

Memo			
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Subject:	Scope of Work to Optimize Uranium and Molybdenum Extraction from Soils: Dam to Ditch Area, Cotter Uranium Mill, Cañon City, CO.		

1.0 INTRODUCTION

This memorandum presents a brief Scope of Work (SOW) to identify chemical reagents that can be used to optimize uranium and molybdenum extraction from subsurface soils and geologic materials in the Cotter Corporation (Cotter) Dam to Ditch Area (DDA). Routine monitoring has shown that both uranium and molybdenum groundwater concentrations at several DDA locations exceed Colorado Groundwater Quality Standards (CGWQS) of 0.03 mg/L and 0.035 mg/L, respectively. As a result, a field investigation was conducted in 2010 to better delineate areas of impacted groundwater and to characterize potential sources and pathways for migration of uranium and molybdenum to the north. The results from the 2010 investigation were used to update the existing conceptual model with respect to the geologic, hydrologic, and water quality conditions within the DDA (HydroSolutions, 2010).

Drill cuttings from investigative borings were subsequently used in a column study to characterize the mobility of uranium and molybdenum from DDA subsurface materials. The results showed that a portion of the total uranium and molybdenum is readily released by either natural precipitation or local groundwater (AMEC, 2011). Most columns produced initial leachate concentrations exceeding CGWQS for uranium and molybdenum, but with concentrations that decreased with increased leaching. Higher uranium and molybdenum concentrations were often associated with weathered claystone (WCS) and overlying sands, silts, and clays (SSC), compared to the underlying claystone and sandstone. Mass balance calculations show that only a small fraction of the total uranium was released, while molybdenum was more soluble. Geochemical modeling results suggested that uranium and molybdenum exist as adsorbed species on mineral surfaces. Although the results indicate the potential for natural leaching of elevated uranium and molybdenum concentrations from DDA soils, only a small fraction of their total mass appeared to be released by natural leaching (AMEC, 2011). These findings suggest that leaching with a selective extraction solution more aggressive than water could be used to enhance the extraction of total uranium and molybdenum from DDA soils.

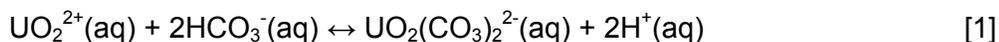
The objectives of this SOW are to: (1) Present a brief summary of chemical reagents that have been used to effectively extract uranium from contaminated soils, and (2) recommend supplemental column leaching and laboratory batch testing procedures for identifying chemical reagents that can be used to effectively extract uranium and molybdenum from DDA soils. As part of the ongoing remedial action investigations for the DDA, Cotter may consider implementing a field-scale pilot test to examine the feasibility of *in situ* soil flushing for removing uranium and molybdenum from the soils. The batch test results will be used to provide reagent recommendations for use in future field-scale pilot tests for remediation of uranium- and molybdenum-contaminated soils in the DDA.

2.0 URANIUM EXTRACTION FROM SOILS

Chemical extraction of uranium from contaminated soils involves the conversion of uranium into a water soluble form, which is then extracted from the soil. Efficient uranium removal from soils can be achieved provided that the extracting solution enhances the solubility of uranium, and that the uranium predominantly exists in the oxidized state [U(VI)] (Gavrilescu et al., 2009).

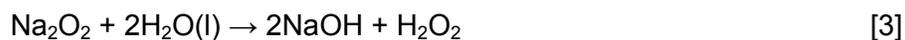
2.1 Extraction Using Carbonate

One of the most commonly-used reagents for removal of uranium from contaminated soils is sodium bicarbonate (NaHCO₃). Sodium bicarbonate is also used in the mining industry to extract uranium from certain ores, because carbonate forms strong solution complexes with uranium:



Consequently, the formation of stable dissolved uranium-carbonate complexes enhances the solubility and subsequent removal of solid-phase uranium(VI) from contaminated soils. In a soil column leaching study, Mason et al. (1997) used 0.5 M NaHCO₃ to achieve 75 to 90% uranium removal efficiency, corresponding to the percentage of uranium in the oxidized form. Even though varying the solution ratios of HCO₃⁻:CO₃²⁻ (1:0, 2:1, and 1:1) produced pH values of 8.3, 9.9, and 10.3, respectively, uranium removal efficiencies did not change significantly within the pH range of 8.3 to 10.3 (Mason et al., 1997).

Recognizing that bicarbonate extraction only dissolves the oxidized form of uranium [U(VI)], Mason et al. (1997) used an oxidizing agent (sodium peroxide, Na₂O₂) to further enhance uranium removal by oxidizing the reduced forms of uranium [U(IV)] present as solid UO₂ (Gavrilescu et al., 2009):



By incorporating solid Na_2O_2 into the contaminated soil prior to leaching, the uranium removal was enhanced by 20% compared to columns where Na_2O_2 was not added (Mason et al. 1997).

In a bench-scale experiment, Kulpa and Hughes (2001) demonstrated 90% removal of uranium from contaminated soils using a solution of 0.2 M NaHCO_3 and a retention time of 1.5 hours. Based on their bench-scale results, a pilot-scale and subsequent full-scale soil washing facility was designed which achieved uranium removal efficiencies of approximately 80 to 95%.

2.2 Extraction Using Citric Acid

Organic acids also have a tendency to form strong solution complexes with uranium, and hence can be used to mobilize uranium from contaminated soils. A number of studies have shown that citric acid is very effective in dissolving uranium, and that the removal efficiency generally improves with increasing citric acid concentration. For example, Francis and Dodge (1998) utilized citric acid extraction of uranium, in conjunction with both biodegradation and photodegradation, to remove uranium from contaminated soil. Sixty percent of the uranium was extracted using 0.2 M citric acid, while 80% of the uranium was extracted when using 0.4 M citric acid. Use of 0.6 M citric acid did not result in any further significant removal of uranium.

Batch experimentation by Kantar et al. (2006) has indicated that even low citric acid concentrations (0.001 M) can increase the extraction of uranium from contaminated soils by a factor of 3 times greater than distilled water. Citric acid was particularly effective in cases where uranium is associated with Fe-oxide coatings on soil minerals. Kantar et al. (2006) also noted that greater solution:solid ratios and higher citric acid concentrations were required to achieve the same column removal efficiencies observed in batch tests. Citric acid has also been used to treat depleted-uranium contaminated soils with removal efficiencies ranging from 85 to 99% (Gavrilescu et al., 2009).

Citric acid is environmentally-compatible and the uranium-citrate complexes will biodegrade rapidly when the pH is maintained between 8 and 9. Once the extraction process is complete, however, biodegradation of residual uranium-citrate complexes does not promote additional uranium mobility from the treated soils (Gavrilescu et al., 2009).

3.0 MOLYBDENUM EXTRACTION FROM SOILS

Reported incidences of molybdenum contamination in soils are not as common when compared to uranium, and therefore less information exists regarding the effectiveness of soil flushing to remove molybdenum from soils. Rather, excavation/disposal or phytoremediation techniques are more frequently used to remediate molybdenum-contaminated soils. Column leaching results (AMEC, 2011) indicate that DDA soils are a potential source of elevated molybdenum in groundwater north of the Cotter Mill, and therefore molybdenum removal efficiencies will be evaluated in conjunction with uranium under this SOW.

Under oxidizing soil conditions, dissolved molybdenum exists mainly as the molybdate ion (MoO_4^{2-}). Molybdate does not tend to form strong solution complexes with inorganic ions or organic acids, and is generally mobile in the soil environment. In calcareous soils, dissolved molybdenum concentrations may be controlled by calcium molybdate (CaMoO_4). More commonly, molybdenum occurs as adsorbed molybdate on mineral surfaces. Molybdenum adsorption by soil minerals is generally greatest at low pH (3 to 5) but decreases rapidly with increasing pH, and with very little adsorption occurring above pH 7 (Goldberg et al., 1996).

The DDA column leaching study (AMEC, 2011) demonstrated that the soil column leachates were undersaturated with respect to solid CaMoO_4 , and that the majority of the molybdenum occurs as molybdate adsorbed to soil minerals. In addition, a larger fraction of the total molybdenum was leached from the soil when compared to uranium. Therefore, the batch testing methods recommended in this SOW are primarily designed to identify a candidate uranium extraction solution. It is assumed that adequate molybdenum removal efficiencies will also be achieved simply based on the favorable mobility of molybdenum under oxidizing conditions.

4.0 RECOMMENDED PROCEDURES

Two methods are suggested for identifying potential chemical reagents that can be used to optimize removal of uranium (and molybdenum) from the DDA soils: (1) Supplemental column leaching and (2) laboratory batch testing.

4.1 Supplemental Column Leaching

In the recent DDA column leaching study, 10 pore volumes of either synthetic meteoric precipitation or groundwater were passed through columns containing representative vadose- and saturated-zone aquifer materials (AMEC, 2011). Most of the columns produced leachates whose initial concentrations exceeded CGWQS for uranium (0.03 mg/L) and molybdenum (0.035 mg/L), but with concentrations that continued to decrease with increased leaching. Higher observed uranium and molybdenum leachate concentrations were typically associated with SSC and WCS from the vadose zone. As shown on Figure 1, Column 1 (SSC) displayed rinse-out behavior of uranium that decreased asymptotically to concentrations below 0.03 mg/L, whereas the WCS material in Columns 4 and 5 produced leachates with linear decreases in uranium concentration that remained above 0.03 mg/L after 10 pore volumes.

Supplemental leaching of Columns 1, 4, and 5 with four additional pore volumes is proposed as a preliminary test to evaluate the effects of enhanced uranium leaching by complexation with carbonate. The results of mass balance calculations indicated that a significant fraction of the initial total uranium remains in the columns, and that the uranium likely exists as adsorbed uranium(VI) (AMEC, 2011). Therefore, additional leaching of the existing columns with carbonate solution should produce a concentration “spike” in the column effluents, provided that

the residual uranium exists in the oxidized form. If no spikes are observed in the column effluents, this may indicate that much of the residual uranium is present in the reduced form.

4.2 Laboratory Batch Testing

Laboratory batch testing is proposed as a controlled method to identify an efficient uranium and molybdenum extraction solution for use in future pilot-scale testing. The proposed testing will utilize two of DDA materials that were previously evaluated in the column tests (AMEC, 2011): (1) Unconsolidated sands, silts, and clays (SSC) used to prepare Column 1 (C1), and (2) weathered claystone materials (WCS) used to prepare Column 4 (C4) (Table 1).

Samples of both C1 and C4 material will be extracted using two concentrations of sodium bicarbonate (0.2 and 0.5 M) and citric acid (0.2 and 0.5 M). Treatments will be repeated using an approximate 100:1 molar ratio of Na_2O_2 to uranium (50 mg Na_2O_2) for a total of 16 tests (Table 1). A solution:solid ratio of 5:1 will be used, and all tests will be run in triplicate to account for variability in extractable uranium and molybdenum concentrations.

To improve uniformity of the results, the reactive fraction (<2-mm) will be isolated by sieving and used for all batch tests. Four subsamples of each material will be analyzed for total uranium and molybdenum to characterize their initial total concentrations. The efficiency of uranium and molybdenum removal for each test will be defined as the ratio of the uranium and molybdenum removed to their initial levels, expressed as a percentage. Recommended detailed procedures for the proposed laboratory batch tests are provided in Attachment A.

5.0 SUMMARY AND SCHEDULE

This Scope of Work outlines recommended procedures for identifying an efficient extraction solution that can be used in future pilot-scale testing for DDA soil remediation. The SOW assumes that all testing will be conducted at the Cotter Corporation Mill Site in Cañon City, CO and that Cotter will purchase all required equipment and conduct all analytical testing. AMEC will provide project oversight, data assimilation/interpretation, and reporting.

A reasonable schedule for completing both supplemental column leaching and laboratory batch testing is approximately 12 weeks:

- Obtain laboratory equipment, chemical reagents, and prepare soil materials - **3 weeks**
- Conduct supplemental leaching and batch testing – **4 weeks**
- Complete analytical testing of solutions and solids – **3 weeks**
- Data assimilation, evaluation, and reporting – **2 weeks**

6.0 REFERENCES

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Table 1 Experimental Matrix of Proposed Batch Testing.

Test No.	Material ^a	Sample Mass(g)	Solution Volume (mL)	NaHCO ₃ (M)	Citric Acid (M)	Na ₂ O ₂	H ₂ O
1	SSC	50	250	0.2	-----	-----	-----
2	SSC	50	250	0.2	-----	50 mg	-----
3	SSC	50	250	0.5	-----	-----	-----
4	SSC	50	250	0.5	-----	50 mg	-----
5	SSC	50	250	-----	0.2	-----	-----
6	SSC	50	250	-----	0.2	50 mg	-----
7	SSC	50	250	-----	0.5	-----	-----
8	SSC	50	250	-----	0.5	50 mg	-----
9 (control)	SSC	50	250	-----	-----	-----	Deionized
10	WCS	50	250	0.2	-----	-----	-----
11	WCS	50	250	0.2	-----	50 mg	-----
12	WCS	50	250	0.5	-----	-----	-----
13	WCS	50	250	0.5	-----	50 mg	-----
14	WCS	50	250	-----	0.2	-----	-----
15	WCS	50	250	-----	0.2	50 mg	-----
16	WCS	50	250	-----	0.5	-----	-----
17	WCS	50	250	-----	0.5	50 mg	-----
18 (control)	WCS	50	250	-----	-----	-----	Deionized

^a SSC = archived sands, silts, and clays used for Column 1. WCS = archived weathered claystone used for Column 4 (AMEC, 2011).

ATTACHMENT A
DETAILED BATCH TESTING PROCEDURES

Laboratory Batch Testing Procedures

Uranium and Molybdenum Extraction from Dam-to-Ditch Area Soils

Laboratory Materials

<ul style="list-style-type: none"> • Archived soils used for Columns 1 and 4 	<ul style="list-style-type: none"> • Oscillating table shaker
<ul style="list-style-type: none"> • 2-mm (10 mesh) sieve 	<ul style="list-style-type: none"> • Balance, spatula, weighing vessel
<ul style="list-style-type: none"> • 27- Nalgene wide mouth extraction bottles (250 mL or 8-oz) 	<ul style="list-style-type: none"> • Filtering apparatus and 0.45 micron pore size filtration membranes
<ul style="list-style-type: none"> • 60 – small clean sample bottles for collection of filtered batch test leachates (100 to 200 mL) 	<ul style="list-style-type: none"> • Labware cleaning supplies (soap, brushes)
<ul style="list-style-type: none"> • Sodium peroxide (Na_2O_2) (several grams) 	<ul style="list-style-type: none"> • Clean plastic beakers for solution transfer
<ul style="list-style-type: none"> • Sodium bicarbonate (NaHCO_3) (approx. 200 g) to prepare 2 L of 0.2 and 0.5 M solution 	<ul style="list-style-type: none"> • 250 to 500-mL graduated cylinder
<ul style="list-style-type: none"> • Citric Acid ($\text{C}_6\text{H}_8\text{O}_7$) (approx. 250 g) to prepare 2 L of 0.2 and 0.5 M solution 	<ul style="list-style-type: none"> • Plastic storage bags (quart or gallon size), Sharpee, clear tape
<ul style="list-style-type: none"> • Distilled or deionized (DI) water 	

Procedures

1. Prepare approximately 2 kg of fresh, air-dried material previously used for Column 1 (C1) by sieving to pass a 2-mm (10 mesh) screen. Place the sieved soil into a plastic Ziploc bag and thoroughly homogenize. Remove four separate 10 g subsamples using a small spatula, place into an appropriate sample container, and submit each sample to the laboratory for analysis of total uranium and molybdenum.
2. Prepare 27 Nalgene extraction bottles (250-mL capacity) by thoroughly cleaning the bottles and caps with warm soapy water and brushes (even if new). Rinse both bottles and caps thoroughly with tap water to remove soap, followed by rinsing a minimum of three times with DI water. Allow the bottles to dry upside down and replace the caps during storage.
3. Using DI water, prepare 2 Liters each of the respective NaHCO_3 and citric acid solutions:
 - a. 0.2 M NaHCO_3 : dissolve 16.8 g NaHCO_3 per Liter (33.6 g for 2 Liters).
 - b. 0.5 M NaHCO_3 : dissolve 42.0 g NaHCO_3 per Liter (84.0 g for 2 Liters).
 - c. 0.2 M citric acid: dissolve 38.4 g per Liter or 76.8 g for 2 Liters (42.1 g per Liter or 84.2 g per 2 Liters, respectively, if using citric acid monohydrate).

- d. 0.5 M citric acid: dissolve 96.1 g per Liter or 192 g for 2 Liters (105 g per Liter or 210 g per 2 Liters, respectively, if using citric acid monohydrate).
4. Filter 100 mL of each solution through a 0.45 micron pore-size filter and into a small clean plastic sample bottle, acidify using nitric acid (HNO₃). Submit to the laboratory for analysis of dissolved uranium and molybdenum.
5. Label the 27 clean Nalgene extraction bottles for Tests 1 through 9 specified in Table 1. (triplicates should be labeled 1a, 1b, 1c, 2a, 2b, 2c, etc.). Place clear tape over the labels to prevent them from wearing off during the extraction process.
6. Weigh exactly 50.0 g of the prepared soil from Step 1 into each of the 27 extraction bottles.
7. Add 50 mg of solid Na₂O₂ reagent to the 12 extraction bottles labeled 2a,b,c; 4a,b,c; 6a,b,c; and 8a,b,c (Table 1).
8. Add 250 mL of the appropriate extraction solution to the extraction bottles according to Table 1. Rinse all glassware and plastic ware with DI water in between the various extraction solutions.
9. Cap all bottles tightly and place them on their sides into the oscillating table shaker such that the bottles oscillate end-to-end. At a minimum, the shaker should be set at a speed in which the soil and solution are continuously agitated with no observed settling of the sediment in the bottles. Shake the bottles for 8 hrs, remove from the shaker, and allow to settle while standing upright.
10. Filter a minimum of 100 mL of each supernatant solution through a 0.45 micron pore size filter and into a small clean plastic sample bottle (sample bottles should be cleaned by brushing with warm soapy tap water, followed by thorough rinsing with tap water, acid washing with 0.10 M HCl, and rinsing a minimum of three times with DI water). A fresh filter membrane should be used for each sample. Preserve the sample accordingly using a minimal amount of nitric acid (HNO₃) to achieve a pH less than 2 and submit to the laboratory for analysis of dissolved uranium and molybdenum.
11. Repeat Steps 1 through 10 using fresh material that was previously used to prepare Column 4 (AMEC, 2011).