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Evaluation of the Potential for Precipitation of Solids during Storage of Non-Aluminum SNF Solutions

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EXECUTIVE SUMMARY

Non-aluminum clad spent nuclear fuels (NASNF) stored in the L-Area basin will be dissolved in H-Canyon using the 6.3D electrolytic dissolver. The solutions will be stored in either the hot or warm canyon until the preparation of a sludge batch for the Defense Waste Processing Facility. Spent nuclear fuel solutions could be stored for 1-2 years before transfer to the H-Area Tank Farm depending on the interval between sludge batches. The solution level in the storage tanks will be maintained; therefore, precipitation of solids due to evaporation is not an issue. However, the precipitation of solids from completely dissolved SNF due to solution instabilities has been observed during intermediate storage of solutions generating hydrated oxides. The presence of fissile material in these solids is generally associated with zirconium molybdate, which is known to act as a host lattice for Pu and can carry the actinides upon precipitation.

The formation of zirconium molybdate solids which carry fissile material is a potential concern for the storage of NASNF solutions. To address this concern, the Savannah River National Laboratory performed a literature review to identify knowledge gaps which may require experimental work to determine if the formation of solids is a concern during storage of these solutions. Based on the literature review, the precipitation of zirconium molybdate solids from the Campaign 1 NASNF solutions during intermediate storage is expected. This conclusion is supported by the identification of zirconium molybdate solids found on the H-Canyon 6.1D Dissolver MK-12 insert spacer. The formation of the zirconium molybdate solids is attributed to hydrolysis and radiolytic processes in the nitric acid solution. As the molybdate solids form, U and Pu can substitute for Zr in the crystal lattice resulting in co-precipitation. Generally, the Pu substitutes directly into the crystal lattice during precipitation while the U associated with the molybdate solids more likely absorbs from the solution. The U in the NASNF solutions is present as uranyl nitrate, a 2+ cation which will not substitute as easily into the molybdate crystal lattice for the Zr^{4+} ion.

Assuming that zirconium molybdate solids will precipitate during the interim storage of NASNF solutions, a bounding analysis was performed to estimate the amount of Pu which could co-precipitate with zirconium molybdate solids from the Campaign 1 NASNF solutions. The assessment was prepared using calculations performed to estimate the fission and activation product inventory of the Campaign 1 fuels, the maximum extent of precipitation of the zirconium molybdate from the NASNF solutions, and the bounding concentrations of fissile material in the precipitated solids based on the literature review. The estimated masses of Zr and Mo in the Campaign 1 assemblies indicated that Mo is the limiting reagent for the formation of zirconium molybdate. The maximum amount of zirconium molybdate solids which can be produced from the fuels is only 2193 g which would contain 430 g of Zr. Even if the Pu replaces 10 wt % Zr in the solids, an amount which is greater than the values reported for irradiated light water reactor fuels in the literature, the total mass of Pu precipitated from all the Campaign 1 solution will be less than 50 g.

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LIST OF ABBREVIATIONS

ABD	Accelerated Basin De-inventory
BOL	beginning of life
CPM	cesium phosphomolybdate
FBR	fast breeder reactor
HAL	high active liquor
HLLW	high level liquid waste
ID	identification
LWR	light water reactor
NASNF	non-aluminum spent nuclear fuel
MOX	mixed oxide
NNL	National Nuclear Laboratory
PWR	pressurized water reactor
SNF	spent nuclear fuel
SRNL	Savannah River National Laboratory
SRP	Savannah River Plant
XRD	X-ray diffraction
ZM	zirconium molybdate
ZMH	zirconium molybdate hydrate

1.0 Introduction

The Accelerated Basin De-inventory (ABD) Program is designed to expedite the removal of spent nuclear fuel (SNF) from L-Basin and accelerate its disposition leading to the eventual closure of H-Canyon. As part of the program, H-Canyon will disposition non-aluminum spent nuclear fuels (NASNF) using the 6.3D electrolytic dissolver. These fuels have stainless steel, Zircaloy, or Hastelloy cladding which will be dissolved using the electrolytic dissolver prior to either chemical or electrolytic dissolution of the fissionable components of the fuel. Once the fuels are dissolved, the solutions will be transferred to tanks in either the hot or warm canyon for storage. Spent nuclear fuel solutions could be stored for 1-2 years before transfer to the H-Area Tank Farm depending on the interval between the preparation of sludge batches for the Defense Waste Processing Facility. The level of the storage tanks will be maintained in compliance with the Interim Storage Program;[1] therefore, precipitation, due to exceeding the solubility limit of a solution component due to evaporation is addressed. However, the precipitation of solids from dissolved SNF due to solution instabilities has been observed during the intermediate storage of solutions and several hydrated oxides have been identified.[2,3] The presence of fissile material in the solids was generally associated with zirconium molybdate, which is known to act as a host lattice for Pu and can carry the actinides upon precipitation.[4,5,6] The generation of solids characterized as a zirconium molybdate hydroxide hydrate ($Zr[Mo_2O_7(OH)_2(H_2O)_2]$) has also been observed in the support structure of the physical spacers of the H-Canyon 6.1D dissolver MK-12 insert. Small amounts of U (0.1 wt %) and Pu (0.05 wt %) were associated with the solids.[7]

The Savannah River National Laboratory (SRNL) was requested to perform a literature review and identify knowledge gaps which may require subsequent experimental work to determine if the formation of zirconium molybdates and other solids which carry fissile materials are a concern during the storage of dissolved NASNF.[8] In addition to the literature review, SRNL was requested to perform a bounding assessment of the mass of fissile material which could potentially precipitate with zirconium molybdates during the storage of NASNF solution. The assessment was applied to the NASNF designated for dissolution during Campaign 1; although, the methodology used for these fuels could also be used to assess the fuels dissolved in subsequent campaigns once the SNF bundles are identified.

The bounding assessment of the mass of fissile material which could potentially precipitate with zirconium molybdate solids during the storage of the Campaign 1 NASNF was based on conservative estimates of the fission product inventory of the fuels, extent of precipitation of Zr and Mo from solution, and the concentration of fissile material in the solids. The SRNL was also requested to evaluate whether the addition of a material (e.g., Fe) can be used to complex molybdate and prevent its precipitation if the bounding analysis indicates the precipitation of fissile bearing solids is a concern during storage of NASNF. If the complexation of molybdate to prevent precipitation is needed, the amount of complexant required in the dissolver should be identified which would likely require experimental work.

1.1 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

2.0 Literature Review

2.1 Characterization of Precipitates/Residue from Solutions of Dissolved Fuel and Waste

A large amount of research has been performed on characterizing the solid residues from spent fuel dissolution, using both actual fuel material and simulated fuel. The amount and types of residue are very dependent on the type of fuel dissolved, burnup level, dissolution conditions, etc. Research has also focused

on precipitation of solids in high-level liquid waste (HLLW) solutions, which can be similar to the conditions in fuel dissolution. The first type of study discussed looks at the fragments of fuel casings that are left over in the type of reprocessing where fuel is chopped into segments and the fuel meat dissolved. Then, studies of undissolved solids from reprocessing of irradiated fuel are summarized.

2.2 Characterization and Processing of Fuel Hulls

Considerable effort has gone into the characterization and disposal of the leftover casing fragments, or hulls, from dissolution of the fuel inside the casings.[9,10,11,12,13,14,15] Chips and fines of Zircaloy in the dissolver and headend process at the Tokai plant were characterized by Gonda et al.[11] They found residual solids of 5.3 kg Zircaloy fines, 1.8 kg crud and 1.0 kg fission product residues for each ton of spent fuel reprocessed. The U and Pu contents of the undissolved solids were low, with 0.0075 wt % U and up to 0.000375 wt % Pu. Restani et al.[14] performed an analysis of the isotopic composition of spent fuel hulls and structural component residue from dissolution of Obrigheim pressurized water reactor (PWR) Zircaloy-clad fuel. They found an average of 1130 ppm of U in the Zircaloy, and a 1:85 Pu:U ratio. Gue et al.[10] reported the results of characterization of hulls leftover from dissolution of Obrigheim PWR fuel. They noted that the hulls and fines of Zircaloy have a high surface area and potentially explosive reactivity with oxygen. The hulls contained up to 0.147 wt % U and up to 0.00262 wt % Pu. Complete dissolution of Zircaloy fuel casing leads to formation of a large amount of ZrO_2 sludge, as reported by Hyder et al.[15]

Since the empty fuel casing fragments take up a lot of storage space with large amounts of void volume, several methods have been tested for volume reduction of the hulls. Campbell[12] reported on the results of melting processes for cladding and other parts left over from acid leaching of chopped fuel bundles. The melting of cladding and hull residues from fuel dissolution to reduce waste volume was reported by Nelson and Griggs.[13] Taylor[9] reviewed a variety of reported characterization results from and methods for dealing with Zircaloy fuel hulls.

2.3 Irradiated Fuel Dissolution Studies

In dissolution of U-Mo (3% Mo) alloy fuels in 12-14 M nitric acid, Schulz[16] found that 80-95% of the Mo precipitated as molybdic oxide. In 11 M nitric acid, in addition to molybdic oxide, uranyl molybdate precipitate also formed. About 0.05% of the U and 2.3% of the Pu stayed with the precipitate. In another dissolution study of U-Mo fuels, Amos[17] observed that uranium molybdate precipitate can be formed by incorrect dissolver conditions.

Plodinec[18] found that dissolution of irradiated UO_2 gave a solution with fine residue particles of fission products. Organic flocculants were used to clarify solution for the solvent extraction step, which was determined to be a better treatment than a MnO_2 precipitation step due to lower waste amounts.

Three different phases were observed by Kleykamp[19] in residues from the dissolution of irradiated fast breeder reactor (FBR) mixed oxide (MOX) fuel: (1) incompletely dissolved Pu-rich $(U,Pu)O_2$, with CaF_2-type structure; (2) incompletely dissolved metallic fission products with a hexagonal structure and containing Mo, Tc, Ru, Rh, and Pd; and (3) oxide phases consisting mainly of Mo and Ru, which had been reprecipitated out from the nitric acid solution. The Pu content of the residues was approximately 40%, which amounts to between 1.9% and 4.55% of the total Pu in the fuel.

Gonda et al.[11] characterized the amount of undissolved solids from the reprocessing of Zircaloy-clad fuel at the Tokai reprocessing facility in Japan using the chop and leach dissolution method. They found 5.3, 1.8, and 1.0 kg/t U of zircaloy chips, crud and undissolved fission products, respectively. About 75 g/t U was in the residues, with up to 0.05 weight ratio of Pu to U, giving up to 4 g Pu in the residue per ton U. The overall percentage of Pu in the fuel was up to 1%, giving 0.04% of the Pu and 0.0075% of the U in fuel carried in the undissolved solids.

De Regge et al.[20] studied the dissolution of MOX fuels and further dissolution of the residues. They found 6.1% of the initial fuel weight was left undissolved after boiling for 12 hours in 10 M nitric acid to a final metal concentration of 0.2 M. For these conditions, 3.4% of the U and 6.2% of the Pu remained undissolved. They also found 6.8% of the initial fuel weight was left undissolved after boiling for 15 hours in 10 M nitric acid to a final metal concentration of 1 M. For these conditions, 5.7% of the U and 10.3% of the Pu remained undissolved. The remaining residues were treated with 10 M nitric acid containing 0.1 M HF but did not completely dissolve.

Residues from dissolution of irradiated MOX FBR fuel were analyzed by Kleykamp[19] using X-ray diffraction (XRD). Oxide fuel particles, Mo-Tc-Ru-Rh-Pd alloys, and reprecipitated fission product oxide hydrates were observed. X-ray microanalysis of the reprecipitated solids showed the composition $(Ba_{1-x-y}Sr_xCs_y)(U,Pu,RE,Zr,Mo)O_3$. The rare earths only appeared in significant concentration at high burnup levels.

Kleykamp[2] reviewed the results of work performed at the Karlsruhe Plant to study fission products in LWR and FBR fuels. Solids residues were observed after the dissolution process in nitric acid within the headend of reprocessing of irradiated nuclear fuels. This material was predominantly composed of fuel particles and a metallic fission product phase. The metallic phases contained fission product Mo, Tc, Ru, Rh, and Pd and were identical with those that were generated in the fuel during reactor operations. Reprecipitation phenomena have been observed on completely dissolved fuels during the intermediate storage of the solutions of both LWR and FBR fuels. The reprecipitation phenomena may be explained by hydrolysis and radiolytic processes in the nitric acid solutions during intermediate storage.

Kleykamp[3] examined the residues from dissolution of Zircaloy-clad UO_2 LWR fuel in nitric acid at Karlsruhe. The mass of the residues from dissolution averaged 0.6% of the total fuel. About 13% of the total residues were composed of the incompletely dissolved metallic Mo-Tc-Ru-Rh-Pd inclusions. The remaining 87% of the residues were reprecipitated oxides or oxide hydrates. Reprecipitation of U and Pu was confirmed by the analyzed 7:1 ratio of U:Pu in the solids compared to the expected ratio of 70:1 in undissolved fuel.

Residues from the dissolution of irradiated UO_2 fuel pellets with Zircaloy cladding were examined by Adachi et al.[21] Fuel burnup was from 7,000 to 39,000 MWd/t U. The amount of insoluble residue increased with increasing burnup, up to 0.4 wt % at 39,000 MWd/t U. X-ray diffraction analysis showed that oxide hydrates such as zirconium molybdate hydrate (ZMH) were not produced in significant quantities due to the short dissolution time (2 h) of cut up pieces of fuel and a relatively low nitric acid concentration of 4 M. The residue was mainly metallic ruthenium alloy. Plutonium content in the residue was 0.03% to 0.08%, attributed to a lack of washing.

Magnaldo et al.[22] examined the precipitates in the spent fuel dissolvers at the La Hague reprocessing plant in France. Most of the solids found remaining in the fuel dissolvers at La Hague were Zr cladding, from 30% to 70% of the total mass. The rest of the solids were mainly ZMH. The solids contained from 0.3% to 1.2% Pu, mostly in the ZMH. Analysis found that Pu probably integrated into ZMH as a solid solution. Uranium content of the solids was 0.2% to 1.7%, likely from solution absorbing into the solids. Studies found that the solubility of ZMH increased as nitric acid concentration increased from 1 M to 3 M, and solubility of ZMH remained about the same at temperatures from 60 ˚C to 90 ˚C.

Dissolution experiments were conducted by Liu et al.[23] on Zircaloy-clad LEU fuel with a burnup of 40,433 MWd/t U. Dissolution of UO_2 pellets was carried out in 6.5 M nitric acid at 95 ˚C for 5 h. Residue was filtered using a 3-µm pore filter. Solid residue from dissolution was 0.2185 wt % of the original fuel. The residue contained 2.4% U and 0.24% Pu, with the bulk composed of O, N, Ru, Mo, Tc and Rh.

McNamara et al.[24] characterized residues from the dissolution of high-burnup LWR fuel as mainly noble group metals, with minor quantities of Se, Te, Zr, Ag, I, U, Pu. Fluorination treatment of the residues extracted all of the Mo, Tc and Ru.

Buravand and Reynier-Tronche[25] reported the composition of solid residues left over from nitric acid dissolution of irradiated Sodium Fast Reactor MOX fuel. Residues from dissolution were from 1.5% to 2.5% of the original fuel mass. The residues contained 0.7% to 2.5% Pu and 2.4% to 5.3% U, with the bulk of the residue being platinum group metals. Residues from the most irradiated portions of the fuel had the lowest U and Pu content. Pu was found to combine with insoluble intermetallic phases of platinum group metals. Oxidizing Ag(II) digestion was used to further dissolve the residues left over from nitric acid dissolution.

Aihara et al.[26] performed analysis of residual solid sludge from dissolution of FBR MOX fuel. Only 0.04% or less of the total U remained in the undissolved solids, and 0.05% to 0.25% of the Pu. The sludge was mainly $Mo_4Ru_4RhPdTc$ alloy with some other unidentified component, but no ZMH was present in the sludge, possibly due to low Zr and Mo concentrations. Molybdenum is known to evaporate in high burnup fuel. Goode and Stacy[27] found that in the dissolution of irradiated Zircaloy-clad UO_2 fuel at ORNL, about 0.2% of the material remained as undissolved residue. This residue contained about 0.001% of the total U and 0.004% of the total Pu.

In dissolution studies of high-burnup UO_2 LWR fuel in nitric acid, Campbell and Buxton[28] found a fine black powder residue. The powder was composed of Ru and Mo mainly, with smaller amounts of Tc, Pd, Rh, Fe and Si. Very little Zr was in the residue. A total of 0.2% to 0.3% of the UO_2 was undissolved, along with about 0.01% of the Pu. Nitric acid dissolved the residue very slowly, while hydrochloric acid easily dissolved the residue. They observed ZMH formation when the dissolver solution was allowed to sit. Keeping the temperature below 60 ˚C reduced precipitation as the solution aged. In a study of the dissolution of irradiated MOX fuels, Gue et al.[29] observed that the residual solids were 4 to 4.5 kg per ton of fuel. The maximum Pu content of the residual solids was 0.3%.

Jenkins and Brown[30] studied the irradiated fuel cladding and insoluble residues arising from the dissolution of stainless steel-clad fast reactor fuel. The insoluble residues, 0.3% to 0.6% of the initial fuel weight, were mostly small spherical particles (or conglomerates) which were mainly composed of alloys of the noble metal fission products – Mo, Tc, Ru, Rh and Pd. All of the U and Pu associated with the undissolved solids was present as undissolved fuel and was not a constituent phase of the fission product alloys. The amount of undissolved fuel increased with Pu content of the fuel, with very little undissolved fuel for 15% Pu fuel, and up to 25% undissolved fuel content in the residue for 25% Pu fuel.

Lausch et al.[31] reported on the solids remaining in the dissolver solution for spent LWR fuel at Karlsruhe. The solids consisted of a metal fraction (Mo, Tc, Pd, Ru, and Rh) and an oxide phase (Zr, Mo, and Pu). Total solids were about 8 kg/t U, containing 6-33% feed clarification sludge, 60-84% fine solids and 7-10% post-precipitates. Experimental results suggested the presence of ZMH, given the Zr:Mo ratio in the oxide phase and that ZMH is known to act as a host lattice for Pu. From 0.01% to 0.02% of the total U in the fuel element was carried in the solids, and from 1.42% to 3.54% of the total Pu. Less residue was generated in solutions which had been centrifuged compared to solutions which had been filtered. The amount of metal solids increased with fuel burnup.

Glatz et al.[32] analyzed the residue from dissolution of very high burnup fuel (70 GWd/t U) in 3-7 M nitric acid. Residues were from 1.67% to 2.25% of the fuel mass. From 1.1% to 8.2% of the total U in the fuel remained in the residue, and from 0.3% to 6.5% of the total Pu. Two residue morphologies were observed: (1) oxide phase – Mo, Ru, Zr, Tc, Rh and U, Pu, Pd as traces, and (2) metallic phase – Mo, Ru, Zr, Tc, Pd,

Rh and U, Pu as traces. The higher Pu content was found in dissolution at 4 and 5 M nitric acid, likely due to reprecipitation of ZMH containing Pu at lower acidity.

Penneman et al.[33] conducted experiments on solutions containing U, Pu, Zr, Mo and other fission products in nitric acid solutions from 1 M to 4 M. ZMH was formed preferentially over Pu molybdate. Pu substitution for Zr in the precipitate ranged from 0.9% in 4 M nitric acid with 1 g/L Mo, 1.5 g/L Zr and 1.5 g/L Pu, up to 12.2% in 1 M nitric acid with 1.5 g/L Mo, 1 g/L Zr and 1.47 g/L Pu. The Pu cannot be leached out without dissolving the precipitate, so the Pu is incorporated into the chemical structure.

A study by Fang et al.[34] found that secondary precipitates from dissolution of high-burnup fuel were about 0.01% to 0.3% of original fuel mass. No Pu or U was detected in the secondary precipitate. Work was performed at Harwell Laboratories by Gue et al.[10] to characterize the insoluble residues remaining after the dissolution of FBR fuel in nitric acid. Irradiation ranged between 2.7% and 7.8% burnup of heavy metal atoms in the fuel sectioned from the pin. The principal constituents of the residues were the alloys of noble metal fission products, which were formed as particles or inclusions in the fuel during irradiation and which resisted dissolution in nitric acid. The main components were Ru, Rh, Pd, Mo, and Tc.

Usami et al.[35] observed the precipitation in dissolution of irradiated PWR fuel solutions. They found Pu incorporated into ZMH, with 3.6 mol % substitution of Pu in place of Zr. Washing did not remove the Pu, so it was incorporated into the chemical structure. The precipitate was dissolved with HNO_3-H_2O_2 solution at 80 ˚C.

Residues from dissolution of spent fuel in nitric acid were examined by Pokhitonov et al.[36] Fuel burnup ranged from 15 to 54 MWd/kg U. Total residual solids were from 0.03% to 0.5% of total fuel mass. Reprecipitated solids were from 0.01% to 0.3% of total fuel mass. The residues contained 0.2% to 4% U and 0.1% to 3% Pu. The most residue was obtained from the higher burnup fuel. More residue remained at lower concentration of nitric acid and lower dissolution temperature. Lower dissolution temperature also led to more U and Pu in the residues. The ZMH did not precipitate at ambient temperature, only when the dissolved fuel solution was heated.

Restani et al.[14] performed analysis of the isotopic composition of spent fuel hulls and structural component residue from the dissolution of PWR Zircaloy-clad fuel. They found an average of 1130 ppm of U in the Zircaloy, and a 1:85 Pu:U ratio. Hyder et al.[15] reported that for the electrolytic dissolution of fuel at SRP with Zircaloy cladding, 85 wt % of the Zr forms ZrO_2 sludge, which carries up to 0.5% of the total U. For dissolution of stainless steel-clad cermet fuel, 7 wt % of the stainless steel forms fine sludge particles. For other stainless clad fuels, 2 wt % of the stainless steel formed sludge.

In a report by Perkins and Christman,[37] fission products in HEU fuel with high burnup and in solutions in which the fuel had been dissolved were measured. This data was used to validate computer codes to predict the fission product concentrations in the fuel based on reactor data. Comparison of the measured and predicted Zr-95 and Nb-95 were not as good as other fission products. The amount of Nb-95 which was accounted for was only 10-15%. Previous experience at Savannah River showed that Zr-95 + Nb-95 activities in process solutions were routinely lower than predicted, but Nb-95/Zr-95 ratios were not routinely measured. The Nb-95 discrepancy was attributed to efficient scavenging of Nb-95 from solution by the siliceous solids that form whenever high-burnup U-Al alloy fuels are dissolved.

2.4 Simulated Fuel Dissolution Studies

Using Ce as a surrogate for Pu to simulate dissolver solution, Jakab-Costenoble et al.[38] studied precipitation of ZMH in nitric acid with Ce substituted in place of Zr from 0% to 100%. They found that Ce incorporates into the solid, substituting in the compound in place of Zr, at only half the concentration in solution below

60 mol % Ce in solution. The Mo to Zr/Ce ratio is 2.5 when the concentration of Ce in the solid is below about 35%, showing a stoichiometry different than the accepted formula for ZMH of $ZrMo_2O_7(OH)_2.2H_2O$.

In a report on Pu losses due to solids formation in dissolver solutions, Fellows et al.[39] found that ZMH contained up to 3 wt % Pu when precipitated from Pu-containing nitric acid solutions. ZMH was the first solid to precipitate from solution. The solubility of ZMH was a complex function of nitric acid, Zr and Mo concentrations, ionic strength of the solution, and temperature. ZMH had low solubility at nitric acid concentrations of 1 to 7.5 M, but higher solubility at nitric acid concentrations below 1 M and above 7.5 M. The report discussed data showing regions of Zr, Mo and nitric acid concentrations that minimize ZMH precipitation, but did not give specifics.

Fellows et al.[40] used Th as a surrogate for Pu to study precipitation in a simulated dissolver solution. Studies of Th, Zr, and Mo in nitric acid solution found ZMH precipitation containing up to 6% Th, in preference to thorium molybdate precipitation which forms in the absence of Zr.

Rao et al.[6] found that ZMH was the main precipitation product from simulated fuel reprocessing solutions containing Zr and Mo in nitric acid. Ammonium nitrate was added as a salting reagent. The solution was refluxed at 100 °C for normally 6 hours. The ratio of Mo to Zr varied between 2 and 4.15. In solutions with the largest excess of Mo, another precipitate was formed in addition to ZMH. Ionic strength did not seem to influence the yield. The yield of ZMH decreased with increasing nitric acid concentration. In further work by Rao et al.,[5] simulated process solutions contained Zr, Mo, U, Ru, and Pu under initial conditions. Solutions containing the actinide and fission product elements were heated to 100 °C and the percent precipitated was measured as a function of time (t = 0 to 250 min or 450 min). In solutions containing an excess of Mo relative to Zr, the solid residues consist of a mixture of ZMH and MoO_3, while in the absence of Zr mainly uranium molybdate and/or plutonium molybdate was formed.

Simulated irradiated fuels were produced by heat-treating pellets of composition similar to irradiated fuel in a study by Adachi et al.[41] It was found that dissolution of simulated fuel treated at 2,073 K or higher leads to some of the U remaining in the insoluble residue. The amount of residue increased with increase in simulated burnup. ZMH was found in the insoluble residue. Kim et al.[42] performed dissolution of simulated irradiated LWR fuel. The residue and precipitate from dissolution were mainly Mo and Ru, with smaller amounts of Zr, Rh, Pd and Cd. ZMH was found in the precipitated solids.

Sakurai et al.[43] performed an experimental study to evaluate the interaction of iodine with insoluble residues during the dissolution of simulated spent fuel pellets. The primary residues were not characterized. Secondary precipitation of metal molybdates was observed in solutions with greater than 170 g/L U. Between 2% and 5% of the iodine is carried by the insoluble residue by compounding with silver or palladium. By leaching in nitric acid with introduction of NO_2, 50% to 90% of the iodine can be removed. The remainder of the iodine is trapped inside the residue.

Sreenivasulu et al.[44] studied the dissolution of U-Zr and U-Pu-Zr alloys in nitric acid. In dissolution of U-Zr alloy samples in nitric acid at 130 °C, over 98% of the U was dissolved while at most 73.7% of the Zr was dissolved. Kolobov et al.[45] studied the dissolution rate of U alloyed with Mo, Zr, Si and other elements as a function of nitric acid concentration and temperature. The residual precipitate after dissolution was up to 10 wt % of the original sample and contained 0.8% to 1% of the U in the original sample. The bulk of the precipitate was made up of Zr, U, O and Al.

2.5 High Level Waste Studies

In treatment of simulated high level liquid waste (HLLW), Kondo and Kubota[46] studied precipitation of platinum group metals (Ru, Rh and Pd) during denitration with formic acid. Most of the Ru, Rh and Pd was recovered in the precipitate along with smaller amounts of the other metals in solution. In another study by

Kondo et al.,[47] reflux boiling of simulated HLLW in 2 M nitric acid was performed and the precipitate collected periodically. The Mo and Zr precipitated at a 2:1 ratio, with most of the Mo precipitated after 150 min of refluxing. Filtration of the refluxed mixture before denitration gave improved removal of Zr and Mo. Kondo et al.[48] also found that reflux boiling of simulated HLLW in 0.5 and 2 M nitric acid created precipitates containing Zr, Mo, Te and Ru. For the 2 M nitric acid solution, in the absence of Zr, very little precipitate was formed. For the 0.5 M nitric acid solution, without Mo in solution, no precipitate was formed, and removing Zr resulted in very little precipitate formation. Aging the solution for 30 days at 0.5 M nitric acid precipitated most of the Zr and Mo, while for the 2 M nitric acid solution about 6% precipitated after aging. Also using simulated HLLW, Shirahashi and Kubota[49] studied precipitation of Pu, Np and Am during denitration with formic acid. The amounts of Pu, Np and Am precipitated increased with increasing pH and formic acid concentration. Up to 90% of the Pu was observed to coprecipitate with Zr and Mo, but they were not sure in what form.

Xuegang et al.[50] studied precipitation of Mo and Zr solids in simulated HLLW during evaporation and denitration with addition of formic acid. Precipitation of Mo increased as the solution was concentrated. Precipitation of Zr increased until a concentration factor of 5x, then decreased. The precipitate was mainly ZMH, with some amorphous Mo precipitate not seen by XRD. Russell et al.[51] conducted a precipitation study in simulated HLLW samples. The experiment was conducted using caustic solution with sodium nitrate, nitrite, carbonate, hydroxide and aluminate. The experiments increased the concentration of phosphate, oxalate, sulfate, silicate and fluoride in solution to saturation levels, then observed precipitation rates of sodium salts.

Using simulated HLLW, Izumida and Kawamura[52] observed precipitate formation during evaporation and aging. This resulted in precipitation of Ba/Sr nitrate, phosphomolybdic acid and ZMH. Precipitation of ZMH increased at higher temperature and lower acidity. Whyatt et al.[53] performed an analysis of the likelihood of criticality when transferring Hanford tank sludge. They found that Pu can coprecipitate with La in Hanford cladding removal wastes. In a study by Bradley et al.[54] the conversion of cesium phosphomolybdate (CPM) to ZMH in simulated high active liquor (HAL) was carried out in highly acidic conditions. The conversion rate increased at higher temperature and lower acidity. Modeling software by OLI System Inc. was successfully used by Takeuchi et al.[55] to predict the precipitation of solids, mostly ZMH, in simulated HLLW. Quemet et al.[56] monitored dissolution of the last part of the Pu fuel residues in a dissolution solution using thermal ionization mass spectrometry isotope dilution.

2.6 Aging Studies of Solutions and Irradiation Effects

Kinetics experiments were performed on dissolved fuel solutions of irradiated UO_2 fuel in 6.6 M nitric acid by Baghdadi et al.[57] Observation over 40 hours showed the concentration of Zr in solution drop by 20% in one solution sample and 16% in a second sample.

In a study of the effects of gamma and high energy electron irradiation on ZMH, Fourdrin et al.[58] found no change was observed in the crystalline structure, but possibly a change in solubility. A color change was observed in the solid caused by changes in oxidation state of some of the atoms.

Kubota and Fukase[59] found that aging of simulated HLLW with 2 M nitric acid showed 30% of Mo, Zr and Te precipitated in 5 months. Irradiation with Co-60 gamma rays accelerated precipitation, with 4 days of irradiation producing as much precipitate as 30 days of aging.

A study of the treatment and long-term storage of simulated HLLW by Jin et al.[60] found that reflux boiling of simulated HLLW in 3 M nitric acid created a ZMH precipitate, while no other elements of the solution formed a precipitate. Storage of simulated HLLW at 60 ˚C for 90 hours showed no precipitation of solids. At higher temperature ZMH precipitated. Addition of phosphoric acid to above 100 ppm concentration created a zirconium phosphate precipitate.

Campbell et al.,[28] in dissolution studies of high-burnup UO_2 LWR fuel in nitric acid, observed ZMH formation when dissolver solution was allowed to sit. Keeping the temperature below 60 ˚C reduced precipitation as the solution aged. Thomson et al.[61] observed that precipitated solids formed in HAL tanks over time including ZMH, CPM, zirconium hydrogen phosphate, barium/strontium nitrate, and magnesium lanthanide nitrates. Experiments show that CPM formed in real HAL waste converts to ZMH over time. The authors describe results from two different solutions used to wash solids from tanks after the liquid has been removed, but do not give the recipes for the solutions.

2.7 Structure, Synthesis, and Characterization of ZMH

Esbelin[62] found that in a strongly acidic solution, a Zr:Mo complex with 1:1 ratio forms before the slower formation of ZMH. ZMH precipitation experiments in simulated dissolved fuel performed by Doucet et al.[63] found that ZMH forms preferentially on a surface rather than precipitating in the bulk solution. ZMH and CPM were synthesized in a 2 M nitric acid solution by Shiels et al.[64] Two forms of ZMH were found, ZM-a with formula $ZrMo_2O_7(OH)_2 \cdot 3H_2O$ and ZM-b with formula $ZrMo_2O_7(OH)_2 \cdot 4H_2O$. CPM was found to form rapidly, within a few hours, while ZMH formed in several days while consuming the CPM.

In a study of the precipitation of ZMH, Zhang et al.[65] found that nitric acid concentration and temperature do not affect the crystal size of ZMH. ZMH solubility was higher at lower temperature (343 K, tested up to 373 K). ZMH was more soluble in 5 M nitric acid than in 3 M nitric acid at 343 K, but at higher temperature was more soluble in 3 M nitric acid.

In a study by Yasuike et al.,[66] a simulated spent fuel was made by reducing 2% of Zr and Mo oxides in UO_2 powder to create an alloy metal. The simulated fuel was dissolved in nitric acid. The ZMH precipitate was then separated from the solution. The ZMH was dissolved effectively in a mixture of H_2O_2 and nitric acid to study the reaction kinetics. Adding Ru to the solution decomposes H_2O_2, but adding more H_2O_2 can compensate for the decomposition and still dissolve ZMH.

As the subject of a thesis, Masheder[67] studied crystal growth and morphological control of ZMH in solutions typical of HAL. It was found that the faster the growth rate of ZMH, the more it forms needle-shaped crystals along the 001 axis. Slower crystal growth, typical of the conditions in HAL, leads to cubic crystals. Adding telluric acid changes the shape of ZMH crystals and reduces formation of ZMH at higher concentrations of telluric acid. Lind et al.[68] observed a phase transition to monoclinic structure in ZMH at high pressure. Zhou et al.[69] performed synthesis and structural characterization of the citratomolybdate complex. Cruywagen et al.[70] studied the formation of various citratomolybdate complexes in solution at varying pH.

2.8 Settling and Flow Properties of Solids in Dissolver and Waste Solutions

For the main focus of a Ph.D. dissertation, Shiels[71] synthesized and characterized settling and aggregation properties of zirconium molybdate (ZM) and CPM. It was found that certain forms of ZM and CPM tend to aggregate and form solid beds that are difficult to compress. Paul et al.[72] studied the sedimentation and flow properties of CPM and ZMH. In a report on the flow and settling behavior of ZMH, CPM and their mixtures in waste solution, Dunnett et al.[73] found that the morphology of ZMH varied. More elongated particles led to higher viscosity and yield stress, which hindered solution transport. In a study of Hanford fuel dissolution, Amos[17] reported on the settling properties of various precipitates in dissolver solution under gravity and centrifugation.

In studies of the formation and filtration properties of precipitates from HLLW, Kondo and Kubota[74,75] measured particle sizes and filtration characteristics. During the denitration of simulated HLLW, precipitates were formed of Mo, Te, Ru, Fe, and the Pt group metals. As the solution became more acidic,

less precipitates were in the mixture, except for Mo which precipitated across the range of pH. Zirconium precipitated only when phosphate ion was in solution. They found ZMH and zirconium telluride precipitated as larger particles that were easy to filter, while phosphomolybdic acid and strontium and barium nitrates were much smaller particles and difficult to filter from solution. In a similar study, Kondo[76] found that preheating simulated HLLW before denitration reduces the amount of precipitate and leads to larger particles that are easier to remove by filtration.

2.9 Reduction or Prevention of Formation of ZMH and Other Precipitates in Solutions of Dissolved NASNF

Jerden et al.[77] used thermodynamic modeling to predict precipitation of solids in a uranyl nitrate reactor for medical Mo-99 production. It was found that increasing pH in the solution could lead to precipitation of U and Mo solids. The authors suggested adding nitric acid to prevent precipitation. It was predicted that precipitation of uranyl molybdate or zirconium molybdate would occur above pH 1, but they did not have adequate solubility data to provide firm numbers. Peroxide concentration above 0.001 M can lead to uranyl peroxide precipitation at pH less than 1.

Ferris[78] found low solubility of molybdic oxide in nitric acid and uranyl nitrate/nitric acid solutions. Limited formation of uranyl molybdate in nitric acid-uranyl nitrate solution was observed. During processing of enriched U fuels at SRP, Hyder et al.[15] reported that maintaining a minimum nitric acid concentration of 0.3 M in the dissolvers helps prevent U or Pu precipitation.

Schulz et al.[79] found that for the dissolution of U-Mo fuels in 3-5 M nitric acid, the presence of 0.5-1.0 M $Fe(NO_3)_3$ prevents precipitation of solids. In 12 M nitric acid, most of the Mo precipitates as MoO_3. To reduce deposits of ZMH, Arai et al.[80] varied solution parameters including temperature, nitric acid concentration and Zr/Mo ratio. The amount of ZMH precipitate decreased with increasing nitric acid concentration from 1.0 to 3.8 M, and stayed about constant from 80 to 100 °C. The amount of ZMH encrustation on surfaces decreased as temperature or initial Mo/Zr mole ratio increased, or as the concentration of nitric acid was reduced from 3.8 M to 1.0 M. Similarly, Jakab-Costenoble et al.[38] found an increase in solubility of ZMH at higher concentration of nitric acid. They recommended increasing acidity to reduce fouling. In a study to reduce the precipitation of ZMH, Abe et al.[81] found that addition of molybdenum trioxide hemihydrate crystals to solutions containing Zr and Mo in nitric acid can reduce deposits of ZMH on process surfaces.

With the goal of preventing precipitation of KBF_4, Crooks et al.[82] used software modeling to predict precipitation of KBF_4 in SRS dissolver solutions. Jerden et al.[83] found that for dissolution of Zr-bonded U-10Mo irradiated fuel with >0.0031 M fluoride in solution, modeling predicted precipitation of fission product fluorides, aluminum fluorides and uranium fluorides. To reduce precipitation of MoO_3 and UO_2MoO_4, the optimum nitric acid concentration is about 4 M. Zirconium fluoride is predicted to precipitate at initial HF concentrations greater than 0.5 M.

In a dissertation by Paul,[84] reference was made to work by Franklin (1999, internal National Nuclear Laboratory (NNL) report) who found that excess U in solution increased acidity and slowed growth of ZMH (p. 93). Denniss (2000, internal NNL report) found that seeding agents delayed the precipitation of ZMH. Barium/strontium nitrate precipitated at highly acidic conditions (Orley, 2009) (p. 33).

Geckeis et al.[85] studied the dissolution of noble metal simulated dissolver residues containing Mo, Ru, Rh and Pd in nitric acid. Sparging with ozone and/or use of an electrolytic dissolver accelerated dissolution. Addition of silver nitrate as an oxidation catalyst increased the rate of dissolution.

Paul et al.[86] observed that the addition of citric acid into the reaction mixture in 2 M nitric acid can inhibit the growth of zirconium molybdate and produce zirconium citratomolybdate. Schulz and Duke[87] found that dissolution of Mo-U alloy fuels in a ferric nitrate-nitric acid mixture inhibited formation of uranyl

molybdate precipitate. They found that the solution is more stable at 25 °C than at 50 °C on prolonged storage. Iron-molybdenum complex anions that form in solution appear to be less stable at higher temperature. Long-term stability was better at higher acidity. The addition of sodium dichromate to 0.2 M also appeared to improve stability on storage. Magnaldo et al.[88] looked at the nucleation of crystal growth of ZMH to find out how to prevent surface fouling. Only 20% of the fouling is ZMH, the ZMH acts as a cement to bind up insoluble zircaloy cladding residues and inter-metallic particles. ZMH formation was inhibited by keeping the acidity high and temperature low.

2.10 Summary of Literature Review Applied to Storage of NASNF Solutions in H-Canyon Tanks

Reprecipitation phenomena have been observed for completely dissolved fuels during the intermediate storage of solutions of both LWR and FBR fuels. Reprecipitation of fission and activation products may be explained by hydrolysis and radiolytic processes in the nitric acid solutions during intermediate storage. The solids remaining in the spent fuel dissolvers at the La Hague reprocessing plant in France were characterized. Most of the remaining solids found in the dissolvers were from Zircaloy cladding ranging from 30 to 70% of the mass. The rest of the solids were mainly ZMH. The solids contained from 0.3 to 1.2% Pu, mostly in the ZMH. The U content of the solids was 0.2 to 1.7%, likely from solution absorbing into the solids. Studies found that the solubility of ZMH increased as the nitric acid concentration increased from 1 to 3 M, and the solubility of the ZMH remained about the same at temperatures from 60 to 90 °C.

Characterization studies from residues generated during the dissolution of LWR fuel at the Karlsruhe facility in Germany have also been reported. In a study with Zircaloy-clad UO_2 LWR fuel, about 13% of the total residues were composed of incompletely dissolved metallic fission products (e.g., Mo, Tc, Ru, Rh, and Pd). The remaining 87% of the residues were reprecipitated oxides or oxide hydrates (e.g., ZMH). Reprecipitation of U and Pu was confirmed by the analyzed 7:1 ratio of U:Pu in the solids compared to the expected ratio of 70:1 in undissolved fuel. In a second study at Karlsruhe, solids remaining in the dissolver solution for spent LWR fuel were characterized. The solids consisted of a metal fraction (Mo, Tc, Pd, Ru, and Rh) and an oxide phase (Zr, Mo, and Pu). Total solids were about 8 kg/t U, containing 6-33% feed clarification sludge, 60-84% fine solids and 7-10% post-precipitates. Experimental results suggested the presence of ZMH, given the Zr:Mo ratio in the oxide phase and that ZMH is known to act as a host lattice for Pu. From 0.01% to 0.02% of the total U in the fuel element was carried in the solids, and from 1.42% to 3.54% of the total Pu. Less residue was generated in solutions which had been centrifuged compared to solutions which had been filtered. The amount of metal solids increased with fuel burnup.

In a study with irradiated PWR fuel, precipitation in solution was observed. The researchers found Pu incorporated into ZMH, with 3.6 mol % substitution of Pu in place of Zr. Washing did not remove the Pu; therefore, a conclusion was reached that the Pu was incorporated into the chemical structure. The precipitate was dissolved with HNO_3-H_2O_2 solution at 80 ˚C. In controlled laboratory experiments, solutions containing U, Pu, Zr, Mo and other fission products in 1 M to 4 M nitric acid, ZMH was formed preferentially over Pu molybdate. Plutonium substitution for Zr in the precipitate ranged from 0.9% in 4 M nitric acid with 1 g/L Mo, 1.5 g/L Zr and 1.5 g/L Pu, up to 12.2% in 1 M nitric acid with 1.5 g/L Mo, 1 g/L Zr and 1.47 g/L Pu. The Pu could not be leached out without dissolving the precipitate, so the Pu was incorporated into the chemical structure.

Characterization of solids from the dissolution of simulated reactor fuels have been performed to understand the precipitation of ZMH solids containing fissile materials. In a study to evaluate Pu losses due to solids formation in dissolver solution, ZMH solids contained up to 3 wt % Pu when precipitated from nitric acid solutions. The solubility of ZMH was a complex function of nitric acid, Zr, and Mo concentrations, ionic strength of the solution, and temperature. The ZMH had low solubility at nitric acid concentrations of 1 to 7.5 M, but higher solubility at nitric acid concentrations below 1 M and above 7.5 M. In a study in which Th was used as a surrogate for Pu in a simulated dissolver solution, the ZMH precipitate contained up to 6 wt % Th, in preference to Th molybdate precipitation which occurs in the absence of Zr.

Kinetic experiments have been performed to evaluate the rate at which ZMH precipitates form. Experiments using dissolved fuel solutions of irradiated UO_2 in 6.6 M nitric acid showed that the concentration of Zr in solution dropped by 16-20% over 40 hours. In an aging study with simulated HLLW in 2 M nitric acid, 30% of the Mo, Zr, and Te precipitated in 5 months. Irradiation with a Co-60 source accelerated precipitation, with 4 days of irradiation producing as much precipitate as 30 days of aging. In dissolution studies of high-burnup UO_2 LWR fuel in nitric acid, ZMH formed when the dissolver solution was allowed to sit. Keeping the temperature below 60 ˚C reduced precipitation as the solution aged.

Experimental programs have characterized the structure and synthesis of ZMH. In a strongly acidic solution, a Zr:Mo complex with a 1:1 ratio forms before the slower precipitation of ZMH. Precipitation experiments in simulated dissolved fuel found that ZMH forms preferentially on a surface rather than precipitating in the bulk solution. In experiments in which ZMH and CPM were synthesized in a 2 M nitric acid solution, two forms of ZMH were found, ZMH-a with formula $ZrMo_2O_7(OH)_2 \cdot 3H_2O$ and ZMH-b with formula $ZrMo_2O_7(OH)_2 \cdot 4H_2O$. The CPM was found to form rapidly, within a few hours, while ZMH formed in several days while consuming the CPM. In a ZMH precipitation study, the nitric acid concentration and temperature did not affect the ZMH crystal size. The ZMH solubility was higher at lower temperature (70 °C versus 100°C). The ZMH was also more soluble in 5 M nitric acid than 3 M nitric acid at 70 °C, but at higher temperature, the ZMH was more soluble in 3 M nitric acid.

Studies have been performed to identify methods to reduce or prevent the formation of ZMH and other precipitates in solutions of dissolved fuel. During the development of a dissolution flowsheet for U-Mo fuels, the solubility of uranyl molybdate was increased by adding Fe to the solution. Iron forms a negatively charged Fe-Mo complex which prevents precipitation. The Fe-Mo complex appeared more stable at lower temperature (25 versus 50 °C). Long-term stability was also better at higher acidity. The addition of Fe to dissolved fuel solutions could prevent the formation of ZMH; although, this type of mitigation has not been tested. Other studies have tried to minimize the formation of ZMH in dissolved fuel by varying solution parameters including temperature, nitric acid concentration, and the Zr/Mo ratio. The amount of ZMH precipitate decreased with increasing nitric acid concentration from 1.0 to 3.8 M, and stayed about constant from 80 to 100 °C. The amount of ZMH deposited on surfaces decreased as temperature or initial Mo/Zr mole ratio increased, or as the concentration of nitric acid was reduced from 3.8 M to 1.0 M. In a study to reduce the precipitation of ZMH, researchers found the addition of $MoO_3 \cdot ½H_2O$ to solutions containing Zr and Mo in nitric acid can reduce deposits of ZMH on process surfaces. The addition of citric acid into a reaction mixture in 2 M nitric acid inhibited the growth of ZMH and produced Zr citratomolybdate. The addition of 0.2 M sodium dichromate also appeared to improve the stability of dissolver solution during storage.

3.0 Bounding Assessment for Precipitation of Fissile Material from NASNF Solutions

A bounding assessment was performed to calculate the mass of fissile material which could potentially co-precipitate with zirconium molybdate solids from solutions generated during the dissolution of Campaign 1 NASNF. The assessment was prepared using calculations performed to estimate the fission and activation product inventory of the Campaign 1 fuels, the maximum extent of precipitation of the zirconium molybdate, and the bounding concentrations of fissile material in the precipitated solids based on the literature review.

3.1 Campaign 1 NASNF Assemblies

The fuel bundles which will be dissolved in Campaign 1 of the electrolytic dissolver were identified by Corcoran.[89] The bundle identifications are provided in Appendix A. To perform the bounding analysis, the fission and activation product inventory of the assemblies stored in each bundle must be estimated. Estimates for the radionuclide inventories in the assemblies which will be dissolved in Campaign 1 were

calculated by Langton et al.[90] for an evaluation of disposition path options for Zircaloy and stainless steel residues generated during electrolytic dissolution. The Campaign 1 fuels were initially broken into 15 representative subgroups, each featuring assemblies with identical construction and enrichment. The fuel burnups for each subgroup were also very similar. The maximum burnup was selected from the assemblies in each subgroup to represent the subgroup's bounding exposure. The reactor exposure data for the Campaign 1 subgroups are provided in Table 3-1.[90] The number of assemblies in each subgroup which are stored in the fuel bundles are also provided in Appendix A.

Table 3-1. Reactor Exposure Data for Campaign 1 Subgroups

Subgroup Name	Number of Assemblies in Subgroup	Max BOL U (g)	U-235 Enrich. (%)	Burnup (%)	Time in Reactor (days)	Cooling Time (days)
CVTR-2%	32	2,026	2.02	60	240	20,819
CVTR-4%	2	1,913	3.82	28	240	20,819
EBWR-Plates	4	432	93.24	0	1	24,106
EBWR-6%	56	24,127	5.97	7	275	21,185
EBWR-Nat	50	26,730	0.71	11	275	20,454
OT-Nat	1	19,513	0.71	15	43	22,646
OT-1	3	21,240	1.54	47	185	22,280
SOT-1-2	2	2,027	1.5	68	204	22,036
SOT-1-4	7	2,125	1.5	54	141	22,036
SOT-8	10	3,924	1.2	26	80	22,036
SOT-9	4	3,263	1.2	26	204	22,036
SOT-6-2	3	3,250	0.71	45	143	22,036
SOT-6-3	6	3,276	0.71	28	65	22,036
SPRO-high	6	5,579	0.71	30	100	22,036
SPRO-low	8	6,419	0.71	9	77	23,563

Langton et al.[90] created depletion models for each fuel subgroup using the Standardized Analysis for Licensing Evaluation (SCALE) code, specifically using the Transport Rigor Implemented with Time-dependent Operation for Neutronic depletion (TRITON) sequence to generate time-dependent three-dimensional neutronic models for the 15 fuel assembly subgroups which comprise the Campaign 1 NASNF. A decay date of January 1, 2025, was assumed for the elemental and radionuclide distributions in the fuel subgroups.

Although the SCALE depletion models developed for the 15 fuel subgroups tracked over 1,000 nuclides, Langton et al.[90] calculated the elemental inventory for 35 fission and activation products. For the bounding assessment for the Campaign 1 fuels, only the fission products Zr and Mo and the actinides U, Np, Pu, and Am were of interest. The elemental masses of these elements are provided in Table 3-2 for an assembly for each of the 15 subgroups. The masses of Zr, Mo, U, Np, Pu, and Am in each fuel bundle were subsequently calculated using the number of assemblies in each subgroup present in the bundle (Appendix A) and the masses of the elements in an assembly from the respective subgroup provided in Table 3-2. The masses of the elements in each fuel bundle are provided in Appendix B and the total masses of Zr, Mo, U, Np, Pu, and Am in all Campaign 1 fuel bundles are summarized in Table 3-3.

Table 3-2. Masses of Zr, Mo, and Selected Actinides for an Assembly in Each Fuel Subgroup

Subgroup Name	Zr (g)	Mo (g)	U (g)	Np (g)	Pu (g)	Am (g)
CVTR-2%	3.80E+00	3.23E+00	1.98E+03	3.35E-01	1.42E+01	1.57E+00
CVTR-4%	2.50E+00	1.94E+00	1.88E+03	1.48E-01	9.07E+00	4.50E-01
EBWR-Plates	1.56E-04	1.14E-04	4.32E+02	5.32E-09	1.82E-06	5.65E-16
EBWR-6%	1.41E+01	1.05E+01	2.70E+04	2.63E-01	2.48E+01	6.54E-02
EBWR-Nat	2.63E+00	1.99E+00	2.67E+04	6.12E-02	1.71E+01	2.36E-02
OT-Nat	2.61E+00	1.97E+00	1.95E+04	2.81E-02	1.59E+01	3.46E-02
OT-1	2.20E+01	1.79E+01	2.10E+04	1.29E+00	9.45E+01	6.09E+00
SOT-1-2	3.39E+00	2.90E+00	1.98E+03	2.47E-01	1.31E+01	1.15E+00
SOT-1-4	2.43E+00	1.97E+00	2.10E+03	1.14E-01	8.91E+00	4.98E-01
SOT-8	1.59E+00	1.23E+00	3.90E+03	4.05E-02	7.98E+00	1.10E-01
SOT-9	1.34E+00	1.03E+00	3.25E+03	2.81E-02	5.83E+00	7.22E-02
SOT-6-2	1.53E+00	1.25E+00	3.23E+03	5.06E-02	8.76E+00	2.34E-01
SOT-6-3	8.86E-01	6.94E-01	3.26E+03	1.95E-02	5.67E+00	5.85E-02
SPRO-high	1.55E+00	1.19E+00	5.56E+03	1.90E-02	7.57E+00	3.48E-02
SPRO-low	5.05E-01	3.72E-01	6.41E+03	4.02E-03	2.61E+00	7.29E-04

Table 3-3. Total Amount of Zr, Mo, and Selected Actinides in All Campaign 1 Fuel Bundles

Element	Mass (g)	Moles
Zr	1.18E+03	1.30E+01
Mo	9.04E+02	9.43E+00
U	3.18E+06	1.34E+04
Np	3.49E+01	1.47E-01
Pu	3.33E+03	1.39E+01
Am	8.27E+01	3.43E-01

3.2 Bounding Analysis for Co-Precipitation of Pu with Zirconium Molybdate

The bounding analysis for the amount of fissile material which could potentially co-precipitate with zirconium molybdate during the intermediate storage of the Campaign 1 NASNF solution was performed for Pu. The U which is present as uranyl nitrate ($UO_2(NO_3)_2$), a 2+ cation (i.e., UO_2^{2+}), will not substitute as easily into the molybdate crystal lattice for the Zr^{4+} ion. This chemistry is supported by an evaluation of undissolved solids generated during the reprocessing of LWR fuel at the La Hague plant. The U content of the solids was 0.2% to 1.7% and likely was from solution absorbing into the solids.[22] In addition, the U enrichment of the Campaign 1 fuels is generally low with the exception of the EBWR plates (Table 3-1). The U in the combined solutions will have an estimated U-235 content of less than 3.2% based on the beginning of life (BOL) enrichment. For solutions generated from the dissolution of HEU fuels, the U-235 can be assumed to behave as Pu in the presence of zirconium molybdate, a conservative assumption. The percentages of U and Pu which were associated with zirconium molybdate reported in the literature for LWR fuel were not significantly different.[22,31,36] Therefore, calculation of the maximum amount of Pu which could co-precipitate with zirconium molybdate would be bounding for elemental U for the HEU fuels. The masses of Np and Am in the Campaign 1 NASNF are factors of 95 and 40, respectively, less than the mass of Pu, and these actinides do not present a nuclear safety issue.

The chemical formula of the zirconium molybdate hydroxide hydrate determined from the material found on the H-Canyon 6.1D dissolver MK-12 insert was used as the basis for the bounding analysis. The

chemical formula of the solids determined by XRD analysis was $Zr[Mo_2O_7(OH)_2(H_2O)_2]$. Based on the formula, the ratio of Zr:Mo is 1:2. From Table 3-3, the limiting reagent for the formation of zirconium molybdate in the Campaign 1 fuels is Mo. Therefore, the maximum amount of zirconium molybdate solids which can be produced from the fuels is only 2193 g which would contain 430 g of Zr. If Pu^{4+} replaces the Zr^{4+} in the zirconium molybdate crystal lattice, Table 3-4 provides a summary of the maximum amount of Pu which could precipitate for a range of Zr masses between 2 and 20 wt %.

Table 3-4. Maximum Pu Co-Precipitation with Zirconium Molybdate for Campaign 1 NASNF

Zr Replacement (wt %)	Pu Co-Precipitated (g)
2	8.60
4	17.2
6	25.8
8	34.4
10	43.0
12	51.6
14	60.2
16	68.8
18	77.4
20	86.0

The bounding analysis summarized in Table 3-4 shows there is only the potential to co-precipitate a minimal amount of Pu with the zirconium molybdate in the Campaign 1 NASNF. Even if the Pu replaces 10 wt % Zr in the solids, an amount which is greater than the values reported for irradiated LWR fuels in the literature, the total mass of Pu precipitated from all the Campaign 1 solutions will be less than 50 g.

4.0 Conclusions

Precipitation of zirconium molybdate solids from the Campaign 1 NASNF solutions during intermediate storage prior to disposal to a Defense Waste Processing Facility sludge batch is expected based on a review of the literature. This conclusion is supported by the identification of zirconium molybdate solids found on the H-Canyon 6.1D Dissolver MK-12 insert spacer. The formation of the zirconium molybdate solids is attributed to hydrolysis and radiolytic processes in the nitric acid solution. As the molybdate solids form, U and Pu can co-precipitate. Generally, the Pu substitutes directly into the crystal lattice during precipitation while the U associated with the molybdate solids more likely absorbs from the solution. The U in the NASNF solutions is present as uranyl nitrate, a 2+ cation, which will not substitute as easily into the molybdate crystal lattice for the Zr^{4+} ion.

A bounding analysis was performed to estimate the amount of Pu which could co-precipitate with zirconium molybdate solids during interim storage of the Campaign 1 NASNF solutions. The assessment was prepared using calculations performed to estimate the fission and activation product inventory of the Campaign 1 fuels, the maximum extent of precipitation of the zirconium molybdate from the NASNF solutions, and the bounding concentrations of fissile material in the precipitated solids based on the literature review. The estimated masses of Zr and Mo in the Campaign 1 assemblies indicated that Mo is the limiting reagent for the formation of zirconium molybdate. The maximum amount of zirconium molybdate solids which can be produced from the fuels is only 2193 g which would contain 430 g of Zr. Even if the Pu replaces 10 wt % Zr in the solids, an amount which is greater than the values reported for irradiated LWR fuels in the literature, the total mass of Pu precipitated from all the Campaign 1 solutions will be less than 50 g.

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Appendix A. Campaign 1 NASNF Bundles

The fuel bundles identified for dissolution during Campaign 1 of the NASNF in the electrolytic dissolver are listed in Table A-1. The table includes the reactor facility, bundle identification (ID), and the number of assemblies in each of the 15 subgroups.

Table A-1. Campaign 1 NASNF Bundle and Assembly Subgroup Identification

Facility	Bundle ID	Number and Type of Assembles
CVTR	RL-CVTR 1062	(8) CVTR-2%
CVTR	RL-CVTR 1063	(13) CVTR-2%
CVTR	RL-CVTR 1064	(11) CVTR-2%, (2) CVTR-4%
EBWR	RB-EBWR-5469	(1) EBWR-Plates
EBWR	RB-EBWR-5470	(1) EBWR-Plates
EBWR	RB-EBWR-5471	(1) EBWR-Plates
EBWR	RB-EBWR-5472	(1) EBWR-Plates
EBWR	RL-EBWR 0953	(1) EBWR-6%
EBWR	RL-EBWR 0954	(1) EBWR-6%
EBWR	RL-EBWR 1135	(2) EBWR-Nat
EBWR	RL-EBWR 1136	(2) EBWR-Nat
EBWR	RL-EBWR 1137	(2) EBWR-Nat
EBWR	RL-EBWR 1138	(2) EBWR-Nat
EBWR	RL-EBWR 1139	(2) EBWR-Nat
EBWR	RL-EBWR 1140	(2) EBWR-Nat
EBWR	RL-EBWR 1141	(2) EBWR-Nat
EBWR	RL-EBWR 1142	(2) EBWR-Nat
EBWR	RL-EBWR 1143	(2) EBWR-Nat
EBWR	RL-EBWR 1144	(2) EBWR-Nat
EBWR	RL-EBWR 1145	(2) EBWR-Nat
EBWR	RL-EBWR 1146	(2) EBWR-Nat
EBWR	RL-EBWR 1147	(2) EBWR-Nat
EBWR	RL-EBWR 1148	(2) EBWR-Nat
EBWR	RL-EBWR 1153	(2) EBWR-6%
EBWR	RL-EBWR 1154	(2) EBWR-6%
EBWR	RL-EBWR 1155	(2) EBWR-6%
EBWR	RL-EBWR 1156	(2) EBWR-6%
EBWR	RL-EBWR 1157	(2) EBWR-6%
EBWR	RL-EBWR 1158	(2) EBWR-6%
EBWR	RL-EBWR 1159	(2) EBWR-6%
EBWR	RL-EBWR 1160	(2) EBWR-6%
EBWR	RL-EBWR 1161	(2) EBWR-6%
EBWR	RL-EBWR 1162	(2) EBWR-6%
EBWR	RL-EBWR 1163	(2) EBWR-6%
EBWR	RL-EBWR 1164	(2) EBWR-6%
EBWR	RL-EBWR 1165	(2) EBWR-6%
EBWR	RL-EBWR 1198	(2) EBWR-6%
EBWR	RL-EBWR 1199	(2) EBWR-6%
EBWR	RL-EBWR 1200	(2) EBWR-6%
EBWR	RL-EBWR 1201	(2) EBWR-6%
EBWR	RL-EBWR 1202	(2) EBWR-6%
EBWR	RL-EBWR 1203	(2) EBWR-6%
EBWR	RL-EBWR 1204	(2) EBWR-6%

Facility	Bundle ID	Number and Type of Assembles
EBWR	RL-EBWR 1205	(2) EBWR-6%
EBWR	RL-EBWR 1206	(2) EBWR-6%
EBWR	RL-EBWR 1207	(1) EBWR-6%
EBWR	RL-EBWR 1208	(2) EBWR-6%
EBWR	RL-EBWR 1209	(2) EBWR-6%
EBWR	RL-EBWR 1210	(2) EBWR-6%
EBWR	RL-EBWR 1211	(2) EBWR-6%
EBWR	RL-EBWR 1212	(1) EBWR-6%, (1) EBWR-Nat
EBWR	RL-EBWR 1213	(2) EBWR-Nat
EBWR	RL-EBWR 1214	(2) EBWR-Nat
EBWR	RL-EBWR 1215	(2) EBWR-Nat
EBWR	RL-EBWR 1216	(2) EBWR-Nat
EBWR	RL-EBWR 1217	(2) EBWR-Nat
EBWR	RL-EBWR 1218	(2) EBWR-Nat
EBWR	RL-EBWR 1219	(2) EBWR-Nat
EBWR	RL-EBWR 1220	(2) EBWR-Nat
EBWR	RL-EBWR 1221	(2) EBWR-Nat
EBWR	RL-EBWR 1222	(2) EBWR-Nat
EBWR	RL-EBWR 1223	(1) EBWR-Nat
HWCTR	RL-HWCTR-0849	(1) OT-Nat, (1) OT-1
HWCTR	RL-HWCTR-0850	(2) OT-1
HWCTR	RL-HWCTR-1057	(3) SOT-6-2, (6) SOT-6-3
HWCTR	RL-HWCTR-1065	(10) SOT-8
HWCTR	RL-HWCTR-1067(1)	(2) SOT-1-2, (7) SOT-1-4, (4) SOT-9
HWCTR	RL-HWCTR-1049	(7) SPRO-low
HWCTR	RL-HWCTR-1050	(6) SPRO-high, (1) SPRO-low

(1) Bundle RL-HWCTR-1067 was removed from the Campaign 1 inventory of NASNF which will be dissolved in H-Canyon; however, the bundle was included in the analysis to estimate the amount of Pu which could co-precipitate with zirconium molybdate solids during interim storage of the Campaign 1 NASNF solutions. The additional fuel bundle results in a bounding mass of Pu.

Appendix B. Masses of Zr, Mo, and Selected Actinides in Campaign 1 Fuel Bundles

The calculated masses of Zr, Mo, U, Np, Pu, and Am in each of the Campaign 1 fuel bundles are provided in Table B-1. The total mass of each element in all bundles is provided at the bottom of the table.

Table B-1. Masses of Zr, Mo, and Selected Actinides in Campaign 1 Fuel Bundles

Bundle ID	Zr (g)	Mo (g)	U (g)	Np (g)	Pu (g)	Am (g)
RL-CVTR 1062	3.04E+01	2.58E+01	1.58E+04	2.68E+00	1.14E+02	1.26E+01
RL-CVTR 1063	4.94E+01	4.20E+01	2.57E+04	4.36E+00	1.85E+02	2.04E+01
RL-CVTR 1064	4.68E+01	3.94E+01	2.55E+04	3.98E+00	1.74E+02	1.82E+01
RB-EBWR-5469	1.56E-04	1.14E-04	4.32E+02	5.32E-09	1.82E-06	5.65E-16
RB-EBWR-5470	1.56E-04	1.14E-04	4.32E+02	5.32E-09	1.82E-06	5.65E-16
RB-EBWR-5471	1.56E-04	1.14E-04	4.32E+02	5.32E-09	1.82E-06	5.65E-16
RB-EBWR-5472	1.56E-04	1.14E-04	4.32E+02	5.32E-09	1.82E-06	5.65E-16
RL-EBWR 0953	1.41E+01	1.05E+01	2.70E+04	2.63E-01	2.48E+01	6.54E-02
RL-EBWR 0954	1.41E+01	1.05E+01	2.70E+04	2.63E-01	2.48E+01	6.54E-02
RL-EBWR 1135	5.26E+00	3.98E+00	5.34E+04	1.22E-01	3.42E+01	4.72E-02
RL-EBWR 1136	5.26E+00	3.98E+00	5.34E+04	1.22E-01	3.42E+01	4.72E-02
RL-EBWR 1137	5.26E+00	3.98E+00	5.34E+04	1.22E-01	3.42E+01	4.72E-02
RL-EBWR 1138	5.26E+00	3.98E+00	5.34E+04	1.22E-01	3.42E+01	4.72E-02
RL-EBWR 1139	5.26E+00	3.98E+00	5.34E+04	1.22E-01	3.42E+01	4.72E-02
RL-EBWR 1140	5.26E+00	3.98E+00	5.34E+04	1.22E-01	3.42E+01	4.72E-02
RL-EBWR 1141	5.26E+00	3.98E+00	5.34E+04	1.22E-01	3.42E+01	4.72E-02
RL-EBWR 1142	5.26E+00	3.98E+00	5.34E+04	1.22E-01	3.42E+01	4.72E-02
RL-EBWR 1143	5.26E+00	3.98E+00	5.34E+04	1.22E-01	3.42E+01	4.72E-02
RL-EBWR 1144	5.26E+00	3.98E+00	5.34E+04	1.22E-01	3.42E+01	4.72E-02
RL-EBWR 1145	5.26E+00	3.98E+00	5.34E+04	1.22E-01	3.42E+01	4.72E-02
RL-EBWR 1146	5.26E+00	3.98E+00	5.34E+04	1.22E-01	3.42E+01	4.72E-02
RL-EBWR 1147	5.26E+00	3.98E+00	5.34E+04	1.22E-01	3.42E+01	4.72E-02
RL-EBWR 1148	5.26E+00	3.98E+00	5.34E+04	1.22E-01	3.42E+01	4.72E-02
RL-EBWR 1153	2.82E+01	2.10E+01	5.40E+04	5.26E-01	4.96E+01	1.31E-01
RL-EBWR 1154	2.82E+01	2.10E+01	5.40E+04	5.26E-01	4.96E+01	1.31E-01
RL-EBWR 1155	2.82E+01	2.10E+01	5.40E+04	5.26E-01	4.96E+01	1.31E-01
RL-EBWR 1156	2.82E+01	2.10E+01	5.40E+04	5.26E-01	4.96E+01	1.31E-01
RL-EBWR 1157	2.82E+01	2.10E+01	5.40E+04	5.26E-01	4.96E+01	1.31E-01
RL-EBWR 1158	2.82E+01	2.10E+01	5.40E+04	5.26E-01	4.96E+01	1.31E-01
RL-EBWR 1159	2.82E+01	2.10E+01	5.40E+04	5.26E-01	4.96E+01	1.31E-01
RL-EBWR 1160	2.82E+01	2.10E+01	5.40E+04	5.26E-01	4.96E+01	1.31E-01
RL-EBWR 1161	2.82E+01	2.10E+01	5.40E+04	5.26E-01	4.96E+01	1.31E-01
RL-EBWR 1162	2.82E+01	2.10E+01	5.40E+04	5.26E-01	4.96E+01	1.31E-01
RL-EBWR 1163	2.82E+01	2.10E+01	5.40E+04	5.26E-01	4.96E+01	1.31E-01
RL-EBWR 1164	2.82E+01	2.10E+01	5.40E+04	5.26E-01	4.96E+01	1.31E-01
RL-EBWR 1165	2.82E+01	2.10E+01	5.40E+04	5.26E-01	4.96E+01	1.31E-01
RL-EBWR 1198	2.82E+01	2.10E+01	5.40E+04	5.26E-01	4.96E+01	1.31E-01
RL-EBWR 1199	2.82E+01	2.10E+01	5.40E+04	5.26E-01	4.96E+01	1.31E-01
RL-EBWR 1200	2.82E+01	2.10E+01	5.40E+04	5.26E-01	4.96E+01	1.31E-01
RL-EBWR 1201	2.82E+01	2.10E+01	5.40E+04	5.26E-01	4.96E+01	1.31E-01
RL-EBWR 1202	2.82E+01	2.10E+01	5.40E+04	5.26E-01	4.96E+01	1.31E-01
RL-EBWR 1203	2.82E+01	2.10E+01	5.40E+04	5.26E-01	4.96E+01	1.31E-01
RL-EBWR 1204	2.82E+01	2.10E+01	5.40E+04	5.26E-01	4.96E+01	1.31E-01
RL-EBWR 1205	2.82E+01	2.10E+01	5.40E+04	5.26E-01	4.96E+01	1.31E-01

Bundle ID	Zr (g)	Mo (g)	U (g)	Np (g)	Pu (g)	Am (g)
RL-EBWR 1206	2.82E+01	2.10E+01	5.40E+04	5.26E-01	4.96E+01	1.31E-01
RL-EBWR 1207	1.41E+01	1.05E+01	2.70E+04	2.63E-01	2.48E+01	6.54E-02
RL-EBWR 1208	2.82E+01	2.10E+01	5.40E+04	5.26E-01	4.96E+01	1.31E-01
RL-EBWR 1209	2.82E+01	2.10E+01	5.40E+04	5.26E-01	4.96E+01	1.31E-01
RL-EBWR 1210	2.82E+01	2.10E+01	5.40E+04	5.26E-01	4.96E+01	1.31E-01
RL-EBWR 1211	2.82E+01	2.10E+01	5.40E+04	5.26E-01	4.96E+01	1.31E-01
RL-EBWR 1212	1.67E+01	1.25E+01	5.37E+04	3.24E-01	4.19E+01	8.90E-02
RL-EBWR 1213	5.26E+00	3.98E+00	5.34E+04	1.22E-01	3.42E+01	4.72E-02
RL-EBWR 1214	5.26E+00	3.98E+00	5.34E+04	1.22E-01	3.42E+01	4.72E-02
RL-EBWR 1215	5.26E+00	3.98E+00	5.34E+04	1.22E-01	3.42E+01	4.72E-02
RL-EBWR 1216	5.26E+00	3.98E+00	5.34E+04	1.22E-01	3.42E+01	4.72E-02
RL-EBWR 1217	5.26E+00	3.98E+00	5.34E+04	1.22E-01	3.42E+01	4.72E-02
RL-EBWR 1218	5.26E+00	3.98E+00	5.34E+04	1.22E-01	3.42E+01	4.72E-02
RL-EBWR 1219	5.26E+00	3.98E+00	5.34E+04	1.22E-01	3.42E+01	4.72E-02
RL-EBWR 1220	5.26E+00	3.98E+00	5.34E+04	1.22E-01	3.42E+01	4.72E-02
RL-EBWR 1221	5.26E+00	3.98E+00	5.34E+04	1.22E-01	3.42E+01	4.72E-02
RL-EBWR 1222	5.26E+00	3.98E+00	5.34E+04	1.22E-01	3.42E+01	4.72E-02
RL-EBWR 1223	2.63E+00	1.99E+00	2.67E+04	6.12E-02	1.71E+01	2.36E-02
RL-HWCTR-0849	2.46E+01	1.99E+01	4.05E+04	1.32E+00	1.10E+02	6.12E+00
RL-HWCTR-0850	4.40E+01	3.58E+01	4.20E+04	2.58E+00	1.89E+02	1.22E+01
RL-HWCTR-1057	9.91E+00	7.91E+00	2.93E+04	2.69E-01	6.03E+01	1.05E+00
RL-HWCTR-1065	1.59E+01	1.23E+01	3.90E+04	4.05E-01	7.98E+01	1.10E+00
RL-HWCTR-1067	2.92E+01	2.37E+01	3.17E+04	1.40E+00	1.12E+02	6.07E+00
RL-HWCTR-1049	3.54E+00	2.60E+00	4.49E+04	2.81E-02	1.83E+01	5.10E-03
RL-HWCTR-1050	9.81E+00	7.51E+00	3.98E+04	1.18E-01	4.80E+01	2.10E-01
Totals	1.18E+03	9.04E+02	3.18E+06	3.49E+01	3.33E+03	8.27E+01

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