Electrodialysis of Highly Concentrated Brines: Effects of Calcium

¹Thomas D. Hayes, Ph.D., ²Blaine F. Severin, Ph.D., P.E.

ABSTRACT

Electrodialysis (ED) is an electrochemically driven membrane technology that is usually used for treating feed water containing several thousand mg/l total dissolved solids (TDS). This research investigated the use of ED for the treatment of flowback water from shale gas hydro fracture. Shale brines contain tens of thousands of mg/l TDS and contain a mixture of multivalent cations, such as calcium, magnesium, barium, strontium, radium, iron, and manganese. This paper covers efforts undertaken to mitigate problems associated with high concentrations of calcium (4,000 mg/l) in the presence of 30,000 mg/l NaCl. Eight baseline ED tests were performed with sodium chloride. Seven additional runs were designed to understand the effect of calcium on the electrodialysis process. Initial tests showed strong incursion of calcium into the electrolyte using a CMX barrier membrane. The apparent calcium fouling (in and around) the electrode cells was indicated by a rapid degradation of process efficiency, observed as a decrease in current. The single cathode boundary membrane was replaced with a membrane that was more selective against multivalent cations (CMX-S). Calcium flux into the electrolyte was reduced by 47-73% and the ion flux from the concentrate to the diluate improved by approximately 40% compared to the baseline. Additionally, the replacement of the single cathode boundary membrane imparted an apparent immunity to direct fouling by addition of calcium directly into the electrolyte.

¹Gas Technology Institute, Des Plaines, IL 60018

²Environmental Process Dynamics, Inc., Okemos, MI 48864

KEY WORDS

Electrodialysis, shale gas flowback, seawater, sodium chloride, calcium, demineralization, separations, produced water, fouling prevention.

ABBREVIATIONS AND NOMENCLATURE

Term	Definition	Units
RFI	Relative Flux Index, ratio of flux into electrolyte to flux into concentrate	%
Calcium Rejection	% calcium rejected at the cathode membrane	%
CBM	Coal Bed Methane	
ED	Electrodialysis	

BACKGROUND

This project was a part of a larger investigation into the quantity and quality of the flowback water and produced water from shale gas hydraulic fracture processes, and the alternatives available to maximize the reuse of recovered water, minimize the volume of deep well disposal, and reduce the cost and environmental impact associated with the disposal of flowback and produced water (Hayes and Severin, 2012). As part of this project, we investigated the potential to utilize electrodialysis (ED) for partial treatment of these types of saline waste water. (Severin and Hayes, 2012). We approached the investigation from the standpoint of providing 1) acceptable power utilization (0.22-0.33 kWh/kg salt) using standard equipment, 2) insights into means of minimizing equipment size (area of membrane), and 3) means of overcoming difficulties, either anticipated or encountered in the field. These goals led the research down one path that included 1) methods to maximize salt transfer by changing the ionic strength and pH of the electrolyte rinse solution (Severin and Hayes, 2016 A *IN PREPARATION*), 2) mitigation of calcium incursion into the catholyte (*THIS PAPER*), and mitigation of problems associated with other multivalent cations (Severin and Hayes, 2016 B *IN PREPARATION*). In following this research path, we chose to solve the problems associated with calcium incursion into the electrolyte by using a more selective barrier membrane at the cathode cell boundary.

There has been some discussion in the literature about mitigating fouling by changes to the chemistry utilized as the electrolyte rinse solution. One such alternative is sulfamic acid. Sulfamic acid (HSO_3NH_2) is commonly used as an industrial cleanser and has some application in home cleanser products. Because sulfamic acid is a strong acid and relatively non-corrosive compared to sulfuric or hydrochloric acid, it has been evaluated as a descalant in large electrodialysis plants (Anees et al 1994). Due to the relatively higher solubility of calcium and barium salts of sulfamic acid (Brooks King et al 1946) compared to the sulfate salts, sulfamic acid or its sodium salt has been suggested as an alternative electrolyte rinse solution to mitigate electrolyte fouling. Sodium sulfamate has been used in at least one study (Elazhar et al 2013) instead of sodium chloride to limit corrosion of the electrodes. However, the solution concentration was not mentioned in the article. In another study, 0.05M sulfamic acid was used as the electrode rinse solution in an ED application to recover Ni and Cu from plating wastes (Yajima and Kume, 1999). As part of our overall research effort to improve the ion flux in treating highly concentrated brines (Severin and Hayes 2012), we concentrated efforts on the electrolyte system (disodium sulfate) recommended by the manufacturer of the ED pilot unit. Due to the relatively low solubility of sodium sulfamate and sulfamic acid and the relatively poor-conductive nature of the sulfamate anion (Taylor et al 1951) we contend that this would have been a poor choice for our research needs.

Hydraulic Fracture of Shale

The hydraulic fracture of shale formations for the capture of natural gas melds decades old hydro fracture technology with new advances in horizontal drilling. Work on North American shale formations, such as the Barnett and the Marcellus, has demonstrated the potential to capture trillions of cubic feet of high value gas. During the fracture process, between 1 and 5 million gallons (4,000 - 19,000 cubic meters) of water and sand are expended “down hole” into each well to aide in the fracture. A portion of this water (termed flowback) is recovered during the initial extraction of the gas. As the well matures, it continues to generate low volumes of concentrated brine (termed produced water). The recovered fluids contain high concentrations of complex mixtures of dissolved salts, plus trace concentrations of residual anti-oxidants and lubrication fluids. Therefore, recovered flowback water presents a disposal problem, of which there are presently few non-controversial disposal methods.

The range of TDS expected in flowback water and produced water encountered in the shale industry is several tens of thousands mg/l (Hayes and Severin 2012.) A number of problems were encountered that were systematically addressed as the project proceeded from the treatment of synthetically simulated flowback/produced water containing pure sodium chloride (30,000-60,000 mg/l) to the treatment of solutions with sodium, calcium (up to 4,000 mg/l), barium (up to 400 mg/l), iron (up to 50 mg/l), and magnesium (up to 600 mg/l) (Severin and Hayes 2012). This paper addresses some of the problems associated with calcium in the presence of sodium in carbonate poor water.

The ED process is typically operated on brackish water sources that are less concentrated than seawater (Xu and Huang, 2008). Operation of ED under the high salt conditions of flowback and/or produced water places the process in a regime of relatively low electrical resistance, requiring lower voltage and allowing higher amperage (current flow) compared to the normal range of operation. This has led to an understanding of the relation between ion flux and applied voltage that allowed for a number of process improvements for operation in this regime (Severin and Hayes, 2016A). Another challenge to the desalinization of shale flowback water is the potential for process poisoning by soluble calcium and other multivalent cations. This challenge was addressed by other process improvements aimed at mitigating the effects of divalent cations on the electrolyte cell. For this portion of the development program, eight electrodialysis runs were performed with pure sodium chloride. Seven runs were dedicated to understanding the relation of calcium to the electrodialysis process. The effects of other multivalent cations are the topic of another paper (Severin and Hayes 2016B).

Effects of Calcium on Electrodialysis

The adverse role of calcium on the duration of a process run was expected, and demonstrated. The chemical nature of flowback water from 19 wells in the Marcellus Shale has been reported by Hayes and Severin (2012). The median total dissolved solids was about 67,300 mg/l with a median soluble calcium concentration of about 4,950 mg/l. Importantly, the median calcium carbonate hardness of 17,700 mg/l as CaCO_3 was balanced against only 122 mg/l alkalinity as CaCO_3 , implying that the majority of the hardness was soluble and balanced against the chloride ligand. The waters are typically devoid of carbonate species. Major contributions to this hardness were Mg (559 mg/l), Ba (686), Sr (1,080 mg/l), and Ca (4,950 mg/l). In these types of brine, the sulfate ion is also usually present in low concentrations. The barium content is dictated (inversely) by the relative concentration of sulfate. The concentrations of the various soluble salts are well above the usual range of operation of ED.

As an example of ED fouling experienced in complex waters, Kaakinen (1984) experienced difficulty in treating water from two sources of hydraulic fracture flowback water. One source had a TDS range of 3,200-3,400 mg/l with calcium (7-18 mg/l) and magnesium (15-30 mg/l). The sulfate concentration was about 980 mg/l balanced against 1160 mg/l chloride. The second source had a TDS range of 9,140-9,180 mg/l, with calcium (35-60 mg/l) and magnesium (52-55 mg/l). The sulfate concentration was about 2040 mg/l with 3660 mg/l chloride. The author attributed membrane fouling in the concentrate stream to gypsum-like precipitation, and recommended that either the water be pretreated with chemical precipitation to remove divalent cations, or treated in parallel with ion exchange.

Bazinet and Araya-Farias (2005) studied the fouling of calcium on cation-selective membranes (CMX-S) in a two cell (three membrane) ED unit in which a model solution containing potassium and calcium at pH 11-12 was desalinated into a solution of sodium chloride at pH 11-12 across a cation selective membrane. The process was meant to mimic application of ED to the food industry (milk purification). They observed no fouling using either 400 or 800 mg/l solutions of

calcium chloride in the absence of carbonate in the model solution, but fouling occurred with 400 mg/l calcium chloride in the presence of carbonate (1,000 mg/l Na_2CO_3). The fouling material appeared to be calcium hydroxide, which was easily cleaned with an acid rinse. They surmised that the carbonate slowed the treatment time sufficiently to allow increased incursion of calcium across the selective cationic membrane.

Firdaus et al. (2007) investigated commercially available monovalent cationic perm-selective membranes for the separation of calcium and magnesium salts from sodium using electrodialysis. They performed systematic research into the ionic competition that can occur at the membrane surfaces due to ionic radii, hydrated radii, and hydration energies. With perm-selective membranes they reported that in solutions with sodium, magnesium, and calcium salts that the relative flux was $J_{\text{Na}} > J_{\text{Ca}} > J_{\text{Mg}}$. However, the presence of calcium abates sodium transport by as much as 33%, whereas, the presence of sodium has little influence on the rate of calcium transport. The interference of calcium and magnesium on sodium transport are attributed to the preferential occupancy of membrane transfer sites on the perm-selective by calcium and magnesium.

Hayes and Moon (2009) examined the desalination of coal bed methane (CBM) produced waters using the same ten cell pilot plant as used in the present study. CBM produced waters typically are only 10% of the ionic strength of produced waters from non-conventional gas production sites that have been created through hydraulic fracturing. The selected test water to represent CBM produced water from the Powder River Basin in Wyoming prepared with the following composition (670 mg/l Na^+ , 6.7 mg/l Ca^{++} , 2.3 mg/l Mg^{++} , 140 mg/l Cl^- , and alkalinity 1,300 mg/l as CaCO_3 at a pH of 8.4). The ED unit was operated at a constant current of 4 m-Amp per square centimeter of membrane surface (about 0.8 amps) with the voltage set not to exceed 15V. Tests proceeded until about 90% of the TDS was transferred from the diluate to the concentrate. One purpose of their testing was to determine if choice of membranes could influence the fate of calcium and magnesium. When all cationic membranes were conventional CMX non-exclusionary membranes, both calcium and magnesium in the diluate were about 10% of the initial concentration. The power utilization was 0.14 kWh/lb (0.31 kWh/kg) NaCl removed. The CMX-S membranes with the ability to retard the passage of multivalent cations resulted in the retention of about 30% of the calcium and magnesium in the diluate. However, the power consumption increased 30% to 0.2 kWh/lb (0.44 kWh/kg) NaCl removed.

Mitigating the Effects of Calcium

A generic cation selective membrane (CMX, Neosepta® manufactured by Astom Corporation, Japan) was initially installed at the boundary to the cathode cell. High rates of calcium incursion into the electrolyte were encountered, causing calcium fouling of the electrode cells. This type of fouling was reversed by acid washing of the electrode cells. The cathode boundary membrane was replaced with a membrane that selected against multivalent cations (CMX-S monovalent-selective membrane, Neosepta® Astom Corporation, Japan). Calcium flux into the electrolyte was reduced by 47-70%. An apparent added benefit was that calcium deliberately introduced into the electrolyte, both as free ions or as a precipitate, no longer interfered with ion flux. This indicated that the initial calcium poisoning was at the surfaces of the cathode boundary. As described above, Hayes and Moon (2009) found replacement of all the cation membranes with CMX-S material resulted in a 30% loss in power efficiency. The data presented below with only the cathode barrier membrane did not result in appreciable loss of efficiency.

METHODS

Electrodialysis Pilot Plant

This project was performed using an Eurodia Industrie, S.A (Rungis, France) Ameridia Eur2B-10 electrodialysis unit (Figure 1). The main component is the Eur2B-10 Electrodialysis ddialysis stack that consists of twenty-one alternating cationic and anionic selective membranes, beginning and ending with cationic selective membranes, forming 10 diluate and 10 concentrate cells. All selective membranes were provided and installed by the vendor. Individual membranes had an area of 200 cm².

The diluate was collected in a 10L diluate tank. A pump, a control valve, and a rotameter were used to deliver and control the flow of diluate to the diluate manifold within the stack that connects all the diluate cells. A diluate tube returns the diluate to the diluate tank. The nominal volume of diluate within the rotameter cell pairs associated with the diluate flow loop is about 0.5L. The recommended flow of diluate through the manifold is about 1.0-1.5 L/minute. The concentrate loop and associated hardware and flow rate is similar to that of the diluate loop. The normal operation is a batch mode where the diluate from the electrodialysis cells was continuously remixed to the diluate tank. A similar approach to fluid management was used for the concentrate.

The electrolyte that passed through the anode cell was collected in the anolyte tank. Likewise the electrolyte that passed through the cathode cell was collected in the catholyte tank. The production of oxygen at the anode and hydrogen at the cathode required that these two tanks be isolated from each other for degassing. In the Eur2B-10 Electrodialysis Pilot Plant, the feed of electrolyte to the electrode cells was provided by a single electrolyte pump that captures electrolyte from both the anolyte and catholyte tanks in roughly the same proportions. This single pump fed a pair of control valves and flow indicators that provide electrolyte separately to the cathode and anode.

The anode and cathode electrodes were connected to a 0-40 V direct current power supply with a maximum current of 25 amps. The recommended maximum potential for this Eur2B-10 was 1.5 volts per cell pair, or 15 volts.

Figure 1: Simplified Diagram of the Batch Electrodialysis Pilot Unit

Electrodialysis Membranes

The CMX cation-exchange, the CMX-S monovalent-selective membranes, and the ACS anion-exchange membranes were all Neosepta® membranes manufactured by Astom Corporation, Japan. All membranes were installed by the stack manufacturer, Eurodia.

Instrumentation

Oakton Instruments Con 110 meters were used to continuously measure conductivity and temperature in the diluate and concentrate. The conductivity meters were calibrated by setting all meters to a 12.50 mS/cm (milli-Semens per centimeter) standard (Oakton Instruments). Subsequently, a series of sodium chloride solutions ranging from 120,000 mg/l to about 8000 mg/l NaCl were prepared. Calibration curves were generated for each conductivity meter. Calibrations were regenerated at least once each week and spot checked against a single solution daily before each test. Temperature changed throughout each test run by a few degrees,

usually increasing as each test proceeded. The conductivity probes were sensitive to temperature so an Arrhenius relation was developed to correct for minor changes in temperature. The corrections were made automatically by the software. Three Oakton Instruments pH 110 meters were occasionally used to measure the pH of the diluate, the concentrate, and the electrolyte. The pH probes were calibrated to pH7.

Voltage Selection

One goal of this research project was to demonstrate that the electrodialysis process could work satisfactorily at a power utilization rate of between about 0.1 and 0.15 kWh/lb of salt transferred (0.22-0.33 kWh/kg), which was estimated to represent a power cost acceptable to the gas and oil industry for treating saline wastewater. At a starting point of 3% NaCl and 200 cm²/cell pair with 10 cell pairs, application of Faraday's Law predicts that a target of 0.104 kWh/lb (0.23 kWh/kg) salt transferred is achieved with an applied potential of 5V, assuming 100% transfer efficiency. Thus, the target of 5V was established as a reasonable potential use in this pilot ED skid.

Electrolyte Solution

There is a dearth of information in the open literature concerning the effects of the electrolyte chemistry within the electrode cells (or electrode rinse) on the overall efficiency of ED performance. As one objective of the overall project we examined the chemistry of the sodium sulfate electrolyte system for the purpose of improving the rate of salt transfer at feed water concentrations that exceed seawater concentration. Increasing the electrolyte rinse concentration to an ionic strength exceeding that of the feed water improved the ion flux. Lowering the overvoltage of the electrodes by operation of the electrolyte at a pH greater than pH 11.5 yielded an additional improvement (Figure 2). In this figure we show a systematic improvement in ion flux (vis. amperage) with higher concentrations of sodium sulfate in the electrode rinse. The data also show that the addition of sodium hydroxide allows an additional 15% flux improvement.

Figure 2: Relative flux (as amperage) versus applied voltage for disodium sulfate electrolyte rinse solutions, initial conditions 3% NaCl

The preferred electrolyte was prepared with disodium sulfate as recommended by the vendor of the commercial electrodialysis process tested in this study. Most electrolyte solutions used in this study also contained 1 g/l sodium hydroxide. Tests with 3% NaCl were performed with electrolyte with 90 mg/l disodium sulfate, whereas, tests with 6% disodium sulfate were performed with 120 g/l disodium sulfate. The relatively high disodium sulfate concentration and the increased pH > 11.5 results in a superior ion transport rate between the diluate and the concentrate. The high pH of the electrolyte also presented the potential for amplification of the effects of calcium within the electrolyte solution. In three tests (M,N, and O) that were designed to identify the mechanism of calcium interference, the electrolyte chemistry was altered changed throughout the test. This will be described in the results section. In all tests except Test N, the

electrolyte volume was 10.5 liters. In Test N the electrolyte volume was 3.4 liters in an effort to accelerate the rise in calcium concentration within the electrolyte.

Membrane Selection

The Initial tests (D, F, G, H and I) were performed with a cathode barrier membrane (CMX) that was non-selective for divalent cations. The remaining tests (J, K, L, M, N, and O) were performed with a cathode barrier membrane (CMX-S) with increased selectivity against divalent cations. The CMX cation-exchange, the CMX-S monovalent-selective membranes, and the ACS anion-exchange membranes were all Neosepta® membranes manufactured by Astom Corporation, Japan and installed by the stack manufacturer, Eurodia under service contract.

Test Descriptions

Two types of tests were conducted, 1) volt-amp profiles and 2) continuous runs in batch mode. The volt-amp profiles were performed by quickly ramping the power source down, in one volt increments, from 15 to 2 volts. The amperage was recorded at each voltage and provided a snapshot of the ED process under the extant conditions over a short period of time. The VA profile was taken at the start and at the end of each continuous run, or during a run if of interest. Continuous batch run tests were performed at a constant 5 volts stack potential. When in continuous-mode, the instruments were polled once every minute by data collection software. All continuous run tests were performed in batch mode where the concentrate recycled to the concentrate tank and the dilute recycled to the diluate tank.

RESULTS

This phase of the research into the use of electrodialysis of highly concentrated brine is based on a series of eleven electrodialysis runs using either 3% or 6% sodium chloride as the baseline feed stock. Some of the test waters (seven tests) were amended with either 1,000 or 4,000 mg/l calcium. In the first five tests, the single barrier cation selective membrane (CMX) at the cathode was non-exclusionary to divalent cations. In the final six tests, the single cathode barrier membrane was changed to a membrane (CMX-S) with more selectivity against multivalent cations. Table 1 is a summary of the eleven tests described in this development effort. For brevity only a few of these tests will be presented in full as highlights to the overall discussion. The reader is referenced to the report of Severin and Hayes (2012) for a more detailed review of the data.

Table 1:Summary Results

Water Creep:

In full test runs lasting 6 to 8 hours, there was a tendency for the diluate volume to become depleted by between about 250 and 400 ml, and for the concentrate to pick up this additional volume. In general, about 25 g/l of sodium chloride was transferred from the 10.5 liters of diluate to the concentrate during these tests. It is commonly understood that the hydration shell of sodium consists of 5 waters. This would represent an expected volume change of about 1.2 liters if all ions were transferred in the fully hydrated state. However, it is estimated that many ions are transferred across the membrane are stripped of the hydration shell (Kotov et al, 2002) as many cations lose the hydration shell near to ion transfer materials (Horne, 1969). There is also tendency for the membranes to leak water due to a build-up of osmotic pressure as the diluate

and concentrate concentrations change over time. The results in the present paper, especially the data for the voltage-amp profiles and the temperature data which were collected with the diluate and concentrate at equal concentrations are unaffected by volume changes from water creep. The data for the full batch runs reflect salt concentrations based on calibrated conductivity meter readings. These concentration data do not reflect considerations of water creep.

Problem Definition

Test D (Figure 3) with an initial TDS of 31,000 mg/l NaCl represents the baseline with a standard CMX membrane at the cathode boundary. The initial current is 2.3 amps, which falls off to about 1.8 amps as the concentration difference between the concentrate and diluate streams increases throughout the test. This is a very typical experimental run with a high efficiency of salt transfer of around 0.24 kWh/kg, and a relatively short duration (6 hr) to achieve 85% transfer from the diluate to the concentrate. Also seen in Figure 3 are the results for Test J at 31,000 mg/l NaCl which is the counterpart experiment to Test D, but with the CMX-S membrane at the cathode boundary. There is very little difference between the two tests indicating that the single change in one membrane did not appreciably effect the performance of the ED stack when treating sodium.

Figure 3: Comparison of Test D Baseline ED run with non-selective CMX membrane at the cathode boundary versus Test J with CMX-S membrane at the cathode boundary, test water 3% NaCl.

At the high TDS levels in the feed stock, and with the relatively low applied voltage (5 volts), all tests in Table 1 had current efficiencies nearing 100%. Therefore, plots of amperage versus diluate concentration represent an effective means of visualizing the overall trends in these experiments. Figure 4 is a plot of the amperage averaged at ½ hour intervals versus diluate concentrations for tests with the CMX membrane at the cathode boundary.

Test F in Figure 4 is presented as an example of the disruptive influence of the addition of 4,000 mg/l calcium to the feed stock. In this example, the TDS of the feed was around 43,500 mg/l. Even though the transfer efficiency remained high, around 0.24 kWh/kg, the rate of transfer was severely affected, compared to the baseline case (Test D). The loss of ion transfer rate is observed immediately. This is evident with a decreased initial current of just over 1.9 amps. After 7.5 hours, the current had fallen to just over 1.1 amps and less than 50% of the TDS had been transferred from the diluate stream. A number of other tests are also presented in this figure to demonstrate the dramatic effect of calcium on ED performance. Test G was conducted with 3% sodium chloride plus 1,000 mg/l calcium such that the total dissolved solids was around 33,000 mg/l. The loss of ED ion transfer rate was less than that with 4,000 mg/l calcium (Test F) but still a substantial 20% loss compared to the reference Test D.

Figure 4 also includes results from two tests with 6% NaCl with the non-selective CMX membrane at the cathode barrier. Test I represents the base case without calcium addition. Test H was performed with 4000 mg/l added calcium. As seen in this figure, there is a marked decrease in current caused by the addition of 4,000 mg/l Ca^{++} . The amperage data at 55,000 mg/l diluate concentration indicate that 4,000 mg/l Ca^{++} caused a 50% decrease in ion flux.

Figure 4: Calcium degradation of ED ion transport efficiency with the non-exclusionary CMX membrane at the cathode boundary

Electrolyte Cell as the Problem Area

Calcium transport into the electrolyte was identified as the source of the problems with loss of ion transfer rate. One of the tests performed with the ED unit was a volt-amp profile which consisted of rapidly ramping the stack voltage from 15 V down to 2 V and measuring the amperage. This gave a snap-shot of performance at any desired condition.

Test H was performed with 6% NaCl with 4,000 mg/l calcium (see Figure 4) and showed severe degradation of the ion transport rate compared to the baseline (Test I). The following example (Figure 5) shows a series of volt-amp profiles taken before and after Test H. A profile taken at the initiation of the test shows that with the concentration of the diluate equal to the concentrate, the current at 15 V exceeded 12 amps. At the end of the 7.5 hr test the concentrate and diluate were remixed to reconstitute the concentration of the initial feed stock. The end condition profile showed that the 15 volt potential could only generate 7.5 amps.

The feed flow was shut down and the stack power supply to the electrodes was turned off. A clean-in-place method was instituted by acidifying the electrolyte to pH 2.9 using hydrochloric acid (35 ml 35 HCl into 10.5 liters electrolyte). After only 5 minutes of flow through the electrode cells, a volt-amp profile showed that the 15 volt potential could generate nearly 10 amps.

The acidified electrolyte was then allowed to flow through the electrode cells for 24 hours. The volt-amp profile showed that the performance of the ED stack was restored to the initial condition. These observations suggested that some sort of calcium precipitation was occurring and that this condition could be reversed by acidification of the electrolyte. It was further speculated that reducing the flux of calcium into the electrolyte could mitigate the problem.

Figure 5: Restoration of ED performance by acid cleaning of the electrolyte as exemplified by Test H (6% NaCl with 4000 mg/l calcium).

CMX-S Cathode Barrier Membrane

CMX-S selective membranes are known to control the transport of multivalent cations (e.g. Hayes and Moon (2009) and Firdaous et al. (2007)). It was therefore suspected that a more selective membrane at the cathode barrier could mitigate the process degradation caused by calcium. The cathode barrier membrane (CMX) was replaced with a membrane that was more selective against calcium (CMX-S). Referring again to Figure 3, Test J compares directly with to Test D (3% NaCl with no added calcium). There is very little difference in the two tests, indicating that there is very little impact of using the more exclusive membrane with sodium chloride.

Figure 6 shows the results of Test F with 3% NaCl plus 4,000 mg/l calcium using the CMX barrier membrane against the results of Test K using the more selective CMX-S membrane. The more exclusionary membrane allowed for a higher overall amperage and improved overall ion transport rate throughout the entire test. For example, at 7.5 hours operation, Test K had a diluate concentration of about 10,000 mg/l (76% salt transfer from the diluate), whereas, Test F had a diluate concentration of about 23,000 mg/ (46% salt transfer from the diluate). This

indicates that the more exclusionary boundary membrane imparted a 65% improvement in overall process efficiency compared to the non-exclusionary membrane under these experimental conditions.

Figure 6: Comparison of Test F with a CMX cathode boundary membrane versus Test K with the protective CMX-S cathode boundary under calcium challenged conditions.

The results of these and of other tests comparing the exclusionary membrane (Tests J and K) to the non-exclusionary membrane (Tests D, F, and G) are summarized by an analysis of the progression of the current during the treatment process (Figure 7). In these tests, the current was representative of the rate of ion transport from the diluate to the concentrate. The current in each test was averaged in ½ hour intervals and plotted versus the concentration in the diluate. As seen in this figure, there was a marked decrease in current caused by the addition of 1,000 mg/l Ca^{++} (Test G vs Test D) with the non-exclusionary membrane. The amperage data at 30,000 mg/l diluate concentration indicate that 1000 mg/l Ca^{++} causes a 15-20% decrease in ion flux. A calcium concentration of 4000 mg/l causes a decrease of about 45% ion flux (Test F versus Test D). Protecting the cathode with a more exclusionary membrane yields very similar ion transfer rates compared to the non-exclusionary membrane with pure sodium chloride (Test J versus Test D). With the more exclusionary CMX-S membrane, there is only a small influence (<10% decrease in ion transport capacity, flux, as measured by amperage) caused by the addition of 4,000 mg/l calcium to the feed stock (Test J versus Test K).

Figure 7: Summary of results for 3% sodium chloride tests comparing the non-exclusionary CMX membrane versus CMX-S membrane at the cathode boundary.

Figure 8 is a summary of the tests performed comparing the use of the non-exclusionary membrane (Test H and I) versus the more exclusive membrane (Test L) using 6% sodium chloride. Tests I and H were previously presented in Figure 4 and are included herein as direct comparison to Test L with the more exclusionary membrane. There is about a 10% loss in efficiency caused with the addition of 4000 mg/l calcium with the more exclusionary CMX-S membrane compared to the baseline test (Test L versus Test I). However, this compares favorably to the non-exclusionary membrane (Test H versus Test L) where the more exclusionary membrane imparts about a 60% improvement in ion flux in the presence of 4000 mg/l calcium.

Figure 8: Summary of results for 6% sodium chloride tests comparing the non-exclusionary CMX membrane versus CMX-S membrane at the cathode boundary.

Calcium Migration to the Electrolyte

In order to better understand the relation of calcium transport across the cathode cell boundary to loss of ion flux, grab samples were taken for the Tests F, H, K and L. Data for calcium in the initial and final feed, diluate, concentrate, and electrolyte are presented in Table 2.

It is expedient to define the relative flux of an ion, such as calcium, between the diluate and the concentrate, as compared to flux of the ion from the water to the electrolyte. The relative flux index (RFI) is defined as the change in electrolyte calcium concentration compared to the change in calcium concentration between the concentrate and the diluate.

$$RFI = \frac{\Delta C_{electrolyte}}{C_{concentrate} - C_{diluate}}$$

With the non-exclusionary membrane, the relative flux index of calcium between the process water and the electrolyte was about 0.023-0.24. With the more exclusionary membrane, the relative flux of calcium was reduced to 0.006 to 0.013, when comparing the 3% and 6% NaCl data. This indicates the more exclusionary membrane was effective in reducing the flux of calcium into the electrolyte by 47-73%.

Table 2: Exclusion of calcium from the electrolyte caused by cathode boundary membrane selection

Fate of Calcium within the Electrode Cell

If the more exclusionary CMX-S membrane rejects 47-73% of the calcium from the electrolyte, this means that 27-53% of the calcium still enters the electrolyte. Long term operation of an electrolyte bath, therefore, should still be impacted by incursion of multivalent cations. The following three tests (Tests M, N, and O) were performed to investigate the fate of calcium into and out of the electrolyte with the cathode protection CMX-S membrane in-place.

Test M (Table 3) was performed based on the premise that the electrolyte could become fouled and, therefore, present impedance to ion flux. In this test, the preferred electrolyte, 90 g/l Na₂SO₄ with 1 g/l NaOH at pH 12.5 was used. The salt solution was 3% NaCl with no calcium, and presented no challenge to the electrolyte. At ½ hour, the electrolyte was challenged with 400 mg/l Ca⁺⁺. A white precipitate immediately formed. While the composition precipitate was not investigated, it is likely to be either calcium hydroxide or calcium sulfate or both. The test continued for another hour when the pH of the electrolyte was then dropped to pH 3.2 with 3 g/L HCl. The test continued for an additional 4½ hour with no indication of flux inhibition (Figure 10). Therefore, the act of creating calcium precipitate within the electrolyte solution does not appear to represent an operational problem. Furthermore, when the calcium precipitate was dissolved with acid, the soluble calcium caused no inhibition. In fact, quite an opposite effect was noted. Calcium was observed to leave the electrolyte and become concentrated in the concentrate stream. It is fair to question the use of the high pH electrolyte in these tests. Test M is an example of the advantages of higher pH electrolyte. Initially at pH 12.5, the amperage exceeded even the initial amperage of the reference standard Test J at around pH 11.5. When the pH of the electrolyte was dropped to pH 3.2 at about 1.5 hours into the test, the amperage began to fall below that of the reference Test J.

Table 3: Test M, Effect of Precipitated and Soluble Calcium in Electrolyte: Test for Transport of Calcium from Electrolyte into Concentrate

Test N (Table 4) was performed to determine if the rate of transport of soluble calcium from the diluate to the electrolyte or if the transport from the electrolyte to the concentrate could present an ion flux inhibition. In this test, a reduced volume (3.4 L instead of 10.5 L) electrolyte was used in order better measure the rate of calcium change across the hydraulic boundaries. The salt solution treated was 3% NaCl with 4,000 mg/l Ca^{++} . The electrolyte rinse was 90 g/L Na_2SO_4 at pH 6.8 with an initial concentration of 100 mg/l Ca^{++} . As seen in Table 4, the electrolyte slowly collected calcium from an initial concentration of 110 mg/l to a concentration of 400 mg/l at 7.5 hours in the small volume of electrolyte. This is consistent with the approximate rate of calcium incursion seen in Test K (initially 45 mg/l increased to 97 mg/l in 10.5 L electrolyte).

The entire run Test N (Figure 9) was efficient, indicating that soluble calcium in the treated water and soluble calcium in the electrolyte did not cause an ion flux inhibition. It should be noted that this test utilized electrolyte at pH 6.8 and the amperage was initially about 2.1. In previous tests, the preferred electrolyte was prepared at a pH around 12, in which case, the initial amperage at 3% NaCl was about 2.3-2.4 amps. The lower overall amperage in Test N is attributed to the pH effect, as noted in the previous results with electrolyte improvements (Severin and Hayes, 2016 *in preparation*).

Table 4: Test N: Effect of Soluble Calcium in Electrolyte: Test for Transport of Soluble Calcium from Diluate to Electrolyte and from Electrolyte to Concentrate

Test O (Table 5) was performed to determine if bicarbonate or carbonate in the electrolyte, in the presence of calcium, could cause degradation of ion flux with a protected cathode. The electrolyte was initially at pH 6.8 and consisted of 90 g/L Na_2SO_4 with 100 mg/l Ca^{++} . The salt water to be treated was initially 3% NaCl with 4,000 mg/l Ca^{++} . At ½ hour into the run, 200 mg/l NaHCO_3 was added to electrolyte. No degradation of performance was noted. At 1 hour, 1 g/L NaOH was added to the electrolyte to precipitate the calcium. Although a white precipitate formed that could have been calcium carbonate, calcium sulfate, or calcium hydroxide, or a combination; there was no degradation of performance.

Table 5: Test O: Effect of Bicarbonate and Carbonate on the Electrolyte Solution

Tests M, N, and O, demonstrate that once the calcium exclusionary CMX-S membrane was placed to protect calcium incursion into the catholyte, there was very little that could be done to the electrolyte chemistry to further impede ion flux. This is illustrated in Figure 9. Test M can be compared to Test J; the difference being that Test M had calcium added to the electrolyte. Test N can be compared to Test K, the difference being, again, the addition of calcium to the electrolyte in Test N. Test O can be compared to Tests K and N, with the difference that the calcium added to the electrolyte was deliberately precipitated with bicarbonate and sodium hydroxide.

Figure 9: With the CMX-S membrane placed at the cathode barrier, alterations of the electrolyte composition in Tests M, N, and O, failed to diminish performance as compared to reference Tests J and K.

DISCUSSION:

Electrodialysis is conventionally limited to waters containing several thousand mg/l TDS and not more than several hundred mg/l calcium. Literature suggests that as little as 20 mg/l calcium influences the process. Flowback waters contain tens of thousands of mg/l TDS and thousands of mg/l calcium, magnesium and other multivalent cations. This paper focused on problems associated with relatively high concentrations of calcium in highly concentrated brines.

A generic non-exclusionary cation selective membrane (CMX) was installed at the boundary to the cathode cell. High rates of calcium incursion into the electrolyte were encountered causing calcium fouling of the electrode cell. Figure 4 shows the loss of current (ion flux) in 3% sodium chloride as 1,000 mg/l and 4,000 mg/l Ca^{++} was added to the test water. Similar results were obtained with 6% sodium chloride and 4,000 mg/l Ca^{++} . Calcium poisoning of the electrolyte can be reversed with acid wash (pH around 3) through the electrode cells. This indicates that the mechanism of calcium poisoning is likely caused by a precipitate. In these tests, the most likely precipitate is calcium sulfate.

The cathode boundary membrane was replaced with a membrane that selected against multivalent cations (CMX-S). This single change in the stack configuration caused immediate improvement in performance in the presence of calcium. Figure 8 shows the dramatic improvement in ion flux with tests with sodium chloride and calcium when the more selective cation membrane was installed.

The chemistry of the electrolyte and test waters was analyzed to determine the extent of the calcium exclusion to the electrolyte. A relative flux index (RFI) was defined as the ratio of the flux of calcium into the electrolyte and the flux of calcium from the diluate to the concentrate. A low RFI index indicates a higher rate of rejection at the cathode barrier membrane. Between 47 and 73% of the calcium incursion into the electrolyte was achieved with the CMX-S membrane.

In further tests with the multivalent exclusionary membrane, calcium was deliberately introduced into the electrolyte to achieve an electrolyte concentration of >100 mg/l calcium, both as free ions or as a precipitate. These additions of calcium, surprisingly, did not interfere with the ED performance. This suggests that the weak link in the electrolyte system is precipitation of calcium on the internal surface of an unprotected cathode membrane. The placement of a more selective membrane at the cathode boundary creates a very robust electrolyte system that is virtually undisturbed by calcium. Since soluble calcium does cross the exclusionary membrane, it is interesting that process degradation does not occur. This may indicate that the more exclusionary membrane additionally acts to discourage the precipitation of calcium on the internal cathode cell boundary.

No experiments were performed using an external filtration or external ion exchange system to continuously clean the electrolyte solution of precipitates or soluble multivalent cations, however, such a filtration system could be beneficial.

CONCLUSIONS:

The presence of calcium in feed water has traditionally been a problem for concentrated brines, such as seawater. The findings in this paper suggest a means of mitigating exposure to calcium. A generic non-exclusionary cation selective membrane was installed at the boundary to

the cathode cell. High rates of calcium incursion into the electrolyte were encountered causing calcium fouling of the electrode cell. Calcium poisoning of the electrolyte can be reversed with acid wash (pH around 3) through the electrode cells.

The cathode boundary membrane was replaced with a membrane that selected against multivalent cations. This single change in the stack configuration caused immediate improvement in performance in the presence of calcium. Between 47 and 73% rejection of the calcium incursion into the electrolyte was achieved with the more selective membrane.

Calcium was deliberately introduced into the electrolyte to achieve an electrolyte concentration of >100 mg/l calcium, both as free ions or as a precipitate. These additions of calcium, surprisingly, did not interfere with the ED with the more selective membrane installed. performance. Since soluble calcium does cross the exclusionary membrane, it is interesting that process degradation did not occur. This strongly suggests that the more exclusionary membrane additionally acts to discourage the precipitation of calcium on the internal cathode cell boundary.

These results are potentially of value as the basis for a means of mitigating calcium interference in the ED process by a combination of clean-in-place electrolyte treatment along with a selective cation exchange membrane at the cathode boundary.

REFERENCES

Bazinet, L. and Araya-Farias, M. (2005) Effect of Calcium and Carbonate Concentrations on Cationic Membrane Fouling During Electrodialysis. *Journal of Colloid and Interface Science* 281, pp 188-196.

Brooks King, G., and Hooper, J.F. (1941). The Solubility in Water of Barium, Calcium and Magnesium Salts of Sulfamic Acid., *J. Phy. Chem.* 45 (6) 938-942.

Elazhar, F., Tahaikt, M., Zouahri, A., Taky, M., Hafs, M., and Elmidaoui, A. (2013). Defluorination of Moroccan Groundwater by Nanofiltration and Electrodialysis: Performances and Cost Comparison, *World Applied Sciences Journal* 22 (6): 844-850

Hayes, T.D., and Moon, P. (2009) Electrodialysis Process Development for the Demineralization of Coal Bed Methane Produced Water, Chapter 10, 33pp. In Produced Water Management and Beneficial Use, DOE-NETL Final Report, DOE DE-FC26-05NT15549, Landkamer, L.L and Thyne, G., Project Managers.

Hayes, T. D., and Severin, B.F., (2012) Barnett and Appalachian Shale Water Management and Reuse Technologies <http://www.rpsea.org/projects/08122-05/> RPSEA Final Report No. 08122-05.FINAL.03. March 30, 2012, 145 pp.

Horne, R., (1969). *Marine Chemistry*; Wiley: New York. Chapter 12, Section 2 pp 361-369.

Firdaous, L., Molérait, J.P., Schlumpf, J.P., and Quéméneur, (2007) Transfer of Monovalent and Divalent Cations in Salt Solutions by Electrodialysis. *Separation Science & Technology*, 42, pp 931-948.

Kaakinen, J., (December 1984), High Recovery Desalting of Brackish Water by Electrodialysis, Field Tests at Yuma Desalting Test Facility & at La Verkin Springs, Report REC-ERC-84-24, Bureau of Reclamation Energy and Research Center, Denver Colorado.

Kotov, K.K., Peregonchaya, O.V., and Selemenev, V.F. (2002). Electrodialysis of Binary Electrolyte Mixtures with Membranes Modified by Organic Species. *Russian Journal of Electrochemistry*, Vol. 38, pp. 927.

Malik, A.U., Andijani, I.N., Siddiqi, N.A., Ahmed, S. and Al-Mobayaed, A.S. (1994), Studies on the Role of Sulfamic Acid as a Descalant in Desalination Plants. Saline Water Conservation Corporation presented at VI Middle East Corrosion Conference, January 23-26, Vol. 1, pp 65-78.

Severin, B.F., and Hayes, T.D. (2016 a in preparation), Electrodialysis for Highly Concentrated Brines: Electrolyte Considerations.

Severin, B.F., and Hayes, T.D. (2016 b in preparation), Electrodialysis for Highly Concentrated Brines: Effects of Multivalent Cations. *Separation and Purification Technology* Submitted October, 2015.

Severin, B.F., and Hayes, T.D., (2012) Evaluation of Electrodialysis for the Desalination of Shale Gas Flowback Water. <http://www.rpsea.org/projects/08122-05/> RPSEA Report No. 08122-05.12. March 16, 2012, 156 pp.

Taylor, E.G, Desch, R.P., AND Catotti, A.J. (1951). The Conductance of Sulfamic Acid and Some Sulfa mates in Water at 25° and Conductance Measurements of Some Long Chain Sulfamates in Water and in Water-Acetone Mixtures at 25° J. Am. Chem. Soc. Vol 73, pp 74-77.

Xu, T., and Huang, C. (2008), Electrodialysis-Based Technologies, a Critical Review, *AIChE J.*, 54, pp. 3147-3159.

Yajima, K., and Kume, M., (1999). Electrodialysis Recovery of Nickel, Copper, and Water from Rinse Water of Copper/Nickel Sulfamate Multilayer Plating. *J. Surface Finishing, Japan*, Vol 50 (12) pp. 1162-1166.

ACKNOWLEDGEMENTS

The authors express their appreciation for the contributions of Jennifer Yang, Development Engineer, GTI, for developing the data acquisition system.

Funding for this project was provided by RPSEA through the “Ultra-Deepwater and Unconventional Natural Gas and Other Petroleum Resources” program authorized by the U.S. Energy Policy Act of 2005 contract 08122-05 . RPSEA (www.rpsea.org) is a nonprofit corporation whose mission is to provide a stewardship role in ensuring the focused research, development and deployment of safe and environmentally responsible technology that can effectively deliver hydrocarbons from domestic resources to the citizens of the United States. RPSEA, operating as a consortium of premier U.S. energy research universities, industry, and independent research organizations, manages the program under a contract with the U.S. Department of Energy’s National Energy Technology Laboratory.

Figure 1: Simplified Diagram of the Batch Electrodialysis Pilot Unit

Figure 2: Relative flux (as amperage) versus applied voltage for disodium sulfate electrolyte rinse solutions, initial conditions 3% NaCl

Figure 3: Comparison of Test D Baseline ED run with non-selective CMX membrane at the cathode boundary versus Test J with CMX-S membrane at the cathode boundary, test water 3% NaCl.

Figure 4: Calcium degradation of ED ion transport efficiency with the non-exclusionary CMX membrane at the cathode boundary

Figure 5: Restoration of ED performance by acid cleaning of the electrolyte as exemplified by Test H (6% NaCl with 4000 mg/l calcium).

Figure 6: Comparison of Test F with a CMX cathode boundary membrane versus Test K with the protective CMX-S cathode boundary under calcium challenged conditions.

Figure 7: Summary of results for 3% sodium chloride tests comparing the non-exclusionary CMX membrane versus CMX-S membrane at the cathode boundary.

Figure 8: Summary of results for 6% sodium chloride tests comparing the non-exclusionary CMX membrane versus CMX-S membrane at the cathode boundary.

Figure 9: Failure to cause ion transfer rate loss by attempts to alter the electrolyte by conditions as imposed in Tests M, N, and O which were designed to poison the electrolyte compared to reference Tests J and K when the CMX-S membrane is placed at the cathode barrier.

Table 1: Summary Results												
Test	Start TDS mg/L Feed	Finish TDS mg/L Diluate	Finish TDS mg/L Concentrate	Hours	Amps Start	Amps Finish	Amps Avg.	kWh/kg	NaCl %	Ca ⁺⁺ mg/l added	Electrolyte Na ₂ SO ₄ g/l	Cathode Membrane
D	31,000	4,750	49,300	6.0	2.32	1.79	2.09	0.24	3		90	CMX
F	43,500	23,500	65,000	7.6	1.93	1.13	1.50	0.24	3	4,000	90	CMX
G	33,000	6,000	56,600	7.5	2.09	1.24	1.64	0.23	3	1,000	90	CMX
H	66,750	50,500	93,000	7.5	2.76	1.43	1.74	0.31	6	4,000	120	CMX
I	58,000	10,000	83,200	9.3	2.84	1.84	2.50	0.24	6		120	CMX
J	31,500	3,200	52,600	6.0	2.24	1.26	1.88	0.24	3		90	CMX-S
K	41,500	9,500	52,600	8.0	2.24	1.60	2.03	0.27	3	4,000	90	CMX-S
L	64,000	36,400	88,300	8.5	2.50	2.28	2.44	0.30	6	4,000	120	CMX-S
M	30,100	3,000	49,700	6.0	2.47	1.09	1.93	0.24	3		90	CMX-S
N	39,800	7,000	68,000	8.5	2.13	1.56	1.98	0.26	3	4,000	90	CMX-S
O	39,800	6,200	76,000	8.0	2.07	1.98	1.67	0.26	3	4,000	90	CMX-S

Table 2: Exclusion of calcium from the electrolyte caused by cathode boundary membrane selection									
	Cathode Boundary Membrane	NaCl	Calcium (mg/l)					Relative Flux Index	Calcium Exclusion*
			Feed	Final Diluate	Final Concentrate	Initial Electrolyte	Final Electrolyte		
Test F	CMX	3%	4,400	750	6,100	38	160	0.023	
Test H	CMX	6%	3,500	1,600	5,100	47	130	0.024	
Test K	CMX-S	3%	3,500	14	6,600	56	97	0.006	73%
Test L	CMX-S	6%	3,800	800	8,000	100	190	0.013	47%
*Calcium Exclusion (%) = 100 x (1-(RF _{CMX-S} /RF _{CMX}))									

Table 3: Test M, Effect of Precipitated and Soluble Calcium in Electrolyte: Test for Transport of Calcium from Electrolyte into Concentrate						
Time	Action				Response	
0-Hour	Initial Condition Electrolyte; vol. =10.5 L, 90 g/L Na ₂ SO ₄ With 1 g/L NaOH pH 12.5 Salt Solution; 3% NaCl only				Represents Baseline Conditions	
½ -Hour	Added 1 g/L CaCl ₂ (400 mg/l) into Electrolyte Tank				Immediate white ppt. in electrolyte	
1 ½ Hour	Added 0.3 g/L HCl to Electrolyte Tank				pH 3.2 in electrolyte, ppt cleared	
1 ½- 6 Hour	Continued Test at 5V				Efficient operation recorded	
Sample	Time Hour	Na	Ca	Cl	TDS	pH
Feed	0	11,000	29	18,000	29,000	10.0
D4 Diluate	1.5	8,900	23	14,000	22,000	10.2
D5	2.5	7,200	10	11,000	18,000	10.2
D6	3.5	6,200	4	8,600	13,000	10.2
D7	4.5	3,000	<2.5	5,500	8,100	10.2
D8	6	1,500	<2.5	2,900	3,900	10.1
C4 Concentrate	1.5	15,000	110	22,000	37,000	9.6
C5	2.5	15,000	110	24,000	42,000	9.3
C6	3.5	18,000	130	26,000	44,000	9.3
C7	4.5	16,000	110	30,000	48,000	9.2
C8	6	19,000	120	30,000	54,000	9.3
E1 Electrolyte	0	34,000	<2.5	27	98,000	12.4
E2	0.5	25,000	15	47	96,000	12.5
E3	1	25,000	490	1,700	86,000	11.8
E4	1.5	29,000	610	1,500	87,000	11.4
E5	2.5	26,000	350	1,800	85,000	2.7
E6	3.5	31,000	380	1,700	86,000	2.7
E7	4.5	29,000	390	1,700	88,000	2.8
E8	6	29,000	390	1,800	90,000	2.8

Table 4: Test N: Effect of Soluble Calcium in Electrolyte: Test for Transport of Soluble Calcium from Diluate to Electrolyte and from Electrolyte to Concentrate						
Time		Action			Response	
0-Hour		Initial Condition Electrolyte; vol. = 3.4 liter, 90 g/l Na ₂ SO ₄ ,pH 6.7 Plus 100 mg/l Ca ⁺⁺ Salt Solution; 3% NaCl plus 4000 mg/l Ca ⁺⁺			Represents Challenged Condition	
0-7 ½ Hour		Continued Test at 5 V			Appeared a normal run for neutral pH electrolyte	
(Note low electrolyte volume to increase rate of change in concentration)						
	Time Hour	Na	Ca	Cl	TDS	pH
Feed	0	12,000	3,600	25,000	68,000	3.8
D2 Diluate	3	8,400	1,700	17,000	42,000	6.6
D3	6	4,800	110	7,300	16,000	6.6
D4	7.5	3,300	12	5,300	8,500	6.7
C2 Concentrate	3	8,400	3,600	30,000	86,000	6.1
C3	6	14,000	6,100	38,000	100,000	6.3
C4	7.5	17,000	6,600	38,000	110,000	6.4
E1 Electrolyte	0	25,000	110	230	100,000	4.5
E2	3	24,000	180	250	100,000	3.7
E3	6	27,000	330	300	98,000	3.8
E4	7.5	22,000	400	340	98,000	3.8

Table 5: Test O: Effect of Bicarbonate and Carbonate on the Electrolyte Solution						
Time	Action				Response	
0-Hour	Initial Condition Electrolyte; vol. = 10.5 Liter 90 g/l Na ₂ SO ₄ With 0 g/l NaOH pH 6.7 Plus 100 mg/l Ca ⁺⁺ Salt Solution; 3% NaCl plus 4000 mg/L Ca ⁺⁺				Represents Challenged Condition	
½- Hour	Added 220 mg/l NaHCO ₃ to electrolyte tank				No change	
1-Hour	Added 1 g/L NaOH to electrolyte tank				pH to 12.5, no change in performance	
1-7 ½ Hour	Continued at 5 V				Good performance	
	Time Hour	Na	Ca	Cl	TDS	pH
Feed	0	9,800	3,300	25,000	65,000	6.6
D4 Diluate		3,200	27	4,800	9,500	27.0
C4 Concentrate		16,000	5,900	41,000	110,000	6.7
E1 Electrolyte		26,000	110	200	99,000	7.5
E2		25,000	150	270	99,000	7.2
E3		26,000	190	290	100,000	12.2
E4		27,000	150	310	100,000	12.2