

SEPARATION OF TECHNETIUM AND RARE EARTH METALS FOR CO-DECONTAMINATION PROCESS

Actinide Separations Conference

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SEPARATION OF TECHNETIUM AND RARE EARTH METALS FOR CO-DECONTAMINATION PROCESS

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Introduction

There are several technologies that are under consideration for separating the useful components of used nuclear fuel in the United States. However, although the behavior of the actinide elements is reasonably well defined in these systems, the same is not true for the fission products. The behavior of technetium (Tc) in particular is poorly defined in these separations systems. In dissolved fuel, Tc is present as pertechnetate (TcO_4^-) and as such, does not follow the normal behavior of positively charged metal ions in a solvent extraction process. Further, TcO_4^- is the most stable form of Tc under aerobic conditions [1] 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 [2]. The Co-Decontamination process is based on a liquid-liquid extraction process where uranium (U), neptunium (Np) and plutonium (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 also extracts most of the Tc, along with the U product, which can be removed in a separate step creating a separate Tc waste stream for disposal.

Co-Decontamination research is currently focused on reproducibly controlling the behavior of key actinides, and TcO_4^- , in the presence of other metals inherent to dissolved used fuel feed to a PUREX type process. The extraction behavior of TcO_4^- in the Co-Decontamination process is assessed in the presence of metals that can strongly affect the TcO_4^- extraction. The presence of zirconium (Zr), ruthenium (Ru), fluoride (F), as well as U may affect the extraction product path for TcO_4^- in the raffinate. The behavior of both TcO_4^- and Np are also affected by the type of reagent used for Pu stripping which will determine whether TcO_4^- , or Np, follow the U stream or the Pu stream, respectively. 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 [3]. To this end, solvent extraction contacts have been performed to experimentally evaluate the behavior of the TcO_4^- within the Co-Decontamination process allowing for the design of an optimal extraction path.

Methods

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. A single batch contact test, Figure 1, was performed for each combination of elements, shown in Figure 2, in 2.83 M HNO_3 . The acid concentration for the simulant throughout the extractions was 2.83 M HNO_3 which represents the acidity of the feed to Co-Decontamination.

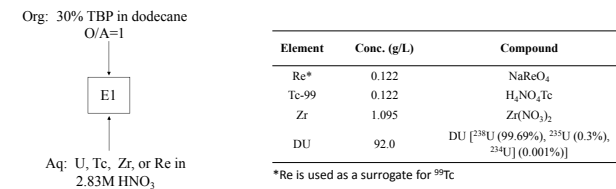
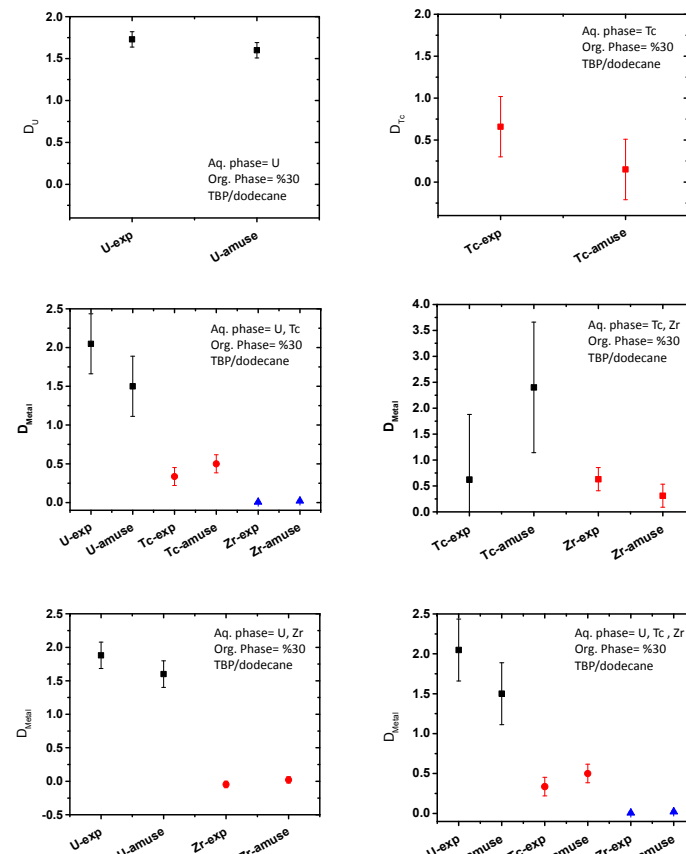


Figure 1. Batch contact schematic for Co-Decontamination process separations

Figure 2. Target metals of interest with in the Co-Decontamination process

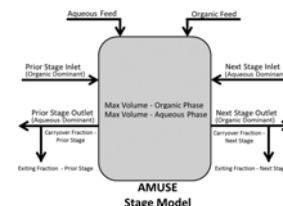


Results

The Argonne Model for Universal Solvent Extraction (AMUSE) is used to simulate multi-stage aqueous liquid-liquid solvent extraction processes for components of interest to spent nuclear fuel reprocessing and was used to analyze the Co-Decontamination process. A series of batch contact tests were conducted to experimentally compare the results of U, Zr, and Tc extracted with 30% TBP against the AMUSE modeling code. The resulting interactions of U, with both Tc and Zr, are shown below. The plots are divided up by metal combinations and both the AMUSE and experimental data are shown side-by-side. The results show a reasonable comparison between experimental and modeled distributions for U and Zr for the different contacts, however, Tc in the presence of only Zr does not follow the AMUSE code results compared to experimental. Technetium extracted alone also shows variance from the AMUSE analysis, but this may be attributed to issues related to ICP-MS analysis.

Predicted AMUSE model distributions for the extractions using varied metal combinations experimentally.

Organic Phase	Aqueous Phase	Experimental Distributions	AMUSE model Distributions
30% TBP/dodecane	U	1.73	1.6
30% TBP/dodecane	Tc	0.66	0.15
30% TBP/dodecane	Tc	0.62	2.4
30% TBP/dodecane	Zr	0.63	0.31
30% TBP/dodecane	U	1.88	1.6
30% TBP/dodecane	Zr	ND	0.021
30% TBP/dodecane	U	1.83	1.6
30% TBP/dodecane	Tc	0.22	0.35
30% TBP/dodecane	U	2.05	1.5
30% TBP/dodecane	Tc	0.34	0.5
30% TBP/dodecane	Zr	0.006	0.021
30% TBP/dodecane	U	1.93	1.5
30% TBP/dodecane	Zr	ND	0.021
30% TBP/dodecane	Re	0.032	na



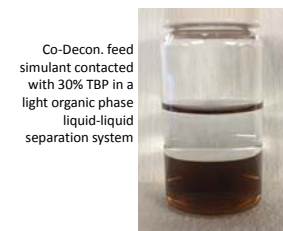
Representation of the stage model used in the AMUSE model code.

Element	New sim. conc. (g/L)	Compound
Ba	0.551	$\text{Ba}(\text{NO}_3)_2$
Ce	0.774	$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$
Cs	0.036	CsNO_3
Eu	0.054	$\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$
La	0.397	$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$
Mo	0.542	H_2MoO_4 (161.95g/mol)
Nd	1.316	$\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$
Rb	0.111	RbNO_3
Re	0.122	NaReO_4
Ru	0.372	$\text{Ru}(\text{NO})_2(\text{NO}_3)_3(\text{OH})_3$
Sm	0.269	$\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$
Sr	0.260	$\text{Sr}(\text{NO}_3)_2$
Y	0.145	$\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$
Zr	1.095	$\text{Zr}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$
U	159.0	$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
Tc	0.122	Tc-99 in 0.01M HNO_3

Co-Decon. feed simulant composition for continuing work on Tc and rare earth metals separations.



Co-Decon. feed simulant prepared for batch contacts. To this simulant will be added both U and Tc used in the baseline experiments.



Co-Decon. feed simulant contacted with 30% TBP in a light organic phase liquid-liquid separation system

Conclusions

The experimental results are generally in good agreement with the predicted AMUSE model for the extraction of Tc, U, and Zr in various combinations, with a few exceptions. Future work will expand on these initial tests by incorporating U, Tc, and Zr in the full metal spectrum of Co-Decontamination feed raffinate which will be compared to AMUSE model distributions.

Acknowledgements

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