Experimental Plan for ANL Electrochemical Corrosion Studies

Used Fuel Disposition – Engineered Barrier Systems

Prepared for
U.S. Department of Energy
Used Fuel Disposition Campaign

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SUMMARY

This report documents Argonne's FY2013 experimental plan for tests supporting the extension an optimization of the electrochemical model for oxide fuel degradation that was implemented as part of Argonne's FY2012 activities. The processes targeted by the experimental and modeling plans described in this document were identified in a data gap analyses performed in FY2011 to "provide an up-to-date and comprehensive review of the pertinent scientific literature and on this basis identify the scientific information needs for assessing fuel degradation and radionuclide mobilization" (Jerden et al. 2011). This work is being performed as part of the U.S. DOE's Used Fuel Disposition (UFD) Campaign's Engineered Barrier Systems (EBS) evaluations work package: FT-13AN080601 Rev 0, milestone: M4FT-13AN0806011.

The objective of the ANL experiments and modeling activities is to produce an experimentally verified process model for the rate of degradation of used oxide fuel that is based on fundamental electrochemistry and thermodynamics. A specific objective of this work is to account for the role of the noble metal bearing fission product alloy phase or noble metal particles (NMP) present in spent oxide fuel in catalyzing reactions that inhibit the oxidative dissolution of the fuel matrix and thus significantly slow the release of radionuclides. The catalyzed oxidation of dissolved hydrogen and associated reduction (destruction) of radiolytic oxidants such as H_2O_2 may provide electrochemical protection against fuel degradation by lowering the electrochemical potential at the fuel surface such that the radionuclides in the spent fuel (i.e., U, Tc, Np, Pu, etc.) remain in or are reduced to sparingly soluble oxidation states (e.g., as UO_2, TcO_2, NpO_2, and PuO_2). Although the natural conditions of a disposal system contribute to the electrochemical potential at the fuel surface through the groundwater composition, the effects of radiolysis and corrosion products can overwhelm the influence of the natural environment at the fuel surface and control the fuel degradation mechanism and rate.

The process model we are working on will be an extension of the mixed potential model (MPM) that was developed for the oxidative dissolution of UO_2 fuels (Shoesmith et al., 2003). As part of Argonne's FY2012 work on this project the mixed potential model of Shoesmith et al., 2003 was implemented and its performance verified relative to the experimental data on which the Shoesmith model was based: see Jerden et al., 2012 for details on implementation and verification of Argonne's mixed potential model.

The following report presents the FY2013 plan for electrochemical testing at Argonne in support of extending Argonne's MPM to account for the role of NMP in the rate of used oxide fuel degradation. In FY2012 a series of electrochemical experiments were performed on UO_2 and NMP electrodes (see Ebert et al., 2012) included. These experiment provide a thorough base-line data set on which FY2013 experiments will build. The FY2013 tests will expand on the FY2012 data sets by quantifying the temperature and pH dependence of UO_2 matrix dissolution both in the presence and absence of H_2 gas and the NMP phase (Table 1).

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Experimental Plan for Electrochemical Corrosion Studies

1.   OBJECTIVES AND SCOPE

The context for the experimental and modeling tasks described in this report is shown in Figure 1, which was adapted from Freeze et al. (2010). Our work has important implications for the rates of waste form degradation and radionuclide release from used oxide fuels, which will largely determine the radionuclide source terms used in disposal system performance models.
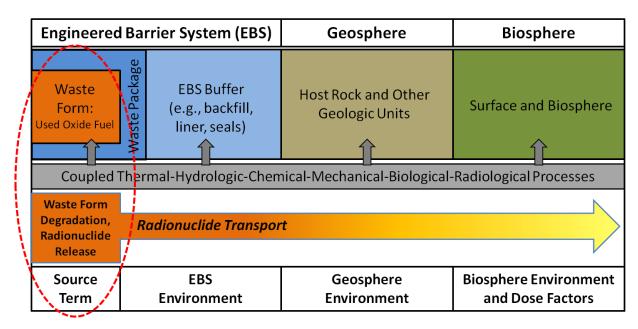

Figure 1. Components of a generic disposal system for used oxide fuel (adapted from Freeze et al. 2010). The red circle identifies the components and associated processes targeted by the experiments described in this report.

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The FY2013 work for this project will focus on producing experimental data that facilitates extending the Argonne's mixed potential model for used fuel degradation (ANL-MPM) to determine analytical forms form the temperature and pH dependencies of the reaction kinetics as well as the role of NMP in catalyzing H_2 oxidation which may protect the fuel from oxidative dissolution.

The technical approach used for this project combines standard electrochemical measurements in controlled environments with direct measurements of the UO_2 dissolution rate from solution analyses. This links the electrokinetic model for oxidative dissolution to the source term for radionuclide release. Separate electrodes have been fashioned from ceramic UO_2 and an alloy having a composition representing the NMP found in used oxide fuel. The electrochemical measurements provide data sets that are used to optimize and extend our process level mixed potential model for used fuel degradation (ANL-MPM). For a detailed discussion of the Argonne mixed potential model see Jerden et al., 2012.

Our established experimental approach (see Ebert et al., 2012) of using separate electrodes in various electrically and chemically coupled systems allows for detailed characterization and quantitation of various effects on the fuel dissolution rate, such as the composition of the fuel matrix, the relative surface areas of the fuel and NMP, the composition of the NMP, corrosion of the NMP, poisoning of the catalytic efficiency of the NMP due to the sorption of groundwater solutes, etc.

Our FY2012 electrochemical test results provide benchmark responses with which the responses in coupled systems can be compared. Those tests have established the baseline behavior of the UO_2 and NMP alloy electrodes under a range of conditions that can be used for comparisons of test responses in the coupled system. As part of the FY2012 work we successfully developed the experimental and analytical methodologies that will be used in future tests, gained experience using the UO_2, NMP electrodes to identify testing artifacts and limitations, estimated the sensitivity of the electrochemical and solution analytical methods to the electrode responses, and demonstrated the roles of the experiments to provide insights, validation, and kinetic information to the degradation model.

Experiments in FY2013 will include measurements Using separate electrodes in a coupled system. This will allow different potentials to be imposed on each material, different electrical resistances to be imposed between the materials to simulate the weathering of phase boundaries, pre-test corrosion of one or both materials, and separate couplings to other materials to measure galvanic effects, such as steels used in canisters and various cladding materials.

2.   FY2013 ELECTROCHEMICAL EXPERIMENTS

The methodology, materials and an initial dataset for Argonne's electrochemical studies of oxide fuel dissolution are discussed in Jerden et al., 2012 and Ebert et al., 2012. The following section identifies the new samples and variables that will be tested in the FY2013 matrix of experiments. The FY2013 tests will expand on the FY2012 data sets by quantifying how the corrosion/dissolution rate of UO_2 matrix is influenced by the following:

- Temperature
- pH
- Presence of lanthanides in the UO_2 matrix (simulated fission products)
- Electrical coupling of UO_2 matrix and NMP electrode
- Composition of the NMP electrode (new Ru-Mo-Pd-Rh-Tc bearing alloy materials will be used)
- Presence/absence of dissolved H_2
- Concentration of H_2O_2 (dominant radiolytic species in silicate repository groundwaters)
- Electrode surface area changes throughout the test (electrode will be examined by SEM, light microscopy before and after each electrochemical test)

The FY2013 tests will be used to extend and optimize the second version of the ANL-MPM code, which takes into account processes that may slow or even inhibit the oxidative dissolution of used fuel, specifically the oxidation of H_2 and the catalytic role of the NMP phase. Table 1 summarizes the FY2013 experimental work in the context of previous and envisioned future tests: the purpose of each test is identified and the link to the ANL-MPM is briefly described (columns 7, 8 on Table 1). The materials and test conditions shown in bold font are planned for FY2013 and those shown in italics are planned for out years. The experiments indicated in plain font were completed in FY2012.

A number of the FY2013 tests will be performed using new electrode materials that contain surrogate fission products that may play important roles in the rate of oxidative dissolution of the oxide fuel matrix. These materials include technetium bearing NMP and a lanthanide doped UO_2 (~2% Nd > Ce > La). The materials to be used for electrode materials are summarized as follows:

- UO_2: pure cut from standard UO_2 fuel pellet (produced at UNLV by cold pressing purified UO_2 powder). This material was used for FY2012 tests and will continue to be used for FY2013 tests with combined electrode set up until new lanthanide doped UO_2 is obtained.
- Lanthanide doped UO_2: sintered pellet containing ~0.9% Nd_2O_3, ~0.5% Ce_2O_3, ~0.2% La_2O_3. This material will be produced and used in FY2013 and future tests.
- NMP-W: two phase alloy of 40Mo-30Ru-15Pd-10Re-5Rh (atomic %) describe in Wonkiewicz et al., 2002. This material was used for FY2012 tests and will continue to be used for FY2013 tests with combined electrode set up until new Tc bearing NMP is obtained.
- NMP-E: Tc bearing alloy with target composition: 55Ru-20Mo-10Rh-10Pd-5Tc (mass %). This material will be produced and used in FY2013 and future tests.

Table 1. Summary of multi-year experimental matrix for Argonne's electrochemical tests being performed in support of the optimization of the ANL-MPM for used fuel matrix degradation. Experiments with materials and test conditions shown in plain font were completed in FY2012, experiments planned for FY2013 are shown in bold font, and conditions for future experiments are shown in italics.

Test Type	Working Electrodes*	$[H_2O_2]$ (initial, molar)	pH	T (°C)	Purge gas	Purpose	Link to ANL-MPM
Open circuit corrosion	UO_2, **Doped-UO_2**	10^{-6}, 10^{-4}, 10^{-2}, **1.0**	9.5, *7.0*, 4.0	30, **50**, *90*	Air, Ar, >2% H_2 in Ar	Base-line behavior (potential and dissolution current) of electrode for a given solution/gas composition	Results test model accuracy: compare predicted and measured dissolution current and electrode potential
Cyclic voltammetry	UO_2, **Doped-UO_2**, NMP	10^{-6}, 10^{-4}, 10^{-2}, **1.0**	9.5, *7.0*, 4.0	30, **50**, *90*	Air, Ar, >2% H_2 in Ar	Identify voltage range for key redox reactions, identify preferential (non-uniform) dissolution of electrode surface (by microscopy).	Results test conceptual basis for ANL-MPM parameter database: identify key redox reactions for oxidative dissolution of UO_2.
Potentiostatic	UO_2 **Doped-UO_2,**	10^{-6}, 10^{-4}, 10^{-2}, **1.0**	9.5, *7.0*, 4.0	30, **50**, *90*	Air, Ar, >2% H_2 in Ar	Corrosion rate for given solution/gas composition at fixed potential (monitor dissolution current)	Results test overall accuracy of ANL-MPM: compare predicted and measured dissolution rates, precipitation of corrosion product phases
Potentiodyamic, Linear polar. resistance, Tafel	UO_2, **Doped-UO_2**, NMP	10^{-6}, 10^{-4}, 10^{-2}, **1.0**	9.5, *7.0*, 4.0	30, **50**, *90*	Air, Ar, >2% H_2 in Ar	Electrochemical characterization of electrodes, quantify electrochemical parameters for key reactions	Results will provide Tafel constants and charge transfer coefficients for surface reactions in ANL-MPM parameter database
Coupled open circuit	**UO_2 + NMP Doped-UO_2 + NMP**	**10^{-6}, 10^{-4}, 10^{-2}, 1.0**	**9.5,** *7.0*, **4.0**	**30,** **50**, *90*	**Air, Ar, >2% H_2 in Ar**	Base-line behavior (potential and dissolution current) of UO_2 in coupled system for a given solution/gas composition	Results test model accuracy: compare predicted and measured dissolution current and electrode potential
Coupled potentiostatic	**UO_2 + NMP Doped-UO_2 + NMP**	**10^{-6}, 10^{-4}, 10^{-2}, 1.0**	**9.5,** *7.0*, **4.0**	**30,** **50**, *90*	**Air, Ar, >2% H_2 in Ar**	Corrosion rate for UO_2 at fixed potential when electrically coupled with NMP for given solution/gas composition	Results test overall accuracy of ANL-MPM: compare predicted and measured dissolution rates, precipitation of corrosion product phases, catalytic properties of NMP
Coupled potentiostatic	**Doped-UO_2 + pre-corroded NMP**	**10^{-6}, 10^{-4}, 10^{-2}, 1.0**	**9.5,** *7.0*, **4.0**	**30,** **50**, *90*	**Air, Ar, >2% H_2 in Ar**	Corrosion rate for UO_2 at fixed potential when electrically coupled with corroded NMP for given solution/gas composition	Results test overall accuracy of ANL-MPM: compare predicted and measured dissolution rates, precipitation of corrosion product phases, catalytic properties of corroded NMP

*Both lanthanide doped and non-doped UO_2 will be used and both Tc bearing and non-Tc bearing NMP electrodes will be used in tests.
**Each test will be timed and the concentration of key species (U, lanthanides for UO_2, Ru, Mo, Pd, Rh, Tc for NMP) will be measured by ICP-MS when the test is terminated. All electrodes will be examined using SEM before and after tests. Starting and final H_2O_2 concentrations will be measured by UV-Vis.
***Electrolyte chemistry for all tests will be $1x10^{-3}$ NaCl with pH adjusted using NaOH or HCl.

3   EXPERIMENTAL APPROACH AND METHODS

The following summarizes the experimental approach and methods for a more detailed discussion see Ebert et al., 2012 and Jerden et al., 2012.

The experimental method utilizes separate electrodes fabricated from alloys made to represent a range of NMP composition and UO_2 or lanthanide-doped UO_2 ceramics made to represent UOX fuel (without NMP). The electrodes are immersed in a solution containing known concentrations of dissolved H_2 and H_2O_2. Potentials are imposed on the NMP and UO_2 electrodes using separate potentiostats and various configurations. The measured current will provide a measure of UO_2 or NMP that is oxidized during the test and the solution will be analyzed for U and components of the NMP after the test. In this way, the NMP and UO_2 remain electrically coupled (effectively, through the potentiostats) but physically separated to differentiate chemical and physical effects and isolate interactions with the solution. This allows the currents from reactions between the solution and fuel and between the solution and NMP to be measured separately. The initial tests were conducted with different H_2O_2 concentrations at different potentials. Subsequent tests will be conducted using solutions that are held at different temperatures, are adjusted to different pH values, may contain additional solutes to identify variables that affect the UO_2 dissolution rate and quantify the effects of environmental variables. Measurements will be made for different NMP alloy compositions, with different electrode surface areas, with NMP electrodes that have been electrochemically corroded, and without the NMP electrode to characterize the dissolution behavior of UO_2 alone and determine the contribution of NMP-catalyzed reactions.

The steps for our experimental approach are summarized as follows:

- Fabricate electrodes with surrogate Tc-bearing alloy representing NMP (subcontract to INL)
- Fabricate electrodes with doped UO_2 representing UOX fuel (subcontract to UNLV)
- Measure UO_2 dissolution rate in test solution in absence of NMP
- Measure effect of (clean) NMP-catalyzed reactions on UO_2 dissolution
  Electrochemically characterize kinetics of UO_2 dissolution at various T, pH, H_2O_2 and H_2 concentrations, electrode surface areas, and imposed potentials
  Measure concentrations of U, Mo, Tc, etc. in solutions after electrochemical tests
- Measure effects of solutes likely to poison catalytic efficiency
  Control potentials, T, pH, solutions with H_2O_2, H_2, and added NaCl, NaBr, NaI, S, Se, etc.
- Corrode surface of NMP electrode under controlled conditions (*ex situ*)
- Measure dissolution of UO_2 into solutions in presence of corroded NMP alloy
- Characterize electrode surface electrochemically, with electron microscopy and X-ray absorption spectroscopy, etc.

4.   RECORDS AND QUALITY ASSURANCE

The experimental and modeling activities in FY 2013 will be conducted at QA Level 3 as research and development activities. It is expected that these activities will establish the experimental design and identify the data that will be used to establish the mathematical form of the process model and identify the key environmental variables that will be included.

Dedicated scientific notebooks will be used to document the experimental and modeling activities, and experimental work will follow good laboratory practices. Progress will be reported during monthly teleconferences, entered into the PICSNE project management system, and presentations made at campaign meetings. Testing results and data interpretation will be reviewed by collaborators at ANL, PNNL, and SNL and documented in reports submitted to the Used Fuel Disposition Campaign national directors and DOE Fuel Cycle Research and Development managers.

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