WATER TREATMENT FOR SMALL PUBLIC SUPPLIES

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Technical Completion Report Project Number T-0009

New Mexico Water Resources Research Institute in cooperation with the Department of Chemical Engineering New Mexico State University

The work on which this publication is based was supported in part by funds provided through the New Mexico Water Resources Research Institute by the United States Department of the Interior, Office of Water Research and Technology, as authorized under the Water Research and Development Act of 1978, Public Law 95-467, and by the state of New Mexico through state appropriations.

Project Numbers: T-0009, C-90016-T, 1423639, 1423635, 1345616, and 3109-161.

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ACKNOWLEDGEMENTS

Two persons need formal acknowledgement for their contributions to this project - Dr. Harry G. Folster and Mr. Steven W. Hanson. Dr. Folster initiated the project when he was an Associate Professor in Chemical Engineering at New Mexico State University. Dr. Folster is currently Head of the Energy Department of the Fiber Products Division R & D for Weyerhaeuser Company, Tacoma, Washington. Mr. Hanson served as the project staff engineer during the first two and one-half years of the project. His dedication and enthusiasm were greatly appreciated. Mr. Hanson is currently a project engineer with Continental Water Corporation, El Paso, Texas.

ABSTRACT

The project successfully demonstrated the application of reverse osmosis and electrodialysis as methods for small New Mexico communities to upgrade current drinking water supplies to meet the National Drinking Water Act standards. Nine communities were visited. In each community the mobile demonstration unit was operated from 500 to 2000 hours using feed from the present drinking water supply. In all cases product water, as certified by the appropriate state agency (EID), met drinking water standards. Operating data has been reported. This report presents engineering design data for the evaluation of electrodialysis, reverse osmosis and ion exchange unit operations for application in New Mexico's drinking water systems. The 9 communities are used as example cases.

In addition this project evaluated the potential for selectively removing ionized contaminants (cations) through precipitation as sulfides. Cadmium, mercury and zinc were examined. Experimental studies were conducted by developing a technique appropriate for a stopped-flow spectrophotometer. The initial data indicate that such a method would be appropriate under specialized conditions, e.g. the water has low TDS and high concentrations of only one or two of the cations. This experimental technique was also applied to study the removal of fluoride as calcium fluoride. To achieve reasonable precipitation rates and sedimentation rates a large excess of calcium must be used. Consideration of the effect of calcium on the drinking water quality would be required.

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WATER TREATMENT FOR SMALL PUBLIC SUPPLIES

I. Introduction

In 1977, the Chemical Engineering Department at New Mexico State University in cooperation with the New Mexico Water Resources Research Institute (WRRI) and with the assistance of the New Mexico Environmental Improvement Division (EID), initiated a project to evaluate and demonstrate advanced water treatment methods for small community drinking water supplies not meeting the standards of the National Drinking Water Act (Appendix A). The New Mexico EID had identified approximately 800 public water supplies (operating year round) which did not meet these standards. The extent of non-compliance ranged from supplies high in a single solute to supplies failing to meet several standards, e.g. total dissolved solids, (TDS), radioactivity and several cations or anions in excess. Funding for the project was obtained from the Office of Water Research and Technology, the Interstate Streams Commission, the WRRI, and New Mexico State University.

Demineralization of drinking water can occur either by removing water via a phase transformation or by removing solute via ultrafiltration, chemical adsorption or chemical reaction. The advanced treatment methods selected for demonstration were reverse osmosis and electrodialysis. Laboratory work was to include ion exchange and solute precipitation. The range of solute concentrations in the drinking water supplies available for demonstration of the equipment are given in Table 1.

The specific project objectives were:

- to develop operating conditions and data for an engineering evaluation or reverse osmosis, electrodialysis and ion exchange as appropriate methods for producing the required quality drinking water;
- to develop specific cost data;
- 3. to extend water treatment technology in the area of single solute removal from supplies containing a large number of ionic and dissolved species;
- 4. to provide the necessary material for assimilation of this unit or comparable equipment into the educational activities of water supply and water treating operator training;
- 5. to survey brine disposal methods in compliance with New Mexico groundwater regulations (Appendix B).

Objectives (1) and (2) were to be achieved through the construction and operation of a reverse osmosis system and an electrodialysis system in nine New Mexico communities. [1,2,3] Objective (3) resulted in two Master of Science theses in chemical engineering. [4,5] After the operational phase of the project, the demonstration reverse osmosis system equipment was released to the Dona Ana Vocational Technical Branch of New Mexico State University. This equipment will be used in the Waste Water and Water Supply Operators Training program, i.e. Objective (4).[6] Appendix (C) of this report constitutes the survey of disposal methods to be provided as Objective (5).

Table 1. Feed Water Solute Concentration Ranges

	Limit	<u>:s</u>
	(Concentrati	ons, $mg/1$)
	•	
Sodium	46.00 -	697 . 90
Potassium	0.78 -	25.35
Calcium	31.00 -	385.00
Magnesium	11.60 -	229.40
Iron - Total	0.30 -	22.50
Manganese	0.05 -	0.40
Chloride	26.10 -	
Fluoride	0.29 -	
Nitrate		16.30
Bicarbonate	209.00 -	
Carbonate		one
Sulfate		1700.00
Phosphate		
Total Hardness	165.00 -	1410.00
Alkalinity	171.00 -	
Total Dissolved Residue	663.00 -	
Surfactants	0.02 -	0.06
рН	7.60 -	8.25
Odor		one
Color	No	one
Turbidity	0.03 -	
Conductance Micromhos/cm 25°C	540.00 -	
Arsenic	0.010-	
Barium	Negative -	
Boron	Negative -	
Cadmium	Negative -	
Chromium	Negative -	
Copper	Negative -	
Cyanide		
Lead	0.010-	0.130
Mercury	0.005-	
Molybdenum	_	
Nickel	Negative -	0.10
Silver	Negative -	
Selenium	Negative -	
Zinc	Negative -	0.350
Silica (SiO ₂)	0 -	80.
D11100 (D10\(\infty\)	J	~~ .

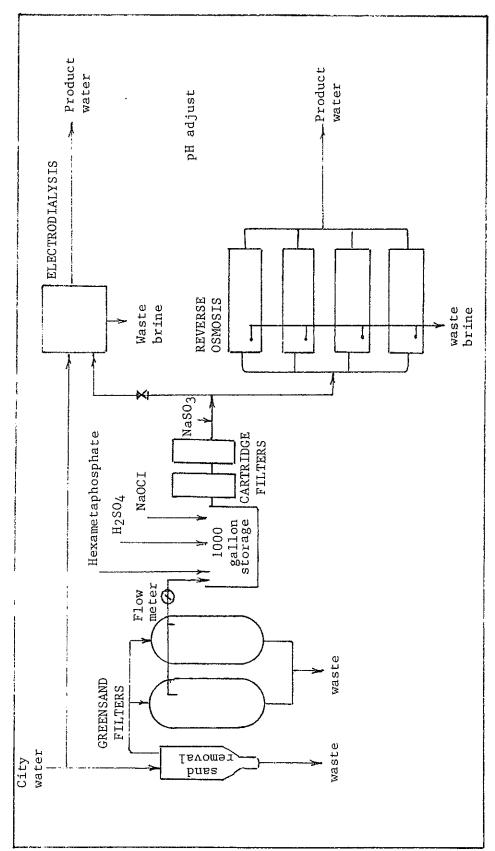
A. Summary Description of Demonstration Van

The demonstration water treating systems were designed and constructed in a standard forty-foot semi-trailer van. The system was designed so that feed water, electricity and brine discharge were all external connections for the van. Competitive bids were received and a contract was awarded to Saltech, Inc. of El Paso, Texas, for turn-key construction of the reverse osmosis system. Figure 1 shows the simplified flow schematic of the RO system. Table 2 lists the equipment components. A complete description including operating procedure is in Reference 1.

Table 2. Reverse Osmosis System Components

1. Manufactured by: Saltech, Inc. Air Injection System Flocculant Injection System Sand Separator System KMnO4 Removal System 1000 gal. Feed Tank Feed pH Control System Feed Water Pressure System (see pump below) Sodium Hexametaphosphate Injection System Sodium Hypochlorite Injection System Cartridge Filter System Pressure Maintenance System (see OSMO pumps below) 4 Spiral Wound R. O. Systems 2 Hollow Fine Fiber R. O. Systems Conductivity Instrumentation Measurement Electrical Control System Electrical Power System Permeate Flush System Product pH Control System Product Iodination System Product Storage Vessel 750 gal

- 2. Pumps:
 - 2 OSMO (R.O) 18H2312 8771031, 8771032
 - 1 Price (feed) 100100 B Mod 5Kc39126431X Stock No. C321
 - 1 Teel (flush) 1P778
- 3. Feed Pumps: LMi Liquid Metronix Feed Acid B51192 l ea. Others All1191 4 ea.



Process Flow Schematic Small Community Water Treatment Van Figure 1.

4. Austic Pump: Precision Control
Model No. 12781-11
Serial No. 77070287

Water pump W. W. Grainger Supplied by NMSU Flowcontroller James & Cooke Engineers

- 5. Heating and Cooling: W. W. Grainger 1 heating & cooling unit
 - l heating unit

Figure 2 shows the reverse osmosis sytem as assembled in the van. Two types of reverse osmosis membranes were used during the demonstration period-spiral wound (SW) (ROGA and Environgenics, Inc.) and hollow-fine fiber (HFF) (Dow and Dupont). Individual membrane operation was not monitored at each location; however, the performance of the two types of membranes was monitored.

The electrodialysis system was an Ionics, Inc. Aquamite V on loan from the company for the duration of the demonstration project. Table 3 gives the system specifications. [6] The unit was installed in the demonstration van by the Ionics, Inc. engineers. Figure 3 shows the van interior after installation of all the ED equipment.

Table 3. Electrodialysis Major Component List

- 1. Feed Pump Goulds Model 3655, 5 gpm
- 2. Brine Pump Same as 1.
- 3. Cartridge Filter 10 micron rating
- 4. Motor operated valves 5 second response time
- 5. Product Conductivity Controller Range 0-3000 micromhos/cm
- 6. Aquamite V Membrane Stack (short)
 Anion membranes Ionics 103-PZL-183
 Cation membranes Ionics 61-AZL-183
- 7. Control Panel Rectrifies
- B. Summary of Operation in Nine New Mexico Communities

Nine communities from the possible 800 plus public water supplies were selected in consultation with the Water Quality Group of the EID (New Mexico).

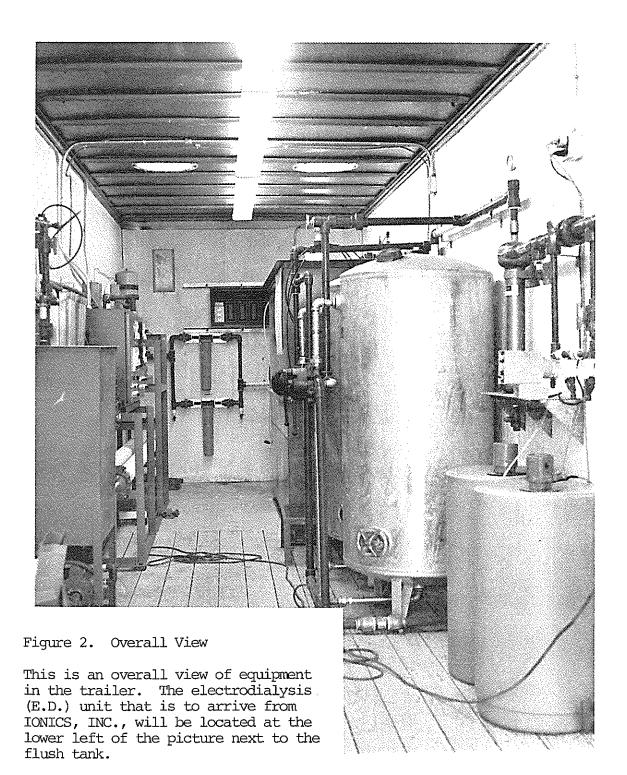


Table 4. Community Water Supplies

CURRENT TREATMENT	Surge-setting tank, non-regenerated green sand filters	Mixing tank (CaOC1, Alum), Sand Filter	Sand Filters	Settling Tank	Storage Tank	Storage Tank	Storage Tank	Settling Tank	*
QUALITY, $\mathfrak{mg}/\mathcal{L}$	TDR 780; Iron 1.6; Mn 1.4;	TDR 950; SO ₄ 374; Strontium 2.5	TDR 1994; SO ₄ 1004; Strontium 2.5	TDR 1100; Ar 0.05; Fluoride 1.4	TDR 908; SO_4 402 Radioactivity 1. pc/ℓ	${ m TDR}\ 1000;\ { m SO}_4\ 383$	TDR 1280; SO ₄ 492; H ₂ S .15; Ströntium 2.1 Turbidity	TDR 1180; Fluoride 3.8	TDR 1250; SiO ₂ 40. CaSO ₄ 450
SOURCE OF WATER, GPD	Wells - 180,000	Wells + Bonita Lake (summer) 200,000	Wells (daytime) Bonita Lake (night) 100,000	Jemez River (shallow) Wells - 13,220	Wells - 400,000	Wells -135,000	Wells 175,000	Wells - 50,000	Well
SIZE POPULATION	1200	1250	750	250 (summer) 100 (winter)	2500	1750	750	300	10000
LOCATION	l. Cuba	2. Carrizozo	3. La Luz	4. San Ysidro	∞ 5. Bluewater	6. Moriarity	7. Hagerman	8. San Jon	9. Alamogordo

^{*} Alamogordo is not a "small community". The demonstration at this site was in support of the proposed Tularosa Basin Brackish Water Desalting Plant.

Table 5. Operation Summary

perol	LOCATION	PERIOD	SYSTEMS OPERATED	Gal Prod AP %TDS Gal Feed	Rejected	QUALITY
1.	Cuba	Nov-Dec 1977	RO - Spiral Wound (SW) ED Green Sand Filters		88% 31% 22%	Certified-EID Certified-EID
2.	Carrizozo	Jan-Feb 1978	RO - SW RO - Hollow-fine fiber (HFF) ED	.55 .55	91% 91% 77%	Certified-EID Certified-EID Certified-EID
m,	La Luz	Mar-Apr 1978	RO – SW RO – HFF ED	.75 .75 .73	94% 74%	Certified-EID Certified-EID Certified-EID
. 4	San Ysidro	Aug 1978*	RO – SW RO – HFF ED	.71 .71 .78	80% 80% 82%	Certified-EID Certified-EID Certified-EID
5.	Bluewater*	Sept-Oct 1978	RO - SW RO - HFF ED	.53	96% 96% 75%	Certified-EID Certified-EID Certified-EID
9	Moriarity	Oct-Nov 1978	RO - SW RO - HFF ED	.58 .58	97% 97% 77%	Certified-EID Certified-EID Certified-EID
7.	Hagerman	Nov-Dec 1978	RO – SW RO – HFF ED	.63 .63	%96 %96	Certified-EID Certified-EID Certified-EID
∞ ∞	San Jon**	June-July 1978	RO - SW RO - HFF ED	.63 .63 .72	93% 96% 84%	Certified-EID Certified-EID Certified-EID
.6	Alamogordo	Apr-Dec 1979	RO – SW RO – HFF ED	.51 .70 .74	94% 96% 90%	Certified-EID Certified-EID Certified-EID
•		,		, t	:	

^{*} Community water supply would not support summer population and the demonstration RO/ED units.

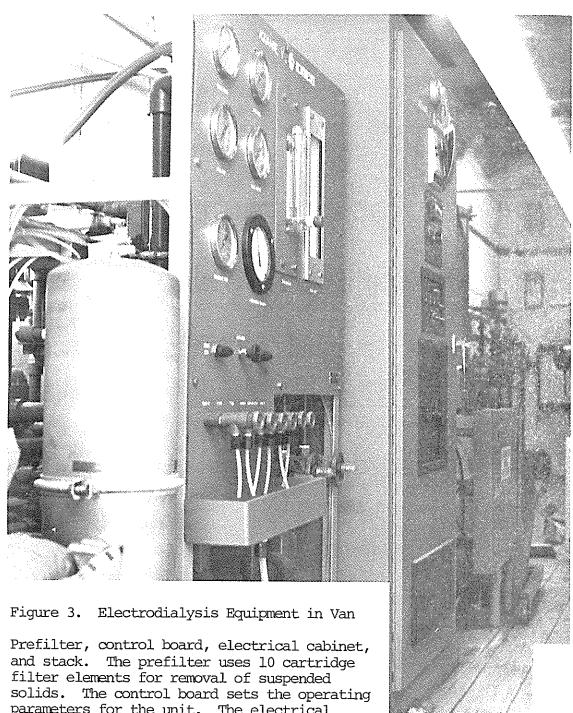
Other community systems would not accomodate product ** Product water introduced into community distribution system. water reintroduction without piping revision.

Figure 4 is a map showing the location of these communities. Operation periods for the communities ranged from 500 hours (San Ysidro) to 2000 hours (Alamogordo). In addition the demonstration van was operated for several days on two different occasions at New Mexico State University. Table 4 gives the description of the nine community water supplies. Table 5 describes the van operation in each community.

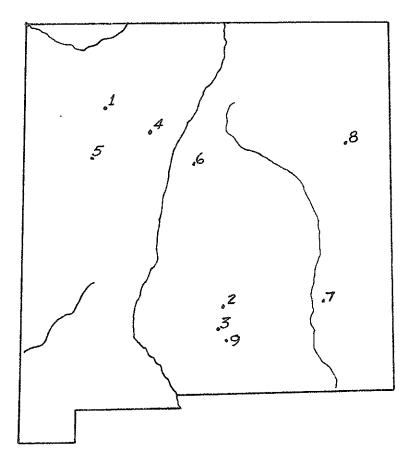
The demonstration unit was operated by a chemical engineer (Mr. Steve Hanson, B.S. 1977). At each location change, Ionics, Inc. field engineers, supervised the start-up of the ED system. Both Dupont and Dow personnel were available to suggest operation conditions for the HFF-RO units. Saltech, Inc. engineers provided similar advice for the SW-RO units, however the system design did not permit optimizing the performance of the individual RO module.

II. Engineering Design Methodology

One of the critical phases in the early, conceptual stage in planning water treatment processes occurs when an economic evaluation must be prepared. Often many cost studies of water treatment projects are generated and analyzed for process alternatives before a good picture of the economic structure of a project emerges. It is important at this stage to have capital cost estimates that are as accurate as possible. It is equally important to use consistent estimating techniques so that alternatives can be compared on the same basis, and subsequently comparisons can be made between projects. One such technique for capital cost estimation is the modular technique.[7]



parameters for the unit. The electrical cabinet controls power to pumps, and the stack. The stack is the basic desalinization unit.



- Cuba 1.
- Carrizozo
 La Luz
- 4. San Ysidro
- 5. Bluewater
- Moriarty 6.
- 7.
- Hagerman San Jon 8.
- 9. Alamogordo

Figure 4. Location of Operations

The application of the module concept to process plant estimation is shown in Table 6. All major cost elements are grouped into six distinct modules, five direct and one indirect, as follows:

Chemical (Water) processing
Solids handling
Site development
Industrial buildings
Offsite facilities
Project indirects

For the present purposes, i.e. the evaluation of RO, ED and IX for producing drinking water of the required quality, only the capital cost of the water processing equipment will be presented. Each of the nine communities visited have vastly different types of operations for providing the community with water. It would be impossible to adequately and consistently compare other than a specific process' equipment.

There are available many federally-funded studies of demineralization of water. Four of these are used as primary references for this portion of this report. They are listed as References 8, 9, 10 and 11. Cost estimations will be based on the 1980 (final quarter) Chemical Engineering Cost Index (Appendix D).

The above analysis will provide a consistent capital cost estimation. The operation and maintenance cost requirements must also be developed. The above references provide guidelines for developing these costs. The component categories to be used are:

Energy Electrical, Process related kw-hr/year
 (The three processes RO, ED, IX all operate using electrical energy).

- 2. Chemicals \$/year
- 3. Maintenance material (excludes chemicals) \$/yr
- 4. Labor, hr/year

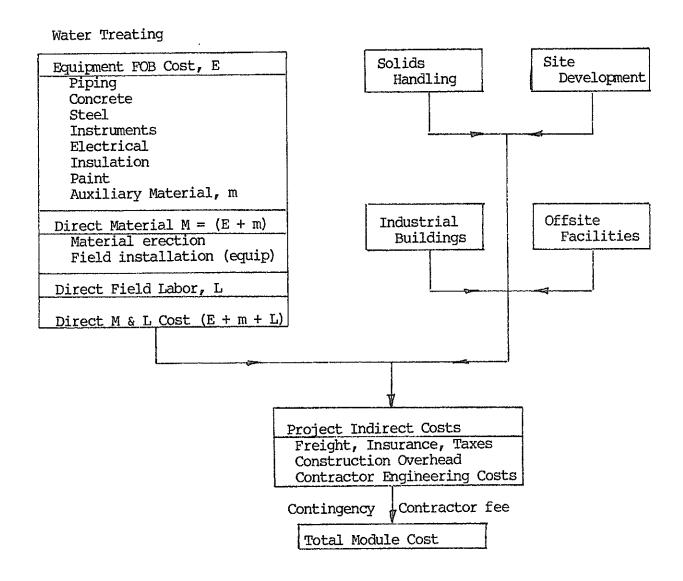
Water treatment plants seldom operate at full capacity. While it is feasible to prorate costs associated with items 1, 2 and 3 based on percent of full capacity, labor usually cannot be adjusted as easily. In the communities rated in the demonstration phase of the project, only Alamogordo had full-time experienced water treatment plant personnel. For small communities, labor associated with demineralization processes will be a major expense. Brine disposal costs are not included in these cost analyses.

The efficient operation of RO, ED or IX units will produce a product water which will greatly exceed some of the drinking water quality standards, i.e. for 2000 mg/l TDR in the feed, RO will remove better than 90% giving a 200 mg/l TDR product. This is two and one-half times the national standard. Thus only 40 percent of the total water used would require processing through the RO unit. For the purposes of this study all water treatment processes will be designed with a 50 percent margin of safety, i.e. if the standard is .20 mg/l design will produce .10 mg/l.

A. Reverse Osmosis Systems

Reverse osmosis will remove a high percentage of all inorganic ions, Table 7, turbidity, bacteria, and viruses. Most organic matter is also removed, with the exception of most halogenated and low molecular weight compounds. The efficiency of the membrane elements in RO systems may be impaired by scaling because of slightly soluble or insoluble compounds, e.g.

Table 6. Module Method of Capital Cost Estimating



CaCO3, CaSO4, MgSO4 etc. Fouling of the membrane can result as the deposition of colloidal or suspended materials, e.g. SiO2, Fe/Mn compounds. Bacteria as well as chlorine, can cause membrane deterioration. [12] Because of these potential effects, a major consideration in the design of a reverse osmosis system is the provision of adequate pretreatment to protect the membranes. At the same time the design should include provision for cleaning of the membranes (without disassembling the module housings). Figure 1 showed the typical RO system with pretreatment.

Table 7. RO Efficiencies for Certain Inorganic Ions

Ion	Percentage Pomona, Calif.[13]	Reduction La Luz**	Alamoo SW	jorđo* HFF
		(SW+HFF)	DW	
Nitrate	80.6	88.	52.5	81.4
Ammonium	94.0	-	-	-
Phosphate	98.8	C ***	-	***
Calcium	97. 5	98. 5	98.7	90.5
Magnesium	91.8	98.5	98.2	98.2
Potassium	93.4	86.4	99.9	99.9
Sodium	92.8	82.6	88.1	91.1
Sulfate	100.0	97.7	98.	97.1
Chloride	90.6	94.8	87.6	91.7
TDR	93.7	93.5	95.2	92.8

^{*}Representative operations

The behavior of semipermeable RO membranes can be described by two basic equations.[14] The product water flow through a semipermeable membrane may be expressed as:

$$F_{W} = A(\Delta p - \Delta \pi) \tag{1}$$

where

 F_W = water flux

A = water permeability constant

Δp = pressure differential across the membrane

 $\Delta\pi$ = osmotic pressure differential across the membrane.

^{**}Scaled membranes with CaSO4. All SW modules replaced.

The salt flux through the membrane may be expressed as:

$$F_S = B(C_1 - C_2)$$
 (2)

where

Fs = salt flux

B = salt permeability constant

 C_1-C_2 = concentration gradient across the membrane.

The water permeability and salt permeability constants are characteristic of the particular membrane which is used and the processing which it has received. Values for A and B as determined for the RO module used in the demonstration van are given in Appendix E.

These equations show that the water flux is dependent upon the applied pressure, while the salt flux is not. As the pressure of the feedwater is increased, the flow of the water through the membrane should increase while the flow of salt remains essentially constant. It follows that both the quantity and the quality of the product water should increase with increased driving pressure.

The water flux increases as the available pressure differential increases; and the water flux decreases as the salinity of the feed increases because the osmotic pressure contribution increases with increasing salinity). As more and more water passes through the membrane, the salinity of the feedwater becomes higher and higher; the osmotic pressure contribution of the concentrate becomes correspondingly higher, and this results in a lower water flux with increasing percentage water recovery.

While $\Delta\pi$ in Equation (1), the osmotic pressure, can be calculated, a rule of thumb, which is based on sodium chloride, is that the osmotic pressure increases by approximately 0.01 psi for each mg/l. This approximation

works well for most natural waters. High molecular weight organics, however, produce a much lower osmotic pressure. For example sucrose gives approximately 0.001 psi for each mg/l. Most drinking water supplies would use the first approximation.

Commercial suppliers of reverse osmosis equipment have usually programmed simple algorithms for solving Equations (1) and (2). Their design specifications would include number and type of membrane modules, based upon appropriate pretreatment.

B. Electrodialysis Systems

The Aquamite V is the packaged electrodialysis system loaned to the project by Ionics, Inc. The water to be demineralized is pumped at low pressure (30 to 60 psi) between the ion permeable membranes. Within the membrane assembly (called the membrane stack) DC electric current drives the solutes through the membranes to a concentrate water stream. Ion selective membranes are essentially ion exchange (IX) resin in sheet form. Some membranes are made by mixing IX resins with a polymeric binder and casting or extruding a sheet from the mixture. The ionic properties of an IX membrane are identical to those of the resin on which they are based.

Passage of water between the membranes of a single stack, on stage, usually requires 10 to 20 seconds. The actual percentage removal achieved varies with water temperature, type and amounts of ions present, flow rate of the water and stack design.[15] Typical removals per stage range from 25 to 60 percent. Practical systems currently employ one to six stages.

Water temperature is the most important factor affecting desalting efficiency. Mineral removal increases at the rate of slightly more than 1 percent/°F. Aquamite V membranes are stable up to 110°F. If inexpensive thermal energy is available operation should approach this temperature.

According to Faraday's law, 100 mg/l of dissolved ionized solids can be removed from 1000 gal. of water by 200 amp-ohms of direct electric current. Since 1-2 volts per membrane or cell pairs are generally required in modern ED plants to achieve practical removal rates (for low TDR, e.g. 1000 mg/l), the amount of energy required to remove 100 mg/l of dissolved minerals from 1000 gal. of water is 0.2-0.4 kwh. To this must be added 23 kwh/1000 gal. for pumping the product and waste streams through the stack.[16] Table 8 gives the Aquamite V operating data as published by Ionics Inc.[17] Appendix F compiles the corresponding ED operating efficiencies obtained in this demonstration project.

Table 8. AQUAMITE V-2 Operating Specifications [17]

Feed Water TDS Number of Stages	1500 4	(ppm) 6	2500 4	(ppm)	
80°F — Product Flow (in thousands USGPD) Product TDS (ppm) Per Cent TDS Removal Per Cent Water Recovery	30 160 89	15 70 95	30 275 89	15 115 95	
(Product to Feed Water Quantity) Electrical Energy Consumption	76	73	70	66	
(KW-Hr/1000 US Gal)	8	12	13	15	
100°F - Product Flow (in thousands USGPD)	30	15	30	15	
Product TDS (ppm) Per Cent TDS Removal	100 93	50 97	170 93	75 97	
Per Cent Water Recovery (Product to Feed Water Quantity) Electrical Energy Consumption	76	73	70	66	
(KW-Hr/1000 US Gal)	8	11	12	15	

The most commonly encountered problem in ED operation is scaling (or fouling) of the membranes by both organic and inorganic materials. Alkaline scales are troublesome in the concentrating compartments when the diffusion of ions to the surface of the anion membrane in the diluting cell is

insufficient to carry the current. Water is then electrolyzed and hydroxide ions pass through the membrane and raise the pH in the cell. This increase is often sufficient to cause precipitation of magnesium hydroxide, calcium carbonate, etc. and limits the allowable current density. The Aquamite V system employs electrical polarity reversal in place of continuous chemical feed for control of scaling and membrane fouling substances. This operation reverses the DC current direction and the flow path of the diluting and concentrating streams every 15 minutes. In addition, during the later stages of the demonstration project, recycle of brine was facilitated to improve overall efficiency. This effect is shown in Appendix F data.

C. Ion Exchange Systems

Ion exchange processes have been used for many years to soften hard water and to demineralize water for various industrial uses. The demonstration van did not include ion exchange as a unit operation. Laboratory work was performed under a related project on an industrial waste water using ion exchange. [18] The demonstration van did include green sand filters for iron/manganese control. The design of fixed bed, regenerable unit operation equipment is described.

The exchange zone method of Michaels[19] for designing ion exchange beds has been widely accepted by industry. The exchange zone is defined as that region of the bed within which (at steady state) the specified ion concentration in the liquid flowing through the bed falls from 95 percent (exhaustion) to 5 percent (break-through) of its value in the effluent. Figure 5 shows the concentration profile in a fixed-bed ion exchange column. The

choice of the concentration limits for defining the exchange zone is arbitrary. Michaels recommends values which have an arithmetic average of 50 percent, and which are not so close to 0 and 100 percent that experimental measurement of concentration becomes difficult.

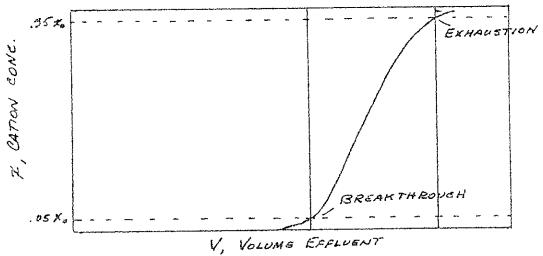


Figure 5. Fixed-bed Ion Exchange Concentration Profile

Figure 1 provides the necessary design information. The concentration of the specified ion in the effluent is plotted as a function of the total volume of effluent collected. The significant design information is shown. If an IX bed is operated to the breakthrough point the only portion of the bed not essentially exhausted will be the band at the bottom of the bed corresponding to the exchange zone. The breakthrough capacity of the bed may be determined by:

$$C_{E} = C_{T} \frac{(h_{T} - (1 - F)h_{Z})}{h_{T}}$$
 (3)

where C_T = specific molal total capacity of exchanger (milliequivalents per cubic centimeter of solid); h_T = mean bed height, cm.; h_Z = height of the exchange zone, cm; F = fraction of the exchanger in the zone which still possesses the ability to remove ions. Table 9 gives a listing of contaminants that can be treated by ion exchange.

The specific ion exchange material used in the demonstration van was "greensand." A "greensand" filter was used for removal of iron and manganese. This material is a natural occurring zeolite (glauconite).[20] These zeolites have been conditioned to have a surface coating of MnO2. In use the particle surface "matures," i.e. becomes coated with hydrous oxides of Fe(III) and Mn(IV), and subsequent sorption of Fe(II) and Mn(II) becomes more rapid and more complete. When the sorption capacity of the greensand becomes exhausted, e.g. breakthrough, regeneration can be accomplished by flushing with a permanganate solution. Back flushing greensand filters removes the precipitated iron and manganese compounds.

Table 9. Upper Limiting Raw Water Concentrations of Various Contaminants
That Can Be Treated by Ion Exchange without Exceeeding the MCL

Contaminant to be Removed	Upper Limiting Raw Water Concentration	MCL	Remarks
Arsenic, Trivalent	Unknown	0.05 mg/l	Activated alumina or bone char
Barium	45 mg/l. Generally by blending of raw & finished water for corrosion & hardness control	1.0 mg/l	Softening resins
Fluoride		1.4 to 2.4 mg/l	Activated alumina or bone char
Manganese	Unknown	0.5 mg/l	Secondary MCL
Inorganic Mercury	0.1 mg/l	0.002 mg/l	Cation and anion resins
Organic Mercury	0.1 mg/1	0.002 mg/l	Cation and anion resins
Nitrate - as N	50 mg/l	10.0 mg/l	NO ₃ selective resin
Radium	100.0 pCi/l	5.0 pCi/l	Softening
Selenium, Quadrivalent	0.33 mg/1	0.01 mg/l	
Selenium, Hexavalent	0.33 mg/l	0.01 mg/l	
Sodium	133.0 mg/l	20.0 mg/1	No MCL set
Sulfate	8,300 mg/l	250.0 mg/1	Secondary MCL

III. Evaluation of RO, ED, or IX for New Mexico Communities

To reduce the unit cost of treating water in small quantities, different types of treatment techniques or treatment configurations are normally utilized for small treatment systems. For example, package plants, e.g. pre-assembled, skid-mounted or modular construction, are commonly employed to reduce capital costs for small treatment facilities. This type of unit lends itself to those processes which were analyzed (demonstrated) in this study—reverse osmosis, electrodialysis and ion exchange.

The equipment cost evaluation, as shown in Table 6, will only be evaluation as direct equipment, material, labor cost. The specifics of each system will be detailed in the subsections. No indirect costs will be applied because each community tax and capital-equipment budgeting is different. Finally, this report is not recommending one type of equipment. Each unit operated to produce water of the required quality; and the actual installed equipment cost and operating costs are subject to a wide range of market factors not available to this study. The economic data is updated to March 1981 and is representative of the best available information in the open literature. Specific equipment suppliers should be consulted for actual cost information.

A. Reverse Osmosis Systems

The capital equipment costs for the reverse osmosis system represent the cost of a complete self-contained system, e.g. includes acid and polyphosphate feed equipment, and also cleaning equipment. RO systems however, are subject to scaling and fouling and may require more extensive pretreatment. For those locations where pretreatment is advisable, the capital

cost for a prepackage pressure filtration system is used. These filters could be particulate control or greensand, iron-manganese control.

The equipment cost data are almost independent of the total dissolved solids over the range of brackish waters up to 10000 mg/liter TDR. Other considerations, such as calcuim sulfate and silica concentrations are more important since they will effect the recovery, i.e. too high a recovery of high sulfate raw water can lead to calcium sulfate precipitation and total scaling of the membranes.

Further considerations in the cost data are: the temperature of the feedwater is assumed to be between 65° and 95°F [in Cuba and La Luz, feedwater was 40-45°F]; and the pH of the feedwater is adjusted to about 5.5 to 6.0; a singlepass treatment system is used and operating pressure is in the range 400 to 450 psi.

The operating and maintenance cost data in Appendix G have the items mentioned in Section II, excluding chemicals. Costs for pretreatment chemicals vary widely from community to community and are added in for each community separately. Again each community will develop its own labor force; however the O & M costs have been based on \$10/hr.

a. LOCATION #1: CUBA

Table 10. Water Supply Data - Cuba

Consumption	180,000 gallons per day
Quality	maa /3
TDR	780 mg/l
Iron	1.6 mg/l
Manganese	1.4 mg/l
рĦ	6.5

Table 10 shows the water supply data for the community of Cuba, N.M. Although there is an occasional turbidity problem the following design does not consider it as a separate unit. Iron and manganese must be removed before treating with an RO unit; therefore a pre-package pressure filtration system is considered. Although New Mexico standards allow 1000 TDS, the federal standard 500 mg/l TDS will be used. (Note: As described previously a design safety factor will be used, i.e. for TDR the design value is 250 mg/l for final drinking water). Table 11 gives the estimated equipment capital cost and appropriate O & M costs.

Table 11. RO System Equipment Cost - Cuba

1.	Prepackage Filter Unit (195,000 GPD/5 gpm per : Reverse Osmosis Equipment (195,000 GPD) (produces 136,000 GPD To Be Blended to give 180,0000 GPD)	ft ²)	\$1.44	х 10 ⁵ х 10 ⁵
3.	O & M (Filter Unit) (RO System)	TOTAL	\$4.64 \$1.1 \$6.6	x 10 ⁵ x 10 ⁴ /year x 10 ⁴ /year
			\$7.7	x 10 ⁴ /year

b. LOCATION # 2: CARRIZOZO

Table 12 gives the consumption and water quality for Carrizozo, New Mexico. This community has actively sought alternatives to its present water supply but has not implemented any of them as yet. The present

Table 12. Water Supply Data - Carrizozo

Consumption	200,000 GPD
Quality	
TDR	950 mg/l

system removes suspended solids only. The RO system is all that would be required. Appropriate costs are shown in Table 13.

Table 13. RO System Equipment Cost - Carrizozo

1. Reverse Osmosis Equipment (234,000 GPD) \$3.5 x 10^5 \$7.5 x 10^4 /year

c. LOCATION #3: LA LUZ

Table 14 gives the consumption and water quality data for La Luz, N.M. A major problem occurred in the operation at La Luz in that the community supply was intermittent (shut down at night). Combined with the very high sulfate, careful operation was required. During the demonstration project, one unit of spiral wound modules was scaled shut with calcium sulfate. Table 15 gives the 0 & M costs and these have been increased to reflect the project experience.

Table 14. Water Supply Data - La Luz

Consumption	100,000 GPD
Quality	
TDR	1994 mg/l
Sulfate	1004 mg/l

Table 15. RO System Equipment Cost - La Luz

1.	RO Equipment	(140,000 GPD)	\$2.35	
_	O & M T	•	\$5.2	x 10 ⁴ /year

d. LOCATION #4: SAN JON

The demonstration van operation was most successful during its operation in San Jon. The quantity of product water was sufficient that when it was blended into the community supply the quality of the water was noticeably improved. Table 16 gives the raw water data and Table 17 gives the appropriate cost data.

Table 16. Water Supply Data - San Jon

Consumption	50,000	GPD
Quality		
TDR		mg/1
Sodium	420.	mg/1
Fluoride	3.8	mg/1

Table 17. RO System Equipment Cost - San Jon

1. RO Equipment (67,400 GPD) $$1.33 \times 10^5$ 2. O & M $3.5 \times 10^4/\text{year}$

e. LOCATION #5

Table 18 is the water supply information for San Ysidro. The demonstration van operation was terminated early due to lack of water, i.e. product water could not be blended and returned to community system. The community system supplies a few permanent residents but mostly the area is a summer vacation area. Table 19 gives the cost data.

Table 18. Water Supply Data - San Ysidro

Consumption	13250	GPD
Quality		
TDR	1100	
Fluoride	1.4	mg/1

Table 19. RO System Equipment Cost - San Ysidro

1.	RO Equipment	(17500 GPD)	\$4.7 x	
_	O & M	•	\$1.45 x	10 ⁴ /year

f. LOCATION #6: BLUEWATER

Bluewater is in the uranium belt of New Mexico. It was selected for that reason. Table 20 gives the water quality data and Table 21 the appropriate cost.

Table 20. Water Supply Data - Bluewater

Consumption	400,000 GPD
Quality TDR	908 mg/l
Se	.009 mg/l
Gross Alpha	1. pc/1

Table 21. RO System Equipment Cost - Bluewater

l.	RO Equipment	(461,000 GPD)	\$6.0 x 10 ⁵
_	O & M		\$1.2 x 10 ⁵ /year

q. LOCATION #7: MORIARTY

Moriarty is a small farming community 40 miles east of Albuquerque on Interstate 40. Tourist facilities have raised the population to 1500 and the community is growing. Additional water consumption will require treatment systems because current water supplies are not adequate and other available water is of a lower quality. Table 22 gives the water supply data and Table 23 gives the RO system cost.

Table 22. Water Supply Data - Moriarty

Consumption	135,000 GPD
Quality TDR	1,000 mg/l

Table 23. RO System Equipment Cost - Moriarty

1.	RO Equipment	(161,000 GPD)	\$2.6 x 10 ⁵	
	O & M -		\$5.8 x 10 ⁴ /yea	ar

h. LOCATION #8: HAGERMAN

Hagerman was a replacement for Puerto de Luna in the project demonstration phase. Puerto de Luna was supplied with 110 volt power only. The major problem at Hagerman was sulfide in the system, but this was associated with the piping network not the supply. Table 24 is the water quality data. Table 25 is the RO system cost.

Table 24. Water Supply Data-Hagerman

Consumption	175,000 GPD
Quality	7000
TDR	1280
H ₂ S	0.15 mg/l

Table 25. RO System Equipment Cost - Hagerman

1.	RO Equipment	(224,000 GPD)	\$3.4 x 10 ⁵
	O & M -		$$7.2 \times 10^4/year$

i. LOCATION #9: ALAMOGORDO

Alamogordo cannot be considered a "small" public supply. The operation of the demonstration unit at this location unit was to supply experimental data for consideration in conjunction with a proposed 2 million gallon per day demineralization plant. Table 26 is the water supply data and Table 27 is the RO system cost.

Table 26. Water Supply Data - Alamogordo

	(Proposed Plant)	2,000	,000 GPD
Quality TDR		1800	MG/L

TABLE 27. RO System Equipment Cost - Alamogordo

_	RO Equipment O & M	(2,740,000 GPD)	\$2.45 x 10 ⁶ + \$5.0 x 10 ⁵ /year +

+Extrapolated on curves in Appendix D

B. Electrodialysis Systems

The electrodialysis system considered in this evaluation is the self-contained unit typified by the Aquamite V unit used in the demonstration project, e.g. capacity would change principally the stack configuration. There is very little equipment and cost data published in the open literature. The curves in Appendix G are an approximation generated from two points; because of this there is no comparison made between systems and the available data do not warrant such comparisons. The data given in Table 28 are representative of the equipment and operating costs associated with electrodialysis operation.

The demonstration project found the electrodialysis system to be reliable and durable. On one occasion in moving the van between locations the system was frozen, e.g. membranes, etc. While some piping and rotameters were fractured and required replacements, the membranes continued to perform at very acceptable levels of solute rejection and throughput.

During the course of the demonstration phase of the project the operation of the ED system was modified to incorporate polarity reversal and Performance of the system was very satisfactory. brine recycle.

Table 28. Electrodialysis Unit Costs

		Plant Capacity ^a		Annual Operating & Maintenance
Con	munity	GPD	Equipment Cost	Cost
1. 2. 3. 4. 5. 6.	Cuba ^b Carrizozo La Luz San Jon San Ysidro Bluewater Moriarty	195,000 234,000 140,000 67,000 17,500 400,000 161,000	\$5.94 x 10 ⁵ \$5.4 x 10 ⁵ \$3.2 x 10 ⁵ \$1.6 x 10 ⁵ \$6.4 x 10 ⁴ \$9.4 x 10 ⁵ \$3.7 x 10 ⁵	\$5.9 x 10 ⁴ \$5.4 x 10 ⁴ \$3.7 x 10 ⁴ \$2.15 x 10 ⁴ \$1.06 x 10 ⁴ \$7.8 x 10 ⁴ \$4.2 x 10 ⁴
8. 9.	Hagerman Alamogordo ^C	224,000 2,740,000	\$5.3 x 10 ⁵	\$5.3 x 10 ⁴

a Based on 90% TDR removal and 70% recovery as product water.

C. Ion Exchange Systems

In drinking water systems in which the standard exceeded is total dissolved solids (TDR) the use of ion exchange would not improve the TDR, in fact under certain circumstances ion exchange could increase the TDR of the product water. Ion exchange, therefore, has not been analyzed as a general method of demineralization. It will be discussed further in Section IV Single Solute Control.

b Includes package pressure filteration c NOT AVAILABLE AS A RELIABLE EXTRAPOLATION

IV. Specific Ion Precipitation

A number of conventional water treatment techniques may be used to selectively remove a single contaminant. Table 29 lists the most effective treatment methods for contaminant removal.[21] These conventional techniques as well as a variety of other new techniques have been researched in considerable detail by EPA funded projects and the results are available in EPA publications.[2225] This project examined three contaminants for removal by sulfide precipitation, e.g. cadmium sulfide, mercuric sulfide and zinc sulfide. Zinc has no primary MCL and was used to develop the test method; fluoride was precipitated as calcium fluoride. Table 29 shows that cadmium, mercury and fluoride are all treated by precipitation and coagulation. The necessary design information, therefore, is the nucleation/crystal growth/coagulation rate of each of the ions as a function of the temperature and concentration of the other reactant, e.g. sulfide or calcium. Experimental data is not available and standard procedures have not been established to measure such rates.

A. Theoretical Development

Measurement of nucleation, crystal growth and coagulation (or flocculation, agglomeration) remains one of the less well-defined experimental problems. The most reliable methods involve "lightscattering" and the experimentalist's work is to develop the appropriate equipment/instrumentation to give the required sensitivity. Theories of light scattering by small particles are associated with the names Rayleigh and Mie.[26,27]

When a beam of light is passed through a solution, its intensity is reduced due to (a) selective or consumptive absorption and to (b) conservative

Table 29. Most Effective Treatment Methods for Contaminant Removal

Most Effective Treatment Methods Contaminant As+5 - ferric sulfate coagulation, pH 6 to 8; Arsenic alum coagulation, pH 6 to 7; excess lime softening As+3 ferric sulfate coagulation, pH 6 to 8; alum coagulation, pH 6 to 7; excess lime softening. NOTE: Oxidation required before treatment for As⁺³. Lime softening, pH 10 to 11; ion exchange sof-Barium Ferric sulfate coagulation, pH 8; alum coagula-Cadmium tion pH 9; lime softening; excess lime softening. Cr+3 - ferric sulfate coagulation. pH 6 to 9; Chromium alum coagulation, pH 7 to 9; excess lime softening. Cr+6 - ferrous sulfate coagulation, pH 7 to 9.5. Disinfection; coagulation plus disinfection. Coliform Organisms Ion exchange with activated alumina; lime sof-Fluoride Ferric sulfate coagulation, pH 6 to 9; alum Lead coagulation, pH 6 to 9; lime softening; excess lime softening. Inorganic - oxidation/sedimentation/filtration. Manganese Organic - lime softening. Inorganic - ferric sulfate coagulation. pH 7 Mercury Organic - ion exchange. Ion exchange. Nitrate Powdered activated carbon; granular activated Organic Contaminants Lime softening; reverse osmosis. Radium Se+4 - ferric sulfate coagulation, pH 6 to 7; Selenium ion exchange; reverse osmosis. Se+6 - ion exchange; reverse osmosis. Ferric sulfate coagulation, pH 6 to 8; alum Silver coaqulation, pH 6 to 8; lime softening; excess lime softening. Ion exchange; reverse osmosis. Sodium Ion exchange; reverse osmosis. Sulfate

Turbidity

Alum coagulation, filtration.

absorption or light scattering (the light is re-emitted in all directions, hence the transmitted light intensity is reduced.) Usually, both factors operate simultaneously. Both can be caused by the colloidal particles as well as by the solvent; however, generally speaking, the effect of the solvent is negligible with respect to that of the particles. The transmitted light, i.e. light of incident intensity, I_O, is directed through a cell, length, L, containing the suspended particles, is related to the experimental parameters by the Beer-Lambert Law.

$$I = I_0 \exp(-\alpha^* L) \tag{4}$$

where α^* is called the absorptivity. The absorptivity of a suspension may be expressed in terms of the effective or absorption cross section of the particles C; $\alpha^* = NC$ where N is the number of particles per unit volume. The effective cross section is not identical with the geometrical cross section πa^2 of the particle by $C = Q\pi a^2$ in which Q is a dimensionless efficiency factor. The value of Q may be evaluated by applying either the theory of Rayleigh or the theory of Mie.

Rayleigh arrived at the following formula for QR:

$$Q^{R} = 8/3 \times \frac{m^{2}-1^{2}}{4^{2}m^{2}+2}$$
 (5)

in which m is the relative index of refraction of the particle with respect to that of the medium; X is the relative size of the particle with respect to the wavelength of the light in the medium λ_O/n (n = refractive index of the medium, and λ_O the wavelength of the light in vacuum):

$$X = 2\pi n \cdot a/\lambda_0 \tag{6}$$

In Rayleigh's theory the scattering is treated as light emission by an oscillating dipole induced in the particle by the electro-magnetic field of the incident light. The amplitude of the induced dipoles, and hence the amplitude of the scattered light, is proportional to the polarizability of the particle. The factor \mathbf{X}^4 can be understood as follows; the polarizability of the particle is proportional to its volume, hence the intensity of the scattered light increases with the square of the volume or with \mathbf{a}^6 . After dividing by the geometrical cross section of the particle, the factor \mathbf{a}^4 or \mathbf{X}^4 is obtained.

Rayleigh's theory is derived for small spherical particles, but it is also valid for isotropic particles of different shapes provided that the refractive indices of particle and solvent are not too different, and that the largest dimension of the particle is smaller than about 0.1λ . It is further assumed that there is no consumptive absorption of light, and that the particles scatter independently. Secondary scattering, i.e., scattering by one particle of light scattered previously by another particle, is assumed to be negligible. The last conditions will only be fulfilled by very dilute suspensions.

Mie has developed a theory of scattering by larger particles (up to sizes of the order of the wave length of light), taking also consumptive absorption into account. Mie talked about turbidity, i.e. $\tau \equiv \alpha^*$ in Equation 4, where $\tau \equiv K^*\pi r^2 N_p$ which means K^* in equivalent conceptually to Q_R . K^* is a function of the two parameters m and α where m has the same meaning as in Equation 5 and $\alpha = 2\pi r/\lambda_m = \pi d/\lambda_m$, with d as the particle diameter and λ_m the wavelength of light in the medium. If [C] is the concentration of scattering particles in gms per cc and p their density, then p the concentration of scattering particles in gms per cc and p their density,

$$\tau = 3K^*C/(4pr) = 3K^*C/2pd$$
 (7)

Rearrangement gives:

$$(2\pi\lambda m/3\pi) (\tau/C)_{\Omega} = K^{*}/\alpha$$
 (8)

The zero subscript means that this ratio has been extrapolated to zero concentration, i.e. no mutual interactions among the particles and no secondary scattering.

Since all the quantities on the left side of Equation (8) are experimentally observable, a value for K^*/α can be obtained. Mie solved the Maxwell equations to give plots of K^*/α vs $d/\lambda m$. Using the experimental value of K^*/α and the appropriate Mie plot a value, d, can be obtained.

In particulate nucleation and particle growth experiments both d and N will be changing with respect to time; hence the experimental method must provide a sufficient method for handling this problem.

B. Experimental System

All light-scattering instruments contain as their base elements a light source, a sample holder, and a light detector. There are the angular light-scattering photometers which measure relative intensities at various angles. These instruments are also capable of measuring absolute intensities. Transmission ($\theta = 0^{\circ}$) measurements can be carried out in these instruments. There are photometers which measure only the forward scattering and therefore are particularly useful for large particles. The Stopped-Flow Spectrophotometer measures both forward scattering/transmission, Fig. 6, and approximately right-angle measurements, Fig. 7. Figure 8 is a schematic drawing of this instrument.

The sample cell is fabricated around a fused silica tube to permit scattered radiation to be observed in a direction orthogonal to the incident radiation. The cell has a standard 2 cm optical path length and 2 mm diameter for Rayleigh ratio measurements as well. Incident radiation from the monochromator traverses the cell along the length of the tube and the scattered radiation passes through the side of the tube where it is detected when the photomultiplier is mounted directly above the cell.

The photomultiplier is a Hamamatsu R-376 which has an end-window photo-cathode 25 mm in diameter and an S-20 spectral response. In order to gain sufficient room to mount the detector very close to the cell, it is necessary to move the mirror box of the stopped-flow system 20 mm away from the cuvette. The mirror is repositioned within the mirror box, moving it close to the cuvette.

The photomultiplier is contained in a metal tube which is clamped in a bracket, positioning it above the cell, i.e., Fig. 6. It is easily repositioned in the alternative location coaxial with the observation tube in the cuvette, i.e., Fig. 7. In this way the same cuvette and transferoptics may be used for absorption measurements as well as light-scattering measurements.

The specifications for the stopped-flow spetrophotometer are:

- Mixing rate 99.5 percent complete within 2 milliseconds for solutions with relative viscosity of 1.0.
- 2. Maximum mixing dead time 2 milliseconds with 20-mm cuvette, 1.0 milliseconds with 2-mm cuvette.
- 3. Reaction half time (in 20-mm cuvette) less than 5 milliseconds to approximately 15 minutes, depending on stability of readout device for longer reaction times. (Half-times of less than 2 milliseconds are possible with 2-mm cuvette).

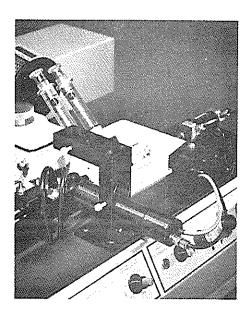


Fig. 6. Stopped-Flow Spectro-photometer - 90° measurement

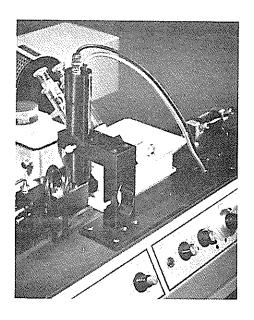


Fig. 7. Stopped-Flow Spectro-photometer - Transmission

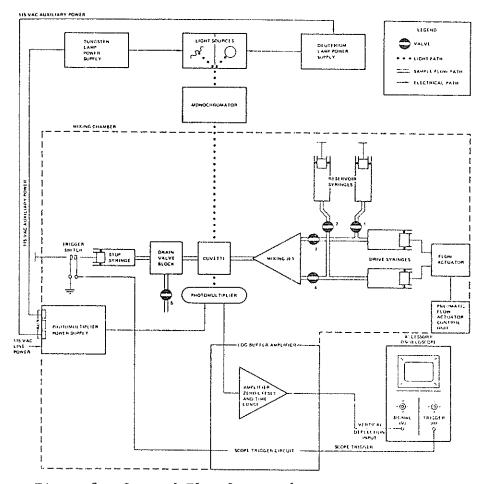


Figure 8. Stopped-Flow Spectrophotometer

- 4. Wavelength Range 300 nm -800 nm with standard tungsten lamp source;
 200 nm 300 nm with deuterium lamp source.
- 5. Power requirements 500 watts, 115 volts, 60 Hz, single phase, 3 wire grounded outlet; one transformer with two plugs provided if equipped for operation with 240 volts, 50 Hz power.
- 6. Tektronix 5111 storage oscilloscope single beam cathode-ray tube (CRT) with a storage unit which can be operated in the storage mode for a maximum storage time of one hour; with a 5A20N differential amplifier and a 5B10N time base amplifier, maximimum writing speed 20 divisions/millisecond.
- 7. Temperature control closed circuit liquid recirculating system, including pump, with heat exchanger coil suspended outside the instrument for convenient immersion in water bath.
- 8. Blue M Model PCC 13A portable cooling unit temperature range, -23 C° to ambient ± 0.15C°; Blue M Model 110-A Constant temperature unit, temperature range, ambient to 100C° ± 0.15 C°.

C. Measurements of Rayleigh Ratio

The Rayleigh ratio at 90° is given by Rg0° = $Ig0 \circ b^2/I_{0°}$, hence the Rayleigh ratio can be correctly determined. The development of the suspension was followed by light-scattering measurement (λ = 529 nm). The reaction for calcium fluoride is rapid and consists of nucleation and growth of particles. A typical oscilloscope trace is shown in Figure 9. The signal is proportional to the amount of light-scattered at 90° to the incident beam.

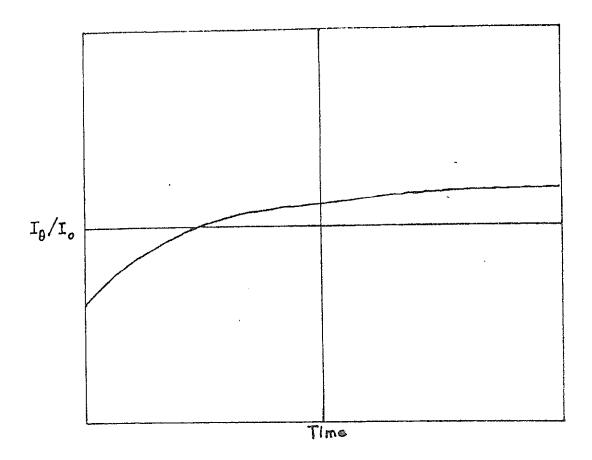


Figure 9. Light scattering from reaction of $4.9 \times 10^{-3} \text{M}$ calcium chloride with $2.0 \times 10^{-2} \text{M}$ sodium fluoride. Wavelength 529 nm, 0.1 volts/division, 0.5 sec/division.

In making a series of light-scattering measurements, the working standard should be used for calibrating the particle solution in absolute terms. The ideal working standard should be stable and easy to handle. It is more convenient to use a standard which gives a depolarization factor close to zero, and gives no angular dissymmetry of scattering, so that the relation between its turbidity and its Rayleigh intensity may be accurately given as shown in the following Equation:

$$\tau = (8 \pi/3) I b^2/I_{O^\circ} = (16 \pi/3) I_{90} b^2/I_{O^\circ}$$

$$\tau = 8 \pi R_{O^\circ}/3 = 16 \pi R_{90}^\circ/3$$
(9)

Calcium fluoride and barium sulfate were used as the working standards for this research. The standard solution concentration is determined by the following relation:

C' (Accurate concentration) =
$$(CV_o - SV_t)/V_t$$
 (10)

where C is the concentration of the source solution

S is the solubility of the standard sample

Vo is the volume of source solution

Vt is the final volume of solution

1). Preparation of calcium fluoride

To prepare the concentration, 1.5×10^{-3} g/c.c. of calcium fluoride, pour 1.5 grams of calcium fluoride into a 1000-ml volumetric flask. The solubility of calcium fluoride is 1.7×10^{-5} g/c.c. at 25 °C.

$$C' = 1.5 \times 10^{-3} - 1.7 \times 10^{-5} = 1.483 \times 10^{-3} \text{g/c.c}$$

Dilute the solution, 10 ml of 1.483×10^{-3} g/c.c. to 100 ml final solution.

$$C'' = (1.483x10^{-3}x10 - 1.7x10^{-5}x100)/100$$

= 1.313x10⁻⁴q/c.c.

Since the range of particle size for Rayleigh scattering measurement is approximately 10^{-5} ~ 10^{-6} cm, we will use a series of particle solutions, 3.96×10^{-5} , 4.9×10^{-5} , 6.28×10^{-5} g/c.c. of calcium fluoride, to prepare a standard curve (R_{90} ° vs. concentrations of particle solutions). The particle size of standard particle solutions is calculated as follows:

Conc. of particle	
solution, g/c.c.	<u>Radius, cm</u>
3.9x10 ⁻⁵	5.85x10 ⁻⁵
.9x10 ⁻⁵	5.79x10 ⁻⁵
6.3×10^{-5}	5.95x10 ⁻⁵

The data about the standardization of calcium fluoride are shown in Reference 5.

2). Preparation of barium sulfate

Working up as above, a series of particle solutions, 3.7x105g/c.c., 4.7x105g/c.c., 7.6x105g/c.c., are used to plot a standard curve for barium sulfate. The detailed calculations and the plot are shown in Reference 5.

D. Determination of Instrumental Factor

The instrumental factor can be obtained by using some system of known intensities of isotropic and anisotropic scattering, or known particle size in solution. Such a substance is also termed the standard. A standard substance should be stable and hopefully of large scattering power. More important is the requirement that the substance of identical quality should be obtainable without the need for complicated purification procedures. The precipitation kinetics and mechanism of the formation of barium sulfate precipitates have been studied extensively over the past few years. [28] The results of Walton and Hlalse [29] will be used for determining the instrumental factor for the stopped-flow spectrophotometer.

Equal volumes of barium chloride and sodium sulfate solutions of the required concentration were injected into, and mixed in, a 2-cm stopped-flow spectrophotometer cell. The daily setup and calibration for the stopped-flow spectrophotometer is described in Reference 5. The development of the suspension was followed by measuring the extinction of transmitted light ($\lambda = 546$ nm). The theoretical interpretation of the data obtained by this method has been outlined elsewhere[30], but consists of conversion of the turbidity data to particle numbers and sizes. A typical equation for the calculation of the instrumental factor is described as follows:

F (instrumental factor) = R90 0 R90 0 R90

where R_{90} ° is the Rayleigh ratio of the standard solution (theoretical value) and R_{90} ° is the Rayleigh ratio of the standard solution (the experimental value).

E. Results and Discussion

The mechanism of nucleation proceeds by a series of bimolecular collisions between precipitating ions and subcritical embryos. They obtained the nucleation rate as

$$dN_p^*/dt = K_n C_m^q$$
 (11)

where $K_{\rm n}$ is the rate constant, and $C_{\rm m}$ is the concentration of monomers. In logarithmic form Equation (11) becomes

$$\ln(dN_{\rm D}^*/dt) = \ln K_{\rm n} + q \ln C_{\rm m}$$
 (12)

The term in parentheses on the left side of Equation (12) may be determined from the data in experiment. The rate of nucleation may be plotted as a function of the monomer concentration and the slope of the curve at various rates of nucleation determined graphically. Typical data for a run is shown in Table 30.

Figure 10 is a plot of the nucleation rate versus mean calcium fluoride concentration using logarithmic coordinates. The slope of this plot, q, is 5.44 and $K_{\rm n}=6.24{\rm x}10^{30}\,({\rm ml/g})^{5.44}{\rm ml}^{-1}{\rm sec}^{-1}$.

Table 30. Nucleation Data

Time,sec	Run	#9 [Ca ²⁺] Np*, ml ⁻¹	= $1.0 \times 10^{-2} M_{\bullet}$ $C_{m_{\bullet}} g/ml$	$[F^{-}] = 2.0 \times 10^{-3} M$ $\frac{\ln(dNp^{*}/dt)}{\ln(dNp^{*}/dt)}$	<u>lnC</u> m
0.5 1.0 1.5 2.0 2.5 3.0		1.465x10 ⁷ 1.829x10 ⁷ 2.011x10 ⁷ 2.065x10 ⁷ 2.083x10 ⁷ 2.111x10 ⁷	5.10x10 ⁻⁵ 4.10x10 ⁻⁵ 3.20x10 ⁻⁵ 3.00x10 ⁻⁵ 2.55x10 ⁻⁵ 2.30x10 ⁻⁵	17.19 15.80 15.11 13.89 12.79 13.23	- 9.883 -10.101 -10.349 -10.414 -10.576 -10.680

F. Kinetics of Growth

Experiments have been carried out using, as the kinetic reaction, the formation of calcium fluoride solutions.

Nielsen[31] has used an approximated method for very large barium sulfate particles where r is of the order of a few microns. Using this method, the fraction precipitated is defined as

$$X = (r/r_f)^3 \tag{13}$$

and

$$(dx/dt)/x^{2/3} = K_p(1 - x)p$$
 (14)

$$ln[(dX/dt)/X^{2/3}] = lnK_p + p ln(1 - X)$$
 (15)

The straight line drawn in Figure 11 is used to determine the parameter p and K_p . A typical example of the results is shown in Table 31. Therefore, the parameter p is 1.72 and K_p is 13.87 \sec^{-1} .

Table 31. Growth Data

Run #1
$$[Ca^{2+}] = 4.9x10^{-3}M$$
, $[F^{-}] = 2.0x10^{-2}M$

Time, sec	<u>Np*, ml</u> -l	r*, cm	X	<u>ln(dx/dt)/x^{2/3}</u>	<u>ln(l-X)</u>
0.5	1.574x107	5.35x10 ⁻⁵ 5.64x10 ⁻⁵ 5.84x10 ⁻⁵ 5.87x10 ⁻⁵ 5.89x10 ⁻⁵	0.731	0.5887	-1.313
1.0	1.601x107		0.856	-1.2826	-1.937
1.5	2.029x107		0.950	-1.6371	-2.995
2.0	2.220x107		0.965	-3.4822	-3.352
2.5	2.293x107		0.975	-3.8951	-3.688

Table 32 summarizes the results of kinetic studies for calcium fluoride formation. The magnitudes of q and p changed with concentrations of reactants. It is implied that the nucleation of small particles may be considered to take place in two steps, the first being the production of supersaturation within the system and the second the formation of the nucleus within the supersaturated solution. The $K_{\rm n}$ values are very large and tend

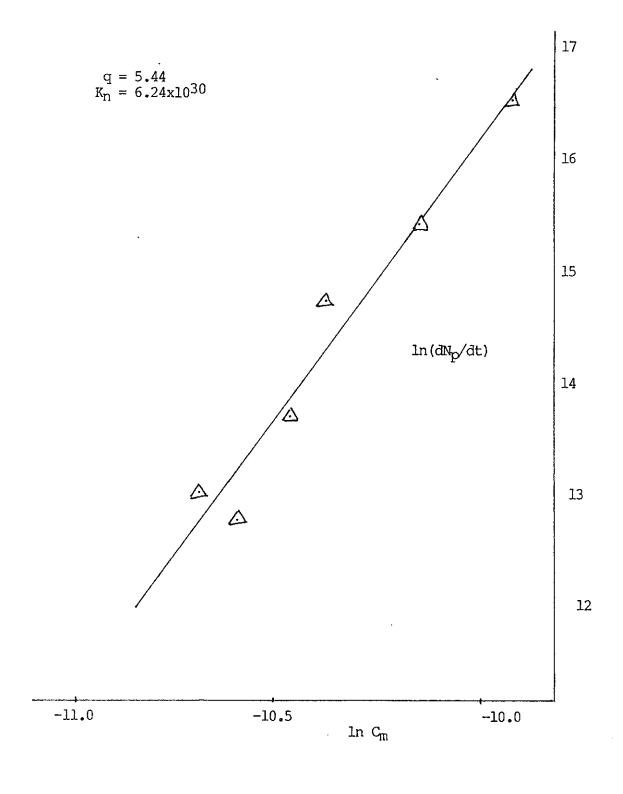


Figure 10. A Plot of Equation for... $ln(dN_p/dt) = lnK_n + q lnC_m$

toward infinity. In this situation, the nucleation may be increased very rapidly with supersaturation. At the critical supersaturation ratio the spontaneous formation of crystalline particle results.

On the other hand, with the depletion of supersaturation at the end of the induction period, the nucleation rate, because of the relatively low stability of nuclei and initial crystallites, decreases rapidly and its effective contribution to the precipitation rate is eliminated at a concentration substantially greater than the macro-solubility. Accordingly, growth is the sole precipitation reaction beyond a certain intermediate stage in the process.

Table 32. Summary of Results on CaF2

<u>Run</u>	<u>Ca</u> 2+	<u>F</u> 1-	<u>(N</u> p*)f	g	<u>K</u> p	₫	Kn
1 2 3 4 5 6 7 8 9	4.9x10 ⁻³ 1.0x10 ⁻³ 4.9x10 ⁻³ 1.0x10 ⁻³ 4.9x10 ⁻³ 1.0x10 ⁻² 1.0x10 ⁻³ 4.9x10 ⁻³ 1.0x10 ⁻² 1.0x10 ⁻²	2.0x10 ⁻² 1.0x10 ⁻² 1.5x10 ⁻² 1.5x10 ⁻² 1.0x10 ⁻² 2.0x10 ⁻³ 2.0x10 ⁻³ 2.0x10 ⁻³ 1.5x10 ⁻²	2.29x107 1.81x107 2.00x107 1.81x107 2.04x107 2.04x107 1.77x107 2.00x107 2.11x107 2.11x107	1.72 1.09 1.17 0.99 1.31 3.22 0.64 0.67 0.84 0.95	13.87 5.04 5.31 2.03 5.00 49.00 1.47 1.29 1.10 2.19	10.43 6.00 44.91 5.09 46.18 1.57 5.44 74.61	7.2x1042 1.3x1033 ******** 9.7x1028 ******* ******* 3.4x1013 6.2x1030 *******

where ****** means infinite ($>>10^{99}$)

Units: All concentrations are expressed in molarity

$$(N_p^*)_{final}$$
 is ml^{-1}

$$K_n$$
 is $(ml/g)^q ml^{-1}sec^{-1}$

$$K_{\rm D}$$
 is ${\rm sec}^{-1}$

The work on the selective removal of cadmium, mercury and zinc cations from drinking water by sulfide precipitation followed along the same lines as the work on calcium fluoride. The initial rate of precipitation was

considered to be predominatly due to the nucleation reaction. The rate of nucleation and thus precipitation was followed using the rapid mixing Multi-Mixing Stopped Flow Spectrophotometer.

Precipitation reactions were accomplished by initially oxidizing a sulfide solution with excess hydrogen peroxide to obtain the polysulfide solution with excess hydrogen peroxide to obtain the polysulfide in the form of $S_{\rm x}^2$ which was then rapidly mixed with a solution containing the metal cation. The initial rates of absorbance versus reaction time were calculated and converted to precipitation rates by using the molecular absorptivities of the polysulfides at the specific solution pH levels.

Analysis of variance or F-tests were performed for each set of rate data. From these tests and other investigations the following conclusions can be made:

- The most significant effects on the precipitation rate for all three metals occurred when the pH level of the sulfide solution was 9.0.
 - A) At this pH the predominant polysulfide species present (90 percent) are $\rm S_4{}^2$ and $\rm S_5{}^{2-}$ which appear to selectively remove the metals in the form of the highly insoluble metal sulfide.
 - B) At the lower pH level (7.0) these polysulfide species are less predominant due to the presence of S^O and H_2S which also act to remove the metals. At the high pH (11.0) the precipitation rate may be somewhat affected by precipitation of the metals as the hydroxide salts, but this effect is probably very small compared to the sulfide precipitation due to the greater affinity of the metals for the S_x^2 ligand over the OH ligand.
- Precipitation rates are highly dependent upon the concentration level of the metal present in the solution.

- A) Highest rates occurred where the concentration ratio of metal to polysulfide were equivalent (1:1).
- B) At the highest concentration of the metals the precipitation rate was dramatically reduced due to the high supersaturation level which limited the deposition of $S_{\rm x}^{2-}$ ligands on the cation, decreasing the number of nuclei formed. Dissolution of the preformed nuclei might also explain the lower rates.
- 3. The temperature of the reaction system when increased tends to result in lower precipitation rates of the metals.
 - A) Highest precipitation rates and also percentage removal rates tend to occur at the lowest temperature $10\,^{\circ}\text{C}$.
 - B) Values fall significantly when the reaction system is at 21.1°C due to increased solubility of the cations caused by the increased temperature.
- 4. The critical nucleus size, n, or the number of primary (metal) ions that must be in the nucleus before precipitation can occur, is a function of solution saturation by the metal cation species. The smallest critical nucleus occurs when metal and ligand concentration are equal.

V. <u>Summary and Conclusions</u>

The principal conclusion of the demonstration phase of this project was that reverse osmosis and electrodialysis as demineralization methods are particularly well-suited for use in drinking water systems. At the same time it should be recognized that the use of such systems will require

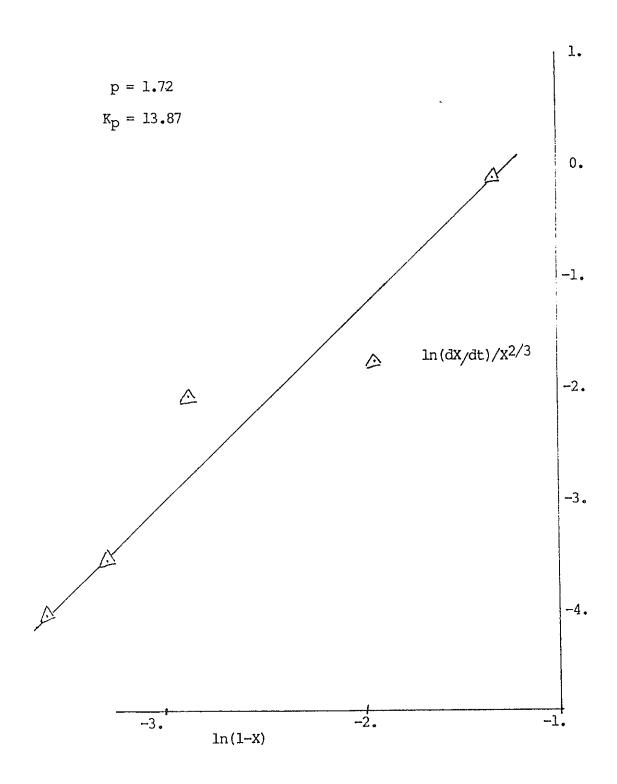


Figure 11. A Plot of Equation for... $ln[(dX/dt)/X^{2/3}] = lnK_p + p ln(1-X)$

a higher level of skill on the part of water treatment plant operators. In all the small communities visited with the demonstration van and its equipment the current water plant operators are part-time employees. The systems are such that prompt adjusting or careful operation, i.e. pH, additives, etc. are not required and if the operating personnel do not make such adjustments the system will still operate. In the case of RO or ED, while scaling or fouling of membranes can be partially recovered by cleaning operations, poor operation will seriously effect the units performance.

The second major consideration in planning reverse osmosis or electrodialysis as methods for upgrading drinking water supplies to meet the National Drinking Water Act Standards is the additional cost. The data presented on capital equipment cost and operating and maintenance costs for
these systems are consistent with published information. The actual cost
to the consumer is contingent on many factors not available to this project, i.e. method of financing by a particular community, tax rate, current water treatment plant operating personnel, etc. The data, therefore,
were limited to capital equipment cost for the demineralization system and
the usual experience O & M costs. Commercial manufactures should be solicited for bids for actual costs.

The tests conducted to determine the feasibility of selectively precipitating calcium fluoride, cadmium sulfide and mercuric sulfide were successful. Two students received Master of Science degrees in which this work contributed as their thesis research. The utilizing of a stopped-flow spectrophotometer proved effective in following nucleation and particle growth rates. Work is continuing on this instrumental technique.

Table 33 summarizes the performance of the demonstration van in the nine New Mexico communities. Included in the table are the approximated capital equipment costs and operating and maintenance costs. These again should be evaluated as estimates only.

Table 33. Summary of Demineralization

(ALYSIS O & M	\$1.1 × 104 \$4.8 × 104	\$5.4 × 10 ⁴	\$3.7 × 10 ⁴	\$2.15 × 10 ⁴	\$1.06 × 10 ⁴	\$7.8 × 10 ⁴	\$4.2 × 10 ⁴	\$5.3 × 10 ⁴	rd 1
ELECTRODIALYSIS CE	\$1.44 \times 10 ⁵ \$4.50 \times 10 ⁵ .	\$5.4 × 10 ⁵	\$3.2 × 10 ⁵	\$1.6 × 10 ⁵	\$6.4 × 10 ⁴	\$9.4 × 10 ⁵	\$3.7 × 10 ⁵	\$5.3 x 10 ⁵	ı
OSMOSIS 0 & M	\$1.1 × 104/year \$6.6 × 104/year	\$7.5 × 10 ⁴ /year	\$5.2 x 10 ⁴ /year	\$3.5 × 10 ⁴ /year	\$1.45 x 10 ⁴ /year	\$1.2 x 10 ⁵ /year	\$5.8 x 10 ⁴ /year	\$7.2 x 10 ⁴ /year	\$5.0 x 10 ⁵ /year
REVERSE (C	\$1.44 × 10 ⁵ \$3.20 × 10 ⁵	\$3.5 × 10 ⁵	\$2.35 x 10 ⁵	\$1.33 × 10 ⁵	\$4.7 × 10 ⁴	\$6.0 × 10 ⁵	\$2.6 × 10 ⁵	\$3.4 × 10 ⁵	\$2.45 × 10 ⁶
DESIGNED WATER SYSTEM CAPACITY GPD	195,000	234,000	140,000	67,400	17,500	461,000	161,000	224,000	2,740,000
POPULATION	1200	1250	750	300	250 (summer) 100 (winter)	2500	1750	750	10,000
LOCATION	Cuba	Carrizozo	La Luz	San Jon	San Ysidro	Bluewater	Moriarty	Hagerman	Alamogordo
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^aSee Note C Table 28

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APPENDIX A*: New Mexico Drinking Water Quality Standards

^{*} Hernandez, J. W. and W. A. Barkley, "The National Safe Drinking Water Act," for Training Seminar, U.S. Environmental Protection Agency, New Mexico State University, July 1976.

Maximum Contaminant Levels for Inorganic Chemicals other than Fluoride

The maximum contaminant level for nitrate is applicable to both community water systems and non-community water systems. The levels for the other inorganic chemicals apply only to community water systems.

Contaminant	<u>Level (mg/l)</u>
Arsenic Barium Cadmium Chromium Lead Mercury Nitrate (as N) Selenium	0.05 1. 0.010 0.05 0.05 0.002 10. 0.01
Silver	0.00

Maximum Contaminant Levels for Fluoride

The MCL's for fluoride were established at two times the concentration which is desirable for protecting teeth. The maximum contaminant levels of fluoride are a function of the maximum daily air temperature of the location of community water systems and are given below:

Temperature (in °F)	Level (mg/l)
53.7 and below 53.8 - 58.3 58.4 - 63.8	2.4 2.2 2.0
Temperature (in °F)	Level (mg/l)
63.9 - 70.6 70.7 - 79.2 79.3 - 90.5	1.8 1.6 1.4

Maximum Contaminant Levels for Organic Chemicals

The following are the maximum levels for organic chemicals. They apply only to community water systems.

Chlorinated Hydrocarbons	Level (mg/l)
Endrin (1,2,3,4,10,10-Hexachloro- 6,7-epoxy-1,4,4a,5,6,7,8,8a- octahydro-1,4-endo,endo-5,8- dimethano naphthalene)	0.0002
Lindane (1,2,3,4,5,6-Hexachloro-cyclohexane, gamma isomer)	0.004
Methoxychlor (1,1,1-Trichloro-2,2-bis [p-methoxyphenyl]ethane)	0.1
Toxaphene (C ₁₀ H ₁₀ Cl ₈ -Technical chlorinated camphene, 67-69% chlorine)	0.005
Chlorophenoxys	
2,4-D (2,4-Dichlorophenoxyacetic acid)	0.1
2,4,5-TP Silvex (2,4,5-Trichlorophenoxypropionic acid)	10.01

Maximum Contaminant Level of Turbidity

The maximum contaminant levels for turbidity are applicable to both community water systems and non-community water systems using surface water sources in whole or in part. The maximum contaminant level of turbidity at representative entry point(s) into the distribution system is a monthly average of one turbidity unit (1 TU). A maximum of five turbidity units (5 TU) may be allowed if the supplier can demonstrate to the state that this higher turbidity does not do any of the following:

- 1. interfere with disinfection;
- prevent maintenance of an effective disinfectant agent through the distribution system; or
- 3. interfere with microbiological determinations.

Maximum Microbiological Contaminant Levels

Two methods applicable to community water systems and non-community water systems are used to describe the maximum coliform levels that must be met. The parameters used to judge compliance with these levels for each method are given in the following paragraphs.

Membrane filter. When the membrane filter (MF) technique is used, coliform densities shall not exceed any of the following:

- one per 100 milliliters as the arithmetic mean of all samples examined per month;
- 2. four per 100 milliliters in more than one sample when less than 20 are examined per month; or
- 3. four per 100 milliliters in more than 5 percent of the samples when 20 or more are examined per month.

<u>Fermentation tube method</u>. When the fermentation tube method is used and when 10 milliliter standard portions are analyzed, coliform bacteria shall not be present in any of the following:

- 1. more than 10 percent of the portions in any month;
- 2. three or more portions in more than one sample when less than 20 samples are examined per month; or
- 3. three or more portions in more than 5 percent of the samples when 20 or more samples are examined per month.

When 100 milliliter standard portions are analyzed, coliform bacteria shall not be present in any of the following:

- 1. more than 60 percent of the portions in any month;
- five portions in more than one sample when less than five samples are examined per month; or

five portions in more than 20 percent of samples when five samples or more are examined per month.

Maximum Contaminants Level for Radioactivity

Section 141.15 and 141.16 of the regulations established the following maximum contaminant levels:

Contaminant

Combined Radium-226 and Radium-228
Gross alpha particle activity
(including Radium-226)
Beta Particle and photon radioactivity from man-made radionuclides.

<u>Level</u>

5 picocuries per liter

15 picocuries per liter Annual dose equivalent to the total body or any internal organ not to exceed 4 millirems

Compliance with Maximum Contaminant Levels

Gross alpha, Radium-226 and 228. A gross alpha screening level of 5 picocuries per liter has been established as being capable of assuring compliance with both the combined radium and the gross alpha levels, provided that the measured gross alpha particle activity does not exceed a confidence level of 95 percent (1.65 times the standard deviation of the net counting rate of the sample).

If the 5 picocuries per liter value is exceeded then an equivalent sample is to be analyzed for Radium 226. If this sample exceeds a concentration of 3 picocuries per liter, then an equivalent sample is to be analyzed for Radium-228.

Gross beta and photon radioactivity. Compliance with this maximum contaminant level may be assumed if:

- there is a gross beta particle activity of less than 50 picocuries per liter and if
- 2. the average annual concentration of tritium in the total body is less than 20,000 picocuries per liter and an

- average annual concentration of Strontium-90 in the bone marrow of 8 picocuries per liter, provided that
- 3. if both radionuclides are present the sum of the annual dose equivalent to the bone marrow does not exceed 4 millirems.

If the gross beta particle activity exceeds 50 picocuries per liter, an analysis of the sample must be performed to identify the major radio-active constituents present and the appropriate organ and total body doses shall be calculated.

APPENDIX B: New Mexico Groundwater Regulations

Part 3

- 3-100. REGULATIONS FOR DISCHARGES ONTO OR BELOW THE SURFACE OF THE GROUND
- 3-101. PURPOSE.--

A. The purpose of these regulations controlling discharges onto or below the surface of the ground is to protect all ground water of the state of New Mexico which has an existing concentration of 10,000 mg/l or less TDS, for present and potential future use as domestic and agricultural water supply, and to protect those segments of surface waters which are gaining because of ground water inflow, for uses designated in the New Mexico Water Quality Standards. The regulations are written so that in general:

- 1. If the existing concentration of any water contaminant in ground water is in conformance with the standard of Section 3-103 of these regulations, degradation of the ground water up to the limit of the standard will be allowed; and
- 2. If the existing concentration of any water contaminant in ground water exceeds the standard of Section 3-103, no degradation of the ground water beyond the existing concentration will be allowed.
- B. Ground water standards are numbers that represent the pH range and maximum concentrations of water contaminants in the ground water which still allow for the present and future use of ground water resources.
- C. The standards are not intended as maximum ranges and concentrations for use, and nothing herein contained shall be construed as limiting the use of waters containing higher ranges and concentrations.

3-102. AUTHORITY.—Standards are adopted by the commission under the authority of Section 75-39-4, N.M.S.A., 153 Comp. (the New Mexico Water Quality Act, Chapter 326, Laws of 1973, as amended). Regulations are adopted by the commission under the authority of Section 75-39-4 and 75-39-4.1 of the New Mexico Water Quality Act.

3-103. STANDARDS FOR GROUND WATER OF 10,000 mg/l TDS CONCENTRATION OR LESS.—The following standards are the allowable pH range and the maximum allowable concentration in ground water for the contaminants specified unless the existing condition exceeds the standard or unless otherwise provided in Subsection 3-109D or Section 3-110. When an existing pH or concentration of any water contaminant exceeds the standard specified in Subsection A, B or C, the existing pH or concentration shall be the allowable limit, provided that the discharge at such concentrations will not result in concentrations at any place of withdrawal for present or reasonably forseeable future use in excess of the standards in this section.

These standards shall apply to the dissolved portion of the contaminants specified with a definition of dissolved being that given in the publication "Methods for Chemical Analysis of Water and Waste of the U.S. Environmental Protection Agency," with the exception of mercury which shall be total.

A. HUMAN HEALTH STANDARDS - Ground water shall meet the standards of Section A and B unless otherwise provided.

```
0.1 \, \text{mg}/1
Arsenic (As)
                                                   1.0 \text{ mg/}1
Barium (Ba)
                                                   0.01 \, \text{mg/l}
Cadmium (Cd)
                                                   0.05 \, \text{mg/l}
Chromium (Cr)
                                                   0.2 \, \text{mg/l}
Cyanide (CN)
Fluoride (F)
                                                   1.6 \text{ mg/l}
                                                   0.05 \text{ mg/l}
Lead (Pb)
                                                   0.002 \, \text{mq/l}
Total Mercury (Hg)
                                                  10.0 \text{ mg/1}
Nitrate (NO3 as N)
                                                   0.05 \text{ mg/l}
Selenium (Se)
                                                   0.05 \text{ mg/l}
Silver (Ag)
                                                   5.0 \text{ mg/l}
Uranium (U)
Radioactivity: Combined
Radium-226 and Radium-228
                                               30.0 pCi/1
```

B. Other Standards for Domestic Water Supply

Chloride (C1)	250. mg/l
Copper (Cu)	1.0 mg/1
Iron (Fe)	$1.0~\mathrm{mg/1}$
Manganese (Mn)	0.2 mg/1
Phenols	0.005 mg/l
Sulfate (SO _A)	600. mg/l
Total Dissolved Solids (T	DS) 1000. $mg/1$
Zinc (Zn)	10.0 mg/l
Ha	between 6 and 9

C. Standards for Irrigation Use - Ground water shall meet the standards of subsections A, B and C unless otherwise provided.

Aluminum (Al)	5.0 mg/l
Boron (B)	0.75 mg/1
Cobalt (Co)	0.05 mg/l
Molybdenum (Mo)	1.0 mg/1
Nickel (Ni)	0.2 mg/l

3-104. DISCHARGE PLAN REQUIRED.—Unless otherwise provided by these regulations, no person shall cause or allow effluent or leachate to discharge so that it may move directly or indirectly into ground water unless he is discharging pursuant to a discharge plan approved by the director. When a plan has been approved, discharges must be consistent with the terms and conditions of the plan.

- 3-105. EXEMPTIONS FROM DISCHARGE PLAN REQUIREMENT.—Sections 3-104 and 3-106 of these regulations do not apply to the following:
- A. effluent or leachate which conforms to all the listed numerical standards of Section 3-103, has a total nitrogen concentration of 10 mg/l or less, and does not contain toxic pollutants. To determine conformance, samples may be taken by the agency before the effluent or leachate is discharged so that it may move directly or indirectly into ground water; provided that if the discharge is by seepage through non-natural or altered natural materials, the agency may take samples of the solution before or after seepage. If for any reason the agency does not have access to obtain the appropriate samples, this exemption shall not apply;
- B. effluent which is discharged from a sewerage system used only for disposal of household and other domestic waste which receives 2,000 gallons or less of liquid waste per day;
- C. water used for irrigated agriculture, for watering of lawns, trees, gardens or shrubs, or for irrigation for a period not to exceed five years for the revegetation of any disturbed land area, unless that water is received directly from any sewerage system;
- D. discharges resulting from the transport or storage of water diverted, provided that the water diverted has not had added to it after the point of diversion any effluent received from a sewerage system, that the source of the water diverted was not mine workings, and that the director has not determined that a hazard to public health may result;
- E. effluent which is discharged to a water-course which is naturally perennial; discharges to dry arroyos and ephemeral streams are not exempt from the discharge plan requirement, except as otherwise provided in this section;

- F. those constituents which are subject to effective and enforceable effluent limitations in a National Pollutant Discharge Elimination System (NPDES) permit, where discharge onto or below the surface of the ground so that water contaminants may move directly or indirectly into ground water occurs downstream from the outfall where NPDES effluent limitations are imposed, unless the director determines that a hazard to public health may result. For purposes of this subsection, monitoring requirements alone do not constitute effluent limitations:
 - G. discharges resulting from flood control systems;
- H. leachate which results from the direct natural infiltration of precipitation through disturbed or undisturbed materials, unless the director determines that a hazard to public health may result;
- I. leachate from solids disposed of in accordance with the Solid Waste Management Regulations adopted by the New Mexico environmental improvement board on April 19, 1974;
- J. natural ground water seeping or flowing into conventional mine workings which re-enters the ground by natural gravity flow prior to pumping or transporting out of the mine and without being used in any mining process; this exemption does not apply to solution mining;
- K. effluent or leachate discharges resulting from activities regulated by a mining plan approved and permit issued by the New Mexico coal surface mining commission, provided that this exemption shall not be construed as limiting the application of appropriate ground water protection requirements by the New Mexico coal surface mining commission;
- L. effluent or leachate discharges which are regulated by the oil conservation commission and the regulation of which by the water quality control commis-

Section 65-3-11, N.M.S.A., 1953 Comp. or under other laws, to the oil conservation commission.

3-106. APPLICATION FOR DISCHARGE PLAN APPROVAL

A. Any person who, before or within 120 days after the effective date of these regulations, is discharging any of the water contaminants listed in Section 3-103 or toxic pollutants so that they may move directly or indirectly into ground water shall, within 120 days of receipt of written notice from the director that a discharge plan is required, or such longer time as the director shall for good cause allow, submit a discharge plan to the director for approval; such person may discharge without an approved discharge plan until 240 days after written notification by the director that a discharge plan is required or such longer time as the director shall for good cause allow.

B. Any person who intends to begin, more than 120 days after the effective date of these regulations, discharging any of the water contaminants listed in Section 3-103 or toxic pollutants so that they may move directly or indirectly into ground water shall notify the director giving the information enumerated in Subscription 1-201B,; the director shall, within 60 days, notify such person if a discharge plan is required; upon submission the director shall review the discharge plan pursuant to Sections 3-108 and 3-109; for good cause shown the director may allow such person to discharge without an approved plan for a period not to extend beyond one year after the effective date of these regulations; after one year after the effective date of these regulations; for good cause shown the director may allow such person to discharge without an approved discharge plan for a period not to exceed 120 days.

C. A proposed discharge plan shall set forth in detail the methods or techniques the discharger proposes to use or processes expected to naturally occur which will ensure compliance with these regulations.

APPENDIX C: Survey of Brine Disposal Methods

Reverse osmosis, electrodialysis and ion exchange all produce a concentrated waste water (reject or regenerate) stream that can add appreciably to the cost of the product water depending on the method used for safe disposal. As is true in all waste-handling practices if arrangements can be made for someone else to dispose of the stream, it usually is the most economical and efficient method, i.e. in the case of water demineralization if the reject or regenerate stream can be sent to the community waste water treatment plant through the available sewer systems. Unfortunately, many small community water supplies are not located where such an arrangement would be convenient. In the nine New Mexico communities visited with the demonstration van in only one community, Alamogordo, would the above method of disposal be practical and it would have required about one-half mile of new sewer line. Location of the water treatment (demineralization) plant where its waste brine could conveniently enter the sewer system may not be possible without excessive pumping, i.e. raw water or product water. A second consideration in evaluating this method us whether the community has a community waste water treatment plant. Many small New Mexico communities which are effected by the Drinking Water Act do not.

An alternative to discharge to a community sewer system would be direct to surface drainage and into natural waterways. This method of disposal would require compliance with effluent standards and permit requirements of the appropriate state discharge regulations. Seven of the nine communities visted by the demonstration project were in areas with no continuously running surface waters, i.e. only intermittent arroyo flow occurred usually associated with rain in the immediate area.

The demonstration project received permission from the State Environmental Improvement Division to dispose of reject brine through surface

and discharge subsequent percolation (infiltration) to ground water. The recently adopted regulations for control of ground water quality (Appendix B) would have to be met for subsequent community demineralization projects. The methods of reject brine disposal reviewed therefore in this appendix are:

- 1. Deep-well injection
- 2. Evaporation/percolation using either unlined ponds or playas
- 3. Evaporation using lined ponds
- 4. Zero discharge with product recovery

A. Deep-well Injection

Section 1421 of the Public Health Service Act as amended by the Safe Drinking Water Act authorizes regulations governing State underground injection control programs. Proposed regulations seek to prevent the injection of materials which may enter a present or potential drinking water source and pose a threat to human health or otherwise render a present or potential water source unfit for human consumption. Necessarily, the regulations seek to prevent the injection of materials which may force a public water system to expend funds to comply with any national primary drinking water regulation or otherwise to avoid endangerment to the public health. A further stipulation is that regulations for State underground injection programs may not prescribe a requirement which interferes with or impedes underground injection in connection with oil or natural gas production or the secondary or tertiary recovery of oil or natural gas unless such a requirement is essential to assure that underground sources of drinking water will not be endangered by such injection.

Determining the feasibility of deep-well injection (DWI) would require extensive geological (hydrological) information. The State of New Mexico

has determined that aquifers containing waters with less than 10,000 mg/l TDR (Total dissolved residue) are potential sources of drinking water, therefore DWI is contingent upon finding a geologic zone that meets the State regulations; that will accept reject brine at the required rate and whose own chemical composition will not result in precipitation of the reject brine mineral constituents. Such precipitation potentially would plug the injection zone.

Other possible problems in using DWI include scaling and the need for high injection pressures for disposal in artesian aquifers; in addition, scaling could possibly occur in the injection equipment due to high TDS levels in the brine. This scaling could result in significant maintenance costs.

The cost associated with DWI is difficult to generalize. One recent study indicates that the operating cost of a DWI system is in the range of \$0.45 to \$0.90 per 1000 gallons of brine. Adjust to March 1981 costs these values would be \$0.54 to \$1.07 per 1000 gallons of brine. Considerations that would affect these costs are the following:

- 1. Current status of the injection aquifer, i.e. whether there are existing wells that can be used, whether there are wells that would need to be plugged; whether there are adequate monitoring wells.
- 2. Stand-by facilities. Federal regulations do not make specific requirements regarding stand-by facilities. They specify, however, that a permit must ensure that adequate procedures for detecting failure of the system in a timely fashion, and "adequate contingency plans to cope with malfunction or failure of the underground injection system "are included on the permit. Possible stand-by facilities and programs included (1) lined ponds, (2) tanks, (3) surfactant treatment plants, (4) stand-by injection wells, and (5) plant shutdown.

3. Change in State or Federal regulations. Experience has shown that what was unregulated or approved for one time period may not be acceptable for future time periods, i.e. regulations will change.

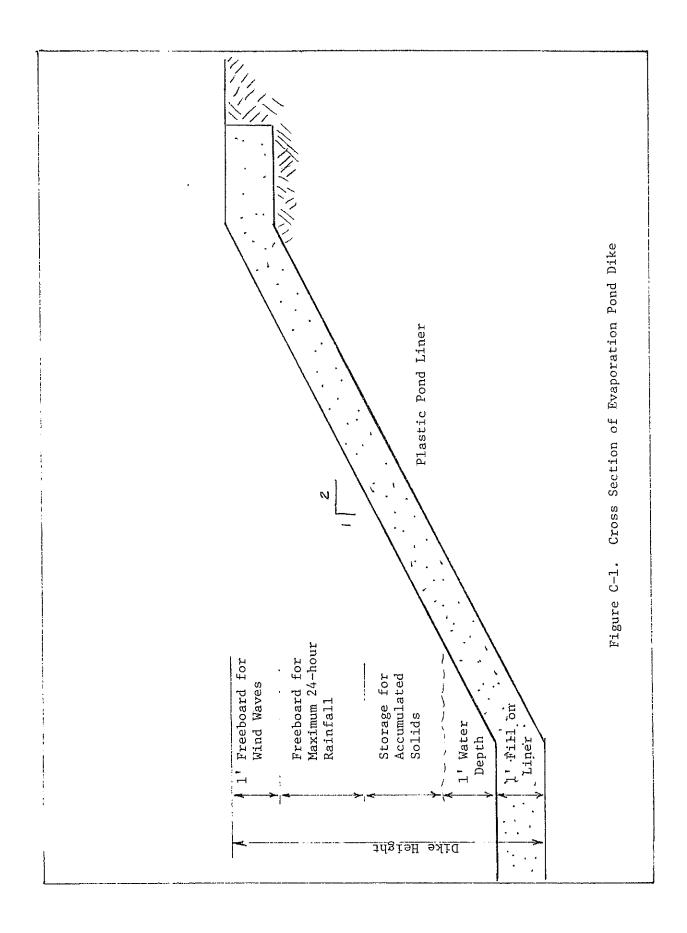
B. Evaporation/percolation Using Either Unlined Ponds or Playas

The net annual evaporation for New Mexico ranges between 50 and 60 inches. Combined with percolation this method would provide adequate treatment provided percolation of the reject brine does not intercept ground water of less than 10,000 TDR. There are areas in New Mexico where this does occur, e.g. Tularosa Basin, and this method was the chosen method for the proposed Tularosa Basin Demineralization Demonstration Plant. In this case approximately 25 areas of evaporation/percolation ponds would be required to dispose of 0.5 million gallons per day of reject brine. A pipeline approximately 5 miles long would be required to transport brine to this disposal area. The use of playas would encounter the same constraints – area and transportation. It is very clear however, that where available this is the least experience method of reject brine disposal.

C. Evaporation in Lined Ponds

The disposal of reject brine into a lined-solar evaporation pond requires an engineered pond. Figure C-l shows the typical earth structure which forms the dike surrounding the pond. The earth covering for the linear is applied when periodic precipitated solids removal is required.

There is much variation in the design of evaporation ponds although all are built on the basis of the evaporation rate characteristic of the site. Reject brine evaporation ponds can very likely be operated at depths which are shallow enough so that the evaporation rate approaches that obtained in pans; however,



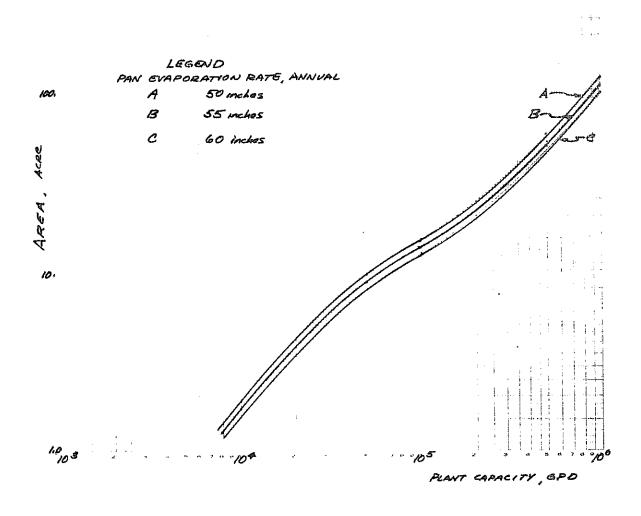


Figure C-2. Pond Area vs. Plant Capacity

salinity, there is a decrease in the rate of evaporation. A ratio of 0.7 for reject brine evaporation rates relative to fresh water is regularly used. Figure C-2 shows the relationship for evaporation pond area versus demineralization plant capacity with the parameter inches of fresh water evaporate per year (the 0.7 factor has been used to calculate the area).

The cost of lining evaporation ponds is the most significant single cost item in construction of the pond. There are many manufacturers of pond liners. Table C-1 lists several and briefly describes some of the materials used. The major reason for excluding brine disposal costs in the analysis is the uncertainty in such costs.

Table C-1. Pond Liner Manufacturers

Company	<u>Address</u>	<u>Material</u>
1. Burke Rubber Company	Pond Liner Division 2250 South Tenth Street San Jose, CA 95112	Hypolon Synthetic Rubber
2. Chevron U.S.A.	Asphalt Division Chevron U.S.A. 576 Standard Avenue Richmond, CA 94802	Chevron Industrial Membrane, mondithic elastomer
3. E. I. DuPont	Elastomer, Chemical Dept. Suite 724 Bank of Delaware Building Wilmington, Delaware 19898	Hypalon, Nordel, Neoprene, 3110,311
4. IU Conversion Systems, Inc.	115 Gibralter Road Horsham, PA 19044	Pozzolanic encapsulation of Waste materials
5. Kote-line, Inc.	9225 Katy Freeway Suite 325 Houston, TX 77024	Fiberglass reinforced plastic
6. Misco Industries, Inc.	United Supply Inc. Misco Building Wichita, Kansas 67202	(flexible membrane)

7. Palco Linings, Inc. 7571 Santa Rita Circle (flexible membrane) Stanton, CA 90680

8. Staff Industries, Inc. The Snow Company (flexible membrane)
P.O. Box 3915
Albuquerque, NM 87190

D. Zero Discharge (with product recovery)

The words "zero discharge" imply reuse of waste waters. For reject brine from demineralization operations it means, evaporation (and recovery of vapor) and crystallization. While there will be a solid to dispose of, it may be feasible that most of the solid is a useful chemical e.g. product recovery. For the nine communities visited in New Mexico this approach would not be economically feasible. It is described simply for completness.

1. Evaporators: Conventional evaporators used in waste water treatment, are limited in the degree of permissible concentration by scale forming chemicals such as calcium, carbonate, calcium sulfate and silica which begin to precipitate when their saturation limits are reached. Further concentration forms undesirable deposits on heat transfer surfaces thereby reducing transfer efficiency and unit capacity. The extremely hard scale, once formed, must be mechanically or chemically removed.

A flat plate vapor compression evaporator can be operated to concentrate brine to higher levels without depositing scale by using a seed slurry method which provides preferential sites for crystal growth. Brine concentrators should be designed for at least 90 percent water recovery. Since the solubility of calcium sulfate and silica is generally exceeded at these concentrations, a slurry of calcium sulfate seeds is continuous by circulated overall wetted surfaces of the concentrator to provide preferential sites for crystal growth. Successful application of seed slurry scale prevention techniques requires careful control of scaling parameters such as

the solids production rate, system volumes, slurry concentration and seed characteristics. In addition, local concentration and temperature change rates must be controlled, and phase changes must occur in controlled locations.

2. Product Recovery: The particular process developed involves a partial deionization of brine, sufficient to allow recycle of the residual aqueous stream to the feed step. During the processing, the various components of the brine are largely converted to products or wastes as follows:

calcium, magnesium to calcium carbonate and
magnesium oxide (waste)

sodium, bicarbonate to sodium carbonate (product)

sulfate to calcium sulfate (waste)

chloride to calcium chloride (product)

In cases where the sodium carbonate produced is equal or less than that required in the pretreatment (softening step, the process consists of three major operations:

- a. Precipitation of calcium sulfate with calcium chloride;
- b. Exchange of chloride in the brine for bicarbonate ions by liquidliquid extraction with an anion exchange extraction. The extractant is stripped with lime to produce calcium chloride, and regenerate with carbon dioxide.
- c. The bicarbonate solution is recycled to the pretreatment step,

APPENDIX D*: Engineering Cost Index

^{*} Chemical Engineering, April 1981.

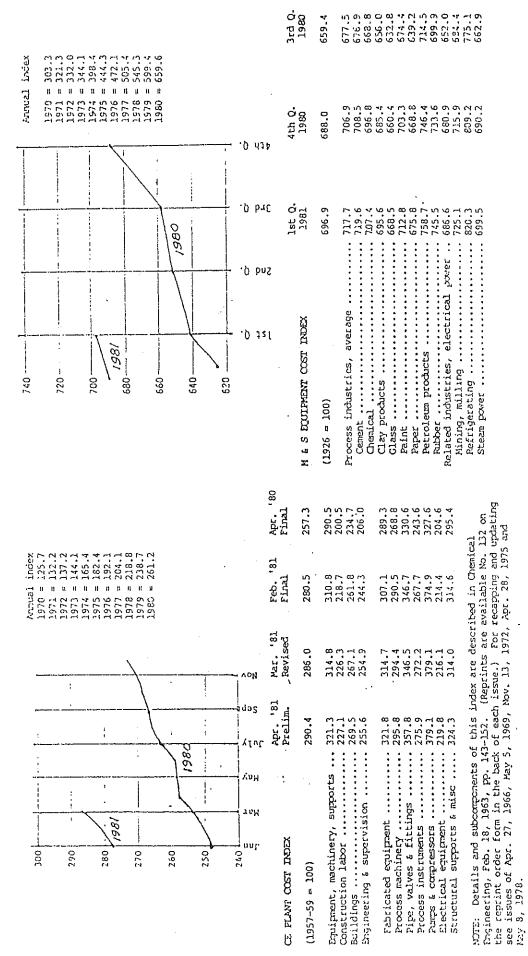


Table D-2. Equipment Cost Index

APPENDIX E: Reverse Osmosis Data

Table E-1. Calculation for RO System Capacity

Q,	Capacity =	onsumption TD Recovery .	<u>R - 250</u> 9*TDR	
1.	Cuba:	$Q = \frac{180,000}{.7}$	780 - 250 •9 x 780	= 1.95 x 10 ⁵ GPD
2.	Carrizozo:	$Q = \frac{200,000}{.7}$	950 - 250 .9 x 950	$= 2.34 \times 10^{5}$ GPD
3.	La Luz:	$Q = \frac{100,000}{.7}$	<u>1994 - 250</u> .9 x 1994	$= 1.4 \times 10^{5} GPD$
4.	San Jon:	$Q = \frac{50.000}{.65}$	<u>1180 - 250</u> •9 x 1180	$= 0.647 \times 10^{5}$ GPD
5.	San Ysidro:	$Q = \frac{13,250}{.65}$	<u>110 - 250</u> .9 x 1100	= 0.175 x 10 ⁵ GPD
6.	Blue Water:	$Q = \frac{400,000}{.7}$	908 - 250 .9 x 908	= 4.61 x 10 ⁵ GPD
	Moriarty:		1000 - 250 .9 x 1000	= 1.61 x 10 ⁵ GPD
		$Q = \frac{175,000}{.7}$	<u>1280 - 250</u> .9 x 1280	= 2.24 x 10 ⁵ GPD
	Alamogordo:	2,000,000	<u>1800 - 250</u> .9 x 1800	$= 27.4 \times 10^{5} GPD$

Table E.2. Salt Permeability Values, B

	11	2	3	4	5*	6	7	8	9	Avg.
SODIUM	.24	.17	.20	.17	_	.1	.06	.05	.11	.14
POTASSIUM	.12	.15	.14	_		.06	.08	.05	.05	.09
CALCIUM ·	.04	.05	.02	.01	_	.01	.01	.02	.05	.03
MAGNESIUM	.05	.04	.01	.04	_	.01	.01	.02	.02	.02
IRON			-	_				-	-	-
MANGANESE				_	_					-
CHLORIDE		.13	.05	.41		.14	.01	.11	.11	.12
FLUORIDE	_	_	-	.22	_		_	.25	_	.23
NITRATE	_	1.31	.07	1.78	-	.30	.05		.52	.45
BICARBONATE	.04		.15	.12	_	.01	.01	.06	.10	.07
SULFATE	_	.13	.02	.16	_	.25	.04	.04	.02	.08
ARSENIC	-	.29	.03	_		.05	_	_	.06	.10
BARIUM	_	.11	.05	-	-	-	-		_	.09
BORON		_		_	_			_	-	-
SELENIUM	.25	_	.11	-	-	.28	-	_	.43	.25
ZINC	.11	.25	_		_	_	.25	-	.37	.23
RADIUM	_	-	-	_	-	<5. Pc	-	-	-	
STRONTIUM	.02	.03	.01	_	-	.01		.01	.05	.02
SILICA	.20	.30	.22	.49		.11	.03	.02	.14	.18
TDR	.09	.16	.06	.10	.06	.04	.02	.02	.06	.06

⁺ Calculation based on a factor of 1.5 used as a representative area for each type of module; 2 types of SW membranes and 2 types of HFF membranes; not all units were run at each location. ++ B = $Ms/(C_1 - C_2)$, gallons/minute * Not available

Table E.3. Ionl Rejection (Fractional)

	1	2	3	4	5 ²	6	7	8	9	Avg.
SODIUM	.82	.86	.82	.85	-	.92	.94	.96	.90	.88
POTASSIUM	.9	.87	.86			.95	.93	.96	.95	.92
. CALCIUM	.96	.95	.98	.99	-	.99	.99	.98	.95	.97
MAGNESIUM	.95	.96	.99	.96		.99	.99	.98	.98	.98
IRON	.95	- -	-	_		<u></u>	-	-		
MANGANESE	.973	-	-						-	-
CHLORIDE	_	.89	.95	.68	-	.87	.99	.9	.9	.88
FLUORIDE	_	-	484	.82		-		.8		.81
NITRATE	-	.44	.93	.36	-	.78	.95	-	.66	.69
BICARBONATE	.96	_	.86	.89		.99	.99	.94	.9	.93
SULFATE	-	.88	.98	.86	_	.80	.96	.96	.98	.92
ARSENIC	-	.78	.97	_	_	.95	-	-	.94	.91
BARIUM	_	.9	.95	_	_	_				.92
BORON ⁴	1.20	1.05	_	.08		.46		1.5	1.4	-
SELENIUM	.80	_	.90	_		.78		.	.70	.8
ZINC	.90	.80	_	-	-	~	.80	_	.73	.81
RADIUM	_	-	_	_	-	<.5 Pc		_	_	_
STRONTIUM	.98	.97	.99	-	_	.99	-	.99	.95	.98
SILICA	.83	.77	.82	.67	_	.9	.97	.98	.88	.85
TDR	.92	.86	.94	.91	.94	.96	.98	.98	.94	.94

¹ Only those ions that material balance showed consistancy

² No component analysis was available from San Ysidro 3 Removed via Greensand filter

⁴ Boron appeared to increase in the product water

^{*} No product analysis

APPENDIX F: Electrodialysis Efficiency Constants

Table F.1 Electrodialysis Ion Separation (Fraction)

Para contraction of the contract	1*	2	3	4	5	6	7	8	9	Avg.#
SODIUM		.61	.58	.74	-	.73	.75	.86	.89	
POTASSIUM	.31	. 78	.77	.68	•••	. <u>8</u> 5	.82	.95	<u></u>	
CALCIUM	.52	.85	.84	.86	<u>-</u>	.91	.78	.96	.97	
MAGNESIUM	.41	.86	.82	.92		.9	.87	.95	.96	
IRON		_	-	****	_	-	_	_		-
MANGANESE		-	_	_	****	_	_		_	
CHLORIDE		.79	.8	.91	-	.87	.86	. 96	.94	
FLUORIDE	_	_	_	.74			.5	.85	silver	
NITRATE	.75	.80	.82	.90	_	.92	.98		.97	
BICARBONATE	.90	.61	.42	.80		.76	.58	.91	.85	
SULFATE	_	.86	.72	.89	_	.92	.91	.93	. 94	
ARSENIC	_	.67	.83	.75	_	.86	.90	-	.82	
BARIUM	.58	.9	.94	_		-	_	-	. 🛶	
BORON ⁺	1.28		-	_	_		_			
SELENIUM		_	_	.80	-	_	_	-	_	
ZINC	_	-	_	_	_	_	-	-	-	
RADIUM	-		_	_		_	_		_	
STRONTIUM	.59	.92	.84	_	-	.96	.98	.99	.99	
SILICA	0.	0.	0.	0.	_	0.	0.	0.	.06	
TDR	.31	.80	. 74	.81		.75	.77	.92	.94	

^{*} Unit installed at this location; operator training period

⁺ Boron appeared to increase in product water

^{*} Average not computed because method of operation changed after Moriarty (7)

APPENDIX G: Equipment Cost Curves

Table G-1

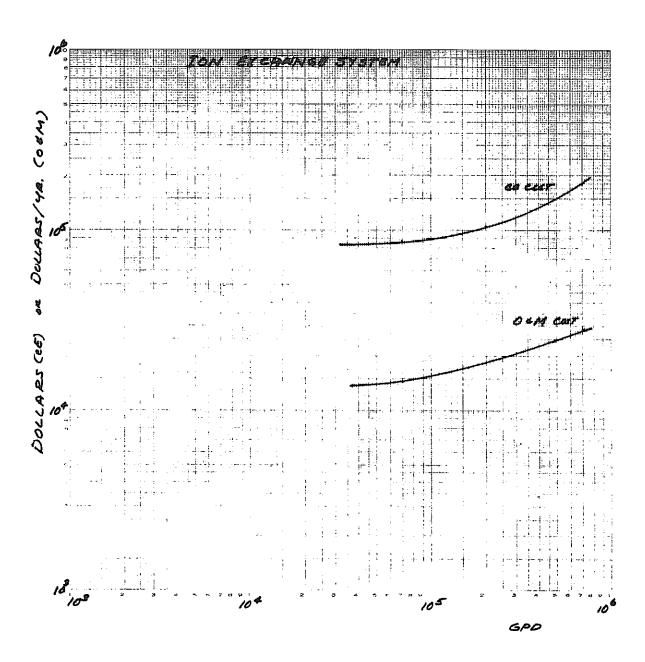


Table G-2

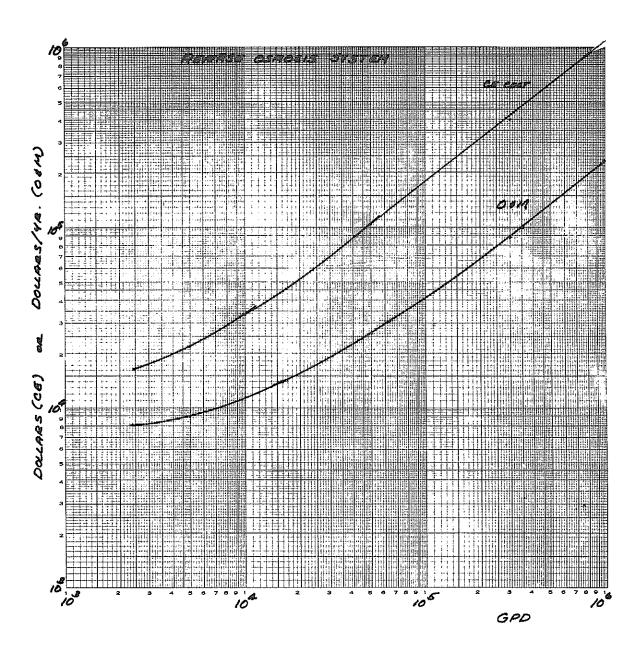


Table G-3

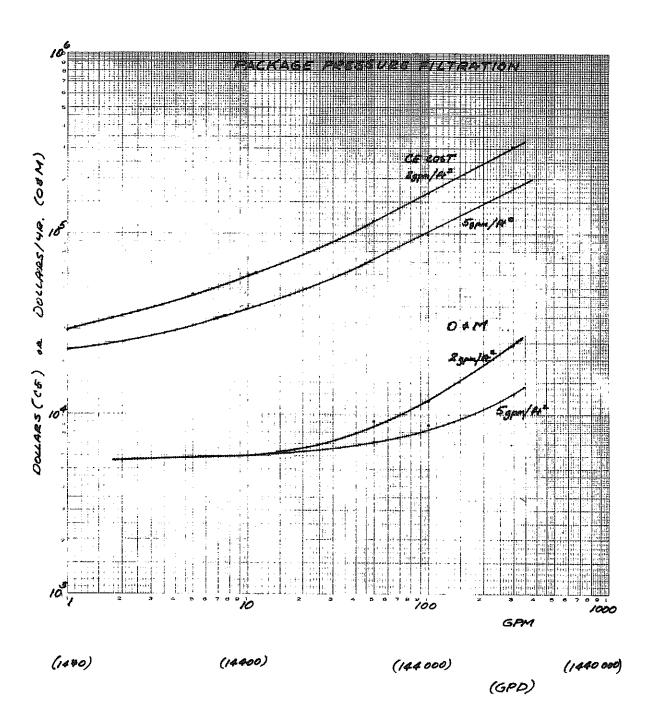
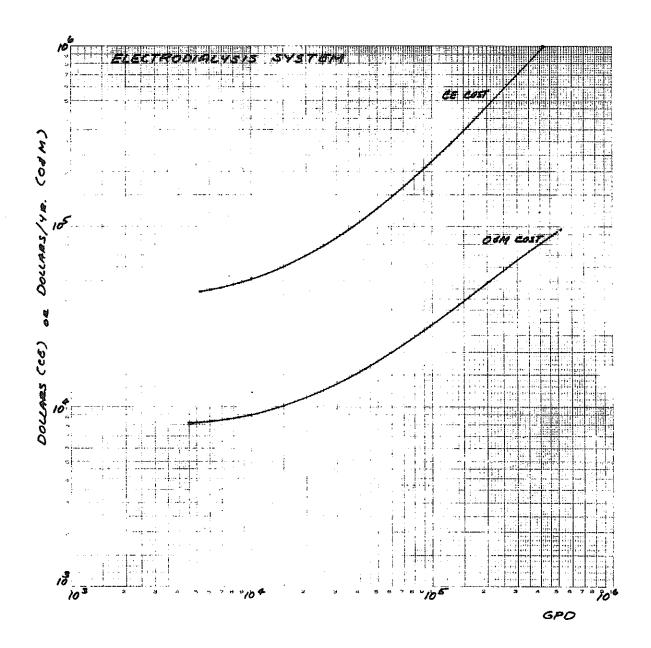


Table G-4



APPENDIX H: Electrodialysis Cost Data

Table H-1. Electrodialysis Cost Data

1. NMSU Demonstration Van (Oct. '77)

Aquamite VI (short stack) 10000 gpd 10000 gpd declared cost \$36,000. \$51,200.

2. Unpublished Fluor Report

Seawater

\$3.03/GPD

3. Kaiser Engrs (Alamogordo Project)

 2×10^6 GPD

 $$8.3 \times 10^6$ Total

The total included engineers fees, contingency etc. to place on same basis as 1 & 2 used 50% factor.

%2.08/GPD \$2.39/GPD \$1 x 10⁶ 420,000 gpd

4. Aquamite XX unit capacity 264,000 gpd

CE Cost should be linear on log-log plot above this figure.