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Subject: various articles re Fernald and K-65

articles attached

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Company Set to Remove Fernald Waste Without Leaking Radon

[By Katie Taft](#) Thursday, March 25, 1999

The Foster Wheeler Environmental Corp., the company that has been contracted to clean up two of the silos at the Fernald site, is about to put a system in place that will remove the silos' contents without leaking high levels of radon.

The silos contain about 8,900 cubic yards of low-level uranium ore residues that emit radon. Radon is an odorless, colorless radioactive gas that, in high levels, has been linked with lung cancer. It is produced by the decay of naturally occurring uranium and thorium in the soil.

But at the former Fernald uranium-processing plant in Crosby Township, which operated from 1953 until 1988, the radon is from radium in the silos at high concentrated amounts. The Centers for Disease Control and Prevention released a study last year that reported the radon gas leaking from the silos caused the largest health risk to residents surrounding the site.

"The material in the silos is unique, it's the only material like it in the world," said Wayne Potter, engineer manager for the company. "The process and technique (for cleanup) has a long history. We are using similar applications of past practices. The material is new to us, but the technique is not."

The New Jersey-based company received a \$50 million, four-year contract from the U.S. Department of Energy (DOE) on Feb. 26 to remove the potentially deadly sludge wastes from two concrete silos at the site. The contract calls for the company to design, build and implement the retrieval system and a transfer system to remove the radium-bearing waste from the two silos and place it into new storage tanks. The company already has a preliminary design in place, Potter said.

"Because the material is unique, there have been a number of samples and tests that have been done on the material so that we will be prepared," he said.

And the unique material calls for some other preparation, Potter said.

There are two other silos at the Fernald site. One contains about 5,100 cubic yards of cold metal oxides and the other is empty. Potter said that the empty silo will be useful to gain experience in dealing with the silos and the removal procedure.

"There is a significant advantage to having that extra (empty) silo there because it gives us the ability to have a full-scale mockup system," Potter said. "We can field an exact replica on the fourth silo, and we can verify the operation."

The first part of the process of removing the waste from the silos, he said, will involve the radon control system. The company will use negative pressure to remove the gas and will remove the radon from the gas through carbon filters.

"It will be a completely sealed air-lock system where there will be two layers of pipes," Potter said.

The reason for a pipe-within-a-pipe system is to make sure the gas cannot escape, he said.

The retrieval system for the solid waste in the silos will use a hydraulic retrieval process and a slurry pumping system. The waste water generated from this process will be collected and treated before it is discarded.

"These silos are fragile and were not meant to hold this type of material for this long," Potter said.

Because of this, the company will use only openings that already are in place on the silos. ©

Title: Recycling radium

Creator/Author: Blair, J.A.

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Description/Abstract: The Technology Programs Department of Fluor Daniel Fernald investigated alternatives for dealing with the World's largest concentrated supply of radium, the K-65 silos at Fernald, the United States Department of Energy's (DOE) former uranium processing facility near Cincinnati, Ohio. These two silos contain nearly 3,770 curies (by definition 3,770 grams) primarily of Ra-226 ($T_{1/2} = 1600$ a) within 10,000 metric tons of material. Material contents of the silos were to be vitrified according to a Record of Decision (ROD) between the DOE and the United States Environmental Protection Agency (EPA). Because of cost considerations, that alternative must be reconsidered. Research showed that although Ra-226 had come mostly into disfavor as a therapeutic agent for cancer, isotopes derived from the neutron bombardment of pure Ra-226 and radioactive decay of the resulting purified isotopes could be used to good effect. One of these isotopes, bismuth-213 (Bi-213, $T_{1/2} = 45.6$ m), is being used in clinical trials against acute myelogenous leukemia. The isotope is attached to an antibody that seeks out cancer cells. Because alpha particles dissipate most of their energy within the space of one or a few cells, virtually all the surrounding healthy tissue remains unharmed. Because of the short half life, waste disposal is no problem. Because of past policies, radium for feedstock is difficult to find. A new policy is needed in the United States acknowledging radium's value for feedstock while continuing to control its health and environmental consequences.

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Personal and Environmental Exposure Assessment Measurements at Fernald

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Specific DOE Problem Addressed

This research provides the specific instruments required to accurately determine the dose and therefore the risk from inhaled radionuclides during D&D in any environment. Fernald is now the only site to have these data, provided by two entirely new personal exposure instruments. The first is a lightweight (20 gram) passive, badge type detector measuring both radon and thoron, the exposures of relevance at Fernald. The second is a miniature aerosol particle size sampler that can be worn with a belt pump or used for long periods of time as an area sampler.

Although the inhaled particle size is the major determinant of bronchial dose, no other DOE site is attempting to do the particle size distribution measurements. Prior to the development of this instrument, the labor intensive effort needed, and the cost, precluded the measurement.

Research Objective

The research is directed to developing state-of-the-art personal and environmental exposure assessment for inhaled radionuclides at Fernald during D&D. An additional objective is the radiochemical analyses of soil samples taken around the radium (K-65) silos before and after removal of the material. Lead-210, the long lived decay product of radon released during the removal, provides a sensitive tracer to determine the entire inventory of radon released.

Research Progress and Implications (Summarizing year 3 of a 3 year project)

Two new radiation detection instruments have been developed. The first is a lightweight (20 gram) radon (Rn-222) and thoron (Rn-220) detector, This is the only monitor of its kind. The radon and thoron detector is tri-lobed and shaped like a cloverleaf. There are 3 alpha track detection chambers, 2 chambers have a diffusion barrier to prevent short-lived thoron gas entry (55 second half life). These 2 chambers provide a duplicate measurement of radon (3.8 day half-life). The third chamber measures the total gas signal and thoron is measured by signal difference of the 2 chambers. The CloverLeaf monitor

was designed for use at Fernald but has wider application wherever radon or thoron exposures exist. It is either a personal monitor, clipped to the lapel or deployed as a field area monitor. It is presently being used both outdoors as an area monitor around the radium (K-65) silos to determine the relevant compliance dose perimeter, and indoors to determine personal exposure where thoron and/or radon concentrations are known to exist..

The second instrument is a particle size sampler for inhaled airborne particles. This newly developed particle size monitor is also the only one of its kind. It is a commercial sampler head modified with 4 added filtration stages of our design. The inlet air jets focus on an impactor stage, modified with a ZnS alpha phosphor cover. All large particles (> 2 micrometer diameter) deposit on the impactor stage. Four, very fine mesh screen filters, follow the impactor stage. The screens filter the small size particles selectively. An exit Millipore backup filter collects any residual particles. A low flow pump (4 LPM) draws air through the sampler head. We count the radioactivity from all 6 filtration elements, in our very low background (5 counts per day) alpha counters at NYU.

The long lived radon decay products, Pb,Po-210, is a unique tracer for atmospheric aerosol particles, and this is used to trace the particle size around the silos or other locations having even background concentrations of radon. During the excavation of pit3, two samplers along with the radon thoron detectors were located on either side of the removal area. In late 1999, a low level excursion at the drying facility occurred, while drying material from pit3 (mainly thorium-230 waste). Thorium-230 was the radionuclide measured by our particle size sampler at the drying facility, using alpha spectrometry in this case. Although the air concentrations were very low, this is the only particle size sampler that could accurately measure both the concentration and size distribution.

This particle size sampler measures over long periods of time without intensive labor or costly down time. The same is true for the passive, alpha track radon and thoron detector. These new instruments provide a means to measure, in a simple non-invasive way, the detailed information needed to describe the environmental and worker exposure before, during, and after remediation. The sensitivities are such that normal background environments can be measured by both instruments.

Planned Activities

We have been asked by the Radiation Control Section at Fernald to redesign both the radon thoron monitor and the particle size sampler. Measurements so far are initial to the remediation at Fernald. The major waste removal effort (silos, pits, buildings) is ready to commence. The radon thoron monitor is to be redesigned to have 4 detection chambers to provide duplicate measurement for both radon and thoron. The particle size detector is to be redesigned with fabrication material of lightweight conducting plastic rather than metal, and with more filtration elements to provide the complete range for the spectrum of inhaled particles.

Additional Information

NYU School of Medicine is seeking a patent for the personal radon and thoron detector.

DEMONSTRATION OF PACKAGING OF FERNALD SILO I WASTE IN CHEMICALLY BONDED PHOSPHATE CERAMIC

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ABSTRACT

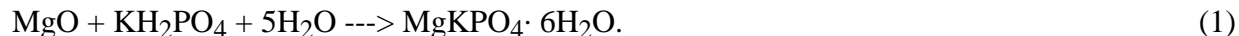
This paper summarizes our experience in bench-scale packaging of Fernald Silo I waste in chemically bonded phosphate ceramics. The waste was received from the Fernald Environmental Management Project (FEMP), and its treatability was studied in our laboratory. This waste contained As^{5+} , Ba, Cr^{6+} , Ni, Pb, Se^{4+} , and Zn as the hazardous contaminants. In addition, the total specific activity of all the radioactive isotopes in the waste was $3.85 \mu\text{Ci/g}$, of which that of radium alone was $0.477 \mu\text{Ci/g}$. This indicated that radon (a daughter product of the radium) in the waste could present a serious handling problem during this study. For this reason, the waste was handled and stored in a flowing-air glovebox. We made waste form samples with an actual waste loading of 66.05 wt.% and subjected them to the Environmental Protection Agency (EPA) Toxicity Characteristic Leaching Procedure (TCLP). The results showed excellent stabilization of all contaminants. Actual levels detected in the leachate were well below the EPA's most stringent Universal Treatment Standards and in almost all cases were one order of magnitude below this limit. Radioactivity in the leachate was also very low. Alpha activity was $25 \pm 2.5 \text{ pCi/mL}$, while beta activity was $9.81 \pm 0.98 \text{ pCi/mL}$. This very low activity was attributed to the efficient stabilization of radium as insoluble radium phosphate in the waste form, thus prohibiting its leaching. This study indicates that the chemically bonded phosphate ceramic process may be a very suitable way to package Silo I waste for transportation and storage or disposal.

INTRODUCTION

Fernald Silo wastes are residues from the processing of pitchblende ores during 1949-1958. The wastes are stored in silos in Operable Unit 4 (OU4) at DOE's Fernald Experimental Management Facility (FEMP) in Ohio.

Recently, the Mixed Waste Focus Area (MWFA) of DOE funded a feasibility project to assess several technologies to treat the wastes from these silos. The chemically bonded phosphate ceramic (CBPC) process developed at Argonne National Laboratory (1-3) was one such technology. This paper provides an overview of this work on Silo I waste.

The CBPC process is based on acid-base reactions used to form compounds that mimic phosphate minerals found in nature and that have very low solubility. It is based on the reaction between calcined magnesium oxide (MgO) and a solution of monopotassium phosphate (KH_2PO_4). The reaction product is magnesium potassium phosphate ($\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$) that is formed by dissolution of MgO in the solution of KH_2PO_4 and its eventual reaction to form the product according to the reaction



This product is the binder that can be used to form the matrix material to host wastes.

Wastes with a wide range of pH can be stabilized by this process and hence setting is possible with a range of feedstock from acidic to basic wastes. The process uses commercially available low-cost powders and mixing equipment and can be scaled up to any size and operations and carried out at waste sites with mobile equipment. The cost of treating wastes is low and comparable to that of cement grouting. No secondary waste streams are generated in the process and no volume increase occurs during stabilization. For these reasons, this technology is a good candidate for packaging OU4 waste streams at Fernald.

There have been earlier attempts to thermally treat the OU4 waste streams. Jantzen et al. (4), Janke et al., (5), and Merrill and Janke (6) have reported results on vitrifying simulated OU4 waste streams. The approach taken in our work is distinct from theirs. We demonstrate stabilization and packaging of actual Silo I waste at room temperature. The advantages of this approach are several:

- No secondary waste streams result from this process due to volatility of any components of the primary waste stream.
- Glovebox operation is easier because no heating elements are required.
- In general, the cost of this process is lower than that of vitrification (7).

The study was conducted in two steps. Surrogate waste formulated by FEMP experts was used in this study to tailor the process for maximum waste loading. The results were then used to fabricate waste forms with actual Silo I waste, which were evaluated using the standard Toxicity Characteristic Leaching Procedure (TCLP) (8). While a large number of samples are being tested by FEMP for complete evaluation, we present here the results of the TCLP test performed in our laboratory, because this test has been very conclusive in establishing that the CBPC process is one of the most suitable approaches for packaging Silo I waste.

COMPOSITION OF SILO I WASTE

Considerable characterization work has been done on Silo waste streams. The general composition given by Jantzen et al. (4) is shown in Table I.

The data in Table I show that the main component in the waste is silica, which accounts for two-thirds of the waste stream. The Fe_2O_3 (haematite) gives the waste its red color. In addition, alumina, lime, and alkali metals are present in low but significant concentrations.

The major hazardous components in the waste are lead and barium. Their very high concentrations make this waste very difficult to stabilize. Most of the lead is in the form of carbonate. In addition, the waste also contains other hazardous components such as nickel and zinc, and in addition, metals in higher oxidation states such as As^{5+} , Cr^{6+} , and Se^{4+} . These metals in higher oxidation states are easily leachable, unless they are reduced during the stabilization process. One purpose of this work was to demonstrate stabilization of these metals in higher oxidation states.

Table I. General composition of Silo I and II wastes

| Nonhazardous components | | Hazardous components | |
|--------------------------------|-------|------------------------|--|
| Oxide | Wt. % | Oxide | Wt. % |
| Al ₂ O ₃ | 3.7 | BaO | 6.3 |
| CaO | 1.5 | PbO | 12.3 |
| Fe ₂ O ₃ | 4.8 | Oxides of | All at trace levels and in parts per million (ppm) |
| K ₂ O | 0.9 | As ⁵⁺ , | |
| MgO | 1.7 | Cr ⁶⁺ , | |
| Na ₂ O | 1.7 | Ni, | |
| P ₂ O ₅ | 0.8 | Se ⁴⁺ , and | |
| SiO ₂ | 62.9 | Zn | |

RADIOACTIVITY IN THE WASTE

The major radioactive component in the waste was radium (²²⁶Ra). Its specific activity was 0.477 $\mu\text{Ci/g}$, and the total specific activity of all the isotopes in the waste was 3.85 $\mu\text{Ci/g}$. This high activity was a concern while dealing with this waste in our laboratory. In particular, due to the high activity of radium, emanation of its gaseous daughter product radon (²²²Rn) into the laboratory atmosphere was a serious concern.

SAMPLE PREPARATION

When the sealed container was received from FEMP, it was opened and exhaled in a fume hood for three days to allow the trapped radon to escape. The entire treatability study had to be performed in the fume hood. Each time, only a precalculated amount of waste was removed from the container and the remainder was kept in the closed container. The operators wore double layers of gloves. Before and after each session of the work, the room was surveyed to detect any stray contamination in the room; if detected, the room was decontaminated.

Our initial study was done with the surrogate waste provided by FEMP. It was a mixture of oxides that simulated the actual waste very closely. Determining treatability with the surrogate waste was necessary to avoid expensive failure with the real waste streams. Various waste loadings were attempted with the surrogate waste and, based on physical and mechanical properties, the highest waste loading was selected for the treatability study to be done with actual waste.

As shown in Table II, the optimal waste loading achieved with the dry surrogate waste was 60.5 wt.%. At this level, the samples set well into homogeneous monoliths. The density of the samples was 1.986 g/cm³, and open porosity measured by the water intrusion technique was

Table II. Composition (wt.%) of test samples

| Sample identity | Waste, dry | Waste, actual | Binder | Total water |
|---------------------------|------------|-----------------|--------|-------------|
| Surrogate waste | 60.5 | NA ^a | 26.2 | 13.3 |
| Actual waste ^b | 53.5 | 66.05 | 24 | 23.55 |

^aNA: not applicable.

^bActual waste contains 19 wt.% of water.

4.8%. Compressive strength was 3318 psi; the land disposal requirements for compressive strength are only 500 psi and the strength obtained in our study is nearly one order of magnitude higher than that. Therefore, even this high waste loading was considered to be feasible and safe. Using this high loading as a guideline, we could make samples of the actual waste with a loading of 66.05 wt.%. This higher loading was possible partly because of the 19 wt.% water in the actual waste, which partly compensated for the stoichiometric water needed for the reaction represented in Eq. 1. As one may notice in Table II, the total water content in the slurry of the actual waste was higher than that in the slurry of the surrogate waste. Despite this difference, the slurry of the actual waste had the same consistency as that of the slurry of the surrogate waste.

A 5-gal concrete mixer placed in the fume hood was used for this study. The actual waste received from FEMP was first homogenized by mixing it for ≈ 30 min. The waste was then mixed with the binder powders and water, and the reactions were allowed to occur during mixing of the components for another 30 min. The resulting slurry was a smooth paste that could be poured into molds to form 2 x 2 x 2 in. cubes; or cylinders of 1.0 in. diameter. The slurry set in ≈ 2 h and formed hard samples. Slurry temperature rose to $\approx 55^\circ\text{C}$ during setting. The samples were allowed to cure for several weeks before they were removed from the molds and tested.

EXPERIMENTAL RESULTS

The main criterion used for testing good packaging of a mixed waste is the Toxicity Characteristic Leaching Procedure (TCLP) (8). To evaluate containment of the radioactive isotopes, we also tested the leachate for radioactivity at the end of the TCLP test. Normally, leaching of radionuclides is done by using American Nuclear Society's 16.1 90-day immersion test (9) on the monolithic sample. It is expected that FEMP will perform this test on a large number of samples made by us and provided to them. In our evaluation, however, because the leachate water was collected from crushed samples, the TCLP test was more severe and came closer to the worst-case scenario than did the ANS 16.1 immersion test. Results from the TCLP test are presented in Tables III and IV.

The TCLP results in Table III show that the samples passed the test at the UTS limits for all metals. This indicates that the phosphate bonded ceramic process is a very good candidate for stabilizing all of the hazardous metals shown in Table III. In particular, the Pb concentration in the waste was ≈ 12 wt.% . As a result, at the dry waste loading of 53.5 wt.% in waste form, Pb

Table III. TCLP results on stabilized samples (mg/L)

| Contaminant | As | Cd | Cr | Co | Cu | Ni | Pb | Se | Sr |
|-------------------|------|------|------|------|------|------|------|------|------|
| Level in leachate | 0.22 | <0.1 | 0.05 | 0.55 | 0.01 | 2.31 | <0.1 | 0.82 | 0.13 |
| UTS limit | 5.0 | 0.2 | 0.85 | - | - | 13.6 | 0.75 | 5.7 | - |

content was 64,200 ppm in the waste form that was tested. In spite of this high content in the waste form, the Pb level in the leachate was below the detection limit of 0.1 ppm. This demonstrates the effectiveness of the process in stabilizing hazardous metals in the waste.

Table IV gives the specific activities in various samples, including those in the TCLP leachate. The total specific activity in the leachate was calculated on the basis of the measurement of alpha and beta activity in the leachate and then estimating the gamma activity as equal to that of beta. With this total specific activity of the leachate, we could then estimate the total activity in the leachate, which was 20 times (by weight) that of the waste form subjected to the leaching procedure. This amounted to 4.42 $\mu\text{Ci/g}$ of the waste form. When this is compared with the specific activity in the waste (2.06 $\mu\text{Ci/g}$), one finds that the leaching activity is lower by three orders of magnitude, or containment of the radioactive isotopes due to stabilization of the waste by the phosphate bonded ceramic process is higher by three orders. The radium content in the waste was 0.477 $\mu\text{Ci/g}$. Because radium is water-soluble, the leachate would be a pathway for it. Despite this, the leachate activity is extremely low, implying that the radium and most other isotopes are well stabilized in the waste forms. This is possible because radium would form its insoluble phosphate form in the leachate; hence, the chemically bonded phosphate process is a good method for arresting leaching of radioactive contaminants.

Table IV. Specific activities ($\mu\text{Ci/g}$) in various samples^a

| Sample code | Alpha | Beta | Total |
|--|------------|-------------|----------------|
| Waste as received | | | |
| Total specific activity | --- | --- | 3.85 |
| Specific activity of ^{226}Ra | --- | --- | 0.477 |
| Calculated activities in waste form | | | |
| Total specific activity | --- | --- | 2.06 |
| Specific activity of ^{226}Ra | --- | --- | 0.255 |
| Specific activities in TCLP leachate (pCi/g) | 25 ± 2 | 98 ± 10 | 221 ± 22^a |

^aAs an approximation, we have assumed that activity of gamma radiation is nearly equal to that of beta activity.

DISCUSSION AND CONCLUSIONS

This study has demonstrated that the CBPC process has the potential for stabilizing both hazardous contaminants and radioactive isotopes from the Fernald Silo I waste. High waste loadings of ≈ 60 dry wt.% and ≈ 66 actual wt.% are feasible. Even at such high waste loadings, contaminant concentrations in the TCLP leachates have remained well below the UTS limit. This implies that the above waste loadings may be used for packaging the Silo wastes.

Even at the higher waste loading of 66 wt.%, there is no effective increase in volume of the waste form. The waste forms had the same volume as that of the waste. The binders simply occupied the space of the voids in the waste. This means that disposal costs are not increased because of the stabilization.

The Silo wastes, though low-level waste streams, are difficult to handle because of the radon emanation. Several difficulties were encountered while handling this waste. For example, radon accumulated in the closed containers. Therefore, while opening the container, care had to be taken to ensure that radon did not diffuse into the room.

During storage and handling of the samples, we also noted that radon permeated through the airtight polyethylene bags. This indicates that such bags are probably not suitable for handling this waste or its waste forms. And because the contamination might have permeated through a single glove layer, double gloves and double shoe covers were used by the workers.

Aside from these problems related to the activity of the waste, the surrogate waste and the actual waste behaved very similarly during stabilization. For future work on this waste with the CBPC process, the surrogate formulation used in this study is very appropriate.

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DEMONSTRATION OF PACKAGING OF FERNALD SILO I WASTE IN CHEMICALLY BONDED PHOSPHATE CERAMIC*

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ABSTRACT

This paper summarizes our experience in bench-scale packaging of Fernald Silo I waste in chemically bonded phosphate ceramics. The waste was received from the Fernald Environmental Management Project (FEMP), and its treatability was studied in our laboratory. This waste contained As^{5+} , Ba, Cr^{6+} , Ni, Pb, Se^{4+} , and Zn as the hazardous contaminants. In addition, the total specific activity of all the radioactive isotopes in the waste was $3.85 \mu\text{Ci/g}$, of which that of radium alone was $0.477 \mu\text{Ci/g}$. This indicated that radon (a daughter product of the radium) in the waste could present a serious handling problem during this study. For this reason, the waste was handled and stored in a flowing-air glovebox. We made waste form samples with an actual waste loading of 66.05 wt.% and subjected them to the Environmental Protection Agency (EPA) Toxicity Characteristic Leaching Procedure (TCLP). The results showed excellent stabilization of all contaminants. Actual levels detected in the leachate were well below the EPA's most stringent Universal Treatment Standards and in almost all cases were one order of magnitude below this limit. Radioactivity in the leachate was also very low. Alpha activity was $25 \pm 2.5 \text{ pCi/mL}$, while beta activity was $9.81 \pm 0.98 \text{ pCi/mL}$. This very low activity was attributed to the efficient stabilization of radium as insoluble radium phosphate in the waste form, thus prohibiting its leaching. This study indicates that the chemically bonded phosphate ceramic process may be a very suitable way to package Silo I waste for transportation and storage or disposal.

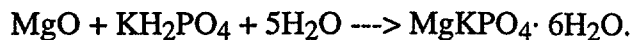
INTRODUCTION

Fernald Silo wastes are residues from the processing of pitchblende ores during 1949-1958. The wastes are stored in silos in Operable Unit 4 (OU4) at DOE's Fernald Experimental Management Facility (FEMP) in Ohio.

Recently, the Mixed Waste Focus Area (MWFA) of DOE funded a feasibility project to assess several technologies to treat the wastes from these silos. The chemically bonded phosphate

ceramic (CBPC) process developed at Argonne National Laboratory [1-3] was one such technology. This paper provides an overview of this work on Silo I waste.

The CBPC process is based on acid-base reactions used to form compounds that mimic phosphate minerals found in nature and that have very low solubility. It is based on the reaction between calcined magnesium oxide (MgO) and a solution of monopotassium phosphate (KH_2PO_4). The reaction product is magnesium potassium phosphate ($\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$) that is formed by dissolution of MgO in the solution of KH_2PO_4 and its eventual reaction to form the product according to the reaction



This product is the binder that can be used to form the matrix material to host wastes.

Wastes with a wide range of pH can be stabilized by this process and hence setting is possible with a range of feedstock from acidic to basic wastes. The process uses commercially available low-cost powders and mixing equipment and can be scaled up to any size and operations and carried out at waste sites with mobile equipment. The cost of treating wastes is low and comparable to that of cement grouting. No secondary waste streams are generated in the process and no volume increase occurs during stabilization. For these reasons, this technology is a good candidate for packaging OU4 waste streams at Fernald.

There have been earlier attempts to thermally treat the OU4 waste streams. Jantzen et al. [4], Janke et al., [5], and Merrill and Janke [6] have reported results on vitrifying simulated OU4 waste streams. The approach taken in our work is distinct from theirs. We demonstrate stabilization and packaging of actual Silo I waste at room temperature. The advantages of this approach are several:

- No secondary waste streams result from this process due to volatility of any components of the primary waste stream.
- Glovebox operation is easier because no heating elements are required.
- In general, the cost of this process is lower than that of vitrification [7].

The study was conducted in two steps. Surrogate waste formulated by FEMP experts was used in this study to tailor the process for maximum waste loading. The results were then used to fabricate waste forms with actual Silo I waste, which were evaluated using the standard Toxicity Characteristic Leaching Procedure (TCLP) [8]. While a large number of samples are being tested by FEMP for complete evaluation, we present here the results of the TCLP test performed in our

laboratory, because this test has been very conclusive in establishing that the CBPC process is one of the most suitable approaches for packaging Silo I waste.

COMPOSITION OF SILO I WASTE

Considerable characterization work has been done on Silo waste streams. The general composition given by Jantzen et al. [4] is shown in Table 1.

Table 1. General composition of Silo I and II wastes

| Nonhazardous components | | Hazardous components | |
|--------------------------------|-------|------------------------|--|
| Oxide | Wt. % | Oxide | Wt. % |
| Al ₂ O ₃ | 3.7 | BaO | 6.3 |
| CaO | 1.5 | PbO | 12.3 |
| Fe ₂ O ₃ | 4.8 | Oxides of | All at trace levels and in parts per million (ppm) |
| K ₂ O | 0.9 | As ⁵⁺ , | |
| MgO | 1.7 | Cr ⁶⁺ , | |
| Na ₂ O | 1.7 | Ni, | |
| P ₂ O ₅ | 0.8 | Se ⁴⁺ , and | |
| SiO ₂ | 62.9 | Zn | |

The data in Table 1 show that the main component in the waste is silica, which accounts for two-thirds of the waste stream. The Fe₂O₃ (haematite) gives the waste its red color. In addition, alumina, lime, and alkali metals are present in low but significant concentrations.

The major hazardous components in the waste are lead and barium. Their very high concentrations make this waste very difficult to stabilize. Most of the lead is in the form of carbonate. In addition, the waste also contains other hazardous components such as nickel and zinc, and in addition, metals in higher oxidation states such as As⁵⁺, Cr⁶⁺, and Se⁴⁺. These metals in higher oxidation states are easily leachable, unless they are reduced during the stabilization process. One purpose of this work was to demonstrate stabilization of these metals in higher oxidation states.

RADIOACTIVITY IN THE WASTE

The major radioactive component in the waste was radium (^{226}Ra). Its specific activity was $0.477\ \mu\text{Ci/g}$, and the total specific activity of all the isotopes in the waste was $3.85\ \mu\text{Ci/g}$. This high activity was a concern while dealing with this waste in our laboratory. In particular, due to the high activity of radium, emanation of its gaseous daughter product radon (^{222}Rn) into the laboratory atmosphere was a serious concern.

SAMPLE PREPARATION

When the sealed container was received from FEMP, it was opened and exhaled in a fume hood for three days to allow the trapped radon to escape. The entire treatability study had to be performed in the fume hood. Each time, only a precalculated amount of waste was removed from the container and the remainder was kept in the closed container. The operators wore double layers of gloves. Before and after each session of the work, the room was surveyed to detect any stray contamination in the room; if detected, the room was decontaminated.

Our initial study was done with the surrogate waste provided by FEMP. It was a mixture of oxides that simulated the actual waste very closely. Determining treatability with the surrogate waste was necessary to avoid expensive failure with the real waste streams. Various waste loadings were attempted with the surrogate waste and, based on physical and mechanical properties, the highest waste loading was selected for the treatability study to be done with actual waste.

As shown in Table 2, the optimal waste loading achieved with the dry surrogate waste was 60.5 wt.%. At this level, the samples set well into homogeneous monoliths. The density of the samples was $1.986\ \text{g/cm}^3$, and open porosity measured by the water intrusion technique was 4.8%. Compressive strength was 3318 psi; the land disposal requirements for compressive strength are only 500 psi and the strength obtained in our study is nearly one order of magnitude higher than that. Therefore, even this high waste loading was considered to be feasible and safe. Using this high loading as a guideline, we could make samples of the actual waste with a loading of 66.05 wt.%. This higher loading was possible partly because of the 19 wt.% water in the actual waste, which partly compensated for the stoichiometric water needed for the reaction represented in Eq. 1. As one may notice in Table 2, the total water content in the slurry of the actual waste was higher than that in the slurry of the surrogate waste. Despite this difference, the slurry of the actual waste had the same consistency as that of the slurry of the surrogate waste.

Table 2. Composition (wt.%) of test samples

| Sample identity | Waste, dry | Waste, actual | Binder | Total water |
|---------------------------|------------|-----------------|--------|-------------|
| Surrogate waste | 60.5 | NA ^a | 26.2 | 13.3 |
| Actual waste ^b | 53.5 | 66.05 | 24 | 23.55 |

^aNA: not applicable.

^bActual waste contains 19 wt.% of water.

A 5-gal concrete mixer placed in the fume hood was used for this study. The actual waste received from FEMP was first homogenized by mixing it for ≈ 30 min. The waste was then mixed with the binder powders and water, and the reactions were allowed to occur during mixing of the components for another 30 min. The resulting slurry was a smooth paste that could be poured into molds to form 2 x 2 x 2 in. cubes; or cylinders of 1.0 in. diameter. The slurry set in ≈ 2 h and formed hard samples. Slurry temperature rose to ≈ 55 °C during setting. The samples were allowed to cure for several weeks before they were removed from the molds and tested.

EXPERIMENTAL RESULTS

The main criterion used for testing good packaging of a mixed waste is the Toxicity Characteristic Leaching Procedure (TCLP) [8]. To evaluate containment of the radioactive isotopes, we also tested the leachate for radioactivity at the end of the TCLP test. Normally, leaching of radionuclides is done by using American Nuclear Society's 16.1 90-day immersion test [9] on the monolithic sample. It is expected that FEMP will perform this test on a large number of samples made by us and provided to them. In our evaluation, however, because the leachate water was collected from crushed samples, the TCLP test was more severe and came closer to the worst-case scenario than did the ANS 16.1 immersion test. Results from the TCLP test are presented in Tables 3 and 4.

The TCLP results in Table 3 show that the samples passed the test at the UTS limits for all metals. This indicates that the phosphate bonded ceramic process is a very good candidate for stabilizing all of the hazardous metals shown in Table 3. In particular, the Pb concentration in the waste was ≈ 12 wt.% . As a result, at the dry waste loading of 53.5 wt.% in waste form, Pb content was 64,200 ppm in the waste form that was tested. In spite of this high content in the waste form, the Pb level in the leachate was below the detection limit of 0.1 ppm. This demonstrates the effectiveness of the process in stabilizing hazardous metals in the waste.

Table 3. TCLP results on stabilized samples (mg/L)

| Contaminant | As | Cd | Cr | Co | Cu | Ni | Pb | Se | Sr |
|-------------------|------|------|------|------|------|------|------|------|------|
| Level in leachate | 0.22 | <0.1 | 0.05 | 0.55 | 0.01 | 2.31 | <0.1 | 0.82 | 0.13 |
| UTS limit | 5.0 | 0.2 | 0.85 | - | - | 13.6 | 0.75 | 5.7 | - |

Table 4 gives the specific activities in various samples, including those in the TCLP leachate. The total specific activity in the leachate was calculated on the basis of the measurement of alpha and beta activity in the leachate and then estimating the gamma activity as equal to that of beta. With this total specific activity of the leachate, we could then estimate the total activity in the leachate, which was 20 times (by weight) that of the waste form subjected to the leaching procedure. This amounted to $4.42 \mu\text{Ci/g}$ of the waste form. When this is compared with the specific activity in the waste ($2.06 \mu\text{Ci/g}$), one finds that the leaching activity is lower by three orders of magnitude, or containment of the radioactive isotopes due to stabilization of the waste by the phosphate bonded ceramic process is higher by three orders. The radium content in the waste was $0.477 \mu\text{Ci/g}$. Because radium is water-soluble, the leachate would be a pathway for it. Despite this, the leachate activity is extremely low, implying that the radium and most other isotopes are well stabilized in the waste forms. This is possible because radium would form its insoluble phosphate form in the leachate; hence, the chemically bonded phosphate process is a good method for arresting leaching of radioactive contaminants.

Table 4. Specific activities ($\mu\text{Ci/g}$) in various samples^a

| Sample code | Alpha | Beta | Total |
|--|------------|-------------|----------------|
| Waste as received | | | |
| Total specific activity | --- | --- | 3.85 |
| Specific activity of ^{226}Ra | --- | --- | 0.477 |
| Calculated activities in waste form | | | |
| Total specific activity | --- | --- | 2.06 |
| Specific activity of ^{226}Ra | --- | --- | 0.255 |
| Specific activities in TCLP leachate (pCi/g) | 25 ± 2 | 98 ± 10 | 221 ± 22^a |

^aAs an approximation, we have assumed that activity of gamma radiation is nearly equal to that of beta activity.

DISCUSSION AND CONCLUSIONS

This study has demonstrated that the CBPC process has the potential for stabilizing both hazardous contaminants and radioactive isotopes from the Fernald Silo I waste. High waste loadings of ≈ 60 dry wt.% and ≈ 66 actual wt.% are feasible. Even at such high waste loadings, contaminant concentrations in the TCLP leachates have remained well below the UTS limit. This implies that the above waste loadings may be used for packaging the Silo wastes.

Even at the higher waste loading of 66 wt.%, there is no effective increase in volume of the waste form. The waste forms had the same volume as that of the waste. The binders simply occupied the space of the voids in the waste. This means that disposal costs are not increased because of the stabilization.

The Silo wastes, though low-level waste streams, are difficult to handle because of the radon emanation. Several difficulties were encountered while handling this waste. For example, radon accumulated in the closed containers. Therefore, while opening the container, care had to be taken to ensure that radon did not diffuse into the room.

During storage and handling of the samples, we also noted that radon permeated through the airtight polyethylene bags. This indicates that such bags are probably not suitable for handling this waste or its waste forms. And because the contamination might have permeated through a single glove layer, double gloves and double shoe covers were used by the workers.

Aside from these problems related to the activity of the waste, the surrogate waste and the actual waste behaved very similarly during stabilization. For future work on this waste with the CBPC process, the surrogate formulation used in this study is very appropriate.

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Title: Overview of Remote Retrieval Equipment and the Strategy for removal of Radon Bearing Waste from Silos 1 and 2 at the Fernald Site

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Description/Abstract: This document provides an overview of the remote retrieval equipment and strategy for the retrieval of waste from Silos 1 and 2 at the Department of Energy's Fernald site in southwestern Ohio. The scope of this paper is limited to general descriptions of remote equipment specifically related in-silo retrieval. The retrieval strategy describes how the contractor team is planning to utilize the various remote subsystems to efficiently remove the waste from the silos from a philosophical standpoint as opposed to a procedural and operational standpoint. The retrieval strategy and approach is based upon the successful tank retrieval operations conducted at DOE's Oak Ridge and Hanford Sites. Lessons learned from these previous operations have been utilized in planning an approach for the Fernald Silo Retrieval Project. The equipment overview includes discussion of the retrieval system configurations together with descriptions of the robotic arm and retrieval end effectors, the conditioning and transfer pumping system, the sluicer and sluicing pump, as well as the debris retrieval system. A unique challenge being addressed as part of this project is the waste contents. Silos 1 and 2 contain two distinct layers of material that need to be retrieved. The first layer is a Bentonite (trade name BentogROUT™) cap that was placed in the silos to prevent radon migration into the dome space and out of the silos. The Bentonite layer varies, but in general it is approximately six inches deep in the center of the silo and thirty-six inches near the silo walls. The material may have dried out on the surface, and may still be wetted near the bottom of the bentonite layer. The K-65 ore tailings, which were slurried into

the silos, are the remainder of the waste that is over 20' in depth. This paper provides an overview of the retrieval strategies, technologies, and techniques that will be used to safely and efficiently retrieve the waste from the Fernald Silos.

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