

REDUCTION OF CESIUM AND COBALT-ACTIVITY IN LIQUID RADWASTE PROCESSING USING CLINOPTILOLITE ZEOLITE AT DUKE POWER COMPANY

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ABSTRACT

Duke Power Company (DPC) operates three PWR nuclear power stations. All of them have recently started using natural clinoptilolite zeolite which has a high selectivity for cesium in their miscellaneous liquid radwaste process train. This paper discusses in detail the physical characteristics of the media and DPC's full-scale process experience with the zeolite at its Catawba Nuclear Station (CNS), and in summary on the media's performance at McGuire (MNS) and Oconee (ONS).

The use of clinoptilolite zeolite has resulted in large throughputs to a cesium breakthrough, e.g., > 45,000 gallons/ft³ for clinoptilolite zeolite bed compared with a normal 10,000 gallons/ft³ for conventional cation exchange resin bed. For 25 ft³ bed, these figures are equivalent to about 6,000 bed volumes for clinoptilolite zeolite compared to 1,300 bed volumes for strongly cation exchange resin. The zeolite lasts 3-5 times longer than cation exchange resin; therefore, sluicing frequency is reduced by 60 to 80%. Reduction in sluicing frequency has also contributed to reduction in personnel radiation exposure. The complete immobilization of cesium in large throughputs has also contributed to a reduction of curies released to the environment via liquid releases.

The changeover from cation exchange resin to clinoptilolite zeolite for cesium removal from liquid radwaste can save DPC about \$250,000 in process and burial costs in one year. The economic advantage and impact of including clinoptilolite zeolite in the process train to the entire liquid radwaste process are also discussed in detail.

Clinoptilolite zeolite has its own process drawbacks. One of them is its tendency to slough off fines which could create differential pressure problems in the demineralizer. However, at DPC, the zeolite was carefully backwashed to remove fines and carefully loaded into process vessels to avoid generation of fines. These activities required considerable manpower. After the fines have been removed no differential pressure problems were experienced at the nuclear stations. In addition, this paper discusses the unique physical and chemical characteristics and properties of the natural clinoptilolite pertinent to the operation of the liquid radwaste system.

INTRODUCTION

From 1984 to 1986 Duke Power Company in cooperation with Electric Power Research Institute (EPRI) conducted several bench-scale column tests of liquid radwaste pretreatments and selective bed materials for improved processing of PWR liquid radwaste (1). A number of bed materials including cation exchange resins, chelate resins, porous glass material, etc., claimed by the vendors to have high selectivity for cesium were tested to determine their capacity and service life for cesium removal. Figure 1 displays some of the results.

The process life of some of the bed materials either ended abruptly (< 200 bed volumes; 1 bed volume = 10 ml) or developed differential pressure problems (flow stopped), and so could not be represented in Fig. 1. Those zeolites that did not present such characteristics are shown in Fig. 1 and are clinoptilolite, chabazite, mordenite and Type X zeolite. They demonstrated their affinity for cesium; their service life was greater than 800 bed volumes without cesium breakthrough, whereas cation exchange resin broke on cesium at around 450 bed volumes. (Fig. 1) It is now known from full scale processing experience at CNS that the actual values are about 6,000 bed volumes for clinoptilolite zeolite and 1,300 bed volumes for strongly acidic cation exchange resin. A look at Fig. 1 shows that the naturally occurring clinoptilolite, zeolite, synthetic chabazite and mordenite would be equally effective in removing cesium from liquid radwaste. However, the price of clinoptilolite is less than 1/2 the price of chabazite. The decision was, therefore, made to take a closer look at clinoptilolite, that is, ascertain its service life and its physical and chemical properties before plant application.

PHYSICAL AND CHEMICAL PROPERTIES OF CLINOPTILOLITE

The physical and chemical properties of clinoptilolite considered necessary for evaluation for full scale application in liquid radwaste system included the following: acceptable

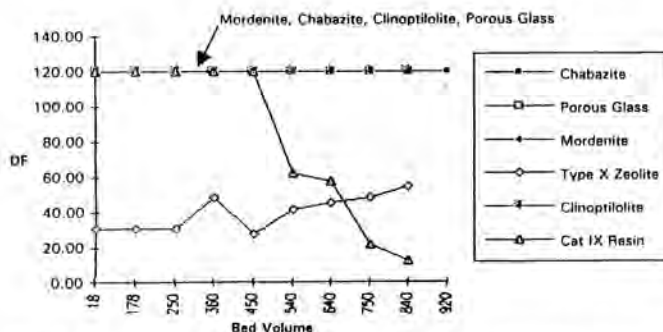


Fig. 1. Cs-134 removal; comparative service life of bed materials.

levels of fines, water retention capacity, friability, cesium exchange capacity, and solubility at different pH values.

Clinoptilolite samples from two different suppliers, Producer "A" and Producer "B", were evaluated. Both materials were described as 20 to 35 mesh in size. Note that some of the laboratory work was performed in the Epicor, Incorporated, laboratory by Mr. Gary A. Matthews. The methods and results are summarized as follows:

PHYSICAL PROPERTIES

Percent Moisture and Water Retention Capacity of Clinoptilolite

Water retention capacity is a measure of water retained in the lattices and pores of the zeolite. It represents a fairly constant property of the zeolite. Water retention capacity was determined using ASTM Method D21-2187. Table I gives the results relative to the referenced values for strong acid cation exchange resin. Percent moisture of clinoptilolite was determined in the usual manner.

TABLE I

Percent Moisture and Water Retention Capacity of Clinoptilolite

Producer	% Moisture, As Received	Water Retention Capacity %
"A"	6.1	15.6
"B"	7.5	22.0
Cation Exchange Resin, H ⁺ form	---	49-56

Sieve Analysis of Clinoptilolite Samples

Screen analysis of the free flowing "as received" zeolite and the backwashed material was made to enable the zeolite particle size distribution specifications to be written.

The samples were sieved on a dry as-received and on a wetted basis. The results obtained are shown in Table II.

After Epicor backwashed Producer "B" sample to remove entrained fines, their sieve analysis indicated the particle size distribution shown also in Table II. The material was supplied to DPC by Epicor, Incorporated, for full scale use. During a column test of this zeolite at ONS, fines were found sloughing off from the zeolite bed, impeding the flow of the test liquid radwaste through the bed. The fines were considered a potential source of process problems and so it was decided to backwash the Epicor zeolite again at DPC before plant use. Table II also includes the DPC screen analysis result of the zeolite after the second backwash.

The method used at DPC to backwash clinoptilolite will be described later. The twice backwashed Producer "B" zeolite having the particle size distribution shown in Table II has performed well in the liquid radwaste system at MNS, CNS and ONS. Consequently, a DPC specification for this material is no more than 0.3% fines by weight passing through No. 100 U.S. Standard sieve.

Friability of Clinoptilolite

Friability is a measurement of the physical strength of a particle, and hopefully, indicates the ability of an ion exchange material to resist fracturing during field operation. For years, the friability of ion exchange resin beads has been measured using the Chatillon DPP-1 crush tester. This is a device that measures the force in grams required to physically break an ion exchange resin bead. The particle size of each bead tested is important. In the present test, two particle sizes were used in testing: 16-20 mesh and 20-30 mesh (U.S. Standard Sieves). Although there was some question as to whether or not this instrument could be used to measure the fragility of an irregular crushed particle, it was thought that it would be interesting to test the materials supplied by Producer "A" and Producer "B" on the instrument. The results obtained are shown in Table III.

When this technique was discussed with the two producers of clinoptilolite, they questioned the Chatillon's applicability to crush clinoptilolite particles. They advised that the test method they use is to place a sample in a container with water and shake it on a paint shaker for a short period of time. Particle size distribution is determined before and after shaking. This method may well be more reproducible than the Chatillon Instrument when working with granular crushed particles rather than spherical particles. There is a plan to make some comparisons in the laboratory.

CHEMICAL PROPERTIES

Solubility of Clinoptilolite at Different pH Values

Solubility of clinoptilolite was determined at pH of 4, 5, 7 and 9. The pH of the D1 H₂O was 7 at 24.3°C.

Clinoptilolite is an aluminum silicate having the chemical composition (Na₂,K₂)O · Al₂O₃ · 10SiO₂ · 8H₂O(2). Its solution will, therefore, contain Na, Al and Si. These parameters were analyzed for in the solubility testing phase.

A 5 gram dry sample of clinoptilolite was allowed to soak in 50 ml of buffered solution or deionized water for 16 hours. All of the zeolite and solution mixes were covered with Saran Wrap while soaking to avoid CO₂ pick-up. The solution was then analyzed for Si and Al. The results are shown in Table IV from which the graph in Fig. 2 was plotted.

Conclusions may be drawn from Table IV and Fig 2. As pH decreased, more Al is released by clinoptilolite, and as pH increased more silica is released.

Preferably, the pH of the influent to clinoptilolite bed should be kept between 6 and 8 to discourage significant dissolution of the material. Note that by keeping the pH > 6,

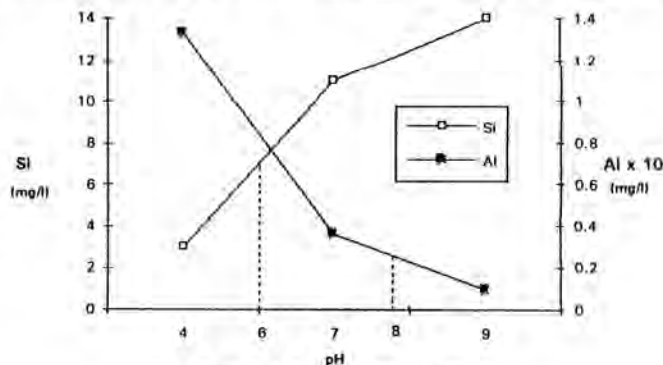


Fig. 2. Solubility of Clinoptilolite.

TABLE II

Screen Analysis of Clinoptilolite

Mesh Size (U.S. Standard) Sieve Producer	As Received (Free flowing) by Epicor		Free Flowing Wetted and Sieved by Epicor		Backwashed by Epicor and Sieved	Backwashed Twice* and Sieved
	"A"	"B"	"A"	"B"	"B"	"B"
% By Weight Retained on Sieve						
+14	0	0	0.1	0	--	--
+16	0	0.02	0.03	1.08	16.7	12.5-13.4
+20	1.33	32.45	4.68	33.14	38	--
+25	--	--	--	--	--	57.3-58
+30	43.19	26.63	39.00	26.56	29.7	--
+40	47.68	34.07	44.00	33.67	14.8	--
+50	5.95	5.38	4.68	5.22	0.7	--
>50	--	--	--	--	0.1	--
+60	--	--	--	--	--	28.8-29.4
+70	0.1	0.19	0.06	0.31	--	--
>70	1.75	0.34	7.43	0.02	--	--
+100	--	--	--	--	--	0.1-0.13
>100	--	--	--	--	0.8**	0.2-0.3

*Note: Backwashed first by Epicor, then second time by DPC after high levels of fines were detected in the consignment from Epicor.
**Note: As analyzed by DPC on Epicor backwashed zeolite.

TABLE III

Chatillon Values: As Received Clinoptilolite Compared with Bead Resin

	Clinoptilolite		Bead Resin 20-30 Mesh Grams Force
	16-20 Mesh, Dry Grams Force	20-30 Mesh, Dry, Grams Force	
Producer "A"	736	631.7	450-600
Producer "B"	963.2	708.4	
Bead Resin	--	--	

the dissolution of aluminum is minimized. In the case of ion exchange, aluminum (Al^{+3}) is of much greater concern than silica due to relative selectivity. The pH of floor drain tank (FDT) liquid radwaste at Duke Power is typically in this range (Fig. 3). Figure 3 demonstrates that FDT pH presents no processing concern with respect to clinoptilolite zeolite solubility. The values reported in Table IV were obtained from the static test described above in which the zeolite was "soaked" in water. The results of Table V were obtained by dynamic testing in which the zeolite was not only soaked but also "rinsed down." A pH 5.0 solution of D1 H_2O and acetic acid was passed through a 10 ml bed of clinoptilolite. The flow rate was 2 ml/min, thus simulating the large scale process. Samples were taken every 100 ml and analyzed for Na, Al and Si. It can

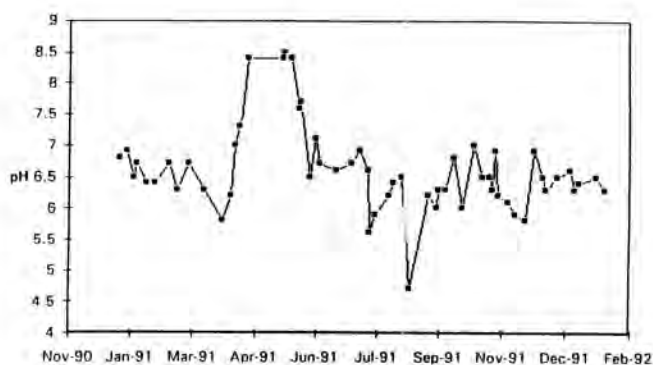


Fig. 3. pH of floor drain tank liquid radwaste-Catawba Nuclear Station.

be seen from Table V that the concentrations of Al, Si and Na decreased as throughput increased, and that as 800 ml (80 bed volumes) is approached, the values leveled to a plateau at low concentrations. Thus, it would appear in this dynamic test, that solubles in the zeolite were being removed via rinsing. It also appears that if the zeolite is allowed to soak in deionized water 24 hours before backwashing, a good portion of the solubles are removed before placing the zeolite bed in service. Therefore, the clinoptilolite was soaked in D1 water for at least 24 hours prior to being backwashed. The backwashing operation not only removed fines but also rinsed down the zeolite and rid it of the solubles which could shorten the service life of the ion exchange resin beds downstream in the liquid process system.

TABLE IV

Solubility of Clinoptilolite at Various pH Values
(Raw Data)* (mq/L)

Producer	pH	Si		Al	
		"A"	"B"	"A"	"B"
	4	3.1	5.1	1.3	2.4
	7	11.2	9.0	0.4	0.3
	9	14	13.2	1.0	0.2

Figure 2 is a graph of Producer "B" raw data.

Cation Exchange Capacity of Clinoptilolite

One other chemical property of clinoptilolite needs to be mentioned. That is cesium exchange capacity. One producer reported a cation exchange capacity of 1.85 meq/gram of dry clinoptilolite. Since the interest was in the zeolite's capacity for cesium the total capacity was determined in the present test using a solution of cesium chloride which contained 4,370 ppm (0.44%) of cesium. Total cation exchange capacities are usually obtained in the laboratory using 4% solutions. The procedure used was very similar to that used in determining the total exchange capacity of a strongly acidic cation exchange resin. The volume of solution was one liter of solution which was passed through 5 dry grams of clinoptilolite. The total cation exchange capacity of clinoptilolite obtained for cesium compared with that of cation exchange resin is shown in Table VI.

The amount of ion exchange capacity utilized is affected to some degree by the solution concentration. However, clinoptilolite's relatively high selectivity for cesium and the small amount of radioactive cesium ($\sim 10^{-10}$ gram/liter) to be removed from liquid radwaste means that very large volumes of waste can be treated by a small volume of clinoptilolite. The zeolite's high selectivity for cesium is the key parameter. As seen in Table VI, cation exchange resin has a higher cation

exchange capacity than clinoptilolite, but the zeolite has a higher relative selectivity for cesium (Table VII).

POTENTIAL PROBLEMS WITH CLINOPTILOLITE

Fines and solubles in improperly backwashed clinoptilolite have been identified as potential sources of problems with application of clinoptilolite in liquid radwaste processing. The following discussions address ways to avoid or reduce the sources of potential problems.

Backwashing Clinoptilolite for Large Scale Use at DPC

In 1990, 50 cubic feet of vendor backwashed clinoptilolite zeolite delivered to DPC for large scale processing of liquid waste at CNS was found to have intolerable amount of fines. It was not advisable to backwash the material in process vessel, which had 200 mesh lateral screens. Therefore, it became necessary to construct a column for batch backwashing of the material. Figure 4 is a sketch of the column.

Previous laboratory work conducted independently at Epicor, Incorporated, and at CNS gave an indication of the bed expansion characteristics and flow rate for effective backwash of clinoptilolite. The results are presented in Table VIII. From the Table, Epicor and CNS results for 50% and 100% bed expansion, 19-20 gpm/ft² and 32 gpm/ft² respectively, are essentially the same for Producer "B". However, in actual practice with the backwash column depicted in Fig. 4, the useful flow rate for 200% bed expansion to allow the slow overflow of fines was 90-100 gpm/ft² or 18-20 gpm for the 6 in. ID column. Each zeolite loading for backwash was approximately 0.6 ft³ in volume.

When backwashing it was necessary to avoid generating a significant amount of very fine particles. This was done by gradually increasing flow rate so that the clinoptilolite bed was slowly expanded and turbulence minimized.

Natural Clinoptilolite Specification for Radioactive Liquid Waste Processing

Natural clinoptilolite zeolite having the following properties has been found suitable for use at DPC plants:

TABLE V

Solubility of Clinoptilolite at pH 5

Sample No.	Throughput (ml)	Na (ppm)	Al (ppm)	Si (ppm)
1	100	6.00	0.4	6.15
2	200	5.85	0.285	4.73
3	300	5.52	0.19	3.67
4	400	4.84	0.113	2.82
5	500	4.50	0.095	1.57
6	600	3.31	-	1.20
7	700	2.22	0.05	0.858
8	800	1.37	0.042	0.373
9	900	0.098	0.036	0.228
10	1000	-	0.035	0.220

Note: All measurements for Na, Al, and Si shown in Tables VII and VIII were made using a Beckman Spectraspan IV, direct current plasma emission spectrophotometer.

TABLE VI

Cation Exchange Capacity of Producer "B" Clinoptilolite

Producer	Clinoptilolite Cation Exchange Capacity	Strong Acid Cation Exchange Resin Capacity
	Influent 4370 ppm Cs ⁺ , Meq/gram	Meq/gram
"A"	1.32	2.0
"B"	1.42	2.0

TABLE VII

Cation Exchange Selectivity of Clinoptilolite and Cation Exchange Resin

Clinoptilolite	Cation Exchange Resin	
Cs	Ba	Increasing Preference for cations by media at low concentrations
K	Sr	
NH ₄ ⁺	Ca	
Na	Cs	
Sr	K	
Ca	Na	
Mg	Li	

- Sieve Analysis of Backwashed Clinoptilolite (U.S. Standard Sieve) as shown in Table II for twice backwashed Producer "B".
- No foreign debris or humus material in the media.

All other physical and chemical parameters cannot be specified because clinoptilolite is a naturally occurring material, i.e., no specifications can be stated except fines limitations.

The above specifications apply only to clinoptilolite mined from a certain area in the United States.

DPC PLANT APPLICATION OF RESINS AND CLINOPTILOLITE

Two results which have found applications in the nuclear industry arose from the DPC-EPRI investigations mentioned earlier in this paper (1). One was the pretreatment of liquid radwaste with polyelectrolyte coupled with deep bed filtration and/or ion exchange resin to reduce particulate and colloidal cobalt activity (3, 4, 5). The other was the realization that

optimization of the liquid radwaste processing system would be achieved by staging the process configuration as follows:

- Stage 1: Colloid Filtration Stage utilizing a deep bed. This is primarily a depth filtration stage in which particulates and some transition metals (e.g., cobalt) are partially removed especially if the liquid waste is pretreated with cationic polyelectrolyte as indicated above.
- Stage 2: Cesium Stage - Natural Clinoptilolite Zeolite
- Stage 3: Transition Metals Stage - Cation Exchange Resin
- Stage 4: Iodine Stage - Anion Exchange Resin

The present general layout of the liquid waste process at DPC's nuclear stations is as follows:

1. Colloid Filtration Stage = Deep bed carbon-based filter, 25-60 ft³ and bag filters up-stream of the deep bed
2. Cesium Stage = Clinoptilolite zeolite bed, 25 ft³

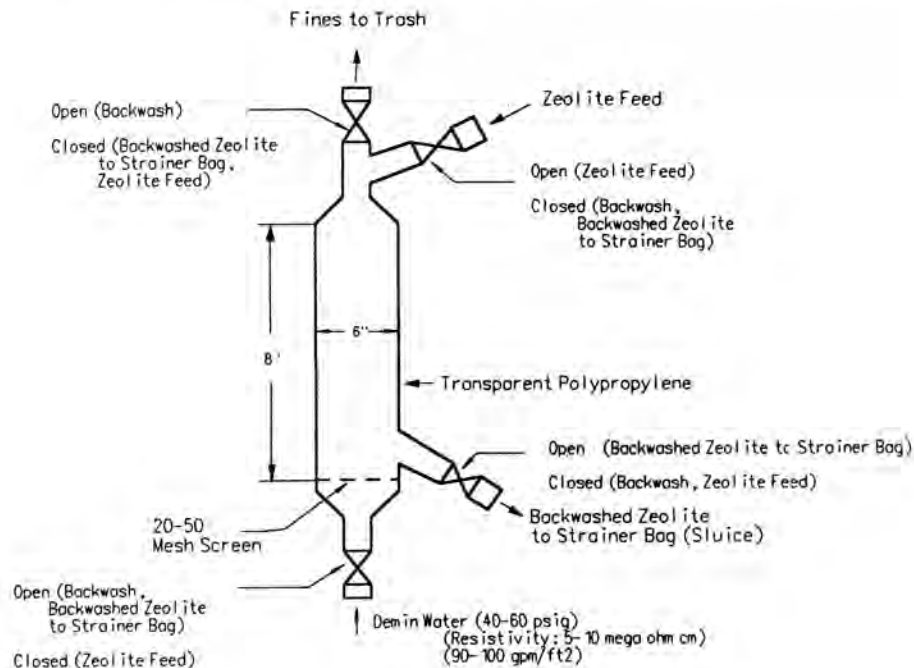


Fig. 4. Zeolite backwash column used at Duke Power Co.

TABLE VIII

Bed Expansion Characteristics and Flow Rate
For Backwashing Clinoptilolite Zeolite at
Epicor, Inc. Laboratory

% Bed Expansion	Flow Rate, GPM/Ft ²	
	Producer "A"	Producer "B"
25	8.52	13.50
50	14.91	20.80 (18.6)*
75	18.40	26.20
100	24.00	32.20 (31.6)*

3. Transition Metals Stage = Cation Exchange Resin Bed, 25 ft³

4. Iodine Stage = Anion Exchange Resin bed, 25 ft³

All three DPC nuclear stations - McGuire, Catawba and Oconee - have adopted the above staged approach in processing liquid radwaste and have found it satisfactory. Bench tests of various media configurations carried out at MNS in 1991 before full scale application at that station confirmed that the above processing scheme had merit. The results showed that the processing scheme is a significant improvement over the previously used scheme at MNS in both radionuclides removal and service life. The previous scheme at MNS involved cation beds upstream of mixed beds. The MNS 1991 bench scale column test results also determined that if the cation exchange resin in Stage 3 above is a macroreticular, high capacity strongly acidic cation exchange resin, and 20% crosslinked, the overall radionuclide removal (particularly cobalt) could improve significantly. The vessels for each stage in the full scale processing contain only one unlayered, unmixed bed of ion exchange or adsorbent material. Since the implementation of clinoptilolite, MNS and CNS have had no process problems due to differential pressure caused by fines. MNS and CNS which have 200 mesh lateral screens have also not experienced loss of materials from the vessels, nor has ONS which has 80 mesh lateral screens. MNS and CNS stations have recorded the cesium concentration in the zeolite effluent below level of detection (LLD) and an average zeolite bed throughput of 45,000 gallons per cubic foot of clinoptilolite. At ONS the performance of clinoptilolite has been less than that at CNS and MNS. A recent loading of the media gave effluent results with a net cesium DF of approximately 100 and not close to the LLD levels experienced at the other two stations. Lab-scale testing at ONS showed the zeolite to perform similar to CNS and MNS. There is question whether this discrepancy is due to the zeolite or operational problems. This noted difference is currently under evaluation.

The following deals with DPC full scale experience with the natural clinoptilolite zeolite (Cesium Stage) at CNS, service life, media cost, dewatering and overall cost savings.

Clinoptilolite Throughput

The use of clinoptilolite zeolite in the cesium stage instead of conventional cation exchange resin has resulted in large throughputs to a cesium breakthrough. At CNS, for example, in 1991, a year after full scale use of clinoptilolite began, throughput for the bed was 45,000 gallons/ft³. The cesium

concentrations in the zeolite bed effluent were below the level of detection (LLD) until cesium breakthrough. In previous years when cation exchange resin was used in the Cesium Stage the average throughput was 10,000 gallons/ft³. Thus the zeolite lasts about 4.5 times longer. The volume of strong acid cation exchange resin required to process a certain volume of liquid radwaste would be 4.5 times that needed for clinoptilolite for similar volume of waste. Strong acid cation exchange resin costs less than clinoptilolite (approximately \$80/ft³ versus \$120/ft³). However, 50 ft³ of clinoptilolite are used per year to remove radioactive cesium from about 2,160,000 gallons of liquid radwaste at CNS. A similar figure for strong acid cation exchange resin would be 225 ft³. Consequently, 175 ft³ of cation exchange media are saved from burial by the use of clinoptilolite per year and the downstream cation bed can be kept in service until exhaustion on cobalt. The approximate total cost of burial of the media is \$420/ft³. From the foregoing, it can be calculated that each DPC nuclear station can save about \$86,500 by changing from cation exchange resin to clinoptilolite zeolite to remove radioactive cesium from liquid radwaste. The bulk of this savings is in reducing the volume of class B waste that gets buried. The total potential savings for the three DPC nuclear stations is \$256,500 per year.

Other Benefits of Clinoptilolite

Before the implementation of zeolite in the liquid radwaste process system, cation exchange resin was located immediately downstream of the carbon-based deep bed filter. Its function was to remove cesium and some cobalt. Under the present configuration, zeolite has replaced the cation exchange resin solely to remove cesium entirely from the waste stream. In this way the need on the other cation exchange resin bed downstream is reduced and the life of the bed extended.

Reduction of Dose and Curies Released Due to Use of Zeolite

By not having to sluice the cation exchange bed as often, the use of zeolite in liquid radwaste processing has contributed to the reduction of exposure to radwaste personnel. The consistent, efficient removal of cesium by the zeolite has also reduced the curies released to the environment.

Clinoptilolite Zeolite Dewatering

There are a number of proprietary methods available for dewatering zeolites alone or mixed with other granular or powdered materials.

CONCLUSION

Natural clinoptilolite zeolite, which has been backwashed such that it has no more than 0.3% (by weight) fines passing through No. 100 U.S. Standard sieve and only 9-13% of the zeolite retained on No. 16 U.S. Standard Sieve, has been successfully used at DPC nuclear plants to remove cesium from liquid radwaste. The cesium concentration in the zeolite effluent has consistently been in the lower levels of detection (LLD). The average throughput of the zeolite bed has been 45,000 gallons of liquid waste per cubic foot of zeolite compared to 10,000 gallons (i.e., more than 4 times the throughput of cation exchange resin) of liquid per cubic foot of cation exchange resin pre-zeolite use. This translates to a total potential savings of about \$256,000 per year at the three DPC nuclear stations.

Clinoptilolite reduces the off-site dose due to cesium since the overall cesium concentration in liquid releases is minimized. It has also reduced personnel exposure and manpower requirements because the stet sluicing frequency has been reduced more than 40%.

Clinoptilolite zeolite use has its drawbacks. Fines generation during processing of the liquid radwaste can be a potential source of process troubles. Care must be taken in loading the vessel, otherwise turbulence and careless mishandling can cause fines generation. Zeolite materials can partially dissolve in liquid radwaste processed at low and high pH values. The recommended pH range is 6-8. The cited deficiencies of clinoptilolite have been successfully overcome. Zeolite use has provided positive results in radwaste liquid processing. Clinoptilolite zeolite itself has great potential to serve the industry both economically and environmentally.

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