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**OAK RIDGE
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MARTIN MARIETTA

**Bench-Scale Treatability Studies
for Simulated Incinerator Scrubber
Blowdown Containing Radioactive
Cesium and Strontium**

**A. C. Coroneos
P. A. Taylor
W. D. Arnold, Jr.
D. A. Bostick
J. J. Perona**

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Chemical Technology Division

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INCINERATOR SCRUBBER BLOWDOWN CONTAINING
RADIOACTIVE CESIUM AND STRONTIUM**

A. C. Coroneos
P. A. Taylor
W. D. Arnold, Jr.
D. A. Bostick
J. J. Perona*

*Department of Chemical Engineering, The University of Tennessee, Knoxville.

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OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6285
managed by
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EXECUTIVE SUMMARY

The purpose of this report is to document the results of bench-scale testing completed to remove ^{137}Cs and ^{90}Sr from the Oak Ridge K-25 Site Toxic Substances Control Act (TSCA) Incinerator blowdown at the K-25 Site Central Neutralization Facility (CNF). The report presents results of bench-scale testing using chabazite and clinoptilolite zeolites to remove cesium and strontium; using potassium cobalt ferrocyanide (KCCF) to remove cesium; and using strontium chloride coprecipitation, sodium phosphate coprecipitation, and calcium sulfate coprecipitation to remove strontium.

Low-range, average-range, and high-range concentration blowdown surrogates were used to complete the bench-scale testing. The composition of these surrogates is listed in the following table. All surrogates were traced with low levels of ^{137}Cs and ^{85}Sr ; ^{85}Sr was used because it behaves the same chemically as ^{90}Sr but is less toxic and easier to analyze.

	Surrogate Compositions				
	Concentration (mg/L)				
	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Sr^{2+}
Low range	3	1	8	1	0.3
Average range	65	19	360	6	0.3
High range	400	150	7000	20	0.3

The following conclusions can be made after reviewing the experimental results.

- Additional column equilibrium testing should be done to define maximum loading of chabazite and clinoptilolite zeolites in low-range surrogates if wastewater that resembles low-range surrogate compositions will be treated at CNF. Stable cesium and strontium should be added to the surrogates.
- Chabazite and clinoptilolite zeolite are not good sorbent materials for removal of ^{85}Sr from average-range and high-range surrogates. In both surrogates, ^{85}Sr breakthrough occurred after a relatively small amount of surrogate solution was processed.

- Chabazite zeolite may be appropriate for removal of ^{137}Cs from both average-range and high-range surrogates. Further bench-scale column testing is required to determine ^{137}Cs breakthrough characteristics.
- Rapid changes from low to high sodium concentrations in CNF wastewater will cause ^{137}Cs and ^{90}Sr to be displaced from zeolite, causing a high concentration of radioactive contaminants in the effluent.
- KCCF effectively removed ^{137}Cs from a wide concentration range of salt solutions that were used for bench-scale testing.
- Strontium and calcium coprecipitation processes were not effective for ^{85}Sr removal from low-range and high-range surrogates that were at a near-neutral pH.

Before additional testing can be accomplished, some basic studies need to be completed to determine how to upgrade CNF to treat wastewater contaminated with ^{137}Cs and ^{90}Sr generated from burning Oak Ridge National Laboratory (ORNL) organic waste at the K-25 Site TSCA Incinerator. ORNL organic waste that is contaminated with ^{137}Cs and ^{90}Sr must be characterized. Future CNF influent metals and salt concentrations need to be estimated since these parameters have a significant effect on the various treatment methods tested. After the ORNL waste is characterized, the information gained from the recent TSCA Incinerator partitioning study can be used to estimate what concentration of ^{137}Cs and ^{90}Sr (as well as other potential contaminants) will be transferred to CNF in the incinerator blowdown. This information can be used to determine what treatment is necessary to meet derived concentration guideline limits for ^{137}Cs and ^{90}Sr in the CNF discharge.

Depending on what treatment is needed, the following items need to be considered:

- Chabazite zeolite may be useful for ^{137}Cs and ^{90}Sr removal, depending on the volume and composition of water contaminated with ^{137}Cs and ^{90}Sr . A study that considers the costs of equipment design, installation, and operation and the cost of

spent zeolite for final waste disposal generated might show that zeolites could be an economical treatment for small volumes of wastewater. This treatment method might fit easily into the current plant configuration.

- If chabazite zeolite were to be implemented at CNF, changes in process control at CNF or TSCA would be required to maintain a constant salt concentration in wastewater that is transferred to CNF. Swings in sodium concentration (from relatively low to relatively high concentrations) can cause ^{137}Cs and ^{90}Sr to be displaced from zeolite.
- KCCF treatment is the most promising method of ^{137}Cs removal tested. This treatment method would require further development work before it could be implemented at CNF. Further development work is necessary to determine if free cyanide left in the treated wastewater is a potential problem; if cyanide is a problem, testing of cyanide removal methods would become necessary. Further testing is also needed to optimize KCCF concentrations to minimize sludge volume and to optimize polymer addition for solids settling.
- The KCCF treatment could be implemented within the current CNF configuration if equipment for cyanide removal is not necessary. The existing polymer addition system and sludge thickener could be used. If cyanide removal is necessary, the selection of a treatment process should be based on ease of implementation.
- Previous tests have shown that ^{90}Sr can be removed from ORNL wastewaters if the wastewater can be adjusted to a high pH. If ^{90}Sr concentrations are expected to be a problem, having tank space to remove the ^{90}Sr at a high pH might be useful. Bench-scale testing would be required to determine what chemicals to use for this treatment step. The CNF process layout would have to be reviewed to determine if existing tank capacity and piping could be modified to do this or if additional tank space and piping would be needed.
- New sorbents are currently being developed by the U.S. Department of Energy Office of Technology Development that may be appropriate to treat CNF

wastewaters; these technologies should be considered if further development work is necessary.

1. INTRODUCTION

The Central Neutralization Facility (CNF) at the Oak Ridge K-25 Site is designed to remove heavy metals and uranium from various wastewaters. One of the main wastewater influents is a sodium hydroxide-based solution generated by the off-gas scrubbing system of the Toxic Substances Control Act (TSCA) Incinerator at the K-25 Site. Presently, uranium is the principal radioactive contaminant in incinerator scrubber blowdown. In the future it is anticipated that cesium (^{137}Cs) and strontium (^{90}Sr) will also be present in the incinerator blowdown as a result of incinerating Oak Ridge National Laboratory (ORNL) solid and aqueous organic wastes. An FY 1997 line item project is scheduled to enhance capabilities for removal of these radionuclides at CNF.

There are several issues to consider before the TSCA Incinerator burns ORNL organic wastes. First, it is unknown how ^{137}Cs and ^{90}Sr will partition into the blowdown which is treated at CNF. Second, CNF does not have the capability to remove ^{137}Cs and ^{90}Sr from the incinerator liquid effluents. To gain a better understanding of ^{137}Cs and ^{90}Sr partitioning, a study was performed at the TSCA Incinerator to determine how ^{137}Cs and ^{90}Sr partition into the blowdown water that is transferred to CNF.¹ This test was completed in December 1993 (ref. 2).

In June 1993 the Engineering Development Section of the Chemical Technology Division at ORNL was requested to do bench-scale and pilot-scale testing to define and demonstrate ^{137}Cs and ^{90}Sr removal methods for CNF by September 1994. Due to the accelerated schedule for development work, testing began before the TSCA Incinerator partitioning study was completed, and only demonstrated treatment methods or promising treatment methods that could be easily implemented within the limited space available at CNF were considered.

In April 1994, uncertainties associated with the incineration of ORNL wastes resulted in the inability to justify the CNF upgrades for additional radionuclide removal capability. As a consequence, development testing for radionuclide removal was brought to a close, allowing only for the completion of a limited number of bench-scale tests. The purpose of

this report is to document the results of bench-scale testing completed to date. Results are presented for bench-scale testing using zeolites to remove ^{137}Cs and ^{90}Sr ; potassium cobalt ferrocyanide (KCCF) to remove ^{137}Cs ; and strontium chloride coprecipitation, sodium phosphate coprecipitation, and calcium sulfate coprecipitation to remove ^{90}Sr from CNF wastewaters. Descriptions of the TCSA Incinerator and CNF processes, the wastewaters presently treated at CNF, the reasons for selecting the ^{137}Cs and ^{90}Sr removal methods that were tested, and the surrogates used in completing the bench-scale testing are also presented.

Details of the bench-scale testing are recorded in ORNL technical notebook A-106198-G, "CNF Studies."

2. TSCA INCINERATOR PROCESS

The K-25 Site TSCA Incinerator is a rotary kiln incinerator that is designed to treat solids, sludges, and liquid waste forms. A process flowsheet is shown in Fig 1. As combustion gases and solid ash exit the kiln, they enter a mix chamber where gas velocity is significantly reduced, allowing much of the ash to drop out of the gas suspension and fall into a water-filled ash pit. The secondary combustion chamber receives hot flue gases from the primary combustion chamber and secondary liquid wastes fired by a burner.

After the secondary incineration process, off-gases pass into a process gas cleaning system that reduces both acidic gas and particulate emissions. The off-gases pass through a refractory-lined aqueous quench chamber that cools the gases to 187°F. The venturi scrubber receives the cooled flue gas and removes entrained particulates with particle sizes greater than about 1 μm . Subsequently, a mist eliminator minimizes entrained water before the flue gases pass onto a packed-bed scrubber that neutralizes acid gases such as HCl, HF, and H_2SO_4 . The off-gas is further cleaned with the use of two wet ionizing scrubbers to remove particles less than 1 μm in diameter. An induced draft fan pulls the off-gases through the air pollution control system and forces the purified gases out of a 100-ft emission stack.

Fig. 1. Flowsheet for the Oak Ridge K-25 Site TSCA Incinerator.

A caustic scrubber solution is used in the off-gas cleaning system. The scrubber solution is recirculated; part of the scrubber solution is removed, and fresh scrubber fluid is added to the system. The part of the scrubber fluid that is removed is referred to as scrubber blowdown and is transferred to CNF for treatment. Heavy metals, including uranium, are present in the ash entrained in the scrubber blowdown as small (typically <1- to about 3- μ m-diam) insoluble particulates.

3. DESCRIPTION OF CNF OPERATIONS

CNF has unit operations for precipitation of heavy metals and pH adjustment of wastewater streams. A process flowsheet is shown in Fig. 2. Noncontaminated and contaminated wastewaters are treated at CNF. Noncontaminated wastewaters include hydrogen and sodium softener regenerant continuous blowdown and mud drum blowdown from the steam plant. These wastewaters are treated in 17,000-gal batches in a reaction tank with 20 wt % lime slurry. If the pH of the wastewater is above 5, it is lowered to below 5 with sulfuric acid before lime slurry is added. This step ensures that enough lime is added to precipitate any metals present. Betz 1138 polymer is added to the wastewater at 10-ppm final concentration as it is being transferred to a sludge thickener. The clarified wastewater from the sludge thickener is transferred to one of two settling basins. Four batches of wastewater are transferred to a basin before discharge through pressure filters to a National Pollutant Discharge Elimination System (NPDES) monitoring station and then to a mixing zone, where the wastewater is augmented with 3500 gal/min Clinch River water before being discharged to Poplar Creek.

Contaminated wastewaters (wastewaters that contain radioactivity) include the TSCA Incinerator scrubber blowdown, rainwater and wash water collected in the TSCA Incinerator sumps, TSCA Incinerator cooling wastewater, and miscellaneous wastewaters that meet CNF waste acceptance criteria. The primary treatment of these wastewaters is iron coprecipitation. Specific treatment steps are as follows. The pH of the wastewater is lowered to below 5 by addition of hydrochloric acid (HCl) to drive off any carbonate that might form soluble uranium complexes. Ferri-floc [$\text{Fe}_2(\text{SO}_4)_3$] is then added to a final dosage of 14 ppm iron to coprecipitate heavy metals present in the wastewater. The

Fig. 2. Flowsheet for the Oak Ridge K-25 Site Central Neutralization Facility.
 NPDES = National Pollutant Discharge Elimination System

solution is stirred with a mechanical agitator, and air is sparged through the solution to remove any carbonate that remains after the pH adjustment step. Lime slurry is then added to readjust the pH to a value between 7.5 and 8.5. After the pH adjustment step, Betz 1138 polymer is added at a final dosage of 10 ppm as the treated waste is being transferred to the sludge thickener. The rest of the treatment is the same as described previously for noncontaminated wastewaters.

4. COMPOSITION OF WASTEWATER TREATED AT CNF

Unit operations for ^{137}Cs and ^{90}Sr removal could be installed at the beginning or end of the CNF process; therefore, an understanding of CNF influent and effluent compositions is necessary to begin selecting treatment methods. Outside of additional radionuclides that might be present due to the incineration of ORNL organic wastes, the characteristics of wastewater treated at CNF are not expected to change much in the future. Therefore, a review of historical data concerning the K-25 Steam Plant, the TSCA Incinerator effluent, and the CNF effluent was completed to determine how to make the nonradioactive component of the surrogate.³ Since a wide variation existed in the salt and metals concentrations, three different wastewater compositions were chosen for testing. The wastewater characteristics of importance for treatability studies are summarized in Table 1.

To determine what radionuclides might be present in future CNF wastewaters, ORNL waste generators were surveyed to determine the composition of the ORNL organic waste.⁴ This survey resulted in a list of radionuclides that might be present in the waste. Concentrations and quantities of the radionuclides were not available. The most frequently cited radionuclides in 647 drums of ORNL organic waste are listed in Table 2.

If the radionuclides listed in Table 2 are present in the ORNL waste, some will probably not require new treatment methods at CNF for the following reasons:

- The radionuclides ^3H and ^{14}C are volatile and will not be in the blowdown water.
- The iron coprecipitation treatment and hydroxide precipitation steps currently used at CNF should remove uranium, thorium, and cobalt that might partition into the blowdown water transferred to CNF.
- Technetium-99 is as likely to be in the K-25 wastewater already treated at CNF as in that from ORNL. No problems with ^{99}Tc releases at CNF have occurred to date, which indicates that the existing treatment will remove any ^{99}Tc present in the blowdown.
- If ^{51}Cr is present in the blowdown, it could be removed by reinstating ferrous sulfate treatment, which was formerly used at CNF.

Table 1. Surrogate compositions

	Concentration (mg/L)				
	Ca^{2+}	Mg^{2+}	Na^+	K^+	Sr^{2+}
Low range	3	1	8	1	0.3
Average range	65	19	360	6	0.3
High range	400	150	7000	20	0.3

Note: All surrogates were made at pH 8 (see ref. 1).

It is likely that ^{131}I and ^{125}I , ^{32}P and ^{33}P , ^{137}Cs , and ^{90}Sr could require treatment at CNF. Of these radionuclides, ^{137}Cs and ^{90}Sr are used the most at ORNL and are likely to be present at the highest concentrations in the organic wastes; therefore, these isotopes were the focus of the bench-scale treatability studies.

The results of TSCA Incinerator partitioning study confirmed that both ^{137}Cs and ^{90}Sr will be present in the blowdown.² The study used 15,000 L of aqueous feed containing 108 $\mu\text{g/g}$ of strontium as strontium chloride and 52 $\mu\text{g/g}$ of cesium as cesium chloride. Of the total amount of strontium in the feed, approximately 75% partitioned to the scrubber blowdown. Of the total amount of cesium in the feed, approximately 64% partitioned to

Table 2. Radionuclides in ORNL organic waste

Isotope	Number of drums
^3H	307
^{14}C	290
^{131}I , ^{125}I	238
^{32}P , ^{33}P	197
U (all)	151
^{137}Cs , ^{134}Cs	128
^{90}Sr	83
^{60}Co	62
^{51}Cr	52
Th (all)	24
^{99}Tc	17

the scrubber blowdown. Of the portion partitioning to the scrubber blowdown, nearly all the cesium (88-96%) and about one third of the strontium (26-37%) were soluble.

It should be noted that the concentrations of cesium and strontium in the test burn feed were relatively high compared with the concentrations that might actually be in the waste. At lower concentrations all of the cesium and strontium present in the scrubber blowdown may be soluble.

5. SELECTION OF CESIUM AND STRONTIUM REMOVAL METHODS

As stated previously, because of the fast schedule for development work, only previously demonstrated treatment methods or promising methods that could be easily implemented were tested. Several methods have been developed for separation of ^{137}Cs and ^{90}Sr from ORNL wastewater that is similar to CNF wastewater: zeolite ion-exchange

treatment for removal of ^{137}Cs and ^{90}Sr (refs. 5-8), KCCF ion-exchange treatment for removal of ^{137}Cs (refs. 9, 10), and strontium chloride coprecipitation for removal of ^{90}Sr (ref. 10). These methods, in addition to calcium sulfate coprecipitation and sodium phosphate coprecipitation for the removal of ^{90}Sr (methods which had not been previously demonstrated but were easy to test and showed promise), were the methods selected for bench-scale testing.

6. DESCRIPTION OF WASTEWATER SURROGATE

CNF wastewater surrogates were prepared for the bench-scale testing studies. The compositions listed in Table 1 were used to make the surrogates; the review of CNF wastewater characterization had indicated that Cl^- , SO_4^{2-} , and F^- were present in the wastewater. A surrogate made with these anions contained CaSO_4 and CaF_2 precipitates; therefore, only soluble chloride salts were used to prepare the surrogate.

Since the ORNL waste characterization data were not available at the time testing began, the surrogates were traced with low levels of ^{137}Cs and ^{85}Sr . The radionuclide concentrations used were selected to ensure detection using available counting methods. The ^{85}Sr was used because it behaves the same chemically as ^{90}Sr but is a less toxic isotope. Also, ^{85}Sr is a gamma emitter and is more readily counted than ^{90}Sr , which is a beta emitter.

7. CESIUM AND STRONTIUM REMOVAL USING ZEOLITES

7.1 DESCRIPTION OF ZEOLITE

Zeolites have several characteristics that are unique compared with those of ion-exchange resins. They are porous aluminosilicates with rigid frameworks and open crystal lattice containing pores of precisely uniform dimensions. Therefore, zeolites exhibit both molecular-sieve and ion-exchange properties. They also tend to be less expensive than many organic resins and are resistant to thermal and radiation degradation. The ion-

exchange sites are primarily sodium, but there are calcium and magnesium ion-exchange sites as well.

The zeolites tested in these bench-scale studies are currently used in ORNL wastewater treatment plants and have been used in previous bench-scale and pilot-scale treatability studies at ORNL. Natural chabazite (TSM-300, 12 × 50 mesh) and natural clinoptilolite (TSM-140-D, 20 × 40 mesh) were obtained from Steelhead Specialty Minerals Company in Spokane, Washington. The compositions of these zeolites are listed in Table 3.

Table 3. Zeolite composition
(Expressed as percent unless otherwise indicated)

Chemical	Chabazite ^a	Clinoptilolite ^b
SiO ₂	55.97	66.03
Al ₂ O ₃	13.34	10.47
Fe ₂ O ₃	2.83	1.12
MgO	1.01	0.58
CaO	3.29	1.55
Na ₂ O	2.57	3.25
K ₂ O	1.56	1.81
Sr, ppm	1150	4000

^aTSM-300 Zeolite, Steelhead Specialty Minerals, Spokane, Washington. Composition from phone conversation with Wally McGregor, Steelhead Specialty Minerals, Spokane, Washington.

^bTSM-140-D Zeolite, Steelhead Specialty Minerals, Spokane, Washington. Composition from Data Sheet No. 211, Steelhead Specialty Minerals.

Samples of the zeolites were screened to verify particle sizes only; that is, zeolites used for equilibrium and column testing were not screened. Zeolites used for equilibrium

testing were washed by gently mixing the zeolites with deionized water in a beaker until a visual inspection showed that all the fines had been removed. Zeolites used in column testing were backwashed with deionized water in the test column until a visual inspection of the backwash water showed that fines had been removed. Removal of fines is especially important for column testing, since small particles can plug the frits used to retain the zeolite in the column.

7.2 EQUILIBRIUM TESTS

7.2.1 Test Equipment and Procedure

Equilibrium tests were completed using a batch method. The batch method involves using varying amounts of zeolite in a constant volume of solution. Chabazite and clinoptilolite zeolites and CNF low-range and high-range surrogates traced with 500 Bq/L of ^{137}Cs and 250 Bq/L of ^{85}Sr were used to complete these tests; stable cesium and strontium were not added to the surrogate for these tests. The amount of zeolite used was determined by using a zeolite equilibrium model to predict zeolite loading capacities.¹¹ In this case, the model predicted that 5, 25, 50, and 100 g of chabazite zeolite per liter of solution should provide appropriate equilibrium data. The model is not set up to predict equilibrium loadings for clinoptilolite, but since the two zeolites are similar in physical and chemical properties, the model results for chabazite testing were applied to clinoptilolite testing.

The weighed amounts of zeolite were added separately to 1-L samples of traced surrogate and were placed on a jar roller for a 24-h contact time. Previous testing had shown that this was more than adequate time to reach equilibrium. At the end of the contact time, the solution was decanted from the spent zeolite. Betz 1138 polymer was then added to the solution to separate any remaining spent zeolite from the solution; the solution from each sample was then filtered through 0.45- μm filter paper followed by 0.2- μm filter paper to remove the solids.

To determine the effects of fluctuating sodium concentrations on the zeolite performance, the 25 g of spent zeolite from each of the four equilibrium tests was split

into two 12.5-g samples at the end of the equilibrium test. One sample was soaked in 1 L of high-range surrogate and the other in 1 L of low-range surrogate. The surrogate used for soaking the zeolite did not contain any radioactive components. These samples were then handled in the same manner as the samples for the equilibrium test described above.

Samples were submitted to the ORNL Analytical Services Department for analysis of radioisotope and chemical concentrations. Solutions from all four tests were analyzed for ^{85}Sr and ^{137}Cs concentrations by gamma spectroscopy.

7.2.2 Experimental Results from Equilibrium Tests

Results of the equilibrium studies completed using chabazite and clinoptilolite zeolites in CNF low-range and high-range surrogates are shown in Tables 4–8. Clinoptilolite and chabazite zeolite are effective for removing ^{137}Cs and ^{85}Sr from low-range surrogate. These results support earlier test results that show zeolites are effective in treating ORNL wastewaters that have characteristics similar to those of the CNF low-range surrogate.

Chabazite is fairly effective at removing ^{137}Cs from high-range surrogate, although relatively high amounts of zeolite are necessary to achieve ^{137}Cs removal compared with the amounts necessary using low-range surrogate. However, chabazite does not work well at removing ^{85}Sr from high-range surrogate. Clinoptilolite is not as effective as chabazite at removing ^{137}Cs from high-range surrogates. Clinoptilolite is also not effective at removing ^{85}Sr from high-range surrogate, although it shows better results than chabazite with this surrogate.

The zeolite probably had greater sorption capacity for ^{137}Cs and ^{85}Sr because stable cesium and strontium had not been added to the surrogate. The stable cesium and strontium compete for the same exchange sites as the ^{137}Cs and ^{85}Sr ; therefore, if stable cesium and strontium are not present, the zeolite will have a higher capacity for ^{137}Cs and ^{85}Sr . However, even if stable cesium and strontium had been added to the surrogate, the equilibrium loading of ^{137}Cs and ^{85}Sr probably would have decreased by only about 10%

(ref. 12), because the concentrations of sodium, calcium, and magnesium are still relatively high compared with the concentrations of stable cesium and strontium.

The results of the tests to determine the effects of fluctuating sodium concentrations on the zeolite performance are shown in Table 9. These results show that ^{137}Cs and ^{85}Sr will not be displaced from chabazite and clinoptilolite if the sodium in the feed suddenly drops from high to low concentrations. However, ^{137}Cs and ^{85}Sr will be displaced from chabazite and clinoptilolite if the sodium in the wastewater increases from low to high concentrations.

Table 4. Loading of ^{137}Cs and ^{85}Sr on chabazite zeolite in equilibrium with CNF high-range surrogate

Zeolite (g/L)	^{137}Cs			^{85}Sr		
	Bq/L in solution	Bq/g on zeolite	Percent removed	Bq/L in solution	Bq/g on zeolite	Percent removed
0	790	0	0	120	0	0
5	80	142	89.8	110	2	8.3
25	19	31	97.6	100	0.8	16.7
50	14	16	98.2	63	1	47.5
100	17	8	92.8	59	0.6	50.8

Table 5. Loading of ^{137}Cs and ^{85}Sr on chabazite zeolite in equilibrium with CNF low-range surrogate

Zeolite (g/L)	^{137}Cs			^{85}Sr		
	Bq/L in solution	Bq/g on zeolite	Percent removed	Bq/L in solution	Bq/g on zeolite	Percent removed
0	670	0	0	170	0	0
1 ^a	9.1	650.9	98.6	1.3	1.7	100
5	15.0	131	97.8	0	3.4	100
25	7.3	26.5	98.9	0	6.8	100
50	8.4	13.2	97.7	0	34	100
100	8.5	6.6	98.6	0	98.7	98.7

^aThe equilibrium test using 1 g of zeolite was completed at a later date than the test with the other zeolite samples; the radionuclide concentrations in the corresponding 1-g sample blank solution were 660 Bq/L ^{137}Cs and 100 Bq/L of ^{85}Sr .

Table 6. Loading of ^{137}Cs on clinoptilolite zeolite in equilibrium with CNF high-range surrogate

Zeolite (g/L)	^{137}Cs — Test 1			^{137}Cs — Test 2			^{137}Cs — Test 3		
	Bq/L in solution	Bq/g on zeolite	Percent removed	Bq/L in solution	Bq/g on zeolite	Percent removed	Bq/L in solution	Bq/g on zeolite	Percent removed
0	880	0	0	840	0	0	800	0	0
5	230	130	73.9	220	120	73.8	200	120	75
25	78	32	91.1	57	31	93.2	52	30	93.5
50	45	17	94.9	26	16	96.9	30	15	93
100	20	8.6	97.7	17	8.2	97.9	19	7.8	97.6

Table 7. Loading of ^{85}Sr on clinoptilolite zeolite in equilibrium with CNF high-range surrogate

Zeolite (g/L)	^{85}Sr — Test 1			^{85}Sr — Test 2			^{85}Sr — Test 3		
	Bq/L in solution	Bq/g on zeolite	Percent removed	Bq/L in solution	Bq/g on zeolite	Percent removed	Bq/L in solution	Bq/g on zeolite	Percent removed
0	190	0	0	170	0	0	140	0	0
5	140	10	26.3	150	4.0	11.8	110	6.0	21.4
25	63	5.1	66.8	99	2.8	41.8	54	3.4	61.4
50	62	2.6	67.4	64	2.1	62.4	42	2.0	70.0
100	33	1.6	82.6	46	1.2	72.9	25	1.2	82.1

Table 8. Loading of ^{137}Cs and ^{85}Sr on clinoptilolite zeolite in equilibrium with CNF low-range surrogate

Zeolite (g/L)	^{137}Cs			^{85}Sr		
	Bq/L in solution	Bq/g on zeolite	Percent removed	Bq/L in solution	Bq/g on zeolite	Percent removed
0	700	0	0	150	0	0
1 ^a	5	651	99.2	0	100	100
5	12	140	98.3	0.7	30	99.5
25	20	27	97.1	1	6	99.3
50	11	14	98.4	0.3	3	99.7
100	7	7	99.9	0	15	100

^aThe equilibrium test using 1 g of zeolite was completed at a later date than the test with the other zeolite samples; the radionuclide concentrations associated with the 1-g sample blank solution were 660 Bq/L ^{137}Cs and 100 Bq/L of ^{85}Sr .

Table 9. Impact of sodium concentration changes on zeolite performance

Equilibrium test	Activity in 25-g sample at end of test (Bq/g) ^a		High-range surrogate soak (% removed)		Low-range surrogate soak (% removed)	
	^{137}Cs	^{85}Sr	^{137}Cs	^{85}Sr	^{137}Cs	^{85}Sr
Chabazite in high-range surrogate	31	0.8	-	-	0.2	0
Chabazite in low-range surrogate	26.5	6.8	6.6	63.5	-	-
Clinoptilolite in high- range surrogate	10	0	-	-	1.6	NA
Clinoptilolite in low- range surrogate	27	6	15.1	42.7	-	-

^aThe 25-g sample from each equilibrium test was split into two samples. One sample was contacted with 1 L of high-range surrogate, and the other was contacted with 1 L of low-range surrogate that had not been traced with radioactive cesium and strontium.

7.3 COLUMN TESTS

Bench-scale column testing was performed to determine if the ^{137}Cs and ^{85}Sr removal efficiency could be improved over the equilibrium testing removal efficiencies.

Equilibrium test results, general column design guidelines, and results of previous testing were used to estimate these design parameters for initial column testing. Details of the selection of column design parameters are found in Sect. 7.3.1.

7.3.1 Test Equipment and Procedure

A total of four column tests were performed; chabazite and clinoptilolite were tested using both average-range and high-range surrogates. Average-range surrogate was used rather than low-range surrogate since equilibrium testing showed that ^{137}Cs and ^{85}Sr removal in low-range surrogate could be expected to be similar to the performance of chabazite and clinoptilolite in ORNL wastewaters with similar compositions. Also, the composition of the average-range solution better approximates actual CNF operating conditions. Both surrogates contained stable cesium and strontium for these tests. Ion-exchange column test parameters are summarized in Table 10; these parameters were estimated for chabazite and clinoptilolite column testing with average-range and high-range surrogates in the following manner.

Since the equilibrium testing was done with low-range surrogate and the time schedule for testing did not permit additional equilibrium testing, alternate methods were used for estimating column test parameters for average-range surrogates. Previous test results using chabazite zeolites to treat ORNL Process Waste Treatment Plant wastes were used to estimate column design parameters for both chabazite and clinoptilolite testing with average-range surrogates.⁸ These column tests showed strontium breakthrough at about 3000 bed volumes (solution volume treated/zeolite volume). The zeolite volume for the present test was estimated using this information and estimating that about 10 L of surrogate (ten 1-L samples) would provide enough points to obtain a breakthrough curve for strontium. The zeolite volume was calculated by dividing the total amount of solution to be processed by the total number of bed volumes until

Table 10. Ion-exchange column testing parameters

Test description	Column diameter (cm)	Bed height (cm)	Zeolite amount (g)	Average flow rate (mL/min)	Superficial velocity (gal · min ⁻¹ · ft ⁻²)	Length of test (min)	Bed volume (cm ³)	Volume treated (mL)
Chabazite, average-range surrogate	1.0	10.0	4.3	4.1	1.3	1062	7.9	4299
Clinoptilolite, average-range surrogate	1.0	10.0	6.0	4.0	1.3	1500	7.9	5807
Chabazite, high-range surrogate	2.5	10.8	30.6	20.0	1.0	252	55.4	4729
Clinoptilolite, high-range surrogate	2.5	10.8	40.1	20.6	1.0	240	52.9	4578

breakthrough, which indicated the bed should be 3.9 mL, or 2.8 g of zeolite; this resulted in a 5-cm bed height in a 1-cm-ID column. A preliminary column test using 2.8 g of chabazite zeolite reached ^{85}Sr breakthrough almost immediately; therefore, the zeolite bed depth for subsequent testing was increased by a factor of two, increasing the zeolite volume to 7.9 mL.

A rule-of-thumb column design parameter is that the superficial velocity should be maintained at $1\text{--}5 \text{ gal} \cdot \text{min}^{-1} \cdot \text{ft}^{-2}$ (ref. 13). A 1.0-cm-diam test column was used for the average-range surrogate tests. The feed rate was set at 4 mL/min to maintain a superficial velocity of $1 \text{ gal} \cdot \text{min}^{-1} \cdot \text{ft}^{-2}$.

The equilibrium test results described in the previous section were used for estimating column testing parameters for high-range surrogates. Equilibrium test results showed that 5 g chabazite in 1 L of high-range surrogate can remove 2 Bq ^{85}Sr per gram of zeolite. To remove 2000 Bq ^{85}Sr (200 Bq/L) in 10 L of surrogate requires about 1000 g of chabazite.

The equilibrium test results showed that 5 g of clinoptilolite in 1 L of high-range surrogate could remove about 8 Bq ^{85}Sr per gram of zeolite. Therefore, about 250 g of clinoptilolite zeolite would be necessary to remove 200 Bq ^{85}Sr per liter from 10 L of high-range surrogate.

Since stable cesium and strontium were not in the surrogates used for equilibrium testing, more zeolite than predicted by the equilibrium model would have been necessary to achieve the desired radionuclide removal levels. However, since the bench-scale columns readily available did not have the capacity for the amount of zeolite needed for these tests, and since radionuclide removal is expected to be improved in using columns, the maximum amount of zeolite that would fit in the columns available was used for column testing with high-range surrogates. The largest column available (2.5 cm ID $\times$ 10.8 cm tall) was used for these tests; a column of this diameter and length would hold about 40 g of zeolite. A flow of 20 mL/min was selected to maintain a superficial velocity of $1 \text{ gal} \cdot \text{min}^{-1} \cdot \text{ft}^{-2}$.

The test equipment configuration is shown in Fig. 3. Surrogate was pumped from a feed reservoir to the test column using a peristaltic pump. The surrogate was pumped into the bottom of the column. In bench-scale testing, upward flow is used because it is easier to prevent column plugging and channeling effects. The effluent from the top of the column went to a Rainin model F2-1 sample fractionator. The fractionator could be programmed to collect the desired volume of sample based on the column flow rate. The test column had Teflon frets at the top and bottom to keep the flow distributed through the bed and to help support the bed. The pump flow rate was verified at the beginning of each test by running deionized water through the column. Verifying the flow rate also showed if air pockets that would slow or stop flow through the column may have developed during the zeolite loading.

A Canberra series 90 multichannel analyzer was used to analyze samples for ^{137}Cs and ^{85}Sr . The ORNL Analytical Services Department measured metals concentrations by inductively coupled plasma analysis.

7.3.2 Experimental Results from Zeolite Testing

The ^{137}Cs and ^{85}Sr breakthrough curves for each column test are shown in Figs. 4 through 7. In all four tests ^{85}Sr breakthrough occurred early in the run. In the column tests with chabazite in average-range and high-range surrogates, the tests ended before ^{137}Cs breakthrough occurred. In the column test with clinoptilolite, ^{137}Cs breakthrough occurred at about 550 bed volumes in average-range surrogate and at about 20 bed volumes in high-range surrogate. It is clear that the relatively high salt concentrations in the surrogate interfered with loading of ^{85}Sr on both chabazite and clinoptilolite zeolite and that they interfered with ^{137}Cs loading on clinoptilolite, causing early breakthrough of the radioisotopes.

The metals breakthrough curves for each column test are shown in Figs. 8 through 11. In all four tests, metals naturally occurring on the zeolite, particularly strontium, were displaced from the zeolite, causing the metals to exceed 100% breakthrough. This effect became more pronounced when high-range surrogate wastewater was treated with zeolites.

Fig. 3. Bench-scale column testing equipment.

Fig. 4. Breakthrough curve for ^{137}Cs and ^{90}Sr in column test with chabazite in CNF high-range surrogate.

Fig. 5. Breakthrough curve for ^{137}Cs and ^{90}Sr in column test with chabazite in CNF average-range surrogate.

Fig. 6. Breakthrough curve for ^{137}Cs and ^{90}Sr in column test with clinoptilolite in CNF high-range surrogate.

Fig. 7. Breakthrough curve for ^{137}Cs and ^{90}Sr in column test with clinoptilolite in CNF average-range surrogate.

Fig. 8. Breakthrough curve for metals in column test with chabazite in CNF high-range surrogate.

Fig. 9. Breakthrough curve for metals in column test with chabazite in CNF average-range surrogate.

Fig. 10. Breakthrough curve for metals in column test with clinoptilolite in CNF high-range surrogate.

Fig. 11. Breakthrough curve for metals in column test with clinoptilolite in CNF average-range surrogate.

It is not known how this effect impacts the radionuclide removal capacity of the zeolites. Another series of tests, using zeolite that was prewashed with NaCl, is currently being conducted at ORNL to address this issue.

8. CESIUM REMOVAL USING POTASSIUM COBALT FERROCYANIDE

8.1 KCCF Test Description

Potassium cobalt ferrocyanide is prepared by mixing solutions of potassium ferrocyanide [$K_4Fe(CN)_6$] with cobalt nitrate [$Co(NO_3)_2$] to precipitate $K_2CoFe(CN)_6$ or KCCF. Previous testing used several different preparation methods for KCCF indicated that in situ formation of KCCF was one of two methods of preparing KCCF that worked the best.⁹ This method was chosen for bench-scale testing with CNF wastewater because it could be easily implemented at CNF. In situ KCCF is formed by adding $K_4Fe(CN)_6$ to the wastewater and then adding $Co(NO_3)_2$ to form KCCF, which then removes the cesium by ion exchange.

The KCCF treatment process is shown in Fig. 12. Tests were performed with low-range surrogate and high-range surrogate traced with 1,442,450 Bq/L ^{137}Cs and 936,700 Bq/L ^{85}Sr ; 0.26 mg/L stable cesium and 0.3 mg/L stable strontium were also added. The KCCF process was integrated into the normal CNF treatment steps described in an earlier section. The pH of the solution was adjusted to below 5 with HCl. $Fe_2(SO_4)_3$ was added to a final iron concentration of 10 ppm. Calcium hydroxide was added to adjust the solution to pH 8. The $K_4Fe(CN)_6$ was added first and followed by a stoichiometric amount of $Co(NO_3)_2$ to achieve a KCCF concentration of 100 ppm. After $Fe_2(SO_4)_3$ and $Co(NO_3)_2$ additions, samples were taken and centrifuged to remove solids, and the resulting solutions were analyzed for ^{137}Cs and ^{85}Sr using a Canberra series 90 multichannel analyzer.

An additional test was performed with low-range and high-range surrogates that were not traced with ^{137}Cs and ^{85}Sr to determine if free cyanide would be present in the treated wastewater. The CNF process with KCCF treatment incorporated was simulated as

Fig. 12. Flowsheet for KCCF treatment.

described above. The ORNL Analytical Services Department measured free cyanide using colorimetric analysis.

8.2 KCCF Experimental Results

The results of the KCCF testing are shown in Tables 11 and 12. Three separate tests showed that $\text{Fe}_2(\text{SO}_4)_3$ removed small amounts of ^{137}Cs and ^{85}Sr from both low-range and high-range surrogates. The KCCF treatment removed greater than 99.9% of the ^{137}Cs from both surrogates; KCCF treatment did not remove any ^{85}Sr .

Table 11. $\text{Fe}_2(\text{SO}_4)_3$ and KCCF test in CNF high-range surrogate

	^{85}Sr % removal after $\text{Fe}_2(\text{SO}_4)_3^a$	^{137}Cs % removal after $\text{Fe}_2(\text{SO}_4)_3^b$	^{85}Sr % removal after $\text{Fe}_2(\text{SO}_4)_3$ and KCCF ^a	^{137}Cs % removal after $\text{Fe}_2(\text{SO}_4)_3$ and KCCF ^b
Test 1	13.7	12.6	14.5	99.9
Test 2	11.4	9.7	11.1	99.9
Test 3	10.2	9.1	12.6	100

^aInitial ^{85}Sr concentration was 936,700 Bq/L, and initial strontium was 0.3 mg/L.

^bInitial ^{137}Cs concentration was 1,142,450 Bq/L, and initial cesium was 0.26 mg/L.

Table 12. $\text{Fe}_2(\text{SO}_4)_3$ and KCCF test in CNF low-range surrogate

	^{85}Sr % removal after $\text{Fe}_2(\text{SO}_4)_3^a$	^{137}Cs % removal after $\text{Fe}_2(\text{SO}_4)_3^b$	^{85}Sr % removal after $\text{Fe}_2(\text{SO}_4)_3$ and KCCF ^a	^{137}Cs % removal after $\text{Fe}_2(\text{SO}_4)_3$ and KCCF ^b
Test 1	5.0	8.2	6.4	100
Test 2	3.0	7.8	4.7	99.9
Test 3	9.6	11.1	11.6	100

^aInitial ^{85}Sr concentration was 936,700 Bq/L, and initial strontium was 0.3 mg/L.

^bInitial ^{137}Cs concentration was 1,142,450 Bq/L, and initial cesium was 0.26 mg/L.

A single cold test showed that 0.01 ppm free cyanide remained in the low-range surrogate and that 0.004 ppm remained in high-range surrogate after KCCF treatment.

9. STRONTIUM REMOVAL USING STRONTIUM CHLORIDE COPRECIPITATION

9.1 Strontium Chloride Coprecipitation Test Description

The basis of strontium chloride (SrCl_2) coprecipitation is that the potential exists to add enough stable strontium to the wastewater so that the solubility limit for strontium in solution will be exceeded; the stable strontium that precipitates will then coprecipitate radioactive strontium. Previous bench-scale testing with wastewaters similar in composition to CNF low-range surrogate indicated that SrCl_2 coprecipitation at pH 11 could remove enough strontium from the waste to meet discharge criteria.¹⁰ Since implementing a coprecipitation process at a high pH would be difficult at CNF, bench-scale testing for SrCl_2 was conducted at a neutral pH.

The CNF process with SrCl_2 coprecipitation incorporated is shown in Fig. 13. Tests were performed with low-range and high-range surrogates traced with 814,000 Bq/L of ^{85}Sr and 1,115,000 Bq/L ^{137}Cs ; 0.26 mg/L stable cesium and 0.3 mg/L stable strontium were also added to the surrogate. The standard CNF treatment steps were followed, except that SrCl_2 was added with the $\text{Fe}_2(\text{SO}_4)_3$ at a low pH. The previous tests¹⁰ had shown that adding 100 ppm SrCl_2 would remove most of the strontium in the starting solutions. The present bench-scale tests were conducted using 250 ppm SrCl_2 initially. If this concentration proved effective at removing the strontium, then lower concentrations would be tested. The SrCl_2 was added at a low pH because it was easier to dissolve when this was done. The KCCF treatment was incorporated into the flowsheet to make sure the overall process steps would be compatible. Samples were taken after $\text{Fe}_2(\text{SO}_4)_3$, SrCl_2 , and KCCF additions. The samples were centrifuged, and the resulting solutions were analyzed for ^{137}Cs and ^{85}Sr using a Canberra series 90 multichannel analyzer.

Fig. 13. SrCl_2 coprecipitation.

9.2 Experimental Results

The results of the SrCl_2 coprecipitation testing are shown in Tables 13 and 14. Comparison of these results with test results in Tables 11 and 12 shows that the addition of SrCl_2 along with $\text{Fe}_2(\text{SO}_4)_3$ did not improve the ^{85}Sr removal achieved by using $\text{Fe}_2(\text{SO}_4)_3$ alone in high-range surrogates; in low-range surrogates, a slight increase in ^{85}Sr removal was achieved. The KCCF test results verified the previous test results; greater than 99% of the ^{137}Cs can be removed and no additional ^{85}Sr can be removed by using KCCF.

Table 13. SrCl_2 coprecipitation in CNF high-range surrogate

	^{85}Sr % removal after $\text{Fe}_2(\text{SO}_4)_3/\text{SrCl}_2^a$	^{137}Cs % removal after $\text{Fe}_2(\text{SO}_4)_3/\text{SrCl}_2^b$	^{85}Sr % removal after KCCF addition ^a	^{137}Cs % removal after KCCF addition ^b
Test 1	12.0	11.8	19.0	99.2
Test 2	16.3	15.7	14.2	99.5
Test 3	14.1	13.7	16.9	99.5

^aInitial ^{85}Sr concentration was 814,000 Bq/L, and initial strontium was 0.3 mg/L.

^bInitial ^{137}Cs concentration was 1,115,000 Bq/L, and initial cesium was 0.26 mg/L.

Table 14. SrCl_2 coprecipitation in CNF low-range surrogate

	^{85}Sr % removal after $\text{Fe}_2(\text{SO}_4)_3/\text{SrCl}_2^a$	^{137}Cs % removal after $\text{Fe}_2(\text{SO}_4)_3/\text{SrCl}_2^b$	^{85}Sr % removal after KCCF addition ^a	^{137}Cs % removal after KCCF addition ^b
Test 1	18.2	18.8	-	-
Test 2	28.2	29.8	22.9	100.7
Test 3	20.1	19.9	23.5	100.7

^aInitial ^{85}Sr concentration was 814,000 Bq/L, and initial strontium was 0.3 mg/L.

^bInitial ^{137}Cs concentration was 1,115,000 Bq/L, and initial cesium was 0.26 mg/L.

10. STRONTIUM REMOVAL USING SODIUM PHOSPHATE COPRECIPITATION

10.1 Strontium Phosphate Coprecipitation Test Description

The basic principle underlying sodium phosphate (NaH_2PO_4) coprecipitation is that strontium phosphate (SrHPO_4) is very insoluble in pure water. By adding NaH_2PO_4 to CNF surrogates, the potential exists for SrHPO_4 to form and to coprecipitate radioactive strontium.

The CNF process with sodium phosphate coprecipitation incorporated is shown in Fig. 14. Tests were performed with low- and high-range surrogates traced with 936,700 Bq/L of ^{85}Sr and 1,142,000 Bq/L of ^{137}Cs ; 0.26 mg/L stable cesium and 0.3 mg/L stable strontium were also added. The standard CNF treatment steps were followed, incorporating KCCF and NaH_2PO_4 addition. The bench-scale tests were conducted using 100 ppm NaH_2PO_4 initially. If this concentration proved effective at removing the strontium, then lower concentrations would be tested. The KCCF treatment was incorporated into the flowsheet to make sure the overall process steps would be compatible. Samples were taken after $\text{Fe}_2(\text{SO}_4)_3$ treatment, KCCF treatment, and NaH_2PO_4 treatment. The samples were centrifuged, and the resulting solutions were analyzed for ^{137}Cs and ^{85}Sr using a Canberra series 90 multichannel analyzer.

10.2 Experimental Results

The results of the NaH_2PO_4 coprecipitation testing are shown in Tables 15 and 16. The $\text{Fe}_2(\text{SO}_4)_3$ and KCCF steps showed comparable ^{137}Cs and ^{85}Sr removal for other tests in this series of experiments. In high-range surrogate, no additional ^{137}Cs and ^{85}Sr were removed using NaH_2PO_4 than were already removed using $\text{Fe}_2(\text{SO}_4)_3$. In low-range surrogate, a small additional amount of ^{85}Sr was removed by NaH_2PO_4 . The KCCF test results verified the previous test results; greater than 99% of the ^{137}Cs can be removed and no additional ^{85}Sr can be removed by using KCCF.

Fig. 14. Sodium phosphate coprecipitation.

Table 15. NaH₂PO₄ coprecipitation in CNF high-range surrogate

	⁸⁵ Sr % removal after Fe ₂ (SO ₄) ₃ ^a	¹³⁷ Cs % removal after Fe ₂ (SO ₄) ₃ ^b	⁸⁵ Sr % removal after KCCF ^a	¹³⁷ Cs % removal after KCCF ^b	⁸⁵ Sr % removal after SrHPO ₄ ^a	¹³⁷ Cs % removal after SrHPO ₄ ^b
Test 1	13.7	12.7	14.5	99.9	15.3	99.7
Test 2	11.4	9.7	11.1	99.9	17.2	99.7
Test 3	10.2	9.1	12.6	100.0	15.6	99.8

^aInitial ⁸⁵Sr concentration was 936,700 Bq/L, and initial strontium was 0.3 mg/L.

^bInitial ¹³⁷Cs concentration was 1,142,000 Bq/L, and initial cesium was 0.26 mg/L.

Table 16. NaH₂PO₄ coprecipitation in CNF low-range surrogate

	⁸⁵ Sr % removal after Fe ₂ (SO ₄) ₃ ^a	¹³⁷ Cs % removal after Fe ₂ (SO ₄) ₃ ^b	⁸⁵ Sr % removal after KCCF ^a	¹³⁷ Cs % removal after KCCF ^b	⁸⁵ Sr % removal after SrHPO ₄ ^a	¹³⁷ Cs % removal after SrHPO ₄ ^b
Test 1	5.0	8.0	6.4	100	18.6	100
Test 2	3.0	8.0	4.7	100	-	-
Test 3	9.6	11.0	11.6	100	18.4	100

^aInitial ⁸⁵Sr concentration was 936,700 Bq/L, and initial strontium was 0.3 mg/L.

^bInitial ¹³⁷Cs concentration was 1,142,000 Bq/L, and initial cesium was 0.26 mg/L.

11. STRONTIUM REMOVAL USING CALCIUM SULFATE COPRECIPITATION

11.1 Calcium Sulfate Coprecipitation Test Description

This process is similar to sodium phosphate coprecipitation. Calcium sulfate (CaSO₄) is fairly insoluble in pure water. By using sulfuric acid (H₂SO₄) rather than HCl in the pH adjustment step in CNF wastewater treatment, the potential exists to add enough sulfate

to react with calcium already present in the wastewater so that CaSO_4 will form and coprecipitate radioactive strontium.

The CNF process with the CaSO_4 coprecipitation incorporated is shown in Fig. 15. Tests were performed with low-range and high-range surrogates traced with 573,300 Bq/L of ^{85}Sr and 598,650 Bq/L of ^{137}Cs ; 0.26 mg/L stable cesium and 0.3 mg/L stable strontium were also added. No additional calcium was added to high-range surrogate tests, and CaCl_2 was added to the low-range surrogate to bring the final calcium concentration to 100 ppm.

The standard CNF treatment steps were modified: H_2SO_4 was used to lower the pH, and NaOH was used to adjust the pH to 8. The H_2SO_4 was used to make SO_4 available to react with the calcium. Because of a recent determination that CNF will use NaOH , rather than $\text{Ca}(\text{OH})_2$, in the future, NaOH was used in this testing. The KCCF treatment was incorporated into the flowsheet to make sure the overall process steps would be compatible.

11.2 Experimental Results

The calcium sulfate coprecipitation test results are presented in Tables 17 and 18. These results indicate that no additional ^{85}Sr was removed beyond the amount removed by $\text{Fe}_2(\text{SO}_4)_3$ in other tests. The KCCF test results verified previous results: greater than 99% of the ^{137}Cs can be removed by using KCCF, and no additional ^{85}Sr is removed.

Table 17. CaSO_4 coprecipitation in CNF high-range surrogate

	^{85}Sr % removal after $\text{Fe}_2(\text{SO}_4)_3/\text{H}_2\text{SO}_4^a$	^{137}Cs % removal after $\text{Fe}_2(\text{SO}_4)_3/\text{H}_2\text{SO}_4^b$	^{85}Sr % removal after KCCF ^a	^{137}Cs % removal after KCCF ^b
Test 1	4.9	1.8	13.3	99.9
Test 2	3.7	2.5	10.9	99.9
Test 3	4.9	4.6	11.6	99.9

^aInitial ^{85}Sr concentration was 573,300 Bq/L, and initial strontium was 0.3 mg/L.

^bInitial ^{137}Cs concentration was 598,650 Bq/L, and initial cesium was 0.26 mg/L.

Fig. 15. CaSO_4 coprecipitation flowsheet.

Table 18. CaSO_4 coprecipitation in CNF low-range surrogate

	^{85}Sr % removal after $\text{Fe}_2(\text{SO}_4)_3/\text{SrCl}_2^{\text{a}}$	^{137}Cs % removal after $\text{Fe}_2(\text{SO}_4)_3/\text{SrCl}_2^{\text{b}}$	^{85}Sr % removal after KCCF addition ^a	^{137}Cs % removal after KCCF addition ^b
Test 1	8.8	12.3	8.4	100
Test 2	6.9	12.0	6.8	100
Test 3	5.3	6.3	8.9	100

^aInitial ^{85}Sr concentration was 573,300 Bq/L, and initial strontium was 0.3 mg/L.

^bInitial ^{137}Cs concentration was 598,650 Bq/L, and initial cesium was 0.26 mg/L.

12. CONCLUSIONS

The following conclusions can be made after reviewing the experimental results.

- Additional column equilibrium testing should be done to define maximum loading of chabazite and clinoptilolite in low-range surrogates if wastewater that resembles low-range surrogate compositions will be treated at CNF. Stable cesium and strontium should be added to the surrogates.
- Chabazite and clinoptilolite zeolite are not good sorbent materials for removal of ^{85}Sr from average-range and high-range surrogates. In both surrogates, ^{85}Sr breakthrough occurred after a relatively low volume of solution was processed.
- Chabazite zeolite may be appropriate for removal of ^{137}Cs from both average-range and high-range surrogates. Further bench-scale column testing is required to determine ^{137}Cs breakthrough characteristics.
- Rapid changes from low to high sodium concentrations in CNF wastewater will cause ^{137}Cs and ^{90}Sr to be displaced from zeolite, causing a high concentration of radioactive contaminants in the effluent.

- KCCF effectively removed ^{137}Cs from a wide concentration range of salt solutions that were used for bench-scale testing.
- Strontium and calcium coprecipitation processes were not effective for ^{85}Sr removal from low-range and high-range surrogates that were at a near-neutral pH.

13. RECOMMENDATIONS FOR FURTHER TESTING

There are some basic studies that need to be completed to determine how to upgrade CNF to treat wastewater contaminated with ^{137}Cs and ^{90}Sr from burning ORNL organic waste at the K-25 Site TSCA Incinerator. ORNL organic waste must be characterized to determine radionuclide concentrations. Future CNF influent metals and salt concentrations need to be estimated since these parameters have a significant effect on the treatment method chosen. After the waste is characterized, the information gained from the recent TSCA Incinerator partitioning study can be used to estimate what concentration of ^{137}Cs and ^{90}Sr (as well as other potential contaminants) will be transferred to CNF in the incinerator blowdown. This information can be used to determine what treatment is necessary to meet derived concentration guideline limits for the CNF discharge.

Depending on what treatment is needed, the following items need to be considered:

- Chabazite zeolite may be useful for ^{137}Cs and ^{90}Sr removal depending on the volume and composition of water contaminated with ^{137}Cs and ^{90}Sr . A study that considers the costs of equipment design, installation, and operation and the disposal cost of spent zeolite generated might show that zeolites could be an economical treatment for small volumes of wastewater. This treatment method might fit easily into the current plant configuration.
- If chabazite zeolite treatment were to be implemented at CNF, changes in process control at CNF or the TSCA Incinerator would be required to maintain a constant salt concentration in wastewater that is transferred to CNF. Swings in sodium

concentration (from relatively low to relatively high concentrations) can cause ^{137}Cs and ^{90}Sr to be displaced from zeolite.

- KCCF treatment is the most promising method of ^{137}Cs removal tested. This treatment method would require further development work before it could be implemented at CNF. Further development work is necessary to determine if free cyanide left in the treated wastewater is a potential problem; if cyanide is a problem, testing of cyanide removal methods would become necessary. Further testing is also needed to optimize KCCF concentrations to minimize sludge volume and to optimize polymer addition for solids settling.
- The KCCF treatment could be implemented within the current CNF configuration if equipment for cyanide removal is not necessary. The existing polymer addition system and sludge thickener could be used. If cyanide removal is necessary, the selection of a treatment process should be based on ease of implementation.
- Previous tests have shown that ^{90}Sr can be removed from ORNL wastewaters if the wastewater can be adjusted to a high pH. If ^{90}Sr concentrations are expected to be a problem, having tank space to remove the ^{90}Sr at a high pH might be useful. Bench-scale testing would be required to determine what chemicals to use for this treatment step. The CNF process layout would have to be reviewed to determine if existing tank capacity and piping could be modified to do this or if additional tank space and piping would be needed.
- New sorbents are currently being developed by the U.S. Department of Energy Office of Technology Development that may be appropriate to treat CNF wastewaters; these technologies should be considered if further development work is necessary.

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