

Feasibility Study for EDR Wastewater Treatment and Recovery

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Introduction and Background

The City of Sherman currently operates an 11 million gallon per day (MGD) water treatment plant (WTP) to treat surface water from Lake Texoma. The plant uses electro dialysis reversal (EDR) to demineralize a portion of the filter effluent from the conventional treatment portion of the WTP. The EDR process produces a continuous brackish wastewater of approximately 1 MGD that is currently discharged to the City's sewer system, using critical sewer transmission and treatment capacity. The wastewater consists of three streams: concentrate, off-spec product water, and electrode waste. Concentrate comprises more than 90% of the waste flow. The City desires to treat this wastewater to reduce sewer and wastewater plant loadings and recover a portion of the wastewater as high quality water than can be used to increase plant finished water capacity. The EDR wastewater contains several sparingly soluble salts (barium sulfate, calcium sulfate, strontium sulfate and calcium carbonate) at concentrations greatly in excess of their theoretical solubility. The presence of these salts makes treatment and recovery of the wastewater impractical by conventional desalting technologies (EDR and reverse osmosis (RO)) using standard, commercially-available scale inhibition chemicals because of the high likelihood of membrane scaling. Thus, alternative methods are required to meet the City's objectives. The purpose of this technical memorandum (TM) is to document a bench/pilot scale feasibility study of two innovative treatment technologies for EDR wastewater treatment and recovery. The technologies are:

- GrahamTek RO, manufactured by Mineral Water Development (MWD) of Stellenbosch, South Africa; and
- Zeta Rod, manufactured by Zeta Corporation of Tucson, Arizona

Only the results of the ZetaRod testing are presented in this document.

Purpose and Objectives

The primary objective of the testing was to assess the ability of the innovative products to operate reliably on the EDR wastewater (i.e. provide stable productivity and TDS rejection without rapid or significant fouling or scaling). The study was structured to perform a longer-term (3 month) evaluation of the GrahamTek system using a pilot unit outfitted with full-scale treatment components and operated on a continuous basis. This type of evaluation was intended to determine if RO performance could be maintained over a period of three

months of operation, and to assess membrane cleaning frequency and cleaning effectiveness. The Zeta Rod /RO system testing was short-term (two weeks) and intended to provide data to enable a “go/no-go” decision regarding feasibility. If a “go” decision was made, a longer-term test would be necessary to develop the same applicability information as was to be developed for GrahamTek in this study. If a “no-go” decision was made, additional testing of the Zeta Rod would not be recommended.

Specific testing objectives included:

- Operate the GrahamTek pilot-scale unit for a period of approximately three months on a continuous basis.
- Operate the Zeta Rod (with downstream bench-scale unit) for a period of two weeks on a continuous basis.
- Monitor critical performance parameters for each unit as a function of operating time. These parameters included:
 - permeate and concentrate flow;
 - feed and concentrate (and where applicable, permeate) pressure; and
 - feed, concentrate and permeate conductivity and analyze these data as a function of operating time to determine if and to what extent membrane fouling and/or scaling occurs during the testing period
- Periodically collect samples of unit feed, concentrate and permeate and measure levels of the following constituents (GrahamTek system only). Together with this data and unit flows, perform a mass balance on the constituents to estimate their recovery and indirectly assess the likelihood of mineral precipitation by sparingly soluble salts containing these constituents:
 - barium
 - strontium
 - calcium
 - alkalinity
 - sulfate
- Measure the quality of the product water to determine if it (1) meets selected federal and state drinking water regulations or (2) is of a quality that when blended with plant finished water will meet drinking water regulations
- For the MWD unit, assess process operability (on-line factor)
- Autopsy a membrane element from operation of each unit to determine the presence / absence of mineral scales
- Assess the chemical stability of the MWD waste discharge relative to its tendency to precipitate minerals in the time required for waste conveyance from the WTP to the WWTP. (Due to the difficulty in maintaining suitable performance of the test units, this objective was not addressed in this testing.)

Test Equipment and Methodology

Analytical

Field

Field data was collected for both the GrahamTek RO system and the Zeta Rod system to evaluate performance. The data that was collected included:

- Membrane and concentrate pressure
- Feed pH
- Feed temperature
- Permeate, concentrate, and concentrate recycle (Zeta Rod system only) flowrate
- Feed, permeate, concentrate, and concentrate recycle (Zeta Rod system only) conductivity
- Feed total and free chlorine (GrahamTek system only)
- Feed turbidity(GrahamTek system only)
- Feed SDI (GrahamTek system only)

All of the data collected for the GrahamTek system except the free and total chlorine, feed turbidity, and feed SDI was read from the GrahamTek pilot unit. The free and total chlorine were determined by the DPD method.

For the Zeta Rod system, only the feed temperature, feed pH, flowrates, and pressures were read from the unit. Each of the conductivity measurements was made using a conductivity meter.

Laboratory

Weekly and monthly samples were taken of the feed, permeate, and concentrate of the GrahamTek system. These samples were shipped to the CH2M HILL Applied Sciences Lab for analysis. Combined with flow data, these samples were used to perform a mass balance on constituents to determine if precipitation is occurring. Table 1 summarizes the analysis performed for each sample event.

TABLE 1
Laboratory Analysis Sampling Schedule

Weekly Sampling	Monthly Sampling
Anions	
Total Alkalinity	Total Alkalinity
Sulfate	Sulfate
	Chloride
	Fluoride

TABLE 1
Laboratory Analysis Sampling Schedule

Weekly Sampling	Monthly Sampling
Other	
Total Dissolved Solids	Total Dissolved Solids Silica, Reactive
Cations	
Barium, Ba	Barium, Ba
Calcium, Ca	Calcium, Ca
Strontium, Sr	Strontium, Sr
	Aluminum, Al
	Iron, Fe
	Magnesium, Mg
	Manganese, Mn
	Potassium, K
	Sodium, Na

Pilot Plant Description

A process schematic of the pilot plant is shown in Figure 1. With minor exceptions, all equipment was set up and operated in the WTP demineralization building.

Feedwater Extraction, Pumping and Storage

Wastewater from the four full-scale EDR units served as feedwater to the GrahamTek and Zeta Rod/RO systems. Wastewater was extracted from the plant waste header and pumped to the feedwater holding tank. The tank was necessary to provide a continuous supply of feedwater to the desalting systems when a clean-in-place (CIP) was performed on the EDR units. Initially, a 600-gal tank was installed adjacent to the GrahamTek unit. This volume was determined to be insufficient to maintain flow to the GrahamTek unit when one or more EDR units were removed from service for CIP and the tank was subsequently replaced with a larger, 2,100-gal tank, located outside the demineralization building.

Feedwater Dechlorination

The EDR system feedwater is chlorinated to provide a low free chlorine residual through the EDR stacks (0.5-1.0 mg/L target range). This is necessary to control biofouling of the membranes and spacers. The polyamide RO membranes used in this study (and most applicable to the treatment and recovery of the high salinity EDR wastewater) have very limited tolerance to free chlorine. Koch/Fluid Systems recommends that the free chlorine residual of feedwater to their elements be maintained at <0.1 mg/L. To accommodate this requirement, the EDR wastewater was initially dosed with aqueous ammonia to convert the free chlorine to combined chlorine as the latter has been shown to be compatible with

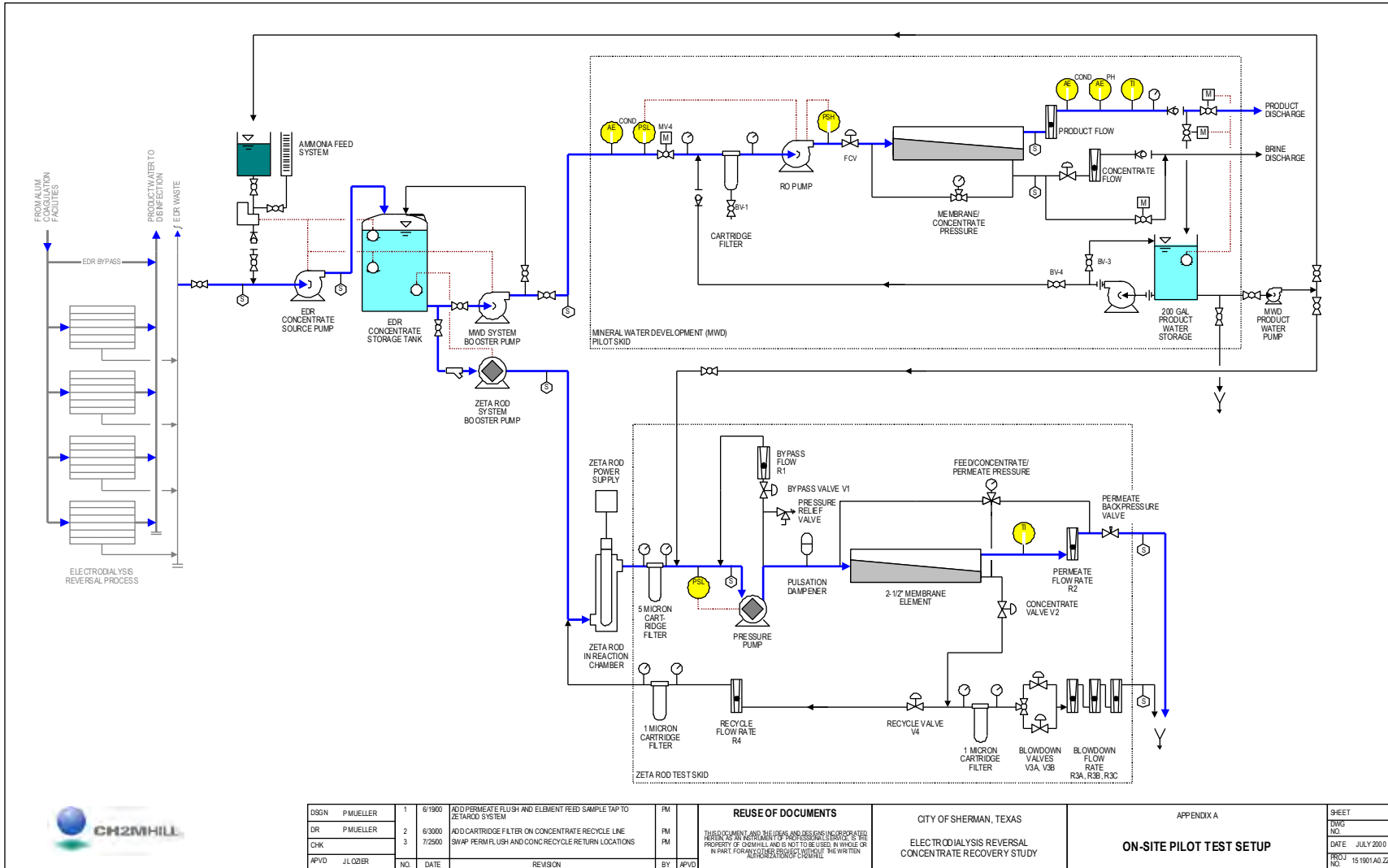
polyamide RO membranes and also provide excellent biofouling control. Despite the dosing of ammonia in doses well in excess of the stoichiometric requirement for free chlorine conversion, it was determined that not all of the free chlorine was being successfully converted. The presence of the residual free chlorine was considered a contributing factor to the increase in GrahamTek permeate conductivity during the first run. Consequently, dechlorination was performed with sodium metabisulfite (SMBS), a strong reducing agent, during the second GrahamTek run. SMBS proved more effective for dechlorinating the EDR wastewater, reducing the free chlorine residual from an average of 0.80 mg/L with ammonia to 0.10 mg/L.

Zeta Rod/RO System

Zeta Rod is a patented ceramic electrode that uses capacitance and electrostatic dispersion of mineral and colloidal dispersion to prevent scaling and fouling of surfaces. The electrode converts 110 volt alternating current to 35,000 volts direct current (at 600 microamperes) and uses this electrical potential to charge organic and inorganic particles passing by the electrode. When coupled with downstream conventional RO technology, the Zeta Rod acts as a capacitor to elevate the surface charge of particles in the RO feedwater and prevent their interaction, with the intent of eliminating or greatly inhibiting fouling and scaling of the RO membrane surface. The device has been shown to reduce biological fouling in an industrial RO facility (2) and has found to be compatible with both hollow fine fiber and spiral wound RO elements (3), (4). The device serves to pretreat the feedwater to a conventional RO system.

A model ZR18S electrode (1-in diameter, 18-in long) and a model ZRPOV power supply was installed as part of the Zeta Rod system to treat flow from the feedwater holding tank. The Zeta Rod system consisted of a power supply, ceramic electrode and PVC flow-through housing for the electrode. Tank flow was pressurized by a transfer pump, flowed through the Zeta Rod and into the CH2M HILL bench scale RO unit.

FIGURE 1
Process Schematic for Pilot EDR Wastewater Treatment Systems

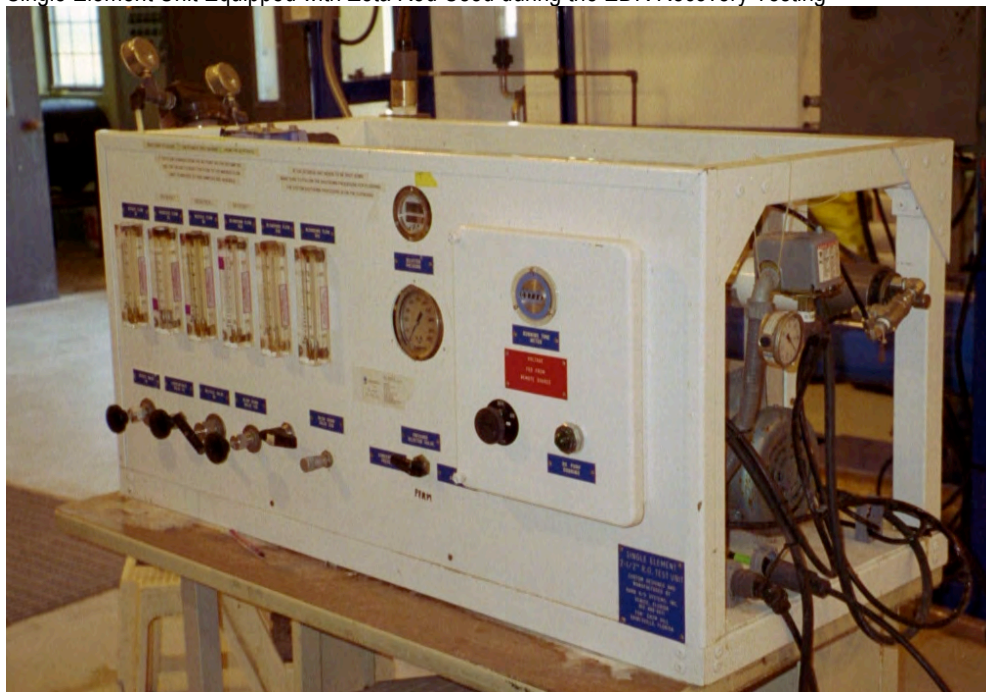


Single Element Bench-Scale RO Unit

EDR wastewater pretreated by the Zeta Rod was then treated using a single element bench-scale RO unit (SETU) provided by CH2M HILL. A photo of the SETU is shown in Figure 2. Major components of the SETU included a cartridge filter, high pressure feed pump, pressure vessel containing one 2.5"-diameter by 40"-long RO spiral wound element, Koch/Fluid Systems model 2540HR thin film composite polyamide type membrane, and flowmeters and pressure gauges. Unlike, the GrahamTek unit, which operates in a single pass mode (feed flow entering the pressure vessel is converted to permeate and concentrate and wasted from the system), the SETU operated in both single pass and concentrate recycle modes (a portion of the concentrate exiting the pressure vessel is recycled back and blended with the incoming feed) depending on feedwater recovery¹. At feedwater recoveries >15%, concentrate recycle was employed. Permeate and waste concentrate flows from the SETU were directed to the EDR wastewater holding pond. When required, the SETU element was chemically cleaned to remove foulants and scalants accumulated during operation. No chemical treatment was applied to the Zeta Rod/RO feedwater.

FIGURE 2

Single Element Unit Equipped with Zeta Rod Used during the EDR Recovery Testing



Start-Up/Shutdown

From June 16 to 25, 2000, the Zeta Rod/RO system was operated intermittently for equipment start-up and shutdown. During this period, several mechanical issues were addressed with the RO unit.

Element No. 1 was operated for 317 hours from the period June 26 through July 16, 2000 at 50% system recovery. During this period, it became apparent that particulates were forming during treatment and impacting the operability of the system by plugging orifices of the

¹ Feedwater recovery is defined as (permeate flowrate/feedwater flowrate) x 100, expressed as a percentage.

small valves used to set and maintain concentrate waste and recycle flows. The pluggage problem made it very difficult to maintain steady state operation, with feed pressures increasing, permeate flow increasing and concentrate flow decreasing. To alleviate this problem, a 5-um cartridge filter was installed upstream of the concentrate control valves to capture the particulates. Later the rating of the filter was reduced to 1-um to improve solids retention.

The system was off line from July 17 through August 6, 2000, during which time the cartridge filter was replaced with a stainless steel, higher pressure rated unit, and the concentrate recycle stream was re-located to blend concentrate and feedwater directly upstream of the Zeta Rod. (This was done to enable the Zeta Rod to assist in particle formation.) A second 1-um cartridge filter was also installed downstream of the Zeta Rod to capture solids present in the combined feed / concentrate recycle stream. A flush line from GrahamTek permeate tank was installed to allow RO unit flushing with permeate prior to or following shutdowns. A process and instrumentation diagram for the modified Zeta Rod / RO system is shown in Figure 1.

On August 7, 2000, element No. 2 was installed and the system operated at target conditions until September 1 for a total of 468 hours. During this period, the unit experienced shutdowns caused by failure of the system feedwater supply pump and of the pulse dampener. In addition, a portion of discharge flow from the high pressure pump was diverted to waste from the pressure relief valve being set at too low a blowoff pressure. The unplanned shutdowns resulted in the unit not being flushed with product water until the next calendar day, potentially resulting in mineral precipitation within the RO element. Consequently, on August 22, 2000 (at 274 hours of operation), the RO element was chemically cleaned using a 2% citric acid solution.

To determine if the Zeta Rod was contributing to the increased permeate conductivity observed during operation of elements 1 and 2, on October 11, a third RO element was installed and operated at 15% element and system recovery on EDR wastewater not pre-treated by the Zeta Rod. Element No. 3 was operated for 626 hours until December 7, 2000. This concluded Zeta Rod / RO system testing.

Testing Protocol

Table 2 presents the protocol used to evaluate the feasibility of the Zeta Rod / RO systems for EDR wastewater treatment. The main intent of the protocol was to operate each unit at increasing feedwater recovery, monitoring system performance at each recovery to determine if performance declines were evident.

TABLE 2
Zeta Rod System Operating Conditions

Recovery	Permeate Flow (gph)	Concentrate Flow (gph)	Concentrate Recycle Flow (gpm)
50%	12	12	1.0
15%	12	68 (1.13 gpm)	--

Given the short planned operating duration, the Zeta Rod / RO system was operated at a

target system recovery of 50% and an element recovery of 15%.² A follow-on, negative-control test was conducted at system and element recoveries of 15% with the Zeta Rod power supply inactive to determine if the Zeta Rod was contributing to the membrane performance degradation observed in the first run.

Data on the flows, pressures, and conductivities was collected twice daily to evaluate membrane scaling and/or fouling. One of the membrane elements used in the testing was sent to the Bureau of Reclamation Engineering and Research Center (BORERC) for an autopsy.

Results

Zeta Rod/RO System

Water Quality Characterization

No characterization of the quality of the Zeta Rod /RO system feed, permeate or concentrate was performed during the study as the focus of this testing was to characterize performance changes only.

System Performance

The Zeta Rod /RO system was evaluated for a total of 1,461 hours in which three separate RO elements were operated. The operational results for elements No. 1, 2, and 3, respectively, are summarized in Figures 3 through 10. (Performance results for element No. 2 span 0 to 468 hours of run time, and performance results for element No. 3 span 516 to 1143 hours of run time, as shown in Figures 7 through 10.)

² System recovery is calculated as $[\text{permeate flow}/\text{feed flow}] \times 100$ where feed flow does not include concentrate recycle. Element recovery is defined similarly, except feed flow includes both feed and concentrate recycle flows.

FIGURE 3
Zeta Rod Element No. 1 Feedwater Recovery

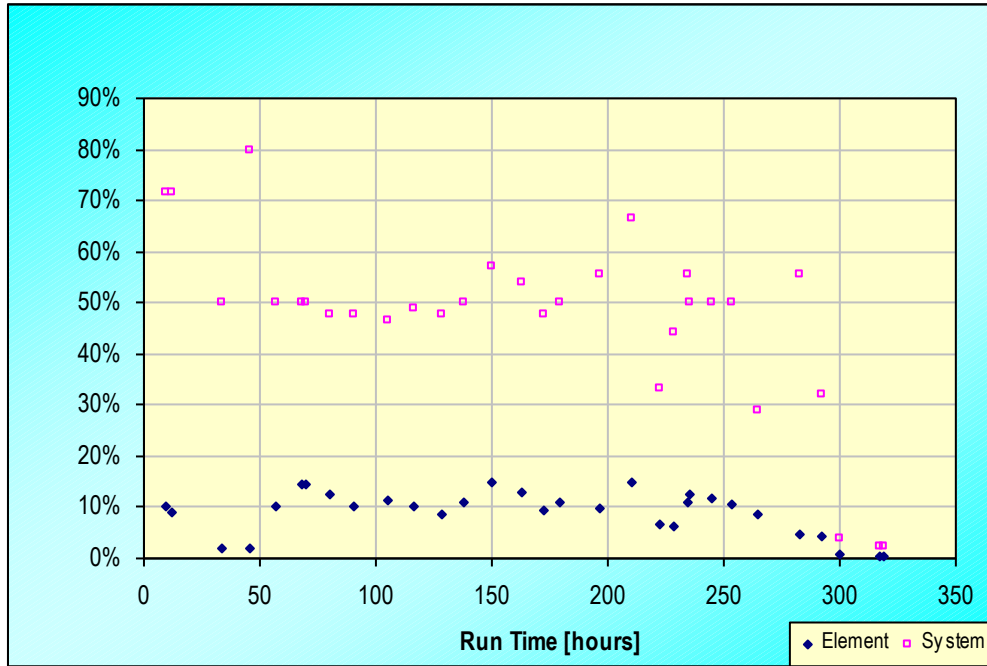


FIGURE 4
Zeta Rod Element No. 1 Feed Pressure

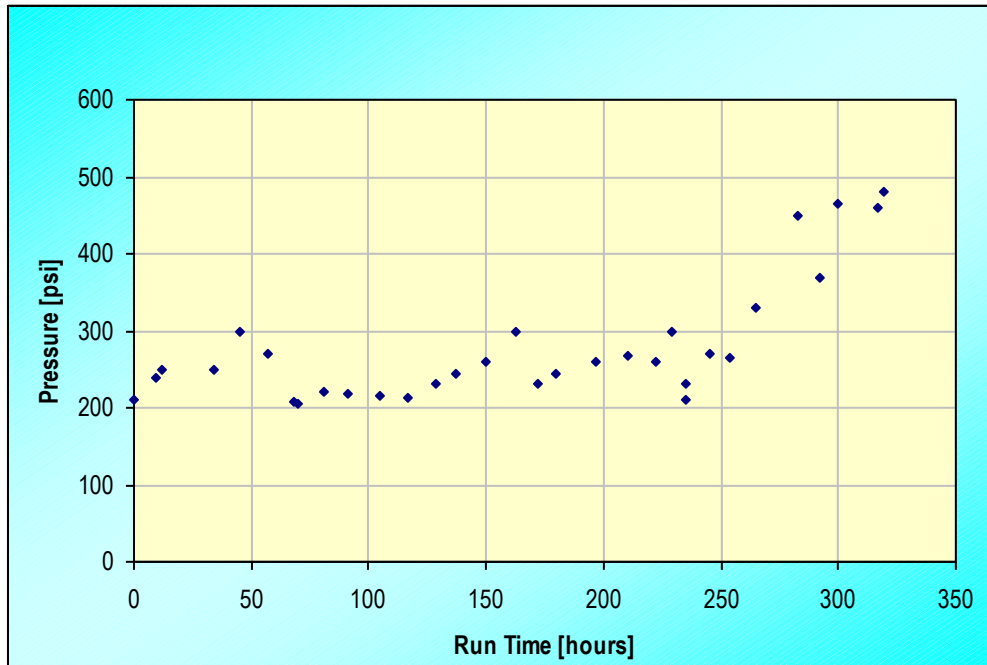


FIGURE 5
Zeta Rod Element No. 1 Feed and Permeate Conductivities

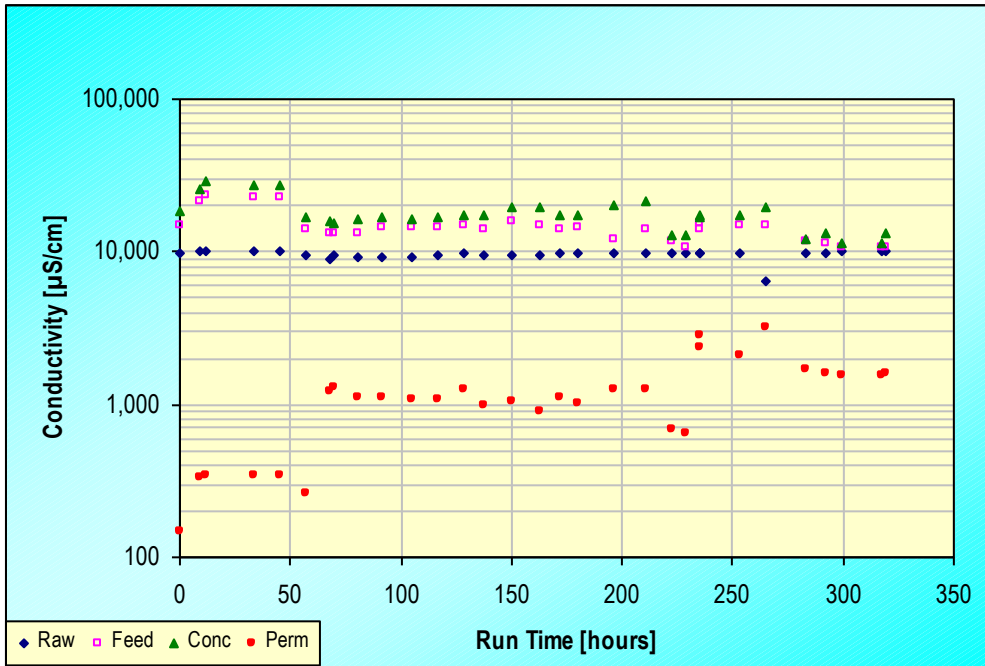


FIGURE 6
Zeta Rod Element No. 1 Water and Salt Transport Coefficients

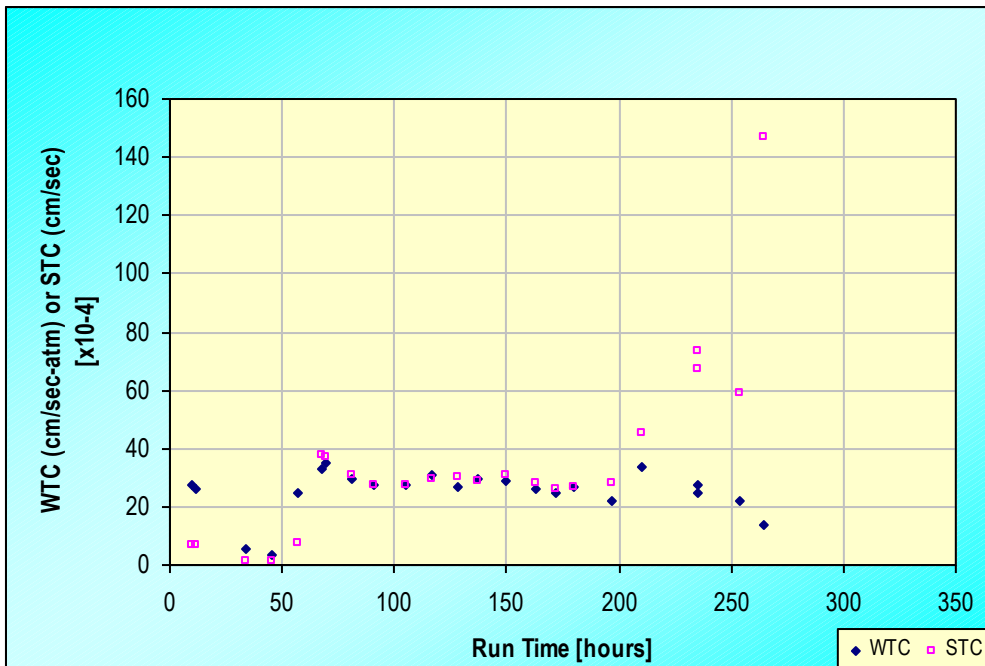


FIGURE 7
Zeta Rod Element Nos. 2 and 3 Feedwater Recovery

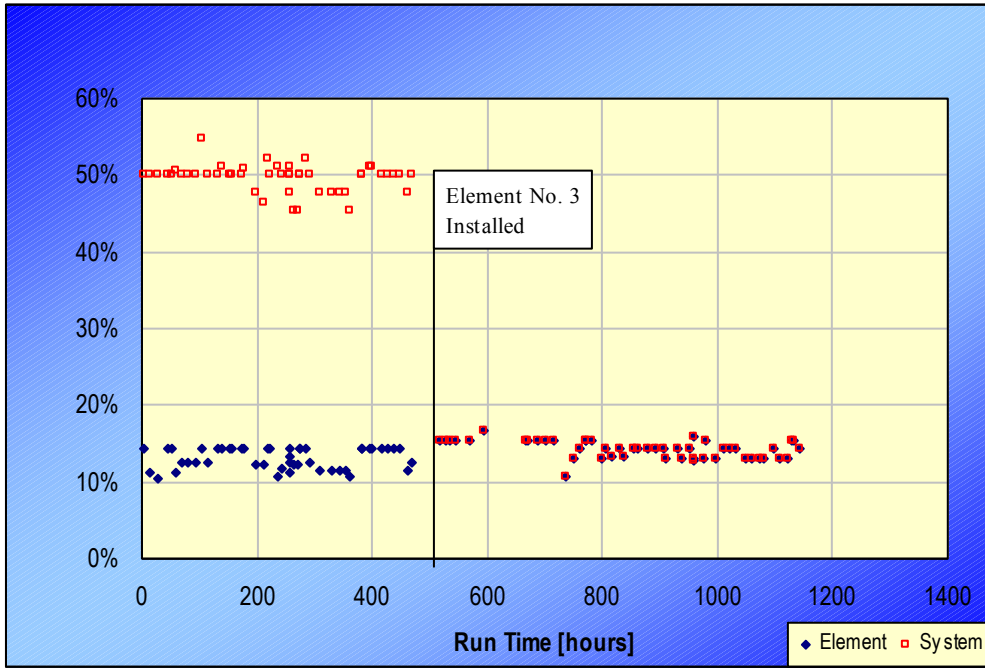


FIGURE 8
Zeta Rod Element Nos. 2 and 3 Feed Pressure

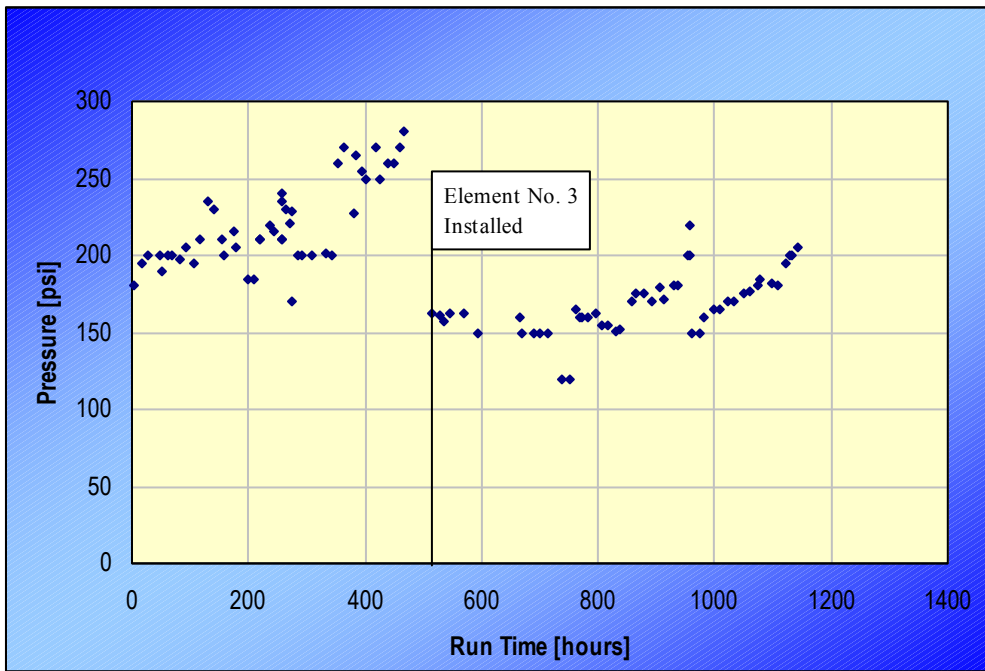


FIGURE 9
Zeta Rod Element Nos. 2 and 3 Feed and Permeate Conductivities

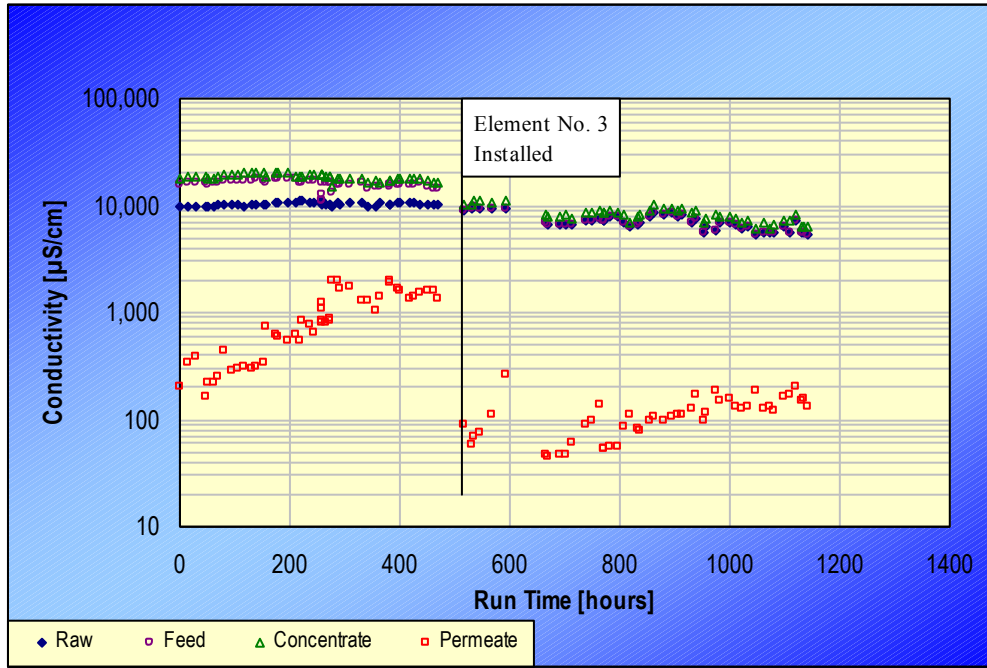
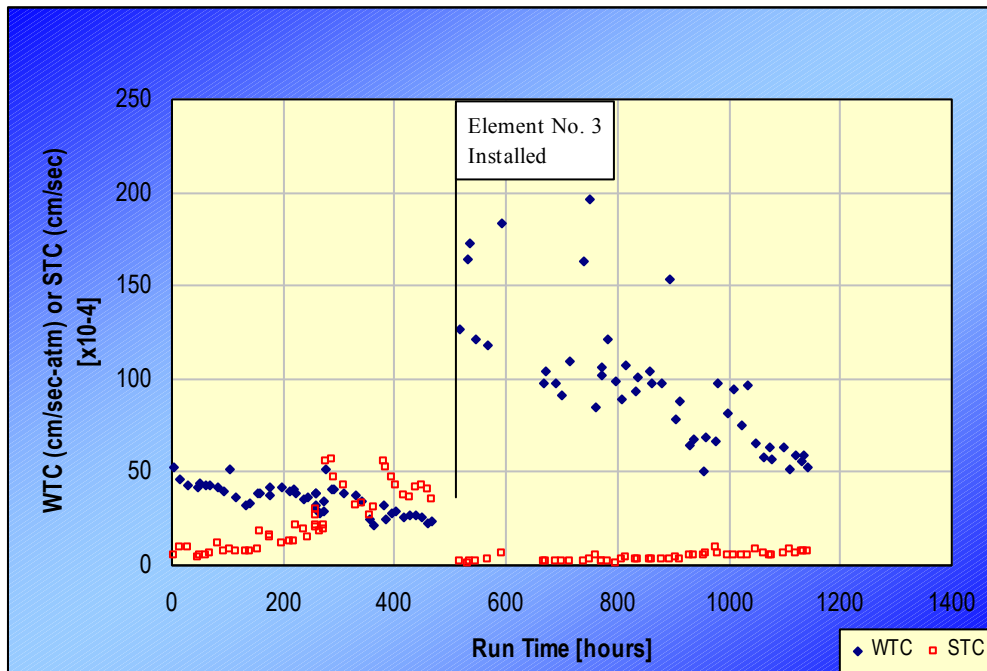


FIGURE 10
Zeta Rod Element Nos. 2 and 3 Water and Salt Transport Coefficients



Element No. 1

Feedwater recovery was consistently maintained at the target value of 50% although some variations did occur. These were associated with the difficulty of adequately controlling the very low waste concentrate flows. Feed pressure was quite stable during the first 250 hours of operation, at which time it increased dramatically. Product water conductivity showed a step increase from 350 to 1,300 uS/cm at ~60 hours. WTC was stable until feed pressure increased at which time it declined rapidly. Likewise, STC changes mirrored those of product water conductivity. The increases in feed pressure and product conductivity and decline in WTC are attributed to unplanned shutdowns and lack of timely feedwater flush associated with valve plugging. Following these uncontrolled shutdowns, supersaturated salts would have an opportunity to precipitate within the feed channels of the element. Based on the results of the autopsy of element No. 1 (see subsequent section titled Element Autopsy), calcium sulfate was the predominant precipitated salt.

Element No. 2

In contrast to that of element No. 1, the performance of element No. 2 showed no period of stability. Feed pressure and permeate conductivity increased and WTC decreased steadily from start-up through the end of testing. No autopsy was performed with this element to determine if precipitated salts were accumulating at the feed end the element (like element No. 1), however ΔP was stable during the entire period of operation. This indirectly indicates that any salt buildup was minor. The cartridge filters did show a pressure drop increase indicating retention of particulate material. It may be more likely that the performance declines resulted from precipitation of sparingly soluble salts from concentration at the membrane surface (which would be more noticeable at the concentrate end), chemical oxidation of the membrane, or a combination.

Element No. 3 (Without Zeta Rod)

Element No. 3 performance was stable for the first 320 hours at which time, feed pressure increased and WTC declined steadily. Product water conductivity did increase during this latter period of operation but at a much lower rate and to a much lesser extent than for element No. 2. Further, chemical cleaning was successful in reducing feed pressure and increasing WTC (see step change at 960 hours run time) but not the increase in product water conductivity. These changes indicate that fouling, rather than scaling was causing the decrease in WTC, but oxidation was responsible for the conductivity increase. Following the cleaning, the element exhibited the same rate of fouling as prior.

Element Autopsy

Element No. 1 was shipped to the Bureau of Reclamation Engineering and Research Center (BORERC) following completion of testing. The element was flushed with product water prior to shipping. The BORERC autopsied the element and produced a report on their findings which is presented as Appendix A. Scanning electron microscopy (SEM) of the membrane surface, originally planned as part of the autopsy, was not performed. The major findings from the autopsy are:

- A large amount of salt was present in the feed channel (vexar) of the elements.
- The salt was predominantly calcium sulfate. When dissolved in acid, the solubilized fraction of this salt was 97% percent calcium sulfate.
- The manner in which the salt was deposited within the feed channel (predominant at

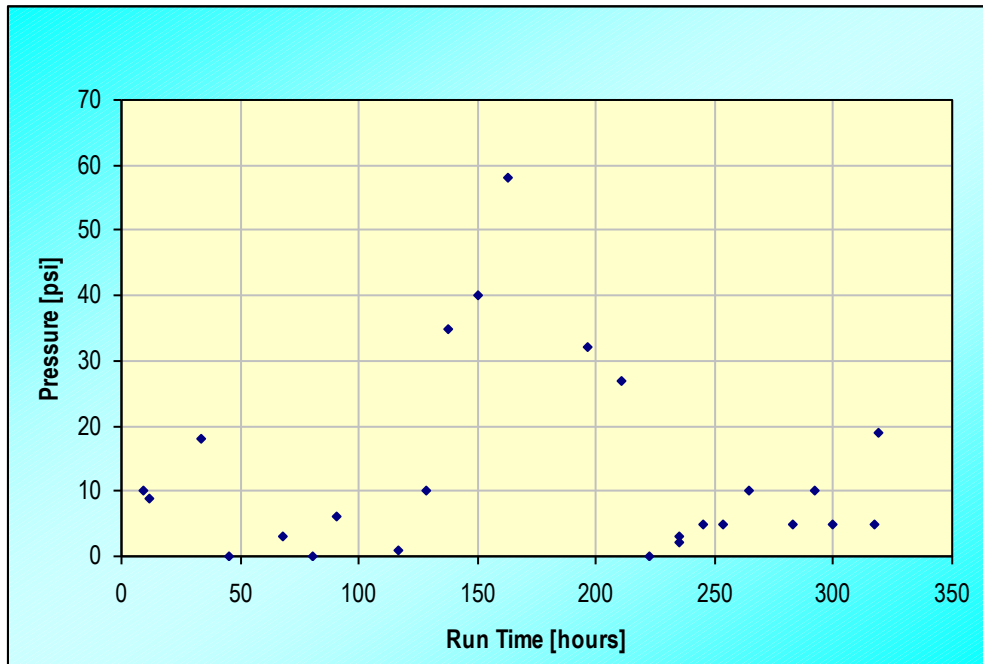
feed end of element) suggests the salt was already present as a precipitate in the element feed and was not precipitated at the membrane surface from soluble calcium sulfate.

- The mass of deposited salt would have caused a significant increase in the feed / concentrate differential pressure (ΔP).

The BORERC staff postulated that four salts, barium sulfate, calcium sulfate, strontium sulfate and calcium carbonate, were supersaturated in the element feed. The degree of supersaturation was not above that allowed with the use of a scale inhibitor, however. At 50% recovery, the calcium sulfate was estimated to about 2.2 times saturation in the concentrate. This degree of supersaturation could have caused calcium sulfate to precipitate in the concentrate recycle loop. Three alternatives are possible to explain the presence of precipitated salts in the element: (1) the salts present in the water held in the element precipitated when the RO unit was shut down and the supersaturated feed / concentrate solution was not flushed prior to element removal and draining, (2) precipitation occurred during or after EDR treatment or (3) precipitation occurred in the concentrate recycle loop. Alternative (1) is not feasible as it would produce a precipitation pattern different from that observed from the autopsy and could not produce the mass of salt collected.³ There is no way of knowing whether alternative (2) or (3) was the cause, however alternative (3) is more likely given the higher concentration of calcium sulfate in this stream. It should be noted that the ΔP did increase from 5 to 10 psi to 30 to 40 psi near the latter period of testing, consistent with the BORERC's conclusion (see Figure 11).

³ The mass of salt present in the hold-up volume of the element is calculated as follows:
(1.25in/12in/ft)²* π *(40in/12in/ft)*7.48gal/ft³*3.785L/gal* 0.5 = 1.6L*6.5 g/L = 10.4 grams. This is <20% of the salt mass removed from one leaf and there are multiple leaves in the element.

FIGURE 11
Zeta Rod Element No. 1 Differential Pressure



Conclusions and Recommendations

General

1. At 50% feedwater recovery, RO treatment of the EDR wastewater produces a high quality treated water that should be acceptable for direct blending with the existing water treatment plant's filtered water. This is based on the low TDS and hardness of the RO permeate (<100 mg/L and ~15 mg/L as CaCO₃). If such treatment were to be implemented in the future, it is recommended that additional permeate testing be conducted to confirm that all applicable drinking water regulations can be met. Production of potable water from the EDR wastewater by RO appears to be limited by the scaling potential not the permeate quality. Salt removal should be sufficiently high that treatment to 80% recovery is feasible for direct product water blending assuming an effective scale control method can be demonstrated at this recovery.
2. The EDR wastewater cannot be effectively treated by RO as it currently exists. The wastewater is characterized by a high oxidation potential and contains significant concentrations of free chlorine caused primarily by the high chlorine concentration of the electrode waste stream and to a lesser extent by chlorination of the EDR feedwater. The high oxidation potential caused chemical degradation of the thin-film rejecting layer of the RO membrane and cannot be practically controlled by addition of a reducing agent (e.g., sodium bisulfite). A suitable control strategy, that would require demonstration, would be to change from free chlorine addition to chloramination of the EDR feedwater and to segregate the electrode waste stream from the EDR wastewater.

3. RO membrane degradation caused by exposure to the high oxidation potential of the wastewater did not allow a clear assessment of the feasibility of either EDR wastewater treatment technology (GrahamTek and Zeta Rod). Performance changes resulting from the degradation, which include increased salt passage and potentially decreased WTC, would mask similar performance changes that are expected to occur from the precipitation of sparingly soluble salts, the main concern in treating the wastewater with RO. The conclusions presented below for the GrahamTek and Zeta Rod/RO systems should be considered in this context.

Zeta Rod/RO System

1. The Zeta Rod improved operability of the conventional RO treatment (relative to no pretreatment) although the mechanism responsible for the observed reduction in membrane fouling is not well understood. Feed pressures and WTC were more stable during Zeta Rod use at 50% recovery than without its use at 15% recovery. By increasing the surface charge of the ions and colloids in the EDR wastewater, the Zeta Rod may actually de-stabilize the sparingly soluble salts, resulting in their precipitation in the feedwater, thereby reducing the potential for these salts to scale the membrane surface. Such precipitation was evident from membrane autopsies and indirectly from valve orifice clogging and solids loading on 1-um cartridge filters. If the precipitated salts can be effectively captured before they reach the RO element so that clogging of the feedwater spacer can be minimized, a low-cost approach to EDR treatment and recovery may be available. Longer-term testing will necessary to successfully demonstrate this approach before a full-scale system could be implemented.
2. As observed with the GrahamTek system, salt passage increased dramatically during testing with and without the Zeta Rod, indicating the RO membrane was being degraded by oxidants in the EDR wastewater. The rate of increase in RO salt passage appears to be proportional to feedwater recovery, again an observation consistent with GrahamTek test results, suggesting that whatever is oxidizing the RO membrane is concentrated by RO treatment.

Recommendations

- 1) Prior to the testing and evaluation of any RO-based treatment and recovery system, the EDR system should be modified as follows to eliminate the high oxidation potential of the wastewater:
 - a) Provide an ammonia addition point in the filter effluent line to provide the capability to dose the effluent with ammonia as well as chlorine to form chloramines. It is recommended that a 1-2 mg/L combined chlorine residual be applied to the EDR feedwater to adequately control biological growth in the EDR stacks. CH2M HILL has discussed the use of continuous chloramination with Ionics technical representative (Bob Allison) and have been told that chloramination is compatible with the EDR membranes and has been used previously with full-scale EDR installations.
 - b) Isolate the electrode waste streams exiting each unit degasifier, manifold these together in a dedicated waste line and discharge this line directly to the EDR wastewater holding pond.
- 2) Conduct a three-month pilot test of the Zeta Rod in combination with a larger-scale RO system to reduce the probability of process upsets that occurred with the small-scale (2.5") unit. This could be a single 4" element based unit or a multi-stage 4" system

similar to what is being contemplated for use in plant expansion pilot testing. A potentially cost attractive approach is to obtain a 4" single element unit from Osmonics for such testing. Osmonics is currently providing such a unit to CH2M HILL, complete with RO membranes, at no charge for testing at both Abilene and Wichita Falls. Either system will require outfitting with appropriate cartridge filters to retain precipitated solids that may form from Zeta Rod treatment. To better understand the effect of Zeta Rod treatment on supersaturated salts in the EDR wastewater, it is recommended that such testing incorporate filtering of the Zeta Rod inlet, outlet and RO concentrate through 0.45-um pore size (or smaller) filter discs to quantify the extent to which Zeta Rod use is causing mineral precipitation, directly in the RO feedwater or during RO treatment.

References

- (1) Kalish, P., Graham, W. and A. van Vugt. Novel Low Cost Reverse Osmosis System for Seawater and Brackish Water Desalination. Proceedings of the 1997 IDA World Conference. Madrid, Spain.
- (2) Romo, R.F.V., and M.M. Pitts. Application of Electrotechnology for Removal and Prevention of Reverse Osmosis Biofouling. Environmental Progress. 18 (2) 107-112. Summer 1999.
- (3) Letter from T.J. Eckman, DuPont Fabrics & Separations, to M. Michael Pitts, Zeta Corp, dated September 10, 1998.
- (4) Letter from W.T. Bates, Hydranautics, to Rodrigo Romo, Zeta Corp, dated May 6, 1999.

Appendix A

Zeta Rod Element Autopsy

SPIRAL WOUND MEMBRANE ELEMENT AUTOPSY

PURPOSE AND LOCATION OF AUTOPSY
<p>Purpose of Autopsy: To determine if there is any material on the membrane surface or in the membrane and, if so, what and where it is.</p>
<p>Date and Place: August 28, 2000 Pilot Plant Laboratory, Room 1755, Building 56, DFC</p>
<p>Date of This Report: December 7, 2000</p>
<p>Names of Observers: Susan Martella (recorder) Frank Leitz</p>

ELEMENT IDENTIFICATION	
Manufacturer:	Koch Membrane Systems/Fluid Systems
Element Type:	2540 TFC® HR
Serial Number:	560881
Element Dimensions:	Nominal size: 2.5 inches by 40 inches Measured size at anti-telescoping devices: 2.45 inches by 38 inches Membrane bundle size: about 2.2 inches by 36.75 inches
Number of Leaves:	Two
Size of Leaves:	Overall size: 36 3/4" by 27 3/4" = 7.08 ft ² = 0.659m ² Active area (per face): 33.67" by 23.56" = 793 in ² = 5.51 ft ² = 0.512 m ²

Total active area in element: $3,172 \text{ in}^2 = 22.0 \text{ ft}^2 = 2.05 \text{ m}^2$

OPERATING HISTORY

Information on the operating history and events leading to the autopsy was supplied by CH2M Hill who requested the autopsy.

The element was operated in a pilot unit installed at the Sherman, Texas, water treatment plant. The unit consists of a Zeta-Rod treatment system followed by a single 2.5 by 40 inch test vessel connected in a feed-and-bleed mode. This unit is fed with the concentrate stream from an electro dialysis reversal system used in the water treatment plant. The purpose of this test is to determine whether additional water can be recovered from this concentrate stream by use of these technologies.

The feed water sampled on June 19, 2000, was analyzed as follows:

Total dissolved solids	6,500	mg/L
Sulfate	1,730	mg/L
Alkalinity	339	mg/L as CaCO ₃
Calcium	712	mg/L
Strontium	14	mg/L
Barium	0.391	mg/L

DESCRIPTION OF EVENTS LEADING TO AUTOPSY

Our understanding is that the element had been in service for about a week. During that week the inlet pressure was slowly increasing. This increase in pressure caused the element to be removed from the unit. Pressure, flow and recovery data are not available to us.

WET TEST DATA

Test Number	Procedure	Date	Element Rejection %	Product Flow GPD	Product Flux GFD
None					

SUMMARY OF WET TEST PROCEDURE(S)

Not applicable.

NARRATIVE DESCRIPTION OF AUTOPSY PROCEDURE

Note: Observations made during the autopsy are recorded in the next section of this report.

Bagged element was removed from refrigerated storage.

Element bag was cleaned on the outside and then opened. A single plastic bag was used to transmit the element.

The identifying label was recorded, removed from the element, and retained.

Feed and reject ends of product water tube were marked. *Note:* We assumed that the end of the element on which the chevron ring brine seal was mounted was the feed end. If this is incorrect, then references to feed and reject end should be reversed.

The element was examined for damage, odors etc. A sample of the crystalline material found on the outside of the element was preserved as Sample 1.

The element was dried with a Kleans™ tissue wipe.

The brine seal was removed, examined, and retained. This was marked as Sample 2.

We marked feed end (brine seal) and reject end of product water tube as well as the corresponding sides of the autopsy table.

Element outer wrap, blue tape, was removed. A piece of this tape was retained in the envelope with Sample 2.

Anti-telescoping devices from each end of the element were removed, examined, and retained.

We unrolled Leaf 1. By our convention, the first leaf unrolled is called Leaf 1. Unrolling Leaf 1 exposes the concave side of the leaf. Since the element is lying on the autopsy table at that point, any features on the convex side of the last leaf, in this case Leaf 2, are spoiled. The leaf is unrolled so that the vexar sheet lies on top of the concave surface.

A portion of the salt from the membrane was collected as Sample 3.

After examination of the feed/brine passage, the vexar lying on top of Leaf 1 was removed and set aside to provide a smooth surface to work on. Some salt remained in the vexar when it was removed. A swatch of the vexar with included salt was kept as Sample 5.

NARRATIVE DESCRIPTION OF AUTOPSY PROCEDURE (continued)

Leaf 1 was turned over carefully to expose the concave side of Leaf 2.

We made as complete a collection as possible of all the salt deposit in the feed/reject flow channel between two leaves. This was obtained by scraping with a dry squeegee the concave side of Leaf 2 and the convex side of Leaf 1 and teasing the crystals out of the intervening vexar. This was Sample 6.

A piece of sticky tape just under 2 inches wide is used to protect the fold in the membrane between leaves from puncture by the edges of the vexar sheet. At this time we removed the tape, and preserved in the envelope with Sample 2.

Two pieces of membrane, including both membrane faces and the product water carrier in between were cut from the feed end of Leaf 2. These were identified as Sample 7.

After removing the salt from Leaf 2, we attempted to remove some of the yellowish brown material by going over the surface with a squeegee and deionized water. This produced a very dilute suspension identified as Sample 8.

Measurements were made on Leaf 2. Since the glue lines, which define the active area, are usually not straight but tend to be wavy, we typically take two or more measurements across the active area and average them.

Total leaf length = 36 3/4"

Total leaf width = 27 3/4"

Active leaf length: 33 1/2", 33 3/4", 33 3/4" Average = 33.67"

Active leaf width: 23 1/4", 23 7/8" Average = 23.56"

At the end of the autopsy, the element was rebagged, labeled, and stored. The remnants of the autopsied elements and samples not consumed in analysis are typically stored for about one year in case there is any further inquiry.

OBSERVATIONS

There was a modest amount of white, crystalline material scattered over the outside of element. After removing the element, a few milliliters of liquid with some crystalline material in it remained in the bag.

Once the element was removed from the bag, no liquid drained from the element.

There were no obvious smells anywhere on the element.

The chevron ring brine seal was found to be flexible and strong, with no nicks or cracks.

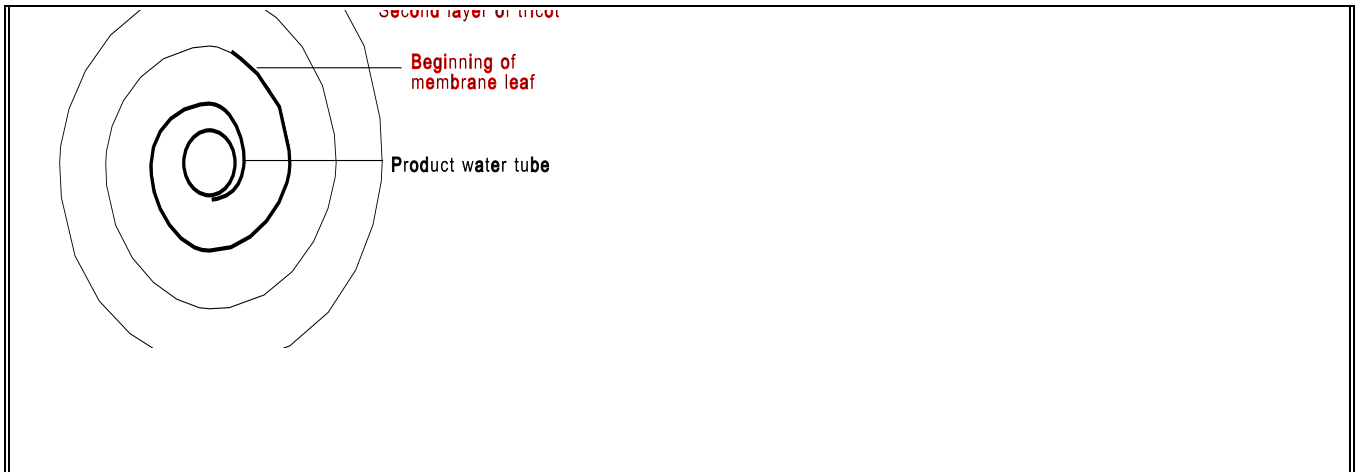
The blue tape used to wrap the element was still strong and reasonably adhesive. It was not discolored; the color of the portion on the outside of the element was consistent with that of the unexposed portion.

The anti-telescoping devices had not been glued in place, but rather had been taped in place using about a yard of blue tape (ends retained). Once the tape was removed, the devices easily slid off the ends of the product water tube. The devices were not found to be damaged in any easily detectable way.

A piece of salt a little larger than a dime had accumulated between the flange of the anti-telescoping device and outer wrap on the feed end of the element. There was no similar accumulation on the reject end.

The outer wrap of the element consisted of a single piece of blue tape, the same kind used for securing the anti-telescoping devices, about 2" wide and tapered at both ends. This was wrapped in a helical manner, each layer overlapping the previous layer by about 50%.

A layer of tricot material was wrapped entirely around the element. Outer layer of tricot material was glued or welded in a strip about $\frac{1}{2}$ inch wide along entire length of element and around entire circumference at both ends. The element leaves began at third wrap, see detail below.



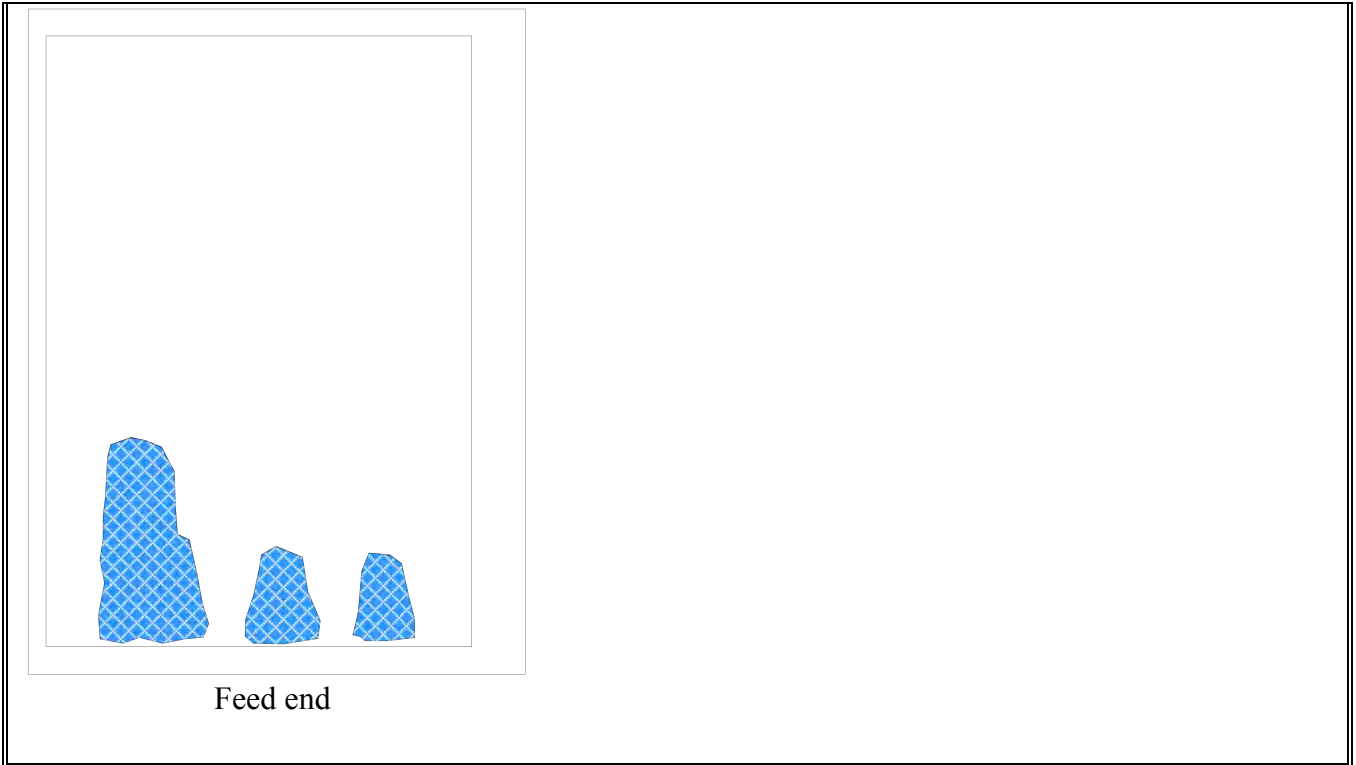
OBSERVATIONS (continued)

There was no visible accumulation of material on the front (feed) face of the element bundle.

When Leaf 1 was unrolled, heavy deposits of salt were found along the feed end of the leaf. The salt was not evenly distributed across the leaf but was concentrated across what we believe was the feed end of the leaves. Where there was a deposit, it appeared to be almost solid from one membrane surface through the vexar to the other leaf. The solidity of the deposit is uncertain visually since salt stuck to the membrane surfaces and thus broke into several layers, one on each membrane, with a modest amount still adhering to the vexar. The deposition appeared to be only on the active area, starting essentially at the downstream edge of the glue line on the feed end. While it is not possible to say that the distribution of salt that we saw was not influenced by the process of unrolling the element leaf, it appears that even across the entrance to the leaf, the salt was not evenly distributed. There was a region 3 to 4 inches from the product water tube where there was no deposit. Further out into the element, measured from the tube, was the heaviest deposit, which extended some 11 to 12 inches from the feed end.

In places, salt appeared to fill the voids in the vexar completely. The sketch below shows the location of heavy salt deposits. The outer rectangle represents the outer edges of the leaf; the inner rectangle represents the edge of the active area. The cross-hatched areas represent the salt deposits.

Reject or concentrate end



OBSERVATIONS (continued)

A piece of black foreign matter was found almost exactly in the center of the leaf. This was saved as Sample 4.

There was a small amount of dark material which appeared to be biological growth at, or perhaps in, the feed end glue line.

A very light yellowish brown deposit was found on the membranes reflecting the pattern in the vexar. This appeared to become more intense toward the reject end.

The sticky tape in the membrane crease on Leaf 2 was not folded in half as expected, but at one end was quite far off center.

A similar pattern of salt deposits was found on Leaf 2 as on Leaf 1. If anything, the deposit on Leaf 2 was heavier, i.e., more of the vexar was filled. As before, there was very little salt deposit within 3-4" of the product water tube along the entire length of the tube. There were patches of heavy salt deposit across the remainder of the feed end of the leaf. Again the caveat remains that unrolling the leaf broke apart the salt layer.

TESTS PERFORMED AFTER AUTOPSY

<p>1. Test and Test Objective: To get a general chemical analysis of the salt found on the membrane surfaces, 8.5 grams from Sample 6 (salt scraped from the membrane surfaces, was given to Barb Frost of D-8290. She was requested to do an ICP test to analyze for metals, including calcium and sodium and to measure alkalinity, chloride and sulfate, all on a dry basis.</p>
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<p>She extracted this sample with 85 milliliters of water overnight with agitation and obtained the following results.</p>
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<p>Organization Performing Test: Fisheries Application Research Group</p>

<p>Date: September 7, 2000</p>

<p>Observations from Test:</p>

1:10 water leach -

Concentrations in mg/kg

Metals detected	Metals below detection limits	Anions
Al 6.72	Ag < 0.04	HCO ₃ ⁻ 541.
B 0.14	As < 0.70	SO ₄ ⁻ 16,730.
Ba 0.72	Be < 0.005	Cl ⁻ 167.
Ca 6350.	Cd < 0.04	CO ₃ ⁻ < 10.0
Cu 1.06	Co < 0.03	
Fe 0.226	Cr < 0.04	Other parameters
K 23.3	Mo < 0.10	pH 7.38
Li 0.07	Ni < 0.10	EC µs/cm 2260.
Mg 59.6	Pb < 0.30	
Mn 0.12	Sb < 0.20	
Na 566.	Se < 0.30	
Si 1.82	V < 0.04	
Sr 204.		
Zn 0.12		

2. Test and Test Objective: Because of concerns about the initial analysis, the remainder of Sample 6 was given to Barb Frost to analyze using similar procedures but generating the extract with different and stronger procedures. The sample was finely ground prior to extracting, a greater dilution 1:100 was used for the water extraction and a nitric acid extract was made.

Organization Performing Test: D-8290

Date: October 3, 2000

Observations from Test:

1:100 water leach -

Metals detected	Metals below detection limits	Anions
Al 4.40	Ag < 0.04	HCO ₃ ⁻ 1,530.
B 0.14	As < 0.70	SO ₄ ⁻ 160,000.

Ba	5.85	B	< 1.00	Cl ⁻	120.
Ca	51000.	Be	< 0.05	CO ₃ ⁻	< 100.0
Cu	0.85	Cd	< 0.04	Other parameters	
Fe	0.226	Co	< 0.03	pH	7.39
K	691.	Cr	< 0.04	EC μs/cm	2260.
Li	1.20	Fe	< 0.05		
Mg	53.7	Mn	< 0.40		
Mn	0.12	Mo	< 1.00		
Na	500.	Ni	< 1.00		
Si	6.80	Pb	< 3.00		
Sr	776.	Sb	< 2.00		
Zn	1.40	Se	< 3.00		
		V	< 0.40		

1:100 water + 0.5% HNO₃ leach –

Metals detected	Metals below detection limits	Anions
Ag 0.53	As < 7.00	
Al 22.6	B < 1.00	SO ₄ ⁻ 293,000.
Ba 5.95	Be < 0.05	Cl ⁻ 4,760.
Ca 97800.	Cd < 0.04	
Co 0.87	Mo < 1.00	
Cr 1.20	Ni < 1.00	
Cu 23.1	Pb < 3.00	
Fe 23.7	Sb < 2.00	
K 768.	Se < 3.00	
Li 1.38		
Mg 76.9		
Mn 0.82		
Na 522.		
Si 3.90		
Sr 1170.		
V 0.76		
Zn 42.6		

3. Test and Test Objective: A sample of salt were saved for Karl Krill to analyze by SEM EDS to determine the composition of the deposit found on the membrane. A sample of membrane was also preserved to be scanned generally to see if there was anything unusual on the surface.

Organization Performing Test:D-8340

Date:

Observations from Test:

DISCUSSION and CONCLUSIONS [*in italics*]

The outer part of the element was in good condition. The small amount of salt found on the outside of the element was not any indication of any abnormal operation, but was typical of what is found on elements used in high salinity feeds. The chevron ring used for a brine seal was still flexible enough to provide a reasonable seal and strong enough not to have undergone any apparent degradation. The tape used for an outer wrap was still adherent. It was not discolored to any noticeable degree. Comparison with an unused element might indicate differently, but the inner layers of the tape were not differentiable in color from the outer layers. The glue strips used to close up the element were strong enough to give us some difficulty in opening the element.

The striking change that this element had undergone during the test period was the accumulation of a significant deposit of salt on both leaves. We assume that the element was new, and thus clean, when put into the unit at the beginning of the test. The salt deposits on Leaves 1 and 2 were very similar in appearance. Descriptions, even photographs of the salt deposits are imprecise because the act of unrolling the leaves splits the deposit into three parts, that which remains on the convex part of the membrane, that which is caught up in the vexar and that which adheres to the concave part of the adjacent membrane leaf.

The analysis of the sample delivered on September 7, 2000 indicated that *the dominant species in the salt deposits is calcium sulfate.* Anions were predominantly sulfates (96%), while cations were mostly calcium with a little sodium, strontium and magnesium. However, since only about 2.5% of the material appeared in the extract and since some species like calcium sulfate were clearly solubility limited while others like sodium sulfate were not, the distribution of metal ions is probably not representative. Consequently the analysis was redone.

A quantity of 53 grams was found between one pair of leaves. *The amount of solid salt found in the feed/reject channel would have caused a significant increase in pressure drop along the length of the element.*

Based on the measured weight of a piece of vexar (0.5755 gram for 10 square inches) and the handbook density for polypropylene (0.90), the vexar was calculated to occupy 13% of the space between the membranes. We assume that the distance between the membranes in operation is determined by the thickness of the vexar. This cannot be too bad an assumption since the measured thickness of crystals lodged in the vexar is not significantly different from the measured thickness of the vexar itself, 0.0295 inch. The vast majority of the salt was found to be calcium sulfate. The specific gravity of calcium sulfate dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, which is the species we would expect to occur from the temperature and pressure under which the element was used, is 2.32. Using this specific gravity, we can estimate that the 53 grams of salt would cover 54 square inches, if closely packed, i.e., having the density of crystalline salt without occluded water or air. Since the area covered with salt appears to be somewhat greater than 54 square inches, we can conclude that *the salt found in the element is not closely packed but is almost closely packed.*

DISCUSSION and CONCLUSIONS [*in italics*] (continued)

In the second analysis (with the 1:100 water leach), a larger fraction of the solids, just over 20%, was dissolved. A few more metals fall below the detection limits because of the dilution. Calcium and sulfate dominate the results even more strongly. In the second analysis (with the 1:100 water + 0.5% HNO₃ leach), almost 40% of the material was dissolved. During the acid leach we lose the bicarbonate and we appear to gain some chloride, due to slight contamination of the nitric acid. From the results of these two leaches we can state reasonably definitively that the salt found in the element is predominantly calcium sulfate (cation equivalent fraction is over 98% calcium and anion equivalent fraction is over 97% sulfate). There is a little strontium sulfate (the second largest cation equivalent fraction is 0.5% strontium).

Since neither the ion product in the feed analysis shown on page 2 is below the solubility product both for calcium ($IP/K_{SP} = 0.76$) and for strontium ($IP/K_{SP} = 0.81$), this was assumed to be feed to the system not feed to the element. However, the ion product for barium sulfate is well above the solubility product ($IP/K_{SP} = 39.53$) and the Langelier index is +1.61, so the feed has the potential to deposit calcium carbonate. We don't have enough data to calculate the concentrations of species in the feed to the element. However, it appears that the feed to the element was above saturation with respect to four compounds: calcium sulfate, strontium sulfate, calcium carbonate and barium sulfate. These are all compounds which precipitate slowly and which supersaturate significantly. The process of deposition requires a bit of speculation. The distribution of solids in the flow path suggests that some or all of these compounds were already in the solid form in the feed to the element. Typically in a scaled element the deposits are heaviest at the reject end where the ion products are highest. In this element the deposits occurred at the front of the element. This suggests that particles small enough to enter the flow path uninhibited were carried to the membrane surface by the flow of water through the membrane. When sufficient solids have accumulated the flow slows down locally. The solids then can act as nucleation sites for further solid accumulation and for cementing together of the salt mass.

The final conclusion relates to the effect operation during this test has had on the element. As stated above, the individual components have suffered no apparent damage. The membrane transport properties might have been affected, but, although swatches could have been tested, they were not. The major damaging effect was the very thorough scaling of the element. In principle, this scale could be washed out by passing low salinity water, possibly with a divalent ion complexing agent in it through the element. But, because there is a clear passage for water along the element's length and because the scale is tightly packed in parts of the vexar, it would take an extraordinarily long time to wash the scale out of the element. *For all practical purposes, the element has been damaged beyond repair.*

DISCUSSION and CONCLUSIONS [*in italics*] (concluded)

There are some loose ends on this autopsy. We don't know what the yellowish brown material is. Experience suggests that it is iron, which is a common contaminant and is present in low concentration in the deposited salt. We don't know what the black spec is. All kinds of things can get into elements both during manufacture and during use. We don't know if the dark biological material in the glue line is really biological. In terms of the major questions asked at the beginning of this autopsy, these questions are not very meaningful. If elements were to be put into this kind of service for a long time, these features might take on more meaning.

Major questions remaining are when did the damage occur and what was the sequence of events which led to the existing condition? The autopsy provides a picture of the condition of an element at a particular point in time. Determining how that condition was reached requires information on the initial conditions and on the operation as well as on the final condition.

Autopsy Photographs



Figure 1. View of concave side of Leaf 2 (on right) and convex side of Leaf 1 (on left). Product water tube runs from lower left to top center. The feed end of the leaf is at the bottom (as marked on the autopsy table). The vexar netting lies on top of Leaf 2. The darker beige blotches are the accumulations of salt on the leaf.



Figure 2. View of vexar being lifted from the concave side of Leaf 2. The crease on the left side of the photo is the membrane crease that separates Leaf 1 (left side of photo) from Leaf 2 (right side). The preference for the salt to adhere to the membrane can be seen from the large fraction of salt that remains on the membrane while comparatively little sticks to the vexar. Salt can also be seen on the convex side of Leaf 1