EMSP
Environmental Management Science Program
Project Summary Fact Sheet • April 2000

MATERIALS SCIENCE AND GEOCHEMISTRY

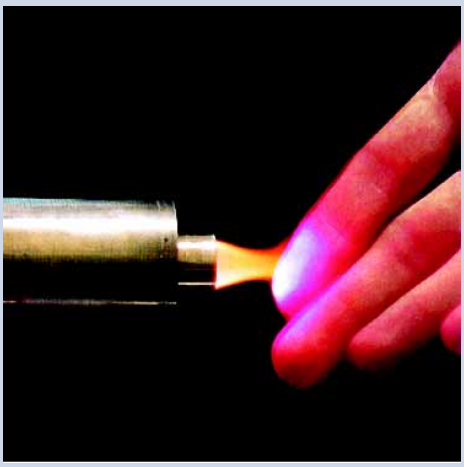
UNDERSTANDING PROPERTIES OF MATERIALS IS IMPORTANT FOR LONG-TERM STORAGE OF WASTES AND MANY OTHER REMEDIATION PROGRAMS

A major role for research in material science is to understand the properties of materials that may be used for long-term storage of radionuclides. One EMSP project has explored the possibility that oxygen could be produced in the vicinity of flammable metals by long-term irradiation, and another has investigated the effects of irradiation on the clays or zeolites that may be backfill materials around a repository. Fortunately, alpha emitters with relatively short half-lives were prepared in host matrices about 20 years ago; these materials have now experienced the same dose of alpha radiation as would be experienced by materials containing plutonium-239 in many thousands of years, so they provide an excellent subject for studies of long-term radiation damage. One group is exploring iron phosphate glass as an alternative to borosilicate glass for long-term storage, and another is studying the properties of lanthanide phosphates that might make them viable alternatives. Another project involved improved analytical methods for detecting surface leaching processes in glass.

One group has investigated why small changes in the composition of salt cakes and slurries in waste storage tanks can result in big changes in ease of pumping these materials.

Projects relevant to decontamination of surfaces include a study of the chemical and physical properties of an atmospheric pressure plasma jet for removing transuranic wastes from surfaces. Etching rates ten times faster than conventional plasma systems have been demonstrated. Another project has studied the chemistry of hydrous oxides surface layers on metals in order to improve chemical and electrochemical methods for removal of radionuclides from metal surfaces.

Tiny crystals or nanoclusters of certain semiconductors are potential catalysts for using sunlight to power oxidation and reduction reactions that decompose hazardous organic compounds in water, and this is the subject of one project.



Atmospheric-Pressure Plasma Cleaning of Contaminated Surfaces
A UCLA project (54914) is developing an atmospheric-pressure plasma jet for removing transuranic wastes from surfaces. This photo of the first-generation technology illustrates the low effluent temperature.

Problems/Solutions

- Demonstration of long-term stability of waste storage media is essential before these materials are sent to a permanent repository. One EMSP project investigated the properties of 17-year-old materials that had been subjected to the same number of alpha decays as would occur in 23,000 years if plutonium were the alpha emitter. No material damage was found.
- Cesium-137 is the most common radionuclide in the water soluble portion of tank wastes, and it decays by beta emission to barium with a half-life of about 30 years. Some cesium-containing solids were prepared about 20 years ago for other uses, but they are now available to EMSP researchers who are investigating whether this change in chemical properties has increased the danger of release of the remaining cesium.

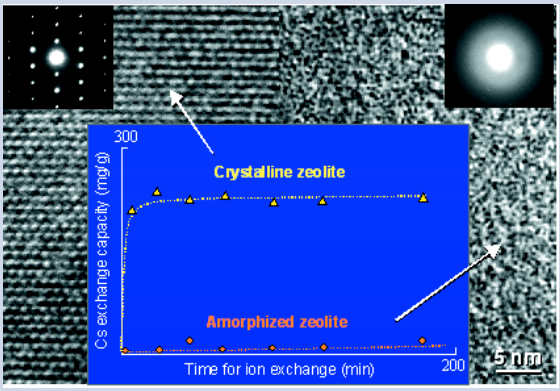
Anticipated Impact

- Storage tanks at the Hanford and Savannah River Sites contain more than 650 million curies of radioactivity (mainly ^{137}Cs and strontium-90), so studies of the long-term stabilities of materials that will be used for immobilization contribute to remediation of the tanks.
- Retrieval of 54 million gallons of waste from the Hanford tanks should be done with as little added water as possible to avoid more leaks and unnecessary added volume. But concentrated slurries can form gels that could plug transfer pipes, so basic science to understand the relationships between chemical composition and physical properties will assist in the design of safe retrieval operations.
- Most metal decontamination techniques are slow and ineffective, and metal worth millions of dollars may have to be disposed of as low-level waste if radionuclides are not removed from the surface. One EMSP project is developing an improved atmospheric pressure plasma jet for removing radionuclides from surfaces, and another is exploring the chemical methods to improve electrochemical and chemical surface cleaning methods.

Effects of Radiation Damage on Waste Storage Materials

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 and plutonium residues, and other highly radioactive wastes. Theoretical and modeling studies investigated topics such as point defect migration in glass and crystalline ceramics, threshold energies to create displaced atoms in magnesium oxide and zircon, and the stable configurations for different oxidation states of plutonium in zircon. Experimental work included detailed studies of changes in properties of zircon and glass samples that were prepared over 18 years ago with different ratios of ^{238}Pu and ^{239}Pu. The plutonium-containing glass samples were used to study the effects of radiation dose on structural properties in chemically identical samples. In zircon samples containing ten weight percent plutonium, 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 the amorphization process in zircon were in excellent agreement with experimental results. Annealing studies indicate that decomposition of zircon into constituent oxides should not occur under repository conditions. Glass and ceramics were also irradiated with electrons and ions to accelerate the radiation damage process and to provide a broader range of data for developing fundamental understanding and predictive models. A study of ion-irradiated pyrochlore samples confirmed that radiation-induced amorphization increases 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 work described above did not find evidence for any such bubbles. The objective of Naval Research Laboratory (NRL) 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 that had been subjected to three and fifteen billion rads of gamma irradiation, respectively. Three 17-year-old high-iron glasses from PNNL containing plutonium 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 Damage Effects on Waste Storage Materials
As demonstrated by a University of Michigan project (54691), zeolite lost 95% of its cesium exchange capacity after solid-state amorphization. (In the background are high-resolution transmission electron micrographs and electron diffraction patterns from crystalline zeolite and amorphized zeolite.)

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 in a high-level waste repository. 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. Larger volumes of amorphous materials were prepared by neutron irradiation and by thermal means. The ion exchange capacity for cesium in the thermally amorphized samples was reduced by about 95%, presumably due to the blockage of access to exchangeable cation sites. However, for the same reason, samples that contained cesium prior to becoming amorphous also had an enhanced retention capacity for cesium. The ion-exchange capacities of neutron-irradiated zeolites as well as thermally-amorphized bentonite and silicotitanate are also being studied.

Another approach to the study of radiation damage in nuclear waste forms has been taken in an Argonne National Laboratory study (55367). They studied alpha-decay induced damage in 17-year-old lutetium and yttrium phosphate samples that had been doped with about 1% of curium-244. These samples had experienced the same number of alpha decays as would be experienced by a sample with the same amount of ^{239}Pu in about 23,000 years, but they did not find significant damage to these crystalline materials. Their 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.

In addition to damage to the host matrix due to alpha decay, for example, there may be problems with long-term stability of stored waste because of transmutation effects. Thus, ^{137}Cs decays by beta emission to form barium-137, which has chemical properties quite different from cesium. 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.

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. Both infrared and Raman spectroscopy were used to interrogate the surfaces of several glasses with low chemical durability with 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. Raman spectroscopy has the potential to study glass surfaces while the glass is immersed in water, and preliminary tests showed that the Raman approach has promise for the examination of such samples.

The corrosion of glass has been extensively studied in U.S. Department of Energy (DOE) laboratories because the prediction of the long-term stability of radionuclide-containing glass is crucial to its use for long-term storage. The goal of the Georgia Tech project (55042) is to develop a comprehensive model of amorphous silica reactivity. They find that amorphous silica dissolves in pure water at rates up to 30 times faster than crystalline quartz, and they have begun studies of dissolution rates as a function of temperature, pH, and concentrations of ions, such as sodium, calcium, and magnesium, that are most likely to be found in groundwater.

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
- University of Missouri – Rolla
  PI: Delbert E. Day (55110)
- Naval Research Laboratory
  PI: David L. Griscom (55188)
- Argonne National Laboratory
  PI: Guokui Liu (55367)
- Argonne National Laboratory
  PI: Carlos A. Melendres (55380)
  Northern Illinois University
- Argonne National Laboratory
  PI: Don Reed (55382)
  Pacific Northwest National Laboratory
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  PI: J. P. Wilcoxon (55387)
  Colorado State University

Waste Forms for Long-Term Storage

The University of Missouri – Rolla group (55110) has investigated the properties of iron phosphate glasses as a possible alternative to borosilicate glasses for waste vitrification. They have incorporated a wide variety of metal oxides into the glasses, i.e., uranium, strontium, molybdenum, sodium, bismuth, and cesium oxides. They have shown certain wastes that are not suitable for borosilicate glasses can be incorporated into iron phosphate glasses, and the resulting leach rates are considerably lower than with borosilicate glasses. The waste composition for some components was as high as 35 weight percent without seriously degrading the properties of the iron phosphate glass. Detailed structural studies have been performed using Mossbauer spectroscopy, x-ray absorption and photoelectron spectroscopies, Raman spectroscopy, and high-energy x-ray scattering. These studies suggest that the addition of waste components does not cause major changes in the chemical bonding or durability of the iron phosphate materials.

Natural monazites are mixed crystalline lanthanide orthophosphate minerals that almost always contain thorium or uranium, so natural monazites have been subjected to alpha-decay damage over geologic time and are known to be highly resistant to leaching and to becoming amorphous. The objective of the Rockwell International/ORNL study (55094) was to study the ceramic science of monazite to explore its use as a sequestering host for actinides and other radionuclides. Studies have ranged from practical preparation techniques for lanthanum phosphate from water-soluble precursors to fundamental investigations of the physical and chemical characteristics of single crystals. The determination of diffusion rates of impurities in these ceramics was deemed to be essential to establish that these materials will remain closed

systems over long times. Radiation damage studies showed that monazite materials have lower critical temperatures for amorphization than their zircon analogues, so they remain crystalline more easily at temperatures above 25°C.

Properties of Alkaline Salt Cakes and Slurries

The relationship between the chemical species present in alkaline wastes and the macroscopic properties of the wastes is the subject of a LANL/Purdue University project (54773). The major focus of their work has been to explore the chemistry of gels and slurries of alkaline aluminates. Raman spectroscopy was used to study the formation of dimers and oligomers of aluminate, and infrared spectroscopy has been used to monitor water activity. Aluminum nuclear magnetic resonance studies were used to elucidate the geometry of the oxygen atoms surrounding the aluminum atoms. It is known that dilution of supernatant can result in the formation of precipitates under some conditions, and experiments were underway to complete key regions of a phase diagram for the aluminate system.

Atmospheric-Pressure Plasma Cleaning of Contaminated Surfaces

The goal of the UCLA/LANL project (54914) is to develop an atmospheric pressure plasma jet for removing transuranic wastes from surfaces. Improvements to the plasma source design have enabled stable operation with several different gas mixtures, so the plasma jet can be used to produce oxygen atoms and radicals for removal of paint films from surfaces or to produce fluorine atoms for removal of metals. Spectroscopic characterizations of the effluent from a helium/oxygen plasma have shown that oxygen atoms are produced downstream of the plasma by reactions of electronically excited helium atoms with molecular oxygen, so the plasma may be used at relatively large distances from surfaces for reactive etching. The etching of actinide metals has been simulated using tantalum as a surrogate, and etching rates ten times faster than conventional plasma systems have been demonstrated. Ongoing work included installation in a radioactive material research laboratory for studies of etching of actinide metals.

Studies of Radionuclide-Contaminated Surface Films on Metals

The objective of the ANL/Northern Illinois project (55380) is to gain a fundamental understanding of the structure, composition, and mechanism of formation of contaminated surface films on metals to improve methods to decontaminate piping systems and waste storage tanks. Thin films of nickel hydroxide and nickel oxyhydroxide have been prepared and used as models of the hydrous oxide surface layers on metals. Some metal hydroxides or oxides were found to form separate domains when codeposited with the nickel, whereas chromium ions were incorporated into lattice vacancies in the nickel hydroxide structure and would probably be more difficult to remove. Studies were underway to understand correlations between the local structures of incorporated metal ions and the ease of removal by electrochemical and chemical dissolution methods.

Semiconductor Nanoclusters as Photooxidation Catalysts

Light with sufficient energy can excite an electron into the conduction band of a semiconductor, and if the electron and hole do not rapidly recombine, then the electron and hole may be available for redox reactions with other molecules at the surface. Molybdenum sulfide, MoS_2, has sufficient stability to make it attractive as a photocatalyst, but it absorbs light in the near infrared region, so it gains insufficient energy to oxidize most organic compounds. However, the absorption edge can be shifted into the visible region of the spectrum if individual MoS_2 crystals have dimensions less than 10 nanometers. The SNL/Colorado State investigators (55387) have found that such nanoclusters can be deposited onto titania supports and used with visible light to oxidize phenol in aqueous solutions to carbon dioxide. In these studies, bypyridine was used as the sacrificial electron acceptor, and some alternate would need to be found for practical photooxidation reactions using sunlight as an energy source.

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