

Accelerated testing of the CSNF waste form: Applicability to Yucca Mountain

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Brady Hanson¹, Edgar Buck¹, Patrick Brady²

- 1) Pacific Northwest National Laboratory
- 2) Sandia National Laboratory

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Spent fuel tests in support of Yucca Mountain have been performed for many years. Most of these tests have been either single-pass flowthrough (SPFT) or unsaturated drip tests that have been used to elucidate waste form degradation rates. In general, the tests have been considered accelerated tests per the definition found in ASTM Standard C1174 in that either the temperature or flow rate has been increased in order to increase the rate of alteration. However, as the design and models for the proposed repository have solidified, it is clear that much of what was originally considered an accelerated test is, in reality, either a service condition test or a test that determines bounding conditions that grossly overestimate radionuclide degradation and release rates under repository relevant conditions. This presentation will examine the factors that need to be considered for future waste form, including waste package internals, degradation tests.

One of the most important factors for CSNF degradation is the temperature of the fuel and the water contacting it. Recent models predict fuel temperatures in excess of 50°C even at the end of the proposed 10,000-year regulatory period. For early failed waste packages, the fuel temperature will be 95°C when the waste form is first contacted by water. Even then, the decay heat of the fuel will ensure that it will be at least a degree or two warmer than its surroundings. This phenomenon should limit contact of water with the waste form but might accelerate corrosion of the surrounding waste package internals. Temperature also plays an important role in determining the secondary phases that form and the ability of these phases to incorporate or sequester key radionuclides such as Tc and Np. Thus, while it is tempting to increase temperature for an accelerated test, one must carefully examine the effects on the alteration mechanisms to assure they are still relevant for the proposed repository.

A second major factor for CSNF degradation is the effective surface area of the fuel exposed to moisture. Recent evidence indicates that the surface area is strongly affected by microscopic properties such as fuel burnup and chemistry far more than the macroscopic geometric surface area. CSNF is not simply UO₂ with some impurities in it. The fission products and actinides soluble in the uranium matrix can grossly affect the oxygen (i.e., chemical) potential of the fuel. Less soluble elements such as Zr and Pu may serve to decrease the effective surface area as they are concentrated at the surface of the corroding fuel. These same elements, combined with the rare earth elements, which are difficult, if not impossible, to oxidize to higher states will serve to effectively block their nearest-neighbor uranium ions from oxidizing because of the effective negative charge they exhibit. The changes in semiconductor properties also make it more difficult for oxygen reduction at the fuel surface by decreasing the density of donor-acceptor sites. In total, these factors show that normalizing the reaction rate to the surface area may

introduce significant error and uncertainty. The use of artificially increasing the surface area of samples to accelerate the rate may result in non-realistic rates and mechanisms.

A third factor that is critical in controlling not only degradation rates, but also the water chemistry to which the waste forms are subjected, is the radiolytic components generated by radiolysis. Radiolysis products generated can greatly accelerate the corrosion rate of CSNF, even under SPFT conditions. Similarly, radiolytically-produced peroxide has been shown to result in formation of the uranyl peroxide, studtite, instead of the uranyl oxyhydroxides such as schoepite. Studtite has been shown to incorporate Np in much larger quantities than schoepite, although this effect may be because of the higher Np oxidation state in the presence of the peroxide. If the waste package or cladding can prevent contact of CSNF with water for at least 300 years, the radiolytic contribution from β - and γ -decay will be significantly reduced. It remains to be determined how important the α contribution is under oxidizing conditions, but the existence of studtite in nature suggests that it is still significant. Because all tests using spent fuel will have significant contributions to radiolysis since most fuels have had at most 30 years decay, PNNL has developed the concept of RADFUEL to simulate the fuel chemistry and radiolytic fields of spent fuels at various decay times. The importance of unannealed radiation damage in the fuel and the affect on degradation rates and mechanisms need to be examined.

A final important factor for CSNF degradation is the water flux to which the fuel is subjected. SPFT tests may be ideal in determining the dependence of the rate on individual parameters, but the anticipated water flux in the proposed Yucca Mountain repository are such that the fuel will never undergo degradation at the forward rate of reaction. Under low flow scenarios, the formation of alteration phases on the waste form surface will affect the degradation rate of the underlying fuel matrix by limiting the surface area of the matrix exposed, providing a diffusion barrier for water and oxygen in and radionuclides out, and by limiting water contact because of the hydrophobic behavior of some of the alteration phases. The same process will likely control corrosion of the non-fuel internals.

The net result is that in order to determine the actual rates and mechanisms for CSNF degradation under repository-relevant scenarios, PNNL and SNL are beginning a series of mock-up tests that include simulated fuel and waste package components. Ongoing tests as part of the OCRWM Science and Technology Source Term Thrust Area will more precisely determine the dependence of CSNF degradation on these parameters and determine which factors can be changed to allow accelerated testing. Our underlying hypothesis is that under these relevant conditions, the waste form degradation rate will be much less than presently modeled and, when combined with reduction of radionuclides by the altered waste package materials, radionuclide release from a failed waste package will be minimal.