EMSP
Environmental Management Science Program
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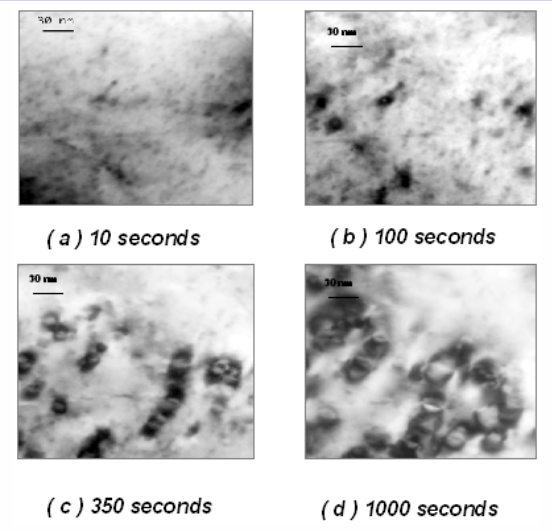
IMMOBILIZATION OF HIGH-LEVEL WASTES AND NUCLEAR MATERIALS

PREDICTIONS OF LONG-TERM STABILITY OF WASTE STORAGE MEDIA REQUIRE A FUNDAMENTAL UNDERSTANDING OF THE PROPERTIES OF MATERIALS

Pretreatment should separate tank wastes into a portion with high levels of radionuclides and a much larger portion that contains low levels of radioactivity. There are many research issues related to immobilization of both types of waste, both with respect to the initial processing of the waste into a form intended for long-term storage and with respect to the prediction of the long-term stability of the waste forms.

The sources of radiation in high-level wastes are primarily from beta decay of cesium-137 and strontium-90 plus lesser contributions from many others, including alpha decay of the actinide elements. ^{137}Cs and ^{90}Sr have half-lives of about 30 years, so they account for most of the activity during the early storage years; however, alpha-decay will account for most of the activity after several hundred years. Radiation damage in host materials can result in swelling, increased leachability, formation of bubbles, and other chemical changes, so a primary area of concern is whether radionuclides can be leached from the storage materials over long times. Several projects were oriented toward detailed studies of damage mechanisms in glass and ceramics, and two of these studies had radionuclide-containing samples that had been prepared about 20 years ago. Another investigation concentrated on radiation-induced changes to the clays and other materials that might be placed around the long-term storage media.

Corrosion processes on glass and on pure amorphous silica are being studied by two EMSP projects to provide improved predictions of long-term stability. Another project is exploring the properties of monazite ceramics as an alternate waste form for immobilization of actinides.



Radiation Effects on Waste Storage Materials
Observed by an ANL project (55367) under a transmission electron microscope, an electron beam facilitates bubbles aggregation in a 17-year-old sample of (1 wt%) $^{244}Cm:YPO_4$, which experienced alpha decays equal to the same amount from ^{239}Pu in about 23,000 years.

Problems/Solutions

- Plutonium-239 has a half-life of almost 25,000 years, so reliable determinations of radiation damage to storage media are difficult. An EMSP project had available some 17-year-old samples that contained a short-lived alpha emitter, curium-244. The ^{244}Cm-containing sample had been subjected to the same number of alpha decays as would have been a 23,000-year-old sample containing the same amount of ^{239}Pu. No significant damage to the host materials was found.
- Alternates to borosilicate glass for immobilization of actinides are once again of considerable interest. An EMSP project has continued to explore the virtues of monazite ceramics for this purpose.
- Cesium-137 undergoes beta decay to form barium-137, so the stability of a host material might be changed by this transmutation. An EMSP project had available 20-year-old samples in which nearly 40% of the ^{137}Cs had decayed to barium, so detailed studies of the stability of the host material could be made.

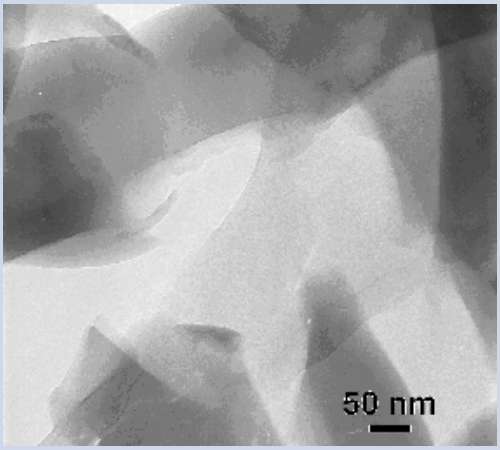
Anticipated Impact

- If oxygen bubbles could form as a result of alpha irradiation in glasses used for immobilization of high-level wastes, the result could be the formation of a dangerous mixture of flammable metals in an oxygen atmosphere inside of a sealed steel canister. If this were found to be a likely occurrence, the entire vitrification program would be in jeopardy. This issue has been investigated by several EMSP projects described here.
- Most of the high-activity waste at the Savannah River Site (400 million curies) and Hanford Site (200 million curies) must be concentrated and then encased in glass or other material intended for long-term storage. Acceptance by the scientific and stakeholder communities requires the best possible knowledge concerning the consequences of radiation damage to long-term stability of the waste media.

Radiation Effects on Waste Storage Materials

There are still many fundamental questions related to reliable predictions of the long-term performance of glass or ceramic materials that contain radionuclides. The goal of a multidisciplinary project (54672) led by a group at PNNL was to develop the basic science necessary to predict the performance of the glass or ceramic materials that are proposed for immobilization of high-level tank wastes, weapons-grade plutonium (Pu) and Pu residues, and other highly radioactive wastes. Theoretical and modeling studies investigated several topics related to the creation and mobility of defects in silica and zircon, as well as the stable configurations for different oxidation states of Pu in zircon. Experimental studies included detailed structural studies of the properties of zircon and glass samples that were prepared 18 years ago and that have been subjected to different radiation doses because of different ^{238}Pu and ^{239}Pu concentrations. The Pu-containing glass samples were used to study the effects of radiation dose on structure and stored energy. In the zircon, alpha decay induced a crystalline-to-amorphous transformation, in which both long-range order and edge-sharing relationships between molecular units were lost, leading to 18% swelling. Computer simulations of amorphization in zircon were in excellent agreement with experimental results. Glass and ceramic samples were irradiated with electrons and ions to accelerate the radiation damage processes and to provide data over a wider range of experimental conditions. A study of ion-irradiated pyrochlore samples confirmed that radiation-induced amorphization increased the aqueous dissolution rate by a factor of ten.

Although there have been suggestions that electron-beam irradiation of glasses could lead to the formation of oxygen bubbles, the project work described above did not find evidence for such bubbles. The objective of the Naval Research Laboratory project (55188) was to look for signs of radiation-induced decomposition in vitreous materials proposed for immobilization of high-level wastes or plutonium. An iron-free boro-aluminosilicate glass was subjected to gamma rays and to implantation by helium ions. By using electron spin resonance (ESR) methods, the presence of peroxy radicals (a precursor of oxygen bubbles) was detected in both cases, though in about 100 times greater numbers in the implanted samples. No induced defects or other changes were found in Savannah River borosilicate glasses nor in similar high-iron glasses from PNNL which had been subjected to three and fifteen billion rads of gamma irradiation, respectively. Three 17-year-old high-iron glasses from PNNL containing Pu in different isotopic proportions exhibited changes in the amplitudes of the ESR signatures of ferric iron proportional to their ^{238}Pu contents, indicative of changes in glass structure to be expected from alpha decays of ^{239}Pu during 4,700 years of storage.



Radiation Effects on Waste Storage Materials
This TEM micrograph, provided by an ANL project (55382), shows a radioactive pollucite containing 16% radiogenic barium. The pollucite was shattered during the thin sectioning process, but each fragment has a homogeneous appearance.

Another approach to the study of radiation damage in nuclear waste forms has been taken in an ANL study (55367). They studied alpha-decay-induced damage in 17-year-old samples that had been doped with about 1% of relatively short-lived alpha or beta emitters. Lutetium and yttrium phosphate samples containing ^{244}Cm had experienced the same number of alpha decays as would be experienced by a sample containing the same amount of ^{239}Pu in about 23,000 years, but they did not find significant damage to these crystalline materials. The results suggested that much of the anticipated alpha-decay-induced damage had been reversed by self-annealing mechanisms. Although they found little evidence of crystalline amorphization, they did find numerous microscopic bubbles of helium from the alpha decay. Related studies in progress included studies of alpha-decay damage in borosilicate glass samples and damage induced in a transmission electron microscope.

The objective of the ANL/PNNL project (55382) was to examine the transmutation of ^{137}Cs to ^{137}Ba in crystalline pollucite ($CsAlSi_2O_6$) that had been stored for more than 20 years. One sample chosen for transmission electron microscopy (TEM) examination contained the most radiogenic barium—nearly 16% of the total cesium, exceeding the solubility of barium in pollucite achievable by direct synthesis. Bright field TEM images revealed a

homogeneous, crystalline matrix, with no evidence of distinct barium phases or ex-solution phenomena resulting from the transmutation. Electron diffraction patterns from several portions of the sample were in excellent agreement with literature values for pollucite. This null result was later confirmed by x-ray absorption spectroscopy, where several aged, radioactive samples failed to show significant differences from a nonradioactive pollucite standard.

Radiation Effects on Backfill Materials in a Nuclear Waste Repository

If high-level waste materials are incorporated in glasses or ceramics that are sealed inside of metal containers, then clays or similar materials that could retard the migration of radionuclides if the primary containment vessels fail will surround these containers. The objective of the University of Michigan project (54691) was to study radiation-induced changes in the structure and properties of clays and zeolites that are potential backfill materials. Several zeolites as well as crystalline silicotitanate and bentonite were subjected to high-energy electron and ion bombardment, and the rate at which these substances formed disordered or amorphous phases was studied. The consequences of the amorphization on the ion-exchange capacity for cesium were investigated by using thermally amorphized zeolite samples. It was found that amorphized samples had an enhanced retention capacity for cesium because they lost about 95% of their ion-exchange capacity after becoming amorphous.

Project Teams

Lead Principal Investigator (Award Number)

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  PI: Patricia M. Dove (55042)
- Rockwell International Corporation
  PI: P. E. D. Morgan (55094)
  Oak Ridge National Laboratory
- Naval Research Laboratory
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- Argonne National Laboratory
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Analysis of Corrosion Processes in Glass

The objective of a University of Florida project (54982) was to develop optical methods for real-time testing of corrosion processes on the surface of glass without having to remove any of the glass surface. Both infrared and Raman spectroscopy were used to interrogate the surfaces of several glasses with low chemical durability and enhanced leach rates of alkali metals in water. The infrared spectra of dried glass samples clearly showed changes attributable to loss of surface sodium or lithium ions. The possibility of using Raman spectroscopy to study leaching processes in real-time for glass samples immersed in water was being investigated, and preliminary tests showed promise for achieving this goal.

The corrosion of glass has been extensively explored in U.S. Department of Energy (DOE) laboratories for some time because of the importance of predictions of long-term stability of vitrified waste. The Georgia Tech project (55042) has measured dissolution rates of pure, amorphous silica as a function of temperature, pH, and the concentration of various salts that are most likely to be present in groundwater. They find that the dissolution rate for amorphous silica in pure water is up to 30 times greater than crystalline quartz. The goal of the project is to develop an experimentally based comprehensive model of amorphous silica reactivity.

Safe Storage of Actinides Using Monazite

The Rockwell International/ORNL project (55094) began with the assertion that “monazite ceramics will provide the most safe, most secure, geologically tested, very long term containment for actinides.” Mineral monazites are mixed lanthanide orthophosphates, but the work in this project has focused on the preparation and properties of synthetic monazites, especially lanthanum monazite. They have studied the preparation of lanthanum phosphate from various water stable precursors, and they have investigated conditions for the most efficient sintering of the powders. A variety of monazite orthophosphates were irradiated by high-energy krypton ions in order to study the amorphization of these materials, and it was found that the monazites were more considerably more difficult to amorphize than the analogous zircons at room temperatures. Phosphates were also found to be more difficult to amorphize than the corresponding silicates. Studies were underway to determine the thermal expansion properties up to 1,400°C and to determine the diffusion rates of impurities in monazite ceramics.

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