PNNL Engineered Barrier Systems International Collaborations

Spent Fuel and Waste Disposition

SUMMARY

This report discusses the progress made in FY20 at Pacific Northwest National Laboratory (PNNL) in the program focused on the dissolution of UO_2 fuel with various dopants. Previous work has shown that radiolysis of water has a significant impact on the dissolution rate of spent nuclear fuel under oxidizing conditions due to the generation of a range of oxidizing (O_2, •OH, HO_2•, H_2O_2) and reducing species (•e_{aq}^-, •O_2^-, •H) at concentrations dependent on dose rate [a,b]. Following long time periods in geologic disposal environments the gamma source will subside quickly, and long-lived radionuclides will dominate, emitting alpha radiation, which generates products such as H_2O_2 and influences UO_2 dissolution rates. Under oxidizing conditions, the primary dissolution mechanism is oxidative dissolution; work has illustrated that fission products and actinides soluble in the UO_2 matrix of spent nuclear fuel (SNF) delays solid state oxidation with an increasing resistance to oxidation to form U_3O_8 with increasing burnup [c]. Oxidation resistance has also been observed in Gd doped-UO_2[d].

To simulate fuel chemistry, dopants in the UO_2 matrix are representative of fission products and actinides, and are soluble in the UO_2 matrix. This report discusses PNNL's progress towards testing fuels using a single pass flowthrough (SPFT) system to determine the effects of dopants on the dissolution kinetics of UO_2 fuel samples and doped-UO_2 fuels. The efforts to develop and build the SPFT are nearly complete and nearing the initiation of testing. The deployment of the system has been delayed due in part to the COVID-19 pandemic and associated precautions.

Movement to studying fuel dissolution in anoxic reducing conditions at PNNL is under development to support studies that replicate both repository type conditions. In order to adapt to the alternative environment, the SPFT system would likely be replaced with an electrochemical cell set up, autoclave, or a smaller single pump system in an oxygen free environment, such as an environmental chamber or glovebox.

Results from experimental data in both conditions can be used to populate the Fuel Matrix Dissolution Model (FMDM), which provides calculations of radionuclide source terms for use in repository performance assessments based on fundamental chemical and physical principles.

In support of the UO_2 dissolution program, PNNL attended the 3rd annual meeting of Modern Spent Fuel Dissolution and Chemistry in Failed Container Conditions (DisCo) to leverage technical information from European collaborators. The DisCo project goal is to close the gap in knowledge regarding spent fuel dissolution from novel fuel types, in particular Cr/Al-doped fuels and mixed oxide (MOX) fuels. The 3rd annual meeting of the project was held virtually on the 23rd of April, 2020. The meeting aim was to provide a forum to facilitate the discussion of project results and planning of project direction, as well as to communicate with the broader scientific community on progress. Results of fuel pellet production, pellet spent fuel dissolution, dissolution of model materials, and computational simulations of dissolution

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[a] Jégou, C., et al., *Effect of external gamma irradiation on dissolution of the spent UO2 fuel matrix.* Journal of Nuclear Materials, 2005. **341**(1): p. 62-82.

[b] Casella, A., B. Hanson, and W. Miller, *The effect of fuel chemistry on UO2 dissolution.* Journal of Nuclear Materials, 2016. **476**: p. 45-55.

[c] Hanson, B. D. (1998). *The burnup dependence of light water reactor spent fuel oxidation*, PNNL-11929; Pacific Northwest National Lab., Richland, WA

[d] Kim, J-G., et al., *Effect of trivalent dopant, Gd3+, on the oxidation of uranium dioxide*. Journal of Nuclear Materials, 2001. **297**(3): p. 327-331.

were all discussed and presented. A summary of the technical portions of the meeting are summarized in this report.

ACKNOWLEDGEMENTS

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ACRONYMS

ADOPT	Advanced Doped Pellet Technology
BET	Brunauer-Emmett-Teller
CEA	Atomic Energy and Alternatives Energies Commission
Ciemat	Centro de Investigaciones Energeticas, Medioambientales y Tecnologicas
COVID-19	coronavirus disease 2019
CF	cumulative fraction
DGR	deep geological repository
DisCo	Modern Spent Fuel Dissolution and Chemistry in Failed Container Conditions
DOE	Department of Energy
EDX	Energy dispersive X-ray Spectroscopy
Eh	redox potential
FMDM	Fuel Matrix Dissolution Model
GDSA	Geologic Disposal Safety Assessment
IRF	instant release fraction
JRC	Joint Research Center
KIT	Karlsruhe Institute of Technology
KPA	Kinetic Phosphorescence Analyzer
LWR	light water reactor
MOX	mixed oxide fuels
NDR	normalized dissolution rate
NNL	National Nuclear Laboratory
PNNL	Pacific Northwest National Laboratory
PSI	Paul Scherrer Institut
R&D	research and development
SCK•CEN	Studiecentrum voor Kernenergie
SEM	scanning electrochemical microscopy
SNF	spent nuclear fuel
SPFT	single pass flowthrough
TGA	thermogravimetric analysis
WP	work package
XRD	x-ray diffraction
YCWCa	young cement water with calcium

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1.   INTRODUCTION

In a geologic repository, if a waste package holding spent nuclear fuel (SNF) failed, the SNF could be exposed to any water present and has the potential to dissolve and migrate radionuclides. The rate of dissolution of the fuel depends on a combination of the redox conditions near the fuel surface, the temperature, and the chemical composition of the contacting water. The conditions within the repository and within a failed container are fluid as time progresses and concentrations of chemicals are generated and evolve. The UO_2 matrix of the SNF dictates the release of many radionuclides from the SNF. When in the reduced form of U^{IV}, the solubility of UO_2 by groundwater is low. However, the environment within the failed container and the redox conditions greatly impact the UO_2 matrix solubility; the near field conditions of the fuel can rapidly evolve.

During its lifetime the SNF will emit gamma, beta, and alpha radiation, which results in self-radiation damage and can alter the near field environment [1]. When exposed to ionizing radiation, water decomposes into a range of oxidizing (O_2, $\bullet OH$, $HO_2\bullet$, H_2O_2) and reducing species ($\bullet e_{aq}^-$, $\bullet O_2^-$, $\bullet H$). Previous work has shown that the radiolysis of water has a significant impact on the dissolution rate of spent nuclear fuel under oxidizing conditions [2, 3]. The radicals formed have short lifetimes due to their reactivity, resulting in recombination to produce stable species. Thus, molecular products of water radiolysis, such as H_2O_2, H_2, and O_2 are anticipated as the predominant species at or near the liquid:SNF interface. These species can oxidize U^{IV} to U^{VI}; U^{VI} is much more soluble than its reduced counterpart. A stability diagram for U systems is shown in Figure 1.1.
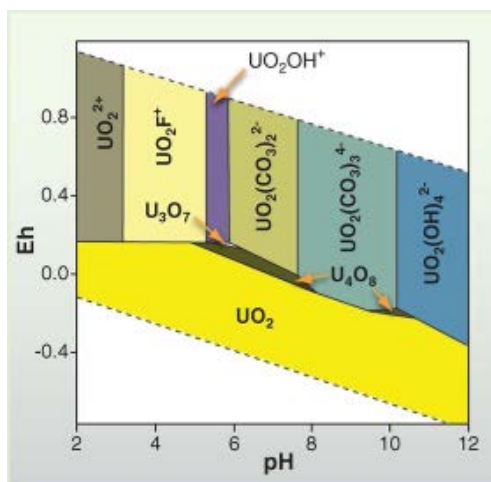
Figure 1.1 A stability diagram for U systems: speciation of U in a hypothetical groundwater at 25°C. Source: Ref [4]

In repository relevant conditions the bicarbonate species in groundwater is likely to increase the rate of UO_2 dissolution as it strongly complexes with $U^{VI}O_2^{2+}$, and $OH\bullet$ can generate $CO_3^{\bullet-}$, which is a strong oxidant [5, 6]. The enhanced matrix dissolution is of critical importance as it could expose other radionuclides within the SNF and lead to their enhanced release.

The concentration of products from radiolysis is dependent on the dose rate and energy. With increased gamma dose rate, radicals such as $\bullet OH$ and O_2 form, which affect UO_2 dissolution via oxidation. However, the gamma irradiation will cease early upon disposal. At longer times the alpha irradiation from long-lived radionuclides will be the dominant irradiation source, which as well, generates products such as H_2O_2, which also influences UO_2 dissolution rates [5, 7, 8]. With this knowledge, and because H_2O_2 is not as efficient in driving fuel matrix dissolution compared to the radicals formed in water radiolysis, fuel dissolution rates should decrease with increased time. However, limited assessments of this hypothesis are available, and any trends would be highly dependent on fuel composition and the presence of dopants. Analysis of fuel samples exposed to different dose rates and sources (or simulated

radiolysis products) can assist in determining the effects of alpha, beta, and gamma radiation and determine their influence on dissolution rate.

The chemistry of spent nuclear fuel also heavily impacts the dissolution rate. Within a fuel pellet the elemental distribution in the microstructure is not uniform and is influenced heavily by its in-service conditions and burnup [1]. Due to these compositional and microstructural variations; fractures can easily occur while in the reactor along with grain size coarsening [1]. Volatile elements are likely to migrate to grain boundaries and fractures within the pellet, resulting in their immediate release upon contact with groundwater and resulting dissolution. These radionuclides and elements contribute to the instant release fraction (IRF), which also include fission gases. The long-term release of less volatile radionuclides from the fuel matrix is slower and occurs over a longer period. Studying this release process requires a technique which can accelerate dissolution while allowing solution monitoring for radionuclides released.

The Fuel Matrix Dissolution Model (FMDM) in Geologic Disposal Safety Assessment (GDSA) Framework (a repository simulation software tool used to assess geologic disposal of nuclear waste) provides calculations of radionuclide source terms for use in repository performance assessments based on fundamental chemical and physical principles [9]. The model is an electrochemical reaction/diffusion model for the dissolution of used UO_2 developed by Argonne National Laboratory (ANL) and Pacific Northwest National Laboratory (PNNL) that is coded in Matlab [10]. One goal of the GDSA Framework is to study realistic repository simulations to determine areas of needs and uncertainty to aid in research and development (R&D) direction. It calculates spent fuel dissolution rates as a function of radiolysis, alteration layer growth, reactant diffusion through the alteration layer, interfacial corrosion potential, and temperature [11]. Results based on laboratory studies on fuel chemistry in realistic repository environments are important to add to the FMD model to improve fidelity. The results collected in this effort will aid in the simulation of fuel dissolution, especially in the case of doped fuels.

The Single Pass Flowthrough (SPFT) system testing allows for the measurement of dissolution rates of fuels [3, 12]. Leachate solution is passed through a reactor at various rates to adjust the level of saturation in the reactor. By increasing the flow rate : material surface area ratio during the test, conditions within the reactor become more dilute. With increased dilution the solubility of the material being tested, in this case UO_2 in the SNF, will increase and prevent back reactions and secondary phase formation. In these conditions the forward dissolution rate of the material can be measured.

Current research often focuses on the effects of radiolysis under reducing conditions (simulating a deep geologic repository post-closure). While these tests are beneficial and relevant to many disposal programs, they often ignore the effect of the decaying radionuclides on the fuel chemistry and the effects of surface area and water volume. Radiolysis can alter the chemistry of water interacting with spent fuel, turning a reducing environment into a locally oxidizing environment [8, 12]. This test effort plans to use doped-UO_2 fuels to more realistically mimic the scenario that may occur in a geological repository when water is in contact with fuel in oxidizing conditions or when localized oxidizing conditions are generated due to radiolysis. The sample matrix will investigate the effect of grain size (which will vary depending on dopant), water chemistry, and dopant effects on fuel chemistry. Chromium and Al will be the primary dopants of interest included in the sample matrix. Ideally the results of this study can be added to the FMD model and aid in future simulation of spent fuel dissolution.

2.   EFFECTS OF ENVIRONMENT ON SPENT FUEL DISSOLUTION

The local environment that the failed spent fuel canister is exposed to affects the dissolution of the spent nuclear fuel. The solubility of UO_2 in an aqueous environment is highly dependent on the oxidation state of the uranium and near field chemistry (e.g. pH, redox potential (Eh), CO_3^- presence). As noted previously, U^{VI} has a higher solubility than U^{IV}; therefore when UO_2 is oxidized it increases solubility dramatically [13].

In the US, the presumed repository will place waste packages in open tunnels in unsaturated oxidizing conditions (e.g. Yucca Mountain), however other repository designs are possible [3, 14]. Thus, SNF dissolution would occur in a predominantly oxidizing environment. Under oxidizing conditions, the used fuel will dissolve through oxidative dissolution. Research has focused on using H_2O_2 and/or O_2 as oxidants and to measure the release of U^{VI} with increased time, or to use spent nuclear fuel and to monitor the production of oxidizing species and the dissolved U [5, 15-17].

Alternatively, deep geological repositories (DGRs) in other countries, such as Canada, Sweden, and the UK, reducing conditions will be predominant in the long term [6, 18-20]. Oxidizing conditions will initially prevail until the closure of the repository and subsequent consumption of the remaining O_2 present. The sedimentary materials, such as Callovo-Oxfordian clay, and granitic bedrock environments that are planned for use of DGRs in Europe provide low water permeability and reducing conditions, maintaining a low solubility of UO_2 if conditions remained static post-closure [21]. Figure 2.1 details the anticipated total U solubility depending on the pH conditions at 25°C.
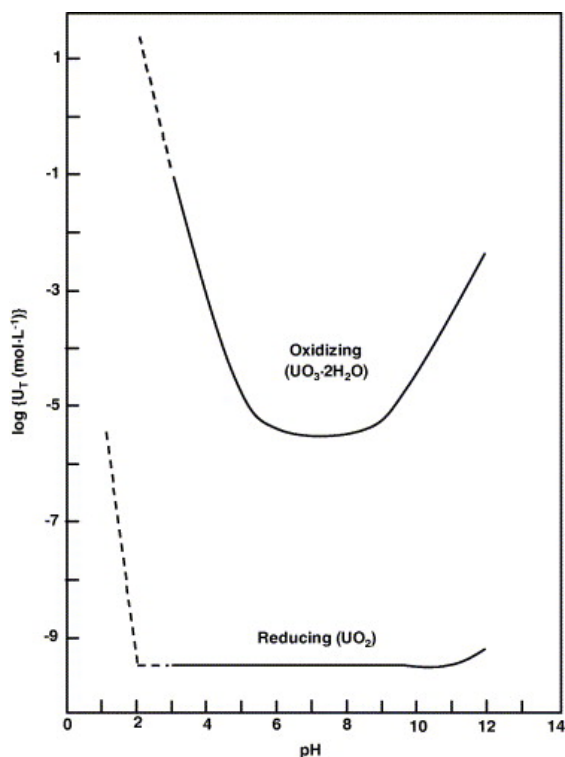
Figure 2.1 Solubility of UO_2 and $UO_3 \cdot 2H_2O$ at 25°C as a function of pH, where U_T is total U [5, 22].

In a DGR, the repository environment is often divided into two phases, first being the warm, oxidizing phase, followed by a cool, long-term, saturated phase [23]. In the event of H_2O infiltration, the resulting corrosion processes of the container and water radiolysis can generate localized oxidizing conditions before the transition to a long-term period, where corrosion processes are uniform and more predictable.

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3.   DisCo ANNUAL MEETING

3.1   PROGRAM OVERVIEW

The 3rd Annual Meeting of Modern Spent Fuel Dissolution and Chemistry in Failed Container Conditions (DisCo) was held in an online meeting format this year due to the outbreak of COVID-19. The meeting was initially paired with a training workshop, that PNNL was planning to attend, for professionals that was to focus on the experimental and modelling details for studying the corrosion of SNF under anoxic and reducing conditions in hot cells. Unfortunately, the workshop has been postponed indefinitely.

The aim of the DisCo project and its collaborators is to close the knowledge gaps in SNF matrix dissolution in relevant repository conditions, thus the project is directly relevant to the PNNL program. The project is subdivided into five work areas: management coordination, and dissemination (Work Package 1 [WP1]); preparation and characterization of samples and experimental systems (WP2); spent fuel dissolution experiments (WP3); model material dissolution experiments (WP4); and chemical modelling (WP5). Each WP has specific objectives to work to. Work package 1 focuses on management and coordination of the project; WP2 aims to prepare model materials through synthesis, prepare and analyze spent fuel samples, and to describe the aqueous phase and experimental set-up; WP3 aims to study and analyze the matrix dissolution and the IRF of different fuel types under different relevant disposal conditions; the goals of WP4 are to understand the matrix corrosion of modern Light Water Reactor (LWR) fuels under DGR relevant conditions (closely linked to WP2 and WP3) through the determination of element release and corrosion rates, characterizing the microstructural evolution upon corrosion by advanced micro-analytical tools, and linking matrix corrosion behavior of UO_2-based model systems and spent fuel; WP5 focuses on chemical modelling and the development and application of thermodynamic and kinetics models as well as reactive transport modelling to provide the basis for understanding the behavior of spent nuclear in the presence of component of the near field. Therefore WP3, WP4, and WP5 are of most relevance to our domestic program.

Much of the historical work on SNF dissolution studied the dissolution of standard UO_2 fuels. Studies have shifted to now focus on the testing of modern fuel types, mixed oxide (MOX) fuels and doped fuels, for comparison with conventional fuels. Novel fuel types of particular interest are those doped with Cr and/or Al (such as Westinghouse ADOPT [Advanced Doped Pellet Technology] UO_2 fuel pellets), and MOX fuels. Chromium, Al, and Gd additives affect the dissolution of spent nuclear fuels as the addition of dopants changes the fuel chemistry and may shift the oxygen potential of the fuel.

To understand the effect of these dopants and the behavior of the novel fuel types, real spent fuel dissolution experimentation has involved the testing of MOX, Cr-doped, Cr/Al-doped, and standard fuel. Model materials used are UO_2 with and without Cr, Al, Gd, and Th dopants, and with and without α emitters. Post experimental dissolution analysis compares the material pre- and post-leaching, and also includes the analysis of failed fuel from spent fuel pools/ponds. In conjunction with the sample analysis, chemical models examine thermodynamics, electrochemistry, chemical kinetics, and reactive transport, and results from models are compared with real analytical results. The project also aims to improve existing models by incorporating Fe corrosion, the effects of hydrogen, and metallic particles. These tasks are split among various European collaborators.

Of particular interest to the DisCo collaborative is the results of SNF dissolution in anoxic reducing conditions, which is relevant to the granitic and sedimentary repository conditions anticipated in Europe. While reducing, anoxic conditions are the main focus, some experimentation on UO_2 is performed in oxidizing conditions with the system equilibrated with air, which is the environment the system will see pre-closure.

Results from the meeting are summarized in the following sections. Many results are currently in progress, and not yet published.

3.2   WP3 PRESENTATION SUMMARY

While results have been delayed from many WP3 spent fuel dissolution experiments due to the pandemic, some results have been collected and analyzed. Preliminary results have been analyzed in some cases to give an idea of the corrosion occurring and release rates under predominantly anoxic conditions. To achieve the conditions relevant to a DGR in an anoxic environment, experiments are typically performed in autoclaves or other airtight vessels, and often in an environmental chamber or glove box. The sample matrix and experimentation performed for the spent fuel dissolution experiments is summarized in Table 3.1.

<div align="center">Table 3.1 Sample Matrix and Conditions for Experiments Under WP3</div>

Leachant	Conditions	Fuel	Burn-Up (GWd/t$_{HM}$)
Bicarbonate water (pH ≈ 8.3)	Anoxic	MOX	40-60
	Reducing with the presence of dithionite as a reductant agent in anoxic atmosphere	UO$_2$	60
	Reducing with the presence of H$_2$ atmosphere	MOX	38
		UO$_2$	57.1
		UO$_2$-Cr&Al doped	59.1
		UO$_2$-Cr doped	60
Young Cement Water with Calcium (pH ≈ 13.5)	Oxidizing, equilibrated with air	UO$_2$	60
	Reducing with the presence of dithionite as reductant agent in anoxic atmosphere	UO$_2$	60

Results from the Joint Research Center (JRC) in Karlsruhe showed the initial release of U, Pu, Cs, Tc, and Mo was high followed by a significantly lower release of elements. The quick release of U and Pu was attributed to the pre-oxidized phases, and in the case of the IRF elements (those elements that dissolve faster than the matrix, which govern the initial radiation dose during the dissolution of SNF), moving to segregated phases in open fuel voids. However, further analysis and sampling is required to fully understand the behavior of some elements, such as Pu and Cs.

The leaching of irradiated MOX fuel is being studied at the Karlsruhe Institute of Technology (KIT), and includes the study of samples with and without cladding. The release of some elements, such as ^{90}Sr and ^{137}Cs, were similar in the clad and de-clad samples, and were both exhibiting slight increases as experimentation continued. Compared to other fission products, ^{137}Cs and [129]I exhibited a relatively fast release. A main difference was observed in the clad and de-clad samples in the fission gas release, with the MOX fragments without cladding exhibiting much higher release.

At Studsvik, the aqueous leaching of an ADOPT fuel pellet and a standard UO$_2$ SNF pellet are being studied under an H$_2$ atmosphere. The ADOPT fuel pellet is an Al/Cr doped-UO$_2$ pellet to compare to the standard UO$_2$. Thus far, both autoclave experiments were displaying similar behavior, with the exception of [129]I release. The standard UO$_2$ spent fuel had released higher amounts of [129]I in comparison to the ADOPT fuel. However, since experiments are ongoing, more data is needed to understand the behavior observed and long-term trends.

3.3   WP4 PRESENTATION SUMMARY

The study of model material dissolution experiments was the focus of WP4. These studies typically prepared two separate samples (manufactured normally from WP2 studies): a doped UO$_2$ pellet, and a

reference pellet that was pure UO_2. Repository relevant conditions were used experimentally and compared different conditions, such as high pH cementitious water, typically Young Cement Water with Calcium (YCWCa, pH = 13.5), or pH-neutral bicarbonate water (pH = 8.5). These studies create the additional challenge of mimicking radiolysis since samples have not been previously irradiated in a reactor. To mimic radiolysis, experiments typically added H_2O_2 which is normally generated with increased radiolysis of samples; this addition is challenging due to the instability of H_2O_2.

Results from Forschungzentrum Julich compared pure UO_2 reference pellets to Cr-doped and Nd-doped UO_2 pellets using a bicarbonate water chemistry with H_2O_2 added to simulate radiolytic oxidative dissolution. Initially, dissolution results from the Cr samples were on the same order of magnitude as the pure UO_2 reference pellets. As the experiment progressed the pure UO_2 generated higher dissolved U in comparison to their Cr-doped counterparts. This difference was attributed to the lower density of the UO_2 pellets. The Nd-doped pellets had much lower dissolution rates in comparison to the pure and Cr-doped UO_2 pellets.

Experimental work at Studiecentrum voor Kernenergie (SCK•CEN) is comparing Cr-doped UO_2 pellets and pure UO_2 pellets in YCWCa and bicarbonate water. In agreement with what was observed at Julich, Cr-doping of UO_2 pellets resulted in lower concentrations of U dissolution. However, when comparing results from YCWCa and bicarbonate water, the Cr had a constant effect on the dissolution of U in the cementitious environment, but only a temporary effect in the bicarbonate medium. Possible mechanisms require surface analysis and modelling calculations to fully understand and determine the cause. To simulate radiolytic oxidation under long periods of time, future experiments will contain ^{238}Pu/Cr-doped UO_2, but experiments have been currently halted.

Long term leaching on MOX fuel pellets at Atomic Energy and Alternatives Energies Commission (CEA) was performed for almost 500 days with an added Fe pre-corrosion step. Experimental work was completed immediately prior to shut down, thus analysis has yet to be performed.

The dissolution of alpha doped-UO_2 with and without Cr is under study at VTT Technical Research Centre of Finland. Using metallic Fe, redox conditions are simulated in natural groundwater and under anaerobic conditions. Alpha doped samples are able to simulate 3000 year old and 10000 year old pellets. Thus far samplings have not presented a high rate of scatter between samples of ^{238}U concentration, but processing on the release rate is still ongoing.

Samples of Cr-doped UO_2, Al/Cr-doped UO_2, and Gd-doped UO_2 pellets were prepared and subjected to dissolution experiments to determine element release and corrosion rates under neutral-alkaline conditions at Centro de Investigaciones Energeticas, Medioambientales y Tecnologicas (Ciemat). Dissolution was performed in autoclaves with bicarbonate water (pH = 8.9), YCW (pH = 13.2) and a blank (pH = 7.2). Solid characterization was performed post leaching, and aliquots were removed from solution for analysis throughout the leaching experiment. Results indicated that U is highly sensitive to the pH/carbonate system as the lowest release was detected at the high pH of YCW, while the highest dissolution was determined in the blank water. The dopants had no significant effect on the release of UO_2, though Gd-doped samples consistently showed the lowest release. While solid characterization is ongoing, samples thus far in bicarbonate water have shown no differences between pre- and post-leached samples by x-ray diffraction (XRD), Raman spectroscopy, or Scanning Electrochemical Microscopy (SEM). Overall, the U concentration release was higher for the high bicarbonate water in comparison to YCWCa, with no significant differences observed between dopants.

Results for Cr-doped UO_2 at the University of Sheffield indicate that the normalized mass loss of U decreased with increased Cr content within the pellet. While trends have been observed in the preliminary data, more information is needed to be collected to understand the results.

Ultimately, results from WP4 are strongly indicating the Cr-doped UO_2 pellets decrease the loss of U from the sample. However, mechanisms explaining why this is occurring are still ongoing.

3.4   WP5 PRESENTATION SUMMARY

Results from WP5, chemical modelling, most commonly illustrated the difficulties presented when modeling spent fuel dissolution with many competing factors. Computational models were compared to experimental results to determine the validity of model results. Model inputs range depending on the theory and software used, but typically aim to integrate some combination of water radiolysis effects, spent fuel chemistry, spent fuel porosity, solute transport, and H_2 effects. Overall, trends were accurately depicted in the modelling of the dissolution, such as increase of fuel corrosion with increased burn up, and the decreased rate of corrosion as the rate of Fe release increased, as shown by modelling results at National Nuclear Laboratory (NNL) in the UK. However, in the same studies by NNL, the comparison of modelling data to the results showed that the model was slightly over predicting the corrosion behavior of samples that experienced a transition from an oxic to an anoxic environment. Results from Amphos 21 showed good agreement between the model presented and experimental data from Studsvik at shorter time periods without the addition of H_2. However, results from longer time periods incorrectly predicted the U concentration released by an order of magnitude. Work by the Paul Scherrer Institut (PSI) indicated that the Cr-doping would not affect the redox state of the fuel and the oxygen potential of UO_2 fuels, and that adverse effects under repository conditions were not to be expected [24]. While the results are promising, they do show the gap between models and laboratory results, and still require work to give reliable data.

4. SINGLE PASS FLOWTHROUGH TESTING

4.1 TEST PLAN FOR OXIDIZING SPFT TESTING

4.1.1 Equipment and Procedure

Work at PNNL in the SPFT system will test the oxidative dissolution of doped-UO2 pellets. The fuel samples will be acquired and contain known compositions and dopants. Samples will be ground by an in-house fabricated sample crusher to reduce the size of the fuel pellets to fragments and powders; testing will include fuel fragments as well as fuel powder. Nominally 1 g of sample fragments (typically 2-3 fragment pieces) will be removed from the sample following grinding in the sample crusher for analysis in the SPFT system (Figure 4.1, Figure 4.2, Figure 4.3). The remainder of the ground pellet will be sieved using a vibratory shaker/tapper sieve system consisting of a 25 µm sieve, a 10 µm sieve, and a catch pan. Powder between the two sieves will be collected and 200 mg samples will be used in the flow cells for powder SPFT analysis.
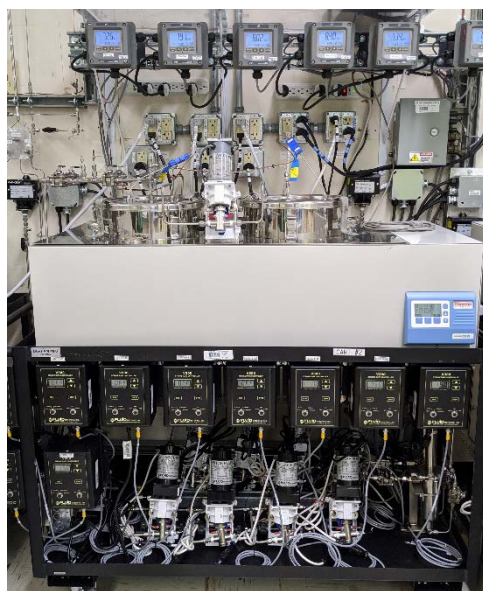

Figure 4.1 The mobile cart containing the recirculation pumps, pre-equilibrated leachate transfer pumps, temperature-controlled water bath, and pre-equilibration and feedstock leachate vessels. Pictured above the cart is the pH sensor read-out and controller.

Figure 4.2 The ventilated canopy housing the oven, effluent taps, and funnels directing leachate to ion exchange columns before proceeding to waste.

Figure 4.3 Flow cells within the oven in a ventilated canopy.

Prior to flow testing, SEM will be performed on the powder samples to aid in the determination of grain size and remaining fines. Energy dispersive X-ray Spectroscopy (EDX) may be utilized on some samples to determine the fuel surface composition. Determination of the surface area will be obtained using the Brunauer-Emmett-Teller (BET) method using a Tristar II Plus BET analyzer (Micromeritics), Figure 4.4.

Some samples may be analyzed by thermogravimetric analysis (TGA) to better understand physical changes in the sample with temperature over time.

Figure 4.4 Micromeritics Tristar II Plus analyzer for Brunauer-Emmett-Teller (BET) measurements.

The effluent from the SPFT reactors will be collected periodically during testing and analyzed using a Kinetic Phosphorescence Analyzer (KPA, Chemchek Instruments, Inc.), Figure 4.5, to determine U concentrations. Results and data analysis will allow for testing of the cumulative fraction (CF) release rate of U as well as the normalized dissolution rate (NDR) from the leachate samples.
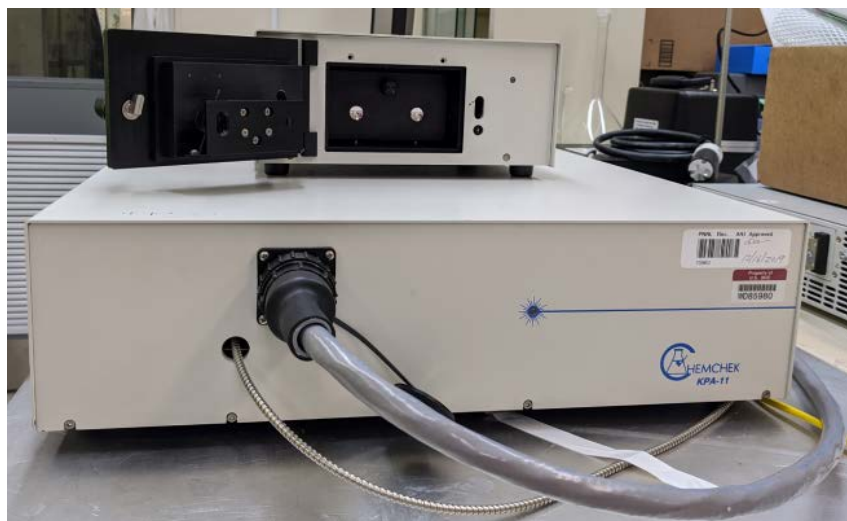

Figure 4.5 Chemchek Kinetic Phosphorescence Analyzer (KPA) instrument with remote attachment.

Post SPFT testing, XRD will be used to determine if any crystalline phases other than UO_2 are present. Using SEM and EDX post-flow testing, altered surface composition will be analyzed on powder samples, fragments will be analyzed for grain boundary attack and cracking, and sample surfaces will be studied for alteration phases that may have formed during the testing.

4.1.2   Testing Matrix

Initial tests solutions will use $2\times10^{-3} \pm 2\times10^{-4}$ M sodium bicarbonate in deionized water with a pH maintained between 7 and 8.5. Sparge gas used will be 20.9% O_2, 2000 ppm CO_2 with a balance of N_2, and 10.3% O_2, 2000 ppm CO_2 with a balance of N_2. Three temperature set points will be analyzed: 25°C,

50°C, and 75°C. The proposed testing matrix is shown in Table 4.1. The organizers of DisCo have asked that we perform testing under oxidizing conditions using our proven SPFT system with the Cr- and Al-doped fuels for direct comparison with previous results on pure UO_2 and Gd-doped UO_2.

Table 4.1 Proposed Testing Matrix

Test #	Powder Mass (g)	Fragment Mass (g)	Water Chemistry (Solution / Concentration)	Temperature (°C)	Dissolved O_2 (ppm)
Cr – doped sample 1					
Cr – doped sample 2					
Cr – doped sample 3					
Cr – doped sample 4					
Al – doped sample 1					
Al – doped sample 2					
Al – doped sample 3					
Al – doped sample 4					

Test fuels with appropriate dopants will be produced by commercial fuel vendors and procured by PNNL.

4.2   REDUCING AND ANOXIC CONDITIONS

4.2.1   Adapting PNNL to Reducing and Anoxic Conditions

The work performed at PNNL is focusing on an oxidizing environment for repository relevant conditions. However, it is of interest to alter and set up a system that would also allow for the study of reducing conditions using the fuels available to study.

Moving to anoxic conditions to achieve a reducing environment creates a challenge. The current SPFT set up is not suitable for such studies because there is no option to seal the system to ensure an anoxic environment – the leachate feedstock drums alone are open to the environment with no option to seal shut. Thus, moving to anoxic environments would require a new system.

Anoxic environments are best controlled within environmental chambers or glove boxes with O_2 free environments. This ensures that the system sees minimal O_2 from the environment, and would only be exposed to oxidants and reductants produced through the corrosion of the container and radiolysis of the groundwater [25]. Initially it is anticipated that the radiolytic oxidants present play a larger role on the redox conditions for the dissolution than the reducing species. Water radiolysis produces hydrogen in a stoichiometric amount equal to oxidizing species, though the main hydrogen source will be produced from anaerobic corrosion of the steel liner of the cannister [26]. Of the species produced, H_2O_2 is the oxidant that is primarily driving the corrosion of the fuel [25].

To adapt to reducing anoxic conditions, experimentation would be moved to an environmental chamber or glove box to control the atmosphere and environment. Two scenarios are available for set up: a miniature SPFT set up could be performed with a pulsed pump to simulate the movement of groundwater

through the samples, or samples could be submerged in a sealed electrochemical cell or autoclave, allowing for electrochemical measurements, chemical measurements, and a final chemical analysis. In the case of the autoclave experiments, samples removed from solution could be replaced with fresh leachate to simulate the flow of leachate through the system. Research to adapt and determine which system fits best is ongoing.

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5.   SUMMARY

Preliminary set up and laboratory preparation for sample analysis has been completed at PNNL. Unfortunately, the outbreak of the COVID-19 pandemic has delayed the start of the system and the resulting dissolution analysis. Under current operating conditions, startup is not anticipated until mid-summer 2020.

The 3rd Annual Meeting of DisCo was moved to an online platform due to the current global circumstance. The meeting was an informative gathering with approximately 60 participants and online presentations regarding different facets of work. The work most relevant to this project was that of spent fuel dissolution and model systems dissolution using doped UO_2 pellets generated in the lab space. Results largely indicated that Cr-doped UO_2 pellets reduce the U loss from the matrix, though mechanisms to explain this result are still under investigation.

The test plan for this work is currently focused on the oxidative dissolution of doped UO_2 using Cr and Al as dopants. To study the system in an anoxic reducing environment, the system would be modified to a smaller set up, or an autoclave. To facilitate SPFT experiments, a small pump apparatus could be adapted to an environmental chamber or glove box. These conditions would severely limit the size of system that could be used, and as such, the testing capacity would be dramatically reduced from the current set up. For this reason, the alternative to move to static testing within an autoclave with solution replenishment may be a more practical option. Results from such a set up would produce results that should, in theory, be comparative to those presented at the DisCo 2020 meeting.

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