Examination of the purification step of the PUREX process with varying HNO_3 concentration

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Detection and quantification of Pu in proliferated material is of great importance to national security. Pu is created through the irradiation of UO_2 in a nuclear reactor and is later separated from fission products and uranium for further usage. One of the primary ways this is accomplished is through the PUREX process [1,2], which has the main objective of separating and purifying U and Pu from each other and the fission products such as ^{137,134}Cs, ^{144}Ce, ^{155,154}Eu, ^{106}Ru, and ^{125}Sb. This separation scheme is a complex process with many conditions that could potentially be varied, which could in turn affect the effectiveness of separation. This change in effectiveness, specifically when comparing the ratio of Pu to other fission products, can give information as to the conditions being used during separation and potentially attribute the proliferated material to a source.

To achieve comparable data, a laboratory mockup of the PUREX process was created based on published data on the Barnwell Nuclear Fuel Plant as there is a large amount of detail known specifically about the concentrations of the aqueous and organic streams used in the extraction processes, including temperature and acid concentration. This fuel reprocessing was constructed in South Carolina but never commercially opened and eventually decommissioned. The fuel that was used for the experiment was obtained from a High Flux Isotope Reactor (HFIR) source. Specifically, studies have been conducted to determine the effect of HNO_3 concentration on extraction yield and decontamination factor in nuclear fuel samples.

The extraction process used in this experiment utilized a sample of irradiated uranium dioxide irradiated in a pseudo-fast neutron spectrum. A working solution containing approximately 0.5% of the fuel pellet activity per 500 μL was created with a HNO_3 concentration of 4 M. This was used in the aqueous phase of the extraction with a total volume of 3 mL with organic phases of 1 mL consisting of n-dodecane. Prior to phase mixing, approximately 100 μg of $NaNO_2$ was added to the aqueous phase containing the HFIR fuel aliquot and both phases were heated to 75 °C using an oil bath to achieve an oxidation state of +4 in Pu necessary for extraction and uniform temperature. After allowing this process to occur for 5 min, the oil bath was turned down to the desired temperature for chemical separation. The phases were then mixed and shaken vigorously for 2 min to ensure thorough mixing for extraction. The phases were then allowed to separate via gravity before being subjected to centrifugation for 1 min at 3000 rpm. The phases were then extracted using a pipette to obtain a 500 μL aliquot of the organic phase and a 1 mL aliquot of the aqueous phase for characterization. One 3 M HNO_3 extraction was conducted at 35 °C for proof of concept and a 1 M, 3 M, 5 M, 7 M, and 9 M HNO_3 series were conducted at 25 °C.

Gamma spectroscopy of the sample was taken of each organic phase and aqueous phase post-extraction using a high-purity germanium (HPGe) detector. All aqueous samples were counted with real times of 1200.00 s. All organic samples were counted with real times between 60000.00 to 90000.00 s to achieve lower error in measurements. A background measurement lasting 87300.00 s was taken and subtracted out of all measurements. The HFIR working solution was counted with a real time of 14400.00 s. The energy and efficiency calibrations of the instrument was performed using a ^{152}Eu source.

All samples used in alpha spectrometry were taken by using a 20 µL aliquot of the final organic phase and performing a back extraction with 1 mL of 0.03 M HNO_3. Once this mixture had been vortexed for 2 min and centrifuged at 3000 rpm for 1 min, a 20 µL aliquot of the aqueous phase containing the extracted Pu was taken, placed on a planchet, allowed to evaporate, and deposited. These samples were then counted using an alpha spectrometer with count times of a minimum of 43200.00 s. A background of the alpha spectrometer was taken for 129600.00 s and subtracted from results. The HFIR working solution was counted for 259200.00 s. The energy and efficiency calibrations of the instrument were determined using a standard containing ^{148}Gd, ^{239}Pu, ^{241}Am, and ^{244}Cm.

The initial trial of the extraction performed at known conditions (35 °C, 3 M HNO_3, 3:1 aq:org phase ratio) proved to be successful in extracting Pu from the other fission products. Alpha spectrometry indicates that approximately 46% of the Pu was successfully extracted from the aqueous phase. Additionally, gamma spectroscopy showed favorable results with regards to the decontamination factor of the fission products in the final organic phase for this single sample.

The series of trials that varied the concentration of HNO_3 from 1 M to 9 M in 2 M increments indicated that there was no significant change in DF for ^{155}Eu, ^{154}Eu, and ^{241}Am between the varying concentrations except for the 1 M trial, which resulted in a significantly lower Pu extraction at 0.40% compared to an average of 47% extraction. This appears to indicate that the fission products have a generally uniform behavior with regards to varying HNO_3 concentration, with the notable exceptions of ^{137}Cs and ^{106}Ru, which can be observed in Fig. 1. These deviances may potentially be due to experimental

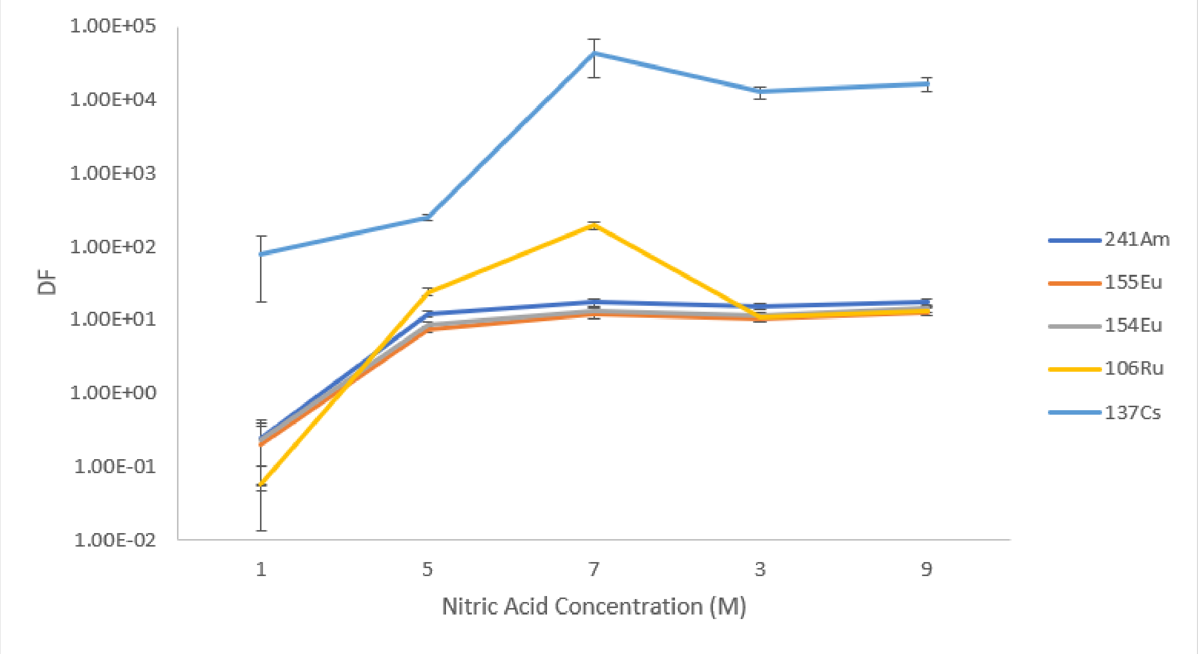

FIG. 1. Decontamination factors of measured fission products performed at 35 °C and varying HNO_3 concentrations.

error as the data was not collected in triplicate to minimize fuel usage, and further studies are being conducted to determine this.

[1] H.A.C. McKay, K.P. Bender, L.L. Burger, and J.D. Navratil, *The PUREX Process*, (CRC Press, Inc. United States, 1990).
[2] M. Benedict, T.H. Pigford, and H.W. Levi, *Nuclear Chemical Engineering*, (McGraw-Hill, New York, 1981).