Removal of depleted uranium from contaminated soils

Christine Chin Choy, George P. Korfiatis, Xiaoguang Meng[*]

Center for Environmental Systems, Stevens Institute of Technology, Castle Point-on-Hudson, Hoboken, NJ 07030, USA

Available online 28 December 2005

Abstract

Contamination of soil and water with depleted uranium (DU) has increased public health concerns due to the chemical toxicity of DU at elevated dosages. For this reason, there is great interest in developing methods for DU removal from contaminated sources. Two DU laden soils, taken from U.S. Army sites, were characterized for particle size distribution, total uranium concentration and removable uranium. Soil A was found to be a well graded sand containing a total of 3210 mg/kg DU (3.99×10^4 Bq/kg, where a Becquerel (Bq) is a unit of radiation). About 83% of the DU in the fines fraction (particle diameter <0.075 mm, total DU 7732 mg/kg (9.61×10^4 Bq/kg)) was associated with the carbonate, iron and manganese oxide and organic matter fractions of the material. Soil B was classified as a sandy silt with total DU of 1560 mg/kg (1.94×10^4 Bq/kg). The DU content in the fines fraction was 5171 mg/kg (6.43×10^4 Bq/kg). Sequential extraction of the Soil B fines fraction indicated that 64% of the DU was present either as soluble U(VI) minerals or as insoluble U(IV). Citric acid, sodium bicarbonate and hydrogen peroxide were used in batch experiments to extract DU from the fines fraction of both soils. Citric acid and sodium bicarbonate were relatively successful for Soil A (50–60% DU removal), but not for Soil B (20–35% DU removal). Hydrogen peroxide was found to significantly increase DU extraction from both soils, attaining removals up to 60–80%.
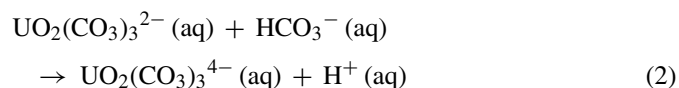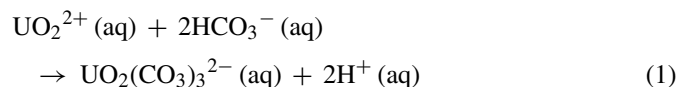© 2005 Elsevier B.V. All rights reserved.

Keywords: Uranium; Soils; Leaching; Sequential extraction

1. Introduction

The presence of high levels of uranium (U) compounds in the human body has been reported to affect renal functions and, at very high concentrations, lead to kidney failure [1]. The primary pathways of U entry into the human body are inhalation of contaminated dust or ingestion of contaminated water. The chemical toxicity of uranium as a heavy metal has raised public health concerns, especially in areas where contamination of local soils and groundwater from radioactive material has taken place. As a result, there is strong interest in re-mediation of depleted uranium (DU) laden areas. Several investigations into the removal of uranium from artificially contaminated soils as well as from anthropogenic sources, such as mine tailings and DU processing facilities, have been published [3,5,6,8]. Several chemical processes used for extracting U from contaminated soils are summarized in Table 1.

Sodium bicarbonate has been used in the mining industry to extract U from carbonate bearing ore material. The bicarbonate

ion forms strong aqueous complexes with U(VI) [2] according to reactions (1) and (2).

$$UO_2{}^{2+} (aq) + 2HCO_3{}^- (aq)$$
$$\rightarrow UO_2(CO_3)_3{}^{2-} (aq) + 2H^+ (aq) \tag{1}$$

$$UO_2(CO_3)_3{}^{2-} (aq) + HCO_3{}^- (aq)$$
$$\rightarrow UO_2(CO_3)_3{}^{4-} (aq) + H^+ (aq) \tag{2}$$

These stable water soluble complexes form easily under ambient conditions. Mason et al. [3] used $NaHCO_3$ solution as an alkaline treatment for U contaminated soils from a processing facility in Fernald, OH, USA. The authors were able to recover 80% of the total DU in the aqueous phase. Residual DU in the soil was determined to be comprised of relatively insoluble minerals, including meta-autunite (Ca–$(UO_2)_2(PO_4)_2 \cdot xH_2O$, log K_{sp} (25 °C) = −48.5), uranium metaphosphate (U$(PO_3)_4$) and uraninite (UO_2) [3,4,20]. It was believed that the autunite formed because the local soil had high phosphate content from prior pollution to the site. Sodium peroxide, Na_2O_2, was also added to the leaching process to promote oxidation of U(IV) by reac-
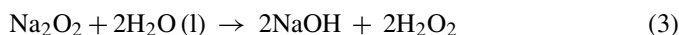
---

* Corresponding author. Tel.: +1 201 216 8014; fax: +1 201 216 8303.
 E-mail address: xmeng@stevens.edu (X. Meng).

Table 1
Literature survey of DU chemical extraction methods from soils

Total U content (mg/kg)	Material	Extraction method	Overall percentage DU removed	Reference
420–1320	Contaminated soil and ash	0.1–0.5 M NaHCO₃	80	Mason et al. [3]
95–708[a]	Acid/mixed/alkaline tailings, contaminated soil	0.1 M NaHCO₃	20–94	Phillips et al. [5]
449–732	Contaminated soil	0.2–0.6 M citric acid	85–99	Francis and Dodge [6]
2629	Radioactive waste	4 M HNO₃ + 0.05 M HBO₃	>99	Nirdosh [8]

[a] Values interpolated from publication.

tions (3) and (4):

$$Na_2O_2 + 2H_2O\,(l) \rightarrow 2NaOH + 2H_2O_2 \tag{3}$$

$$UO_2\,(s) + H_2O_2 + 2H^+ \rightarrow UO_2^{2+} + 2H_2O\,(l) \tag{4}$$

The oxidation of U(IV) to U(VI) occurred by a two electron transfer from U(IV) to H_2O_2. The resulting uranyl ion (UO_2^{2+}) was then available for subsequent complexation with HCO_3^- ions by reaction (1). A 10:1 molar ratio of oxidant to U enhanced the extraction of DU by 20%.

A wide range of U removals (20–94%) using $NaHCO_3$ was reported by Phillips et al. [5]. Various types of U contaminated material, including both acid and alkaline mine tailings, and contaminated soil, were tested. The lowest removals were from a contaminated soil (20%) and alkaline mine tailings (33%). The authors surmised that all accessible U had already been removed from the tailings and therefore further leaching would yield poor results. No reason for the low removal from the contaminated soil was provided. The highest extractions were achieved from acid mine tailings where reaction kinetics and multiple batch leachings were believed to explain the improved removal percentage. Remaining U was considered to be generally unavailable to chemical leaching.

Citric acid ($C_6H_8O_7$, H_3Cit) has also been used to treat DU contaminated soil from two sites in OH, USA, with removals ranging from 85 to 99% [6,19]. The acid formed an aqueous complex with U(VI) under acidic conditions (below pH 5.0) by the reaction below [7]:

$$UO_2^{2+} + Cit^{3-} \rightarrow UO_2Cit^- \tag{5}$$

Another method of DU extraction was reported by Nirdosh [8]. A two-stage acid leaching procedure was developed for treatment of radioactive soil waste. Stage 1 consisted of treatment with 0.4 M HCl or HNO₃ followed by Stage 2 extraction using 0.4 M acid containing 0.05 M H_3BO_3. The aqueous pH of these batch tests was below 1 and the oxidation reduction potential (Eh) was greater than 400 mV. DU levels in the waste decreased by over 99%.

The Eh–pH diagram of an aqueous system containing 2.1×10^{-4} M (50 mg/l) U is shown in Fig. 1. This concentration represents a 1000 mg/kg DU soil where all the DU solubilized during a 20:1 liquid:solid extraction with water and no carbonate present. The reactions used to construct the diagram are provided in Table 2. Below pH 4.25 and above an Eh ∼ 0.25 mV, the uranyl cation dominates in the U–OH system. As the pH increases, the tendency is for uranium hydroxide complexes to dominate under oxidizing conditions (positive Eh). No U(IV) cations are pre-
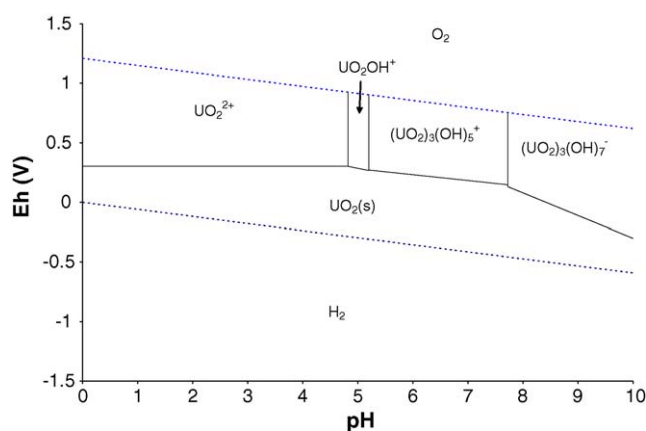

Fig. 1. Eh–pH diagram for U–OH system. Total U = 2.1×10^{-4} M (50 mg/l).

dicted in significant concentrations. However, uraninite should exist under reducing conditions.

After analysis of the Eh–pH diagram for a U system, it appears that the experimental conditions under which Nirdosh [8] performed extractions were optimal for the UO_2^{2+} cation to exist. The low pH and high Eh conditions prevented the formation of solid compounds such as uraninite and schoepite.

The studies summarized in Table 1 indicate that several highly efficient choices exist for the extraction of U from contaminated soils and other materials. Under ambient oxidizing conditions, U(VI) should be easily removed using bicarbonate, a strong inorganic acid or citric acid. The predominance diagram (Fig. 1) indicates that U(VI) cationic complexes are abundant from low to alkaline pH (about pH 8).

In this study, two DU contaminated areas from a U.S. Military site were used to evaluate several chemical leaching options in batch experiments. Each site is unique in terms of its contamination history and the minerals present, making generalization of treatment options difficult. Thus, the soil from each site was characterized and several leaching agents (citric acid, sodium

Table 2
Equations used for Eh–pH diagram of U–OH system, after Grenthe et al. [2]

	Equation	log K [2]
1	$4H^+ + UO_2^{2+} + 2e^- \rightarrow 2H_2O\,(l) + U^{4+}$	9.04
2	$UO_2^{2+} + 2e^- \rightarrow UO_2\,(s)$	13.91
3	$UO_2^{2+} + H_2O\,(l) \rightarrow H^+ + UO_2OH^+$	−5.40
4	$3UO_2^{2+} + 5H_2O\,(l) \rightarrow 5H^+ + (UO_2)_3(OH)_5^+$	−15.55
5	$3UO_2^{2+} + 7H_2O\,(l) \rightarrow 7H^+ + (UO_2)_3(OH)_7^-$	−31

bicarbonate and hydrogen peroxide) were screened for their efficacy of DU removal.

2. Materials and methods

2.1. Physical characteristics of contaminated soils

Soils from two testing areas at a U.S. Military site were selected for analysis due to their high DU content. Site A was once an open air munitions explosion area. DU weapons were sporadically launched into a field and shrapnel were manually recovered and recycled. Smaller fragments were left in the soil. Operations at Site A ceased once Site B was activated in the late 1980s. Site B contains a berm consisting of about 50 metric tonnes of sand with a catchbox, a three-sided enclosure, at the top intended to contain suspended dust and particulates. While larger fragments were collected after each test, smaller metallic pieces remained in the sand. Fewer metallic DU fragments were expected to exist in the Site A soil, due to the site's inactive status and the long period over which weathering reactions may have occurred.

Subsamples of the two soils were characterized for pH and moisture content following ASTM methods D4972 [9] and D2216 [10], respectively. Two kilograms of each soil was oven dried at 60 °C for 4 days, until the dry masses remained unchanged. The particle size distribution was determined following D2487 [11]. Acid digestion of 1.0 g portions of each size fraction was completed using concentrated HNO_3 and 30% H_2O_2, in accordance with EPA method 3050B [12]. The resulting mixture was separated through a 0.45 μm membrane filter, diluted with de-ionized water and analyzed in a Chemchek Phosphorescence Analyzer (Model KPA-11) for determination of aqueous U concentration. The gamma count of a 500 g sample of each soil was also measured over the period of 24 h for the U-238 and U-235 isotopes.

2.2. Sequential extraction

As the fines (<0.075 mm) of the Sites A and B soils contained most of the total DU contamination, this size fraction was selected for sequential extraction analysis. Acid digests of duplicate samples of the fines indicated that the DU distribution was homogeneous. If metallic DU had been present in the samples, large variabilities in total DU would have been found. As this was not the case for either soil, the fines were determined to be suitable for repeated screening tests. The total DU content in the Site A fines was 7732 mg/kg (9.61×10^4 Bq/kg, where a Becquerel (Bq) is a unit of radiation), and it was 5171 mg/kg (6.43×10^4 Bq/kg) for the Site B fines. Using the method of Tessier et al. [13], uranium was classified according to its leaching potential from five general components of soils. For the first phase, "exchangeable cations", 1.0 g of each soil was mixed with 8 ml Mg_2Cl_2 in 50 ml polycarbonate centrifuge tubes for 1 h and centrifuged at 2500 rpm for 20 min. The liquid phase was decanted and stored for analysis, while the residue was subjected to the next extraction stage. The remaining steps of the sequential extraction were as follows: (ii) "bound to carbonates" – extracted by 8 ml of 1 M acetic acid – sodium acetate buffer solution at pH 5 for 5 h; (iii) "bound to Fe–Mn oxides"—extracted by 20 ml of 0.04 M $NH_2OH·HCl$ in 25% acetic acid at 96 °C for 6 h; (iv) "bound to organic matter"—extracted by 3 ml 0.02 M HNO_3 and 5 ml 30% H_2O_2 (adjusted to pH 2 with HNO_3) at 85 °C for 2 h, followed by the addition of 3 ml of 30% H_2O_2 (pH 2) and subsequent continuous heating for 3 h. The H_2O_2 mixture was cooled, mixed with 5 ml of 1.2 M ammonium acetate in 20% HNO_3, diluted to 20 ml with de-ionized water and agitated for 30 min. The final fraction (v) "the residuals" is usually the digestion of the residue with a mixture of HF, $HClO_4$ and HNO_3. This last step was not performed. Alternatively the residues were exposed to 10 ml of 15% H_2O_2 at 75–80 °C for 1.5 h, to determine if a longer oxidation period would improve extraction.

The supernatants from each extraction were analyzed for total U concentration using a Chemchek KPA-11. Dilutions were made with 1% HNO_3. Residual concentrations were considered to be the difference between the cumulative DU removed and the average total DU in the fines.

2.3. Batch experiments

One gram of the soil fines was mixed with varying concentrations of citric acid and sodium bicarbonate. Liquid:solid ratios were 20:1 [v/w] and the samples were mixed in 50 ml polycarbonate tubes in an end-over-end mixer for a minimum of 24 h. Thereafter, 1 ml from each sample was centrifuged for 15 min at 10,000 rpm. The supernatant was then diluted in 1% HNO_3 for uranium analysis with a Chemchek KPA-11 Analyzer.

Hydrogen peroxide treatment consisted of placing 20:1 [v/w] liquid:soil mixtures in loosely capped 50 ml polycarbonate tubes in an oven at 60 °C for 24 h. The H_2O_2 concentration was varied between 0.5 and 15% and the pH was kept between 2 and 3 using H_2SO_4. Batch control tests contained no oxidant and were maintained in the same pH range. As H_2O_2 obstructed the phosphorescence needed for uranium analysis by the Chemchek KPA-11, the following extra step was added to the sample preparation procedure. After centrifuging 1.5 ml aliquots of samples at 10,000 rpm for 15 min, 1 ml of each supernatant was placed in a glass scintillation vial. The samples were heated to dryness on a hotplate in order to remove all hydrogen peroxide. The resulting residue was reconstituted with 1% HNO_3 to 10 ml for a 10-fold dilution. Samples were then analyzed for U with the KPA analyzer. Uranium standard controls indicated that no loss of the metal occurred during this drying process.

Residues from the H_2O_2 batch treatment were collected by centrifuging the bulk sample at 2500 rpm for 45 min, followed by decanting of the supernatant. The residues were next combined with 20 ml 0.1 M $NaHCO_3$. The samples were mixed for 24 h and aliquots were taken for analysis.

Results from these described tests were determined by analysis of the supernatants from each extraction. Percentage removals were based on the total DU concentration determined for the fines by acid digestion.

Table 3
Physical characteristics of the soils samples used in the study

	Methods	Soil A	Soil B
Moisture content (%)	ASTM D2216 [10]	2.94	1.50
Soil classification	ASTM D2487 [11]	Well graded sand with silts	Sandy silt with about 10% finer than 0.075 mm
Total DU (mg/kg)	EPA 3050B [12]	3210 (3.96×10^4 Bq/kg)	1560 (1.93×10^4 Bq/kg)
pH	ASTM D4972 [9]	7.5	7.1

3. Results and discussion

3.1. Physical characterization

Some physical characteristics for both soils are summarized in Table 3. Soil A had a moisture content of 2.94% and is classified as a well graded sand with silt (Unified Soil Classification System (USCS) Symbol: SW-SM). The fines (<0.075 mm) comprised less than 10% of the total mass but accounted for 38% of the DU content. This was determined by acid digestion of each size fraction of the soil sample (data not shown). DU fragments were manually isolated from the coarse sand (0.85–4.75 mm) and fine gravel (4.75–9.5 mm) fractions. The average total DU concentration, based on acid digestion and gamma count, was 3210 mg/kg (3.99×10^4 Bq/kg).

Soil B was classified as a sandy silt with 10% fines (USCS Symbol: SM) with a moisture content of 1.50%. Acid digestion of each soil fraction indicated that uranium was evenly distributed in the fine and medium sand fractions, with 1000–1800 mg/kg DU (1.24×10^4–2.24×10^4 Bq/kg). Fifty-two percent of the total contamination was associated with the fines. A few DU fragments were identified in the fine gravel fraction. Overall, the average DU in the soil was 1560 mg/kg soil (1.94×10^4 Bq/kg).

3.2. Sequential extraction of contaminated fines

Sequential extraction tests yielded different results for the two soils. None of the DU in the Soil A fines was removed in the exchangeable fraction (Fig. 2a). The results indicated that the leachability of DU in the soil was low since exchangeable ions were the most mobile form. Forty-one percent of the DU was associated with carbonates, 26% with Fe and Mn oxides and 16% with the organic matter fraction. All the residuals were recovered by a second treatment with H_2O_2, implying that a longer oxidation period was needed for complete extraction from the organic fraction. Analytical error may account for a small amount of DU recovered; however, the fact that the cumulative amount of DU was the same as the total removed by acid digestion indicates that the analytical and experimental errors were small.

These sequential extraction results were similar to those reported by Sheppard and Thibaulk [14], where DU was not in the exchangeable fraction of U(VI) contaminated soils. These soils were a natural sandy soil and a clay subsoil that were each spiked with $UO_2(NO_3)_2 \cdot 6H_2O$ and aged for 4 years. Sheppard and Thibaulk [14] found U primarily associated with the iron oxides fraction (over 58%) and the carbonates (25–35%). Like Soil A, the amount of U in the residual fraction was very small. In another study [15], an arid alkaline soil located directly below a DU penetrator for 22 years, in the open air, was tested. Sequential analysis of the upper 4 cm of the soil profile showed that at least half of the total DU may be attributed to the carbonate fraction (Stage 2 of the sequential extraction). The relative ease of DU dissolution implied that uranyl hydroxide minerals were present [15]. No DU was in the exchangeable fraction for the first 8 cm below the surface. A comparison of the extraction results of Soil A with these studies implied that Soil A contained mostly
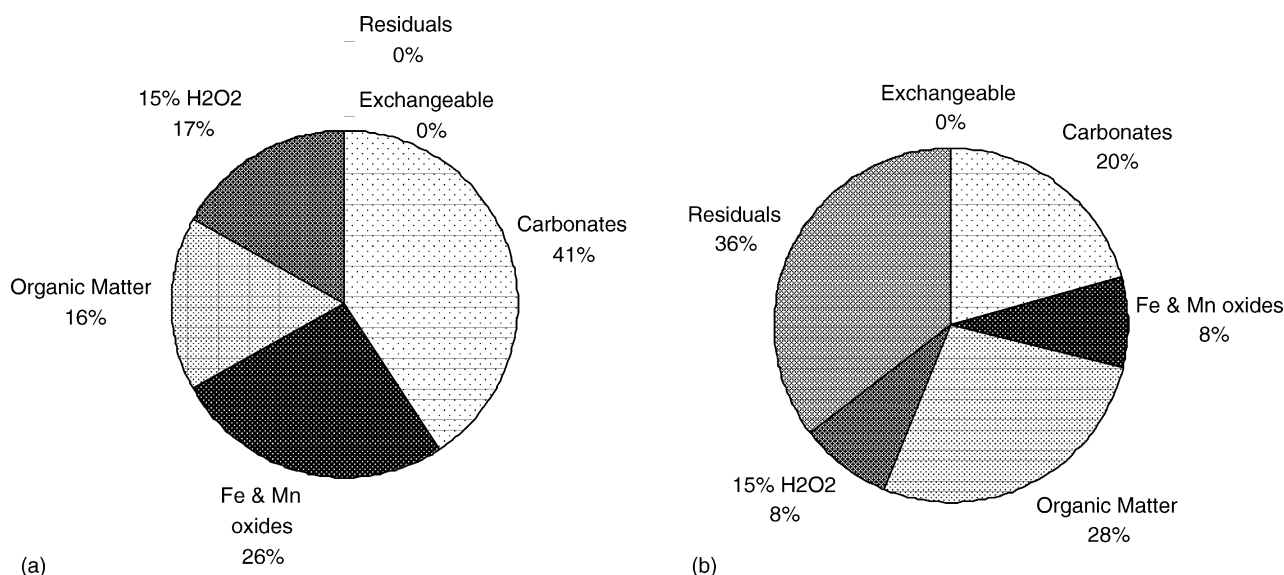

Fig. 2. Sequential extraction results from: (a) Soil A fines and (b) Soil B fines.

U(VI) minerals, with some DU associated with the organic matter fraction. Corrosion of metallic DU may also have led to the formation of U(IV) minerals, which could be oxidized by H_2O_2 treatment.

An insignificant amount of DU was found in the exchangeable fraction of the Soil B fines (Fig. 2b). About 20% of the total DU was bound to carbonates. As discussed earlier, this implied the presence of U(VI) hydroxide minerals. Stage 3 extraction yielded 8% DU associated with Fe and Mn oxides, suggesting that this phase was not a controlling component to the overall extraction. Twenty-eight percent and another 8% were extracted by two batch treatments with H_2O_2. Organic matter was not considered to be a significant portion of this soil, as it was mostly quartz sand. Therefore, the H_2O_2 used to destroy the organic matter in Stage 4 of the sequential analysis test was expected to oxidize any U(IV) minerals which may have formed from slow oxidation of uranium metal fragments. Thirty-six percent of the total DU in the Soil B fines could not be removed by the first four stages of the Tessier method.

Johnson et al. [15] reported 29–52% DU in the residuals fraction of their sequential extraction tests. Coatings of amorphous silica around schoepite particles and aggregates with clays and calcium carbonate were found to inhibit U solubility during extraction experiments and cause it to be recovered in the residual phase. As the soils in that study were alkaline (pH 9–10), silica and carbonates were found to dissolve and re-precipitate as they migrated down the soil profile. A similar mechanism may have been responsible for the large amount of DU in the residual fraction of Soil B, where silica coatings may have developed around DU containing minerals and aggregates. With the neutral pH of Soil B, less dissolution and re-precipitation of silica and carbonates was expected. However, the high localized temperatures induced by DU weapons explosions on the active site may have vitrified the silicates, incorporating DU in the glass matrix.

Recent publications [21–25] have questioned the accuracy of the sequential extraction tests to predict the speciation of metals in soils. While these studies did not consider DU, the qualitative results should be considered for all heavy metal contaminants subjected to the sequential extraction test. Organic matter and other soil minerals can alter the amount of target metal removed during each stage of the sequential tests, because of re-adsorption of the metal onto those surfaces. Thus, the data reported here should be considered first-order estimates of the DU distribution in each particular soil.

3.3. Batch leaching experiments

The extraction results from treatment of each soil fines with citric acid are shown in Figs. 3 and 4. The pH of the citric acid system was between 2.3 and 3.2. Fig. 3 shows that 50% DU was removed in 24 h using 0.01 M citric acid for 24 h. This leveled off to 55% after 3 days and remained at that level after 6 days of mixing. About 60% DU was extracted using 0.1 M acid. An increase in citric acid concentration did not yield a comparable difference in the amount of DU removed from the soil. Equilibrium was attained within 72 h as the aqueous DU concentration remained constant at that time. According to Fig. 1, the uranyl
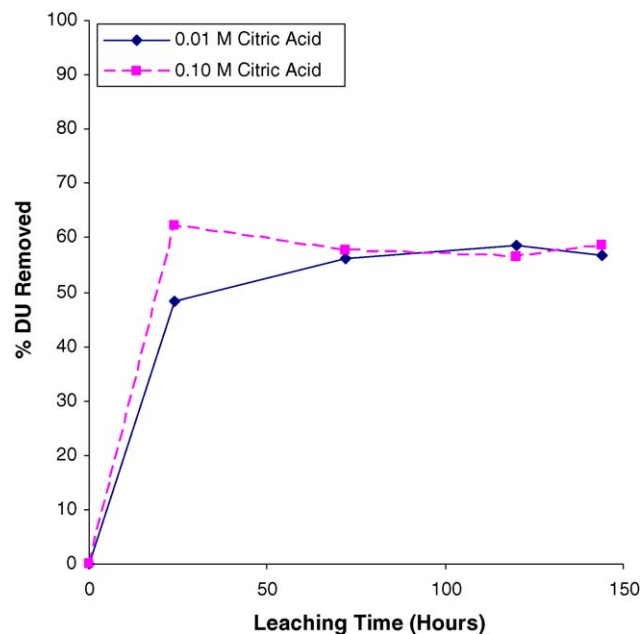

Fig. 3. Effect of time and citric acid concentration on extraction from Soil A fines.

cation was the dominant aqueous form under the pH of the citric acid batch tests, implying that the environment was suitable for reaction (5) to take place.

The amount of DU removed from Soil A corresponded to 57–59%, 10% less than the sum of the carbonate and the Fe and Mn oxides fractions (Fig. 2a). It is likely that citric acid targeted the same DU sites in the soil as those removed in Stages 2 and 3 of the sequential extraction tests, since both stages required acidic conditions.

The Soil B fines were more resistant to DU release in the presence of citric acid. After 24 h of mixing, less than 20% DU
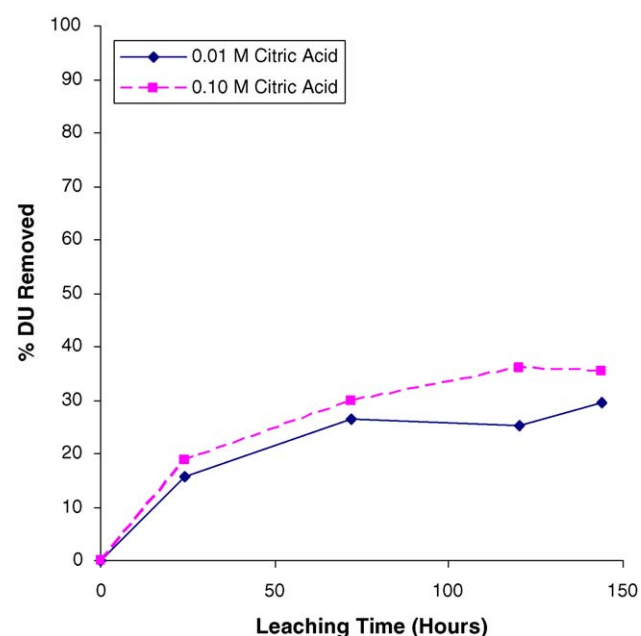

Fig. 4. Effect of time and citric acid concentration on extraction from Soil B fines.
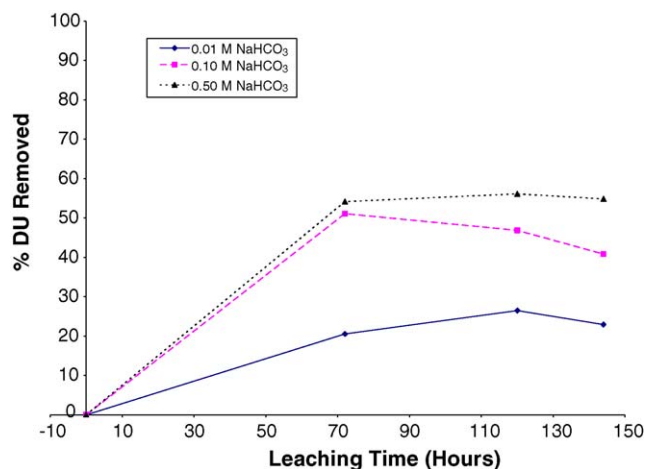
Fig. 5. Effect of concentration of NaHCO$_3$ on removal from Soil A fines.

was removed for both concentrations of acid used. This increased to about 30% after 5 days (120 h) of mixing, using 0.01 M acid and 35% with 0.1 M acid. An increase in mixing time as well as an increase in citric acid concentration did not dramatically impact the 24 h removal of DU from the Soil B fines. The initial 20% removed was the same amount as that extracted in Stage 2 of the sequential extraction (Fig. 2), implying that readily soluble U(VI) represented most of the overall removal by citric acid (reaction (5)). Incremental increases in DU extraction with time were due to citric acid complexation with less mobile DU forms in the soil.

Citric acid extraction from both soils gave results well below 85–99% reported by Francis and Dodge [6] in Table 1. Citric acid is known to target DU in the exchangeable and carbonate fractions [6], consistent with the high carbonate content of the Fernald soils tested [16]. However, the results from the sequential extraction of DU in Soils A and B did not indicate a high percentage of the metal associated with the carbonate fraction (Fig. 2a and b).

Results from DU removal using 0.01, 0.10 and 0.50 M sodium bicarbonate (Figs. 5 and 6) were similar to extractions using citric acid. As shown in Fig. 5, 0.01 M NaHCO$_3$ removed less than
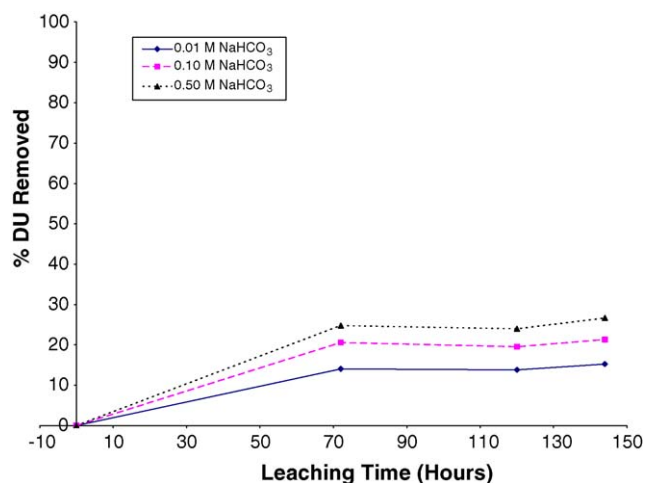
30% DU from Soil A after 6 days of mixing. However, 50–60% removal was achieved with 0.1 and 0.5 M NaHCO$_3$. A decrease in aqueous DU was observed over the 6 day (144 h) period for all the concentrations, with the more pronounced decrease noted for the 0.1 M NaHCO$_3$ mixture. This decrease may be due to re-adsorption of DU onto iron oxides in the soil matrix or some experimental error. DU extraction was low for the Soil B fines. Fig. 6 shows the highest percent removed after 6 days was less than 30%, using 0.5 M NaHCO$_3$. A constant aqueous DU concentration was observed after 3 days. The pH of these batch tests varied between 8.0 and 8.3, as this was the natural pH of the bicarbonate system, under atmospheric conditions.

The percentage DU removals from both Soils A and B fines, using NaHCO$_3$, were comparable to the cumulative amount extracted during the first three stages of the sequential tests (Fig. 2), as well as the amount removed by citric acid. Thus, it seems that the same DU forms were removed in all three chemical treatments. In a carbonate system, the carbonate anion forms several complexes with the U(VI) cation according to reactions (1) and (2). These U(VI) polycarbonate complexes dominate at pH 8 [17]. As with citric acid, easily accessible U(VI) forms were targeted by the bicarbonate anion for complexation, rather than the less mobile U(VI) forms or the less soluble U(IV).

Table 1 reports higher DU removals from bulk soils when using NaHCO$_3$ in another study [3]. These soils were naturally high in carbonate (they originated from the same location as the ones tested by Francis and Dodge [6]) and had significant U contamination in that fraction. The higher removals from those soils, when compared with the Soils A and B fines, should be attributed to their higher amount of leachable DU.

A two-stage extraction procedure was considered, where the first step involved the oxidation of the soil fines using H$_2$O$_2$, followed by treatment using NaHCO$_3$. Results are presented in Figs. 7 and 8. The use of H$_2$O$_2$ in the first stage dramatically improved DU extraction from both soil samples. In the absence of H$_2$O$_2$, only 29% of the DU was leached from Soil A at a final pH of 2.3. The amount of DU extracted increased to 78% with the addition of 15% H$_2$O$_2$. A further 10–30% DU was removed
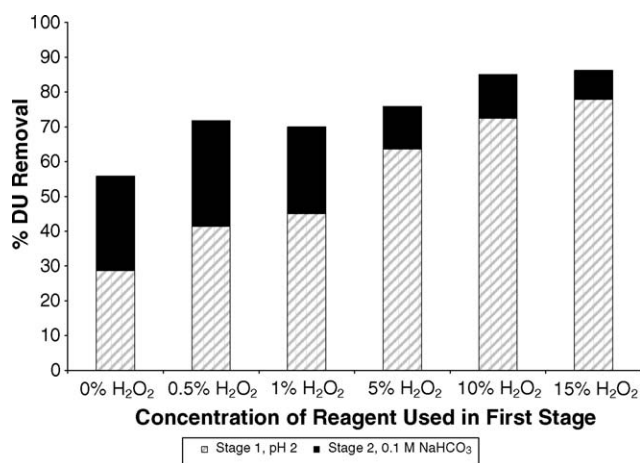

Fig. 7. Cumulative percent removal from Soil A fines by two-stage extraction. Stage 1 = 20 ml of liquid, final average pH 2.33, 0–15% H$_2$O$_2$; Stage 2 = 0.10 M NaHCO$_3$, final average pH 8.84.

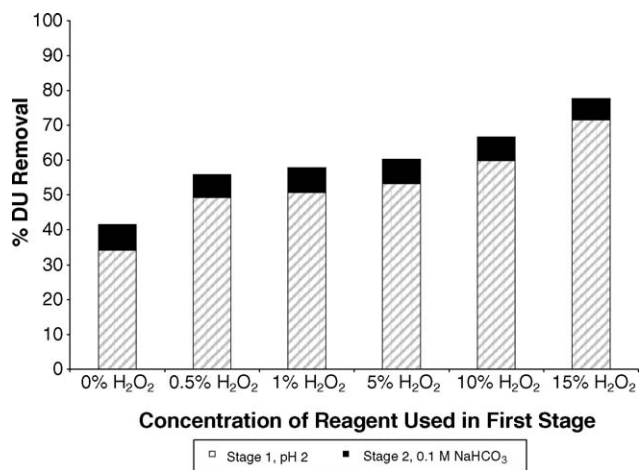Fig. 6. Effect of concentration of NaHCO$_3$ on removal from Soil B fines.

Fig. 8. Cumulative percent removal from Soil B fines by two-stage extraction. Stage 1 = 20 ml of liquid, final average pH 2.33, 0–15% H_2O_2; Stage 2 = 0.10 M $NaHCO_3$, pH 8.58.

in the second stage for Soil A at a $NaHCO_3$ concentration of 0.1 M and final pH of 8.8.

It should be noted that the control solution (no H_2O_2) extracted about the same amount of DU from the Soil B fines, as did treatment with bicarbonate and citric acid (Fig. 8). As the tests were conducted at low pH, this implies that the UO_2^{2+} species was the one available for extraction (Fig. 1). Without oxidant, a maximum of about 35% of the total DU was removed from the Soil B fines, prior to the addition of $NaHCO_3$. Less than 10% was extracted in the second stage for Soil B.

The Haber–Weiss mechanism may assist in explaining the improvement of DU extraction from the soils when H_2O_2 was added to the system. In this reaction, metal ligands on the soil surface (M^{n+}) catalyze the decomposition of H_2O_2 according to reaction (6) [18]:

$$H_2O_2 + M^{n+} \rightarrow \ ^{\bullet}OH + OH^- + M^{n+1} \tag{6}$$
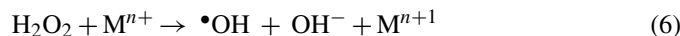
The radicals may oxidize U(IV) bearing minerals and allow UO_2^{2+} to solubilize by reaction (4). Since H_2O_2 is not a very selective oxidant, other soil minerals and organic matter which may have shielded DU from the aqueous phase could also have been partially or completely dissolved by the peroxide solution, thus releasing any trapped DU.

A proportional increase of DU removal from the Soil B fines with increased H_2O_2 concentration was observed. Removals increased from 50 to 70% as the concentration of H_2O_2 was raised. These values correspond to the cumulative DU extracted from the Soil B fines during Stages 1–4 (Fig. 2b). The highest removal was about the same amount as the cumulative amount removed, once the second H_2O_2 treatment was included. Thus, H_2O_2 extracted all of the leachable DU from Soil B. Since this soil consisted mostly of sand, depletion of H_2O_2 by organic matter was not a significant sink for the oxidant. As these removals were more than twice the removals with citric acid and $NaHCO_3$, the results suggested that the U forms in Soil B were different from Soil A.

DU contamination in the Site A soil was more easily removed than that in the Site B soil. This suggests that the Site A soil

may be treated with an environmentally benign leaching agent such as citric acid to remove 60% DU. Based on sequential extraction results, longer leaching times or even multiple batch leaching treatments would target the DU bound to the Fe and Mn oxides, but this may not be enough to remove DU associated with organic matter. This last fraction represents a large percentage of the DU in the Soil A fines. An additional one or two leaching stages should be considered in order to achieve a sufficiently low concentration for the bulk soil to be categorized as clean. Hydrogen peroxide treatment yielded higher extractions, likely due to oxidation of organic material in the sample (Stage 3 of the sequential extraction procedure). Additional amounts of the oxidant would improve extraction from this soil; however, costs and final soil quality will govern the total amount of H_2O_2 employed. The Soil B fines proved to be more resilient to batch extractions by citric acid and $NaHCO_3$. Once H_2O_2 was added at low pH, 60–70% of the total DU was removed. The aggressive nature of these experimental conditions suggests that the DU in this soil was less accessible for extraction. Thus, chemical treatment of soil from this site would be insufficient to remove satisfactory quantities of the contaminant.

The leachates from all the batch tests performed could be added to another process where DU may be recovered and recycled. If bicarbonate or citric acid were used, these may be regenerated and returned to the extraction process. The residues from these tests would need to be neutralized before returning the soils to the environment.

Analysis of other metals extracted during the batch extraction tests would assist in better understanding the role of H_2O_2 on the improved DU extraction from the contaminated soils, as well as in determining the post-treatment soil quality. Identification of DU containing minerals by microscopic or crystallographic study of the minerals would also aid understanding the extraction mechanism in more detail.

4. Conclusions

Soils from two U.S. Army sites were characterized as a well graded sand (Soil A, 3210 mg DU/kg) and a sandy silt with 10% fines (Soil B, 1560 mg DU/kg). Sequential extraction of the fines fraction from both soils indicated that the DU in the Soil A fines was easier to remove than from the Soil B fines. About 33% of the DU in the Soil B fines could not be removed by standard sequential extraction steps, while over 80% was extracted from the Soil A fines by the same method. Higher removals were consistently found when the Soil A fines were treated with different leaching agents. However, a one step treatment with established U(VI) leaching agents, such as $NaHCO_3$ and citric acid, still proved to be insufficient to treat these two soils. Oxidation using H_2O_2 at low pH improved removals to 60–70% for both soils.

The leachable DU in Soil B was mostly in a form not easily removed with strong U(VI) complexing agents such as $NaHCO_3$ and citric acid. It was only when H_2O_2 was applied at low pH that 50–70% removals were observed. This implied that oxidation of U(IV) minerals took place. DU that could not be removed by sequential extraction or by any of the leaching agents was most likely fused into the silicate matrix of the sand.

Acknowledgments

References

[1] N.H. Harley, E.C. Foulkes, L.H. Hilborne, A. Hudson, C.R. Anthony, A Review of the Scientific Literature as it Pertains to Gulf War Illness, vol. 7, National Defense Research Institute MR-1018/7-OSD, Rand, 1999.

[2] I. Grenthe, J. Fuger, R.J. Lemire, A.B. Muller, C. Nguyen-Trung, H. Wanner, I. Forest, Chemical Thermodynamics of Uranium, Elsevier, 1992.

[3] C.F.V. Mason, W.R.J.R. Turney, B.M. Thomson, N. Lu, P.A. Longmire, C.J. Chisholm-Brause, Carbonate leaching of uranium from contaminated soils, Environ. Sci. Technol. 31 (1997) 2707–2711.

[4] E.C. Buck, N.R. Brown, N.L. Dietz, Contaminant uranium phases and leaching at the Fernald site in Ohio, Environ. Sci. Technol. 30 (1996) 81–88.

[5] E.J.P. Phillips, E.R. Landa, D.R. Lovley, Remediation of uranium contaminated soils with bicarbonate extraction and microbial U(VI) reduction, J. Ind. Microbiol. 14 (1995) 203–207.

[6] A.J. Francis, C.J. Dodge, Remediation of soils and wastes contaminated with uranium and toxic metals, Environ. Sci. Technol. 32 (1998) 3993–3998.

[7] J.J. Lenhart, S.E. Cabaniss, P. MacCarthy, B.D. Honeyman, Uranium(VI) complexation with citric, humic and fulvic acids, Radiochim. Acta 88 (2000) 345–353.

[8] I. Nirdosh, Leaching of uranium and 226-Ra from low-level radioactive waste from Port Hope, Ontario, Can. J. Chem. Eng. 77 (1999) 508–514.

[9] ASTM (American Society for Testing and Materials), Standard Test Method for pH of Soils, D-4972-95a, Annual Book of ASTM Standards, vol. 04.08., 2001, West Conshohocken, PA.

[10] ASTM (American Society for Testing and Materials), Standard Test Method for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass, D-2216-98, Annual Book of ASTM Standards, vol. 04.08., 2001, West Conshohocken, PA.

[11] ASTM (American Society for Testing and Materials), Standard Practice for Classification of Soils for Engineering Purposes (Unified Soil Classification System), D-2487-00, Annual Book of ASTM Standards, vol. 04.08., 2001, West Conshohocken, PA.

[12] USEPA (The U.S. Environmental Protection Agency), Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Method 3050B, U.S. EPA, Washington, DC, 1996.

[13] A. Tessier, P.G.C. Campbell, M. Bisson, Sequential extraction procedure for the speciation of particulate trace metals, Anal. Chem. 51 (1979) 844–851.

[14] M.I. Sheppard, D.H. Thibaulk, Desorption and extraction of selected heavy metals from soils, Soil Sci. Am. J. 56 (1992) 415–423.

[15] W.H. Johnson, B.J. Buck, H. Brogonia, A.L. Brock, Variations I depleted uranium sorption with depth in arid soils, Soil Sediment Contam. 13 (2004) 533–544.

[16] M.P. Elless, S.Y. Lee, Uranium solubility of carbonate-rich uranium contaminated soils, Water Air Soil Pollut. 107 (1998) 147–162.

[17] M. Wazne, Ph.D. Dissertation, Stevens Institute of Technology, 2003.

[18] B.R. Petigara, N.V. Blough, A.C. Mignerey, Mechanisms of hydrogen peroxide decomposition in soils, Environ. Sci. Technol. 36 (2002) 639–645.

[19] C.W. Francis, M.E. Timpson, J.H. Wilson, Bench- and pilot-scale studies relating to the removal of uranium from uranium-contaminated soils using carbonate and citrate lixiviants, J. Hazard. Mater. 66 (1999) 67–87.

[20] D.B. Hunter, P.M. Bertsch, In situ examination of uranium contaminated soil particles by micro-X-ray absorption and micro-fluorescence spectroscopies, J. Radioanal. Nucl. Chem. 234 (1998) 237–242.

[21] M. Raksasataya, A.G. Langdon, N.D. Kim, Assessment of the extent of lead redistribution during sequential extraction by two different methods, Anal. Chim. Acta 332 (1996) 1–14.

[22] J.L. Gómez Ariza, I. Giráldez, D. Sánchez-Rodas, E. Morales, Selectivity assessment of a sequential extraction procedure for metal mobility characterization using model phases, Talanta 52 (2000) 545–554.

[23] V. Ettler, A. Vaněk, M. Mihaljevič, P. Bezdička, Contrasting lead speciation in forest and tilled soils heavily polluted by lead metallurgy, Chemosphere 58 (2005) 1449–1459.

[24] K.G. Scheckel, C.A. Impellitteri, J.A. Ryan, T. McEvoy, Assessment of a sequential extraction procedure for perturbed lead-contaminated samples with and without phosphorus amendments, Environ. Sci. Technol. 37 (2003) 1892–1898.

[25] D. Dermatas, G. Shen, M. Chrysochoou, D.G. Grubb, P. Dutko, Pb speciation versus TCLP release in army firing range soils, J. Hazard. Mater. 136 (2006) 34–46.