

REMOVAL OF URANIUM FROM DRINKING  
WATER BY ION EXCHANGE AND  
CHEMICAL CLARIFICATION

by

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## FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water Act, the Safe Drinking Water Act, and the Toxic Substances Control Act are three of the major congressional laws that provide the framework for restoring and maintaining the integrity of our Nation's water, for preserving and enhancing the water we drink, and for protecting the environment from toxic substances. These laws direct EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Water Engineering Research Laboratory is that component of EPA's Research and Development program concerned with preventing, treating, and managing municipal and industrial wastewater discharges; establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storage and distribution; and assessing the nature and controllability of releases of toxic substances to the air, water, and land from manufacturing processes and subsequent product uses. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

This report details the demonstration of ion exchange and chemical clarification technology for the removal of uranium (as  $\text{UO}_2^{2+}$ ) from drinking water. These technologies were shown to be applicable for reduction of uranium concentrations to below 10 pCi/L. This report further describes a strategy for the ultimate disposal of the recovered uranium in a safe manner.

Francis T. Mayo, Director  
Water Engineering Research Laboratory

## ABSTRACT

A research project was conducted to remove uranium solute from drinking water with ion exchange and chemical clarification. Three different ion exchange resins were used: DOWEX SBRP, DOWEX 21K, and IONAC A641. Four ion exchange columns were constructed, each containing 2 ft<sup>3</sup> of resin. Three columns were operated in the conventional down flow mode; the fourth column was operated with upward flow of the feed water. Pretreatment consisted of particulate filtering only. Regeneration was by chloride ion. Resin capacity was represented by bed volumes between 12,000 and 20,000. Four cycles of the resin were completed, processing approximately 4 million gallons of feed containing an average uranium concentration of 300 ug/L.

A small, 1-gpm chemical clarification unit was built consisting of a rapid-mix vessel and a pre-coat rotary vacuum filter. This system was operated continuously over a period of 3 months using various pH values ranging from 6 to 10.0 and various ferric chloride concentrations ranging from 15 to 40 mg/L. Better than 99 percent uranium removal was achieved by operating at a 30 mg/L ferric chloride concentration and pH 10.0. The diatomaceous earth precoat filter achieved complete solid-liquid separation.

Additional work included a review of current drinking water operations for uranium removal, geohydrology studies on the origin of the raw water uranium for this study, fluidization characteristics of upflow ion exchange columns, and ultimate disposal problems associated with the separated uranium.

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## SECTION 1

### INTRODUCTION

#### A. Objectives of the Study

The overall study objective was to demonstrate the operation of the equivalent of commercially available ion exchange equipment and to develop a pilot-scale chemical clarification unit for the removal of uranium from drinking water supplies. Specific objectives were:

1. To demonstrate extended operation of four ion exchange columns (3 to 5 gpm capacity each) using three different resins with one column operated in an up-flow mode. These columns were to be the equivalent of commercially available units and were to include automatic regeneration capability.
2. To develop a pilot-scale chemical clarification unit (5 gpm maximum capacity) and to test selected coagulants and/or flocculating reagents. The system includes continuous solid-liquid separation.
3. To assemble the necessary ion exchange equipment, chemical clarification equipment, monitoring instrumentation, and analytical instrumentation in a self-contained trailer unit.
4. To develop and conduct a monitoring program for several currently operating conventional drinking water treatment plants that have uranium in their feedwater supplies.
5. To prepare a general evaluation of radioactive waste disposal technology that would be appropriate for the selected processes of ion exchange and chemical clarification.
6. To prepare the necessary engineering data for process selection, process design, and cost evaluation for removing uranium from individual community water supplies.
7. To publish the project results. In addition to this final report, research related to this project will provide thesis or dissertation material for graduate students, and appropriate material will be published in the technical literature.

#### B. Uranium Effects and Chemistry in Aqueous Solution

At present, the maximum contaminant level (MCL) for radioactivity in drinking water does not include regulation of naturally-occurring uranium. [1] The MCL for alpha-emitting radionuclides specifies 5 pCi/L for Ra226 and 228 combined and gross alpha activity of 15 pCi/L excluding the alpha contribution from radon and uranium. Establishing a safe unit for human consumption

is the primary goal of the MCL, but it is also based on technology for removal and cost of the technology.

Although the effects of ionizing radiation on humans is much better known than those of many other environmental pollutants, it cannot accurately and definitely be predicted from known animal effects. Our bodies may be exposed to both external and internal radioactivity. For exposures to drinking water, the internal exposures are the most important. Once the radioisotope enters the body through ingestion, it will move to locations determined by the body's metabolism and chemistry. Uranium is considered to concentrate in the kidney rather than in bone marrow; therefore it may have a short biological half-life (e.g., the time duration for the body to eliminate one-half the original concentration). [2]

A recent study of the occurrence of uranium in drinking water in the United States estimates the average concentration as 2 pCi/L. [3] By consuming 2 liters of drinking water per day, the average person would ingest 1440 pCi in 1 year. The average annual ingestion in food is about 240 pCi/year. Current model estimates indicate that the ingestion of 10 pCi/day of radium (i.e., 2 liters of water containing 5 pCi/L) produces a dose of 150 mrem/year to the skeletal bone. [4] Corresponding models for uranium have estimated the risk from ingested uranium to produce  $3 \times 10^{-5}$  excess cancers per lifetime from ingestion of water with a uranium concentration of 10 pCi/L. Therefore current considerations are for limiting uranium concentrations in drinking water to 10 pCi/L. This is the level of activity that must be achieved by current available technology.

Public water supplies are subjected to a variety of treatments, depending on the condition of the raw water and the needs of the consuming community. Several different drinking water treatment processes are available for possible removal of naturally occurring uranium. These processes are classified into conventional water treatment processes and non-conventional water treatment process. Conventional water treatment processes for removal of inorganic contaminants are (1) coagulation (alum or iron) followed by settling and filtration; (2) coagulation (alum or iron) followed by filtration; (3) lime softening (with or without recarbonation). Conventional treatment plant operations on uranium-containing water supplies were surveyed. [5] The results of this survey are summarized in Table 1. [6] The survey indicated that further research and development of chemical clarification and ion exchange should be undertaken.

Before considering the technology of uranium removal a brief review of the aqueous-phase chemistry of uranium is appropriate. Pourbaix [7] gives two potential pH diagrams for uranium-water systems. These are summarized as Figure 1. These diagrams show the region of the  $\text{UO}_2^{2+}$  ion that is the predominant form of the uranium ion in drinking water.<sup>2</sup> Cotton and Wilkinson [8] summarize the aqueous chemistry of uranium as follows:

"Uranium ions in aqueous solution can give very complex species because, in addition to the four oxidation states, complexing reactions with all ions other than  $\text{ClO}_4^-$  as well as hydrolytic

TABLE 1. URANIUM CONCENTRATIONS IN RAW AND TREATED SAMPLES TAKEN FROM SELECTED MUNICIPAL WATER TREATMENT PLANTS

Water Treatment												Uranium	
Location and Name of Treatment Plant	Water Source	Coagulation					Activated Carbon	Lime	NaOH for pH Control	Filtration	Chlorination	Raw Water	Treated Water
		Alum	Iron Salt	Lime	Polymer	Silica							
Arizona (Phoenix)													
Squaw Peak	Si	X					X			X	X	1.70	1.80
Val Vista	Si	X			X		X	X		X	X	4.45, 4.30	4.05
Verde	Si	X					X			X	X	4.30, 4.10	4.20
California (Los Angeles)													
Hawthorne	G			X						X	X	0.74, 0.29, <0.10	0.10, <.10
Jensen	Si	X								X		0.30, 0.27	0.28
Long Beach	G			X						X	X	0.32, 0.30	1.59±0.03
Weymouth	S									X	X	6.61, 6.10	6.06, 6.60
California (San Diego)													
Alvarado	Si		X	X						X	X	1.68, 1.90	2.31, 1.80
Escondido-Vista	Si	X			X					X	X	5.43, 5.10, 8.15	6.25, 5.60
Olay	Si		X						X	X	X	1.05, 1.00	2.10, 2.30
Sweetwater	Si				X					X	X	4.07, 3.30	3.30
Colorado (Denver)													
Harrison	Si		X		X					X	X	1.60, 1.60	1.50
Moffat	Si		X		X					X		15.9±1.58	4.00
Michigan (Midland)	Si			X						X	X	0.27±0.03	0.35
Missouri (Kansas City)	Si			X	X					X	X	5.33±0.23	4.07±0.30
Nebraska (Lincoln)	G					X				X	X	7.29±0.47	7.39
Texas (Houston)	Si		X		X				X	X	X	0.32±0.14	0.28
Utah (Salt Lake City)													
Big Cottonwood	Si		X							X	X	0.90	0.80
City Creek	Si		X							X	X	1.00, 0.30	0.90, 1.00
Little Cottonwood	Si		X			X				X	X	1.70	0.90, 1.00

For replica analyses (n>2), values are mean ± standard deviation.

n = 3

n = 4

-4-

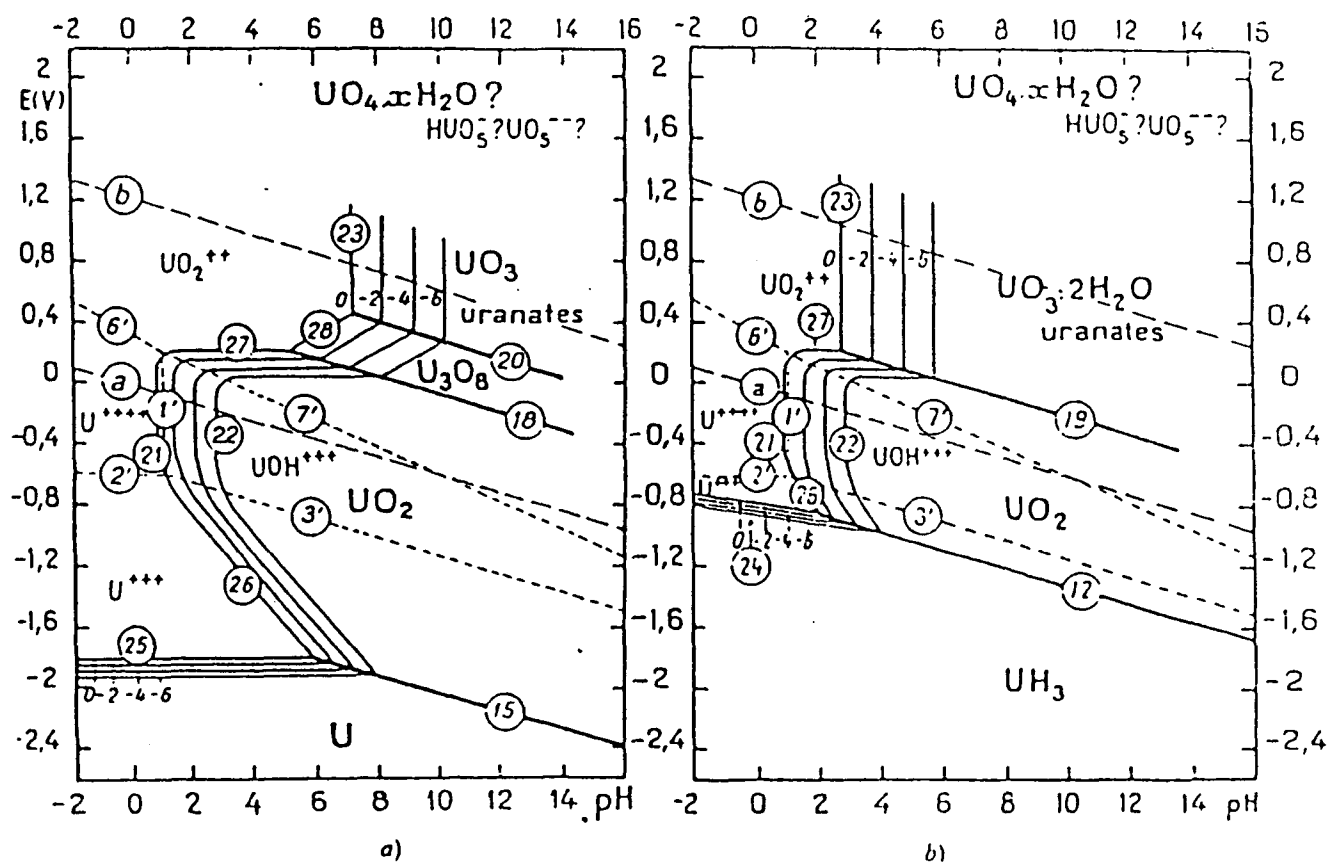


Figure 1. Pourbaix Diagrams for Uranium

reactions leading to polymeric ions occur under appropriate conditions."

Table 2 lists the simple ions and their properties plus the pH dependency of the uranyl complex ions in the presence of carbonate.

TABLE 2. URANIUM IONS IN AQUEOUS SOLUTIONS [8]

Ion	Color	Preparation	Stability
$U^{3+}$	Red-Brown	Na or Zn/Hg on $UO_2^{2+}$	Slowly oxidized by $H_2O$ , rapidly by air to $U^{4+}$
$U^{4+}$	Green	Air or $O_2$ on $U^{3+}$	Stable; slowly oxidized by air to $UO_2^{2+}$
$UO_2^+$	?	Transient species	Stability greatest at pH 2-4; disproportionates to $U^{4+}$ and $UO_2$
$UO_2^{2+}$	Yellow	Oxidize $U^{4+}$ with $HNO_3$ , etc.	Very stable; difficult to reduce

Adjusted pH [6]

(In the presence of carbonate)

pH	4	6	9	10
Uranyl Species	$UO_2^{2+}$	$UO_2CO_3^0$	$UO_2(CO_3)_2^{2-}$	$(UO_2)_3(OH)_5^+$

Aqueous solutions of uranium salts have an acid reaction due to hydrolysis, which increases in the order  $U^{3+} < UO_2^{2+} < U^{4+}$ . The uranyl and  $U^{4+}$  solutions are well studied. The main hydrolyzed species of  $UO_2^{2+}$  at 25° are  $UO_2OH^+$ ,  $(UO_2)_2(OH)_2^{2+}$  and  $(UO_2)_3(OH)_5^+$ , but the system is a complex one and the species present depend on the medium (shown in Table 2). At higher temperatures the monomer is most stable but the rate of hydrolysis to  $UO_3$  of course increases. The solubility of large amounts of  $UO_3$  in  $UO_2^{2+}$  solutions is also attributable to formation of  $UO_2OH^+$  and polymerized hydroxo bridged species. Knowing the uranium ion species actually present is important for successful operation of both chemical clarification and ion exchange.

Table 3 lists the ion composition of a typical drinking water supply containing uranium. All the anions listed will complex with uranium in

TABLE 3. DRINKING WATER SOLUTES

Metals	Ions	Water Parameter
U	$\text{Cl}^-$	P&M Alkalinity
Fe	$\text{F}^-$	Hardness
Ca	$\text{SO}_4^{=}$	SP Conductance
Na	$\text{NO}_3^{=}$	pH
As	$\text{CO}_3^{=}$	TDS
Ra	$\text{HCO}_3^-$	Temperature
Mg	$\text{PO}_4^{=}$	
Si		

species depending on the pH. As shown in Table 2 carbonate complexes can be either neutral or negative in the pH range characteristic of drinking water supplies. Phosphate complexes can be either positive, such as  $\text{UO}_2\text{H}_2\text{PO}_4^+$  and  $\text{UO}_2\text{H}_3\text{PO}_3$ , or negative at higher concentrations. Finally, silica readily adsorbs  $\text{UO}_2^{2+}$  and  $\text{U}^{4+}$  at low pH's [9].

Sorg and Logsdon [10] have published a series of articles summarizing existing treatment technology to meet the inorganic National Interim Primary Drinking Water Regulations. Part 5 of their series covers barium and "radio-nuclides" which are treated as radium 226 and radium 228. Uranium and other members of the actinides are not discussed. Recent work by Oak Ridge National Laboratories has provided the best available data for uranium removal. [11] The Oak Ridge studies addressed the technologies of chemical clarification and ion exchange, supporting the decision that it is these technologies which should be examined further.

### C. Chemical Clarification

In general, chemical clarification is made up of three operations: (1) coagulation, (2) flocculation, and (3) sedimentation [12]. The literature does not make a clear distinction between these operations and in some work 'coagulation' and 'flocculation' are used interchangeably. The description of the process becomes even less clear when chemical reactions occur and filtration is substituted for sedimentation. It is defined in this work that "chemical clarification" will mean "...the addition of coagulants, flocculants or oxidants to cause the precipitation of material which removes inorganic compounds or which adsorbs inorganic compounds (ions) and hence removes them from solution."

Coagulation takes place in rapid mix, or flash mix basins. Some systems use in-line mixers. The primary coagulants that have been used in wastewater treatment are: (1) lime, (2) alum, and (3) iron salts such as ferric chloride, ferric sulfate and ferrous sulfate. While the mechanism of uranium removal via coagulation has not been demonstrated conclusively, it most likely occurs through adsorption of the uranyl ion complex by the coagulant precipitate. Subsequent filtration removes the coagulant precipitate and the adsorbed uranyl ion complex. Depending on the filter media there may also be adsorption of the uranyl ion complex on the filter media. Successful operation requires the uranyl ion complex to remain adsorbed i.e., should not desorb during filtration.

Conventional water treating systems which use coagulants or flocculating agents most often use sedimentation basins for separating the solid-precipitate, agglomerated solids from the water. These systems are selected on the basis that the feed water contains suspended solids. In applications where chemical clarification is used to remove metal ions from water in the absence of suspended solids the resulting precipitates are usually so small that sedimentation alone is not adequate and flocculation and filtration are required.

Filtration is the key process in production of high quality effluents from wastewater. In solid-liquid separation filtration is generally through a very thin layer of porous material deposited by flow on a support septum. [13] While these types of filters have special applications in water treatment, most frequently filtration in water treatment is understood to mean the removal of impurities from water by passage through a relatively deep (2-3 ft) bed of granular material. The major difference in the operation of the two types of filtration is that the mechanical-straining type filter produces a product cake having from 5-8 percent water and the deep bed filter produces a slurry (as a result of back washing to regenerate the bed). Both types of filters will need to be evaluated for ultimate product disposal when separating radioactive nuclides.

A conventional chemical clarification system is shown in Figure 2.

#### D. Description of Ion Exchange

Ion exchange is a separation process in which ions held by electrostatic forces to charged functional groups on the surface of an insoluble solid are replaced by ions of like charge from the solution. Unlike simple physical adsorption phenomena, ion exchange is a stoichiometric process in which every ion removed from solution is replaced by an electrical equivalent amount of another ionic species of the same sign from the solid. Ion exchange is, in general, a reversible process and is selective in the removal of dissolved ionic species. Although many naturally occurring materials exhibit ion exchange properties, synthetic ion exchange resins having a wide range of properties for specific applications have been developed. [14,15]

The characteristic properties of ion exchange materials are due primarily to their structure. These materials consist of a solid matrix held together by chemical bonds. Attached to this framework are soluble ionic functional

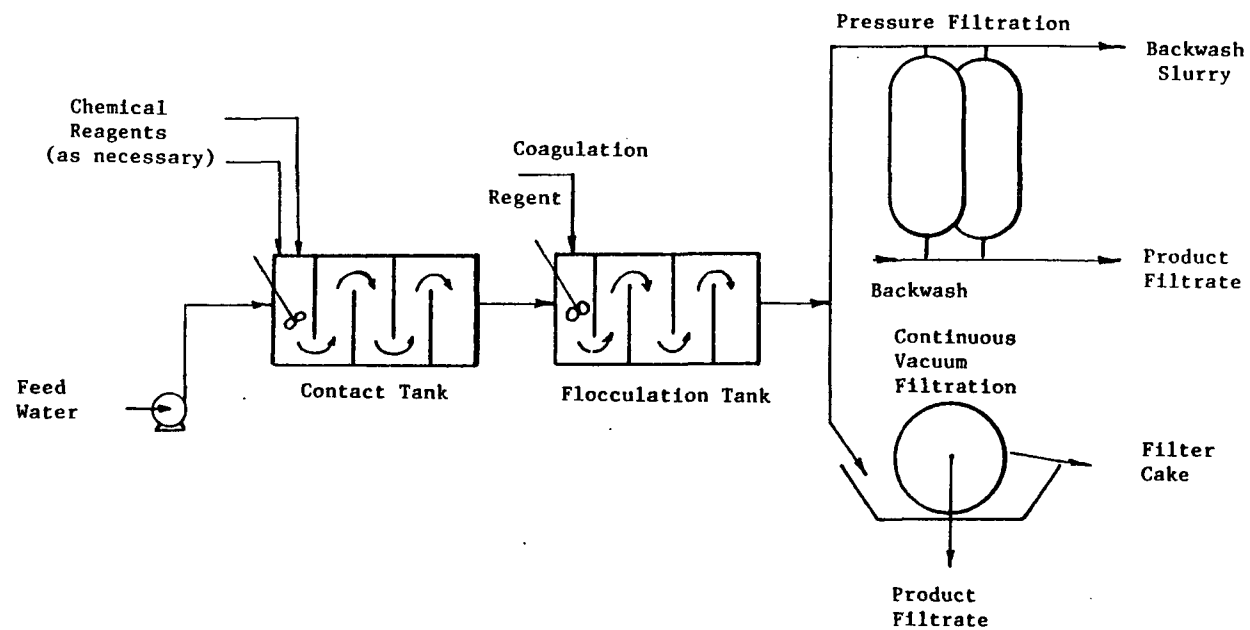


Figure 2. Chemical Clarification



groups containing ions which are relatively free to move and exchange with similarly charged ions in solution. Ion exchange materials must possess the following characteristics:

1. Ion-active sites throughout the entire structure e.g., very uniform distribution of activity;
2. High total capacity, that is, a high degree of ion substitution or low equivalent weight;
3. Good degree of selectivity for ionic species but capable of being regenerated;
4. Extremely low solubility;
5. Good structural chemical stability;
6. Good structural physical stability;
- and 7. Costs competitive with other processes.

Ion exchangers are classified by the type of ionic functional group attached to the structure and the charge sign of the exchanging ion. Five major classes of ion exchange resins, categorized according to functional group, are (1) strongly acidic cationic; (2) weakly acidic cationic; (3) strongly basic anionic; (4) weakly basic anionic; and (5) a broad miscellaneous category of ion-specific structures. In addition to these classes, there exist some intermediate strength acid and base resins.

Normal ion exchange is operated in a column system as shown in Figure 3. There are four distinct steps to one cycle of operation: 1) service period; 2) backwash; 3) regenerate; and 4) rinse.

The primary operating parameters in ion exchange units are shown in Figure 4 e.g., the exchange zone and breakthrough. These parameters provide the necessary operation period before regeneration. The third operating parameter can only be obtained on pilot-scale experiments using the actual water supply and this is the number of generation/regeneration cycles a given charge of ion exchange resin can undergo. Bottle tests can give some indication of the percentage regeneration (aging) of the resin but are not conclusive.

#### E. Description of Current Data on Uranium Removal

As a result of the literature review of removing uranium from drinking water, Oak Ridge National Laboratory undertook bench-scale testing on uranium removal from a natural water. [11] Their work is summarized in Figures 5 through 8 indicating that conventional coagulants i.e., ferric sulfate or aluminium sulfate remove more than 85 percent of dissolved uranium (83  $\mu\text{g/L}$ ) when an optimum pH and dosage were provided. At pH 10 a dosage of greater than 12 mg/L for both coagulants gave maximum removal. In addition, it was verified that a strong base anion-exchange column is a recommended option for the treatment of private well waters containing uranium at higher than desired levels; although the published data did not represent column breakthrough.

Further bench tests on ion exchange were initiated at the Drinking Water Research Laboratory of the Environmental Protection Agency. [1] In addition McClanahan examined ion exchange for removal of uranium from mine waters. [16] These results are summarized in Table 4.

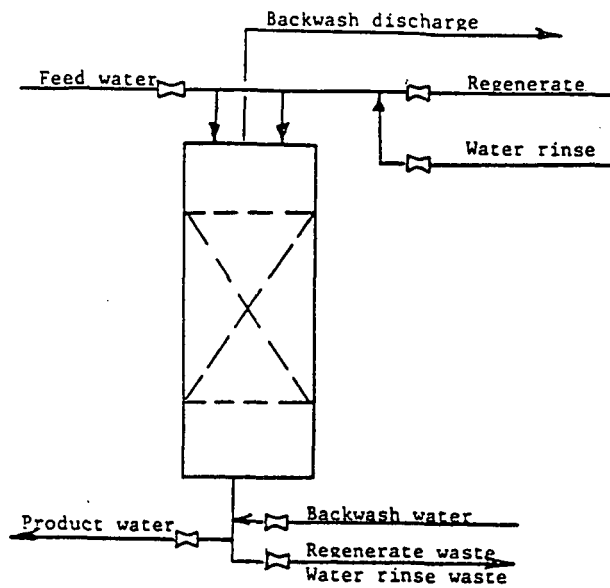


Figure 3. Typical Single-Column Ion Exchanger Flow Diagram

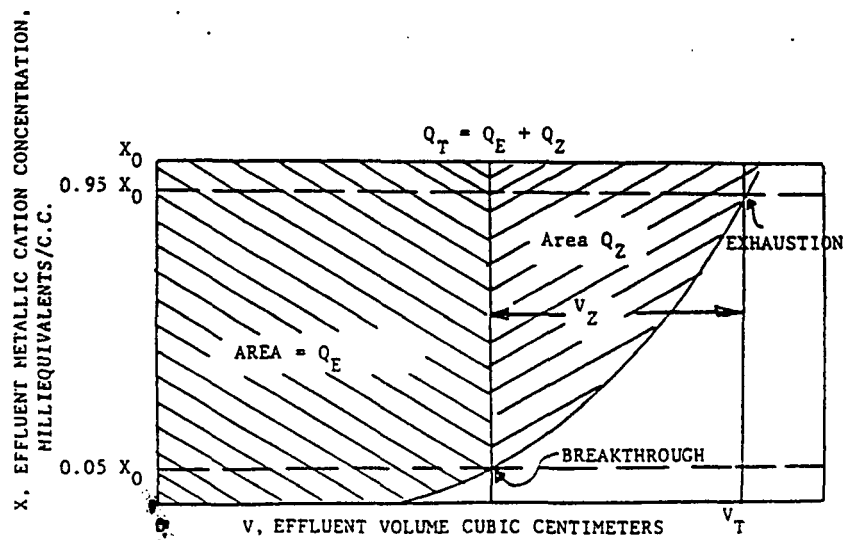


Figure 4. Ion Exchange Column Operation

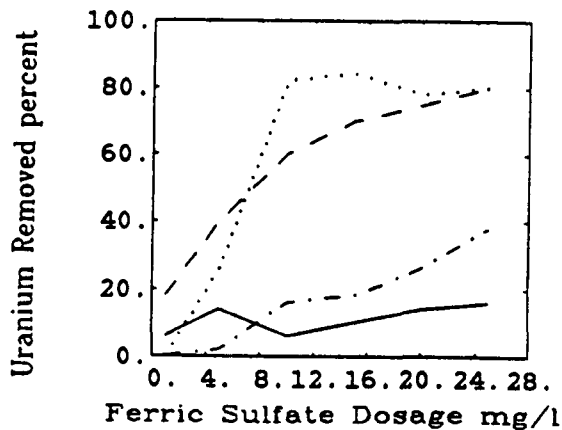


Figure 5. Percentage of Uranium Removed From Pond Water by Ferric Sulfate. — pH 4; --- pH 6; - - pH 8; ... pH 10.

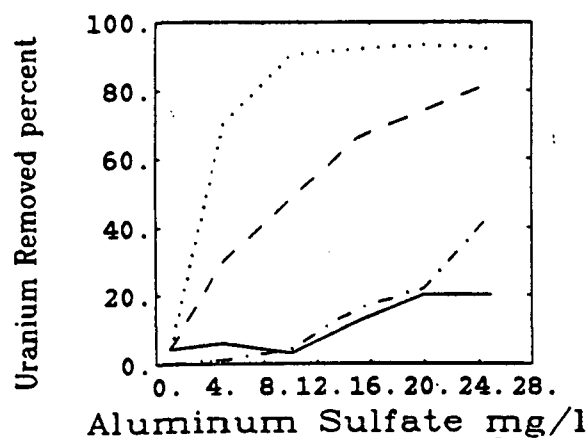


Figure 6. Percentage of Uranium Removed From Pond Water by Aluminum Sulfate. — pH 4; --- pH 6; - - pH 8; ... pH 10.

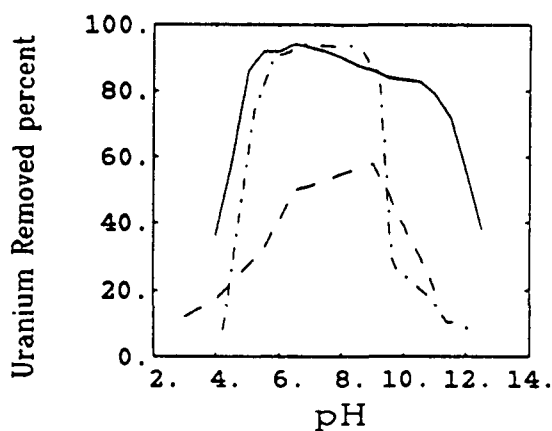


Figure 7. Percentage of Uranium Removed as a Function of pH (Using Ferric Sulfate). —; no coagulant ---; Aluminum sulfate - -

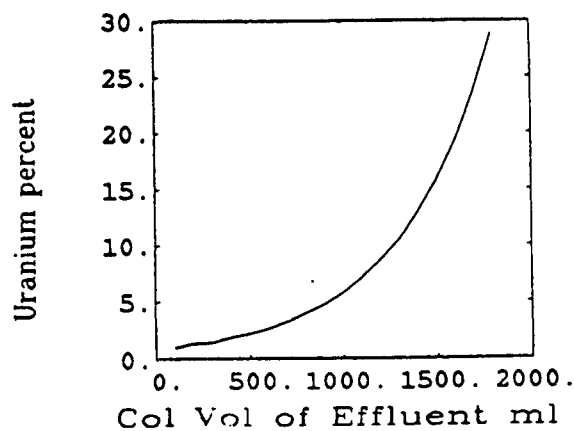


Figure 8. Uranium Breakthrough From An Anion Exchange Column. (DOWEX 1-X2) Influent Contained 23.8 mg U/L and 960 mg  $(\text{NH}_4)_2 \text{CO}_3/\text{L}$ .

TABLE 4. MINE-WATER ION EXCHANGE TESTS

Ion Exchange Material	Uranium Removal, %	Comment	Ref.
DOWEX SBR	99 <sup>+</sup>	Mine Water	16
DOWEX 50W-X8	35.	Mine Water	16
Clinoptilolite	20.	Mine Water	16
DOWEX 21K	97.	Mine Water	16
DOWEX 1-X2	99 <sup>+</sup> (Max)	Parameter Dependent	1
DOWEX SBR-P	99	Column Test	1
IONAC A-641	99 <sup>+</sup>	Column Test	1

The majority of applications of ion exchange and chemical clarification for recovery of uranium (and other radioactive materials) has taken place at uranium ore processing operations or at national laboratories. While ion exchange is a primary unit operation for the recovery of uranium from aqueous solution in ore processing the concentrations considered are several orders of magnitude greater than the equivalent concentration anticipated in drinking water supplies. In fact the IX column effluent from ore processing is usually greater than drinking water supply raw feed.

Chemical clarification and ion exchange for treating radioactive waste solutions have been used extensively at Los Alamos National Laboratory (LANL). [17] Liquid wastes originate at many LANL facilities and are treated at two separate plants in conventional water purification equipment. The treatment removes most of the radioactivity in the wastes by controlled precipitation of ferric hydroxide, followed by ion exchange if necessary. Settling tanks and filtration (precoat) are used to separate the precipitate (called sludge) from the treated water. The piping system permits recycling of the liquid through the plant when additional contamination removal is necessary. This process removes more than 99.9 percent of the original transuranic radioactivity.

#### F. Ultimate Waste Disposal From Uranium Removal From Drinking Water

This topic has not been discussed in the literature. The subject of radioactive waste disposal is a major concern that does not have a universally acceptable solution at present. There are regulations for handling various levels of radioactivity in wastes. The two that are pertinent to this proposed technology are maximum allowable uranium discharge to surface water i.e., the ion exchange regeneration solution and the level of radioactivity in solid waste.

New Mexico restricts the discharge to surface waters of uranium to concentrations of less than 5 mg/L. [18] Solid waste having less than 100 nanocuries per gram can be packaged for ground burial at an approved site. Solid waste having greater than 100 nanocuries per gram must be packaged and eventually transported to an approved waste repository.

Those communities currently using conventional waste treatment operations (Table 1) on uranium containing waters dispose of their sludge similar to non-radioactive sludge disposal practices.

## SECTION 2

### SUMMARY AND CONCLUSIONS

#### A. Ion Exchange

Water treatment using ion exchange technology is a well established operation. Much of the growth, however, has been relatively recent. This current popularity can be attributed to the increasing awareness of declining water quality and the concurrent requirements for meeting water standards. Manufacturers have responded by providing an increasing variety of ion exchange resins to handle these demands. Three resins were selected to demonstrate the effective removal of uranium from a potential drinking water supply.

The resins selected and their operational configuration are shown in Table 5. As shown, three of the four units were operated in the conventional downward mode, while the fourth was operated in an upflow mode. The efficiency (as characterized by the breakthrough curve) of each system was comparable, although the upflow unit processed the most water.

Several physical and chemical characteristics of the resins need to be considered in the selection of ion exchange as a water treatment technology. Physical bead breakage may occur in some applications. For down-flow systems, this results in increased pressure drop and reduced efficiency. In an upflow unit, breakage could result in subsequent downstream problems in addition to the loss of exchange capacity through loss of resin.

Thermal stability of the resins is a second consideration in selecting ion exchange. Weak-base resins are usable up to 212 °F followed by Type I strong bases to 122 °F (the resins of this demonstration). Temperatures in the van housing the units ranged from a winter low of 35 °F and a summer high of 115 °F. The average inlet water temperature was 65 °F.

Although chemical degradation is not normally a problem in most water treatment applications, strong oxidizing agents can rapidly degrade the polymer matrix and should be avoided. Slower degradation with oxygen may be catalytically induced, so ionic iron, manganese, and copper should be minimized. Both equipment manufacturers and resin producers recommend techniques for managing these situations.

Capacity of ion exchange resin is the measure of ionic attraction per volume, and is expressed in a number of ways. Total capacity is the theoretical measure of the total number of exchange sites available and is normally

TABLE 5. DEMONSTRATION ION EXCHANGE UNITS

Resin Type	Flow Condition	Total Gallons Processed	Number of Cycles	Average Bed-Volumes Treated/Cycle	Maximum Removal Efficiency
DOWEX 21K	Down	797,540	4	12920	99%
DOWEX SBR-P	Down	890,600	4	14925	99%
IONAC A-641	Down	853,870	4	16038	99%
IONAC A-641	Up	903,450	4	15370	99%

Inlet water concentration ranged between 200 and 400  $\mu\text{g/l}$  uranyl complex (as uranium).

calculated in three different ways: Dry weight capacity, (milli-equivalents/dry gram), wet weight capacity (milli-equivalents/wet gram), and wet volume capacity (milli-equivalents/milliliter). Regardless of how expressed, operating capacity is the most realistic performance measure for ion exchange resins and in water treatment is usually expressed as kilograins  $\text{CaCO}_3$  per cubic foot of resin.

A final consideration in the selection of an ion exchange resin is the cost of regeneration. Small differences in efficiency will be magnified over the life of the system. Perhaps of equal importance are the potential environmental problems encountered in disposing of waste regenerant. These problems will be addressed after a discussion of the chemical clarification results.

$\text{NaCl}$  in a 10-percent by weight concentration was selected as the regeneration solution.

#### Specific Conclusions

1. When operated under prescribed conditions, all resins performed satisfactorily to produce effluent water that would meet the suggested standard of less than 10 pCi/L (approximately 14  $\mu\text{g/L}$ ). The IONAC A-641 resin had the greater capacity under the operating conditions used.
2. All four systems operated well. No unusual mechanical problems were experienced.
3. The three units operated with downflow showed no resin breakage as determined by pressure drop.
4. The upflow unit exhibited no resin breakage based on no change in pressure drop and examination of the resin.
5. No noticeable change in operation occurred as a result of the temperature of the operation over the range 35°F (winter) to 115 °F (summer).

6. Feed water iron and manganese concentrations (4 mg/L and 1.1 mg/L, respectively) were higher than recommended for operation, however there was no quantitative effect on the measured resin capacity over the four cycles, although the measured capacity was less than the manufacturer's listed capacity
7. Table 6 gives the measured resin capacity for the resins under the operating conditions used.

Table 6. Ion Exchange Resin Capacity

Resin	Uranium Capacity* Kilograins/ft <sup>3</sup>	Uranium Wet Volume Capacity <sup>†</sup> (meq/mL)	Total Wet Volume Capacity <sup>‡</sup> (meq/mL)
DOWEX 21K	2.95	0.03	1.20
DOWEX SBRP	3.15	0.032	1.20
IONAC A641	3.67	0.038	1.16
IONAC A641 (upflow)	3.54	0.037	1.16

\*As  $\text{UO}_2(\text{CO}_3)_2^{2-}$ .

<sup>†</sup>Average over three cycles of operation (i.e., cycles 1,2, and 4).

<sup>‡</sup>Manufacturer's value: 1.2 meq/mL is 26 Kilograins/ft<sup>3</sup> as  $\text{CaCO}_3$ .

#### B. Chemical Clarification

A bench-scale flotation cell was used as the flash mixer and adsorption vessel. Entrained air only was used i.e., no forced air mixing, and no surfactants to enhance bubble stability or flocculation were used. This vessel had a one-minute residence time at 1 gpm feed rate. The effluent was channeled, by gravity flow to the filter vessel, where a continuous rotary vacuum filter separated the ferric hydroxide precipitate.

The filter membrane was 0.45 micron polymer mesh and when operated without precoating allowed precipitate to bleed through into the filtrate. A one-quarter inch pre-coat of diatomaceous earth was used and gave complete solid-liquid separation as measured by our analytical procedures. Additional diatomaceous earth (12% by wgt) was added to the filter feed and mixed by a mechanical agitator with the feed slurry. A stationary knife removed the cake build up. The residual precoat showed (visual inspection), no blinding by the ferric hydroxide precipitate. Sampling the precoat material after a run for uranium showed that all uranium removed was adsorbed on the ferric hydroxide and not on the diatomaceous earth.



Bed filtration was considered and previous work in the Sanitary Engineering program had demonstrated the suitability of mixed media bed filtration for separating ferric hydroxide. Bed filtration was rejected for two reasons: first, successful use required coagulation chemicals and second, back-flushing, which again produces a slurry, is required to regenerate the bed. Ultimate disposal of the uranium suggests that the disposal product should be solid and of minimum volume, hence the selection of pre-coat continuous vacuum filtration. Further discussion of ultimate disposal will occur in Section D.

### Specific Conclusions

1. This work verified the prior work of Oak Ridge, Los Alamos, and EPA that conventional chemical clarification would successfully remove uranium from drinking water.
2. Ferric chloride at a concentration of 30 mg/L removed more than 98 percent of the uranium at concentrations of 300 and 400 µg/L at pH 10.
3. At pH 6, and an average uranium concentration of 300 µg/L, 30 mg/L ferric chloride removed 82 percent of the uranium.

### C. Survey of Current Operations

A detailed search was conducted to locate currently operating conventional water treatment facilities with uranium in their feed supplies. For this search, a minimum level of 15 µg/L of uranium was arbitrarily selected and conventional water treatment facilities were defined as any type of treatment facility more "complex" than sand separation and chlorination. A total of 34 municipal systems and an additional 21 municipal wells were located in a six state area (Table 7). Of these 55 possible study sites, only 4 provide treatment above and beyond sand separation and chlorination.

Three of these cities are located in Colorado (Denver, Arvada and North Table Mountain) and they all draw their water from the uranium contaminated Ralston Reservoir. The fourth city is a small city in South Dakota (Harrisburg). These communities were contacted and with the exception of North Table Mountain they agreed to help with this study.

The city of Arvada treats their water using a microfloc system. The system employs alum and Separan (a polyelectrolyte) to create the microfloc. The water is then passed through mixed media filters. A 125 cc water sample is collected daily from the raw water and the treated water to form monthly composite samples. For the past couple of years, these monthly samples have been tested for uranium. The raw water from Ralston Reservoir contains from less than 1 µg uranium/L to 36 µg uranium/L with an average of  $14.7 \pm 9.6$  (SD) µg/L of uranium.

The Moffat Treatment Facility (Denver) also draws water from Ralston Reservoir and has been keeping uranium records for about two years. Unfortunately, Denver's monthly samples are "grab samples" and correlation between raw and treated waters are less meaningful.

TABLE 7. SURVEY OF CURRENT OPERATIONS ON URANIUM-CONTAINING WATERS

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Colorado, Water Quality Control Division of Colorado Dept. of Health, 3 community composites, <1 - 24 pCi/L, conventional alum systems.

New Mexico, Water Supply Section of New Mexico Environmental Improvement Division, 2 community composites and 15 municipal water sources, 10 - 110 pCi/L, sand filters and chlorination.

Oklahoma, Association of Central Oklahoma Governments, 22 communities (about 200 wells) near Oklahoma City, 10 - 190 pCi/L, sand removal and chlorination.

South Dakota, S.D. Dept. of Water and Natural Resources, 1 community, 12 pCi/L, iron and manganese removal, chlorination.

Texas, Texas Water Hygiene Division, 5 community composites and 6 individual water sources, 10 - 55 pCi/L, sand removal and chlorination.

Wyoming, EPA Drinking Water Branch, Denver, 1 community (Cheyenne), 29 pCi/L, this well water is chlorinated, they also use surface water which is treated with conventional alum.

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NOTE: This survey is representative of existing state and federal records and may not be complete.

Harrisburg, South Dakota treats about 100,000 gpd using aeration,  $\text{KMnO}_4$ -greensand filters, chlorination and fluoridation. No previous data existed on the uranium removal efficiency of this facility.

#### Specific Conclusions.

1. The Arvada facility removed 18 to 90 percent of uranium in the feed with an average efficiency of 67 percent  $\pm$  15 percent.
2. The Denver facility data were inconclusive (probably because their sampling technique was the use of grab samples).
3. Two sets of samples were taken from the Harrisburg facility. Before and after treatment had the same uranium concentration (19  $\mu\text{g/L}$ ).

#### D. Waste Disposal

As previously described, uranium contaminated drinking water is a common problem, particularly in the western United States. If regulations governing the concentration of uranium in drinking water are accepted and enforced, many communities will be required to remove uranium from their drinking water supplies. Removal of uranium produces a new problem for these communities--the ultimate disposal of a radioactive waste. Three disposal alternatives were considered in this study: dilution/release, reuse or resale, and burial.

### Specific Conclusions

1. Environmental considerations aside, dilution and release is easily the least expensive alternative.
2. Depending on the treatment used for removal, a concentrated solution of uranium could be shipped to a standard uranium mill for processing.
3. Solid material containing the uranium could be packaged and shipped for burial at an approved repository.

### SECTION 3

#### RECOMMENDATIONS

1. The recommended process is a combination of ion exchange for primary removal of uranium from the drinking water supply and chemical clarification (with filtration) for recovery of the uranium from the regeneration solution. This is similar to current practice at Los Alamos National Laboratories.
2. During part of the operation, the uranium concentrations in the well reached 450 µg/L. Uranium concentrations in the regeneration solution were measured as greater than 25 mg/L. Research needs to be conducted to establish the operating conditions for successful chemical clarification at these loadings of uranium and solution conditions.
3. Clarification of existing federal (and state) regulations on licensing of uranium processing facilities would be required should recovery of uranium be acceptable practice.
4. Because ultimate disposal of the uranium through an ore-processing facility is an optimal solution, research should be conducted to establish the conditions, (i.e. pH, temperature, etc.) for desorption of the uranyl complex from the ferric hydroxide precipitated.
5. Permissible water content of the filter cake for inter- (or intra-) state shipping should be established, and the necessary research should be supported to demonstrate appropriate technology should the 5 to 8 percent residual moisture of vacuum filtration be unacceptable.
6. Conventional ion exchange operation on waters containing iron suggest prefiltering for iron removal. Green sand filtration is the recommended treatment. The survey data obtained from Harrisburg, South Dakota, showed that green sand filters would pass the uranyl complex through. This should be confirmed by further testing.
7. Alternative quantitative analysis procedures that could be performed by community water treatment personnel would be required. If not available, they, (e.g., equipment and or procedures) need to be developed.
8. This research did not examine the leaching of organic materials from the ion exchange resins used. If this information is not available, it should be obtained before such resins are introduced into water treatment for uranium removal.
9. Kinetic rates and mechanisms of uranyl complex adsorption on precipitating ferric hydroxide compounds should be researched.

## SECTION 4

### EXPERIMENTAL EQUIPMENT AND PROCEDURES

The demonstration objectives of the project were met through the design and construction of three experimental systems:

- (a) Four-column, semi-commercial-scale ion exchange system.
- (b) Pilot-scale chemical clarification unit, and
- (c) Pilot-scale upflow ion exchange unit.

The major ion exchange system was assembled and operated by personnel from the Water Utilities Operator Training program at the Doña Ana Branch of New Mexico State University. The chemical clarification unit and upflow ion exchange were assembled and operated by graduate students in the chemical engineering program, and present treatment and waste disposal studies were conducted by civil engineering students at NMSU.

#### A. Ion Exchange System and Operation

The ion exchange system was shop-fabricated onsite under the supervision of Mr. Steven Hanson. Table 8 is a summary of the equipment used and the cost of the major items including the resins. Figures 9 through 13 show the components of the system and their organization in the trailer.

The basic design criteria for the ion exchange units were as follows:

Downflow columns	2.75 gpm/ft <sup>2</sup>
Upflow column	1.83 gpm/ft <sup>2</sup>

The following is a description of the basic operation of the ion exchange system.

#### Operational Steps

There are five steps in the operation of an anion exchange column, the service cycle and four-step regeneration.

1. Service--The raw water enters the anion columns and passes either up or down through the resin bed and is piped to the product storage tank. The service cycle continues until either: 1) the seven day timer indicates regeneration, or 2) the water quality falls to an unacceptable level which is indicated by performing a water analysis for uranium. (Initially these were daily until experience suggested a weekly sample). Sample frequency increased when breakthrough occurred.
2. Backwash--Flow through the resin bed is reversed - this is true only for the three down-flow units, the flow for the up-flow unit will be

Table 8. Ion Exchange Equipment List (Spring 1983)

Company Name	Amount	Item
CERAC Inc.	27.13	Sodium Sulfide
Fisher Scientific	10.38	Hydrochloric Acid
Sargent-Welch	87.50	D. Earth
McMaster Carr	130.44	Filter Regulator
Meter Service Supply	326.93	Pressure Gauges
Control Devices	553.70	Level Switches
Automatic Switch	2232.50	Solenoid Valves
Plastic Systems Inc.	5815.00	Diaphragm Valve
L. A. Piping System Inc.	3310.00	Centrifugal Pumps
Ronnigen-Potter Corp.	5269.00	Multiplex Filter
Electrical Supply Co.	120.00	Slotted Angle
Cashway	365.50	B-Board Insulation
Great Lakes Inst.	880.00	pH Analyzer
McMaster Carr	332.93	PVC Welding Kit
Great Lakes Inst.	972.50	Conductivity Analyzer
Raven Industries	931.00	Fiberglass Tanks
Aquamatic	2481.00	Programmable Controller
Metro Harrington Plastics	760.00	PVC Pressure Regulators
Unistrut of El Paso	989.32	Unistrut Channel
Southwest Piping Supplies	454.52	PVC Valves
Southwest Piping Supplies	913.04	PVC Fittings
Southwest Piping Supplies	984.00	PVC Pipe

TOTAL \$ 28,706.39

Ion Exchange Resins

IONAC A641	4 cubic feet	\$ 664.00
DOWEX SBRP	2 cubic feet	288.00
DOWEX 21K	2 cubic feet	295.00

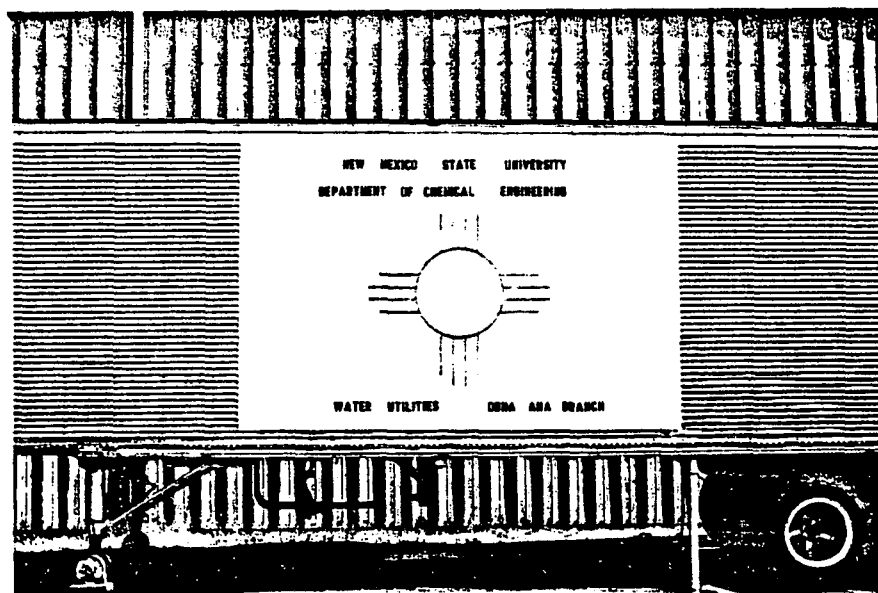


Figure 9. Demonstration Van

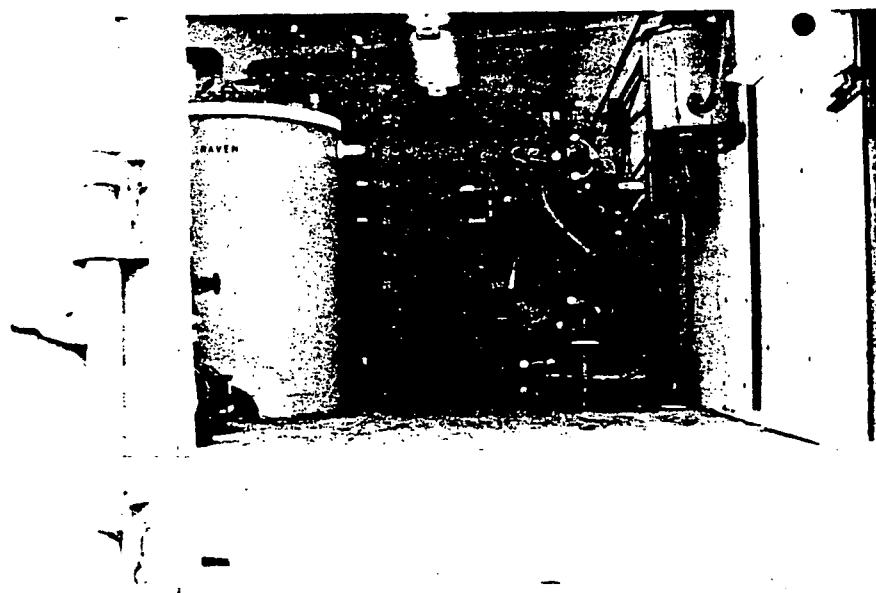


Figure 10. IX Equipment Overview in Trailer

- |                                   |                              |
|-----------------------------------|------------------------------|
| 1. Water Supply                   | 8. Product Tank              |
| 2. Feed Pump                      | 9. Product Discharge         |
| 3. Pre-Filter                     | 10. Regeneration Solution    |
| 4. Chemical Clarification System  | 11. Regeneration Perm        |
| 5. Four Unit Ion Exchange Columns | 12. Waste Discharge          |
| 6. Ion Exchange Control Sytem     | 13. Pilot-Scale Up Flow Unit |
| 7. Product Pump                   |                              |

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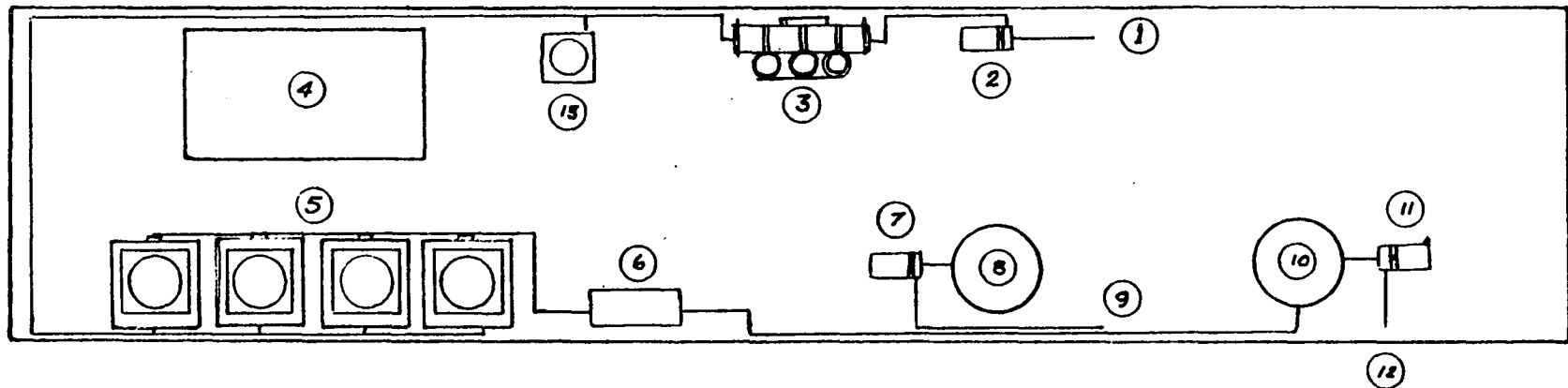


Figure 11. Organization of Van System



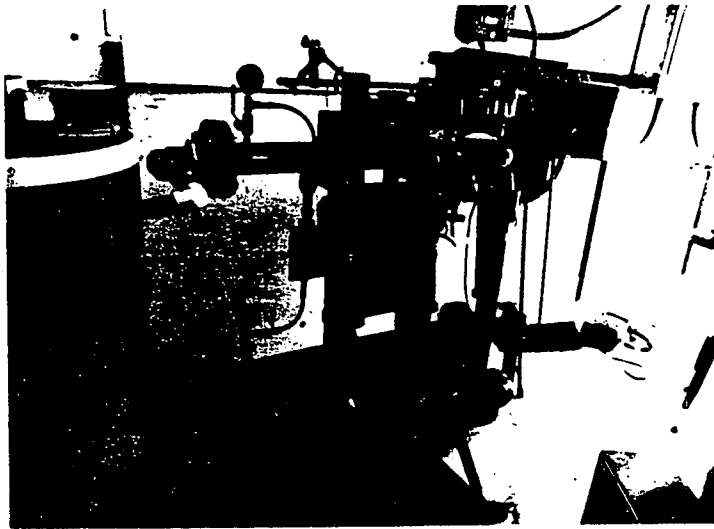


Figure 12. Pre-Filter Equipment Ion Exchange System



Figure 13. IX Columns

the same as the service flow - allowing water to pass upward loosening the particles and flushing away accumulated resin "fines" and sediment.

3. Regeneration--The resin is now regenerated by allowing the brine solution to be pumped from the brine tanks and passed up through the resin bed. This generating procedure displace the ions picked up during the preceding service cycle and exchange chloride ions for them. The anion resin is once again converted to its functional form.
4. Slow Rinse--After the regenerant chemical has passed through the resin, a displacement rinse continues at the same rate and in the same direction through the resin gradually forcing any remaining regenerant out to drain. The step helps insure good chemical utilization.
5. Fast Rinse--The regenerated resin is now rinsed at a flow rate near the service rate until all the residual chemicals are removed. This rinse continues until the water going to drain meets the required effluent quality as determined by analysis.

### Operating Conditions

1. Physical Conditions--The equipment is designed to operate at inlet line pressures of 45 to 75 psig. However, variations in line pressure within these limits cannot be greater than  $\pm 5$  psi. The constant pressure requirement is necessary to insure that the regeneration steps are not upset by erratic flow rates. A pressure regulator has been installed to insure that a constant pressure is kept. The temperature of the incoming water should not fluctuate much during the year, however, the system should not be operated at temperature higher than 105 °F due to the fact that plastic piping is subject to deformation at that temperature and strong base resin should not be operated much above that temperature.
2. Chemical Conditions--Due to the use of the 5-10 micron filter, the turbidity of the incoming water should not be a problem. The chemical composition of the raw water should be checked periodically for dissolved iron and manganese as these ions can and will cause fouling of the anion resin should they exist above 0.3 mg/L.

### B. Start-up

The start-up of the deionizers should proceed smoothly. At any time the system is restarted, however, there may occur minor problems which must be corrected to insure proper operation. Most problems can be easily handled by using good common sense and frequent referral to this procedure.

1. Start-up Preparation
  - a. Close all column valves.
  - b. Water connections should be checked for tightness. Line pressure to the system should be brought to 50 psig.
  - c. Drain lines should be clear of any blockage.

- d. This completes the Start-Up Preparation. The sequence should be repeated for all units.
2. System Fill and Pressurization
  - a. Open main water valve and bottom feed valve and allow the vessel to fill from the bottom with air escaping from the vent. When the vessel is full as evidenced by water flowing from the vent line, close bottom feed valve.
  - b. Now open column valves on the down-flow units - shutting off feed valve. For the up-flow unit, open column valve while leaving feed valve open. The entire system is now pressurized. Carefully go over the entire piping, checking for any leaks and tighten connections as necessary.
  - c. Close all valves. This completes the fill and pressurization for the system.

#### Regenerant Chemical Make-Up

1. Salt (NaCl)--Fill the regenerant tank with 10 percent by weight sodium chloride, NaCl.

#### Initial Start-Up

The following steps will be performed prior to start-up. During these steps, the flows will be set, backwash rates checked and chemical regenerant concentrations verified.

1. Backwash
  - a. Open main valve and column backwash valve on down-flow units. Open bottom valve and column backwash valve on up-flow unit.
  - b. Regulate flow by means of stopwatch and allen wrench, until a flow of 3 gpm is reached. This is the normal backwash rate for the anion units of 60 °F. If the water is cooler, this rate will have to be reduced, while if the water is warmer, the rate must be increased.
  - c. Take a beaker or other suitable container and take a sample every minute or so at the drain and inspect to be sure that no whole beads are being carried over. Resin "fines," small, dust-like particles are expected to be in the sample. If whole beads appear, the backwash rate should be reduced at column backwash valve until the carryover stops.
2. Slow Rinse
  - a. Close main feed valve and column backwash valve on the down-flow units. Close backwash valve on the up-flow unit.
  - b. Open column feed valve on the down-flow units. Open column feed valve on the up-flow unit.
  - c. Adjust the flow rate until a flow of 1 gpm is reached at each unit.
  - d. Allow this step to continue for 5 minutes, then close column feed valve on the down-flow units and column feed valve on the up-flow unit.

3. Fast Rinse
  - a. Now open feed valve on the down-flow units and bottom feed valve on the up-flow unit.
  - b. Adjust the flow rate until a flow of 6 gpm is reached on each unit.
  - c. Allow this step to continue for 3 minutes. This is the end of the rinse step.
4. Service
  - a. Now adjust flow on all columns to desired operating flow. Operation should now begin.

### C. Chemical Clarification System

The study of the removal of uranium ions with ferric chloride was performed using a model D-12 Laboratory Sub-A Flotation Machine attached to a rotary-drum vacuum filter. The flotation machine is manufactured by Joy Manufacturing Company, Denver Equipment Division, Denver, Colorado. The rotary-drum vacuum filter design was adapted from that of an Oliver filter manufactured by Dorr-Oliver, Inc. The vacuum filter system was built in the shop of the Chemical Engineering Department. A schematic showing the main components of the flotation/filtration system is shown in Figure 14. Figure 15 is a photograph of the system. The filtered well water was combined with an appropriate amount of ferric chloride solution and the pH of the influent adjusted to a desired level, then fed directly to the flotation cell. The mixed feed was agitated using the impeller in a cell [20]. Air was sucked into the cell near the impeller zone. The air bubbles dispersed by the impeller, attached to particles which were precipitated as coagulant, rise to the cell top and then flow into the filtration vat. The slurry in the vat was agitated using mechanical stirring to keep the suspension uniform. The drum speed, degree of vacuum and precoat thickness have been adjusted to a suitable value to maintain about 40 percent of the drum surface submerged in the slurry. Continuous operation was achieved by having an automatic level control on the filtrate receiver. At a high level, the pump discharged filtrate to drain, shutting off at the low level. Uranium activity remaining in the filtrate was determined by a fluorometric method using a Turner Filter Fluorometer.

### D. Up-Flow Ion Exchange System

The pilot-scale column for the up-flow ion exchange experiments was constructed in the Chemical Engineering Department. Figure 16 shows the system assembled for operation in the van. This unit was operated as an M.S. Thesis project. [20]

### E. Analytical Procedures

The water used in this experiment was taken from a university well located at the Physical Plant of New Mexico State University, Well Number 8. The chemical composition of the well water is shown in Table 9. The pH and concentration of carbonate and other liquid species in the well water indicate that the dominant uranium species in well water would be uranyl carbonates

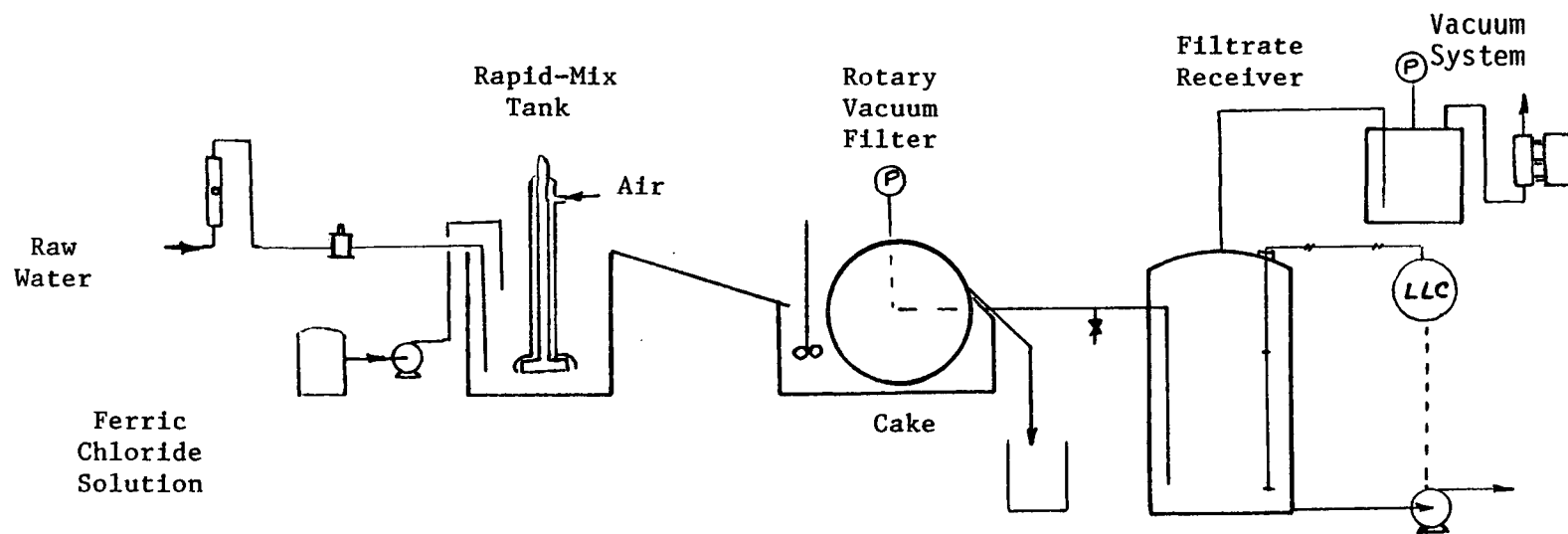


Figure 14. Schematic Diagram of a Flotation/Filtration Unit

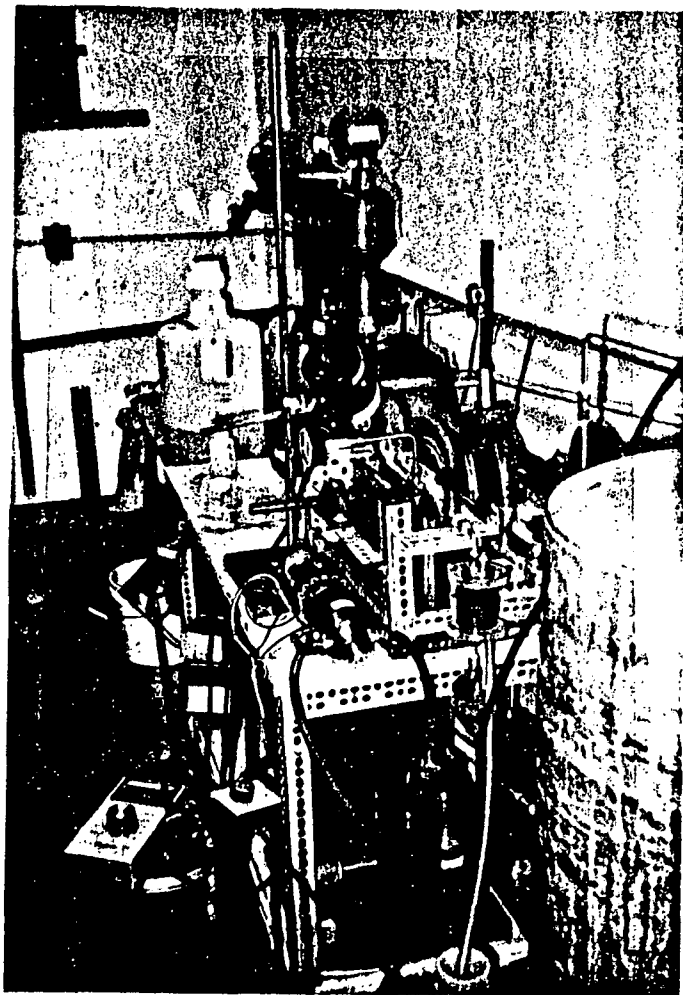


Figure 15. Chemical Clarification System as Installed

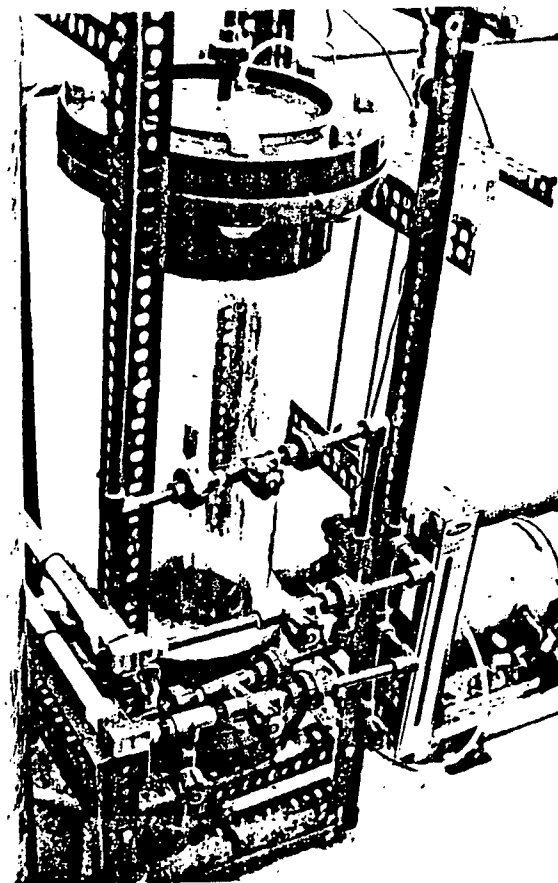


Figure 16. Up-Flow Ion Exchange System

Table 9. Chemical Composition of Well  
Water Used in Demonstration

Component	Concentration (mg/L)	Component	Concentration (mg/L)
U	0.300 (1)	Cd <sup>2+</sup>	<0.005
Na <sup>+</sup>	17.9	Cr <sup>3+</sup>	<0.01
K <sup>+</sup>	18.4	Pb <sup>2+</sup>	<0.005
Ca <sup>2+</sup>	375.2	Hg <sup>2+</sup>	0.0004
Mg <sup>2+</sup>	69.0	Se <sup>2-</sup>	0.005
Cl <sup>-</sup>	555.2	Ag <sup>-</sup>	<0.05
CO <sub>3</sub> <sup>2-</sup>	0	NO <sub>3</sub> <sup>-</sup>	0.01
HCO <sub>3</sub> <sup>-</sup>	96.4	F <sup>-</sup>	0.54
SO <sub>4</sub> <sup>2-</sup>	400.0	Fe <sup>3+</sup>	1.69
TDS	2152	MN <sup>2+</sup>	0.95
AS <sup>5+</sup>	0.005	Hardness (CaCO <sub>3</sub> )	1220
Ba <sup>2+</sup>	0.12	Alkalinity	79

Notes:

1. Uranium concentration in well waters varied and ranged from 180 µg/L to 450 µg/L.
2. pH of well water was 7.62.
3. Electric conductivity of well water was 2.36 m mhos/cm.

([UO<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>]<sup>2-</sup> and [UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>]<sup>4-</sup>). The well water was passed through a pre-filter to remove suspended impurities.

Two standard methods of uranium analysis were used by the student assistants. These are given in the Appendix.

## SECTION 5

### RESULTS AND DISCUSSION

The overall project operation went smoothly, although the well pump did require replacing on two occasions. The student personnel from the Doña Ana Water Utilities Training Program used the ion exchange system operation as part of their technical education. The three graduate students involved wrote Master of Science Thesis on work related to the project and one senior did an independent study project related to the project. All the students stated they gain a great deal from involvement in the project.

#### A. Ion Exchange System

The ion exchange system processed nearly four million gallons of well water which contained on the average 300  $\mu\text{g/L}$  uranium. The ion exchange systems were constructed and operated similar to commercially available equipment. Readily available commercial anion exchange resins were used. Table 10 summarizes the operation (throughput) of the four columns which made up the system. The table shows differential volume treated per period. Units 1, 2, and 3 were operated in a down-flow mode and Unit 4 was operated in an up-flow mode. Although the operation was intended to try and maintain uniform volume flow through all four units, this was not achieved.

Figure 17 gives the overall operation summary for the four units. Figures 18 through 21 show the breakthrough curves for each cycle of each unit. These curves show the total volume of water processed during that cycle by each unit. As seen in these figures, breakthrough to exhaustion did not occur for each column during each cycle. (This is shown by the dashed portion of the curve.) The columns were all regenerated in the same sequence at the same time. The consistency of the four units operation can be seen by the similar behavior as reflected in the breakthrough curves.

All four units operated well. Each resin tested was successful in removing uranium from the raw water supply. Each resin stood up well under the conditions of operation, as shown by the resin capacity calculations summarized in Table 11. There was no degradation of the resin through fouling or decrepitation during the project. As seen in Figure 17 and reflected in Table 11, the results for Cycle 3 were not included. Examination of the effluent sample analysis indicated that regeneration was not complete and there was a period when the influent concentration varied widely, e.g.  $<100 \mu\text{g/L}$  to  $>500 \mu\text{g/L}$ . Also several effluent samples tested at greater concentrations than the corresponding feed.



TABLE 10. SUMMARY OF OPERATION OF ION EXCHANGE SYSTEM

This table shows the operational data taken on the ion-exchange columns as operated between August 1983 and October 1984.

Date	Gal. Treated Per Period	Unit #	Comments
9/15/83	-		Well pump keeps shutting off, not enough flow to run IX and Vac. filter
11/10/83	24,580	1	Still not enough
	78,360	2	Water to run
	88,840	3	System
	84,790	4	
12/12/83	-		Need new well pump Perhaps frozen
1/15/84	42,390		New pump installed
	116,060		Higher Capacity -
	128,780		Needs new wiring
	102,680		
3/6/84	67,020	1	
	128,910	2	
	185,070	3	
	165,780	4	
4/25/84	119,970	1	
	189,280	2	
	236,570	3	
	216,730	4	
5/10/84	130,670	1	
	301,620	2	
	333,090	3	
	369,850	4	
5/15/84	152,670	1	
	343,620	2	
	369,090	3	
	417,850	4	
5/16/84	159,700	1	
	350,540	2	
	374,940	3	
	426,120	4	

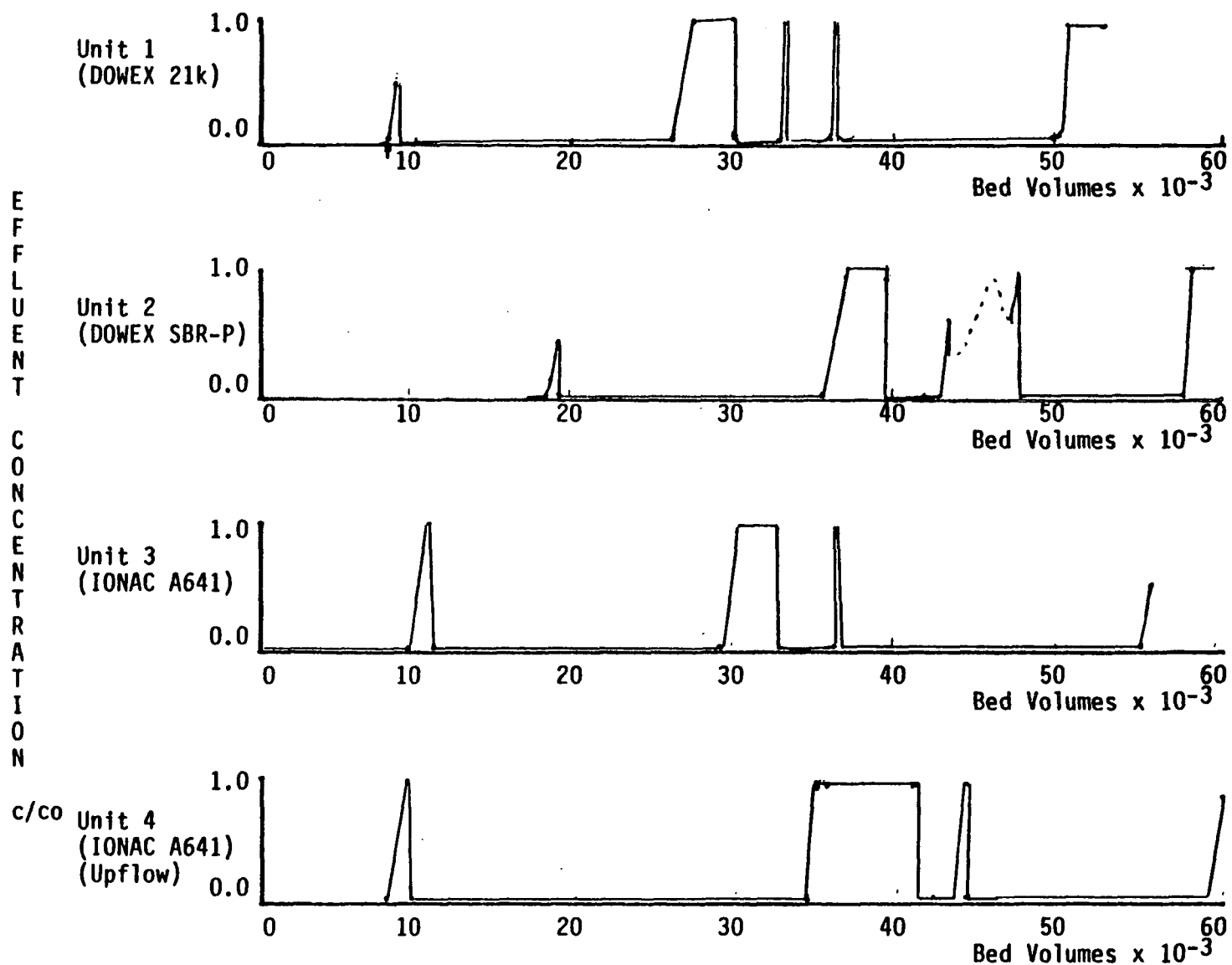


Figure 17. Summary of Operation of Ion Exchange Columns.

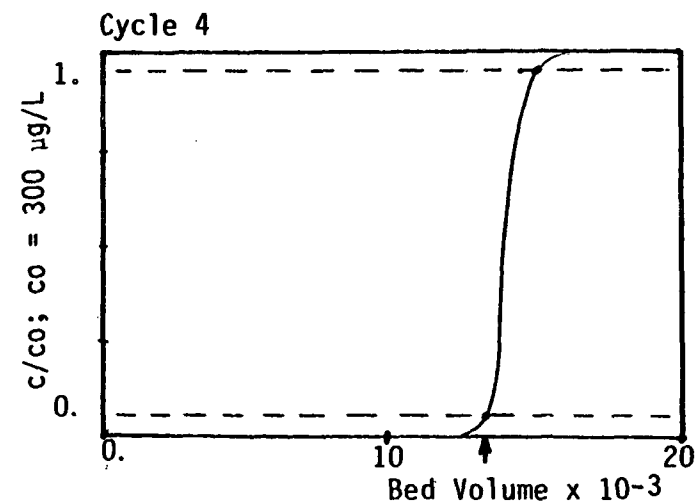
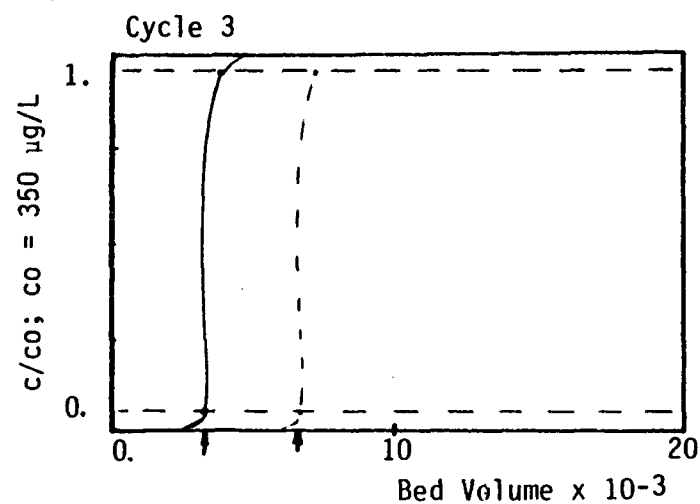
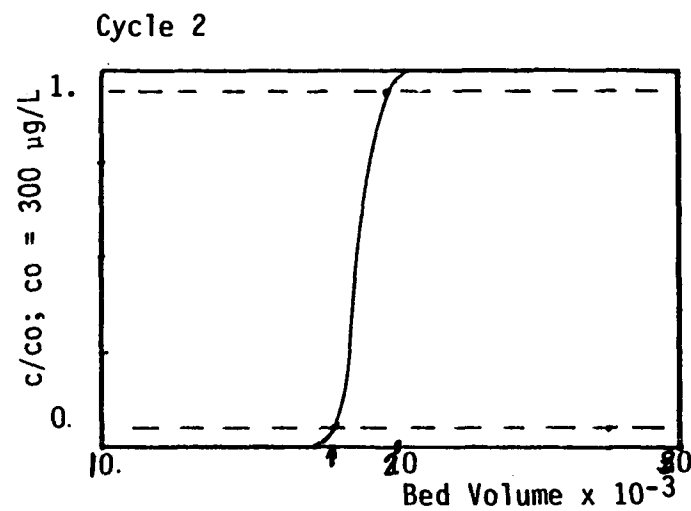
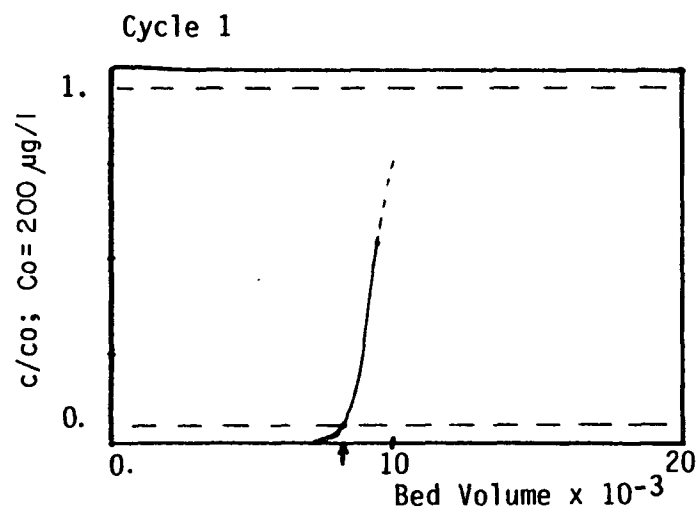


Figure 18. Breakthrough Curves-Unit 1 (DOWEX 21k).  
Bed Volumes Processed Measured for Each Cycle Separately.

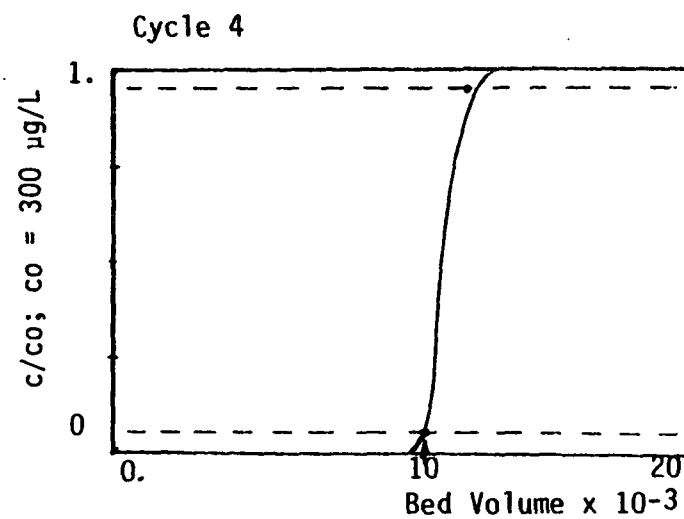
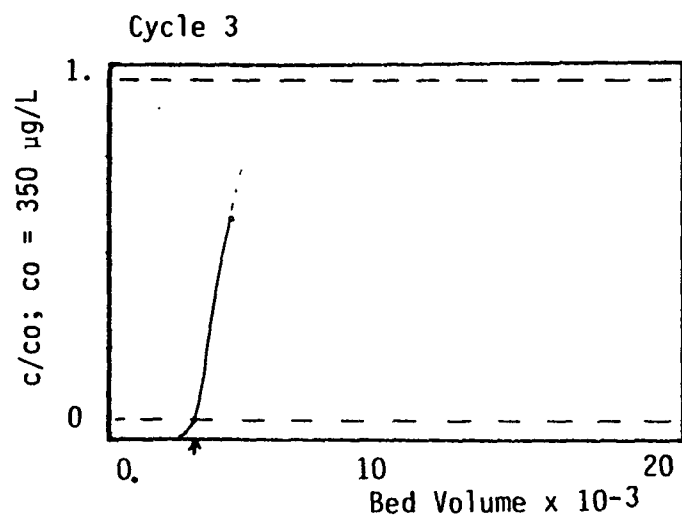
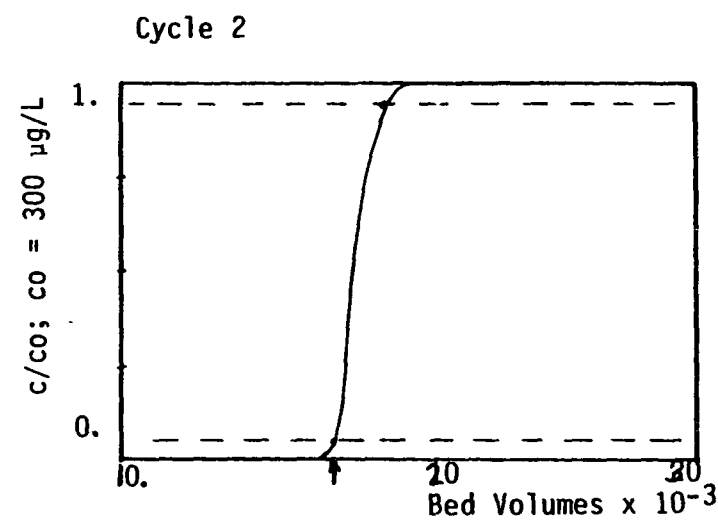
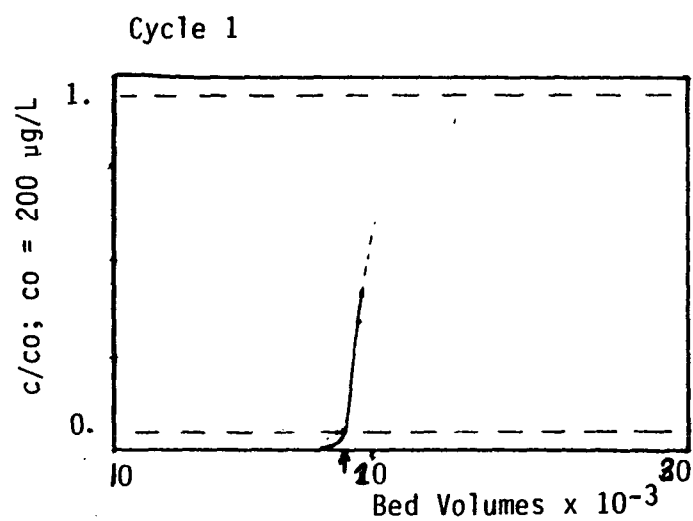


Figure 19. Breakthrough Curves-Unit 2 (DOWEX SBR-P).  
Bed Volumes Processed Measured for Each Cycle Separately.

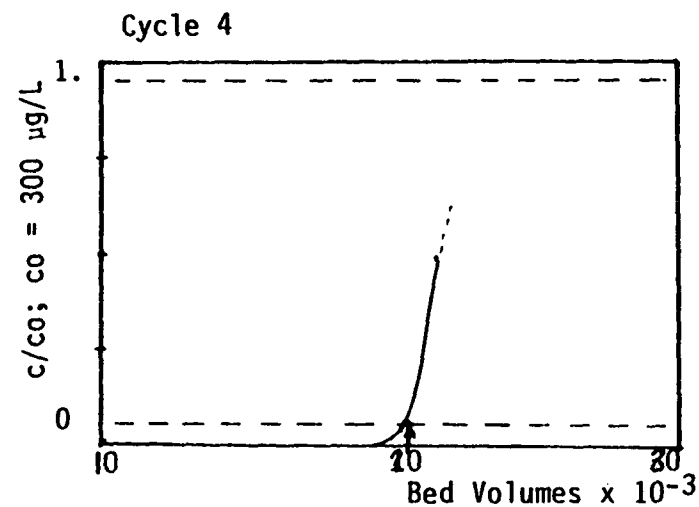
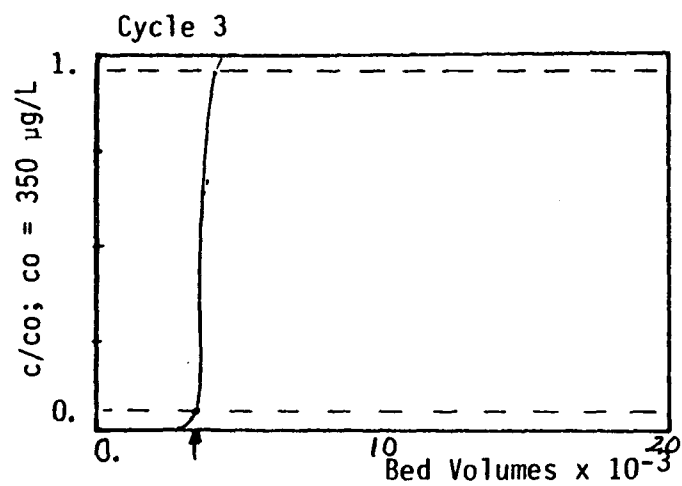
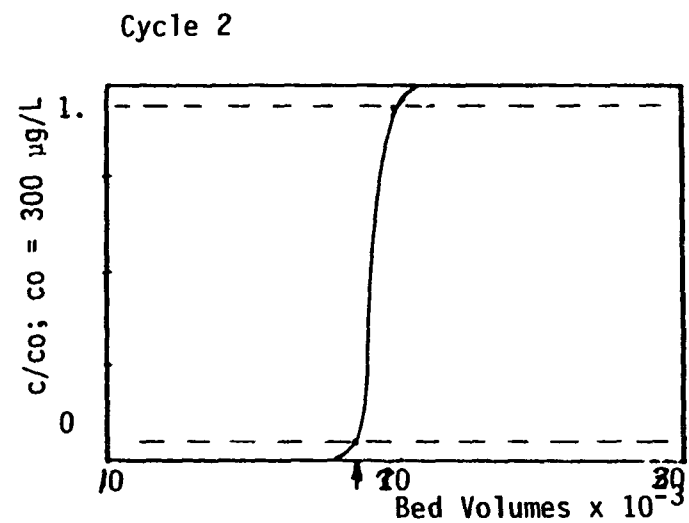
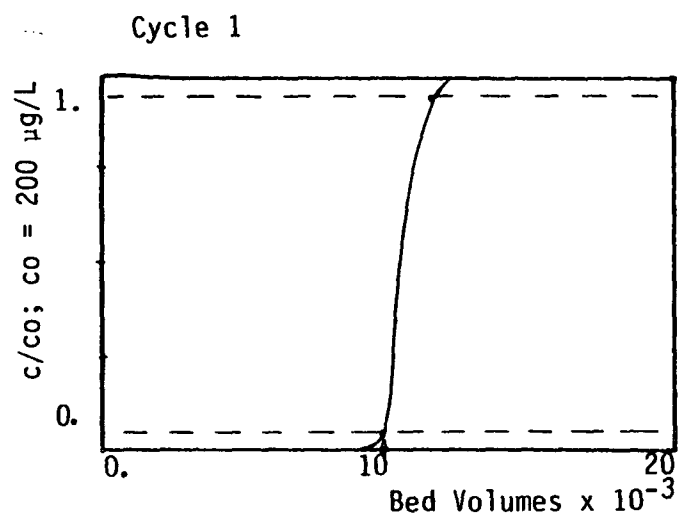


Figure 20. Breakthrough Curves - Unit 3 (IONAC A641-Downflow).  
Bed Volumes Processed Measured for Each Cycle Separately.

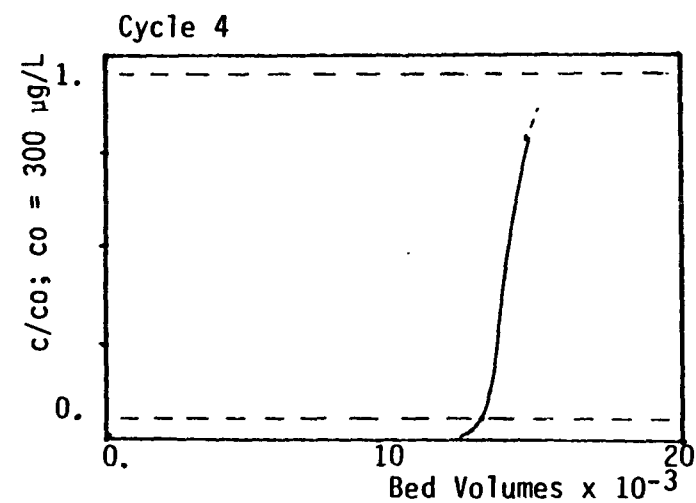
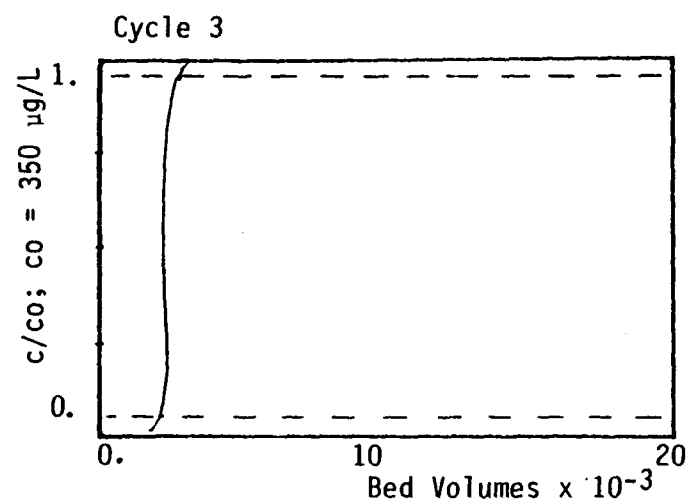
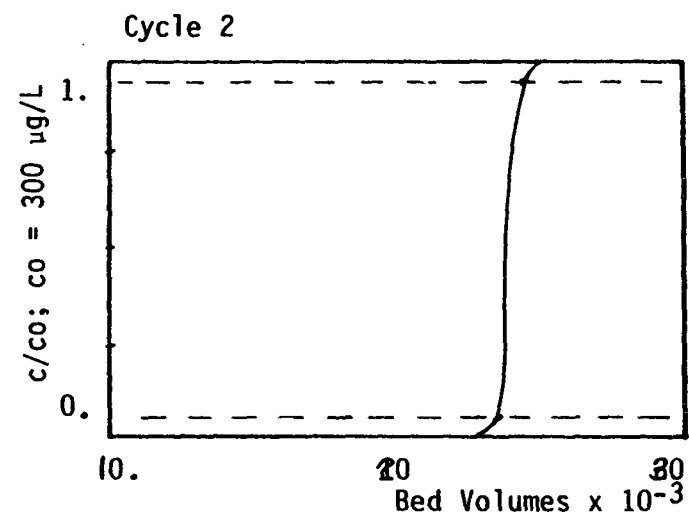
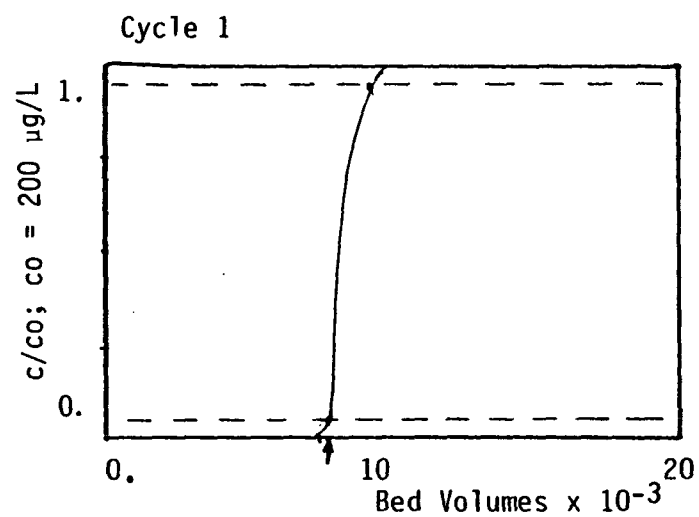


Figure 21. Breakthrough Curves - Unit 4 (IONAC A641-Upflow).  
Bed Volumes Processed Measured for Each Cycle Separately.

Table 11. Resin Capacity for Each Unit Per Cycle

	$C_0$ , $\mu\text{g/l}$	$V_T$ Gallons*	$\frac{\text{meg}}{\text{ml}}$	Bed-Volumes Treated at Breakthrough
Unit 1				
Cycle 1	200	$12 \times 10^4$	0.013	8020
Cycle 2	300	$26 \times 10^4$	0.044	17375
Cycle 4	300	$20 \times 10^4$	0.034	13365
		Average	0.030	12920
Unit 2				
Cycle 1	200	$28 \times 10^4$	0.031	18712
Cycle 2	300	$24 \times 10^4$	0.040	16038
Cycle 4	300	$15 \times 10^4$	0.025	10024
		Average	0.032	14925
Unit 3				
Cycle 1	200	$15 \times 10^4$	0.017	10024
Cycle 2	300	$27 \times 10^4$	0.046	18043
Cycle 4	300	$30 \times 10^4$	0.051	20048
		Average	0.038	16038
Unit 4				
Cycle 1	200	$13 \times 10^4$	0.015	8687
Cycle 2	300	$36 \times 10^4$	0.061	24057
Cycle 4	300	$20 \times 10^4$	0.034	13365
		Average	0.037	15370

\*The volume  $V_T$  is the differential volume processed during the cycle.

While industrial ion exchange columns have been used in an up-flow mode for recovering uranium from mine and mill waters, very few drinking water treating operations have used up-flow in their operation. As seen in Table 10 the up-flow unit, #4, processed a greater volume of water during several cycles than the down-flow units although the operation procedure was to try and balance the load on all units.

To better understand the operation of the up-flow mode, a small bench-scale unit pilot-scale units were constructed and operated on a side stream from the project feed. Table 12 summarizes these experiments. The resin was IONAC A-641, the same as used in the large column. As seen in Table 12, the beds were operated in an expanded mode, e.g. bed porosity  $f_c^0$ , but not in a complete fluidized state (as seen by visual inspection). These runs were operated until at least 50 percent of breakthrough had been achieved and the data analyzed for conventional mass transfer/adsorption parameters. The complete analysis is available in Reference 20. These analyses confirmed that

the Exchange Zone method (Figure 4) gives satisfactory analysis for up-flow ion exchange.

TABLE 12. UP-FLOW COLUMN EXPERIMENT

Run	A	B	C	D
Resin Mesh Size	16-50	16-50	16-50	16-50
Resin Weights, g	29.11	58.4	45.2	1965.
Height of Packed Bed (cm)	2.12	4.32	3.02	10.12
Bed Diameter	5.08	5.08	5.08	19.05
Height of Expanded bed (cm)	4.02	8.02	6.32	22.2
$C_0$ ( $\mu\text{g/ml}$ )	422.	443.	444.	336.
$V$ ( $\text{cm}^3/\text{min}$ )	80.	86.	90.	3785.
$U_0$ (cm/sec)	0.0658	0.0707	0.0740	0.2213
$f_E$ , dimensionless	0.63	0.62	0.67	0.68

## B. Chemical Coagulation

### Effect of pH on Coagulation/Flotation Process

Different percentages of uranium removal were obtained with different pH of solutions in chemical treatment for the samples which have the same dosage of the ferric chloride solution. The results in Table 13 and Figure 22 show the difference observed when pH of solutions were adjusted from 4 to 10 using 0.1 N NaOH and HCl solutions with 30 mg/L  $\text{FeCl}_3$ .

The results in Table 13 show that among these five pH solutions the highest uranium removal efficiency by ferric chloride was found at pH 10 about 98 percent removal was obtained. The same dosage of coagulant was less effective at pH 6 (31 percent of uranium was removed). However, at pH 6 the removal was much higher than at pH 4 and 8. Only 31 percent and 18 percent removals were obtained in pH 4 and pH 8, respectively, with the same dosage of ferric chloride. No data are shown for similar experiments examining the pH dependencies for other dosage of ferric chloride.



TABLE 13. SUMMARY OF THE RESULTS FOR URANIUM  
REMOVAL USING 30 mg/L OF FERRIC  
CHLORIDE SOLUTION AT DIFFERENT pH  
OF WATER SAMPLES.

Adjusted pH	Uranium Remaining in the Tested Water ( $\mu\text{g/L}$ )	Percent of Uranium Removed
4.0	309	31.3
4.9	251	44.2
5.3	180	60.0
5.8	86	80.9
8.2	369	18.0
9.4	6	98.7
10.0	<2	99.0

#### The Effect of Variation of Ferric Chloride Concentration

In order to study the effects of variations in the different dosages of ferric chloride solution, the best conditions of pH dependencies test have been chosen i.e., the solution which had pH 6 and 10.

The results shown in Table 14 indicate that the uranium removal percentage increased with increased dosage in the 30 to 90 mg/L range on the effect of the ferric chloride as a coagulant at the pH 6. The results show the uranium removal efficiency in this range was about 81 percent to 87 percent.

The same experiments also have been done at pH 10 with varying amount of ferric chloride concentration. The results show that greater than 99 percent of the uranium was removed at a ferric chloride dosage of 30 mg/L and above (Table 14).

Experimental data for the effect of dosage of the ferric chloride and the equilibration pH of the solution, show that pH is a major controlling factor in the removal of uranium from drinking water via the coagulation/filtration process. Proper choice of pH is a requirement for effective

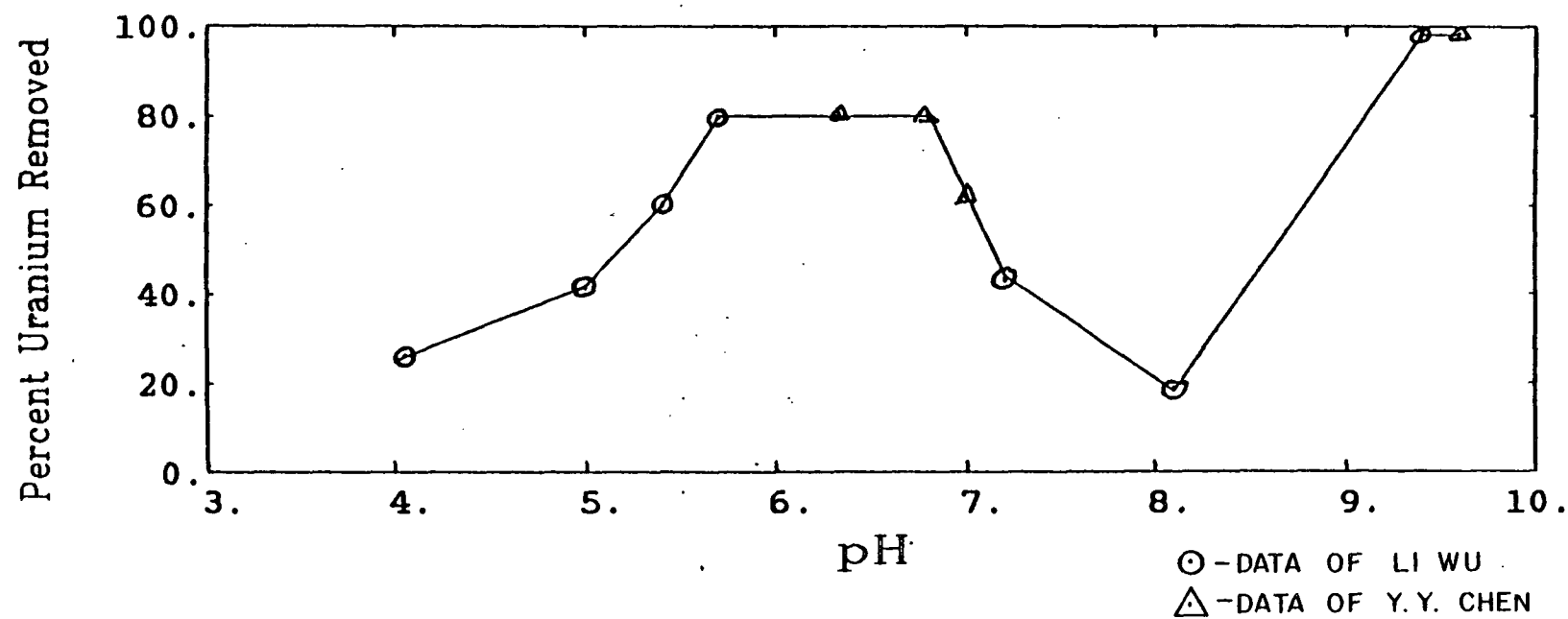


Figure 22. Chemical Clarification Operation

TABLE 14. THE EFFECT OF FERRIC CHLORIDE CONCENTRATION ON URANIUM REMOVAL EFFICIENCY IN A SOLUTION OF pH 6 and pH 10.

FeCl <sub>3</sub> Dosage (mg/L)		Uranium Remaining in the Tested Water (µg/L)	Percent of Uranium Removed
At Ph 6	30	86	80.9
	60	60	86.6
	90	59	86.9
At Ph 10	30	<2	>99.0
	60	<0	100.0
	90	<0	100.0

chemical coagulant treatment. The results of the pH dependence for uranium removal with iron salt can be interpreted by the stability and charge characteristics of uranyl species and metal hydroxide precipitates at the adjusted pH of the solution. No data are shown for similar experiments examining the pH dependencies for other dosages of ferric chloride. However, the similar results can be expected from the physicochemical properties of the metal hydroxide formed during the coagulation process at a given pH and the dominant uranyl species in the solution. The role of ferric hydroxide as a coagulant formed from ferric chloride in aqueous solution as well known. The stability, solubility and reactivity (adsorption) of the hydroxides are pH dependent. The pH dependence of the distribution of uranyl species in natural water is also known. Dominant uranyl species and charge characteristics of iron hydroxide floc at pH 4, 6, 8 and 10 are shown in Figure 23. At a low pH, say, pH < 5, ferric hydroxide has a positive charge,  $\text{Fe}(\text{OH})_3^{w+}$ , and the uranyl carbonate complex also dissociates to a positively charged uranyl ion ( $\text{UO}_2^{+}$ ,  $\text{UO}_2\text{OH}^{+}$ ). Therefore, at pH 4, less adsorption can occur due to the strong repulsion between ferric hydroxide and uranyl ion. As the pH was increased to 6, the dominant uranyl complex would be  $\text{UO}_2\text{CO}_3^0$  with a small positive charge of uranyl ions, and the mixed charge of negative and neutral hydrolyzed ferric iron would be negative. The possible reason is that at least there is no repulsion between the two charge particles,  $\text{UO}_2\text{CO}_3^0$  and  $\text{Fe}(\text{OH})_4^-$ . At pH 8, the same phenomenon was observed as at pH 4 except both interacting species would have negative charges. Therefore, a lower removal efficiency was obtained in both conditions (pH 4 and 8). When the pH exceeds 9.5, the  $\text{UO}_2(\text{CO}_3)_4^{4-}$  species are known to be stable, but  $(\text{UO}_2)_3(\text{OH})_5^{+}$  would be the dominant species in carbonate-depleted water. The carbonate in water

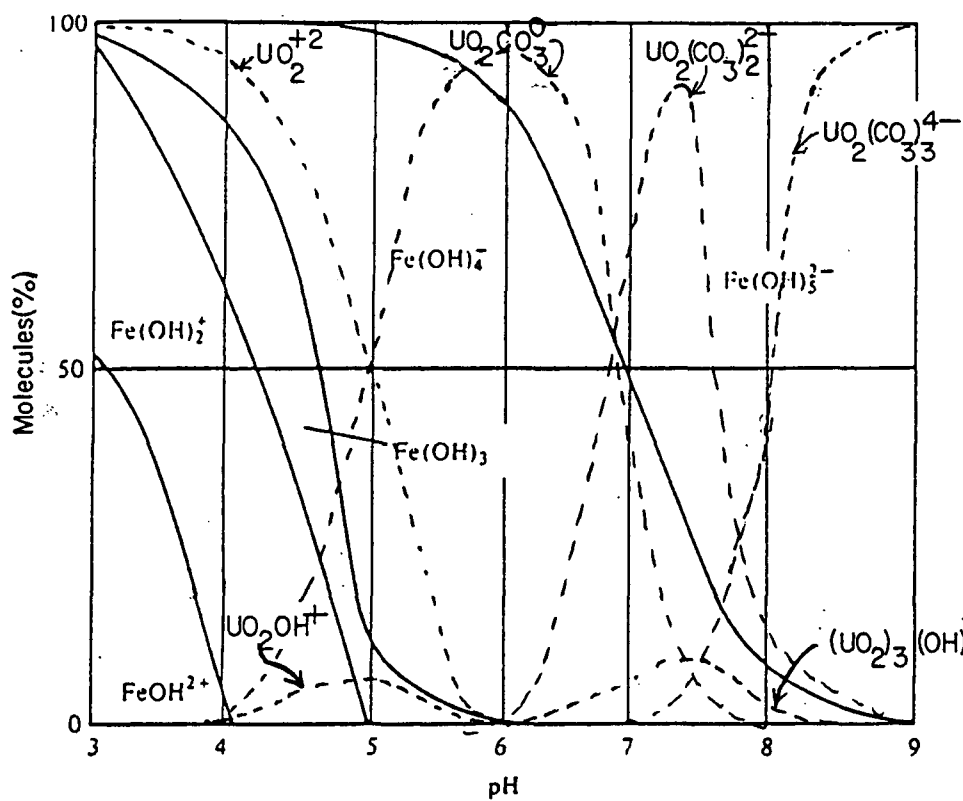
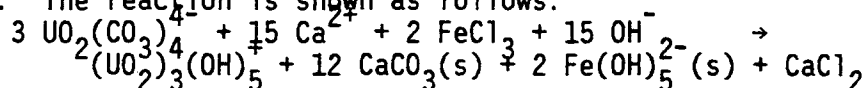


Figure 23. Combined Distribution of Species in Chemical Clarification System

could be depleted by  $\text{CaCO}_3$  precipitation during the coagulant treatment process. The reaction is shown as follows:



Since the charge of the ferric hydroxide is pH-dependent, it should adsorb on its active surface sites the stable uranyl complex through electrostatic attraction. Therefore, minimum uranium removal was observed when the charge of the uranyl species was the same as the charge of the flocs, and maximum removal occurred when the charges were opposite or neutral.

The experiments in this work examining the effects of pH of the solutions and variation of coagulant concentration in the coagulation/filtration continuous process with ferric chloride were similar to previous investigations using ferric sulfate and aluminum sulfate as coagulants in batch tests. The optimum dosage is related to the type of coagulant and the amount of uranium contained in the water. However, for the optimum effectiveness of uranium removal with different iron salts (ferric sulfate and ferric chloride), the results are essentially the same.

### C. Monitoring Program

A detailed search was conducted to locate currently operating conventional water treatment facilities with uranium in their feed supplies. For this search a minimum level of 15  $\mu\text{g/L}$  of uranium was arbitrarily selected and conventional water treatment facilities were defined as any type of treatment facility more "complex" than sand separation and chlorination.

The wide variety of state and U.S. government agencies responsible for the radiological monitoring of water supplies made the search very time consuming. A total of 34 municipal systems and an additional 21 municipal wells were located in a 6 state area (Table 15). Of these 55 possible study sites, only 4 provide treatment above and beyond sand separation and chlorination.

Three of these cities are located in Colorado (Denver, Arvada, and North Table Mountain) and they all draw their water from the uranium contaminated Ralston Reservoir. The fourth city is a small city in South Dakota (Harrisburg). These communities were contacted and with the exception of North Table Mountain they agreed to help us with this study.

The City of Arvada treats their water using a microfloc system. The system employs alum and Separan (a polyelectrolyte) to create the microfloc. The water is then passed through mixed media filters. A 125 cc water sample is collected daily from the raw water and the treated water to form monthly composite samples. For the past couple of years, these monthly samples have been tested for uranium. The raw water from Ralston Reservoir contains from less than 1  $\mu\text{g/L}$  to 36  $\mu\text{g/L}$  with an average of  $14.7 \pm 9.6$  (SD)  $\mu\text{g/L}$  of uranium. The Arvada facility removed from 18 to 90 percent of this incoming uranium with a mean efficiency of  $67 \pm 15$  percent. The meticulous nature of these records and the time span of the monitoring clearly indicates that conven-

TABLE 15. STATE SURVEY FOR URANIUM ENRICHED WATERS

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Colorado, Water Quality Control Division of Colorado Dept. of Health, 3 community composites, 1-24 pCi/L, conventional alum systems.
New Mexico, Water Supply Section of New Mexico Environmental Improvement Division, 2 community composites and 15 municipal water sources, 10 - 110 pCi/L, sand filters and chlorination.
Oklahoma, Association of Central Oklahoma Governments, 22 communities (about 200 wells) near Oklahoma City, 10-190 pCi/L, sand removal and chlorination.
South Dakota, S.D. Dept. of Water and Natural Resources, 1 community, 12 pCi/L, iron and manganese removal, chlorination.
Texas, Texas Water Hygiene Division, 5 community composites and 6 individual water sources, 10-55 pCi/L, sand removal and chlorination.
Wyoming, EPA Drinking Water Branch, Denver, 1 community (Cheyenne), 29 pCi/L, this well water is chlorinated, they also use surface water which is treated with conventional alum.
NOTE: This survey is representative of existing state and federal records and may not be complete.

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tional water treatment facilities can greatly reduce the uranium content of natural waters.

The Moffat Treatment Facility (Denver) also draws water from Ralston Reservoir and has been keeping uranium records for about two years. Unfortunately, Denver's monthly samples are "grab samples" and correlation between raw and treated waters are less meaningful. Using their records, uranium removal efficiency was  $78 \pm 190$  percent.

Harrisburg, S. D. treats about 100,000 gpd using aeration,  $\text{KMnO}_4$  green-sand filters, chlorination and fluoridation. No previous data exists on the uranium removal efficiency of this facility.

Harrisburg, South Dakota, is a town of about 500 people located near Sioux Falls. Because the Harrisburg water supply contains some 3 parts per million (ppm) of iron and quite a bit of manganese, a small water treatment facility was constructed in 1970. In late 1980, the Water Quality Division of the S.D. Department of Water and Natural Resources determined that the Harrisburg water also contained about 20  $\mu\text{g/L}$  uranium.

Harrisburg appeared to meet the two criteria of our study; an elevated concentration of uranium in the raw water and a water treatment facility more involved than sand separation and chlorination. To determine if the Harrisburg system still contained uranium, we requested Ross Abbott of Harrisburg to ship us a raw and a treated water sample. We had these samples

tested fluorometrically in June of 1983. Both samples contained about 19 µg/L of uranium.

A visit to Harrisburg was conducted in July of 1983. In brief, the water treatment process consists of permanganate, counter-flow aerator-degassifier, chlorine, dual green sand filters (66 inches in diameter and 24 inches deep) and fluoridation. This facility treats 0.07 and 0.1 millions gallons per day. A sample of the raw, treated and backwash water was collected.

A standard fluorometric test was run on the raw and treated water samples. Because of the tremendous iron concentration in the backwash sample an isotopic uranium analysis was run on this sample. The isotopic tests includes a U-232 spike, ion exchange column, electrodeposition on a planchet, alpha spectrometer and a multichannel pulse height analyzer.

The test results show that the water contained about 13 µg/L of uranium before treatment and about 15 µg/L after treatment. The increased uranium in the treated water is attributed to the fickle and statistical nature of the fluorometric test. The backwash sample contained  $9.6 \pm 1.1$  picocuries per liter of alpha activity. This radiation is the sum from U-234, U-235 and U-238. The backwash water contains about 15 µg/L of uranium (assuming 1 pCi/L equals 1.5 µg/l). Therefore, the backwash water from the green sand filters contains the same concentration of uranium as the raw water. Since the backwash water is the only possible outlet for the uranium in the water, we can conclude that a permanganate/aeration/green sand filter system does not remove uranium from drinking water. These results are shown in Table 16.

TABLE 16. RESULTS OF HARRISBURG, S.D., OPERATION ANALYSIS

Sample	Date Collected	Type of Analysis*	µ/l
Feed	6/83	Total Uranium	19
Product	6/83	Total Uranium	19
Feed	7/83	Total Uranium	13
Product	7/83	Total Uranium	15
Backwash	7/83	Total Uranium	$9.6 \pm 1.1^{\neq}$

<sup>≠</sup>Backwash was accomplished with product water; measurement pCi/L

The results of these tests are commensurate with theoretical considerations. Dissolved iron in water is in the ferrous state,  $\text{Fe}^{+2}$  (a cation). This iron is removed by aeration which changes the ferrous iron to ferric iron,  $\text{Fe}^{+3}$ . The ferric iron combines with hydroxide to form a filterable solid,  $\text{Fe}(\text{OH})_3$ . In waters of a neutral pH, the uranium exists as uranyl carbonate complex ions (anions),  $\text{UO}_2(\text{CO}_3)_2^{-2}$  and  $\text{UO}_2(\text{CO}_3)_3^{-4}$ . In an oxidizing environment, uranium always changes to the very soluble hexavalent state. In fact, if an insoluble uranium precipitate,  $\text{UO}_2$ , were introduced into the aerator it would quickly dissolve into the water as uranyl carbonate complex ions.

In summary, a permanganate/aeration/green sand filter system does not remove any uranium under normal operating conditions. This conclusion is born-out by both theoretical considerations and as the result of a testing program of an operating greensand filter system in South Dakota.

#### D. Waste Disposal

As previously described, uranium contaminated drinking water is a common problem, particularly in the western United States. If regulations are accepted and enforced, many communities will be required to remove the uranium from their drinking water supplies. Removal of this radioactive element produces a new problem--that is, a problem of radioactive waste disposal. The physical form of this waste and the longevity of uranium cause difficulties in formulating a waste disposal plan. Three disposal alternatives were considered in this study. These include: dilution/release, reuse or resale, and burial; however, the choice must also be based on environmental acceptability. Each participating community will have unique drinking water and waste characteristics. For this reason, it is not possible to prescribe one solution to the problem. Each community must consider their situation and choose the optimum plan on that basis. Two cases are analyzed: (1) 150,000 gallons per day with 30  $\mu\text{g/L}$  uranium, and (2) 150,000 gallons per day with 200  $\mu\text{g/L}$  uranium. Table 17 summarizes the quantity of uranium to be disposed.

TABLE 17. Ultimate Disposal Values for Uranium

System Capacity: 150,000 gallons/day	
Case 1: Concentration 30 $\mu\text{g/L}$	Total Uranium = 1.79 g/day
(a) Ion Exchange Treatment - Regeneration Solution	1500 gallons @0.3 mg/L
(b) Chemical Clarification - Filter Cake	17.03 kg Cake
Case 2: Concentration 200 $\mu\text{g/L}$	Total Uranium = 11.35 g/day
(a) Ion Exchange Treatment - Regeneration Solution	1500 gallons @2.0 mg/L
(b) Chemical Clarification - Filter Cake	17.03 kg Cake



## Dilution and Release

The first alternative considered is to dilute, if necessary, and return the uranium to surface waters. In New Mexico, the New Mexico Water Quality Control Commission regulates such releases. They have established a maximum allowed concentration of uranium of 5 mg/L to be returned to surface waters. In case 1 (Table 15) the ion exchange regeneration solution could be discharged directly to the surface, i.e. 0.3 mg uranium/L concentration. In Case 2, the average regeneration solution could be discharged directly to surface waters, i.e. 2.0 mg uranium/L. Note that this is the average concentration of the regeneration solution. During operation of the ion exchange system, samples of regeneration solution were obtained which exceed 25 mg/L uranium. These samples were taken shortly after starting regeneration and were highly concentrated in uranium.

If the treatment is chemical clarification, the waste product is a filter cake. For Case 1, this cake would contain 0.057 nanocuries uranium per gram and in Case 2 the cake would contain 0.38 nanocuries per gram. (These calculations are based on 0.67 picocuries = 1  $\mu$ g uranium). In both cases these quantities are well below the 100 nano curie per gram definition of low-level waste. (In analyzing the currently operating systems in Section C, the practice was to send the flocculated sludge to sludge beds).

## Reuse and Resale

A second alternative would be to ship liquid waste to a uranium mill, where it could be processed along with the incoming ores. It could be possible to co-dispose sludge waste with the uranium mill tailings. Reuse or sale of the waste would involve several steps. It would involve collection, intermediate storage, shipment and possible packaging of the waste.

Collection does not pose any major problem and should be a relatively inexpensive part of this process. Intermediate storage, however, presents difficulties. A storage facility is necessary to hold waste until a large enough volume is collected for a shipment. This facility would be some type of holding tank from which trucks could be filled. It would require licensing and a permit from the State Hazardous Waste Management division. This is a new situation and would require an indepth study. Since uranium is an alpha emitter, the tank construction material is not a critical factor for preventing radiation exposure under normal operation.

Assume that the regeneration solutions from ion exchange is 1500 gallons per day per 1000 people. Assume, also, that approximately 10,000 gallons of waste will constitute a shipment. The storage period would be 6.5 days. Cost involved in storage will be the initial cost of construction of the tank and any maintenance required thereafter. A current rule of thumb for estimating construction costs of steel tanks is about twenty-five cents per gallon of volume. For a 10,000 gallon holding tank, the construction cost would be about \$2,500.

The next stage of this alternative is shipment. Two mills are currently operating in the U.S., both of which are located in northern New Mexico. Shipping distances would thus be fairly short and feasible for most of New Mexico, Colorado, and Arizona. As distances to the mills increase, however, costs and disadvantages of this plan also increase. The risk associated with accidents during shipping and storing the waste must be considered. Licensing by the State Hazardous Waste Management Division would be reported for shipment on public roads and highways. The following shipping cost estimates are based on the 1983 Book Rental Rates for a 5000 gallon diesel powered truck. The hourly cost for shipment by this means is about \$10.25. This does not include pay for the driver. Actual cost per mile would be about \$1.75 per loaded mile. Obviously this becomes very expensive over any large distance.

### Disposal Through Burial

The third choice available for either liquid or a sludge waste is storage or burial. Burial of the waste at a commercial facility would involve several processes similar to those involved in shipment of the waste to mills. In addition to collection, intermediate storage, and shipment, a solidification and/or volume reduction process would have to be included before shipment could take place.

Collection again would be a relatively simple process. Intermediate storage will be necessary as volumes are accumulated. This also would require the type of structure discussed for use in shipment of the waste to uranium mills. Either solidification or volume reduction is necessary prior to shipment. A solidification process could be implemented for either a liquid or sludge waste. Solidification can be achieved by several methods. In-drum solidification is one process currently being used by the Department of Energy. The waste (either liquid or sludge) is put into drums. Portland cement is added, the drums are sealed and then tumbled for mixing. Vermiculite is also used for solidification of sludge or liquid waste. Waste is added to vermiculite filled drums. The vermiculite will expand and incorporate the waste in its matrix. A method which will solidify sludge waste as well as reduce its volume, is vacuum filtration. Sludge cakes will result from the vacuum filtration system. The filter cake containing 5-8 percent moisture could be further dried or package with a cement binder as above.

It is difficult to predict costs for these processes because of their recent development and difficulties in predicting sludge volumes. Cost of shipment of solid waste would be comparable to that of shipping the liquid waste. The solid form presents a much smaller shipping risk as compared to the liquid waste, thus licensing would be easier to obtain.

In using ion exchange, the uranium is removed through the regeneration solution. Evaporation to dryness would give a greatly reduced volume of solid, i.e. 1.7 g/day Case 1 and 11.35 g/day Case 2, but would be impractical from an energy standpoint. The alternative is to follow the ion exchange process with chemical clarification. Since the volume to be treated is the regeneration solution, the scale of the chemical clarification unit will be

greatly reduced from that of the ion exchange system. Although it was not tested by this project, the quantity of filter cake would be comparable to that previously discussed.

#### E. Design Analysis

The main purpose of this section is to present cost analysis for the application of ion exchange/chemical clarification for removal of uranium from drinking water supplies. Complete cost estimation has been covered by a recent EPA publication "Estimation of Small System Water Treatment Costs." [19] This publication treats ion exchange both for centralized treatment systems and for point-of-use treatment systems. There are currently other projects examining ion exchange point-of-use treatment for removing uranium and this is not included in this section. It should be noted that the exceptional capacity for uranium of standard ion exchange resins makes point-of-use applications feasible on a one-cycle charging of resin, then collection by a service company for regeneration as is practiced in any point-of-use water-softening applications.

#### Ion Exchange

An ion-exchange system usually consists of the exchange resin (cation or anion), with provisions made for regeneration and rinsing. Prior to application to the ion-exchange bed, wastewater may be subjected to pretreatment to remove certain contaminants which may hinder the performance of the exchange bed.

#### Input Data

- (1) Wastewater Flow.
  - (a) Average flow, mgd.
  - (b) Minimum and maximum flows, mgd.
- (2) Cation and anion concentrations, mg/l.
- (3) Allowable effluent concentrations, mg/l.

#### Design Parameters

- (1) Type of resin.
- (2) Resin exchange capacity, lb/ft<sup>3</sup> (manufacturer's specifications).
- (3) Regenerant dosage, lb/ft<sup>3</sup> (consult resin manufacturer's specifications).
- (4) Flow rates.
  - (a) Treatment flow rate (2-5 gpm/ft<sup>3</sup>).
  - (b) Regenerant flow rate (1-2 gpm/ft<sup>3</sup>).
  - (c) Rinsing flow rate (0.5-1.5 gpm/ft<sup>3</sup>).
- (5) Amount of rinse water (30-120 gal/ft<sup>3</sup>).
- (6) Column depth (24-30 in. minimum).
- (7) Operation per day, hr.
- (8) Amount of backwash water, gal/ft<sup>3</sup>.
- (9) Regenerant level, lb/ft<sup>3</sup>.

- (10) Regenerant concentration, percent.
- (11) Regenerant specific gravity.
- (12) Backwash water rate, gpm/ft<sup>3</sup>.

One case study has been summarized in Table 18. Capital equipment cost is given in Figure 24.

#### Chemical Clarification

The chemical clarification system consisted of a flotation cell for ferric hydroxide colloids precipitation and adsorption of the uranyl ion complex and a vacuum filter for solid-liquid separation. The flotation design and filter design are outlined as follows:

Capital equipment for the two systems of this study are shown in Figures 25 and 26.

#### Input Data

- (1) Wastewater flow, mg.
- (2) Solute solids concentration in the feed, mg/l.
  - (a) Average concentration.
  - (b) Variation in concentration.

Design Parameters. From laboratory or pilot plant studies.

- (1) Air-to-solid ratio (A/S).
- (2) Air pressure (P), psig.
- (3) Detention time in flotation tank (DTFT), hr.
- (4) Solids loading (ML, lb/ft<sup>2</sup>/day).
- (5) Hydraulic loading (HL), gpm/ft<sup>2</sup>.
- (6) Detention time in pressure tank (DTPT), min.
- (7) Float concentration (C<sub>F</sub>), percent.

#### Filtration

##### Input Data

- (1) Volume of slurry to be dewatered, gpd.
- (2) Initial moisture content of slurry, percent

##### Design Parameters

- (1) Final moisture content of slurry, percent.
- (2) Specific resistance, sec<sup>2</sup>/gm (Buchner funnel test).
- (3) Applied vacuum, psi.
- (4) Fraction of cycle time for cake formation (formation time/cycle time), depends on degree of submergence.
- (5) Cycle time, min (usually 1.5 to 5 min).
- (6) Filtrate viscosity, centipoises.
- (7) Chemical dose, percent of dry weight in solids fed to filter.
- (8) Operation per week, days.
- (9) Operation per day, hr.

TABLE 18. ION EXCHANGE SYSTEM DESIGN

---

Based on Avg. Influent Conc. of:

84 µg/L as  $(\text{UO}_2)_2(\text{CO}_3)_2^{2-} \cong 50 \text{ µg/L as uranium}$

Using Avg. Capacity of 3.3 KGR./Ft<sup>3</sup> Grains as  $\text{UO}_2(\text{CO}_3)_2^{2-}$

$$600 \frac{\text{gal}}{\text{min}} \times .084 \text{ ppm} \times 0.0547 \frac{\text{grain/gal}}{\text{ppm}} \times 24 \text{ hrs} \times 60 \frac{\text{min}}{\text{hr}} = 3960 \text{ grains}$$

3960 grains feed. (1 day basis)

Resin Needed for 1 Days Operation:

$$\frac{3.96 \text{ KGR}}{3.3 \text{ KGr/Ft}^3} = 1.20 \text{ Ft}^3$$

Size of Tank:

Assume 10 GPM/Ft<sup>3</sup>

$$\frac{600 \text{ GPM}}{10 \text{ GPM/Ft}^2} = 60 \text{ Ft}^2$$

Use 9' diam. Tank = 63.6 Ft<sup>2</sup>

Use 3' Bed Depth

$$\text{Resin Quantity} = 63.6' \times 3' = 191' \text{ Ft}^3$$

Using 100% Freeboard for B/W and/or expansion

60" side shell tank

Tank Size:

9'  $\phi$  x 5' SS.

Approximate Running Time Between Regenerations:

$$\frac{191 \text{ Ft}^3}{1.20 \text{ Ft}^3/\text{day}} = 160 \text{ days}$$

Salt Needed/Regeneration

$$15\#/\text{Ft}^3 \times 191 \text{ Ft}^3 = 2,865\#$$

Estimated Capital Equipment Cost (Figure 24) \$125,000.

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(10) Loading rate, lb/ft<sup>2</sup>/hr.

(11) Number of units.

One case study for chemical clarification is summarized in Table 19.

The cost of curves for the three unit operations considered were updated in 1985 costs using the CE plant, cost index data published in Chemical

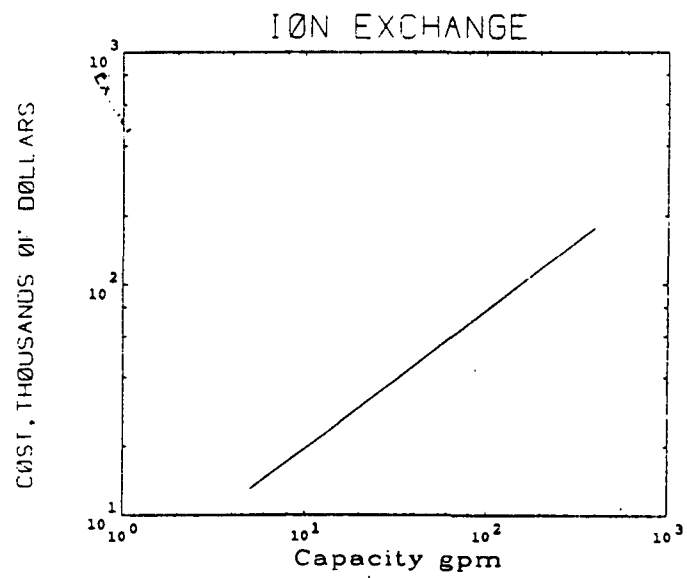


Figure 24. Cost of Ion Exchange (1985)

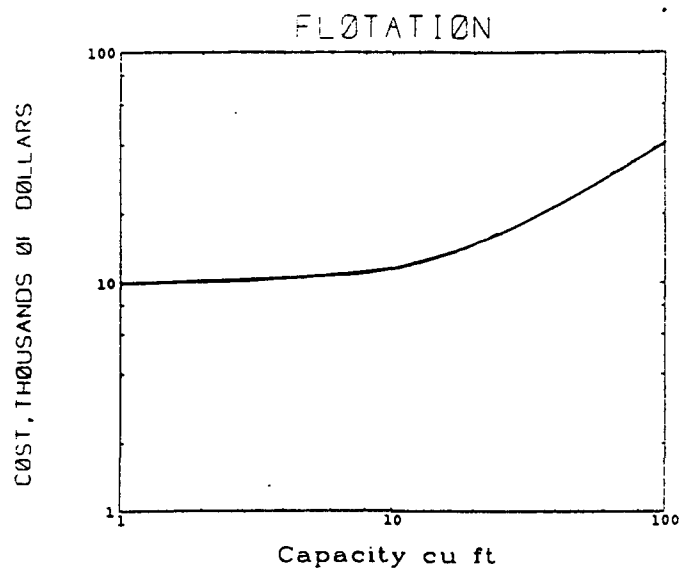


Figure 25. Cost of Flotation (1985)

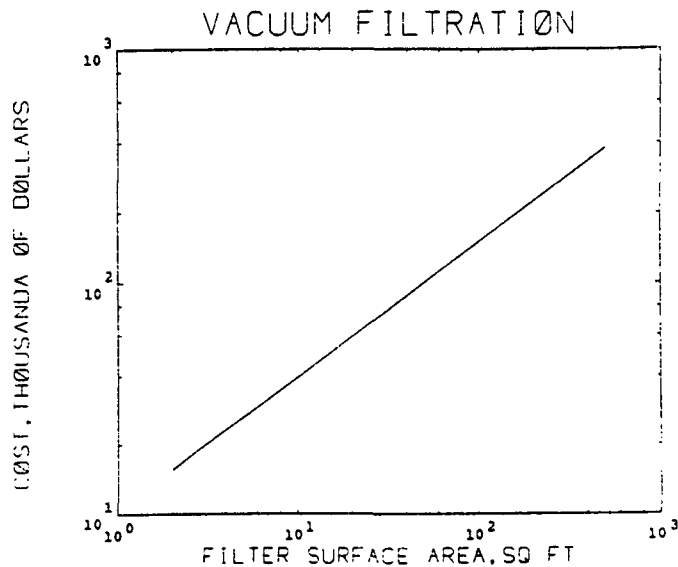


Figure 26. Cost of Filtration (1985)

TABLE 19. CHEMICAL CLARIFICATION SYSTEM DESIGN

---

Based on Avg. Influent Conc. of: 0.5 mg/l  
 Feed Rate: 60 gpm  
 Joy Manufacturing Flotation Cell 16 cu. ft.  
 Approximately two minutes residence time  
 Ferric Chloride Addition 25 mg/l  
 35.7 lbs/day  
 pH Adjustment Assuming Feed at pH 7 → pH 10  
 2 liters Conc (37%) HCl per day  
 Continuous Rotary Vacuum (Precoat) Filter  
 6 ft<sup>2</sup> Total Surface Area  
 Filter-aid Addition 2x weight of Ferric Chloride (Diatomaceous earth)  
 70 lbs/day  
 Total Filter production per day (dry weight and wet weight 8% moisture)  
 106 lbs dry weight  
 115 lbs wet weight  
 Estimated Capital Equipment Cost (Figures 25 and 26) \$44,000

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Engineering. The index used was 375.2 (July 1985) based on 1957 - 59 as 100. These cost curves were scaled for the specific processing of uranium.

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## APPENDIX A. METHOD OF URANIUM ANALYSIS

The first method needs a blank pellet, a sample pellet, and a sample with an uranium spike pellet to analyze a sample. The detailed steps are described as below.

### Reagents

All chemicals were of analytical grade ("Baker Analyzed" Reagent, J. T. Baker Chemical Company, Phillipsburg, New Jersey). Aqueous reagents were prepared in deionized water. The following chemicals were used in the uranium analysis:

1. Flux mixture: Mix together 9 parts of sodium fluoride (NaF), 45.5 parts of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and 45.5 parts of potassium carbonate ( $\text{K}_2\text{CO}_3$ ) by weight in a ball mill until it becomes homogeneous.
2. Nitric acid (1+1): Mix one volume of nitric acid  $\text{HNO}_3$  (sp. gr. 1.42) with one volume of water.
3. Nitric acid (1+9): Mix one volume of nitric acid  $\text{HNO}_3$  (sp. gr. 1.42) with nine volumes of water.
4. Nitric acid (1+99): Mix one volume of nitric acid  $\text{HNO}_3$  (sp. gr. 1.42) with ninety nine volumes of water.
5. Potassium pyrosulfate ( $\text{K}_2\text{S}_2\text{O}_7$ ): For cleaning the platinum dishes.
6. Uranyl nitrate ( $\text{UO}_2(\text{NO}_3)_2$ ): For preparation of uranium standard stock solution.

### Uranium Standard Stock Solution

1. Prepare 1000 mg/l of uranium solution as follows:
  - a. Weight 1.0549 grams of uranyl nitrate and dissolve it in 20 ml of  $\text{HNO}_3$  (1+1) solution.
  - b. Slowly evaporate to near dryness.
  - c. Dissolve residue with 10 ml of  $\text{HNO}_3$  (1+9) solutions.
  - d. Transfer to 500-ml volumetric flask.
  - e. Dilute to 500 ml with  $\text{HNO}_3$  (1+99) solution.
  - f. Mix solution and transfer to a clean polyethylene bottle.
2. Prepare 50 mg/l of uranium solution as follows:
  - a. Pipet 25 ml of 1000 mg/l of uranium standard solution into a 500-ml volumetric flask.
  - b. Dilute to 500 ml with  $\text{HNO}_3$  (1+99).
  - c. Mix well and transfer to a clean dry polyethylene bottle.

3. Prepare more dilute uranium solution as follows:
  - a. Dilute appropriate volumes of 50 mg/l of uranium solution with  $\text{HNO}_3$  (1+99) solution.
  - b. <sup>3</sup>Consecutive tenfold dilutions of the 10 and 5 mg/l uranium standards are used for improving accuracy in preparing the more dilute standards.
  - c. Mix each standard well and transfer to a clean, dry polyethylene container.

#### Procedure of Uranium Assay

0. The procedure is for samples greater than 20  $\mu\text{g/l}$ .
1. Transfer two 100- $\mu\text{l}$  aliquots of the filtered samples to each of two platinum dishes and evaporate to dryness in a drying oven at 103 °C. Drying takes about ten minutes.
2. To one of the platinum dishes add 100  $\mu\text{g/l}$  of uranium standard solution.
3. Evaporate to dryness in a drying oven at 103 °C.
4. Weigh out  $400 \pm 4$  mg flux into each of the two platinum dishes where the flux is the mixture of 9 parts of NaF, 45.5 parts of  $\text{Na}_2\text{CO}_3$  and 45.5 parts of  $\text{K}_2\text{CO}_3$  by weight.
5. Prepare a blank flux sample by weighing out  $400 \pm 4$  mg flux into a clean platinum dish.
6. Place the three platinum dishes on a stainless steel plate and put into a preheated muffle furnace at 625 °C for 15 minutes.
7. Remove from furnace and cool in a desiccator for 30 minutes.
8. Read fluorescence in a fluorometer.

#### Cleaning the Platinum Dishes

1. Remove the disk from the platinum dish.
2. Wash the dish in hot water.
3. Fuse each dish with potassium pyrosulfate ( $\text{K}_2\text{S}_2\text{O}_7$ ).
4. Wait until it cools down.
5. Dissolve the residue in hot water.
6. Store the dishes in dilute  $\text{HNO}_3$  (1+9) solution until needed.
7. Rinse in water prior to use next time.

#### Fluorometric Determination

1. Choose the appropriate lamp and filters (excitation and emission filter) for the analysis to be performed.
2. Select the desired range and pull out the "Range Selector" knob. The numbers IX, 10X, and 30X indicate the approximate increase in sensitivity which is obtained in order to select the appropriate setting for emission energy.
3. Insert the blank disk containing a reagent blank into the "Uranium Pellet Holder Door". (which is designed to accept pellets fused from 0.5 g of flux in platinum dishes).
4. Close the door and turn on the "Power" rocker switch.

5. Momentarily depress the "Lamp Start" button and release. Confirm lamp ignition by observing the lamp indicator.
6. Allow 15 minutes for warming up.
7. Set the End Point or Kinetic Chemistry Mode switch to the appropriate position. In End Point Mode, the QA lamp indicates when to take a reading. In Kinetic Mode, the QA lamp is deactivated and readings are taken as required for the procedure being used.
8. Using the "Coard Blank Control", adjust the display to read any value from -01.0 to +01.0. Then adjust the Fine Zero Control to  $0.000 \pm 0.02$ .
9. Remove the blank sample.
10. Insert the sample into the "Uranium Pellet Holder Door".
11. Repeat steps 4 and 5 and record the output.
12. Note that the pellets should be handled with tweezers.

### Calculation

Calculate the uranium concentration in micrograms per liter as follows:

$$\text{Uranium, } \mu\text{g/l} = (((R_s - R_b)/(T_{ss} - R_s)) * a) / V \quad (3-1)$$

where

$R_s$  = Reading of the blank

$R_b$  = Reading of the blank

$R_{ss}$  = Reading of the spiked sample

$a$  = Mass of the uranium spike,  $\mu\text{g}$

$V$  = Initial sample size in liters.

### Precision

The standard deviation,  $S$ , is calculated from the equation:

$$S = ((\sum(s_i^2) - (\sum x_i)^2 / N) / (N-1))^{1/2} \quad (3-2)$$

where

$\sum(x_i^2)$  = summation of the squares of the individual results

$(\sum x_i)^2$  = square of the summation of the individual results

$N$  = number of results

The coefficient of variation,  $CV$ , is calculated from the equation:

$$CV = 100S/X \quad (3-3)$$

where

$S$  = standard deviation from the equation (3-2)

$X$  = mean value of the individual results.

### Second Method of Uranium Analysis

With the second method, the data can be graphed and the unknown concentration can be read from the graph. The second method resembles the first method except the reagents and procedure of the uranium assay is as below.

## Reagents

Reagents are the same as in the first method except the flux. The flux mixture contains 98 parts of sodium fluoride (NaF) and 2 parts of lithium fluoride (LiF) by weight.

## Procedure of Uranium Assay

1. Pipet 0.1 ml aliquots of blank reagent solution, 0.01, 0.05, 0.75 and 0.1 mg/l uranium standards into five of the platinum dishes.
2. Evaporate blank sample and standard to dryness in a drying oven at 103 °C.
3. Add one scoop of flux into each dish.
4. Put into a preheated muffle furnace of 980 °C for 15 minutes.
5. Remove from furnace and cool in a desiccator.
6. Read fluorescence in a fluorometer.
7. Plot fluorescence versus uranium concentration as a calibration curve.
8. Repeat steps 2, 3, 4 and 5 to make one blank (for setting a zero point) and sample pellets.
9. Repeat step 6.
10. Read concentration from calibration curve.