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EVALUATION OF OPERATING CHARACTERISTICS FOR A CHABAZITE ZEOLITE SYSTEM FOR TREATMENT OF PROCESS WASTEWATER AT OAK RIDGE NATIONAL LABORATORY

T. E. Kent, J. J. Perona, H. L. Jennings,
A. J. Lucero, and P. A. Taylor

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Chemical Technology Division

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OAK RIDGE NATIONAL LABORATORY**

T. E. Kent, J. J. Perona, H. L. Jennings,
A. J. Lucero, and P. A. Taylor

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Waste Management and Remedial Action Division

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ABSTRACT

Laboratory and pilot-scale testing were performed for development and design of a chabazite zeolite ion-exchange system to replace existing treatment systems at the Process Waste Treatment Plant (PWTP) at Oak Ridge National Laboratory (ORNL). The process wastewater treatment systems at ORNL need upgrading to improve efficiency, reduce waste generation, and remove greater quantities of contaminants from the wastewater. Previous study indicated that replacement of the existing PWTP systems with an ion-exchange system using chabazite zeolite will satisfy these upgrade objectives. Pilot-scale testing of the zeolite system was performed using a commercially available ion-exchange system to evaluate physical operating characteristics and to validate smaller-scale column test results. Results of this test program indicate that (1) spent zeolite can be sluiced easily and completely from a commercially designed vessel, (2) clarification followed by granular anthracite prefilters is adequate pretreatment for the zeolite system, and (3) the length of the mass transfer zone was comparable with that obtained in smaller-scale column tests. Laboratory studies were performed to determine the loading capacity of the zeolite for selected heavy metals. These test results indicated fairly effective removal of silver, cadmium, copper, mercury, nickel, lead, and zinc from simple water solutions. Heavy-metals data collected during pilot-scale testing of actual wastewater indicated marginal removal of iron, copper, and zinc. Reduced effectiveness for other heavy metals during pilot testing can be attributed to the presence of interfering cations and the relatively short zeolite/wastewater contact time. Flocculating agents (polyelectrolytes) were tested for pretreatment of wastewater prior to the zeolite flow-through column system. Several commercially available polyelectrolytes were effective in flocculation and settling of suspended solids in process wastewater.

1. INTRODUCTION

Development studies were performed to support the design of a full-scale chabazite zeolite system for removal of ^{90}Sr and ^{137}Cs from ORNL process wastewater. Pilot-scale testing of the zeolite system was performed using a commercial ion-exchange system to evaluate important operating characteristics. These included determining optimum procedures for sluicing spent zeolites from the operating vessel, determining mass transfer zone (MTZ) length with near-full-scale columns, and evaluating the effectiveness of prefiltration equipment. Laboratory tests were performed to evaluate the ability of zeolite for removing heavy metals and to evaluate the performance of various polyelectrolytes in removing suspended solids from wastewater prior to zeolite treatment.

One problem that has been encountered in previous small-scale and near-full-scale column studies at the PWTP is that inadequate removal of spent zeolite from the operating column has caused "contaminant bleed." Contaminant bleed is characterized by high effluent concentrations of radioactive contaminants

after a column has been placed in service after sluicing spent media and reloading with fresh zeolite. This is caused by elution of contaminants from residual spent zeolite that was not removed from the column during sluicing. This behavior can reduce column life and result in the release of treated wastewater which exceeds ^{90}Sr discharge limits. The pilot-scale testing provided the opportunity to optimize column sluicing procedures for removal of all spent zeolite from the column.

The MTZ is the minimum depth of the zeolite required to achieve the required decontamination factor for the wastewater being treated. This was determined for small-scale columns (7.6-cm diameter, 91-cm length) in previous studies.¹ The MTZ length can vary somewhat with column geometry and design. The MTZ length was determined for pilot-scale columns in this study to validate the results of small-column tests and to determine the effect that the larger-scale column has on the MTZ length.

In small-column studies, granular anthracite prefilter columns were found to be effective in removing suspended solids from process wastewater prior to treatment with zeolite. Pilot-scale columns were loaded with the same anthracite material and used in the pilot test program to evaluate operational characteristics and effectiveness in preventing the fouling of downstream zeolite columns.

The zeolite system will eliminate the alkaline-softening process currently used at the PWTP. As a consequence, the trace concentrations of heavy metals which would normally precipitate in the softener will not be removed from the wastewater. Most heavy metals are expected to precipitate, to some degree, at near-neutral pH and be filtered from the wastewater or sorbed onto activated carbon. With the potential for more restrictive discharge limits for heavy metals imposed by the Clean Water Act, the Nonradiological Wastewater Treatment Plant (NRWTP), which treats the wastewater discharged from the PWTP, may have difficulty complying with future discharge permits. Laboratory studies were performed to determine the ability of zeolite to remove these metals from process wastewater. Heavy-metals data was also collected during the pilot-scale testing to evaluate and compare the removal performance for selected heavy metals with laboratory test results.

This report summarizes pilot-plant testing and laboratory studies that were performed in FY 1994 to support zeolite system development and provide design data for the FY 1996 line-item capital project Process Waste Treatment Facility (PWTF) to replace the PWTP.

Wastewater clarification will be a necessary, along with granular prefilters, to prevent fouling and plugging of the zeolite columns. Use of a flocculating agent (polyelectrolyte) will be necessary to facilitate the settling and removal of suspended solids from the wastewater. The current PWTP uses a polyelectrolyte as an additive for the softening process; however, the chemical conditions will be different when zeolites are employed and this polyelectrolyte will not be effective. To identify a new polyelectrolyte for wastewater pretreatment, a laboratory-scale test program was performed.

2. BACKGROUND

2.1 DESCRIPTION OF THE EXISTING PWTP

The PWTP currently uses a chemical water-softening process followed by ion exchange using Dowex HCR-S (Dow Chemical Co.) strong-acid cation resin for removal of radioactive ^{90}Sr from process wastewater. A process flow diagram is shown in Fig. 1. Process wastewater, which consists of

Fig. 1. Existing PWTP process flow diagram.

groundwater, once-through process cooling water, evaporator condensate, and laboratory wastewater, is collected in the two Bethel Valley Storage Tanks (BVST), each with a capacity of 1.32×10^6 L (350,000 gal). Table 1 summarizes the typical composition of PWTP feed process wastewater. The primary radioactive contaminants of the wastewater include ^{90}Sr and ^{137}Cs at concentrations of about 750 and 350 Bq/L, respectively. The wastewater is generated and treated at an average flow rate of 8.8 L/s (140 gal/min). The minimum flow of wastewater is 5 L/s (80 gal/min). The current maximum treatment capacity is 14.5 L/s (230 gal/min), though near-term upgrades will increase the capacity to 22 L/s (350 gal/min). In the current operation, the wastewater first enters the softener/clarifier unit where the pH is elevated to 11.5, causing calcium, magnesium, and strontium compounds to precipitate. Flocculants are added to enhance settling, and the precipitates are separated by sludge-blanket clarification. The sludge consists primarily of calcium carbonate, magnesium hydroxide, smaller quantities of other precipitated metals, and 80 to 90% of the influent ^{90}Sr . It is dewatered in a recessed plate filter press and drummed for storage. The wastewater effluent from the softener/clarifier is routed through granular anthracite filters and ion-exchange columns containing the Dowex resin. The Dowex removes the remaining ^{90}Sr to a concentration below the discharge limit of 37 Bq/L. The PWTP also uses an auxiliary zeolite system to treat process wastewater when the generation rate of the wastewater feed exceeds the treatment capacity of the softening process. The flow capacity of this zeolite system is about 5 L/s (80 gal/min). Due to design limitations, the auxiliary zeolite system is inefficient to operate and is used infrequently. After ion-exchange treatment, the PWTP effluent flows to a basin for pH adjustment and transfer to the NRWTP for removal of trace organic contaminants. The NRWTP effluent is discharged to the environment.

2.2 BENEFITS OF THE ZEOLITE SYSTEM

In previous development studies, many different flowsheets were evaluated for improved treatment of process wastewater.² The chabazite zeolite system was chosen because of the many process advantages it offers from the standpoint of waste reduction, economics, safety, environmental protection, and operating simplicity.

The PWTP currently generates significant quantities of radioactive secondary solid and liquid wastes. The softening process generates approximately 146 m³ of filter cake each year. From regeneration of the Dowex resin with nitric acid, about 28,400 L (7500 gal) of concentrated spent nitric acid is generated each year. Both these secondary wastes are being stored for later disposal. The auxiliary zeolite system generates about 23 m³ (800 ft³) of spent zeolite per year. The spent nitric acid, which falls in the category of liquid low-level waste (LLLW), will be particularly difficult and expensive to dispose of. It is now being stored in underground storage tanks with other highly concentrated LLLW. Future processing will likely involve additional separations and stabilization in grout, which could cost more than \$10.50/L (\$40/gal) for nontransuranic supernate liquids or as much as \$158/L (\$600/gal) for tank sludges which contain transuranic isotopes.³ Because of limited storage capacity and costs for LLLW treatment, the new treatment method for process wastewater must reduce or eliminate LLLW generation. Zeolite is nonregenerable and will be disposed of as a solid waste. The waste zeolite meets the criteria for on-site disposal on the Oak Ridge Reservation, which significantly reduces disposal costs. The volume of spent zeolite expected to be generated each year is about 90 m³ (3000 ft³), which is more than 40% less than the volume of softener sludge and spent zeolite currently generated. Assuming on-site disposal costs of about \$1400/m³ for solid low-level waste, a cost savings of \$112,000/year could be realized from solid-waste disposal costs alone. Replacing the existing PWTP

Table 1. Typical composition of PWTP influent wastewater^a

Radionuclides, Bq/L		Metals, mg/L	
Gross alpha	5	Ag	<0.005
Gross beta	1000	Al	0.23
⁹⁰ Sr	750	As	<0.05
¹³⁷ Cs	350	B	<0.08
⁶⁰ Co	25	Ba	0.032
¹⁵² Eu	30	Be	<0.0003
¹⁵⁴ Eu	8	Ca	39
¹⁵⁵ Eu	5	Cd	<0.005
¹⁰⁶ Ru	10	Co	<0.004
Other components, mg/L		Cr	0.016
		Cu	0.018
		Fe	0.4
		K	1.0
		Li	0.003
		Mg	8.0
		Mn	0.069
		Mo	<0.04
		Na	14
		Ni	<0.01
		P	0.85
		Pb	<0.05
		Sb	<0.05
		Se	<0.05
		Si	3.1
		Sn	<0.05
		Sr	0.10
		Ti	<0.02
		V	<0.002
		Zn	0.08
Alkalinity	112		
SO ₄	21		
Cl	9		
NO ₃	5.3		
F	0.8		
PO ₄	2.1		
TOC	1.9		
TDS	250		
TSS	80		

^aThe pH is in the range of 7.5 to 9.0. TOC = total organic carbon; TDS = total dissolved solids; TSS = total suspended solids. Alkalinity is measured as CaCO₃.

processes with the chabazite zeolite system completely eliminates generation of LLLW. The PWTP spent nitric acid LLLW contains significant quantities of calcium salts which form insoluble sludges upon pH elevation. These sludges increase the volume of Melton Valley Storage Tank (MVST) transuranic sludges, which will be much more expensive to treat and dispose of. Conservatively assuming that the spent nitric acid is stabilized as a non-TRU grout which is disposed of on site, the yearly cost of treatment and disposal would be about \$360,000. Combined with the solid LLW disposal savings, the total savings from reduced secondary wastes is about \$472,000 per year.

The PWTF zeolite operation will eliminate the ion-exchange regeneration, nitric acid recovery, and softening processes currently used at the PWTP. Eliminating these processes will virtually eliminate the handling of concentrated nitric acid and greatly reduce the quantities of concentrated sulfuric acid and sodium hydroxide used at the facility. Consequently, the potential for worker exposure to these hazardous materials will be greatly reduced.

The PWTP softening process and subsequent pH adjustment of the wastewater currently adds significantly to the concentration of dissolved sulfate and nitrate salts in the wastewater effluent. Although regulatory limits have not been imposed, it is known that high salt concentrations can significantly impact the quality of the aquatic environment. By eliminating the softening process and reducing the pH adjustment requirement, the zeolite operation will significantly reduce the concentration of dissolved salts and improve effluent water quality.

The zeolite system also simplifies the PWTP treatment operation by eliminating the softening process, ion-exchange regeneration process, nitric acid recovery process, and several chemical makeup processes and by reducing the frequency of filter press operation. The only added unit operation involves dewatering the exhausted zeolite prior to disposal. Simplifying this operation may result in cost savings from reduced chemical, utility, and manpower requirements.

2.3 DESCRIPTION OF THE ZEOLITE SYSTEM

The zeolite will remove both strontium and cesium, though the throughput to exhaustion for the system will be governed by strontium breakthrough. Compared with the Dowex resin, strontium uptake by the zeolites is relatively slow. Removal effectiveness and efficiency will be improved by reducing the superficial velocity of the wastewater, increasing residence time in the zeolite bed, and using several columns piped in series. The system will include three columns piped in series, with each column designed for a maximum flow of 22.1 L/s (350 gal/min). A flow diagram for this system is shown in Fig. 2. The initial treatment of the wastewater will involve clarification and filtration to prevent plugging and channeling of the zeolite columns. The zeolite system will be operated using two columns piped in series with a third on standby. When strontium in the effluent reaches the allowable discharge limit, the lead column is taken off line and reloaded with fresh zeolite. The second column in the original configuration is moved to the lead position, and the standby column containing fresh zeolite is placed in the lag position downstream of the former lag column. The spent zeolite will be transferred to a dewatering bin, where the bulk of the free water will be drained through a screen at the bottom of the bin. The dewatered zeolite will then be transferred to a disposal container in which the zeolite will be further dewatered to meet disposal criteria.

3. PILOT PLANT TESTS USING A COMMERCIAL ION-EXCHANGE SYSTEM

Larger-scale pilot testing was necessary to evaluate physical operating parameters and to validate the Results of laboratory and small-column studies. In January 1993, procurement specifications were developed for purchase of a 1/10 full-scale ion-exchange system with which to demonstrate several aspects of the chabazite zeolite application. Specific areas of development included (1) developing sluicing procedures for spent zeolite, (2) determining if contaminant bleed would be a problem for large-scale columns, (3) validating MTZ length obtained from previous small-column tests, and (4) evaluating the performance of granular anthracite prefilters.

Fig. 2. ORNL process waste treatment facility with zeolite system.

Initial responses from the potential vendors included a proposal to lease a commercial ion-exchange system which was specifically designed with zeolite application in mind. This system, designed and constructed by Chem Nuclear Systems, Inc., for nuclear power plant wastewater treatment, was leased and delivered to ORNL in September 1993. A flow diagram for the system is shown in Fig. 3. The system consists of three 0.91-m (36-in.)-diam. stainless steel tanks, 0.85-m³ (30-ft³) capacity columns, and a pump/control skid. The columns are designed for down-flow ion exchange or granular media filter applications and are equipped for backwashing, air sparging, flow control, flow totalizing, and sluicing of media into and out of the columns. Two of the columns are used as prefilters and were loaded with granular anthracite, while the third column is loaded with TSM-300® natural chabazite zeolite. The system has a process wastewater influent and an effluent header with tie-in for service water and service air. The pump/control skid is housed in a shelter to protect the electrical and electronic components of the control system. The system also includes pressure indicators, sample ports, and a pressure relief valve. Bypass valves are provided so each column can be taken out of service when it is not needed. Capability is provided to backwash the media in all three columns.

3.1 SYSTEM DESCRIPTION

The Chem Nuclear system, referred to as the Zeolite Demonstration System (ZDS), was initially assembled on site at the ORNL BVST facility. The system was connected to one of the two 12.2-m (40-ft)-diam., 1.32×10^6 -L (350,000-gal) collection tanks used as a surge/feed tank for the PWTP. During normal operation, process wastewater is continuously collected in one of the tanks at a rate of about 8.8 L/s (140 gal/min) and allowed to equalize before transferring to the PWTP for treatment. The physical layout for the system is shown in Fig. 4. The influent connection point for the ZDS was located at a tap normally used for continuous pH monitoring. The ZDS return connection was installed on the same tank at a bottom drain fitting located 120 degrees circumferentially from the influent connection. The two columns to be used as prefilters were connected in parallel such that either could be in service while the other was being backwashed. The column to be used for the zeolite was located downstream from the prefilter columns. The flow indicator/totalizer was installed downstream from the zeolite column so that its operation would not be compromised by suspended solids in the feed wastewater. Since a significant source of filtered wastewater or tap water was not available, the backwash system was designed for backwashing the columns using system feed wastewater. It was decided that backwashing with system feed would not be detrimental due to the low concentrations of suspended solids and the short duration of contact with the zeolite and filter media.

The unit was successfully leak tested at 5.5×10^5 Pa (80 psig) using clean service water. The two prefilter columns were then loaded with granular anthracite and the other column with zeolite. The anthracite columns were loaded with 0.57 m³ (20 ft³) of media, while the zeolite column received 0.43 m³ (15 ft³) of chabazite zeolite sized to 20 × 50 Tyler mesh (0.841- to 0.297-mm diameter). This media was introduced to the columns by pouring it as a dry material through the top access port of the columns. The media was then backwashed to remove excess fines. This backwash was conducted using process wastewater at a flow rate of approximately 3.2 L/s (50 gal/min). One prefilter column and the zeolite column were then placed into service as Run No.1 began on December 20, 1993, at 9:00 a.m. The system was operated at a flow rate of 1.26 L/s (20 gal/min) to coincide with the flow per unit area used in previous small-scale column tests.

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Fig. 4. Layout of the Zeolite Demonstration System.

3.2 PROCESS MONITORING

The flow control system for the ZDS was equipped with audible alarms and also an automatic system shutdown in the event of low flow. This allowed for unattended operation of the system. Wastewater sampling and recording of operating data by engineering technicians were performed every 12 h. Column backwashing was performed manually when pressure drop across a column reached 6.9×10^4 Pa (10 psi). Operating parameters recorded included flow rate, total throughput, wastewater pH, pressure drop across each column, and operating status of the collection tank.

Samples of plant feed, filter column effluent, and zeolite column effluent were collected every 12 h. These samples were submitted to the ORNL Analytical Chemistry Division for analysis of total beta emitters (gross beta), which was primarily ^{90}Sr , and Inductively Coupled Plasma (ICP) metals scan, which included the major interfering cations for zeolite (Ca, Mg, Na, and Sr) and most heavy metals (Ag, As, Cd, Cr, Cu, Fe, Ni, Pb, Se, and Zn). Heavy-metals concentrations were determined to evaluate the affinity of the zeolite for these metals under actual operating conditions.

3.3 SYSTEM OPERATION—EXHAUSTION CYCLE 1

The initial test, designated EC1, took place during a period of very cold weather. Since the demonstration project was located outdoors and exposed to these cold temperatures, it was decided that heat-tracing and insulation should be installed on lines leading to and from the columns. Dead-legs in the system were of special concern in this regard. On one occasion prior to heat tracing, with the system shut down and empty of wastewater, an end coupling for one of the hoses froze and cracked where a pocket of water had collected. The system was also shut down intermittently due to heavy rain which accumulated in the diked area, making access to the system impossible. Despite the weather conditions, however, the system operated extremely well. No problems were encountered with the pump, piping, hoses, valving, or control system of the ZDS. A total of $2.4\text{E}+06$ L [5633 bed volumes (BV)] of process waste was processed during EC1. Scheduled backwashing of the prefilter and zeolite columns was not necessary during normal operation due to the low solids content of the influent wastewater and low pressure drop across the media beds. Backwashing was instead performed on an as-needed basis when the pressure drop across the prefilters approached $6.9\text{E}+04$ Pa (10 psi). The BVST collection tank jet mixer was not energized during the run due to the limitations of filtration systems at the PWTP. This allowed for some clarification of the wastewater within the tank. The pressure drop across the clean anthracite prefilter at the beginning of the run was between $6.9\text{E}+03$ and $1.38\text{E}+04$ Pa (1 and 2 psi), which was difficult to measure due to the wide pressure range (0 to $6.9\text{E}+05$ Pa) for the inlet and outlet pressure gauges. At a throughput of $2.27\text{E}+06$ L (5341 BV), the pressure drop across the prefilter had gradually increased to $8.3\text{E}+04$ Pa (12 psi). The zeolite column pressure drop was too low to measure for throughputs ranging from zero up to $1.89\text{E}+06$ L (4441 BV). From 4441 BV through the end of the run at 5633 BV, the pressure drop for the zeolite column increased to $2.1\text{E}+04$ Pa (3 psi). The ZDS anthracite prefilter required backwashing on only one occasion during the run.

Column breakthrough data is shown in Fig 5. For the graph, each data point for the feed wastewater gross beta was averaged with the previous three data points to dampen the fluctuation in concentration and give an improved indication of breakthrough. The gross beta concentration of the wastewater was effectively reduced to acceptable levels during the first several days of operation. On the third day, a sudden increase in gross beta concentration occurred at a throughput of 591 BV. During the next 48 h,

Fig. 5. Breakthrough data for Exhaustion Cycle 1.

the gross beta concentration gradually decreased to acceptable levels. At a throughput of $6.7\text{E}+05$ L (1580 BV), the fractional breakthrough (effluent gross beta concentration/influent gross beta concentration) began to increase to a consistent level of 30 to 40%, where it remained until the throughput of the system reached $1.96\text{E}+06$ L (4630 BV). At this point, the effluent gross beta suddenly increased to levels that far exceeded the influent concentration. Gross beta concentrations gradually fell to levels corresponding to 40 to 50% breakthrough, at which point the test was terminated at a throughput of $4.2\text{E}+06$ L (5630 BV).

At the conclusion of EC1, the spent zeolite was sluiced from the zeolite column using the operational procedure developed by the vendor. The sluicing procedure was preceded by backwashing the zeolite to fluidize the bed and break up any agglomerated media. The media was sluiced from the bottom of the column by first introducing a mixture of wastewater and air into the column through the outlet collector while opening the bottom sluice port to allow it to be forced into a waste disposal container. During the sluicing procedure, the media exiting the column was observed through a sight glass installed on the bottom sluice port. When zeolite was no longer visible in the sight glass, the column valving was changed to divert the flow to the top of the column through the inlet distributor. This removed media from the walls and internals by washing it to the bottom of the column and out of the sluice port. The column was then purged with air until empty. This was followed by several alternating water flushes and air purges while observing the sight glass on the sluice line. When the liquids leaving the column were free of suspended zeolite, the sluice was considered complete. Following the sluice, the column access port on top of the vessel was opened for visual inspection. The column internal surfaces were found to be free of all spent zeolite except for a few particles which had settled on top of the small, flat inlet diffuser plates. It is worthy to note that the sluicing operation could be stopped and restarted at any point in the operation, even if the sluice hoses were filled with zeolite slurry. The zeolite would remobilize easily upon reestablishing the water flow to the column.

3.4 SYSTEM OPERATION—EXHAUSTION CYCLE 2

Although the zeolite sluicing operation was very successful after EC1, there remained the potential that the small amount of residual zeolite, perhaps not detected during the visual inspection, could cause contaminant bleeding into the column effluent. To investigate further, the column effluent was sampled on a more frequent basis after loading with fresh zeolite and placing the column back in service for the second exhaustion cycle. Results of the initial sampling showed no evidence of column breakthrough. Gross beta concentrations were reduced to levels equal to or less than those from EC1, which began with clean equipment.

As in the first test, the second test (EC2) was also shut down intermittently due to heavy rain which accumulated in the diked area. At one point, the system was shut down for an entire month to allow rainwater to be pumped from the containment. Once again, no equipment problems were encountered. A total of about $5.9\text{E}+06$ L (14,000 BV) was processed during EC2, though part of this throughput was accumulated during recirculation of the tank contents. By deducting the approximate volume of water recirculated, the actual throughput processed is about $3.8\text{E}+06$ L (8900 BV).

A significant amount of suspended solid material was introduced to the ZDS when the BVST collection-tank jet mixer was energized during the test. The jet mixer is designed to maintain a uniform mixture in the collection tank. The solid materials that had settled in the tank over the previous months were resuspended in the wastewater at a high concentration. The solids broke through the prefilters and

collected in the zeolite column, causing a high pressure drop across both columns of up to $1.2\text{E}+05$ Pa (17 psi) for the prefilter and $5.5\text{E}+05$ Pa (8 psi) for the zeolite column. Frequent backwashing of both prefilters and the zeolite column was necessary to maintain adequate flow through the system. The suspended solids in the wastewater also caused high pressure drop across the column collector screens during the backwash cycle. This led to inadequate backwash flow and accumulation of solids in the columns. Air and water were forced through the screens in upflow and downflow directions in an effort to clear the screens. Repeating this procedure several times seemed to clear the screens sufficiently to allow moderate backwash flow and a reduction in column pressure drop. The ZDS was shut down temporarily to allow displacement of the high solids content wastewater in the collection tank. After this delay, system operations improved with lower column pressure drop and less frequent backwash cycles.

The high solids content of the wastewater and breakthrough of the prefilters during EC2 caused the zeolite to bind together in a somewhat gelatinous state. Under these conditions, the zeolite could not be sluiced from the column using the Chem Nuclear procedure, even after repeated efforts. It was necessary to remove the lid from the vessel and use water pressure from a garden-type hose to break up the zeolite, which was then pumped from the column using a diaphragm pump. This situation is not expected to be encountered in a full-scale system and was therefore deemed not to be a systematic or procedural failure for this test. For the intended future application, adequate clarification and prefiltering will be provided to eliminate the possibility of a solids buildup on the zeolite bed.

Breakthrough data for EC2 is shown in Fig. 6. Early in the test, heavy rainfall and subsequent collection of water in the containment area prevented sampling of the system for several days, starting at a throughput of about $2.5\text{E}+05$ L (600 BV). The contour of the containment prevented water from collecting around the test system, so operation of the system continued. Sampling resumed at a throughput of about $7.6\text{E}+05$ L (1800 BV). A sudden drastic increase in effluent gross beta concentration occurred at a throughput of $1.8\text{E}+06$ L (4200 BV). This behavior was consistent with data collected during EC1 where a similar drastic breakthrough was indicated at a throughput of $2.0\text{E}+06$ L (4630 BV). However, the fractional breakthrough declined rapidly over the next several days to a level of less than 30%. Upon investigating the concentrations of other cations in the effluent wastewater (whose analytical results were several weeks behind the radiochemical results), it was discovered that an increase in sodium concentration from 16 to 130 mg/L coincided with the sudden 240% fractional breakthrough. It is well known that sodium concentration strongly influences the equilibrium between the zeolite and other cations in the wastewater.⁴ In this case, the increase in sodium concentration caused elution of contaminants from the zeolite, resulting in high-effluent gross beta concentrations. The exhaustion cycle was continued until the sodium perturbation passed. At a throughput of $2.5\text{E}+06$ L (6000 BV), a steady decrease in the gross beta concentration for the system feed was noted. This behavior was due to the diversion of the wastewater feed to the alternate BVST collection tank, resulting in recirculation of wastewater in the ZDS feed tank and the subsequent exponential decay curve. The process waste feed was diverted back to the ZDS feed tank at a throughput of about $4.9\text{E}+06$ L (11,500 BV). Final breakthrough was confirmed at a throughput of $5.1\text{E}+06$ L (12,000 BV). Upon review of other cation data for EC1, it was discovered that a similar sodium concentration increase occurred at a throughput of $2.0\text{E}+06$ L (4630 BV). The gross beta increase at this throughput was mistaken for actual breakthrough, and EC1 was terminated prematurely. Sodium concentration data is shown along with breakthrough data in Figs. 7 and 8. As shown in these plots, the sodium concentration profile and effluent gross beta profile are closely related.

Fig. 6. Breakthrough data for Exhaustion Cycle 2.

Fig. 7. Sodium concentration and effluent gross beta concentration for Exhaustion Cycle 1.

Fig. 8. Sodium concentration and effluent gross beta concentration for Exhaustion Cycle 2.

Based on this behavior, it will be important that the sodium concentration of the plant feed wastewater be monitored and carefully controlled to avoid sudden variations. Sources of high-sodium wastewater additions include PWTP filter backwash and building sump recycle streams. Since the use of sodium hydroxide for softening and pH adjustment will not be necessary for the zeolite system, sodium additions for the PWTF wastewater are not expected to be high enough to cause elution of contaminants from zeolite.

3.5 SYSTEM OPERATION—EXHAUSTION CYCLE 3

After sluicing the agglomerated zeolite from EC2, the column was reloaded with zeolite and backwashed according to procedure for removal of fines before starting the next run. The final test, EC3, was undertaken only to verify removal of all spent zeolite from the filter vessel during sluicing after EC2. This data was collected to verify that removal of all visual amounts of spent zeolite would be sufficient to prevent contaminant bleed into the column effluent. EC3 was not conducted over a period of time sufficient for breakthrough of strontium. A total of 3601 BV of process wastewater was pumped through the system during this run. Sluicing of the spent zeolite using the procedure provided by Chem Nuclear was successful in this case without manual sprays and pumping. The two anthracite prefilter columns were also sluiced using this procedure. No difficulty was experienced during prefilter sluicing even though they were exposed to very high solids loading during EC2.

Prior to EC3, the collection-tank jet mixers were deenergized to accommodate process needs at the PWTP. As a consequence, column pressure drop remained low and very few backwash cycles were necessary.

Effluent gross beta data for EC3 are shown in Fig. 9. As indicated by the data, there is no evidence of contaminant bleed into the zeolite column effluent. Gross beta concentrations are equal to or below those experienced during EC1, which was begun with clean equipment.

3.6 EQUIPMENT RECOMMENDATIONS

A helpful addition for this application would be to have on-line monitoring of wastewater pH and conductivity. It has been shown in other studies and in this study that increases in sodium concentration can adversely affect the performance of the zeolite for loading of strontium and cesium. The pH of our influent process wastewater increased during operation due to high levels of sodium hydroxide introduced to the feed tank from the PWTP. This is not expected to occur when the new plant is in service due to reduced acid/base requirements for the treatment. However, on-line pH/conductivity monitors would assist in troubleshooting should these salts be added from other feed sources. As noted above, difficulty with backwashing occurred when the collector screens plugged during the backwash procedure after being loaded with high solids from the influent waste. Removing these solids from the back side of the collector screen was somewhat time-consuming and laborious. Another recommended addition to the system would be a cleanout port in the discharge pipe at its lowest elevation as it exits the column. This would facilitate removal of solids that clog the back side of the collector screens.

The site glass installed on the column sluice outlet pipeline was invaluable in determining completion of the sluice operation. It is strongly recommended that this be included in the design of the full-scale system. Full-open ball valves were used on the sluice line to minimize pipeline obstructions. It should

Fig. 9. Influent and effluent gross beta data for Exhaustion Cycle 3.

be noted that pipeline plugging was not a problem, even when the sluice was temporarily halted with the transfer line filled with sluiced zeolite. The zeolite that settled in the transfer line remobilized easily once the flow of sluice water was resumed.

3.7 MASS TRANSFER ZONE LENGTH

An important objective for the pilot testing was to determine the length of the MTZ and compare it with MTZ lengths determined from smaller scale column tests. At any time in the loading process, a column can be divided into three zones: a saturated zone, a MTZ, and an unused zone. The solid loading in the MTZ is near saturation in the direction of the water inlet end of the column and near zero toward the outlet end. The MTZ moves down the column during loading, and breakthrough occurs when it reaches the end of the column. Ideally, the MTZ will occupy a relatively short fraction of the column length so that nearly all of the column is saturated at the time of breakthrough, when the column must be taken off stream and loaded with fresh zeolite. Experiments using 7.6-cm-diam columns gave strontium MTZ lengths ranging from 10 to 30 cm, depending on wastewater velocity. The Rosen long-bed solution adequately predicted these MTZ lengths in an earlier study.¹ The long-bed solution of Rosen is a simpler model which accounts for both equilibria and flow rate variations. This model was used to determine MTZ length for the ZDS column using the data collected in EC2.

Rosen solved the partial differential equations for unsteady-state column adsorption for the case of a linear isotherm. A study of the equilibria of the present five-component system showed that the distribution coefficients for strontium and cesium were constant even when their concentrations were increased by several orders of magnitude, provided the calcium and sodium concentrations were constant.⁵ The Rosen solution for long beds is shown in Eq. (1) as follows:

$$\frac{C_A}{C_{Ao}} = \frac{1}{2} \left[1 + \operatorname{erf} \left(\frac{(3Y/2X) - 1}{2 \sqrt{v/X}} \right) \right] , \quad (1)$$

where

$$X = \frac{3D_A K_D \rho_S (1 - \epsilon) Z}{\epsilon U_z R^2} \quad (\text{bed-length parameter}) , \quad (2)$$

$$v = \frac{D_A K_D \rho_S}{R k_f} \quad (\text{film resistance parameter}) , \quad (3)$$

and

$$Y = \frac{2D_A}{R^2} (t - Z/U_z) \quad (\text{contact-time parameter}) . \quad (4)$$

NOTATION

- C_A = concentration of strontium in liquid (Bq/L or meq/L)
 C_{Ao} = concentration of strontium in feed stream (Bq/L or meq/L)
 D_A = diffusivity of strontium in pellet (cm²/s)
 k_f = mass transfer coefficient at pellet surface (cm/s)
 K_D = equilibrium distribution coefficient
 R = pellet radius (0.0285 cm)
 t = time (s)
 U_z = interstitial liquid velocity (cm/s)
 X = bed length parameter (dimensionless); see Eq. (2)
 Y = contact-time parameter (dimensionless); see Eq. (4)
 Z = bed length (cm)
 ϵ = void fraction in bed (0.4 dimensionless)
 v = film resistance parameter (dimensionless)
 ρ_s = solid density (1150 g/L)

The following steps were used to determine MTZ length for EC2.

1. The superficial velocity through the bed is calculated ($U_2\epsilon$).

bed diameter = 3 ft
 area (A_c) = $(\pi/4)(3)^2 = 7.07 \text{ ft}^2$ or 6570 cm^2
 flow rate = 20 gal/min or $1260 \text{ cm}^3/\text{s}$
 velocity = $1260/6570 = 0.192 \text{ cm/s}$

2. The mass transfer coefficient is calculated. From a study by Robinson,⁴ the mass transfer coefficient (k_f) was determined to be 0.006 cm/s at a lower velocity of 0.0914 cm/s.

k_f is proportional to $Re_p^{1/3}$ for pellet radius = 0.0285 cm (avg) and velocity = 0.0914 cm/s,
 $k_f = 0.006 \text{ cm/s}$.

$$\frac{k_f}{0.006} = \left(\frac{0.192}{0.0914} \right)^{1/3} \quad (5)$$

Since the pellet radius is the same, the Reynolds number varies only with velocity.
 $k_f = 0.00769 \text{ cm/s}$.

3. K_D is determined. A log-log plot of K_D versus total salt concentrations in solutions from other zeolite treatment studies gives a fairly straight-line relationship (shown in Fig. 10). To estimate K_D for this case, total salt concentration for the wastewater of EC2 was estimated, and the corresponding K_D was determined from the graph. From the graph, $K_D = 10.2 \text{ L/g}$.

Fig. 10. Strontium distribution coefficient versus total equivalent salt concentration.

4. A time or position in the bed is chosen to calculate the length of the MTZ. The Rosen solution is valid only for "long beds," so a position near the end of the bed is chosen. For the present example, breakthrough occurs at about 3×10^6 L. At a flow rate of 1.26 L/s (20 gal/min), the corresponding time is about 40,000 min. Let us choose $t = 30,000$ min, or 1.78×10^6 s.

The parameter ratios that occur in the Rosen long-bed solution can be simplified as follows:

$$\frac{Y}{X} = \frac{2\epsilon U_z \left(t - \frac{z}{U_z} \right)}{3K_D \rho_s (1 - \epsilon)z} \quad (6)$$

$$\frac{v}{X} = \frac{\epsilon U_z R}{3k_f(1 - \epsilon)z} \quad (7)$$

The strontium diffusivity in the pellet (D_A) drops out of the ratios.

5. An expression is obtained for $v/X = f(z)$.

$$\frac{v}{X} = \frac{\epsilon U_z R}{3k_f(1 - \epsilon)z} = \frac{(0.192)(0.0285)}{3(0.0077)(0.6)z} = \frac{0.395}{z}$$

6. An expression is obtained for $Y/X = f(z)$.

$$\frac{Y}{X} = \frac{2\epsilon U_z \left(t - \frac{z}{U_z} \right)}{3K_D \rho_s (1 - \epsilon)z} = \frac{2(0.192)(1.78 \times 10^6)}{3(10.2)(690)z} = \frac{32.4}{z}$$

7. The MTZ should be near the end of the bed for the time selected. By trial and error, the range of z values (distance along the bed) is found at the locations of the MTZ.

z (cm)	v	Y/X	Q	$\text{erf } Q$	C_a/C_{A0}
40	0.00987	0.810	1.082	0.873	0.937
45	0.00878	0.720	0.427	0.454	0.727
50	0.00790	0.648	-0.157	-0.209	0.395
60	0.00658	0.540	-1.17	-0.901	0.0495

The length of the MTZ at this point in the bed is about 20 cm between 94% and 5%. In earlier small-column tests,⁵ the length of the MTZ between 70% and 5% breakthrough was 15 cm, which agrees reasonably well with the results obtained in the demonstration. However, the lengths of the MTZs should not necessarily be consistent between the small-column test and the demonstration test, since the feed water compositions, and therefore the K_D s, were not the same.

For a system whose equilibrium behavior is characterized by a constant K_D , such as this one, the MTZ exhibits "square-root spreading" as it moves along the bed. For example, comparing the length of the MTZ at the end of a 3-m-long bed versus a 1.5-m-long bed, the MTZ should be $\sqrt{2} = 1.414$ times as long. This is in contrast to a system with a "favorable" isotherm, where the MTZ does not spread. So when scale-up design is done for the PWTF full-scale columns from the pilot-scale data, the square-root spreading factor should be applied. Comparing the expected bed depth of 3 m for the full-scale zeolite system (1.5 m per column with two columns in series) with the bed depth for the demonstration tests (0.67 m), the ratio is $3/0.67$ or 4.5 and $\sqrt{4.5} = 2.13$. The MTZ of 20 cm is multiplied by 2.13 to obtain the MTZ length expected for the full-scale system. The result is 42.6 cm, which is only a 14% fraction of the total bed height; therefore, good zeolite utilization should be achievable for the new plant.

4. HEAVY-METALS REMOVAL BY ZEOLITE

4.1 LABORATORY EQUILIBRIUM TESTING

Laboratory testing was conducted to determine the capacity of zeolite for removal of heavy metals expected to be dissolved in process wastewater at small concentrations. As discussed in Sect. 2, in planned upgrades of the ORNL process waste system, alkaline precipitation treatments are expected to be discontinued to minimize generation of radioactive sludges. Most heavy metals are expected to precipitate, to some degree, at near neutral pH and be filtered from the wastewater or sorbed by the NRWTP granular activated carbon system. However, the NRWTP may not be capable of meeting discharge limits for such metals.

Several experiments were conducted with Ag, Cd, Co, Cu, Fe, Hg, Ni, Pb, and Zn. Previous experiments were conducted with surrogate wastewater which was spiked Ag, Ni, Pb, and Cd at a concentration of 100 mg/L. These were the only metals that would not precipitate at neutral pH at that concentration. The experiments showed that the zeolite is capable of removing significant quantities of these metals from water.⁶ Since the normal concentrations of the metals that are encountered at the PWTP are generally too low to be measured in milligrams per liter, a new series of experiments was performed using a neutral pH surrogate wastewater with concentrations of 0.5 to 1.0 mg/L of Ag, Cd, Co, Cu, Fe, Hg, Ni, Pb, and Zn. The samples were submitted to ORNL Analytical Chemistry for analysis by ICP to obtain the lower detection limits needed. The results of these experiments are described in the following.

4.2 EXPERIMENTAL PROCEDURE

Four series of experiments were conducted with slightly different methods of preparing the surrogate wastewater. A fresh surrogate solution was prepared for each series of experiments using either nitrate salts of the metals or atomic absorption standards of the metals dissolved in nitric acid. The first three series of experiments were conducted with surrogate solutions at a nominal concentration of 0.5 mg/L.

The surrogate solution for series 1 was prepared from the atomic absorption standards. The surrogates for series 2 through 4 were prepared from nitrate salts of the metals. For series 3 the pH of the surrogate solution was not adjusted to 7 so that no sodium would be added. The pH for that series of experiments was 4.0. For series 4 the concentration of the metals was increased to 1.0 mg/L.

Each individual experiment was conducted by contacting a predetermined weight of zeolite with a 30 mL aliquot of the surrogate solution in plastic 50-mL centrifuge tubes. The weights of zeolite tested were 10, 100, 500, and 1000 mg (and 2000 mg for series 3 and 4). Triplicate experiments were conducted for each weight of zeolite tested. A control (no zeolite) was used for each test. The values reported are calculated from averages of the three experiments at each weight of zeolite. Each series of experiments included measuring the nine metals mentioned (and sodium and calcium) in 16 separate samples for series 1 and 2 and 20 samples for series 3 and 4.

After contacting the zeolite with the surrogate solution for 24 h, each sample was centrifuged to remove the zeolite then decanted into a plastic sample jar. The pH was adjusted to 2.0 with 0.1 N HNO₃ prior to submitting the samples to Analytical Chemistry.

4.3 RESULTS OF LABORATORY TESTS

In general, the experiments showed that the zeolite is capable of removing each of the metals tested. A summary of the percentage of each metal removed in experiments is shown in Table 2. The removal rates for Ag and Cd appeared to be consistently high, followed by Co, Pb, Ni, Cu, Zn, and Hg. Figures A-1 through A-8 in Appendix A show loading curves for each metal except iron. Typical loadings ranged from 0.01 to 1.0 mg/g zeolite for each metal with a corresponding solution concentration of approximately 0.01 mg/L. Increased concentrations of sodium tended to decrease the amount of each metal loaded on the zeolite. The curves appear to have a large amount of scatter except for mercury, but Table 2 reveals that nearly all of each metal (except mercury) was removed with very little zeolite. Final concentrations of the metals after contact with the zeolite were generally close to detection limits. Results for copper and iron exhibited substantial scatter. Results for iron removal testing (not given in table or graphs) seemed to indicate that iron was eluted from the zeolite. Further investigation indicated that the zeolite was not completely centrifuged from the samples. A nitric acid digestion used by Analytical Chemistry may have dissolved zeolite and associated iron present in the samples, thus producing the unusual results. Additional tests are needed to evaluate iron removal and also evaluate the interference of other cations such as calcium.

4.4 HEAVY-METALS DATA FROM THE ZDS

Characterization data in Table 1 indicate that the concentrations of heavy metals in process wastewater is very low. However, for metals such as Cu, Zn, and Fe, the concentrations shown are higher than the Water Quality Standards (WQS) used by the Tennessee Department of Environment and Conservation (TDEC). Under the Clean Water Act, TDEC will be using the WQS as a basis for revising the existing National Pollutant Discharge Elimination System (NPDES) permits for wastewater treatment facilities. This means that the capacity of the zeolite for removal of these metals may become important for meeting the more restrictive discharge limits in the future permit. Another reason for

**Table 2. Equilibrium test results for removal of heavy metals
from simulated wastewater using chabazite zeolite**

Sodium concentration (mg/L)	Grams of zeolite per 30 mL of solution	Percent metal removed							
		Ag	Cd	Co	Cu	Hg	Ni	Pb	Zn
57	0.011	27.4	55.8	57.7	73.4	8.2	35.1	47.6	61.1
	0.100	95.5	100	97.9	74.0	46.2	100	100	95.4
	0.501	98.2	98.5	97.8	74.5	83.8	100	60.4	93.9
	1.002	97.4	98.0	95.8	64.0	88.6	94.4	55.4	90.1
0.0	0.010	96.4	98.0	90.8	55.0	16.5	88.0	100	76.6
	0.100	98.1	94.1	58.5	E ^a	50.1	34.6	33.3	11.4
	0.500	100	95.2	76.8	E	87.9	69.1	49.2	40.3
	1.000	100	95.2	67.4	E	87.8	56.1	46.6	49.4
5.8	0.010	97.7	100	100	100	19.0	100	100	100
	0.101	100	100	100	100	55.2	100	100	98.0
	0.500	100	100	100	94.1	85.2	100	100	96.1
	1.001	100	100	100	92.6	89.1	93.6	79.8	95.3
	2.001	100	100	98.0	92.0	92.6	85.7	100	92.4
15.7	0.010	86.1	84.1	79.5	E	7.6	75.7	52.7	71.5
	0.101	100	98.0	94.7	24.0	39.7	100	100	100
	0.500	99.1	97.5	89.2	E	82.0	91.8	100	88.1
	1.001	100	96.8	90.8	17.9	90.0	100	100	92.0
	2.000	100	97.2	87.8	8.8	93.7	94.0	100	85.9

^aE = final concentration higher than initial concentration, possibly due to dissolution of metal from zeolite matrix.

evaluating heavy-metal loading capacity of the zeolites is to ensure that heavy metals do not accumulate in the zeolite to concentrations that would cause it to become characteristically hazardous under the Resource Conservation and Recovery Act (RCRA).

During the ZDS operation, samples of the system influent and effluent were taken and analyzed for heavy metals. Only two of the RCRA-regulated metals, silver and chromium, were detectable in more than 10% of the samples. Only chromium was detected routinely, and the data shown in Figs. A-9 and A-10 in Appendix A indicate no appreciable removal of chromium from the wastewater. Iron, copper, and zinc, though not regulated under RCRA, are typically regulated in NPDES permits and are routinely detected in process wastewater. Plots of influent, filter effluent, and zeolite effluent iron, copper, and zinc are shown in Figs. A-11 to A-16 in Appendix A for the two exhaustion cycles. Table 3 gives minimum, maximum, and mean concentrations for metals which were routinely detected. Most of the metals are removed by the prefilter. The zeolite is not particularly effective in the removal

Table 3. Concentrations of heavy metals in the Zeolite Demonstration System wastewater samples

Metal	No. Detect ^a	Unfiltered wastewater			Filtered wastewater			Zeolite effluent		
		Min ^b	Max	Avg	Min ^b	Max	Avg	Min ^b	Max	Avg
Exhaustion Cycle 1										
Iron	41	0.094	2.2	0.423	0.050	1.7	0.218	0.050	1.5	0.124
Chromium	33	0.004	0.023	0.0075	0.004	0.012	0.0067	0.004	0.020	0.0069
Silver	7	0.005	0.01	0.0061	0.005	0.37	0.065	0.005	0.0075	0.0059
Copper	42	0.007	0.130	0.0286	0.007	0.410	0.024	0.007	0.094	0.012
Zinc	42	0.027	0.230	0.076	0.005	0.098	0.022	0.005	0.039	0.011
Exhaustion Cycle 2										
Iron	69	0.050	6.4	0.728	0.050	2.0	0.133	0.050	0.79	0.067
Chromium	18	0.004	0.094	0.0066	0.004	0.015	0.0044	0.004	0.019	0.0044
Silver	7	0.005	2.2	0.043	0.005	0.005 ^b	0.005 ^b	0.005	0.066	0.0061
Copper	42	0.007	0.19	0.023	0.007	0.057	0.0099	0.007	0.032	0.008
Zinc	42	0.005	0.76	0.087	0.005	0.20	0.022	0.005	0.084	0.0113

^aNo. Detect = total number of sample sets where analytical results showed at least one detectable result for any of the unfiltered, filtered, or zeolite effluent samples.

^bThe value given is the detection limit for the analytical method and not a positively identified metal concentrator.

of these metals, though the concentrations are reduced by an additional 40 to 50%. It is possible that removal efficiencies will be improved in the full-scale system, which will use a much deeper zeolite bed.

5. TESTING OF POLYELECTROLYTES FOR WASTEWATER CLARIFICATION

The PWTF will include a clarifier and dual media filters for removal of suspended solids prior to treatment through the zeolite columns. A flocculating agent (polyelectrolyte) will be used to promote settling in the clarifier. The current PWTF uses alkaline (pH=11.5) softening and flocculation with Betz 1100 anionic polyelectrolyte (Betz Laboratories, Trevose, Pa.) to remove solids and hardness compounds. The new PWTF will use clarification at a near-neutral pH to remove suspended solids from the wastewater. Laboratory-scale tests were performed to identify polyelectrolytes that could be used to clarify the wastewater.

5.1 POLYELECTROLYTE TEST PROCEDURE

Lab-scale tests were performed on a jar-test apparatus, which consists of six stirring paddles with a variable speed drive. One-liter samples of process wastewater were placed on the stirrer and mixed at 150 rpm for 10 min after the polyelectrolyte was added, then the stirring speed was reduced to 50 rpm for 1 h. The stirrer was then stopped, and the solids were allowed to settle for 10 min. Samples of water were then decanted from the top of the beaker and filtered through 0.45- μ m pore size, pre-weighed filters. The filters were dried at room temperature for 24 h, weighed again, and the solids weight calculated. For each test, one filter was wetted with deionized water and then dried the same as the others to check for weight changes in the filters. Table 4 lists the polyelectrolytes that were tested. Both Betz products are dry powders that are dissolved prior to use. The Calgon products are liquids

Table 4. Polyelectrolytes tested

Identification	Company	Description ^a
Betz 1100	Betz Labs (Trevose, Pa.)	High MW, low CD, anionic
Betz 1138	Betz Labs	High MW, high CD, anionic
Cat Flocc A	Calgon Corp. (Pittsburgh, Pa.)	Medium MW, high CD, cationic
Cat Flocc L	Calgon Corp.	Med-high MW, high CD, cationic
Cat Flocc T2	Calgon Corp.	Low MW, high CD, cationic
Pol-E-Z 652	Calgon Corp.	High MW, nonionic
Pol-E-Z 2706	Calgon Corp.	High MW, medium CD, anionic
Pol-E-Z 7736	Calgon Corp.	High MW, high CD, anionic
WT-2466I	Calgon Corp.	High MW, high CD, cationic

^aMW=molecular weight, CD=charge density.

that can be pumped directly to the point of use. For the lab-scale tests, a 0.5 wt% dilution of the polyelectrolytes was prepared. These solutions were then added to the wastewater.

5.2 RESULTS OF POLYELECTROLYTE TESTS

Samples of process wastewater were collected about twice each week from 9/15/94 through 12/28/94. Initial screening tests showed that three of the polyelectrolytes (Betz 1138, Pol-E-Z 652, and Pol-E-Z 2706) produced the best results in terms of settling time and decant clarity. Tests using various concentrations of these polyelectrolytes showed that a concentration of 0.5 mg/L was sufficient for each. These three polyelectrolytes were then tested on 15 samples of wastewater to determine if they would work dependably. Eight other wastewater samples did not contain any measurable suspended solids and were discarded.

In each of these tests all three polyelectrolytes produced large floc particles that settled rapidly and left a clear decant solution. Settling tests without any polyelectrolyte eventually gave similar decant clarity, but the settled solids were not as compact and were resuspended more easily than when polyelectrolyte was used. Figure 11 illustrates the results of the suspended solids measurements for the 11 settling tests with the highest initial solids concentrations. Generally Pol-E-Z 2706 produced a decant with a slightly lower concentration of suspended solids, but the differences between the three polyelectrolytes were minor.

Fig. 11. Results of settling tests using various polyelectrolytes.

5.3 POLYELECTROLYTE RECOMMENDATIONS

Three different polyelectrolytes (Betz 1138, Pol-E-Z 652, and Pol-E-Z 2706) successfully flocculated the solids in 15 different sample of process wastewater over a three-month period. The polyelectrolytes produce large floc particles from the suspended solids in the wastewater that settle rapidly and yield a clear decant solution. Pol-E-Z 2706 generally performed slightly better than the other polyelectrolytes, but the differences were minor. Any of these polyelectrolytes should perform well in the clarifier of the new PWTF.

6. CONCLUSIONS AND RECOMMENDATIONS

Pilot-scale testing of the zeolite system was performed to evaluate operating characteristics and to validate smaller-scale column test results. The pilot test system, leased from Chem Nuclear Systems, Inc., was installed in the containment area surrounding the ORNL BVSTs and successfully operated for three zeolite exhaustion cycles. Sluicing tests performed after each exhaustion cycle indicated that spent zeolite can be sluiced easily and completely from the zeolite vessel. Contaminants that elute from tiny quantities of residual spent zeolite left in the column (unseen during visual inspection) do not reach significant concentrations in the system effluent. The granular anthracite prefilters performed adequately when wastewater is pretreated by clarification. Breakthrough data were used to determine the MTZ length of 20 cm. This length was comparable with that obtained from small column tests, even though the distribution coefficient for the pilot test was significantly higher. These results showed that the zeolite system can be expected to perform at least as good or better than what was achievable in previous laboratory and small column studies. The pilot testing also illustrated the importance of the sodium concentration of the wastewater. The radioactive strontium concentration in the zeolite column effluent was influenced greatly by sodium concentration. Sudden increases in sodium concentration of the wastewater must be prevented; otherwise, premature breakthrough of strontium from the zeolite system could result.

Laboratory tests to determine zeolite capacity for heavy-metals removal indicate that the zeolite can remove significant quantities of heavy metals from wastewater. Heavy-metals data from pilot-scale testing also indicated removal of iron, copper, and zinc, though fractional removal efficiencies were not impressive under pilot test conditions. This was due to the greater quantities of interfering cations in the actual wastewater and also due to the much shorter wastewater/zeolite contact time compared with the equilibrium testing. Concentrations of arsenic, cadmium, lead, silver, and selenium were typically below detection limits for the pilot-scale tests, and removal efficiencies could not be determined. Since it has been shown that zeolite will remove heavy metals, it would be prudent to determine the leach resistance of such metals under the conditions used in the RCRA Toxicity Characteristic Leaching Procedure (TCLP) test. The cost of storage and disposal of the spent zeolite will be much greater if it must be managed as a mixed (RCRA and radioactive) waste. Due to the typically low concentrations of RCRA heavy metals in process wastewater, however, it is very unlikely that heavy metals will reach regulatory concentrations in the TCLP leach solutions.

Testing with samples of actual wastewater indicated that several different polyelectrolytes would be effective in removing suspended solids from process wastewater prior to zeolite treatment. Three different polyelectrolytes (Betz 1138, Pol-E-Z 652, and Pol-E-Z 2706) successfully flocculated the solids in actual samples of process wastewater.

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Appendix A
Data from Heavy-Metals Removal Study

Fig. A-1. Equilibrium isotherm for removal of silver from simulated neutral wastewater in the presence of varying sodium concentrations.

Fig. A-2. Equilibrium isotherm for removal of cadmium from simulated neutral wastewater in the presence of varying sodium concentrations.

Fig. A-3. Equilibrium isotherm for removal of cobalt from simulated neutral wastewater in the presence of varying sodium concentrations.

Fig. A-4. Equilibrium isotherm for removal of copper from simulated neutral wastewater in the presence of varying sodium concentrations.

Fig. A-5. Equilibrium isotherm for removal of mercury from simulated neutral wastewater in the presence of varying sodium concentrations.

Fig. A-6. Equilibrium isotherm for removal of nickel from simulated neutral wastewater in the presence of varying sodium concentrations.

Fig. A-7. Equilibrium isotherm for removal of lead from simulated neutral wastewater in the presence of varying sodium concentrations.

Fig. A-8. Equilibrium isotherm for removal of zinc from simulated neutral wastewater in the presence of varying sodium concentrations.

Fig. A-9. Influent and effluent chromium concentrations for Exhaustion Cycle 1.

Fig. A-10. Influent and effluent chromium concentrations for Exhaustion Cycle 2.

Fig. A-11. Influent and effluent iron concentrations for Exhaustion Cycle 1.

Fig. A-12. Influent and effluent iron concentrations for Exhaustion Cycle 2.

Fig. A-13. Influent and effluent copper concentrations for Exhaustion Cycle 1.

Fig. A-14. Influent and effluent copper concentrations for Exhaustion Cycle 2.

Fig. A-15. Influent and effluent zinc concentrations for Exhaustion Cycle 1.

Fig. A-16. Influent and effluent zinc concentrations for Exhaustion Cycle 2.

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