Report on the Behavior of Fission Products in the Co-decontamination Process

Fuel Cycle Technology

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SUMMARY

This document was prepared to meet FCT level 3 milestone M3FT-15IN0302042, “Generate Zr, Ru, Mo and Tc data for the Co-decontamination Process.” This work was carried out under the auspices of the Lab-Scale Testing of Reference Processes FCT work package. This document reports preliminary work in identifying the behavior of important fission products in a Co-decontamination flowsheet. Current results show that Tc, in the presence of Zr alone, does not behave as the Argonne Model for Universal Solvent Extraction (AMUSE) code would predict. The Tc distribution is reproducibly lower than predicted, with Zr distributions remaining close to the AMUSE code prediction. In addition, it appears there may be an intricate relationship between multiple fission product metals, in different combinations, that will have a direct impact on U, Tc and other important fission products such as Zr, Mo, and Rh. More extensive testing is required to adequately predict flowsheet behavior for these variances within the fission products.

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FCT	Fuel Cycle Technology
FP	Fission Products
ICP-MS	Inductively Coupled Plasma-Mass Spectroscopy
INL	Idaho National Laboratory
LSC	Liquid Scintillation Counting
MOX	Mixed Oxide Fuel
O/A	Organic to Aqueous phase volume ratio
PUREX	Plutonium Uranium Reduction Extraction
TBP	Tri-n-Butyl Phosphate
TRU	Transuranic

REPORT ON THE BEHAVIOR OF FISSION PRODUCTS IN THE CO-DECONTAMINATION PROCESS

1. INTRODUCTION

A unique characteristic of nuclear energy is that used fuel may be reprocessed to recover fissile and fertile materials, thereby providing fresh fuel for existing nuclear reactors or fuel storage for future reactors [1]. Over the last 50 years, various countries around the globe have operated a partially closed nuclear fuel cycle to recover unused uranium (U) and plutonium (Pu) for future fuel use. By closing the fuel cycle, it is estimated that 25% to 30% more energy is captured from the original U, as well as Pu through the manufacture of mixed oxide fuel (MOX), [2]. Closing the fuel cycle may also reduce the volume of material to be disposed of as high-level waste (HLW) [3]. In addition, removal of the minor actinides (MAs) continues to be an important step additional step in fully closing the used nuclear fuel cycle. Separating the Am from dissolved used nuclear fuel matrixes would also reduce the heat load on future repositories. In the last decade there has been a significant effort in developing processes to recover U and the trans-uranic (TRU) elements from used fuel so they can be recycled as mixed oxide fuel (MOX) or burned in fast reactors [3].

There are several technologies that are under consideration for separating the useful components of used nuclear fuel in the US. Although the behavior of the actinide elements is reasonably well defined in these systems, the same is not true for some of the fission products. The behavior of technetium (Tc), in particular, is poorly defined in these separations systems. In dissolved fuel, Tc is present as the pertechnetate (TcO_4^-) and, as such, does not follow the normal behavior of positively charged metal ions in a solvent extraction process. Furthermore, TcO_4^- is the most stable form of Tc under aerobic conditions [4] making it highly mobile in the environment. To complicate matters, ^{99}Tc is produced in significant quantities in nuclear fuel and, hence, accurate modeling of its behavior is essential for waste management purposes[5].

The Co-decontamination process is based on a liquid-liquid extraction process where U, Np and Pu are removed from used nuclear fuel by tri-n-butyl phosphate (TBP) in an isoparaffinic diluent (such as dodecane) leading to two product streams. The two product streams are produced by selective stripping of U/Pu/Np from the TBP extraction followed by a second product stream containing any residual U. The Co-decontamination process should also extract most of the Tc, along with the U product, which can be removed in a separate scrub step creating a separate Tc waste stream for disposal [6].

Co-decontamination research is currently focused on reproducibly controlling the behavior of key actinides (primarily Np), and TcO_4^-, in the presence of other metals inherent to dissolved used fuel from a PUREX type process. The extraction behavior of TcO_4^- in the Co-decontamination process is assessed in the presence of species present in used fuel that can strongly affect the TcO_4^- extraction. The presence of Zr, Ru, F, as well as U, may affect the extraction product path for TcO_4^- in the raffinate. The concentration dependence of these metals and U have a direct impact as to whether the TcO_4^- follows the majority of the fission products, follows the U steam, or ends up alone in a separate waste stream [6].

The behavior of both TcO_4^- and Np are also affected by the type of reagent used for Pu/U/Np stripping which will determine whether TcO_4^-, or Np, follow the U stream or the

Pu/U/Np stream, respectively. Since acetohydroxamic acid (AHA) is used as a reduction/complexation reagent, it is generally observed that the Tc should follow the U stream while Np will follow Pu/U/Np stream. Even though U is the highest concentration metal in the feed, it is important to evaluate the effects of other lower concentration metals that could potentially interfere with the ability of TcO_4^- to strip out of the U product stream [6]. To this end, batch contact experiments were designed to evaluate the behavior of the TcO_4^- within the Co-decontamination process, allowing for the design of an optimal extraction path during FY14. Results from the previous year's experimental testing revealed Zr and Tc distributions differed from the AMUSE predictions in the presence of a simulant containing all of the fission product metals. In order to ascertain which fission product metal(s) were causing the deviation in distribution ratios from projected, experiments were designed to pair Tc with individual or small groups of key fission products in order to find which metal, or combination of metals, is the cause of the difference.

2. EXPERIMENTAL

All diluents and compounds were reagent grade and used as received. Nano-pure deionized water was used to prepare all aqueous acid solutions. The nitric acid (HNO_3) was trace metal grade from Sigma-Aldrich Chemical Co. (Milwaukee, WI). The aqueous simulant, for all extractions, contains U, Zr, molybdenum (Mo), ruthenium (Ru), and Tc in various combinations or individually. In previous Co-decontamination work, rhenium (Re) was used as a surrogate for Tc; however, the Re surrogate resulted in less accurate results in the presence of other fission product metals and was replaced with a Tc-99 radiotracer for all current work. The simulants were prepared using metal concentrations based on the Co-decontamination simulant feed, listed in Table 1, with the metals of interest in bold with the exception of Tc. The simulant metal concentrations are representative of U, and selected important fission products, present in a dissolved used nuclear fuel composition. The dissolved nuclear fuel composition is estimated as feed to the Co-decontamination process, after scrub dilution, in the recent case study flowsheet analysis performed for the Material Recovery and Waste Form Development Campaign [6]. Stable salts of fission products were used for the simulant, with the exception of a ^{99}Tc radioisotope and depleted U (DU). Nitric acid solutions, as well as the final simulant, were stored in glass to reduce the potential for metal complexation with plasticizers from the degradation of polymer bottles in contact with high acid concentrations. The acid concentration for the simulant throughout the extractions was 2.83 M HNO_3 which represents the acidity of the Co-decontamination process feed after scrub dilution.

Table 1. Dissolved used fuel simulant component concentrations for Co-decontamination. Elements in red are the only metals used for baseline investigations in this experimental work.

Element	New sim. conc. (g/L)	Compound
Ba	0.552	$Ba(NO_3)_2$
Ce	0.774	$Ce(NO_3)_3 \cdot 6H_2O$
Cs	0.036	$CsNO_3$
Eu	0.054	$Eu(NO_3)_3 \cdot 5H_2O$
La	0.397	$La(NO_3)_3 \cdot 6H_2O$
Mo	**0.542**	**H_2MoO_4**
Nd	1.316	$Nd(NO_3)_3 \cdot 6H_2O$
Rb	0.111	$RbNO_3$
Ru	**0.372**	**$Ru(NO)(NO_3)_3(OH)_3$**
Sm	0.269	$Sm(NO_3)_3 \cdot 6H_2O$
Sr	0.260	$Sr(NO_3)_2$
Tc*	**0.552**	**(^{99}Tc) $NH_4[TcO_4]$**
Y	0.145	$Y(NO_3)_3 \cdot 6H_2O$
Zr	**1.095**	**$Zr(NO_3)_2$**
U	**159.0**	**DU [^{238}U (99.69%), ^{235}U (0.3%), ^{234}U] (0.001%)]**

*The Tc-99 used in this work was in tracer concentrations only.

The aqueous phase simulant components were dissolved in 2.83M HNO_3 in varied combinations of metals, with and without the presence of U. The exclusion of U in the initial tests allowed for baseline extraction behavior of the metals to be measured without interference from the dominant U species. A uranyl nitrate solution (100g $UO_2(NO_3)_2$ in 145mL 0.1 M HNO_3) was used to prepare the U containing simulant. The uranyl nitrate solution was diluted from stock to obtain a simulant concentration of 159g/L. The organic phase solvent was 30% TBP in dodecane, which was washed multiple times with a 1 M $NaCO_3$ solution and rinsed with nano-pure water prior to use [7]. The 30% TBP/dodecane solvent was pre-equilibrated three times, at equal volumes, with 2.83M HNO_3 prior to extraction contacts.

The feed simulant and organic 30% TBP/dodecane solvent were contacted at an O/A=1 for 1 minute using a vortex mixer, followed by centrifuging for 5 minutes and separation of the two phases. Two types of batch contact tests were performed, shown in Figures 1 and 2, using the feed simulant, with and without U, and 30% TBP/dodecane.

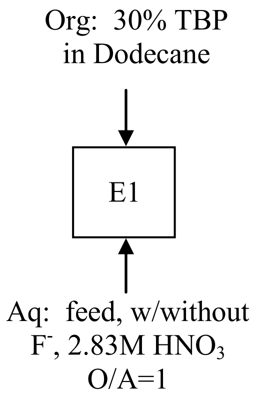


Figure 1. Baseline extraction (E1) testing using varied metals in the feed simulant, with/without U present.

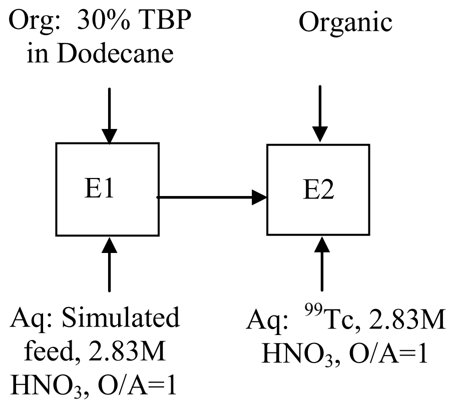


Figure 2. Extraction flowsheet with one initial extraction and a second extraction contact of the organic with Tc only.

A variety of metal combinations were used for each experiment. By limiting the amount of metals in individual experiments, it is possible to observe which fission product metals enhance or interfere with each other, as well as the extraction of U and Tc. For extractions shown in Figure 1, the fission product simulants were contacted as single metals, in metal pairs, or in groups of metals within a single extraction. All tests were run in triplicate and included a non-contacted feed sample for mass balance comparison. The flowsheet tests, using the flowsheet from Figure 2, included varied concentrations of fluoride anion (F^-) added to the simulant in order to duplicate the potential presence of hydrofluoric acid (HF) in the Co-decontamination feed if it were included in the dissolution process. The F^- concentrations used, in the form of sodium fluoride (NaF), were 0.02, 0.04, and 0.06M F^-.

The analysis of metals in all aqueous phase samples was performed using inductively coupled plasma-mass spectroscopy (ICP-MS) as well as analysis of organic and aqueous phases using liquid scintillation counting (LSC) for the U and Tc containing samples. Mass balances for the ICP-MS aqueous phase samples were determined by calculation of the organic phase metals through use of a standard feed solution as a baseline measurement.

3. RESULTS AND DISCUSSION

A series of tests were conducted using a narrowed group of simulant components with metal concentrations equivalent to the estimated Co-decontamination process feed. Individual and group component tests with U, Zr, Mo, Ru, and Tc were performed in order to provide information on the behavior of key fission product constituent interactions with Tc. Included in this work were batch contact flowsheet tests performed with one extraction contact for loading U and Zr followed by a second contact of the loaded solvent with Tc. Tests were also performed with a stimulant that included NaF for varied groupings of metals in order to identify how F^- impacts U, Zr, Mo, Ru, and Tc components individually and together. The distribution ratios for each metal are based on the aqueous phase ICP-MS analysis and the mass balance calculated organic phase concentration as well as direct activity measurements by LSC for U and Tc radiotracers. All distribution ratio points are the mean of triplicate extractions with an average percent error of <3%.

A series of batch contact tests, using the E1 extraction scheme in Figure 1, were conducted to experimentally compare the distribution ratios of U, Zr, and Tc extracted with 30% TBP with results predicted by the AMUSE code. The resulting interactions of U, with both Tc and Zr, are shown in Figure 3. The distribution coefficients obtained show reasonable agreement between experiment and AMUSE predictions for U and Zr for the different contacts. However, Tc in the presence of Zr does not follow the AMUSE code results. Technetium extracted alone, represented in Figure 3a Tc-neat, also shows variance from the AMUSE prediction, but this may be attributed to issues related to ICP-MS analysis. Because of the potential for analysis issues from ICP-MS, an LSC analysis protocol was added as a check for continuity for radionuclide tracers to future experiments. Alpha-beta discrimination was employed on the LSC for detection of U and Tc radionuclide tracers while all of the stable metals, as well as U and Tc, were analyzed by ICP-MS.

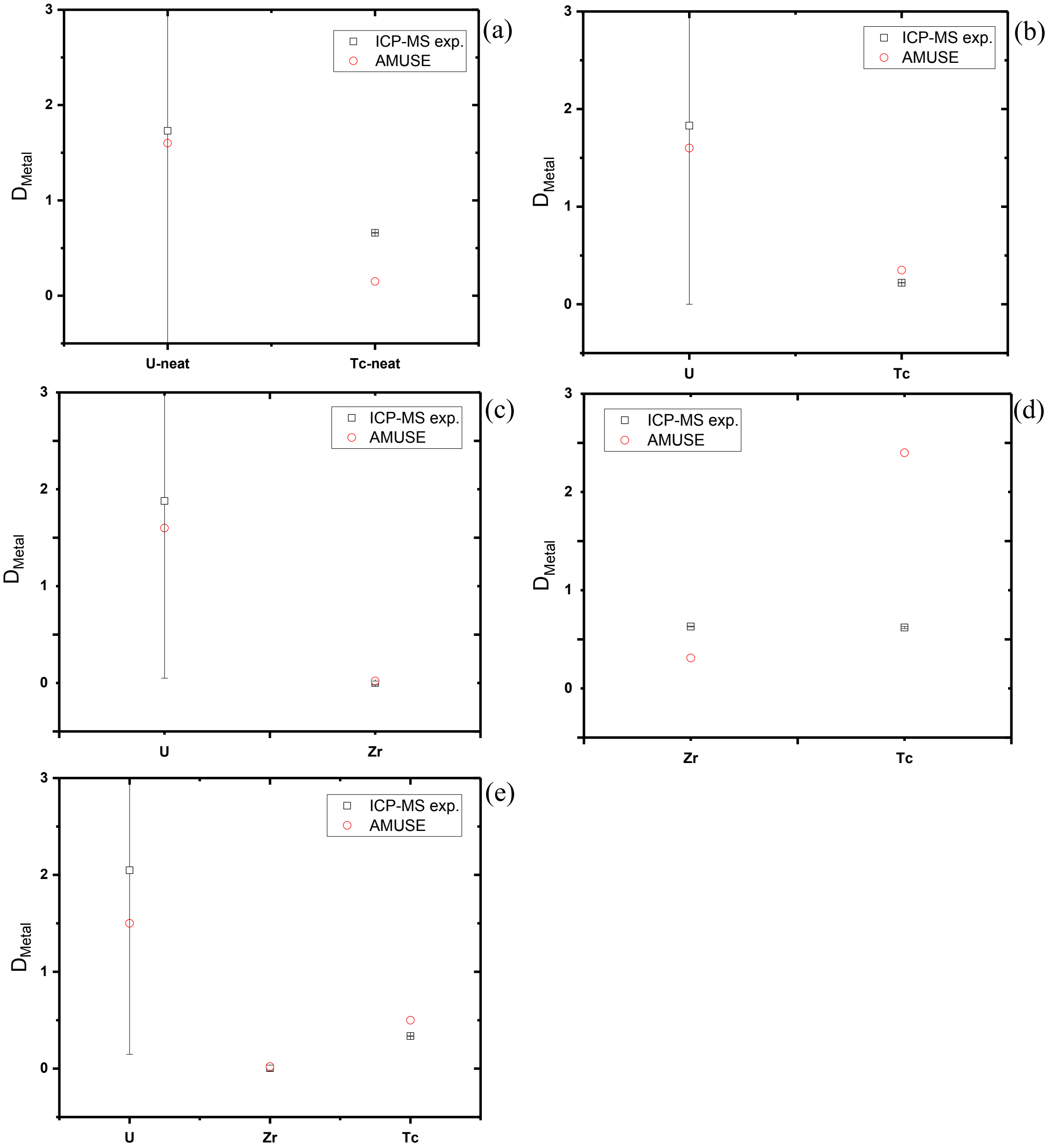


Figure 3. Distributions for varied metal combination extractions in 2.83M HNO_3 contacted with 30% TBP/dodecane. (a) Neat contacts of U and Tc extracted separately. (b) Combined U and Tc extraction. (c) Combined sample of U and Zr extraction. (d) Combined sample of Zr and Tc extraction. (e) Combined sample of U, Zr, and Tc extraction.

The next phase of extraction experiments, based on results shown in Figure 3, employed a batch contact flowsheet design. The flowsheet experiment, Figure 2, was performed in order to evaluate the extraction behavior of Tc in the presence of U, Zr, and a combination of both metals with the respective distributions shown in Figure 4. The first contact, E1, was used to load U in a 30% TBP/dodecane solvent after which the loaded organic solvent was contacted with a 2.83M HNO_3 solution containing Tc (E2). The E1 extraction distributions measured for U compared well with modeling results (U distributions of D=1.9, 1.7, and 1.6 for ICP-MS, LSC, and AMUSE, respectively). However, the distributions for U in the E2 extraction showed variable results between both experimental analysis and the AMUSE prediction, with U distributions of D=6.1, 3.1, and 4.2 for ICP-MS, LSC, and AMUSE, respectively. The distribution ratios for Tc in E2 showed good agreement between experimental and modeling with a standard deviation of ±0.068 for the two analysis protocols. Since the ICP-MS and LSC results for U differ by such a wide margin, further investigation will be needed to establish reproducible results for U within the different analysis protocols.

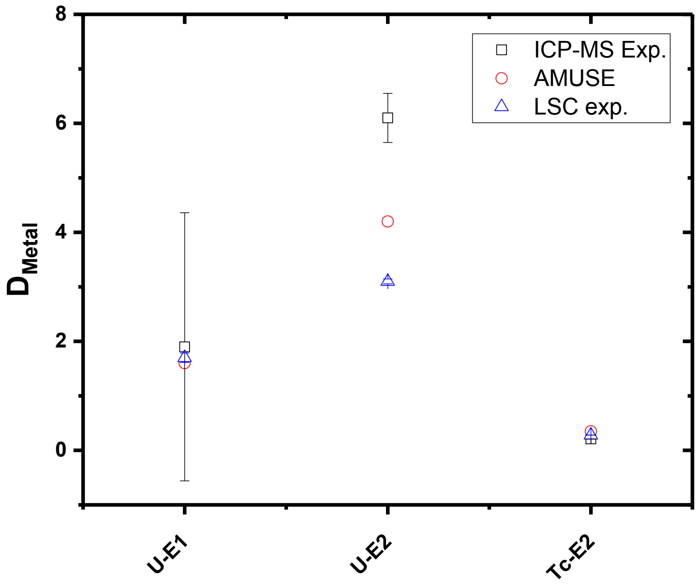


Figure 4. Distributions of U in 2.83M HNO_3 (E1) contacted with organic phase of 30% TBP in dodecane. The organic phase (loaded U organic) is contacted with Tc in 2.83M HNO_3 (E2).

Figure 5 shows extraction distributions for Zr and Tc under the same E1/E2 flowsheet extractions previously used in Figure 4 for U. The AMUSE model predicts distributions for Zr for E1 and E2 of 0.31 and 0.32, respectively, while the distribution for Tc in E2 was 0.70. The experimental test results showed distributions for Zr to be considerably lower than predicted by AMUSE with a D=0.034 for E1 and a distribution at detection limits, for E2.

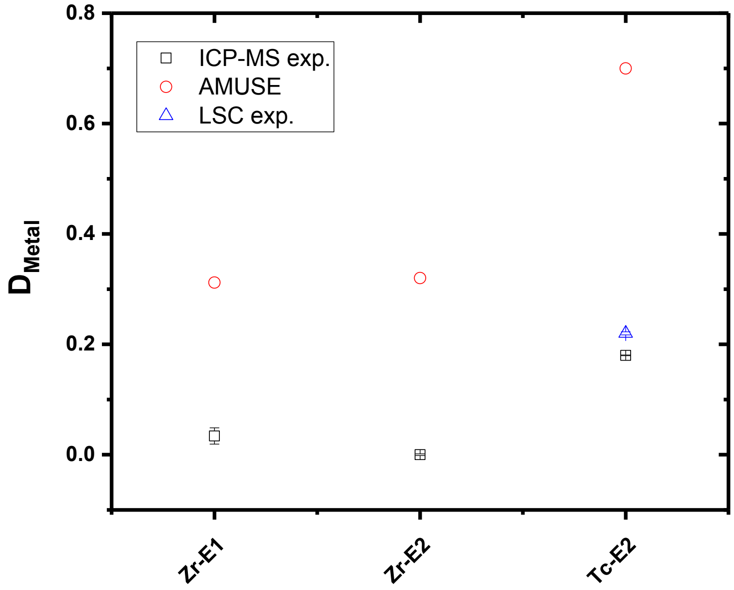


Figure 5. Distributions of Zr in 2.83M HNO_3 (E1) contacted with organic phase of 30% TBP in dodecane. The organic phase (loaded Zr organic) is contacted with Tc in 2.83M HNO_3 (E2).

The final batch contact flowsheet experiment, shown in Figure 6, is a combination of U and Zr in the E1 extraction followed by contact with Tc in E2. This contact was performed in order to evaluate the behavior of loaded U and Zr interactions with Tc. The experimental distributions for Zr in both E1 and E2 are below detection limits at <0.010g/L and these distributions are well below those predicted by AMUSE with D=0.021 and 0.049 for E1 and E2, respectively. The lower distributions for Zr in the presence of U can be attributed to extraction suppression of Zr by vastly larger amounts of U being extracted and loading the TBP.

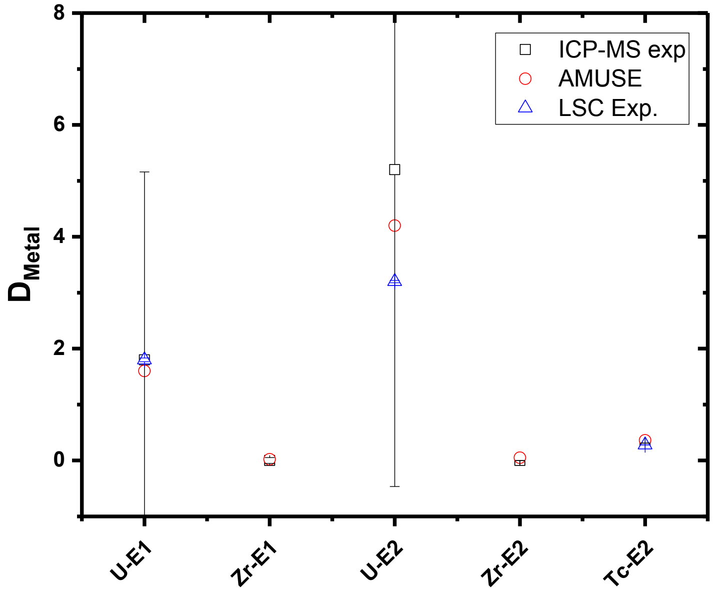


Figure 6. Distributions of U and Zr combined in 2.83M HNO_3 (E1) contacted with organic phase of 30% TBP in dodecane. The organic phase (loaded U and Zr organic) is contacted with Tc in 2.83M HNO_3 (E2).

Results from the flowsheet experiments showed little to no change in the distributions for U between the different tests. For E1, the U distributions were consistent with the AMUSE predictions in all flowsheets; however, U distributions for E2 did vary slightly between the two analysis techniques used with AMUSE predictions sitting between the two experimental techniques. Further investigation is needed to establish a more consistent baseline for the loaded U contacts with the two analysis regimes.

A second set of experiments was conducted that incorporated F^-, which was added in the form of NaF, in order to account for F^- present in dissolved fuel that may result from hydrogen fluoride (HF) added in the dissolution of the fuel. Prior experimental results have suggested that this may impact the distribution of metals present in the simulant. From previous literature [6], it has been shown that Tc should report to the organic phase at concentrations of approximately ≥0.05M F^- and at concentrations of ≤0.04M F^- the Tc will stay with the aqueous raffinate. Figure 7 shows the results of the F^- incorporated simulant batch contact where both experimental and AMUSE distributions are within statistical error for U, Zr, and Tc. However, Tc samples containing no F^- and the lowest concentration of F^-, 0.02M, are lower than predicted by AMUSE. This trend for Tc distributions is only seen in extractions with certain metal pairings and will need to be investigated further in order ascertain the behavior of Tc within these metal combinations.

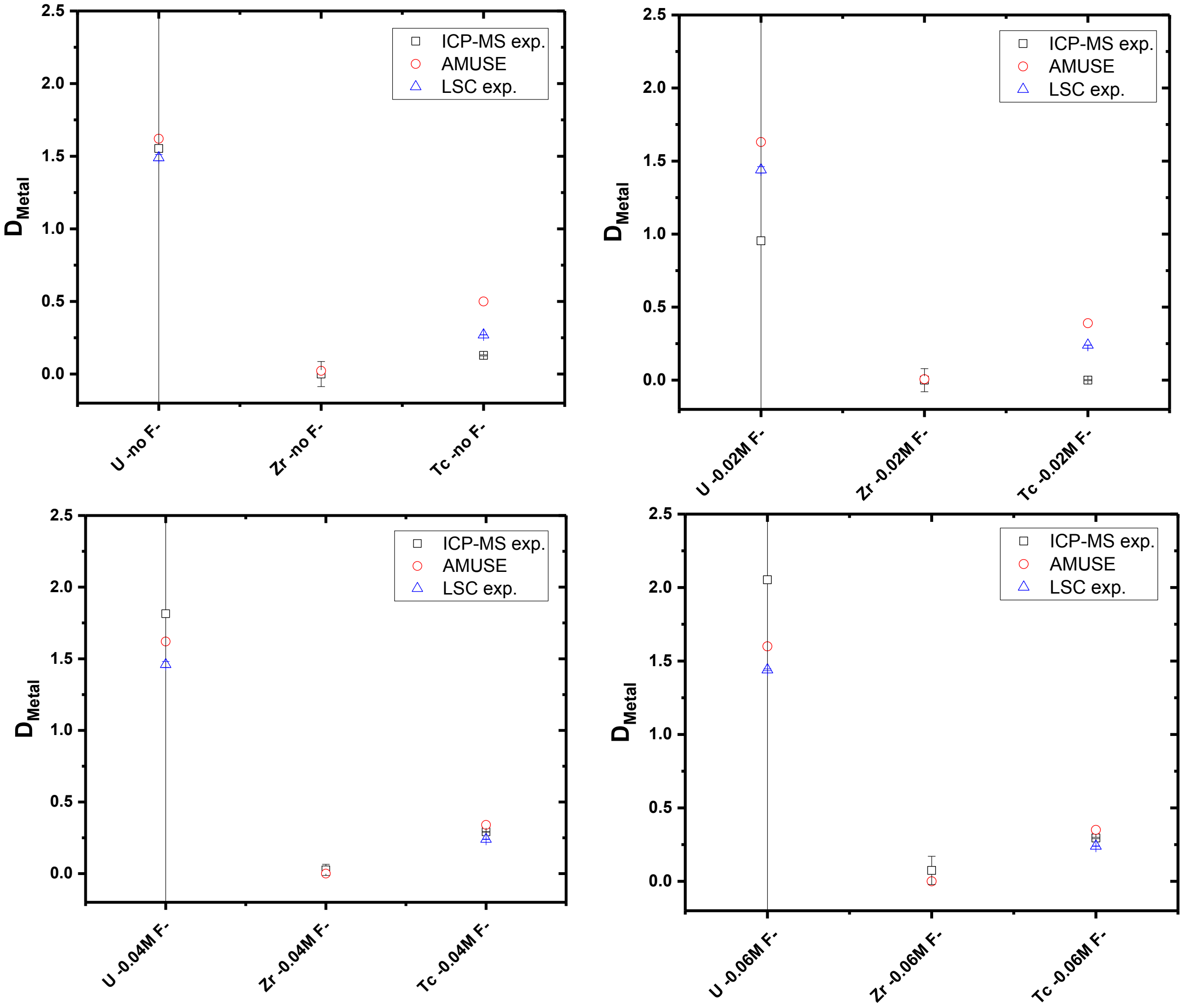


Figure 7. Distributions of U, Zr, and Tc with and without varied concentrations of F$^-$present in the form of NaF compared against AMUSE predictions.

An additional experiment using F$^-$ was performed that incorporated U, Zr, Tc, Ru, and Mo with the distribution results shown in Figure 8. The distribution for Ru is considerably higher than predicated by AMUSE and is most likely due to the nitrosyl ruthenium trinitrato [$RuNO(NO_3)_3$] complex. Nitrosyl Ru complexes have been shown to exhibit high distribution at higher concentrations of nitric acid using TBP. Tri-butyl phosphate complexes with ruthenium and forms $RuNO(NO_3)_3 \cdot 2TBP$. As a general rule, the more nitrato groups (NO_3^- groups) present in the molecule, the better the compound is extracted by TBP, while nitro-compounds (NO) are relatively unextractable [8]. It has been shown that Ru will complex easily with F$^-$ to form the RuF_3 complex at dilute concentrations of F$^-$ which reports to the organic phase. However, the results for Ru show very low distributions across all of the F$^-$ concentrations. These low distributions for Ru in the presence of F$^-$ maybe due to interference with the high levels of nitrosyl causing a suppression of Ru distributions.

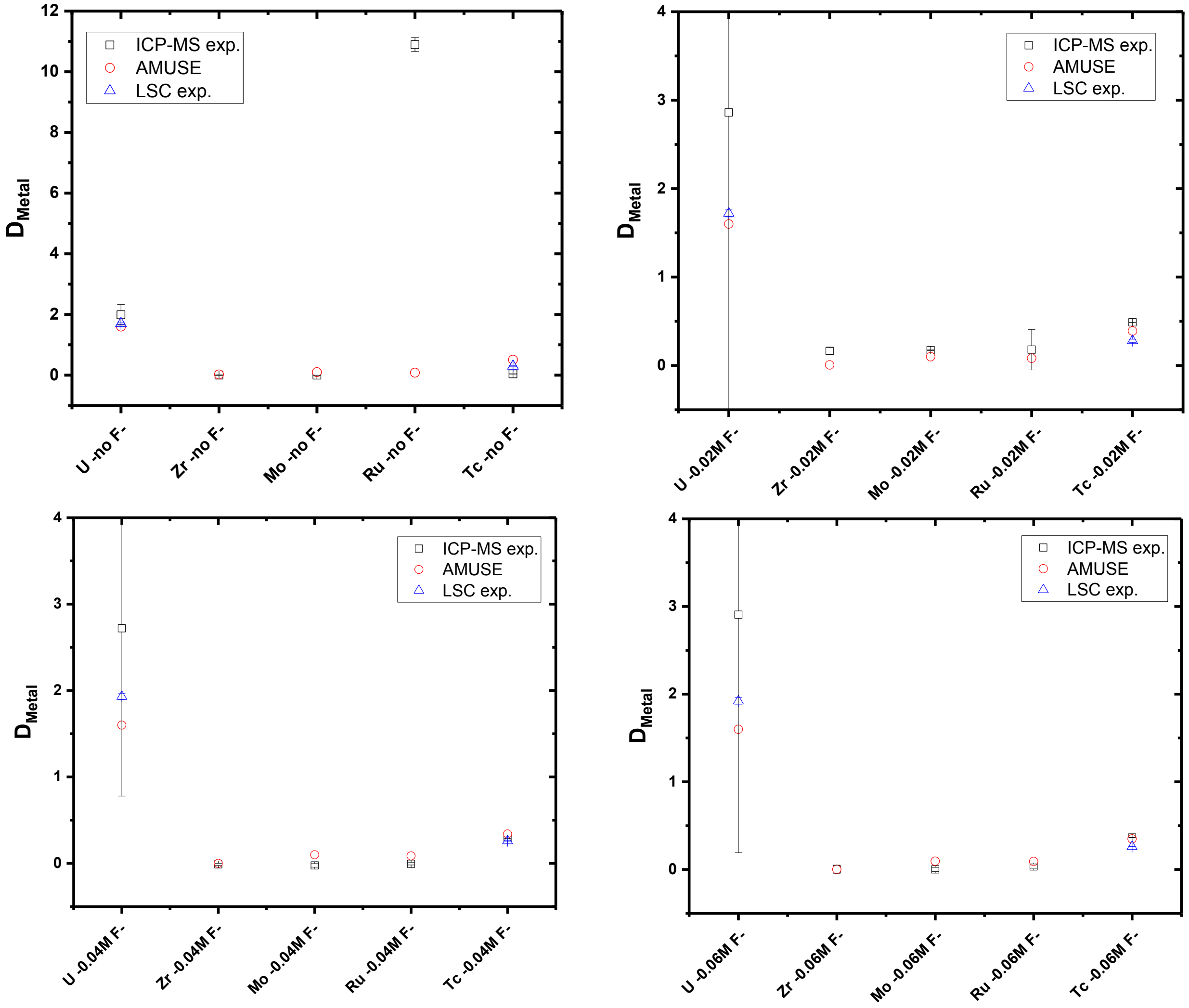
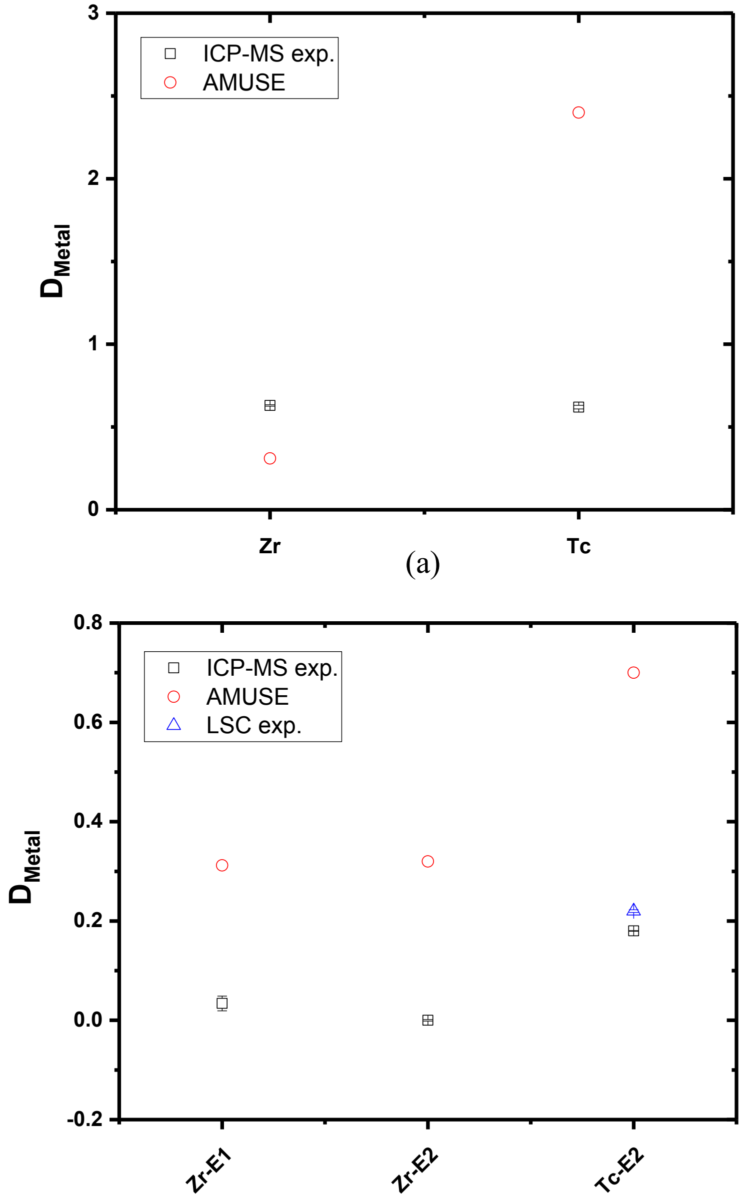


Figure 8. Distributions of U, Zr, Mo, Ru, and Tc with and without varied concentrations of F$^-$ present in the form of NaF.

Ruthenium also showed different extraction behavior when compared to previous Co-decontamination experimental work performed in FY14 [7], using a complete metal simulant as opposed to contact with only U, Zr, Mo, and Tc. Distributions for Ru in the presence of all metals, from Table 1, was D=0.24 and, in the presence of the limited metal composition, shown in Figure 8, the distribution is D=10.9. This behavior for Ru in the presence of both F$^-$ and varied metal concentrations is not typical and warrants further investigation.

From previous Co-decontamination work, shown in Figure 9, a comparison can be made with respect to the relationship between Tc and Zr distributions when no other metals are present. Zirconium is seen to enhance the extraction of Tc; Figure 9a shows this trend in the



(a)

(b)

Figure 9. Comparison of Tc distributions, in the presence of Zr, for experimental and AMUSE modeling. (a) Tc and Zr in 2.83M HNO_3, where Zr is contacted with 30% TBP/kerosene, from previous work, and (b) Tc and Zr contacted with 30% TBP/dodecane.

experimental data; Zr with D=0.63, and Tc with a D= 0.62. Although the AMUSE predictions are lower for Zr and substantially higher for Tc, it has been shown in previous literature [9], that the experimental values in 9a reflect enhanced distribution ratios for both Zr and Tc.

This trend for Tc is repeated in Figure 9b where Zr is extracted once and the organic contacted with Tc. Although the distribution ratios for Zr are lower than predicted by AMUSE, the Tc distribution shows a similar pattern with the plot in 9a. The change in Zr distribution ratios, compared between the two plots, may possibly be explained by the difference in extraction set up for the different experiments.

Figure 10 depicts simulants and extraction solvent combinations for both full metal simulant as well as the baseline limited metal simulant extractions.

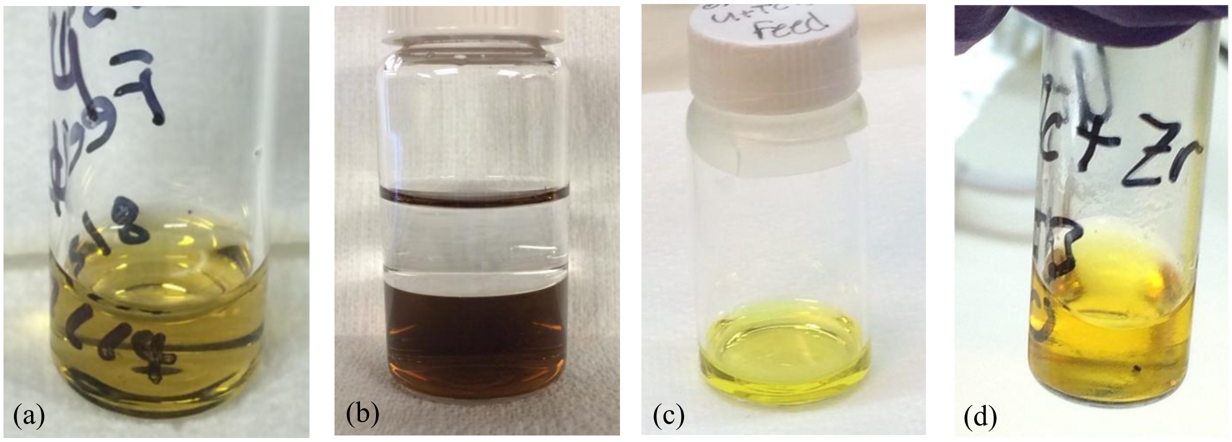


Figure 10. (a) Co-decontamination simulant containing all elements from Table 1. (b) Metal simulant, excluding U, after extraction with 30% TBP/dodecane where the top fraction is a light phase organic with the aqueous phase on the bottom. (c) Co-decontamination simulant containing only U, Zr, and Tc in 2.83M HNO_3. (d) Organic phase, 30% TBP, after separation from 2.83M HNO_3 solution containing U, Zr, and Tc.

4. CONCLUSIONS AND CONTINUING WORK

Experimental data and computational values matched in many of the experiments performed and new experimental work will be designed based on these outcomes. Experiments that did not match well with the AMUSE code will need to be studied in more detail to layout a matrix that will reconcile experimental results and AMUSE in areas of; acid dependence data, Zr and Tc concentration, and F^- for additional input into AMUSE to update the code. For the experimental data that did match well, it may be more appropriate to consider a full simulant study at this point to ensure that the experimental data does not vary from the baseline with all raffinate ions present. Future work will also require an expansion of the flowsheet tests to incorporate multiple extraction steps as this may lead to other differences observed between the AMUSE code and experimental results.

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