Electrodialysis-Ion Exchange for the Separation of Dissolved Salts

**Final Report
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**By:
Jeffery L. Harrison
C.J. Baroch
John Litz**

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Office of Environmental Management
Office of Technology Development
1000 Independence Avenue
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U.S. Department of Energy
Office of Fossil Energy
Federal Energy Technology Center
Morgantown Site
P.O. Box 880
Morgantown, West Virginia 26507-0880

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By
WASTREN, Inc.
Norwest Blank Plaza
12000 North Pecos,
Suite 250
Westminister, Colorado 80234

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1.0 EXECUTIVE SUMMARY

Electrodialysis and ion exchange are two well-established commercial water treatment processes. Electrodialysis-Ion Exchange (EDIX) is an emerging technology in which ion-exchange resins are placed in the electrodialysis compartments; cation resins in the catholyte compartment, ion resins in the anolyte compartment, and mixed bed resins in the feed compartment. Theoretically, EDIX should be an improvement over the two individual processes in sequence. The presence of the ion-exchange resins improves the efficiency of electrodialysis by reducing resistance and improving ion transfer.

EDIX has been successfully demonstrated on a laboratory scale using a solution containing sodium nitrate and nitric acid. This program was conducted for EG&G at the Rocky Flats Plant in 1992. Because of this success, *WASTREN* obtained funding from DOE in response to the ROA DE-AR21-95MC32112 to determine if EDIX might be suitable for treating waste water containing low levels of radioactivity, acids, heavy metals, dissolved salts, and soluble organics. If it is successful, then *WASTREN* would design a 30 gpm system and determine the overall economics of the process.

The laboratory work on this program was performed at the Colorado Minerals Research Institute (CMRI) since *WASTREN* does not have any laboratory facilities. *WASTREN*, in conjunction with CMRI, designed and procured a 1 L/minute EDIX system. The system was designed based on the experience gained in the EG&G project. Scaling from the 1 L/minute to the 30 gpm was considered possible based on the discussions with the supplier of the electrodialysis system.

A series of 37 bench scale tests were run to select the most suitable resins and membranes and to establish the conditions necessary to produce a product stream of the desired quality when starting with feed solutions containing 20-200 ppm Na^+ , 30-3,000 ppm NO_3^- , 20-200 ppm Cr^{+6} as $\text{CrO}_4^{=}$, or Cr^{+3} as $\text{Cr}(\text{NO}_3)_3$. The bench scale tests indicated that the combination of $\text{CrO}_4^{=}$ and HNO_3 destroyed the anion membranes and that $\text{Cr}(\text{OH})_3$ precipitated in both the feed and catholyte compartments when testing a feed solution containing $\text{Cr}(\text{NO}_3)_3$.

Although some useful data were obtained, the principal objectives of the program were not met. Therefore, the program was terminated at the convenience of the DOE part way through the

program. EDIX still may have potential for processing waste streams containing dissolved salts if the cation does not form an insoluble hydroxide at any pH and if membranes are resistant to strongly oxidizing acidic solutions.

This report describes in details the results that were obtained during the bench scale testing of a variety of simulated waste streams.

2.0 INTRODUCTION

The Department of Energy generates and stores a significant quantity of low level, high level, and mixed wastes. As some of the DOE facilities are decontaminated and decommissioned, additional and possibly different wastes will be generated. A significant portion of these wastes are aqueous streams containing acids, bases, and mixed salts, or are wet solids containing inorganic salts. Some of the wastes are mixed as they contain hazardous constituents: heavy metals, organics, or both; and radioactive contamination.

The disposal and treatment of these wastes are expensive and difficult because of radiation hazards and complexity of the processes required to produce a stable waste form. For example, some of the current aqueous streams are combined with cement to produce grout. The grout has limited capacity for water and the dissolved salts. Thus, producing grout yields a substantially larger volume and weight of waste that must be stored. Vitrification can be used to process wet solids. However, many salts in the wet solids either decompose, producing a gaseous effluent that requires an elaborate off gas treatment system, or produce a low melting and unstable product.

DOE is continuing to study, develop, and seek processing techniques that are simpler and less expensive and produce small volumes of radioactive and hazardous waste.

Electrodialysis-Ion Exchange (EDIX) was believed to be a possible process that should be more cost effective in treating aqueous wastes. EDIX is a process developed by Mr. Phil Grant of *WASTREN* in the 1970s while he was employed by the Babcock & Wilcox company. The process was developed to control the boron and lithium content of the primary coolant in Pressurized Water Reactors. This technique was never commercialized. A small Research and Development (R&D) program was conducted by *WASTREN* for EG&G Rocky Flats in 1992 to determine the suitability of EDIX for processing streams containing low levels of nitric acid and small amounts of sodium nitrate (~ 1.5 g/l). The program was exploratory in nature and was not very

comprehensive. It did, however, yield some very promising results that justified conducting additional R&D.

Based on the earlier results, the DOE-METC funded the program described in this report to study the suitability to treat aqueous streams containing heavy metals and radioactive cations in a solution containing sodium and nitrates. The goal of the program was to produce a cation stream containing sodium, heavy metals, and the radioactive cations; an anion stream of nitric acid free of heavy metals and radioactive cations; and a product stream that meets the discharge criteria approved by DOE.

The program was designed to assess the suitability of EDIX to process streams containing 20-2,000 ppm Na^+ , 20-2,000 ppm chromium as CrO_4^- , and 30-3,000 ppm NO_3^- . Some of the solutions were to contain small quantities of depleted uranium and methyl alcohol. Following these tests, two 100-hour continuous runs were planned. The data from these runs were to be used to design a 30 gpm system.

The experimental results described in Section 6.0 indicated that the original program objectives could not be met, and that EDIX was not a suitable process for treating wastes containing metals that formed insoluble hydroxides in a basic solution. The test program was therefore terminated prior to running the two 100-hour continuous runs. This report does provide a detailed description of the results obtained from the program. It does not, however, include the design of a 30 gpm system

3.0 SUMMARY AND CONCLUSIONS

The experimental program conducted on this contract did yield some interesting results and a few conclusions can be drawn from the data.

1. The presence of ion-exchange resins in the electrodialysis cell improves the removal efficiency of both sodium and nitrate, but they have a much greater effect on nitrate removal. The resins also reduce the resistivity of the cell, thus reducing the power requirements for the ion removal.
2. The solution adjacent to the catholyte membrane, both in the feed and catholyte compartments, is apparently quite basic, possibly because of polarization of the water. Because of this, metals that form insoluble hydroxides precipitate in the catholyte and feed compartments and in the cathode membrane. Thus, this EDIX cell configuration cannot be used for processing solutions containing these metals.
3. The solution adjacent to the anolyte membrane, both in the feed and anolyte compartments, is very acidic, possibly because of the polarization of the water. The acidic conditions in the presence of chromic acid are so severe that the Neosepta and Membrane International membranes were attacked by the solution, and thus destroyed. Feed solution could pass from the feed compartment into the anolyte compartment without any significant ion removal.
4. The ion-exchange resins do not appear to be affected by the solutions in either the feed, anolyte, or catholyte compartments, even when the solution caused deterioration of the membranes.

5. The degree of ion removal in the EDIX system is dependent upon—

Flow Rate: The lower the flow rate, thus the longer residence time in the system, the greater is the ion removal efficiency in terms of total amount removed and the resulting water quality.

Power: The degree of ion removal increases with power, but the power efficiency decreases as the power increases.

Ion Mixed Bed Composition: Changing the ratio of cation to anion ratio of the resins in the mixed bed affects the degree of anion and cation removal.

Ion Concentration: The electrical resistivity of the cell decreases with increasing ion concentration, and thus the cell efficiency improves. However, the increased power efficiency does not necessarily yield a higher quality product.

6. The EDIX cell used in this program still seems to be viable for the separation of salts, providing that the cation in the salt does not form an insoluble hydroxide.
7. An EDIX cell designed to improve diffusion and turbulence in the liquid streams may reduce the effects of polarization, thus reducing precipitation of metal hydroxides in the feed compartment. However, it is not known what affect the polarization caused by the mixed-bed resins has on the metals forming insoluble hydroxides.

4.0 EDIX THEORY

The fundamental principals that were believed to be applicable to the EDIX process are discussed below. The experimental results discussed in Section 5.0, however, do not support all of the theory that was used in the design of the program.

EDIX is a water/waste water treatment technology that combines ion-exchange resins and membranes with the conventional electrodialysis process. The ion-exchange resins can be either organic or inorganic and provide the removal mechanism for all ionic forms within a given feed stream. Electrodialysis is a voltage driven process which is used to separate and transport ions to their respective compartments for the separation and concentration of specific salts. The collective EDIX process can be used to split waste salt streams into acids and bases, or concentrate waste salts with substantial volume reduction. The use of ion-exchange resins provide substantial decontamination factors across the cell and can provide very pure effluent water.

Several unique features are provided by EDIX. The cell, resins, and membranes can be selected and configured to provide the optimum ion exchange and concentration factors. The process provides, in a single step, water purification/recycle, acid-base recovery, and waste volume reduction. The resins and membrane materials are regenerated continuously in the process which eliminates the need for regenerant chemicals. For selective recovery of acid and base applications, the ion-exchange resins can also be used to purify the recovered chemicals. The conventional ion exchange and electrodialysis processes are very efficient and cost effective processes for treating various waste and mixed waste streams. The EDIX technology, which combines proven conventional processes, appears both technically and economically competitive with other waste water processes including reverse osmosis, evaporators, and membrane treatment systems.

The basic EDIX cell unit is illustrated in Figure 4.1. This cell contains three compartments, each separated by a cation or anion permeable membrane. A cation membrane allows passage of cations but not anions. The opposite is true for anion membranes (A). The outer compartments contain a cathode (-) or an anode (+). The center compartment is the deionization section containing mixed-bed ion-exchange resins.

The anolyte compartment contains anion resins and the catholyte compartment contains cation resins. The basic cell unit can be arranged in parallel or in series with similar cell units to provide either a larger flow capacity or greater degree of water purification.

4.1 Process Chemistry

Figure 4.1. Electrodialysis-Ion Exchange (EDIX).

The process involves two basic mechanisms: ion exchange by resin, and ion migration induced by current flow. The operation of the cell is best described by assuming the feed stream contains sodium (Na^+) and nitrate ions (NO_3^-). The Na^+ ions exchange on the cation resin in the center compartment and displace hydronium (H_3O^+) ions. Under the induced current, the Na^+ ions migrate toward the cathode (-) through the porous resin particles, through the cation membrane, and into the catholyte compartment. In conjunction with the Na^+ transport, the hydroxyl ions (OH^-) are generated at the cathode from the electrolysis of water. The OH^- combines with the Na^+ to form a concentrated stream of sodium hydroxide (NaOH).

Similarly, the NO_3^- exchanges on the anion resin in the center mixed-bed compartment and then migrates with the induced current to the anolyte compartment. H_3O^+ generated from the electrolysis of water combines with the NO_3^- in the anolyte compartment to form nitric acid (HNO_3). If the solution residence time in the center compartment is sufficiently long, complete deionization occurs and all Na^+ and NO_3^- ions are removed from the feed. In this mode, the unit operates as a 3-in-1 process producing concentrated HNO_3 , NaOH , and deionized water.

The mixed-bed resins are constantly regenerated in place, as shown in Figure 4.2. In the feed compartment, Na^+ and NO_3^- exchange on their respective cation and anion resins. The dissociation of water molecules produces OH^- and H_3O^+ . These ions displace their similarly charged Na^+ and NO_3^- from the cation and anion resins. The Na^+ and NO_3^- ions migrate to their respective anolyte and catholyte compartments. This mechanism is a continuous electrolytical regeneration that precludes the need for regeneration by conventional acid and base techniques.

Another unique feature of this process is the ability to clean the system without disassembly. Cleaning, or purging in this instance, involves reversing the cell polarity similar to the process for conventional electrodialysis. Reversing cell polarity transports the contaminants along with Na^+ and NO_3^- into the feed compartment where they are flushed as unrecovered waste. This operation can be monitored automatically and does not require the operator's attention.

Figure 4.2. EDIX Cell Resin Regeneration.

If the goal is to produce high quality water and the composition of the anolyte and catholyte is unimportant, it may not be necessary to regenerate the resins. In treating waste streams containing low levels of radioactivity, it is the goal to have these contaminants transported to the catholyte compartment.

4.2 Previous Application

EDIX was initially developed to recover boric acid and lithium hydroxide from very dilute aqueous streams in pressurized water power plants. The technology was demonstrated in a pilot plant at Babcock & Wilcox in the 1970s, but it was never put into commercial operation. In 1992, *WASTREN* conducted a program for EG&G at the Rocky Flats Plant in which surrogate aqueous streams containing small quantities of NaNO_3 and HNO_3 were processed. The test results were encouraging in that over 90% of the sodium and nitrate were removed from the feed stream and concentration factors as high as 10 were achieved. The process was not optimized because resumption of weapons production at Rocky Flats was terminated and processing of this particular stream was not necessary. Therefore, the overall operating conditions were not established.

4.3 Conceptual Design of Equipment

The EDIX cell and associated support system are designed to collect and store highly concentrated chemicals. The EDIX system consists of a stack of cells, an electrical rectifier, holding tanks, pumps, flowmeters, pressure gauges, and conductivity meters. The EDIX system is configured in a three-loop flow configuration as shown in Figure 4.3. The alkaline and acid streams are circulated through individual tank systems to increase the concentration of the ions. The solutions are collected in the acid tank for the acid loop and the alkaline tank for the alkaline loop. These solutions are piped to their respective pumps and pumped through control valves and flowmeters to the cell stack. During continuous operation, a portion of these streams are bled off for further treatment and deionized water is added to reduce the ion concentrations in the tanks.

Figure 4.3. EDIX System—Three-Loop Flow Configuration.

After the solutions leave the cell stack, they discharge into their respective tanks.

Heat can build up in these loops from the pumps and the cell power. If necessary the heat can be removed with cooling coils submerged in the acid and alkaline tanks.

The feed solution is introduced into the EDIX system via the feed tank. When the cell is energized, the stream will become demineralized through the loss of anions through the anion membranes and the loss of cations through the cation membrane.

The EDIX system is equipped with instrumentation for regulating and monitoring the operating parameters. In-line conductivity and temperature probes are installed approximately two feed

downstream from the cell exit for each of the liquid streams. Flowmeters and control valves regulate the flow of solution to the cell stack. Pressure gauges monitor the pressures in the three compartments of the cell.

The AC to DC rectifier provides power to the stack of cells. The positive lead is connected to the anode and the negative lead is connected to the cathode. The cell current and cell voltage are recorded.

The stack assembly consists of electrodes and one or more cell pairs. A cell pair is made up of an anode, an anolyte compartment, an anion membrane, a feed compartment, a cation membrane, a catholyte compartment, and a cathode (or bipolar membrane). The cell is arranged in a stack unit assembled and compressed by end plates and tie-rods as shown in Figure 4.4.

The feed stream enters the feed compartment that is filled with a bed of mixed anion and cation ion-exchange resins. The ratio of the anion to cation resins can be varied, but normally it would be in the same ratio of the anions to cations that are in the feed stream. The ratio is based on the equivalent weights of the ions in the feed stream.

The catholyte compartment is filled with cation resins. Likewise, the anolyte compartment is filled with anion resins.

Figure 4.4. EDIX Cell Stack Configuration.

5.0 PROGRAM DESCRIPTION AND EQUIPMENT SELECTION

5.1 Recommended Testing Program

The initial objectives of this program are to determine if EDIX can be used

- (1) to produce water meeting discharge criteria from a variety of waste streams containing small quantities of nitrates, heavy metals, organics, sodium, and radioactive materials.
- (2) to produce two waste streams—one containing the anions, and the other containing the radioactive wastes, heavy metals, and other cations. The volume of these two waste streams is to be less than 1/10 of the volume of the feed stream.
- (3) to run two 100-hour tests on two different surrogate solutions.
- (4) to design a system for treating 30 gpm of one of the streams tested in Item 3.
- (5) to develop capital and operating cost estimates for treating 30 gpm of the feed used in Item 4.

The necessary equipment to conduct the program was not available at DOE or *WASTREN*.

Therefore, a system was designed, procured, assembled, and checked out before the actual testing began. *WASTREN* does not have a laboratory facility. Therefore, the laboratory portion of the program was conducted at the Colorado Minerals Research Institute in Golden, Colorado. The basic tasks involved in this program are summarized below. As a result of problems encountered during Phase 2 of Task 3, the experimental program was terminated by DOE. Therefore, Phase 3 of Task 3, and Tasks 4, 5, and 6 were not completed.

Task 1: Design of the EDIX System

For the laboratory experiments, a system having a capacity of at least one liter per minute was required. The system was required to process a variety of waste streams. The basic hardware was designed and selected for the expected conditions. *WASTREN* selected the membranes and resins that have the highest probability of performing as required.

Task 2: Procure, Assemble, and Check Out the System

After the equipment was received, it was assembled into a complete EDIX system. The system was checked out using deionized water and very dilute salt solutions to determine if there were leaks; determine the throughput of the system; and the ability of control flow, pressure drop, voltage, and other operational parameters.

Task 3: Conduct Bench Scale Tests

The experimental program is divided into three phases. Phase 1 was a series of about 10 tests determining the most suitable resins and membranes, voltages, and flow rates to transfer the anions and cations.

Phase 2 is a series of about 40 tests in which the composition of the feed stream is varied with the chief variables being levels of nitrate, sodium, and heavy metals. A proposed test matrix, that was recommended by *WASTREN* and approved by DOE, is shown in Table 5.1, and the desired water quality discharged from the EDIX cell is shown in Table 5.2.

These experiments are designed to

- (1) determine if the anions and cations are removed selectively or in bulk.
- (2) establish the conditions necessary to achieve the desired water quality.

- (3) determine what concentration factors can be achieved for both the cation and anion streams.
- (4) determine if precipitates are formed in the cation compartment because of the high pH, and determine what effect, if any, these cations have on overall system performance.
- (5) determine the operating conditions that are needed to preclude the deleterious effects of precipitates in cation cells.

Table 5.1. Experimental Program as Defined in the Proposal and Contract.

Nitrate Level ppm	Heavy Metal* Conc, ppm	Sodium Concentration, ppm		
		20	200	2000
30	20	X	X	X
30	200	X	X	X
30	2000	X	X	X
300	20	X	X	X
300	200	X	X	X
300	2000	X	X	X
3000	20	X	X	X
3000	200	X	X	X
3000	2000	X	X	X

* ppm chromium as $\text{CrO}_4^{=}$

**Table 5.2. Specification for Water Quality Discharge
from EDIX Cell.**

Composition of Product Stream	Water Quality Standard
Nitrate concentration, ppm	< 45
Chromium as Cr^{+3} , ppm	< 0.05
Chromium as $\text{CrO}_4^{=}$, ppm	< 20
Total Dissolved Solids, ppm	< 500
pH	6.0 - 8.5

Phase 3 is a series of 12 tests in which one of the solutions tested in Phase 2 is spiked with various levels of organics and/or depleted uranium to see if organics adversely affect the process and to

see if the uranium concentration in the discharge streams (product and anion streams) is low enough to label them as non-radioactive.

Task 4: 100-Hour Extended Runs

After the bench scale tests are completed, two 100-hour continuous campaigns on two different surrogate solutions will be conducted. These campaigns will determine if the performance of the cell changes with time, how frequently it will be necessary to regenerate the resins, and what corrosion problems are encountered.

Task 5: Recommend processes for Treating the Catholyte and Anolyte Streams

The results of the 100-hour runs will provide information on the composition of the anolyte and catholyte streams. *WASTREN* will suggest a means of processing these streams.

Task 6: Design of a 30 gpm System

Based on the results from the 100-hour extended runs, an EDIX system to process 30 gpm of feed solution will be designed. The design will not include any processing schemes for the anolyte and catholyte solutions generated in the EDIX system. The system designs will be used to develop capital and operating costs.

5.2 Tasks 1 and 2: Design and Procurement of the EDIX System

The design of the system used for the EG&G-sponsored project at Rocky Flats in 1992 provided *WASTREN* with valuable information that could be used in the design of the system for this project. The system used for the EG&G project was provided by Ionics and had a very low flow rate (< 100 cc/min) and had a number of design deficiencies.

Based on the EG&G project, a preliminary process flow diagram was developed that defined in general terms the equipment requirements. This preliminary flow diagram is shown in Figure 5.1. Based on discussions with suppliers of electrodialysis cells, it was decided that a nominal flow rate of one liter per minute would provide sufficient information to design a commercial unit of 30 gallons per minute or more.

The various pieces of equipment were therefore designed for the one liter per minute electrodialysis cell with the possibility of increasing the flow rate to 3 liters per minute. The system used on the EG&G project often required several hours to reach equilibrium. Thus, the tanks in this project were designed to have sufficient capacity to run for up to ten hours (3 liters per minute for 10 hours). The size of the tanks and piping are shown in Figure 5.2.

The composition of the feed solution could vary from fairly acidic to fairly basic. The acid (anolyte stream) loop and alkaline (catholyte stream) loop could be handling solutions up to 1 normal. The feed solution could be slightly basic to slightly acidic. Based on this information, most of the system was constructed of PVC including the various storage tanks and valves. The metallic components of the electrodialysis cell were made of stainless steel. The cooling coils were designed but not fabricated, as they were not needed.

5.2.1 Selection of the Electrodialysis Cell

The electrodialysis cell used for the EG&G project was provided by Ionics. *WASTREN* personnel were familiar with the Electrosynthesis Corporation, a known supplier of electrodialysis cells. The *Thomas Register* was reviewed for other possible suppliers of electrodialysis equipment. Although the proposal recommended a system having a capacity of up to 3 liters per minute, *WASTREN* was willing to purchase an off-the-shelf unit having an even larger capacity if such a system were suitable for the test programs, was readily available, and could be purchased with the funds allocated for the equipment.

Figure 5.1. Conceptual Design of EDIX System.

Figure 5.2. Equipment Size and Flow Diagram.

Requests for quotations were sent to six different suppliers of electrodialysis systems. Some of the suppliers did not provide units of 3 liters per minute, others did not provide units that were acceptable for an experimental program. For example, one supplier supplied a completely sealed unit; thus, changing resins and membranes was not possible.

Electrosynthesis was able to provide a modular unit satisfactory for the test program. The modular unit included flow meters, temperature gauges, pressure gauges, piping, valves, and the electrodialysis cell. The actual cell was manufactured by ElectroCell Systems, AB, of Täby, Sweden. Photographs of the cell, various components, power source, individual channels (spacers), etc., are shown in Figures 5.4 through 5.10. The modular unit, as provided, was equipped with Neosepta membranes as discussed in Section 5.2.2. These membranes were recommended by Electrosynthesis based on their knowledge of the proposed composition of the feed stream and the desired removal efficiencies.

The Electrosynthesis unit had three individual compartments for each cell pair, each cell pair having both a cathode and an anode. This is in contrast to other designs where bipolar membranes separated individual cells. A sketch of this unit is shown in Figure 5.3.

Figure 5.3. Schematic Diagram of the ElectroSyn Cell.

Figure 5.4. Modular Unit and Power Supply.

Figure 5.5. Modular Unit showing Gauges, Valves, and Piping.

Figure 5.6. EDIX Cell showing Inlet and Outlet Connections and Power Supply Hook-ups.

Figure 5.7. EDIX Cell showing Anolyte and Catholyte Outlets (top) and Feed Inlets (bottom).

Figure 5.8. EDIX Cell Disassembled showing One of the Electrodes.

Figure 5.9. EDIX Cell Disassembled showing an Inner Frame and O-Ring Seals.

Figure 5.10. Drawing of an Individual Spacer (either Anolyte or Catholyte).

5.2.2 Selection of Resins and Membranes

Discussions were held with the various suppliers of electrodialysis systems to determine what membranes might be suitable for the test solutions being considered in this test program. The *Thomas Register* was reviewed to locate suppliers of both electrodialysis membranes and ion-exchange resins. It was soon learned that very few companies made resins or electrodialysis membranes. Many of the companies contacted were sales agents for the manufacturers.

5.2.2.1 Selection of Resins

The program conducted for EG&G at Rocky Flats in 1992 used Dowex M-33 as the cation resin and Reillex HPQ as the anion resins. These were selected because of their ability to process a stream containing sodium nitrate and nitric acid. Discussions with personnel at Reilly and Dow indicated that no one had any knowledge of what resins to use with a solution containing chromium as chromate (CrO_4^-). These companies recommended that the following resins be evaluated in the test program.

Resin Type	First Choice	Second Choice
Anion	Dowex 21K	Reillex HPQ
Cation	Dowex G-26	Dowex M-33

Based on these recommendations, these four resins were selected for inclusion in the test program.

5.2.2.2 Selection of Membranes

The electrodialysis cell purchased from Electrosynthesis included the necessary membranes for processing the solution containing sodium, nitrate, and chromate. Electrosynthesis recommended the use of Tokuyama Soda Neosepta membranes, CMX as the catholyte membrane, and AMX as the anolyte membrane. The characteristics of these membranes are shown in Table 5.3.

Table 5.3. Characteristics of Neosepta Membranes.

Type	CMX Strongly Acidic Cation Permeable Na Form	AMX Strongly Basic Anion Permeable Cl Form
Electrical Resistance, ohm-cm ² ¹	2.5 - 3.6	2.5 - 3.3
Water Content ²	0.25 - 0.30	0.25 - 0.30
Exchange Capacity, meq/g	1.5 - 1.8	1.4 - 1.7
Thickness, mm	0.17 - 0.19	0.15 - 0.18

- Notes: 1. Equilibrated with 0.5 N NaCl solution at 25° C.
 2. Equilibrated with 0.5 N NaCl solution [g H₂O/g Na⁺ form dry membrane (or Cl⁻ form)].

Requests for quotes for other membranes for treating the reference solution were sent to several other suppliers that were listed in the *Thomas Register*. Only Electrosynthesis and Membranes International provided quotes for alternate membranes. *WASTREN* reviewed the information received and decided to purchase an alternate set of membranes from Membranes International. These "Ultrex" membranes had catalogue designations of CMI-7000 for the cation membranes and AMI-7001 for the anion membranes. The characteristics of these membranes are shown in Table 5.4.

Table 5.4. Characteristics of Ultrex Membranes.

Type	CMI-7000 Cation Membrane	AMI-7001 Anion Membrane
Electrical Resistance, ohm-cm ² ¹	6	8
Water Permeability, ml/hr/ft ² /5psi ²	< 10	< 10
Exchange Capacity, meq/g	1.3	1.1
Thickness, mm	0.43	0.43

- Notes: 1. Equilibrated with 1 N NaCl solution at 25° C.

6.0 EXPERIMENTAL PROGRAM

Thirty-seven bench scale test runs were completed in the experimental program using a combination of EDIX and electrodialysis systems. The various pieces of equipment were shipped to the Colorado Minerals Research Institute where the EDIX system was assembled. The test runs are divided into three categories. The first category consists of four tests that were completed to check out the system and to understand its operation (Task 2 is described in Section 5.0). The second category includes fourteen tests that were performed using sodium nitrate in the feed stream, and experimenting with different combinations of ion-exchange membranes and resins. The third category comprises several test runs using a feed solution containing sodium, nitrate, and a heavy metal. A summary of the experimental program which includes test conditions, results, observations, and conclusions for each test is provided in Appendix A. A summary describing the cell configuration and the targeted composition of the various streams is shown in Table 6.1.

6.1 Category 1: System Check-Out

This first category of tests was performed to check out the EDIX system and become familiar with the operation of the system. These four tests (Tests A through D) were performed between September 20, 1995, and September 27, 1995. Tokuyama Soda Neosepta AMX (anion) and CMX (cation) membranes were used for each of these tests. These were the membranes provided with the system. Tests A and B were run without ion-exchange resins in the cell to observe the performance of the system as an electrodialysis unit. Test C was performed with resins in the cell which were preconditioned with solutions approximating the concentration of the feed solution. This test was conducted with the rectifier off initially and then with the rectifier on in order to observe the effect resins had on the system performance. Test D was run using NaNO_3 feed containing chromium (as sodium chromate). The purpose of this test was to see if the chromium as chromate would be transferred into the anolyte compartments, or if it would be reduced and

the chromium transferred into the catholyte compartments. Dowex G-26 (cation) and 21K (anion) ion-exchange resins were used for these tests.

Several observations were made during these tests. During Test B, the current and feed flow rate were held constant while varying the flow rates of the anolyte and catholyte streams. The flow rates of the anolyte and catholyte streams appear to have very little, if any, effect on the conductivity (an indication of change in composition) of the product stream. It was also observed that when the current and flow rates were held constant, the voltage would initially fluctuate and then stabilize. When the voltage stabilizes, the system appears to be in equilibrium, indicating the maximum number ions that can be removed from the feed under a given condition. Before resins were introduced into the cell (Test C), they were soaked in a solution containing about 210 mg/L of sodium and 390 mg/L of nitrate. The total wet volume capacity of the anion and cation resins is approximately 51 g/L of sodium and 81 g/L of nitrate, respectively. Therefore, the resins could not have been loaded to capacity. The effect resin loading has on the function of the system is not clearly understood and is discussed further in this section.

Table 6.1. Summary of Test Conditions.

Test Number	Ion-Exchange Resins		Ion-Exchange Membranes	Target Composition of Ions (ppm)						
	Anion ¹	Cation ²		Feed			Anolyte		Catholyte	
				Na ⁺	NO ₃ ⁻	Cr	NO ₃ ⁻	Cr ⁺⁶	Na ⁺	Cr ⁺³
System Check-Out										
A	None	None	Neosepta	70	130	0	100	0	100	0
B	None	None	Neosepta	210	390	0	1000	0	1000	0
C	21K	G-26	Neosepta	210	390	0	≈1,000	0	≈1,000	0
D	21K	G-26	Neosepta	210	390	250 Cr ⁺⁶	≈1,000	0	≈1,000	0
Evaluation of Membrane and Resin Combinations										
1	21K	G-26	Neosepta	500	500	0	500	0	500	0
2	21K	G-26	Neosepta	100	100	0	5000	0	5000	0
3	21K	G-26	MI	210	390	0	1000	0	1000	0
4	21K	G-26	MI	210	390	0	1000	0	1000	0
5	21K	G-26	MI	500	500	0	500	0	500	0
6	21K	G-26	MI	100	100	0	1000	0	1000	0
7	HPQ	M-33	MI	500	500	0	500	0	500	0
8	None	None	MI	500	500	0	500	0	500	0
9	HPQ	M-33	MI	500	500	0	500	0	500	0
10	HPQ	M-33	Neosepta	500	500	0	500	0	500	0

Test Number	Ion-Exchange Resins		Ion-Exchange Membranes	Target Composition of Ions (ppm)						
	Anion ¹	Cation ²		Feed			Anolyte		Catholyte	
				Na ⁺	NO ₃ ⁻	Cr	NO ₃ ⁻	Cr ⁺⁶	Na ⁺	Cr ⁺³
11	None	None	Neosepta	500	500	0	500	0	500	0
12	21K	G-26	Neosepta	500	500	0	500	0	500	0
13	21K	G-26	Neosepta	500	500	0	500	0	500	0
14	21K	G-26	Neosepta	100	100	0	1000	0	1000	0
Testing With Sodium Chromate										
15	21K	G-26	MI	2000	3000	2000	30000	20000	20000	0
16	21K	G-26	MI	2000	3000	2000	30000	20000	20000	0
17	21K	G-26	MI	20	30	20	300	200	200	0
18	21K	G-26	MI	20	30	20	300	200	200	0
19	21K	G-26	MI	20	30	20	300	200	200	0
20	21K	G-26	MI	20	30	20	300	200	200	0
Testing Without Resins in Anolyte and Catholyte Compartments										
21	21K	G-26	MI	500	200	0	200	0	500	0
22	21K	G-26	MI	500	200	0	2000	0	5000	0
23	21K	G-26	MI	500	500	0	2000	0	5000	0
Testing With Chromium Nitrate										
24	21K	G-26	MI	20	750	20	7500	0	200	200
25	21K	G-26	MI	20	750	20	7500	0	500	200
26	21K	G-26	MI	20	750	20	7500	0	500	200
27	21K	G-26	MI	200	3000	200	30000	0	2000	2000
28	21K	G-26	MI	200	3000	200	30000	0	2000	2000
29	None	None	MI	200	3000	200	30000	0	2000	2000
Testing With Iron Nitrate										
30	None	None	MI	200	3000	200 Fe ⁺²	30000	0	2000	0 Fe ⁺²
31	None	None	MI	200	3000	200 Fe ⁺²	30000	0	30,000 NO ₃ ⁻	0 Fe ⁺²
32	None	None	MI	200	3000	200 Fe ⁺²	30000	0	30,000 NO ₃ ⁻	0 Fe ⁺²
33	21K	G-26	MI	200	3000	200 Fe ⁺²	30000	0	30,000 NO ₃ ⁻	0 Fe ⁺²

Notes: 1. Anion Resins: 21K is Dowex 21K and HPQ is Reillex HPQ
2. Cation Resins: G-26 is Dowex G-26 and M-33 is Dowex M-33

These screening tests did show that sodium, nitrate, and chromate could be removed from the feed solution, and that the chromate ion migrated into the anolyte compartments. The screening tests, however, gave qualitative results, not quantitative, as the purpose of the tests was to gain an understanding of the system.

During these four tests, it was determined that several system modifications were needed. Prior to assembling the EDIX cell with resins, it was noticed that the mesh size of the inlet and outlet

screens on the feed compartments allowed resin to pass through and exit the cell. Also, the inlet and outlet on the anion and cation compartments did not have screens. To solve this problem, fine mesh screens were heat-welded over the inlet and outlet openings.

Another problem was the in-line conductivity probes did not work. The probes were installed about two feet downstream from the cell exit. The reason the probes did not work was not determined. The failure apparently was caused by stray current from the EDIX cell following the solution discharging the cell. This problem was never solved so periodic samples were collected and a hand-held conductivity probe was used throughout the program.

The valves used to control the flow rate of the feed, anolyte, and catholyte streams were diaphragm-type valves and would not maintain constant flow rates. Needle valves were installed to provide the necessary degree of flow rate control.

6.2 Category 2: Evaluating Various Combinations of Ion-Exchange Resins and Membranes

This second category of tests was conducted to observe the effects of the many different variables on the performance of the system. These seventeen tests (Tests 1-14 and 21-23) were performed from October 4, 1995 to November 16, 1995, and from December 28, 1995 to January 1, 1996. For these tests, several concentrations of NaNO_3 were used in the feed stream. The anolyte and catholyte streams contained different concentrations of nitric acid and sodium hydroxide, respectively.

Several problems developed during this phase of the program that prevented the use of some of the test results for quantitative analyses. Only the analytical results from Tests 7, 8, and 9 were used for quantitative analyses. For Tests 3, 4, 5, and 6, the nitrate analyses were suspect because of problems with analytical testing. Because of problems with the Neosepta membranes (Tests 1, 2, 10, 11, 12, 13, and 14), discussed later in this report, quantitative data are suspect. The analytical results from Tests 21 and 22 appear to be lower than they should be because the initial cell resins were only slightly loaded. Results from Test 23 were not used because a valid

comparison could not be made with other tests because of different variables. Qualitative observations were made for some of these tests and are discussed in this section. Data collection logs and analytical results are presented in Appendix B for those tests that *WASTREN* believes provide accurate results.

6.2.1 Evaluation of Ion-Exchange Membranes

Two different types of anion- and cation-exchange membranes were to be evaluated: Tokuyama Soda Neosepta AMX (anion) and CMX (cation) membranes, and Membranes International (MI) CMI-7000 (cation) and AMI-7001 (anion) membranes.

Neosepta membranes were used in Tests 1 and 2. Following these two tests, the cell was disassembled. A tear along the sealing surface of one of the cation membranes was observed. The cause of the tear in the membrane was not determined and, because the cell was not disassembled between Tests 1 and 2, it was not known when the perforation occurred. This tear allowed feed solution to enter the catholyte compartment without being processed. Because of the leakage, the results of these tests were considered to be invalid.

The torn Neosepta cation membrane was replaced with a new one, and additional tests (Tests 10-14) were conducted. During these next several tests, the liquid levels in the catholyte and anolyte tanks rose slowly. Because the solutions in the anolyte and catholyte tanks recirculate continuously, the tank volumes should essentially remain constant. Material balances were calculated for these five tests which indicated there was an internal leak in the cell. Feed solution was flowing into the anolyte and catholyte compartments. These calculations showed that the leak into the anolyte circuit was more severe than the leak into the catholyte circuit.

To determine the cause of this leak, a bench-scale test was performed in which a Neosepta anion membrane from the previous test was placed over the mouth of a Buchner flask that was under a vacuum. Water was then poured onto the membrane surface. Results of this test showed that a substantial amount of water passed through the membrane. Although ion-exchange membranes

are not completely impermeable, the amount of water passing through the membrane indicated that there was some membrane deterioration. The three hour internal leak test performed during Test A of the system check-out showed no change in the liquid levels of the tanks. The chromium VI in the feed stream of Test D, also conducted during the system check-out, is believed to be the cause of the membrane deterioration. Subsequent testing using chromium VI appears to confirm this assumption. The effect of chromium VI on the system is discussed later in this report.

Tests 3-9 were run using the MI membranes. Beginning and ending tank liquid levels were recorded for most of these tests which indicated no internal leakage. A vacuum test was also performed on a new MI membrane. Results of this vacuum test demonstrated that water did not pass through the membrane.

Because of the problems that resulted with the Neosepta membranes, the test results for Tests 1, 2, and 10-14 are suspect. Therefore, a valid comparison could not be made between the Neosepta and MI membranes.

6.2.2 Evaluation of Ion-Exchange Resins

Two different types of anion- and cation-exchange resins were evaluated. The anion-exchange resins tested were the Dowex 21K and Reillex HPQ, and the cation-exchange resins tested were the Dowex G-26 and Dowex M-33.

One of the difficulties in combining electrodialysis and ion exchange was understanding resin loading in terms of total wet volume capacity (ion milliequivalents [MEQ] per unit volume of resin). With a one to one ratio of anion to cation resin in the feed compartments, the EDIX cell has a capacity of approximately 1.5 L each of anion and cation resins. This results in an anion resin capacity of 1875 MEQ and cation resin capacity of 3,000 MEQ, on average. The feed streams that were tested contained an average of 22 MEQ/L of sodium (Na^+) and 8 MEQ/L of nitrate (NO_3^-).

The as received anion-exchange resins are in the chloride (Cl^-) form, and the cation-exchange resins are in the hydrogen (H^+) form. If the resins are placed in the cell in this form, the Na^+ and NO_3^- from the feed stream would load onto the resins, displacing H^+ and Cl^- ions until the resins are exhausted. At this point, equilibrium is reached, and the solution conductivities should be equal in the feed stream and the product stream. Resin saturation can be achieved by soaking the resins in a solution containing the appropriate amount of sodium nitrate. Saturation can also be reached by reversing the polarity of the system, electrolytically transporting ions from the anolyte and catholyte to the feed.

Another variable that can effect equilibrium is power consumption. The point at which equilibrium is reached is different for each current setting, and appears to be affected by the resin loading. It appears that if the resins are only slightly loaded, substantial Na^+ and NO_3^- removal from the feed stream will occur. These results, however, do not indicate how well EDIX works because a large percentage of the Na^+ and NO_3^- ions are loading on the resins (displacing H^+ and Cl^- ions) and not migrating through the membranes by electro-transport. There does seem to be a point where the resins are partially loaded, although not to capacity, and the analytical results would suggest that equilibrium has been achieved.

The effect resin loading has on the operation of the EDIX system is not clearly understood. Because the resins were only slightly loaded in a few of the tests, it was apparent that electrodialysis and ion exchange were not working together effectively, and the analytical results of these tests were not used in any of the quantitative evaluations.

To evaluate which type of anion- and cation-exchange resins were more effective for sodium and nitrate removal, Tests 5 and 7 were compared. MI membranes were used in both tests. Test 5 used the Dowex 21K and G-26 resins, and the Reillex HPQ and Dowex M-33 resins were used in Test 7. For both tests, approximately equal ion concentrations were used in the feed, anolyte, and catholyte streams. The comparison of nitrate results is only qualitative because of problems with the analytical procedure.

Imprecise nitrate results from Test 5 were a result of using a colorimeter for direct nitrate readings. For direct readings, a precalculated diagram is used to give direct values in nitrogen content. This diagram assumes a linear curve between 0 and 30 ppm. It was later determined that the nitrogen reading was very dependent on the concentration and that by running different dilutions (still within the 0 to 30 ppm range) the values would be different. For subsequent tests (including Test 7), nitrate values were obtained by reading absorbance. A blank plus three standards were used to plot a curve showing absorbance versus nitrogen concentration.

When comparing Tests 5 and 7, the following observations were made.

- The Dowex 21K and G-26 resin combination provides lower resistance at every flow rate and current setting.
- Cell resistance decreased as current increased at every flow rate and current setting for the Dowex 21K and G-26 resin combination, indicating that there is no limiting current density over the current range tested (30 to 160 amps).
- At a flow rate of 1 L/min., the Reillex HPQ and Dowex M-33 resins showed an increase in resistance with increasing current, indicating that there is a limiting current density.
- Sodium ion transfer rates (ITR) are essentially the same for both resin types. However, the Reillex HPQ and Dowex M-33 resins appear to provide better nitrate ITR.

This evaluation does not clearly support a preferable resin combination. The Reillex HPQ and Dowex M-33 resins demonstrate better nitrate ITR. However, this observation may not be accurate because of the uncertainties in the nitrate results from Test 5.

The Reillex HPQ and Dowex M-33 resins seem to have a lower limiting current density than the Dowex 21K and G-26. The limiting current density, also called the "polarization point," can be determined by plotting cell resistance versus reciprocal current. The region in which a sharp increase in resistance occurs is the polarization point. In the case of Test 7, the resistance increases from the beginning of the test. Test 5, on the other hand, shows a continual decrease in resistance (Figure 6.1). The effects of the limiting current density may increase power consumption. Water dissociation occurs more readily when polarization occurs, and thus will decrease ion removal efficiency. Polarization can also cause problems with membrane fouling or poisoning.

6.2.3 Effect of Mixed-Bed Resin Ratio

To determine the effect of the ratio of mixed-bed ion-exchange resins, Tests 7 and 9 were compared. Both tests used MI membranes, Reillex HPQ anion-exchange resins, and Dowex M-33 cation-exchange resins. The ion concentrations in the feed for both tests were comparable as was the ratio of ion concentrations in the feed versus anolyte and catholyte tanks.

The ratio of cation to anion resin in the feed compartments was 1:1 for Test 7 and 2:1 for Test 9. The significance of this resin ratio can be seen when assessing ions removed and ITR. Figure 6.2 shows that nitrate ion removal is better with a 1:1 resin ratio, while sodium ion removal improves with the 2:1 resin ratio. Similarly, a higher nitrate ITR is achieved using a 1:1 resin ratio, and a higher sodium ITR is attained using a 2:1 resin ratio (See Figure 6.3).

The results of this comparison were not unexpected because the nitrate ion exchanges on the anion resins, and the sodium ion exchanges on the cation resins. With a larger amount of cation-exchange resin, one would expect to see better sodium ion removal and a declining nitrate ion removal. Presumably, a larger amount of anion resin would provide better nitrate removal.

Based on these findings, it seems that changing the ratio of mixed-bed resin may be a technique used in controlling the amount of ions removed from the feed stream.

Figure 6.1. Evaluation of Ion-Exchange Resin.

Figure 6.2. Effect of Mixed-Bed Resin Ratio—Current versus Ion Removal.

Figure 6.3. Effect of Mixed-Bed Resin Ratio—Current versus Ion Transfer Rate.

6.2.4 Effect of Operating without Ion-Exchange Resins in the Anolyte or Catholyte Compartments

Three tests (Tests 21-23) were run without ion-exchange resins in the anolyte or catholyte compartments to determine if the system's performance was affected by resins in these compartments. The analytical results from Tests 21 and 22 were not used because the resins were only slightly loaded during these two tests. As explained previously, if the resins are only slightly loaded, the results appear to be low when compared to tests in which the resins were known to be loaded near capacity. For Test 23, the resins were sufficiently loaded, and the results suggest that equilibrium had been reached. However, a valid quantitative evaluation could not be made because Test 23 used the Dowex 21K and G-26 resins, while the tests with reliable data (Tests 7 and 9) used the Reillex HPQ and Dowex M-33 resins.

Even though the effect of not having resins in the anolyte and catholyte was not determined, in theory, having ion-exchange resins in the anolyte and catholyte compartments will decrease the danger of scaling on the surface of the membranes (Belfort 1984).

6.2.5 Evaluation of the Ratio of Feed Concentration to Anolyte and Catholyte Concentrations

Because the anolyte and catholyte streams are closed-loop systems, ions in these streams continually become more concentrated in this experimental program. One of the parameters to be evaluated was the effect of the ratio of feed concentration to anolyte and catholyte concentrations. It was desirable to know whether ions could be electrolytically transferred from the feed stream to the anolyte and catholyte streams as the concentration gradient became larger.

In comparing results of several tests (especially Tests 2, 6, and 14), sodium and nitrate ions did migrate through the membranes from the feed stream into the anolyte and catholyte streams regardless of the ion concentration ratio. In fact, both sodium and nitrates were removed from the feed stream even when the concentration of the ions in the anolyte and catholyte streams were a factor of 50 over the respective ions in the feed stream (Test 2). It does appear, however, that

ITR decreases as the concentration gradient increases. Only qualitative results were obtained as some of these tests were run using Neosepta membranes that had been damaged by the chromate ion (Test D).

6.2.6 Effect of Flow Rate

Another variable examined was the flow rate into the feed compartment. To determine the effect of the feed stream flow rate, results from Tests 7 and 9 were evaluated. MI membranes and a 1:1 ratio of Reillex HPQ and Dowex M-33 resins were used for Test 7. Test 9 used MI membranes and a 2:1 ratio of Dowex M-33 (cation) and Reillex HPQ (anion) resins.

As previously discussed, flow rates for the anolyte and catholyte streams have essentially no effect on ion removal from the feed stream. In these tests, the flow rates in the anolyte and catholyte compartments were maintained at a rate necessary to maintain proper differential pressure across the membranes.

When comparing flow rates in Test 7, several observations were made.

If the flow rate is reduced from 2 L/min to 1 L/min,

- the sodium and nitrate ion removal increases by about 30% to 80% depending on the current (Figure 6.4).
- sodium ion concentrations in the product stream are reduced by factors of 2 to 3 and nitrate by 3 to 4 (Figure 6.5).
- sodium and nitrate ITR decrease by about 10% to 60% depending on current (Figure 6.6).

If the flow rate is reduced from 3 L/min to 1 L/min,

- sodium ion removal increases by almost 100%, and nitrate ion removal increases by about 65% (Figure 6.4).
- sodium ion concentrations decrease by 2 to 4 times and nitrate by 3 to 5 times (Figure 6.5).
- sodium ITR increases by about 50% to 80% and nitrate ITR by 80% to 120% depending on current (Figure 6.6).

As can be seen in Figure 6.4, the slopes of the various curves are not parallel, nor are the sodium ion removal curves linear. However, the nitrate ion removal curve at 1 L/min. is linear. In Figure 6.5 it can be seen that none of the slopes of the curves are parallel, and none are linear functions. Also, no ITR slopes are parallel, but at 2 L/min., the nitrate ITR is linear (Figure 6.6). The reason for these differences is not clear, but it could possibly be that equilibrium was not achieved in all tests.

Similar observations regarding ion removal percentage and product ion concentration reductions were made when comparing flow rates in Test 9. The ITR for Test 9, however, appeared different than Test 7. As was previously discussed, sodium ITR is much better than nitrate ITR in Test 9 because the mixed-bed resin ratio was 2:1 cation to anion. Another observation made when comparing different flow rates was that changes in flow rate have almost no effect on nitrate ITR for this test (Figure 6.7). This is probably because there is insufficient exchange capacity with the smaller amount of anion resin in the feed compartments.

Based on this analysis, the lowest flow rate (1 L/min.) gives the best results in terms of contaminants removed from the feed stream.

Figure 6.4. Effect of Feed Stream Flow Rate—Current versus Ion Removal.

Figure 6.5. Effect of Feed Stream Flow Rate—Current versus Product Concentration.

Figure 6.6. Effect of Feed Stream Flow Rate—Current versus Ion Transfer Rate.

Figure 6.7. Effect of Feed Stream Flow Rate—Current versus Ion Transfer Rate.

6.2.7 Comparison of Electrodialysis and EDIX

To evaluate the effect ion-exchange resins have on the performance of an electrodialysis cell, a test (Test 8) was performed without resin in any of the compartments. Test 8 was compared to Test 7. The feed stream concentration was approximately the same for both of these tests, as was the ratio of ions between the feed and anolyte/catholyte streams.

When comparing electrodialysis (Test 8) with EDIX (Test 7), the following observations were made. As shown in Figure 6.8,

- electrodialysis removes approximately 30% more sodium ions than EDIX at a flow rate of 1 L/min.
- EDIX removes approximately 85% more nitrate ions than electrodialysis at 1 L/min.

As shown in Table 6.2, EDIX consumes 15% to 30% less power, and provides 15% to 25% less ohmic resistance than conventional electrodialysis.

Table 6.2. Electrodialysis Versus EDIX.

Feed Flow Rate (L/min)	ELECTRODIALYSIS			EDIX		
	Current (amps)	Power (watts)	Resistance (ohms)	Current (amps)	Power (watts)	Resistance (ohms)
3	40	840	0.525	30	420	0.467
	50	1220	0.488	60	1320	0.367
	63	1827	0.46	79	2291	0.367
2	40	812	0.508	30	357	0.397
	50	1225	0.49	60	1410	0.392
	60	1740	0.483	78	2270	0.373
1	20	262	0.655	30	450	0.5
	40	940	0.5875	45	1089	0.538
	46	1334	0.63	55	1628	0.538

Figure 6.8. Electrodialysis versus EDIX.

It can be concluded that for streams containing nitrates, EDIX is much more effective than conventional electrodialysis systems. Although electrodialysis seems to provide better sodium removal, sodium is typically not a contaminant of concern since limits on sodium are substantially higher than nitrates.

6.3 Category 3: Testing Using Heavy Metals in the Feed Stream

This category of tests was conducted to observe the effects of a heavy metal in the system. These tests were performed from November 30, 1995 to December 20, 1995, and from January 15, 1996 to February 6, 1996. MI membranes were used for all of the heavy metal tests.

None of the tests in Category 2 used heavy metals (i.e., Cr^{+6}) because disposal of wastes containing the chromate ion is difficult and expensive. Neither Electrosynthesis, Colorado Minerals Research Institute (where the program was conducted), nor *WASTREN* suspected that the chromate ion in concentrations of less than 2,000 ppm would damage the membranes. Therefore, testing to select the resins and membranes did not include any chromate ions. The testing of the matrix included in the program and approved in the original contract began with Test 15. The planned test matrix is shown in Table 6.3. The approach was to run a few tests at the extremes of concentrations and some in the middle to determine if one could predict the ion removal rates at other concentrations. If this could be done, then the full matrix of 27 tests would not be needed.

Table 6.3. Approved Test Matrix.

Sodium (ppm)	Chromate (ppm)	Nitrates (ppm)		
		30	300	3000
18	20	X	X	X
18	200	X	X	X
18	2000	X	X	X
200	20	X	X	X
200	200	X	X	X
200	2000	X	X	X
2000	20	X	X	X

Sodium (ppm)	Chromate (ppm)	Nitrates (ppm)		
		30	300	3000
2000	200	X	X	X
2000	2000	X	X	X

6.3.1. Chromium VI

Tests were run using different concentrations of NaNO_3 and nitric acid containing chromium VI (as sodium chromate) as the feed stream. The chromate ion (CrO_4^{2-}) is negatively charged and migrates through the anion membranes into the anolyte compartments. For these tests, the anolyte stream was comprised of nitric acid containing the chromate ion (chromic acid).

The first of these tests (Tests 15 and 16) used approximately 2,000 mg/L Na^+ , 2,600 mg/L NO_3^- , and 200 mg/L chromium VI in the feed. The anolyte contained about 30,000 mg/L NO_3^- and 2,000 mg/L chromium VI, and the catholyte contained about 20,000 mg/L Na^+ . After a short time, it was evident that the level of the anolyte tank was rising. Upon disassembly of the cell, it was found that the anion membranes had deteriorated. The cation membranes looked normal, as did the resins. A bench-scale vacuum test was performed on a used MI anion membrane and a new MI anion membrane. While placed over a vacuum, water was poured onto the membrane surface. Results of this test showed that the new membrane did not let any water pass through, while the used membrane leaked substantially.

To determine if lower chromium and nitrate concentrations would solve the membrane deterioration problem, the next tests conducted (Tests 17-20) used only about 20 mg/L Na^+ , 30 mg/L NO_3^- , and 20 mg/L chromium VI in the feed. The anolyte contained about 300 mg/L NO_3^- and 200 mg/L chromium VI, and the catholyte contained about 200 mg/L Na^+ . An internal leak from the feed to the anolyte was again noted. The cell was disassembled, and the same characteristics were seen with the anion membranes as the previous tests. However, there was also a localized area in several of the mixed-bed compartments where the resins appeared "moldy." Examination of these resins under a microscope revealed that the resin beads were broken. An explanation for this occurrence was not determined.

Following these tests, another vacuum test was conducted. In this test, various concentrations of solutions of nitric acid, chromic acid, and a combination of the two were made up in graduated cylinders. Approximately 5 in.² pieces of MI anion membranes were soaked in the solutions overnight. The vacuum tests showed that membrane soaked in 30,000 mg/L nitric acid did not leak. Membrane soaked in 20,000 mg/L chromic acid also did not let water pass through. However, the membrane saturated with a combination of 200 mg/L chromic acid and 300 mg/L nitric acid leaked severely. It was concluded that the extremely corrosive environment achieved with the combination of nitric and chromic acids caused the deterioration and subsequent leakage of the membranes.

The effects from low levels of chromium as chromate were completely unexpected. However, when the membranes were destroyed by low concentrations of chromate in the presence of nitric acid, *WASTREN* recommended to the DOE that the program be redirected. In the new program, *WASTREN* recommended the use of chromium nitrate, $\text{Cr}(\text{NO}_3)_3$, as the source of chromium. The revised test program, approved by the DOE, is shown in Table 6.4. Chromium precipitates at a pH of about 3, thus the feed solution must contain sufficient nitric acid to maintain this low pH.

Table 6.4. Revised Test Program.

Sodium (ppm)	Chromium (ppm)	Nitrates (ppm)		
		750	1500	3000
20	20	✓	✓	✓
20	100	✓	✓	✓
20	200	✓	✓	✓
200	20	✓	✓	✓
200	100		✓	✓
200	200		✓	✓
400	20		✓	✓
400	100		✓	✓
400	200			✓

✓ Tests to run - assumes solutions will have a pH low enough to keep the chromium in solution.

6.3.2 Chromium III

Tests were run using different concentrations of NaNO_3 containing chromium III (as chromium nitrate) in the feed stream. The chromium ion (Cr^{3+}) is positively charged and should migrate through the cation membranes into the catholyte compartments if the EDIX system performs as predicted.

The first of these tests (Tests 24-26) used approximately 50 mg/L Na^+ , 700 mg/L NO_3^- , and 10 mg/L chromium III in the feed. The anolyte contained about 6,000 mg/L NO_3^- , and the catholyte contained about 500 mg/L Na^+ and 200 mg/L chromium III. Each of these tests used about the same ion concentrations but different flow rates. It was thought that the chromium would stay in solution at these feed concentrations, but the feed was cloudy which indicated that there was suspended chromium, presumably chromium hydroxide. In other words, a stream containing chromium hydroxide was introduced into the cell. The analytical results showed that chromium ion concentration in the catholyte fluctuated up and down (between 135 and 166 ppm) throughout the three tests. The sodium ion concentration in the catholyte increased throughout the tests indicating some level of ion migration through the membranes.

Subsequent tests (Tests 27 and 28) were conducted to determine if EDIX would remove higher chromium concentrations (making sure there was enough acidity to keep the chromium in solution). The feed contained approximately 200 mg/L Na^+ , 3,000 mg/L NO_3^- , and 200 mg/L chromium III. The anolyte contained about 30,000 mg/L NO_3^- , and the catholyte contained about 650 mg/L Na^+ and 140 mg/L chromium III. These two tests used about the same ion concentrations but different flow rates. During these tests, the chromium ion concentration in the catholyte fluctuated slightly (between 134 and 141 ppm) throughout the two tests. And, as was the case for the previous three tests, the sodium ion concentration increased in the catholyte throughout Tests 27 and 28.

The cell was not disassembled after Tests 24-26, but was disassembled following Tests 27 and 28. Disassembly of the cell revealed that the cation membranes on the feed side were plated with

chromium hydroxide, and the resins near the cation membrane were coated with the precipitate. The cation membrane on the catholyte side also contained the chromium hydroxide precipitate but was not plated as in the feed compartment. The precipitate was hung up in the plastic "grids" in the catholyte compartments. It was not known if the chromium precipitate on the feed side of the cation membranes was a result of the first tests in which the feed contained suspended chromium or if it was due to the formation of chromium hydroxide from polarization at the cation membrane. The chromium data did not reveal the level of ion transfer. The results may be skewed because of the chromium hydroxide caught in the plastic grids in the catholyte compartments.

The EDIX cell was reassembled with new membranes using approximately the same concentrations as Test 28. However, ion-exchange resins were not put into the cell. Thus, the cell operated as an electrodialysis unit. This was done to determine the effect of chromium without resins. Following this test (Test 29), the cell was again disassembled. Without resins, the chromium still plated out on the feed side of the cation membrane. In fact, the chromium plating on the membranes appeared to be even worse than before.

It was speculated that the chromium precipitate was a result of the limiting current density. The limiting current density is a function of fluid velocity in the flow path, stream temperature, and types of ions present. While most of the ions are transported through the membranes in electrodialysis by electrical transport, only about half of the ions arriving at the membrane surfaces from the bulk of the solution are carried by electrical transport. The remaining ions arrive at the membrane surfaces from the flowing stream as a result of diffusion and convection processes. As ions are electrically transferred from the feed compartments through the membranes, the concentration of ions in the feed compartments in the boundary layer (thin layer immediately adjacent to the membrane surfaces) becomes depleted. As the current density is increased, the boundary layer becomes so depleted in ions that the electrical resistance rises sharply. The increased resistance results in increased voltage which eventually exceeds the breakdown voltage for water molecules, causing them to dissociate, forming hydrogen (H^+) and hydroxyl (OH^-) ions. When such dissociation of water molecules occurs, the "polarization" point has been

reached. Polarization of cation membranes results in transfer of hydrogen ions into the catholyte compartments, increasing the pH in the boundary layer due to excess hydroxyl ions. This increase in pH causes the formation of chromium hydroxide precipitate (Baddour and others 1959).

6.3.3 Iron II

Because chromium forms a hydroxide at a pH of 2 to 3, it was decided to run a series of experiments using iron II. Iron II does not form an insoluble hydroxide until the pH of the solution is 5 or higher. Tests were run using a feed stream made up of NaNO_3 containing iron II (as iron nitrate). The iron ion (Fe^{2+}) is positively charged and migrates through the cation membranes into the catholyte compartments as does chromium III.

The first of these tests (Test 30) used approximately 200 mg/L Na^+ , 3,000 mg/L NO_3^- , and 200 mg/L iron II in the feed. The anolyte contained about 30,000 mg/L NO_3^- , and the catholyte contained about 2,000 mg/L Na^+ . Iron was not added to the catholyte at the start of this test. In addition, resins were not used in this test in order to see the affect of iron without resins as a variable. Analyses indicated that no iron migrated to the catholyte tank. Disassembly of the cell showed that the iron did form a hydroxide on the feed side of the cation membrane. The iron precipitate was much easier to remove from the membrane surface than was the chromium.

Because no iron migrated to the catholyte tank in the previous test, the catholyte solution was changed to nitric acid in Test 31 rather than the sodium hydroxide that had been used in all of the previous tests. This was a recommendation from two consultants who suggested that an acid in the catholyte compartments might inhibit the formation of the hydroxide on the feed side of the cation membranes. The feed and anolyte stream concentrations were the same as the previous test. The catholyte contained 30,000 mg/L NO_3^- . Again, iron was not added to the catholyte tank, and resins were not used for the test. Current was increased throughout the test from 10 to 60 amps. A sharp increase in resistance was noted between 30 and 40 amps which was possibly the polarization point. There was also an increase in resistance between 20 and 30 amps but not as severe. Analytical data showed that a small amount of iron did migrate to the catholyte tank.

However, the cell was disassembled and iron hydroxide had formed on the feed side of the cation membranes again. The voltage at 30 amps, which was the point where the sharp increase in resistance occurred, was 8 volts. If this was the polarization point, theoretically, a test run at about 8 volts would not form the iron hydroxide.

Therefore, Test 32 was run at a constant 8 volts for a two-hour period. This test used approximately 200 mg/L Na^+ , 3,000 mg/L NO_3^- , and 200 mg/L iron II in the feed. The anolyte contained about 30,000 mg/L NO_3^- , and the catholyte contained about 20,000 mg/L NO_3^- . The catholyte also contained about 92 mg/L Na^+ and 26 mg/L iron II which had migrated through the membranes from the last test. Resins were not used for this test. During this two-hour period, cell resistance increased from 0.333 to 0.381 ohms. Disassembly of the cell revealed an iron precipitate on the feed side of the cation membrane. The amount of iron on the cation membrane was small; however, the theory that the iron would not precipitate at 8 volts did not hold true.

The final test, Test 33, was also run at a constant 8 volts and approximately the same concentrations for the same two-hour period. However, a mixed-bed resin was used in the feed compartments for this test. As determined earlier in the experimental program, ion-exchange resins in the electrodialysis cell reduce the electrical resistance. Because of this, it was thought that the limiting current density would be higher and, therefore, polarization would occur at a voltage greater than 8 volts for this condition. During this test, much greater currents were achieved than in the previous test. When the cell was disassembled, iron hydroxide was again formed on the feed side of the cation membranes. In addition, the ion-exchange resins near the cation membrane were coated with the iron hydroxide precipitate.

6.4 Discussion and Technical Improvements

Although problems were experienced during the EDIX program, some valuable data were obtained. The amount of ions removed from the feed stream can be controlled by the ratio of anion to cation resin in the feed compartments. Another observation made was that ions can be transported across the membranes against an increasing concentration gradient between the feed

and anolyte/catholyte streams. The most significant observation was that EDIX is much more effective for the removal of nitrates than conventional electrodialysis.

The problems experienced with EDIX were poor cell efficiencies, membrane deterioration in a strong oxidizing environment, and precipitation of heavy metals as hydroxides in the feed compartments. There are many factors that contributed to these problems. The EDIX cell was configured with six cell pairs with only one cell pair between each electrode pair, resulting in very low cell efficiencies. Energy consumption can likely be reduced by use of a large number of cell pairs between each set of electrodes, using bipolar membranes to separate each cell pair.

The distance between each anion and cation membrane in the feed compartments was about 3/8 inches. The cell thickness should be kept small because it is the main cause of ohmic resistance in the cell pair (Belfort 1984).

As discussed previously, polarization occurs due to the depletion of ions in the boundary layers, and can cause the formation of metal hydroxides in the feed compartments. Polarization can also cause several other inefficiencies. The electrical resistance increases so that the energy consumption increases. The current efficiency decreases, since the transfer of hydrogen and hydroxyl ions is not the desired object of the operation. As the current density is increased into the region of polarization, each additional increment of current is less efficient in transferring ions into the anolyte and catholyte streams (Baddour 1959).

Care must be taken in the design to improve diffusion and turbulence in the liquid streams. Thickness of the boundary layer is a function of linear velocity of the solution in the cell and spacer geometry. An increase in ion flux by diffusion will reduce polarization, and can be achieved by decreasing the thickness of the boundary layer. This can be accomplished by raising the linear velocity of the solution in the cell (Belfort 1984). Decreasing the spacer thickness will increase the stream velocity, and should reduce the effects of polarization. Introducing ion-exchange resins into the electrodialysis cell was believed to promote turbulent flow.

It was demonstrated that ion-exchange resins introduced between the membranes decreased the resistance of the cell. Because there is no inhibition of diffusion rate on the resin surfaces, the limiting current density for resin-membrane electro-transport is much greater than for electrodialysis. Polarization, however, can take place on the surface of every ion-exchange resin bead in the cell in the same manner that it occurs on the membrane. However, if the anion-exchange resin is introduced next to the anion membrane and cation-exchange resin next to the cation membrane in the feed compartments, polarization near both membranes will decrease markedly and a higher electrical efficiency can be obtained (Belfort 1984).

7.0 REFERENCES

- Baddour, R. F., et. al. 1959. Adsorption, Dialysis, and Ion Exchange. *Chemical Engineering Progress Symposium Series*. vol. 55, no. 24.
- Belfort, G., ed. 1984. *Synthetic Membrane Processes: Fundamentals and Water Applications*. Academic Press, Inc.

APPENDIX A

Summary of each test, including test conditions,
results, and observations

TEST DATE	TEST CONDITIONS	RESULTS	OBSERVATIONS
9/20/95 Test A	Resins: None Membranes: Neosepta Starting Solution Concentrations Feed: 200 mg/L NaNO ₃ /150 gal Catholyte (Cat): 100 mg/L NaOH/30 gal Anolyte (An): 100 mg/L HNO ₃ /30 gal Product Destination: Recycled back to feed tank Run Time: 1 hr 45 min	At 37 volts and 19 amps (703 W), flowing at 1 to 2 L/min, the feed was reduced from 600 to 500 μ S	Results from this test are inconclusive. Because the operation of the rectifier was unfamiliar, insufficient power was applied on the cell to see any substantial results. Also only conductivity readings were taken, because analytical capabilities were not in place yet. Qualitatively, the test did show that the cell was reducing the feed conductivity. Also, the conductivity meter used for Tests A-D shows 0 μ S when < 50 μ S. A more accurate conductivity meter was used for the other tests.
9/21/95 Test B	Resins: None Membranes: Neosepta Starting Solution Concentrations Feed: 600 mg/L NaNO ₃ /150 gal Cat: 1000 mg/L NaOH/30 gal An: 1000 mg/L HNO ₃ /30 gal Product Destination: Recycled back to the feed tank Run Time: 4 hrs	Initial conductivity of the feed was 1700 μ S. At 2.0 L/min and 69 A/54.7V (3774 W) product was 500 μ S. At 0.5 L/min and 30 A/ approx. 40 V (1200 W) product was 100-200 μ S. Ran test holding power and feed flow rate constant at 40 A/35 V and 1.5 L/min respectively, while varying the flow rates of the anolyte and catholyte from 0.5 to 2.5 L/min. The product was consistently between 600 and 700 μ S.	Again, results are only qualitative, because only conductivity measurements were taken. The test did show that the reduction of the feed conductivity was approaching the conductivity of the labs DI system of less than 100 μ S. Also, the conductivities of the anolyte and catholyte continually increased at each flow rate as current increased. This test also showed that varying the flow rate of the anolyte and catholyte streams has little effect, if any, on the conductivity of the product. It was also observed that as current was held constant at each increment, the voltage steadily increased and then stabilized. This indicates the cell is functioning correctly, since a decrease in conductivity of the feed would cause greater resistance in the cell, thus causing the voltage to rise. When the voltage stabilizes, the cell is apparently in equilibrium, where the number of ions leaving the feed compartment is equal to number of ions exiting the cell from the electrode compartments. This point is probably the maximum number ions that can be removed from the system for that amperage.

TEST DATE	TEST CONDITIONS	RESULTS	OBSERVATIONS
9/26/95 Test C	<p>Resins: Dow G-26(cat) and Dow 21K(an) and a 1:1 ratio in the feed compartment (conditioned with solutions approximating the concentrations of the test solutions).</p> <p>Membranes: Neosepta</p> <p>Starting Solution Concentrations - used ending solutions from the 9-21-95 test</p> <p>Feed: <600 mg/L NaNO₃</p> <p>Cat: >1000 mg/L NaOH</p> <p>An: >1000 mg/L HNO₃</p> <p>Product Destination: recycled back to the feed tank</p> <p>Feed Flow Rate: 2.2 L/min and 1 L/min</p> <p>Run Time: 3 hrs 30 min</p>	<p>Initial conductivity of the feed was 1200 μS. Running with ion-exchange (IX) only at between 1.0 and 3.0 L/min for approximately one hour the product varied from 1200 to 1400 μS. With the rectifier on and flowing at 2.2 L/min, the product conductivity readings were:</p> <p>450 μS at 10 amps 200 μS at 20 and 30 amps 100 μS at 40 and 60 amps 0 μS at 100 A</p> <p>Changed the flow rate to 1 L/min and conductivity was 0 μS at 5 and 10 amps.</p>	<p>Again only conductivity measurements were taken so results are qualitative. When the rectifier was turned on, immediate drops in product conductivity were noted, and the conductivities of the anolyte and catholyte continually increased at each flow rate as current increased. After the maximum power to the cell was applied (100 A, 28.2 V), conductivity of the product remained below 100μS as power was gradually reduced to zero. This indicates that we had stripped the resins and the cell was basically operating as an IX unit. Future tests will need to take this occurrence into consideration. Tests should start out at low current settings and high flow rates, and move towards high power and low flows.</p> <p>I believe conductivity of feed compared to product w/o rectifier on is a good indication of whether the resins are loaded to capacity. After running IX for 1 hr (120 L), conductivity seemed stable so it appeared resins were loaded. However, if resins were conditioned in solutions approximating our feed solution, I don't think 120 L is enough to load them. If this is true, our conductivity readings with power applied are not accurate.</p>
9/27/95 Test D	<p>Resins: Dow G-26(cat) and Dow 21K(an) and a 1:1 ratio in the feed compartment</p> <p>Membranes: Neosepta</p> <p>Starting Solution Concentrations - used ending solutions from 9-26-95 test plus 250 mg/L Cr(VI) as CrO₃ (forms chromic acid when added to water with a negatively charged chromate ion CrO₄⁻²).</p> <p>Feed: 1000mg/L NaNO₃, 250 mg/L Cr(VI)/ 150 gal</p> <p>Cat: 600 mg/L NaNO₃/30 gal</p> <p>An: 1000 mg/L HNO₃/30 gal</p> <p>Product Destination: recycled back to the feed tank</p> <p>Feed Flow Rate: 1 L/min</p> <p>Run Time: 2 hrs 30 min</p>	<p>Initial conductivity of the feed was 3000 μS. Began test with the rectifier off. Flowed at 1.0 L/min for approx. 40 minutes and the conductivity of the product went from 1900 to 2000 μS. With the rectifier on and flowing at 1.0 L/min the product conductivity was 700 μS at 10 amps, 200 at 40 amps and 100 at 60, 80, and 100 Amps. Chromium content in product at this point was found to be 4.4 mg/L. Conductivities of the anolyte and catholyte continually increased as current increased.</p>	<p>Chemical analysis was only done for chrome (total Cr by AA). It was evident that during the initial portion of test when the rectifier was off, the resins were not completely loaded. The reduction in conductivity at this time was probably due to the loading of Cr on to the resin. When the rectifier was turned on, a reduction in conductivity of the product was noticed immediately. The ending concentration of the anolyte tank was only 1 mg/L, indicating that the majority of the Cr taken out of the feed was taken up by anion resins in the feed and/or anolyte compartment.</p> <p>With a 1:1 ratio of mixed bed resin in the feed compartments, the capacity of the anion resin is 113 g of the chromate ion or 121 g of nitrate. The chromate has a higher affinity for the resin than the nitrate because of the higher valence of chromate. The amount of chromium processed through the cell was about 37 g so the resins were no where near capacity. Therefore, the 4.4 ppm Cr(VI) in the product is not an accurate assessment of the ability of EDIX to remove chromium.</p>

TEST DATE	TEST CONDITIONS	RESULTS	OBSERVATIONS
10/4/95 Test 1	<p>Resins: Feed Compartments — Dow G-26(cat) and Dow 21K(an) at a 1:1 ratio (conditioned in 285 g HNO₃ and 126 g NaOH) Anolyte Compartments — Dow 21K (conditioned in 285 g HNO₃) Catholyte Compartments — Dow G-26 (conditioned in 126 g NaOH) Membranes: Neosepta Starting Solution Concentrations Feed: 538 mg/L Na⁺, 559 mg/L NO₃⁻/867 L Cat: 219 mg/L Na⁺/124 L An: 738 mg/L NO₃⁻/133 L Product Destination: recycled back to the feed tank Feed Flow Rate: 4, 3, 2, and 1 L/min Run Time: 5 hrs</p>	<p><u>Flow Rate=4 L/min:</u> Current = 5, 10, and 20 amps resulted in product concentrations of 400-490 mg/L Na and 441-536 mg/L NO₃⁻. Resistance started at 0.62 and decreased to 0.24 as current was increased.</p> <p><u>Flow Rate=3 L/min:</u> Current = 5, 10, and 20 amps resulted in product concentrations of 380-480 mg/L Na and 482-513 mg/L NO₃⁻. Resistance started at 0.64 and decreased to 0.25 as current was increased.</p> <p><u>Flow Rate=2 L/min:</u> Current = 5, 10, and 20 amps resulted in product concentrations of 350-460 mg/L Na and 485-508 mg/L NO₃⁻. Resistance started at 0.66 and decreased to 0.27 as current was increased.</p> <p><u>Flow Rate=1 L/min:</u> Current = 5, 10, 20, 40, 80, 100, and 120 amps resulted in product concentrations of 70-400 mg/L Na and 151-470 mg/L NO₃⁻. Resistance started at 0.68 and decreased to 0.14 as current was increased; no dramatic increase in resistance implies no polarization.</p>	<p>Cell efficiency is 45% at 5 amps and drops to 28% at 20 amps and 4L/min. Cell efficiency is 41% at 5 amps and drops to 28% at 20 amps and 3L/min. Cell efficiency is 41% at 5 amps and drops to 22% at 20 amps and 2L/min. Cell efficiency is 33% at 5 amps and drops to 4% at 120 amps and 1L/min. Ion transfer rates for both Na and NO₃ decrease with increasing amperage at each flow rate. Na removal was 87% and NO₃ was 74% at 1 L/min and 120 amps. Water Quality Standards (WQS) were not met at any current.</p> <p>See OBSERVATIONS for Test 2 below.</p>
10/5/95 Test 2	<p>Resins: Dow G-26(cat) and Dow 21K(an) and a 1:1 ratio in the feed compartment Membranes: Neosepta Starting Solution Concentrations (by analysis) Feed: 46 mg/L Na⁺, 127 mg/L NO₃⁻/336 gal Cat: 2166 mg/L Na⁺/31.5 gal An: 6870 mg/L NO₃⁻/34.8 gal Product Destination: recycled back to the feed tank Feed Flow Rate: 1 L/min Run Time: 1 hr 25 min</p>	<p>Cell resistance decreased at each current from 0.63 to 0.15. Only one product sample was taken with rectifier on which was at 120 amps. Concentrations were 25 mg/L Na and 38 mg/L NO₃⁻. Another product sample was taken 4 minutes after rectifier was shut off; results were 32 mg/L Na and 24 mg/L NO₃⁻.</p>	<p>Because there was no increase in cell resistance throughout the test, it appears that for this current range, there is no limiting current density at which polarization occurs. Na removal was 46% and NO₃ removal was 53% at 120 amps. However, the cell efficiency at 120 amps was only 0.2%. Resins were not preconditioned so I am not sure if they were loaded to capacity. Feed concentrations were much lower than the previous test (Test 1) and WQS were still not achieved. WQS were achieved with power off at the end of the test, but this is because the resins were stripped during the test, and with the rectifier off, the resins began loading again.</p> <p>Upon disassembly of the cell, a crack was found along the sealing surface of one of the cation membranes. Because the cell was not disassembled between Tests 1 and 2, the crack may have also been there during Test 1.</p>

TEST DATE	TEST CONDITIONS	RESULTS	OBSERVATIONS
10/12/95 Test 3	Resins: Dow G-26(cat) and Dow 21K(an) at a 1:1 ratio in the feed compartment Membranes: MI Starting Solution Concentrations (by analysis) Feed: 147 mg/L Na ⁺ , 617 mg/L NO ₃ ⁻ Cat: 938 mg/L Na ⁺ An: 2215 mg/L NO ₃ ⁻ Product Destination: recycled back to the feed tank Feed Flow Rate: 2 L/min Run Time: 1 hr 40 min	Current was varied from 10 to 80 amps and conductivity of the product decreased from 1050 μ S to 134 μ S. The largest decrease was from 10 to 20 amps when the conductivity went from 675 to 351 μ S, and at 60 and 80 amps the conductivity was constant at 134 μ S. The only sample taken of the product with the rectifier on was taken at 80 amps which resulted in concentrations of 25 mg/L Na and 97 mg/L NO ₃ .	The conductivities of the anolyte and catholyte continually increased throughout the test which indicates some ion transfer, however, only qualitative. There was no increase in cell resistance throughout the test, it appears that for this current range, there is no limiting current density. Na removal at 80 amps was 83 % and NO ₃ removal was 91 %. However, the cell efficiency at 80 amps was only 10.9 %. WQS were not achieved.
10/16/95 Test 4	Resins: Dow G-26(cat) and Dow 21K(an) at a 1:1 ratio in the feed compartment Membranes: MI Starting Solution Concentrations (by analysis) - used ending solutions from 10/12/95 test Feed: 159 mg/L Na ⁺ , 365 mg/L NO ₃ ⁻ Cat: 1110 mg/L Na ⁺ An: 2126 mg/L NO ₃ ⁻ Product Destination: recycled back to the feed tank Feed Flow Rate: 1 L/min Run Time: 1 hr 35 min	At 40 amps, product concentrations were 25 mg/L Na and 45 mg/L NO ₃ . At 84 amps, product concentrations were 24 mg/L Na and 27 mg/L NO ₃ . At 100 amps, product concentrations were 14 mg/L Na and 10 mg/L NO ₃ . Cell resistance continually decreased as current increased. Ion transfer rates for both ions decreased as current increased.	Cell efficiency was poor and also decreased during test; 3.9 % at 40 amps, 1.9 % at 84 amps, and 1.7 % at 100 amps. WQS were met at each amperage. It doesn't appear as if the resins were loaded to capacity at the start of the test, and the results may not be accurate.

TEST DATE	TEST CONDITIONS	RESULTS	OBSERVATIONS
10/18/95 Test 5	<p>Resins: Dow G-26(cat) and Dow 21K(an) at a 1:1 ratio in the feed compartment</p> <p>Membranes: MI</p> <p>Starting Solution Concentrations (by analysis)</p> <p>Feed: 473 mg/L Na⁺, 341 mg/L NO₃⁻</p> <p>Cat: 420 mg/L Na⁺</p> <p>An: 368 mg/L NO₃⁻</p> <p>Product Destination: to product tank</p> <p>Feed Flow Rate: 4, 3, 2, and 1 L/min</p> <p>Run Time: 7 hr 55 min</p>	<p><u>4.0 L/min:</u> Current varied from 30 to 110 amps, resulted in concentrations of 328-163 mg/L Na and 255-153 mg/L NO₃. Resistance decreased from 0.25 to 0.21 as current increased. Na ion transfer rate decreased from 1.4E-5 to 7.6E-6 meq/amp*sec as current increased. NO₃ ion transfer rate decreased from 30 to 50 amps but then increased at 70, 90, and 110 amps. Cell efficiency decreased from 22.5% to 12.2% as current increased.</p> <p><u>3.0 L/min:</u> Current varied from 30 to 110 amps, resulted in concentrations of 322-128 mg/L Na and 277-142 mg/L NO₃. Resistance decreased from 0.26 to 0.22 as current increased. Na ion transfer rate decreased from 1E-5 to 6.8E-6 meq/amp*sec as current increased. NO₃ ion transfer rate fluctuated throughout test. Cell efficiency decreased from 16.4% to 11% as current increased.</p> <p><u>2.0 L/min:</u> Current varied from 30 to 110 amps, resulted in concentrations of 293-58 mg/L Na and 288-13 mg/L NO₃. Resistance decreased from >0.29 to 0.23 as current increased. Na ion transfer rate decreased from 9.13E-6 to 5.47E-6 meq/amp*sec as current increased. NO₃ ion transfer rate increased from 30 to 70 amps but then decreased at 90 and 110 amps. Cell efficiency decreased from 14.7% to 8.8% as current increased.</p> <p><u>1.0 L/min:</u> Current varied from 30 to 160 amps, resulted in concentrations of 156-34 mg/L Na and 135-2 mg/L NO₃. Resistance decreased from >0.36 to 0.18 as current increased. Na ion transfer rate decreased from 7.66E-6 to 1.99E-6 meq/amp*sec as current increased. NO₃ ion transfer rate decreased from 1.85E-6 to 5.7E-7 meq/amp*sec as current increased. Cell efficiency decreased from 12.3% to 3.2% as current increased.</p>	<p>As current increased, there was no increase in resistance at any flow rate; no polarization point noted. Na ion transfer rates decreased as current increased at all flow rates, but NO₃ ion transfer rates fluctuated except at 1.0 L/min where they also decreased with increasing current. Cell efficiency decreased at each flow rate and also decreased with increasing current. WQS were not met at 3 and 4 L/min. WQS were met at 2 and 1 L/min. Na removal at 160 amps and 1 L/min was 93% and NO₃ was >99%. NO₃ is at 45 mg/L at around 95 amps at 2 L/min. At 1 L/min, NO₃ reaches 45 mg/L at about 50 amps but then increases at 70 amps before reaching 45 mg/L again about 80 amps. Efficiency at these points is <10% at 2 L/min, and 9% (50 amps) and ~6% (80 amps) at 1 L/min.</p>

TEST DATE	TEST CONDITIONS	RESULTS	OBSERVATIONS
10/20/95 Test 6	<p>Resins: Dow G-26(cat) and Dow 21K(an) at a 1:1 ratio in the feed compartment</p> <p>Membranes: MI</p> <p>Starting Solution Concentrations (by analysis)</p> <p>Feed: 95 mg/L Na⁺, 121 mg/L NO₃⁻</p> <p>Cat: 975 mg/L Na⁺</p> <p>An: 742 mg/L NO₃⁻</p> <p>Product Destination: to product tank</p> <p>Feed Flow Rate: 3, 2, and 1 L/min</p> <p>Run Time: 2 hr 50 min</p>	<p><u>3.0 L/min:</u> Current varied from 20 to 56 amps, resulted in concentrations of 26-18 mg/L Na and 9.3-15 mg/L NO₃. Resistance decreased from 0.71 to 0.53 as current increased. Na ion transfer rate decreased from 7.5E-5 to 2.8E-6 meq/amp*sec as current increased. NO₃ ion transfer rate fluctuated throughout test. Cell efficiency decreased from 12.1% to 4.5% as current increased.</p> <p><u>2.0 L/min:</u> Current varied from 20 to 59 amps, resulted in concentrations of 10-16 mg/L Na and 1.8-5.8 mg/L NO₃. Resistance decreased from 0.83 to 0.5 as current increased. Na ion transfer rate decreased from 6.16E-6 to 1.94E-6 meq/amp*sec as current increased. NO₃ ion transfer rate decreased from 1.94E-6 to 6.21E-7 meq/amp*sec as current increased. Cell efficiency decreased from 9.9% to 3.1% as current increased.</p> <p><u>1.0 L/min:</u> Current varied from 20 to 68 amps, resulted in concentrations of 6-14 mg/L Na and 1-4 mg/L NO₃. Resistance decreased from 0.88 to 0.43 as current increased. Na ion transfer rate decreased from 3.22E-6 to 8.63E-7 meq/amp*sec as current increased. NO₃ ion transfer rate decreased from 9.81E-7 to 2.84E-7 meq/amp*sec as current increased. Cell efficiency decreased from 5.2% to 1.4% as current increased.</p>	<p>As current increased, there was no increase in resistance at any flow rate; no polarization point noted. Na and NO₃ ion transfer rates decreased as current increased at all flow rates, except at 3 L/min where the NO₃ ion transfer rate fluctuated during test. Cell efficiency decreased at each flow rate and also decreased with increasing current. WQS were met at every flow rate as well as every current. Typically however, the lowest ion concentrations were at the lowest current and increased as current increased which is not like previous tests.</p> <p>Even though the initial feed concentrations were fairly low, the WQS were achieved almost immediately at the lowest current. I believe this is an indication that our resins were not loaded to capacity, and because of the dilute feed solution, the resins never were loaded. Therefore, it is likely that these results are inaccurate.</p>

TEST DATE	TEST CONDITIONS	RESULTS	OBSERVATIONS
10/26/95 Test 7	<p>Resins: Dowex M-33-H(cat) and Reillex HPQ(an) with a 1:1 ratio in the feed compartment</p> <p>Membranes: MI</p> <p>Starting Solution Concentrations (by analysis)</p> <p>Feed: 458 mg/L Na⁺, 682 mg/L NO₃⁻</p> <p>Cat: 450 mg/L Na⁺</p> <p>An: 647 mg/L NO₃⁻</p> <p>Product Destination: to product tank</p> <p>Feed Flow Rate: 3, 2, and 1 L/min</p> <p>Run Time: 2 hr 50 min</p>	<p><u>3.0 L/min:</u> Current varied from 30 to 79 amps, resulted in concentrations of 175-307 mg/L Na and 244-280 mg/L NO₃. Resistance decreased from 0.57 to 0.37 as current increased. Na ion transfer rate decreased from 1.96E-5 to 7.72E-6 meq/amp*sec as current increased from 30 to 60 amps but increased to 8.05E-6 at 79 amps. NO₃ ion transfer rate decreased from 1.4E-5 to 5.89E-6 meq/amp*sec as current increased. Cell efficiency decreased from 31.5% to 12.4% as current increased from 30 to 60 amps but increased slightly at 79 amps to 12.9%.</p> <p><u>2.0 L/min:</u> Current varied from 30 to 78 amps, resulted in concentrations of 105-290 mg/L Na and 134-374 mg/L NO₃. Resistance decreased from 0.40 to 0.37 as current increased. Na ion transfer rate decreased from 7.71E-6 to 6.23E-6 meq/amp*sec as current increased. NO₃ ion transfer rate decreased from 7.29E-6 to 4.37E-6 meq/amp*sec as current increased. Cell efficiency decreased from 12.4% to 10% as current increased.</p> <p><u>1.0 L/min:</u> Current varied from 30 to 55 amps, resulted in concentrations of 65-160 mg/L Na and 59-122 mg/L NO₃. Resistance <u>increased</u> from 0.5 to 0.538 as current increased. Na ion transfer rate decreased from 7.2E-6 to 4.6E-6 meq/amp*sec as current increased. NO₃ ion transfer rate decreased from 6.09E-6 to 3.24E-6 meq/amp*sec as current increased. Cell efficiency decreased from 11.6% to 7.4% as current increased.</p>	<p>As current increased, there was an increase in resistance at 1 L/min; however, it is not dramatic and may not be the polarization point. Na removal at 55 amps and 1 L/min was 86% and NO₃ was 93%. Cell efficiency decreased at each flow rate. Although ion removal was good, WQS were not met at any flow rate.</p>

TEST DATE	TEST CONDITIONS	RESULTS	OBSERVATIONS
<p>10/27/95</p> <p>Test 8</p>	<p>Resins: none</p> <p>Membranes: MI</p> <p>Starting Solution Concentrations (by analysis)</p> <p>Feed: 503 mg/L Na⁺, 562 mg/L NO₃</p> <p>Cat: 520 mg/L Na⁺</p> <p>An: 479 mg/L NO₃</p> <p>Product Destination: to product tank</p> <p>Feed Flow Rate: 3, 2, and 1 L/min</p> <p>Run Time: 2 hr 30 min</p>	<p>3.0 L/min: Current varied from 20 to 63 amps, resulted in concentrations of 465-210 mg/L Na and 605-290 mg/L NO₃. Resistance decreased from 1.32 to 0.46 as current increased. Na ion transfer rate increased from 4.13E-6 to 1.09E-5 meq/amp*sec as current increased from 20 to 40 amps, decreased slightly at 50 amps to 9.96E-6, and increased to 1.01E-5 at 63 amps. NO₃ ion transfer rate increased from 4.84E-7 to 4.97E-6 meq/amp*sec as current increased from 20 to 50 amps but decreased at 63 amps to 4.19E-6. Cell efficiency increased from 6.6% to 17.6% as current increased from 20 to 40 amps, decreased to 16% at 50 amps, and increased to 16.3% at 63 amps.</p> <p>2.0 L/min: Current varied from 20 to 60 amps, resulted in concentrations of 111-350 mg/L Na and 278-333 mg/L NO₃. Resistance decreased from 0.65 to 0.48 as current increased. Na ion transfer rate decreased from 1.11E-5 to 9.22E-6 meq/amp*sec as current increased from 20 to 50 amps and increased to 9.47E-6 at 60 amps. NO₃ ion transfer rate decreased from 8.12E-6 to 3.04E-6 meq/amp*sec as current increased from 20 to 50 amps and increased to 4.14E-6 at 60 amps. Cell efficiency decreased from 17.8% to 14.8% as current increased from 20 to 50 amps and increased to 15.2% at 60 amps.</p> <p>1.0 L/min: Current varied from 20 to 47 amps, resulted in concentrations of 244-21 mg/L Na and 309-179 mg/L NO₃. Resistance decreased from 0.655 to 0.588 as current increased from 20 to 40 amps, but increased to 0.63 at 46 amps, and then decreased to 0.617 at 47 amps. Na ion transfer rate decreased from 9.38E-6 to 7.37E-6 meq/amp*sec as current increased. NO₃ ion transfer rate decreased from 4.14E-6 to 2.44E-6 meq/amp*sec as current increased. Cell efficiency decreased from 15.1% to 3.9% as current increased.</p>	<p>As current increased from 40 to 46 amps, there was an increase in resistance at 1 L/min. When plotting resistance as a function of inverse current, it appears that polarization occurs around 40 amps at 1 L/min. Na removal at 46 amps and 1 L/min was 96% and NO₃ was 71%. WQS were not met at any flow rate, but were not expected to w/o resins.</p>

TEST DATE	TEST CONDITIONS	RESULTS	OBSERVATIONS
11/8/95 Test 10	Resins: Dowex M-33-H(cat) and Reillex HPQ(an) with a 1:1 ratio in the feed compartment Membranes: Neosepta Starting Solution Concentrations (by analysis) Feed: 480 mg/L Na ⁺ , 713 mg/L NO ₃ ⁻ Cat: 530 mg/L Na ⁺ An: 542 mg/L NO ₃ ⁻ Product Destination: to product tank Feed Flow Rate: 1 L/min Run Time: 2 hr 45 min	Current varied from 10 to 40 amps, resulted in concentrations of 274-87 mg/L Na and 812-187 mg/L NO ₃ . Resistance decreased from 0.65 to 0.59 as current increased from 10 to 20 amps, and <u>increased</u> to 0.673 at 30 amps, then to 0.738 at 40 amps. Current then "kicked" down to 39 amps and resistance continued to increase to 0.756. Na ion transfer rate decreased from 1.57E-5 to 6.83E-6 meq/amp*sec as current increased from 10 to 40 amps, but then increased at 40 amps over 1/2 hour to 7.12E-6. There appears to be a problem with the NO ₃ results because the concentration of the first product sample (P1) taken (with rectifier off) was higher than the NO ₃ in the feed. Cell efficiency decreased from 17.2% to 5.1% as current increased (efficiency was negative at 10 amps because of the problem with the results). There was an internal leak from the feed into the anolyte.	When plotting resistance as a function of inverse current, it appears that polarization occurs between 20 and 30 amps. Na removal was 82% and NO ₃ was 74%. WQS were not met at any flow rate. Because of the internal leak during this test, the analytical results are suspect.
11/8/95 Test 11	Resins: none Membranes: Neosepta Starting Solution Concentrations (by analysis) Feed: 485 mg/L Na ⁺ , 622 mg/L NO ₃ ⁻ Cat: 495 mg/L Na ⁺ An: 685 mg/L NO ₃ ⁻ Product Destination: to product tank Feed Flow Rate: 1 L/min Run Time: 1 hr	Current varied from 5 to 44 amps, resulted in concentrations of 420-41 mg/L Na and 413-200 mg/L NO ₃ . Resistance decreased from 1.3 to 0.645 as current increased from 5 to 20 amps, and <u>increased</u> to 0.683 at 40 amps before decreasing slightly to 0.67 at 44 amps. Na ion transfer rate increased from 9.42E-6 to 9.6E-6 meq/amp*sec as current increased from 5 to 20 amps, then decreased to 7.31E-6 at 44 amps. NO ₃ ion transfer rate decreased from 1.12E-5 to 2.55E-6 meq/amp*sec as current increased from 5 to 20 amps, increased at 40 amps to 2.79E-6, then decreased to 2.58E-6 at 44 amps. Cell efficiency was slightly better at 20 amps (15.4%) than at 5 amps (15.2%), but decreased to 4.1% current increased to 44 amps. There was an internal leak from the feed into the anolyte of > 3 L/hr.	When plotting resistance as a function of inverse current, it appears that polarization occurs between 20 and 40 amps. Na removal was 92% and NO ₃ was 68%. WQS were not met at any flow rate, but were not expected to w/o resins. Because of the internal leak during this test, the analytical results are suspect.

TEST DATE	TEST CONDITIONS	RESULTS	OBSERVATIONS
11/9/95 Test 12	Resins: Dow G-26(cat) and Dow 21K(an) at a 1:1 ratio in the feed compartment Membranes: Neosepta Starting Solution Concentrations (by analysis) Feed: 490 mg/L Na ⁺ , 635 mg/L NO ₃ ⁻ Cat: 610 mg/L Na ⁺ An: 518 mg/L NO ₃ ⁻ Product Destination: to product tank Feed Flow Rate: 1 L/min Run Time: 3 hr 55 min	Current varied from 10 to 91 amps, resulted in concentrations of 160-91 mg/L Na and 374-226 mg/L NO ₃ . Resistance decreased from 0.6 to 0.26 as current increased. Na ion transfer rate decreased from 2.6E-5 to 2.79E-6 meq/amp*sec as current increased. NO ₃ ion transfer rate decreased from 6.31E-6 to 1.21E-6 meq/amp*sec as current increased. Cell efficiency decreased from 12.2% at 10 amps to 6.7% at 20 amps, increased to 16.8% at 30 amps, and then continually decreased to 5.4% at 91 amps. There was an internal leak from the feed into the anolyte and catholyte.	As current increased, there was no increase in resistance; no polarization point noted. Na and NO ₃ ion transfer rates decreased as current increased. The lowest Na concentrations were at the lowest current and increased as current increased to 60 amps then decreased at 75 amps, and increased again at 91 amps which is not like previous tests. Even though WQS were not met, NO ₃ concentrations decreased with increasing current with a 65% ion removal. Because of the internal leak during this test, the analytical results are suspect.
11/14/95 Test 13	Resins: Dow G-26(cat) and Dow 21K(an) at a 1:2 ratio in the feed compartment Membranes: Neosepta Starting Solution Concentrations (by analysis) Feed: 425 mg/L Na ⁺ , 545 mg/L NO ₃ ⁻ Cat: 365 mg/L Na ⁺ An: 601 mg/L NO ₃ ⁻ Product Destination: to product tank feed tank Feed Flow Rate: 1 L/min Run Time: 2 hr 40 min	Current varied from 20 to 160 amps, resulted in concentrations of 243-36 mg/L Na and 328-51 mg/L NO ₃ . Resistance decreased from 0.375 to 0.139 as current increased. Na ion transfer rate decreased from 6.59E-6 to 1.76E-6 meq/amp*sec as current increased. NO ₃ ion transfer rate decreased from 2.92E-6 to 8.3E-7 meq/amp*sec as current increased. Cell efficiency decreased from 10.6% to 2.8% with increasing current.	As current increased, no increase in resistance was noted which indicates that there is no limiting current density in this current range. Na removal was 92% and NO ₃ was 91%, but WQS were not met (NO ₃ was 51 mg/L which is close). There may have been an internal leak; not sure because the mass balance was off by the same amount as the accuracy of the tank measurement. However, because of the internal leak during other tests using the Neosepta membranes, the analytical results are suspect.

TEST DATE	TEST CONDITIONS	RESULTS	OBSERVATIONS
11/15/95 and 11/16/95 Test 14	Resins: Dow G-26(cat) and Dow 21K(an) at a 1:1 ratio in the feed compartment Membranes: Neosepta Starting Solution Concentrations Feed: 82 mg/L Na ⁺ , 122 mg/L NO ₃ ⁻ Cat: 735 mg/L Na ⁺ An: 891 mg/L NO ₃ ⁻ Product Destination: to product tank Feed Flow Rate: 1.0 and 0.5 L/min Run Time: 4 hr 45 min	<u>1.0 L/min:</u> Current varied from 40 to 135 amps, resulted in concentrations of 31-8.3 mg/L Na and 38-13 mg/L NO ₃ . Resistance decreased from 0.44 to 0.191 as current increased. Na ion transfer rate decreased from 9.24E-7 to 3.79E-7 meq/amp*sec as current increased from 40 to 130 amps, and increased to 3.96E-7 at 135 amps. NO ₃ ion transfer rate decreased from 5.65E-7 to 2.13E-7 meq/amp*sec as current increased from 40 to 130 amps, and increased to 2.17E-7 at 135 amps. The highest cell efficiency attained was only 0.9% at 40 amps. <u>0.5 L/min:</u> Current varied from 10 to 80 amps, resulted in concentrations of 1.7-4.2 mg/L Na and 5-8 mg/L NO ₃ . Resistance decreased from 1.05 to 0.27 as current increased. Na ion transfer rate decreased from 2.91E-6 to 3.52E-7 meq/amp*sec as current increased. NO ₃ ion transfer rate decreased from 1.57E-6 to 1.92E-7 meq/amp*sec as current increased. Cell efficiency decreased from 2.5% at 10 amps to 0.3% with increasing current.	As current increased, no increase in resistance was noted which indicates that there is no limiting current density in this current range. WQS were met at both flow rates with Na and NO ₃ removal of 90% at 1.0 L/min, and Na removal of 98% and NO ₃ removal of 96% at 0.5 L/min. The lowest ion concentrations attained at 0.5 L/min were at the lowest current (10 amps). This is because 40 and 80 amps were performed before 10 amps. This probably indicates that when going from a high current to a low current, the resins were stripped and are loading causing a lower concentration at the last current setting (10 amps). There may have been an internal leak; not sure because the mass balance was off by the same amount as the accuracy of the tank measurement. However, because of the internal leak during other tests using the Neosepta membranes, the analytical results are suspect. On 12/27/95, bench scale tests were run on a used (from previous test) Neosepta membrane and an unused MI membrane where the membranes were placed over a vacuum (about 10 psi) to see if water would pass through. Water did not pass through the new MI membrane while the used Neosepta membrane showed substantial leakage. It appears that either the chromium (VI) or the combination of chromium and nitrate are destroying the membranes.
11/30/95 and 12/5/95 Test 15	Resins: Dow G-26(cat) and Dow 21K(an) at a 1:1 ratio in the feed compartment (unused) Membranes: MI (unused) Starting Solution Concentrations (by analysis) Feed: 1943 mg/L Na ⁺ , 2617 mg/L NO ₃ ⁻ , 1800 mg/L Cr(VI) Cat: 19320 mg/L Na ⁺ An: 27759 mg/L NO ₃ ⁻ , 13340 mg/L Cr(VI) Product Destination: to product tank Feed Flow Rate: 1.5 L/min Run Time: 6 hrs 40 min	Internal leak from feed into anolyte of > 5 L/hour. Analytical results indicate 44% Na removal, 15% NO ₃ removal, and 21% Cr(VI) removal.	See OBSERVATIONS for Test 16 below.

TEST DATE	TEST CONDITIONS	RESULTS	OBSERVATIONS
12/6/95 to 12/7/95 Tests 16	Resins: Dow G-26(cat) and Dow 21K(an) at a 1:1 ratio in the feed compartment (same as previous test) Membranes: MI (same as previous test) Starting Solution Concentrations (by analysis) - used ending solutions from 12/5/95 test Feed: 2051 mg/L Na ⁺ , 2671 mg/L NO ₃ ⁻ , 1810 mg/L Cr(VI) Cat: 20210 mg/L Na ⁺ An: 25555 mg/L NO ₃ ⁻ , 12050 mg/L Cr(VI) Product Destination: to product tank Feed Flow Rate: 1.0 and 0.5 L/min Run Time: 6 hr 50 min	Internal leak from feed into anolyte of > 7 L/hour. Analytical results indicate 51% Na removal, 35% NO ₃ removal, and 27% Cr(VI) removal at 1.0 L/min, and 79% Na removal, 63% NO ₃ removal, and 54% Cr(VI) removal at 0.5 L/min.	Disassembled cell and found that anion membranes were "deplastisized". The cation membranes looked normal. This fouling of the anion membranes was assumed to be from the chromium (VI). The anion resin was darkened considerable from the chromium.
12/14/95 Test 17	Resins: Dow G-26(cat) and Dow 21K(an) at a 1:1 ratio in the feed compartment (same as previous test) Membranes: MI (unused) Starting Solution Concentrations (by analysis except for Cr) Feed: 18.1 mg/L Na ⁺ , 30 mg/L NO ₃ ⁻ , 20.1 mg/L Cr(VI) Cat: 138 mg/L Na ⁺ An: 158 mg/L NO ₃ ⁻ , 200 mg/L Cr(VI) Product Destination: to product tank Feed Flow Rate: 1.5 L/min Run Time: 4 hr 30 min	Internal leak from feed into anolyte of > 3 L/hour. Analytical results indicate 43% Na removal. Cr(VI) in the product actually increased by more than twice.	See OBSERVATIONS for Test 18 below.
12/15/95 Test 18	Resins: Dow G-26(cat) and Dow 21K(an) at a 1:1 ratio in the feed compartment (same as previous test) Membranes: MI (same as previous test) Starting Solution Concentrations Feed: 18 mg/L Na ⁺ , 30 mg/L NO ₃ ⁻ , 20 mg/L Cr(VI) Cat: 180 mg/L Na ⁺ An: 300 mg/L NO ₃ ⁻ , 200 mg/L Cr(VI) Product Destination: to product tank Feed Flow Rate: 1.0 L/min Run Time: 7 hr 15 min	Internal leak from feed into anolyte of around 4 L/hour.	Disassembly of the cell showed that there was a localized area of the resin in most of the compartments that looked "moldy". Examination under a microscope showed that the resin beads were broken. There were also several anion membranes that had places that were "deplastisized". On 12/12/95, bench scale tests were run on used (from previous test) and unused MI anion membranes where the membranes were placed over a vacuum to see if water would pass through. Water did pass through the used MI membranes while the unused MI membranes did not let water pass through. It appears that either the chromium (VI) or the combination of chromium and nitrate are destroying the anion membranes.

TEST DATE	TEST CONDITIONS	RESULTS	OBSERVATIONS
12/19/95 Test 19 (repeat of test on 12/14/95)	Resins: Dow G-26(cat) and Dow 21K(an) at a 1:1 ratio in the feed compartment (unused) Membranes: MI (unused) Starting Solution Concentrations Feed: 18 mg/L Na ⁺ , 30 mg/L NO ₃ ⁻ , 20 mg/L Cr(VI) Cat: 180 mg/L Na ⁺ An: 300 mg/L NO ₃ ⁻ , 200 mg/L Cr(VI) Product Destination: to product tank Feed Flow Rate: 1.0 and 1.5 L/min Run Time: 7 hr 20 min	Internal leak from feed into anolyte of around 5 L/hour.	See OBSERVATIONS for Test 20 below.
12/20/95 Test 20 (repeat of test on 12/15/95)	Resins: Dow G-26(cat) and Dow 21K(an) at a 1:1 ratio in the feed compartment (same as previous test) Membranes: MI (same as previous test) Starting Solution Concentrations Feed: 18 mg/L Na ⁺ , 30 mg/L NO ₃ ⁻ , 20 mg/L Cr(VI) Cat: 180 mg/L Na ⁺ An: 300 mg/L NO ₃ ⁻ , 200 mg/L Cr(VI) Product Destination: to product tank Feed Flow Rate: 1.0 and 1.5 L/min Run Time: 3 hr	Internal leak from feed into anolyte of around 2 L/hour.	Performed a bench scale test on MI membranes. Pieces of the membranes were soaked overnight in beakers of various different concentrations of nitric acid, chromium, and chromium nitrate. The membranes were then placed over a vacuum of about 1 psi. The membranes soaked in nitric acid up to 30,000 ppm did not leak nor did the ones soaked in very high concentrations of chromium solution. However, the membranes soaked in chromic acid (200 ppm chromate and 300 ppm nitrate) did let water pass through. Therefore, it appears that it is the combination of chromium and nitric acid that destroys the integrity of the membranes.
12/28/95 Test 21	Resins: Dow G-26(cat) and Dow 21K(an) at a 1:1 ratio in the feed compartment. No resins in the anolyte or catholyte compartments. Membranes: MI Starting Solution Concentrations (by analysis) Feed: 425 mg/L Na ⁺ , 190 mg/L NO ₃ ⁻ Cat: 420 mg/L Na ⁺ An: 126 mg/L NO ₃ ⁻ Product Destination: to product tank Feed Flow Rate: 1 L/min Run Time: 1 hr 29 min	Current varied from 50 to 85 amps, resulted in concentrations of 7.9-10.5 mg/L Na and 0.0 mg/L NO ₃ . Resistance decreased from 0.644 to 0.469 as current increased. Na ion transfer rate decreased from 6.0E-6 to 3.5E-6 meq/amp*sec as current increased. NO ₃ ion transfer rate decreased from 1.0E-6 to 6.0E-7 meq/amp*sec as current increased. Cell efficiency decreased from 9.7% to 5.7% with increasing current.	As current increased, no increase in resistance was noted which indicates that there is no limiting current density in this current range. Na concentrations decreased from 50 to 70 amps but increased at 80 amps and again at 85 amps. NO ₃ concentrations were 0.0 at every current. Resins were not preconditioned but were loaded by reverse polarity of the cell. However, based on samples of the feed, anolyte, and catholyte tanks taken before circulating through the cell and after reversing the polarity, the resins were not loaded to capacity. In fact, only 12 g of Na was loaded on the cation resin which has a capacity of 76 g Na, and 36 g of NO ₃ was loaded on the anion resin which has a capacity of 121 g NO ₃ . Therefore, the product concentrations are probably inaccurate.

TEST DATE	TEST CONDITIONS	RESULTS	OBSERVATIONS
12/29/95 Test 22	Resins: Dow G-26(cat) and Dow 21K(an) at a 1:1 ratio in the feed compartment. No resins in the anolyte or catholyte compartments. Membranes: MI Starting Solution Concentrations (by analysis) Feed: 420 mg/L Na ⁺ , 178 mg/L NO ₃ ⁻ Cat: 4786 mg/L Na ⁺ An: 2199 mg/L NO ₃ ⁻ Product Destination: to product tank Feed Flow Rate: 1 L/min Run Time: 2 hr 15 min	Current varied from 50 to 85 amps, resulted in concentrations of 43.7-13.6 mg/L Na and 0.0 mg/L NO ₃ . Resistance decreased from 0.584 to 0.498 as current increased. Na ion transfer rate decreased from 5.45E-6 to 3.46E-6 meq/amp*sec as current increased. NO ₃ ion transfer rate decreased from 1.0E-6 to 6.0E-7 meq/amp*sec as current increased. Cell efficiency decreased from 8.8% to 5.6% with increasing current.	As current increased, no increase in resistance was noted which indicates that there is no limiting current density in this current range. Na concentrations decreased with increasing current, but at first current (50 amps) for 1/2 hour, Na concentration was 43.7 mg/L which seems pretty low. NO ₃ concentrations were 0.0 at every current. Cell was not disassembled after Test 21 so the resins are in the condition they were in at the end of Test 21. Only circulated through cell for 15 minutes before turning on power and polarity was <u>not</u> reversed, so the resins were not loaded to capacity. Therefore, the product concentrations are probably inaccurate.
1/3/96 Test 23	Resins: Dow G-26(cat) and Dow 21K(an) at a 1:1 ratio in the feed compartment. No resins in the anolyte or catholyte compartments. Membranes: MI Starting Solution Concentrations (by analysis) Feed: 552.3 mg/L Na ⁺ , 478 mg/L NO ₃ ⁻ Cat: 4093 mg/L Na ⁺ An: 1292 mg/L NO ₃ ⁻ Product Destination: to product tank Feed Flow Rate: 1 L/min Run Time: 3 hr 5 min	Current varied from 50 to 80 amps, resulted in concentrations of 157.1-53.4 mg/L Na and 116-27 mg/L NO ₃ . Resistance decreased from 0.468 to 0.41 as current increased. Na ion transfer rate decreased from 5.7E-6 to 4.5E-6 meq/amp*sec as current increased. NO ₃ ion transfer rate decreased from 1.95E-6 to 1.51E-6 meq/amp*sec as current increased. Cell efficiency decreased from 9.2% to 7.2% with increasing current.	As current increased, no increase in resistance was noted which indicates that there is no limiting current density in this current range. Resins were loaded by reverse polarity of the cell. A product sample (P6) was taken at the end of the test with power off, and the Na and NO ₃ concentrations were 301.1 mg/L and 122 mg/L. This indicates that the resins are not loaded to capacity which is expected since the cell was just running at a high current. However, because the product sample (P6) was greater (by a factor of 4.5-5.5) than the last sample taken (P5), the resins were not stripped to the point where most of the ions were loading back on the resins. Therefore, the product concentrations are probably accurate.

TEST DATE	TEST CONDITIONS	RESULTS	OBSERVATIONS
1/15/96 Test 24	<p>Resins: Dow G-26(cat) and Dow 21K(an) at a 1:1 ratio in the feed compartment. No resins in the anolyte or catholyte compartments.</p> <p>Membranes: MI</p> <p>Starting Solution Concentrations (by analysis)</p> <p>Feed: 32.5 mg/L Na⁺, 693 mg/L NO₃⁻, 7.2 mg/L Cr(III)</p> <p>Cat: 339 mg/L Na⁺, 184 mg/L Cr(III)</p> <p>An: 5978 mg/L NO₃⁻</p> <p>Product Destination: to product tank</p> <p>Feed Flow Rate: 1.5 L/min.</p> <p>Run Time: 6 hr 13 min</p>	<p>Cell resistance decreased from 1.07 to 0.76 from 40 to 60 amps then increased at 65 amps to 0.78.</p> <p>Current was varied from 40 to 65 amps resulting in product water concentrations of Na = 39-29 mg/L, NO₃ = 2164-71 mg/L, and Cr(III) = 1.3-2.4 mg/L.</p>	<p>It was thought that the chromium would stay in solution at these feed concentrations, but in actuality the feed solution was cloudy which indicated that there was suspended chromium. In other words, we introduced a feed solution into the cell that contained a chromium precipitate. At 40, 50, and 60 Amps, the voltage continually increased while the conductivity decreased, and the Na and Cr(III) concentrations decreased; however, the NO₃ concentrations decreased from 40 to 50 Amps and increased from 50 to 60 Amps. At 65 Amps, the voltage decreased by 0.1 while the conductivity increased; Na, NO₃, and Cr(III) concentrations increased. It appears that the best overall results were achieved at 50 Amps; however, these concentrations do not meet the required WQS. I would suspect that the chromium precipitate is causing some problems with the cells performance. The precipitate is probably a result of polarization.</p>
1/16/96 Test 25	<p>Resins: Dow G-26(cat) and Dow 21K(an) at a 1:1 ratio in the feed compartment. No resins in the anolyte or catholyte compartments.</p> <p>Membranes: MI</p> <p>Starting Solution Concentrations (by analysis)</p> <p>Feed: 61 mg/L Na⁺, 671 mg/L NO₃⁻, 10.8 mg/L Cr(III)</p> <p>Cat: 541.7 mg/L Na⁺, 163 mg/L Cr(III)</p> <p>An: 6645 mg/L NO₃⁻</p> <p>Product Destination: to product tank</p> <p>Feed Flow Rate: 1.0 L/min.</p> <p>Run Time: 2 hr 35 min</p>	<p>Cell resistance decreased from 1.09 to 0.842 from 40 to 50 amps then increased at 60 amps to 0.95. The current was then reduced to 55 amps and the resistance continued to increase to 0.98.</p> <p>Current was varied from 40 to 60 amps resulting in product water concentrations of Na = 38-31 mg/L, NO₃ = 269-207 mg/L, and Cr(III) = 3.9-2.9 mg/L.</p>	<p>Same problem as Test 24 with chromium precipitation in solution. At 40 Amps, the voltage continually increased while the conductivity decreased, and the Na, NO₃, and Cr(III) concentrations decreased. At 50 Amps, the voltage decreased and the conductivity decreased, and the Na, NO₃, and Cr(III) concentrations continued to decrease. At 60 Amps, the voltage began increasing again, but the conductivity also increased; Na and NO₃ concentrations increased but the Cr(III) concentration decreased from 3.0 to 2.9. It appears that the best overall results were achieved at 50 Amps (as was with Test 24); however, these concentrations do not meet the required WQS. Again, I would suspect that the chromium precipitate is causing some problems with the cells performance.</p>

TEST DATE	TEST CONDITIONS	RESULTS	OBSERVATIONS
1/16/96 Test 26	<p>Resins: Dow G-26(cat) and Dow 21K(an) at a 1:1 ratio in the feed compartment. No resins in the anolyte or catholyte compartments.</p> <p>Membranes: MI</p> <p>Starting Solution Concentrations (by analysis)</p> <p>Feed: 61 mg/L Na⁺, 671 mg/L NO₃⁻, 10.8 mg/L Cr(III)</p> <p>Cat: 610.5 mg/L Na⁺, 155 mg/L Cr(III)</p> <p>An: 6453 mg/L NO₃⁻</p> <p>Product Destination: to product tank</p> <p>Feed Flow Rate: 0.5 L/min.</p> <p>Run Time: 2 hr 1 min</p>	<p>Cell resistance decreased from 1.305 to 1.01 from 40 to 57 amps; no polarization point noted.</p> <p>Current was varied from 40 to 57 amps resulting in product water concentrations of Na = 21-13 mg/L, NO₃ = 115-63 mg/L, and Cr(III) = 3.2-0.7 mg/L.</p>	<p>Same problem as Test 24 with chromium precipitation in solution. At 40 Amps, the voltage continually increased while the conductivity decreased, and the Na, NO₃, and Cr(III) concentrations decreased. At 45 Amps, the voltage decreased and the conductivity decreased, and the Na, NO₃, and Cr(III) concentrations increased. At 50 and 60 Amps, the voltage began increasing again, and the conductivity decreased; Na and NO₃ concentrations decreased, but the Cr(III) concentration increased between 45 and 50 Amps and then decreased between 50 and 60 Amps. It appears that the best overall results were achieved at the highest power 60 Amps; however, these concentrations do not meet the required WQS. Again, I would suspect that the chromium precipitate is causing some problems with the cells performance.</p>
1/22/96 Test 27	<p>Resins: Dow G-26(cat) and Dow 21K(an) at a 1:1 ratio in the feed compartment. No resins in the anolyte or catholyte compartments.</p> <p>Membranes: MI</p> <p>Starting Solution Concentrations (by analysis)</p> <p>Feed: 219 mg/L Na⁺, 3263 mg/L NO₃⁻, 249 mg/L Cr(III)</p> <p>Cat: 620 mg/L Na⁺, 141 mg/L Cr(III)</p> <p>An: 30,149 mg/L NO₃⁻</p> <p>Product Destination: to product tank</p> <p>Feed Flow Rate: 1.5 L/min</p> <p>Run Time: 2 hr 40 min</p>	<p>Cell resistance was 0.561 at 60 amps, 0.557 at 70, 0.309 at 80, and 0.44 at 90.</p> <p>Current was varied from 60 to 90 amps resulting in product water concentrations of Na = 211-178 mg/L, NO₃ = 2431-1975 mg/L, and Cr(III) = 211-163 mg/L.</p> <p>The Na ion transfer rate to the catholyte was 0 from 60 to 70 amps and increased at 80 amps, but decreased at 90 amps. The NO₃ ion transfer rate to the an. increased at 60, 70, and 80 amps, but decreased at 90 amps. The Cr in the catholyte tank fluctuated throughout test; overall net decrease.</p>	<p>Of the 61.7 g of Na processed (total processed includes Test 28), 16.2 g was removed from feed, and 7.2 g was added to the catholyte. Of the 919 g of NO₃ processed (total processed includes Test 5, 1/22/96), 394 g was removed from feed, and 374 g was added to the anolyte. Of the 70 g of Cr(III) processed (total processed includes Test 28), 30 g was removed from the feed, and 0.3 g was lost from the catholyte tank. And even though the Cr(III) should migrate to the cathode, the anolyte actually gained 177 mg.</p> <p>See Test 28 for cell tear down description and Tests 27 and 28 conclusions.</p>

TEST DATE	TEST CONDITIONS	RESULTS	OBSERVATIONS
1/22/96 Test 28	<p>Resins: Dow G-26(cat) and Dow 21K(an) at a 1:1 ratio in the feed compartment. No resins in the anolyte or catholyte compartments.</p> <p>Membranes: MI</p> <p>Starting Solution Concentrations (by analysis)</p> <p>Feed: 221 mg/L Na⁺, 3096 mg/L NO₃⁻, 244 mg/L Cr(III)</p> <p>Cat: 690 mg/L Na⁺, 138 mg/L Cr(III)</p> <p>An: 33,749 mg/L NO₃⁻</p> <p>Product Destination: to product tank</p> <p>Feed Flow Rate: 0.5 L/min</p> <p>Run Time: 2 hr 25 min</p>	<p>Cell resistance was 0.78 at 40 amps, 0.776 at 50, 0.723 at 60, and 0.654 at 70. No polarization point noted based on resistance change.</p> <p>Current was varied from 40 to 70 amps resulting in product water concentrations of Na = 191-160 mg/L, NO₃ = 1887-1631 mg/L, and Cr(III) = 151-144 mg/L.</p> <p>The Na ion transfer rate to the catholyte fluctuated throughout test; overall net increase. The NO₃ ion transfer rate to the an. fluctuated throughout test; overall net decrease. The Cr concentration in the catholyte tank decreased from 138 mg/L to 134 mg/L during the test.</p>	<p>Mixed bed resins separated within feed compartment; probably due to the fact that the compartment was not completely full of resin. Separation of resins not as severe in compartments containing more resin. Chromium plated on the feed side of cation membranes; where resins separated, the chromium plated mostly under the anolyte resin. Chromium precipitate was hung up in the plastic "grids" in the catholyte compartments.</p> <p>Of the 61.7 g of Na processed (total processed includes Test 27), 31.9 g was removed from feed, and 5.5 g was added to the catholyte. Of the 919 g of NO₃ processed (total processed includes Test 27), 16 g was removed from feed, and 374 g was lost from the anolyte. Of the 70 g of Cr(III) processed (total processed includes Test 27), 42.5 g was removed from the feed, and 0.4 g was lost from the catholyte tank. And even though the Cr(III) should migrate to the cathode, the anolyte actually gained 395 mg.</p> <p>Most of the 70 g of Cr removed from the feed plated on the cation membrane. The loss is Cr in the cat tank is likely due to the precipitate that hangs up in the plastic "grids" in the cell.</p>

TEST DATE	TEST CONDITIONS	RESULTS	OBSERVATIONS
1/25/96 Test 29	<p>Resins: None</p> <p>Membranes: MI (unused)</p> <p>Starting Solution Concentrations (by analysis)</p> <p>Feed: 200 mg/L Na⁺, 2944 mg/L NO₃⁻, 334 mg/L Cr(III)</p> <p>Cat: 641.3 mg/L Na⁺, 123 mg/L Cr(III)</p> <p>An: 30734 mg/L NO₃⁻</p> <p>Product Destination: to product tank</p> <p>Feed Flow Rate: 1.5 and 0.5 L/min</p> <p>Run Time: 3 hr 57 min</p>	<p><u>1.5 L/min:</u> Cell resistance varied from 0.275 to 0.495; no polarization point noted.</p> <p>Current was varied from 20 to 80 amps resulting in product water concentrations of Na = 190.8-151 mg/L, NO₃ = 2944-1659 mg/L, and Cr(III) = 314-256 mg/L.</p> <p>The Na in the catholyte increased at 40, 60, and 80 amps, but decreased at 20 amps (20 amps was done last, after 40, 60, and 80); overall net increase. The Cr in the catholyte tank fluctuated throughout test, as did the NO₃ in the anolyte tank; overall net decrease. The ion transfer rates of all ions fluctuated throughout test.</p> <p><u>0.5 L/min:</u> Cell resistance varied from 0.39 to 0.525 at 0.5 L/min but was most dramatic when current was changed from 50 to 70 amps when the resistance went from 0.39 to 0.47. At 50 amps the voltage was 19.5 and when changed to 70 amps, the voltage increased to 32.9 in 1/2 hour.</p> <p>Current was varied from 40 to 80 amps resulting in product water concentrations of Na = 116.1-18.5 mg/L, NO₃ = 1247-231 mg/L, and Cr(III) = 211-49 mg/L.</p> <p>The Na in the catholyte increased at each current. The Na ion transfer rates were essentially the same at 40 and 50 amps but decreased at 70 and 80 amps. The Cr in the catholyte tank fluctuated throughout test, and the Cr ion transfer rates continually decreased; overall net decrease. The concentrations and ion transfer rates of the NO₃ in the anolyte tank fluctuated throughout test; overall net decrease.</p>	<p>Chromium did precipitate in feed compartments. At 1.5 L/min, there was no dramatic change in the cell resistance which may be an indication that polarization did not occur. However, at 0.5 L/min, there was dramatic increase in resistance between 50 and 70 amps which could be an indication of polarization. It is also possible that this is a false polarization point due to the nonuniform current density through the cell. Additional current settings between 50 and 70 amps would be needed to pinpoint the limiting current density.</p> <p>Of the 54.8 g of Na processed, 18.6 g was removed from feed. A total of 15.5 g of Na was added to the cat; 8.3 g at 1.5 L/min and 7.2 g at 0.5 L/min. Of the 807 g of NO₃ processed, 311 g was removed from feed. 375 g of NO₃ was added to the anolyte; 92 g was lost from the anolyte at 1.5 L/min and 467 g was added at 0.5 L/min. Of the 91.5 g of Cr(III) processed, 24.5 g was removed from the feed. 1 g of Cr(III) was lost from the catholyte tank; 0.8 g at 1.5 L/min and 0.2 g at 0.5 L/min. And even though the Cr(III) should migrate to the cathode, the anolyte actually gained 425 mg; mostly at 0.5 L/min.</p> <p>Most of the 24.5 g of Cr removed from the feed plated on the cation membrane. The loss is Cr in the cat tank is likely due to the precipitate that hangs up in the plastic "grids" in the cell. I can not explain the movement of the NO₃.</p>

TEST DATE	TEST CONDITIONS	RESULTS	OBSERVATIONS
1/30/96 Test 30	<p>Resins: None</p> <p>Membranes: MI (reused from 1/25/96; cleaned of plated chromium)</p> <p>Starting Solution Concentrations (by analysis)</p> <p>Feed: 218 mg/L Na⁺, 3352 mg/L NO₃⁻, 211 mg/L Fe(II)</p> <p>Cat: 1701 mg/L Na⁺, 0.0 mg/L Fe(II)</p> <p>An: 28357 mg/L NO₃⁻</p> <p>Product Destination: product tank</p> <p>Feed Flow Rate: 1.0 L/min</p> <p>Run Time: 3 hr 15 min</p>	<p>Cell resistance varied from 0.31 to 1.45, but was most dramatic when current was changed from 20 to 40 amps when the resistance went from 0.3 to 0.7. At 20 amps the voltage was 6.1 and when changed to 40 amps, the voltage increased to 18.1 in 1/2 hour, to 27.8 in another 1/2 hr and was still increasing. After running at 60 amps, changed back to 40 amps, and after 15 min. the voltage was 45.8.</p> <p>Current was varied from 10 to 60 amps resulting in product water concentrations of Na = 210-151 mg/L, NO₃ = 3271-1856 mg/L, and Fe(II) = 202-162 mg/L.</p> <p>The Na in the catholyte fluctuated throughout the test. No iron migrated to the catholyte tank at all. The NO₃ in the anolyte tank also fluctuated throughout test.</p>	<p>Based on the test objective, iron did precipitate in feed compartments. The dramatic increase in resistance between 20 and 40 amps could be an indication of polarization. It is also possible that this is a false polarization point due to the nonuniform current density through the cell. Additional current settings between 20 and 40 amps would be needed to pinpoint the limiting current density.</p> <p>Of the 45.2 g of Na processed, 8.1 g was removed from feed, 3.9 g was added to the catholyte, and 95 mg was added to the anolyte. Of the 696 g of NO₃ processed, 142.6 g was removed from feed, but 2.1 g was lost from the catholyte and 87.8 g was lost from the anolyte. Of the 43.8 g of iron processed, 6 g was removed from the feed but none was added to the catholyte and almost none (9 mg) was added to the anolyte.</p> <p>The 6 g of Fe removed from the feed is probably the amount that plated on the cation membrane. There is 4.2 g of Na unaccounted for which may be commingled with the iron precipitate on the cation membrane. I can not explain the discrepancies with the NO₃.</p>

TEST DATE	TEST CONDITIONS	RESULTS	OBSERVATIONS
<p>2/1/96 Test 31</p>	<p>Resins: None Membranes: MI (reused from 1/30/96; cleaned of plated iron) Starting Solution Concentrations (by analysis) Feed: 202.9 mg/L Na⁺, 2944 mg/L NO₃⁻, 211 mg/L Fe(II) Cat: 30.5 mg/L Na⁺, 25818 mg/L NO₃⁻, 4.7 mg/L Fe(II) An: 32750 mg/L NO₃⁻ Product Destination: product tank Feed Flow Rate: 1.0 L/min Run Time: 3 hr 5 min</p>	<p>Cell resistance varied from 0.24 to 0.89, but was most dramatic when current was changed from 30 to 40 amps when the resistance went from 0.27 to 0.55. At 30 amps the voltage was 8 and when changed to 40 amps, the voltage increased to 21.9 in 1/2 hour and was still increasing. Current was varied from 10 to 60 amps resulting in product water concentrations of Na = 200.4-141.9 mg/L, NO₃ = 2768-1742 mg/L, and Fe(II) = 207.5-155.2 mg/L. The Na in the catholyte increased at each current from 30.5-82.1 mg/L; the Na ion transfer rate increased at 20 and 30 amps, but decreased at 40 amps before continuing to increase again at 50 and 60 amps. The Fe(II) in the catholyte increased at each current from 4.7-24.9 mg/L; the Fe(II) ion transfer rate decreased at 20 amps, increased at 30 amps, and then continually decreased at 40, 50, and 60 amps. The NO₃ in the anolyte started at 32750 mg/L and changed to 28747, 29737, 29241, 29737, 31739, and 32750 mg/L at 10, 20, 30, 40, 50, and 60 amps, respectively.</p>	<p>Based on the test objective, iron did precipitate in feed compartments. The dramatic increase in resistance between 30 and 40 amps could be an indication of polarization. It is also possible that this is a false polarization point due to the nonuniform current density through the cell. Another possibility is that the polarization point is around 20 amps (4.7 volts) which is where the first increase in resistance was observed, however, not as severe. Of the 45.1 g of Na processed, 8.3 g was removed from feed and 5 g was added to the catholyte. Of the 655 g of NO₃ processed, 116 g was removed from feed, but none was added to the catholyte or anolyte. Of the 46.9 g of iron processed, 5.7 g was removed from the feed and 1.9 g was added to the catholyte. There is 3.8 g of Fe unaccounted for which is likely the amount that plated on the cation membrane. There is 3.3 g of Na unaccounted for which may be commingled with the iron precipitate on the cation membrane. The entire 116 g of NO₃ removed from the feed is unaccounted for. The NO₃ in the anolyte tank decreased some then increased back to where it started with a net ion transfer of 0. The NO₃ in the catholyte tank fluctuated throughout the test, and ended up containing 182 g less than it started with.</p>

TEST DATE	TEST CONDITIONS	RESULTS	OBSERVATIONS
2/5/96 Test 32	<p>Resins: None</p> <p>Membranes: MI (reused from 1/30/96; cleaned of plated iron)</p> <p>Starting Solution Concentrations (by analysis)</p> <p>Feed: 211.6 mg/L Na⁺, 2877 mg/L NO₃⁻, 209 mg/L Fe(II)</p> <p>Cat: 92.3 mg/L Na⁺, 21850 mg/L NO₃⁻, 26 mg/L Fe(II)</p> <p>An: 26911 mg/L NO₃⁻</p> <p>Product Destination: product tank</p> <p>Feed Flow Rate: 1.0 L/min</p> <p>Run Time: 2 hours</p>	<p>Voltage was held constant at 8 volts. Current initially at 65 amps but quickly dropped to 24 amps and over a 2 hour period, dropped to 21 amps.</p> <p>The cell resistance increased over the 2 hours from 0.333 to 0.381.</p> <p>Na in product reduced to 192.6 mg/L in first 1/2 hr, but changed to 194.2 mg/L, 193.8 mg/L, and 195.1 mg/L in 1/2 hr increments. Na in catholyte tank increased to 101.4 mg/L, 106.3 mg/L, 110.7 mg/L, and 118.4 mg/L in 1/2 hr increments which equates to ion transfer rates of 2.75E-7, 1.54E-7, 1.45E-7, and 2.66E-7 meq/amp*sec, respectively.</p> <p>NO₃ in product reduced to 2279 mg/L in first 1/2 hr, and to 2207 mg/L in next 1/2 hour, but increased to 2424 mg/L, and 2573 mg/L in 1/2 hr increments. NO₃ in catholyte did not change in first 1/2 hour, but then changed to 24583 mg/L, 23192 mg/L, and 22294 mg/L in 1/2 hr increments. NO₃ in anolyte changed to 27389 mg/L in first 1/2 hour but did not change in the next 1/2 hour. In the next 1/2 hour it changed to 28357 mg/L and remained constant for the last 1/2 hour. This equates to ion transfer rates of 5.35E-6, 0.0, 1.18E-5, and 0.0 meq/amp*sec, respectively.</p> <p>Fe in product changed to 196.1 mg/L, 194.1 mg/L, 198.7 mg/L, 194.8 in 1/2 hr increments. Fe in catholyte tank increased to 27.6 mg/L, 28.7 mg/L, 29.5 mg/L, and 31 mg/L in 1/2 hr increments which equates to ion transfer rates of 3.98E-8, 2.86E-8, 2.17E-8, and 4.27E-8 meq/amp*sec, respectively.</p>	<p>Based on the test objective, iron did precipitate in feed compartment, but the amount of iron on the cation membrane. was small. However, the theory that the iron would not precipitate at 8 volts did not hold true.</p> <p>Of the 29.8 g of Na processed, 945 mg was removed from feed and 2.4 g was added to the catholyte. Of the 406 g of NO₃ processed, 85 g was removed from feed, 138 g was added to the anolyte, and 93 mg was added to the catholyte. Of the 29.4 g of iron processed, 1.5 g was removed from the feed, 500 mg was added to the catholyte, and 30 mg was added to the anolyte.</p> <p>According to my calculations, 2.5 times more Na migrated to the catholyte than was removed from feed, and 2 times more NO₃ migrated to the anolyte and catholyte than was removed from feed. How could this be?! For the iron, 530 mg of the 1500 mg removed from the feed, migrated to the anolyte and catholyte. The 970 mg unaccounted for could be the amount that precipitated on the membrane.</p> <p>The increasing resistance may be due to continuing iron precipitation in the feed compartments.</p>

TEST DATE	TEST CONDITIONS	RESULTS	OBSERVATIONS
2/6/96 Test 33	<p>Resins: Dow G-26(cat) and Dow 21K(an) at a 1:2 ratio in the feed compartment; conditioned in 20 g/L NO_3^-, 100 g NaOH, and FeNO_3 (add NaOH to 200 g FeSO_4, filter, and dissolve the FeOH_2 in HNO_3).</p> <p>No resins in the anolyte or catholyte compartments.</p> <p>Membranes: MI (reused from 2/5/96; cleaned of iron precipitate)</p> <p>Starting Solution Concentrations (by analysis)</p> <p>Feed: 237.3 mg/L Na^+, 2498 mg/L NO_3^-, 107.5 mg/L Fe(II)</p> <p>Cat: 118.2 mg/L Na^+, 17577 mg/L NO_3^-, 31.5 mg/L Fe(II)</p> <p>An: 25493 mg/L NO_3^-</p> <p>Product Destination: product tank</p> <p>Feed Flow Rate: 1.0 L/min</p> <p>Run Time: 2 hrs</p>	<p>Voltage was held constant at 8 volts. Current initially at 82 amps but quickly dropped to 54 amps and over a 2 hour period, dropped to 41 amps.</p> <p>The cell resistance increased over the 2 hours from 0.148 to 0.195.</p> <p>Na in product reduced to 198.2 mg/L in first 1/2 hr, but increased to 201.8 mg/L, 213.1 mg/L, and 215.2 mg/L in 1/2 hr increments. Na in catholyte tank changed to 141.5 mg/L, 160.5 mg/L, 199.6 mg/L, and 195.8 mg/L in 1/2 hr increments which equates to ion transfer rates of $3.13\text{E-}7$, $2.75\text{E-}7$, $6.44\text{E-}7$, and $-6.72\text{E-}8$ meq/amp*sec, respectively (assume back diffusion during last 1/2 hr.).</p> <p>NO_3^- in product reduced to 1456 mg/L in first 1/2 hr, but increased to 1521 mg/L, 1653 mg/L, and 1925 mg/L in 1/2 hr increments. NO_3^- in catholyte changed to 18407 mg/L, 17577 mg/L, and 18407 mg/L in 1/2 hr increments. NO_3^- in anolyte changed to 26435 mg/L, 26911 mg/L, 27389 mg/L, and 28357 mg/L in 1/2 hr increments which equates to ion transfer rates of $4.69\text{E-}6$, $2.56\text{E-}6$, $2.92\text{E-}6$, and $6.35\text{E-}6$ meq/amp*sec, respectively.</p> <p>Fe in product reduced to 18.6 mg/L in first 1/2 hr, but increased to 23.3 mg/L, 32.9 mg/L, and 41.4 mg/L in 1/2 hr increments. Fe in catholyte tank changed to 43.8 mg/L, 48.2 mg/L, 51.6 mg/L, and 54.2 mg/L in 1/2 hr increments which equates to ion transfer rates of $1.36\text{E-}7$, $5.26\text{E-}8$, $4.62\text{E-}8$, and $3.79\text{E-}8$ meq/amp*sec, respectively.</p>	<p>It was thought that at 8 volts, the resins would reduce or eliminate the iron precipitation, but iron did still precipitate in feed compartment. The amount of iron on the cation membrane was small, but quite a bit of iron appeared to coat the resins near the cation membrane. It is possible that the dissociation of water molecules resulting from anionic and cationic materials in contact with each other (resin-resin and membrane-resin) caused the iron to precipitate.</p> <p>Of the 34.4 g of Na processed, 11.3 g was removed from feed and 7.4 g was added to the catholyte. Of the 362 g of NO_3^- processed, 26 g was removed from feed and 270 g was added to the anolyte. Of the 15.5 g of iron processed, none was removed from the feed, and the product tank actually increased by 26 g.</p> <p>Iron levels in product samples, however, decreased 40-50%, even though the amount of iron added to final product tank was more than the amount of iron processed through the cell. This difference is due to the displacement of iron already in the resin that did not migrate through the cation membrane because of the lack of current.</p> <p>I believe the reason that the initial concentrations of the ions in the feed decreased but the subsequent product sample concentrations increased is that the ions displaced by the resins were exiting the cell faster than the current could pull them through the membrane.</p> <p>The increasing resistance may be due to continuing iron precipitation in the feed compartments. That would explain the decreasing iron ion transfer rate. I do not, however, understand the ion transfer rate changes for Na and NO_3^-.</p>