

# Immobilization of Fission Products in Phosphate Ceramic Waste Forms

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EM Focus Areas: high-level waste tank remediation; contaminant plume containment and remediation

## Task Description

The goal of this project is to develop and demonstrate the feasibility of a novel low-temperature solidification/stabilization (S/S) technology for immobilizing waste streams containing fission products such as cesium, strontium, and technetium in a chemically bonded phosphate ceramic. This technology can immobilize partitioned tank wastes and decontaminate waste streams containing volatile fission products.

Conventional high-temperature immobilization technologies are not feasible for these waste streams because they cause volatilization of contaminants such as technetium and cesium. Therefore, low-temperature processing will be employed to fabricate zirconium-, magnesium-, and titanium- phosphate-based final waste forms for the S/S of waste streams containing fission products.

Contaminants can be chemically fixed in phosphate ceramics because of one or more of the following mechanisms: formation of an insoluble phosphate of the contaminants, elemental substitution in the matrix phosphate, and intercalation reactions within the phosphate matrix. Because the contaminants will be chemically fixed and physically encapsulated in an extremely dense and durable phosphate matrix, the final waste form is expected to have desirable properties.

In this new project, major tasks include 1) demonstrating the S/S of waste streams containing fission products, 2) scaling up the phosphate-bonded immobilization technology for field applications; and 3) transferring the phosphate-bonded immobilization technology to end users. During FY 1996,

we will focus on developing appropriate phosphate-bonded ceramic waste forms with optimized process parameters, using specific surrogate fission-product waste streams, and demonstrating their effective stabilization.

## Technology Needs

The current volume of high-level waste (HLW) across the DOE complex is several hundred thousand cubic meters. The waste includes solids, sludges, liquids, and salt cakes and comprises radionuclides in three broad categories: actinides, lanthanides, and fission products. Because of the diverse chemical and physical nature of these three components, 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  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$ , and  $^{99}\text{Tc}$  in the HLW poses myriad problems. Cesium and strontium are highly volatile and may escape into the offgas system during HLW vitrification, thus generating a secondary waste stream that will require additional S/S. Cesium and strontium radionuclides are also heat generators with half-lives of  $\approx 30$  years; therefore, they will generate considerable heat for 30 to 50 years if disposed of in a repository in vitrified HLW. In contrast,  $^{135}\text{Cs}$  and  $^{99}\text{Tc}$  have much longer half-lives ( $\approx 10^6$  years) and require an appropriate immobilization system.

Removing fission products from the HLW reduces the overall waste volume and radioactivity levels of the HLW, thus simplifying the waste-handling operations. This and other decontamination processes 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 technologies are available to immobilize the fission-product rich wastes. A low-temperature stabilization and immobilization technology can produce durable final waste forms for long-term storage or 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.

## Scientific Background

### Chemically Bonded Phosphate Ceramics

Novel chemically bonded phosphate ceramics have several advantages that make them ideal candidates for containment of 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 also have high radiation stability, are refractory, and will not degrade in the presence of internal heating from fission products. Dense and hard chemically bonded phosphate ceramics can be fabricated inexpensively and at low temperatures by acid-base reactions between an inorganic oxide/hydroxide powder and either a phosphoric acid solution or an acid-phosphate solution. The resulting phosphates are extremely insoluble in aqueous media and have excellent long-term durability. Dual stabilization mechanisms, chemical fixation and physical encapsulation, will provide superior contaminant retainment.

Argonne National Laboratory (ANL) has been developing chemically bonded phosphate ceramics to treat low-level mixed-waste streams, particularly those containing volatiles and pyrophorics that cannot be treated by conventional thermal processes. This work was begun under ANL’s Laboratory Directed Research and Development (LDRD) funds, followed

by further development with support from DOE’s Mixed Waste Integrated Program (Office of Technology Development, EM-50).

As part of our previous work, we developed magnesium-phosphate-based final waste forms with several surrogate waste streams, including ash, salts, and cement sludge (all spiked with contaminants such as cerium, lead, cadmium, chromium, and nickel). A variety of performance tests (TCLP and ANS 16.1, leaching tests, 90-day immersion tests, and ASTM compression-strength tests) conducted on the fabricated final waste forms showed excellent results, thus demonstrating the phosphate-bonded technology as a viable method for disposal of radioactive and hazardous wastes.

### Stabilization of Fission Products in Phosphate Ceramics

To guarantee safe long-term disposal, the radioactive contaminants must be not only incorporated into a dense and thermodynamically stable crystalline matrix but also chemically bound to it. Several mechanisms can be used to chemically fix the contaminants in a mineral phase, including intercalation reactions and elemental substitution.

Intercalation reactions occur in two-dimensional layered crystalline 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 by ion-exchange process and chemically bound. These layered materials have high potential for use as absorbents and ion exchangers. Several phosphate ceramics, including zirconium and titanium phosphates, exhibit intercalative ion exchanges; moreover, they are refractory, have high radiation stability, and can tolerate structural changes caused by the decay of radioactive contaminants because of their unique layered crystal structure. These phosphate binders are being investigated for the immobilization of fission products such as cesium and strontium.

Elemental substitution occurs when the contaminant species substitutes for a benign ion in the host mineral with similar chemical characteristics such as valence, ionic radius, etc., and does not disrupt the atomic arrangement of the crystalline phase. The resulting material is a solid solution with stability of the host mineral phase. The literature suggests that titanium minerals may be the ideal hosts for containment of technetium because titanium and technetium have similar ionic radii. Moreover, oxides of titanium and technetium form solid solutions. Thus, in this project, titanium phosphate system will be investigated as a candidate system for the stabilization of technetium containing wastes.

## Accomplishments

This is a new task for FY 1996.

## Technical Approach

During FY 1996, we will develop durable final waste forms using chemically bonded phosphate ceramics and simulated fission-product-rich waste stream. Three different phosphate systems (zirconium, magnesium, and titanium) will be investigated. We will identify one or more suitable phosphate systems for the waste stream under consideration (based on the requirements of individual waste streams) and then develop the waste forms with optimized properties. The detailed approach for FY 1996 task will be as follows.

### Identification, Fabrication, and Characterization of Candidate Phosphate Systems

- Identify the phosphate systems applicable to particular waste streams, based on physical and chemical properties and thermodynamic stability.
- Fabricate dense and strong monolithic ceramics at bench scale, using low-temperature processing routes.
- Perform microstructural and mechanical characterizations and durability studies of monolithic phosphate ceramics.

## Development of Optimized Simulated Wastes Forms with Radionuclide Surrogates

- Incorporate surrogate wastes in phosphate matrices with various waste loadings at bench scale. These surrogate wastes will be modeled on the compositions of actual fission-product waste streams at DOE sites.
- Determine the integrity of simulated waste forms by standard performance tests such as compression strength (ASTM C 39), leaching behavior (ANS 16.1), 90-day water immersion test, mechanical stability after thermal cycling (ASTM B 553), and radiation stability.
- Collaborate with the University of Illinois at Urbana-Champaign on extensive microstructural and mineralogical evaluations on the simulated final waste forms to establish the stabilization mechanisms and the fate of the contaminants in the waste forms.

## Benefits

This work will provide a novel low-temperature process for treating and stabilizing fission products generated from D&D processes and cleanup of HLW tanks. This technology will complement high-temperature processes to treat fission-product wastes.

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

The technology generates no secondary wastes. Moreover, the approach is relatively low-cost and has only minimal energy requirements, making it extremely attractive for providing a high return on investment.

## Technology Transfer/Collaborations

During the initial stages of the project, the University of Illinois at Urbana-Champaign (Advanced Center

for Cementitious Materials) will collaborate in the mineralogical evaluations and identification of stabilization mechanisms for the contaminants in phosphate ceramics.

After development of laboratory-scale final waste forms, industrial partners involved in waste solidification will be identified and pilot-scale stabilization will be conducted. Successful S/S by chemically bonded ceramics of actual waste streams containing fission products will have immediate use in cleanup efforts at various DOE sites, especially Hanford and Savannah River. Onsite demonstrations will be sought through concurrence from EM staff. Such an association will be a stimulus for collaboration between industry, universities, ANL, and DOE to ensure successful technology transfer to end users.

### **Keywords**

phosphate ceramics, low-temperature, cesium, strontium, technetium, intercalation, partitioned, fission

products, waste forms, solidification, stabilization, zirconium phosphate, magnesium phosphate, titanium phosphate, immobilization, chemical fixation, physical encapsulation

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