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Storing Waste in Ceramic

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Uncertainty Underground: Yucca Mountain and the Nation's High-Level Nuclear Waste

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Chapter 26:
Storing Waste in Ceramic

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Not all the nuclear waste destined for Yucca Mountain is in the form of spent fuel. Some of it will be radioactive waste generated from the production of nuclear weapons. This so-called defense waste exists mainly as corrosive liquids and sludge in underground tanks. An essential task of the U.S. high-level radioactive waste program is to process these defense wastes into a solid material – called a waste form. An ideal waste form would be extremely durable and unreactive with other repository materials. It would be simple to fabricate remotely so that it could be safely transported to a repository for permanent storage. What's more, the material should be able to tolerate exposure to intense radiation without degradation. And to minimize waste volume, the material must be able to contain high concentrations of radionuclides.

The material most likely to be used for immobilization of radioactive waste is glass. Glasses are produced by rapid cooling of high-temperature liquids such that the liquid-like non-periodic structure is preserved at lower temperatures. This rapid cooling does not allow enough time for thermodynamically stable crystalline phases (mineral species) to form. In spite of their thermodynamic instability, glasses can persist for millions of years (see Chapter 24).

An alternate to glass is a ceramic waste form – an assemblage of mineral-like crystalline solids that incorporate radionuclides into their structures. The crystalline phases are thermodynamically stable at the temperature of their synthesis; ceramics therefore tend to be more durable than glasses. Ceramic waste forms are fabricated at temperatures below their melting points and so avoid the danger of handling molten radioactive liquid – a danger that exists with incorporation of waste in glasses.

The waste form provides a repository's first line of defense against release of radionuclides. It, along with the canister, is the barrier in the repository over which we have the most control. When a waste form is designed, the atomic environment of the radionuclides is chosen to maximize chemical durability. Elements such as zirconium and phosphorous can be included in the waste form that react with and make some radionuclides less soluble and therefore less likely to be released.

The long-term performance assessment of radionuclide containment requires the development of models for each part of the barrier system. It is almost certainly easier to model the corrosion and alteration of waste forms than it is to develop coupled hydrologic, chemical, and geophysical models of radionuclide transport away from a repository. Therefore, much time and effort has been spent optimizing the chemical durability of both glass and ceramic waste forms for radionuclide containment (Ewing, 2001). This has not been an easy task. Three problems in particular posed the greatest challenges.

The first is that radionuclides decay, transmuting into daughter elements that may have different chemical properties. These new elements might degrade the existing mineral by making it unstable. A good waste form that works well for uranium may work poorly for lead, its final decay product.

The second problem is that the radioactive decay itself damages the solid over time. Radioactive decay is an energetic process in which ejected particles and the recoiling nucleus disrupt the surrounding atoms. A single alpha-decay event can displace thousands of atoms in the surrounding volume. We know from laboratory measurements that radionuclides are more easily released from radiation-damaged structures than from materials that do not sustain radiation damage.

The third problem is that radioactive waste, particularly the high level waste from reprocessing of spent nuclear fuel to extract plutonium and uranium, contains a variety of elements with widely varying chemistry. The waste form must incorporate the radionuclides, as well as non-radioactive elements such as silicon and sodium that are present in the waste stream as a result of waste processing.

A number of ceramic waste forms have been developed that minimize these problems and provide a potentially useful host for radionuclides (Lutze and Ewing, 1988a). For ceramics, the mineralogy can be tailored to the waste stream by selecting solid mineral phases with structural sites that can accommodate the waste elements, as well as newly formed radioactive decay elements. Radiation damage can be minimized by selecting mineral phases that allow atoms to renew or regain their original crystalline structure, a process known as annealing. For example, actinide phosphate minerals anneal more readily than actinide silicate minerals.

Despite the superior thermodynamic stability of crystalline materials, borosilicate glasses have become the preferred waste forms. One reason is that the processing technologies associated with this glass are believed to be easier to adapt to handling highly radioactive material. In addition, borosilicate glass is relatively insensitive to variability in the composition of the waste stream Hench et al., 1981; Lutze and Ewing, 1988b; Donald et al., 1997; for detailed reviews of waste form development). The United States decided in 1982 to use borosilicate glass as the waste form for storing high-level defense waste at the Department of Energy's Savannah River Site, and in 1990 to use borosilicate glass as the waste form for high-level waste at Hanford, Washington.The other U.S. site having a large amount of high-level waste -- the Idaho National Engineering Laboratory -- is still in the process of choosing a waste form. Until recently, the Department of Energy was considering a titanate-based ceramic waste form for disposal of fissile plutonium and uranium from dismantled nuclear weapons. Work on this waste form was suspended early in 2002 (DOE, 2002), and there are no current plans to include ceramic waste forms in the U.S. high-level waste repository.

Ceramic corrosion

Corrosion refers to the reaction of the ceramic with water. Mechanisms of corrosion include selective leaching of certain elements, dissolution of material, and the breaking of chemical bonds by water molecules (hydrolysis). Any of these reactions may result in the release of radionuclides from the waste form in a repository.

Except for some gaseous radioactive decay products, neither ceramic nor glass waste forms will release radionuclides under dry conditions. Radionuclides will be released only through water contact. In addition, movement of radionuclides through ceramic is so slow that they cannot simply migrate to the surface and escape -- even at the highest anticipated repository temperatures. To release radionuclides, corrosion must be able to penetrate into the ceramic.

Waste forms are subjected to numerous tests to determine their corrosion rates. Generally, the waste form is immersed in water and the concentrations of released species are measured over time. The temperature and composition of the water solution, chosen based on anticipated repository conditions, are varied to gauge their effects on release rates. The measured release rates allow estimates to be made of the release rates from a waste form in a repository. An additional goal is to use the test results to develop a mechanistic understanding of waste form corrosion, including the identification of the rate-limiting corrosion mechanisms. This understanding allows defensible extrapolations of short-term test results to long-term predictions of waste form corrosion rates in a repository.

Radiation Damage

Any prediction of the long-term durability of a ceramic waste form must also consider the effect on the material of radiation damage. The type of radiation that most compromises the ceramic waste form's durability is due to alpha decay. Each alpha decay gives rise to the emission of an alpha particle and the recoil in the opposite direction of a heavy nucleus. As a result, the local environment surrounding the alpha decay site is full of displaced ions and alpha particles. Radiation damage may be accompanied by swelling of the material of 15 volume percent or more. The swelling causes cracking, flaking off of thin layers, and an increase in surface area. All these processes enhance radionuclide release.

Experimental work has shown that materials damaged by alpha decay can corrode ten to a hundred times faster than undamaged materials (Wald and Weber, 1984; Weber et al., 1998). In these tests, the ceramics either are doped with a short half-life radionuclide to accelerate radiation damage or are bombarded with high-energy ions to simulate the effects of radiation.

However, radiation-damaged crystals can and do repair themselves through annealing. If diffusion rates are high enough, ions in the material tend to migrate back and resume their original structure. Whether the damage can be repaired depends on temperature (higher temperatures allow faster annealing) and the rate of further damage. If alpha damage piles on top of previous damage that has not been repaired, the entire structure may become amorphous -- the so-called "metamict" state sometimes found in natural minerals that contain radionuclides.

In addition, some mineral structures are better able to accommodate radiation-induced defects into their structures. Sickafus et al. (2000) have shown that fluorite-structured solids such as zirconates are less perturbed by defects introduced by radiation than comparable pyrochlore structures. Such knowledge allows tailoring of both durability and radiation tolerance of potential ceramic waste forms.

Natural analogs: The long-term data

Fortunately, information is available to help predict the long-term performance of waste forms. Both ceramics (i.e., minerals and rocks) and glasses occur naturally and are millions or, for some ceramics, billions of years old. These materials have compositions and structures similar to those of the proposed nuclear waste forms. The minerals in rocks sometimes contain uranium and thorium that decay and over time generate radiation damage. Therefore, the durabilities of these minerals are thought to be good indicators of long-term durabilities of comparable radiation-damaged nuclear waste forms (Ewing and Jercinovic, 1987).

The major uncertainty in the use of natural analogs is that the environmental history of the samples is often poorly known. Although radiometric dating may supply an age, no information is available to tell anything about either the time-temperature history of the sample or the amount of time spent in contact with water (Lumpkin, 2001). It is known, however, that these mineral phases have the durability needed to survive in a variety of geologic environments for periods much longer than the Environmental Protection Agency's mandated 10,000 year lifetime of a nuclear waste repository.

Corrosion of ceramic waste forms in a repository

As the preceding discussion makes clear, there are significant uncertainties in using laboratory and natural analog data to make long-term predictions of ceramic waste form performance in a repository. There are two main issues.

The first source of uncertainty involves limitations of laboratory corrosion data. The range of anticipated repository conditions, in terms of temperature and fluid chemistry, is very extensive. Because of this, data on waste form corrosion do not cover the entire range of potential repository conditions. This problem is amplified by the underlying uncertainty of model predictions of repository conditions that the waste form will experience.

Most laboratory tests necessarily have durations of only a few years at most, whereas repository lifetimes are on the order of 10,000 to 100,000 years. If the rate-limiting reaction mechanism for the waste form has not been identified, there is no mechanistic basis with which to extrapolate laboratory test results to long time periods. There is currently no consensus in the waste form community that the correct rate-limiting mechanisms have been identified for any of the existing waste forms. Natural analog data, while reassuring, has always been problematic because of the lack of knowledge of the geologic history and in particular the duration of water contact of the natural analog material.

The second uncertainty is the effect of radiation damage. Based on corrosion tests of irradiated materials, radiation damage is known to significantly accelerate ceramic corrosion. Of particular concern is the possibility that the swelling that accompanies the accumulation of radiation damage may break apart the ceramic along the crystal's grain boundaries and greatly increase the exposed surface area (see Figure 26-1). Since release rates of radionuclides are generally proportional to waste form surface area, radiation damage could lead directly to an increase in radionuclide release. It is difficult to quantify this effect from tests of irradiated materials because their radiation damage is induced rapidly and their damage may not be representative of real ceramic waste forms. So while it is known that radiation damage will lessen the ceramic's durability, the magnitude of the effect is unknown.

A ceramic waste form for plutonium immobilization

One ceramic waste form was, until recently, being considered for the Yucca Mountain repository (DOE 2002): the pyrochlore-based titanate ceramic. This waste form was developed as part of the U.S. DOE effort to immobilize as much as 50 metric tons of surplus weapons-usable plutonium and uranium from dismantled nuclear weapons. The waste stream is primarily plutonium and uranium metal. However, it also includes plutonium and uranium alloys, impure oxides, un-irradiated fuel residues, and other materials generated during fissile material processing.

The selected ceramic waste form is titania-based (TiO_2) and contains roughly 10 weight percent plutonium. The solid phases are mainly pyrochlore, with lesser amounts of brannerite and rutile (Table 26-1). The pyrochlore structure is essentially a titanium oxide framework containing two atomic sites that readily accommodate plutonium and uranium. Minor components of the waste stream generally substitute into one or more of the three mineral phases. Figure 26-1 shows a scanning electron microscope image of a section through the ceramic.

The titanate ceramic is fabricated using a cold press and sinter technique. Fine-grained reactive oxide precursors and the waste oxides are mixed and pressed into pellets at 13 to 20 MPa (130-200 atmospheres) and then heated at $1350^{o}C$ for four hours in a non-reactive gas. The process has been automated for remote operation in a glove box.

Before selecting this waste form, DOE considered several other ceramics, including cubic zirconia (ZrO_2), zircon ($ZrSiO_4$), uraninite (UO_2), gadolinium-zirconate ($Gd_2Zr_2O_7$), monazite ($CePO_4$), apatite ($Ca_5(PO_4)_3OH$), and perovskite ($CaTiO_3$). Summaries of the properties of these minerals can be found in Ewing et al., 1996, and Ewing, 1999. The titanate was chosen for four reasons. First, extensive data is available from previous work to develop titanate waste forms for other waste streams. Secondly, uranium and plutonium have high solubilities in titanate (>10% by weight). Third, a simple fabrication method is available for titanate's synthesis. Finally, the titanates have high durability in water. Susceptibility to radiation damage was not a primary consideration. Ceramics were chosen over glasses for several reasons, including their much lower corrosion rates (Cochran et al., 1997).

Two key issues were considered in developing the titanate waste form. First, the waste form must pose an effective barrier that would prevent terrorists from having access to the plutonium in the waste. In 1994, the National Academy of Sciences recommended the use of the "spent fuel standard." This standard mandates that retrieval of fissile elements from the waste should be at least as difficult as retrieving such elements from spent reactor fuel (National Academy of Sciences, 1994). For this reason, the ceramic waste will be placed inside cans of high-level waste; this "can-in-can" approach is illustrated in Figure 26-2. High-level waste contains the highly radioactive elements cesium-137 and strontium-90, which provide a source of penetrating radiation not present in the ceramic waste form. The high-level waste provides the radiation barrier to prevent human access.

The second issue is criticality. The waste consists primarily of fissile plutonium-239 and uranium-235, which could potentially become sufficiently concentrated to provide critical masses and hence accelerated nuclear reactions. Two scenarios deserve consideration. The first is that criticality arises during waste form production and within the waste form itself. The second is that criticality occurs during storage. This could happen, if, for example, plutonium or uranium is leached from the waste form, transported, and deposited in a localized area. A similar process occurs in nature and is responsible for the formation of localized concentrations of metals in ore bodies, such as gold or uranium. Calculations of the transport and deposition of fissile elements in a repository system needed to evaluate the potential for criticality rely on coupled chemical-thermal-hydrologic models of repository evolution. There is considerable uncertainty in interpretation of the results of these calculations, as described in chapters 13 and 16.

Because of these concerns, two neutron absorbers, hafnium and gadolinium, were added to the ceramic. Both of these elements capture neutrons without fissioning and therefore greatly reduce the chance for criticality for both scenarios, as long as these neutron absorbers remain with the plutonium or uranium.

Corrosion tests of the titanate waste form

The titanate waste form has been subjected to a variety of corrosion tests to measure its chemical durability under repository-relevant conditions. These tests show that as long as the ceramic has not been damaged by radiation, radionuclide release rates are extremely slow (Roberts et al., 2000). For many tests, in fact, it is not clear that anything at all is being released because the measured concentrations are too near background levels to distinguish a signal (Bakel et al., 1999). Examination of the surfaces of reacted ceramics using electron microscopy usually show no reacted layer, or, in a few cases, a layer only a few nanometers thick (see Figure 26-3).

Figure 26-4 shows that at the measured corrosion rates, the maximum rates of plutonium and uranium release would, even after a million years, result in penetration and potential release of radionuclides of only about a one-millimeter thick layer of ceramic. At this rate, only a very small fraction of the total radionuclide inventory could be released over the lifetime of the repository.

The tests that were designed to determine the rate-limiting mechanism for corrosion of the titanate were inconclusive. Reaction rates were so slow that it was impossible to quantify the influence of changing environmental parameters and therefore to deduce the rate-limiting mechanism.

Over time, titanates will accumulate radiation damage due to the presence of alpha emitters. For alpha decay in the pyrochlore ceramic, the average alpha particle will travel about 10 micrometers and the average recoil nucleus will travel about 50 nanometers (Weber et al., 1998). Each alpha particle produces about 100 atomic displacements and each recoil nucleus produces about 1,000 displacements. This self-radiation damage will cause the ceramic to become amorphous in as little as 1,000 years (Muller and Weber, 2001) depending on the temperature evolution of the repository.

Even after sustaining radiation damage, however, pyrochlores may be able to retain their radionuclides for long times. Evidence of this capability comes from observations of natural titanium-rich radioactive pyrochlores (betafites). A study of betafites from nine locations including completely amorphous samples, showed that although the minerals had lost or exchanged cations in their "A" sites (see Table 26-1), the minerals were able to retain virtually all of their uranium and thorium in their "B" sites. This was true even in specimens as old as 1.4 billion years (Lumpkin and Ewing, 1985; Lumpkin, 2001).

The long-term effect of radiation damage on the corrosion rate of titanate ceramic is unknown. To account for radiation damage in performance assessment, the measured reaction rates were increased by a factor of 30 above the measured values for undamaged ceramics (DOE, 2001; Shaw et al., 2001). This factor is an average value based on previous measurements of radiation damage effects on the corrosion rates of related ceramics.

The titanate waste form in the repository

It is useful to compare the relative uncertainties of performance predictions of ceramic waste relative to the waste forms currently destined for the repository - borosilicate glass and spent fuel. Glass waste forms are thermodynamically unstable and will always seek to achieve a lower energy state by re-structuring into crystalline forms, at some rate that is difficult to predict. Ceramic degradation rates do not suffer from this uncertainty. They are already in a low-energy ordered state and do not transform. Ceramics have a known solubility that can be used to provide a conservative upper limit to their solubilities, and therefore radionuclide release rates. Glasses have no solubility limit that can be used with certainty to provide these conservative estimates.

Both glass and ceramic waste forms can be engineered to be compatible with the predicted oxidation state of the repository. For Yucca Mountain this will be a relatively oxidized state, that is, some free oxygen will be present. Compatible oxidation states between the waste form and the local environment will avoid the potential for the occurrence of oxidation reactions between the site groundwater and the waste form. Such reactions are known to degrade the waste form and release radionuclides (see Chapter 23 of this volume). These types of reactions are often enzymatically catalyzed by microbes, which could significantly increase the reaction rate. Most spent nuclear fuel is composed dominantly of reduced uranium, that is, uranium that will react with oxygen to form new uranium solids and aqueous species. In a hot humid oxidizing repository, such as is expected for Yucca Mountain, the uranium will oxidize, and in the process, radionuclides are likely to be released. The rate of this process is highly uncertain, but must be estimated in order to predict radionuclide release rates from the spent fuel. Neither glass or ceramic waste form corrosion rate predictions suffer from this uncertainty.

Summary

The waste form is one component of the repository that we have a great deal of control over. It can be engineered to be durable in site groundwaters and resistant to radiation damage. Ceramic waste forms are preferable to borosilicate glass due to their greater intrinsic durability. Both glass and ceramic are preferable to spent fuel because they will not undergo oxidation reactions that are likely to release radionuclides. Long-term predictions of waste form performance are limited both by uncertainties in extrapolation of short-term tests to long time periods, and by the inadequacies of our mechanistic models of waste form corrosion. An even more severe uncertainty may be that the calculations of waste form corrosion rely on and are limited by the uncertainties in the results of thermohydrologic model predictions of repository conditions over time.

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Figure Captions

Figure 26-1. Scanning electron microscope (SEM) image of titanate ceramic.

Figure 26-2. Ceramic can-in-canister concept.

Figure 26-3. Transmission electron microscope image of unreacted (upper) and reacted (lower) pyrochlore sample. Lower sample was reacted for 28 months in pH 4 solution at 250C and shows a thin amorphous alteration layer (photos courtesy of David Chamberlain, Argonne National Laboratory).

Figure 26-4. Corrosion rates of three repository wasteforms; spent fuel, defense high level waste (borosilicate) glass, and the titanate ceramic (Roberts et al., 2000).

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Figure 26-1. SEM image of titanate ceramic. Dark gray = rutile, light patches = brannerite, groundmass = pyrochlore. Darkest spots are holes.

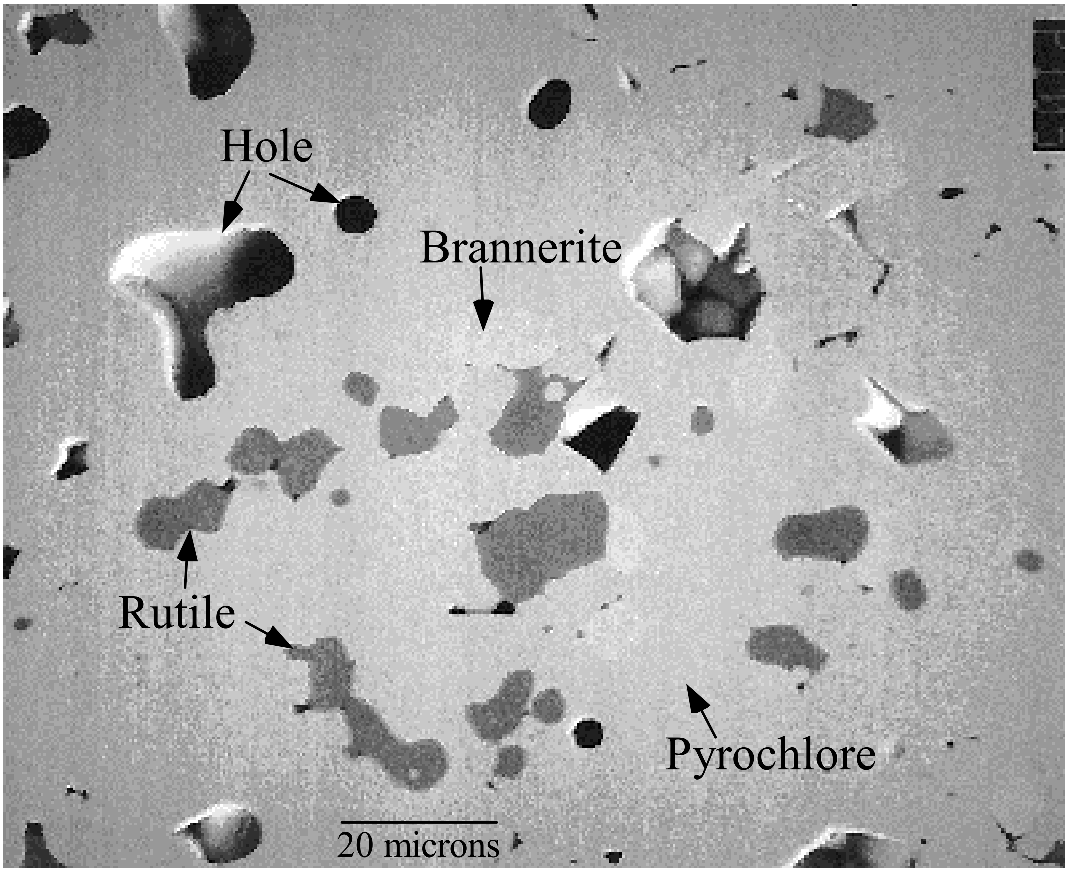
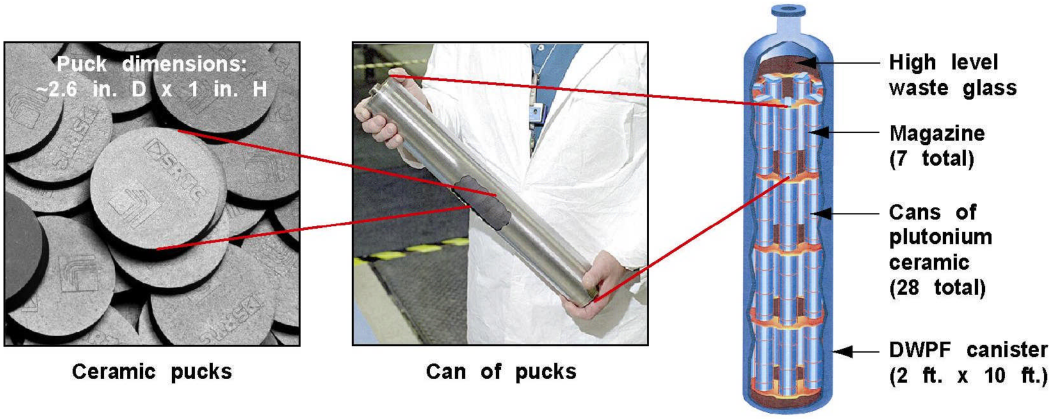


Figure 26-2. Ceramic can-in-canister concept. Ceramic pucks are placed into cans that are then emplaced into high-level waste glass that provides radiation barrier to prevent unauthorized recovery of fissile elements.



Ceramic pucks

Can of pucks

Canister

Figure 26-3. High resolution transmission electron microscope image of unreacted (upper) and reacted (lower) pyrochlore sample. Lower sample was reacted for 28 months in pH 4 solution at 25^0C. The extremely thin alteration layer on the reacted sample appears to be amorphous.

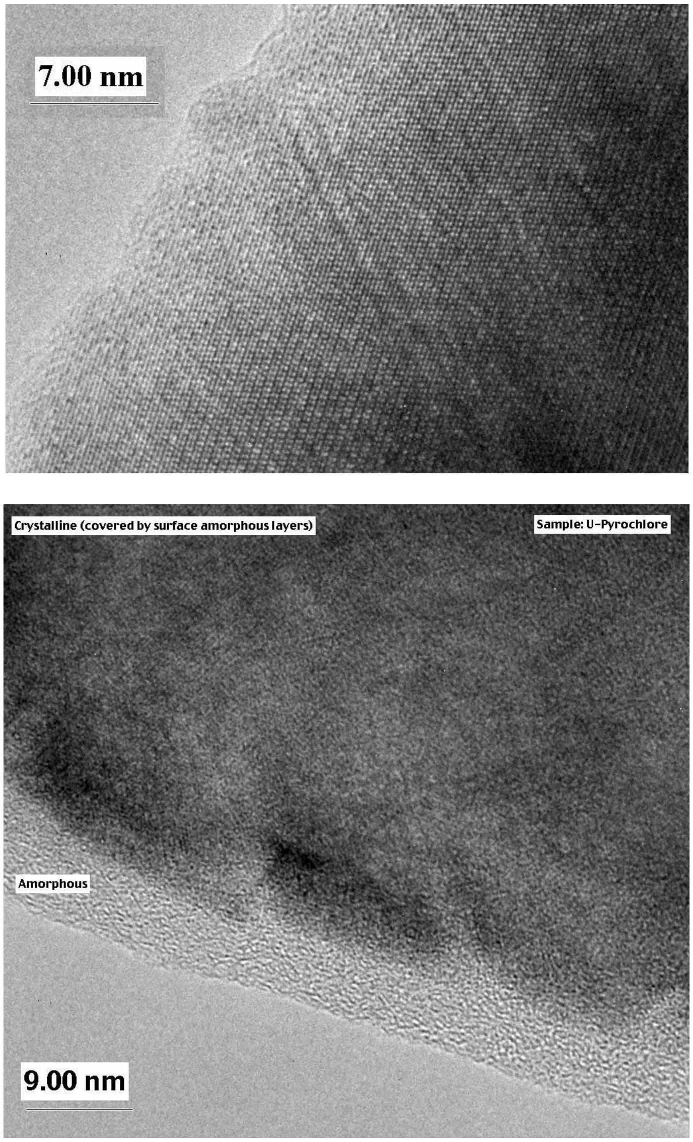


Figure 26-4. Corrosion rates of three repository wasteforms. Symbols show release rates of Pu and U from ceramic waste form.