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Sequential extraction of uranium metal contamination

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Abstract Samples of uranium contaminated dirt collected from the dirt floor of an abandoned metal rolling mill were analyzed for uranium using a sequential extraction protocol involving a series of five increasingly aggressive solvents. The quantity of uranium extracted from the contaminated dirt by each reagent can aid in predicting the fate and transport of the uranium contamination in the environment. Uranium was separated from each fraction using anion exchange, electrodeposition and analyzed by alpha spectroscopy analysis. Results demonstrate that approximately 77 % of the uranium was extracted using NH_4Ac in 25 % acetic acid.

Keywords Sequential extraction · Uranium contamination · Uranium · Alpha spectroscopy

Introduction

The primary objective of nuclear forensics analysis is to reveal the chemical, physical, and radiological attributes of a material so that its provenance can be determined. Although a sample can be analyzed using a variety of methods and procedures, there is no simple relationship between the results of these analyses and the origin and provenance of the material. Samples collected at former nuclear weapons legacy sites contain quantities and types of radioactive contamination from historical operations and processes that are well described in site historical documents. For example, Linking Legacies, a document published by the U. S. Department of Energy, provides the history and the relationship between the measured attributes of a sample collected at a legacy site and its provenance [1].

This project has analyzed residual uranium contamination in samples of the dirt floor collected at a former uranium metal rolling mill, where hot forged uranium metal billets were rolled into rods between 1948 and 1956 for the U. S. Atomic Energy Commission. Fortunately, historical documents are available to describe the type and amount of uranium metal that was rolled at this mill so that the provenance is well defined such that analysis of residual contamination can be directly attributed to the source materials [2, 3]. The metal rolling mill operated from 1910 until 1958, so samples also contain remnants stable metals in addition to uranium. The building and its contents were abandoned in situ and is now part of the Formerly Utilized Sites Remedial Action Program (FUSRAP). Contamination from uranium and other stable metals in the dirt floor of the mill have been exposed to rain, ice, snow, and animal infestation for over 50 years. Exposure to resuspended dirt and dust during eventual remediation of this legacy site represents a potential risk to workers, the environment, and general population. Environmental mobility of the residual uranium contamination was investigated by exposing samples of the dirt to a sequence of increasingly aggressive reagents and measuring the quantity of uranium that was extracted from each fraction.

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Experimental

Sequential extraction

Approximaly 1.5 g of uranium metal contaminated dirt was dried overnight at 100 °C. Four replicate 0.28 g samples of the dried uranium dirt were placed into labeled 125 mL Nalgene plastic bottles. Each bottle was subjected to a sequential extraction protocol involving 40 mL of a series of five progressively aggressive reagents to evaluate uranium extracted [4, 5]. Table 1 lists the extracting reagents, concentrations, temperature, duration of the extraction, function of the extracting reagent and average fraction extracted. Each extracting reagent was made using 18 MΩ cm DI H_2O and certified ACS grade reagents and acids.

Extraction was performed with each sample in a temperature controlled shaking water bath with the exception of the fourth extracting fraction which was performed on a hotplate. For this extracting fraction the sample was transfered to a 50 mL glass beaker in a slurry with 0.05 M HNO_3 (15.6 mL), and covered with a watch glass while dropwise adding 30 % H_2O_2 (24.4 mL) throughout the reaction period. After each extraction period, samples were centrifuged at 3000 rpm for 20 min and the supernatant was withdrawn by vacuum through a 5 mL Finntip filter into new 125 mL Nalgene bottle. Any residual sample remaining after completing the extraction sequence was transferred in a slurry with H_2O to a platinum dish and fused with 3 g KF until a clear melt was achieved. Silica was removed by adding 4 mL of concentrated sulfuric acid to the fusion cake and heating over a low flame to evolve silicon tetrafluoride. The cake was heated again with an additional 0.5 g of KF until fuming subsided to volatilize any remaining silica. Two grams of sodium sulfate was added and heated until a clear melt was achieved [6, 7]. The fusion cake was cooled, transferred to a 250 mL glass beaker, and dissolved in 1:3 ratio of HNO_3:HCl. After allowing the sample to dry overnight, 50 mL of concentrated HNO_3 was added and dried again. The sample was reconstituted with 50 mL of 8 M HNO_3.

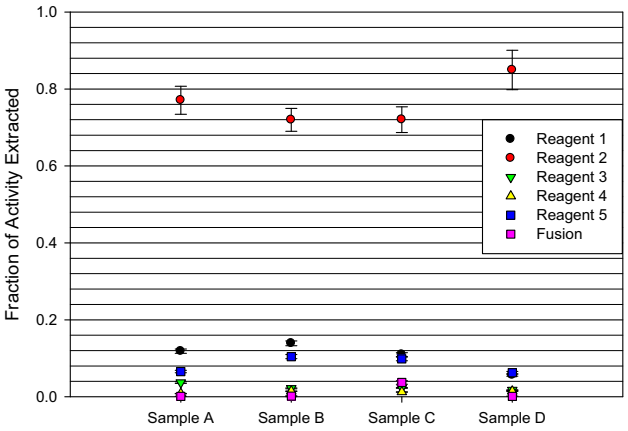

Fig. 1 Fraction of ^{238}U activity extracted by all reagents and fusions from each sample of uranium contaminated dirt analyzed by Alpha Spectroscopy

Separations

Gross alpha activity in 1 mL aliquots of each extraction fraction was determined using liquid scintillation counting (LSC) to establish the appropriate sample volume for further radiochemical analysis. The 8 M HNO_3 fused solutions were diluted to 1.33 M before LSC counting to minimize quenching. Initial radiochemical analysis involved addition of approximately 10–20 disintegrations per minute (dpm) of NIST SRM 4324B 232U tracer to each sample followed by wet ashing with concentrated HNO_3. Each sample was reconstituted in conc. HNO_3 and dried twice to promote thorough mixing. Dried samples were reconstituted and wet ashed in concentrated HCl and then dried three times to convert to chloride form. Uranium was separated from each sample solution using an anion exchange procedure described below [8, 9].

Twenty milliliter Bio-Rad columns were prepared for each sample by adding 6 mL of pre-cleaned resin (AG1×4 100–200 mesh chloride-form P/N 140-1341). Samples extracted in NH_4Ac in 25 % acetic acid required using 12 mL of resin to accommodate increased saturation of the resin. The resin was conditioned by rinsing the column

Table 1 List of reagents and extraction conditions [4, 5]

Extracting reagent	Concentration (M)	Temperature	Time (hr)	Function	Average fraction extracted	1σ
$MgCl_2$	0.1	25 °C	1	Exchangables	0.11	3.52e−2
NH_4Ac in 25 % HAc	1	50 °C	2	Carbonates	0.77	6.10e−2
NH_2OH in 25 % HAc	0.1	70 °C	6	Reducing	0.02	8.44e−3
30 % H_2O_2 in 0.02 M HNO_3	–	70 °C	3	Organics	0.01	2.88e−3
HNO_3	4	70 °C	4	Oxidizing	0.08	2.17e−2

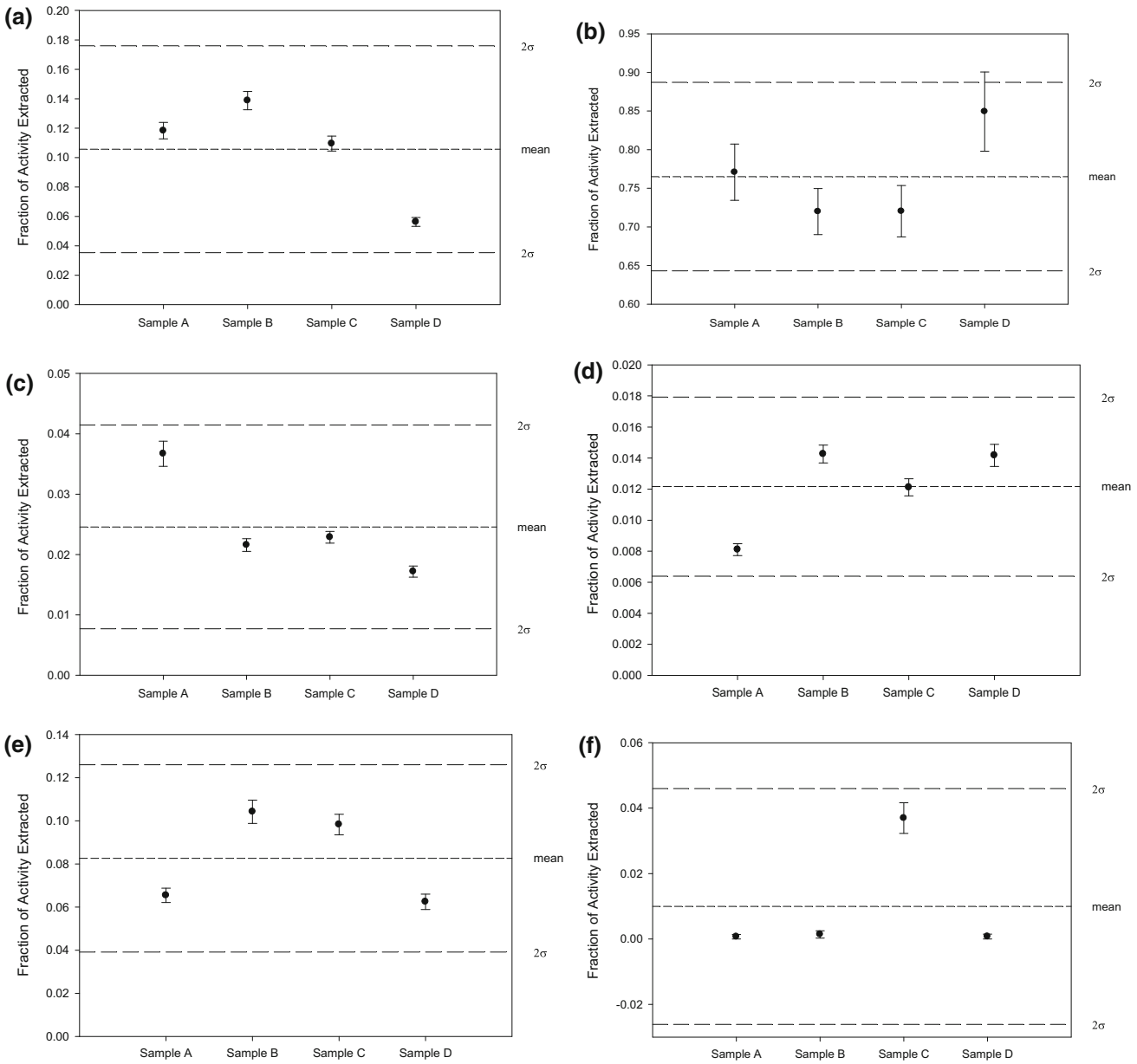

Fig. 2 Fraction of ^{238}U activity extracted from each sample using **a** Reagent 1, **b** Reagent 2, **c** Reagent 3, **d** Reagent 4, **e** Reagent 5, **f** Fusion

with five column volumes of 9 M HCl. Each dried sample was reconstituted in 9 M HCl and loaded onto a conditioned column. Each sample beaker was rinsed twice with 5 mL of 9 M HCl and loaded onto the column. An additional five column volumes of 9 M HCl was loaded onto the column to elute any ions not in the chloride form. Iron was eluted using three column volumes of 8 M HNO_3. Uranium was eluted from the column into a new glass beaker using seven column volumes of 8 M HNO_3. The uranium was kept in solution to avoid losses to the wall by addition of 2 mL of 0.36 M $NaHSO_4$ to the beaker. The sample was dried and reconstituted in conc. HNO_3 with 5 drops of H_2SO_4. The solution was heated to 150° C for 1 h and 300°C for 3 h to drive off the H_2SO_4. The cooled sample was reconstituted in 5 mL conc. HNO_3 and heated to 150°C. Any remaining organics were evolved by adding 30 % H_2O_2 dropwise until bubbling subsided. The sample was reconstituted with conc. HNO_3 and taken to dryness twice to obtain a white crystal sample. The resulting samples were reconstituted in 5–6 mL 0.75 M H_2SO_4, the pH was adjusted to 2–2.3 with NH_4 OH, and samples were electrodeposited on 17.50 mm diameter stainless steel planchete [10, 11]. A collodion film was applied to each planchete for alpha counting to minimize the recoil ion contamination of the detector. [12] The fraction of ^{238}U activity extracted by each sequential extraction reagent was

determined by alpha spectroscopy using a Canberra Alpha Analyst™ system. All extraction samples, quality control samples, and reagent blanks were analyzed and counted for 60,000 s.

Results and discussion

Figure 1 demonstrates that reagent 2 (NH_4Ac in 25 % HAc) extracted the largest fraction of uranium. Table 1 lists the average fraction of uranium extracted using each reagent. The mean fraction of uranium activity extracted for each sample is shown in Fig. 2 and demonstrates that the contamination is relatively homogeneous within the sample. The fusions contained less than 1 % of the activity. It is likely that soluble carbonate complexes increased the leaching and mobility of the uranium in the 50 year period of time during which the uranium contamination was in contact with the dirt floor and exposed to environmental elements, especially rainwater [13]. These results suggest that without remediation, the uranium contamination is likely to be easily transported in the environment.

Conclusions

The average ^{238}U activity in the sample of contaminated dirt was 106 ± 22 Bq. Approximately 77 % of the uranium contamination in the sample was dissolved in the second fraction using NH_4Ac in 25 % acetic acid. Although the origin of the uranium contamination was associated with hot-forged metal billets, the surface of the metal particles in contact with dirt and water for over 50 years would likely be oxidized. Unlike the insoluble tetravalent form of uranium [U(IV)], the hexavalent state of uranium [(U(VI)] forms a highly soluble carbonate complexes at alkaline pH which leads to increased mobility in groundwater.

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