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Immobilization of Fission Products in Phosphate Ceramic Waste Forms

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EM Focus Areas: high-level waste tank remediation; mixed-waste characterization, treatment, and disposal; subsurface contaminants; decontamination and decommissioning

Technology Need

The current volume of high-level waste (HLW) across the DOE complex is several hundred thousand cubic meters. This wastes includes solids, sludges, liquids, and salt cake and comprises radionuclides in three broad categories: actinides, lanthanides, and fission products. Because of the diverse chemical and physical nature of the components in these three categories, the HLW cannot be effectively and inexpensively stabilized and disposed of by a single-step process or technology.

The presence of fission products such as ^{99}Tc, ^{137}Cs, and ^{90}Sr in the HLW poses myriad problems. These radionuclides are highly volatile and may escape into the offgas during HLW vitrification, thus generating a secondary waste stream that will require additional stabilization/solidification (S/S). Technetium is readily oxidized to a highly soluble pertechnetate form that is very difficult to immobilize. Technetium and cesium (^{135}Cs) have extremely long half-lives ($\approx 10^6$ years) and require an appropriate durable immobilization system. Moreover, ^{137}Cs and ^{90}Sr are also heat generators with half-lives of $\approx$30 years; therefore, they will be sources of considerable heat loads for 30 to 50 years if disposed of in a repository in vitrified HLW.

The approach under consideration is to remove fission products from HLW and dispose of them separately. Removing fission products from the HLW reduces the overall waste volume and radioactivity levels of HLW, thus simplifying waste-handling operations. In this regard, several separation technologies are being developed as part of the ESP-CP. These separation technologies, along with other decontamination activities, result in waste streams that are rich in fission products and, if not returned to the bulk HLW stream, require S/S for safe disposal in compliance with federal regulations. Currently, no robust and reliable low-temperature technology is available to immobilize the fission-product wastes. Such a technology could produce durable waste forms for long-term storage and disposal of the fission products and/or the "loaded" separating agents used to remove fission products from the HLW streams. To this end, we are developing and demonstrating a low-temperature treatment and stabilization technology based on chemically bonded phosphate ceramics. Specifically, the focus of this task is to develop phosphate ceramics to immobilize ^{99}Tc eluted from sorption processes.

Technology Description

Chemically bonded phosphate ceramics (CBPCs) have several advantages that make them ideal candidates for containing radioactive and hazardous wastes. In general, phosphates have high solid-solution capacities for incorporating radionuclides, as evidenced by several phosphates (e.g., monazites and apatites) that are natural analogs of radioactive and rare-earth elements. The phosphates have high radiation stability, are refractory, and will not degrade in the presence of internal heating by fission products. Dense and hard CBPCs can be fabricated inexpensively and at low temperature by acid-base reactions between an inorganic oxide/hydroxide powder and either phosphoric acid or an acid-phosphate solution. The resulting phosphates are extremely insoluble in aqueous media and have excellent long-term durability. CBPCs offer the dual stabilization mechanisms of chemical fixation and physical encapsulation, resulting in superior waste forms.

Argonne National Laboratory (ANL) is developing CBPCs to treat low-level mixed wastes, particularly those containing volatiles and pyrophorics that cannot be treated by conventional thermal processes. This work was begun under ANL's Laboratory Directed Research

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and Development funds, followed by further development with support from EM-50's Mixed Waste Focus Area.

As part of our previous work, we developed magnesium- and magnesium-potassium-based final waste forms containing several surrogate waste streams, including ash, salts, and cement sludge (all spiked with contaminants such as Ce, Cs, Pb, Ni, Cr, Cd, and Hg). A variety of performance tests (TCLP, ANS 16.1, 90-day water immersion tests, and ASTM compression-strength tests) conducted on the fabricated final waste forms showed excellent results, thus demonstrating that the CBPCs are a viable approach for disposal of radioactive and hazardous wastes.

The goal of this task is develop and demonstrate the feasibility of CBPCs for S/S of wastes containing fission products. The focus of this work is to develop a low-temperature CBPC immobilization system for eluted ^{99}Tc wastes from sorption processes.

Benefit to DOE/EM

This task will provide a novel low-temperature process for treating and stabilizing fission products generated from cleanup of HLW tanks and D&D processes. CBPC technology will complement the various separation technologies used to remove fission products (especially Tc) from HLW tanks by immobilizing the separated volatile radionuclides in a durable final waste form. Also, CBPC can be used to treat mixed wastes to meet land disposal restrictions for waste streams that are incompatible with high-temperature processing, particularly wastes containing volatiles, pyrophorics, and heavy-metal chlorides and fluorides. Therefore, this technology will complement high-temperature treatment processes (e.g., plasma hearth and vitrification) and fill a gap in DOE's strategy to treat wastes that contain volatile contaminants, thus becoming an integral part of a complete system for stabilizing both high- and low-level wastes.

This technology addresses waste streams at various DOE sites, primarily Hanford and Savannah River. In addition, the work will be critical to ongoing cleanup activities at Rocky Flats, Idaho National Engineering Laboratory, Los Alamos National Laboratory (LANL), and Oak Ridge National Laboratory.

Results to date on radionuclide surrogates have shown excellent retainment of contaminants in the CBPCs. The technology generates no secondary wastes; moreover, it is relatively low cost and has only minimal energy requirements, providing an extremely attractive high return on investment.

Technology Transfer/Collaborations

In FY 1997, we are collaborating with Northwestern University to study phase analysis and pore structure of the fabricated waste forms and establish the speciation and valence state of ^{99}Tc in the final waste form. This collaborative work will provide critical insights into leaching behavior of the radionuclide and durability of the final waste form.

Collaborative work is already under way with LANL and Savannah River Site (SRS). The CBPC technology is being targeted for the ^{99}Tc-containing wastes generated by LANL's complexation-elution process, and a treatability study on the eluted wastes containing actual radionuclides is being conducted at LANL. During FY 1996, we used the CBPC process to successfully demonstrate the stabilization of phosphoric acid residue waste generated by the SRS process for destroying ion-exchange resins. We expect this collaboration to continue in FY 1997.

Successful demonstration of CBPC technology on actual wastes during FY 1997 will lead to the development of the technology at the pilot scale. For this work, industrial partners in waste solidification and DOE site(s) for demonstration will be identified. An onsite demonstration will be sought with concurrence from EM staff that will stimulate collaboration between industry, ANL, and DOE to ensure successful technology transfer to end users.

Scientific Background

Based on thermodynamic predictions and evidence from nature, it is clear that only crystalline waste forms will survive under relatively modest temperatures ($\approx$100°C) and in the presence of water. Therefore, to guarantee safe long-term disposal, it is necessary to not only incorporate the contaminants in a dense crystalline matrix but also chemically bind them. Several mechanisms are available to chemically fix contaminants in a mineral phase, including elemental substitution, conversion of the contaminant to an insoluble form, and intercalation reactions.

Elemental substitution occurs when the contaminant species substitutes for a benign ion with similar characteristics such as valence or ionic radius and does not disrupt the atomic arrangement of the crystalline ceramics. The resulting material is a solid solution with similar stability properties.

In general, phosphates are extremely insoluble. If by chemical reactions, contaminants are converted into their phosphate form, they can then be prevented from dissolving in a liquid phase and leaching out. Intercalation reactions occur in two-dimensional layered structures. The guest ions or molecules can be accommodated within the interlayers and are bound. Because a layered host lattice is easily deformable in the third dimension, a wide range of ions and molecules can be incorporated in such a material system.

Because phosphate ceramics exhibit one or more of the above-mentioned mechanisms, they are being considered for the S/S of fission products. CBPCs are refractory, have high radiation stability, and can tolerate structural changes caused by decay of radioactive contaminants. Moreover, it is expected that in CBPC technology, contaminants will be first chemically fixed and then microencapsulated in a dense phosphate matrix, resulting in a superior waste form.

Technical Approach

During FY 1996, CBPCs were used to stabilize two target wastes: separated Tc wastes from LANL's complexation-elution process and an acid residue waste from oxidation of ion-exchange resins. Radionuclide surrogates were used for this effort. Dense and durable magnesium and magnesium-potassium phosphates were developed. Waste forms were fabricated at room temperature through acid-base reactions. Various standard performance tests for leachability, strength, and durability in aqueous environments were conducted on the forms. Parametric studies were conducted to optimize the waste loadings, radionuclide surrogate, and Resource Conservation and Recovery Act metal content that could be stabilized in the phosphate ceramic. Based on this developmental work in FY 1996, the CBPC technology will be applied to eluted waste with ^{99}Tc in FY 1997. The detailed approach for the FY 1997 task is as follows.

Development of final waste forms with actual radionuclides:

- A treatability study will be conducted on eluted Tc waste from LANL's complexation-elution process. A mixture of ^{95m}Tc/^{99}Tc from solutions of NaOH/ethylenediamine/Sn^{2+} will be incorporated in a phosphate matrix to determine the performance of reduced and complexed Tc. The NaOH/ethylenediamine/Sn^{2+} solution is the material that results from eluting Tc from a Reillex™-HPQ anion exchanger column. In a separate study, Tc will be incorporated directly into the phosphate matrix. These treatability studies will be conducted in collaboration with LANL.
- Fabricated waste forms will be tested for mechanical stability/compression strength (ASTM C 39), water immersion, leaching behavior (ANS 16.1, PCT, and MCC-1), radiation stability, and thermal cycling (ASTM B 553).
- Extensive microstructural and mineralogical evaluations will be carried out to determine the fate of Tc in the phosphate matrix. Specifically, the speciation and valence state of Tc in the waste form will be established through sophisticated analytical techniques.
- Based on the treatability studies, process limits and merits will be defined, and applicability limits will be established. These studies will be aimed at determining acceptability of the stabilized product and the bench-scale technology.

Accomplishments

The project was initiated in March 1996. Using radionuclide surrogates (Re for Tc), we demonstrated successfully during FY 1996 that CBPCs can be used for the S/S of Tc-containing wastes and other low-level mixed wastes. Specifically, two waste streams were targeted: separated Tc wastes from LANL's complexation-elution process, and an acid residue waste from oxidation of ion-exchange resins.

Highlights of FY 1996 results include:

- CBPCs are easily fabricated under ambient conditions. The technology is extremely rugged and can treat waste with a wide range of compositions. Waste loadings can be as high as 40 wt% for LANL's eluted Tc and 55 wt% acid residue waste streams. The presence of NaOH, ethylenediamine, and $SnCl_2$ in the LANL waste does not affect the phosphate solidification process.

- CBPCs are very dense, strong, and insoluble in aqueous environments. Compression strengths of 2500 to 4500 psi were measured for the waste forms. These strengths are similar to those for portland cement without any waste loading.
- CBPCs are extremely effective in the stabilization of Re (surrogate of Tc). A product consistency test conducted on CBPC-LANL eluted waste forms showed the leaching rates of Re to be 3 to 9 x 10^{-4} g/m^2-d. These values are significantly lower than those reported for Tc stabilized in borosilicate glass (0.12 g/m^2-d), but are comparable to those for SYNROC ($\approx 10^{-4}$ g/m^2-d). Similarly, ANS 16.1 tests on the waste forms indicated a leachability index (LI) for Re of >12. For comparison, LI for Tc in cement waste forms is 7 to 9. In addition, TCLP on CBPC-acid residue waste shows excellent stabilization of RCRA metals such as Cr and Ni in the phosphate matrix.
- CBPC waste forms show excellent long-term durability. Ninety-day water immersion tests show <0.5% change in sample weight, indicating no apparent dissolution of the matrix material.
- Microstructural and mineralogical characterization show the presence of both crystalline and amorphous phases in the waste forms. There is uniform distribution of the contaminants in the matrix, and no agglomeration. Contaminants are believed to be microencapsulated in the dense phosphate matrix.

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