EFFECT OF PROCESS VARIABLES ON THE REMOVAL OF CONTAMINANTS FROM RADIOACTIVE WASTE STREAMS USING ZEOLITES

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ABSTRACT

A variety of low level radioactive waste streams are being generated from the decontamination and decommissioning of the former nuclear fuel reprocessing plant at West Valley, New York. The radioactive contaminants from these wastes will be removed and concentrated using zeolites. A study was conducted using representative waste streams to evaluate and compare various zeolites and to provide operating data for the ion exchange process. The testing showed that the contaminant removal was strongly dependent upon waste composition and residence time. Even seemingly slight variations in waste composition resulted in significantly different contaminant loading characteristics. It was found that to obtain the desired cesium and strontium decontamination factors for the waste streams of interest, mixtures of zeolites (i.e. phillipsite and Union Carbide's A-51) had to be used. The required residence time is found to be 20 to 40 minutes depending on the waste stream. The testing also indicated that thousands of bed volumes of the waste solutions could be processed under the required conditions before any significant contaminant breakthrough occurred.

INTRODUCTION

A commercial nuclear fuel reprocessing plant was operated in West Valley, New York at the Western New York Service Center from 1966 to 1972. West Valley Nuclear Services Company, Incorporated, a wholly-owned subsidiary of Westinghouse Electric Corporation, was formed to carry-out the solidification of the high-level radioactive wastes generated from the reprocessing operation and presently stored at the plant. A variety of low level radioactive waste streams are being generated from the decontamination and decommissioning activities. A Liquid Waste Treatment System (LWTS) is being developed to treat these low level waste streams. This system will use a non-regenerative ion exchange process to remove and concentrate the contaminants from these waste streams. Zeolites have been chosen as the ion exchange media for the process (1). Testing was conducted in this study to evaluate and compare various zeolites and to provide operating data for the full-scale ion exchange system.

EXPERIMENTAL METHODS

Two simulated waste streams were tested: 1) the overheads from the evaporation of the decontaminated and diluted supernatant, which is the largest waste stream to be treated, and 2) a nitric acid waste stream which is the most radioactive waste stream to be handled. The composition of these streams are given in Table I.

TABLE I

Composition of West Valley Waste Streams

a. Decontaminated Supernatant Overheads

$NaNO_3/NaNO_2$ - 0.0130 wt%
Na_2SO_4 - 0.0011 wt%
Other salts - 0.0020 wt%
Cs-137 - 2.41 μCi/ml
Sr-85 - 1.00 μCi/ml

b. HNO_3 Evaporator Overheads*

HNO_3 - 0.5 wt%
Cs-137 - 13.7 μCi/ml
Sr-85 - 3.40 μCi/ml

*pH adjusted to 5.

Initial testing was performed on a variety of zeolites. The results of the initial tests, which were presented in an earlier paper (2), indicated that optimum results were likely to be obtained with any of several zeolites, which included the following:

- Phillipsite
- Clinoptilolite
- A-51

Only the testing conducted on these zeolites will be discussed here.

The natural zeolites tested, phillipsite and clinoptilolite, were supplied by Tenneco Specialty Minerals (formerly Phelps Dodge Zeolites). The A-51 is a processed zeolite supplied by Union Carbide. The materials used were in the -20 to +50 mesh size range. The A-51 was soaked in water for at least one day prior to testing. No pretreatment of the natural zeolites was performed.

Batch equilibrium tests were performed using a given weight of ion exchange material and varying volumes of waste solution to determine the equilibrium loading of the various isotopes (i.e., Cs-137, and Sr-85) as a function of solution concentration. The mixtures, in capped sample bottles, were well agitated for 24 hours using a variable speed shaker table at ambient temperature and pressure.

The batch equilibrium test is a rapid method for comparing the various ion exchange materials based on their selectivity for the radionuclides of interest. From the data generated in the tests, a sorption coefficient (Kd) is determined for each of the radionuclides as follows:

$$Kd = \frac{C_s}{C_l}\ ,\ ml/g \qquad (1)$$

where C_s = radioactive concentration on the ion exchange material (meq/g)

C_l = final radioactive concentration in solution (meq/ml)

This sorption coefficient is a measure of the ability of the ion exchange material to selectively remove each of radioactive contaminants.

Ion exchange column testing was performed to determine radioactive contaminant kinetic data, capacity values, and decontamination factors.[a] The testing was conducted using a gravity feed system which permitted as many as four tests to be performed simultaneously. Each of the 2.5 cm (1 in) I.D., 30.5 cm (12 in) long columns were fitted with valves to permit flow control.

Samples generated in both the equilibrium and column tests were placed in Marinelli beakers to permit more accurate radioactive analysis. The activity in each of the samples was determined by counting the gamma rays emitted by each of the isotopes with an intrinsic Germanium detector.

RESULTS

Supernatant Waste Stream

The results of the batch equilibrium tests using the supernatant waste stream are summarized in Table II. All of the zeolites produced average cesium and strontium Kd values greater than 1000. The clinoptilolite had the highest average strontium Kd (8000), and the phillipsite had the highest average cesium Kd (3500). Because of the higher Kd values and of the lower cost of natural zeolites ($800-$3200/ton) compared to the processed zeolite ($8000-$20,000/ton), column tests were initially conducted on only the clinoptilolite and phillipsite.

In each column test, the supernatant was processed through 25 ml of zeolite at a feed rate of 0.5 ml/min (1.0 bed volume (bv)/hr). At this feed rate, the residence time in the zeolite bed was approximately 20 minutes. The cesium and strontium breakthrough curves for these columns are shown in Fig. 1. The results show that for the 2000 bed volumes of solution processed, both materials had cesium and strontium DF's which typically were above 900. No significant contaminant breakthrough had occurred by the conclusion of the test. The results showed no significant differences between the zeolites.

TABLE II

Equilibrium Test Results

	Supernatant Overheads		HNO_3 Overheads	
Zeolite	Sr Kd ml/g	Cs Kd ml/g	Sr Kd ml/g	Cs Kd ml/g
Clinoptilolite	8000	2000	400	3500
Phillipsite	2000	3500	100	4000
A-51	2000	1000	10,000	500

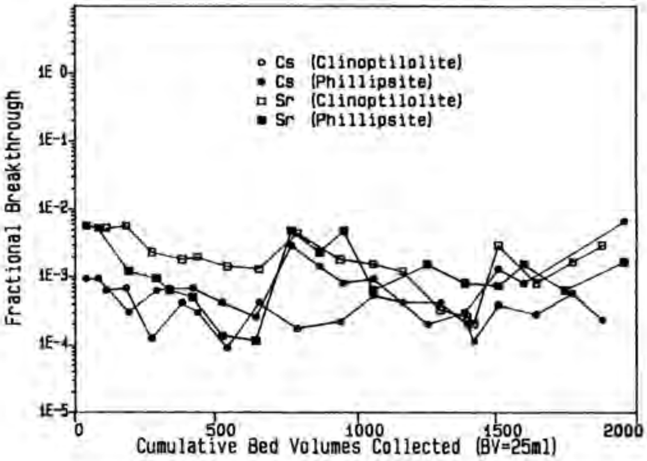

Fig. 1. Effect of Zeolite Type on Supernatant Treatment.

Nitric Acid Waste Stream

The results of nitric acid batch equilibrium tests are summarized in Table II. The two natural zeolites had an average cesium Kd between 3000 and 4000, but an average strontium Kd of only between 100 and 400. The A-51 had a cesium Kd of only 400 but a strontium Kd of 10,000. The high selectivity of A-51 for strontium is not surprising because it is marketed as a strontium-specific material.

Previously performed column tests (2) on the nitric acid waste using another zeolite (i.e. erionite) had shown that while the cesium loading was excellent, the strontium loading was very poor. It had been proposed that perhaps the feed pH (~5) of the nitric acid waste was the cause of the low strontium loading. A study (3) conducted by Savannah River Laboratory (SRL) for the Department of Energy showed that strontium sorption onto clays is greatly affected by the solution pH. At the pH used here the strontium Kd was shown to be low in the SRL study. The optimum pH was found in that study to be in the 6 to 8 range for clays. Tests were

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[a] Decontamination factor = Feed contaminant level/effluent contaminant level.

thus conducted here on the nitric acid waste stream to determine if there is an optimum pH range for zeolites.

Batch equilibrium tests were conducted on the individual zeolites as well as a mixture of phillipsite and A-51 (at a volume ratio of 2). The nitric acid waste stream's initial pH was varied from 6 to 9 using sodium hydroxide. The results, summarized in Table III, show that for all pH's the phillipsite and clinoptilolite had cesium Kd's greater than 1000 but very low strontium Kd's (10-200). For all pH's, the A-51 had a strontium Kd greater than 4000, but cesium Kd's of only about 600. However, the mixture of phillipsite and A-51 had both high strontium (>5000) and cesium (>3000) Kd's. Other studies (4) have also shown that the addition of A-51 to other zeolites (i.e. Union Carbide's IE-96) is required to obtain the desired strontium, as well as cesium, decontamination factors. Column tests were thus conducted here using this zeolite mixture.

TABLE III

Effect of Nitric Acid pH on
Contaminant Loading

Zeolite(s)	HNO_3 Feed pH	Sorption Coefficients Kd(ml/g) Sr	Cs
Phillipsite	6	14	1250
Phillipsite	7	22	1700
Phillipsite	8	21	1550
Phillipsite	9	22	950
Clinoptilolite	6	180	2500
Clinoptilolite	7	180	1800
Clinoptilolite	8	150	850
Clinoptilolite	9	180	2650
A-51	6	5400	600
A-51	7	4450	600
A-51	8	4350	600
A-51	9	8400	600
Phillipsite/A-51	6	11400	3800
Phillipsite/A-51	7	5400	3000
Phillipsite/A-51	8	11800	3500
Phillipsite/A-51	9	5100	3400

Mixed-Zeolite Column Tests

The first mixed bed test was conducted on the nitric waste stream (adjusted to pH 7 with sodium hydroxide) at a feed rate of about 1 bv/hr. The total zeolite volume was 25 ml, which is the volume used in the previously performed column tests. The volumes of phillipsite and A-51 used were 17 ml and 8 ml, respectively. The cesium and strontium DF's produced were both very poor (<200). It was believed that this poor performance was due to the relative short contact time with each of the zeolites in the mixed bed. That is, at a flow rate of about 0.45 ml/min, the 17 ml of phillipsite and 8 ml of A-51 are only in contact with the waste solution for ~14 minutes and ~6 minutes (assuming a voidage of 40%), respectively. This residence time was thus perhaps too short.

A column test was then conducted using a 50 ml mixed bed at about the same waste flow rate (~0.5 ml/min). Approximately 34 ml of phillipsite and 16 ml of A-51 were used. For this test, the contact time with phillipsite and 16 ml of A-51 were ~28 minutes and ~12 minutes, respectively. This test produced excellent cesium and strontium removals. For almost 340 bed volumes, the cesium and strontium DF's averaged 15500 and 9500, respectively. The tremendous improvement using the mixed bed on this waste stream is shown in Fig. 2, where the cesium and strontium DF's obtained in this column are compared to those obtained using just phillipsite.

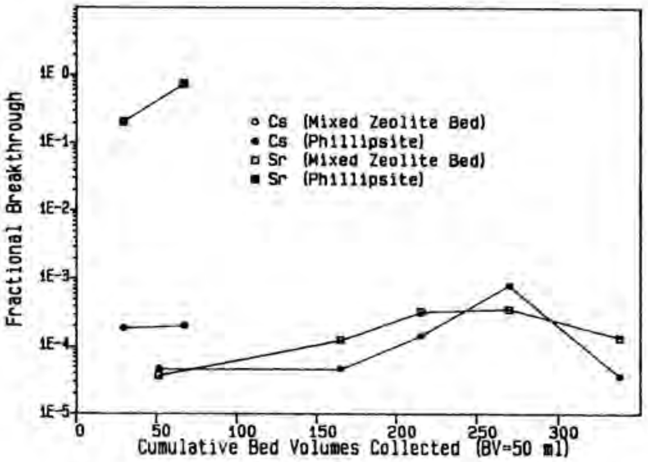

Fig. 2. Effect of Mixed Zeolite Bed on Nitric Acid Waste Treatment.

The supernatant waste stream was also tested using both a 25 ml and 50 ml mixed zeolite bed at a feed rate of 0.5 ml/min. The results of the 25 ml mixed test bed are compared to those obtained with the phillipsite alone in Fig. 3. There are essentially no differences between the two columns. In addition, as shown in Fig. 4, the performance of the 50 ml mixed zeolite bed does not differ significantly from the 25 ml mixed bed. Thus, for the supernatant waste, unlike the neutralized nitric acid waste, there appears to be no advantages to increasing the residence time from 20 to 40 minutes, nor to using a mixed zeolite bed over phillipsite alone.

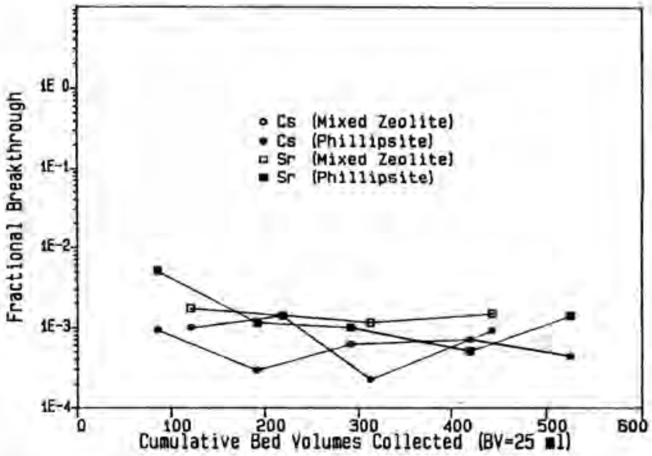

Fig. 3. Effect of Mixed Zeolite Bed on Supernatant Treatment.

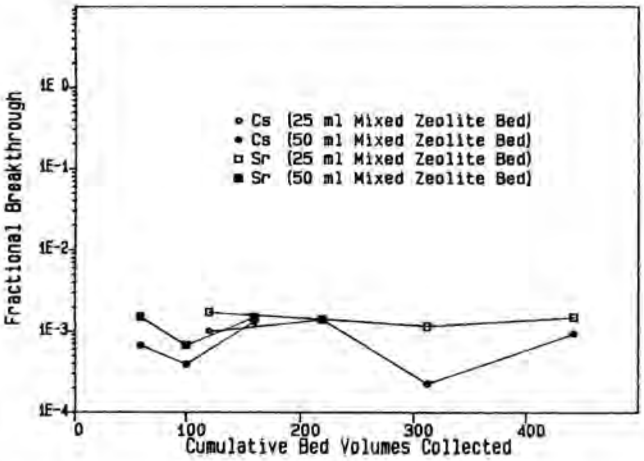

Fig. 4. Effect of Residence Time on Supernatant Treatment.

DISCUSSION

The extremely different contaminant removal characteristics obtained with the neutralized nitric acid waste and the supernatant waste streams were unexpected. It was felt that the contaminant loading characteristics would be similar because the waste streams are very similar in composition. The neutralized nitric acid waste is essentially a 0.5 wt% sodium nitrate solution, while the supernatant is 0.013 wt% sodium nitrate/nitrite plus 0.003 wt% other salts. The cesium and strontium levels in the nitric acid waste are about a factor of five higher. These are seemingly minor differences, yet the sorption characteristics were very different. Using phillipsite alone, acceptable cesium and strontium DF's (500-1000) were obtained for the supernatant for thousands of bed volumes; but the strontium rapidly broke through (<100 bed volumes) with the neutralized nitric acid waste. Using a mixed bed of phillipsite and A-51, the strontium and cesium DF's were improved tremendously for the nitric acid waste; but no improvement was noted for the supernatant waste. The only discernible differences between the waste streams are the slight composition differences noted previously and the feed pH. The nitric acid waste pH was maintained at approximately 7, while the supernatant waste pH would drop from 9 to 7 with each feed batch due to carbon dioxide dissolution from the air. The effect of this varying feed pH has not yet been investigated.

The operating conditions required for the zeolite column appear to be dependent upon the waste stream to be treated. The supernatant waste can be processed in either a phillipsite column or a phillipsite/A-51 column (i.e., phillipsite to A-51 volume ratio of 2) at a residence time of approximately 20 minutes. The nitric acid waste stream (pH ~ 7) must be processed in a phillipsite/A-51 column using a residence time of approximately 40 minutes. To provide the desired flexibility in handling a variety of waste streams, or variations in waste stream compositions, a zeolite mixture of phillipsite and A-51 at volume ratio of 2 will be used in the LWTS at West Valley. It should be noted that, although not tested, a mixture of clinoptilolite and A-51 should also work successfully.

ACKNOWLEDGEMENT

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