REMOVING URANIUM FROM DRINKING WATER SUPPLIES: DEMONSTRATION OF SELECTED ION EXCHANGE AND CHEMICAL CLARIFICATION

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INTRODUCTION

The Interim Primary Drinking Water Regulations for radionuclides issued in 1976 did not set a maximum contaminant level for uranium (1). New Mexico water supply regulations do not set a limit for uranium. Table 1 cites the specific regulation (2). A limit for uranium is specified in New Mexico Water Quality Control Commission Regulations (3). Table 1 includes that limit.

TABLE 1
New Mexico Uranium Standards

Water Supply Regulation 206
Maximum contaminant levels for radium-226, radium-228 and gross alpha particle radioactivity

A. Combined radium-226 and radium-228: 5pCi/l

B. Gross alpha particle activity (including radium-226 but excluding radon and uranium): 15pCi/l

Water Quality Control Commission Regulation 3-103

A. Human Health Standards
Uranium: 5.0mg/l

The proposed standard for uranium has been suggested as 10pCi/l (equivalent to 14.7 μg/l). Before establishing this standard, the U.S. Environmental Protection Agency (EPA) must demonstrate available economical control technology for achieving, in routine municipal and domestic water treating operations, this level of uranium.

After identifying possible control technologies and performing preliminary screening experiments, the EPA moved to demonstrate field (pilot-scale) technology. The Engineering Research Center at New Mexico State University (NMSU) was contracted to demonstrate ion exchange and chemical clarification technology.

URANIUM IN DRINKING WATER SUPPLIES

The chemistry of uranium ions in an aqueous solution can be summarized as stated by Cotton and Wilkinson (4):

> 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 ClO_4^- as well as hydrolytic 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.

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. 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 im-

TABLE 2
Uranium Ions in Aqueous Solutions (4)

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; disproportionate to U^{4+} and UO_2
$UO_2{}^{2+}$	Yellow	Oxidized U^{4+} with HNO_3, etc.	Very stable; difficult to reduce

In the Presence of Carbonate

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

portant for successful operation of both chemical clarification and ion exchange.

As mentioned, all of the common anions anticipated in drinking water supplies will complex with the uranyl species. In the pH range of most drinking water supplies, the complexed uranyl species will be an anion. Some complexes, specifically the phosphate complexes, can be either positive or negative depending on concentration. Finally, silica readily adsorbs $UO_2{}^{2+}$ and U^{4+} at low pHs (5).

The New Mexico Environmental Improvement Division assisted in identifying sources of drinking water containing uranium. Table 3 is a listing of supplies serving 1,000 persons or more which contain uranium (6).

TABLE 3
New Mexico Water Supplies Containing Uranium

SOURCE	URANIUM LEVEL (pCi/l)
Composite	11.2 ± 0.8
Well	16.1
Well	18.9
Well	24.5 ± 2.5
Well	28.0 ± 2.8
Well	1,110. ± 6
Well	23. ± 2
Composite	12.0 ± 1.0
Well	12.6 ± 1.3
Well	22.0 ± 1.0
Well	19.8 ± 1.0
Well	20.0 ± 1.0

While Kerr-McKee Corp. has consented to make one of their mine discharge waters or a process effluent stream available, the levels of uranium in those streams was a factor of 10 greater than anticipated in drinking water. Therefore, the well sampling at a level of 110 pCi/l was selected. This well is located on the NMSU campus and is currently out of service. Detailed analysis of this well water is given in table 4.

Chemical Clarification

Sorg and Logsdon have published a series of articles summarizing existing treatment technology to meet the National Interim Primary Drinking Water Regulations for inorganic solutes (7). Part 5 of their series covers barium and radionuclides. In their review, the radionuclides are treated as radium 226 and radium 228. Apparently, the available work on

TABLE 4
Project Test Well Analysis
(pumped four hours before sampling)

SPECIES	CONCENTRATION (mg/l)
Na^+	17.9
K^+	18.4
Ca^{2+}	375.2
Mg^{2+}	69.0
Cl^-	555.2
$CO_3{}^{2-}$	0
$HCO_3{}^-$	96.4
$SO_4{}^{2-}$	400.0
TDS	2,152
As	0.005
Ba	0.12
Cd	0.005
Cr	0.01
Pb	0.005
Hg	0.0004
Se	0.005
Ag	0.05
$NO_3{}^-N$	0.01
F	0.54
U	0.2 ± 0.1
Fe	1.69
Mn	0.95
Hardness (as $CACO_3$)	1,220
Alkalivity (as $CACO_3$)	79
pH	7.62
E.C.	2.36

uranium removal from drinking waters is the unpublished work of Oak Ridge National Laboratory (8). The Oak Ridge work examined lime softening and coagulation using ferric sulfate and aluminum sulfate with several types of flocculating agents.

In general, chemical clarification is made up of three operations: (1) coagulation; (2) flocculation; and (3) solid-liquid separation, i.e., sedimentation, flotation and/or filtration. 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 less clear when chemical reactions occur and filtration is substituted for sedimentation. In this project, chemical clarification means the addition of coagulants, flocculants or oxidants which remove the uranium ion through its precipitation or through its adsorption on other precipitated material.

The primary coagulants used in wastewater treatment are: (1) lime; (2) alum; and (3) iron salts, e.g., ferric chloride, ferric sulfate and ferrous sulfate. The materials were tested by Oak Ridge National Laboratory. Typical results of their study are summarized in table 5.

TABLE 5
Chemical Clarification for Uranium Removal (8)

		DOSE mg/l	FINAL pH	% URANIUM REMOVED
A.	LIME SOFTENING			
	$CaCO_3$	50	11.5	86
		250	11.5	90
	$CaCO_3 + MgCO_3$	50 + 120	11.2	15
		250 + 120	11.2	99
B.	COAGULATION			
	$Fe_2(SO_4)_3$	25	4	20
		25	6	85
		25	8	45
		25	10	85
	$Al_2(SO_4)_3$	25	4	20
		25	6	85
		25	8	50
		10	10	99+
		25	10	99+

While the mechanism of uranium removal via chemical clarification has not been proven conclusively, it most likely occurs through the adsorption of the uranyl ion complex by the coagulant precipitate. Subsequent solid-liquid separation removes the uranium. If filtration is used on granular media or precoal-mechanical filtration, adsorption of the uranyl complex on the filter media might also occur.

Conventional water treating systems which use chemical clarification use either rapid-mix basins, flash-mix basins or in-line mixers. Sedimentation basins are most frequently applied for solid-liquid separation. This project is using a laboratory scale flotation cell as a mixer followed by either rotary vacuum filtration or gravity-bed filtration. The preliminary work showed that the particulate size required solid-liquid sedimentation instead of normal sedimentation.

Filtration is the key process in production of high quality effluents from water treating (wastewaters [9]). The major difference in the operation of the two types of filtration is that the mechanical-straining (rotary vacuum) type filter produces a product cake having 5-8 percent water and the gravity-bed filter produces a slurry (as a result of backwashing to regenerate the bed). Scale-of-operation and cost will be major considerations although ultimate product disposal is a question when separating radioactive nuclides.

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 in 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 (10).

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 groups containing ions which are relatively free to move and 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
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.

Strong base anion resins have been identified for removing the uranyl complex ion.

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

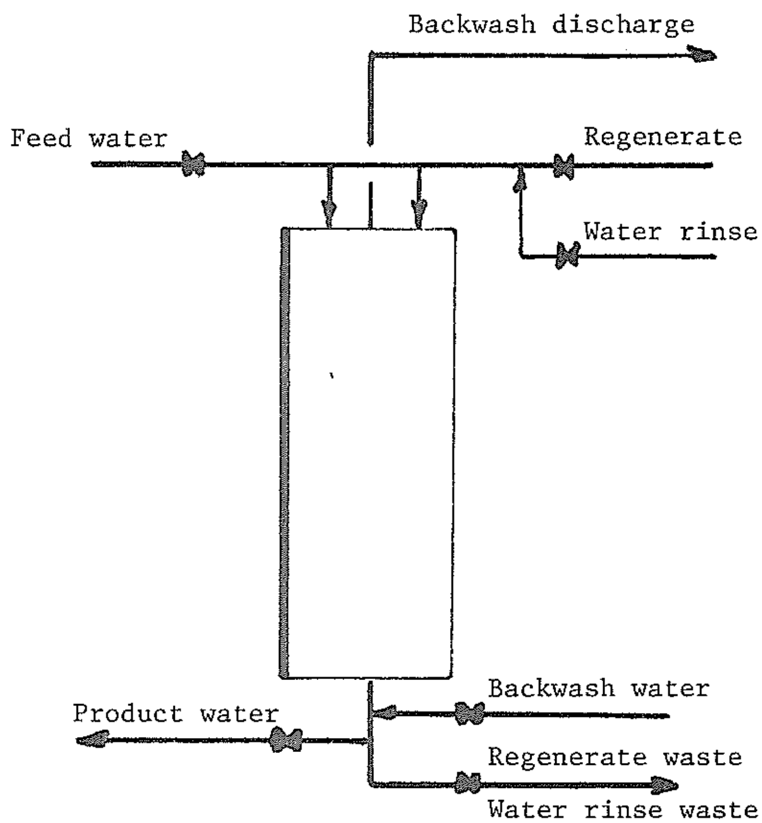

Fig. 1. Typical Single Column Ion Exchanger Flow Diagram

The primary operating parameters in ion exchange units are shown in figure 2, 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.

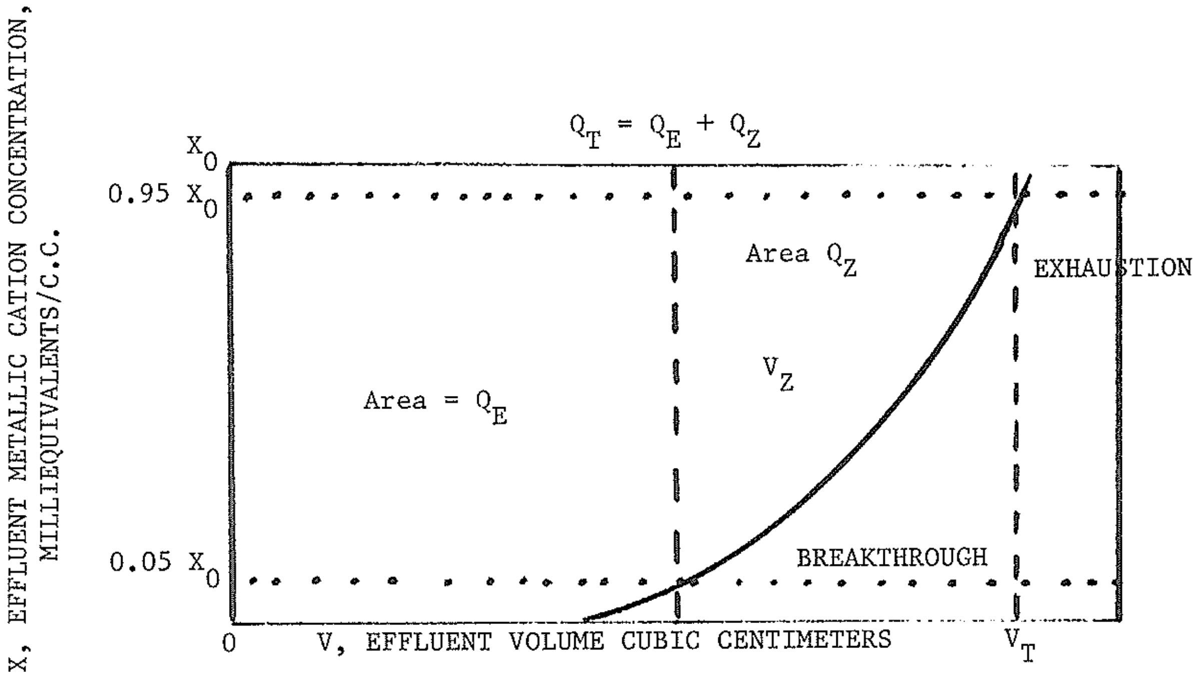

Fig. 2. Ion Exchange Column Operation

Ion exchange has been used as a standard unit operation for the commercial recovery of uranium for many years (11). Recent work by McClanahan (12) used ion exchange for treating uranium mine discharge water. Oak Ridge National Laboratories performed bench scale tests on a synthetic water containing uranium. This work was extended to column tests by the Drinking Water Group of the EPA (8). Table 6 summarizes the results of these tests.

TABLE 6
Ion Exchange Tests

ION EXCHANGE MATERIAL	% URANIUM REMOVAL	COMMENT	REF.
DOWEX SPR	99+	Mine Water	8
DOWEX 50W-X8	35.	Mine Water	8
Clinoptilolite	20.	Mine Water	8
DOWEX 21K	97.	Mine Water	8
DOWEX 1-X2	99+ (Max.)	Parameter Dependent	8
DOWEX SPRB	99	Column Test	8
IONAC A-641	99+	Column Test	8

The project system consists of four 2-cubic feet beds of synthetic resin, i.e., DOWEX SBR, DOWEX 21K and IONAC A-641 (two beds). One IONAC A-641 resin bed will be operated in an upflow mode. Pretreatment for solid filtration and possible iron/manganese control are included. Automatic regeneration using NaCl is included. Previous work indicates 2,000-5,000 bed-volumes of water can be treated before regeneration. Regeneration produces 40-50 bed-volumes of effluent.

PROJECT OPERATION

This project is being conducted with the active participation of personnel from the Water Utility Operation Program located at the Dona Ana Branch of NMSU. Steve Hanson, an instructor, has supervised the construction of the ion exchange system and will supervise its operation by students from the Water Utility program. Doug Roby, an assistant professor in that program, is supervising and monitoring the analytical analysis (chemistry) of the operation.

Graduate students in chemical engineering and civil engineering are assembling the necessary equipment for the chemical clarification evaluation experiments. Suitable Master of Science thesis topics have been identified and their work is progressing.

The project equipment (ion exchange) is on location and operation is commencing. Figure 3 is the project van (used previously for a water treating project under WRRI sponsorship [13]).

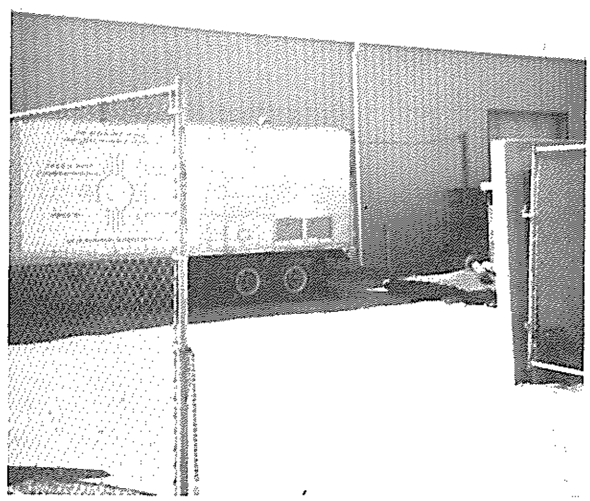

Fig. 3. Project Van. Graduate students in chemical engineering are assembling the necessary equipment for the chemical clarification evaluation experiments. Suitable Master of Science thesis topics have been identified and their work is progressing. The project equipment (ion exchange) is on location and operation in commencing. Figure 3 is the project van (used previously for a water treating project under WRRI and OWRT sponsorship [13]).

The project location is well no. 8 adjacent to the NMSU Physical Plant building. Figure 4 is an interior picture of the ion exchange system

The project covers an 18-month period which began November 1982.

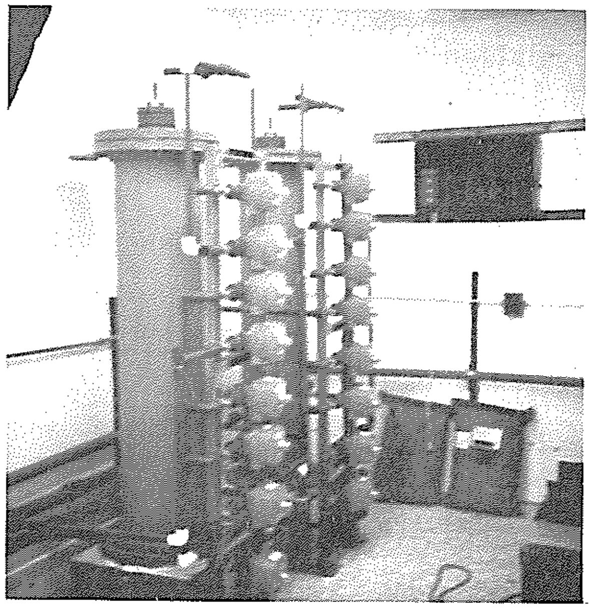

Fig. 4. Ion Exchange System. Project duration is scheduled for 18 months from November 1982. The project location is Well #8 adjacent to the New Mexico State Physical Plant building. Figure 4 is an interior picture of the ion exchange system.

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