**Desalination & Water Purification Research
And Development Program Report No. XXX**

Investigating and Understanding the Selectivity of the Conventional Ion-exchange Membranes used in Electrodialysis Process

Prepared for Reclamation Under Agreement No. R10AC80283

by

Leila Karimi, Abbas Ghassemi

**U.S. Department of the Interior
Bureau of Reclamation
Technical Service Center
Water and Environmental Services Division
Water Treatment Engineering Research Team
Denver, Colorado**

December 2014

MISSION STATEMENTS

The mission of the Department of the Interior is to protect and provide access to our Nation's natural and cultural heritage and honor our trust responsibilities to Indian tribes and our commitments to island communities.

The mission of the Bureau of Reclamation is to manage, develop, and protect water and related resources in an environmentally and economically sound manner in the interest of the American public.

Disclaimer

Acknowledgements

Table of Contents

Glossary

Variable	Description
ΔC	desired ion concentration difference between feed and dilute streams
C	ion concentration
D	ion diffusion coefficient
D	desalting cell width
F	Faraday constant
f	molar activity
I	electrical current
i	total current density
IEC	anion exchange membrane
J	total flux of ion i
L	flow path length
N	number of cell pairs
n	number of anions and cations in the solution
P	swelling pressure of the membrane
Q	flow rate
R	molar gas constant
T	temperature
t	transport number of ion i
t	residence time
u	ion mobility
v	velocity of bulk flow
V	solution linear velocity in the dilute chamber
z	electrical charge
$\dfrac{d\bar{\phi}^{CM\ or\ AM}}{dx}$	electrical potential gradient in the cation or anion exchange membrane

iv

PS_i^j permselectivity of ion i against j in the membrane phase

Greek Variable

μ	chemical potential
φ	electrical potential
α	ion activity
ν	partial molar volume
η	current efficiency
λ	individual ion conductivity
ξ	a dimensionless number
Λ	equivalent conductivity

Superscript

m	membrane phase
s	solution phase

Subscript

i	ion type
j	ion type
cp	cell pair
diff	diffusion
mig	migration
AM	anion exchange membrane
CM	cation exchange membrane
resid	residence time
conv	convection
Don	Donnan

Executive Summary

Drinking water shortage is a worsening issue in the world. After surface water resources, groundwater supplies are very important sources of drinking water in many parts of the world as well as southwest region of the United States. One of the common technologies used for the desalination of brackishwater is electrodialysis/electrodialysis reversal (ED/EDR). The basic design of ED and EDR is the same, except that in ED the direction of the electrical current and ion flow is constant, while in EDR the direction of the electrical current and ion flow is reversed periodically. The reversal of the electrical current and ion flow in EDR gives the system self-cleaning characteristics and decreases scaling, a universal problem for membrane-based systems in which minerals create a hard build-up that clogs the filter membrane. Because EDR is relatively resistant to scaling, especially from silica, EDR is better suited for desalination than other membrane-based technologies such as reverse osmosis (RO). This is particularly important in the case of the desalinization of saline water with significantly high silica content. Among the saline water sources (feedwaters) which are desalinated to produce freshwater, the types and quantities of ions vary. Since drinking water standards allow different types of ions to be present at different levels, sometimes desalination plants only need to remove particular types of ions, while other ions can remain. Consequently, the development of preferential ion removal in the ED/EDR process could increase the efficiency of the technology in cases where the ion composition of a feedwater is well-known. Additionally, the selective removal of ions would help reduce the cost of desalination or anionic contaminant removal by reducing the number of moles of ions that must be removed to get appropriate results.

In this study, the experiments were conducted at the Brackish Groundwater National Desalination Research Facility (BGNDRF) in Alamogordo, NM, on a General Electric Company pilot-scale EDR system with an influent flow rate capacity of 12 gpm (0.775 L/s). Brackish feedwater with a conductivity of 1700 µS/cm was acquired from the aquifer in Tularosa Basin. The experiment operated with a single electrical/hydraulic stage using CR67HMR cation-exchange membranes and three types anion-exchange membranes - AR908, AR204, and aged-AR204 – as well as a Spacer-Mark IV with an effective membrane surface area of 3,540 cm^2.

The objective is to study the effect of operating conditions on the removal of ions in EDR, and to investigate the selective removal of different ions in this process. Additionally, three different types of anion exchange membranes were used to show their behavior in the removal of ions. Then, the sensistivities of selectivity values for cations and anions were explored. Finally, the influence of two different phases, solution phase and membrane phase, were defined using a dimensionless number.

1

Chapter 1: Introduction

1.1 Background

Drinking water in the southwestern region of the United States is heavily dependent upon groundwater (United States Geological Survey, 2011). Groundwater supplies have various water chemistries. Depending on the geological formation, the regional precipitation level, and an aquifer's characteristics, groundwater can contain various amounts of anions such as chloride, sulfate, and alkalinity species (i.e., carbonate/bicarbonate), which contribute to high total dissolved solids (TDS) and/or salinity. In addition to these regular species, the presence of small contamination levels from some other anions such as nitrate, perchlorate, and fluoride poses a risk to public health. If the amount of one or more of these anions in a groundwater resource is higher than the levels established in national primary/secondary drinking water standards (EPA, 2011) or local standards, there is a need to reduce the level of the ions that have exceeded the maximum allowed level.

Reverse osmosis (RO), electrodialysis (ED), ion-exchange (IX), and coagulation/filtration are efficient technologies for removing both: 1) anionic species that cause high TDS/salinity, and 2) contamination from some specific anions (MWH, 2005; Clifford and Ghurye, 2002). Although some development has occurred, the lack of selectivity is a considerable issue in these technologies. In general, there are always competitor ions that interfere with the removal of ion(s) of interest, which makes the process more costly. For instance, if there is some nitrate contamination in a groundwater, but other anions in that groundwater are at acceptable levels, then the other ions would interfere in nitrate removal using IX, RO, or ED technologies, making the actual cost of nitrate removal much higher than the theoretical cost of nitrate removal might have been. Another example is Tularosa Basin's typical groundwater, wehere most of its salinity is due to sulfate salts and chloride is in acceptable level; therefore, the removal of sulfate using RO or ED technologies encounters interference from other ions including chloride, and this interference imposes extra cost to this desalination technology. Thus, selectively removing ion(s) of interest is an area that needs more research.

Selective IX resins have been produced and are available to remove nitrate and perchlorate. Nitrate-selective resins are developed by increasing the length of the functional group from trimethyl amines to triethyl amines and/or tributyl amines (Guter, 1984). The distance between functional groups affects the divalent/monovalent selectivity (Guter, 1984). For perchlorate-selective resins, the order of the selectivity is known to be perchlorate > nitrate > chloride > bicarbonate (Gu and Coates, 2006). Still, there are interferences of other ions in selective resin applications. For instance, increasing the sulfate/nitrate ratio in water from 1 to 10 decreases the percent capacity of the resin allocated to nitrate adsorption from 98% to 85%, and the unwanted removal of sulfate increases.

2

RO membranes are more selective for divalent ions than monovalent ions. In natural waters, the order of ion rejection using conventional RO membranes is $SO_4^{-2} > Ca^{+2} > Mg^{+2} > HCO_3^- > Na^+ > K^+ > Cl^- > Br^-$ (Sata et al., 1997). Although RO membranes reject more divalent ions, there are always amounts of monovalent ions that are removed from water. This removal causes more osmotic pressure in the RO chamber, which increases pressure drop and makes the desalination process more costly.

Some advancements have been reported in the manufacturing of ion-exchange membranes used in the ED systems, increasing the process selectivity for some ions of interest compared to the rest of the ionic species. Monovalent and divalent species separation has been studied (Van der Bruggen et al., 2004; Sadrzadeh et al., 2007). Charge repulsion, attraction, and ionic size are important factors that affect separation between monovalent and multivalent anions (Sata et al., 1997). In addition, operating conditions such as current density, influent flow rate, and acidity (pH) have influences on the permselectivity of the ED ion-exchange membranes used to separate monovalent and multivalent anions. It has been demonstrated that a decrease in current density increases the selectivity of both conventional (non-selective) and monovalent selective ED anion-exchange membranes (Zhang et al., 2009). Still, these membranes are not 100% selective for divalent or monovalent anions and there is always interference of other ions involved in ED removing anions of interest.

To the best of available knowledge, there has not been an extensive study that investigates the selectivity of anion-exchange membranes for various divalent (e.g., sulfate (SO_4^{2-}) and selenate (SeO_4^{2-})) or various monovalent (e.g., nitrate (NO_3^-) and chloride (Cl^-)) species. There is a need to understand the selectivity of available anion-exchange membranes for various divalent and various monovalent species in the case of desalination. In addition, there is a need to comprehend and characterize the selectivity of available anion-exchange membranes for removing trace amounts of anion contaminants, such as fluoride, in the presence of other anions that are normally present in drinking water. The reason is that the amount of energy used in the ED process for desalination or contaminant removal is proportional to the number of moles of ions that are removed from water. The selective removal of ions would help to reduce the cost of desalination or anionic contaminant removal by reducing the number of moles of ions needed to be removed to get appropriate results.

The ion removal not only depends on the selectivity of the ion exchange membranes, but also on how quickly ions move toward the boundary layers and ion exchange membranes. Therefore, the ion removal rate depends on both the affinity of membrane for a certain ion in aqueous solution and the ion movement in the solution phase.

In membrane phase, the selectivity is the affinity of a membrane for a certain ion in aqueous solution, and depends on physical and chemical characteristics of the ion. The magnitude of the valence and the atomic number of the ion are two important factors in determining selectivity (Crittenden et al., 2005). The pore size distribution and the types of functional groups on the polymer chain are also determinant factors for the selectivity. The most important

3

factor affecting the selectivity is the spacing of functional groups (Clifford and Weber, 1986). A divalent ion requires two adjacent active functional groups to connect to and to satisfy the electroneutrality of the exchange chemical reaction. Therefore, increasing the distance between active functional groups decreases the selectivity for divalent ions (e.g. sulfate) (Crittenden et al., 2005). Alternately, monovalent selectivity can be obtained by coating the surface of the anion exchange membrane with a negatively charged layer (Strathmann, 2004).

Both monovalent and divalent selective membranes have been developed. Commercially, monovalent selective membranes are mostly used in the desalination of sea water.

1.2 Conclusions and Recommendations

Conclusion

- Operating parameters, such as applied voltage, solution superficial velocity, temperature, and ion characteristics, have a significant effect on ion removal in the EDR process.

- Increasing the applied voltage in the stack improves ion removal before reaching the limiting current conditions.

- Increasing the solution flow rate (velocity) has an adverse effect on the removal of all ions, due to decreases in the residence time of ions in the EDR stack.

- Increasing the temperature has a positive influence on ion removal due to increases in the ion mobility in both membrane and solution phases.

- Ion characteristics, such as ion size and charge, have a significant effect on the removal of ions; ions with a smaller size and larger charge are removed more than the others.

- The selectivity values of cations, compared to Na^+ removal, and anions, compared to Cl^- removal, are as follows using CR67 and AR204 cation and anion exchange membranes, respectively:

  $$Ca^{2+} \geq Sr^{2+} \geq Mg^{2+} > K^+ > Na^+$$
  $$SO_4^{2-} > Cl^- > HCO_3^- > F^-$$

- Sensitivity analysis of selectivity shows that selectivity values for cations and anions were more sensitive at lower values of ξ compared to its higher values, with ξ representing the operating conditions. Therefore, the selectivity studies can be investigated better at mild operating conditions.

- The obtained results confirmed that the aged anion exchange membranes (aged-AR204) which were used in a waste water treatment plant, showed lower selectivity values for divalent ions compared to the new anion exchange membranes, which showed higher selectivity values for divalent

4

anions. This observation strengthens the idea of a negative surface charge on the aged-AR204 anion exchange membranes, which cause divalent anions' repulsion.

- The removal of ions in the EDR process can be considered in three distinct regions based on the ξ values. In the first region, the membrane phase has a strong role in the selective removal of ions. In the second region, a combination of the membrane phase and the solution phase affects the ion removal. However, in the high values of ξ (region III), all ions are removed simultaneously regardless of the type of ion, or the effects of solution phase and ion exchange membrane phase.

Recommendations

- Characterization of aged-AR204 membranes can confirm, or reject, the hypothesis of a negative surface charge on the membrane surface.

- Testing different water compositions can add more valuable results to this study.

- Studying the removal of ions individually, and mixture of ions, can provide a better picture of ion removal and the role of ions' interaction in selectivity studies.

- Theoretical models can be developed for the selective removal of ions in the EDR process, and these models can be verified with experimental work.

- The selectivity behavior of cation exchange membranes can be investigated using the same approach as for anion exchange membranes.

Chapter 2: Literature Review

2.1 Introduction

2.1.1 Fresh Water Scarcity

Water is an essential chemical material for every living organism on this planet, and it is necessary to maintain proper body function. Naturally, fresh water resources are limited by their quantity. However, there are other factors – such as population increase, industrial development, environmental parameters, and pollution introduction – that affect its availability. Today, fresh water scarcity has drawn the world's attention. It presents the most significant challenge to economic and social development in many countries. By the year 2030, it is estimated that world water needs will increase from 4500 billion cubic meters to 6900 billion cubic meters, 40% greater than current supplies (Addams et al., 2009).

2.1.2 Different water categories and availabilities

With regard to their levels of total dissolved solids (TDS), water resources are categorized into four types, as shown in table 2-2 (Anon., 2014).

2.2 Desalination as a solution to drinking water scarcity

Desalination is the physical-chemical process of removing salt from water. There are different desalination technologies, and the applicability of each depends on factors such as saline water type, energy availability, product application, and required treatment capacity. One of the most applicable desalination technologies across many conditions, especially brackish water treatment, is electrodialysis/ electrodialysis reversal.

2.2.1 Electrodialysis/ Electrodialysis Reversal

Electrodialysis is a membrane-based separation process in which ions are transferred through an ion exchange membrane under the influence of an applied electrical field (Mulder, 1951).

2.2.1.1 *Ion Exchange Membrane*

Ion exchange membranes are divided into two main groups: cation exchange membranes (CEM) and anion exchange membranes (AEM). Cation exchange membranes are negatively charged polymeric membranes, mostly charged with sulfonic or carboxylic acid groups. In contrast, anion exchange membranes are positively charged with quaternary ammonium salts. Co-ions, the ions with similar charges, are repelled from the membrane surface as a result of

6

interaction with these fixed charged groups. These ion exchange membranes can be synthesized in two different forms, as either heterogeneous or homogenous structures. Due to a higher mechanical strength and lower electrical resistance, the homogeneous structure tends to be preferred. The synthesis of these membranes is achieved through the introduction of an ionic group into a polymeric film. The charges are distributed uniformly in the polymer matrix, while a degree of cross-linking sufficient enough to prevent excessive swelling should be present in the polymer structure (Mulder, 1951). Although ion exchange membranes were designed for electrodialysis applications, they are also used extensively in several other processes such as fuel cells, bipolar membrane electrodialysis, and electrodeionization (Tanaka, 2007). Ion exchange membranes are characterized by their properties of electrical resistance, ion exchange capacity, water content, ion transport number, solute permeability coefficient, electrosmotic coefficient, water permeation coefficient, swelling ratio, and mechanical strength (Tanaka, 2007).

2.2.1.2 *Donnan Potential*

As discussed in the previous section, the two groups of ion exchange membranes contain counter ions in their polymeric structures; cation exchange membranes have fixed anions and mobile cations, while anion exchange membranes have fixed cations and mobile anions. When a cation exchange membrane is placed into a strong electrolyte solution, a significant difference in the concentration of ions between the membrane and solution phases occurs. Specifically, the concentration of cations in the membrane phase far exceeds that of the solution phase, while the concentration of anions in the solution phase is much greater than that of the membrane phase. The tendency to eliminate this concentration difference causes the cations to diffuse into the solution phase while the anions diffuse into the membrane phase. However, during the diffusion of the first few ions, a very strong electrical potential occurs that pulls the counter ions (cations) back into the membrane phase, and co-ions (anions) back into the solution phase; this is known as the Donnan potential. Through this, equilibrium is achieved because the tendency of ions to eliminate the concentration difference is neutralized by the effect of the electrical field. As a result, the co-ions are repelled from the membrane, and effect that is called Donnan exclusion (Strathmann, 1995; Helfferich, 1962). The Donnan potential cannot be measured experimentally, but it can be calculated from electrochemical equilibrium between the two phases as follows (Strathmann, 1995):

$$\eta_i^M = \eta_i^s \qquad\qquad \text{Eq. 2-1}$$

where η is the electrochemical potential. The superscripts *m* and *s* are membrane and solution phases and the subscript i, represents the ion type. The electrochemical potential of ion i can be calculated using the following equation:

$$\eta_i = \mu_i + z_i F \varphi \qquad\qquad \text{Eq. 2-2}$$

where μ_i, z_i, F, and φ are chemical potential, electrical charge, Faraday constant, and electrical potential. By assuming that the temperature of the membrane and

solution phases are equal, the Donnan potential can be calculated by the following equation:

$$\Delta\varphi_{Don} = \varphi^M - \varphi^s = \frac{1}{z_i F}\left(RT ln\frac{a_i^s}{a_i^M} - v_i P_s\right)$$

<div align="right">Eq. 2-3</div>

where $\Delta\varphi_{Don}$, φ^M, φ^s, $\alpha^s{}_i$, $\alpha^M{}_i$, v_i, and P_s are Donnan potential, electrical potential in membrane, electrical potential in solution , temperature, activity of ion i in solution, activity of ion i in the membrane, partial molar volume of the ion i, and swelling pressure of the membrane phase, respectively.

2.2.1.3 *Electrodialysis Applications*

The ED process has been applied commercially for more than 50 years (Strathmann, 2010). This technology is the most applicable desalination process when the total TDS of feed water is within 400-6000 ppm (Kalogirou, 2005). However, some researchers have reported success in desalinating saline water with TDS of 30,000 ppm (Tanaka et al., 2003). Nonetheless, very wide applications for electrodialysis exist aside from desalination, including the removal of Cr, Cu (Barakat, 2011; Mohammadi et al., 2005), Co(II), Ni(II) (Tzanetakis et al., 2003), and Cd (Marder et al., 2004), (Jakobsen et al., 2004), Pb^{2+} (Abou-Shady et al., 2012). There have also been demonstrations in Japan and Korea of several applications that use this process for the production of sodium chloride. ED also has several advantages for the treatment of wastewater loaded with heavy metals, including the ability to recover valuable metals such as Cr and Cu, and the benefit of easier disposal due to the production of a highly concentrated waste stream. Additionally, ED processes are also used to recover acids and bases from industrial waste water (Kedem et al., 2010).

2.2.1.4 *Electrodialysis stack*

The electrodialysis stack is the major unit of an electrodialysis system. It is composed of alternating series of cation and anion exchange membranes. These ion exchange membranes are the walls of dilute and concentrate chambers. Between each pair of ion exchange membranes, a spacer is used which creates the thickness of the desalting and concentrating chambers as well as introducing the turbulence to the flows. The stack of ion exchange membranes and spacers is placed between two electrodes which are in contact with electrode rinse solutions. An electrical field is then created by applying differential electrical potential on these electrodes; this generates ionic movement, with the anions attempting to move toward the anode, and the cations attempting to move in the opposite direction toward the cathode. The affected anions pass through the anion exchange membranes, but are blocked by cation exchange membranes in the next chamber. Similarly, the cations pass through the cation exchange membranes but are blocked by the anion exchange membranes in the same chamber where the cations are trapped. This results in what is known as the concentrate chamber, where cations are held on one side by the anion exchange membrane, and anions are held on the other side by the cation exchange membrane. The other type of chamber, which now has far fewer cations and anions, is referred to as the dilute

<div align="center">8</div>

chamber. Therefore, two different solutions, one dilute and the other concentrate, are generated in the electrodialysis process. The schematic figure of the electrodialysis stack is shown in figure 1-1.

The electrodialysis reversal (EDR) process utilizes the same fundamentals that electrodialysis (ED) does. However, it has an additional feature, which is polarity reversal. This feature adds more advantages to the electrodialysis process due to decreases in the scaling risk and increases in the recovery rate of the process (Kalogirou, 2005; Tanaka et al., 2003).

2.2.1.5 *Mass Transport in Electrodialysis Process*

The quantity of ion transport in electrodialysis processes is correlated with the electrical current density in the process based on Faraday's law as shown below:

$$I = \frac{zFQ\Delta C_i}{\eta N_{cp}}$$ Eq. 2-4

where I, z, F, Q, ΔC_i, η, and N_{cp} are electrical current (A), ion valence, Faraday constant (As.eq^{-1}), flow rate (cm^3/s), desired ion concentration difference between feed and dilute streams (eq.cm^{-3}), current efficiency, and number of cell pairs, respectively (Mulder, 1951).

Assuming the bulk solution is mixed well due to spacer design, the ion removal is influenced by the ion transport rate in both the solution boundary layer and the membrane phase. Therefore, separately studying ion transport through the boundary layer and through the membrane is crucially important.

2.2.1.6 *Ion Transport in the Solution Phase*

According to Nernst-Planck equation, the total flux of ion i in the EDR process is composed of three components, as follows:

$$J_i = J_{i,diff} + J_{i,mig} + J_{i,conv}$$ Eq. 2-5

where J_i, $J_{i,diff}$, $J_{i,mig}$, and $J_{i,conv}$ are total, diffusion, migration, and convection flux through an ion exchange membrane, respectively.

The three diffusion, migration, and convection fluxes are represented by equations 2-6 through 2-8, respectively.

$$J_{i,diff} = -D_i \frac{dC_i}{dx}$$ Eq. 2-6

$$J_{i,mig} = -\frac{F}{RT} D_i z_i C_i \frac{d\phi}{dx} = u_i C_i \frac{d\phi}{dx}$$ Eq. 2-7

$$J_{i,conv} = C_i v_i$$ Eq. 2-8

9

These ion transport mechanisims occur due to concentration gradient, electrical potential gradient, and imbalanced forces on the ion in the solution, respectively (Bard & Faulkner, 2001).

Due to the significant role of two first ion transfer mechanisms, the convection term in the above equation can be neglected (Strathmann, n.d.).

$$J_{i,diff} = -D_i \frac{dC_i}{dx}$$
Eq. 2-6

$$J_{i,mig} = -\frac{F}{RT} D_i z_i C_i \frac{d\phi}{dx} = u_i C_i \frac{d\phi}{dx}$$
Eq. 2-7

$$J_{i,conv} = C_i v_i$$
Eq. 2-8

where D_i, C_i, F, R, T, ϕ, z_i, u_i, and v are ion diffusion coefficient, ion concentration, Faraday constant, molar gas constant, temperature, electrical potential, charge magnitude and sign of the ion, ion mobility, and velocity of bulk flow (Bard & Faulkner, 2001; Strathmann, 2004). The ion mobility applied in the above equation can be calculated using Nernst– Einstein equation as follows (Tanaka, 2003):

$$u_i = \frac{|z_i|FD_i}{RT}$$
Eq. 2-9

The electrical current is carried by ions that are transferred through the ion exchange membrane. The component of current which is carried by ion i shown as below.

$$i_i = z_i F J_i$$
Eq. 2-10

According to the Nernst-Planck equation, $ii= z_i F J_i$ Eq. 2-10 can be written as equation 2-11

$$i_i = z_i F \left(D_i \frac{dC_i}{dx} + \frac{z_i F}{RT} D_i C_i \frac{d\phi}{dx} \right)$$
Eq. 2-11

The fraction of total electrical current that is carried by each individual species is called transport number. The transport number of each ion can be calculated from following equation:

$$t_i = \frac{i_i}{i} = \frac{|z_i| u_i C_i}{\sum_k |z_k| u_k C_k} = \frac{|z_i| \lambda_i C_i}{\sum_k |z_k| \lambda_k C_k}$$
Eq. 2-12

where t_i, i, u_i, and λ_i are transport number of ion i, total current density, ion mobility, and individual ion conductivity, respectively. Most researchers consider the transport number as the current portion from occurred ion flux due to the migration mechanism only, as shown in $ti= \frac{i_i}{i} = \frac{|z_i| u_i C_i}{\sum_k |z_k| u_k C_k} = \frac{|z_i| \lambda_i C_i}{\sum_k |z_k| \lambda_k C_k}$
Eq. 2-12, while the total flux includes diffusion and migration mechanisms. Consequently, the ion transport number of each ion in the whole process can be described by the following equation:

10

$$t_i = \frac{z_i F J_i}{\sum_k z_i F J_k}$$

Eq. 2-13

where J_i is the total flux of ion i from dilute cell to concentrate cell.

Additionally, the total flux can be defined by the extended Nernst-Planck equation as follows:

$$-D_i \left(\frac{dC_i}{dx} + z_i C_i \frac{F}{RT} \frac{d\emptyset}{dx} + C_i \frac{dlnf_i}{dx} \right) + C_i v$$

Eq. 2-14

where the D_i, c_i, ϕ, f_i and v are ion diffusion coefficient, ion concentration, electrical potential, molar activity, and velocity of bulk flow, respectively.

The governing ion transport mechanisms in ion movement toward the ion exchange membrane are Electrical migration and diffusion in the desalting solution; however, convection has greater influence in the direction of flow. Therefore, migration and diffusion can be neglected due to great Pecklet number (Moon et al., 2004).

2.2.1.7 *Transport models and selectivity in membrane phase*

The ion transport through the ion exchange membrane as well as the solution phase is explained by Nernst-Plank equation as follows:

$$\bar{J}_i = -\bar{D}_i \left(\frac{d\bar{C}_i}{dx} + n_i \frac{F \bar{C}_i}{RT} \frac{\overline{d\phi}}{dx} \right) - \frac{RT}{F} \bar{u}_i \frac{d\bar{C}_i}{dx} - z_i \bar{u}_i \bar{C}_i \frac{d\psi}{dx}$$

Eq. 2-15

where J_i, $\bar{u}_i$, $\bar{C}_i$, z_i, ϕ , and v are the flux, mobility, concentration, electrical charge, and electrical potential in the membrane phase. In equation 2-15, ion diffusion, migration, and convection through the membrane phase are introduced by the first, second, and the third terms of the equation, respectively. Although all of these three mechanisms occur, the two diffusion and convection terms can be neglected because of the compact and solid structure of ion exchange membranes, so the ion transfer through the membrane can be simplified as the following equation (Tanaka, 2007):

$$J_i = -\bar{D}_i \left(\frac{z_i F \bar{C}_i}{RT} \frac{d\phi}{dx} \right)$$

Eq. 2-16

Assuming ideal passing of counter ions through the membranes, resulting in the replacement of all co-ions, the current density is described by following equation:

$$\sum_i |z_i| \bar{J}_i = \frac{\bar{I}}{F}$$

Eq. 2-17

where $\bar{I}_i$ is current density in the membrane phase. Multiplying equation 2-16 by z_i and combining by Eq. 2-17 will present the following equation as below:

11

$$\frac{\bar{I}}{F} = \sum_i \left(-z_i \overline{D}_i \left(\frac{z_i F \bar{C}_i}{RT} \frac{d\phi}{dx}\right)\right)$$ Eq. 2-18

therefore, the electrical potential gradient in the membrane phase is calculated as follows:

$$\frac{d\bar{\phi}^{CM \ or \ AM}}{dx} = -\frac{RT\bar{I}}{-\sum z_i^2 \bar{C}_i^2 F^2 \overline{D}_i}$$ Eq. 2-19

where $\dfrac{d\bar{\phi}^{CM \ or \ AM}}{dx}$ is the electrical potential gradient in the cation or anion exchange membrane.

By assuming that the ion exchange membranes are ideally selective to counter ions, and co-ions are completely repelled with functional groups, only counter ions are absorbed to fixed charge sites. If it is assumed that only a monolayer of counter ions is absorbed to the fixed charged sites, the ion exchange capacity of membranes is equal to concentration of counter ions in the membrane phase as equation 2-20. The absorbed counter ions on the fixed changed sites migrate through the membranes when an electrical potential gradient is applied.

$$\sum_i |z_i| \bar{C}_i = IEC_{AM} \quad or \quad IEC_{CM} \quad i = 1, 2, \dots, n$$ Eq. 2-20

where IEC_{AM}, IEC_{CM}, and n are ion exchange capacity for anion exchange membrane and cation exchange membrane, and number of anions and cations in the solution, respectively (Moon et al., 2004).

The term permselectivity refers to the different rates at which different ions move through the ion exchange membrane. In the membrane phase, the permselectivity term can be defined by the following equation (Tanaka, 2007):

$$PS_j^i = \frac{\bar{t}_i / \bar{t}_j}{C_i / C_j}$$ Eq. 2-21

where the $\bar{t}_i$, C_i, C_j, and PS_i^j are transport number through the ion exchange membrane, concentration of ions i and j in the dilute solution, and the permselectivity of ion i against j in the membrane phase, respectively (Sata et al., 2002). The ion transport number, defined as the portion of current carried by a particular ion passing the membrane, can be written as follows (Tanaka, 2007).

$$\bar{t}_i = \frac{z_i J_i}{\sum z_i J_i} = \frac{z_i^2 \bar{u}_i \bar{C}_i}{\sum z_i^2 \bar{u}_i \bar{C}_i}$$ Eq. 2-22

where the parameters of the aforementioned equation were defined before.

Several factors affect ion transfer in the membrane phase, where the mobility of monovalent and divalent ions is approximately 1/10 and 1/20, respectively, of their mobility in the solution phase. This decrease in mobility can be attributed to the pore size distribution of ion exchange membranes (0.005-0.1

12

μm), electrical interaction between counter ions and fixed functional groups in the membrane structure and hydrated radius of monovalent and divalent counter ions - not including proton and hydroxide ions (Tanaka, 2007).

The divalent ions are kept in the membrane phase longer than monovalent ions due to their stronger interactions between divalent ions and fixed charged groups, so the divalent ions move more slowly than monovalent ions in the membrane phase (Kabay et al., 2002; Kabay, İpek, et al., 2006). In addition to ion charge, the hydrated ion size affects the ion transport through the membrane phase. The larger ions pass through membranes more slowly than smaller ones (Kabay, İpek, et al., 2006).

Additionally, Donnan equilibrium theory explains the movement of ions through the cation and anion exchange membranes, describing permselectivity both for ions with different charge types and ions with the same charge type. In the concentrated solutions, the effect of Donnan exclusion decreases (Mulder, 1951).

2.2.1.8 *Selectivity in ED/EDR process*
ED/EDR is one of the most selective membrane-based processes for the removal of ions (Aponte & Colón, 2001). Although ED is a high-cost process for removing F^- and NO^-_3, it is also highly efficient in selectively removing these species (Oldani et al., 1992; Kesore et al., 1997). According to the well-defined definition of selectivity in the membrane phase, the overall selectivity term for the ED process can be defined as follows.

$$S^i_j = \frac{t_i/t_j}{c_i/c_j}$$
Eq. 2-23

where t and C are observed transport number of ion in the ED process, and the concentration of ions in the dilute chamber. The subscripts i and j are related to the two ions whose removals are compared.

The membrane characteristics that affect ion transport through the IEM are the characteristics of the polymer matrix, the type and concentration of fixed ions, and the degree of crosslinking in the membrane structure (Bataillon, 2002).

2.2.1.9 *Effective Parameters in the Selective Removal of Ions in ED/EDR process*
On the one hand, the controllable factors such as flow rate, temperature, applied voltage, and membrane type can affect the EDR process. On the other hand, some of the noise factors such as pH, concentration polarization, ambient temperature, fouling, and electrolysis effects can also have an influence on the process.

2.2.1.9.1 Voltage
Applied voltage is the most important factor that affects the rate of separation. Walker demonstrated that at higher applied voltages, sodium and

13

sulfate ions are removed faster in relation to total ion removal. Applying greater voltage, which increases current density, causes a greater concentration gradient for each ion in the diffusion boundary layer (Walker, 2010). Monovalent ion removals were greater affected by voltage variation than are divalent ions under their experimental condition (Kabay, Kahveci, et al., 2006). Kabay et al. showed that voltage variation significantly affects the specific energy consumption (Kabay, Kahveci, et al., 2006). Demircioglu et al. demonstrated the significant role of applied voltage on K^+ removal in their experiments, and also showed that the effect is similar for the removal of Na^+ ions (Demircioglu et al., 2002). Balster et al. showed that calcium transport through the positively charged CEM is low at lower current densities, while it strongly increases at higher current densities (Balster et al., 2005). Banasiak et al. stated that the removal of F^- was affected by voltage changes, while the NO_3^- removal was not influenced significantly by voltage variation. However, they explained that the observed results was due to different initial concentration of the ions and the ion features (Banasiak et al., 2007a).

2.2.1.9.2 Velocity

There are two different reasons for which the rate of ion removal is affected by flow velocity. First, an increased flow velocity can change the thickness of the diffusion boundary layer and cause a positive effect on the rate of ion removal. Particularly, a decrease in the diffusion boundary layer along with an increase in the dilute concentration on the membrane surface occurs from an increasing velocity; in turn, the electrical resistance decreases and a higher current density results in higher rates of ion removal (Walker, 2010). The positive effect of feed velocity variation was distinctly detected on sulfate and sodium removal, along with a negligible and barely detectible effect on calcium and chloride removal (Walker, 2010). Furthermore, the significant effect of velocity was observed at higher concentration polarizations which occurs at applied higher voltage, due to thicker diffusion boundary layer (Walker, 2010). However, Kabay et al. could not observe any specific effect of velocity on ion removal in their experiments (Kabay, Kahveci, et al., 2006), and Demircioglu and et al. did not report any signifcant effect of flow velocity on K^+ and Na^+ ions in their experiments (Demircioglu et al., 2002). The second means by which flow velocity may affect ion removal is a lower residence time for ions at increased flow rates, which can have negative effects on ion removal. Different researchers have reported the unfavorable effect of increased velocity on ion removal rate and separation performance. It is assumed that ions do not have enough time to pass through the membrane at higher feed flow rates, and are instead rinsed from the membrane surface before passing (Sadrzadeh et al., 2006). Aponte and Colon used the ED process to examine sodium chloride recovery from urine; they reported that at a lower flow velocity, which causes higher residence time, greater sodium chloride removal from urine was achieved (Aponte & Colón, 2001). The negative effect of velocity on the separation of different ions was reported (Sadrzadeh et al., 2006),(Sadrzadeh et al., 2007),(Mohammadi et al., 2004). On the other hand, both positive and negative effects of velocity on current effeciency

14

in sea water treatment using small ED was reported by Sadrzadeh and Mohammadi at different flow rates and different feed concentrations (Sadrzadeh & Mohammadi, 2009).

2.2.1.9.3 Ion Type

Ions with lower diffusivity reach limiting current faster than the ions with greater diffusivity, due to faster depletion on the membrane surface (Walker, 2010). In the matter of specific energy consumption in electrodialysis, the effect of ion valance on the separation was investigated (Kabay et al., 2003). Due to interaction between ion exchange membrane characteristics, ion charge also affects ion removal. Balster et al. studied the effects of the feed composition's current density and calcium ion concentration on the selectivity of different commercial ion exchange membranes. They demonstrated that calcium ion transport through the membrane is affected by the membrane's charge density and conductivity, as well as its water uptake and ion exchange capacity. It was also mentioned that IEMs with lower charge density have a greater tendency to remove monovalent ions selectively. Additionally, it was reported that membrane charge density also affects multivalent ion removal rate more than monovalent ion removal rate (Balster et al., 2005).

2.2.1.9.4 Feed composition

Kabay et al. examined the feed composition effect in the electrodialysis process using different 0.01 N binary mixtures on monovalent and divalent ion removal at room temperature, and at a constant flow rate of 1.6 l/min. It was shown that at lower voltage, the monovalent cations are removed more efficiently in the presence of only monovalent anions than under conditions where divalent anions are present in the feed solution; this is because the monovalent cations are more strongly attracted by divalent anions, thus affecting their removal rate. At higher voltages, however, this effect disappeared (Kabay, İpek, et al., 2006). While investigating the effect of initial NaCl concentrations in the feedwater, Banasiak et al. demonstrated the efficiency of removing F^- and NO_3^- ions from brackish water through the use of electrodialysis processes. The results confirmed that the rate of removal was greater at higher initial concentrations of NaCl (Banasiak et al., 2007b).

2.2.1.9.5 Pressure

Most electrodialysis manufacturers recommend that static head difference between the dilute and concentrate solutions be kept close to zero to prevent convection mechanisms and water transport from a dilute stream to a concentrate one. Despite this, the differential pressure at the inlet and outlet points of the stack between the dilute and concentrate chambers in the real large-scale operation of EDR systems is kept within the 0.5-1 psi range. Although the recommended difference can be applied well in the lab-scale EDR process, this is done in the large-scale operation in order to prevent any leakage from the concentrate chamber to the dilute chamber (Murray, 1996).

15

2.2.1.9.6 pH

Removal of anions occurs best in acidic, low-pH environments while removal of cations works best in alkaline high-pH environments; this effect is explained by the tendency of OH^- to compete with anions, and likewise of H^+ with cations. The effect of pH on important parameters such as current efficiency, concentration polarization, and energy consumption in the ED process was investigated by About-Shady et al.; it was shown that pH variations influence the distribution of NO_3^- and Pb^{2+} on the surface membrane, and thus affects their removal (Abou-Shady et al., 2012). Additionally, Kabay et al. investigated the effect of pH on the separation of monovalent ions such as NaCl and KCl, and divalent ions such as $MgCl_2$ and $CaCl_2$, at pH levels of 6.5, 6.0, 4.0, and 2.0 (Kabay et al., 2003). It was shown that a higher energy consumption was required to remove ions at a lower pH (defined as less than 4), regardless of whether the ions where monovalent or divalent. However, pH changes did not affect competitive separation of monovalent and divalent ions (Kabay et al., 2003).

Chapter 3: Material and Methods

3.1 Pilot Scale Experiment Site

The Bureau of Reclamation constructed the Brackish Groundwater National Desalination Research Facility (BGNDRF), a federal research facility located in Alamogordo, New Mexico, to provide national and international researchers an environment where they can conduct work on brackish ground water desalination. The facility's location in the Tularosa Basin provides access to four brackish groundwater wells with a wide range of salinity, ranging from 1000 to 6400 ppm. One of the wells, well 1, is a geothermal well with a normal temperature of 40 ºC. The brackish water from this well can be supplied at two different temperatures: 24 ºC after passing the cooling tower which is subject to change due to seasonal temperature changes, or 40 ºC straight from the storage tank. At this facility test bay number 4, where the pilot-scale EDR set-up was installed, was used for the EDR experiments.

In the process of well water delivery to the test bays, water from the aquifer was pumped to a storage tank, where it was then sent to a hydrostatic tank to be pressurized to 350 kPa. With the use of a valve, the pressure was then reduced to less than 70 kPa before it was delivered to the test bay.

3.2 Pilot-Scale Experimental Set-up

A General Electric EDR set-up with an influent flow rate capacity of 12 gallons per minute (0.775 L/s) was used to conduct these pilot-scale experiments. figures 3-1 and 3-2 present a schematic and a photograph of the entire set-up. The nature and purpose of each component is explained in the following sections.

3.2.1 Pretreatment Process Before EDR

Before being sent to the EDR stack, the feed water is pressurized in the feed pump and then sent to the Multi-Media filter (MMF) and cartridge filter. Generally, the EDR process does not need special pretreatment. However, applying a MMF can help prevent potential damage and fouling of the membranes from sands and suspended solids in the feed water; filters of different pore sizes in the MMF provide the means in which the suspended solids can be removed. The feed water then passes through the cartridge filter, which contains a pore size of 10 μm, to remove any remaining suspended or dissolved particles before finally entering the stack.

3.2.2 EDR Stack

The GE electrodialyzer that was used in this set-up was composed of spacers and anion and cation exchange membranes. These stack components are of industrial-size, but the number of cell pairs differs from that of industrial stacks; the stack used in the experiments had 40 cell pairs, while the number of cell pairs in industrial applications exceeds 600. A cell pair is constituted of three ion exchange membranes that provide two dilute and two concentrate chambers. The spacers serve to separate the ion exchange membranes from each other, and establish the required channel thickness for dilute and concentrate streams to flow in the channels; they also introduce turbulence in the streams. The membranes are fixed between two top and bottom electrodes. Both streams pass once through the chambers and exit the stack as shown in figure 3-1. Therefore, the stack is constituted of one hydraulic and one electrical stage. Heavy spacers and heavy cation exchange membranes precede the electrodes whose coatings give them the capability of charge reversal. The reason behind the use of the heavy spacers and heavy cation exchange membranes is to facilitate the flow of the electrode rinse solution over the top and bottom electrodes. This flow washes out the produced gases from electrode chambers' reactions and sends them to the degasifier to prevent any damage to membranes, especially from the chlorine produced in the cathode. Although the electrode solution conductivity should match that of the feed water in order to decrease the effect of osmotic pressure (Abou-Shady et al., 2012), large scale operations dose the electrode rinse solution with 15% hydrochloric acid. The injected acid is consumed in order to neutralize the hydroxide ions formed in the cathode, which prevents scaling problems in the electrodes. After leaving the stack, the electrode rinse solution is sent to the degasifier and is then either disposed of as waste, or recycled, in order to improve the process's recovery rate. The detailed specification of the EDR components is introduced in table 3-1.

3.2.3 Analytical Analysis

The operating conditions were monitored and recorded during the experiments. By using inline float type flow meters, made by Plast-O-matic valves, Inc., product flow rates and concentrate blow down were measured and then recorded manually. The set-up was equipped with Mettler Toledo inline pH and conductivity sensors, and temperature sensors were used to monitor these parameters during the experiments to ensure a steady system operation. Additionally, an oscilloscope from Fluke Co. was used to measure the applied voltage between the two electrodes on the stack. The DC current probe, also from Fluke Co., was used to measure the direct current in the stack.

During the experiments, water samples were collected and analyzed using the Dionex ICS-5000 Dual Channel IC System, an ion chromatography system with the capability of measuring the cations and the anions via analytical channels and capillary channels, respectively. Additionally, pH levels of the samples were analyzed to detect the amount of carbonate. Titration was then performed for water samples to determine the amount of any possible carbonate. However, for very small mounts of species, the titration procedure cannot be considered as an

accurate method of analysis. Therefore, the samples were analyzed to determine the inorganic carbon source using Total Organic Carbon Analyzer, Shimadzu TOC-Vcsh.

3.3 Pilot-Scale Experiments

The pilot-scale experiments were conducted at BGNDRF using brackish well water. The used feed water was provided from well 1, and as explained previously, could be delivered at two different temperatures. The feed water composition is given in table 3-2; it can be seen from the data that the water composition slightly varies at each operating temperature. These small differences were observed because some of the water in the cooling tower evaporates, further concentrating the feed water to some extent.

3.4 Design of Experiments

The experiments were designed in two different sets. The first set was preliminary experiments at pilot-scale, and the next set will be at laboratory-scale.

3.4.1 Pilot-Scale

In order to show the effect of operating parametes, such as velocity, temperature, and voltage on ion removal in EDR process, the experiments were conducted at two levels of temperature and velocity, and six levels of voltage, as shown in table 3-3. The ratios of dilute and concentrate streams were chosen based on the manufacturer's recommended numbers. The experiments were conducted at four different combinations of temperature and flow. In order to detect the effect of velocity (flow rate), and temperature, the experiments were run at the same voltage levels for all four combinations. The overall design of the conducted experiments is shown in table 3-4.

The most significant operating factors will be determined after conducting the experiments, shown in table 2-8, and analyzing the obtained results. Then another set of detailed experiments will be designed to obtain an empirical model for ion removal in EDR process.

However, for the purpose of anion exchange membrane comparison, the next phase of experiments were conducted in a wider range of operating conditions and used three different anion exchange membranes, but used the same cation exchange membranes in the pilot-scale EDR. The first set of conducted experiments consitsted of using AR204 under a wide range of operating conditions. The second and third sets of experiments were done using AR908 and aged-AR204. The aged-AR204 were used anion exchange membranes from a San Diego wastewater treatment site (North City Water Reclamation). In order to assure that the aged-AR204 membranes were in good condition, the membranes were carefully scrubbed, washed, and tested with the leakage test.

Chapter 4: Results and Discussion

4.1 Effect of Applied Voltage and Ion Size on Ion removal

As discussed in the first chapter, ions are removed in the EDR process because of the applied voltage in the stack. Under normal operating conditions before limiting current is reached, increasing the amount of applied voltage increases the removal of ions. The effect of applied voltage on ion removal depends on some of the ion characteristics such as charge and hydrated radius. According to the literature mentioned in the first chapter, ions with greater electrical charges are affected more strongly by an electrical field than ions with a smaller electrical charge. This effect is distinctly shown for cations in figures 4-1 and 4-2.

The data from all these figures depicts that the divalent cations, Ca^{2+} and Mg^{2+}, are removed better than monovalent cations, such as K^+ and Na^+. However, while this trend is shown in almost all of the figures at lower voltage, at higher applied voltages the percent removal of the ions converges to a unique value, especially at lower velocity and high temperature under which the greatest amount of removal is observed. According to all of these figures, the effect of applied voltage on the removal of ions is not constant in all ranges of applied voltage. Additionally, it is shown that when applied voltage is constant, the percent removal of Ca^{2+} is greater than percent removal of Mg^{2+} due to the smaller hydrated radius of Ca^{2+} in comparison to Mg^{2+}, as shown in table 4-1 (Nightingale & Nightingale Jr., 1959; Railsback, 2006). The effect of the hydrated radius of ions is also observed in the higher removal percentage of K^+ as compared to the removal percentage of Na^+, an effect which is due to the greater hydrated radius of Na^+ in comparison to K^+ (Nightingale & Nightingale Jr., 1959; Railsback, 2006). The same effects from voltage, electrical charge, and hydrated ion size that are observed with cations are also observed in the removal of anions, as shown in figures 4-3 and 4-4. Although it was predicted to observe less removal of HCO_3^- in comparison to F^- due to its bigger hydrated radius (Kielland, 1937), in some experiments the removal of HCO_3^- is higher than, or close to, the F^- removal. The observed difference in the removal of these two monovalent anions implies that the negligible amount of CO_3^{2-} was counted in the obtained results from total inorganic carbon analysis which was initially assumed as HCO_3^- concentration; however, its concentration could not be detected by pH measurements and titration method due to its very small amount.

20

4.2 Effect of Superficial Velocity on Ion Removal

As discussed in chapter 1, one of the other parameters that affect ion removal in the EDR process is superficial velocity, or flow rate. The impact of this effect on the removal of cations and anions is shown in figures 4-5 through 4-12 based on the results obtained from this experiment.

The plotted curves show that when linear velocity increases from 8.8 to 13.1 cm/s, the removal rate decreases for both cations and anions. This reduction trend in the removal of ions can be explained by decreased residence time, a characteristic which can be defined as follows:

$$t_{resid} = \frac{L}{V}$$ Eq. 4-1

which t_{resid}, L, and V are residence time, flow path length, and linear velocity, respectively.

According to this equation, the residence time decreases 33% over the constant flow path in the EDR stack when the linear velocity is increased from 8.8 to 13.1 cm/s. The observed reduction in the ion removal due to the decrease in the residence time means the ions have less time to pass through the membranes and transfer from dilute stream to the concentrate stream. The ions which reach the membrane's surface are washed from the surface without being able to pass through the membranes.

4.3 Effect of Temperature on Ion Removal

One of the impactful operating factors in ion removal is temperature. According to the shown curves in figures 4-13 to 4-20, increasing the temperature of feed water from 24 to 38 ℃ improves ion removal. The experimental results from pilot-scale experiments confirm this effect for the removal of both cations and anions.

The observed effect of temperature can be explained theoretically by considering the positive effect of temperature on ion diffusion coefficient in the solution phase as shown in equation 2-15. By incorporating the effect of temperature on the diffusion coefficient of ions into the Nernst- Einstein equation, the ratio of ion mobility was calculated, confirming that when temperature was increased from 24 to 38 ℃, ion mobility increased 1.3 times for both cations and anions, when the diffusion coefficient of ions are assumed independent of each other. However, because of the nature of the Nernst-Planck equation in which the temperature term is the denominator term of ion flux, this ratio is not the same as the observed ratio of ion removal increasing under the effect of temperature.

21

4.4 Comparing the Effect of Linear Velocity and temperature on Ion Removal

The percent removal of all cations and anions was also plotted in order to compare the effect of linear velocity and temperature in the proposed levels. According to the plotted results in figure 4-21, it seems that increasing temperature from 24 to 38 $^{\circ}$C can compensate for the negative effect of velocity increase on the removal of divalent ions Ca^{2+}, SO_4^{2-}, and Mg^{2+}.

The effects of linear velocity and temperature on the removal of monovalent ions are compared in the figures 4-22 and 4-23. Based on the removal results for monovalent anions and cations, shown in these figures, the greatest removal of ions is obtained at a low linear velocity of 8 cm/s; this causes higher residence time and higher temperature, which creates higher ion mobility. For the removal of monovalent ions, low velocity and low temperature was the second most effective set of operating conditions. It appears that, due to the important role of residence time in the removal of monovalent ions, increases in the operating temperature cannot compensate for the way higher flow velocity decreases the residence time of ions in the stack at higher velocity, as what was observed in the removal of divalent ions.

4.5 Selectivity of different Ion exchange membranes under different conditions

In order to show the effect of operating conditions on ion removal in a combined form, a dimensionless number, ξ was applied. This number was introduced by Kitamato and Takashima (Kitamoto & Takashima, 1970) using the following equation.

$$\xi = \frac{\Lambda \Delta \varphi}{2FDV}$$

Eq 4-2

where Λ, $\Delta \varphi$, F, D, and V are equivalent conductivity, effective applied voltage, Faraday constant, desalting cell width, and solution linear velocity in the dilute chamber.

4.5.1 Selective Removal of Cations

In order to show the preferential cation removal in the EDR process, Na^+ was chosen as the reference cation. The selectivity of the EDR process toward different ions was calculated using equation 2-23, as introduced in the previous chapter. The results of the conducted pilot-scale experiments using the CR-67 cation exchange membrane showed the following order in removal of cations, as shown in figure 4-24.

$Ca^{2+} \geq Sr^{2+} \geq Mg^{2+} > K^+ > Na^+$

22

4.5.2 Selective Removal of Anions

In order to show the preferential anion removal in the EDR process, Cl^- was chosen as reference anion. Similar to cations, the selectivity of the EDR process toward different anions was calculated using equation 2-23. The results of the conducted pilot-scale experiments using the AR204 anion exchange membranes showed the following order in removal of anions as shown in figure 4-25.

$$SO_4^{2-} > Cl^- > HCO_3^- > F^-$$

4.5.3 Selectivity Sensitivity for Cations Vs. Na^+

In order to investigate the sensitivity of selectivity values for different cations at different operating conditions, the selectivity values were calculated when the removal of Na^+ was increased 0.5 ppm at differernt ξ values. As it is shown in figures 4-26 through 4-29, the selectivity values for cations are more sensitive at lower values of ξ compared to its higher values. This observation confirms that the removal of cations in a selective way is more feasible in lower values of ξ, which means the mild operating conditions, specifically lower voltage values, because, as shown in previous figures, the selectivity values approach to one at higher levels of applied voltages.

4.5.4 Selectivity Sensitivity for Anions Vs. Cl^-

The similar sensitivity analysis was conducted to verify the selectivity sensitivity for different anions at different operating conditions. The selectivity values were calculated when the removal of Cl^- was increased 0.5 ppm at differernt ξ values. As it is shown in figures 4-30 through 4-32, the selectivity values for cations are more sensitive at lower values of ξ compared to its higher values. The anions' removal results showed that the selectivity of anions using AR204 anion exchange membranes is more sensitive at lower values of ξ which confirms divalent selective behavior of this type of membrane. Like cations' removal, this observation confirms that the removal of anions in a selective way is more achievable at lower values of ξ which means the mild operating conditions, specifically lower voltage values.

4.5.5 Ion Exchange Membrane Selectivity Comparison

The next phase of experiments was conducted to compare the performance of different anion exchange membranes under different operating conditions. The examined anion exchange membranes in the pilot-scale experiments were AR204, AR908, and aged-AR204. However, the same type of cation exchange membranes, CR-67, was used in all of the experiments. The operating conditions, as explained before, are shown in the form of ξ. The obtained results are shown in the following figures. Figures 4-33 through 4-35 show the selectivity of EDR process using different anion exchange membranes.

As depicted in figure 4-33, the new AR204 and AR908 membranes showed more selective behavior toward SO_4^{2-} compared to Cl^- at lower ξ values, which represent mild operating conditions. This behavior can be explained

23

according to the type of functional groups in the structure of these ion exchange membrane types and the electrical charge of SO_4^{2-}, which causes their fast migration under the influence of an electrical field. However, aged-AR204 anion exchange membranes showed values less than 1 for selectivity of SO_4^{2-} over Cl^- in a wide range of ξ. This observation can be explained hypothetically by the nature of microorganisims built up on the surface of anion exchange membranes, which are negatively charged. The accumulation of negative charge on the surface of the membrane can cause a repulsion force between the anions with greater electrical charge as SO_4^{2-}, but let monovalent ions as Cl^- pass through them much faster and more easily.

Figures 4-33 and 4-35 show that the selectivity of EDR process for monovalent ions, such as F^- and HCO_3^-, are less than Cl^- due to their larger hydrated sizes as compared to Cl^- hydrated size. Additionally, the graphs confirm that the selectivity of the Anion exchange membranes for F^- were not affected by aging and the negative layer of microorganisims on the aged-AR204 anion exchange membranes.

Figures 4-36 through 4-39 showed that the type of used anion exchange membrane did not have any significant effect on selectivity of cations while the type of cation exchange membrane was same. However, the electronuetality is affected when one of the anion or cation exchange membranes are selective toward any specific species.

These figures confirmed that the EDR process is more selective for removal of divalent cations, such as Ca^{2+}, Mg^{2+}, and Sr^{2+} compared to monovalent cations as Na^+ when CR-67 cation exchange membranes are used. However, at higher values of ξ, which mostly represent higher applied voltage in the process, the selectivity values approach to 1 for all species.

In general, three different regions can be assumed for the effect of ξ as shown in figures 4-40 through 4-48. These figures depict that at small ξ values (Region I) the removal of ions is mostly under the influence of ion exchange membrane types rather than other factors. In the mid-range of ξ values (region II) both solution phase and ion exchange membranes play a significant roe in ion removal. This means factors the behavior of ions in the solution phase and afflity of ion exchange membrane to the ion and the behavior of ion in the membrane have a significant role on ion removal. In the high values of ξ (region III) all ions are removed simultaneously regardless of the type of ion, or effects of solution phase and ion exchange membrane phase.

As it is shown in the figures 4-40 through 4-43, the range of ξ values for three different regions is constant in removal of divalent cations. The small ξ values which represent the first region are ξ values less than 6.5×10^{-5}. If ξ parameter is in the range of $6.5 \times 10^{-5} < \xi < 5.9 \times 10^{-4}$, it is called region II. ξ values great than 5.9×10^{-4} represent region III.

24

As shown in figures 4-44 through 4-47, the lower range of ξ values is slightly different for the removal of monovalent ions. However, this difference cannot be strongly claimed due to variation of the data.

Chapter 5: References

Abou-Shady, A. et al., 2012. Effect of pH on separation of Pb (II) and NO3− from aqueous solutions using electrodialysis. *Desalination*, 285, pp.46–53.

Addams, L. et al., 2009. *Charting Our Water Future Economic frameworks to inform decision-making*,

Anon, 2014. Salinity. Available at: http://www.seagrassli.org/ecology/physical_environment/salinity.html.

Aponte, V.M.M. & Colón, G., 2001. Sodium chloride removal from urine via a six-compartment ED cell for use in Advanced Life Support Systems (Part 1: salt removal as a function of applied voltage and fluid velocity). *Desalination*, 140(2), pp.121–132.

Balster, J. et al., 2005. Preparation and characterisation of monovalent ion selective cation exchange membranes based on sulphonated poly(ether ether ketone). *Journal of Membrane Science*, 263(1-2), pp.137–145.

Banasiak, L.J., Kruttschnitt, T.W. & Schäfer, A.I., 2007a. Desalination using electrodialysis as a function of voltage and salt concentration. *Desalination*, 205(1-3), pp.38–46.

Banasiak, L.J., Kruttschnitt, T.W. & Schäfer, A.I., 2007b. Desalination using electrodialysis as a function of voltage and salt concentration. *Desalination*, 205(1-3), pp.38–46.

Barakat, M.A., 2011. New trends in removing heavy metals from industrial wastewater. *Arabian Journal of Chemistry*, 4(4), pp.361–377.

Bard, A.J. & Faulkner, L.R., 2001. *Electrochemical Methods: Fundamentals and Applications* second., John Wiley an Sons, INC.

Bataillon, P.E., 2002. Conductivity and selectivity of ion exchange membranes : *Desalination*, 147, pp.359–361.

Demircioglu, M. et al., 2002. Demineralization by electrodialysis (ED) - separation performance and cost comparison for monovalent salts. *Desalination*, 153, pp.329–333.

Helfferich, F.G., 1962. *Ion Exchange*, New York: Courier Dover Publications.

Jakobsen, M.R. et al., 2004. Electrodialytic removal of cadmium from wastewater sludge. *Journal of Hazardous Materials*, 106(2–3), pp.127–132.

Kabay, N. et al., 2003. Effect of feed characteristics on the separation performances of monovalent and divalent salts by electrodialysis. *Desalination*, 158, pp.95–100.

Kabay, N., İpek, Ö., et al., 2006. Effect of salt combination on separation of monovalent and divalent salts by electrodialysis. *Desalination*, 198(1-3), pp.84–91.

Kabay, N. et al., 2002. Removal of calcium and magnesium hardness by electrodialysis. *Desalination*, 149(1), pp.343–349.

Kabay, N., Kahveci, H., et al., 2006. Separation of monovalent and divalent ions from ternary mixtures by electrodialysis. *Desalination*, 198(1-3), pp.74–83.

Kalogirou, S., 2005. Seawater desalination using renewable energy sources. *Progress in Energy and Combustion Science*, 31(3), pp.242–281.

Kedem, O., Wilf, M. & Strathmann, H., 2010. Electrodialysis, a mature technology with a multitude of new applications. *Desalination*, 264(3), pp.268–288.

Kesore, K., Janowski, F. & Shaposhnik, V.A., 1997. Highly effective electrodialysis for selective elimination of nitrates from drinking water. *Journal of Membrane Science*, 127(1), pp.17–24.

Kielland, J., 1937. Individual Activity Coefficients of Ions in Aqueous Solutions. *Journal of the American Chemical Society*, 58(9), pp.1675–1678.

Kitamoto, A. & Takashima, Y., 1970. Preferential ion transport through ion exchange membranes by electrodialysis. *Journal of Chemical Engineering of ...*, 3(1957), pp.54–61.

Marder, L., Bernardes, A.M. & Ferreira, J.Z., 2004. Cadmium electroplating wastewater treatment using a laboratory-scale electrodialysis system. *Separation and Purification Technology*, 37(3), pp.247–255.

Mohammadi, T. et al., 2005. Modeling of metal ion removal from wastewater by electrodialysis. *Separation and Purification Technology*, 41(1), pp.73–82.

Mohammadi, T., Razmi, a. & Sadrzadeh, M., 2004. Effect of operating parameters on Pb2+ separation from wastewater using electrodialysis. *Desalination*, 167, pp.379–385.

Moon, P. et al., 2004. Computational Modeling of Ionic Transport in Continuous and Batch Electrodialysis. *Separation Science and Technology*, 39(11), pp.2531–2555.

Mulder, M., 1951. *Basic Principles of membrane technology* first., Enschede: Kluwer Academic Publishers.

Murray, P. ed., 1996. *Electrodialysis and Electrodialysis Reversal* first., Denver: American Water Works Association.

Nightingale, E.R. & Nightingale Jr., E.R., 1959. Phenomenological Theory of Solvation. Effective Radii of Hydrated Ions. *The Journal of Physical Chemistry*, 63(9), pp.1381–1387.

Oldani, M. et al., 1992. On the nitrate and monovalent cation selectivity of ion exchange membranes used in drinking water purification. *Journal of Membrane Science*, 75(3), pp.265–275.

Railsback, B.L., 2006. Some Fundamentals of Mineralogy and Geochemistry. *Department of Geology, University of Georgia Athens, Georgia 30602-2501 U.SA.* Available at: www.gly.uga.edu/railsback/FundamentalsIndex.html.

Sadrzadeh, M., Kaviani, A. & Mohammadi, T., 2006. Mathematical Modeling of Desalination by Electrodialysis. In *Tenth International Water Technology Conference, IWTC10*. Alexandria, Egypt, pp. 221–233.

Sadrzadeh, M. & Mohammadi, T., 2009. Treatment of sea water using electrodialysis: Current efficiency evaluation. *Desalination*, 249(1), pp.279–285.

Sadrzadeh, M., Razmi, A. & Mohammadi, T., 2007. Separation of monovalent, divalent and trivalent ions from wastewater at various operating conditions using electrodialysis. *Desalination*, 205(1-3), pp.53–61.

Sata, T., Sata, T. & Yang, W., 2002. Studies on cation-exchange membranes having permselectivity between cations in electrodialysis. *Journal of Membrane Science*, 206(1-2), pp.31–60.

Strathmann, H., Assessment of Electrodialysis Water Desalination Process Costs.pdf. Available at: http://gwri-ic.technion.ac.il/pdf/IDS/82.pdf.

Strathmann, H., 2010. Electrodialysis, a mature technology with a multitude of new applications. *Desalination*, 264(3), pp.268–288.

Strathmann, H., 2004. *Ion-exchange Membrane separation processes* first., Elsevier.

Strathmann, H., 1995. *Membrane Separation Technology- Principles and Applications* second. S. Noble, R.D., Stern, ed., New York: Elsevier.

28

Tanaka, Y., 2003. Concentration polarization in ion-exchange membrane electrodialysis—the events arising in a flowing solution in a desalting cell. *Journal of Membrane Science*, 216(1-2), pp.149–164.

Tanaka, Y., 2007. *Ion Exchange Membranes: Fundamentals and Applications* First., Amesterdam: Elsevier.

Tanaka, Y. et al., 2003. Ion-exchange membrane electrodialytic salt production using brine discharged from a reverse osmosis seawater desalination plant. *Journal of Membrane Science*, 222(1), pp.71–86.

Tzanetakis, N. et al., 2003. Comparative performance of ion exchange membranes for electrodialysis of nickel and cobalt. *Separation and Purification Technology*, 30(2), pp.113–127.

Walker, W.S., 2010. *Improving Recovery in Reverse Osmosis Desalination of Inland Brackish Groundwaters via Electrodialysis*. Austin: University of Texas at Austin.

Tables

Chapter 2

TABLE 2-1 Water resource categories regarding the salinity [2]

Water Type and Salinity				
Water Type	Fresh Water	Brackish Water	Saline Water	Brine
TDS (ppt*)	<0.5	0.5-30	30-50	>50

* parts per thousands

Chapter 3

TABLE 3-1 Specification of the EDR stack

Component	Detail	
EDR Stack	One Electrical Stage	Two Electrodes
	One Hydraulic Stage	40 Cell pairs
Ion Exchange Membranes	Anion Exchange Membranes	GE AR908 114×60×0.6 (cm)
	Cation Exchange Membranes	GE CR67-HMR 114×60×0.6 (cm)
Spacer	Normal	Mk-IV Effective Membrane Area: 0.3 m^2/IEM
	Heavy	

TABLE 3-2 Feed water composition

Brackish Ground Water BGNDRF well 1									
Temperature (ºC)	Cations (ppm)					Anions (ppm)			
	Ca^{2+}	Mg^{2+}	Na^+	Sr^{2+}	K^+	Cl^-	SO_4^{2-}	HCO_3^{-*}	F^-
24	50.5	8.6	376.9	<2	2.1	35.9	664.0	185.1	2.0
38	47.0	7.5	363.6	<2	2.0	31.6	628.2	187.2	2.0

* It may have a negligible source of CO_3^{2-}

30

TABLE 3-2 Operating conditions levels in the pilot-scale experiments

Factor	Level	Real Value
Feed Linear Velocity (V: cm/s)	1	8.8
	2	13.1
Temperature (°C)	1	24
	2	38
	1	2.6
	2	9.8
	3	21.7
Voltage (V)	4	33.4
	5	45.3
	6	57.7

TABLE 3-3 Overall design of preliminary experiments in the pilot-scale experiments

Feed Linear Velocity	Temperature (°C)	Applied Voltage (V)
		1
		2
		3
1	1	4
		5
		6
		1
		2
		3
1	2	4
		5
		6

31

Chapter 4

2   1

1
2
3
4
5
6

TABLE 4-1
Hydrated radii
of examined
cations and
anions

2   2

1
2
3
4
5
6

Ion hydrated radius (ºA)						
Cations				Anions		
Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	SO_4^{2-}	F^-
4.12	4.28	3.58	3.31	3.32	3.79	3.52
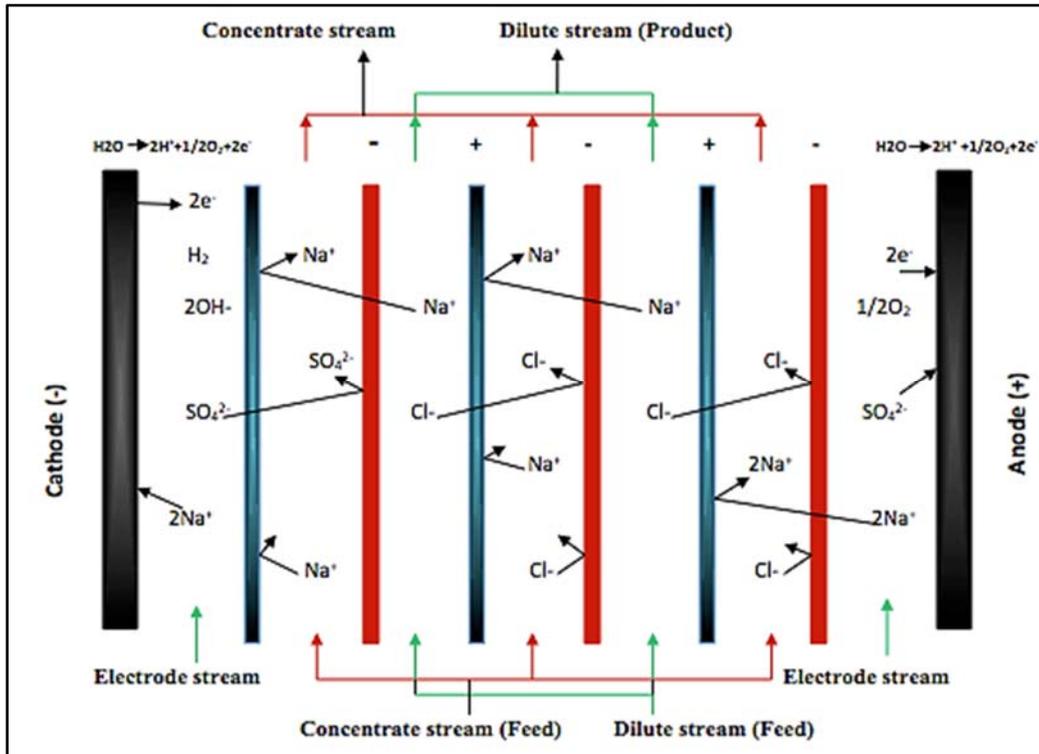
Figures

Chapter 2

FIGURE 1-1 Schematic of electrodialysis process

Chapter 3
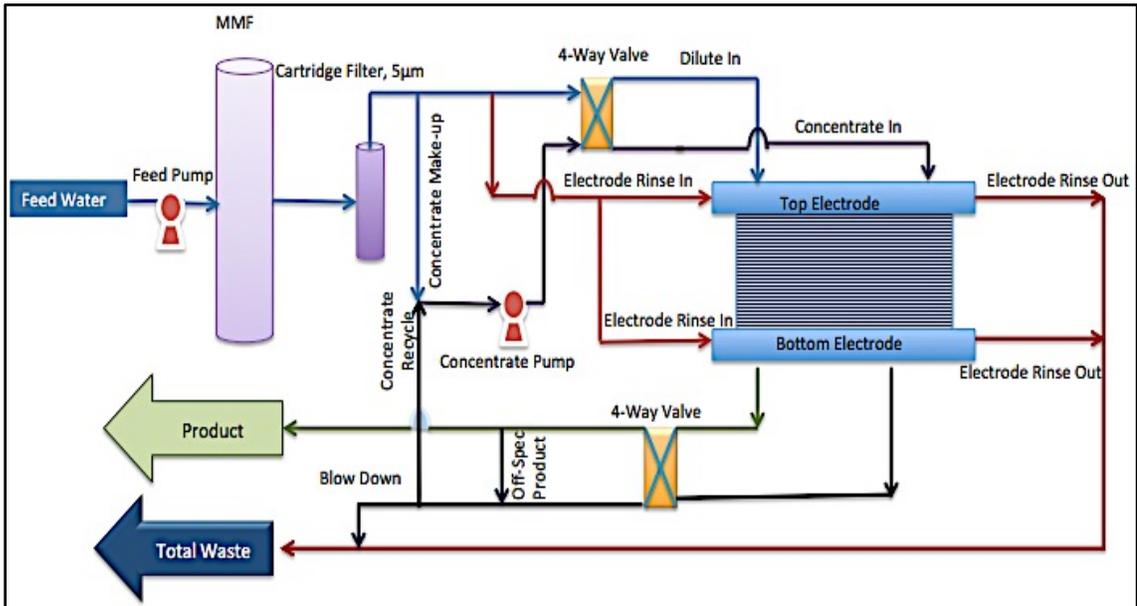
FIGURE 3-1 Schematic of the pilot-scale EDR set-up
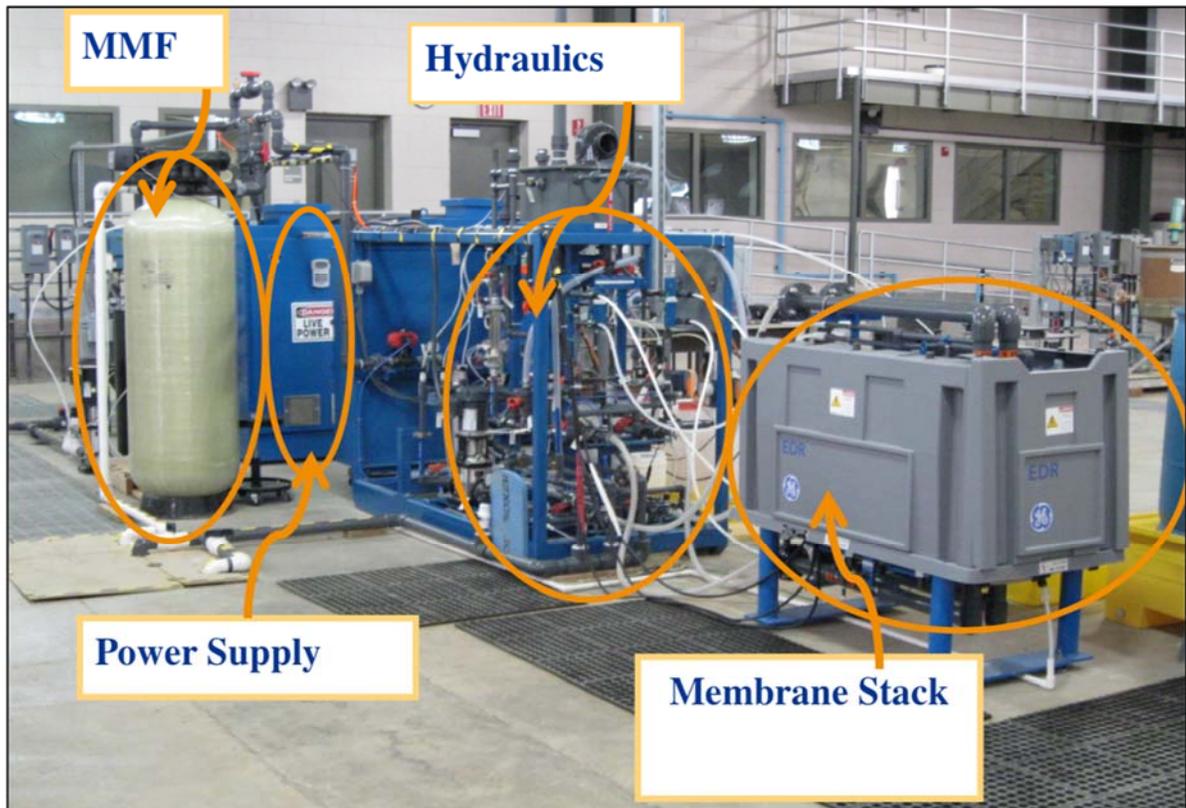
FIGURE 3-2 Pilot-scale EDR set-up

34

Chapter 4
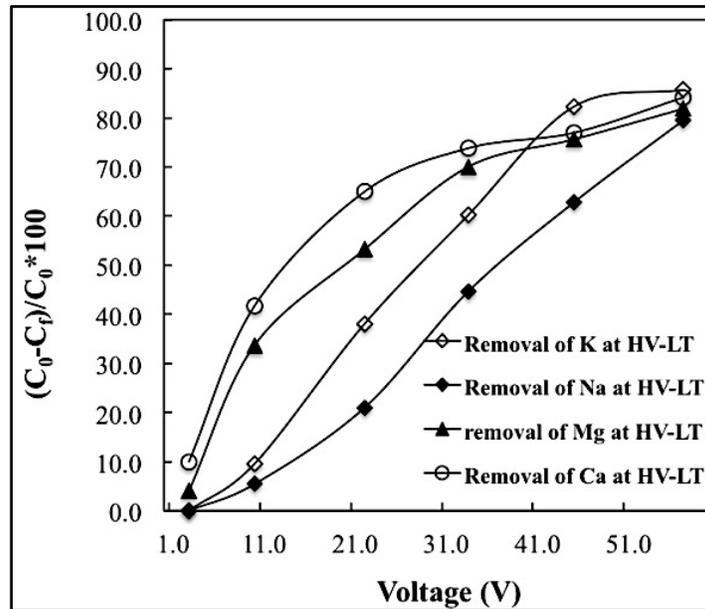
(a)
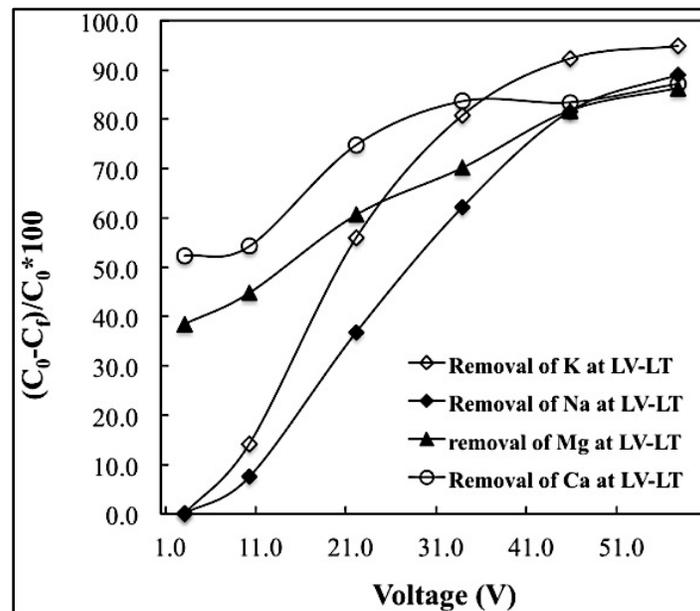
(b)

FIGURE 0-3 Effect of voltage on removal of cations at low temperature, high velocity (a), and low velocity (b)

35
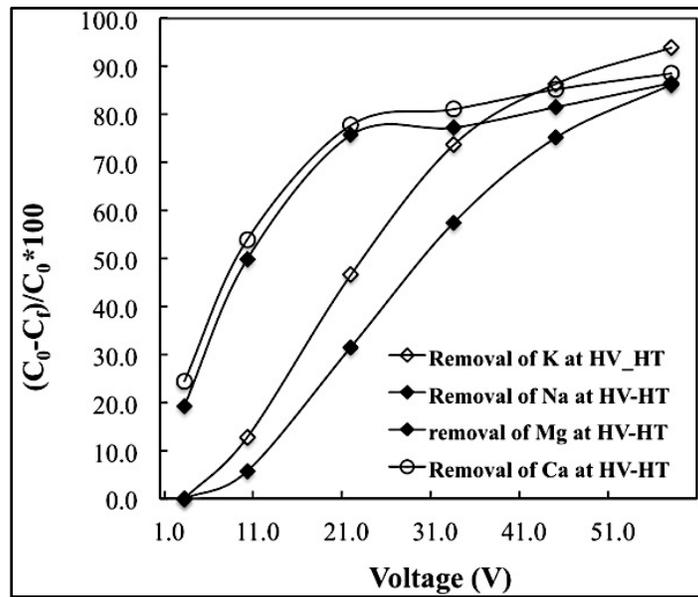
(a)
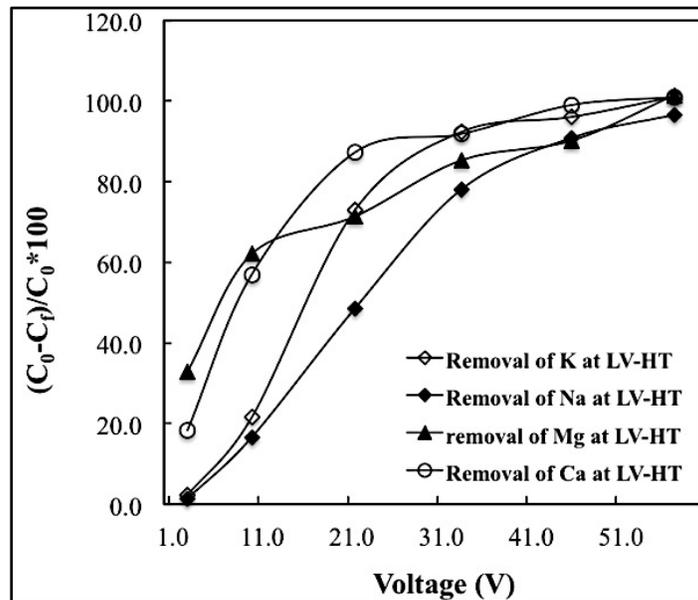
(b)

FIGURE 0-4 Effect of voltage on removal of cations at high temperature, high velocity (a) and low velocity (b)
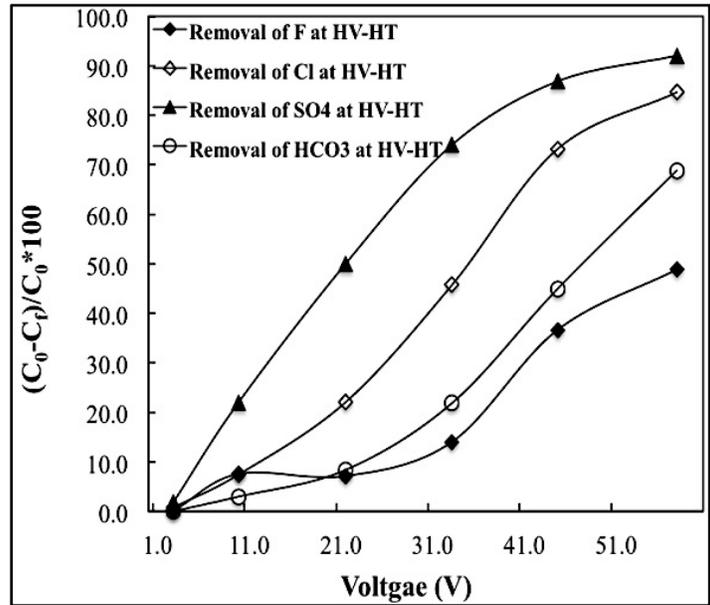
(a)
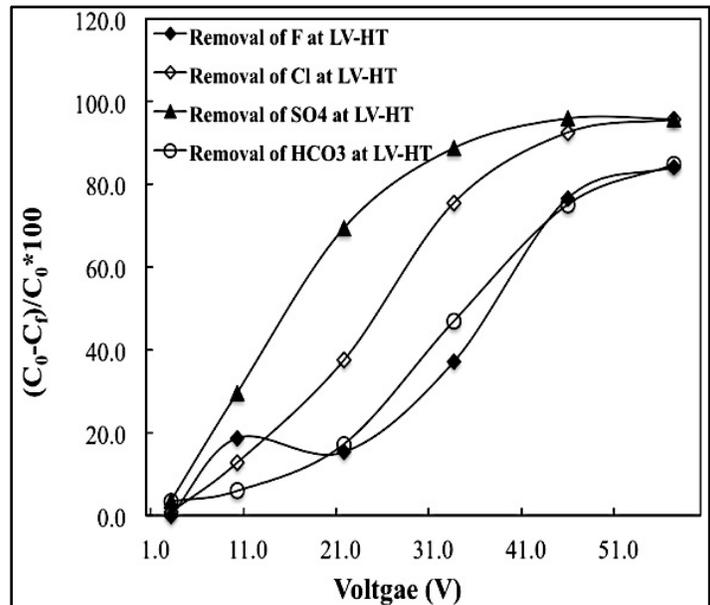
(b)

FIGURE 0-5 Effect of voltage on removal of anions at high temperature, high velocity (a), and low velocity (b)

37
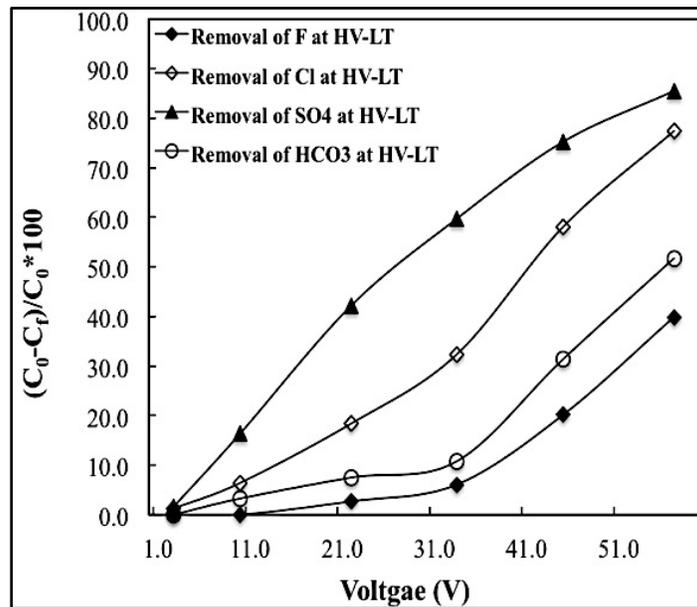
(a)
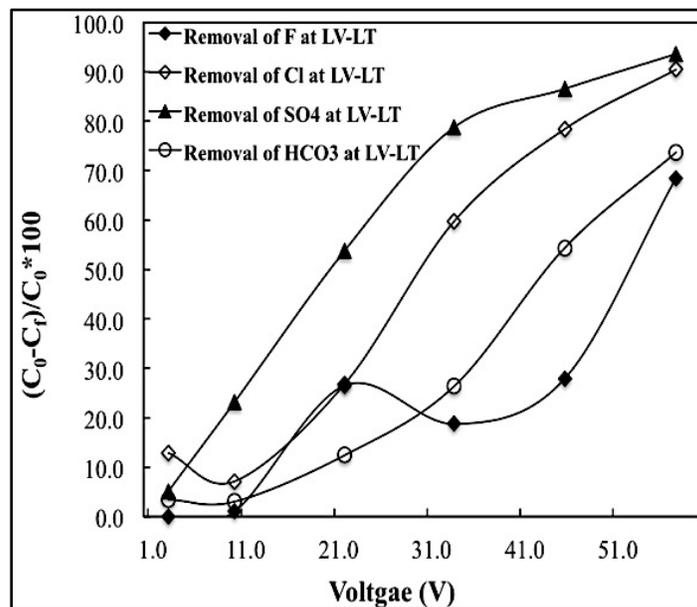
(b)

FIGURE 0-6 Effect of voltage on removal of anions at low temperature, high velocity (a), and low velocity (b)
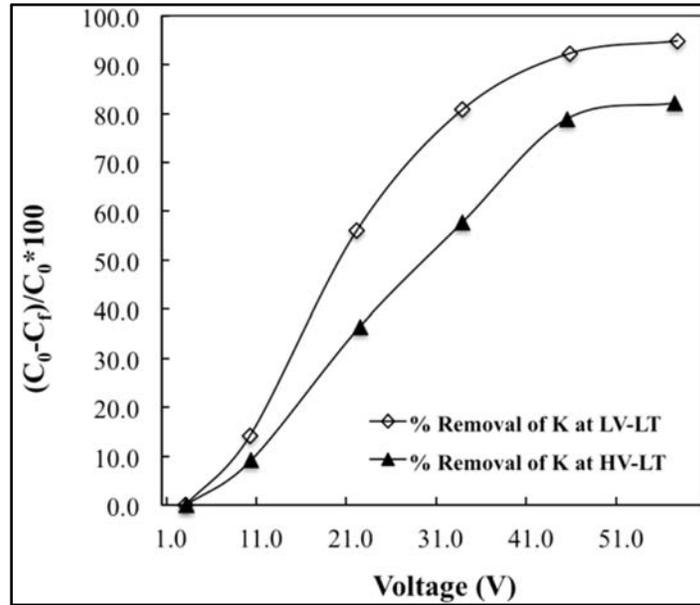
(a)
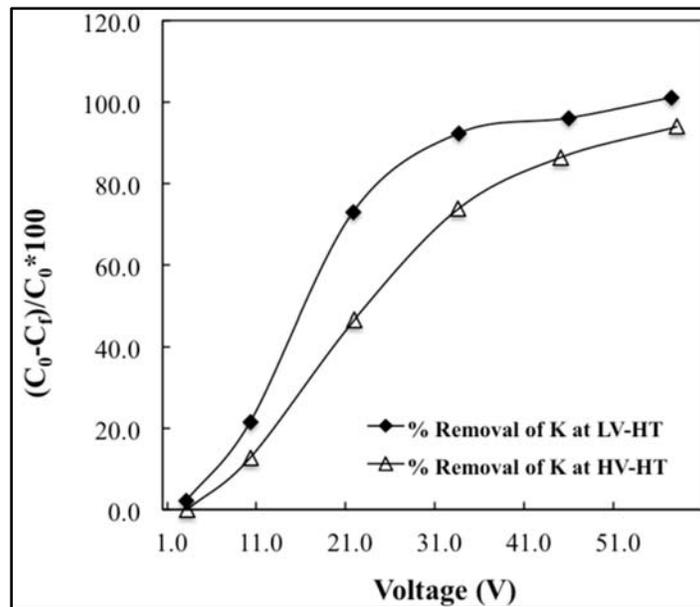
(b)

FIGURE 0-7 Effect of velocity on removal of K$^+$ at low temperature (a),
and at high temperature (b)

39
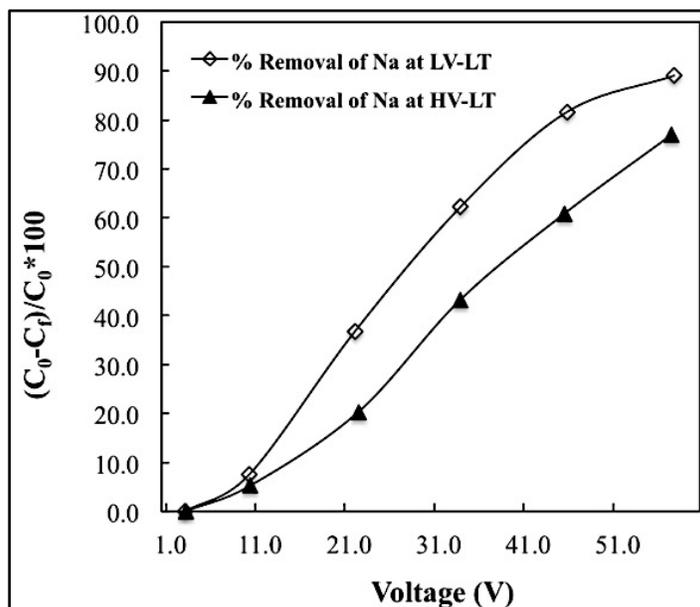
(a)
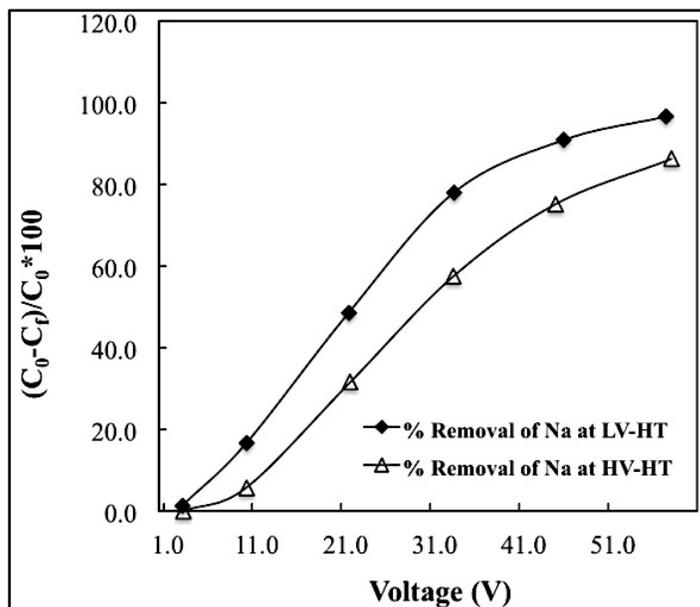
(b)

FIGURE 0-8 Effect of velocity on removal of Na^+ at low temperature (a), and at high temperature (b)

40
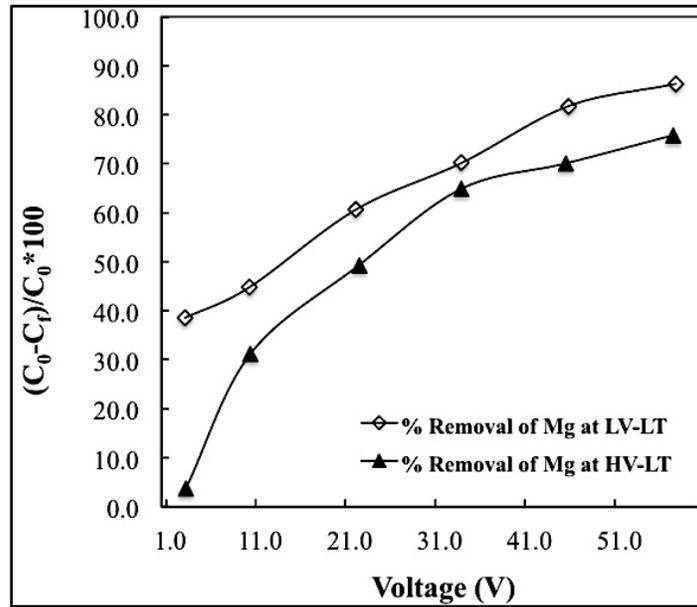
(a)
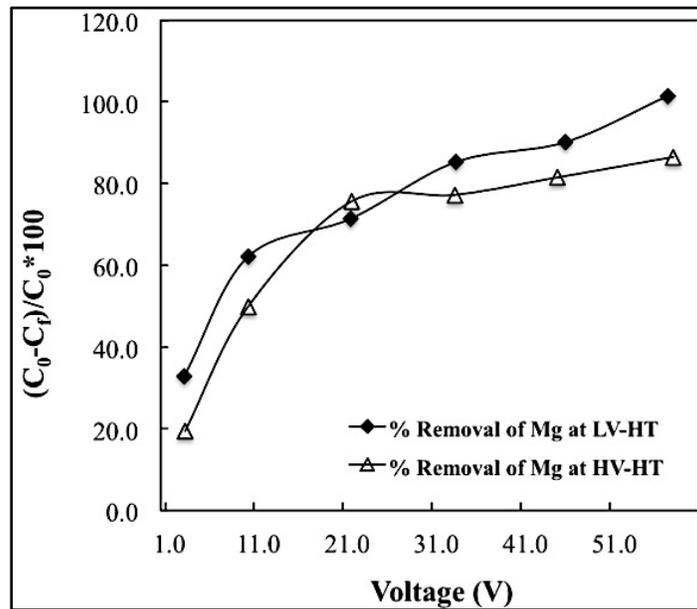
(b)

FIGURE 0-9 Effect of velocity on removal of Mg^{2+} at low temperature (a), and at high temperature (b)

41
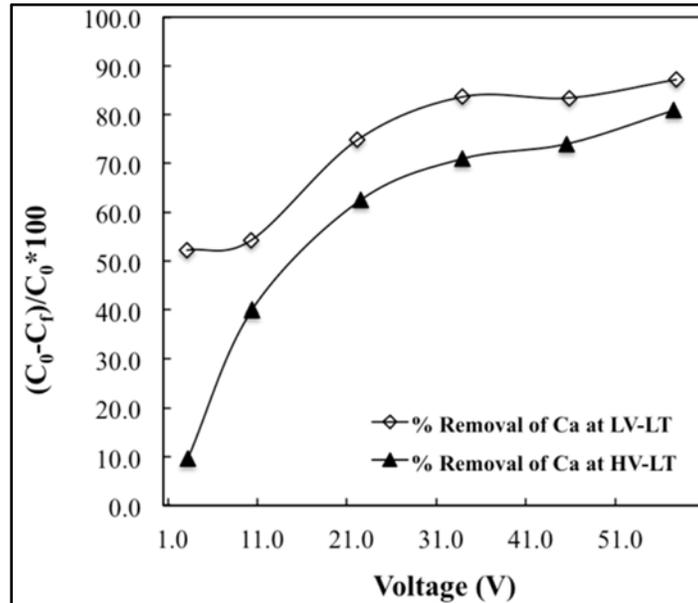
(a)
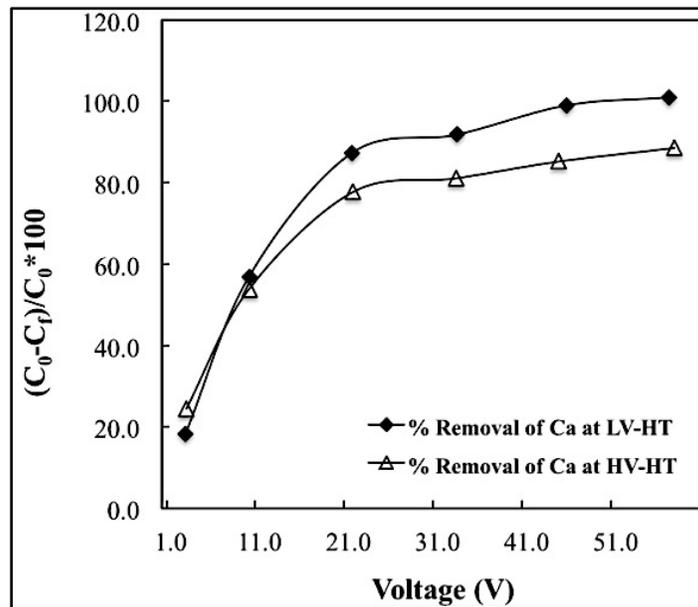
(b)

FIGURE 0-10 Effect of velocity on removal of Ca^{2+} at low temperature (a),
and at high temperature (b)
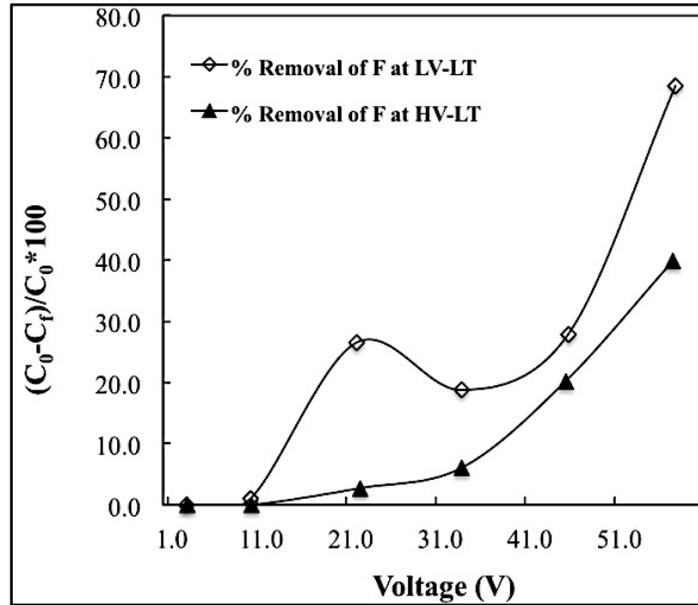
(a)
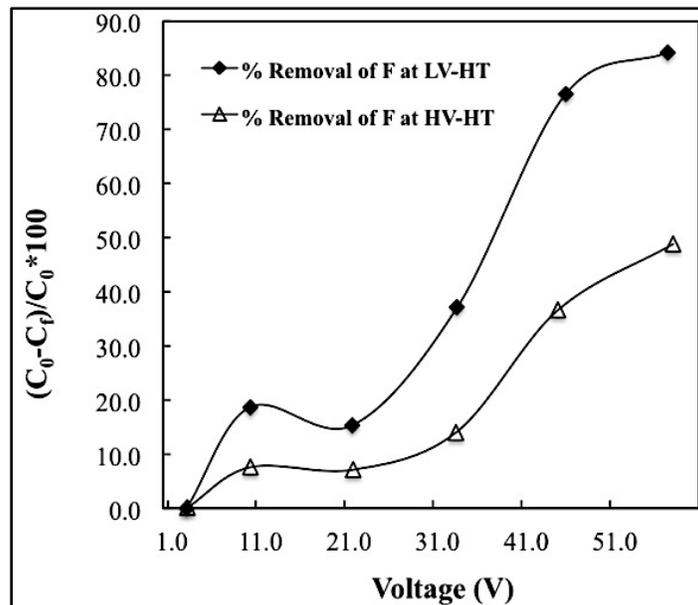
(b)

FIGURE 0-11 Effect of velocity on removal of F⁻ at low temperature (a), and at high temperature (b)
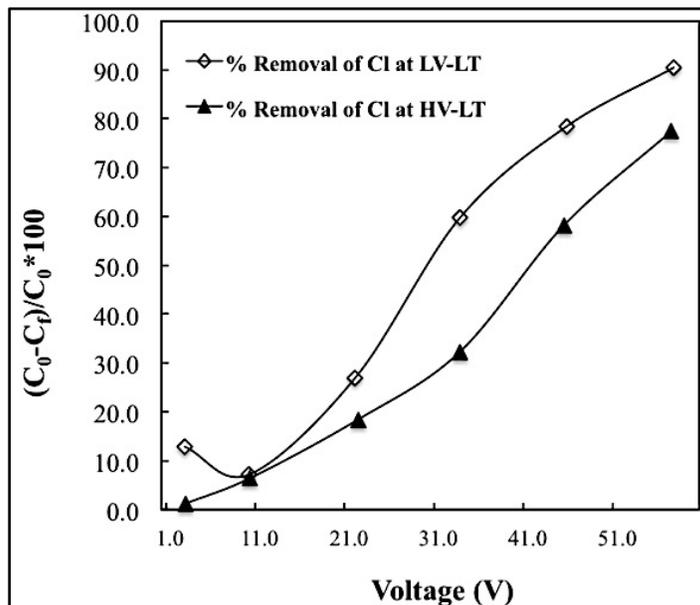
(a)
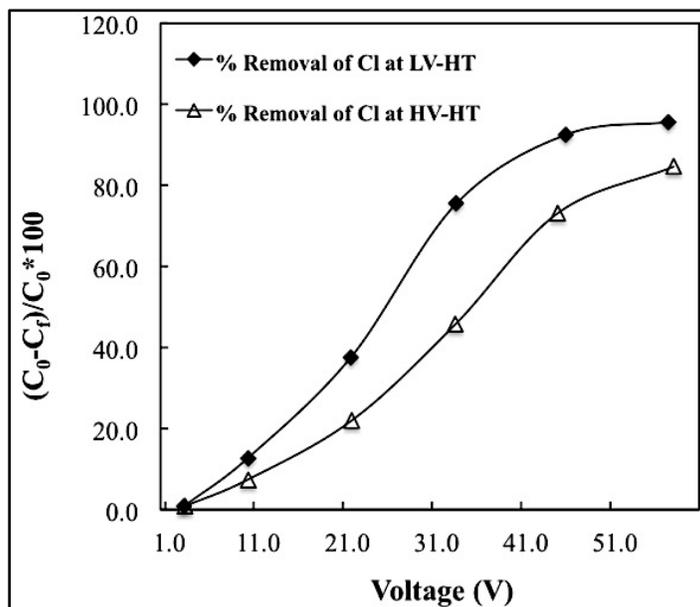
(b)

FIGURE 0-12 Effect of velocity on removal of Cl⁻ at low temperature (a),
and at high temperature (b)

44
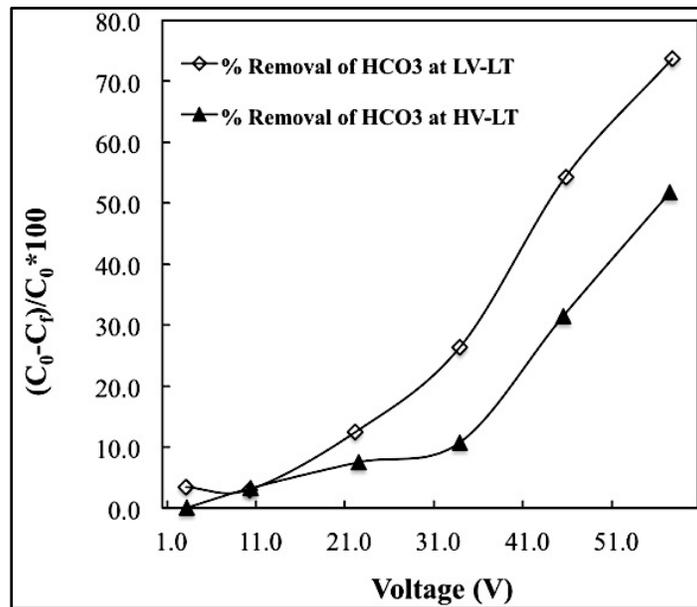
(a)
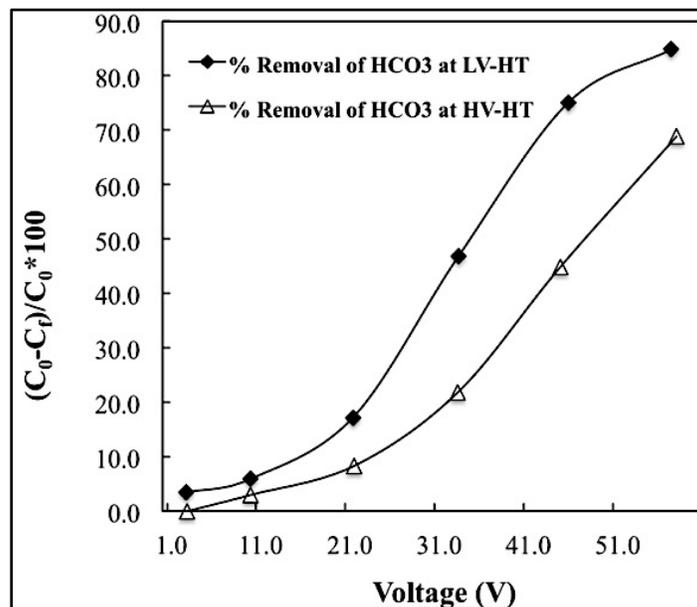
(b)

FIGURE 0-13 Effect of velocity on removal of HCO_3^- at low temperature (a), and at high temperature (b)

45
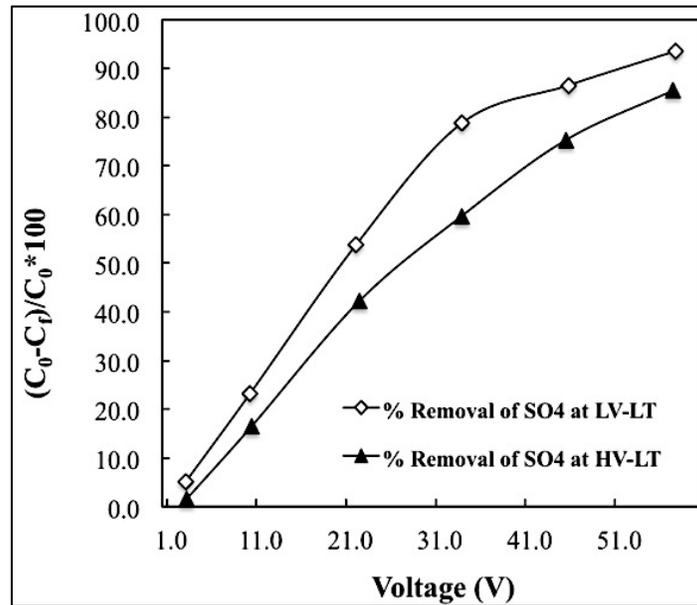
(a)
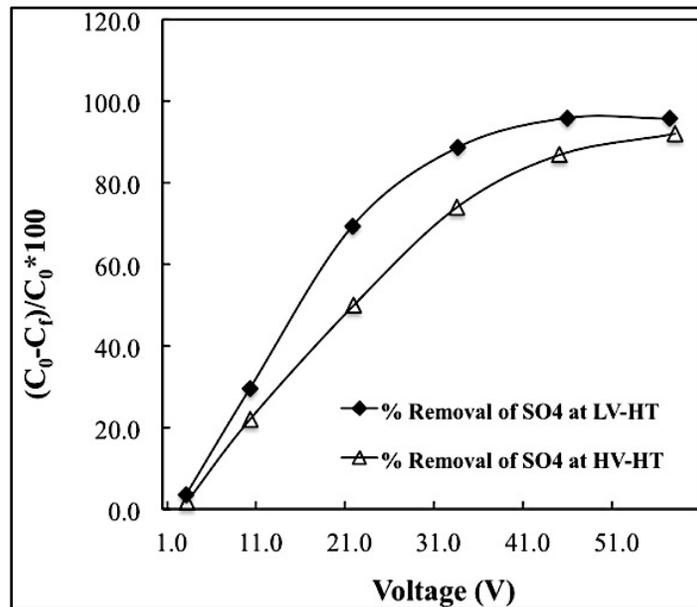
(b)

FIGURE 0-14 Effect of velocity on removal of SO_4^{2-} at low temperature (a), and at high temperature (b)
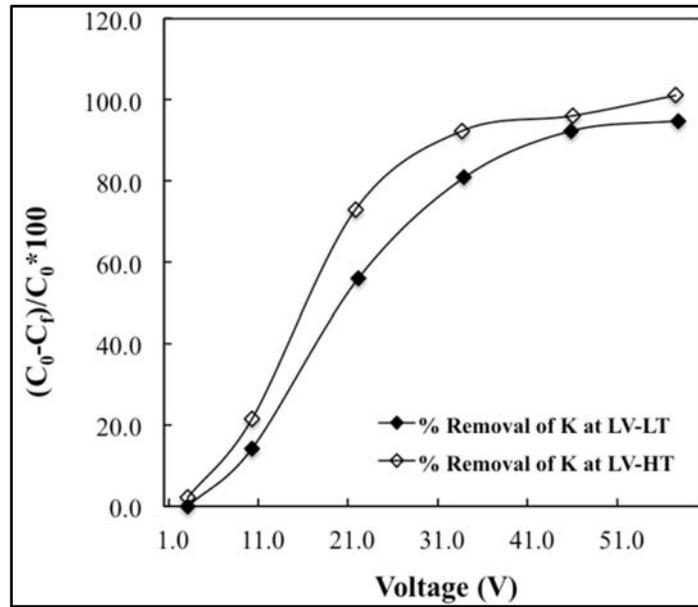
(a)
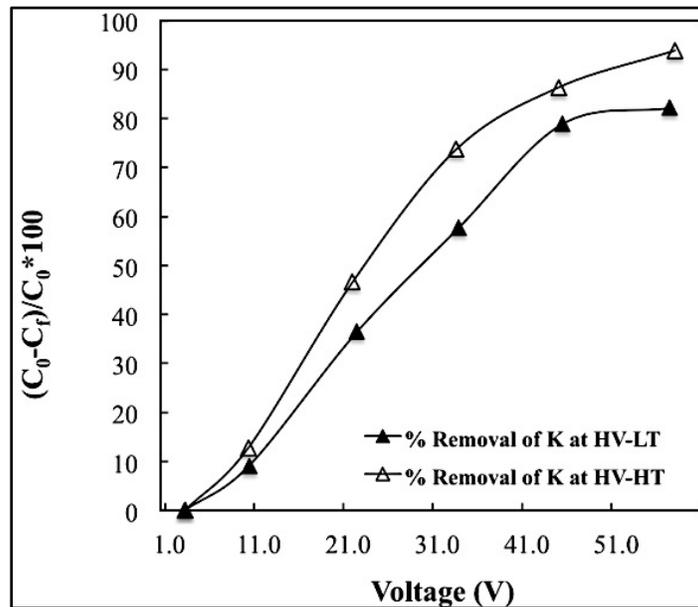
(b)

FIGURE 0-15 Effect of temperature on removal of K$^+$ at low velocity (a), and high velocity (b)
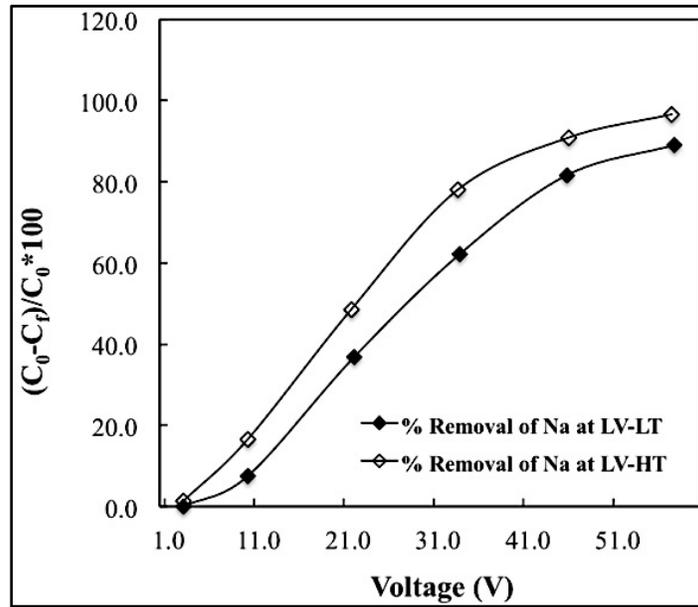
(a)
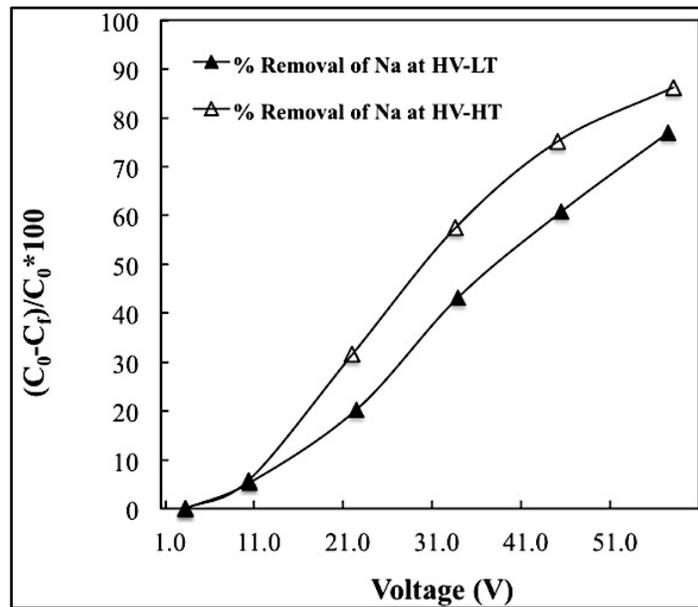
(b)

FIGURE 0-16 Effect of temperature on removal of Na^+ at low velocity (a), and high velocity (b)

48
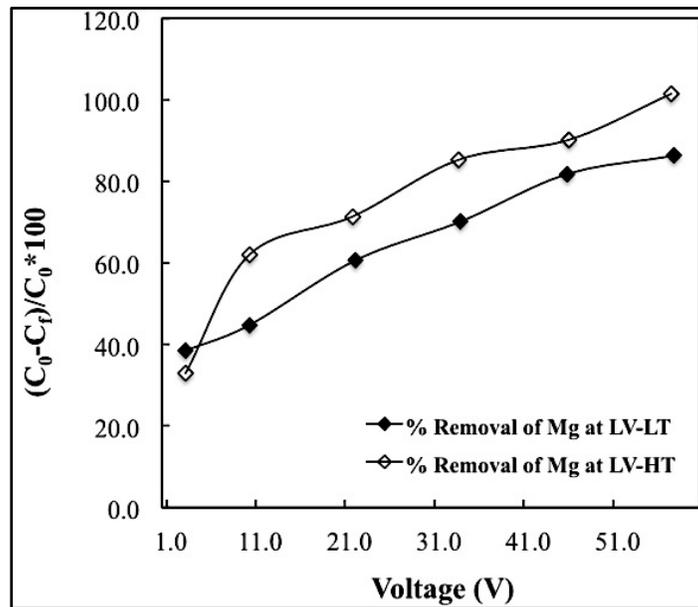
(a)
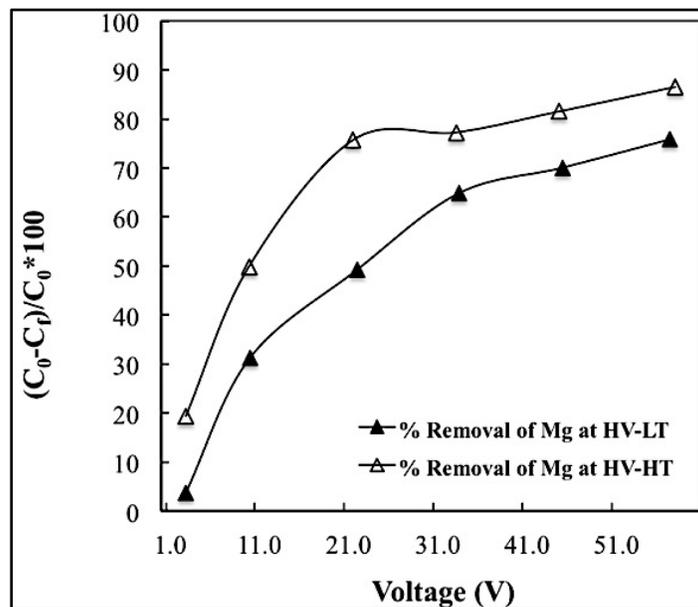
(b)

FIGURE 0-17 Effect of temperature on removal of Mg^{2+} at low velocity (a),
and high velocity (b)

49
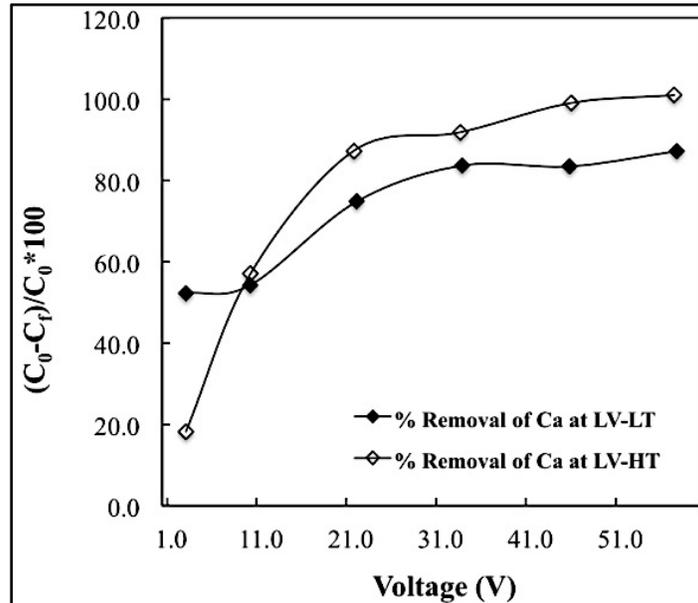
(a)
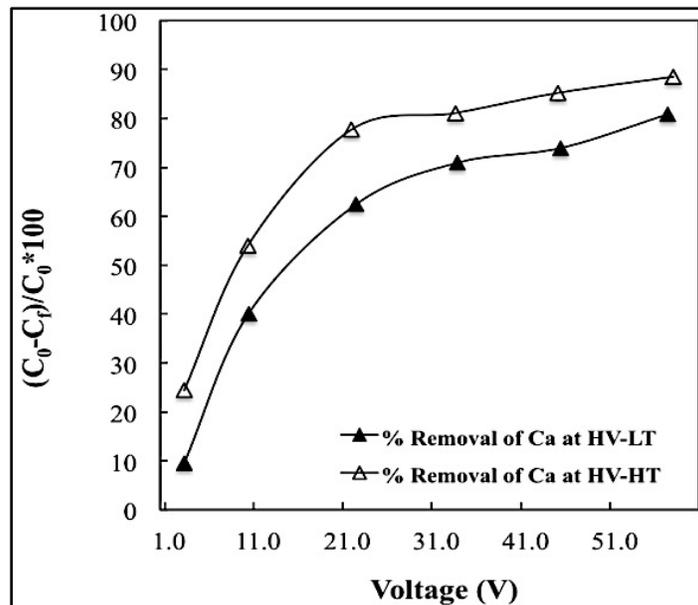
(b)

FIGURE 0-18 Effect of temperature on removal of Ca^{2+} at low velocity (a), and high velocity (b)

50
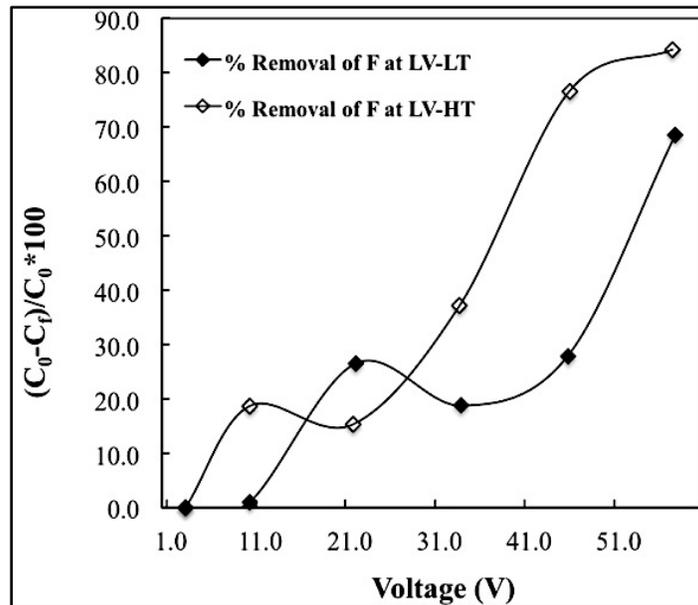
(a)
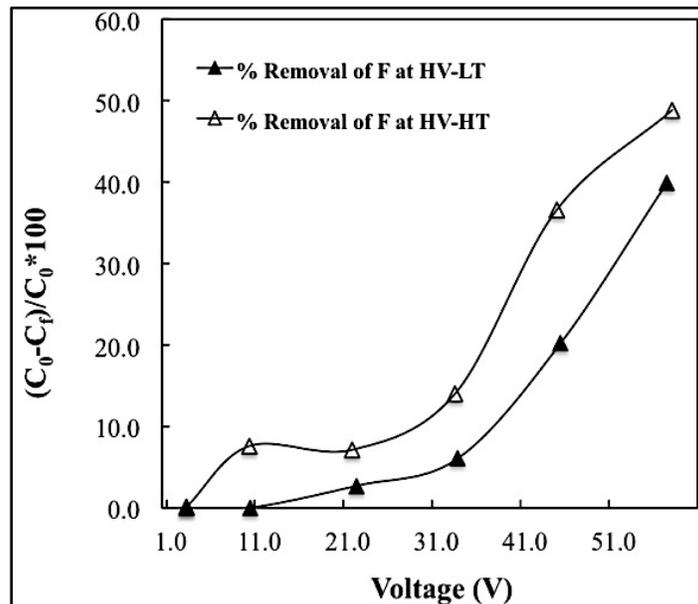
(b)

FIGURE 0-19 Effect of temperature on removal of F⁻ at low velocity (a), and high velocity (b)
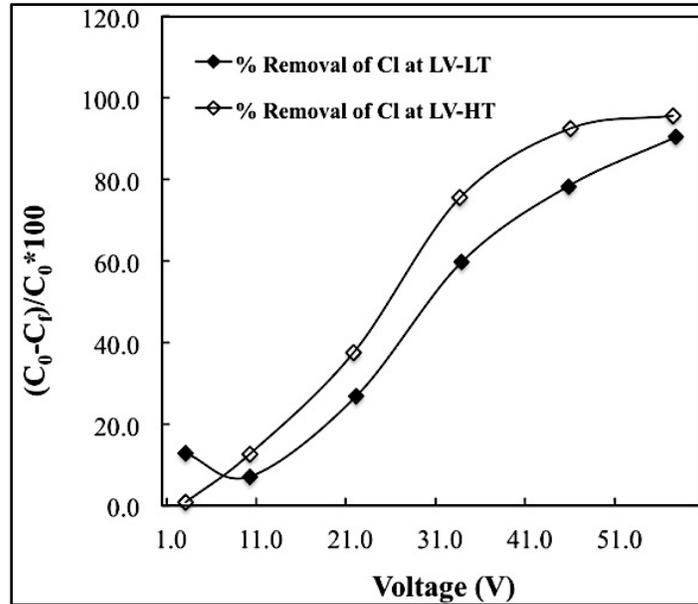
(a)
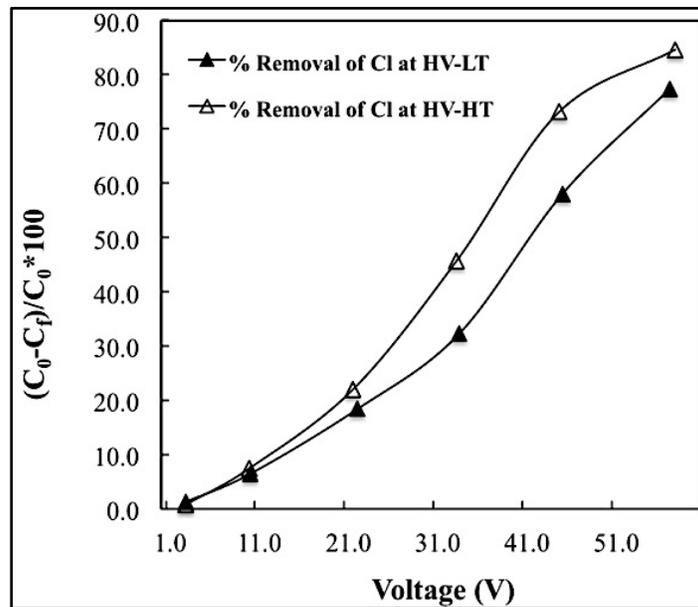
(b)

FIGURE 0-20 Effect of temperature on removal of Cl⁻ at low velocity (a), and high velocity (b)
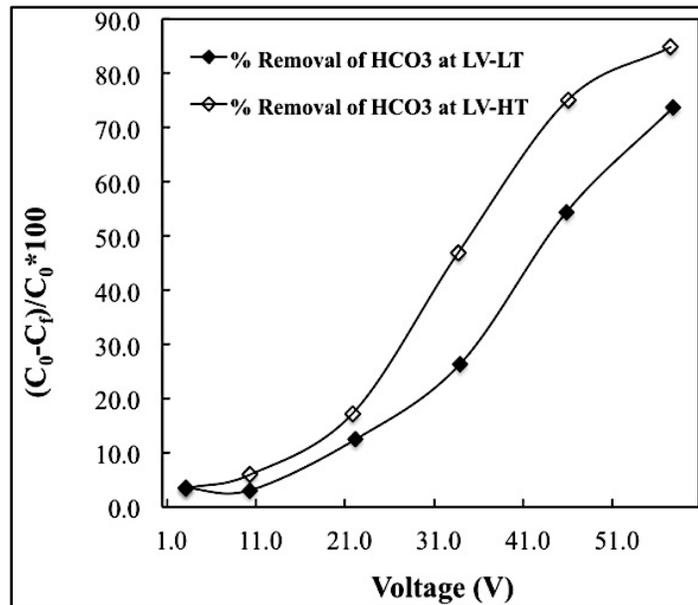
(a)
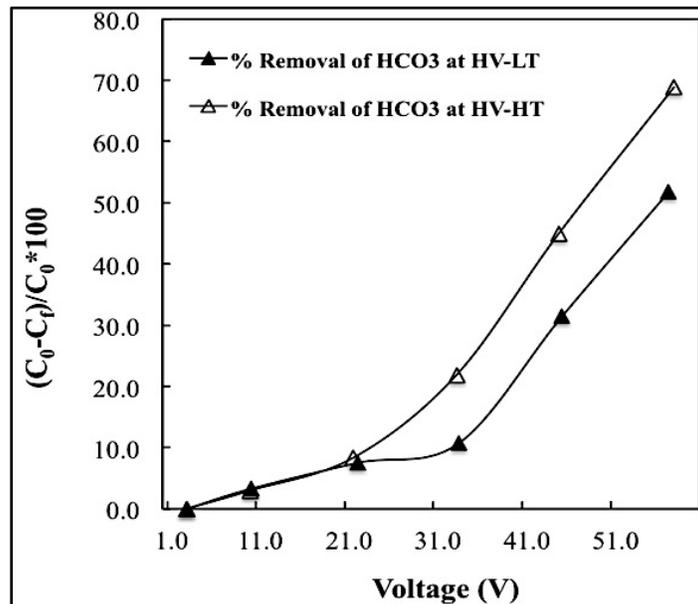
(b)

FIGURE 0-21 Effect of temperature on removal of HCO_3^- at low velocity (a), and high velocity (b)
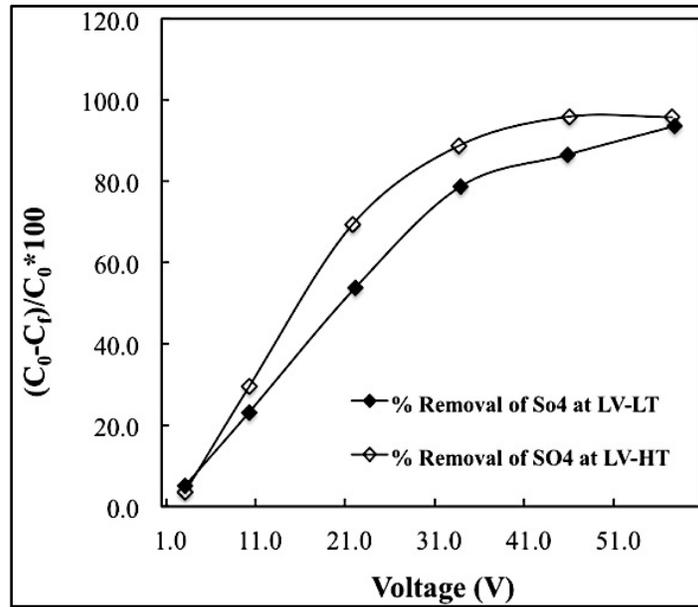
(a)
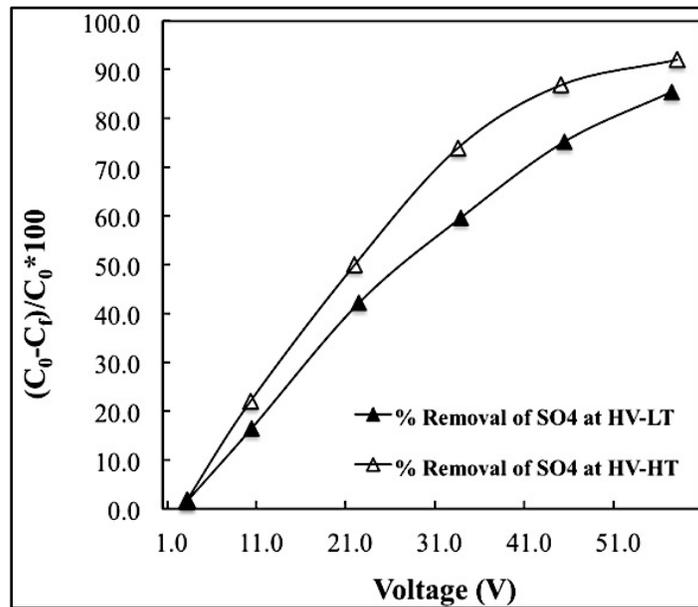
(b)

FIGURE 0-22 Effect of temperature on removal of SO_4^{2-} at low velocity (a), and high velocity (b)
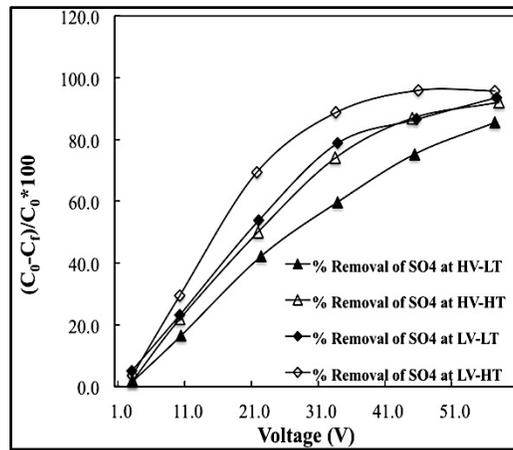
(a)
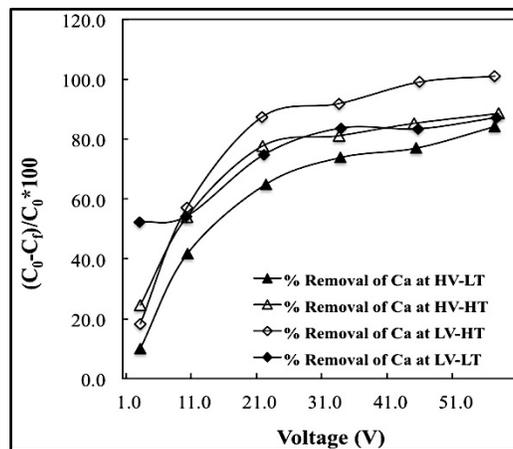
(b)
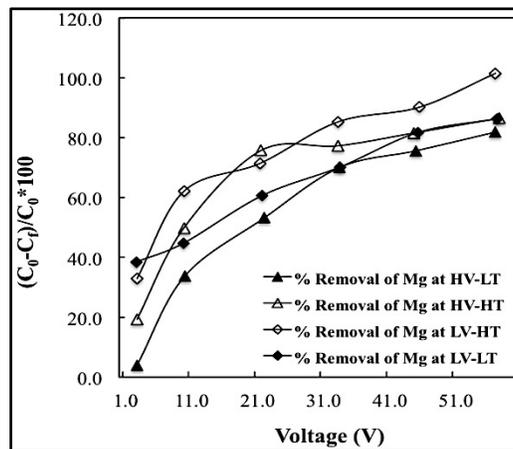
(c)

FIGURE 0-23 Comparison of the effects velocity and temperature on removal of SO_4^{2-} (a), Ca^{2+} (b), and Mg^{2+} (c)

55
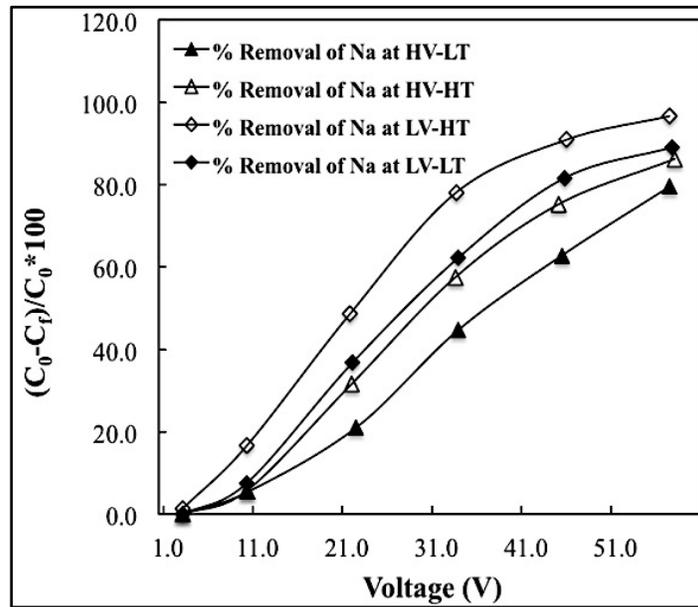
(a)
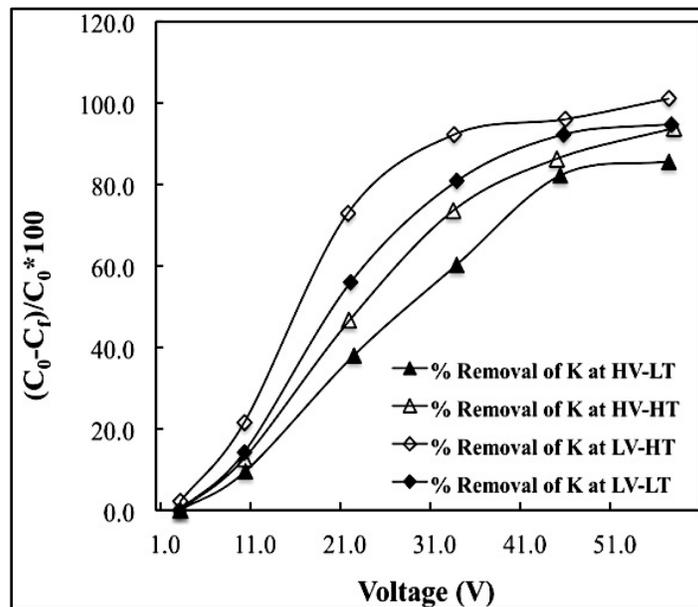
(b)

FIGURE 0-24 Comparison of the velocity and temperature effects on removal of Na$^+$ (a), and K$^+$ (b)

56
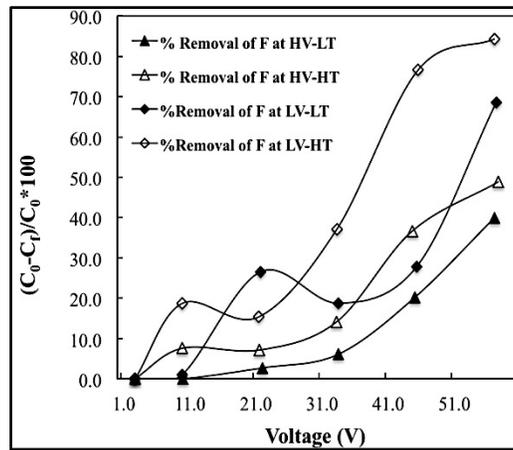
(a)
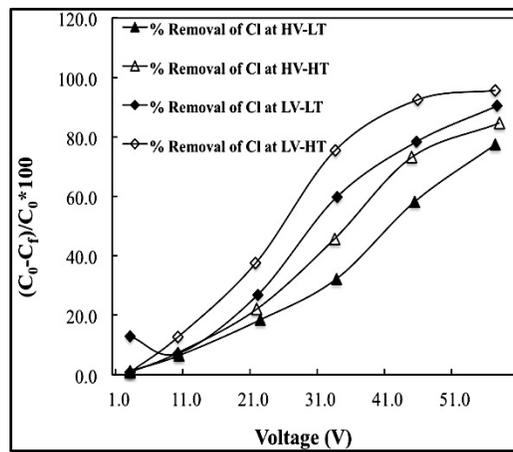
(b)
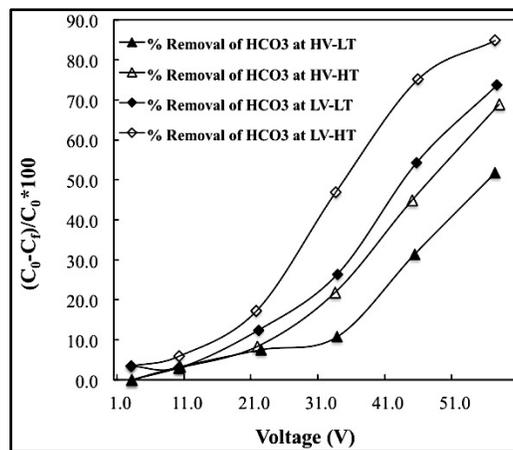
(c)

FIGURE 0-25 Comparison of the effects of velocity and temperature on removal of F$^-$ (a), Cl$^-$ (b), and HCO$_3^-$ (c)

57
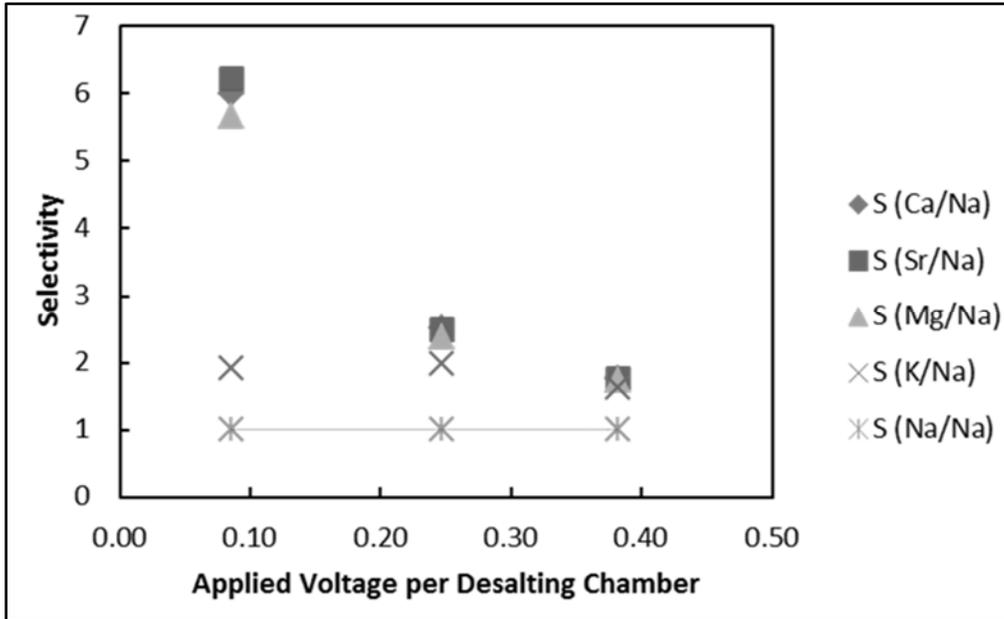
FIGURE 0-26 The general trend of cations' selective removal in the EDR
process using CR-67 cation exchange membrane
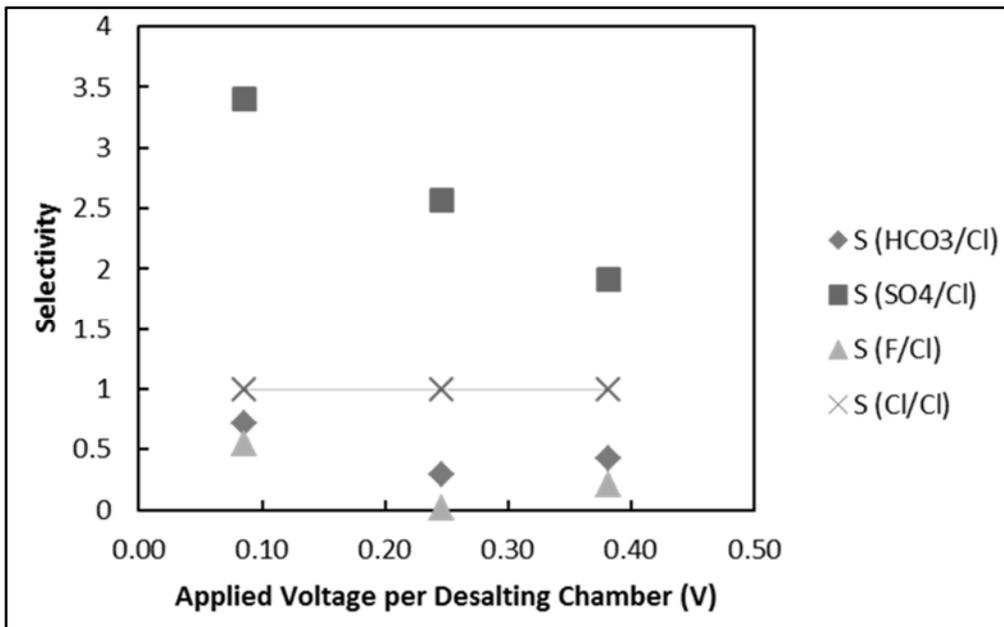
FIGURE 0-27 The general trend of anions' selective removal in the EDR
process using AR204 anion exchange membrane

58
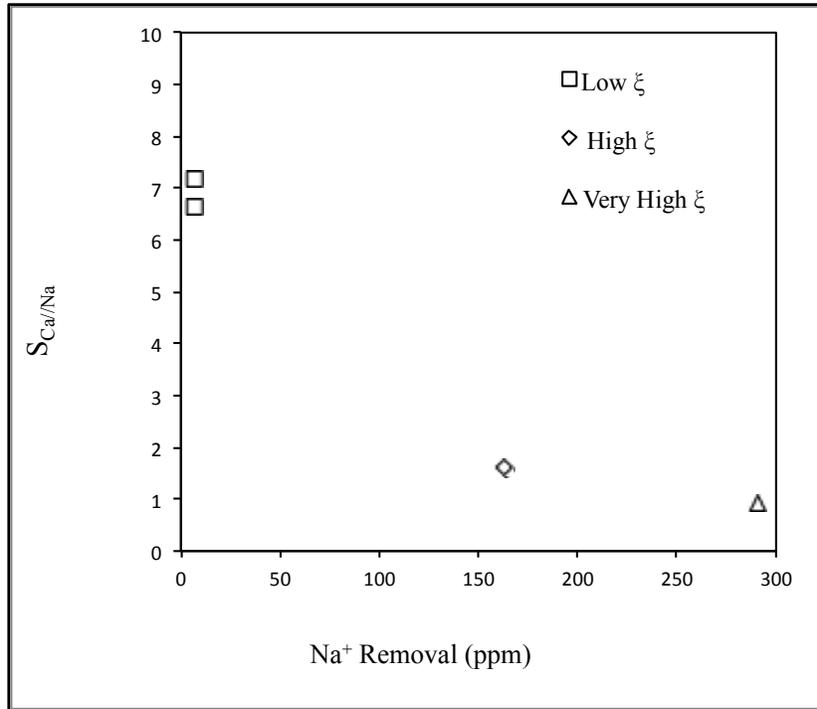
FIGURE 0-28 Selectivity sensitivity for Ca $^{2+}$ vs. Na$^+$
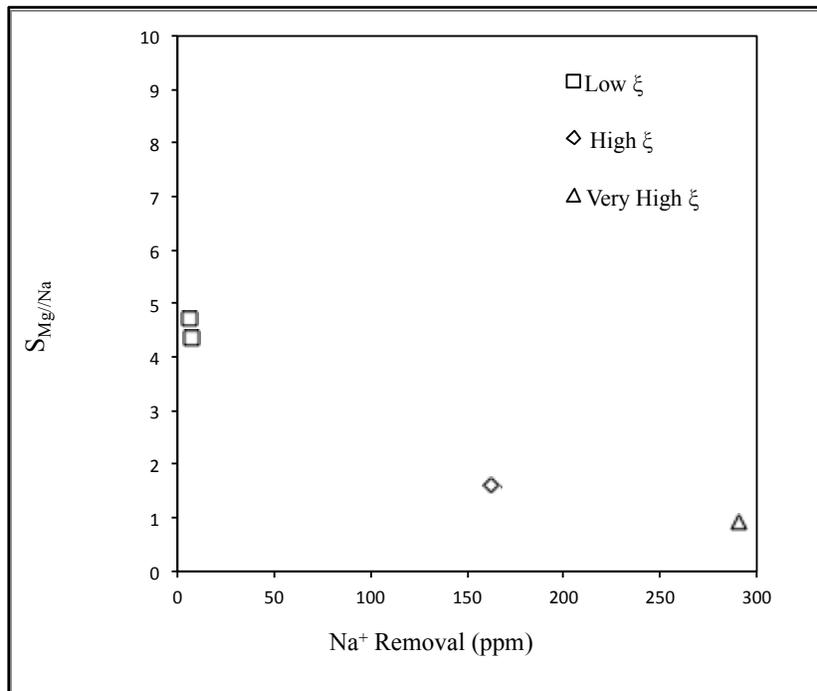
FIGURE 0-29 Selectivity sensitivity for Mg $^{2+}$ vs. Na$^+$

59
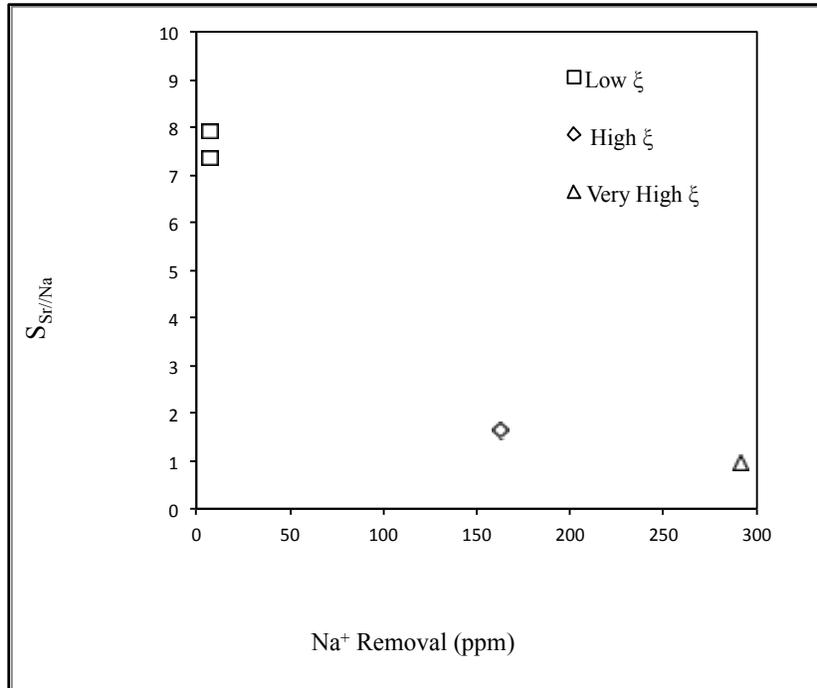
FIGURE 0-30 Selectivity sensitivity for Sr^{2+} vs. Na^+
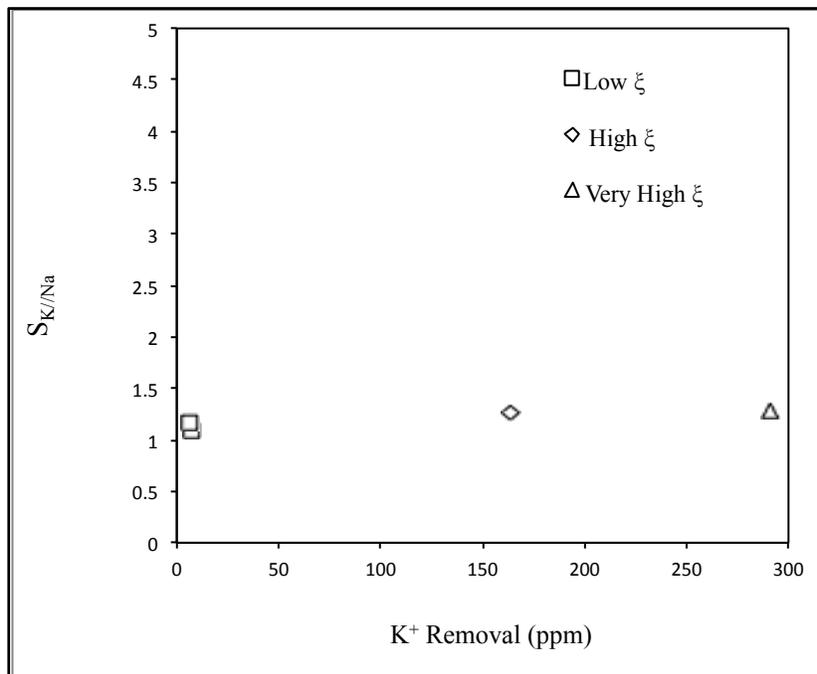
FIGURE 0-31 Selectivity sensitivity for K^+ vs. Na^+

60
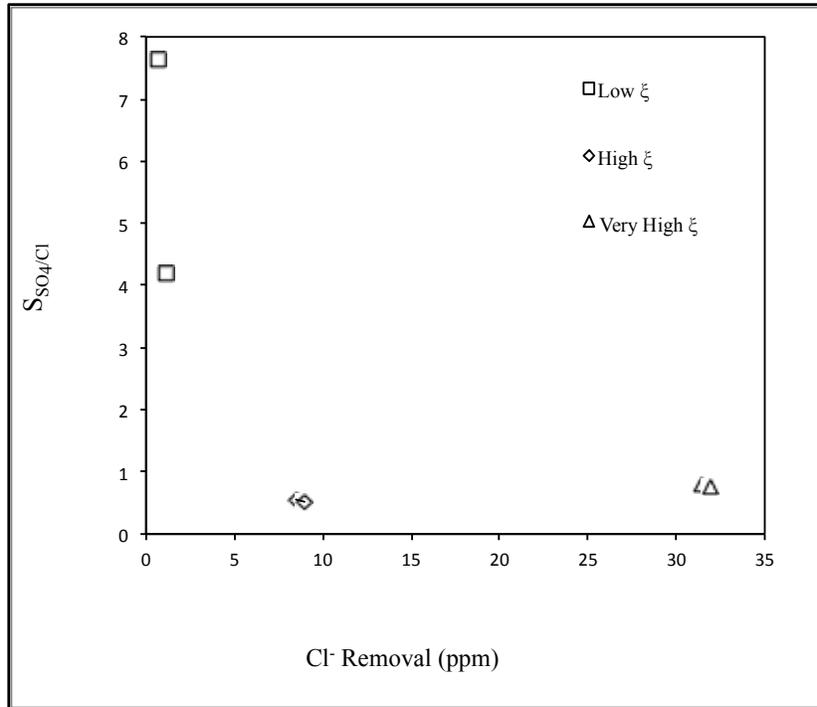
FIGURE 0-32 Selectivity sensitivity for SO_4^{2-} vs. Cl^-
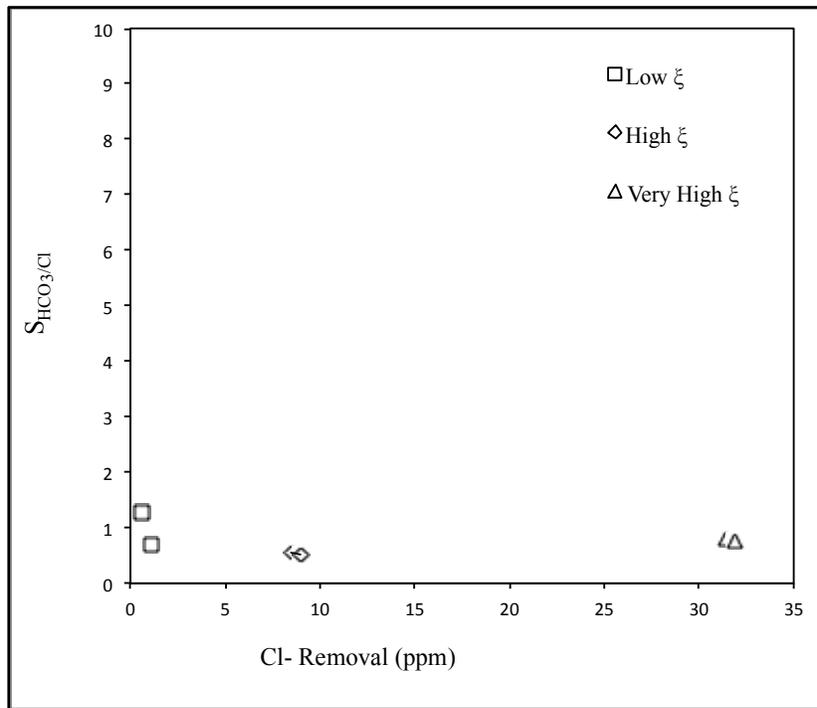
FIGURE 0-33 Selectivity sensitivity for HCO_3^- vs. Cl^-

61
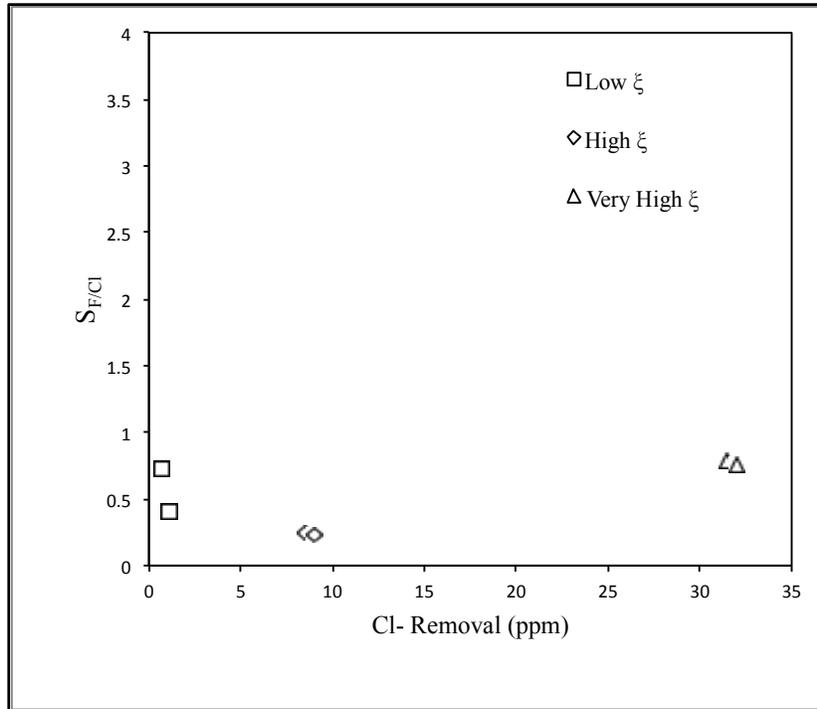
FIGURE 0-34 Selectivity sensitivity for F⁻ vs. Cl⁻
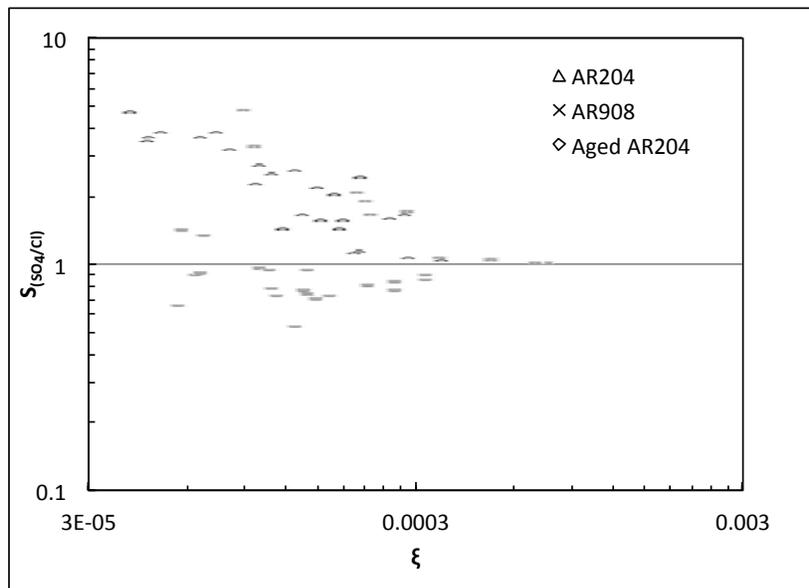
FIGURE 0-35 Selectivity values of SO_4^{2-} vs Cl⁻ in EDR process, using different anion exchange membranes

62
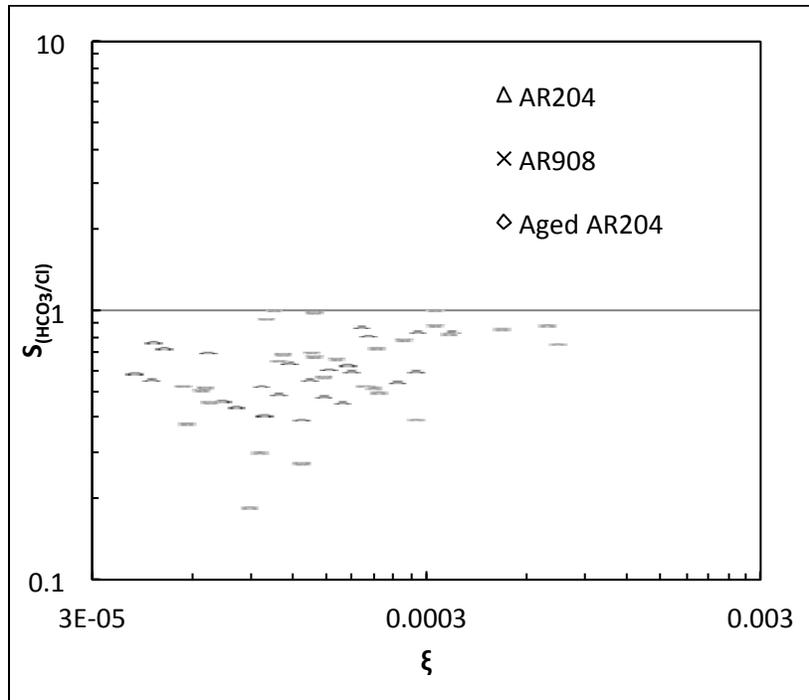
FIGURE 0-36 Selectivity values of HCO_3^- vs Cl^- in EDR process, using different anion exchange membranes
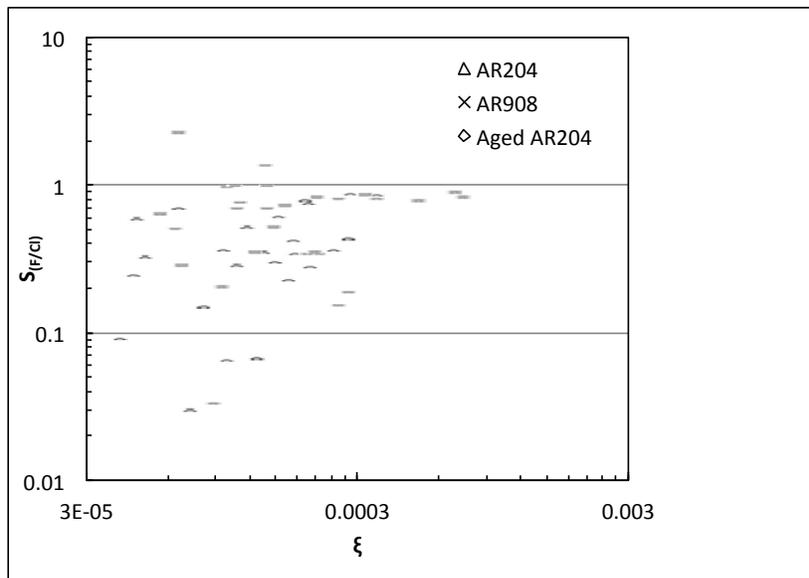
FIGURE 0-37 Selectivity values of F^- vs Cl^- in EDR process, using different anion exchange membranes

63
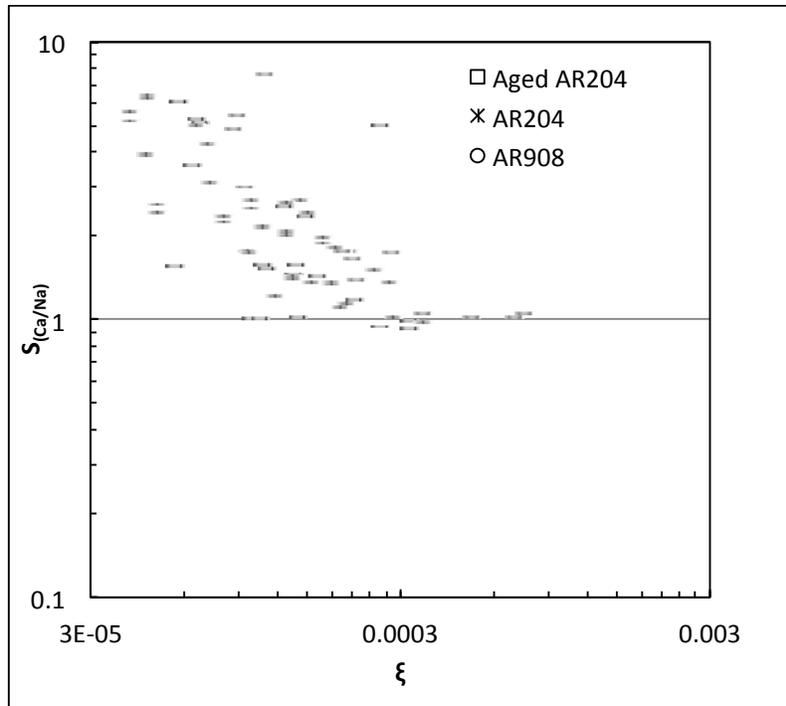
FIGURE 0-38 Selectivity values of Ca^{2+} vs Na^+ in EDR process, using cation exchange membrane type CR-67 and different anion exchange membranes
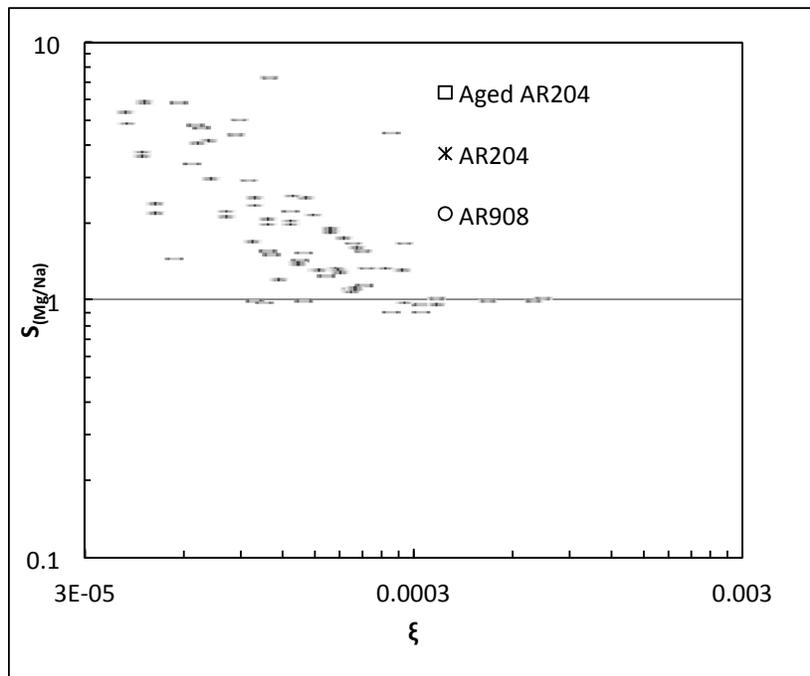
FIGURE 0-39 Selectivity values of Mg^{2+} vs Na^+ in the EDR process, using cation exchange membrane type CR-67 and different anion exchange membranes
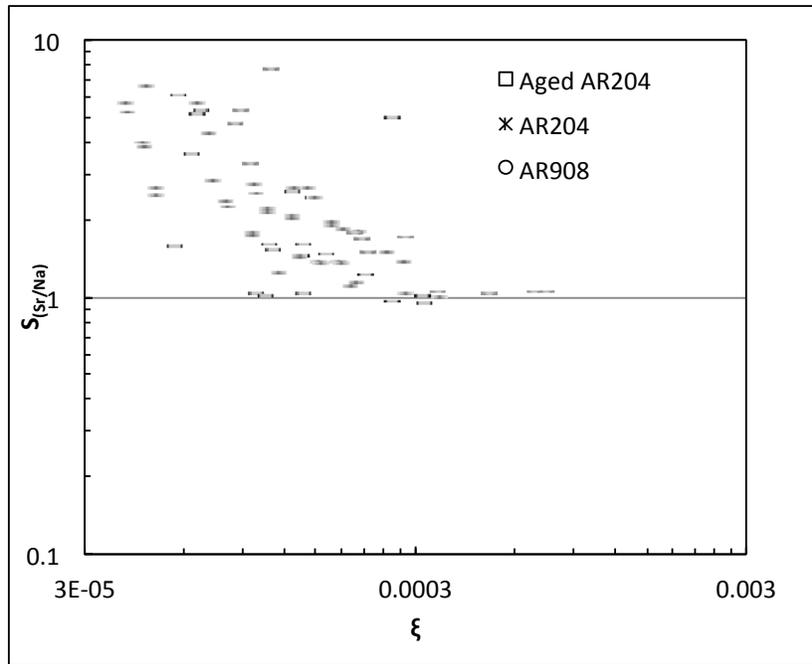
FIGURE 0-40 Selectivity values of Sr^{2+} vs Na^+ in EDR process, using cation exchange membrane type CR-67 and different anion exchange membranes
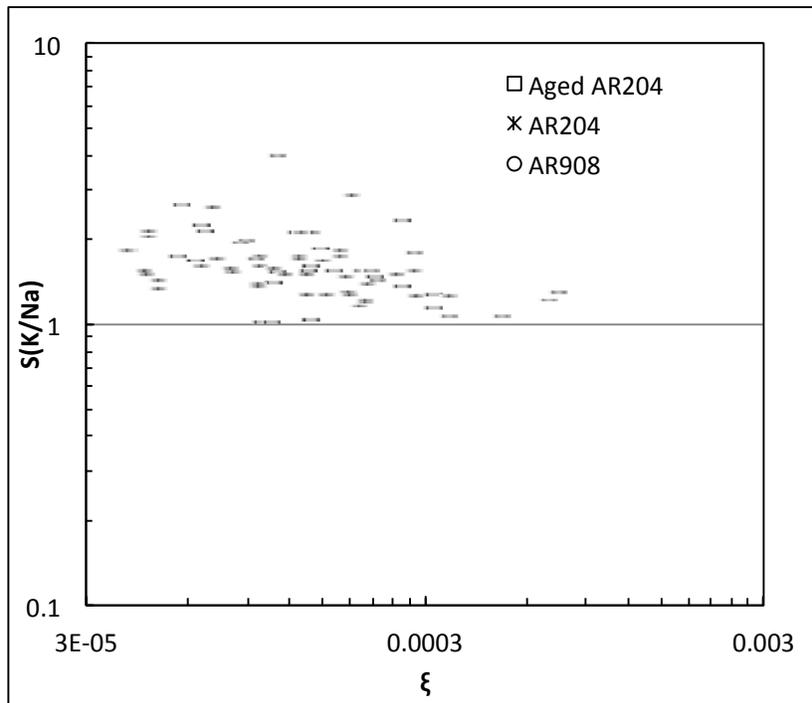
FIGURE 0-41 Selectivity values of K^+ vs Na^+ in the EDR process, using cation exchange membrane type CR-67 and different anion exchange membranes

65
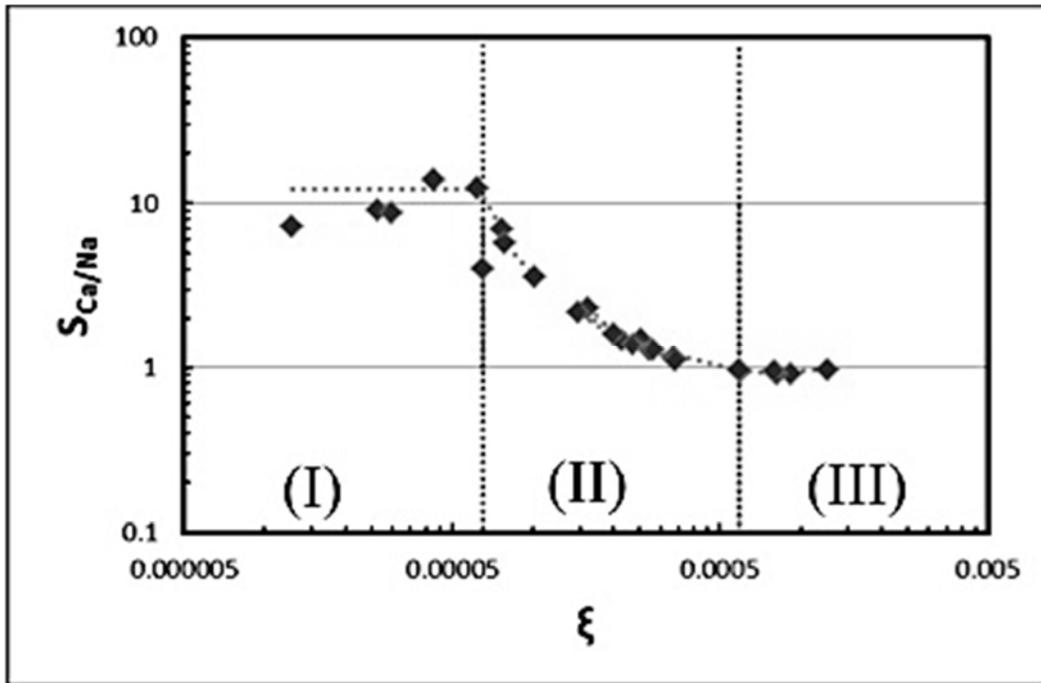
FIGURE 0-42 Different regions for effect of dimensionless number, ξ, in selectivity of Ca^{2+} vs Na^+
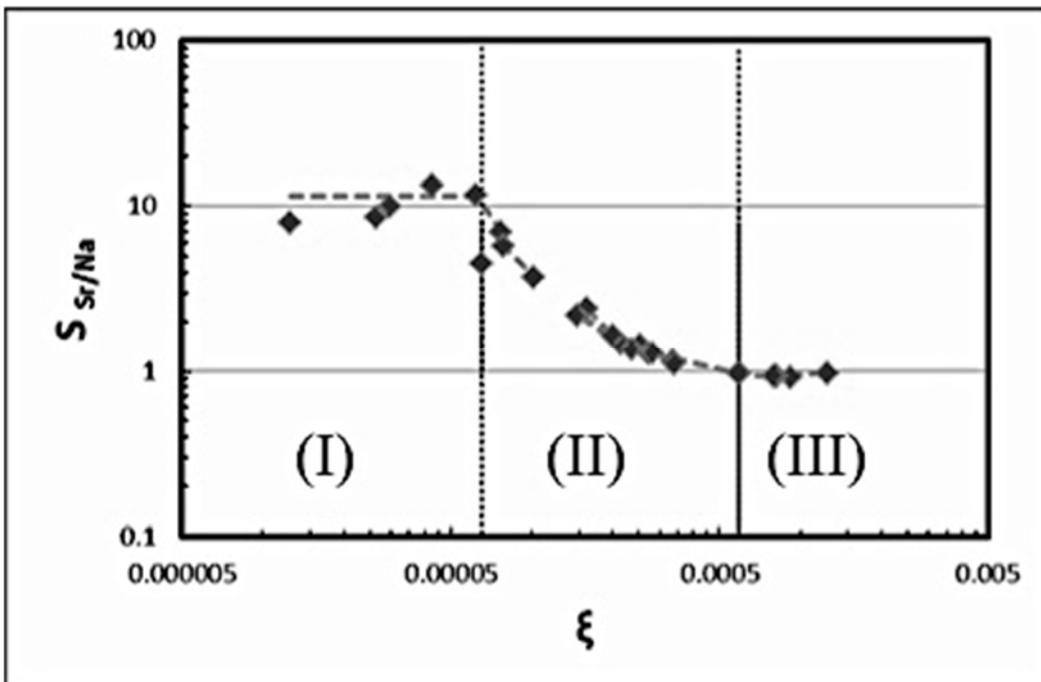
FIGURE 0-43 Different regions for effect of dimensionless number, ξ, in selectivity of Sr^{2+} vs Na^+

66
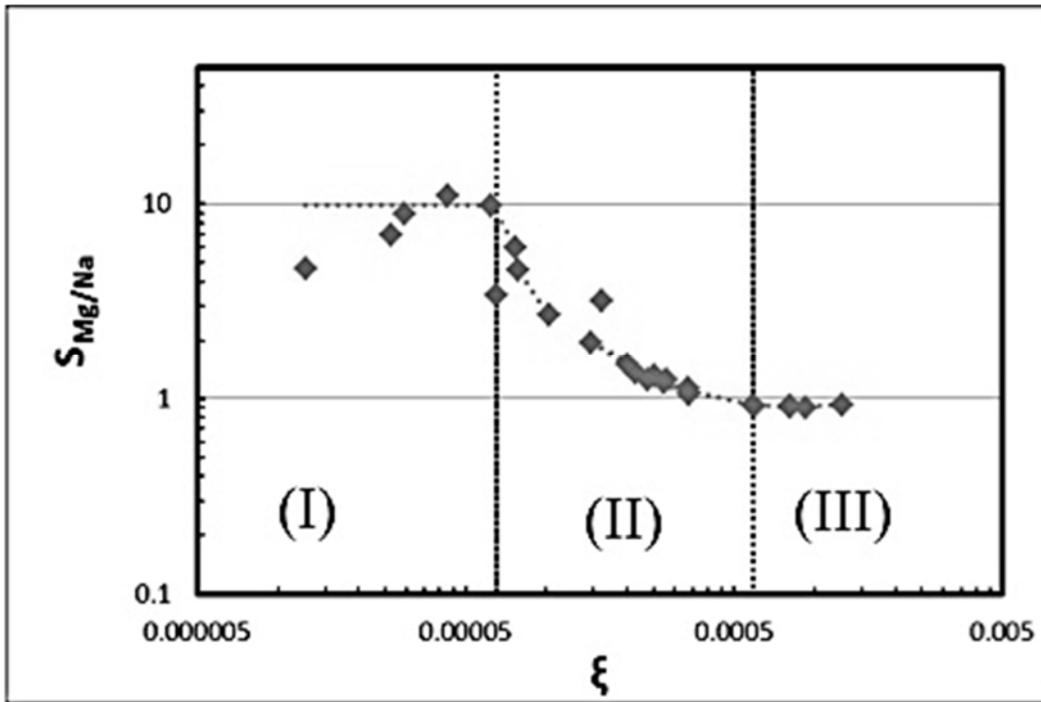
FIGURE 0-44 Different regions for effect of dimensionless number, ξ, in selectivity of Mg^{2+} vs Na^+
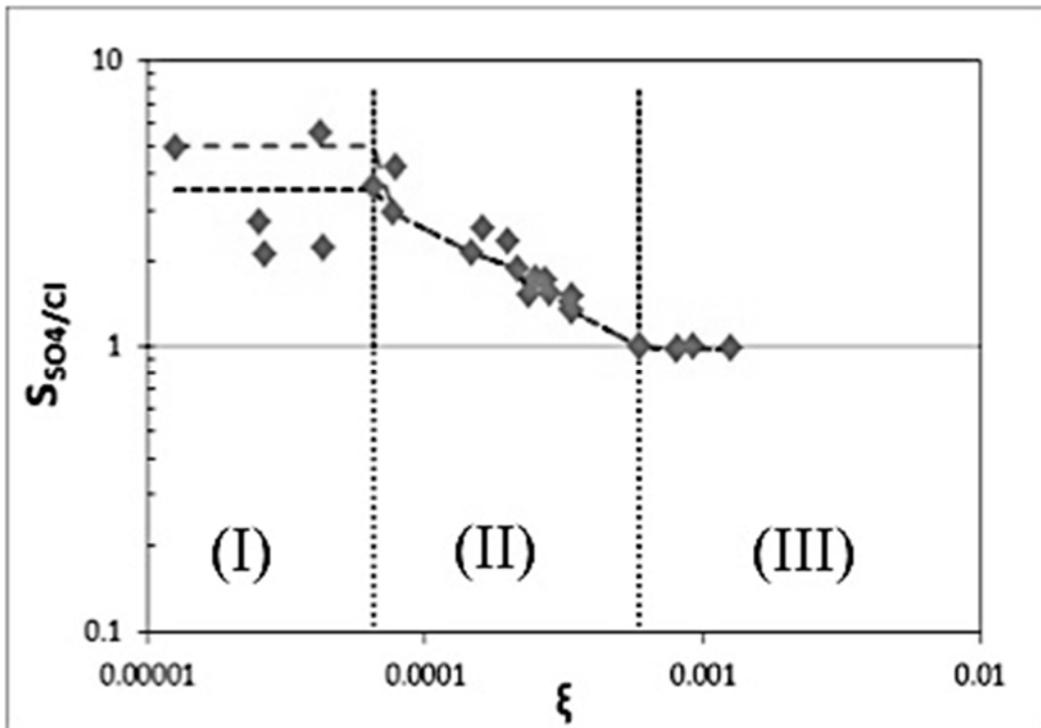
FIGURE 0-45 Different regions for effect of dimensionless number, ξ, for selectivity of SO_4^{2-} vs Cl^-

67
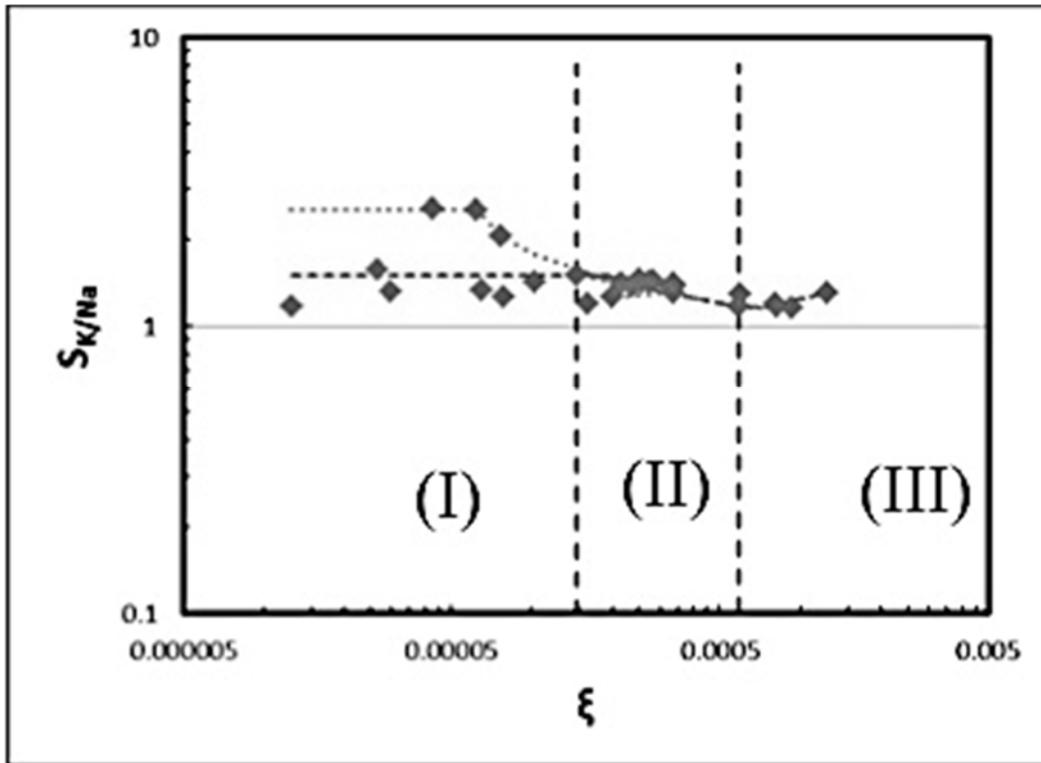
FIGURE 0-46 Different regions for effect of dimensionless number, ξ, in selectivity of K^+ vs Na^+
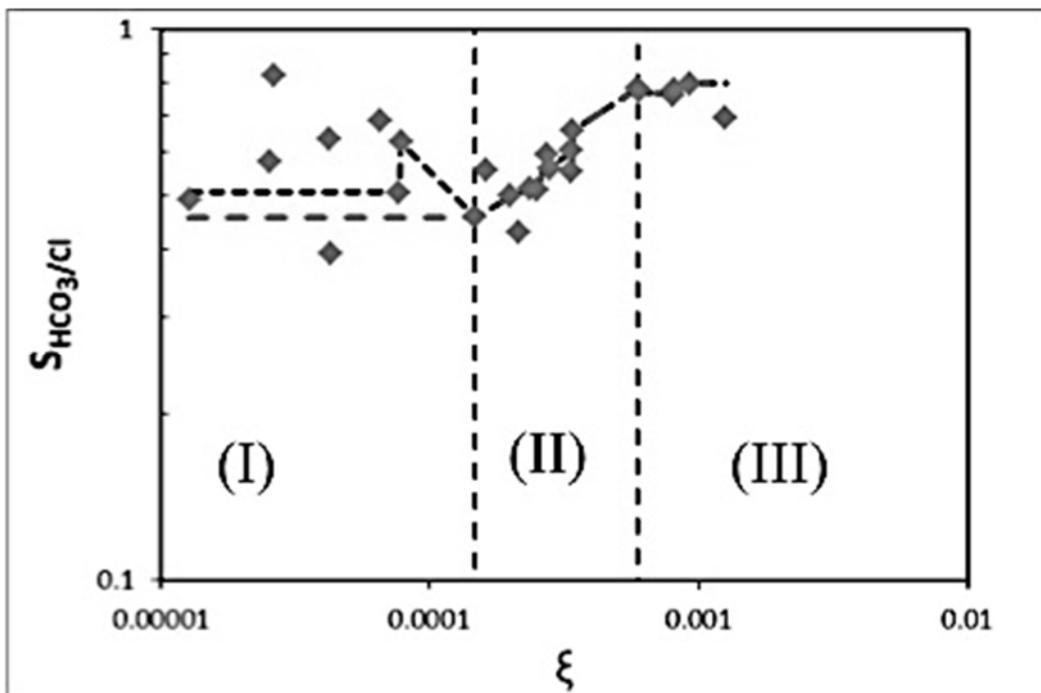
FIGURE 0-47 Different regions for effect of dimensionless number, ξ, for selectivity of HCO_3^- vs Cl^-

68
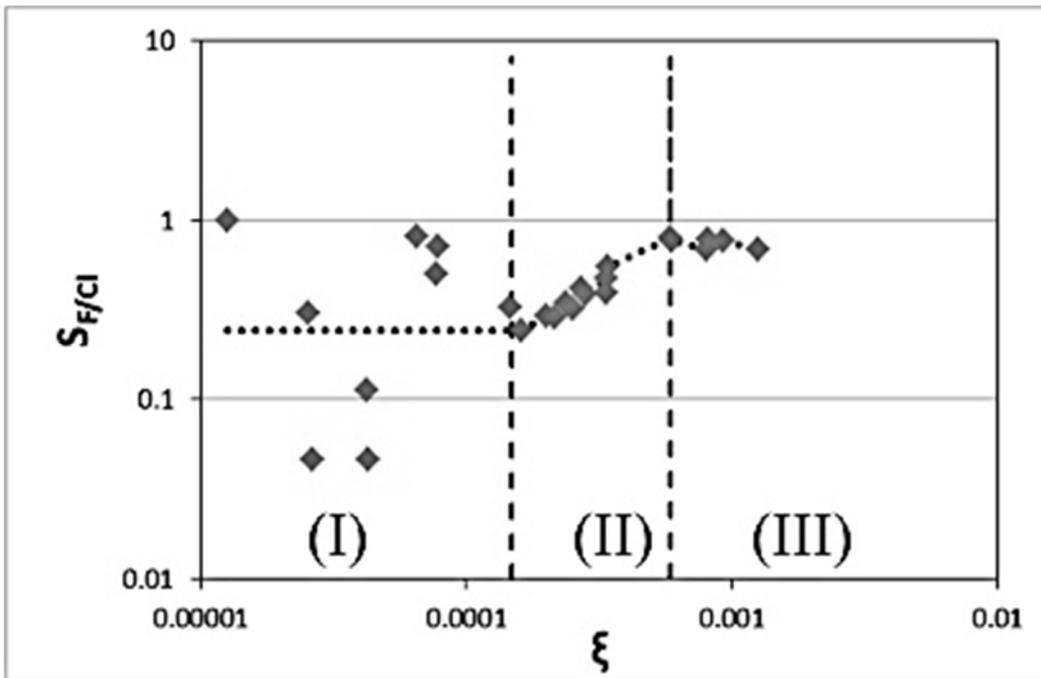
FIGURE 0-48 Different regions for effect of dimensionless number, ξ, for selectivity of F⁻ vs Cl⁻

Appendix

Data Record

Effect of Operating Conditions on Cation Removal

High Temperature-Low Velocity				
Voltage (volts)	K^+ (ppm)	Na^+(ppm)	Mg^{2+}(ppm)	Ca^{2+}(ppm)
2.67	0.0	5.0	2.4	8.5
9.81	0.4	60.2	4.4	26.6
21.34	1.5	176.4	5.1	40.8
33.2	1.8	283.3	6.1	42.9
45.5	1.9	329.7	6.5	46.2
57	2.0	350.6	7.3	47.1
High Temperature-High Velocity				
Voltage (volts)	K^+ (ppm)	Na^+(ppm)	Mg^{2+}(ppm)	Ca^{2+}(ppm)
2.7	0.0	0.0	1.5	11.5
9.81	0.3	20.8	3.9	25.5
21.5	0.9	114.9	5.9	36.7
33.1	1.5	209.4	6.1	38.3
44.6	1.7	273.8	6.4	40.2
57.6	1.9	314.1	6.8	41.8

Low Temperature -Low Velocity				
Voltage (volts)	K^+ (ppm)	Na^+(ppm)	Mg^{2+}(ppm)	Ca^{2+}(ppm)
2.6	0.0	0.0	3.3	27.1
9.8	0.3	28.3	3.9	28.1
21.7	1.2	139.1	5.3	38.8
33.4	1.7	235.0	6.1	43.4
45.3	1.9	308.1	7.1	43.3
57.3	2.0	336.3	7.5	45.2
Low Temperature -High Velocity				
Voltage (volts)	K^+ (ppm)	Na^+(ppm)	Mg^{2+}(ppm)	Ca^{2+}(ppm)
2.7	0.0	0	0.3	4.7
9.94	0.2	19.8	2.6	19.7
22	0.8	76.4	4.2	30.7
33.4	1.2	162.6	5.5	34.9
45	1.6	228.7	5.9	36.3
57	1.7	289.5	6.4	39.7

71

High Temperature-Low velocity				
	Removal/Initial*100			
Voltage (volts)	K^+ (ppm)	Na^+(ppm)	Mg^{2+}(ppm)	Ca^{2+}(ppm)
2.7	2.2	1.4	32.9	18.2
9.8	21.5	16.6	62.1	57.0
21.3	73.0	48.6	71.4	87.3
33.2	92.3	78.1	85.3	91.9
45.5	96.1	90.9	90.2	99.0
57.0	101.1	96.6	101.5	101.0
High Temperature-High Velocity				
	Removal/Initial*100			
Voltage (volts)	K^+ (ppm)	Na^+(ppm)	Mg^{2+}(ppm)	Ca^{2+}(ppm)
2.7	0.0	0.0	19.3	24.4
9.81	12.7	5.7	49.8	53.9
21.5	46.6	31.6	75.7	77.7
33.1	73.7	57.5	77.2	81.1
44.6	86.4	75.2	81.5	85.2
57.6	93.9	86.2	86.5	88.5

Low Temperature-Low Velocity				
	Removal/Initial*100			
Voltage (volts)	K^+ (ppm)	Na^+(ppm)	Mg^{2+}(ppm)	Ca^{2+}(ppm)
2.6	0.0	0.0	38.5	52.2
9.8	14.2	7.5	44.8	54.2
21.7	56.0	36.8	60.6	74.8
33.4	80.8	62.2	70.2	83.7
45.3	92.3	81.6	81.7	83.4
57.3	94.9	89.1	86.3	87.2
Low Temperature-High Velocity				
	Removal/Initial*100			
Voltage (volts)	K^+ (ppm)	Na^+(ppm)	Mg^{2+}(ppm)	Ca^{2+}(ppm)
2.7	0.0	0.0	4.0	10.0
9.9	9.6	5.4	33.7	41.7
22.0	38.0	21.0	53.2	65.0
33.4	60.2	44.6	70.0	73.8
45.0	82.3	62.8	75.6	77.0
57.0	85.7	79.5	81.8	84.1

Effect of Operating Conditions on Anion Removal

High Temperature-Low Velocity				
Voltage (volts)	F^- (ppm)	Cl^- (ppm)	SO_4^{2-} (ppm)	HCO_3^- (ppm)
2.67	0.0	0.3	23.0	6.4
9.81	0.4	4.3	189.7	11.1
21.34	0.3	12.8	445.6	32.4
33.2	0.8	25.8	569.7	88.9
45.5	1.7	31.6	615.7	141.2
57	1.8	32.7	614.6	159.4
Low Temperature-Low Velocity				
Voltage (volts)	F^- (ppm)	Cl^- (ppm)	SO_4^{2-} (ppm)	HCO_3^- (ppm)
2.6	0.0	4.7	34.6	6.4
9.8	0.0	2.6	157.0	5.6
21.7	0.5	9.8	364.4	23.1
33.4	0.4	21.9	533.3	49.2
45.3	0.6	28.7	585.7	101.1
57.3	1.4	33.2	633.5	137.2

74

High Temperature-High Velocity				
Voltage (volts)	F^- (ppm)	Cl^- (ppm)	SO_4^{2-} (ppm)	HCO_3^- (ppm)
2.7	0.0	0.3	11.0	0.0
9.9	0.2	2.5	137.1	5.5
22.0	0.1	7.5	312.5	15.6
33.4	0.3	15.6	462.5	40.8
45.0	0.7	24.9	542.6	83.8
57.0	1.0	28.8	575.1	128.4
Low Temperature-High Velocity				
Voltage (volts)	F^- (ppm)	Cl^- (ppm)	SO_4^{2-} (ppm)	HCO_3^- (ppm)
2.7	0.0	0	10.0	0.0
9.9	0.0	2.3	106.9	6.0
22.0	0.1	6.5	275.1	13.8
33.4	0.1	11.4	388.7	19.8
45.0	0.4	20.4	490.2	57.8
57.0	0.8	27.2	556.9	95.2

75

High Temperature-Low Velocity			
	Removal/Initial*100		
Voltage (volts)	F^- (ppm)	Cl^- (ppm)	SO_4^{2-} (ppm)	HCO_3^- (ppm)
2.67	0.0	0.8	3.6	3.4
9.81	18.7	12.7	29.6	5.9
21.34	15.3	37.5	69.4	17.2
33.2	37.1	75.5	88.8	46.9
45.5	76.6	92.5	95.9	75.1
57	84.3	95.7	95.8	84.8
Low Temperature-Low Velocity			
	Removal/Initial*100		
Voltage (volts)	F^- (ppm)	Cl^- (ppm)	SO_4^{2-} (ppm)	HCO_3^- (ppm)
2.6	0.0	12.9	5.1	3.4
9.8	1.0	7.1	23.2	3.0
21.7	26.5	26.9	53.8	12.4
33.4	18.8	59.8	78.8	26.4
45.3	27.9	78.4	86.5	54.3
57.3	68.5	90.5	93.6	73.7

High Temperature-High Velocity				
	Removal/Initial*100			
Voltage (volts)	F^- (ppm)	Cl^- (ppm)	SO_4^{2-} (ppm)	HCO_3^- (ppm)
2.7	0.1	0.8	1.8	0.0
9.81	7.6	7.4	22.0	3.0
21.5	7.1	22.0	50.0	8.4
33.1	14.0	45.7	74.0	21.9
44.6	36.6	73.2	86.9	44.9
57.6	48.8	84.7	92.1	68.9
Low Temperature-High Velocity				
	Removal/Initial*100			
Voltage (volts)	F^- (ppm)	Cl^- (ppm)	SO_4^{2-} (ppm)	HCO_3^- (ppm)
2.7	0.0	1.2	1.5	0.0
9.94	0.0	6.4	16.4	3.3
22	2.7	18.4	42.2	7.5
33.4	6.1	32.3	59.7	10.7
45	20.2	58.1	75.3	31.4
57	39.9	77.4	85.5	51.7

Anion Exchange Membrane Comparison

AR204 Membrane Tests							
Temp	Applied effective Volt	Velocity (cm/s)	ξ	HCO3/Cl	SO4/Cl	Cl/Cl	F/Cl
17	0.08	14.13	4.56625E-05	0.72	3.41	1.00	0.54
17	0.08	14.13	4.57191E-05	0.48	2.53	1.00	0.41
17	0.31	14.25	0.000168124	0.43	1.91	1.00	0.20
17	0.31	14.25	0.000167604	0.37	1.93	1.00	0.18
30	0.13	14.13	7.28511E-05	0.43	3.58	1.00	0.03
31	0.24	14.13	0.000127302	0.37	2.46	1.00	0.06
33	0.33	14.13	0.000174793	0.58	1.35	1.00	0.38
33	0.33	14.13	0.000182984	0.49	1.71	1.00	0.34
22	0.13	14.25	6.59202E-05	0.65	3.39	1.00	0.62
22	0.30	14.25	0.000148946	0.45	2.07	1.00	0.27
24	0.39	13.89	0.000202162	0.49	2.29	1.00	0.25
24	0.49	14.25	0.000246722	0.49	2.29	1.00	0.25
13	0.07	8.50	4.9391E-05	0.67	3.59	1.00	0.29
13	0.07	8.50	4.93667E-05	0.57	3.21	1.00	0.44
13	0.13	8.98	9.82558E-05	0.38	2.58	1.00	0.06
13	0.13	8.98	9.83541E-05	0.45	2.53	1.00	0.12
22	0.24	8.62	0.000177674	0.56	1.47	1.00	0.31
22	0.24	8.62	0.000179681	0.55	1.50	1.00	0.36
31	0.11	8.38	8.09165E-05	0.41	3.01	1.00	0.13
31	0.11	8.38	8.0354E-05	0.40	3.02	1.00	0.08
32	0.19	8.98	0.000134198	0.52	1.56	1.00	0.32
32	0.19	8.98	0.000133633	0.52	1.55	1.00	0.27
33	0.28	8.98	0.000192475	0.81	1.05	1.00	0.71
33	0.28	8.98	0.000192636	0.81	1.05	1.00	0.71
25	0.36	8.97	0.000277602	0.56	1.54	1.00	0.39
25	0.16	9.34	0.000116476	0.60	1.35	1.00	0.48
23	0.37	8.98	0.000283017	0.78	1.01	1.00	0.80
23	0.48	9.34	0.00035501	0.78	0.99	1.00	0.78
32	0.07	10.78	4.4827E-05	0.52	3.31	1.00	0.22
32	0.07	10.78	4.50794E-05	0.71	3.55	1.00	0.16
34	0.17	11.61	9.63874E-05	0.49	2.12	1.00	0.33
34	0.17	11.61	9.64512E-05	0.49	2.11	1.00	0.33
34	0.36	11.73	0.000199366	0.76	1.08	1.00	0.68
34	0.36	11.73	0.000199583	0.76	1.07	1.00	0.68
24	0.07	11.97	4.013E-05	0.55	4.44	1.00	0.08
24	0.07	11.97	3.99063E-05	0.45	3.33	1.00	0.03
24	0.19	11.97	0.000107795	0.46	2.37	1.00	0.26
24	0.19	11.97	0.000107576	0.45	2.55	1.00	0.30
31	0.28	12.09	0.000153463	0.57	1.47	1.00	0.56
31	0.28	12.09	0.000154488	0.56	1.51	1.00	0.35

78

AR908 Membrane Tests						
Linear velocity	Feed T	Applied effective Volt	ξ	SO4/Cl	HCO3/Cl	F/Cl
8.98	19.20	0.33	2.80E-04	1.59	0.37	0.17
8.98	19.40	0.88	7.45E-04	0.95	0.71	0.76
14.37	24.25	0.20	9.48E-05	3.12	0.28	0.18
14.37	24.47	0.46	2.16E-04	1.56	0.47	0.31
14.37	24.48	1.52	6.93E-04	0.96	0.83	0.81
8.98	33.97	0.12	8.88E-05	4.47	0.17	0.03
8.98	33.91	0.31	1.96E-04	1.94	0.49	0.31
8.98	33.77	0.59	3.53E-04	1.01	0.77	0.73
14.37	33.72	0.37	2.09E-04	1.79	0.48	0.32
14.37	33.81	1.11	5.05E-04	0.99	0.79	0.72

Aged-AR204 Membrane Tests									
	% Removal in Conductivity	Feed Temp	Effective Applied Voltage per desalting cell	ξ	HCO3/Cl	SO4/Cl	Cl/Cl	F/Cl	velocity in desalting chamber (cm/s)
7.5/3.5	30	11.29	0.26	1.4778614E-04	0.52	0.66	1.00	0.48	9.27
7.5/3.5	60	11.32	0.62	2.1243066E-04	0.67	0.76	1.00	0.75	9.39
7.5/3.5	85	11.33	1.95	3.1849595E-04	0.93	0.85	1.00	0.80	9.34
12/5.3	30	9.85	0.46	1.6219957E-04	0.62	0.68	1.00	0.66	14.76
12/5.3	60	9.8	1.13	2.5595399E-04	0.72	0.78	1.00	0.74	14.83
12/5.3	70	9.84	1.86	3.1903570E-04	0.83	0.80	1.00	0.78	15.08
7.5/3.5	30	31.32	0.09	5.7604390E-05	0.36	1.33	1.00		9.25
7.5/3.6	60	31.73	0.26	1.0798076E-04	0.61	0.73	1.00	0.62	9.67
7.5/3.7	90	30.95	0.77	9.8831609E-05	0.87	0.90	1.00	0.88	9.17
12/5.3	30	30.68	0.16	6.3460618E-05	0.48	0.85	1.00	0.46	14.71
12/5.3	60	30.89	0.42	1.1089885E-04	0.64	0.68	1.00	0.70	14.55
12/5.3	90	31.15	1.34	1.0563340E-04	0.94	0.89	1.00	0.90	14.60
7.5/3.5	30	21.96	0.10	6.7394326E-05	0.43	1.26	1.00	0.26	9.12
7.5/3.5	60	21.9	0.30	1.3847771E-04	0.63	0.70	1.00	0.63	9.12
7.5/3.5	90	22.13	1.02	1.3861039E-04	0.92	0.89	1.00	0.90	9.22
12/5.3	30	22.02	0.16	6.5341490E-05	0.49	0.86	1.00	2.10	14.97
12/5.3	60	21.98	0.47	1.3607558E-04	0.65	0.72	1.00	1.25	14.82
12/5.3	90	21.81	1.79	1.5844046E-07	1.01	0.90	1.00	1.01	14.84