5/14/04

Note to: Andy Campbell

From: Richard Codell

Subject: Use of unirradiated uranium dioxide for spent fuel dissolution experiments

See my writeup addressing Savio's comments on the use of unirradiated UO_2 in the Center's research on spent fuel dissolution.

Introduction

The NRC and CNWRA staff recognize that the current abstractions for performance assessments proposed by the Department of Energy (DOE) and the model abstraction implemented by the CNWRA/NRC provide conservative approaches for spent fuel dissolution. Dissolution of spent fuel has been judged to be of "medium" importance in the current Risk Baseline Report (NRC, 2004). As part of its overall approach to performance assessment, the staff continues to (i) increase its understanding of the physical processes affecting performance and (ii) where appropriate, improve the level of realism (in contrast to conservatism) present in the models.

The Center proposed research to study the influence of iron on the dissolution rate of spent UO_2 fuel. Several cited reports indicate that the presence of iron or iron oxides in solution could reduce UO_2 dissolution rates (Quinones 2001, Stroes-Gascoyne 2002). Additionally, carbon steel components of the fuel assemblies could further reduce UO_2 dissolution rates by consuming oxygen in the waste package, thereby depriving the spent fuel of needed oxygen for the dissolution process. The proposed research would confirm that this phenomenon can be reproduced independently, for the sake of realism in the source term models. The Center proposed to use unirradiated UO_2 in its experiments. Should the study show that the dissolution rate is significantly altered by the presence of Fe or Fe-oxides in solution, NRC could ask the DOE to provide an evaluation of potential effects of Fe and Fe-oxides on irradiated nuclear fuel of simulated aged spent fuel.

In May 2004, R. P. Savio, Senior Technical Advisor Memorandum to the Advisory Committee on Nuclear Waste (ACNW) states that the Executive Director's Office (EDO) response to the ACNW Recommendation 2 is not adequate. The memorandum states *"... the EDO has essentially rejected the ACNW concerns, without providing justification other than a statement that the use of unirradiated fuel is justified by 'numerous studies.' I believe that this response is unsatisfactory. I recommend that the Committee inform the EDO that the Committee is not satisfied with this response and intends to have additional discussions on this matter with the cognizant NRC and CNWRA staff"*. A subsequent E-mail message (R. Savio to P. Justus and S. Jones, 5/11/04) implied that only irradiated spent fuel would provide the necessary data. The following paragraphs respond to this criticism and defend the Center's original plan to use unirradiated UO_2 in its experiments.

Center's Choice of Unirradiated UO_2 for Experiments

The Center chose to use unirradiated UO_2 for several reasons: (1) unirradiated uranium is only slightly radioactive and would not require expensive handling techniques and equipment; (2) irradiated spent fuel is both highly radioactive and also not necessarily representative of spent fuel under long-term repository conditions, and (3) a number of experiments indicate that dissolution rates measured from irradiated and unirradiated UO_2 samples are not that different, especially in the oxidizing environment expect at Yucca Mountain. There have been numerous studies, conducted worldwide, that have used a combination of unirradiated UO_2, SIMFUEL, and spent fuel samples to enhance the understanding of spent fuel dissolution. In a recent review article, Oversby and Konsult (1999) indicated that while dissolution data shows a wide range of results, unirradiated UO_2 provides more coherent relationships.

Different needs for reactor accidents and waste disposal

It is clearly worthwhile to use irradiated spent fuel when studying severe reactor accidents. However, the needs for severe reactor accidents and long-term disposal of spent fuel differ in several important respects. For a reactor accident, the biggest concerns are short-lived fission products, especially volatile ones like cesium, iodine and nobel gasses. Most of these radionuclides are γ and β emitters with half lives of days to a few tens of years. The volatile elements collect in fractures, pore spaces and cladding gaps in the fuel and can be released quickly during accidents. Conversely, HLW repositories are expected to protect the fuel long enough that nearly all of the γ and short-lived β emitters would have decayed. The remaining radionuclides of concern are mostly long-lived β emitters like Tc-99, I-129 and Np-237, and long-lived α emitters like plutonium and americium. Although there are some volatile radionuclides that would collect in the open spaces in the fuel, notably I-129 and Cs-135, the contribution to the peak doses in the 10,000 year regulatory time frame from these inventories are not likely to be important.

Effects of Radiation on Dissolution Results

If we can assume that the short-lived radionuclides are unimportant for the long-term performance of the repository, then experiments with relatively fresh irradiated fuel may be misleading because the high γ and β fluxes won't be present later on. This radioactivity can influence fuel-dissolution experiments because in can generate oxygen, peroxide and OH radicals by radiolysis (Bruno et al, 2004, Allia and Oversby, 2004), that would tend to enhance dissolution of fuel, especially for disposal under reducing conditions. This is less of a concern at Yucca Mountain because conditions in the repository are expected to be generally oxidizing already. In its spent nuclear fuel dissolution model abstraction, DOE used a combination of unirradiated UO_2 and spent fuel data. The review of DOE data (CRWMS M&O, 2000) indicates that the dissolution rate from unirradiated UO_2 is similar to spent nuclear fuel samples under similar conditions as shown in Table 1. The only exception observed was in high carbonate solution that showed high dissolution rate for un-irradiated samples compared to spent fuel sample. However, other data point to larger differences caused by high radiation fields. Even under aerated conditions, experiments on UO_2 with high artificial γ radiation simulating fresh spent fuel (650 Gy/hr) shows uranium corrosion rates two orders of magnitude greater than uranium dioxide without γ radiation (Jegou et al, 2004).

If it were possible, the best samples for experiments on spent fuel dissolution would be on samples old enough that most of the short-lived fission and activation products had decayed. Howver, no "old" irradiated fuel exists; spent nuclear fuel today is not representative of aged fuel. After removal of the fuel from the reactor environment, decay of fission and activation

products will result in changes to fuel composition. In addition, α decay will produce increasing amounts of helium and accumulate micro-structural defects at low temperature (Rondinella et al, 2001). There will be less defect recovery from α decay after removal from the reactor than during fission in the hot reactor because of annealing and relatively short exposure time.

To overcome this conundrum, some experiments have used UO_2 samples that have been artificially doped with short-lived α emitters like Pu-238 and U-233 (e.g., Grey, 1987, Mineo, 2004, Ollia and Oversby, 2004, Stroes-Gascoyne, 2002). The difference in dissolution for α-doped UO_2 in the work of Jegou et al (2004) was only about a factor of 2.5 greater than for unirradiated UO_2 as contrast to the two order-of-magnitude increase for γ radiation. Grey (1987) found relatively little effect of α radiolysis in oxigenated brines for Pu doped samples. Overall, the presence of β and γ radiation in spent fuel seems to be a more serious detractor to the experiments than the lack of α radiation.

Difference in Physical Properties between Irradiated and Unirradiated UO_2

There are clearly differences in the physical and chemical properties of irradiated and nonirradiated UO_2. There will be damage to the crystal lattice of the UO_2 from radiation, and kinetic impact of fission products. Also, the UO_2 fuel pellets are known to crack, increasing the surface area of the pellet by a factor estimated to be between 1.5 to 3.5 (Mineo et al, 2004). The planned experiments at the CNWRA are aimed at a very specific data need; i.e., the effect of iron products on the dissolution rate of the fuel. This would appear to have relatively little to do with the radionuclide content of the fuel, and is not specifically looking for radionuclide releases. Since dissolution data are collected on a per-area basis, the difference in surface area between unirradiated and irradiated UO_2 can be easily handled. The long-term effects of α decay of actinides in the fuel will not be possible with unirradiated UO_2, but this appears to be a lesser problem than the complications caused by the short-lived radionuclides in relatively young spent fuel.

Conclusions

The Center's proposed research should be able to use unirradiated UO_2 samples to collect useful data on the effects of iron on spent fuel dissolution. The use of irradiated fuel samples appears to have no benefit for this research, and may in fact be less appropriate because of its high radiation levels from decaying short-lived fission and activation products. Differences in physical properties between irradiated and unirradiated samples like increased fracturing do not appear to be overwhelmingly important and can be handled during the analysis of the data. The possible long-term effects of decay cannot be examined with unirradiated spent fuel samples, but experiments with α-doped samples could be requested of DOE if necessary.

Table 1. Comparison between Un-irradiated UO_2 fuel and spent nuclear fuel dissolution rate. (CRWMS M&O, 2000)

Test Conditions	Spent Fuel Dissolution Rate (g/m^2-d)	Un-irradiated UO_2 fuel Dissolution Rate (g/m^2-d)
75 °C, 0.0002 M CO_3, 0.2 M O_2, pH range between 8-10	8.6, 11.0, 9.5, 6.0	10.9, 6.48
25 °C, 0.0002 M CO_3, 0.2 M O_2, pH range between 8-10	0.63, 2.6, 2.9, 2.9	2.55
75 °C, 0.02 M CO_3, 0.2 M O_2, pH range between 8-10	14.2, 4.6,	77.3, 54.0
25 °C, 0.02 M CO_3, 0.2 M O_2, pH range between 8-10	1.5, 4.0, 3.5, 3.8, 3.2, 3.8	2.42, 6.72
75 °C, 0.02 M CO_3, 0.02 M O_2, pH range between 8-10	2.89, 4.75	5.11,
25 °C, 0.02 M CO_3, 0.02 M O_2, pH range between 8-10	2.05,	1.87

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