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DECONTAMINATION OF RADIOACTIVE EFFLUENT WITH CLINOPTILOLITE

D. W. Rhodes and M. W. Wilding

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A B S T R A C T

The removal of strontium-90 and cesium-137 from fuel storage basin effluent by ion exchange using the mineral clinoptilolite as the exchanger is described. The concentration of cesium-137 in the effluent after decontamination was less than its drinking water tolerance, and the concentration of strontium-90 was approximately equal to its tolerance.

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I. SUMMARY

Removal of the fission products strontium-90 and cesium-137 from fuel storage basin effluent at the Idaho Chemical Processing Plant (ICPP) is necessary before this effluent can be released to the environs. This removal was accomplished by using ion exchange columns containing the mineral clinoptilolite as the exchanger. The exchanger was used on a "once through" basis, after which the column was sealed and buried with other solid radioactive wastes.

The actual operation of a unit handling about 100,000 gallons per month of effluent indicated that approximately 24 cubic feet of mineral were required to obtain an effluent with an average concentration of strontium-90 near drinking water tolerance and a concentration of cesium-137 well below drinking water tolerance. Continued close surveillance of the fuel stored in the basin and general "basin clean-up" procedures are expected to reduce the concentration of strontium-90 and cesium-137 in all of the water in the basin below drinking water tolerances within about five years.

II. INTRODUCTION

Water slightly contaminated with cesium-137 and strontium-90 results from the storage of a large number and a wide variety of irradiated fuel elements under water at the ICPP. Each month, approximately 100,000 gallons of this water is removed from the basin for corrosion control purposes, decontaminated, and released to the environs. Both cesium-137 and strontium-90 are removed by passing this effluent through an ion exchange bed using the naturally occurring mineral clinoptilolite as the ion exchanger. No other fission product is above its drinking water tolerance in the basin water, so these are the only two contaminants of concern.

Clinoptilolite is a naturally occurring zeolitic mineral having the general composition $(M, N)_2O \cdot Al_2O_3 \cdot nSiO_2 \cdot mH_2O$, where M is an alkaline earth and N an alkali metal⁽¹⁾; both M and N are exchangeable with ions in solution. The value of n is usually between 8.5 and 10.5 and the

value of m between 6 and 7. This mineral has been studied extensively at Chalk River⁽¹⁾ and at Hanford⁽²⁾ for possible use as an ion exchanger to remove cesium, and to a lesser extent strontium from radioactive waste solutions. Although it has been shown to be less efficient for strontium than for cesium, the availability of this material in large natural beds in southern Idaho suggested that it might be used to remove strontium-90 from ICPP storage basin water economically.

III. LABORATORY STUDIES

1. Storage Basin Water

The contaminated storage basin water at the ICPP consists of raw water with sufficient chlorine added to produce a concentration of about 0.5 ppm of residual chlorine and sufficient sodium nitrate to produce about 200 ppm nitrate. The chlorine is added to inhibit growth of microorganisms, and the sodium nitrate is added for corrosion control purposes. The approximate chemical composition of the raw water and the storage basin water is given in Table I.

Table I
CHEMICAL COMPOSITION OF RAW WATER AND ICPP
STORAGE BASIN WATER

	Composition in ppm						pH
	<u>Ca⁺⁺</u>	<u>Mg⁺⁺</u>	<u>Na⁺</u>	<u>NO₃⁻</u>	<u>Cl⁻</u>	<u>SO₄⁼</u>	
Raw water	35	12	7	Nil	6	22	8.0
Storage basin water	39	12	95	200	30	26	8.2

The radiochemical constituents are principally strontium-90, at a concentration of about 3.5×10^{-4} to 10×10^{-4} microcuries per ml and cesium-137, at about 0.8×10^{-3} to 1.3×10^{-3} microcuries per ml. These two long-lived radioisotopes are the only two that exceed drinking water tolerances. Both cerium-144 and ruthenium-106 are present in a thin layer of particulate matter on the bottom of the basin, but are not present in the water in significant concentrations.

2. Laboratory Experiments

Both batch equilibrium and column experiments were performed using Idaho clinoptilolite and actual storage basin water. The batch equilibrium experiments consisted of adding one gram of clinoptilolite and 20 ml of basin water to a 50 ml centrifuge tube, then agitating the mixture for 24 hours on a mechanical shaker. All experiments were run

at room temperature. After equilibration, the samples were filtered through a millipore filter, and the clear supernatant solution was analyzed to determine the distribution coefficients for cesium-137 and strontium-90. The distribution coefficient (K_d) was taken to be,

$$K_d = \frac{\text{grams of metal ion/gram of solid}}{\text{grams of metal ion/milliliter of solution.}}$$

The results of this work are shown in Table II. The high affinity for cesium and the moderate affinity for strontium are evident in the data.

Table II

DISTRIBUTION COEFFICIENTS DETERMINED BY EQUILIBRATION FOR CESIUM AND STRONTIUM USING CLINOPTILOLITE AND STORAGE BASIN WATER

<u>Sample No.</u>	<u>K_d</u>		<u>Equilibrium pH</u>
	<u>Cs-137</u>	<u>Sr-90</u>	
1	> 1500	311	8.0
2	> 1860	450	8.1

The clinoptilolite used for the column experiments consisted of particles 0.35 to 2.0 mm diameter. The mineral particles were packed in a glass column (1-inch ID x 48 inches long), and the feed solution was passed downward through the column. The variation in flow rate as a function of hydrostatic head on the column is shown in Figure 1. A constant head of three feet was used in the rest of the experimental work to maintain the flow rate at approximately 1 gal/ft²-min.

The breakthrough curves⁽³⁾ for cesium and strontium in a clinoptilolite column are shown in Figures 2 and 3. The column had sampling ports at one-foot intervals; thus samples were, in effect, collected from four columns of different length. From the data in Figure 3, it is apparent that cesium, as anticipated, has been removed so efficiently that it will never be of concern in the column effluents. Strontium, on the other hand, shows a definite breakthrough. The data in Figure 2 suggest that a four-foot column will exhibit a breakthrough of about $C/C_0 = 0.001$, the decontamination required to reduce the strontium-90 concentration to below drinking water tolerance, somewhere between 500 and 1,000 bed volumes.

IV. OPERATING EXPERIENCE

1. Installation and Operation of Columns

Using the laboratory results as a guide, a unit was designed

CPP-S-3500

Fig. 1 Variation in flow rate through a clinoptilolite column as a function of hydrostatic head

CPP-S-3025

Fig 2. Strontium breakthrough in clinoptilolite columns

CPP-S-3501

Fig. 3 Cesium and strontium breakthrough from fuel storage basin water in clinoptilolite columns

and installed at the storage basin to remove cesium and strontium from the basin effluent. This unit, called the Isotope Removal System (IRS), consists of four columns in parallel, each column consisting of two 55-gallon mild steel drums connected in series. Each drum contains about a 24-inch depth of clinoptilolite, making an effective total column length of about four feet. The bottom drum, when exhausted, is drained and used to replace the top drum. When removed from the system, the top drum is capped, the drain plug on the bottom is sealed, and the drum with its contents is buried with other solid radioactive wastes.

Inasmuch as all of the cesium is retained in the top drum, and strontium, which is retained in both drums, is only a

beta emitter, radiation is significant only in the top drum. The usual radiation level of the top drum when loaded is about 2 R per hour at one inch.

A single unit consisting of two drums in series is shown in Figure 4. Water is pumped from the basin to a header pipe and is then metered to the drums through a flow-meter located at the top of each column. The piping is arranged to maintain each drum about one-half full of water. In addition, a siphon break loop for each drum extends from the drain line up above the drum, then returns to the drum and terminates with the open end of the siphon break just below the lip. If water backs up in the drum to the siphon opening, the siphon effect of about two feet of water is added momentarily. As soon as the water level drops below the lip of the siphon break, normal flow conditions again prevail. In testing, the siphon break functioned very well; however, the flow rate through the column during actual operation was never high enough to require the siphon break to function. When the clinoptilolite is exhausted, a drain valve is opened to remove excess water.

Fig. 4 Clinoptilolite column consisting of two drums connected in series

The actual clinoptilolite used in the drums is essentially all in the size range 0.25 to 2.0 mm diameter. The minimum diameter of the particles is slightly smaller than that used in the laboratory experiments; however, the flow rate is always less than that used in the laboratory experiments and is never a limiting factor during operation. The water is distributed evenly over the surface of the bed by means of a perforated aluminum disk, which rests on the surface of the clinoptilolite. Samples are obtained weekly from two sets of columns, and a monthly composite is obtained from all four columns using a proportional sampler.

2. Results of "On-Line" Operation

Initially, the clinoptilolite used in the columns was oversize (~ 1 to 6 mm diameter) because of inadequate crushing and sieving procedures; consequently, the removal of strontium was inadequate as shown by the January, February, and March, 1964 data in Figure 5. Removal of cesium-137 was well below drinking water tolerance⁽⁴⁾ for every month after startup of the IRS as shown in Figure 6. After the proper size material was obtained for the columns (May, 1964), the strontium concentration in the effluent averaged approximately 2.5×10^{-6} microcuries

Fig. 5. Concentration of strontium-90 in basin water and effluent

per ml (near drinking water tolerance) for the rest of the operating period shown in Figure 5, although occasionally the concentrations for strontium-90 varied from this value by factors ranging from < 0.4 to about 8.5. Using an average influent concentration for strontium-90 of about 5×10^{-4} microcuries per ml for the period April, 1964 through April, 1965 (Figure 5) and an average effluent concentration for the same period of about 2.5×10^{-6} microcuries per ml, the average decontamination factor for strontium-90 was about 200. The total volume of effluent discharged during this thirteen-month period was about 1,300,000 gallons.

The operational results for a single column unit consisting of two drums are shown in Figure 7. The breakthrough curves for the top half of the column and the total column for a two-month cycle are depicted. The breakthrough of strontium-90 was fairly rapid in the top drum which had been used as a bottom drum in the previous cycle; however, essentially all of the cesium was retained in the top drum during the two-month period. The breakthrough curve for strontium-90 in the total column (Figure 7) was rather gradual, with most of the decontamination occurring in the bottom drum. Although only a very small fraction of

Fig. 6 Concentration of cesium-137 in basin water and effluent

the total cation exchange capacity is occupied by strontium-90, the large quantities of calcium, magnesium, and sodium which compete for the exchange sites resulted in a breakthrough of 3×10^{-6} microcuries per ml (the limit used at the ICPP for disposal to the ground) at about 400 column volumes. Assuming that the bottom drums receive an equal volume when they are used as the top units, the total life of each drum is about 800 column volumes

3. Material Costs

Whether or not this type of "throw-away" usage can be justified depends on the cost of the clinoptilolite to the user. The last shipment received at the ICPP is probably representative of the costs that can be expected in the future. These are detailed in Table III.

The sieving and loading of the drums is done at the ICPP by personnel in their free time from other assigned duties. Thus, it does not actually represent an "out-of-pocket" cost.

Organic ion exchange resins may also be used for removing strontium ion from water; however, the cyclic use of resins would require a much more elaborate installation than that currently used. For example,

Fig. 7 Breakthrough curves for strontium-90 in a clinoptilolite column

stainless steel equipment would be required for handling acidic regenerating solutions, and tank storage would be required for the highly contaminated regenerating solutions whether acids or salts were used in the regeneration step. If, however, the capacity of the resin was sufficiently better than the clinoptilolite to make it economically competitive, the resin could also be used as a "throw away" unit utilizing existing equipment. This approach is being investigated.

V. LONG TERM CONTROL OF CONTAMINATION OF BASIN WATER

The ultimate objective is to reduce the contamination in the basin water to such a low value that decontamination of the effluent will not be necessary. A continuing program to accomplish this is underway at the ICPP. Fuel elements that are considered to be susceptible to fission

Table III

COST OF CLINOPTILOLITE AS USED AT THE ICPP

<u>Operation</u>	<u>Cost Per Cubic Foot</u>
Mining rock and transporting to crusher	\$1.82
Dry crushing and delivery to ICPP	2.43
Sieving clinoptilolite and loading drums	4.50*
Total	<u>\$8.75</u>

* Includes \$.50 for oversize and undersize material discarded.

product leakage are tested in special equipment⁽⁵⁾, and faulty elements are sealed in special containers for storage. In addition, contaminated sludge residues on the bottom of the basin are being removed. The effectiveness of this program is evident in the top curve of Figure 5. Extrapolation of this curve indicates that the concentration of strontium-90 in the basin water should reach drinking water tolerance in about five years assuming that the reduction in strontium-90 concentration continues at the same rate for the five year period.

VI. CONCLUSIONS

Ion exchange columns containing clinoptilolite to decontaminate storage basin effluent have been operated satisfactorily at the ICPP for about one year. The removal of cesium has been more than adequate; this was anticipated since clinoptilolite is highly selective for cesium. The removal of strontium, while less effective than removal of cesium, has been adequate (near drinking water tolerance) for this particular geographical location. Additional strontium decontamination occurs as the liquid waste percolates downward through the underlying earth materials, and some dilution is achieved when the waste reaches the groundwater aquifer. However, the most desirable approach is to consider dilution and soil adsorption as secondary safety measures, which requires that only effluent with radioactive isotope concentrations less than drinking water tolerances be released to the environs. At the fuel storage basin, this can be accomplished by obtaining a high operating efficiency for the ion exchange columns and, eventually, by essentially complete decontamination of all water in the storage basin.

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