Final Technical Report

Project Title: Radioactive Waste Management: A Study of Spent Fuel Dissolution Rates in Geological Storage Using Dosimetry Modeling and Experimental Verification

Contract Period: 5/01/07 – 4/30/11 (with no cost extension to 7/31/2011)

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Award Number: DE-FG07-07ID14763

Subcontractors: None

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Project Objective:

This research will provide improved predictions into the mechanisms and effects of radiolysis on spent nuclear fuel dissolution in a geological repository through accurate dosimetry modeling of the dose to water, mechanistic chemistry modeling of the resulting radiolytic reactions and confirmatory experimental measurements. This work will combine efforts by the Nuclear Science and Engineering Institute (NSEI) and the Missouri University Research Reactor (MURR) at the University of Missouri-Columbia, and the expertise and facilities at the Pacific Northwest National Laboratory (PNNL).

Background:

Due to its high radiation field, fresh spent nuclear fuel in contact with water will undergo oxidative dissolution under both oxidizing and reducing environments through the formation of OH•, H_2O_2 and other radiolysis products. Within 300–1000 years, this radiation field will decrease 100–1000 times, significantly reducing the rate of oxidative dissolution. Many present-day corrosion models extrapolate results from tests with fresh fuel that are dominated by beta/gamma radiolytic effects, mainly because of the presence of short-lived ^{90}Sr and ^{137}Cs isotopes. These artificially increase the dissolution rate and also change the behavior of the fission products and actinides in the fuel. Thus, it is probable that these dissolution rates will decrease significantly after the 300–1000 year time period due to decreased activity and the change from predominantly beta/gamma irradiation to predominantly alpha irradiation which will decrease the resulting radiolytic field. Although alpha radiolysis will still occur after 300-1000 years, the production rate of the more reactive radicals is much lower than that of a beta/gamma field, and this should make alpha radiolysis less important than has been suggested. There are also several mechanisms of radiolytic enhancement that need to be examined, including possible morphological changes such as grain boundary disintegration. Fundamental data are also needed on the actual radiolytic generation rates after the decay of ^{90}Sr and ^{137}Cs in a repository-relevant environment.

Students Supported:

Five graduate students received funding and support from this grant:

- Amanda Kline Casella, Nuclear Engineering, Ph.D. in 2008
- Richard Clark, Chemistry, current Ph.D. student
- Benjamin White, Nuclear Engineering, current Ph.D. student
- Jenny Schutte, Nuclear Engineering, current M.S. student
- Chung-Hao (Curtis) Huang, Nuclear Engineering, current M.S. student

Publications:

Six publications resulted from this research, and one final publication is pending:

- Miller, W.H., A. Kline and B. Hanson, "Dosimetry Modeling for Predicting Radiolytic Production at the Spent Fuel – Water Interface," *International High-Level Radioactive Waste Management Conference*, Las Vegas, Nevada (April 30 - May 4, 2006).
- Kline, A., B. Hansen, W.H. Miller, R. Wittman, "Modeling the Radiolysis Effect of CSNF Dissolutions Kinetics," Trans. Am. Nucl. Soc., 95, 177-8 (November 12-16, 2006).
- Kline, A., B. Hanson, B. and W.H. Miller, "Characteristics of UO_2 Dissolution as Determined by SPFT Tests," Trans Am. Nucl. Soc., 96 (June 2007).
- Kline, A., B. Hanson and W.H. Miller, "The Temperature, Oxygen, and Fuel Chemistry Dependence of UO2 Dissolution under Repository Conditions," Trans. Am. Nucl. Soc., 98. 131-2 (June 2008).
- Casella, Amanda, B. Hanson, W.H. Miller, "Factors Affecting UO2 Dissolution Under Geologic Disposal Conditions," 2008 International High-Level Radioactive Waste Management Las Vegas, NV (September 7-11, 2008).
- Casella, Amanda, B. Hanson, W.H. Miller, "Fuel Matrix Chemistry Effects on UO_2 Dissolution," Trans. Am. Nucl. Soc., 102 (November 2009).

Research Program

The purpose of this research effort was to duplicate, as nearly as possible, experimental, unirradiated tests performed at Pacific Northwest National Laboratory (PNNL) to measure the rate of uranium dissolution in powered uranium in flow through samples under irradiation. Quarterly reports have given a detailed description of progress during the term of this project. An overview is given here.

First, baseline dosimetry calculations were performed to provide a range of Co-60 radiation fields that would mimic dose rates expected in a repository. Four Co-60 sources were available in the pool at the Missouri University Research Reactor (MURR) to provide the needed dose field. MCNP calculations were performed to design the placement of these four sources in proximity to uranium dissolution samples to give doses ranging from 800 to 5000 Gy/hour. By comparison, 23 year old spent fuel experiences a dose rate of about 2000 Gy/hr.

The experimental apparatus for inserting samples into the pool at the MURR was then designed and fabricated. This fixture includes positions for inserting 3 single pass, flow through samples into a holder containing the four Co-60 sources, generating dose rates up to 5000 Gy/hour. A picture of this fixture is shown below. The positions for the samples and sources are contained by the top and bottom support “pucks.” The rod extending out of the top supports the irradiator in the Missouri University Research Reactor pool approximately 12 feet below the surface to allow adequate shielding of the sources. This rod also houses the 1/16” stainless steel lines that allow water flow into and out of the sample cells.

Figure 1: Photo of experimental sample holder

All safety reviews for use of this fixture at the MURR were completed and this system was prepared for installation.

Natural uranium dioxide fuel samples were prepared by PNNL consistent with sample preparation for the non-irradiated samples previously used at PNNL. The samples were repeatedly crushed and washed to produce powders approximately 15 microns in size. These were not delivered until the second quarter 2009.due to delays at PNNL which postponed the beginning of experimental runs. A total of approximately 1.6 grams of sample powder was delivered, which was subdivided into eight, 0.2 gram lots.

Some modifications to the system were envisioned to simplify the system that was used at PNNL. A 30 gallon, stainless steel, header tank was used to eliminate the need for replenishing the flow through water during experiments. The water in this tank as monitored for O_2, pH and temperature and was delivered to the uranium samples through 1/8" stainless steel lines. It was assumed that there would be sufficient vertical

space at the MURR to allow gravity feed through the samples. This would have eliminated the need for feed pumps and would provide flow even in the event of loss of power (which occurred at PNNL). .

Considerable work was given to calibrating the analysis procedures for measuring dissolved uranium content in the flow through water. Uranium concentrations in the dissolution samples were accurately quantified down to approximately 20 ppb using uv-vis and were benchmarked against mass spectrometer results.

Initial experiments were begun during Q2 of 2009 on unirradiated samples to benchmark these new results against the previous measurements at PNNL. Almost immediately it was found that gravity feed was insufficient to get adequate flow through the frits used to hold the uranium powder in the columns. This necessitated the purchase and installation of a constant flow pumps and pressure relief valves (similar to what was used at PNNL), and also required additional approvals from MURR operations staff. Unfortunately, back pressure developed almost immediately and the pumps quickly exceeded the 10 psia limit imposed by the approved procedure. (This pressure was implemented to reduce the possible contamination of the reactor pool should a leak occur.) Additional testing was performed and ultimately approval was given for back pressures up to 100 psia. This was used throughout the rest of the experimental protocol with limited success. Some sample flows could be regulated to provide the desired 0.2 ml/min of flow at less than 100 psia, and other samples appeared to clog the frits almost immediately upon starting a run. Water filters (0.5 microns) were installed to ensure that impurities in the header tank were not clogging the filters, but this did not improve the results. This flow problem existed throughout all experimental runs and data taken at low flow rates was analyzed against desired flow rate data.

After working six months to try to solve the flow problems, data on three unirradiated samples was begun in Q4 2009. This run lasted 90 days. The first three irradiated samples (exposed to approximately 800, 2000 and 5000 Rads respectively, were started in Q2 of 2010.and ran through Q3 2010. A final irradiation test was conducted in Q1 2011 with two samples at irradiated at dose rates of approximately 750 and 4700 Gy/hr.

Some trends can be made as summarized in the two figures below: Figure 2 addresses the issue of changing flow rates over the experimental runs. All experimental runs are shown here except for Unirradiated Sample #1, which had unacceptably low flow rates throughout the entire experiment.

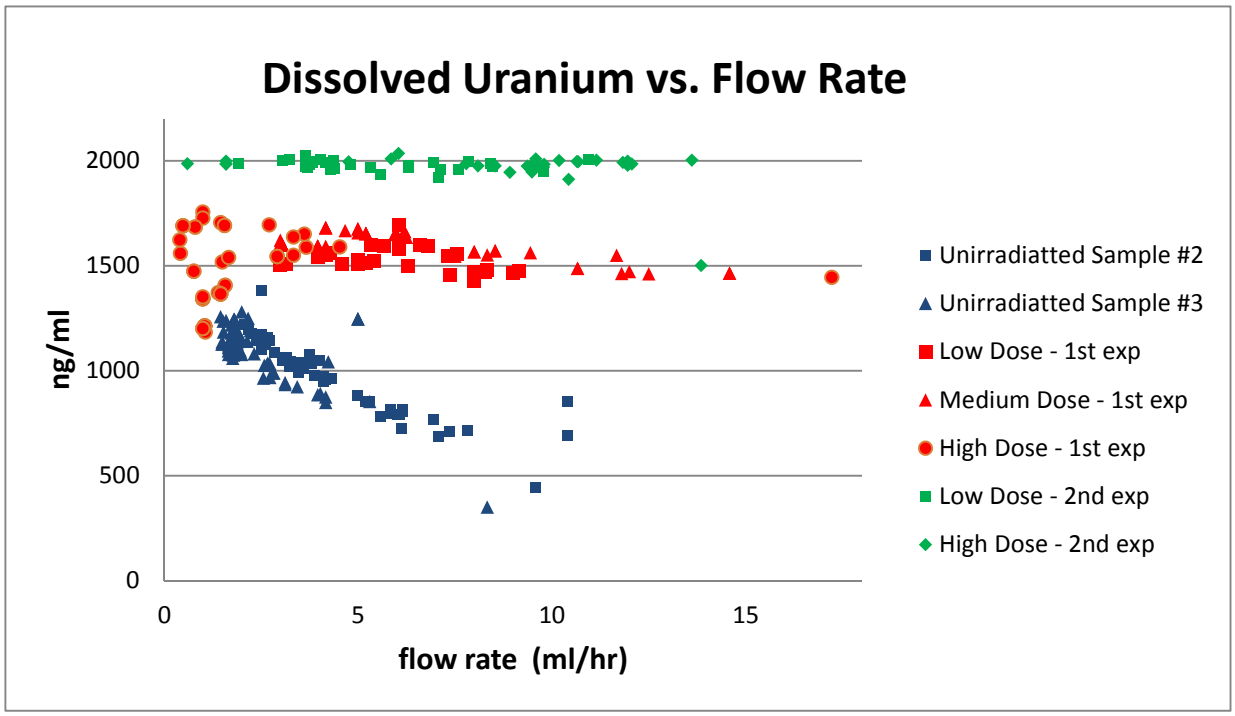

Figure 2 – Dissolved Uranium Concentration vs. Flow Rate

The unirradiated samples demonstrate previously observed behavior identified in Amanda Kline Casella's dissertation from data at PNNL in that lower flow rate samples tend to have higher dissolution rates. Interestingly, this effect is not seen for irradiated samples. Also, Irradiated samples show higher dissolution rates as expected.

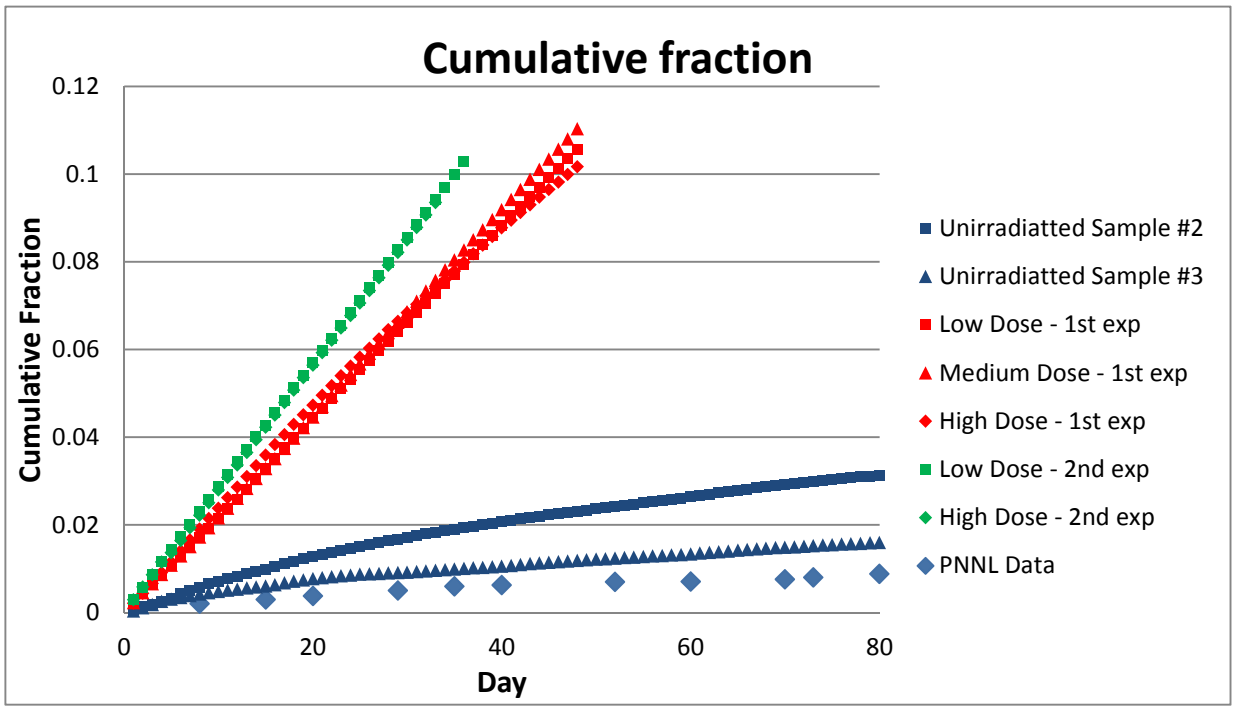

Figure 3 – Cumulative dissolved fraction assuming constant 0.2 ml/min flow

Figure 3 shows the cumulative amount of uranium dissolved for: 1) previous PNNL data taken by Dr. Casella, 2) two unirradiated samples at the MURR and 3) five irradiated samples at the MURR. For the unirradiated samples, the data was corrected to 0.2 ml/min of flow to be consistent with PNNL data. This normalization involved first correcting the dissolved concentration by the flow rate correction implied from Figure 1 and then multiplying this daily

dissolved concentration by an assumed daily flow rate of 288 ml. This data is in reasonable agreement with previous, unirradiated PNNL data.

The irradiated samples at the MURR showed a significant increase in the dissolution rate as would be expected. Corrections for dissolution rate as a function of flow were not applied since the irradiated samples did not show flow rate dependence. An interesting observation is that the irradiated samples show no dose rate dependence, in spite of the fact that the dose rate ranged over almost an order of magnitude from 750 to 5000 Gy/hr. The second set of irradiated samples also showed increased dissolution rates, somewhat greater than the previous irradiated samples. The reason for this offset is unknown.

Summary of Experimental Results

Tests were completed to determine the effect of irradiation on the dissolution of uranium oxide in flow through samples. These results were compared to previous unirradiated data from PNNL and similar unirradiated data takes at the MURR, for which there was reasonable agreement. Irradiated samples showed significantly higher dissolution rates, as would be expected, but showed no dose rate dependence.

Future Research

Ph.D. student Richard Clark will be using this experimental work as part of his dissertation in Radiochemistry. He will be developing models in an attempt to account for the experimental results. Upon completion of this analysis, a final publication will be prepared.

Milestone Status Table:

ID Number	Task / Milestone Description	Planned	Actual	Comments
1	First Year Activities			
1.1	Calculate, using Monte Carlo techniques, the dose to water in contact with spent nuclear fuel as a function of radiation type, fuel geometry and the fuel-to-water ratio for baseline geometry.	12/1/07	9/15/07	Completed
1.2	Predict the radioactive decay rates in the repository for all emission types from the average spent nuclear fuel composition (as defined by the Yucca Mountain Final Environmental Impact Statement) as a function of time.	1/1/08	9/15/07	Completed
1.3	Acquire equipment for experimental tests	1/1/08	3/31/09	Completed
1.4	Using mechanistic models for UO_2 oxidation in water solutions under-going radiolysis, the resulting interactions among radiolytic products and the fuel will be calculated.	4/1/08	----	Will continue with other funding past the end of the grant period.
1.5	Begin preliminary experiments with Single Pass Flow Through (SPFT) tests on UO_2.	4/1/08	7/31/09	Completed
2	Second Year Activities			
2.1	Continue dose to water calculations for other possible fuel/water geometries.	9/1/08	7/31/09	Completed
2.2	Perform experiments of UO_2 fuel saturated with water for fuel doped with single isotopes of either alpha or beta emitters using the facilities of Pacific Northwest National Laboratory	1/1/09	----	No longer being considered
2.3	Begin experiments on grains of UO_2 fuel saturated with water with external gamma ray fields using facilities at the Missouri University Research Reactor	4/1/09	3/31/10	Completed
3.	Year Three Activities			

ID Number	Task / Milestone Description	Planned	Actual	Comments
3.1	Perform experiments on grains of UO_2 fuel saturated with water for RADFUEL simulated fuel doped with alpha emitters using the facilities of Pacific Northwest National Laboratory	1/1/10	----	No longer being considered
3.2	Complete experiments on grains of UO_2 fuel saturated with water with external gamma ray fields using facilities at the Missouri University Research Reactor	1/1/10	6/30/11	Completed
3.3	Correlate the experimental results from the experimental program with the dosimetry and chemical modeling to provide predictions into the mechanisms and effects of radiolysis on spent nuclear fuel dissolution in a geological repository	4/30/10	----	Will continue with other funding past the end of the grant period.