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Improving The Environmental Sustainability Of Industrial Processes Through Membrane Processes And Aqueous System Manipulation

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IMPROVING THE ENVIRONMENTAL SUSTAINABILITY OF INDUSTRIAL PROCESSES THROUGH MEMBRANE PROCESSES AND AQUEOUS SYSTEM MANIPULATION.

by

Robert Mervyn Creighton

Presented to the Graduate and Research Committee
of Lehigh University
in Candidacy for the Degree of
Doctor of Philosophy

in

Environmental Engineering

Lehigh University

May 2018

Approval of the Doctoral Committee

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I learned to live by the motto, “Dream Big and make progress every day!”, as this adventure was not a straight path, but a continuous pursuit for answers.

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Abstract

Treatment processes that use membranes to manage the flux of ions in combination with manipulation of aqueous systems allows for increased environmentally sustainability. The first process investigated combining the neutralization reaction and ion exchange membrane processes to offer onsite management of acidic or basic industrial wastes at low operational and capital costs that improved the environmental sustainability of the industrial waste management. The second process investigated combining a solid compound and gas to form an aqueous system with high osmotic pressure. In regard to the first process, many waste generators with low waste volumes and/or low acid or base concentrations struggle to justify the required investment to manage onsite industrial waste management; however, this research was gathered to show that through combination of the neutralization reaction and ion exchange processes, the waste generators benefit from reduced costs while gaining treatment of target waters. Synthetic pickle waste with 10% Fe(III) and 2.5% HCl was used in a diffusion dialysis process to produce purified acid. The purified acid was used in a Donnan dialysis process to treat hard water at 250ppm of Mg^{2+} and brackish water at 2000ppm of NaCl. The flux and percent removal of H^+, Mg^{2+}, Na^+ and Cl^- was determined for all ion exchange processes with varying starting concentration and ion exchange membranes. Removal of Mg^{2+} was as high as 98% after 2 cycles of purified acid. A three-ion model was developed to predict equilibrium of the Donnan dialysis system which, along with flux data, waste generators may use as a tool for system design of an onsite treatment process. Regarding the second process, a system was created with high osmotic pressure that was used in a

Forward Osmosis process to draw water from the target chamber. Traditional Forward Osmosis (FO) processes operate at hydraulic pressures close to zero with the osmotic pressure (OP) gradient between the target and draw solutions providing the driving force for osmosis. A novel FO process, pressurized FO, creates an OP gradient by applying a partial pressure of CO_2 (g) on the draw solution and the same pressure of inert gas on the target solution that enables a reaction in the target cell between $MgCO_3$ and H_2CO_3 to form $MgHCO_3^+$, HCO_3^-. The potential OP is greater than 100 atms with the OP for the system controlled by adjusting the partial pressure of CO_2 (g) in the draw solution. Through experimental results, the key process elements were validated. These key process elements included the cycling of the OP system from formation of a high OP system to the reduction of high OP system, and the operation of FO with the high OP system. Specifically, it was demonstrated that the formation of the high OP system (33 atms) and subsequent reduction of the OP to 0.5 atm at the removal of the CO_2 (g) coupled with air sparging was accomplished with the process. The high OP draw solution was used to draw deionized water across an HTI membrane under CO_2 partial pressure of 8 atm with a flux rate that corresponded with OP of 33 atm for the draw solution. The research objectives were to demonstrate a new configuration of the FO process through the pressurized FO process and a corresponding draw solution that offers less energy consumption versus other conventional FO systems.

Chapter 1 – Improving the environmental sustainability of industrial waste management by harnessing the neutralization reaction to drive water treatment processes through Ion Exchange membrane processes.

1.1 Introduction

1.1.1 Coupling neutralization reaction and ion exchange membrane processes to build environmentally sustainable processes

The researchers of this dissertation examine the use of the neutralization reaction coupled with ion exchange membrane treatment processes for improved management of industrial waste. Industrial managers can increase environmental sustainability with this process by accomplishing two objectives: neutralizing waste products and performing treatment of target waters. Although proven technologies exist to treat industrial wastes, in many scenarios, the total cost of management drives waste generators to less environmentally sustainable solutions compared to Best Available Technologies (BATs). The objective of the research is to demonstrate that, through combining BAT processes with the neutralization reaction, the onsite treatment processes are both environmentally sustainable and are economical for the waste generator.

Industry begets industrial waste; since industrialized regions need industrial processes to support economic growth, the generated wastes pose risks and costs to society. Often the most economic options for waste generators are management processes that are not environmental sustainable e.g. waste generator collects/ships/disposes industrial waste through a deep well injection solution; however, a more environmentally sustainable process is possible by combining BAT processes onsite at the waste generator location (Covino Jr, 1987). An example is the combination of diffusion dialysis, Donnan dialysis, and acid neutralization, in which the waste generator purifies the acid from the salty waste acid (diffusion dialysis) and then uses the purified acid to perform a treatment process on a target water (Donnan dialysis). The driving force for the treatment process results from the neutralization reaction that creates an ion sink between the chambers separated by the ion exchange membranes. Industrial wastes that contain high concentrations of neutralizing ions (H^+, OH^-, HCO_3^-, CO_3^{2-}) provide source ions for the neutralization reactions and this onsite treatment process. Waste acids and waste bases are prevalent in various industrial wastes, e.g. pickling waste from steel plants to treat the surface of the steel (Covino Jr, 1987). This research was interpreted to demonstrate the implementation of a process that harnesses the thermodynamic favorability of the neutralization reactions to create ion sinks. The outcome of ion gradients in the ion exchange membranes and driving forces between the membranes were interpreted to demonstrate the viable use of the industrial waste to promote environmentally sustainability.

1.1.2 Background and chemistry of pickling process management

In the steel production process (Figure 1), steel pickling is used to remove iron oxides from the metal surface and is considered a vital step in the steel production process (Covino Jr, 1987). The outcome of the pickling process is a metal-laden waste acid as a result of soaking an oxidized steel in an acid solution for purposes of cleaning or conditioning the steel (Covino Jr, 1987) as seen in Figures 2 and 3. The origins of the process date back to 1750 when Renman of Sweden (Anderson 1980) proposed soaking scaled steel for several months in acidic wood by-products so that the acidic solution would react with the iron oxide to form iron salts and, therefore, would remove the scale from the steel's surface. By the late 1800's, as the industrialization age spread, steel manufacturers realized the benefits from steel pickling: increased efficiency and quality of finished product. The superior quality of finished produce and reduced cost increased demand for steel in industrialized products and increased demand for processing capacity for those metals (Covino Jr 1987) (Langill 2003). Inventors improved processes; an apt example of this is John Tytus's patent of a metal pickling process in 1925. Tytus improved the industrialization of the pickling process by passing metal components through a mechanism that contacted the metal with an acid solution (US Patent #1544506 1925). As the pickling technology developed, pickling performance improved through combinations of different acids and inhibitors and, in 1956, James Gravell developed a process for streamlining the steel pickling process by varying the concentrations and types of acids and temperatures of the acid bath (US Patent # 1555798. 1956). These innovators increased the amount of metal being processed through pickling and, in turn, increased the amount of pickling waste. The pickling process became an integral part of the metal industry as it remains today.

The pickling process is a metal finishing process, in which oxides that formed on the base metal during the metal production process are removed (Covino Jr, 1987) (Krzywicki, 2003). These oxides are formed during the high temperature processing of the metal in the presence of oxygen (atmospheric). The author explains that during the annealing operation of the steel production process, the interactions of temperature, time at temperature, and oxygen partial pressure affects the thickness, structure, composition, and adhesion of the oxide scale to the metal (Covino Jr, 1987). The oxidation of the metal forms scale as FeO, Fe_3O_4, and Fe_2O_3 oxides on the surface of the metal. As these oxides form on the surface of the metal, cracks develop due to the different formation rates

(Agrawal & Sahu, 2009). The pickling process is assisted by these cracks, as the acid can reach/dissolve the more soluble oxides close to the metal surface, which weakens the support of the top layer of iron oxide scale. Additionally, the researcher understands the hydrochloric acid reaction with the base metal produces hydrogen gas and forms supplementary pressure against the top layer of the iron oxide and breaks off scale flakes (Agrawal & Sahu, 2009).

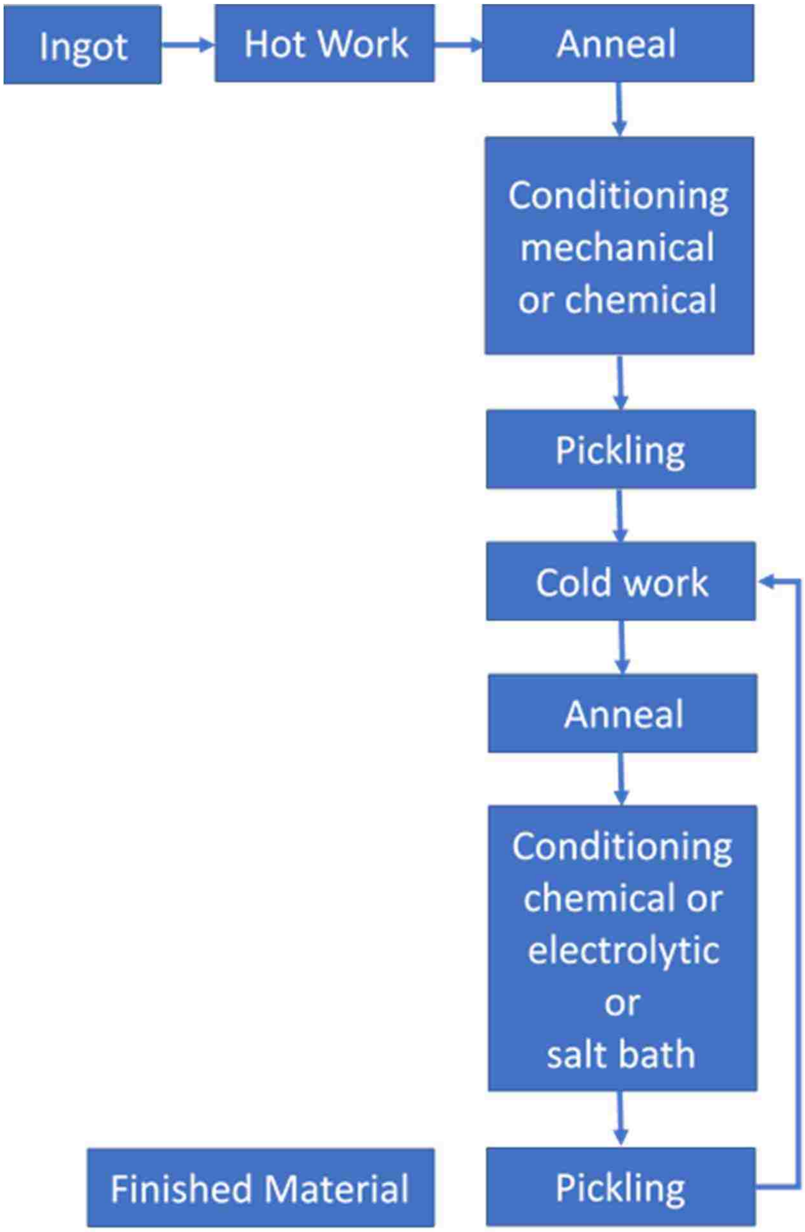


Figure 1. Steel production process steps (Covino Jr, 1987)

Figure 2. Example of steel pickling process (Covino Jr, 1987)

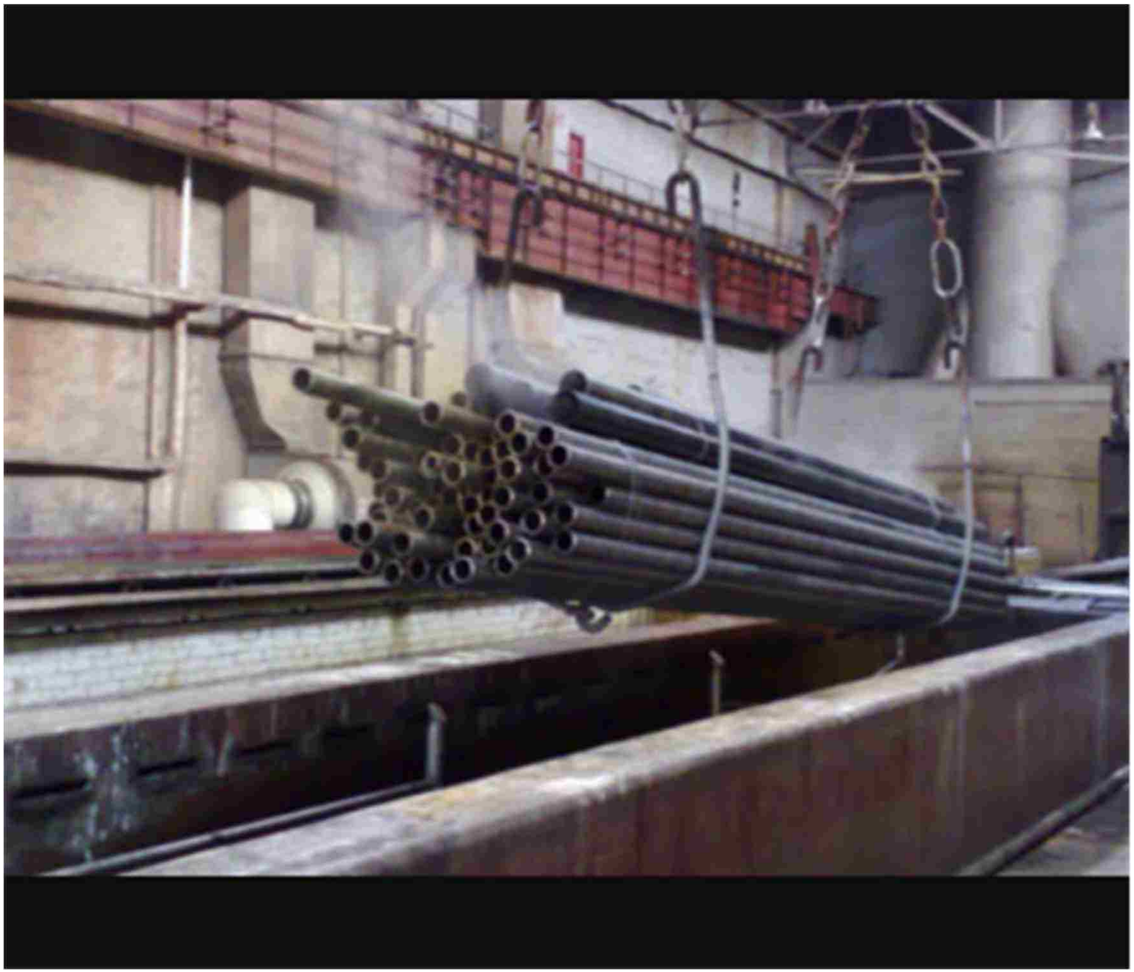


Figure 3. Example of steel pickling process (Covino Jr, 1987)

Chemical reactions between the HCl and iron/ iron oxides include the following (Agrawal & Sahu, 2009),:

Equation 1 $Fe_2O_3 + Fe + 6HCl \rightarrow 3FeCl_2 + 3H_2O$

Equation 2 $Fe_3O_4 + Fe + 8HCl \rightarrow 4FeCl_2 + 4\ H_2O$

Equation 3 $FeO + 2HCl \rightarrow FeCl_2 + H_2O$

Equation 4 $Fe + 2HCl \rightarrow FeCl_2 + H_2$

The researcher understands that through the hydrochloric acid and iron oxide neutralizing reaction, the iron aqueous concentration increases, and the acid concentration decreases, which reduces the utility of the pickling acid. The diminished utility occurs when the ion concentrations achieve 8-10% iron and 3-4% HCl (Agrawal & Sahu, 2009), at which point the pickling acid is considered spent and no longer viable for the metal finishing process, even though there remains a high concentration of acid in the pickling acid.

1.1.3 Available treatment processes for pickling waste

Available treatment processes for spent pickle waste are thoroughly reviewed by Agrawal and Regel-Rosocka (Agrawal & Sahu, 2009) (Regel-Rosocka, 2010). The key technologies and process descriptions for the following technologies in Table 1 include pyrohydrolysis, thermal decomposition, electrolytic precipitation/ deposition, ion exchange/ acid retardation, electro dialysis/ diffusion dialysis, and solvent extraction. Diffusion dialysis is widely accepted as the BAT for treatment of the spent pickling acid (Regel-Rosocka, 2010); however, in the case of small volumes of pickling waste, the most economical option for the producer may not be the BAT, but “pay to dispose” of the waste.

Treatment technology	**Process description**
Pyrohydrolysis	Spent pickle liquor is thermally decomposed at a high temperature in the presence of water vapor and oxygen to form hydrochloric acid and iron (II) oxide.
Neutralization/ precipitation	Remaining acid in spent pickle liquor is neutralized with $CaCO_3$ or CaO, which forms iron oxides as precipitates.
Thermal decomposition	Thermal decomposition sprays the waste acids including metal ion into a furnace heated from 600 ◦C to 1000◦C. HCl is recovered by absorbing the gases decomposed into H_2 gas, Cl_2 gas from chloride pickle liquor. The recovered acids are reused for picking and dissolution of material.
Electrolytic precipitation / deposition	Waste HCl along with Fe metal ions are introduced in the cathodic compartment of the electrolysis cell where metal ions electrodeposit on the cathode and Cl^- ions are transferred through the anion exchange membrane.
Ion exchange technique /acid retardation method	Ion exchange resins adsorb the acid as it passes through the resin bed. In backwashing with water, the adsorbed acid is released because of the difference in osmotic pressure.
Electro-dialysis/ diffusion dialysis	Electro or chemical potentials drive separation processes through membranes that are a semi-permeable barrier through which only selected chemical species may diffuse.
Solvent extraction	Solvent extraction allows specific molecules to be separated from the aqueous phase while others are retained.
Membrane distillation	Partial pressure difference induced by temperature and composition of the layers adjacent to the hydrophobic microporous membrane.

Table 1. Available spent pickle liquor treatments (Regel-Rosocka, 2010) (Agrawal & Sahu, 2009)

1.1.4 A combined approach to industrial waste management; diffusion dialysis and Donnan dialysis driven by the neutralization reaction.

The researcher demonstrates that an alternative industrial waste management process benefits from the combination of BATs that include diffusion dialysis, Donnan dialysis and the neutralization reaction. The combination of the BATs is an environmentally sustainable process and can be implemented at all waste generator plants with minimal capital investment and low operational costs. An example of waste acid that represents a good candidate for this process is spent pickling waste. The spent pickling waste retains acid utility (approximately 3.0%-4.0% HCl) that is available to perform treatment processes by first preparing the purified waste acid through diffusion dialysis and then incorporating the neutralization reaction in a Donnan membrane process to treat a target water. The proposed processes run continuously with no added chemicals and minimal energy required to move solutions through the system. The researcher explains that the chemical potential gradients between the chambers forms the driving force for the processes. The researcher demonstrates that chemical potential gradient across the membrane drives the processes while the neutralization reaction maintains the gradient in the case of the Donnan dialysis process. When the process is finished, the products include a metal solution with low acidity (pH of 4.0 to 5.0), a slightly salty purified acid solution, and a treated target water (softened water or demineralized water). The metal solution has a market value; the salty purified acid can be discharged with minimal acid neutralization treatment and the target water can be used for onsite operations, boiler operations, or other facility functions.

1.1.4.1 Neutralization reactions.

The researcher explains that a key feature of the combined processes is the neutralization reaction. The formation of the hydrogen ion gradient between the target chamber and the waste acid chamber is explained to drive the Donnan dialysis membrane treatment process. The neutralization reactions are kinetically fast and thermodynamically favorable (negative Gibbs free energy) e.g. the hydrogen ion and hydroxyl/bicarbonate ions available in the target chamber. Either carbon dioxide (aqueous) or water is formed by the neutralization reactions. The carbon dioxide (aq) quickly equilibrates with carbon dioxide (g), in which all reactions are thermodynamically favorable and kinetically fast (Eigen, 1954).

1) The hydrogen and bicarbonate reaction has a negative Gibbs free energy of -36.25 kJ/mol.

Equation 5 $H^+ + \quad HCO_3^- \quad \leftrightarrow \quad H_2CO_3^*$

$$\Delta G_f: \quad 0 \quad + -586.85 \quad \leftrightarrow \quad -623.1; \qquad \Delta G^\circ = -36.25\ kJ/mol$$

2) The hydrogen and carbonate reaction has a negative Gibbs free energy of -59.05 kJ/mol.

Equation 6 $H^+ + \quad CO_3^{2-} \quad \leftrightarrow \quad HCO_3^-$

$$\Delta G_f: \quad 0 \quad + -527.8 \quad \leftrightarrow \quad -586.85; \qquad \Delta G^\circ = -59.05\ kJ/mol$$

3) The hydrogen and hydroxyl reaction has a negative Gibbs free energy of -84.7 kJ/mol.

Equation 7 $H^+ + \quad OH^- \quad \leftrightarrow \quad H_2O$

$$\Delta G_f: \quad 0 \quad + -152.7 \quad \leftrightarrow \quad -237.4; \qquad \Delta G^\circ = -84.7\ kJ/mol$$

In addition the researcher explains, the acid-neutralization reaction is applicable over a wide range of pH and the associated free energy change from Equation 7 then can be rewritten as Equation 8.

Equation 8 $$\Delta G = \Delta G^{\circ} + RT\, ln \frac{a_{H_2O}}{a_{H^+} + a_{OH^-}}$$

Under ideal conditions the researcher explains a waste-acid stream of equil-molar OH^- to neutralize excess H^+, Equation 8 is simplified as follows: $a_{H^+} = a_{OH^-}$ and $a_{H_2O} = 1$. Therefore:

Equation 9 $$\Delta G = \Delta G^{\circ} - RT\, ln\, a_{H^+}^2$$

If the waste acid concentration varies in pH from 1 to 7, the computed free energy change (ΔG_R) of the neutralization reaction for different acid strength of the waste acid stream can be plotted as shown in Figure 4. The important aspect of the figure is that even at a pH of approximately 4 or 5, there remains a high negative Gibbs Free energy available to drive the process.

1.1.4.2 Donnan dialysis process coupled with waste acid neutralization

The researcher explains the Donnan dialysis separation process to be a counter diffusion of two or more ions through an ion-exchange membrane to achieve a separation. In this dissertation research, the Donnan dialysis process is used in conjunction with the waste acid neutralization reaction to perform the treatment process; two types of water treatment are possible, demineralization and water softening. In the case of the demineralization treatment, target cations are exchanged for hydrogen ions and target anions are exchanged for hydroxyl or carbonate/bicarbonate ions. The researcher explains there is an addition of an Anion Exchange Membrane (AEM) for the demineralization treatment process. The additional membrane in the process is for the exchange of hydroxide or carbonate/bicarbonate ions with target anions. The researcher explains that the hydrogen ion is combined with hydroxyl ions or carbonate/bicarbonate ions to form water or carbon dioxide (aq). In the case of water softening, the divalent ions in the target water are exchanged with hydrogen while the hydrogen ion is combined with the bicarbonate/carbonate or hydroxide ions in the target water to form carbon dioxide (aq) or water, which only requires a Cation Exchange Membrane (CEM) for the treatment process. Donnan dialysis is a continuous, countercurrent process, whereby a significant amount of the cations/anions can be concentrated in a small volume (Davis 2000b). An example of Donnan dialysis performing a water treatment process is shown in Figure 5 and Figure 6.

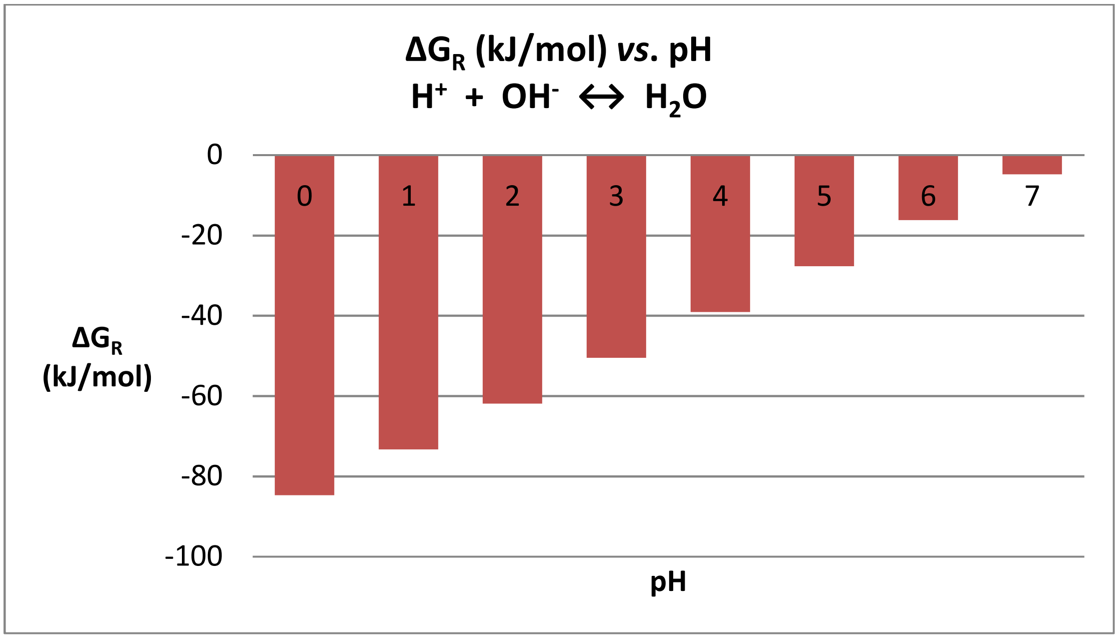


Figure 4. Free energy change *vs*. pH

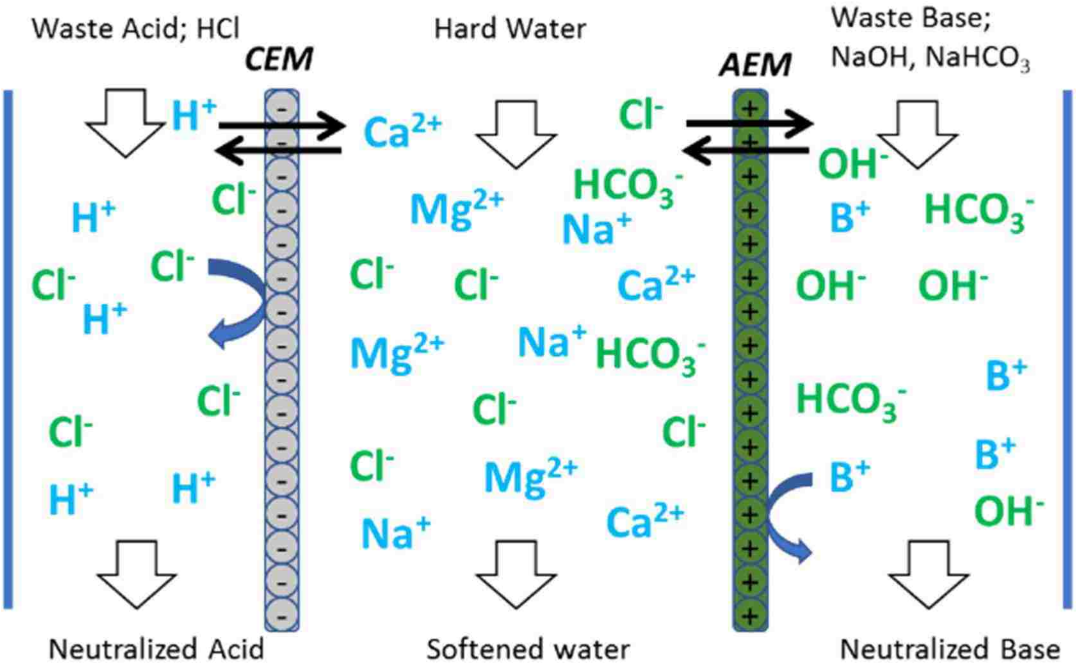


Figure 5. Demineralization water treatment through Donnan dialysis treatment process

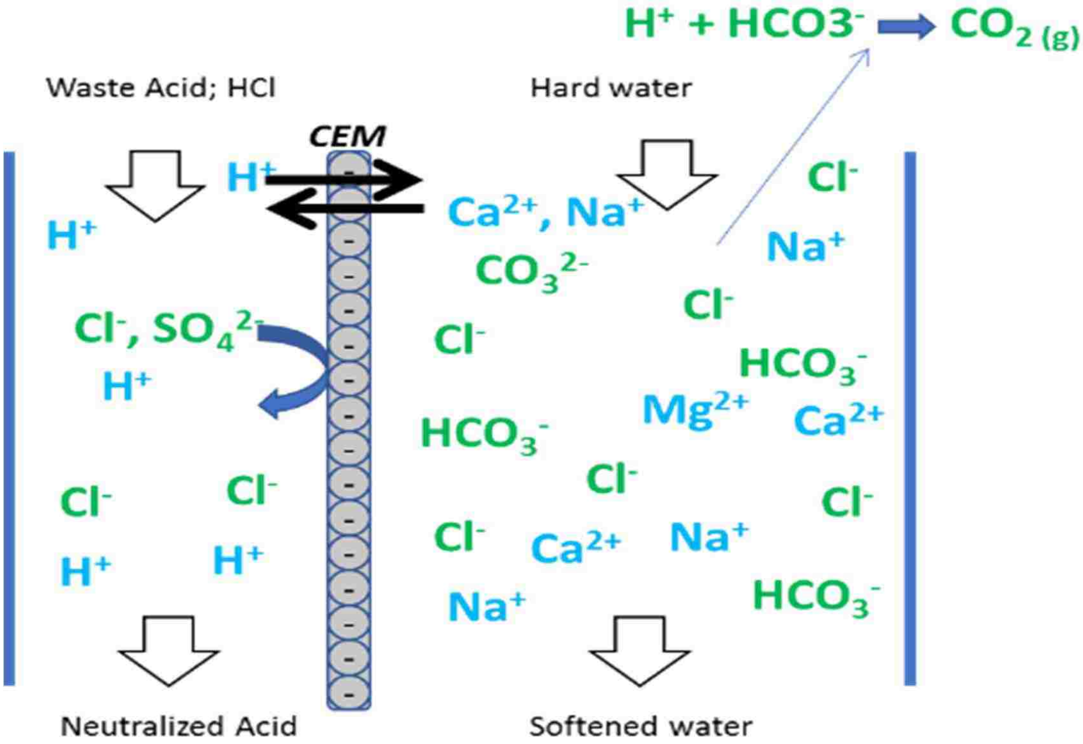
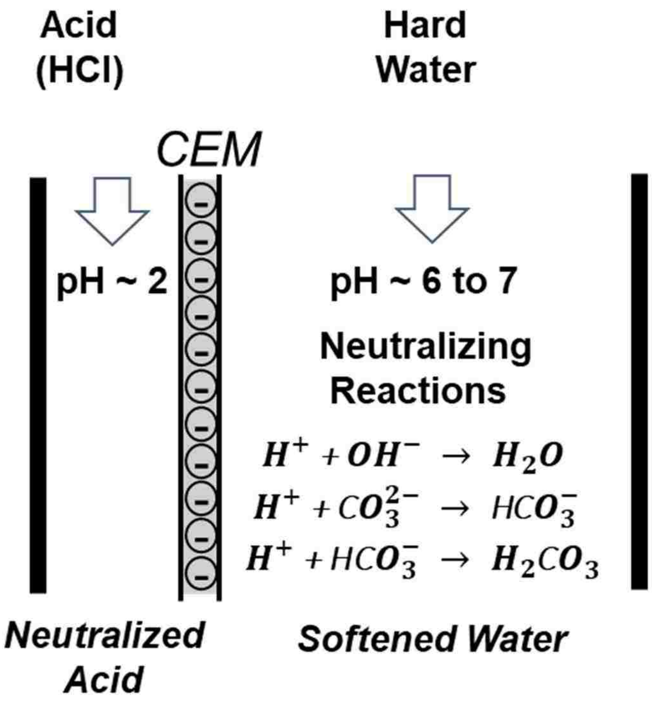


Figure 6. Temporary hardness removal through Donnan dialysis treatment process

Since the neutralization reaction maintains a pH of 6.0 to 7.0 in the target cell, it provides a continuous gradient of hydrogen from the waste acid cell to the target cell. The Donnan equilibrium relationship states that in a two-ion system in equilibrium, the ratios of ions are equal between the two systems. When controlling the pH in the waste acid cell at 2.0 and the pH in the target cell at 7.0, Donnan equilibrium can be used to predict the metal concentration in the waste acid and target cells; the ratio is 10^5 of the waste acid cell to the target cell for a monovalent/monovalent exchange (see Figure 7).



Donnan Equilibrium

$$\frac{C_{Na^+}^{Acid}}{C_{Na^+}^{Target}} = \frac{C_{H^+}^{Acid}}{C_{H^+}^{Target}} \qquad \frac{C_{Na^+}^{Acid}}{C_{Na^+}^{Target}} = \frac{pH\ 2}{pH\ 7} = 10^5$$

Figure 7. Donnan equilibrium determination for mono/mono ion exchange

1.1.4.3 Diffusion dialysis

The diffusion dialysis process allows the transfer of anions across an AEM based on chemical potentials. Waste acids typically contain metal ions: monovalent, divalent, and trivalent cations (e.g., Na^+, Ca^{2+}, Mg^{2+} and Fe^{3+}) (see Figure 8). Waste acids can be separated from metal ions for enhanced purity through appropriate application of the Donnan exclusion principle (Sarkar, SenGupta, & Prakash, 2010) (Sargent, 1963) and through a diffusion dialysis membrane process (Luo, Wu *et al*. 2010, Luo, Wu *et al*. 2011, Palatý, Žáková *et al*. 2000, Palatý, Bendová 2009). Most importantly, the diffusion dialysis process does not require additional chemicals or energy. Water is the only chemical needed in the separation process, while the Donnan co-ion exclusion principle is the heart of the process. In addition, the mass transfer rate for H^+ is 300x faster *versus* the other metals, which provides an effective higher flux to enable the acid purification (Davis 2000b).

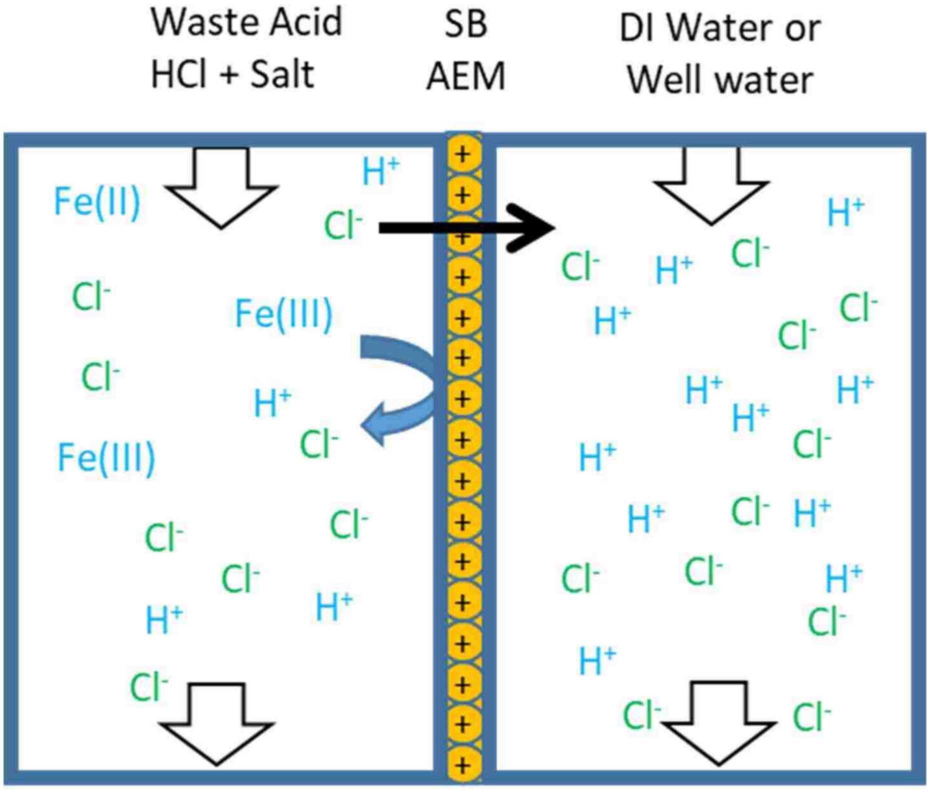


Figure 8. Acid purification diffusion dialysis treatment process

1.1.4.4 Counter current process flow.

An important aspect of both dialysis processes (Donnan and diffusion), is to structure the process to use countercurrent flow in which there is an exchange of ions between the two flowing bodies flowing in opposite directions to each other. The maximum amount of mass transfer that can be obtained is higher with countercurrent than co-current (parallel) exchange because countercurrent maintains a slowly declining difference or gradient. In co-current exchange the initial gradient is higher but falls off quickly, leading to wasted potential, whereas with countercurrent flow the driving gradients can only approach one another. The result is that countercurrent exchange can achieve a greater amount of mass transfer than co-current under otherwise similar conditions. The main advantage is that countercurrent flow maximizes the average driving force, thus increasing the efficiency of the process in question. (Ruthven, 1989). Fick's law is the governing equation for both processes, where the driving force is the chemical potential gradient between the aqueous systems for diffusion dialysis and the gradient in the membrane for the Donnan dialysis system. Through the implementation of counter current flow, the researcher demonstrates optimized performance of the processes.

1.1.5 Research Objectives

The main aspect of the dissertation is to study the applicability of improving the environmental sustainability of industrial waste management through a combination of the neutralization reactions and membrane processes. These studies included:

1) Study diffusion dialysis of synthetic pickle waste with different concentrations of hydrochloric acid combined with ferrous chloride and ferric chloride.
    a) Determine flux, mass transfer coefficients.
    b) Compare results with other peer reviewed studies.
2) Study Donnan dialysis of synthetic hard water and brackish waters with different H^+ concentrations and different membranes.
    a) Determine flux, target ion percent removal.
    b) Compare results with other peer reviewed studies.
3) Study combination of the diffusion and Donnan dialysis processes into a continuous treatment process.
    a) Determine flux, target ion percent removal.
4) Development a three-ion equilibrium iterative model to determine concentrations within the membrane and aqueous phases.

Another important study entailed the comparison or effectiveness of the process in Donnan dialysis water treatment for two types of ion-exchange membrane SA-CEM (standard) and SA-CEM (mono-selective). All the parameters mentioned above were applied to the recovery process using these two membranes.

1.2 – Fundamental principles of the combined treatment processes using ion exchange membrane processes; diffusion dialysis and Donnan dialysis driven by neutralization reaction.

1.2.1 Fundamental principles

The following fundamental principles related to ion exchange build the foundation of the dissertation research, which are derived/developed through Equations.

1.2.1.1 Electrochemical potential

The electrochemical potential gradient is the driving force that moves a system to the Donnan Equilibrium condition.

> *"An electrochemical gradient is a gradient of electrochemical potential, usually for an ion that can move across a membrane. The gradient consists of two parts, the chemical gradient, or difference in solute concentration across a membrane, and the electrical gradient, or difference in charge across a membrane. When there are unequal concentrations of an ion across a permeable membrane, the ion will move across the membrane from the area of higher concentration to the area of lower concentration through simple diffusion. Ions also carry an electric charge that forms an electric potential across a membrane. If there is an unequal distribution of charges across the membrane, then the difference in electric potential generates a force that drives ion diffusion until the charges are balanced on both sides of the membrane* (Nelson & Cox, 2013)*."*

Diffusion dialysis is driven by the chemical potential in which the anion exchange membrane is completely saturated with the common anion and diffusion of the anions related to the concentration gradient move across the membrane accompanied by the H^+ (due to the small size of H^+) to maintain the law of electroneutrality. Large cations in solution are not permitted to cross the membrane due to the exclusion properties of the membrane, referred to as Donnan exclusion (Helfferich 1962). Donnan dialysis is driven by the chemical potential; however, the researcher uses the cation exchange membrane properties and the concentration in the aqueous phase to determine the ion gradients in the membrane that control the driving forces.

1.2.1.2 Separation factor (Helfferich, 1962)

The separation factor is based on characteristics of the membrane and aqueous concentrations. From the separation factor the researcher can predict the behavior of the ion exchange membrane for competing ions. The separation factor value is calculated by the researcher by knowing the concentrations of the two counter ions in both membrane and aqueous phases. The separation factor α_B^A is defined by:

Equation 10 $$\alpha_B^A = \frac{\bar{C}_A C_B}{\bar{C}_B C_A} = \frac{\bar{x}_A x_B}{\bar{x}_B x_A}$$

2.1.3 Mass Action Equation and isotherm development (Helfferich, 1962)

The researcher can use an ion exchange isotherm to determine the ion exchange concentration (Y_i) based on the ion exchange properties of ion affinities (R), ion capacity (Q) and system concentrations. A researcher can use Equation 11 to describe a Monovalent/Divalent ion exchange process and further to develop the concentration mass action Equation 12. Through taking assumptions of a two-ion system and simplifying with equivalent fractions in the aqueous and resin phases, Equation 12 can be transformed into Equation 22. Assuming a two-ion system derives the relationship for one ion in Equation 23, a graphical representation of Equation 23 can be developed by choosing an X value and solving for Y, as shown in Figure 9. Based on the membrane properties related to Ca^{2+} and H^+, the selectively coefficients are given as 1.3 for H^+ and 5.2 for Ca^{2+}. The C_T and R values are properties of the membrane and static for all systems.

Equation 11 $$A + 2\overline{B} \leftrightarrow \bar{A} + 2B$$

Equation 12 $$K_{AB} = \frac{\overline{C_A} {C_B}^2}{\overline{C_B}^2 C_A}$$

Equation 13 $$C = C_A + C_B$$

Equation 14 $X_i = \frac{z_i C_i}{C}$

Equation 15 $X_A = \frac{C_A}{C};\ CX_A = C_A$

Equation 16 $X_B = \frac{2C_B}{C};\ \frac{CX_B}{2} = C_B$

Equation 17 $Y_i = \frac{z_i \bar{C}_i}{R}$

Equation 18 $Y_A = \frac{\bar{C}_A}{R};\ RY_A = \bar{C}_A$

Equation 19 $Y_B = \frac{2\bar{C}_B}{R};\ \frac{RY_B}{2} = \bar{C}_B$

Equation 20 $Y_A + Y_B = 1;\ X_A + X_B = 1$

Equation 21 $K_{AB} = \frac{RY_A\left(\frac{CX_B}{2}\right)^2}{\left(\frac{RY_B}{2}\right)^2 CX_A}$

Equation 22 $K_{AB} = \frac{C}{R}\,\frac{Y_A(X_B)^2}{(Y_B)^2 X_A}$

Equation 23 $K_{AB}\frac{R}{C} = \frac{Y_A(1-X_A)^2}{(1-Y_A)^2 X_A}$

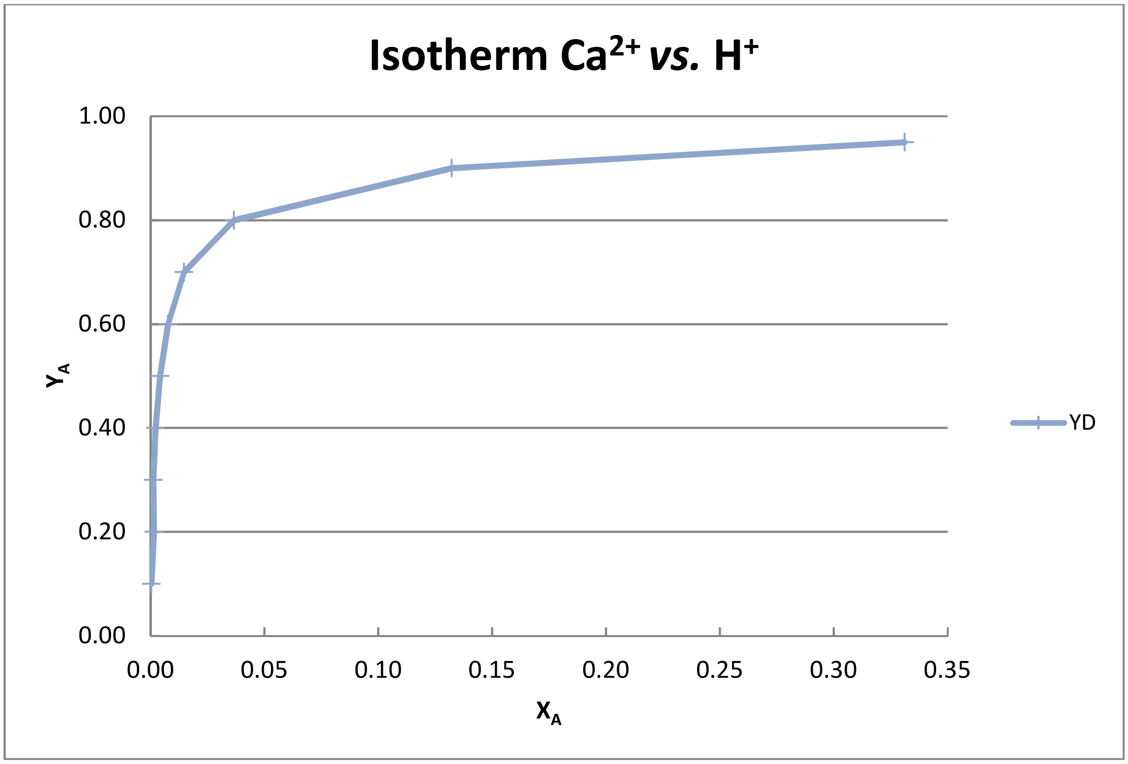


Figure 9. Ion exchange isotherm for Ca^{2+} and H^{+} system

1.2.1.4 Donnan Equilibrium

F.K. Donnan (pictured in Figure 10) exposed the Donnan Equilibrium principle based on ion exchange membranes that enable unique separation processes by incorporating thermodynamic properties and membrane properties (Donnan 1995). The ion exchange membranes are selectively permeable to cations or anions. The researcher explains as two-system separated by ion exchange membranes moves towards equilibrium, the counter ions establish new equilibrium concentrations, called the Donnan equilibrium (Prakash, Hoskins *et al*. 2004, Prakash 2004, Prakash, SenGupta 2005).

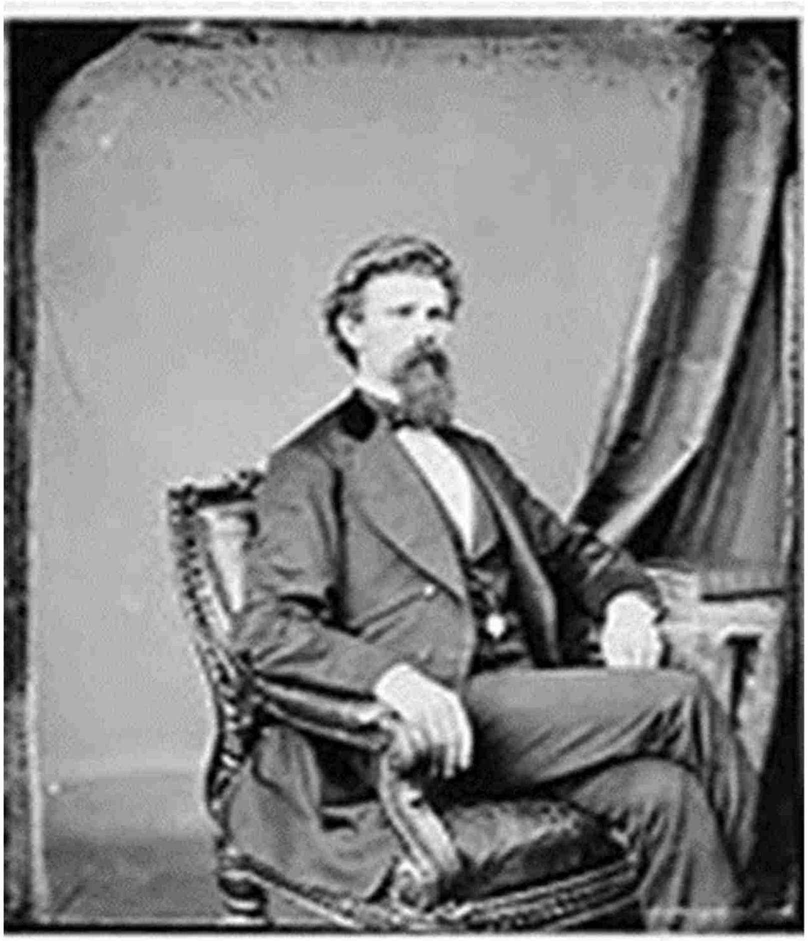


Figure 10. The portrait of F.K. Donnan.

The Donnan equilibrium as defined with two ion aqueous systems separated by a semi-permeable membrane is derived with the following Equations:

- Equation 24, in which the system is shifted towards electrochemical equilibrium, the electrochemical values are equal on the left and right side of the membrane.
- Equation 25, in which the electrochemical term is expanded into electrical potential and chemical potential
- Equation 26, in which the values are further provided for electrochemical potential on the left and right side of the membrane
- Equation 27 is further manipulated to simplify the equation.
- Equation 28 is combined with Equation 13 for two ions
- Equation 29 is derived when considering an ideal system as the activities of the ions can be reduced to concentrations.

Equation 24 $$\bar{\mu}_i^{Left} = \bar{\mu}_i^{Right}$$

Equation 25 $$\bar{\mu}_i = \mu_i^o + RT\,ln\,a_i + z_iF\Phi$$

Equation 26 $$\mu_i^o + RT\,ln\,a_i^{Left} + z_iF\Phi^{Left} = \mu_i^o + RT\,ln\,a_i^{Right} + z_iF\Phi^{Right}$$

Equation 27 $$\frac{F(\Phi^{\ Left} - \Phi^{\ Right})}{RT} = ln\left[\frac{a_i^{\ Right}}{a_i^{\ Left}}\right]^{\frac{1}{z_i}}$$

Equation 28 $$\left[\frac{a_i^{\ Right}}{a_i^{\ Left}}\right]^{z_j} = \left[\frac{a_j^{\ Right}}{a_j^{\ Left}}\right]^{z_i}$$

Equation 29 $$\left[\frac{C_i^{\ Right}}{C_i^{\ Left}}\right]^{z_j} = \left[\frac{C_j^{\ Right}}{C_j^{\ Left}}\right]^{z_i}$$

$\bar{\mu}_i$ is the electrochemical potential of ion *i*, in J/mol.
μ_i is the chemical potential of the ion *i*, in J/mol.
z_i is the valence (charge) of the ion *i*, a dimensionless integer.
F is the Faraday constant, in C/mol.
Φ is the local electrostatic potential, in V.
"^{o}" represents standard state.
"Left" and "Right" determine the system location.
"a" is that activity of the ion.
"C" is the concentration of the ion.

Based on the Donnan Equilibrium relationship established in Equation 29, selective removal of ions from one side of the membrane can be accomplished by increasing the concentration of the exchanging ion *vs*. the target ion. In addition, increased removal of the target ion is possible through incorporation of a neutralization reaction as part of the exchange process. [In addition, ions from the target cell driving towards Donnan Equilibrium by incorporating a neutralization reaction as part of the exchange process, an increased removal of the target ion is possible.] This additional removal is based on the "ion sink" created in the target cell.

1.2.2 Diffusion dialysis

Diffusion dialysis is driven by the chemical potential gradient between two systems that are separated by a semipermeable membrane (Davis 2000a). In the case of acid purification, the Anion Exchange Membrane (AEM) is used, which is fully saturated with anions. The chemical potential difference between the chambers is the driving force, and the diffusion process follows Fick's law with U (the mass transfer coefficient) as the parameter that determines the flux of ions (Davis 2000a):

Equation 30 $$Flux = -U\,\Delta C \quad with\ U\ (L\,t^{-1})$$

The hydrogen ions permeate membranes at U values of 10^{-4} cm sec^{-1} to 10^{-3} while salts have typical U values of 10^{-6} cm sec^{-1}. The salt affect can always be observed in the HCl system (Davis 2000a). In such a scenario, addition of salt (example of Na^+ or Mg^{2+}) chloride can enhance the permeability of HCl, leading to increased HCl concentration at the water side and higher overall dialysis coefficient of HCl (Luo 2010, Luo 2011).

1.2.3 Donnan dialysis

Donnan dialysis is another membrane process that is driven by a chemical potential gradient difference between the two chambers that are separated by a semipermeable membrane. The membrane loading is based on the separation factor and system ion concentrations, which is dynamic and is the driving force for the ion exchange process. As derived in Section 2.1.4, Donnan equilibrium is used to predict equilibrium for a two-ion system, in which the isotherm is used to predict the membrane loading based on the ion concentration in the systems (determine X_i based on ion concentration and then determine Y_i based on the isotherm). The three-ion system is representative of a more complex set of steps to determine the membrane loading, as the membrane loading is a function of the separation factors of the pairs and isotherms of the ion pairs and the ion concentrations in the system. The researcher explains that Donnan equilibrium can be determined from the membrane characteristics and aqueous phase concentrations, which allows for removal of target ions from target cells. Donnan dialysis was originally proposed in 1924 by F. G. Donnan (see Figure 9) who described the resulting equilibrium when a semi-permeable membrane separates two electrolyte solutions, NaA and KA (Donnan 1995). The membrane used was prepared by filling the pores of parchment paper with a gel of copper ferrocyanide, in which ferrocyanide was the common anion A of the two salts (Donnan 1995). The dialysis principle was demonstrated in two simple experiments. In the first experiment with equal initial volumes and concentrations of the two salt solutions, the author explains how the counter diffusion of equal amounts of Na^+ and K^+ through the membrane led to an equilibrium condition in which the two solutions remained at equal concentrations of NaA and KA, In the second experiment, when the initial concentrations were different, the author explained how the counter diffusion of equal amounts of Na^+ and K^+ through the membranes produced solutions with equal ratios of Na^+ and K^+ on both sides of the membrane (Davis, 2000). The author demonstrated how these experiments served as the base of the Donnan dialysis principle.

1.2.4 Kinetics of the Donnan membrane process.

The Nernst-Planck Equation for ionic transport is nonlinear and requires involved mathematical treatment to derive a solution (Prakash 2004). The key assumption is that the process is a “pseudo steady-state process,” in which the solution is simplified. In addition, the following assumptions are made to derive the solution for the transmembrane flux of ions in a batch process Donnan diffusion dialysis:

1. Electroneutrality is maintained in the system.
2. Osmotic transmembrane flux of solvent is negligible.
3. Donnan exclusion principles are applicable to co-ion transport.
4. Membrane concentration of co-ions is negligible.
5. System equilibrium is controlled by membrane-diffusion.
6. Membrane-solution interface is controlled by thermodynamic equilibrium.

The Nernst-Planck Equation has two components: flux due to electrochemical properties of the system and flux due to diffusion.

Equation 31 $$J_{electrical} = -D_i\left(z_i q_i \frac{F}{RT}\frac{\partial\varphi}{\partial x}\right)$$

Equation 32 $$J_{diffusional} = -D_i\left(\frac{\partial q_i}{\partial x}\right)$$

In the Nernst-Planck Equation, which includes electrochemical and diffusion terms, the transmembrane flux of counter-ions in the system is described.

Equation 33 $$J_i = -D_i\left(\frac{\partial q_i}{\partial x} + z_i q_i \frac{F}{RT}\frac{\partial\varphi}{\partial x}\right),\ \ i = A, B$$

Due to electroneutrality:

Equation 34 $$\sum_{i=A}^{B} \ \ z_i q_i - Q = 0,\ i = A, B$$

Due to no electric current:

Equation 35 $$\sum_{i=A}^{B} \ \ z_i J_i = 0,\ \ i = A, B$$

Two terms of flux:

Equation 36 $$J_A = -D_A\left(\frac{\partial q_A}{\partial x} + z_A q_A \frac{F}{RT}\frac{\partial\varphi}{\partial x}\right)$$

Equation 37 $$J_B = -D_B\left(\frac{\partial q_B}{\partial x} + z_B q_B \frac{F}{RT}\frac{\partial\varphi}{\partial x}\right)$$

Using relationships established in Equation 33, 34, and 35, an Equation was derived that is in the form of Fick's law, as shown in Equation 38.

Equation 38 $$J_A = \frac{-D_A D_B\left(z_B^2 q_B\ -.z_A^2 q_A\right)}{D_A z_A^2 q_A\ +\ D_B z_B^2 q_B} \frac{dq_A}{dx}$$

Equation 39 $$J_A = D_{Composite} \frac{dq_A}{dx}$$

Equation 40 $$D_{Composite} = \frac{-D_A D_B\left(z_B^2 q_B\ -\ z_A^2 q_A\right)}{D_A z_A^2 q_A\ +\ D_B z_B^2 q_B}$$

The complete derivation of the Nernst Planck is initiated with the electrochemical relationship for flux for a two-ion system as follows:

Equation 41 $$J_A = -D_A\left(\frac{\partial q_A}{\partial x} + z_A q_A \frac{F}{RT}\frac{\partial \varphi}{\partial x}\right)$$

Equation 42 $$J_B = -D_B\left(\frac{\partial q_B}{\partial x} + z_B q_B \frac{F}{RT}\frac{\partial \varphi}{\partial x}\right)$$

Equation 43 $$\frac{\left(\frac{J_A}{-D_A} - \frac{\partial q_A}{\partial x}\right)}{z_A q_A} = \frac{F}{RT}\frac{\partial \varphi}{\partial x}$$

Equation 44 $$\frac{\left(\frac{J_B}{-D_B} - \frac{\partial q_B}{\partial x}\right)}{z_B q_B} = \frac{F}{RT}\frac{\partial \varphi}{\partial x}$$

Equation 45 $$\frac{\left(\frac{J_A}{-D_A} - \frac{\partial q_A}{\partial x}\right)}{z_A q_A} = \frac{\left(\frac{J_B}{-D_B} - \frac{\partial q_B}{\partial x}\right)}{z_B q_B}$$

From the principle of electroneutrality, the following Equation is developed:

Equation 46 $$(z_A q_A +\ z_B q_B = Q)$$

Taking the derivative of Equation 46 and using the Product Rule:

Equation 47 $$\frac{d}{dx}(z_A q_A +\ z_B q_B = Q)$$

Equation 48 $$\left(z_A\frac{dq_A}{dx} + q_A\frac{dz_A}{dx}\right) + \left(z_B\frac{dq_B}{dx} + q_B\frac{dz_B}{dx}\right) = \frac{dQ}{dx}$$

Equation 49 $$q_A\frac{dz_A}{dx} = 0\ ,\ q_B\frac{dz_B}{dx} = 0\ ,\ \frac{dQ}{dx} = 0$$

Equation 50 $$\left(z_A\frac{dq_A}{dx}\right) + \left(z_B\frac{dq_B}{dx}\right) = 0$$

Equation 51 $$\left(\frac{dq_B}{dx}\right) = \left(\frac{-z_A}{z_B}\frac{dq_A}{dx}\right)$$

From the relationship of no current, a term for J_B is developed:

Equation 52 $$z_A J_A + z_B J_B = 0$$

Equation 53 $$J_B = \frac{-z_A J_A}{z_B}$$

Plug Equation 51 and 53 into Equation 45 to develop Equation 54:

Equation 54 $$\frac{\left(\frac{J_A}{-D_A} - \frac{\partial q_A}{\partial x}\right)}{z_A q_A} = \frac{\left(\frac{\frac{-z_A J_A}{z_B}}{-D_B} - \frac{-z_A dq_A}{z_B\ dx}\right)}{z_B q_B}$$

Solving for J_A, an Equation similar to Fick's law is developed with a diffusion coefficient dependent on the ions in the system:

Equation 55 $$J_A = \frac{-D_A D_B\left(z_B^2 q_B - .z_A^2 q_A\right)}{D_A z_A^2 q_A + D_B z_B^2 q_B} \frac{dq_A}{dx}$$

Equation 56 $$J_A = D_{Composite} \frac{dq_A}{dx}$$

Equation 57 $$D_{Composite} = \frac{-D_A D_B\left(z_B^2 q_B - z_A^2 q_A\right)}{D_A z_A^2 q_A + D_B z_B^2 q_B}$$

1.2.5 Neutralization reactions

The Donnan dialysis process is driven by the neutralization reaction to remove target ions by removing ions from the aqueous phase through the formation of H_2O and CO_2 (aq). As seen in Figure 11, the alkalinity of 15 meq./L buffers the pH of the system from H^+ crossing the membrane. The pH of the target cell is a demonstration of how the added H^+ ions enter the cell, react with either hydroxide or carbonate species, and are removed from the aqueous phase. The titration of a target water is modeled by using the Henderson Hasselbach Equation and demonstrates that, as the removal of alkalinity in the target cell is occurring, the pH of the system remains greater than 5.0. As shown previously in Figure 7, this delta of pH from 5.0 in the target chamber and pH of 2.0 in the waste acid chamber forms a significant driving force and removal potential of ions from the target chamber. As shown in Figure 12, as the H^+ is forming H_2CO_3 to CO_2 (aq), the aqueous phase is not able to retain the CO_2 (aq), and it is released as CO_2 (g) into the atmosphere. Finally, as shown in Figure 13, the neutralization reaction is fast with kinetic reactions on the order of fractions of seconds.

As the neutralization reaction is occurring, the hydrogen concentration in the target chamber is at pH 7 and this is the reason there is a large difference/gradient of pH between the waste acid chamber and the target chamber. The neutralization reaction is the reason there is removal of ions from the target chamber in the aqueous phase through the formation of CO_2 (aq)/H_2CO_3, which is released as CO_2 (g). The "ion sink" is created by this removal mechanism of ions from the aqueous, which, in turn, forms the driving force for Donnan dialysis. An example of the CO_2(g) formation on the probes during one of the "water softening" experiments is shown in Figure 14, which the target chamber has an alkalinity of 15 meq/l.

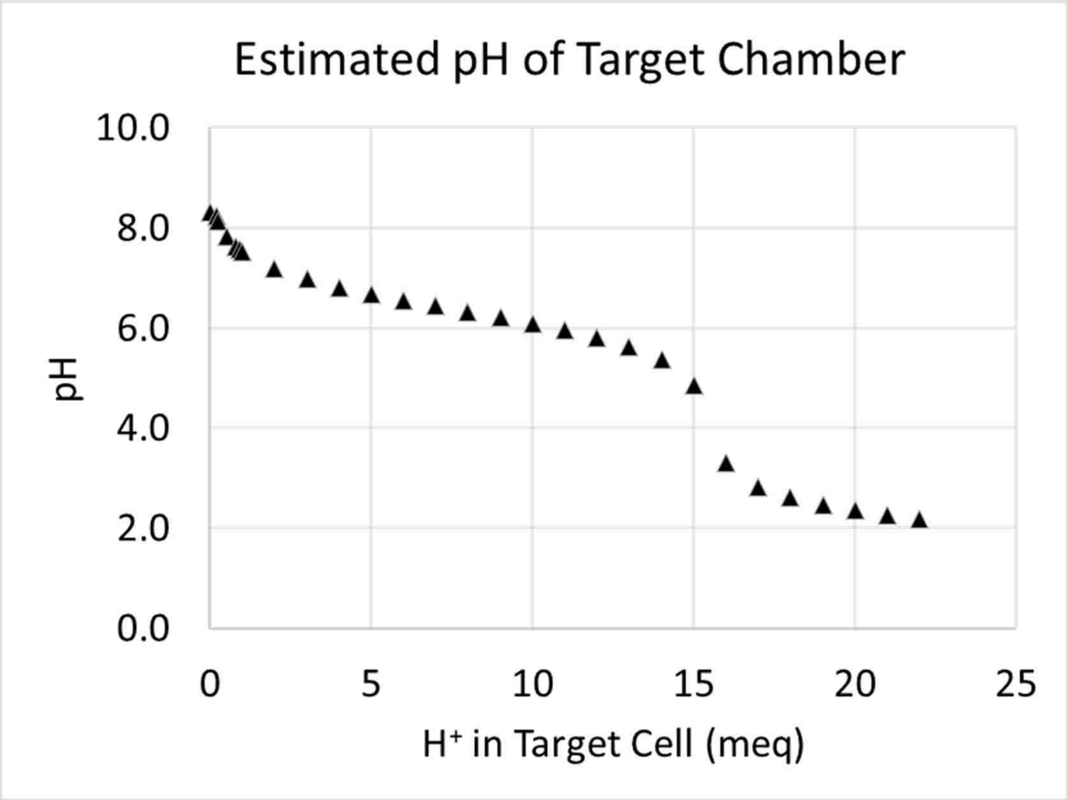


Figure 11. Henderson Hasselbach titration plots

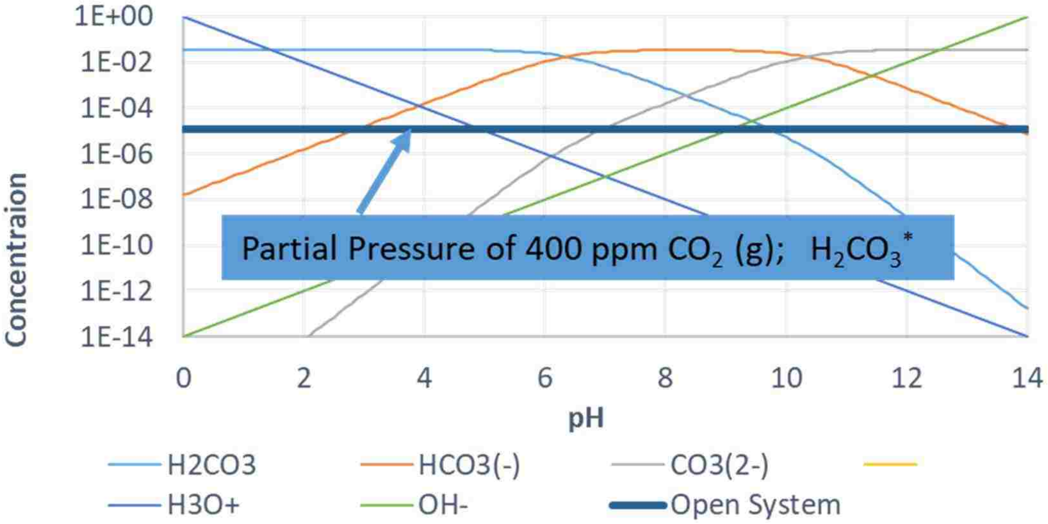
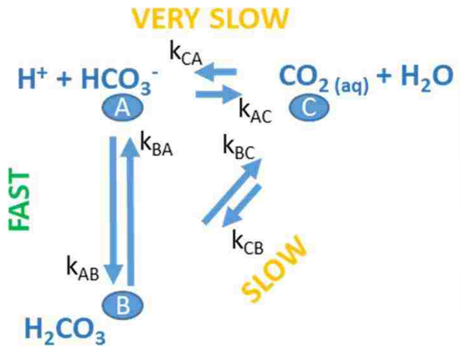


Figure 12. Concentration *vs*. pH plot for target solution



Kinetic Rates	Value	Source
k_{AB}	5×10^{10} M^{-1} s^{-1}	Pocker & Blomkquist
k_{BA}	1×10^{7} s^{-1}	Pocker & Blomkquist
k_{BC}	18 s^{-1}	Stumm & Morgan
k_{CB}	0.04 s^{-1}	Stumm & Morgan

Figure 13. Carbonic acid kinetic information

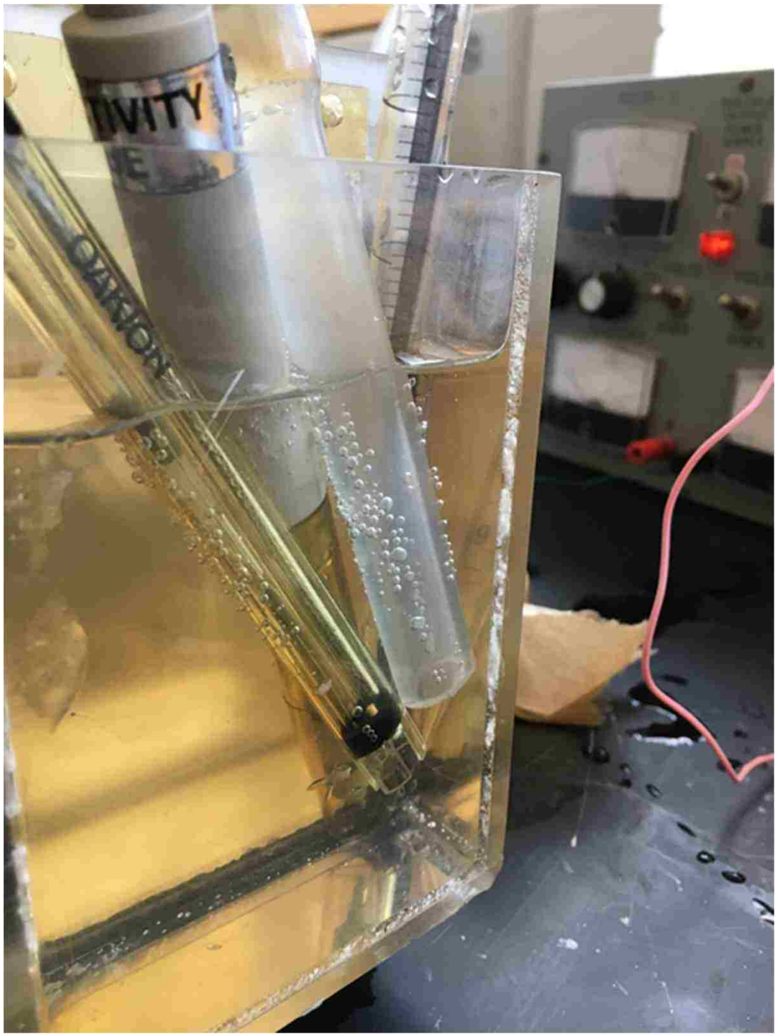


Figure 14. Example of CO_2 (g) formation in a Donnan dialysis experiment

1.2.6 Applications and studies from the literature related to diffusion dialysis, Donnan dialysis and the combination of the two processes.

1.2.6.1 Diffusion dialysis applied to acid purification

Many studies on diffusion dialysis are available in the literature, in which demonstration of waste acid purification is provided.

- Oh (*et al.*) studied the effects of metal species on the performance for recovery of organic acids. He demonstrated HCl recovery increases with increased acid concentration up to 70% recovery for 0.75M and 90% recovery at 5M. He demonstrated that Fe, Ni, Cr, and Cu in the feed solutions were rejected reasonably by the dialysis membrane, the membrane was permeated significantly by Zn in the un-ionized form(Oh, S.J 2000).
- Palaty (*et al.*) and Moon (*et al.*) investigated a model to describe diffusion dialysis. Palaty examined diffusion dialysis of hydrochloric acid in a mixed batch cell with an anion-exchange membrane. He focused on the transport of Cl^- ions in the presence of Fe(III) ions through the anion-exchange membrane if the transport of Cl^- ions in the diffusion films were considered. He found that both the overall dialysis coefficient and the membrane mass transfer coefficient for Cl^- ions decrease with increasing amounts of Fe(III). Palaty documented the "salt effect," that the addition of the salt (example of Na^+ or Mg^{2+}) chloride can enhance the permeability of HCl, leading to increased HCl concentration at the water side and higher overall dialysis coefficient of HCl. Moon developed a lumped parameter model that examined feed concentration, the retention time, and the ratio of feed to water flow rate. He found the model gave good results with the experiment in

predicting the recovery yield and the recovered acid concentration in the range of 0.05 – 3 M (Moon 2000).

- Igawa (*et al.*) investigated using diffusion dialysis to desalinate target waters. He developed an index based on concepts of the ion-exchange reaction rate at the membrane interface and related to the permeation constant in the source-phase boundary layer at the membrane. He found the desalination efficiency increased with the decrease of the desalination compartment thickness and the decrease of linear velocity, which can be estimated by the index (Igawa 1987, Igawa 1986, Igawa 2003).
- Negro (*et al.*) investigated an alternative treatment method based on diffusion dialysis process for free acid recovery and a neutralization process followed by salt splitting for chemical recovery. He observed recovery of 90% of free nitric acid and 50% of free fluoric acid (Negro 2001).
- Zhang (*et al.*) studied HCl recovery from simulated chemosynthesis aluminum foil wastewater with spiral wound diffusion dialysis. He studied the effects of flow rate intensity, diffusate flow rate intensity, dialysate flow rate intensity and initial feed compositions for HCl and $AlCl_3$. He achieved 95% recovery at high HCl concentrations > 2 M (Zhang 2011, Zhang 2012).
- Stachera (*et al.*) investigated the impacts of Divinyl Benzene (DVB) content and impacts to dialysis coefficients and the acid/salt separation. He showed a decrease in the acid and salt dialysis coefficients but a dramatic increase in separation as the DVB content was increased (Stachera 1998).

1.2.6.2 Donnan dialysis applied to water treatment

Many studies on Donnan dialysis are available in the literature, in which demonstration of target ion removal using another available cation and, in some cases, anions is provided.

- Prakash proposed a method to recover $Al_2(SO_4)_3$ through a two-cell system, whereby the acid cell contained sulfuric acid and the feed cell contained acid-treated alum sludge. Prakash attained 90% recovery of the Alum through the process in 24 hours (Prakash, Hoskins, & SenGupta, 2004) (Prakash & SenGupta, 2005) (Prakash, 2004).
- Miyoshi studied various systems, Na^+/K^+, Ca^{2+}/Cu^{2+} to develop a reliable Equation for describing the process and corresponding diffusion coefficients related to the membrane and ions (Miyoshi, 1999).
- Ersoz studied the Co (II)/Ni (II) system using polysulfonated cation exchange membranes. He determined diffusion coefficients for the system and observed that the pH gradient influences the transport of metals and the flux of ions increases with H^+ ion concentrations in the receiver phase (Ersoz & Kara, 2000).
- Hichour studied fluoride removal from diluted solutions by Donnan dialysis with anion-exchange membranes. He determined that chloride was a more efficient driving ion than sulfate. Fluoride was effectively reduced by the system at flowrates lower than 0.6 L h^{-1} (Hichour, Persin, Sandeaux, & Gavach, 1999) (Hichour, Persin, Molénat, Sandeaux, & Gavach, 1999).
- Bleha (*et al.*) determined neutralization dialysis is an effective way to remove both metal salts and anions using OH^- and H^+. He demonstrated a 10-fold increase in the concentration of acid (Bleha 1992).

- Wisniewski (*et al.*) studied Donnan dialysis with cation exchange membranes for the removal of troublesome calcium and magnesium cations before electrodialytic water desalination. He observed 80-88% removal of Ca^{2+} and Mg^{2+} with NaCl in the receiver water at 200 mmol/dm^3 (Wisniewski 2007).

1.2.6.3 Combined diffusion dialysis and Donnan dialysis.

In Figures 15 and 16, the proposed combined BAT process is both an acid purification and a water treatment in a continuous counter current process, which mitigates the remaining acid utility in the pickling acid, while treating a target water. The products of the process include a less acidic solution of ferric or ferrous chloride, a slightly acidic salty purified acid, and a purified target water. In aggregate, compared to an alternative neutralization process that includes costs of a neutralizing compound, this process reduces the total cost of industrial waste management. Oztin studied pickling wastes and determined the indirect costs can be a large portion of the total cost of pickling waste management (Özdemir, Öztin *et al.* 2006a). Therefore, lower total costs and operator benefits are provided by the combined BAT.

The combined processes remain an art and are not practiced in industry as there are a unique set of circumstances required to make the ROI successful. Namely, the operator must be operating an industrial process that is creating waste products that contain neutralizing ions. In addition, that operator must have a need to provide treated target water; either softened hard water or desalinated brackish water. If the circumstances are ideal for the technology, the operator is provided with cost benefits from the combined process. In order to provide a comparison of the combined processes with existing options available to the waste generator, a few of the elements that drive cost in the options are considered. The neutralizing cost of either the industrial waste or the spent purified acid can be determined by examining the cost per neutralizing equivalent using the raw material of $CaCO_3$. Assuming the cost for 2000 (kg) of $CaCO_3$ is approximately $200 (Suresh, 2007), the $/equivalent can be determined, which is provided in Equation 58.

$$2000\, kg\ of\ CaCO_3 \ * \ \frac{1\, mol\ of\ CaCO_3}{0.1001\, kg} * \frac{2\, eq\ of\ CO_3\, 2+}{1\, mol\ of\ CaCO_3} = 40{,}000\, eq\ per\ 2000\, kg$$

Equation 58. Cost per equivalent for neutralization

At $200/2000kg of $CaCO_3$, the cost per equivalent is $0.005/eq.

Table 2 provides the associated costs to treat pickling wastes (100,000 L) with residual acid concentrations.

pH	meq/L	H + Wt%	Cost to Neutralize 100K L (26K gal.)
-0.04	1096.5	4.00%	$ 548.2
0.00	1000.0	3.65%	$ 500.0
0.17	683.9	2.50%	$ 342.0
1.30	50.1	0.18%	$ 25.1
1.70	20.0	0.07%	$ 10.0
2.00	10.0	0.04%	$ 5.0
3.00	1.0	0.00%	$ 0.5

Note: The cost to neutralize is $0.005/eq based on $CaCO_3$ at $200/2000kg.

Table 2. Estimated cost to neutralize residual acid

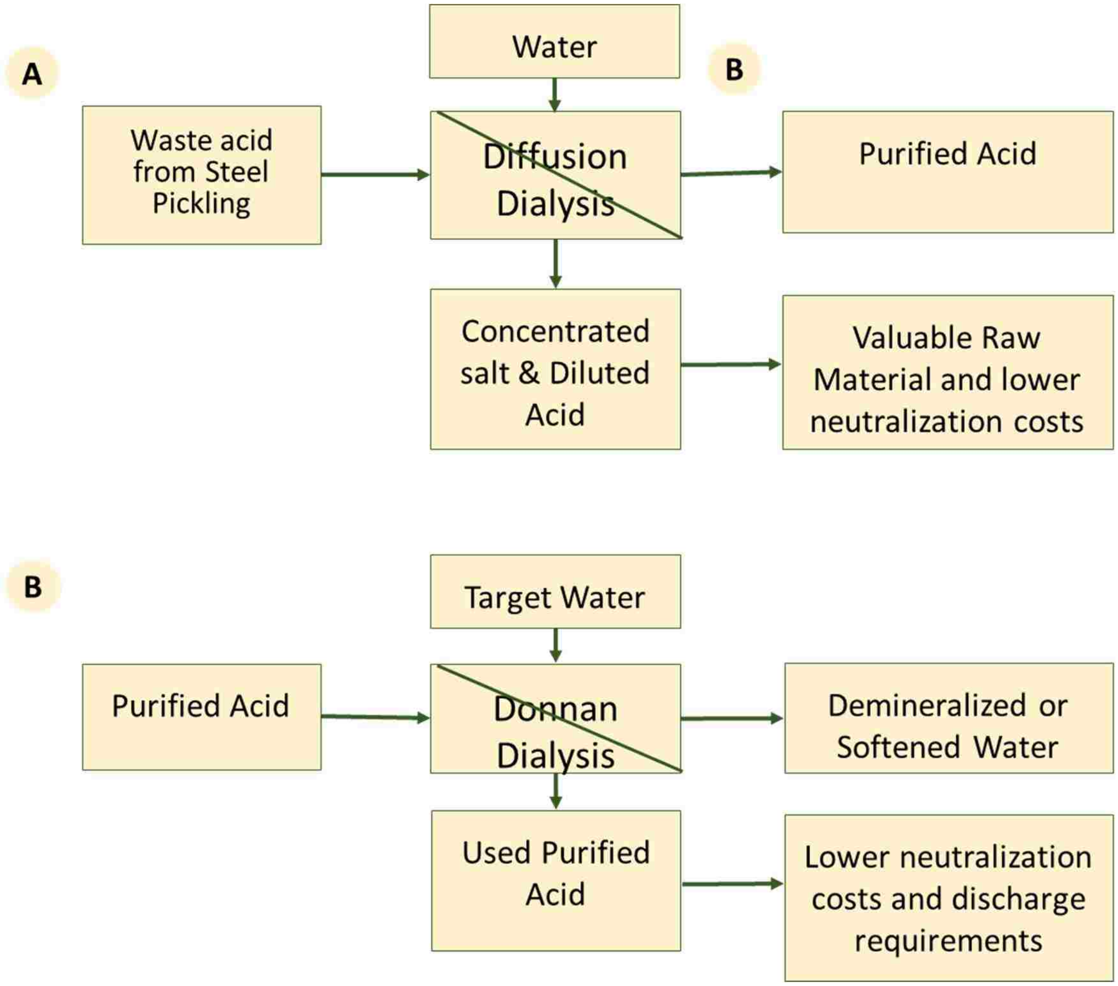


Figure 15. Proposed BAT combined solution; diffusion dialysis and Donnan dialysis

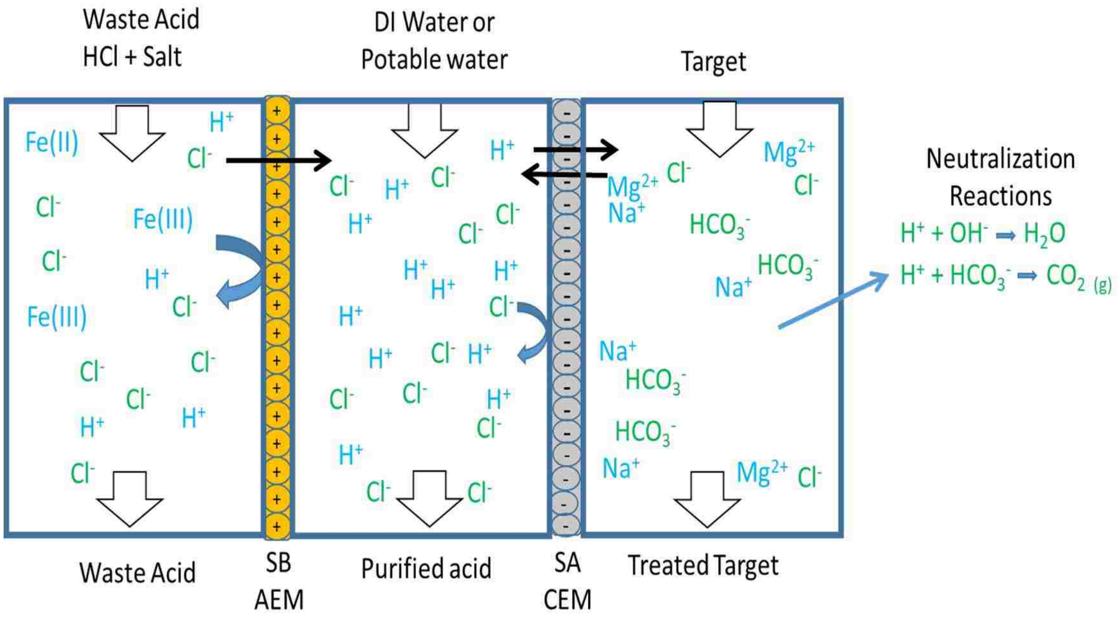


Figure 16. Proposed BAT combined solution; diffusion dialysis and Donnan dialysis

1.2.7 Iterative model of Donnan dialysis applied to a three-ion system

Determining equilibrium in chemical systems provides valuable insight to potential uses/treatments for said systems and the ability to predict equilibrium is greatly enhanced. As discussed previously, the two-ion system equilibrium is defined by Equation 29; however, for a three-ion system the endeavor becomes more complex. A three-ion system was developed and defined by 12 variables, two constants and three interacting Equations that is simplified with assumptions. These simplifications keep the separation factors and isotherms static throughout the operation of the Donnan dialysis process, which develops a system of Equations whereby an iterative process through Excel ("Goal Seek") can solve for the equilibrium condition (Microsoft Excel (2007)).

As discussed in Section 2.4 Donnan Dialysis, Donnan equilibrium is achieved by the three-ion system similar to a two-ion system although with more ion interactions and dependencies. In the three-ion system, the model is reliant on laws of electro-neutrality, the law of mass conservation, and the rule that ion exchangers operate on an equivalent mass exchange principle. An example of an Mg^{2+}, H^+, and Na^+ system is investigated to determine the equilibrium state as determined by Donnan equilibrium. The first step is to use Equation 20 to determine the isotherms for the ion pairs at the determined C_T's and membrane properties. For the starting conditions, the determination of the alphas is provided by Equation 42 and Table. Equation 43 is the membrane loading equation on the face of the membrane based on the system concentrations and alpha values. The model is simplified by an assumption that alpha and isotherm values remain static, as the focus is directed to achieving equilibrium in the membrane as the buffer capacity in the target chamber is consumed by the hydrogen ion through the neutralization reaction. Equilibrium is achieved when the membrane loadings related for each ion are equal. The system concentrations and membrane loadings for two conditions is provided in Table 4, at equilibrium and at maintaining a pH of 7 in the target chamber, which is the equilibrium loadings in the membrane shown in Table 5. Another example is shown in Figures 18 and 19, including the starting, finishing, and equilibrium equivalent fractions /membrane loadings for one of the experiments, which has a strong correlation of the model to the final equilibrium concentrations in the systems.

Equation 59 $$K_{AB}\frac{R}{C_T} = \frac{Y_A(1 - X_A)^2}{X_A(1 - Y_A)^2}$$

Equation 60 $$\alpha_{\frac{b}{d}} = \frac{Y_b X_d}{Y_d X_b}$$

Equation 61 $$Y_d = \frac{X_d}{X_d + \alpha_{\frac{b}{d}} X_b + \alpha_{\frac{c}{d}} X_c}$$

Ions/Reactor	[A] meq/L	[B] meq/L	X_A ratio	X_B ratio	Y Isotherm Value	Alpha
Mg^{2+}/H^+ Acid	7	28	0.20	0.80	0.85	22.7
Mg^{2+}/Na^+ Acid	7	10	0.41	0.59	0.9	12.9
Na^+/H^+ Acid	10	28	0.26	0.74	0.95	53.2
Mg^{2+}/H^+ Target	0.5	1.5	0.25	0.75	0.9	27.0
Mg^{2+}/Na^+ Target	0.5	5.5	0.08	0.92	0.8	44.0
Na^+/H^+ Target	5.5	1.5	0.79	0.21	0.99	27.0

Table 3. Determination of alpha for ion pair

Model simulations	$[Mg]_T$ (meq/L)	$[Na]_T$ (meq/L)	$[H]_T$ (meq/L)	$[Mg]_{WA}$ (meq/L)	$[Na]_{WA}$ (meq/L)	$[H]_{WA}$ (meq/L)
Start	9.4	25.3	0.0	0.0	0.0	0.0
Finish	6.7	23.5	0.0	0.8	3.7	1.20
Equilibrium	1.15	7.1	1.20	8.25	18.25	1.20
Target chamber at pH of 7	1.13	8.3	0.0	8.27	17.03	1.20

Table 4. Model output for speciation concentrations (aqueous) in target and waste acid chambers

Model simulations	X_{Mg}	X_{Na}	X_H	X_{Mg}	X_{Na}	X_H	Y_{Mg}	Y_{Na}	Y_H	Y_{Mg}	Y_{Na}	Y_H
Start	Target			Waste Acid			Target			Waste Acid		
Finish	0.22	0.78	0.00	0.14	0.65	0.21	0.93	0.07	0.00	0.70	0.26	0.03
Equilibrium	0.12	0.75	0.13	0.30	0.66	0.04	0.85	0.12	0.03	0.85	0.15	0.00
Target chamber at pH 7	0.12	0.88	0.00	0.31	0.64	0.05	0.86	0.14	0.00	0.86	0.14	0.00

Table 5. Iterative calculations from model to determine the equivalent fractions on the membrane

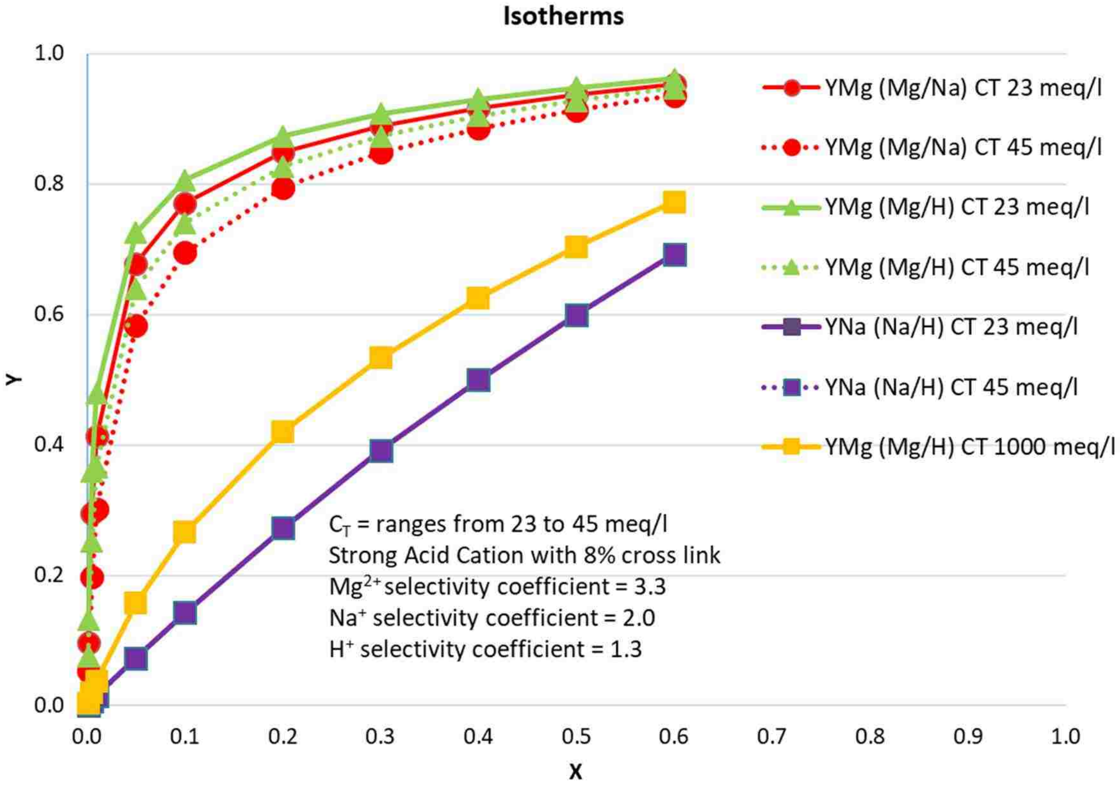


Figure 17. Isotherms for model determination

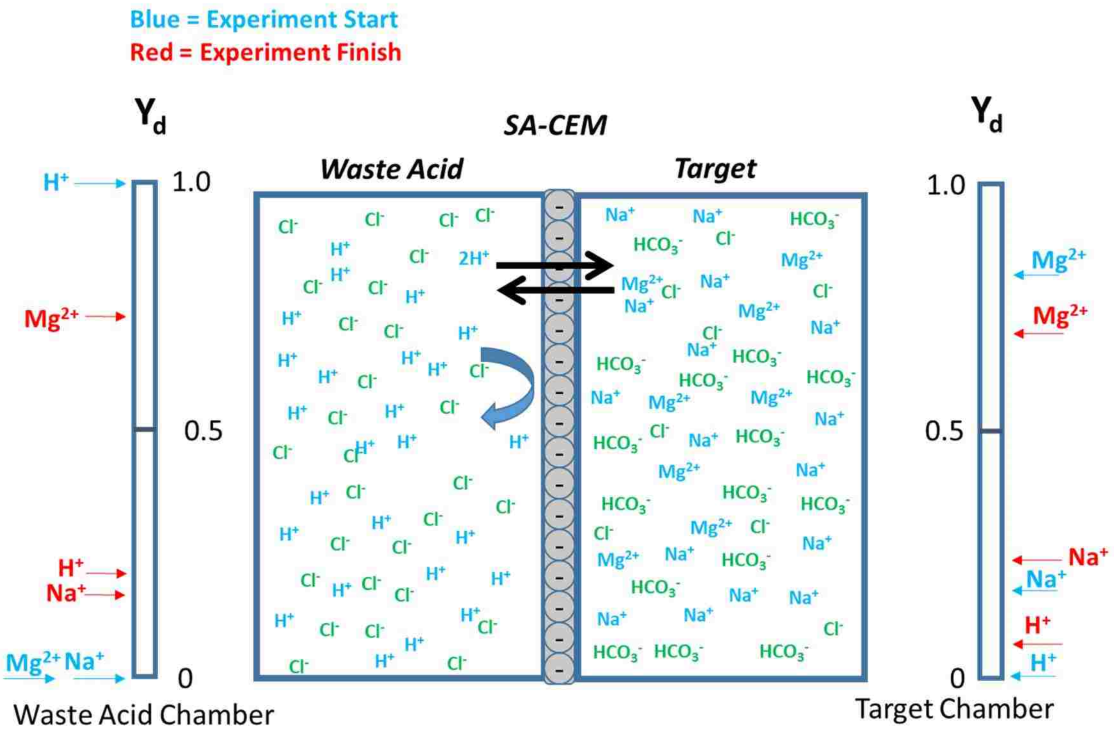


Figure 18. Membrane loadings at end of experiment

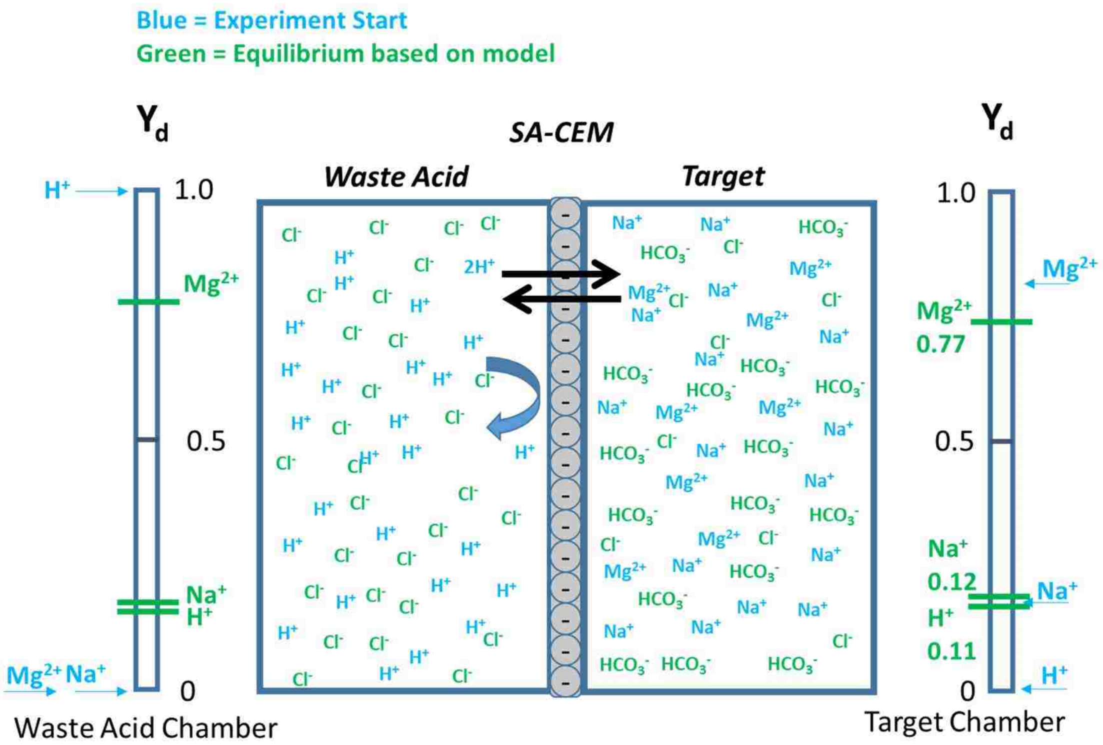


Figure 19. Membrane loadings at model prediction of membrane equilibrium

1.3 Material and Methods

1.3.1 Experimental membrane test set-up

The membrane test set up was made of Plexiglas with configuration options to create two or three chambers by placing membranes between the Plexiglas partitions. The set-up is shown in Figure 20 with each chamber volume based on stated dimensions for the chambers and/or combination of chambers. The test setup was used for all experiments including diffusion dialysis, Donnan dialysis, and the combination of both diffusion and Donnan dialysis experiments. The surface area of the membrane between the chambers was 95 cm^2. Each chamber was equipped with an outlet valve for an option for additional volume through an added chamber and to circulate/mix the chamber solution. The solutions used in all the experiments were synthetically prepared with chemicals purchased from Fisher Scientific and Sigma Chemicals (Reagent grade). Each of the solutions were prepared by measuring specific quantities of the compounds either in liquid or solid form and mixing with deionized water which was purified by reverse osmosis and activated carbon onsite in the lab. The following solutions were prepared for each respective experiment:

- Acid purification: Synthetic steel pickling solution (waste acid) and purified acid (target) is required for diffusion dialysis experiments. The synthetic steel pickling solution consisted of ferrous or ferric chloride and hydrochloric acid; the target solution contained deionized water. Experiment solution concentrations and volumes included:
    i. Experiment DI-1 Waste acid 4.0% HCl, 1.6Wt% $FeCl_2$ and volume of 1L; Target of deionized water volume of 1L.

    ii. Experiment DI-2 Waste acid 2.5% HCl, 13.5Wt% $FeCl_3$ and volume of 1L; Target of deionized water volume of 1L.

- Hard water softening: Donnan dialysis experiments required synthetic target solutions and purified acid solutions. The target solution (hard water) contained magnesium chloride, sodium bicarbonate and deionized water. The purified acid solution contained hydrochloric acid and deionized water. Experiment solution concentrations and volumes included:
    i. Experiment DOH-1; Waste acid of HCl 0.05M (pH ~ 1.3) at 0.78L; Target of $MgCl_2$ 9.2mM, $NaHCO_3$ 38mM at 0.41L
    ii. Experiment DOH-2; Waste acid of HCl 0.02M (pH ~ 1.65) at 0.78L; Target of $MgCl_2$ 9.2mM, $NaHCO_3$ 38mM at 0.41L
    iii. Experiment DOH-3; Waste acid of HCl 0.001M (pH ~ 3) at 0.78L; Target of $MgCl_2$ 9.2mM, $NaHCO_3$ 38mM at 0.41L
    iv. Experiment DOH-4; Waste acid of HCl 0.05M (pH ~ 1.3) at 0.78L; Target of $MgCl_2$ 9.2mM, $NaHCO_3$ 38mM at 0.41L
    v. Experiment DOH-5; Waste acid of HCl 0.02M (pH ~ 1.65) at 0.78L; Target of $MgCl_2$ 9.2mM, $NaHCO_3$ 38mM at 0.41L
    vi. Experiment DOH-6; Waste acid of HCl 0.001M (pH ~ 3) at 0.78L; Target of $MgCl_2$ 9.2mM, $NaHCO_3$ 38mM at 0.41L
    vii. Experiment DOH-7; Waste acid of HCl 0.01M (pH ~ 2.0) at 0.78L; Target of $MgCl_2$ 9.2mM, $NaHCO_3$ 38mM at 0.41L
- Demineralization: Donnan dialysis experiments with synthetic brackish water, purified acids and purified bases. The target solutions included brackish water

containing sodium chloride and deionized water. The purified acid solution contained hydrochloric acid and deionized water. The purified base solution contained sodium hydroxide or sodium bicarbonate and deionized water. Experiment solution concentrations and volumes included:

    i. Experiment DOD-1; Waste acid of HCl 0.05M (pH ~ 1.3) at 0.75L; Target of NaCl 0.034M (0.2%W/V) at 0.41L; Waste base of $NaHCO_3$ 0.5M at 0.75L
    ii. Experiment DOD-2; Waste acid of HCl 0.05M (pH ~ 1.3) at 0.75L; Target of NaCl 0.034M (0.2%W/V) at 0.41L; Waste base of NaOH 0.046M at 0.75L

- Combined acid purification and hard water softening including diffusion and Donnan dialysis used pickling acid solution; industrial waste Fe(III)Cl_3 10%W/V and HCl 2.5% W/V, purified acid solution that started as deionized water, Target solution (hard water) containing magnesium chloride and sodium bicarbonate. Experiment solution concentrations and volumes included:
    i. Experiment CDIDO-1; Industrial waste Fe(III)Cl_3 10% W/V + HCl 2.5% W/V at .78L; Purified acid as deionized water at .44L, Target of $MgCl_2$ 9.2mM, $NaHCO_3$ 38mM at 0.8L
    ii. Experiment CDIDO-2; Industrial waste Fe(III)Cl_3 10% W/V + HCl 2.5% W/V at .78L; Purified acid as deionized water at 10.0L, Target of $MgCl_2$ 9.2mM, $NaHCO_3$ 38mM at 0.78L

1.3.2 Membranes used in experiments.

1. All membranes used in the experiments were Neosepta membranes from Astom Inc., with the membrane characteristics shown in Table 6. There were three types of homogeneous membranes used.
    a. Strong Acid Cation standard (SA-CEM-standard)
    b. Strong Acid Cation mono-selective (SA-CEM-mono-selective)
    c. Strong Base Anion mono-selective (SB-AEM-mono-selective)
2. The membranes were conditioned before each experiment.
    a. Strong Acid Cation Exchange Membranes (SA-CEMs) were conditioned in the sodium form by filling the contact chambers with a sodium chloride solution of 1M to ensure the membrane interfaced the solution. This solution remained in contact with the membranes for 30 minutes and was repeated three times for each experiment. The chambers were then washed with deionized water to remove residual sodium in solution remaining on the membrane.
    b. Strong Base Anion Exchange Membranes (SB-AEMs) were conditioned in chloride form by filling the contact chambers with a sodium chloride solution of 1M to ensure the membrane interfaced the solution. This solution remained in contact with the membranes for 30 minutes and was repeated three times for each experiment. The chambers were then washed with deionized water to remove residual chloride in any solution remaining on the membrane.

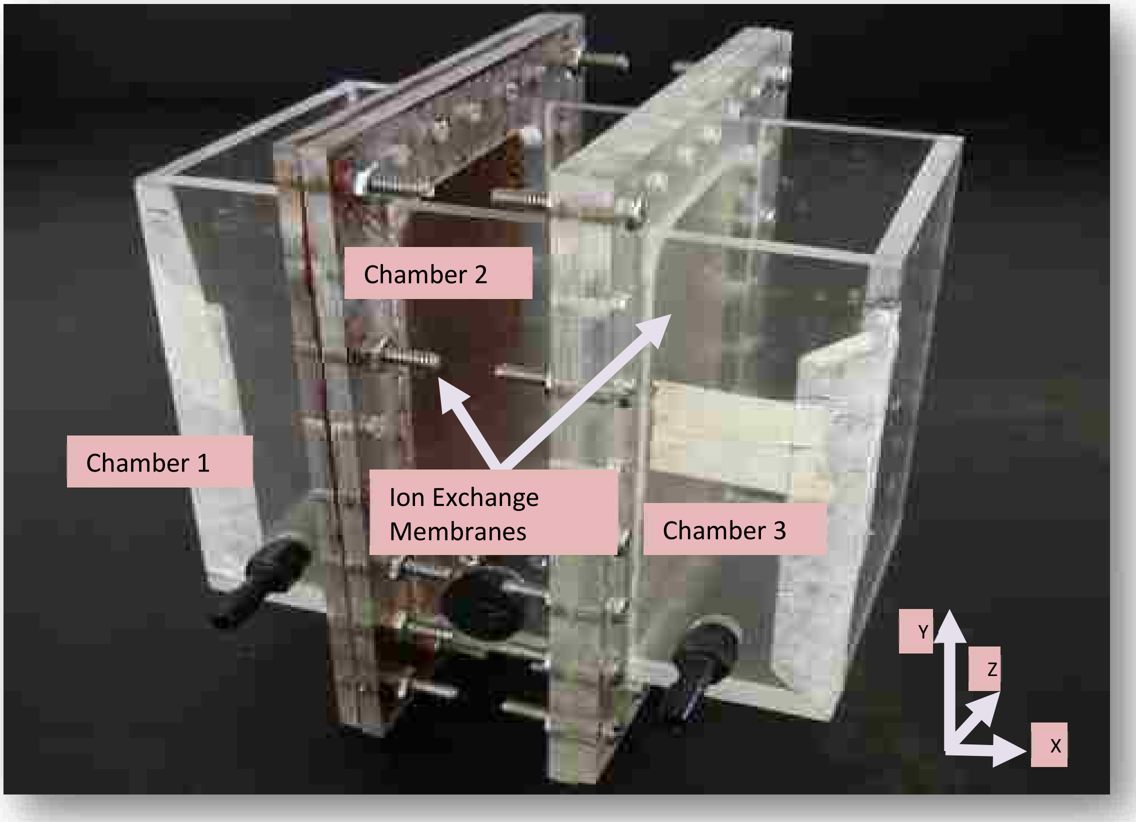


Figure 20. Membrane test set-up.

Neosepta - Astom Inc.	**SA-CEM (Standard)**	**SA-CEM (Mono-selective)**	**SB-AEM (Mono-selective)**
Electric resistance (ohm*cm^2)	3	1.8	3.8
Thickness (mm)	0.17	0.15	0.13
pH, Temp C° range	0-10, <40	0-10, <40	0-8, <40
Functional Group	$-SO_3^-$	$-SO_3^-$	$-N(CH_3)_3^+$
Exchange Capacity (meq/g)	2.0 – 2.5	2.0 – 2.5	1.8 – 2.2
Matrix	Styrene-DVB	Styrene-DVB	Styrene-DVB
Experiments	Softening/ Demineralization	Softening	Demineralization/ Acid purification

Table 6. Membrane properties

1.3.3 Experimental procedures

1.3.3.1 Diffusion dialysis, acid purification of the synthetic industrial waste solution

Two different runs of the diffusion dialysis experiments were performed using a different combination of synthetic solutions and different experiment protocols. The solution used in the experiments were reported in Section 3.1.

The protocol for the first experiment was intended to determine the amount of purified acid at an approximate pH of 2.0 that could be extracted from the synthetic solution over a 24-hour time-frame. Therefore, the target chamber was removed and weighed to determine the amount of solution captured. The pH was recorded at the time of sample extraction and the chloride concentration measured during the sample analysis process. New deionized water was placed in the target chamber immediately following the extraction of the purified acid. The process took place approximately every 24 hours (actual times recorded).

The protocol for the second experiment was intended to determine the amount of purified acid that could be accumulated in the target chamber over the course of the experiment. Therefore, the target chamber remained static through the experiment with only samples (10 mL) being removed on a set frequency. The pH was recorded at the time of sample extraction and the chloride concentration measured during the sample analysis process.

- Purified acid [HCl] (see section 3.1 for concentrations)
    - Experiment DI-1
    - Experiment DI-2
- Target; deionized water and well water
- Membrane; SB-AEM (mono-selective).
- Operation:

    - Experiment DI-1 target chamber replaced every 24 hours through 300 hours. No mixing; Samples drawn from each target chamber.
    - Experiment DI-2 maintained target purified acid over duration of experiment in a batch reactor; no mixing. Samples drawn at 0, 10, 24, 62, 98 hours.
    - Figures 21 and 22 show examples of experiments and test set.

1.3.3.2 Donnan dialysis; water softening

Six different runs of Donnan dialysis water softening experiments were performed using different combinations of purified acid (acid concentrations) and membranes. The target water remained static for all experiments. The membranes were conditioned with NaCl as described in Section 3.2.2. A baseline experiment to determine the impacts of the sodium resident on the membrane at the onset of the experiment was not performed, since the membrane in these experiments function as an ion "gate keeper" and not "removal/retention" of ions. The weight of the membrane and the capacity of the membrane provided in Table 6 were used to account for additional sodium in the system in the mass balance calculations. The experiments ran as batch reactors with a circulation rate of both chambers at 10mL/sec.

- Waste acid [HCl] (see section 3.1 for concentrations):
    - Experiments DOH-1, DOH-2, DOH-3; with mono selective SA-CEM membrane.
    - Experiments DOH-4, DOH-5, DOH-6; with standard SA-CEM membrane.
- Target; $NaHCO_3$, $MgCl_2$ solution, (see section 3.1 for concentrations)
- Operation

        - Solution placed in chambers with circulation pumps operating.
        - Samples taken every 0, 30, 60, 120, 240 minutes.
        - pH and conductivity were measured at determined time frames in the target chamber.

1.3.3.3 Donnan dialysis, water softening with multiple batches.

One run of Donnan dialysis water softening with multiple batches of purified acid was performed. The purified acid at pH of 2.0 was replaced every 60 minutes and the target water remained static for all experiments. The membranes were conditioned with NaCl as described in Section 3.2.2. A baseline experiment to determine the impacts of the sodium resident on the membrane at the onset of the experiment was not performed, since the membrane in these experiments function as an ion "gate keeper" and not "removal/retention" of ions. The weight of the membrane and the capacity of the membrane provide in Table 6 were used to account for additional sodium in the system in the mass balance calculations. The experiments ran as batch reactors with a circulation rate of both chambers at 10mL/sec.

- Waste acid [HCl], (see Section 3.1 for concentrations):
    - Experiment DOH-7; with SA-CEM-standard membrane
- Target; $NaHCO_3$, $MgCl_2$ solution, (see Section 3.1 for concentrations):
- Operation
    - Solution placed in chambers with circulation pumps operating.
    - Waste acid replaced every 60 minutes with samples taken at the end of every batch run
    - Conductivity and pH were measured at determined time frames in the target chamber.

1.3.3.4 Donnan dialysis, demineralization.

Three runs of Donnan dialysis brackish water demineralization were performed using a purified acid at pH of 2.0 and different solution speciation and concentrations for the purified acid (see Section 3.1). The target water remained static for all experiments. The membranes were conditioned with NaCl as described in Section 3.2.2. A baseline experiment to determine the impacts of the sodium resident on the membrane at the onset of the experiment was not performed, since the membrane in these experiments function as an ion “gate keeper” and not “removal/retention” of ions. The weight of the membrane and the capacity of the membrane provided in Table 6 were used to account for additional sodium in the system in the mass balance calculations. The same logic was applied to chloride resident on the SB-AEM. The experiments ran as batch reactors with a circulation rate of both chambers at 10mL/sec.

- Waste acid [HCl], (see Section 3.1 for concentrations):
- Target; [NaCl] 0.034M
- Waste base;
  - Experiment DOD-1; $NaHCO_3$ at 0.5M
  - Experiment DOD-2; NaOH at 0.046M
- Membrane; SA-CEM (standard) and SB-AEM (mono-selective).
- Operation
  - Solution placed in chambers with circulation pumps operating.
  - Samples taken every 0, 30, 60, 120, 240 minutes.
  - Conductivity and pH were measured at determined time frames in the target chamber.

1.3.3.5 Combined diffusion and Donnan dialysis, water softening

Two runs of the combined diffusion and Donnan dialysis water softening experiment were performed using a synthetic industrial waste, deionized water (purified acid) and target with concentrations in Section 3.1. The first experiment was operated with a purified acid chamber of 1L *vs*. the second experiment that included an additional reservoir for the purified acid chamber, thereby increasing the volume to 10L. The synthetic industrial waste and target water remained static for all experiments. The membranes were conditioned with NaCl as described in Section 3.2.2. A baseline experiment to determine the impacts of the sodium resident on the membrane at the onset of the experiment was not performed, since the membrane in these experiments function as an ion "gate keeper" and not "removal/retention" of ions. The weight of the membrane and the capacity of the membrane provided in Table 6 were used to account for additional sodium in the system in the mass balance calculations. The same logic was applied to chloride resident on the SB-AEM. The experiments ran as batch reactors with a circulation rate of both chambers at 10mL/sec.

- Waste acid 2.5% HCl and 13.5% Fe(III)
- Target (purified acid); deionized
- Target (Water treatment); $NaHCO_3$, $MgCl_2$
- Membrane; SB-AEM (mono-selective). Between the waste acid and purified acid cell.
- Membrane; SA-CEM (standard). Between the purified acid and target treated water cell.
- Operation
    - Solution placed in chambers with circulation pumps operating.

- Samples taken every 0, 30, 60, 120, 240 minutes.
- Conductivity and pH were measured at determined time frames in the target chamber.

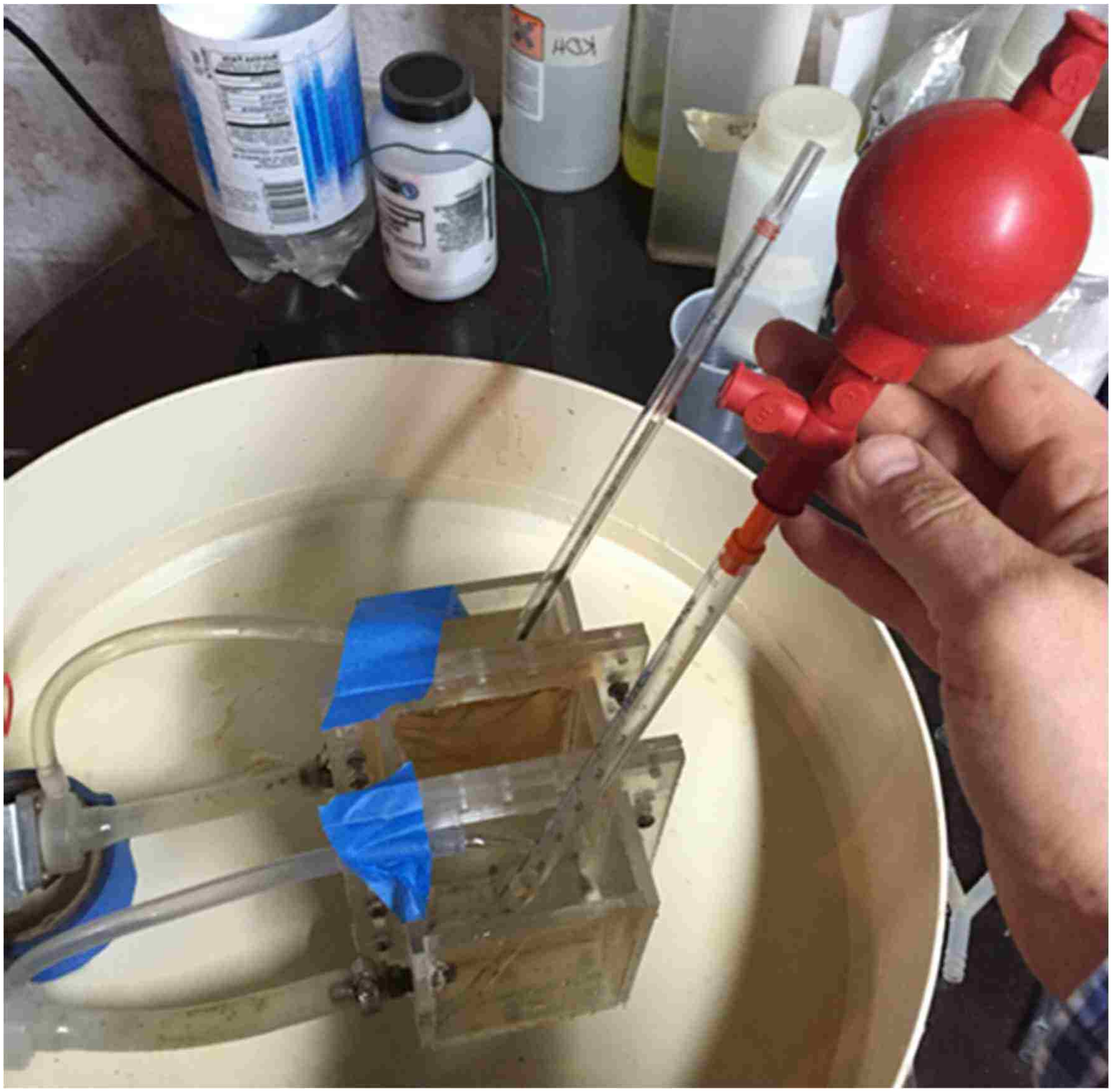


Figure 21. Experimental set up for ion exchange membrane experiments

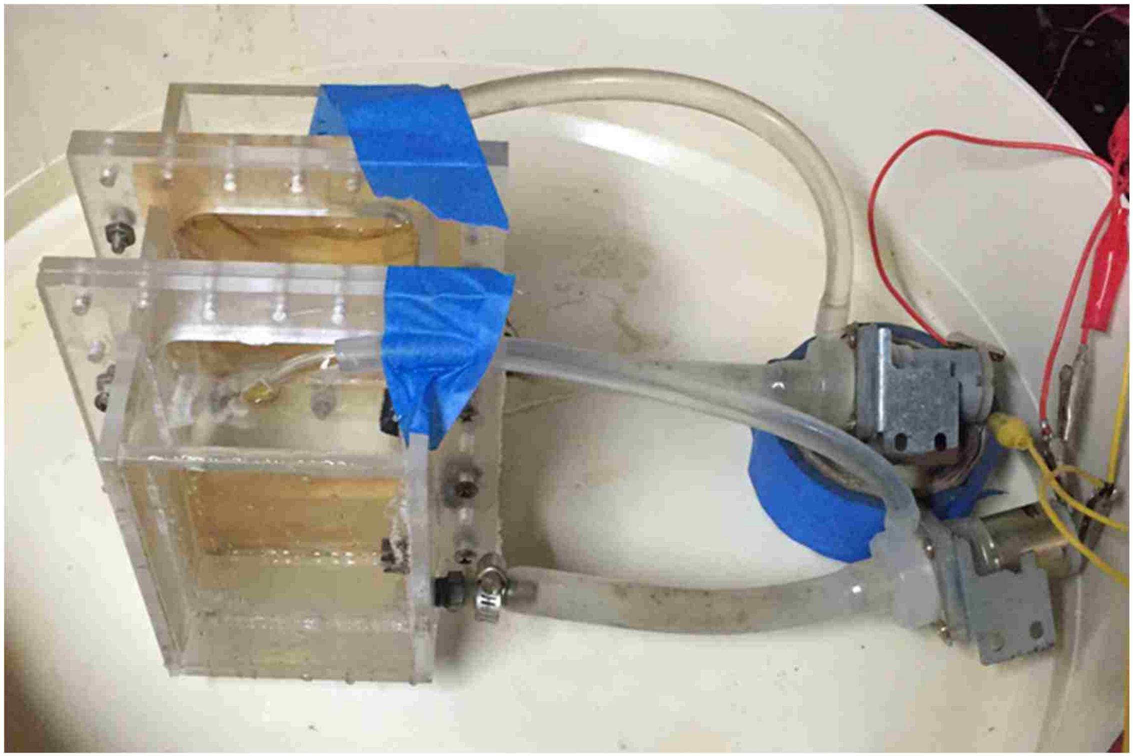


Figure 22. Experimental set up for ion exchange membrane experiments

1.3.4 Analytical Techniques

The analytical techniques employed in this dissertation research used a combination of real-time data acquisition and post experiment sample analysis. The following equipment was used for these analyses.

- Atomic Absorption spectrometer was used to measure total aqueous concentrations of iron, magnesium and sodium; (Perkin Elmer Flame Atomic Absorption Spectrometer: Model AA100). Five-point calibration curves were prepared from primary standards (Ricca Chemical) and for all analyses, an acetylene/air flame was used. In the case of samples exceeding the concentrations set in the five-point calibration curve, the sample was re-prepared from the source with appropriate dilution.

- Dionex Ion Chromatograph (Model 45001) was used to analyze chloride ions. Analysis was performed using chromatography column AS10 and a conductivity detector. Based on the manufacturer recommendations, a 9.0 mM Na_2CO_3 buffer was used as the eluent at a flow rate of 1.0 mL/min
- Hach 2444300 Alkalinity Drop Test Kit was used to measure the alkalinity.
- Fisher Scientific Accumet pH meter 900 was used to measure pH.
- Accumet conductivity meter (Model#AP75) was used to measure conductivity.
- NOTE: All experiments were conducted at ambient temperature and no significant differences in temperature were recorded between the chamber solutions. The relative humidity was maintained at 60%.

1.4 Results

1.4.1 Diffusion dialysis results.

Experiment DI-1 and DI-2 were conducted as batch reactors with waste acid and purified acid cells separated by Strong Base Anion Exchange Membranes (SB-AEM – mono-selective). In experiment DI-1, the waste acid cell remained static through the duration of the experiment, while the purified acid chamber was replaced with deionized water every 24 hours. The accumulated milliequivalents of H^+ and Fe(II) are shown in Figure 23. As shown in Table 7, the flux rates are a consistent value for H^+ of 1.77 ($meq*m^{-2}*min^{-1}$) over 0-10 hours and 10-100 hours, while for Fe(II) the flux decreased from 0.00054 to 0.00041 ($meq*m^{-2}*min^{-1}$) from the first period of 0-10 hours to 10-100 hours. After 130 hours, there was an accumulated volume of 118 meq of H^+ and 0.03 meq of Fe(II). In experiment DI-2, the waste acid cell and the target cell remained static through the duration of the experiment with samples being removed from both chambers on a set frequency. The accumulated milliequivalents of H^+ and Fe(III) is shown in figure 24, with the flux of H^+ at 3.96 ($meq * m^{-2} * min^{-1}$) and Fe(III) at 0.0039 ($meq * m^{-2} * min^{-1}$) and corresponding mass transfer coefficients of $2.7x10^{-5}$ ($cm\ s^{-1}$) for H^+ and $4.6x10^{-9}$ ($cm\ s^{-1}$) for Fe(III). After 100 hours, there was an accumulated volume of 220 meq of H^+ and 0.5 meq of Fe(III).

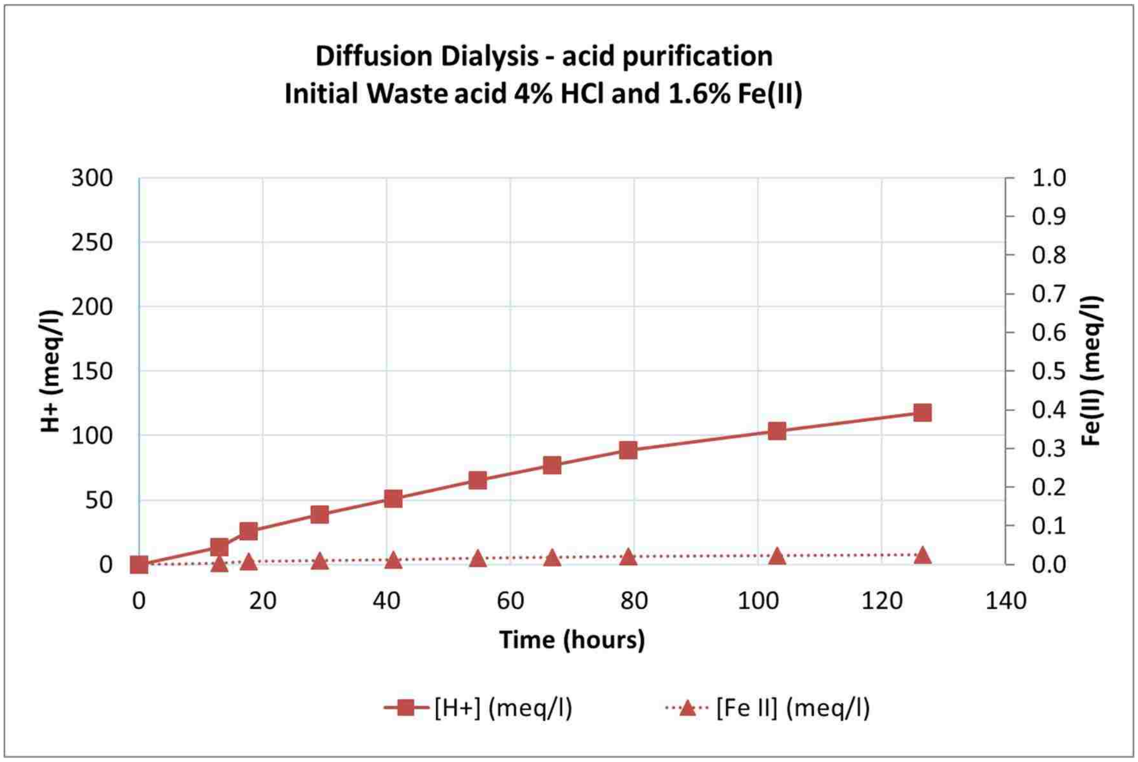


Figure 23. Experiment DI-1, Purified acid cell ion [x] vs. time; Initial pickle waste of 4% HCl and 1.6% Fe(II)

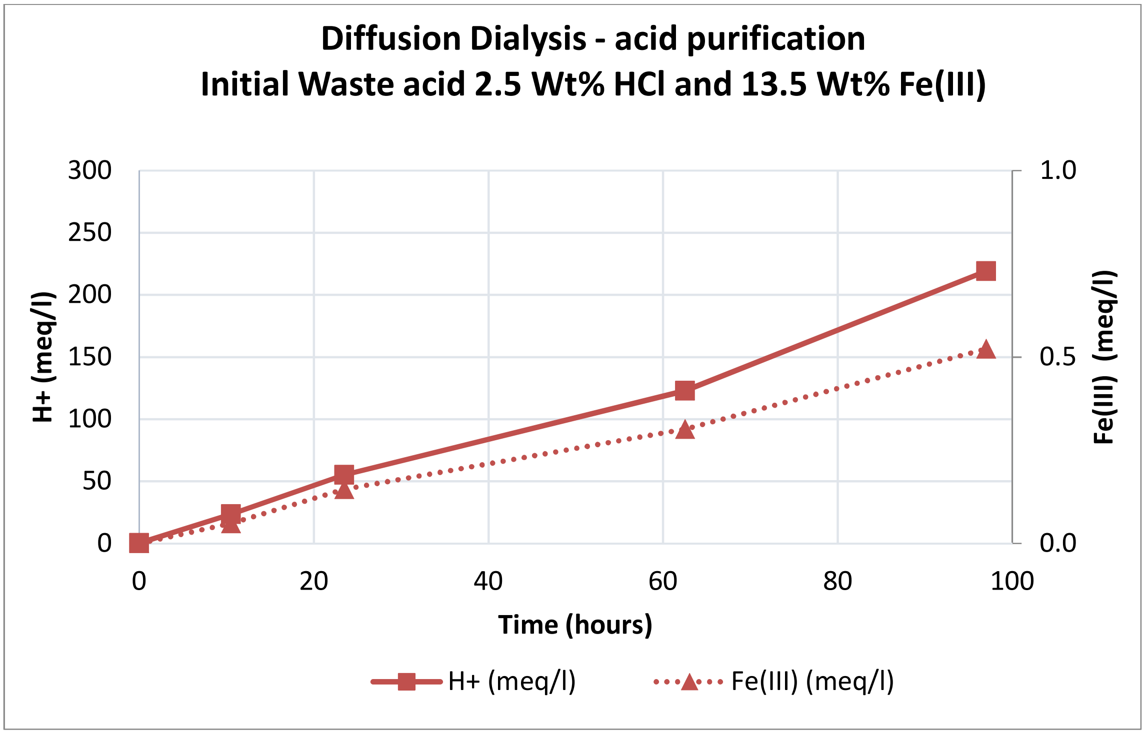


Figure 24. Experiment DI-2, Purified acid cell ion [x] vs. time; Initial pickle waste of 2.5% HCl and 13.5% Fe(III)

Flux rates	H^+		Fe(II)		Fe(III)	
Exp.	(0 - 10 hr)	(10 - 100 hr)	(0 - 10 hr)	(10 - 100hr)	(0 - 10 hr)	(10 - 100hr)
DI-1	1.77	1.77	0.00054	0.00041	N/A	N/A
DI-2	3.90	3.96	N/A	N/A	0.0089	0.0039

Note: Flux units (meq * m^{-2} * min^{-1})

Table 7. Flux rates for combined diffusion and Donnan dialysis experiment

1.4.2 Donnan dialysis results.

1.4.2.1 Donnan dialysis of water softening.

Experiments DOH-1 through DOH-6 were conducted as batch reactors with the purified waste acid and target cells separated by SA-CEM membranes. The results for the target cell ion concentrations as a function of time are shown in Figures 25 through Figure 30.

The flux and removal percentages for the experiments are shown in Table 8 and Table 9, respectively. The experiments were conducted for pH values of 1.3, 1.65 and 3.0 for the purified waste acid with two types of CEMs; standard and mono-selective. Values for Na^+, Mg^{2+}, Cl^- and alkalinity were measured for both the purified waste acid and the target cells.

Experiment DOH-7 was conducted as a batch reactor with the target water static through the duration of the experiment. The purified acid chamber was replaced with stock purified acid every 60 minutes. The flux for Mg^{2+} and Na^+ were recorded for each batch as shown in Table 10. The results for the target ion concentrations as a function of time are shown in Figures 31; the pH and conductivity of the target cell as a function of time are shown in Figure 32. The ion removal percentages after each batch of purified acid are provided in Table 11. The pH of the target remained between 6~7 through the experiment until the alkalinity was depleted. The conductivity reduced over time as the H^+, OH^-, and HCO_3^- ions react as part of the neutralization reaction into H_2O and CO_2 (aq).

The determination of the diffusivity coefficients for DOH-6 were performed with results of -2.1E-08, -1.2E-07, -7.3E-08, and -5.6E-08 (m^2*sec^{-1}) over 0-30 mins, 30-60 mins, 60-120 mins, and 120-240 mins respectively. The results are consistent with diffusivity coefficients found in the literature (Prakash 2004).

Flux rates		Mg $^{2+}$		Na $^{+}$	
Experiment	pH initial	0 – 1 hr	1 – 4 hr	0 – 1 hr	0 – 4 hr
DOH-1	1.3	2.1	0.1	5.0	3.5
DOH-2	1.7	1.9	0.0	1.6	0.7
DOH-3	3.0	1.0	0.0	0.0	0.0
DOH-4	1.3	7.5	1.7	9.4	2.8
DOH-5	1.7	6.6	1.1	14.4	1.0
DOH-6	3.0	1.2	0.9	2.8	0.1

Note: Flux units (meq * m^{-2} * min^{-1})

Table 8. Flux rates for Donnan dialysis – hard water softening

Ion % removal		Mg $^{2+}$	Na $^{+}$
Experiment	pH initial	% removed	% removed
DOH-1	1.3	18.3%	57.1%
DOH-2	1.7	14.3%	13.8%
DOH-3	3.0	7.7%	0.1%
DOH-4	1.3	96.4%	65.5%
DOH-5	1.7	75.6%	63.5%
DOH-6	3.0	30.3%	11.0%

Table 9. Percentage removal of target ions from target chamber

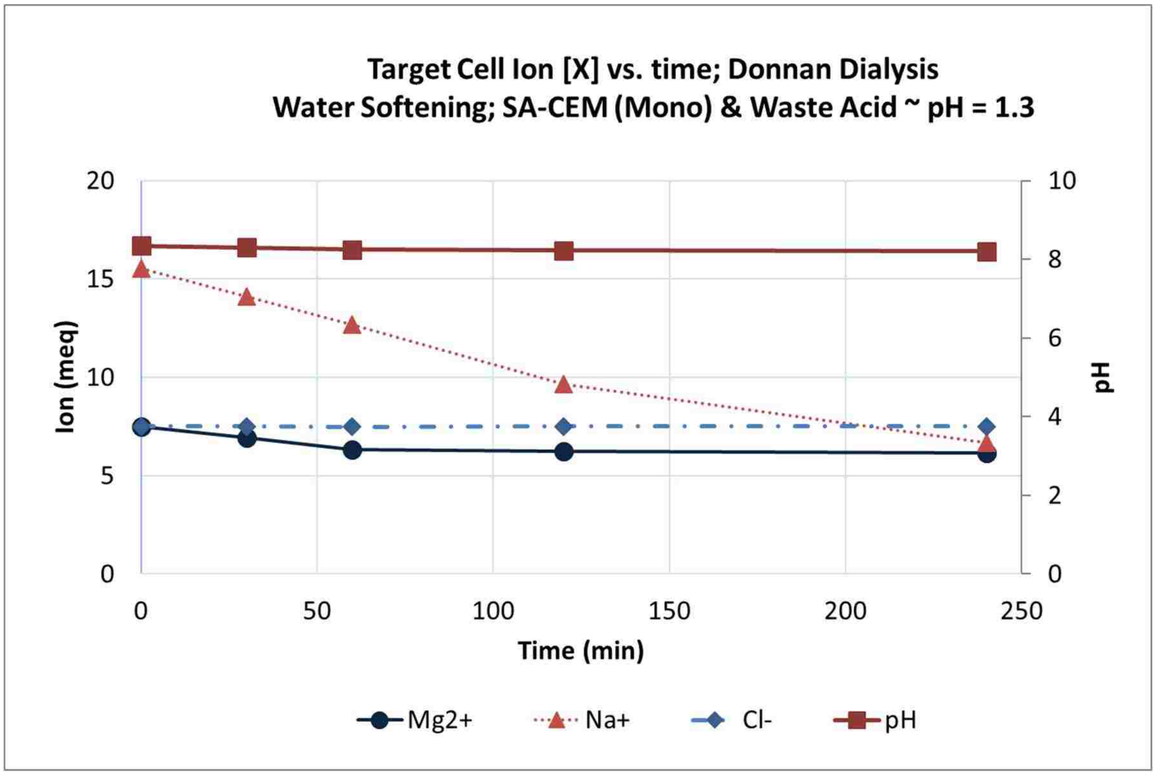


Figure 25. Experiment DOH-1. Target cell ion [x] *vs.* time for Donnan dialysis water softening; SA-CEM (Mono-selective), waste acid 0.18% HCl ~ pH 1.3

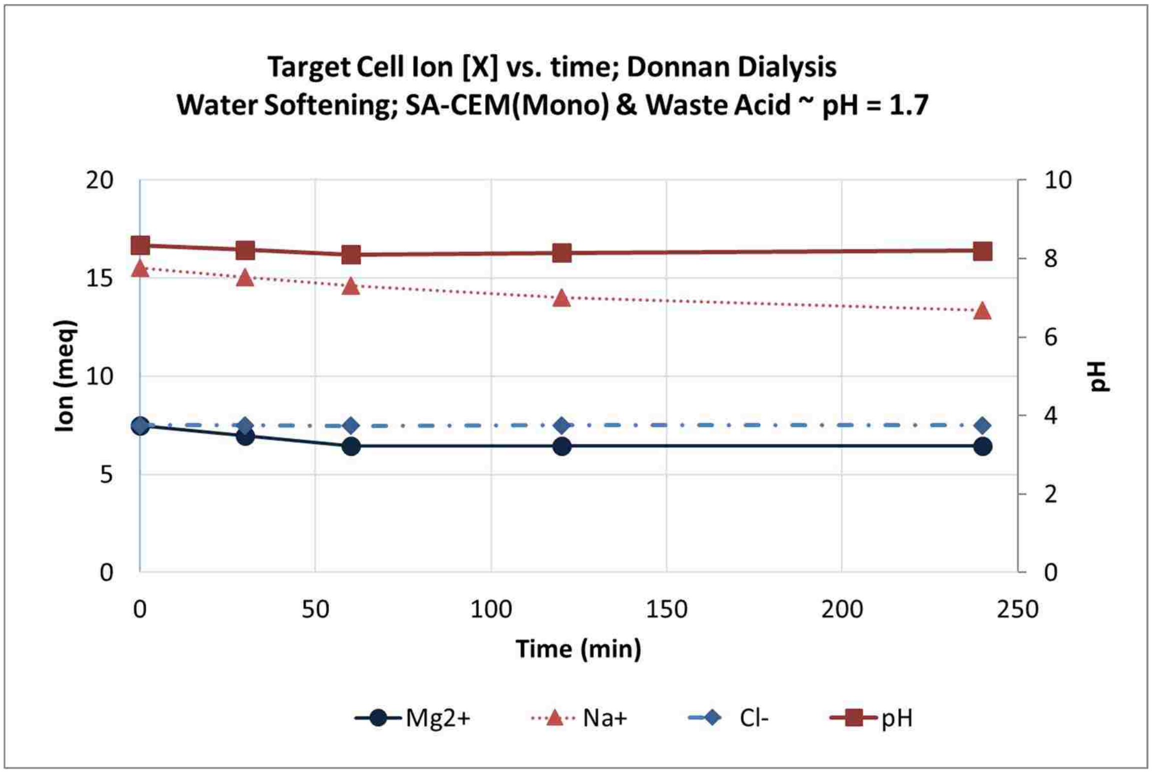


Figure 26. Experiment DOH-2. Target cell ion [x] *vs.* time for Donnan dialysis water softening; SA-CEM (Mono-selective), waste acid 0.073% HCl ~ pH 1.7

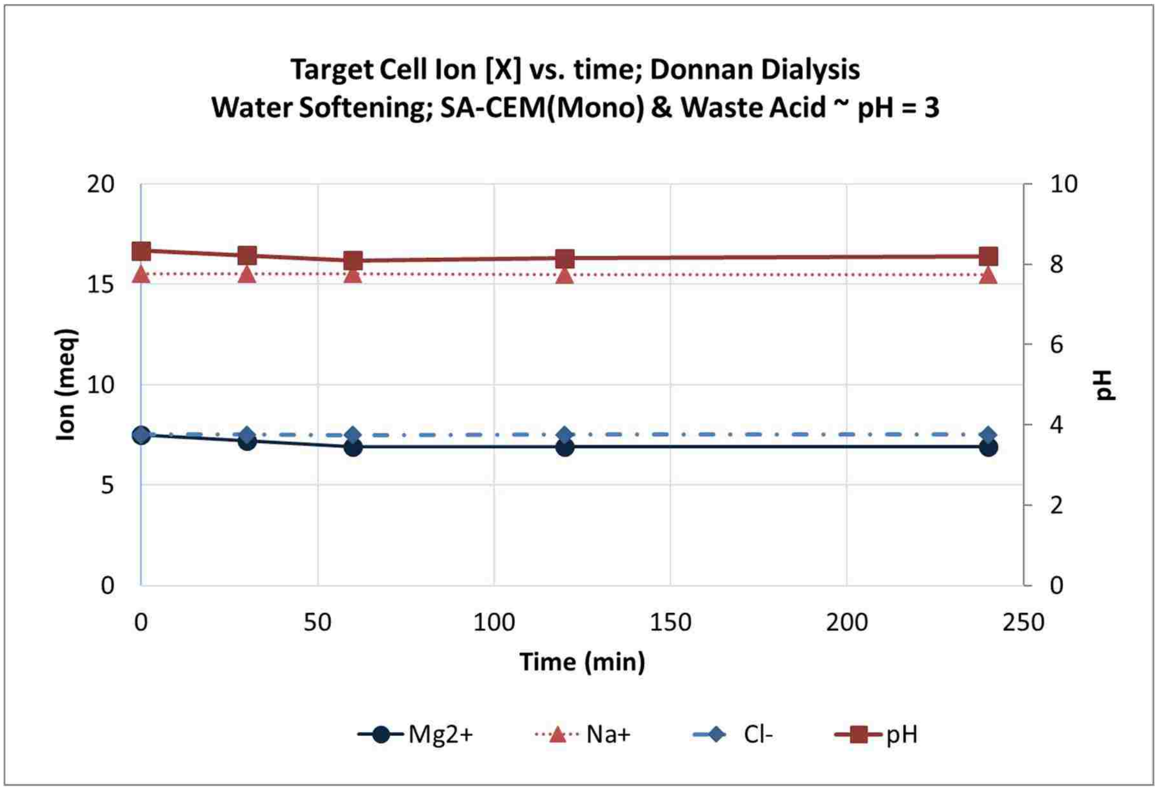


Figure 27. Experiment DOH-3. Target cell ion [x] *vs*. time for Donnan dialysis water softening; SA-CEM (Mono-selective), waste acid 0.0036% HCl ~ pH 3.0

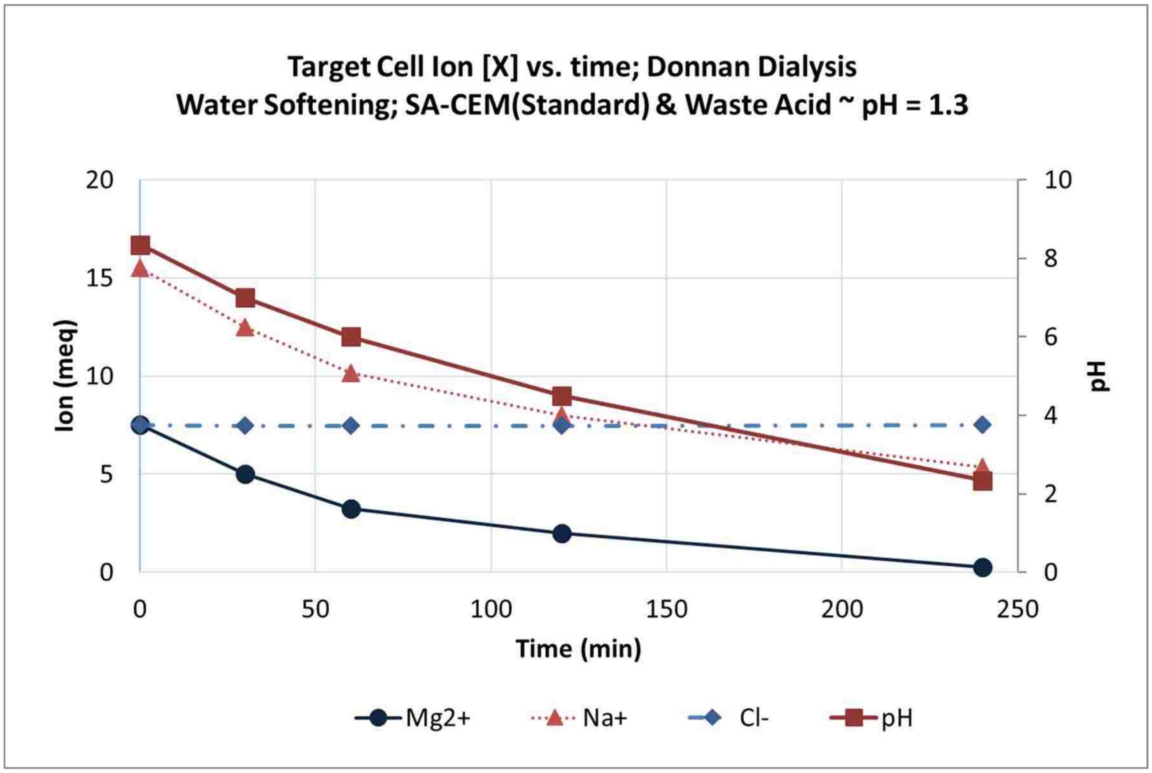


Figure 28. Experiment DOH-4. Target cell ion [x] *vs*. time for Donnan dialysis water softening; SA-CEM (Standard), waste acid 0.18% HCl ~ pH 1.3

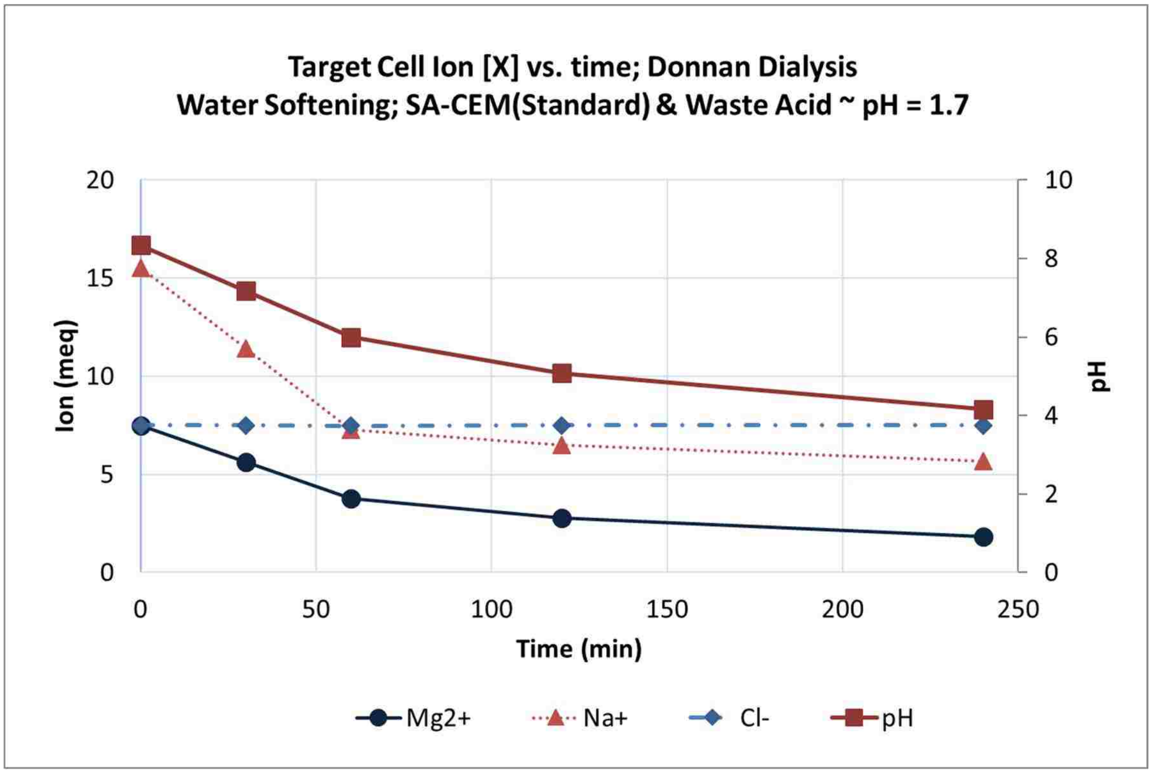


Figure 29. Experiment DOH-5. Target cell ion [x] *vs*. time for Donnan dialysis water softening; SA-CEM (Standard), waste acid 0.073% HCl ~ pH 1.7

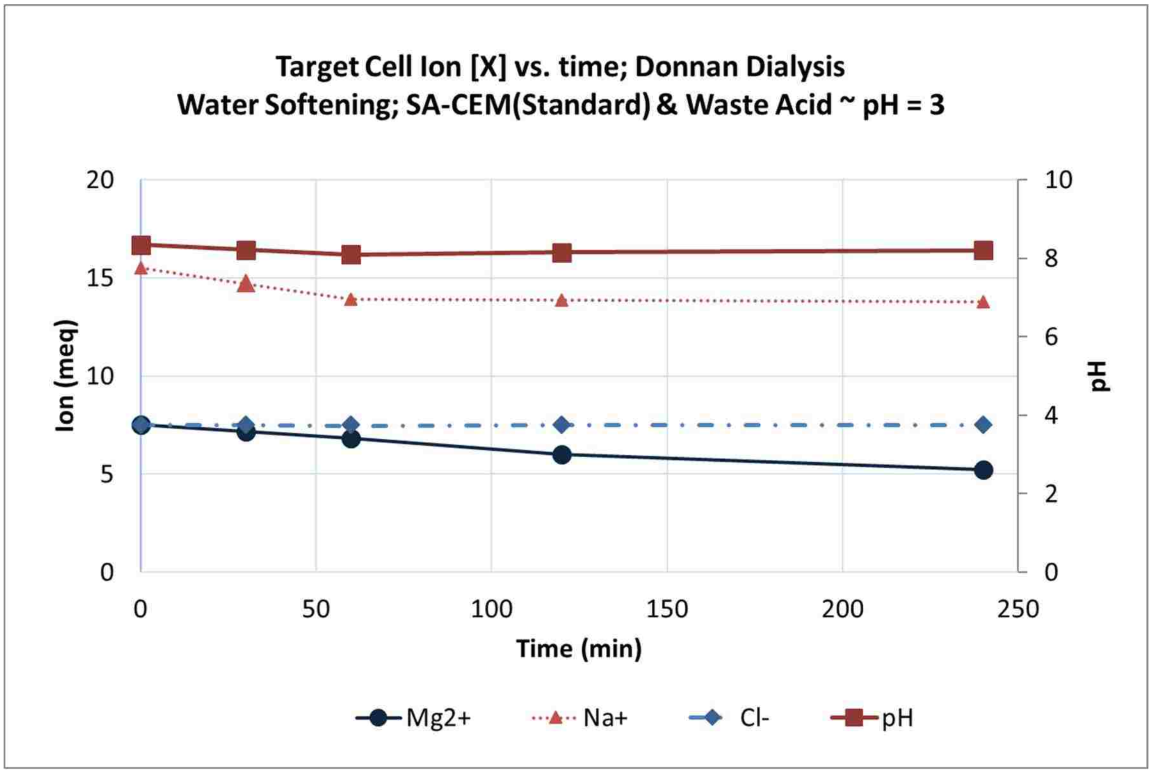


Figure 30. Experiment DOH-6. Target cell ion [x] *vs*. time for Donnan dialysis water softening; SA-CEM (Standard), waste acid 0.0036% HCl ~ pH 3.0

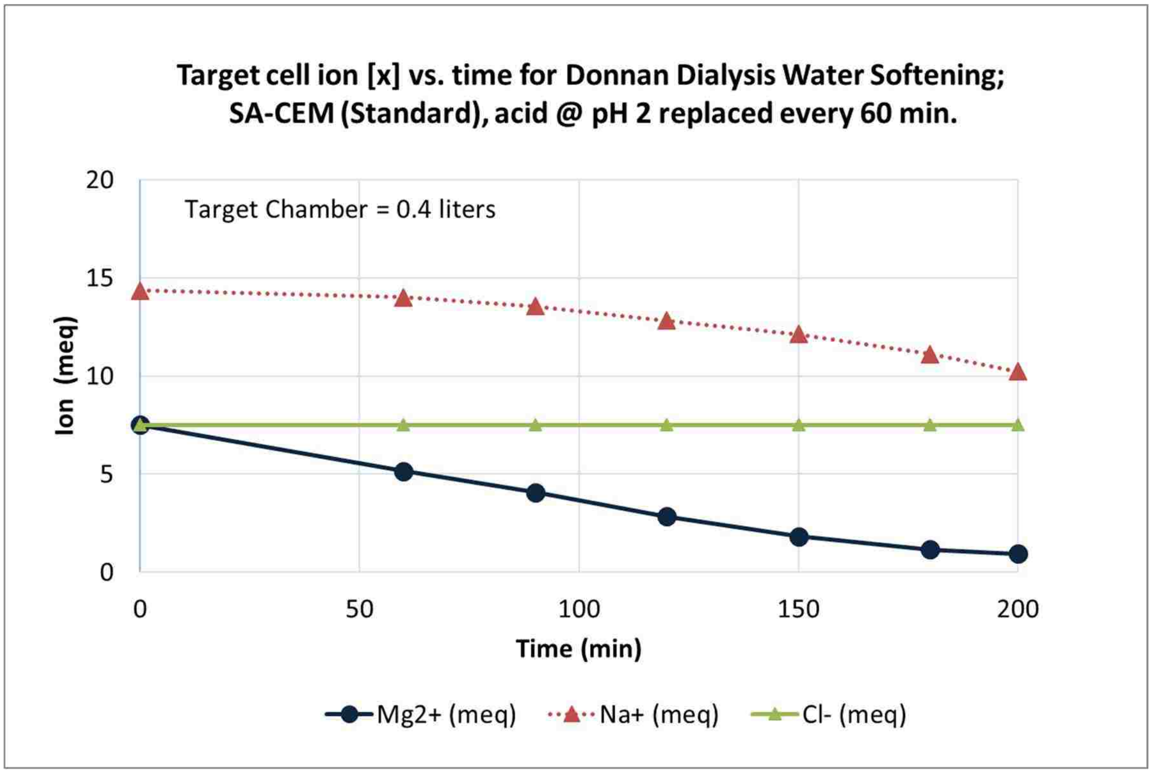


Figure 31. Experiment DOH-7. Target cell ion [x] *vs*. time for Donnan dialysis water softening; SA-CEM (Standard); Waste acid replaced every 60 minutes

Flux Rates	Mg^{2+}	Na+
Exp.DOH-7	(0 - 1 hr)	(0 - 1 hr)
Batch 1	4.10	.58
Batch 2	4.04	2.08
Batch 3	2.95	3.00
Batch 4	1.17	4.70

Note: Flux units (meq * m^{-2} * min^{-1})

Table 10. Flux rates for combined diffusion and Donnan dialysis experiment

Experiment DOH-7	Mg^{2+} % removed	Na^{+} % removed
Batch 1	31.2%	2.3%
Batch 2	61.9%	10.6%
Batch 3	84.3%	22.5%
Batch 4	87.2%	28.7%

Table 11. Experiment DOH-7. Percentage removal of key ions by batch

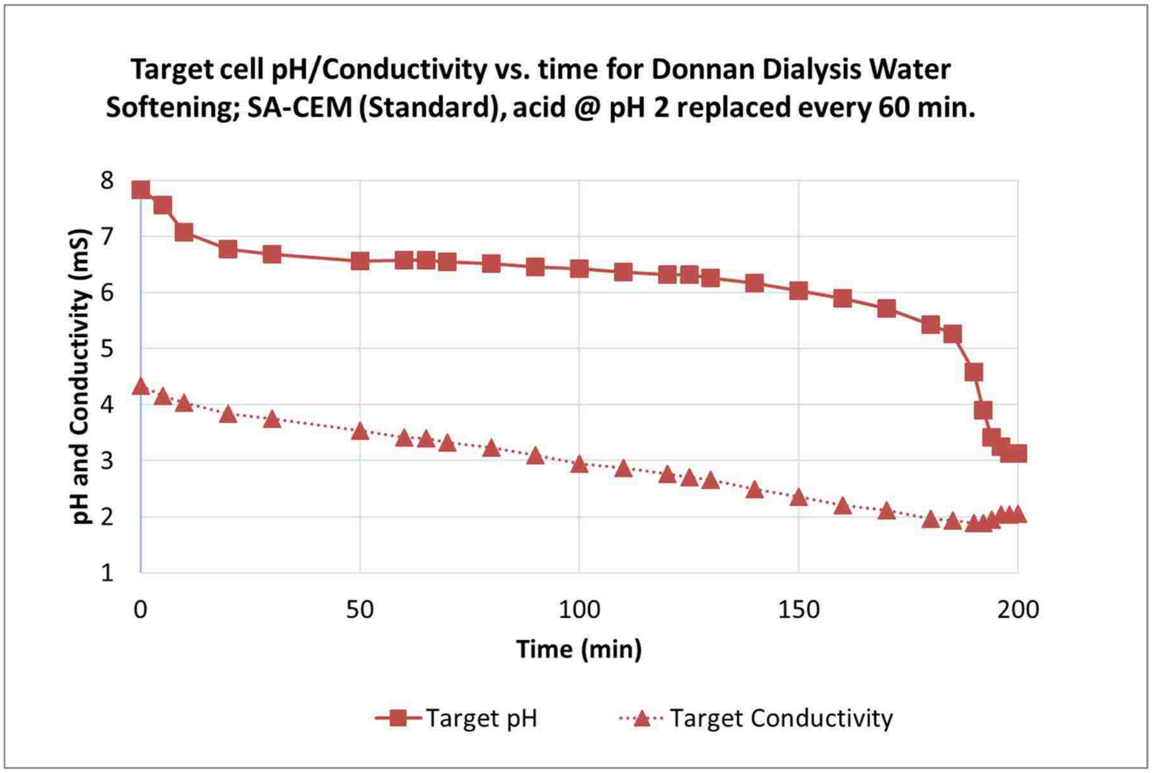


Figure 32. Experiment DOH-7. Target cell pH/Conductivity *vs*. time for Donnan dialysis water softening; SA-CEM (Standard); Waste acid replaced every 60 minutes

1.4.2.2 Donnan dialysis of brackish water demineralization.

Experiments DOD-1 and DOD-2 were conducted as batch reactors with a purified waste acid and target cells separated by a SA-CEM (standard) membrane and the target cell and waste base separated by a SB-AEM (mono-selective) membrane. The test set up is shown in Figure 33.

The results for the target cell ion concentrations as a function of time are shown in Figures 34 and 35; the flux and removal percentages for the experiments are shown in Tables 12 and 13. Values for Na^+, Cl^- and alkalinity were measured for the purified waste acid, purified waste base and target cells; the mass balance of the systems were within expected limits.

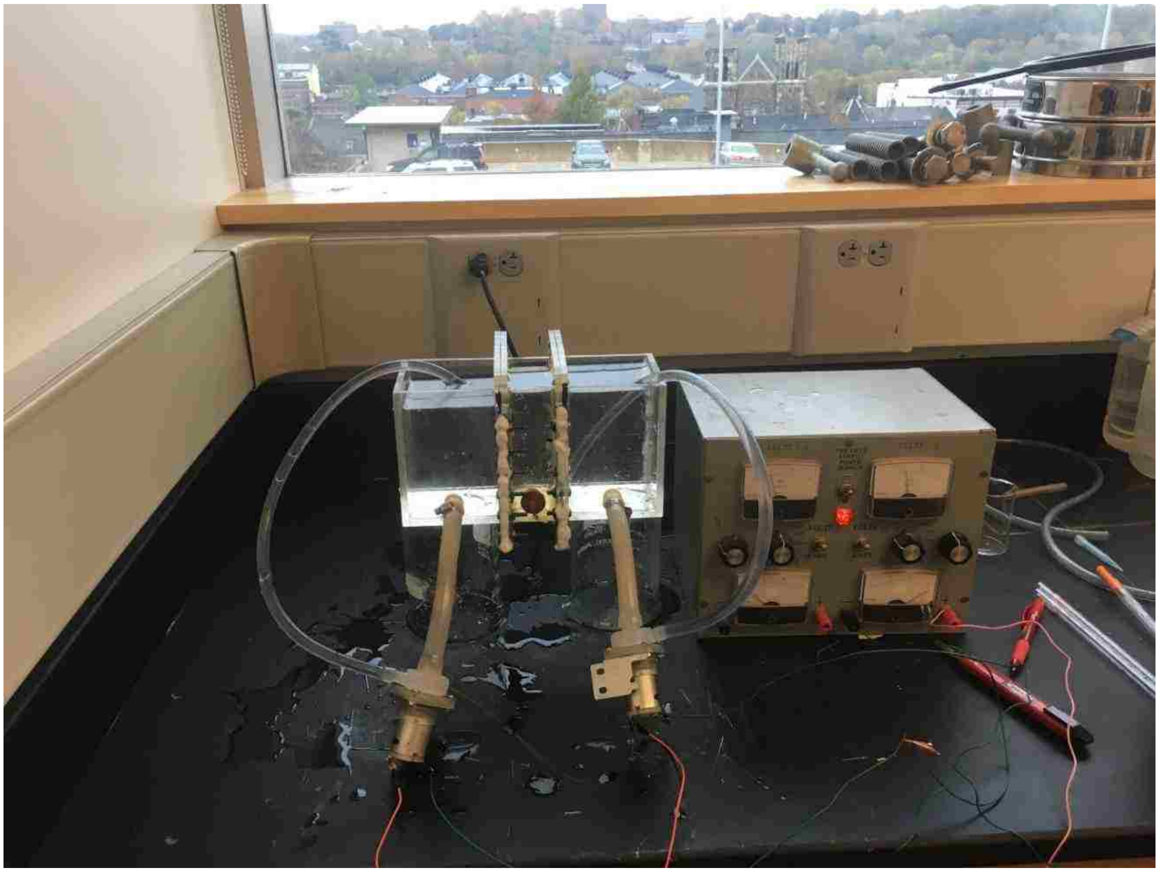


Figure 33. Donnan dialysis experiment set up for brackish water treatment

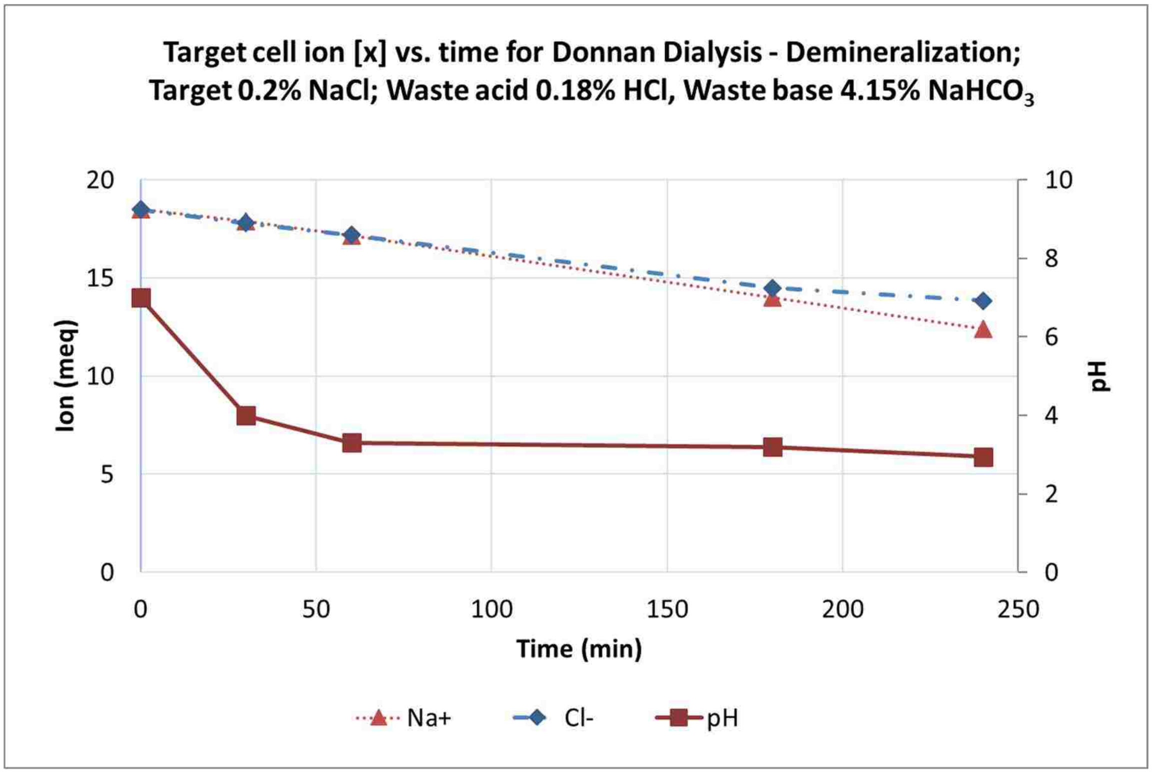


Figure 34. Experiment DOD-1. Target cell ion [x] *vs*. time for Donnan dialysis brackish water demineralization with SA-CEM (standard) and SB-AEM (mono-selective); target 0.2% NaCl; waste acid 0.183% HCl, waste base 4.15% $NaHCO_3$

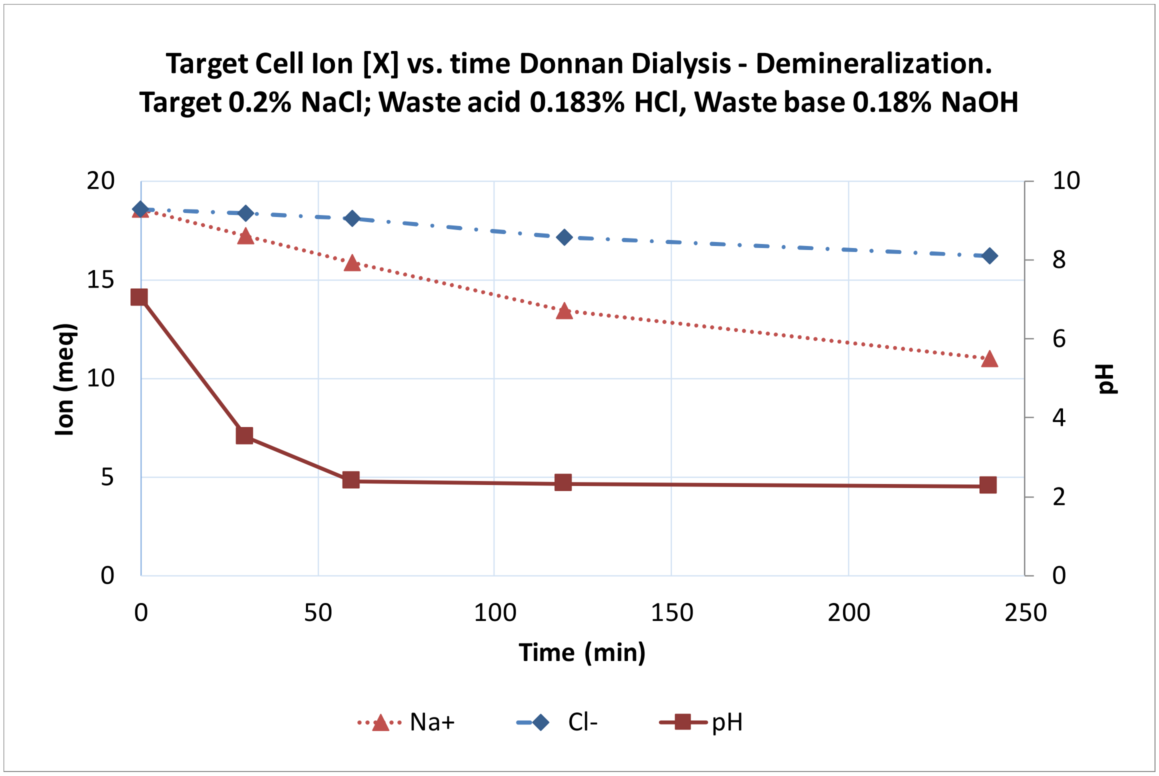


Figure 35. Experiment DOD-2. Target cell ion [x] *vs*. time for Donnan dialysis brackish water demineralization with SA-CEM (standard) and SB-AEM (mono-selective); target 0.2% NaCl; waste acid 0.183% HCl, waste base 0.18% NaOH

Flux Rates	Na^+		Cl^-	
Exp.	(0 - 1 hr)	(1 - 4 hr)	(0 - 1 hr)	(1 - 4 hr)
DOD-1	2.36	2.67	2.29	2.04
DOD-2	3.70	2.64	0.66	0.82

Note: Flux units (meq * m^{-2} * min^{-1})

Table 12. Flux rates for Donnan dialysis brackish water demineralization experiment

Ion % Removed	Na^+ % Removed	Cl^- % Removed
DOD-1	32.9%	25.2%
DOD-2	40.8%	12.6%

Table 13. Percent removal for Donnan dialysis brackish water demineralization experiment

1.4.3 Combined Diffusion and Donnan dialysis experiment performing water softening.

Experiment CDIDO-1 and CDIDO-2 were conducted as batch reactors with the industrial waste chamber and purified acid chamber separated by a SB-AEM mono selective and the purified acid chamber and target chamber separated by SA-CEM (standard). A picture of the experiment set up is shown in Figure 36. The results for the purified waste acid and target cell ion concentrations as a function of time are shown in Figures 37 through Figure 40. The flux and removal percentages from the target cell for the experiments are shown in Tables 14 and 15, respectively. Values for Na^+, Mg^{2+}, Fe(II or III), Cl^- and alkalinity were measured for the waste acid, purified waste acid, and target cells.

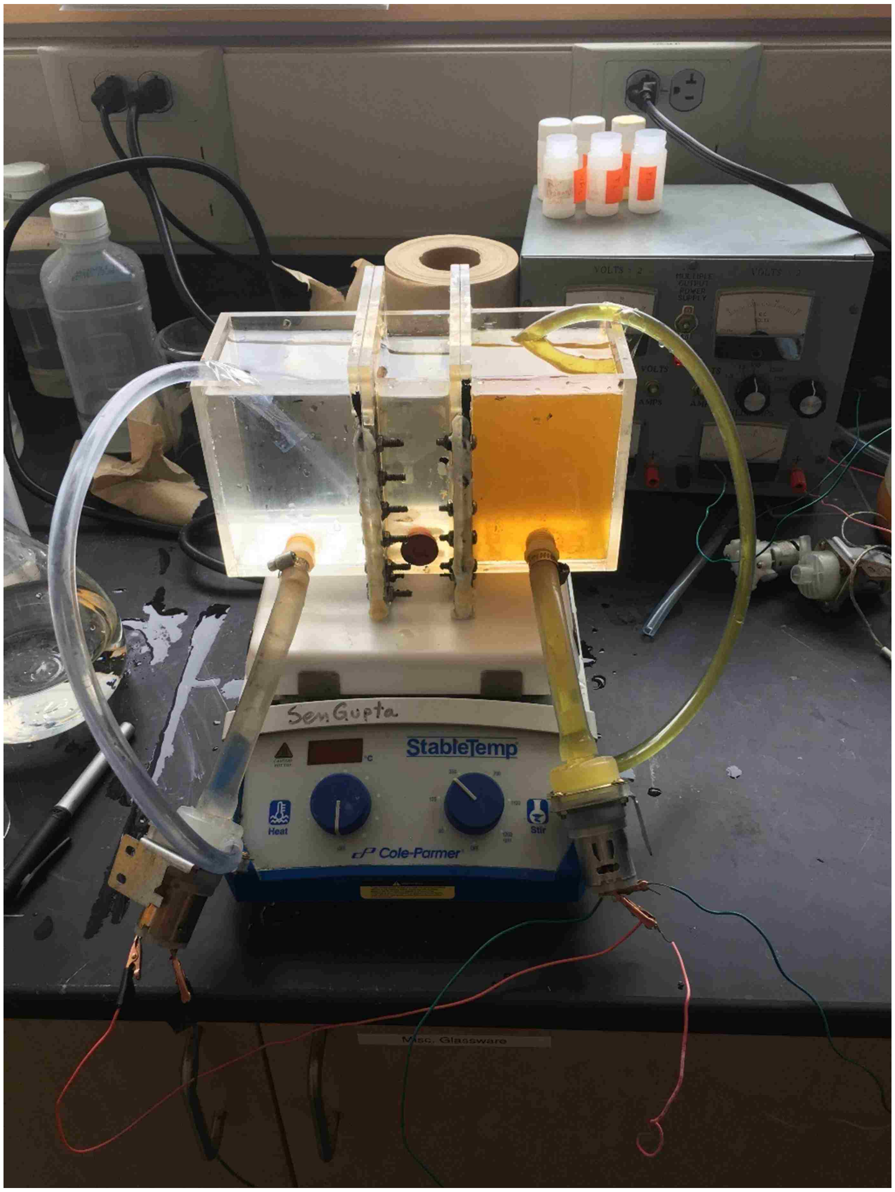


Figure 36. Combined diffusion and Donnan dialysis treatment process

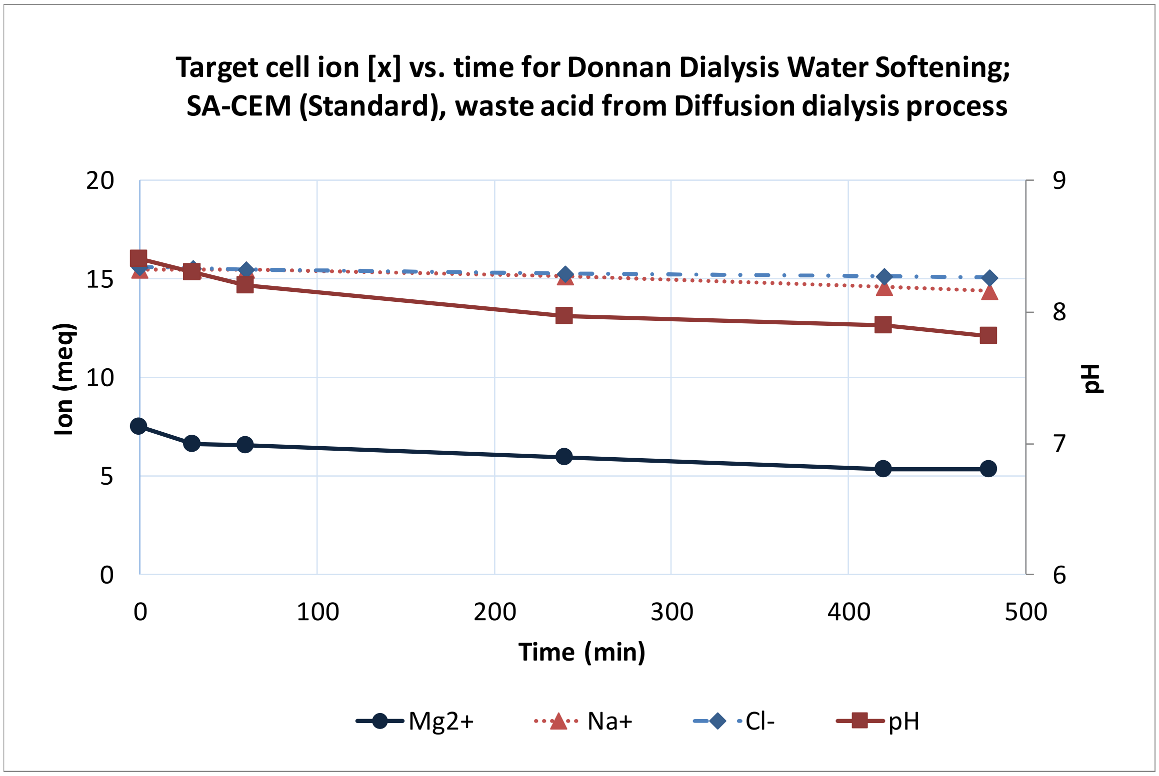


Figure 37. Experiment CDIDO-1. Target cell ion [x] *vs*. time for Donnan dialysis water softening; SA-CEM (standard), waste acid from diffusion dialysis process

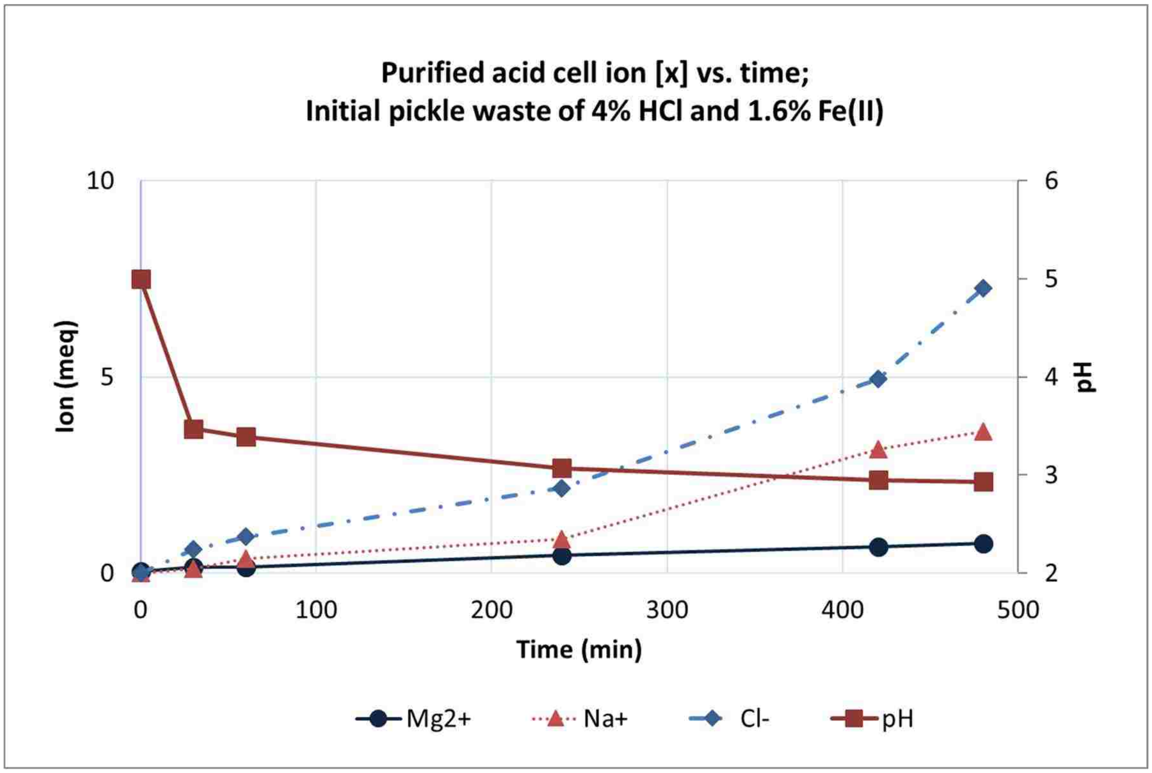


Figure 38. Experiment CDIDO-1. Purified acid cell ion [x] *vs.* time; Initial pickle waste of 4% HCl and 1.6% Fe(II)

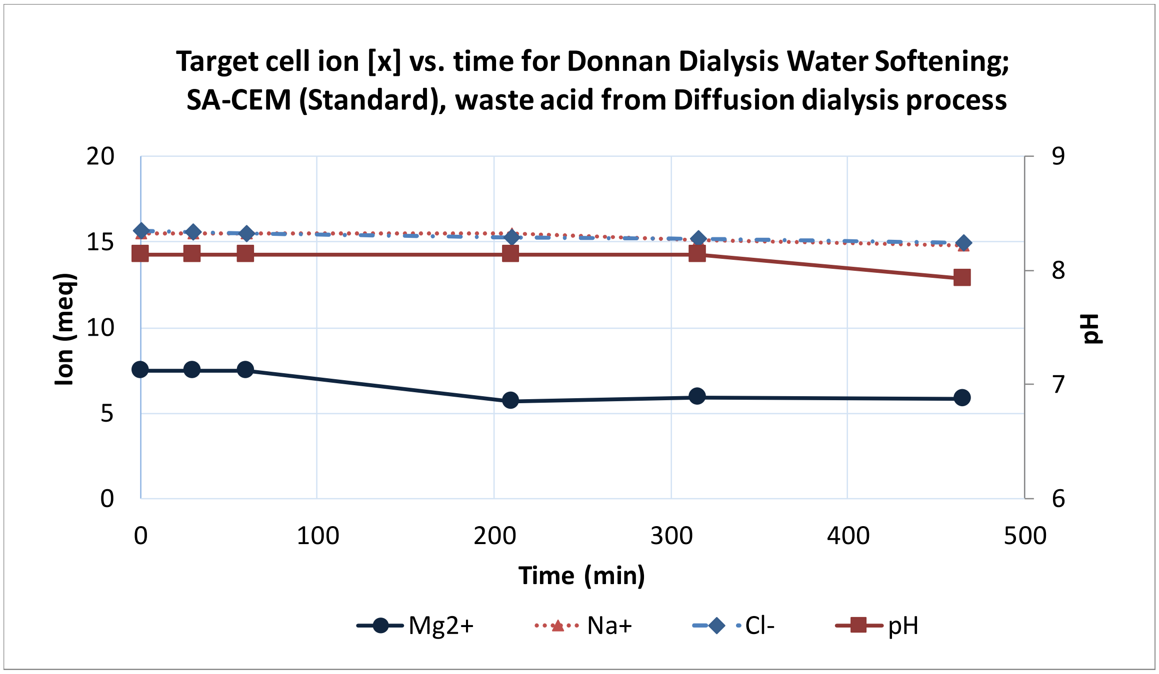


Figure 39. Experiment CDIDO-2. Target cell ion [x] *vs*. time for Donnan dialysis water softening; SA-CEM (standard), waste acid (10L) from diffusion dialysis process

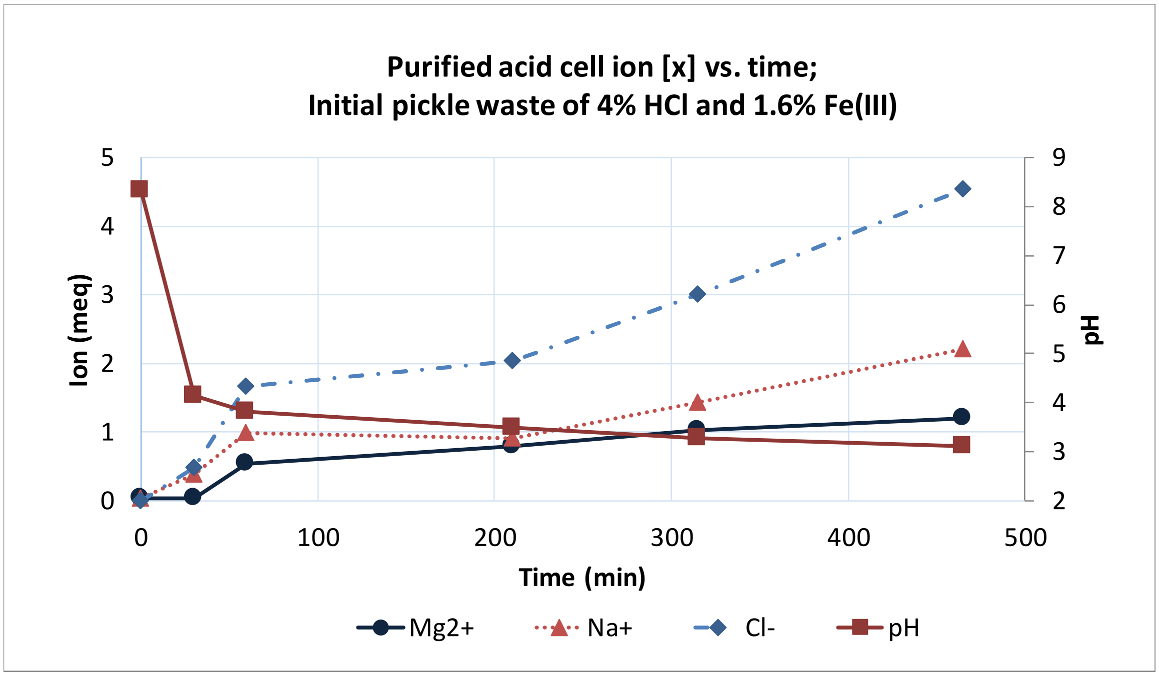


Figure 40. Experiment CDIDO-2. Purified acid cell ion [x] *vs*. time; Initial pickle waste of 4% HCl and 1.6% Fe(III)

Flux Rates	Mg^{2+}			Na^{+}		
Exp.	(0 - 1 hr)	(1 - 4 hr)	(4 - 8 hr)	(0 - 1 hr)	(1 - 4 hr)	(4 - 8 hr)
CDIDO-1	0.035	0.002	0.010	0.000	0.005	0.009
CDIDO-2	0.000	0.018	0.005	0.000	0.000	0.008

Note: Flux units (meq * m^{-2} * min^{-1})

Table 14. Flux rates for combined diffusion and Donnan dialysis experiment

Ion % Removed	Mg2+ % Removed	Na+ % Removed
CDIDO-1	29.1%	25.8%
CDIDO-2	22.6%	14.4%

Table 15. Percent removal for combined diffusion and Donnan dialysis experiment

1.5 Discussion

1.5.1 Interpretation of the results

In this dissertation, the feasibility of combining BATs was examined to demonstrate the economic capability and treatment capability of an on-site treatment process for industrial wastes. The researcher performed experiments to provide a systematic approach to demonstrate the functionality and practicality of the combined BATs to mitigate hydrogen ions in a waste product and to demonstrate performance of water treatment of target waters through the membrane processes of diffusion dialysis and Donnan dialysis. The researcher demonstrated the diffusion dialysis to purify an industrial waste into a purified acid, while demonstrating the Donnan dialysis experiments to use the purified acid to remove target ions from target waters. The researcher was able to demonstrate that the combined processes operating together can neutralized a pickle solution and treat a target water.

1.5.1.1 Acid purification through diffusion dialysis.

The objective of the diffusion dialysis experiments was to demonstrate the feasibility to separate H^+ from the acidic salt under different starting conditions, which bound the operating parameters of an onsite treatment process. In the diffusion dialysis process, the industrial waste is separated into a purified acid (high H^+ concentration and low metal salt concentration) and an acidic salt solution (less acidity), in which experiments were used to determine the relationships between salt and H^+ diffusion across the SB-AEM membrane. In the results of the first experiment, the high HCl and low $FeCl_2$ concentration limit were established. In the results of the second experiment, the low HCl and high $FeCl_3$ concentration limit were tested, which is more representative of spent pickling waste. In both experiments, the mass transfer coefficient for H^+ was over three orders of magnitude greater than for the salt. In Figure 20, the flux for H^+ remains constant over the duration of the experiment with the H^+ flux within 1 to 2% of 3.96 (meq * m^{-2} * min^{-1}) for both time periods. However, Fe(III) flux decreased over the time periods from 0.0089 to 0.0039 (meq * m^{-2} * min^{-1}). In Figure 19, the researcher used a diffusion dialysis experiment protocol in which the target chamber was changed every 24 hours with deionized water. Separation of H^+ and Fe(II) was observed, however the flux rates were less than the previous experiment due to the lower ion concentrations of H^+ and salt in the industrial waste. The researcher was able to demonstrate the effective separation of H^+ from the H^+/salt solution, which is used as a successful step 1 for the onsite process.

In Section 1.2.2, the researcher explained how Fick's law governs the separation of H^+/salt, through controlling the driving force by the concentration gradient between the chambers and the mass transfer coefficient determined by the membrane characteristics. The highest amount of H^+ reclamation was by Zhang, who reported >90% reclamation of H^+ by using DF120 anion exchange membranes and system concentrations of 2.12 mol/L. Therefore, it is understood that the process of H^+/salt separation was validated by the experiments investigated in this dissertation. However, to optimize the amount of H^+ reclamation, the membrane characteristics must be tailored to the system. An example of this includes a higher degree of cross-linking, in which a reduced number of ions cross the membrane both H^+ and Fe, but the ratio of H^+ vs Fe(II or III) increases in relative terms.

1.5.1.2 Hard water treatment through Donnan dialysis.

The objective of the Donnan dialysis experiments was to demonstrate that taking the purified acid from the diffusion dialysis process, the purified acid could be used to treat target waters by removing Mg^{2+} ions in hard waters or removing Na^{+} ions in brackish water. The objective was approached through the following steps:

- Using synthetic purified acid at pH of 1.3, 1.6, and 3.0 with both SA-CEM standard and SA-CEM mono selective to treat hard water.
- Using synthetic purified acid at pH 2.0 with SA-CEM standard with multiple batches of purified acid.
- Using synthetic purified acid at pH 2.0 with SA-CEM standard and waste base to treat brackish water.
- Using a synthetic industrial waste, deionized water and target hard water for a combination of diffusion dialysis and Donnan dialysis system.

Each experiment demonstrated removal of target ions from the target waters through implementing the Donnan dialysis process.

1.5.1.2.1 Target ion removal with varying pH and membranes.

The researcher demonstrated that the first set of Donnan dialysis experiments established relationships between the pH and corresponding flux of ion removal from the target waters for two types of cation exchange membranes. The selection of membrane was considered to understand the impacts related to monovalent/divalent ions, which would be important based on determined target waters. The researcher explains that the determined relationships provide the performance of the onsite systems as related to pH and divalent/monovalent ion concentrations in the target chamber.

As the researcher demonstrated through the experiments the removal of target ions from the target chamber, key parameters will determine the performance of the experiment: pH and membrane characteristics. The researcher demonstrated that the pH influenced the flux to the greatest extent, as the experiment with pH of 1.3 of purified acid had fluxes 6.25 times faster for divalent ions with SA-CEM standard *versus* the experiment with pH of 3.0. The experiment with pH 1.3 had fluxes 5 times faster for monovalent ions using the mono-selective membrane compared to the experiment with pH of 3.0. The low pH of the purified acid had higher ion removal percentage for all cases. The experiments repeatedly had these results as shown in table 8. The selection of membrane had different flux and ion removal rates for the monovalent/divalent ions. The SA-CEM standard membrane had the best results for the divalent ions *versus* the monovalent ions, while the SA-CEM mono-selective membrane had the best results for the monovalent ions. However, the overall removal rate of ions for the monovalent membrane was less than the divalent membrane. The Donnan dialysis process had strong correlation between pH and membrane selection for the removal of target ions; low pH had higher flux and a higher percentage of ion removal.

1.5.1.2.2 Target ion removal with multiple batches of waste acid.

The objective of the multiple batch experiments was to demonstrate that the target ions could be completely removed from the target chamber in an accelerated time frame compared to not replacing the purified acid at a lower pH. A purified acid with a pH of 2.0 was used with a SA-CEM standard membrane with new batches of purified acid added to the purified acid chamber every 60 minutes. The concentration of Mg^{2+} in the purified acid was zero and therefore the surface of the membrane facing the purified acid to not become saturated with Mg^{2+}. The researcher explained that this drove the continual remove of the Mg^{2+} ions from the target chamber. However the researcher explained that as the Mg^{2+} concentration in the target chamber was lowered, the affinity for Na^+ on the membrane increased. which led to an increase of the Na^+ flux over time. The researcher demonstrated this in the results in figure 27, as the Mg^{2+} flux decreased over time and the Na^+ flux increased over time. The researcher explained that multiple batch experiments demonstrated how the system could remove a large percentage of the Mg^{2+}, 87.2%, from the target chamber with a purified acid of pH 2.0 compared to 75.6% removal of the Mg^{2+} result was achievable with a purified acid of pH 1.7.

1.5.1.3 Demineralization treatment through Donnan dialysis.

The objective of the demineralization experiments was to demonstrate that the target ions of Na^+ and Cl^- could be removed through the addition of a SB-AEM and waste base to remove the Cl^- ions. The demineralization experiments had the effectiveness of the onsite treatment process to treat additional target waters as both synthetic hydroxide and bicarbonate were used as the waste base in combination with a synthetic purified acid at pH of 2.0. The chambers were separated from a target chamber of NaCl by SB-AEM and SA-CEM membranes respectively. Removal of both Na^+ and Cl^- were observed for both experiments with the higher concentrations of synthetic anions that had higher rates of Cl^- ion removal. The pH was observed to drop in the target chamber based on the differing rates of ion exchange across the cation and anion exchange membranes. The researcher explained that the final equilibrium state as predicted by Donnan equilibrium would remove essential all the Na+ and Cl-, although the rate of flux would decrease over time as the cation membrane becomes saturated with Na^+ and the anion membrane becomes saturated with Cl^-. Figures 30 and 31 had the removal of both Na+ and Cl- constant over the first 240 minutes of the experiment. Tables 11 and 12 had the flux and percentage of ion removal.

1.5.1.4 Combined acid purification and hard water treatment process.

The objective of the combined experiment was to demonstrate a complete system envisioned for an onsite process. Since the pH in the purified acid chamber (deionized water) starts at pH of 7.0, the Donnan dialysis flux of cations was slow until an appreciable amount of H^+ accumulates in the purified acid chamber. The researcher explained that as the pH drops in the purified acid chamber, the Donnan dialysis process starts to remove target ions from the target chamber, which exchanges the H^+ from the purified acid chamber for target ions. The researcher explained that as the Mg^{2+} enters the purified acid chamber, the membrane loading starts to favor Mg^{2+} and it requires more H^+ to maintain an adequate amount of H^+ on the surface of the membrane facing the purified acid chamber. The researcher explained that since multiple processes were occurring across the membranes and in the target chamber, the results of the flux rates are dynamic; the target chambers increases H^+ due to diffusion dialysis and simultaneously the H^+ concentration decrease as a function of the Donnan dialysis flux. The experiment is an example of possible process configurations of the onsite process compared to optimized performance as multiple parameters can be modified to impact the performance of the combined process.

1.5.1.5 Use of ion exchange membrane equilibrium model

The ion exchange membrane equilibrium model is a tool to understand the Donnan dialysis process by determining the driving forces, the amount of neutralization reaction ions, and the relationships between the interacting ions and has system speciation at any time frame. The researcher explains that the model uses the membrane characteristics/isotherms, aqueous phase concentration, and separation factors to determine the membrane phase concentrations. Once these initial membrane phase and aqueous phase concentrations are determined for a step of the process, the researcher demonstrates that the model iteratively predicts membrane and aqueous phase concentrations as a function of ion exchange processes. The model is a tool to understand when the process achieves equilibrium based on aqueous phase concentrations in the exchanging chambers.

1.5.2 Onsite treatment leads to environmentally sustainable management of industrial waste.

The researcher explains that the primary objective of the onsite treatment process is a process that uses the remaining H^+ utility from the industrial waste to treat target waters. The diffusion dialysis process is a dependable separation process for metal ions and H^+ by only using a membrane and water. From the literature, >80% removal of the H^+ ions can be extracted from an industrial waste acid and can be used for another treatment process (Negro, Blanco *et al.* 2001, Zhang, Li *et al.* 2011, Zhang, Li *et al.* 2012). These treatment processes previously discussed include hard water softening and brackish water demineralization through Donnan dialysis. In addition to the treatment process, a valuable product remains, $Fe(III)Cl_3$, which is used in surface water treatment as a coagulant. This end-product is recoverable with minimal additional treatment requirements (Prakash, Hoskins *et al.* 2004, Prakash 2004, Prakash, SenGupta 2005). Therefore, the researcher explains that the industrial waste serves a purpose of treating target waters and providing a product valuable for the surface water treatment industry.

1.5.3 Approach and Evaluation of the study considered the applicable use cases and demonstrated a better approach to industrial waste management

The objective of the study was to demonstrate that the combinations of BATs is environmentally sustainable for industrial waste management through breaking the onsite process into experiments that the researcher uses to demonstrate the determination of flux rates, diffusivity coefficients, and mass transfer coefficients for the processes. Evaluating the performance of the Donnan dialysis process with different pH of purified acid and membranes is a guideline on flux rates as a function of pH. The researcher demonstrated through performing the multiple batch experiment of purified acid demonstrated the ability to remove target ions. The researcher demonstrated that the three-ion model validates the interactions of the three ions with known starting conditions that serves as a tool to characterize ion exchange systems. Additionally, running the combined diffusion dialysis and Donnan dialysis, the researcher demonstrates the processes work together and only require matching flow rates and membrane surface areas to achieve the desired treatment outcome.

The researcher demonstrates how the dissertation research provides a thorough review of diffusion dialysis and Donnan dialysis processes with a demonstration of those technologies in a real-world application. The practitioners can use the results to design more environmentally sustainable solutions for industrial waste management.

1.6 Key Findings and Future work

1.6.1 Key Findings

The dissertation research has the following conclusions:

1. The combination of BATs, diffusion dialysis and Donnan dialysis in conjunction of the neutralization reactions is an alternative onsite treatment process for industrial waste management, with the following outputs:
    a. Reduce the H^+ concentration in an industrial waste without the use of a neutralizing agent, but through the neutralization reaction as part of the Donnan dialysis process.
    b. Treatment of target waters both brackish and hard water through the Donnan dialysis process to remove target ions.
    c. Industrial waste end-product with high $Fe(III)Cl_3$ concentration with reduced H^+ concentration; possible raw material for surface water treatment.
2. The diffusion dialysis process is an exceptional separation process for waste acids whereby the mass transfer coefficients between H^+ and Fe(III) and Fe(II) are on the order of 300x faster for H^+.
3. The researcher demonstrated that the Donnan dialysis process removes Mg^{2+}, Na^+ and Cl^- from target waters in both water softening and demineralization applications with treatment results matching model equilibrium predictions.
4. Combined BATs are a more environmental sustainable process for industrial waste management.

5. The equilibrium model is a tool to predict treatment outcomes and design parameters.

1.6.2 Future work

1. Model enhancements

The equilibrium model developed for this dissertation was a static model and the isotherms and separation factors were not dynamic but predetermined conditions of the system. The researcher explains that an improved model would recalculate the isotherms and separation factors based on characterizing the membranes and ions used in the systems and the system speciation at a set time. As the researcher explains, these improvements would require a library of membrane characteristics and equations that could approximate the isotherms for various ion combinations and C_T. An ideal model is one that a user has membrane options and speciation options for the industrial waste and target water, while the flow rates, surface areas of membrane, and other design parameters for the project are determined. With additional three-ion model libraries, a less “hands on” approach would be available for users with less knowledge of the ion-exchange fundamentals.

2. Another improvement is to implement the combined BATs process at the waste generator facility. “Steel pickling” facilities are potential case studies, where lab scale tests or onsite systems are implemented to manage the industrial waste through the onsite BAT processes.

Chapter 2 – Applying diffusion dialysis to industrial waste pickle liquor

2.1 Introduction

In order to validate the process developed in Chapter 1, an Industrial waste from Samuel Steel Pickling Group from Cleveland, Ohio was used to in the diffusion dialysis process. Don Drenski, Operations Superintendent (Twinsburg) e. ddrenski@samuelsteel.com (330) 963 3777, provided the samples for the experiments. The objective of the experiments were to use the industrial waste to create a purified waste acid that would serve as the waste acid used in the Donnan dialysis experiments. Appendix B has the chemical composition of the waste pickle liquor.

2.2 Materials and Methods

2.2.1 Experimental membrane test set-up

The membrane test set up was made of Plexiglas with configuration options to create two or three chambers by placing membranes between the Plexiglas partitions. The researcher shows in Figure 20 a picture of the set-up with each chamber volume based on stated dimensions for the chambers and/or combination of chambers. The surface area of the membrane between the chambers was 95 cm^2. Each chamber was equipped with an outlet valve that provided an option for additional volume through an added chamber and to circulate/mix the chamber solution.

The pickle liquor solution came from Samuel Steel Pickling Group and the following solutions were prepared for each respective experiment:

- Acid purification: Diffusion dialysis experiments required steel pickling solution (waste acid) and deionized water (target). The steel pickling solution consisted of ferric and ferrous chloride and hydrochloric acid as the major species, however many other ions were present in the solution (see appendix A for speciation analysis); the target solution contained deionized water. Experiment solution volumes were 1L of waste acid in the Waste Acid cell and 1L of deionized water in the Target cell.

2.2.2 Membranes used in experiments.

1. The membrane used in the experiment was Neosepta membranes from Astom Inc., with the SB-AEM membrane characteristics shown in Table 6. The homogeneous membranes used was Strong Base Anion mono-selective (SB-AEM-mono-selective)
2. The membranes were conditioned before the experiment by putting the SB-AEMs in chloride form by filling the contact chambers with a sodium chloride solution of 1M. This solution was in contact with the membranes for 30 minutes and was repeated 3 times. The chambers were then washed with deionized water to remove residual chloride in solution remaining on the membrane.

2.2.3 Experimental procedures

The diffusion dialysis experiments were performed using the waste acid provided from Samuel Steel Pickling Group. The experimental protocol was that the target chamber remained static through the experiment with only samples (10ml) being removed on a set frequency. The pH was recorded at the time of sample extraction and the chloride concentration measured during the sample analysis process. The details of the experiments are listed below.

- Purified acid [HCl]
- Target; deionized water and well water
- Membrane; SB-AEM (mono-selective).

  - Operation: maintained target purified acid over duration of experiment in a batch reactor; no mixing. Samples drawn at 0, 0.5, 1, 2, 4, and 8 hours.
    - Figures 21 and 22 show examples of experiments and test set.

2.2.4 Analytical Techniques

The analytical techniques employed in this experiment used a combination of real-time data acquisition and post experiment sample analysis. The following equipment was used for these analyses.

- Atomic Absorption spectrometer was used to measure total aqueous concentrations of Iron, Magnesium and Sodium; (Perkin Elmer Flame Atomic Absorption Spectrometer: Model AA100). Five-point calibration curves were prepared from primary standards (Ricca Chemical) and for all analyses, an acetylene/air flame was used. In the case of samples exceeding the concentrations set in the five-point calibration curve, the sample was re-prepared from the source with appropriate dilution.
- Dionex Ion Chromatograph (Model 45001) was used to analyze Chloride ions. Analysis was performed using chromatography column AS10 and a conductivity detector. Based on the manufacturer recommendations, a 9.0 mM Na2CO3 buffer was used as the eluent at a flow rate of 1.0 mL/min
- Fisher Scientific Accumet pH meter 900 was used to measure pH.
- Accumet conductivity meter (Model#AP75) was used to measure conductivity.
- NOTE: All experiments were conducted at ambient temperature and no significant difference in temperature were recorded between the chamber solutions. The relative humidity was maintained at 60%.

2.3 Results

2.3.1 Diffusion dialysis results.

The experiment was conducted as a batch reactor with waste acid and purified acid cells separated by Strong Base Anion Exchange Membranes (SB-AEM – mono-selective). In experiment IWDD-1, the waste acid cell and the target cell were mixed by bubbling air through the chamber through the duration of the experiment with samples being removed from both chambers on a set frequency. The concentration of H^+ and Fe(III) is shown in figure XX, with the flux of H^+ at 0.6 (meq * m^{-2} * min $^{-1}$) and Fe(III) at 0.01 (meq * m^{-2} * min $^{-1}$).

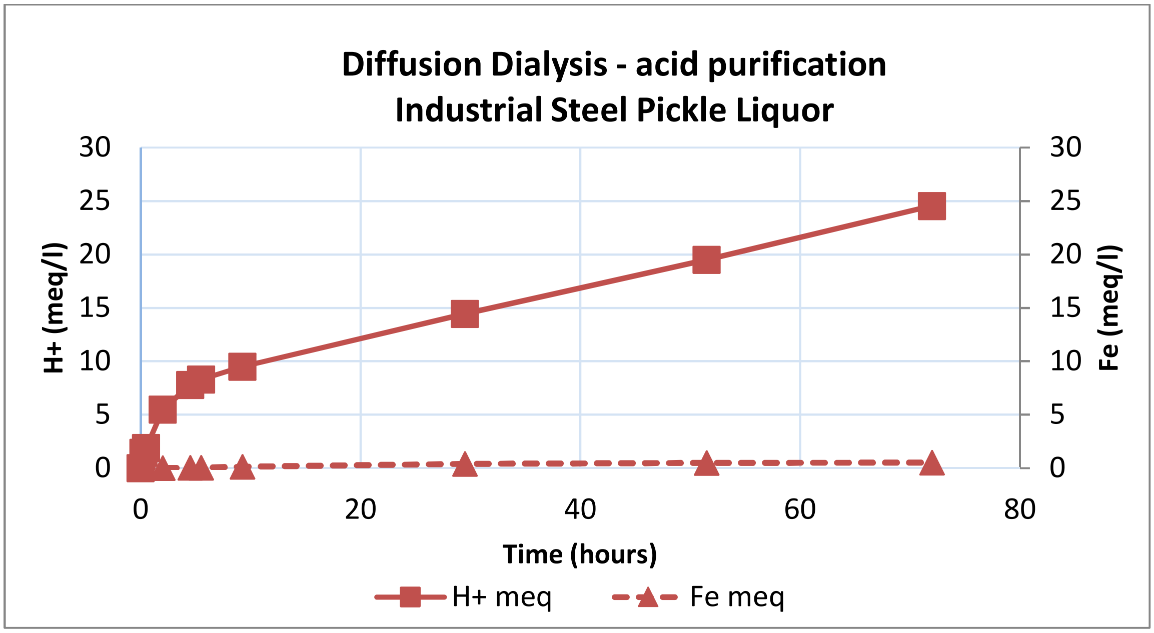


Figure 41. IWDD-1, Purified acid cell ion [x] vs. time; Industrial waste pickle liquor from Samuel Steel.

2.4 Discussion

2.4.1 Interpretation of the results

As demonstrated in earlier experiments using the synthetic waste acid, the researcher demonstrates the diffusion dialysis process effectively purifying the waste acid. The objective of the diffusion dialysis experiment was to demonstrate the feasibility to separate H^+ from the acidic salt (Fe) from a waste produced from an industrial plant. In the diffusion dialysis process the industrial waste is separated into a purified acid (high H^+ concentration and low metal salt concentration) and an acidic salt (Fe) solution (less acidity). In Figure 41, the researcher shows the flux for H^+ decreasing over time. However the researcher shows the Fe(III) flux to be constant over time.

2.5 Key Findings

The industrial waste experiment provides the following conclusions:

1) The diffusion dialysis process provides an exceptional separation process for waste acids whereby the flux between H^+ and Fe(III) and Fe(II) are on the order of 60x faster for H^+.

Chapter 3 – Pressurized Forward Osmosis

3.1 Introduction

Osmosis is a mass transport phenomenon defined by the net movement of water (solvent) across a selectively permeable membrane and is driven by an osmotic pressure gradient across the membrane. Many examples and applications of osmosis impact us today; salt is used to desiccate foods for food preservation as well as the known fact that humans cannot drink seawater without experiencing dehydration (Cath). The two primary sub-technologies of osmosis relevant to water treatment include Forward Osmosis (FO) and Reverse Osmosis (RO) with each concept demonstrated in Figure 41.

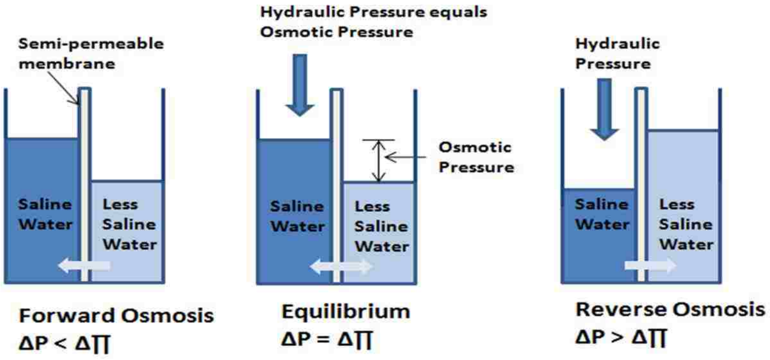


Figure 42: Osmosis schematic.

Osmosis (also known as Forward osmosis) occurs when two systems with different osmotic pressures are separated by a semi-permeable membrane, whereby the system with higher osmotic pressure is diluted by a solvent (H_2O) that has a lower osmotic pressure. Reverse osmosis is a process that requires a hydraulic pressure to be applied to the system with higher osmotic pressure and the resulting hydraulic pressure is greater than the osmotic pressure delta between the systems. Solvent is permeated across the membrane from the system with higher osmotic pressure to the lower osmotic pressure system. RO and FO are commercially viable for specific applications related to water purification and provide alternatives for traditional water treatment processes. However, Reverse Osmosis is predominate for large scale water treatment process for potable water production from seawater or other high salinity feed sources due to optimized energy utilization and quality of the product water. Although the thermodynamic theoretical minimum energy requirement for RO has not been achieved with existing technologies, on a strict cost basis RO provides the most cost-effective water treatment process for saline feed waters (McCutcheon). In cases where waste energy (heat) is available for low cost, other technologies (multi-stage distillation or Forward Osmosis) become competitive with RO. (McCutcheon). In the case of FO, the main advantages are that it operates at low or no hydraulic pressures, it has high rejection of a wide range of contaminants, and it maintains a low membrane fouling potential compared with other pressure driven membrane processes (Cath). Forward Osmosis provides additional benefits since the only pressure is due to flow resistance in the membrane module, the equipment used, and energy requirements are not complex (Achilli). Limitations of FO include the costs associated with draw solution regeneration and membrane performance characteristics (Achilli).

In this investigation, a new process Pressurized Forward Osmosis (PFO) is proposed that uses the chemical potential as the driving force but manages the generation/degeneration of the draw solution osmotic pressure through partial pressure variations with CO_2 (g). Forward Osmosis is the key driver of the process as the draw solution osmotic pressure is created by reacting magnesium carbonate with carbon dioxide (g) at partial pressures greater than 1 atm pressure and the feed solution chamber pressure is counter-balanced with either pump pressure or inert gas pressure. As in traditional FO systems, the sum of the hydraulic pressure terms (P terms) are typically zero and the process is driven by osmotic pressure. In PFO, the P terms are equal and do not drive the osmotic process, but the combination of the $CO_2(g)$ and $MgCO_3$ react to create a high osmotic pressure gradients (π terms), which drives the osmotic process. The researcher shows in Equations 1 and 2, the traditional and pressurized forward osmosis process along with figure 42 with a schematic of the process.

$$\text{Traditional FO; Flux} = \mathrm{D}\,(\Delta \mathrm{P} - \Delta \pi) = \mathrm{D}\left((0-0) - (\pi_{\mathrm{Feed}} - \pi_{\mathrm{Draw}})\right) \quad (62)$$

$$\text{Pressurized FO; Flux} = \mathrm{D}\,(\Delta \mathrm{P} - \Delta \pi) = \mathrm{D}\left((\mathrm{P}_{\mathrm{Feed}} = \mathrm{P}_{\mathrm{Draw}}) - (\pi_{\mathrm{Feed}} - \pi_{\mathrm{Draw}})\right) \quad (63)$$

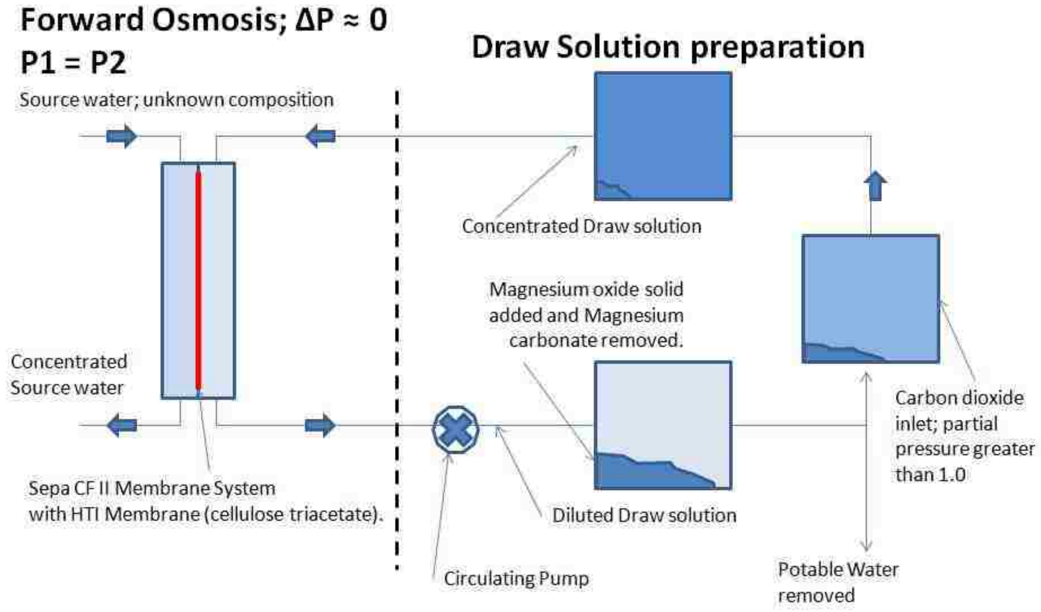


Figure 43: Pressurized Forward Osmosis schematic

3.1.1 Osmotic pressure generation/degeneration and reagent regeneration.

The researcher explains that Forward Osmosis (FO) uses the chemical potential gradient to perform osmosis. In traditional FO, the draw solutions are created by adding salts to water that ionize that results in an increase of osmotic pressure of the system. If the osmotic pressure for the draw solution is greater than the osmotic pressure for the targeted feed solution, osmosis will occur. Achilli provides a systematic approach for selecting a salt for the draw solution, whereby three primary criteria are evaluated; ability to create high osmotic pressure, reverse diffusion of the draw solution is minimal, and there exists a suitable process for effective re-concentration of the draw solution after osmosis. (Achilli). Forward osmosis offers the potential for a less energy consuming process versus Reverse Osmosis.

For PFO, the draw solution is generated by mixing carbon dioxide at partial pressures greater than 1.0 atm with magnesium carbonate. The reaction is not instantaneous and is dependent on temperature, $MgCO_3$ structure, and pH of the system. Once equilibrium is achieved, a mathematical relationship for the $CO_2/MgCO_3$ system can be developed through manipulation of the equilibrium constants and Equations as seen in Equation 64 through Equation 74 (Stumm).

$$\mathrm{Mg(OH)_{2(s)} + 2H^+ \Leftrightarrow \quad Mg^{2+} + 2H_2O; \quad K_{SO} = 10^{16.84}} \quad (64)$$

$$\mathrm{3CO_{2(g)} + 3H_2O \Leftrightarrow \quad 3H_2CO_3; \quad 3 * K_H = 3 * 10^{-1.5}} \quad (65)$$

$$\mathrm{3H_2CO_3 \Leftrightarrow \quad 3H^+ + 3HCO_3{}^-; \quad K_{a1} = 3 * 10^{-6.33}} \quad (66)$$

$$\mathrm{MgCO_{3(s)} \Leftrightarrow \quad Mg^{2+} + CO_3{}^{2-}; \quad K_{SO} = 10^{-7.5}} \quad (67)$$

$$\mathrm{CO_3{}^{2-} + H^+ \Leftrightarrow \quad 3HCO_3{}^-; \quad \frac{1}{K_{a2}} = 10^{10.33}} \quad (68)$$

$$\mathrm{MgCO_{3(s)} + 3CO_{2(g)} + Mg(OH)_{2(s)} \Leftrightarrow \ \ 2Mg^{2+} + \ 4HCO_3{}^{-};\ K = \frac{K_{SO} * 3K_H * \ 3K_{a1}}{K_{a2}}} = 10^{-3.82} \ (69)$$

$$\mathrm{K = \frac{[Mg^{2+}]^2 * [HCO_3{}^{-}]^4}{P_{CO2}{}^3} = \ 10^{-3.82}} \ (70)$$

$\mathrm{[H^+] + 2[Mg^{2+}] = [OH^-] + [HCO_3{}^-] + \ 2[CO_3{}^{2-}]}$ (71) due to electroneutrality.

$\mathrm{2[Mg^{2+}] = [HCO_3{}^-]}$ (72) based on an assumption of pH of 7, the following relationship exists.

$$\mathrm{K = \frac{16[Mg^{2+}]^6}{P_{CO2}{}^3} = \ 10^{-3.82}} \ (73)$$

$$\mathrm{[Mg^{2+}] = \sqrt[6]{\frac{K}{16} * P_{CO2}{}^3}} \ (74)$$

Manipulation of Equation 69 by using the principle of Electroneutrality (Equation 71) and assuming pH is 7, $[H^+]$, $[OH^-]$ << $[Mg^{2+}]$ or $[HCO_3^-]$ (Equations 72 & 73), Equation 74 is developed, which provides a means to develop a theoretical estimate of osmotic pressure per unit mass of $MgCO_3$ and partial pressure of CO_2.

The researcher provides a plot of PCO_2 vs. $[Mg^{2+}]$, $[HCO_3^-]$ and Osmotic pressure of the system in Figure 43. The researcher explains how the osmotic pressure of 50 atm is achievable when the partial pressure of CO_2 is at 23 atm. However, this representation does not account for $MgHCO_3^+$, which further increases the osmotic pressure of the system and is accounted for in Table 16 that provides the estimated osmotic pressure of the CO_2/MgO system based on OLI model.

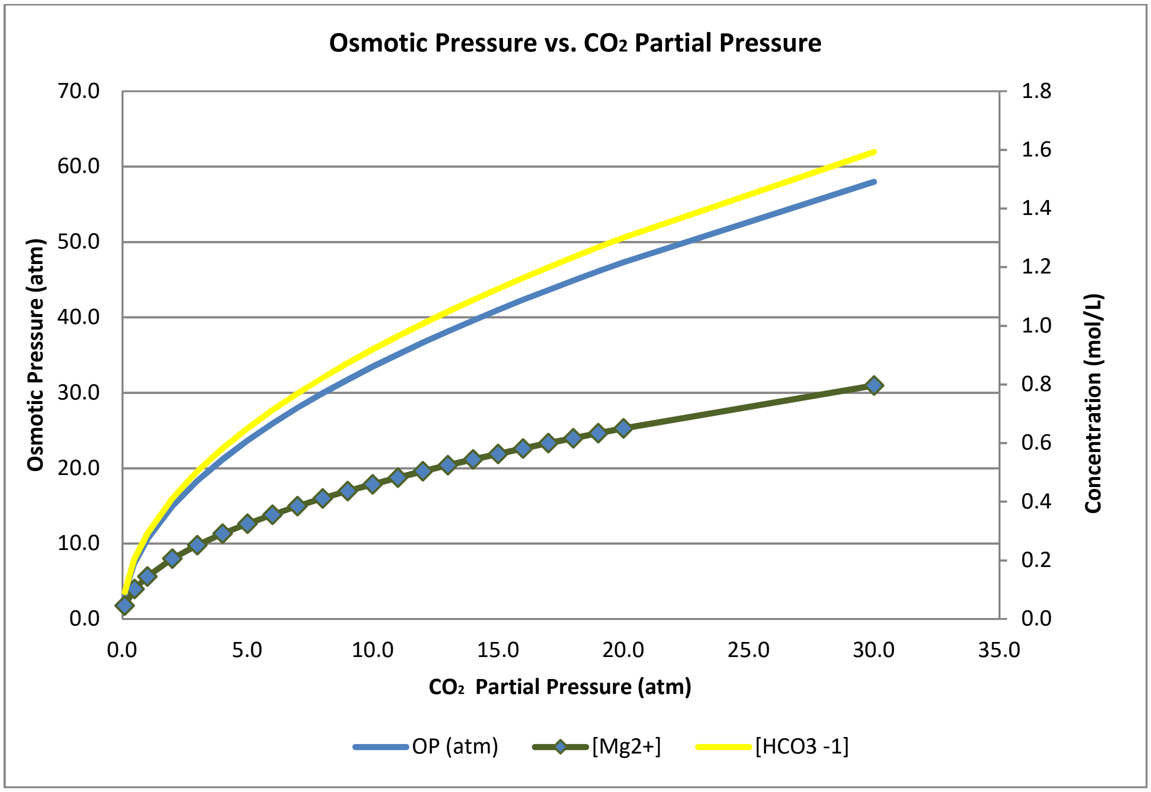


Figure 44. Plot of Osmotic pressure versus CO2 partial pressure based on Equation 13

Temp	.0035 (atm) of CO2; atm	1.0 (atm) of CO2; atm	3.0 (atm) of CO2; atm	8.0 (atm) of CO2; atm	10.0 (atm) of CO2; atm
10’C	1.1	28.7	45.9	83.3	92.6
20’C	1.2	20.1	36.0	59.8	66.9
30’C	1.2	13.7	24.3	40.3	45.1

Table 16. OLI estimations of OP based on 1 mole of MgCO3 and CO2 partial pressure.

The plot in Figure 43 is inconsistent with the OLI estimations of osmotic pressure due to the absence of the Magnesium Bicarbonate ion ($MgHCO_3^+$), which is not included in the K equilibrium assessment, due to simplifying assumptions.

The degeneration of the draw solution is performed by removing the CO_2 (g) from the system; by reducing the partial pressure, while air sparging the residual dissolved CO_2 (g). By removing CO_2 partial pressure, the system immediately starts to form $MgCO_3$, which is an insoluble compound (K_{eq} = 1.4 E-10). The rate of precipitation is increased by purging air or inert gas through the system. The ion concentration can be further reduced by adding MgO or $Mg(OH)_2$ to increase the pH to drive the precipitation process; lime softening.

An important factor related to the process is that $MgHCO_3^+$ has a lower Gibbs Free Energy of formation than $MgCO_3$, which enables the system to remain at the achieved OP if the CO_2 partial pressure remains unchanged. Shoba determined that the Gibbs Free energy for $MgHCO_3^+$(aq) is ΔG = -1048.3 KJ/mol, which is lower than the Gibbs Free energy of Magnesium Carbonate of ΔG = -1012.1 KJ/mol. (Shoba). Therefore, if the conditions that created the $MgHCO_3^+$(aq) ion are maintained, the $MgHCO_3^+$(aq) ion is the preferred species in the system.

3.2.0 Material and Methods

3.2.1. Magnesium carbonate–carbon dioxide draw solution and deionized water feed solution

The draw solution was made by mixing magnesium carbonate ($MgCO_3$), CO_2 (g) at partial pressure of 8 atm and deionized water and is brought to equilibrium. Equilibrium is accelerated by increasing the interactions of H_2CO_3 and $MgCO_3$ in solution. The feed solution was composed of deionized water. The temperature of the draw and feed solution was 25 ˚C.

3.2.2. Forward osmosis membrane

The membrane tested in this investigation was provided by Hydration Technologies Inc. (Albany, OR). The proprietary FO membrane is made from a hydrophilic cellulose-based polymer with a thickness of the membrane less than 50 um.

3.2.3. Forward osmosis crossflow set-up

The apparatus employed in our laboratory-scale FO experiments used a crossflow membrane unit (SEPA CF II Membrane system cell from GE Osmonics, Trevose, PA). The draw solution flowed on the permeate side and the deionized water on the feed side. Co-current flow is used to reduce strain on the suspended membrane. Mesh spacers are inserted within both channels to improve support. The spacers also promote turbulence and mass transport. Pressure vessels from Buchiglas USA Corp. Farmingdale, NY allowed for pressure of 112 psi for both CO_2 (g) and air.

3.2.4 Forward Osmosis performed with Sepa CF II membrane cell system

In the first experiment, the setup consisted of two pressure vessels, ball valves, gas tubing (rated for 250 psi), circulating pumps (rated for 145 psi), the Sepa CF II Membrane cell system and HTI FO membranes. The draw solution pressure vessel was prepared with 200 ml of deionized water with 20 grams of $MgCO_3$ (basic) from Fisher Scientific; 70% $MgCO_3$ and 30% $Mg(OH)_2$. The feed solution vessel was filled with deionized water and the vessels were connected to the Sepa CF II membrane cell system. The pressure vessels were pressurized to 135psi with the target chamber using CO_2 gas and the feed chamber using inert gas. The circulation pumps operated for 60 minutes. After 60 minutes, the solution from the draw solution vessel was collected and measured in a graduated cylinder.

In experiment two, the draw solution consists of NaCl and deionized water. The FO experiment test setup consisted of two pressure vessels, ball valves, gas tubing (rated for 250 psi), circulating pumps (rated for 145 psi), the Sepa CF II Membrane cell system and HTI FO membranes. The draw solution pressure vessel was prepared with 200 ml of deionized water with 100 grams of NaCl. The feed solution vessel was filled with deionized water and the vessels were connected to the Sepa CF II membrane cell system. The pressure vessels were pressurized to 135psi with the target chamber and the feed chamber using inert gas. The circulation pumps were turned on and after 60 minutes, the solution from the draw solution vessel was collected and measured in a graduated cylinder and the conductivity of the feed chamber was recorded.

3.2.5 Draw solution formation and degeneration experiments; CO_2 (g) and MgO

The open atmosphere experiment was conducted in an Erlenmeyer flask with 50 ml of deionized water and Magnesium Oxide in excess as Carbon dioxide gas was bubbled through the solution. After thirty minutes, the CO_2 (g) was stopped and air was bubbled through the solution. After another thirty minutes, CaO and MgO were added to the solution. Conductivity and pH measurements were recorded as a function of time.

The pressure vessel experiment was conducted using the pressure vessel, ball valves, gas tubing (rated at 250 psi) and a conductivity meter. Magnesium oxide in excess and 20 ml of deionized water was placed in the clear gas tubing with one end connected to the pressure vessel and the other end connected to the conductivity meter. The pressure vessel was pressurized to 14 atm of CO_2 (g). The systems were connected by opening the ball valve and conductivity readings were measured as a function of time.

3.2.6 Chemical analysis

The analytical techniques employed included:

- Fisher Scientific Accumet pH meter 900 was used to measure pH.
- Accumet conductivity meter (Model#AP75) was used to measure conductivity.
- NOTE: All experiments were conducted at ambient temperature and no significant difference in temperature were recorded between the chamber solutions. The relative humidity was maintained at 60%.

3.3 Results and Discussion

The researcher explained that the Sepa CF II membrane experiment produced a flux of purified water that equated to an OP of 34.8 atmospheres, while OLI predicted 33.2 atmospheres for the same combination of partial pressure and temperature. In addition, the experiment is a process that can be operated at elevated pressures without rupturing the membrane based on the transmembrane flux and the conductivity measurements in the feed solution. The researcher demonstrated that the open atmosphere experiment with CO_2 and MgO had the ability to create high osmotic pressures that are consistent with the OLI model predictions and demonstrates how the system can return to a low osmotic pressure. The researcher also demonstrated that the pressure vessel experiment could with the CO_2 (g) and MgO system achieve osmotic pressures greater than 25 atmospheres without agitating the system to stimulate the reaction. The researcher used the three experiments demonstrate how the PFO process is applicable for a variety of feed solutions in an FO application.

In Figure 44, the researcher provides the Osmotic pressure versus time for 1 atmosphere of CO_2 (g) with MgO in excess. The OP of the system was sustained while the PP remained constant and the system achieved 20 mS of conductivity.

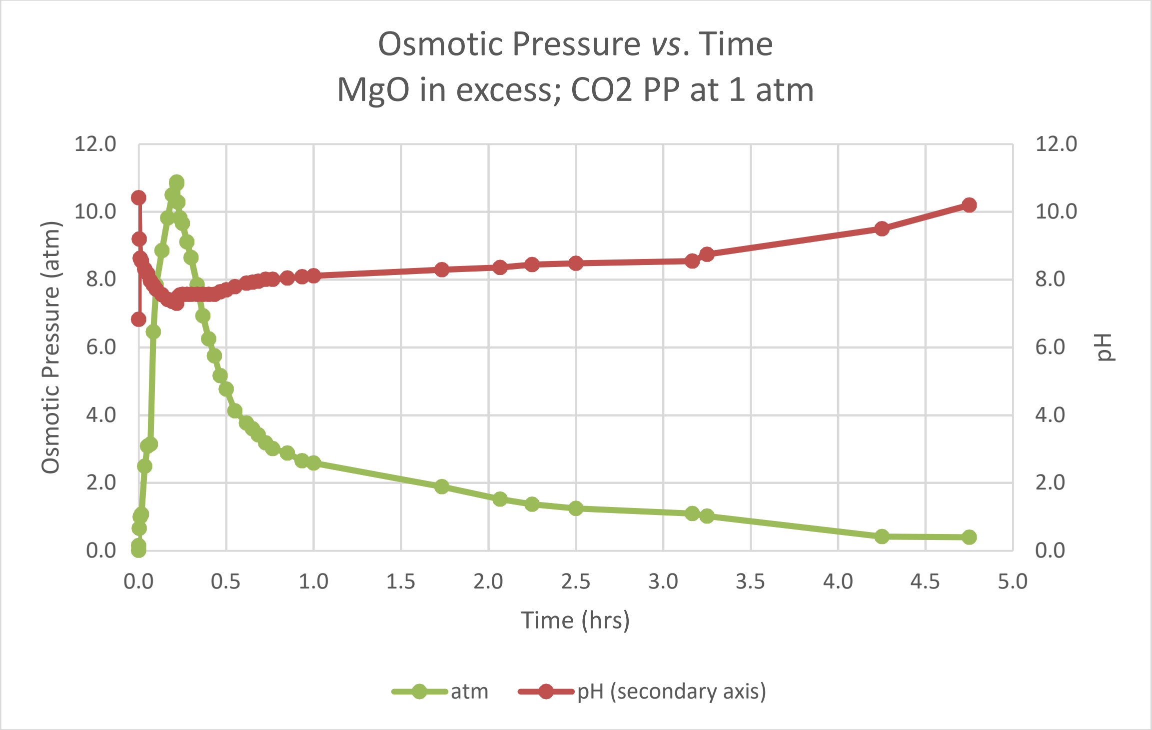


Figure 45 Osmotic pressure *vs*. time for CO_2 PP of 1 atm.; MgO in excess

The researcher demonstrated that the pressure vessel experiment could attain high osmotic pressures as a function of increased PP of CO_2 (g). The partial pressure of CO_2 at 14 atm was sustained for 1 week with the corresponding system OP achieving and sustaining a conductivity of 60 mS or Osmotic pressure of 26 atm. This OP is less than predicted by the OLI model, but attributed to the insufficient mixing of CO_2 and MgO. The researcher shows in Figure 5 the OP versus time for the experiment.

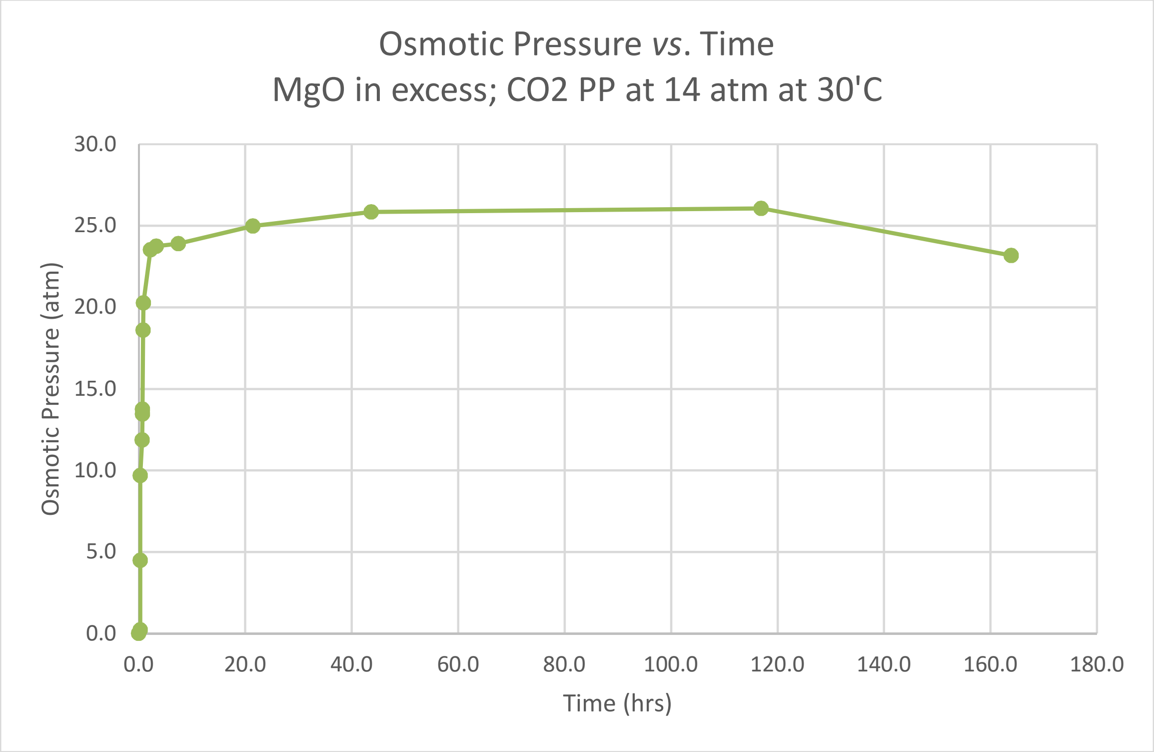


Figure 46 Osmotic pressure *vs*. time for CO2 PP of 14 atm.; MgO in excess

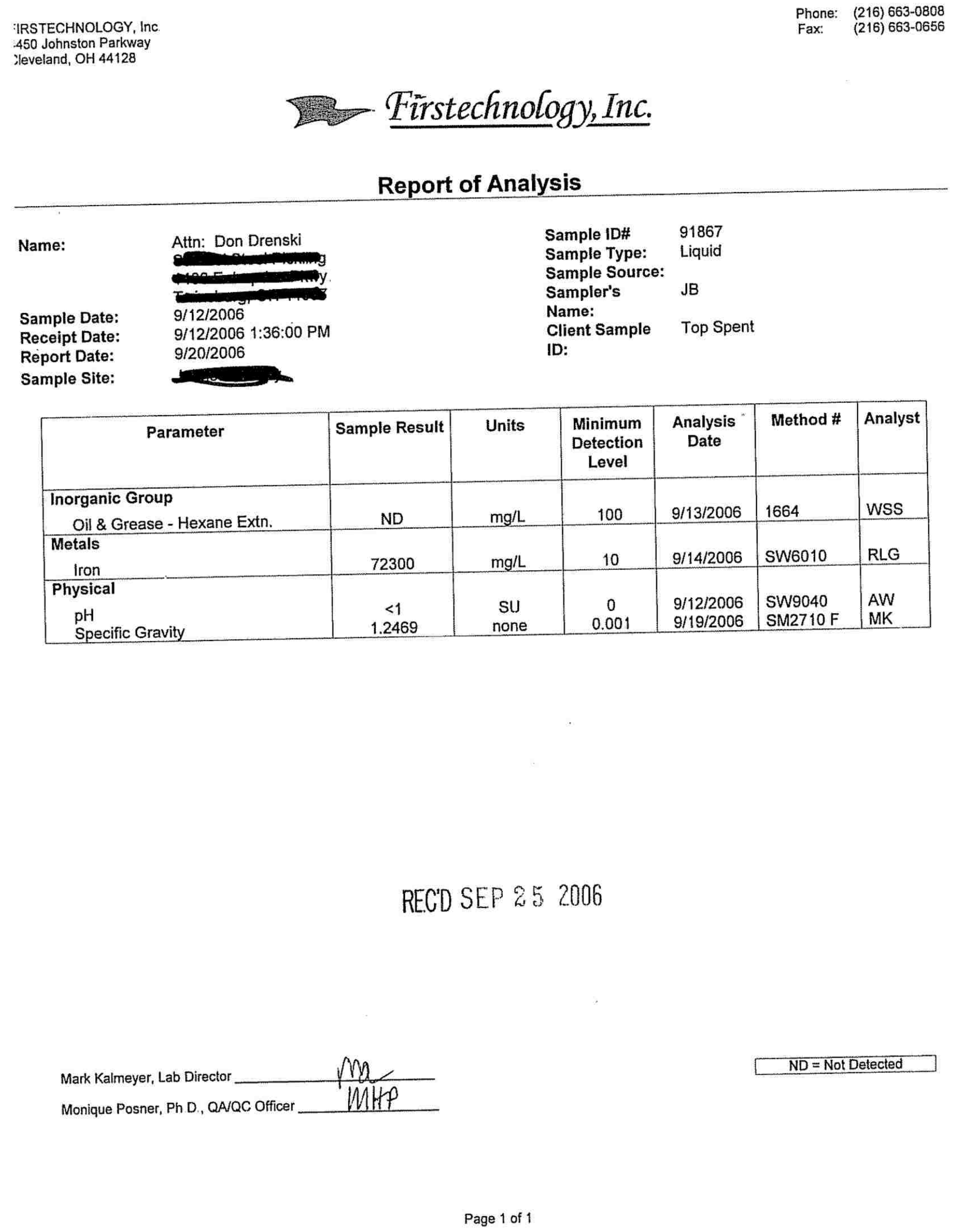
3.4 Conclusions

Through the initial findings, the researcher demonstrated that PFO has the potential for water treatment processes. The specific conclusions include:

- Osmotic pressure is increased by increasing the partial pressure of CO_2 in the $MgCO_3$ system
- Osmotic pressure is a function of unit mass of $MgCO_3$ and partial pressure of CO_2.
- The $MgCO_3$ and CO_2 system is stable until the partial pressure of CO_2 is removed.
- The researcher demonstrated how PFO can perform forward osmosis, if delta P does not exceed 0.5 atm; P_{Feed} approximately equals P_{Draw}.

- Regeneration of $MgCO_3$ and CO_2 are not required as they are the starting points for the process.

Appendix A. Report of Analysis for Waste Pickle Liquor



IRSTECHNOLOGY, Inc.
450 Johnston Parkway
leveland, OH 44128

Phone: (216) 663-0808
Fax: (216) 663-0656

Firstechnology, Inc.

Report of Analysis

Name: Attn: Don Drenski
[redacted]

Sample Date: 9/12/2006
Receipt Date: 9/12/2006 1:36:00 PM
Report Date: 9/20/2006
Sample Site: [redacted]

Sample ID# 91867
Sample Type: Liquid
Sample Source:
Sampler's Name: JB
Client Sample ID: Top Spent

Parameter	Sample Result	Units	Minimum Detection Level	Analysis Date	Method #	Analyst
Inorganic Group						
Oil & Grease - Hexane Extn.	ND	mg/L	100	9/13/2006	1664	WSS
Metals						
Iron	72300	mg/L	10	9/14/2006	SW6010	RLG
Physical						
pH	<1	SU	0	9/12/2006	SW9040	AW
Specific Gravity	1.2469	none	0.001	9/19/2006	SM2710 F	MK

REC'D SEP 25 2006

Mark Kalmeyer, Lab Director
Monique Posner, Ph D., QA/QC Officer MHP

ND = Not Detected

Page 1 of 1

IRSTECHNOLOGY, Inc.
450 Johnston Parkway
leveland, OH 44128

Phone: (216) 663-0808
Fax: (216) 663-0656

Firstechnology, Inc.

Report of Analysis

Name: [redacted]

Sample Date: 9/12/2006
Receipt Date: 9/12/2006 1:36:00 PM
Report Date: 9/20/2006
Sample Site: [redacted]

Sample ID# 91868
Sample Type: Discharge Water
Sample Source:
Sampler's Name: JB
Client Sample ID: Rinse x2

Parameter	Sample Result	Units	Minimum Detection Level	Analysis Date	Method #	Analyst
Metals						
Iron	2960	mg/L	1	9/14/2006	200.7	RLG
Physical						
pH (Lab - Est)	8.17	SU	0	9/12/2006	150.1	AW
Specific Gravity	1.0412	none	0.001	9/19/2006	SM2710 F	MK

Mark Kalmeyer, Lab Director ____________

Monique Posner, Ph.D., QA/QC Officer MHP

ND = Not Detected

Comment: "Est" Parameter: The method for this parameter specifies that it is to be analyzed in the field at the time of sampling. If this parameter is analyzed in the laboratory, the result must be flagged as an estimated value.

FIRSTECHNOLOGY, Inc.
4450 Johnston Parkway
Cleveland, OH 44128

Phone: (216) 663-0808
Fax: (216) 663-0656

Firstechnology, Inc.

Report of Analysis

Name: Attn: [redacted]

Sample Date: 9/12/2006
Receipt Date: 9/12/2006 1:36:00 PM
Report Date: 9/20/2006
Sample Site: [redacted]

Sample ID# 91869
Sample Type: Liquid
Sample Source:
Sampler's Name: JB
Client Sample ID: Dirty Spent

Parameter	Sample Result	Units	Minimum Detection Level	Analysis Date	Method #	Analyst
Inorganic Group						
Oil & Grease - Hexane Extn.	162	mg/L	100	9/13/2006	1664	WSS
Metals						
Iron	92600	mg/L	20	9/14/2006	200.7	RLG
Physical						
pH	4.58	SU	0	9/12/2006	SW9040	AW
Specific Gravity	1.2514	none	0.001	9/19/2006	SM2710 F	MK

Mark Kalmeyer, Lab Director ____________

Monique Posner, Ph D , QA/QC Officer MHP

ND = Not Detected

EA GROUP

EAG Workorder: **0504-00120** c\e

Client Project: **Spent Liquid**

EAG ID: **0504-00120-1** **Client ID:** **Spent-Liquid** **Sampled:** **Received:** **4/12/2005**

Parameter	Result	Sample Reporting Limit	Units	Prep Date	Analysis Date	Analyst
Aluminum	339	100	mg/liter	4/14/2005	4/18/2005	LES
Antimony	<20	20	mg/liter	4/14/2005	4/18/2005	LES
Arsenic	<10	10	mg/liter	4/14/2005	4/18/2005	LES
Boron	<10	10	mg/liter	4/14/2005	4/18/2005	LES
Barium	<5.0	5.0	mg/liter	4/14/2005	4/18/2005	LES
Beryllium	<1.0	1.0	mg/liter	4/14/2005	4/18/2005	LES
Cadmium	22.6	1.0	mg/liter	4/14/2005	4/18/2005	LES
Calcium	129	100	mg/liter	4/14/2005	4/18/2005	LES
Chromium	129	10	mg/liter	4/14/2005	4/18/2005	LES
Cobalt	2.10	1.0	mg/liter	4/14/2005	4/18/2005	LES
Copper	70.0	10	mg/liter	4/14/2005	4/18/2005	LES
Iron	141000	20	mg/liter	4/14/2005	4/18/2005	LES
Lead	<10	10	mg/liter	4/14/2005	4/18/2005	LES
Lithium	<10	10	mg/liter	4/14/2005	4/18/2005	LES
Magnesium	73.8	50	mg/liter	4/14/2005	4/18/2005	LES
Manganese	861	1.0	mg/liter	4/14/2005	4/18/2005	LES
Molybdenum	27.6	5.0	mg/liter	4/14/2005	4/18/2005	LES
Nickel	25.8	5.0	mg/liter	4/14/2005	4/18/2005	LES
Phosphorus	<50	50	mg/liter	4/14/2005	4/18/2005	LES
Potassium	<500	500	mg/liter	4/14/2005	4/18/2005	LES
Selenium	<50	50	mg/liter	4/14/2005	4/18/2005	LES
Silicon	37.6	20	mg/liter	4/14/2005	4/18/2005	LES
Silver	<5.0	5.0	mg/liter	4/14/2005	4/18/2005	LES
Sodium	<500	500	mg/liter	4/14/2005	4/18/2005	LES
Strontium	<1.0	1.0	mg/liter	4/14/2005	4/18/2005	LES
Sulfur	66.0	50	mg/liter	4/14/2005	4/18/2005	LES
Thallium	<20	20	mg/liter	4/14/2005	4/18/2005	LES
Tin	<5.0	5.0	mg/liter	4/14/2005	4/18/2005	LES
Titanium	<10	10	mg/liter	4/14/2005	4/18/2005	LES
Tungsten	<20	20	mg/liter	4/14/2005	4/18/2005	LES
Vanadium	41.7	10	mg/liter	4/14/2005	4/18/2005	LES
Zinc	7.63	5.0	mg/liter	4/14/2005	4/18/2005	LES
Mercury: EPA 245.2	<0.0050	0.0050	mg/liter	4/15/2005	4/15/2005	CMB

EA GROUP

EAG Workorder: 0504-00120

Client Project: Spent Liquid Tw 1

EAG ID: 0504-00120-2 **Client ID:** Spent-Solids **Sampled:** **Received:** 4/12/2005

Parameter	Result	Sample Reporting Limit	Units	Prep Date	Analysis Date	Analyst
Aluminum	<238	238	mg/kg	4/18/2005	4/19/2005	LES
Antimony	<4.75	4.75	mg/kg	4/18/2005	4/19/2005	LES
Arsenic	22.0	4.75	mg/kg	4/18/2005	4/19/2005	LES
Boron	<9.51	9.51	mg/kg	4/18/2005	4/19/2005	LES
Barium	245	2.38	mg/kg	4/18/2005	4/19/2005	LES
Beryllium	<2.38	2.38	mg/kg	4/18/2005	4/19/2005	LES
Cadmium	2.52	2.38	mg/kg	4/18/2005	4/19/2005	LES
Calcium	<238	238	mg/kg	4/18/2005	4/19/2005	LES
Chromium	927	4.75	mg/kg	4/18/2005	4/19/2005	LES
Cobalt	<2.38	2.38	mg/kg	4/18/2005	4/19/2005	LES
Copper	16.7	4.75	mg/kg	4/18/2005	4/19/2005	LES
Iron	14700	9.51	mg/kg	4/18/2005	4/19/2005	LES
Lead	<9.51	9.51	mg/kg	4/18/2005	4/19/2005	LES
Lithium	<4.75	4.75	mg/kg	4/18/2005	4/19/2005	LES
Magnesium	<238	238	mg/kg	4/18/2005	4/19/2005	LES
Manganese	257	4.75	mg/kg	4/18/2005	4/19/2005	LES
Molybdenum	242	2.38	mg/kg	4/18/2005	4/19/2005	LES
Nickel	4.41	2.38	mg/kg	4/18/2005	4/19/2005	LES
Phosphorous	142	23.8	mg/kg	4/18/2005	4/19/2005	LES
Potassium	<238	238	mg/kg	4/18/2005	4/19/2005	LES
Selenium	13.4	9.51	mg/kg	4/18/2005	4/19/2005	LES
Silicon	86.0	4.75	mg/kg	4/18/2005	4/19/2005	LES
Silver	<4.75	4.75	mg/kg	4/18/2005	4/19/2005	LES
Sodium	<238	238	mg/kg	4/18/2005	4/19/2005	LES
Strontium	<23.8	23.8	mg/kg	4/18/2005	4/19/2005	LES
Sulfur	3470	47.5	mg/kg	4/18/2005	4/19/2005	LES
Thallium	<4.75	4.75	mg/kg	4/18/2005	4/19/2005	LES
Tin	5.14	4.75	mg/kg	4/18/2005	4/19/2005	LES
Titanium	73.5	4.75	mg/kg	4/18/2005	4/19/2005	LES
Tungsten	<9.51	9.51	mg/kg	4/18/2005	4/19/2005	LES
Vanadium	94.0	4.75	mg/kg	4/18/2005	4/19/2005	LES
Zinc	40.6	9.51	mg/kg	4/18/2005	4/19/2005	LES
Mercury: SW846-7471A	<0.132	0.132	mg/kg	4/14/2005	4/15/2005	CMB

Firstechnology, Inc.

[redacted]

Attn: [redacted]

Site Location 2b

Work Order #:	0706-00154
Date Sampled:	06/02/2007
Date Received:	06/07/2007
Date Reported:	06/11/2007

Page : 2 of 2

Sample Descriptior 2b **Sample Date & Time** 06/02/2007 00:00

Lab ID: 001

Test Description	Result	Units	Reporting Limit	Method #	Analysis Date	Analyst
Oil & Grease	16.4	mg/L	8.34	1664	06/07/2007	BS

Appendix B. Pressurized Forward Osmosis Patent

US009580337B2

(12) **United States Patent**
SenGupta et al.

(10) **Patent No.: US 9,580,337 B2**
(45) **Date of Patent: Feb. 28, 2017**

(54) **PRESSURIZED FORWARD OSMOSIS PROCESS AND SYSTEM**

(71) Applicants: **Arup SenGupta**, Bethlehem, PA (US); **Robert Creighton**, Manheim, PA (US); **Ryan Smith**, Bethlehem, PA (US)

(72) Inventors: **Arup SenGupta**, Bethlehem, PA (US); **Robert Creighton**, Manheim, PA (US); **Ryan Smith**, Bethlehem, PA (US)

(73) Assignee: **Lehigh University**, Bethlehem, PA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **14/572,956**

(22) Filed: **Dec. 17, 2014**

(65) **Prior Publication Data**

US 2015/0175447 A1 Jun. 25, 2015

Related U.S. Application Data

(60) Provisional application No. 61/920,512, filed on Dec. 24, 2013.

(51) **Int. Cl.**
C02F 1/44 (2006.01)
B01D 61/00 (2006.01)
(Continued)

(52) **U.S. Cl.**
CPC ***C02F 1/445*** (2013.01); ***B01D 61/002*** (2013.01); ***B01D 61/005*** (2013.01); ***B01D 61/58*** (2013.01);
(Continued)

(58) **Field of Classification Search**
CPC C02F 1/445; C02F 2103/08; C02F 1/44; B01D 61/005; B01D 61/002; B01D 61/58; C01F 5/02; C01F 5/14; C01F 5/20; C01F 5/24
See application file for complete search history.

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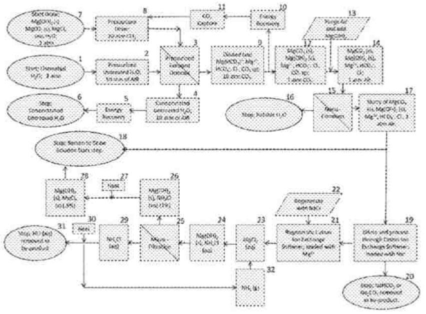
(Continued)

Primary Examiner — Katherine Zalasky
Assistant Examiner — Benjamin Lebron
(74) *Attorney, Agent, or Firm* — Saul Ewing LLP

(57) **ABSTRACT**

A pressurized forward osmotic separation process is disclosed. Generally there are two processes described. One process involves the concentration of a target solute in the first solution; the other process involves the extraction of a solvent from a first solution both by a second solution comprising of water and soluble gas or water, soluble gas, and a compound by creating an osmotic concentration gradient across the semi permeable membrane. The first solution is under pressure from an inert gas and the second solution is under pressure from a soluble gas with equal system pressures greater than 1 atmosphere. The increase or decrease of partial pressure of the soluble gas in the second solution increases or decreases the chemical potential of the

(Continued)



second solution to achieve different solution properties. The soluble gas may be carbon dioxide and the compound may be magnesium hydroxide.

17 Claims, 7 Drawing Sheets

(51) **Int. Cl.**

B01D 61/58	(2006.01)
C01F 5/02	(2006.01)
C01F 5/14	(2006.01)
C01F 5/20	(2006.01)
C01F 5/24	(2006.01)
C02F 1/68	(2006.01)
C02F 103/08	(2006.01)
C02F 103/32	(2006.01)
C02F 103/34	(2006.01)
C02F 103/00	(2006.01)
C02F 1/00	(2006.01)

(52) **U.S. Cl.**

CPC . ***C02F 1/44*** (2013.01); ***C02F 1/68*** (2013.01); *B01D 2311/25* (2013.01); *C01F 5/02* (2013.01); *C01F 5/14* (2013.01); *C01F 5/20* (2013.01); *C01F 5/24* (2013.01); *C02F 1/442* (2013.01); *C02F 2001/007* (2013.01); *C02F 2103/007* (2013.01); *C02F 2103/08* (2013.01); *C02F 2103/32* (2013.01); *C02F 2103/343* (2013.01); *C02F 2209/03* (2013.01); *C02F 2301/06* (2013.01)

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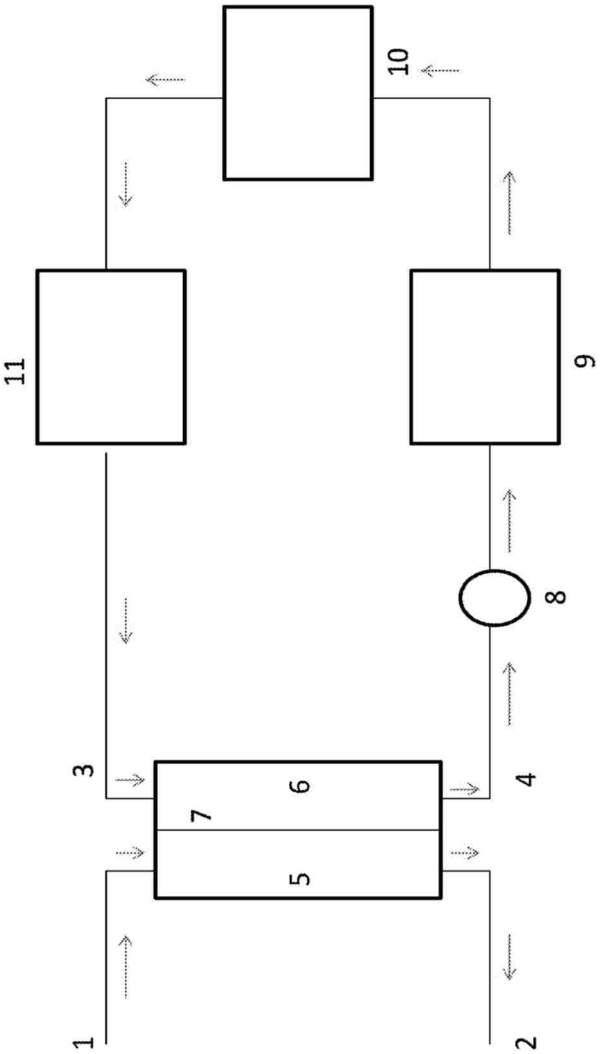

FIGURE 1

$$\text{Traditional FO; Flux} = D\,(\Delta P - \Delta\pi) = D\,((0\text{-}0) - (\,\pi_{\text{Feed}} - \pi_{\text{Draw}}\,)\,) \qquad (2.1)$$

$$\text{Pressurized FO; Flux} = D\,(\Delta P - \Delta\pi) = D\,((\,P_{\text{Feed}} = P_{\text{Draw}}\,) - (\,\pi_{\text{Feed}} - \pi_{\text{Draw}}\,)\,) \qquad (2.2)$$

FIGURE 2

$$Mg(OH)_{2(s)} + 2\,H^+ \longleftrightarrow Mg^{2+} + 2\,H_2O;\ \ K_{SO} = 10^{16.84} \qquad (3.1)$$

$$3CO_{2(g)} + 3\,H_2O \longleftrightarrow 3H_2CO_3\ ;\ 3 * K_H = 3 * 10^{-1.5} \qquad (3.2)$$

$$3H_2CO_3 \longleftrightarrow 3H^+ + 3HCO_3^-\ ;\ \ K_{a1} = 3 * 10^{-6.33} \qquad (3.3)$$

$$MgCO_{3(s)} \longleftrightarrow Mg^{2+} + CO_3^{\ 2-}\ ;\ \ K_{SO} = 10^{-7.5} \qquad (3.4)$$

$$CO_3^{\ 2-} + H^+ \longleftrightarrow 3HCO_3^{\ -}\ ;\ \ \frac{1}{K_{a2}} = 10^{\,10.33} \qquad (3.5)$$

$$MgCO_{3(s)} + 3CO_{2(g)} + Mg(OH)_{2(s)} \longleftrightarrow 2Mg^{2+} + 4HCO_3^-\ ;\ K = \frac{K_{SO} * 3K_H * 3K_{a1}}{K_{a2}} = 10^{\,-3.82} \qquad (3.6)$$

$$K = \frac{[Mg^{2+}]^2 * [HCO3^-]^4}{P_{CO2}^{\ \ 3}} = 10^{\,-3.82} \qquad (3.7)$$

Due to Electroneutrality, the following equation exists

$$[H^+] + 2[Mg^{2+}] = [OH^-] + [HCO_3^{\ -}] + 2[CO_3^{\ 2-}] \qquad (3.8)$$

At pH 7, the following equation exists

$$2[Mg^{2+}] = [HCO3^-] \qquad (3.9)$$

$$K = \frac{16[Mg^{2+}]^6}{P_{CO2}^{\ \ 3}} = 10^{\,-3.82} \qquad (3.10)$$

$$[Mg^{2+}] = \sqrt[6]{\frac{K}{16} * P_{CO2}^{\ \ 3}} \qquad (3.11)$$

FIGURE 3

System Temp.	CO2 Partial Pressure 0.0035 Atm	CO2 Partial Pressure 1.0 Atm	CO2 Partial Pressure 3.0 Atm	CO2 Partial Pressure 8.0 Atm	CO2 Partial Pressure 10.0 Atm
Degree Celcius	OP (Atm)	OP (Atm)	OP (Atm)	OP (Atm)	OP (Atm)
10 deg.	1.1	28.7	45.9	83.3	92.6
20 deg.	1.2	20.1	36.0	59.8	66.9
30 deg.	1.2	13.7	24.3	40.3	45.1

FIGURE 4

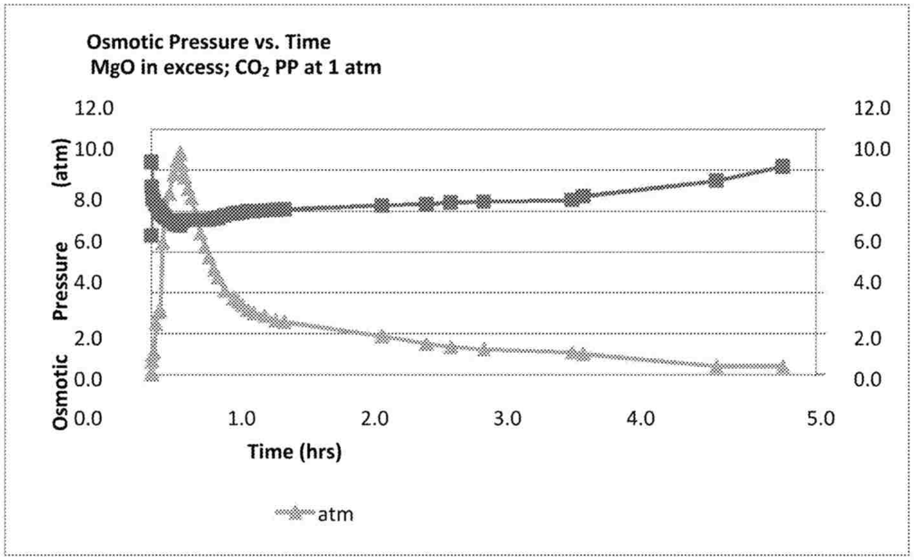
Osmotic Pressure vs. Time
MgO in excess; CO_2 PP at 1 atm
Osmotic Pressure (atm)
12.0
10.0
8.0
6.0
4.0
2.0
0.0
0.0
1.0
2.0
3.0
4.0
5.0
Time (hrs)
atm

FIGURE 5

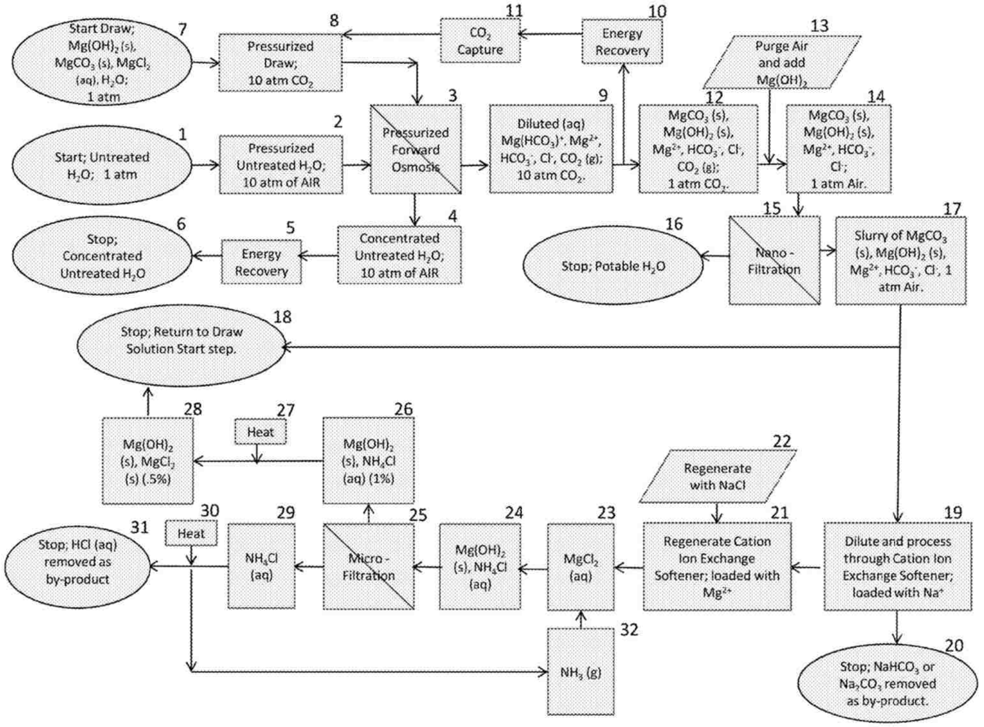
7
Start Draw; $Mg(OH)_2$ (s), $MgCO_3$ (s), $MgCl_2$ (aq), H_2O; 1 atm
8
Pressurized Draw; 10 atm CO_2
11
CO_2 Capture
10
Energy Recovery
13
Purge Air and add $Mg(OH)_2$
1
Start; Untreated H_2O; 1 atm
2
Pressurized Untreated H_2O; 10 atm of AIR
3
Pressurized Forward Osmosis
9
Diluted (aq) $Mg(HCO_3)^+$, Mg^{2+}, HCO_3^-, Cl^-, CO_2 (g); 10 atm CO_2.
12
$MgCO_3$ (s), $Mg(OH)_2$ (s), Mg^{2+}, HCO_3^-, Cl^-, CO_2 (g); 1 atm CO_2.
14
$MgCO_3$ (s), $Mg(OH)_2$ (s), Mg^{2+}, HCO_3^-, Cl^-; 1 atm Air.
6
Stop; Concentrated Untreated H_2O
5
Energy Recovery
4
Concentrated Untreated H_2O; 10 atm of AIR
16
Stop; Potable H_2O
15
Nano - Filtration
17
Slurry of $MgCO_3$ (s), $Mg(OH)_2$ (s), Mg^{2+}, HCO_3^-, Cl^-, 1 atm Air.
18
Stop; Return to Draw Solution Start step.
28
$Mg(OH)_2$ (s), $MgCl_2$ (s) (.5%)
27
Heat
26
$Mg(OH)_2$ (s), NH_4Cl (aq) (1%)
22
Regenerate with NaCl
31
Stop; HCl (aq) removed as by-product
30
Heat
29
NH_4Cl (aq)
25
Micro - Filtration
24
$Mg(OH)_2$ (s), NH_4Cl (aq)
23
$MgCl_2$ (aq)
21
Regenerate Cation Ion Exchange Softener; loaded with Mg^{2+}
19
Dilute and process through Cation Ion Exchange Softener; loaded with Na^+
32
NH_3 (g)
20
Stop; $NaHCO_3$ or Na_2CO_3 removed as by-product.

FIGURE 7

PRESSURIZED FORWARD OSMOSIS PROCESS AND SYSTEM

CROSS REFERENCE TO RELATED APPLICATIONS

The present application claims priority to U.S. Provisional application No. 61,920,512, filed Dec. 24, 2013, the entire contents of which are hereby incorporated by reference as non-limiting example embodiments.

The following patented and non-patented literature are also acknowledged

1. US 2011/0203994 A1
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FIELD OF THE INVENTION

The field of invention relates to osmosis process, more specifically, pressurized forward osmosis process for osmotic separation of aqueous solutions by providing osmotic pressure at different variations for seawater desalination, wastewater purification and product recovery in high purity applications.

BACKGROUND

Prior Art

Osmosis is a mass transport phenomenon that is defined as the net movement of water (solvent) across a selectively permeable membrane driven by a difference in osmotic pressure across the membrane. Forward osmosis and reverse osmosis are commercially viable for water purification and for traditional water treatment process. Forward osmosis provides an advantage over reverse osmosis because it operates at low or no hydraulic pressures, has high rejection of a wide range of contaminants, and it has a lower membrane fouling propensity than pressure driven membrane processes. Additional benefits of forward osmosis are that the only hydraulic pressure applied to the membrane is due to flow resistance in the membrane module and the membrane requires limited support. However, a limitation of forward osmosis is the costs associated with the draw solution regeneration process. In the alternative, pressurized forward osmosis creates a process that increases the competitive advantage over traditional osmosis processes. Pressurized forward osmosis operates the forward osmosis process under a system pressure greater than 1 atmosphere on both the sides of the system. Further using a soluble gas on the draw side of the system, the chemical potential is controlled by the applied partial pressure of the soluble gas. The energy required to pressurize the system can be recovered at high efficiency. The costs to regenerate the draw solutes and the marketable by-products net out a more competitive osmosis process versus other osmosis technologies.

US patent 2011/0203994 A1 describes a process whereby a draw solution is created by mixing ammonia gas and carbon dioxide gas which operates at high osmotic pressures, however the costs for the regeneration of the gases are high as the regeneration process requires heating the diluted draw solution to decompose the soluble ions into gases that leave the aqueous system. Additionally, there is a need for an alternative and improved cost effective method of forward osmosis for various industrial applications such as seawater desalination, wastewater purification and product recovery in high purity applications.

SUMMARY

In accordance with one or more embodiments, a pressurized forward osmosis separation process is disclosed. The process may comprise of introducing a first solution on the first side of a semi-permeable membrane and a second solution on the second side of a semi-permeable membrane with both the first side and second side under a system pressure equal to or greater than 1 atm. Further, the first side of the semi-permeable membrane is under pressure from an inert gas or air and the second side of the semi-permeable membrane is under pressure from a soluble gas or carbon dioxide at partial pressure greater than 0.00035 atmospheres, so that the resulting osmotic pressure in the second side is greater than the first side. This thereby forms an osmotic concentration gradient across the semi-permeable membrane which promotes the flow of at least a portion of the solvent of the first solution across the semi-permeable membrane to form a third solution on the first side of the semi-permeable membrane and a fourth solution on the second side of the semi-permeable membrane.

In some embodiments, the first solution may be an aqueous solution. In some embodiments, the first solution comprises a stream from surface water or wastewater or a pharmaceutical or food grade operation aqueous solution with low osmotic pressure. The target species may comprise of metals, salts, sugars, enzymes, proteins or microorganisms. In some embodiments, introducing the first solution on a first side of the semi-permeable membrane comprises immersing the semi-permeable membrane in the first solution. Introducing the second solution may comprise directing the second solution along the second side of the semi-permeable membrane. In at least one embodiment, the first solution is introduced continuously.

In some embodiments, recovering at least one target species comprises introducing the third solution to a settling vessel, hydrocyclone, precipitator, or force gradient operation. In some embodiments, the process may further comprise introducing the at least one recovered target species to a further treatment unit. At least one treated target species may be supplied to a downstream point of use.

In one or more embodiments, the process may further comprise promoting the flow of at least a portion of the fourth solution to a separation operation thereby releasing a soluble gas leaving a solvent stream. The process may further comprise of capturing the soluble gas or carbon dioxide and returning the soluble gas or carbon dioxide to the second side of the semi-permeable membrane. The process may further comprise a step of processing the solvent stream.

In accordance with one or more embodiments, a pressurized forward osmosis separation process is disclosed. The process may comprise introducing a first solution comprising a solvent and at least one target species on a first side of a semi-permeable membrane under a system pressure greater than 1 atmosphere of inert gas or air. The process may further comprise of introducing a second solution comprising of a magnesium species and carbon dioxide greater than 0.00035 atmosphere partial pressure with a system pressure equal to the first side, so that the resulting osmotic pressure in the second side is greater than the first side. This thereby forms an osmotic concentration gradient across the semi-permeable membrane which promotes the flow of at least a portion of the solvent of the first solution across the semi-permeable membrane to form a third solution on the first side of the semi-permeable membrane and a fourth solution on the second side of the semi-permeable membrane.

In some embodiments, the first solution may be an aqueous solution. In some embodiments, the first solution comprises a stream from sea water or wastewater or a pharmaceutical or food grade operation aqueous solution. The target species may comprise of metals, salts, sugars, enzymes, proteins or microorganisms. In some embodiments, introducing the first solution on a first side of the semi-permeable membrane comprises immersing the semi-permeable membrane in the first solution. Introducing the second solution may comprise directing the second solution along the second side of the semi-permeable membrane. In at least one embodiment, the first solution is introduced continuously.

In some embodiments, recovering at least one target species comprises introducing the third solution to a settling vessel, hydrocyclone, precipitator, or force gradient operation. In some embodiments, the process may further comprise introducing the at least one recovered target species to a further treatment unit. At least one treated target species may be supplied to a downstream point of use.

In one or more embodiments, the process may further comprise promoting the flow of at least a portion of the fourth solution to a separation operation thereby releasing a soluble gas and generating precipitates and a solvent stream. The process may further comprise of capturing the soluble gas and returning the soluble gas to the second side of the semi-permeable membrane. The process may further comprise processing the precipitates and returning the processed precipitates to the second side of the semi-permeable membrane. The process may further comprise a step of processing the solvent stream.

Still other aspects, embodiments, and advantages of these exemplary aspects and embodiments, are discussed in detail below. Moreover, it is to be understood that both the foregoing information and the following detailed description are merely illustrative examples of various aspects and embodiments, and are intended to provide an overview or framework for understanding the nature and character of the claimed aspects and embodiments. The accompanying drawings are included to provide illustration and a further understanding of the various aspects and embodiments, and are incorporated in and constitute a part of this specification. The drawings, together with the remainder of the specification, serve to explain principles and operations of the described and claimed aspects and embodiments.

BRIEF DESCRIPTION OF THE DRAWINGS

Various aspects of at least one embodiment are discussed below with reference to the accompanying figures. In the figures, which are not intended to be drawn to scale, each identical or nearly identical component that is illustrated in various figures is represented by a like numeral. For purposes of clarity, not every component may be labeled in every drawing. The figures are provided for the purposes of illustration and explanation and are not intended as a definition of the limits of the invention. In the figures:

FIG. **1** presents a schematic diagram of a pressurized forward osmosis process.

FIG. **2** describes forward osmosis and pressurized forward osmosis processes.

FIG. **3** describes the key reactions to develop a theoretical estimate of osmotic pressure per unit mass of MgX and partial pressure of CO_2

FIG. **4** describes the table of magnesium oxide and carbon dioxide system osmotic pressure

FIG. **5** provides a graphical representation of osmotic pressure and pH vs. time for CO_2 partial pressure of 1 atm.; MgO in excess. pH on Secondary axis.

FIG. **6** provides a graphical representation of osmotic pressure vs. time for CO_2 partial pressure of 14 atmosphere; MgO in excess

FIG. **7** provides a detailed schematic diagram of pressurized forward osmosis process and a detailed schematic diagram of draw solute regeneration.

DETAILED DESCRIPTION

In the disclosure herein, consideration or use of a particular element number in a given FIG. or corresponding descriptive material can encompass the same, an equivalent, or an analogous element number identified in another FIG. or descriptive material corresponding thereto.

In accordance with one or more embodiments, a pressurized forward osmosis separation process is disclosed herein, which may be used to extract various types of solutes from various types of solvents in solution. The desired products resulting from the disclosed process may include the solvent, the solute or both. In at least one embodiment, products such as metals, salts, sugars, enzymes, proteins, microorganisms, pharmaceuticals or other compounds may be recovered from a process stream. In other embodiments, waste streams such as seawater or wastewater may be treated to recover purified water for downstream use.

In accordance with one or more embodiments, the process may comprise of introducing a first solution with at least one target species on a first side of the semi permeable membrane under a specified system pressure greater than 1 atmosphere of inert gas or air. The process may further comprise of introducing a second solution with an increased concentration of solute relative to that of the first solution, comprising of a soluble gas or carbon dioxide at partial pressure greater than 0.00035 atmosphere or magnesium species and carbon dioxide at a partial pressure greater than 0.00035 atmosphere on the second side of the semi permeable membrane under an equal system pressure of first side forming an osmotic gradient across the semi permeable membrane, which promotes the flow of at least one portion of the first solution, forming a third solution on the first side of the semi permeable membrane and a fourth solution on the second side of the semi permeable membrane.

In another embodiment, the process may further comprise of promoting the flow of at least a portion of fourth solution to a separation operation to isolate and regenerate draw solutes and returning the draw solutes to the second side of the semi permeable membrane. The process may further comprise of recovering at least one or more target species from the third solution.

In some embodiments, the first solution is an aqueous solution and may comprise a stream of natural body of water, sea water, waste water, brackish water, food or pharmaceutical grade solution. The target species may comprise of metal, salt, sugar, protein, pharmaceutical compound, enzyme or microorganism.

In accordance with one or more embodiments, a pressurized forward osmosis separation system may include one or more forward osmosis membranes. The forward osmosis membranes may generally be semi-permeable, for example, allowing the passage of solvent such as water, but excluding dissolved solutes therein, such as sodium, chloride, magnesium, magnesium bicarbonate, bicarbonate, carbonate, other metals, salts, sugars, protein, pharmaceutical compound, enzyme, microorganism or other compounds. Many types of semi-permeable membranes are suitable for this purpose provided that they are capable of allowing the passage of water (i.e., the solvent) while blocking the passage of the solutes and not reacting with the solutes in the solution. The membrane can have a variety of configurations including thin films, hollow fiber membranes, spiral wound membranes, monofilaments and disk tubes. There are numerous well known, commercially available semi-permeable membranes that are characterized by having pores small enough to allow water to pass while screening out solute molecules such as sodium chloride and their ionic molecular species such as chloride. Such semi-permeable membranes can be made of organic or inorganic materials. In some embodiments, membranes made of materials such as cellulose acetate, cellulose nitrate, polysulfone, polyvinylidene fluoride, polyamide and acrylonitrile co-polymers may be used. Other membranes may be mineral membranes or ceramic membranes made of materials such as ZrO2 and TiO2.

In accordance with one or more embodiments, a pressurized forward osmosis separation system may generally be constructed and arranged so as to bring a first solution and a second solution into contact with first and second sides of a semi-permeable membrane, respectively. Although the first and second solutions can remain stagnant, it is preferred that both the first and second solutions are introduced by cross flow, i.e., flows parallel to the surface of the semi-permeable membrane. This may generally increase membrane surface area contact along one or more fluid flow paths, thereby increasing the efficiency of the forward osmosis. In some embodiments, the first and second solutions may flow in the same direction. In other embodiments, the first and second solutions may flow in opposite directions. In at least some embodiments, similar fluid dynamics may exist on both sides of a membrane surface. This may be achieved by strategic integration of the one or more forward osmosis membranes in the module or housing.

In accordance with one or more embodiments, methods may achieve a high yield of solvent extraction without excessive energy demands and/or environmentally harmful waste discharge. Solvent may be extracted to concentrate solutes, such as desirable target species, from a process stream in an energy efficient manner that results in high yields. The solvent and/or recovered solutes from the process stream may be desired end products. Solutes in the draw solution may also be recycled within the process.

In one or more embodiments, the disclosed pressurized forward osmosis process uses the added soluble gas under pressure to modify the chemical potential of the second solution and the gas pressure is not used to drive the osmotic process. Forward osmosis remains the driving force of the process as the second solution osmotic pressure is created by reacting water and magnesium species and carbon dioxide at partial pressures greater than 0.00035 atmosphere, while the system pressure of the first solution and the second solution are equal. In some embodiments, the traditional forward osmosis system has a sum of the hydraulic pressure terms (P terms) equal to zero and the process is driven by osmotic pressure. In pressurized forward osmosis, the P terms are equal and greater than 1 atmosphere and the process is driven by the resulting osmotic pressure. FIG. **1** provides a general schematic of the process. Equations 2.1 and 2.2 in FIG. **2** describe the traditional and pressurized forward osmosis process.

In another embodiment, the focus of the disclosed process is related to the creation of draw solution that is used in the pressurized forward osmosis process. Preferred solutes for the second solution may be magnesium oxide or magnesium hydroxide or magnesium carbonate (basic), or other magnesium species and carbon dioxide and their products; magnesium, magnesium bicarbonate, bicarbonate, carbonate when dissolved in water at various molar ratios and placed under a carbon dioxide partial pressure greater than 0.00035 atmosphere. A theoretical estimate magnesium ion concentration based on the partial pressure of CO_2 is developed by key reactions as illustrated in FIG. **3**, equations 3.1-3.11.

In accordance to one or more embodiments, a theoretical estimate of osmotic pressure per unit mass of magnesium hydroxide and partial pressure of CO_2 is determined from equation 3.11. FIG. **4**. provides the estimated osmotic pressure of the $CO_2/Mg(OH)_2$ system based on a computer model.

In another embodiment, the degeneration of the draw solution is performed by removing the CO_2 from the system; both the increased partial pressure and residual dissolved CO_2. By removing CO_2 from the system, the system immediately starts to form $MgCO_3$, which is an insoluble compound. The rate of precipitation is increased by purging air or inert gas through the system. In some embodiments the ion concentration can be further reduced by adding MgO or $Mg(OH)_2$ to increase the pH to drive the formation and precipitation of $MgCO_3$. In some embodiments, the addition of MgO or $Mg(OH)_2$ is also considered the first step of the process to restart the cycle.

In accordance with some embodiments, flat leaf experiment, open atmosphere experiment and pressure vessel experiment were performed to provide a technical basis for the disclosed process. The flat leaf experiment demonstrated that a transmembrane flux can be operated at elevated pressures without rupturing the membrane or increasing the salt diffusion into the feed solution. According to the process disclosed herein, the test set up for the flat leaf experiment included a test setup consisting of two pressure vessels, ball valves, gas tubing (rated for 250 psi), circulating pumps (rated for 145 psi), the flat leaf chamber and forward osmosis membranes. The draw solution pressure vessel was prepared with 200 ml of deionized water with 20 grams of $MgCO_3$ (basic); 70 percent $MgCO_3$ and 30 percent $Mg(OH)_2$. The draw solution vessel was charged to 135 psi partial pressure (approximate 8 atmosphere) of 99 percent CO_2 gas and allowed to achieve system equilibrium. The feed solution vessel was filled with deionized water and pressurized with air to 135 psi. The vessels were connected to the flat leaf system and pumps were turned on for 60 minutes. After 60 minutes, the solution from the draw solution vessel was collected and measured in a graduated cylinder that correlated to an osmotic pressure of 34.8 atmospheres.

In accordance with some embodiments, the open atmosphere experiment was conducted in an Erlenmeyer flask with 50 ml of deionized water and magnesium oxide in excess as carbon dioxide gas was bubbled through the solution. After a determined time period, the CO_2 was stopped and air was bubbled through the solution. After another determined time period, CaO and MgO were added to the solution. Conductivity and pH measurements were recorded as a function of time. The open atmosphere experiment with CO_2 and MgO demonstrated the ability for the system to cycle from high osmotic pressures to low osmotic pressures based on the partial pressure of carbon dioxide as illustrated in FIG. **5**.

According to some embodiments disclosed herein, the pressure vessel experiment was conducted using the pressure vessel, ball valves, gas tubing (rated at 250 psi) and a conductivity meter. Magnesium oxide in excess and 20 ml of deionized water was placed in the clear gas tubing with one end connected to the pressure vessel and the other end connected to the conductivity meter. The pressure vessel was placed under pressure of 14 atmosphere of 99 percent CO_2 gas. The systems were connected by opening the ball valve and conductivity readings were measured as a function of time. The pressure vessel experiment demonstrated that high osmotic pressures were attainable as a function of increased partial pressure of CO_2. The partial pressure of CO_2 at 14 atmosphere was maintained for 1 week with the corresponding system osmotic pressure achieving and sustaining a conductivity of 60 mS or osmotic pressure of 26 atmosphere as illustrated in FIG. **6**.

In accordance with one or more embodiments, flat leaf, open atmosphere and pressure vessel experiments make the case to use the pressurized forward osmosis process for a variety of feed solutions in pressurized forward osmosis applications.

In accordance with one or more embodiments as shown in FIG. **1**, a solution (**1**), for example, seawater, brackish water, wastewater, contaminated water or other solution, referred to as the first solution, is disposed in a first chamber (**5**). The first chamber is in fluid communication with a semi-permeable membrane. A second solution, the MgX/CO_2 draw solution (**3**), having a concentration greater than the first solution (**1**) is contained in second chamber (**6**). The higher concentration solution enables the solvent, i.e., the water, from the first solution in the first chamber (**5**) to osmosis across the semi-permeable membrane (**7**) into the more concentrated second solution located within the second chamber (**6**). Having lost much of its solvent, the remaining first solution (**1**) in the first chamber (**5**) is concentrated in solute (**2**). The solute (**2**) may be discarded if considered a waste product. Alternatively, the solute (**2**) may be a target compound and may be collected for further processing or downstream use as a desired product. The resulting solvent-enriched second solution (**3**) in the second chamber (**6**) is then introduced, as illustrated by arrow, into a third chamber (**9**). In the third chamber (**9**) magnesium carbonate is removed and magnesium oxide is added and directed into fourth chamber (**10**) where CO_2 at partial pressure greater than 1 atmosphere is added and directed into a fifth chamber (**11**). The solute enriched second solution from the fifth chamber (**11**) is cycled back to second chamber (**6**), as using a pump (**8**), to maintain the concentration of the second solution. The remaining solvent-enriched second solution in the third chamber (**9**), is mixed with inert gas to remove carbon dioxide from the solvent stream. In some embodiments, such as those involving treatment of seawater or wastewater, the solvent stream may be purified water.

In accordance with one or more embodiments, a separation process may begin by bringing the first solution and the second solution into contact with the first and second sides of the semi-permeable membrane (**7**), respectively. Although the first and second solutions can remain stagnant, it is preferred that both the first and second solutions are introduced by cross flow, i.e., flows parallel to the surface of the semi-permeable membrane (**7**). This increases the amount of surface area of the semi-permeable membrane a given amount of the solutions comes into contact with thereby increasing the efficiency of the forward osmosis. Since the second solution in the second chamber has a higher solute concentration than the first solution in the first chamber, the solvent in the first solution diffuses to the second solution by forward osmosis. During the separation process, the first solution becomes more concentrated as it loses solvent and the second solution becomes more diluted as it gains solvent. Despite this occurrence, the concentration gradient between the two solutions remains significant. The depleted solution on the first side of the membrane, and the diluted solution on the second side of the membrane may each be further processed for the recovery of one or more desired products. For example, the depleted solution on the first side of the membrane may contain solutes which are target species whose concentration and recovery is desired. Alternatively, the depleted solution on the first side of the membrane may be discarded as waste. Likewise, the diluted solution on the second side of the membrane may be processed to recover desired solvent.

The process described herein may be conducted continuously, or in batches, to better isolate the solutes from solvent throughout the process.

In accordance with one or more embodiments, wherein the said draw solutes are regenerated after use via at least one process of thermal, membrane, precipitation, aerosol, or gas process.

In accordance with one or more embodiments as shown in FIG. **7**, a detailed process is described that includes pressurized forward osmosis (steps **1**-**18**) and a draw solute regeneration process (steps **19**-**32**). FIG. **7** depicts one scenario that implements the pressurized forward osmosis process for operation in a continuous basis

In accordance with one or more embodiments, a system may be implemented to perform the regeneration of solutes process. One such process comprises of a first chamber, wherein a portion of the fourth solution is fed into the said chamber whereby the fourth solution is heated so that calcination of the solutes forms magnesium oxide and carbon dioxide. A second chamber is used to capture the carbon dioxide for reuse in the forward osmosis process.

In accordance with one or more embodiments, a system may be implemented to perform the regeneration of solutes process. One such process comprises of an ion exchange column, wherein the fourth solution is fed into an ion exchange column to remove the magnesium ions and release sodium ions, whereby forming a solution of sodium carbonate or sodium bicarbonate. A fifth solution of sodium chloride is fed into the ion exchange column to regenerate the column thereby releasing the magnesium ions and removing the sodium ions to form a solution of magnesium chloride, which is placed in the first chamber. A second chamber, wherein the magnesium chloride is mixed with ammonia gas thereby forming magnesium hydroxide (solid) and ammonium chloride. A third chamber, wherein the magnesium hydroxide is captured for reuse in the forward osmosis process. A fourth chamber, wherein the ammonium chloride is heated to form ammonia gas that is removed and captured in a fifth chamber and hydrochloric acid that remains in the fourth chamber for reuse in the regeneration of solutes process.

Any materials may be used to construct the various holding and/or storage devices (chamber, vessels and receptacles), conduits, piping, and related equipment, as long as they will withstand the weight of the solutions, and be unreactive with any solutes within the solutions. Typical materials are non-corrosive, non-reactive materials such as stainless steel, plastic, polyvinyl chloride (PVC), fiberglass, and so forth. The vessels can take any suitable configuration, but are typically cylindrical tanks, contoured or fitted tanks, and so forth. The receptacles are typically water towers, cylindrical tanks, contoured or fitted tanks, and so forth. It is important to note that the chambers are shown as separate units but the invention is not limited to that configuration, and where appropriate, any number of chambers can be contained within a single vessel, for example, partitioned into two chambers separated by the semi-permeable membrane (**7**).

Having now described some illustrative embodiments of the invention, it should be apparent to those skilled in the art that the foregoing is merely illustrative and not limiting, having been presented by way of example only. Numerous modifications and other embodiments are within the scope of one of ordinary skill in the art and are contemplated as falling within the scope of the invention. In particular, although many of the examples presented herein involve specific combinations of method acts or system elements, it should be understood that those acts and those elements may be combined in other ways to accomplish the same objectives.

It is to be appreciated that embodiments of the devices, systems and methods discussed herein are not limited in application to the details of construction and the arrangement of components set forth in the following description or illustrated in the accompanying drawings. The devices, systems and methods are capable of implementation in other embodiments and of being practiced or of being carried out in various ways. Examples of specific implementations are provided herein for illustrative purposes only and are not intended to be limiting. In particular, acts, elements and features discussed in connection with any one or more embodiments are not intended to be excluded from a similar role in any other embodiments.

Those skilled in the art should appreciate that the parameters and configurations described herein are exemplary and that actual parameters and/or configurations will depend on the specific application in which the systems and techniques of the invention are used. Those skilled in the art should also recognize or be able to ascertain, using no more than routine experimentation, equivalents to the specific embodiments of the invention. It is therefore to be understood that the embodiments described herein are presented by way of example only and that, within the scope of the appended claims and equivalents thereto; the invention may be practiced otherwise than as specifically described.

Moreover, it should also be appreciated that the invention is directed to each feature, system, subsystem, or technique described herein and any combination of two or more features, systems, subsystems, or techniques described herein and any combination of two or more features, systems, subsystems, and/or methods, if such features, systems, sub systems, and techniques are not mutually inconsistent, is considered to be within the scope of the invention as embodied in the claims. Further, acts, elements, and features discussed only in connection with one embodiment are not intended to be excluded from a similar role in other embodiments.

The phraseology and terminology used herein is for the purpose of description and should not be regarded as limiting. As used herein, the term "plurality" refers to two or more items or components. The terms "comprising," "including," "carrying," "having," "containing," and "involving," whether in the written description or the claims and the like, are open-ended terms, i.e., to mean "including but not limited to." Thus, the use of such terms is meant to encompass the items listed thereafter, and equivalents thereof, as well as additional items. Only the transitional phrases "consisting of" and "consisting essentially of," are closed or semi-closed transitional phrases, respectively, with respect to the claims. Use of ordinal terms such as "first," "second," "third," and the like in the claims to modify a claim element does not by itself connote any priority, precedence, or order of one claim element over another or the temporal order in which acts of a method are performed, but are used merely as labels to distinguish one claim element having a certain name from another element having a same name (but for use of the ordinal term) to distinguish the claim elements.

CONCLUSION, RAMIFICATIONS, AND SCOPE

While the above description contains many specificities, these should not be construed as limitations on the scope, but rather as an exemplification of one [or several] embodiments thereof. Many other variations are possible. Accordingly, the scope should be determined not by the embodiments illustrated, but by the appended claims and their legal equivalents.

We claim:

1. A pressurized forward osmosis separation method, the method comprising:

providing a semi-permeable membrane comprising a first surface and a second surface, wherein the first semi-permeable membrane surface is opposite to the second semi-permeable membrane surface;

contacting a first solution with the first semi-permeable membrane surface, wherein the first solution comprises a first solvent and a target solute; and

contacting a second solution with the second semi-permeable membrane surface, wherein the second solution comprises a second solvent and a magnesium ion species, wherein the magnesium ion species is at least one selected from the group consisting of magnesium oxide, magnesium hydroxide and magnesium carbonate;

wherein the first and the second semi-permeable membrane surfaces are under the same system pressure, which is equal to or greater than 1 atmosphere,

wherein the first semi-permeable membrane surface is under pressure from an inert gas or air, and

wherein the second semi-permeable membrane surface is under pressure from a gas mixture comprising carbon dioxide at a partial pressure greater than 0.00035 atmosphere, under conditions wherein $Mg(HCO_3)^{+1}$ is formed in the second solution;

whereby an osmotic concentration gradient is formed across the semi-permeable membrane, thus promoting flow of at least a portion of the first solvent from the first solution across the semi-permeable membrane to the second solution,

thereby generating a third solution in contact with the first semi-permeable membrane surface and a fourth solution in contact with the second semi-permeable membrane surface.

2. The method of claim **1**, wherein at least a portion of the fourth solution is processed to release gaseous carbon dioxide and generate a precipitate comprising magnesium carbonate.

3. The method of claim **1**, wherein the target solute is recovered from the third solution.

4. The method of claim **1**, wherein the first solution is an aqueous solution.

5. The method of claim **4**, wherein the first solution is at least one selected from the group consisting of surface water, wastewater, contaminated water, pharmaceutical solution and food grade solution.

6. The method of claim **1**, wherein the first solution contacts the first semi-permeable membrane surface and the second solution contacts the second semi-permeable membrane surface in a cross flow-filtration system.

7. The method of claim **1**, wherein the target solute is at least one selected from the group consisting of salt, sugar, enzyme, protein and microorganism.

8. The method of claim **1**, wherein the first semi-permeable membrane surface is fully immersed in the first solution, and wherein the second semi-permeable membrane surface is fully immersed in the second solution.

9. The method of claim **1**, wherein the semi-permeable membrane comprises organic materials or inorganic materials.

10. The method of claim **2**, wherein the fourth solution is further reacted with at least one selected from the group consisting of magnesium oxide and magnesium hydroxide.

11. The method of claim **1**, wherein the second solution is an aqueous solution.

12. The method of claim **9**, wherein the semi-permeable membrane comprises at least one selected from the group consisting of cellulose acetate, cellulose nitrate, polysulfone, polyvinylidene fluoride, polyamide and acrylonitrile copolymers.

13. The method of claim **9**, wherein the semi-permeable membrane comprises at least one selected from the group consisting of mineral membrane and ceramic membrane.

14. The method of claim **1**, further wherein at least a portion of the fourth solution is subjected to heating to generate a fifth solution and gaseous carbon dioxide.

15. The method of claim **1**, further wherein at least a portion of the fourth solution is subjected to an ion exchange process to generate a sixth solution comprising magnesium chloride.

16. The method of claim **15**, further wherein the sixth solution is treated with ammonia, forming magnesium hydroxide precipitate and a seventh solution comprising ammonium chloride.

17. The method of claim **16**, further wherein the seventh solution is heated to generate gaseous hydrogen chloride and gaseous ammonia.

* * * * *

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Vita

Robert Mervyn Creighton was born on July 15th, 1972 to Thomas Claire Buchannan and Sandra Wunderlich Creighton in Lancaster, PA. He completed a Bachelor of Science Degree in Civil and Environmental Engineering (CEE) in 1994 followed by a Master of Science Degree in CEE from Lehigh University in 1996 under Dr. SenGupta. After two years working in solid waste consulting, he completed a Master of Business Administration from Lehigh University in 2000. He worked in the Telecommunications Industry with Lucent Technologies/Alcatel-Lucent/Nokia in business/engineering operations roles from 2000 to 2017. In 2009, he joined Dr. SenGupta's lab to research membrane technologies including forward osmosis and ion exchange technologies supporting water treatment technologies. He structured joint investigation efforts with industry partners including Hydration Technology Innovations and Fluid Technology Solutions, Inc. and, in 2017, he and Dr. SenGupta were awarded a patent for on novel forward osmosis process, "Pressurized forward osmosis process and system," Publication number US9580337 B2, Application number US 14/572,956. His most recent work includes the use of industrial waste water to perform water softening and brackish water demineralization. His research paper is pending submission to the journal review process, and he intends to file a provisional patent for the technology. During his time at Lehigh, he was a Teaching Assistant for Professional Development CEE203 under Dr. John Wilson.