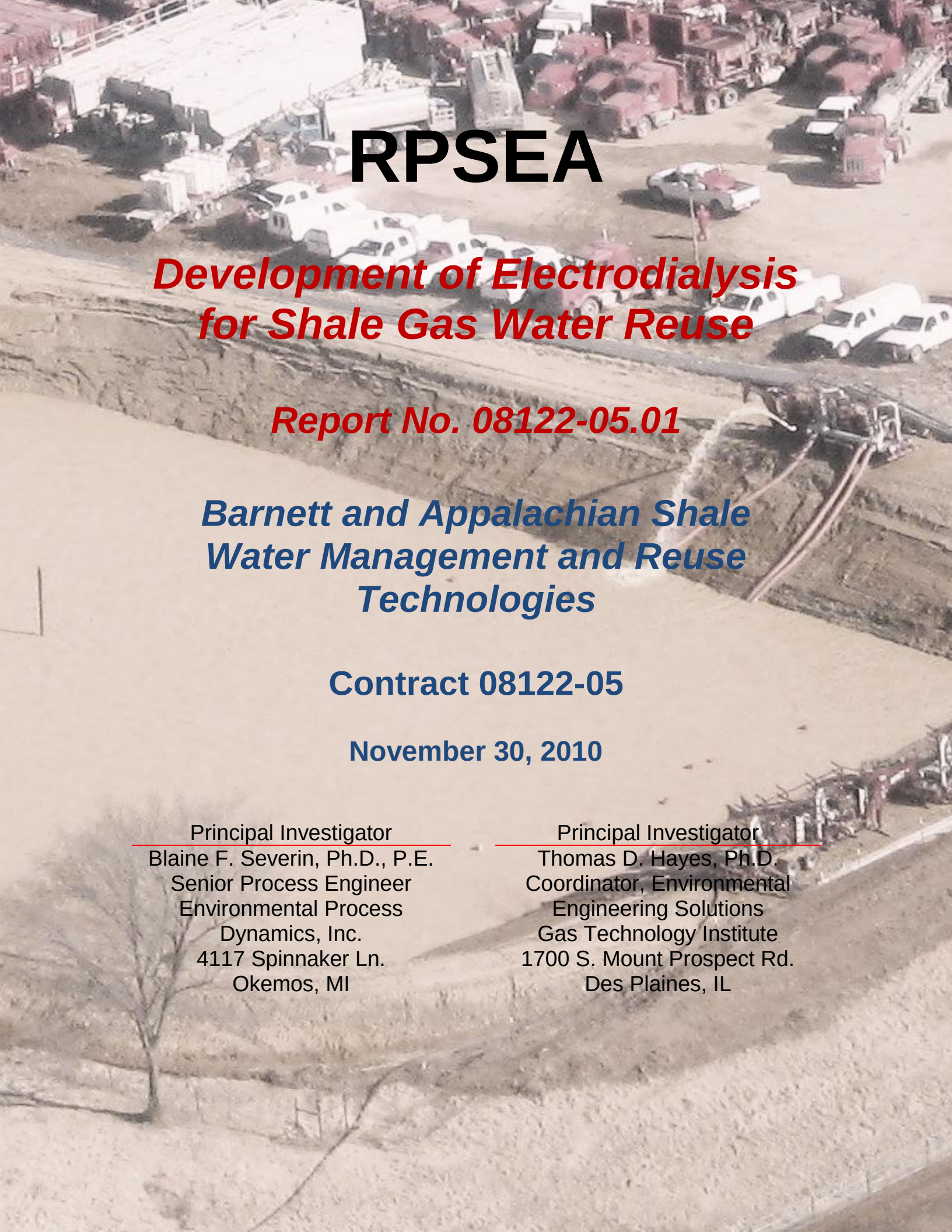

RPSEA

Development of Electrodialysis for Shale Gas Water Reuse

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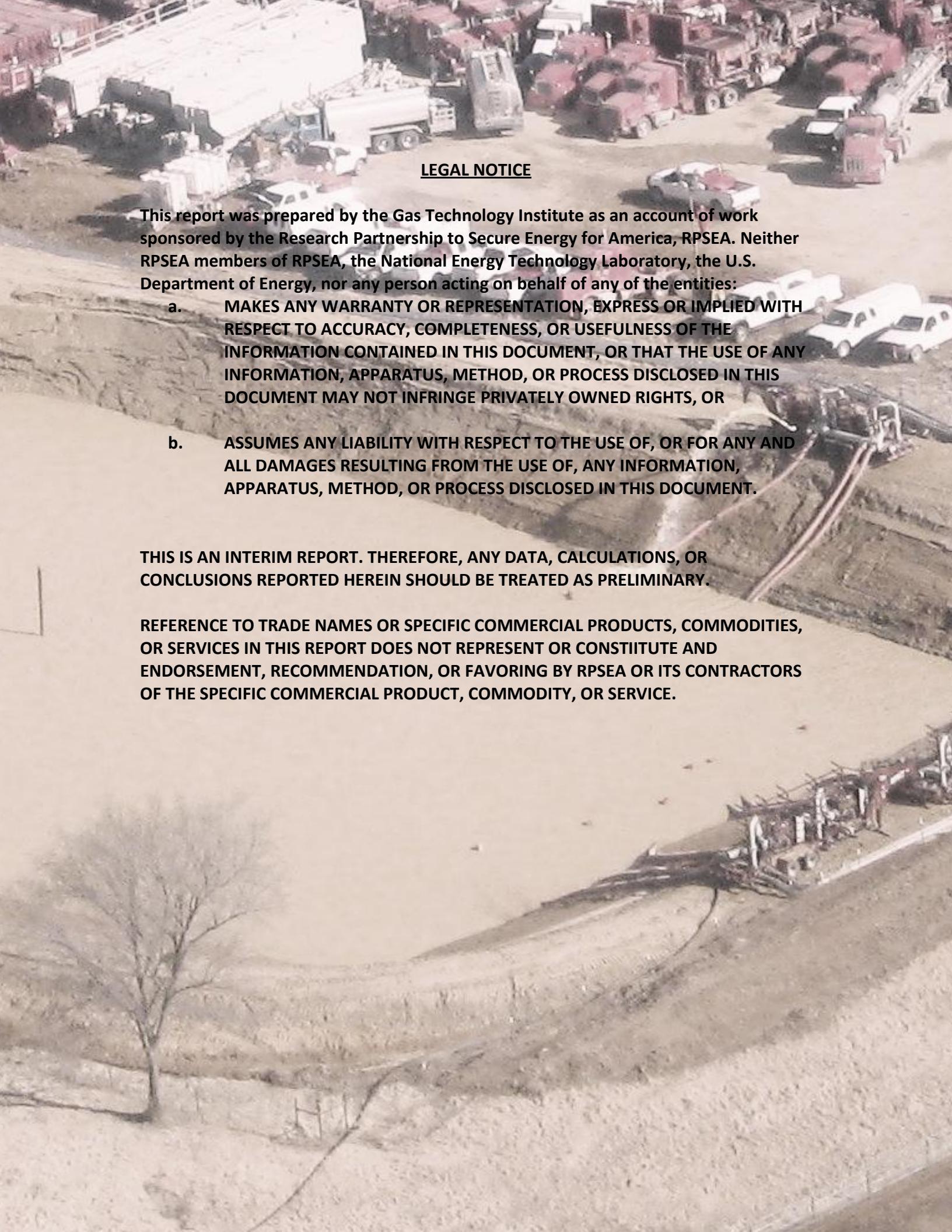

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1. Abstract

This report covers Task 8 of the project, “BARNETT AND APPALACHIAN SHALE WATER MANAGEMENT AND REUSE TECHNOLOGIES.” The purpose of this effort is to evaluate electrodialysis for the desalinization of flowback water. A ten cell pair, semi-batch electrodialysis Eurodia pilot plant was used to investigate a number of suspected challenges under laboratory conditions. The energy efficiency goal of 0.1 to 0.15 kWh per pound of salt removed was consistently achieved in waters containing between 30,000 and 72,000 mg/l TDS (as NaCl plus $CaCl_2$) by limiting the applied stack potential to 5 volts. Ion flux was improved by 24% by increasing the electrolyte concentration to an ionic strength similar to, or greater than, the ionic strength of the process water. Another increment of ion flux improvement of 19% was achieved by adjusting the pH of the electrolyte to reduce the electrochemical overvoltage at the electrodes. Soluble calcium of 1,000 to 4,000 mg/l in the process water caused process inhibition. This challenge was successfully overcome by replacing the single boundary membrane between the final diluate cell and the cathode with a divalent cation exclusionary membrane. One effect of the protection of the cathode by the exclusionary membrane was a rejection of >80% of the flux of calcium into the electrolyte. This produced an overall improvement in ion flux of 29–39% compared to operation without the cathode protection. A second effect of the cathode protection seems to be the inability of calcium within the electrolyte to foul the posterior side (within the electrode cell) of the cathodic membrane. These and other modifications to the electrodialysis process have led to reducing energy demands of the process from 0.20 kWh/lb salt removed observed with conventional ED processing to less than 0.12 kWh/lb salt removed observed in most of the improved process runs, an energy savings of about 40%.

2. Executive Summary

This project is a portion of a larger investigation into the nature (quantity and quality) of the flowback water and the utility of various process alternatives to 1) maximize the reuse of recovered water, 2) minimize the volume of brines requiring deep well disposal, and 3) reduce the cost and environmental impact of disposal of flowback water. The overall objective of this work is to evaluate the feasibility of using electrodialysis (ED) for the recovery of flowback and produced water for reuse in shale gas well completions. The results obtained with the ED laboratory prototype used in this study are directly scalable to the full scale application of the process.

Electrodialysis is an electrically driven membrane separation technology that has been successfully used in the past for the desalination of brackish water containing several thousand mg/l (roughly parts per million, ppm) of total dissolved solids (TDS) to produce a water stream containing several hundred mg/l of TDS for purposes of providing community water or industry water supplies. Application of ED to the conditioning of brines for possible reuse in the shale gas industry, however, involves challenges, risks and opportunities that are quite different from the world of brackish surface water renovation.

The most obvious challenge in the desalination of shale gas waters is represented by the very high levels of salts that are present. Flowback water and produced water contain extremely high concentrations of salts; most flowback water loads hauled from shale gas well completions range from 20,000 to 80,000 mg/l of TDS. Flowback water and produced water can also contain thousands of mg/l of multivalent cations such as calcium, magnesium, barium, strontium, iron and manganese. These metals are known to foul the electrodialysis process at relatively low concentrations (< 100 mg/l total).

There are two challenges to the operation of electrodialysis for the desalinization of flowback water. One is the economic performance at extremely high salt conditions. The second is the high concentrations of calcium and other multivalent cations expected in the flowback water. The first year of this project was used to investigate these challenges under laboratory conditions.

The investigation of electrodialysis, to date, shows that the process can be modified to successfully remove high-salt concentrations extant in flowback waters from fractured shale. Testing assumed that the most practical strategy of applying ED to shale gas waters was to partially demineralize the brine from the influent condition of 20,000–60,000 mg/l TDS down to an effluent (product) stream containing 5,000–10,000 mg/l. Operating the ED process under this condition would maintain excellent conductivity throughout all of the electrolytic cells and minimize resistance to current flow.

Maintaining the ED system under these elevated salt conditions allows process to operate in a regime of relatively low voltage and high amperage compared to conventional operations operating at lower-salt concentrations. This has led to an understanding of the relation between ion flux and applied voltage that allowed for a number of process improvements. Another challenge to the desalinization of the shale flowback water is the potential for process inhibition by soluble calcium and other divalent cations. This challenge was addressed by a simple, low-cost process modification aimed at mitigating the effects of divalent cations on the electrolyte cell.

Specific improvements have been developed to improve energy efficiency and salt separation performance; other improvements were identified that are aimed at creating a system robust enough to operate on shale flowback water. These process enhancements include the following:

1. Improvements to the electrolyte solution by increasing the concentration to an ionic strength similar to, or greater than, the process water to be treated proffered an overall process improvement of 23% over normal electrolyte conditions.
2. Improvement to the electrolyte solution pH was shown to decrease the overvoltage (voltage required for electrochemical initiation) by 0.4 volts. This improvement resulted in an additional 19% process improvement in addition to the already improved electrolyte.
3. Soluble calcium causes process inhibition. A majority of this was observed to be associated with the incursion of calcium into the electrolyte. The point of entry is most likely the boundary between the final diluate cell and the cathode cell. Acidification of the electrolyte was capable of reversing the majority of the inhibition.
4. Replacement of the single membrane at the boundary of the final diluate cell and the cathode cell with a calcium (divalent cation) exclusionary membrane reduced the flux of soluble calcium into the electrolyte by greater than 80%. This translated into improved ion flux (29–39%) greater than observed with the non-exclusionary membrane.
5. The calcium exclusionary membrane at the cathode appears to serve a dual purpose. Conclusion 4 alludes to rejection of calcium into the electrolyte. The challenged the protected cathode system with soluble, externally precipitated, and internally precipitated calcium. It appears that the calcium exclusionary membrane also rejects calcium on the posterior side (inside the cathode cell) such that even calcium that crosses the membrane cannot adhere to the membrane.
6. Development efforts continue to determine the fate of other divalent cations such as magnesium and barium.

3. Introduction

The hydraulic fracture of shale formations for the capture of natural gas is a relatively new technology. Recent work on North American shale formations has demonstrated the potential to capture trillions of cubic feet of high value gas. Other shale formations on other continents have the potential for development, potentially revolutionizing energy economies on a worldwide basis.

In most shale gas plays, completion of wells using large amounts of water introduced down-hole under pressure is a necessary step in the initiation of the release of natural gas from shale rock. During the hydraulic fracture process, between 1–4 million gallons of water and sand is pumped "down hole" into each drilled well to achieve the fractures required for well completion. A fraction of this water is collected during the initial extraction of the gas. The recovered fluid, called flowback water, can contain high concentrations of dissolved salt, plus friction reducing polymers, corrosion inhibitors, scale inhibitors and biocides. These additives facilitate the hydraulic fracturing process and prevent problems with well operation. Therefore, recovered flowback water presents a disposal problem, as well as a major cost in the completion and operation of each shale gas well. The nature of the chemistry and dynamics of recovered flowback water is of vital interest for effective environmental stewardship of a gas field.

In the early management of flowback and produced waters from shale gas plays, transportation to deepwell injection (Class II) facilities was the most frequently used alternative used for water management. In the Barnett, Class II well injection is often an economically attractive option since the Ellenberger formation underlies most of this play and is capable of taking large flows of produced and flowback water. During years of drought, the industry has experienced increased pressure from governmental organizations and stakeholders to explore and develop options that can lead to substantial reductions in the industry's demand for withdrawals from water sources that compete with community water supply systems. This has led a few companies to evaluate technologies that could enable the implementation of the recovery of demineralized water for reuse in future frac jobs on a large scale, if needed.

This project is a portion of a larger effort to define the flowback water chemistry, flow dynamics of recovery, and engineering solutions to lower the cost of water handling and minimize environmental impact. The intent is to develop methods to 1) maximize the reuse of recovered water, 2) minimize the volume of deep well disposal, and 3) reduce the cost and environmental impact of disposal of flowback water.

Flowback water is usually collected in an on-site reservoir for temporary storage. A portion of the water may be reused on-site for re-injection in subsequent fractures. Alternatively, some water may be recycled at neighboring sites. Presently, however, most of the recovered water volume is trucked off-site for deep well injection at some considerable distance from the gas well. Each one million gallons of recovered fracture fluid represents upwards of 250 tanker truck loads and potentially tens of thousands of truck-miles. A set of rational alternatives is needed to reduce traffic and carbon foot print and improve environmental compatibility.

Hayes (2009) compiled flow and concentration data from 19 fracture sites in the Marcellus shale formation (West Virginia and Pennsylvania). Data were collected on Day 1, Day 5, Day 14, and Day 90 after the fracture event. A portion of these data are reproduced in Table 1. Three important conclusions may be immediately drawn from these data.

1. The ultimate recovery of water is less than 25% of the initial charge on a weighted basis of flow from all wells.
2. The flow rate from the wells decreases rapidly with time, such that most of the flowback water (80%) is collected within the first 14 days after fracture. Less than 20% recovery occurs between days 15 and 90.
3. The concentration of salt increases as a function of time after fracture. Four data sets show salt concentrations at 14 and 90 days. The 90-day concentrations are 50% greater than the 14-day concentrations.

The current method of handling the flowback event is to collect the water *en masse*, then make a decision for disposal or reuse. The data in Table 1 suggest that a "triage" evaluation of the water as it emerges from the well may be effectively implemented. Conceptually, low concentration waters (<10,000 mg/l TDS) may be immediately recycled and require minimal treatment (e.g., settling or rough filtration) prior to reuse. Mid-range concentrations (10,000–50,000 mg/l TDS) may be effectively segregated and treated to form two fractions: 1) A demineralized stream suitable for reuse for hydraulic fracturing conducted at future wells, and, 2) A smaller concentrated brine stream for further processing and/or disposal. Highly concentrated brine (>50,000 mg/l) collected later in the well operation can be treated with evaporative processes to make heavy brine (nearly crystalline salt) and water.

The triage concept is developed as a decision tree in Figure 1. Information about the chemistry and quantity of flow forms the basis for a triage decision.

1. Very concentrated water is directed to storage for immediate disposal.

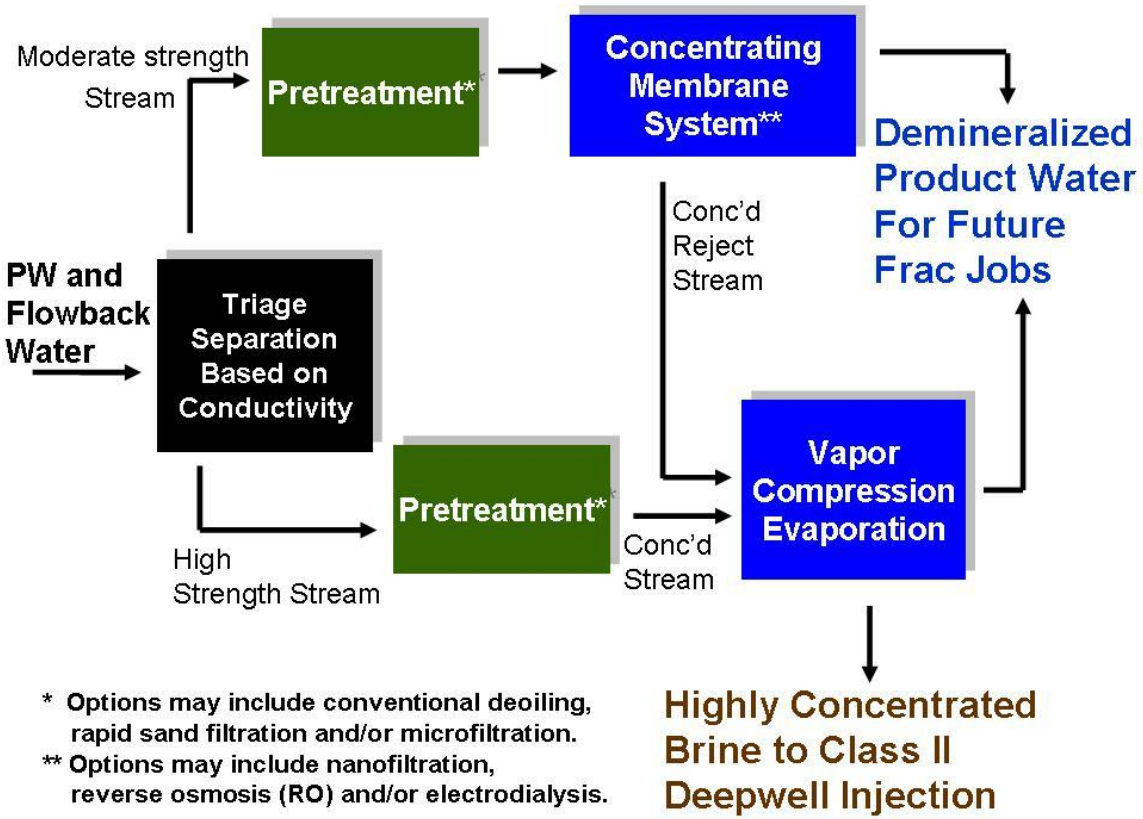
2. Very dilute water is directed to storage for reuse at the next fracture.
3. Intermediate strength water is sent to pretreatment, then desalination.

Desalination may include intermediate concentrating of the brine with a membrane based process such as electrodialysis or reverse osmosis (yellow box, Figure 1). The decision to proceed with the intermediate concentration step is based on the availability of fresh make-up water for dilution, and the economics of operating the membrane system compared to the economics of operating a thermal concentrator such as MVR (mechanical vapor recompression). The decision to include electrodialysis in the triage program requires a through engineering analysis of the capacity, limitations and compatibility of each component in the triage train.

The purpose of the effort described in this report is to evaluate the potential of electrodialysis for demineralizing shale gas waters that can contain 10,000 to 60,000 mg/l of total dissolved solids and more than 4,000 mg/l of calcium.

Table 1: Recovered Flow-back Water Inventory (After Hayes, 2009)											
Site	Total Used Barrels	Barrels Recovered by Day( ) After Fracture				Percent Recovered	Input Fluid mg/l	Well Discharge Concentration (mg/l) Days ( ) After Fracture			
		Day(1)	Day (5)	Day (14)	Day (90)			Day (1)	Day (5)	Day (14)	Day (90)
A	40,046	3,950	10,456	15,023		38	990	15,400	54,800	105,000	216,000
B	94,216	1,095	10,782	13,718	17,890	19	27,800	22,400	87,800	112,000	194,000
C	146,226	3,308	9,652	15,991		11	719	24,700	61,900	110,000	267,000
D	21,144	2,854	8,077	9,938	11,185	53	1,410	9,020	40,700		155,000
E	53,500	8,560	20,330	24,610	25,680	48	5,910	2,890	55,100	124,000	
F	77,995	3,272	10,830	12,331	17,413	22	462	61,200	116,000	157,000	
G	123,921	1,219	7,493	12,471	31,735	26	1,920	74,600	125,000	169,000	
H	36,035	3,988	16,369	21,282		59	7,080	19,200	150,000	206,000	345,000
I							265	122,000	238,000	261,000	
J							4,840	5,090	48,700	19,100	
K	70,774	5,751	8,016	9,473		13	804	18,600	39,400	3,010	
L							221	20,400	72,700	109,000	
M	99,195	16,419	17,935	19,723		20	371			228,000	
N	11,435	2,432	2,759	3,043	3,535	31	735	31,800	116,000		
O							2,670	17,400	125,000	186,000	
P							401	11,600	78,600	63,900	
Q	23,593	1,315	3,577	5,090		22	311	16,600	38,500	120,000	
R							481	15,100	46,900	20,900	
S	16,460	2,094	7,832	9,345	10,723	65	280	680	58,300	124,000	

Figure 1: Treatment System Triage for Flowback Waters



4. Background

4.1 General Description of Electrodialysis

Electrodialysis or ED is an electrically-driven membrane separation process that is capable of separating, concentrating, and purifying selected ions from aqueous solutions (as well as some organic solvents). In this process, as depicted in Figure 2, ions are transferred through ion-selective membranes by means of a dc voltage.

Essentially, electrodialysis is a membrane separation technology containing four distinct components;

1. Pairs of cation and ion selective membrane collectively called the stack.
2. A pair of hydraulic paths to collect demineralized water (the diluate stream) and the concentrated water (the concentrate stream).
3. A pair of electrode cells; one containing an anode and the second containing the cathode.
4. An electrolyte reservoir and hydraulic paths to provide anolyte and catholyte.

A generic depiction of the electrodialysis process is presented in Figure 2. As shown here, the cathode is to the right and the anode to the left. Therefore, the cations move toward the right while anions move toward the left.

Proceeding left to right, the anode is bounded by a cation selective membrane. This membrane provides hydraulic separation of the anolyte from the concentrate stream. An integral part of the process is the free transport of cations from the anolyte into the concentrate. In a typical application, the electrolyte is sodium rich and the preferred cation to cross the anode barrier is sodium. Just as importantly, anions from the concentrate stream cannot diffuse back into the anolyte due to rejection at the cation selective boundary.

The neighboring membrane to the anode boundary is an anion selective membrane. The anion selective membrane and the cation selective membrane at the anode boundary collectively form the first component of the concentrate hydraulic pathway. This pair of membranes naturally causes ion concentration. Cations in the concentrate cannot cross the anion selective membrane to the right. Likewise, anions cross from right to left, compelled by anode potential. But since anions from the concentrate cannot pass into anolyte, the water in this hydraulic path naturally becomes concentrated.

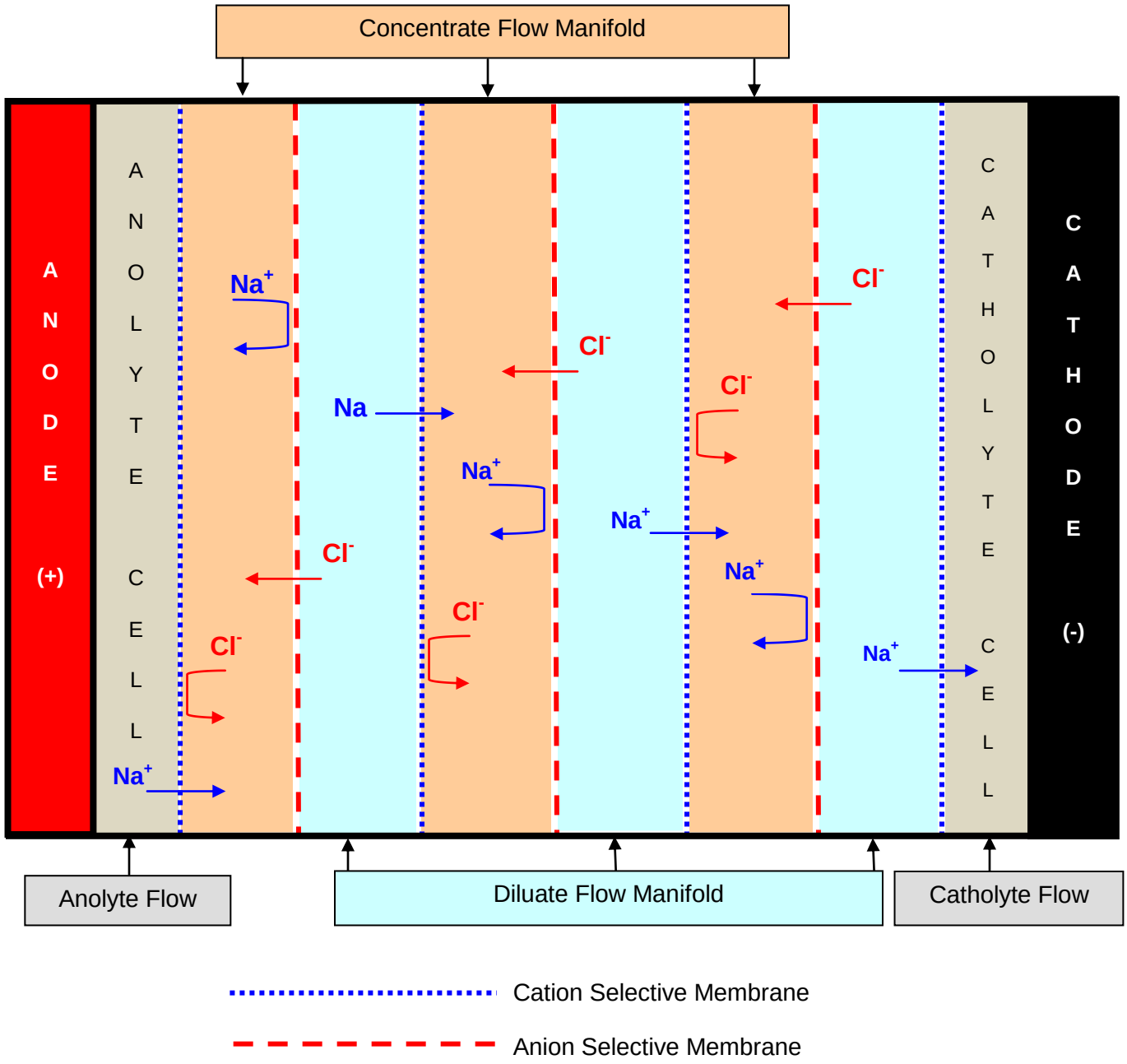


Figure 2: Ion Flow in an Electrodialysis Stack

A cation selective membrane to the right of the first anion selective membrane constitutes the first component of the diluate hydraulic pathway. Water in this space naturally loses anions to the left through the anion selective membrane and loses cations to the right through the cation selective membrane.

The pattern of alternating cation and anion selective membrane creates a pattern of alternating concentrate and diluate streams. The concentrate streams are manifolded together and the diluate streams are manifolded together to form two separate hydraulic pathways.

The final membrane on the right-hand side is also a cation selective membrane and forms the boundary of the cathode cell. This membrane and the anion selective membrane to the left, form the final diluate path. Cations from the diluate stream are compelled to pass into the catholyte, whereas, anions freely pass from the diluate through the anion selective membrane to the left in the diagram of Figure 2.

The passage of ions from the diluate into the concentrate is driven by the electrochemical reactions at the electrodes. The following pair of chemical reactions is often presented as examples of likely reaction at the anode (A1 or A2) and at the cathode (C1).

$$A1)\ H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^- \qquad \mathrm{E_o} = -1.229\,V$$

$$A.2)\ 2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^- \qquad \mathrm{E_o} = -0.401\,V$$

$$C1)\ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad \mathrm{E_o} = -0.8277\,V$$

By oxidizing water to oxygen, the anode provides electrons to the cathode (through the power source). By reducing water to hydrogen, the cathode dumps the electrons and the circuit is complete.

Electronic neutrality must also be maintained throughout the process. It has already been discussed that a cation must leave the anolyte (into the concentrate) and a cation must enter the catholyte from the diluate. If Equation A2 is considered as the predominant anodic reaction, the loss of cations from the anolyte is promoted by the destruction of hydroxide anions. If hydroxide anions are generated at the cathode, then this is balanced by the transport of a cation into the catholyte.

A final observation from this discussion is that the anolyte will become acidic and sodium poor. Likewise, the catholyte will become basic and sodium rich. It is imperative, both for pH control and sodium balance, that the anolyte and catholyte are

remixed into a single electrolyte solution. This is usually done after the catholyte and anolyte are allowed a modest time for degassing (hydrogen and oxygen, respectively).

4.2 Electrodialysis Concepts for Concentrated Brines

ED can be considered as a completed electric circuit. An applied potential (voltage) causes current (amperage vis. Ion flux) across a series of resistors. These resistances are discussed in more detail in the Methods section on the computer model. Under normal operation of ED for application to community water supplies, influent water containing several thousand mg/l TDS and the water is treated to levels below 500 mg/l TDS. The process usually utilizes a high voltage generates a low amperage. The processing objective with the low salinity waters is to remove as much salt as possible in the least amount of time. Low capital cost is traded for higher-energy costs.

On the other hand, the treatment of highly-saline produced waters (with concentrations above 30,000 mg/l) to generate an effluent containing thousands of mg/l of total dissolved solids establishes a processing regime that is quite different than the above conventional system. In this special application of ED, the concentrations of ions and their imparted conductivity are very high throughout the system. Resistance to current flow is very low, even in the cells containing the diluate. Under conditions established by this application, there is a benefit to running a high amperage, with as low a voltage as possible. Given the low volume of the flowback water, there is an economic advantage to trade lower energy costs for slightly higher capital costs.

Under these two operating regimes (high volts, low amps; vs. low volts, high amps) the various electrical resistances extant in the process have different relative influences. A specific case is the concept of “limiting current.” This concept originates from the estimation of the concentration gradients that form as ions are transferred across the membranes. If D is the diffusion coefficient (L^2T^{-1}), δ (L) is the diffusion boundary established between the bulk solution and the membrane, and A (L^2) is the area of a single membrane, then the flow (moles/time) of an ion, such as sodium (Na^+), passing a selective membrane is a function of the concentration gradient (mole L^{-3}) established between the bulk solution and at the surface of the membrane. Using the definition of amp (I) = coulomb/sec and Faraday (F) = 96,500 coulomb/mole, then the amperage needed to cause the ion flow is:

$$I = F\frac{\Delta[Na^+]}{\Delta T} = F\frac{DA}{\delta}\left([Na^+]_{bulk} - [Na^+]_{membrane}\right)$$

The limiting current, I_{lim} occurs as the concentration of the ion at the membrane surface approaches zero.

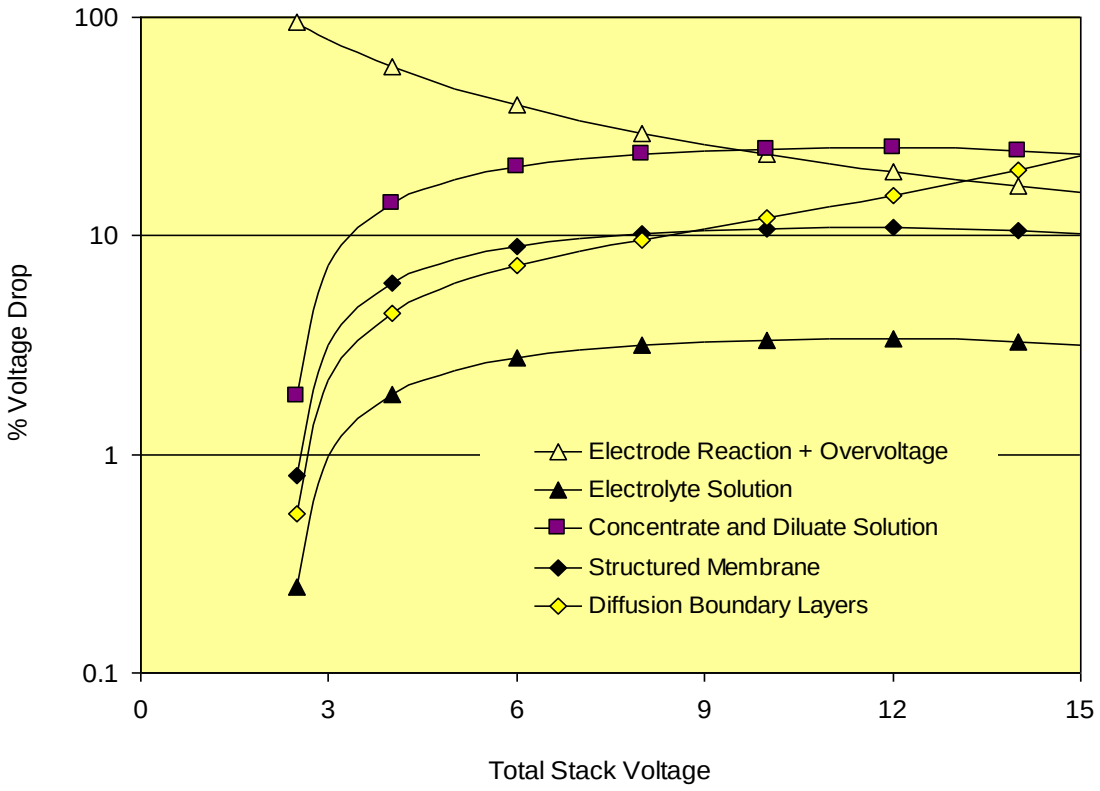
$$I_{\lim} \cong F \frac{DA}{\delta} [Na^+]_{bulk}$$ If too high a voltage is applied, an ion imbalance forms that causes the water near the membrane to polarize or "split" into its conjugate acid proton and caustic hydroxide ions. This allows hydrogen ion (instead of sodium ion) to cross the cation selective membranes; and hydroxide ion (instead of chloride ion) to cross the anion selective membranes. This is inefficient from an energy standpoint and can also be detrimental to the life of the membranes.

If the diffusion coefficient, D, for sodium chloride is taken as about 1.5 x 10^{-5} $cm^2 sec^{-1}$ (CRC, 1973) and δ is on the order of 0.01 cm (Leibovitz, 1977.), then for the pilot system tested in this project the limiting current is approximately;

- 0.5 amps for 1,000 mg/l NaCl;
- 5 amps for 10,000 mg/l NaCl;
- 15 amps for 30,000 mg/l NaCl; and
- 30 amps for 60,000 mg/l NaCl.

Figure 3 is a computer simulation of the ten-cell laboratory prototype of the relative resistances incurred when treating an initial starting condition where the concentrate and diluate concentrations are both 5,000 mg/l NaCl. Under these conditions, there is no resistance due to osmotic pressure between the concentrate and the diluate. The

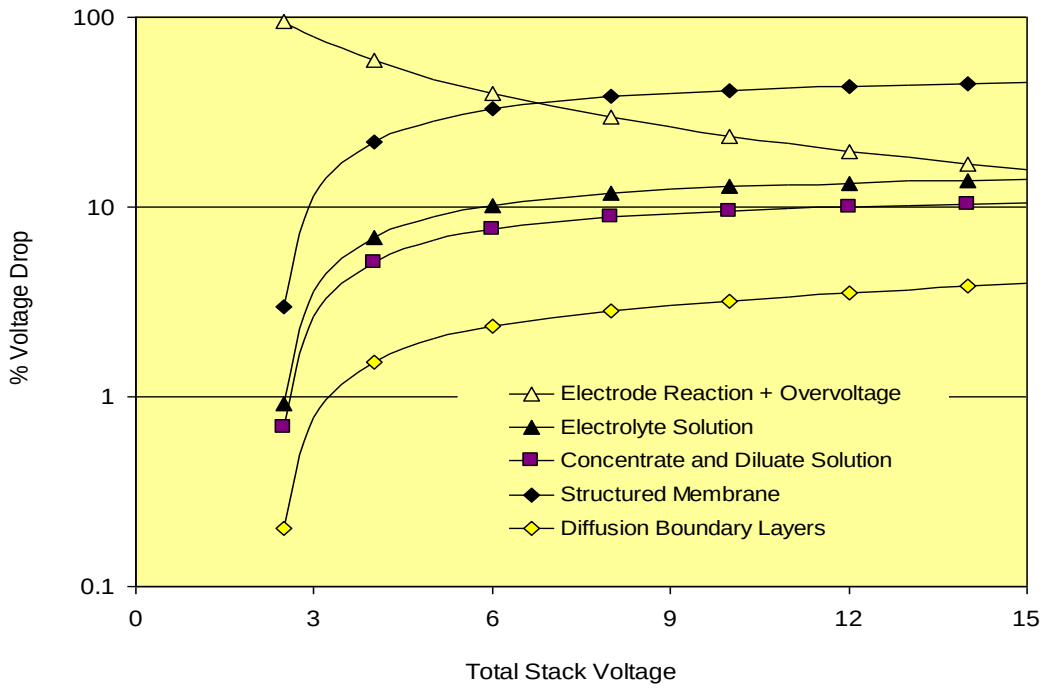
Figure 3 Model Simulation of the Relative Potential Drop At Start (Concentrate = Diluate) with 5,0000 mg/l NaCl



resistance due to the concentrate stream and the diluate stream are equal. It is likely that at the conditions described, the unit would be driven at 10–15 volts in an effort to increase ion flux. At these conditions; the major resistances for the ten-cell prototype are: concentrate solution = diluate solution > overvoltage/electrode > diffusion boundary > membrane > electrolyte solution. Naturally, the relative resistances would be slightly different for an ED unit with more than 10 cell pairs.

Figure 4 is a computer simulation of the relative stack resistances for the ten-cell pair ED unit in this study under high initial salt concentrations (50,000 mg/l NaCl). At the start of the process, the diluate and the concentrate concentrations are equal. Under these conditions, there is no resistance due to osmotic pressure between the concentrate and the diluate. The resistance due to the concentrate stream and the diluate stream are equal. It is likely that at these conditions, the unit would be driven at 5 volts in an effort to minimize the power. Under these conditions; the major resistances are: overvoltage/electrode > membrane > electrolyte > concentrate solution = diluate solution > diffusion boundaries. It is telling the resistance from the electrolyte represents 10–11% of the overall resistance at high-salt concentrations (Figure 4), but only 3% of the overall resistance at low-salt concentrations (Figure 3).

Figure 4: Model Simulation of the Relative Potential Drop at Start (Concentrate = Diluate) with 50,000 mg/l NaCl



4.3 Calcium and Other Multivalent Cations

Very little published literature is available on treating highly-concentrated brine solutions with electrodialysis. However, the presence of several thousands of mg/l of calcium and other divalent cations was expected to present a potential problem in terms of scale formation within the ED process.

A report by Kaakinen (1984) demonstrated extended process runs of 4000 hours on two highly concentrated waters of up to about 3,300 mg/l and 9,150 mg/l TDS on a two-stage ED system. Salt removals up to 92% from the diluate were achieved. The concentrate streams were enriched to 19,000 to 97,000 mg/l. In order to operate at these high-brine levels, brass pump components were replaced with plastic. The electrodes were encased in protective plastic. On top of these challenges, corrosion of the equipment caused amperage leakage that affected the process efficiency.

An economic profile was developed by Kaakinen (1984) for two types of water. Yuma water had a TDS range of 3200–3400 mg/l, with calcium at 7–18 mg/l and magnesium at 15–30 mg/l. The sodium concentration was 960–1,020 mg/l. The conductivity was 5,400–5,797 us/cm. Chloride was 1,114–1,200 mg/l and sulfate was 960–1,020 mg/l. Product water was treated to 430–494 mg/l TDS. Brine was concentrated to 19,000–51,680 mg/l. The current efficiency was 57–73% operating at 154 V and 21–24 amps in stage 1 and 123 V and 7.4–9.6 amps in stage 2. Energy consumption was calculated from the author's data. Based on 85% removal, the consumption was 0.42–0.48 kWh/lb TDS removed. LVS water had a TDS range 9,140–9,180 mg/l, calcium at 35–60 mg/l and magnesium at 52–55 mg/l. The sodium concentration was 3,110–3,170 mg/l. The conductivity was 1,360–1,370 µS/cm. Chloride was 3,660 mg/l and sulfate was 2,040 mg/l. Product water was treated to 1,150–1,280 mg/l TDS. Brine was concentrated to 41,600–96,500 mg/l. The current efficiency was 70–84% operating at 104–109 V and 26.2–31.9 amps in stage 1 and 98–104 V and 15.5–18.1 amps in stage 2. Energy consumption was calculated from the author's data. Based on 85% removal, the consumption was 0.24–0.27 kWh/lb TDS removed.

In summary, the Kaakinen (1984) report describes problems associated with treating brines at 3,300–9,150 mg/l TDS with calcium at 35–60 mg/l and 52–55 mg/l with the ED process. In the 1990s, the Gas Research Institute supported the evaluation of ED for the demineralization of conventional produced waters in laboratory and in pilot prototypes. Field experiments for the effort were conducted in the Wind River Play near Lysite, Wyoming; results from this effort indicated that electrodialysis has the potential of robust performance in the field while exhibiting efficient salt removals from chloride-based brines containing more than 10,000 mg/l total dissolved solids at reasonable

energy inputs of less than 0.25 kWh/lb salts removed (Lawrence, et al., 1998). The same ED process was also evaluated in the treatment of synthetic waters simulating the composition of coalbed methane produced water which is dominated by sodium bicarbonate as the salt. Results of this evaluation indicated that demineralization of a 3,000 mg/l TDS brine down to less than 500 mg/l TDS could be achieved at energy inputs below 0.20 kWh/lb salts removed (Hayes and Moon, 2009). In both of these efforts, soluble calcium was reasonably low at levels less than 20 mg/l; these brines were very low in calcium hardness compared to most shale gas waters that range from 3,000 to above 10,000 mg/l of soluble calcium (Hayes, 2009). The goal of the present research is to develop ED for treatment of water at 30,000 to 60,000 mg/l TDS with calcium exceeding 4,000 mg/l.

5. Approach

Two major challenges were identified for the effective operation of electrodialysis for the desalinization of flowback water.

1. The first challenge was to define the range of operation to be economically compatible at extremely high salt conditions.
2. The second challenge was to mitigate problems associated the high concentrations of calcium and other multivalent cations expected in the flowback water.

A computer model of the electrodialysis process was developed specific to the structure of this pilot plant. The computer results identified a suitable operation range to achieve the goal of reducing energy demand to less than 0.15 kWh/lb salt removed. xperiments were designed to demonstrate that this economic goal could be routinely met under laboratory conditions.

Computer simulations also identified areas for process improvement. More specifically, in treating the highly-concentrated salt, the conductivity of the electrolyte and the electrode overvoltage were identified as major resistances. A development effort was initiated to find means of reducing these resistances.

Problems were expected to arise from the presence of calcium and other multivalent cations in the process water. Indeed, loss of process capacity was observed with 1,000–4,000 mg/l calcium in feed water. In view of this challenge, a development effort was tailored to mitigate the effect of calcium and other divalent, scale-forming cations. Ongoing tests are being developed to determine if magnesium and barium follow the same trends as calcium.

6. Methods

6.1 Electrodialysis Pilot Plant

This project was performed with a Eurodia Industrie, S.A (Rungis, France) Ameridia Eur2B-10 electrodialysis laboratory prototype (Figure 5). The main component was the Eur2B-10 Electrodialysis Dialysis Stack that consists of twenty-one alternating cationic and anionic selective membranes, beginning and ending with cationic selective membranes. All anionic selective membranes were Tokyama AXM. In the first portion of this project, all cationic selective membranes were Tokyama CXM. In the final portion of this project, the single cation selective membrane at the cathode boundary was replaced with a cation selective, multivalent exclusionary membrane (Tokyama CXM-S). Individual membranes had an area of 200 cm^2.

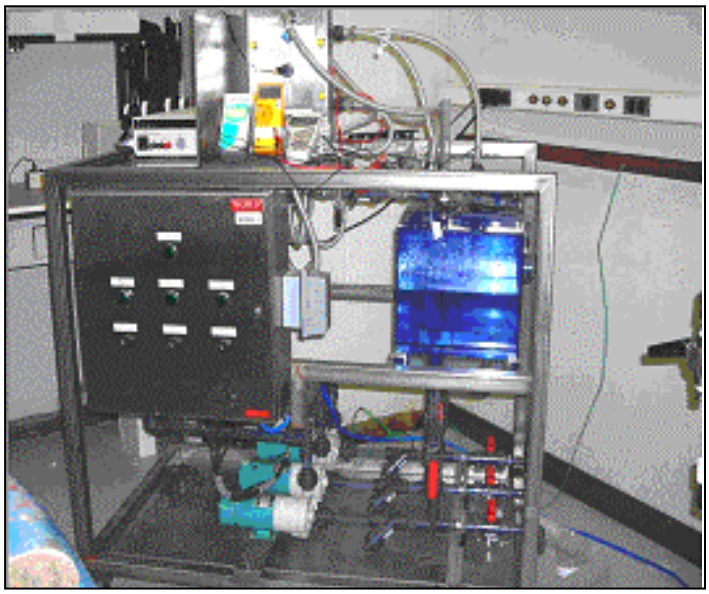


Figure 5: ED Pilot Skid

The unit was a semi-batch operation, meaning that the diluate and concentrate streams were collected in individual tanks. Diluate and concentrate were then cycled at about 1-1.5 liters per minute through the ED stack. Therefore, the dynamics of the system showed elements being of both plug flow (through the stack) and completely mixed (in the tanks.

The electrolyte passed through the anode cell at a flow rate of about 2–2.5 liters per minute and was collected in the anolyte tank. Likewise the electrolyte that passed through the cathode cell (at the same flow rate) 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. The flow of electrolyte to the electrodes was provided by a single electrolyte pump. The pump captured electrolyte from both the anolyte and catholyte tanks in roughly the same proportions.

The anode and cathode electrodes were connected to a power supply that supplied 0–40 volts DC at a maximum of 25 amps. The recommended maximum potential for this

Eur2B-10 was 1.5 volts per cell pair, or 15 volts. Most tests were performed at 5 V across the entire stack.

6.2 Data Collection

Two types of tests were conducted, 1) volt-amp (VA) profile or 2) continuous run. The VA profile was performed by ramping the power source down, in one volt increments, from 15 to 3 volts; then 2.5 volts and 2 volts. The amperage was recorded at each voltage and provided a quick review of the ED process under the extant conditions. The VA profile was taken at the start and end of each continuous run, or during a run as curiosity required. VA profile data were hand recorded.

Continuous run tests were performed by filling the diluate and concentrate tank each with about 10.5 liters of the desired feed water. The electrolyte tank was filled with 10.5 liters in all cases, except Test N, where the volume was 3.5 liters.

When in continuous-mode, the instruments were polled once every minute by data collection software. The master software was LabVIEW® (National Instruments) written for this pilot system by a GTI environmental engineer.

Oakton Instruments Con 110 meters were used to continuously measure conductivity and temperature in the diluate tank, the concentrate tank, and in the anolyte tank (occasionally). 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 5,000 mg/l NaCl were prepared. Calibrations were generated each week with freshly made salt solutions. The conductivity probes were sensitive to temperature (the higher the temperature, the lower the reading for a given salt solution). An Arrhenius relation was developed to correct for minor changes in temperature.

Three Oakton Instruments pH 110 meters were occasionally used to measure the pH of the diluate, the concentrate, and the electrolyte. The pH probes (when used) were calibrated to pH7.

The power source was equipped with a computer interface. The volts and amperage were polled every minute by the LabVIEW® software.

Chemical analyses were occasionally required. These samples were sent to an outside contractor (STAT Analysis Corporation, Chicago, IL). The samples were tested by ion chromatography for sodium, barium, chloride, sulfate and calcium and total dissolved solids.

6.3 Data Analysis

Conductivity data were transposed into concentration (mg/l as NaCl) using the calibration curves. The concentration data were then corrected for temperature influences using an Arrhenius interpolation.

In each test, about 500 ml of diluate was transferred to the concentrate tank. Mass transfer data reflect mathematical corrections for 1) osmotic drift of water across the membranes and 2) a change in the specific volume of the diluate and the concentrate with the change in salt concentration. In general, the osmotic drift accounted for about 90% of the volume shift, whereas, the change in specific volume accounted for 10% of the volume shift based on the mathematical corrections.

The energy used during each test was calculated by summing the product of the volts and amps recorded at each time interval and converted to kWh.

The effectiveness of energy utilization is presented as the energy utilized to transport one pound of salt removed from the diluate (kWh/lb salt removed). This was calculated as the overall average.

6.4 Preliminary Computer Model of the Eurodia Pilot Plant

A simplified series resistance model was developed gain an understanding of the Eurodia pilot plant prior to the initiation of the experimental work. The model included:

1. Boundary diffusion resistance at all membrane surfaces;
2. Resistance to current transmittal in the diluate solution;
3. Resistance to current transmittal in the concentrate solution;
4. Resistance to current transmittal in the electrolyte solution;
5. Osmotic pressure between dilute and concentrate streams;
6. Potential drop across each membrane; and
7. Reaction initiation (overvoltage + electrode potential).

Each of these resistances was assigned a rational mathematical value based on assumptions of boundary diffusion (Fick's Law), electrochemical potential (Nernst's Equation), or Ohms Law.

The model logic was initiated by assuming a voltage across a single diffusion boundary layer on a dilute side of a cationic selective membrane. From this voltage, it was possible to estimate the boundary layer concentrations of hydroxide ion and sodium ion. The boundary layer concentrations yielded an estimation of the amperage attributed to

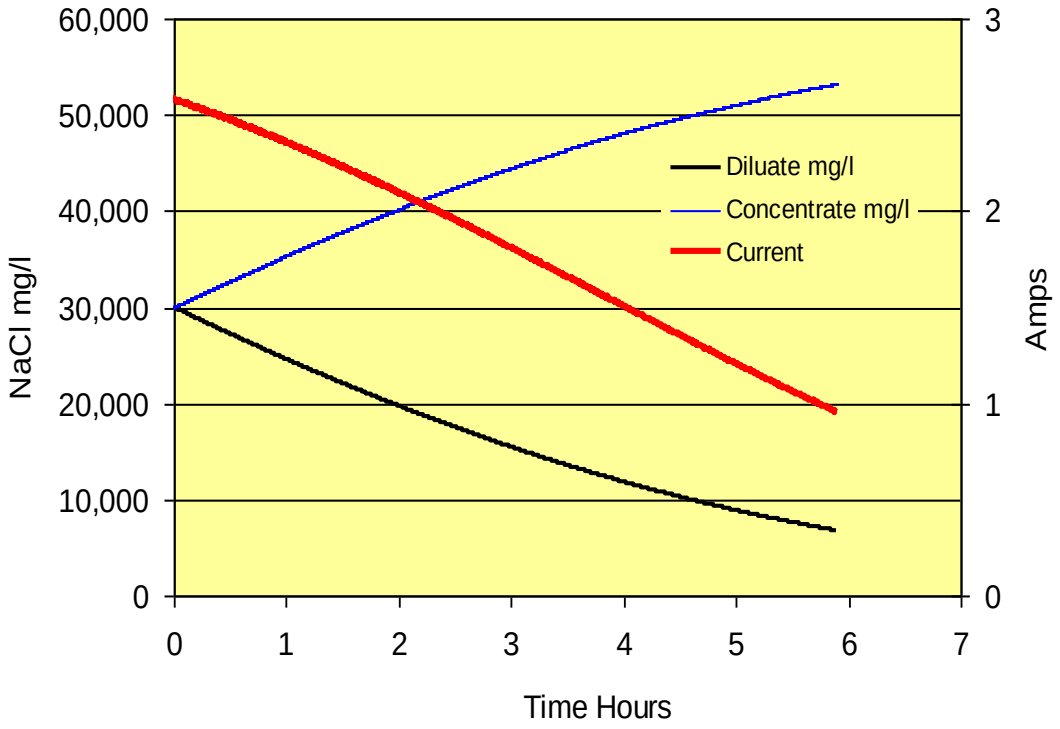
sodium transport and water splitting. The total amperage was then used to estimate the overall stack voltage. The initial single boundary voltage is adjusted until the total stack voltage equals the desired set point.

The calculated amperage was then used to estimate the ion flux across all membranes. The nominal time period was one second, which yielded an estimate of the salt removed during the time increment. This salt mass transferred was mathematically added to the concentrate volume and removed from the dilate volume.

The diluate and concentrate concentrations were then used to recalculate the amperage across the single boundary condition. This yielded a voltage calculation across the boundary from which a total stack voltage was recalculated. If the stack voltage was sufficiently deviant from the set point, an incrementally small change in the boundary voltage was made.

Figure 6 represents a calibrated computer simulation of a test run at 3% NaCl. Similar model runs were made prior to any lab data collection and represented a significant benefit to isolating various effects, either artifacts of the model, or artifacts of the operation of the ED stack.

Figure 6: Model Simulation 3% of NaCl at 5 Volt



7. Results

Figure 7 represents a typical full electrodialysis run. Test B was performed with 3% NaCl using 30 g/l sodium sulfate as the electrolyte. The stack potential was 5 volts.

The operating current efficiency at the 3% salt conditions approached 100%. As such, the amperage is an excellent surrogate for the ion flux. This allowed for easy comparison between test runs: the amperage as a function of the diluate concentration. Most of the remainder of the results will be presented in that format.

In this project period, a total of 15 full ED runs were performed. The results are summarized in Table 2.

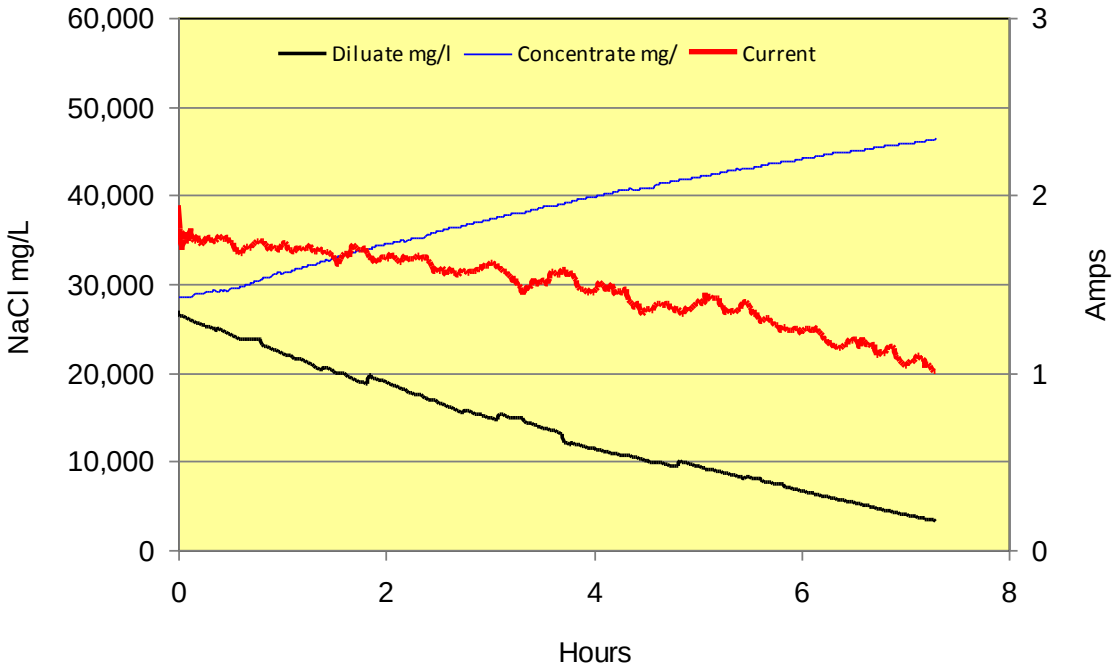


Figure 7: Test B; 3% NaCl with 30/gl Na2SO4 Electrolyte 5V

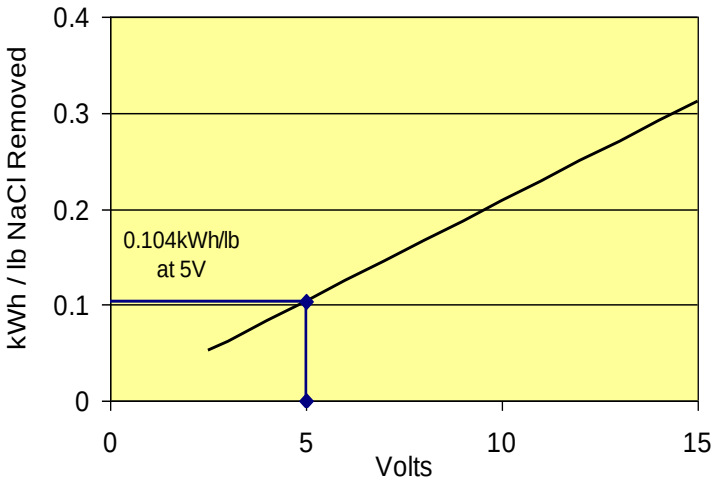
Table 2: Summary of 15 Electrodialysis Runs														
Test	TDS mg/l			Time	Amps			kWh/	NaCl	Ca^{++}	Electrolyte g/l			Cathode
	Start	End Diluate	End Concentrate	Hour	Start	End	Avg.	lb	%	mg/l	Na_2SO_4	NaOH	Na_2HPO_4	Membrane
A	31,000	3,000	64,400	6.8	2.30	1.00	1.66	0.099	3	0	90	1		CMX
B	28,500	3,100	46,200	7.3	1.75	1.05	1.46	0.107	3	0	30			CMX
C	31,500	2,000	48,800	6.6	2.12	1.29	1.73	0.100	3	0	90			CMX
D	31,000	4,750	49,300	6.0	2.32	1.79	2.09	0.108	3	0	90	1		CMX
E	29,600	4,750	50,000	7.5	2.33	1.10	1.62	0.104	3	0	60	2.2	30	CMX
F	43,500	23,500	65,000	7.6	1.93	1.13	1.50	0.111	3	4,000	90	1		CMX
G	33,000	6,000	56,600	7.5	2.09	1.24	1.64	0.106	3	1,000	90	1		CMX
H	67,500	50,500	93,000	7.5	2.76	1.43	1.74	0.132	6	4,000	120	1		CMX
I	58,000	10,000	83,200	9.3	2.84	1.83	2.50	0.134	6	0	120	1		CMX
J	31,500	3,200	52,600	6.0	2.24	1.26	1.88	0.114	3	0	90	1		CMX-S
K	41,500	9,500	52,600	8.0	2.24	1.60	2.03	0.120	3	4,000	90	1		CMX-S
L	64,000	36,400	88,300	8.5	2.5	2.28	2.44	0.149	6	4,000	120	1		CMX-S
M	30,100	3,000	49,700	6	2.47	1.09	1.93	0.109	3	0	90			CMX-S
N	39,800	7,000	68,000	8.5	2.13	1.56	1.98	0.127	3	4,000	90			CMX-S
O	39,800	6,200	76,000	8.0	2.07	1.98	1.67	0.124	3	4,000	90			CMX-S

7.1 Establishment of the Operating Range

The energy used to transfer a given mass of salt is an important economic consideration when dealing with high-brine concentrations. For the present discussion, we establish that a desirable energy utilization rate is from 0.1 to 0.15 kWh/lb NaCl transferred. To put this into perspective, a barrel (42 gallons) of 50,000 mg/l salt brine desalinated to 10,000 mg/l results in the transfer of 14 pounds of salt. At a rate of 0.15 kWh/lb salt and $0.10/kWh, this yields a cost of $0.21/barrel treated.

Figure 8 shows the predicted energy utilization from computer simulations with 3% NaCl. The energy efficiency for 3% NaCl was predicted to be greater than 99%, as typically occurs when operating well below the limiting current. The model predicted that a target voltage of 5.0 in this pilot plant would produce an energy utilization of 0.104 kWh/lb NaCl removed.

Figure 8: Predicted Energy Utilization with 3% NaCl



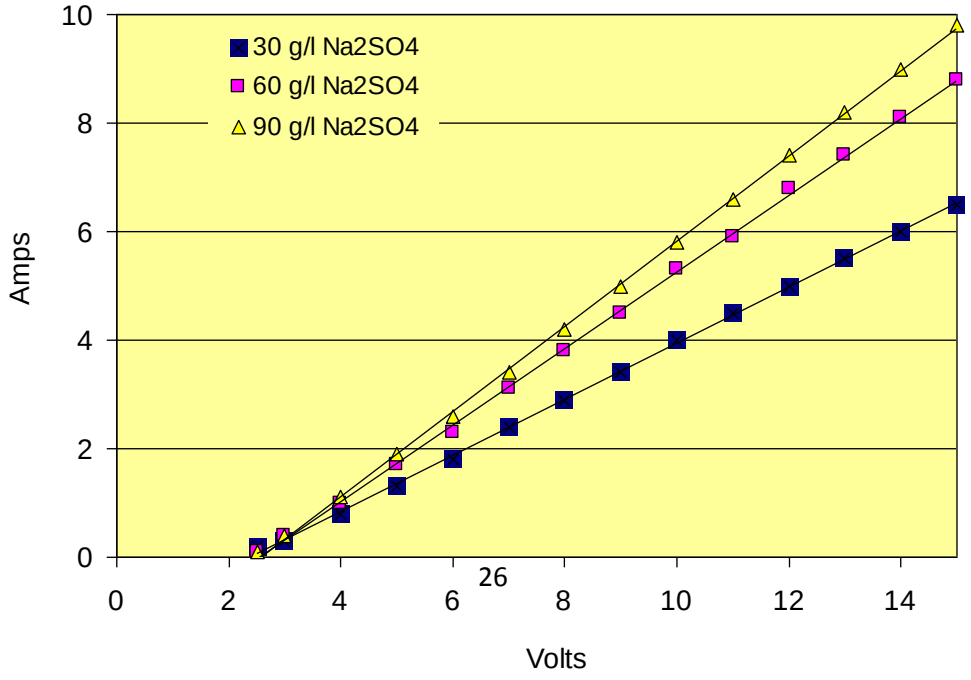
Six runs (A, B, C, D, G and J) were performed starting at 3% NaCl. Three additional tests were performed with 3% NaCl plus additional TDS (E, F and K) as $CaCl_2$, achieving more than 90% NaCl transfer from the diluate to the concentrate. The average energy utilization in these nine tests was 1.07 ± 0.07 kWhr/lb. This is in agreement with the predicted value of 0.104 kWhr/lb, and is given as evidence that the current efficiency in this pilot system approaches 100% when treating 3% salt.

7.2 Effect of Electrolyte Concentration

The pilot plant manufacturer recommended that an electrolyte solution of about 30 g/l Na_2SO_4 should suffice for treatment for a 3% salt solution. The computer analysis of the relative resistances to ion flux (Figures 3 and 4) suggested that improvements to the rate of ion transfer could be achieved by decreasing the electrolyte resistance. A series of tests was designed to improve the process rate through optimization of the electrolyte concentration.

Figure 9 shows a Volt-Amp profile with different strengths of electrolyte. The pH of the electrolytes was about 7.3 units. The concentration of salt in the feed tank and in the concentrate tank were roughly equivalent (3% NaCl) and represented the starting conditions for an ED run. The voltage of the power supply was systematically reduced from the maximum recommended 15 V. The current was measured at each voltage increment until no current was detected. The conventional solution for electrolyte is about 30 g/l Na_2SO_4, as recommended by the producer of the ED prototype equipment. Increasing the electrolyte concentration to 60 g/l and again to 90 g/l had the effect of increasing the system amperage.

Figure 9: Effect of Electrolyte Concentration on Initial Current (3% NaCl)



A pair of runs was performed with 3% NaCl that demonstrate the benefits of improved electrolyte chemistry. Test B was performed with the standard electrolyte consisting of 30 g/l Na_2SO_4. The initial current was 1.75 amps. The final currrent was 1.05 amps, and the average current was 1.46 amps. The feed was initially 28,500 mg/l and treated to 3,100 mg/l in 7.3 hours. Test C was performed treatment with 90 g/l Na_2SO_4 electrolyte. The initial current was 2.12 amps. The final currrent was 1.29 amps, and the average current was 1.73 amps. The feed was initially 31,500 mg/l and treated to 2,000 mg/l in 6.6 hours. These two tests are discussed again in the next section.

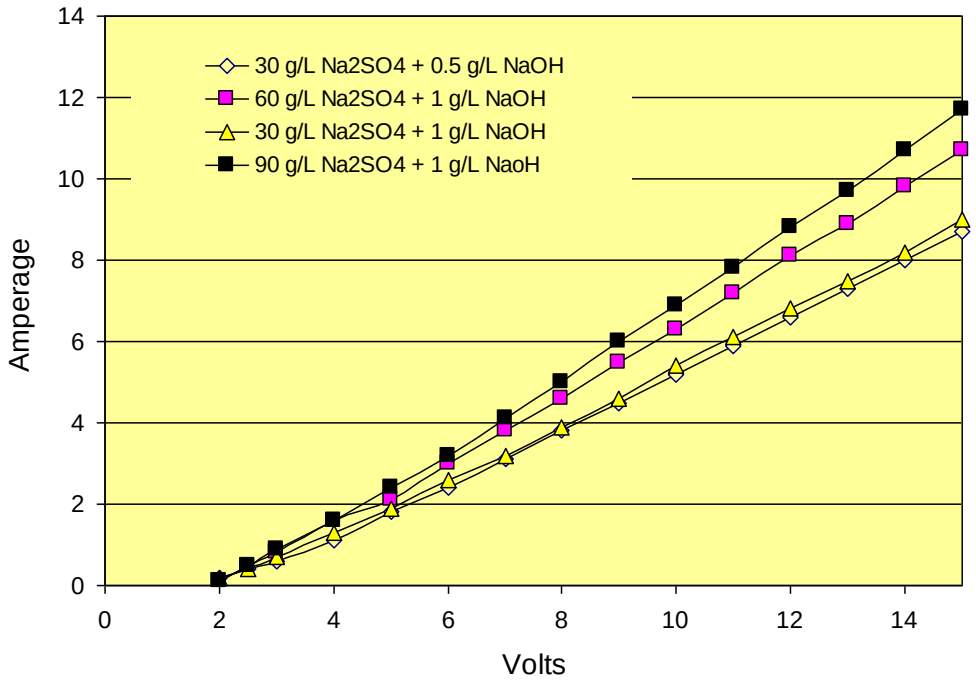
7.3 Optimization of the pH of the Electrolyte

A significant observation from Figure 9 is the position of the intercept on the voltage axis. No current is measured at a voltage of less than about 2.4 V. This represents the minimum voltage to initiate the reactions at the electrode and is presented as the electrode potentials plus "overvoltage." Therefore, the minimum voltage for a neutral pH electrolyte, such as sodium sulfate, is about 2.4 V in this pilot system.

Another series of experiments focused on the pH of the electrolyte solution. The specific tests performed were with 1) 30 g/l Na_2SO_4 with 0.5 g/l NaOH, 2) 30 g/l Na_2SO_4 + 1 g/l NaOH, 3) 60 g/l Na_2SO_4 + 1 g/l NaOH and 4) 90 g/l Na_2SO_4 + 1 g/l NaOH. The feed and concentrate tanks contained 3% NaCl solution. This was sufficient hydroxide addition to increase the pH of the electrolyte from about 7.3 to between 11.5 and 12.4.

Figure 10 shows that even a small amount of sodium hydroxide added to the electrolyte causes improved amperage throughout the entire range of applied voltage potential. Furthermore, as the amperage neared zero, the minimum voltage required shifted downward from 2.4 V range to about 2.0 V. This finding suggests that a fundamental mechanistic change in the reaction had occurred that was not seen at neutral pH.

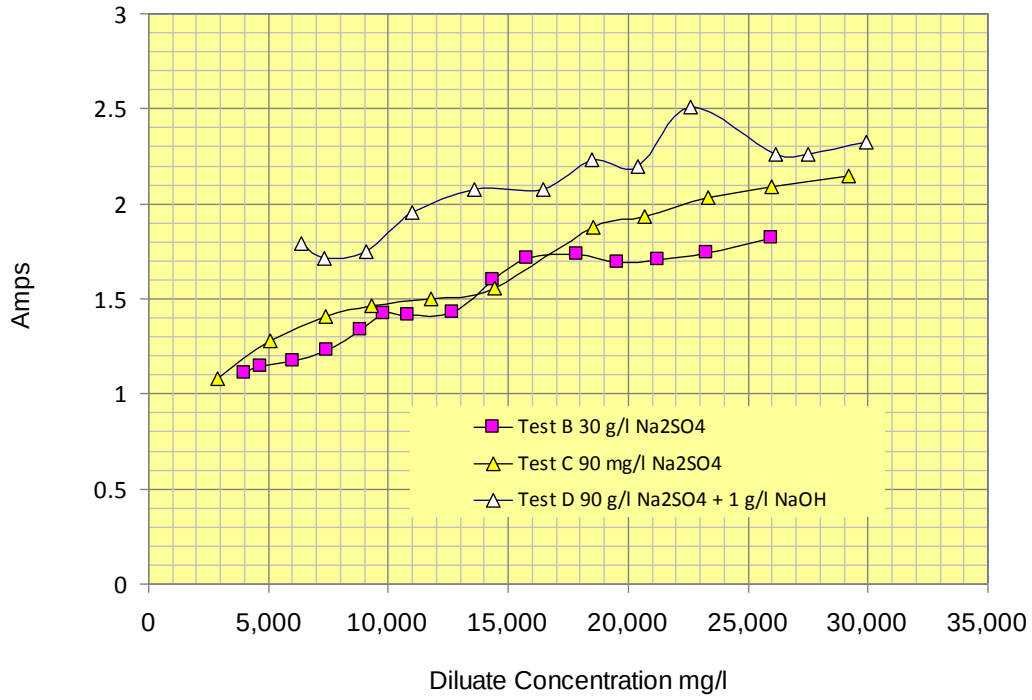
Figure 10: Effect of Sodium Hydroxide Addition to Electrolyte; Initial Conditions 3% NaCl



A full process run at 3% NaCl (Test D) was conducted using the basic electrolyte (90 g/l Na_2SO_4 + 1 g/l NaOH). The initial current was 2.32 amps. The final currrent was 1.79 amps, and the average current was 2.09 amps. The feed was initially 31,000 mg/l and treated to 4,750 mg/l in 6.0 hours.

Figure 11 compares the averages of ½ hour intervals of amperage versus diluate concentration in Tests B (30 g/l Na_2SO_4), Test C (90 g/l Na_2SO_4), and Test D (90 g/l Na_2SO_4 + 1 g/l NaOH). The improved amperage seen with Test D > Test C > Test B is manifested as improved treatment completion rates of 6 hours < 6.6 hours < 7.2 hours for similar test conditions.

Figure 11: Improvements in Electrolyte Chemistry Tests with 3% NaCl at 5V

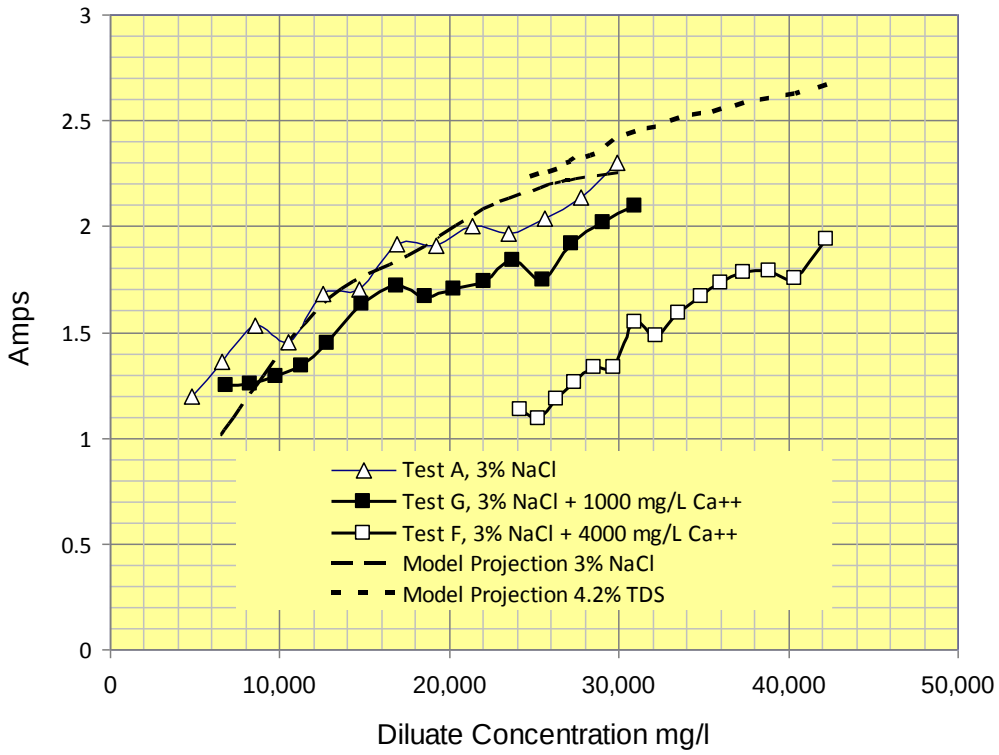


7.4 Effect of Calcium on Electrodialysis

The chemical composition of flowback water (Hayes, 2009) is summarized in the introduction of this document. These data show the median conditions on day five from the fracture. The total dissolved solids is 67,300 mg/l TDS and the median calcium carbonate hardness is 17,700 mg/l as $CaCO_3$. The hardness balanced against only 122 mg/l alkalinity as $CaCO_3$, implying that the majority of the hardness is soluble. Major contributions to this hardness are Mg (559 mg/l), Ba (686), Sr (1,080 mg/l), and Ca (4,950 mg/l). To put this into perspective, Kaakinen (1984) experienced difficulty in treating water from two sources with unbalanced hardness. 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 second source had a TDS range 9140–9180 mg/l, with calcium (35–60 mg/l) and magnesium (52–55 mg/l).

To simulate the problems that might be encountered in flowback waters, calcium chloride was used to represent the unbalanced hardness. A series of three electrodialysis runs with sodium chloride concentrations of 3%, and a pair of test with sodium chloride at 6% were performed. The first of the 3% sodium chloride tests had no

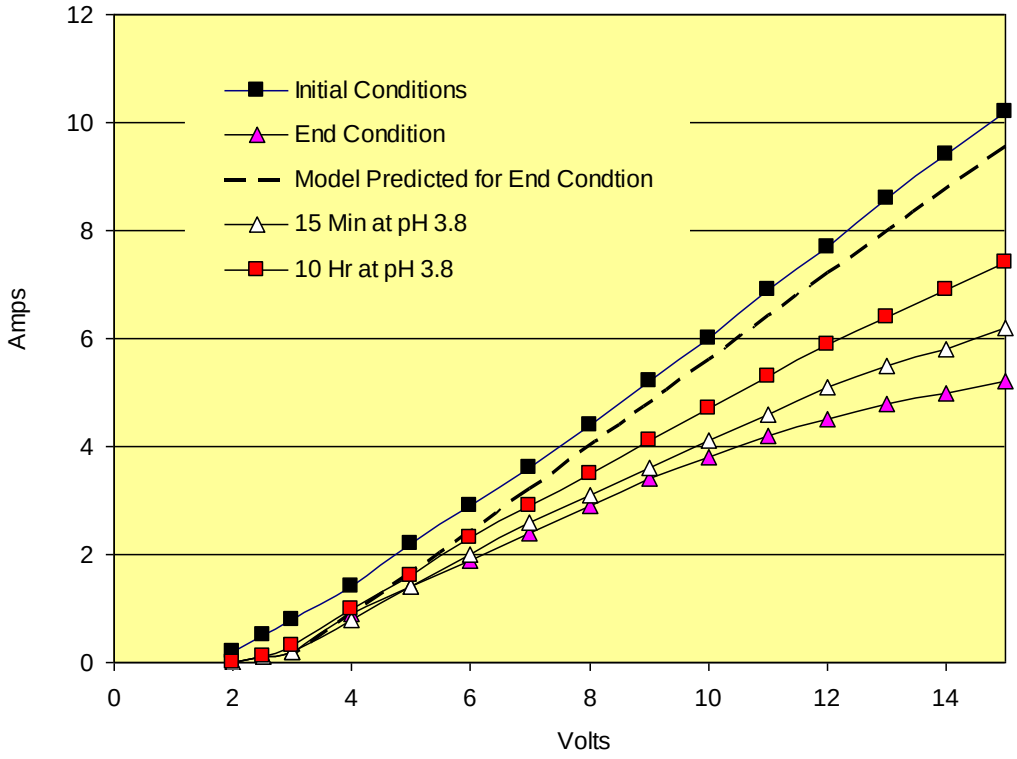
Figure 12: Effect of Calcium on ED Performance with 3% NaCl at 5V



added calcium beyond that present in the tap water. The total dissolved solids in the test solution were around 30,000 mg/l (Test A). Test A and served as the baseline. The second test (Test G) used 3% sodium chloride plus 1,000 mg/l Ca^{++} (from $CaCl_2$) with a total dissolved solids around 33,000 mg/l. The third test (Test F) had 3% NaCl plus 4,000 mg/l Ca^{++} (from $CaCl_2$) with a total dissolved solids concentration around 41,000 mg/l. In all three tests, the electrolyte comprised of 90 g/L Na_2SO_4 plus 1 g/L NaOH and had a pH from 12.2-12.6 units. The volume of the electrolyte was about 10.5 L. All tests were conducted at 5 V.

These results are compared by an analysis of the progression of the current during the treatment process. Figure 12 shows the ½ hour average amperage data versus diluate concentration from the data from Tests A, G and F. There is a marked decrease in current caused by the addition of 1,000 mg/l Ca^{++}. The amperage data at 30,000 mg/l diluate concentration indicate that 1,000 mg/l Ca^{++} causes an 11% decrease in ion flux. A calcium concentration of 4,000 mg/l causes 40% decrease in the current. For reference, computer simulations were also included in Figure 12 for expected results at 3% and 4.2% TDS (as NaCl**).** The loss of ion flux was apparently caused by a change in the electrolyte chemistry from the presence of calcium. Volt-Amp profiles (Figure 13) were collected Test F (3% NaCl plus 4,000 mg/l Ca^{++}). The first profile was an initial condition test at the start of the run. The current at 15 V exceeded 10 amps. By the time the run was terminated, the current at 15 V was only about 5 amps. To test the

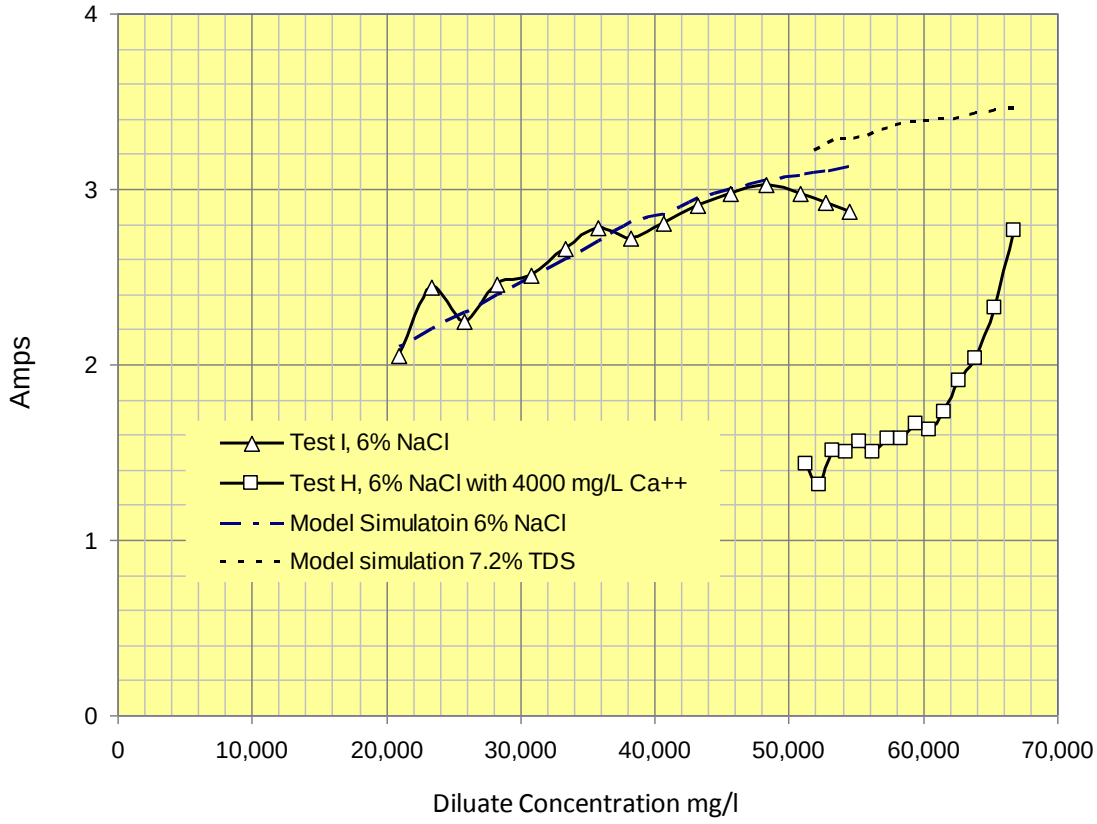
Figure 13: Test F, Recovery of Amperage by Acid Treatment of Electrolyte after Calcium Poisoning (3% NaCl, 4,000 mg/l Ca++)



origin of the fouling, electrolyte was acidified with 30 g HCl (35% wt/wt) was to shift the pH from about 12.5 to 3.8. After 15 minutes the VA profile showed an improvement in current at 15 V to more than 6 amps, a total recovery in terms of current efficiency and ion flux. The acidified electrolyte was cycled (at 0 volt stack potential) overnight for 10 hours. A final VA profile was performed and showed an increased current at 15 volt to greater than 7 amps. These data suggest that a calcium precipitate or other acid soluble precipitate in the electrolyte was interfering with ion flux. A computer simulation was generated for the expected VA profile for final condition. The data suggest that some, but not all, of the resistance was reversed by acid treatment of the electrolyte solution. Two electrodialysis runs with initial sodium chloride concentrations of 6% were also performed to determine the effect of calcium on electrodialysis. The first of these tests (Test I) had no added calcium beyond that present in the tap water. The total dissolved solids concentration in the test solution was around 60,000 mg/l. This represented the baseline. The second test (Test H) had 6% NaCl plus 4,000 mg/l Ca^{++} (from $CaCl_2$). The total dissolved solids was around 71,000 mg/l. The electrolyte was

prepared with of 120 g/l Na_2SO_4 plus 1 g/l NaOH and had a pH from 12.2-12.6 units.

Figure 14: Effect of Calcium on ED Performance with 6% NaCl at 5V Unprotected Cathode

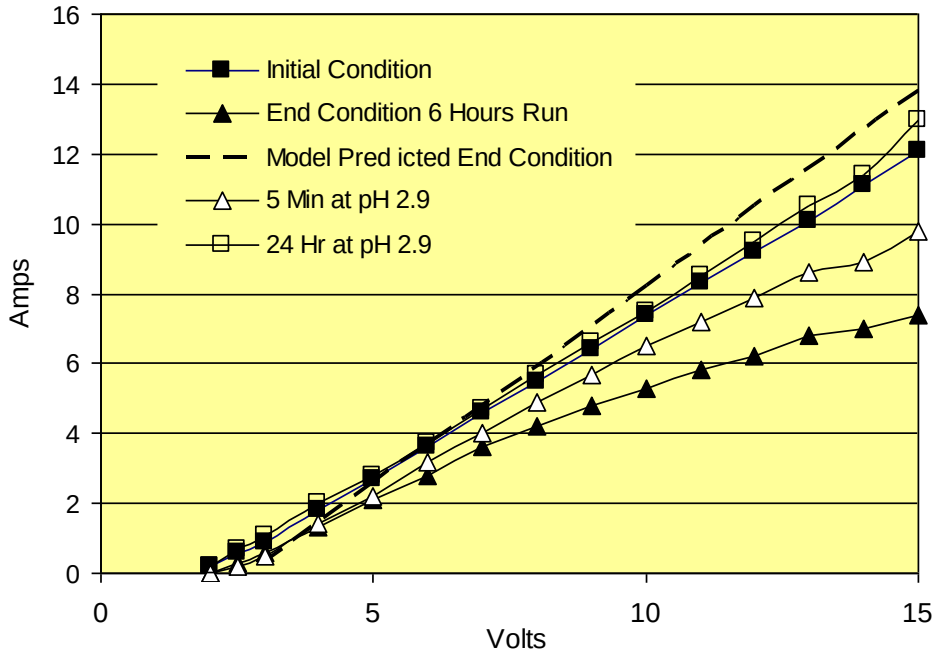


The volume of the electrolyte was about 10.5 liters. Both tests were conducted at 5 V.

Tests I and H are compared by an analysis of the progression of the current during the treatment process. Figure 14 shows the ½ hour average amperage data versus diluate concentration. 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. As a guide to further analysis, computer simulations are presented for 6% NaCl to simulate Test I, and for 7.2% NaCl to simulate the ionic strength conditions of Test H.

To demonstrate again that the loss of ion flux (vis. Amperage) was caused by a change in the electrolyte chemistry, a series of Volt-Amp profiles of current versus voltage were taken for the run (Test H) with 4,000 mg/l calcium (Figure 15). The first test was an initial condition profile taken at the start of the run and shows that the current at 15 V was about 12 amps. By the time the run was terminated, the VA profile showed that the current at 15 V was about 7 amps. About 35 g HCl (35% wt/wt) was added to the

Figure 15: Test H, Recovery of Amperage by Acid Treatment of Electrolyte after Calcium Poisoning (6% NaCl, 4000 mg/L Ca++)



electrolyte to shift the pH from about 12.5 to 2.9. After 5 minutes the VA profile showed an improvement in current at 15 V to more than 9.5 amps. The acidified electrolyte was cycled (at 0 volt stack potential) for 24 hours. The VA profile showed an increased current at 15 volt to greater than 12.5 amps. These data suggest again that a majority of the resistance to ion flux is caused by calcium (possibly in the form of calcium precipitation and scale depositions on the cathode and cathodic membrane) can be reversed by acid treatment of the electrolyte solution.

7.5 Mitigation of the Calcium Problem with Cathode Protection

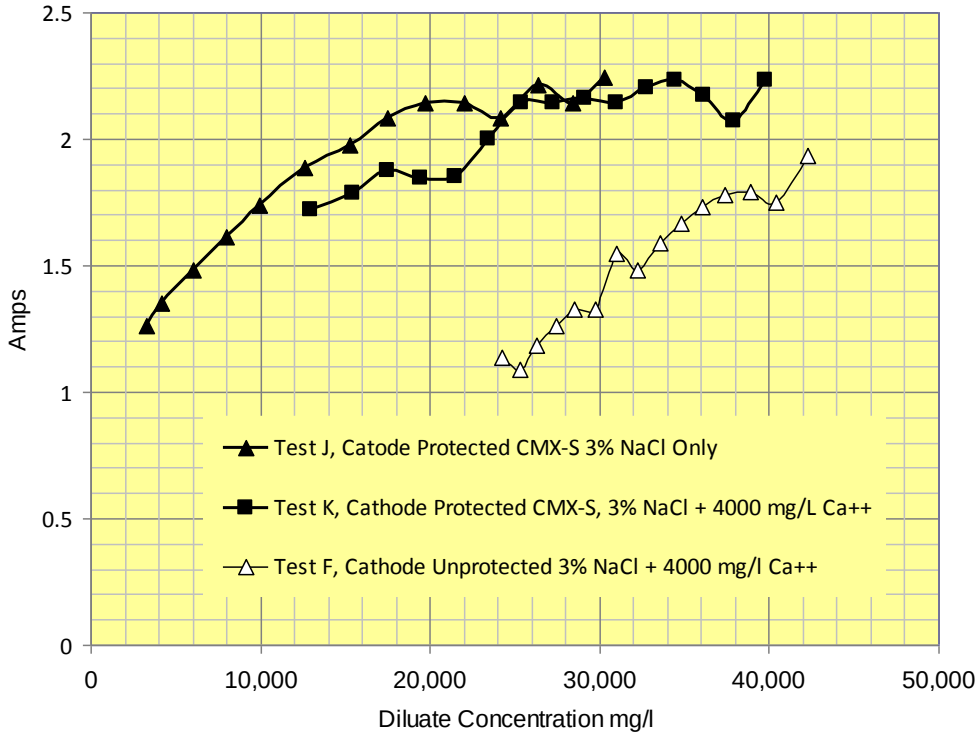
Soluble calcium at the high levels characteristic of many shale gas waters (>1,000 mg/l) appears to be a serious problem for the conventional electrodialysis treatment of highly concentrated brine solutions. Figures 13 and 15, however, suggest that the loss of ion flux can be reversed by acid treatment of the electrolyte. Since there was very little soluble calcium initially in the electrolyte, then calcium problems are likely associated with the transport of calcium into the electrolyte.

The construction of the electrodialysis stack (Figure 2) has only one point of contact between the electrolyte and mobile cations at the boundary of the cathode cell. The membrane at this boundary in all previous tests was a non-exclusionary CMX cation selective membrane (Tokyama).

A potential method of mitigating the effect of calcium transport into the electrolyte is to replace the single cathode boundary membrane with a multivalent exclusionary, cation selective membrane. The remainder of the tests were performed with the cathode cell protected by the replacement of the non-exclusionary membrane with a divalent exclusionary membrane, CMX-S (Tokyama).

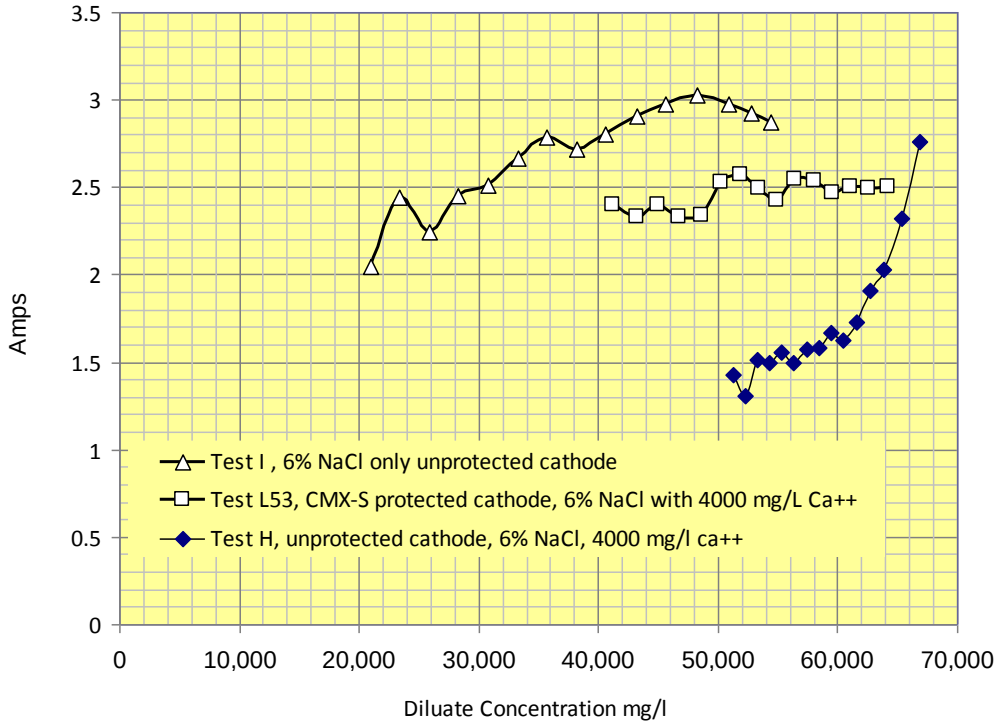
Two runs were performed to determine the capacity of the ED unit to treat calcium rich water with a single multivalent exclusionary membrane (Tokyama CXM-S) placed at the boundary of the cathode cell. Test J was a standard run with 3% NaCl and no added calcium to serve as a new performance baseline with the new membrane. Test K was performed using the protected cathode challenged with 3% NaCl plus 4,000 mg/l Ca^{++} added. This test is a direct comparison to Test F with the unprotected cathode (Figure 17). Compared to Test F, Test K with the protected catholyte showed improved amperage and ion flux throughout the entire run. Figure 16 is the summary of the ½ hour average amperage versus diluate concentration for Tests K (challenged protected cathode) and J (unchallenged protected membrane). The results of test F (challenged, unprotected cathode) are reproduced for comparison. This figure shows little degradation of ion flux when the protected membrane system was challenged with 4,000 mg/l Ca^{++}.

Figure 16: Effect of Calcium on ED Performance with 3% NaCl at 5V Protected Cathode



Test L was performed with 6% NaCl plus 4000 mg/l Ca^{++} and is the counterpart to Test H. The summary of these results are presented in Figure 16. Compared to Test H, Test L with the protected catholyte showed improved amperage and ion flux throughout the entire run. Figure 17 is a plot of the ½ hour average amperage versus diluate concentration for Test L compared to Test I (unprotected cathode, 6% salt and no calcium). The results from Test H are reproduced for comparison.

Figure 17: Effect of Calcium on ED Performance with 6% NaCl at 5V with Protected Cathode



7.6 Reduction of Calcium Flux into the Electrolyte

In order to better understand calcium transport across various points in the ED skid grab samples were taken for the Tests, F, H (Table 3) and Tests K and L (Table 4). It is expedient to define the calcium flux ratio (CFR, dimensionless) that relates the ratio of the flux of calcium crossing the membrane stack from the initial feed stock into the concentrate stream; to the flux of calcium passing from the diluate into the electrolyte. The CFR is estimated as follows:

1. The mass of calcium transported into the electrolyte (CE) is proportional to the final electrolyte minus the average of the tap water and initial electrolyte concentration. The average of the tap water and the initial electrolyte is used to reflect the premise that the only calcium in the initial electrolyte originated from the tap water.

2. The mass of calcium transported across the membrane stack (CW) between the concentrate and the diluate generated by ED is proportional to the concentrate concentration minus the feed concentration.
3. Finally, the relative completion index (RC %) is the degree of completion of the total ion transfer calculated as one hundred minus one hundred times the ratio of the diluate concentration (TDS) to the feed concentration (TDS).
4. CFR = (CW/CE) x RC/100

Table 3: Chemical Analyses: Tests with Unprotected Cathode					
Test F, 3% NaCl with 4000 mg/l Ca++(CMX)	Na^+	Ca^{++}	TDS		
Tap mg/l	26	37	ND		
Feed mg/l	13,000	4,400	55,000	RC=	55%
Diluate mg/l	6,700	750	25,000	CE=	123
Concentrate mg/l	14,000	6,100	63,000	CW=	1,700
Initial Electrolyte mg/l	31,000	38	110,000	CFR=	7.6
Final Electrolyte mg/l	24,000	160	91,000		
Test H, 6% NaCl with 4000 mg/l Ca++ (CXM)	Na^+	Ca^{++}	TDS		
Tap	9	39	ND		
Feed	21,000	3,500	84,000	RC=	37%
Diluate	14,000	1,600	53,000	CE=	87
Concentrate	27,000	5,100	110,000	CW=	1,600
Initial Electrolyte	19,000	47	120,000	CFR=	6.8
Final Electrolyte	34,000	130	110,000		

The relatively completion indices (RC) numbers in Table 3 indicate that without the protective cathode membrane, the removal of salts from the diluate was relatively incomplete (37–55%) in the allocated run time. With the protected cathode, the completion was much higher (61–86%) in Table 4. The flux of calcium incursion into the electrolyte (CFE) was much higher for the unprotected membrane tests (87–123 mg/l) compared to the tests with the protected membrane (46–75) mg/l. The flux of calcium transferred from the diluate to the concentrate (CFP) was much lower with the unprotected membrane (1,600–1,700 mg/l) compared to the protected membrane (3,100–4,200 mg/l). Therefore, the calcium flux ratio (CFR) expressing the relative rate of calcium transport in the membrane stack compared to transport to the electrolyte was small (at a level of 7–8) for the unprotected membrane and higher (at values of 34–57) for the protected membrane.

These estimates allow for an overall evaluation of the effect of using the cathode protection membrane. The final evaluation, the relative rejection rate (RR, %), is calculated as the 100 minus the ratio of the respective calcium flux ratios (X 100). For the tests at 3% NaCl, the protective membrane afforded a rejection rate of 87% of the

calcium into the electrolyte. The rejection rate of calcium by the protecting membrane for the tests at 6% NaCl was 80%.

Table 4: Chemical Analyses, Tests with Protected Cathode					
Test K, 3% NaCl with 4000 mg/l Ca++ (CXM-S)	Na^+	Ca^{++}	TDS		
Tap	11	45	640		
Feed	10,000	3,500	76,000	RC=	0.86
Diluate	2,800	14	11,000	CE=	46.5
Concentrate	18,000	6,600	120,000	CW=	3,100
Initial Electrolyte	24,000	56	98,000	CFR=	57.3
Final Electrolyte	23,000	97	98,000	RR=	87%
Test L, 6% NaCl with 4000 mg/l Ca++ (CXM-S)	Na^+	Ca^{++}	TDS		
Tap	320	130	740		
Feed	25,000	3,800	110,000	RC=	0.61
Diluate	12,000	800	43,000	CE=	75
Concentrate	32,000	8,000	150,000	CW=	4,200
Initial Electrolyte	25,000	100	130,000	CFR=	34.1
Final Electrolyte	36,000	190	130,000	RR=	80%

7.7 Mechanism of Calcium Interference

As previously described, the electrolyte solution that is passed by both electrodes of the ED process is comprised of disodium sulfate at concentrations of 30 to 90 g/l and at an elevated pH 11.5-12.5. The possible precipitation reactions are as follows:

$$Ca^{+2} + SO_4^{-2} = CaSO_4 \quad \mathrm{K_{sp}} = 2.4x10^{-5}$$

$$Ca^{+2} + 2OH^- = Ca(OH)_2 \quad \mathrm{K_{sp}} = 6.5x10^{-6}$$

At a concentration of 30 g/l disodium sulfate (0.21 molar SO_4^{-2}), a build-up of more than 45 mg/l of calcium would cause the solubility constant to be exceeded and a precipitate would be formed. Even at pH 12, the potential for calcium hydroxide precipitation is far exceeded by the concentration dominant sulfate precipitate. Since shale gas waters may contain calcium levels up to 25,000 mg/l, it is probable that even the diluate cells of the process will often contain thousands of mg/l of calcium. In such cases, a flux of even 10 percent of the calcium content of the diluate can potentially result in more than 100 g/l of calcium being transported into the electrolyte solution where nearly 50% of the calcium will be precipitated out with the high concentrations of sulfate anion at the

cathode. Deposits of calcium sulfate scale on the cathodic membrane or on the cathode itself is a possible mechanism of increased resistance to ion flow and reduced current efficiency throughout the ED process. Since this is a possible route of degradation of the ED process, experiments were conducted to elucidate the predominant mechanisms of calcium intrusion, fate of calcium through the electrolyte circulation system and the effects of precipitation formation on process performance with and without the presence of the single exclusionary membrane at the cathode side of the process.

It is evident from the tests evaluated in Tables 3 and 4, that the single exclusionary membrane installed at the cathode boundary is effective at reducing calcium flux into the cathode cell (and, hence, into the electrolyte solution) by about 80%. The corollary to this observation is that 20% of the potential flux of calcium still entered the catholyte.

Long-term operation of an electrolyte bath, therefore, will still be impacted by incursion of multivalent cations. Three tests (M, N and O) were performed to investigate the fate of calcium into and out of the electrolyte with the cathode protection membrane in place.

Test M was based on the premise that the electrolyte could become fouled by direct injection of calcium. In this test, the preferred electrolyte, 10.5 L 90 g/l Na_2SO_4 with 1 g/l NaOH at pH 12.5 was used. The salt solution treated was 3% NaCl with no calcium, and presented no challenge to the electrolyte. At ½ hour, the electrolyte was challenged directly with a charge of 400 mg/l Ca^{++} into the anolyte tank. A white precipitate immediately formed. The test continued for another hour when the pH of the electrolyte was dropped to pH 3.2 with 3 g/l HCl. The test continued for an additional 4 ½ hours with no indication of flux inhibition (Figure 18). Therefore, the act of creating calcium precipitate within the electrolyte solution does not appear to be a problem. Furthermore, if the calcium precipitate is dissolved with acid, the soluble calcium causes no inhibition. In fact, quite an opposite effect was noted. Chemical analysis showed that soluble calcium leaves the electrolyte and become concentrated in the concentrate stream.

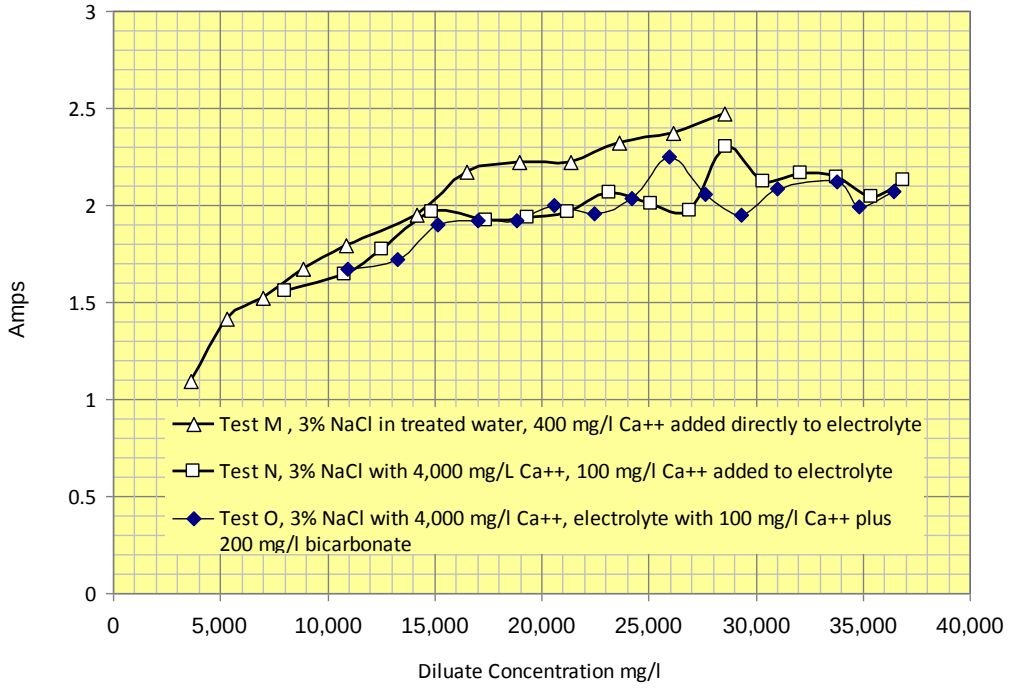
Test N was performed to determine if the transport of soluble calcium from the diluate to the electrolyte, or the transport from the electrolyte to the concentrate, could present an ion flux inhibition. In this test, a reduced volume (3.4 L instead of 10.5L) electrolyte was used in order better measure the rate of calcium change across the hydraulic boundaries and to cause a more rapid rate of electrolyte degradation. The salt solution treated was 3% NaCl with 4,000 mg/l Ca^{++}. The electrolyte was 90 g/L Na_2SO_4 at pH 6.8 with an initial concentration of 100 mg/l Ca^{++}. 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 N (Figure 18) 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 pH 12, in which cases, 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.

Test O 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 4000 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

Figure 18: Effect of Calcium on ED Performance with Protected Cathode



calcium carbonate. No degradation of performance was noted (Figure 18).

In summary, Tests M, N and O demonstrate that once the calcium exclusionary membrane is placed to protect calcium incursion into catholyte, there is very little that can be done to the electrolyte chemistry to further impede ion flux. This strongly suggests that the weak link in the electrolyte system is precipitation of calcium on the internal surface of an unprotected cathode membrane.

8. Discussion

There are two challenges to the operation of electrodialysis for the desalinization of flowback and produced waters associated with shale gas production. One is the economic performance at extremely-high-salt conditions. The second is the high concentrations of calcium and other multivalent cations expected in the flowback water. This discussion will focus on these topics, and try to put the results of this project into perspective relative to the solution of these challenges.

8.1 Meeting the Initial Energy Goals

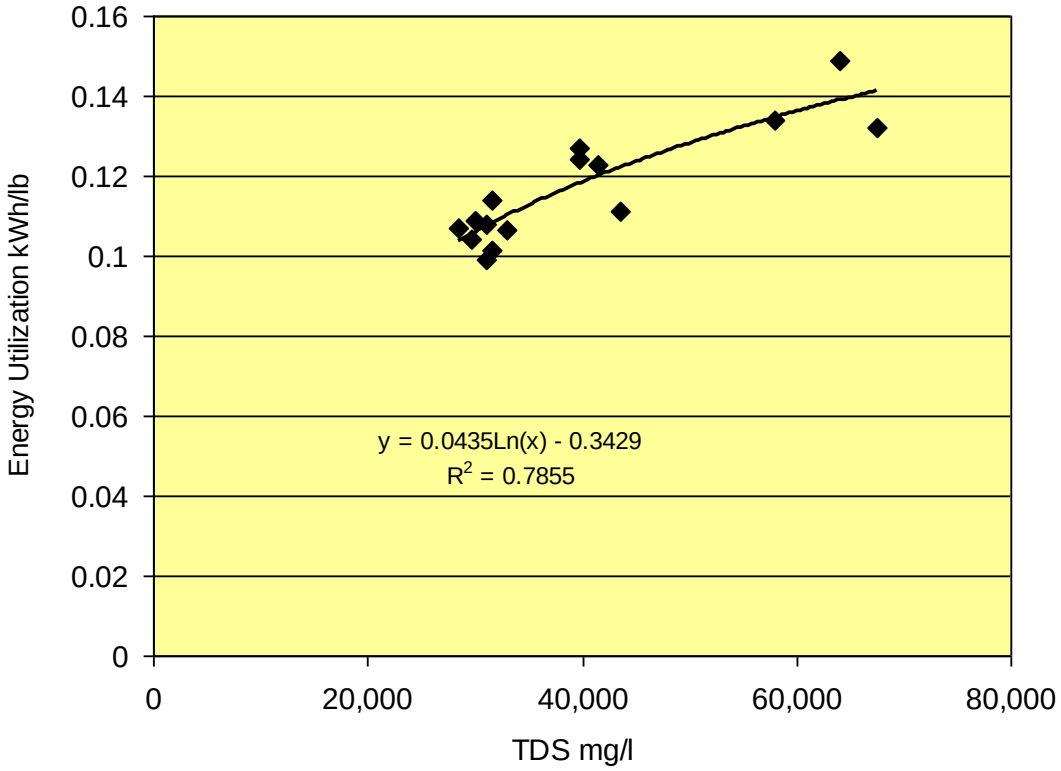
The initial goal was to demonstrate that the electrodialysis process could work satisfactorily at a power utilization rate of between about 0.1 and 0.15 kWhr/lb salt transferred. The energy used to transfer a given mass of salt is an important economic consideration. To put this into perspective, a barrel (42 gallons) of 50,000 mg/l salt brine desalinated to 10,000 mg/l results in the transfer of 14 pounds of salt. At a rate of 0.15 kWh/lb salt and $0.10/kWh, this yields a cost of $0.21/barrel treated.

The goal was approached by running the computer simulation at 3% NaCl to pre-determine the conditions needed to meet the imposed limit. These results demonstrated that the ED prototype can operate at a low electricity demand of less than 0.15 kWhr/ lb NaCl if operated at 5 volts. In nine tests in the range of 3–4.2% TDS an average electricity demand of 0.107 ± 0.07 kWhr/lb TDS was observed, indicating nearly 100% current efficiency was achieved in these tests.

It is instructive to review the energy-efficiency data for all 15 tests summarized in Table 2. Figure 19 shows the energy efficiency as a function of the initial salt concentration. Higher initial salt concentrations appear to command higher-energy requirements. This indicates that the pilot plant performs at less than 100% current efficiency at higher salt concentrations. When current efficiency is below 100%, this is usually blamed on the phenomenon of water splitting. However, these salt concentrations are very far the limiting current conditions. Therefore, other mechanisms must be investigated to explain these results. One likely factor is the loss of water from the diluate to the

concentrate caused by osmotic pressure. Another possible factor is increased current drift or short circuiting within the stack and between the anolyte and catholyte tanks.

Figure 19: Energy Efficiency vs. Initial TDS



This is an obvious area to look for further process improvement.

8.2 Improvements for Extremely Concentrated Salt Solutions

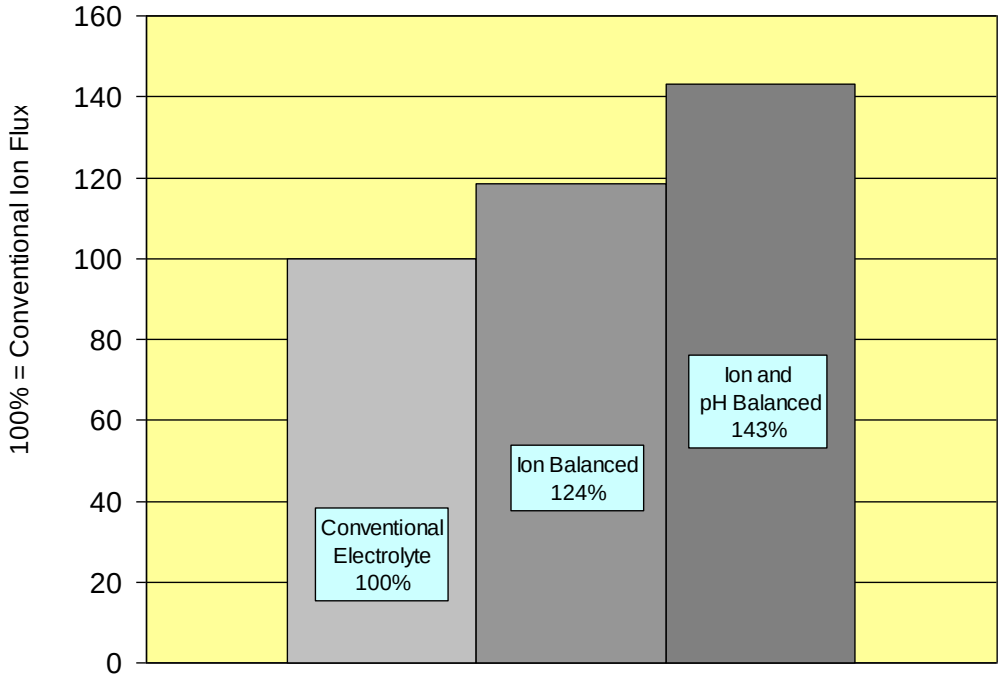
Considerable effort was expended in understanding how electrodialysis should be operated under the extremely concentrated salt conditions expected in flowback waters. In typical operation of electrodialysis, the process encounters salt concentrations of several thousand mg/l TDS with the treatment goal to about 500 mg/l. In the flowback water, the expected median concentration (on Day 5 from the fracture) is in the range of 60,000–70,000 mg/l, with the need to treat to about 10,000 mg/l.

The development of the computer model allowed a good understanding of the electrochemistry of the ED process. At high-salt concentrations, the resistance of the

electrolyte solution and the overvoltage required to initiate the electrode reactions are two of the largest contributors to resistance to ion flux. This understanding helped in defining the early direction of the development effort. Reduction in electrolyte resistance was achieved by increasing the ionic strength of the electrolyte to a concentration similar to that of the water treated. Reduction in overvoltage was achieved by increasing the pH of the electrolyte to better accommodate the electrochemical reaction at the anode.

A summary of the improvements is presented in Figure 20. If the conventional electrolyte solution used under normal operating conditions (about 30 g/l Na_2SO_4 at neutral pH) represents 100%, then increasing the electrolyte concentration to the preferred concentration of 90 g/l Na_2SO_4 (also at neutral pH) increases the ion flux by 24% (at 3% NaCl at 5 volts). The addition of 1 g/l NaOH to the electrolyte has the effect of decreasing the sum of the overvoltage/electrode voltage from 2.4 to 2.0. This is reflected in the improvement observed in the data of an additional 19% over and above the improvements in electrolyte concentration (Figure 20). Together, these economical alterations in the electrolyte solution resulted in an enhancement of ion flux by 43%.

Figure 20: Improvements in Ion Flux by Changes in Electrolyte Chemistry (3% NaCl, 5 Volt, Test Duration 6 Hr.)

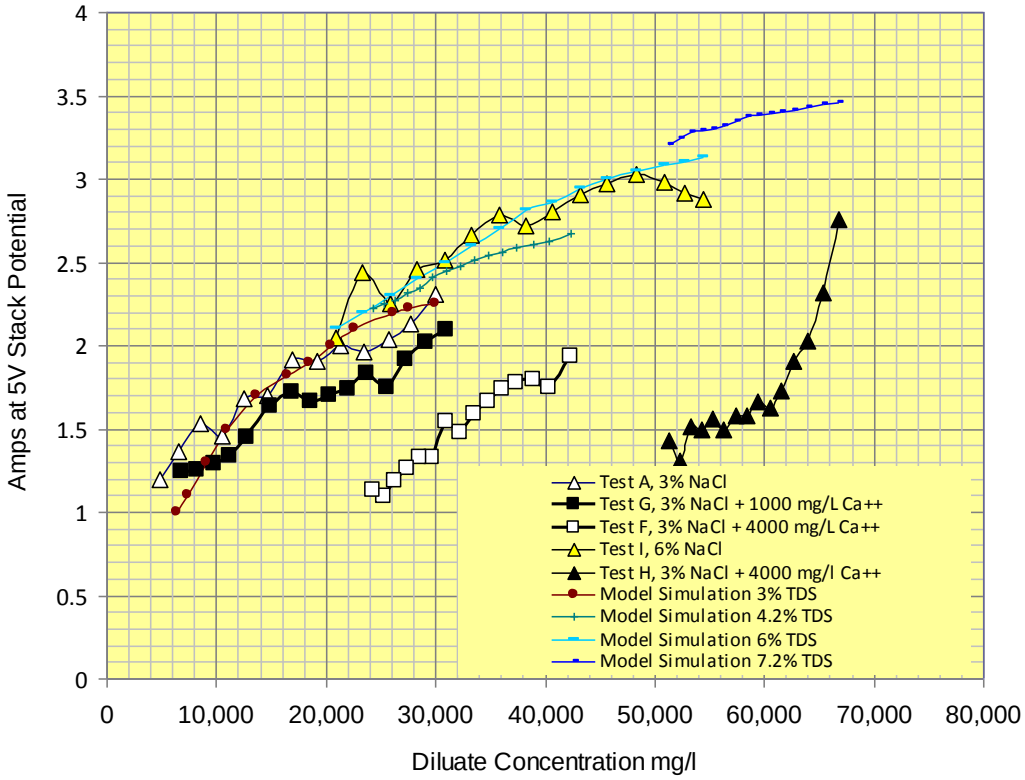


8.3 Problems with Calcium and Other Multivalent Cations

Very little published literature is available on treating highly-concentrated brine solutions with electrodialysis. However, it is expected that the presence of several thousands of mg/l of calcium and other divalent cations will present a problem. Kaakinen (1984) describes problems associated with treating brines at 3,300–9,150 mg/l TDS with calcium at 35–60 mg/l and 52–55 mg/l with the electrodialysis process. The goal of the present research is for treatment of water at 30,000 to 60,000 mg/l TDS with calcium exceeding 4,000 mg/l. Previous literature describes how calcium and magnesium must be removed from the water prior to treatment with electrodialysis.

In expectation of very-high-calcium concentrations the electrodialysis pilot plant was challenged with 3% NaCl with 1000 mg/l and 4000 mg/l soluble calcium added to the process water. In another experiment the ED unit was challenged with 6% NaCl with 4,000 mg/l calcium. Indeed, the calcium caused decreased ion flux. Figure 21 summarizes the results of these tests along side baseline tests with no calcium addition. Amperage (average over 1/2 hour intervals) is used as a surrogate for ion flux. The amperage is presented as a function of the average diluate concentration. Computer simulations are presented showing the expected results. Process poisoning by calcium is evident. Based on median concentrations, 1,000 mg/l Ca^{++} (in 3% NaCl) inflected an 11 % loss of ion flux, 4,000 mg/l Ca^{++} inflicted a 35% loss of ion flux, and 4,000 mg/l inflicted a 48% loss of ion flux.

Figure 21: Effect of Calcium on ED Performance with 3% and 6% NaCl at 5 V with Unprotected Cathode



8.4 Mitigation of the Calcium Problem

Pre-treatment of the entire flowback water stream to remove calcium is prohibitively expensive. For perspective, one million gallons of flowback water with 4,000 mg/l soluble calcium would produce 208 wet tons of calcium carbonate sludge (assuming the sludge is dewatered to form a 20% solids cake). Capital costs, operating costs and disposal costs associated with this volume of sludge should dissuade further consideration of this concept. The best means to dispose of the soluble calcium is along with all the other soluble salts in the concentrate from the electrodialysis process. A significant effort was undertaken to mitigate the calcium poisoning by protecting the integrity of the cathode from calcium incursion.

At the end of Tests H and F (Figure 21), the amperage could be restored by acidification of the electrolyte (Figures 13 and 15). From a mechanistic standpoint, this means that the poisoning from calcium was most likely associated with either the anterior of the boundary membrane between the last diluate cell and the electrolyte cell, or fouling of the electrode.

It was postulated that calcium could be excluded from the electrolyte cell by changing a single cation exchange membrane at the boundary to the cathode with a cation selective membrane that had exclusionary properties for divalent cations. A Tokyama CX-S membrane was selected to replace a non-exclusionary membrane, Tokyama CMX. The pilot ED stack was refurbished with this single membrane change.

A series of tests were performed to compare the response of the ED stack with the protected cathode cell versus the original unprotected cell. These results are summarized in Figure 22. Figure 22 can be compared directly with Figure 21. The protective, exclusionary membrane performed, as expected. The protected cathode performed much better that the unprotected cathode. Tables 3 and 4 in the results section present chemical analyses. These data suggest that the CMX-S exclusionary membrane rejected the passage of about 80% of the calcium from the cathode cell. Based on median results, the protected membrane performed at 29–39% higher ion flux than the unprotected cell.

The single CXM-S membrane at the cathode boundary appeared to confer additional benefits. We challenged the electrode, the electrolyte and the feed solution with a series of tests with soluble and precipitated calcium. A mechanism was suggested; calcium that passed through the membrane was unable to collect at the posterior, and was rejected into the electrolyte where it was able to precipitate before impacting the electrode.

Figure 22 Effect of Calcium on ED Performance with 3% NaCl and 6% NaCl at 5V with Protected Cathode

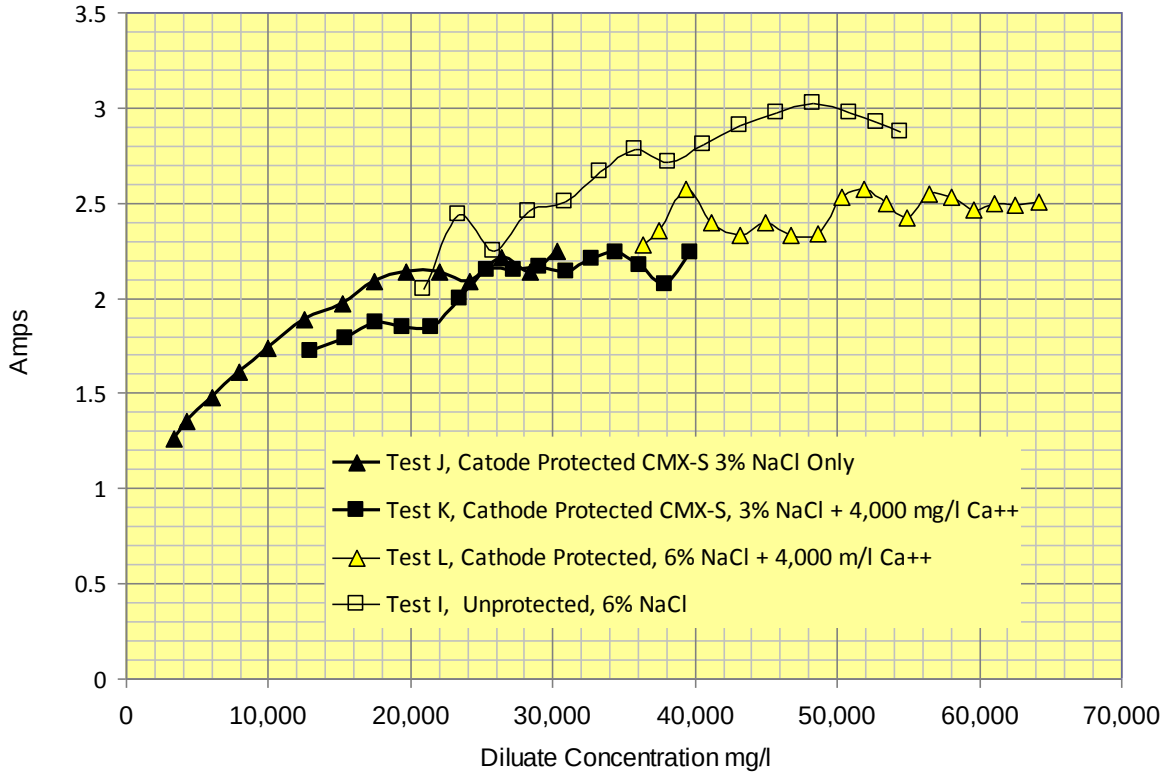
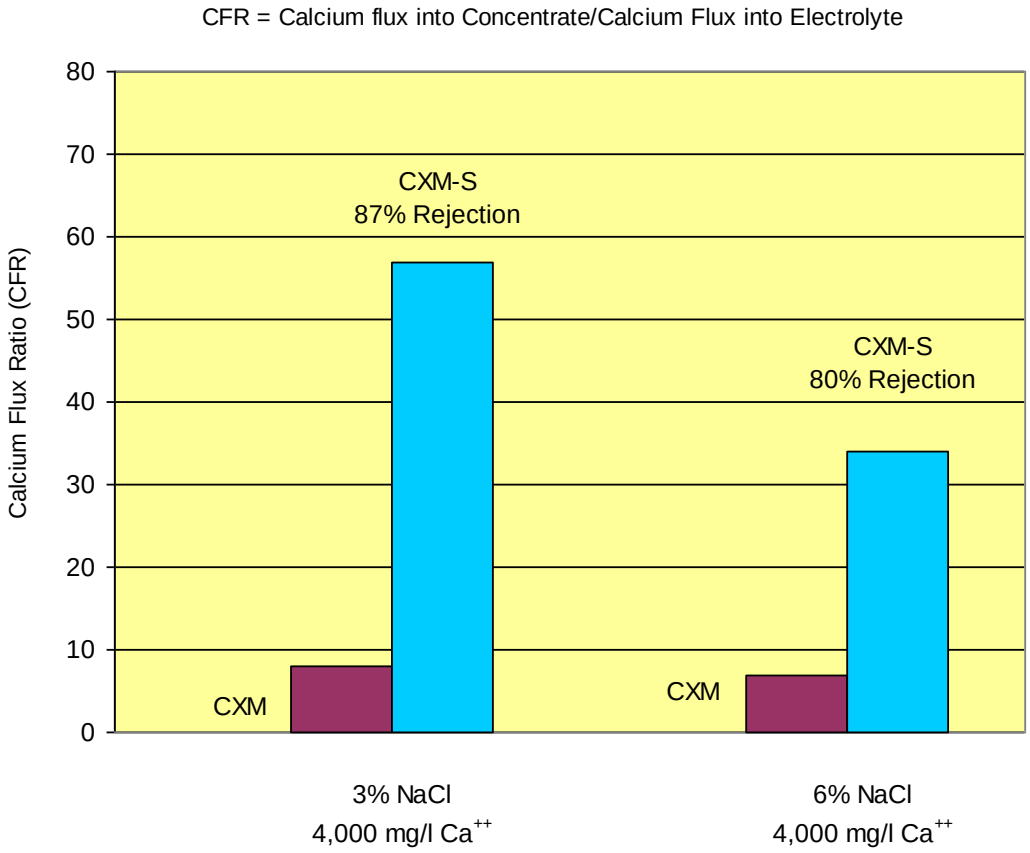


Figure 23: Protection of Electrolyte from Calcium Incursion with Single CXM-S Membrane at the Cathode Boundary



While improvements to the process have been made with respect to the mitigation of calcium incursion into the electrolyte, there remains a need to demonstrate that the other multivalent cations of concern (Ba, Sr, Mg, etc.) follow the same trend as calcium. Further tests are planned to better understand the fate of other important divalent cations.

8.5 Scale-up

There are four issues to be considered for scale-up of the electrodialysis process;

1. Stack voltage (V_s), volts per cell pair (V_{cp}), and electrode/overvoltage (E);
2. Total amps (I_T), surface area per single membrane (A_{cp}), and amp flux (j) per single membrane;
3. Ion transfer capacity (q = charge equivalents/sec) and transfer efficiency (f); and
4. Number of cell pairs (N_{cp}).

The scale factor for voltage is:

$$V_{CP} = \frac{V_S - V_E}{N_{CP}}$$

The scale factors for ion transfer capacity (where F = Faraday = 96,000 coulomb/charge equivalent) are:

$$I_T = jA_{CP}$$
$$q = \frac{fN_{CP}I_T}{F}$$

The pilot data are analyzed as follows:

1. Determine the volume of diluate treated;
2. Determine the time to treat the diluate;
3. Calculate the effective total amperage from total charge equivalents treated per second;
4. Calculate the transfer efficiency from the effective total amperage and the measured average amperage;
5. Determine the volts per cell using the pilot stack voltage and electrode voltage; and
6. Calculate the amps per unit area of a cell (one membrane in a pair).

A full scale unit with the same performance (amps/unit area of a cell) and volts/cell pair treating a larger volume of similar water to a similar end point is calculated as follows:

1. Determine the volume to be treated;
2. Determine the time allowed to treat the water;
3. Calculate the total amperage and effective amperage;

4. Postulate an area per cell (one membrane) to be used;
5. Postulate a number of cell pairs;
6. Calculate the amps/area of a cell (one membrane);
7. Compare the amps/area calculated against the amps/area of the pilot unit;
8. Change the number of cell pairs until the amps/area of the full scale unit equals the amps/area of the pilot unit; and
9. Calculate the stack voltage of the full-scale unit using the volts/cell from the pilot data.

Table 5 shows an example scale-up for treatment of 3% NaCl down to 1% NaCl. Typical pilot results were used to build the parameters. Treatment of 100 barrels per day would require about 80 cell pairs of 1 m^2 per single membrane and operate at a stack voltage of 22 volts and 80 amps. This is a trial and error method and other combinations of unit area and total cells can also be found that would meet the criteria.

Table 5: Example Scale-up

Pilot System				Full Scale		
		0.066	Barrel		100	Barrel
Volume		10.5	Liter	Volume	15890	Liter
Time		6	Hours	Time	24	Hours
Initial		3	% NaCl	Initial	3	% NaCl
Final		1	% NaCl	Final	1	% NaCl
equivalent wt.		58.5	g/eq.	equivalent wt.	58.5	g/eq.
ion capacity	q	0.000166	Eq./sec	ion capacity	0.0629	Eq./sec
current eff.	f	0.99		current eff.	0.99	
cell pairs	N_{CP}	10		cell pairs	76	
stack voltage	V_s	5	volts	stack voltage	20.8	volts
overvoltage	V_E	2	volts	overvoltage	2	volts
volts/cell	V_{CP}	0.3	volts	volts/cell	0.3	volts
area/cell	A_{CP}	0.02	m^2	area/cell	1	m^2
amp/area	j	80	amps/ m^2	amp/area	79.7	amps/m^2
Total amps	I_T	1.6	amps	Total amps	79.7	amps

9. Conclusions

Performance results from the initial testing of electrodialysis on highly-concentrated-salt mixtures representing flowback water and produced water compositions indicate that it is potential feasible to use the ED to partially demineralize brines for purposes of water reuse in shale gas development. A useful niche for ED is in the processing of moderately-concentrated flowback and produced water to recover a partially demineralized water stream that can be combined (and diluted) with fresh waters and

reused for future hydraulic fracturing in shale gas well completions. Laboratory trials showed that ED is capable of achieving rapid reduction of salts concentrations from above 60,000 down to 10,000 mg/l at reasonable energy costs of less than 20 cents per barrel (assuming energy costs of $0.10/kWh-hr).

Specifically, the investigation of electrodialysis shows that the process can be modified to meet the demands of the high-salt concentrations extant in flowback waters from fractured shale. Operation of ED under the high-salt conditions places the process in a regime of relatively low voltage and high amperage 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. Another challenge to the desalinization of the shale flowback water is the potential for process inhibition by soluble calcium and other divalent cations. This challenge was addressed by another process improvement aimed at mitigating the effects of divalent cations on the electrolyte cell.

Significant improvements to the process have already been discovered in this development program. These improvements are aimed at creating a system robust enough to operate on shale flowback water.

1. Improvements to the electrolyte solution by increasing the concentration to an ionic strength similar to, or greater than, the process water to be treated proffered an overall process improvement of 23% over normal electrolyte conditions.
2. Improvement to the electrolyte solution pH was shown to decrease the overvoltage (voltage required for electrochemical initiation) by 0.4 volts. This improvement resulted in an additional 19% process improvement in addition to the already improved electrolyte.
3. Soluble calcium causes process poisoning. A majority of the flux inhibition was associated with the incursion of calcium into the electrolyte. The point of entry is most likely the boundary between the final diluate cell and the cathode cell. Acidification of the electrolyte was capable of reversing the majority of the inhibition.
4. Replacement of the single membrane at the boundary of the final diluate cell and the cathode cell with a calcium (divalent cation) exclusionary membrane reduced the flux of soluble calcium into the electrolyte by more than 80%. This translated into improved ion flux (29-39%) greater than observed with a non-exclusionary membrane in-place.
5. The calcium exclusionary membrane at the cathode appears to serve a dual purpose. Conclusion 4 alludes to rejection of calcium on the anterior side of the membrane. We challenged the protected cathode system with soluble, externally precipitated, and internally precipitated calcium. It appears that the calcium exclusionary membrane also rejects calcium on the posterior side (inside the cathode cell) such that any calcium that crosses the membrane cannot adhere to the membrane.

10. Recommendations

1. Based on the salt separations and energy use performance observed in the initial laboratory trials, it is clear that the process has achieved the initial performance objectives and should proceed to the second year of development for implementing process modifications that improve the capabilities and costs of ED applications to shale gas waters.
2. The ability to mitigate process inhibition by soluble calcium was demonstrated. The ultimate fate of calcium is transport to the concentrate stream. It is imperative that the fate of other multivalent cations, such as Ba, Sr, and Mg, also be understood. A series of tests with a number of multivalent cations in the feed water should be performed under laboratory conditions.
3. Tests on a preliminary clean-in-place method for calcium control in the electrolyte have been initiated. These tests should be continued to test the full utility of the proposed process improvement.
4. Computer modeling of the electrodialysis has indicated that membrane resistance and overvoltage are among the larger resistances to ion flux. It is recommended that investigation on how to reduce these two resistances continue. The approach may include membrane selection and/or hydraulic changes to electrolyte flow to reduce these resistances.
5. An apparent loss of current efficiency with increased salt concentration from 3% to 6% NaCl. The mechanism of the loss of current efficiency needs to be investigated. This may be through selection of membranes less subject to osmotic back pressure, or isolation of short-circuiting within the process hydraulic system.
6. While numerous advances have been achieved in the application of the electrodialysis process to concentrated brines with extreme levels of calcium, the process has yet to be challenged with real flowback waters from the field. A series of tests with field samples should be performed.
7. A better understanding of the pretreatment requirements for ED needs to be acquired.
8. The economics of full scale electrodialysis need to be understood. This would include gaining process economic data from vendors and integration of this knowledge with improved understanding of the concentration and hydraulic profile of the flowback event.

11. Acknowledgements

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12. References

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