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Radionuclide Leaching from Residual Solids Remaining After Acid Dissolution of Composite K East Canister Sludge

CH Delegard
DE Rinehart
CZ Soderquist
SK Fadeff

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Pacific Northwest National Laboratory
Richland, Washington 99352

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Summary and Conclusions

Laboratory tests were performed to examine mixed nitric/hydrofluoric acid leach treatments for decontaminating dissolver residual solids (KECDVSR24H-2) produced during a 20- to 24-hr dissolution of a composite K East (KE) Basin canister sludge in 95ºC 6 M nitric acid (HNO_3). The scope of this testing has been described in Section 4.5 of "Testing Strategy to Support the Development of K Basin Sludge Treatment Process" (Flament 1998). Radionuclides sorbed or associated with the residual solids generated in the K Basin sludge treatment process can restrict disposal of this solid to the Environmental Restoration Disposal Facility (ERDF).

The starting dissolver residual solid for this testing, KECDVSR24H-2, contains radionuclides at concentrations which exceed the ERDF Waste Acceptance Criteria for TRU by about a factor of 70, for ^{239}Pu by a factor of 200, and for ^{241}Am by a factor of 50. The solids also exceed the ERDF criterion for ^{137}Cs by a factor of 2 and uranium by a factor of 5. Therefore, the radionuclides of greatest interest in this leaching study are first ^{239}Pu and ^{241}Am (both components of TRU) and then uranium and ^{137}Cs.

Prior scoping tests examined four alternative leachants for residues created from nitric acid dissolution of composite KE floor and Weasel Pit area sludge (Delegard et al. 1998). The leachant achieving the highest decontamination of the area composite residue, 6 M HNO_3 / 0.3 M hydrofluoric acid (HF) at 90ºC, was therefore used to leach the canister sludge residue (KECDVSR24H-2). The leach tests were performed in duplicate with a 4 hr contact time using approximately 28 mL of leachant per gram of residual solids (4.00 mL of leachant with roughly 0.14 g of solid).

The ^{137}Cs concentrations in the solids decreased by a factor of 5 to less than half the ERDF criterion. Uranium concentrations in the solids decreased about a factor of 10 to less than half the ERDF criterion. The TRU concentrations decreased a factor of ~25 but remain approximately three times the ERDF criterion for direct disposal. The ^{239}Pu concentrations also decreased ~25-fold but remain eight times the ERDF criterion in the residue. The ^{241}Am concentrations decreased about a factor of 16 but exceed the EDRF criterion by a factor of 3.

The decontamination factors achieved for the canister sludge solids are slightly higher (^{137}Cs, uranium, ^{241}Am) to greatly higher (^{239}Pu, TRU) than those previously achieved at comparable conditions for the composite floor / weasel pit area sludge residues. Between 95% and 98% of the TRU (both plutonium and americium) dissolved from the canister sludge residue by HNO_3/HF leaching, as well as 92% to 95% of the uranium and about 82% of the cesium.

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1.0 Background and Approach

Leach tests were performed on the residual solids created by dissolving a composite KE Basin canister sludge in 6 M nitric acid (HNO_3) for 20 to 24 hr at 95ºC. In previous tests on composite KE Basin floor and Weasel Pit sludge residue, four candidate leachants were tested. The leachant most successful in solubilizing the radioelements of interest was found to be 6 M HNO_3/0.3 M hydrofluoric acid (HF) (Delegard et al. 1998). This leachant therefore was used in the present tests with the canister sludge residue. Background information, the experiments performed, and the experimental results are presented in this report.

Solids to be delivered to the Environmental Restoration Disposal Facility (ERDF) must meet established Waste Acceptance Criteria for radionuclide concentration (Bechtel 1998). The radionuclides most likely limiting the ERDF acceptance of K Basin residual solids are ^{137}Cs (32 Ci/m^3 or 32 µCi/mL) and the transuranics (TRU; 100 nCi/g). The TRU isotopes have individual limits: ^{241}Am, 0.05 Ci/m^3 (50 nCi/mL); ^{238}Pu, 1.5 Ci/m^3 (1,500 nCi/mL); and ^{239}Pu and ^{240}Pu, 0.029 Ci/m^3 (29 nCi/mL) each. Because ^{239}Pu represents about 2/3 of the ^{239,240}Pu activity in K Basin materials, and the ERDF activity concentration limits for ^{239}Pu and ^{240}Pu are identical, the ^{239}Pu limit is the more restrictive for ERDF disposal acceptance. The effective uranium limit for disposal to ERDF, 0.0026 g U/mL[1], has the potential to restrict the disposal of certain K Basin residual solids.

The radionuclide contamination in residual solids seems to be most severe for plutonium (i.e., plutonium concentrations are farthest from the relevant acceptance criterion). Therefore, chemical dissolution methods should target plutonium and secondarily be effective for the other key radioelements: ^{241}Am, ^{137}Cs, and uranium. Analyses by inductively coupled plasma (ICP) spectrometry show the major chemical components of the residual solids from nitric acid leaching of K Basin sludge (either floor/Weasel Pit or canister) to be silicon, aluminum, and iron. Therefore, to dissolve plutonium and the other radionuclides, leachants must attack plutonium phases such as PuO_2 or the silica/aluminosilicates and iron (hydr)oxide in which the plutonium may be trapped.

An engineering study was performed to identify chemical agents to leach radioactive components, particularly plutonium, from K Basins sludge dissolver residual solids (Bechtold 1998). Five candidate leachants were identified in that study: Ce(IV) in nitric acid (HNO_3), persulfate ($S_2O_8^{2-}$) with Ag(II) catalyst in HNO_3, HF in HNO_3, Citrox (a combination of citric and oxalic acids), and hydrochloric acid (HCl) in HNO_3. The Citrox process was not selected for the initial studies because its target residue, iron (hydr)oxides, is more readily leached in hydrochloric acid.

The remaining four candidate leachants [Ce(IV), persulfate with Ag(II) catalyst, hydrofluoric acid, and hydrochloric acid, all in HNO_3] were tested on residue remaining from 6 M HNO_3 leaching of a composite K Basin floor and Weasel Pit sludge. Both Ce(IV) and persulfate with Ag(II) are strong oxidants and targeted at PuO_2. They would be effective because they convert the chemically stable solid PuO_2 to dissolved PuO_2^{2+}. However, aside from the slight contribution from the contained nitric acid, neither leachant was expected to be effective in attacking siliceous or ferric residues remaining from prior extensive nitric acid leaching. The HF was thought to be effective for both PuO_2 and siliceous solids

[1] The ERDF Waste Acceptance Criteria limit for ^{238}U *and its daughters* is 0.012 Ci/m^3. With 8 alpha and 6 beta decays in the ^{238}U decay chain and a specific activity of 3.36x10^{-7} Ci ^{238}U /g, the specific activity of the ^{238}U chain is 4.7x10^{-6} Ci/g. The ERDF limit for ^{238}U thus is 0.00256 g ^{238}U/mL. The ERDF limit for ^{235}U (daughters *not* included) is 0.0027 Ci/m^3 and the specific activity of ^{235}U is 2.16x10^{-6} Ci/g. Thus, the ERDF limit for ^{235}U is 0.0013 g ^{235}U/mL. The relative limits of the two uranium isotopes, and the nominal 0.7% enrichment of the K Basins sludge, mean that ^{238}U concentration limits ERDF disposal. Therefore, the effective uranium limit for disposal to ERDF is 0.0026 g U/mL.

because of the strong affinity of the fluoride ion for Pu(IV) and Si(IV) to break down the respective oxide phases. The HCl was targeted at the ferric (hydr)oxides (e.g., goethite, hematite) because of the strong complexing affinity of the chloride ion for Fe(III).

Of the four leachants tested, the 6 M HNO_3/0.3 M HF leachant (4 hr of contact at 90ºC) clearly gave the best decontamination for TRU, plutonium, americium, and uranium. Under the stated conditions, 89% of the plutonium, 95% of the americium, 90% of the TRU, and 91% of the uranium reported to solution. The leached solids were about 1/2 the ERDF criterion for TRU, about 3/2 the ERDF criterion for ^{239}Pu, and about 1/8 the ERDF criterion for ^{241}Am. The ^{239}Pu concentration in the nitric/hydrofluoric acid-leached residue was about 45 nCi /mL to give a decontamination factor of about 8. The ^{241}Am concentration decreased about 16-fold by nitric/hydrofluoric acid treatment. This decontamination was strikingly superior to that attained by any other leachant and left a residue meeting the 50 nCi ^{241}Am/mL ERDF criterion by a factor of about 8.

The 6 M HNO_3/0.3 M HF clearly was the best in leaching the composite K Basin floor and Weasel Pit area sludge residue. Therefore, this reagent, under the same test conditions, also was used to leach the composite KE Basin canister sludge residue.

2.0 Experimental Materials and Methods

All testing and analyses were performed in the Radiochemical Processing Laboratory (RPL). Approved test instructions were followed for executing the leach contact tests. The leach contacts were made in open-faced hoods in the RPL.

2.1 Materials

Leach tests were performed on the residual solids (designated as KECDVSR24H-2) created by treating composite KE canister sludge (KE Can) in 6 M HNO_3 for 20 to 24 hr at 95ºC. The KECDVSR24H-2 material is a pale gray-tan slightly gritty powder.

Leach solutions were prepared using distilled and deionized (DI) water and reagent-grade 15.9 M nitric acid (HNO_3) and 29 M HF solutions. The leachant was 6 M HNO_3/0.3 M HF and 6 M HNO_3 solution was used for rinsing. Reagents were prepared quantitatively (±0.0001 g) using a Mettler AE 240 balance, calibrated pipets, and volumetric glassware. The nitric/hydrofluoric acid solution was prepared and stored in plastic vessels because of its aggressiveness towards glass. The nitric acid rinse solution was prepared and stored in glass vessels.

2.2 Leaching Experimental Procedure

The leach testing was performed in duplicate. First, two ~0.14-g aliquots of dissolver residual solids (KECDVSR24H-2) were weighed (±0.0001 g) into 2-dram glass vials in the RPL Shielded Analytical Laboratory hot cell facility. The aliquots were wetted with about 1 mL of DI water to limit the solids dispersability in air, and the aliquots transferred to an open-face hood for the leach testing. Once in the hood, the aliquots were transferred by pipette into tare-weighed 15-mL capped polypropylene centrifuge cones. Additional DI water was used to aid in the rinse and transfer from the glass vials.

Direct aliquot weighing into the plastic centrifuge cones was not done because of the powder's dispersibility caused by static electricity effects between the dry solids powder and the plastic. Leach tests were not performed in glass because of the glass corrosion caused by hydrofluoric acid. Polypropylene cones were selected because separate tests demonstrated that they could withstand, without deformation or obvious chemical attack, 4 hr contact with a strong oxidant [6 M HNO_3/0.4 M Ce(IV)] at 100ºC.

Following quantitative transfer of the solids to the plastic centrifuge cones, the cones and contents were centrifuged and the supernatant solution withdrawn by transfer pipette. The solutions from each tube were collected separately in labeled vessels. The total amount of transfer and rinse water was around 2 mL. The cones with wet solids were reweighed and found to contain from 0.2 to 0.3 mL residual water. This amount of water would dilute the leachant concentration no more than 7%. The wet solids then were contacted with the nitric/hydrofluoric acid leachant. The leachant, leach temperature, and the weights of KECDVSR24H-2 used in the leach tests are described in Table 1. Also presented in Table 1 for reference in later comparison of results are the corresponding values for the prior HNO_3/HF leaching of the composite KE floor and Weasel Pit area sludge residue, KEACRESID1. The test designations, ACRES and CANRES, refer to the area composite and canister composite residues.

All leach contacts were conducted with 4.00 mL of leachant at 90ºC controlled by a thermostatted water bath. The duration of all leach contacts was 4 hr. The solids and leachants were agitated intermittently (at the beginning and at 0.5, 1, 2, 3, and 4 hr) and left in racks with the caps slightly open between agitations to allow offgassing.

Table 1. Leachants and Material Weights in Leach Testing

Test	Residue Source and ID	Leachant & Temperature, ºC	Mass Residue, g
CANRES1	KE canister; KECDVSR24H-2	6 M HNO_3 / 0.3 M HF 90	0.1447
CANRES2			0.1352
ACRES 5	KE floor and Weasel Pit; KEACRESID1		0.1533
ACRES 6			0.2228

After 4 hr of contact, the tubes were tightly capped and centrifuged, and the supernatant solutions removed by transfer pipette. The leachate solutions were combined with the transfer water. Each leached solid then was washed, centrifuged, and decanted four times with 1-mL portions of 6 M HNO_3 to remove the interstitial leachant. The washes, too, were added to the transfer water and leachate. The weights and volumes of the combined leachates were determined and recorded. The washed solids were transferred into tare-weighed glass vials, dried in a 70ºC oven for about 18 hr, and reweighed. The composited transfer water, leachate, and rinses for each test and the respective leached and dried solids from the CANRES tests were submitted for radiochemical analyses.

2.3 Analyses

The radiochemical analyses were performed in the RPL analytical laboratory using established procedures.

Weighed aliquots of the CANRES residual solids remaining from the leach tests were digested by fusion in molten KOH followed by acidification. The digestates were analyzed for uranium concentration by laser fluorimetry; ^{137}Cs and ^{241}Am concentrations by gamma energy analysis (GEA); and total alpha, ^{239,240}Pu, and ^{238}Pu/^{241}Am concentrations by alpha energy analysis (AEA). The leachates were analyzed to determine uranium, ^{137}Cs, ^{241}Am, total alpha, ^{239,240}Pu, and ^{238}Pu/^{241}Am concentrations by the same analytical measurement techniques as used for the digested solids.

Drying the solutions from the fused and digested solids on radiometric counting planchets left deposits which attenuated the emitted alpha particles and decreased the count rate. Total alpha results from these planchets were about 60% of the sum of the ^{239,240}Pu, ^{238}Pu/^{241}Am, and ^{243,244}Cm alpha peaks found by the radiochemical carrier precipitation analyses[2]. Therefore, the sum of the individual alpha peak data was used to provide the total alpha measurement for the digested solids. The aqueous samples gave total alpha results that agreed within 10% of the sum of the ^{239,240}Pu, ^{238}Pu/^{241}Am, and ^{243,244}Cm alpha activities. To be consistent, however, the summed alpha peak activities also were used to assess the total alpha results for the solutions.

[2] Note: The alpha activity from ^{243,244}Cm is negligible compared with the plutonium and americium activities.

3.0 Experimental Results and Discussion

Experimental observations of the qualitative behavior and radiochemical distributions in the leach testing are presented and interpreted in this section.

3.1 Qualitative Observations

The nitric/hydrofluoric acid leachates from the CANRES tests had slight yellow coloration. The comparable ACRES test leachates had no noticeable coloration. Both the CANRES and ACRES nitric/hydrofluoric leach tests showed no evidence of volatilization of silicon caused by production of SiF_4. Such evidence would have been the formation of a slushy silicic acid deposit in the cooler upper vapor-condensing region of the centrifuge cone caused by hydrolysis of the SiF_4. Silicic acid deposits have been observed to form during plutonium dissolution in silica(te)-bearing scrap by treatment with boiling nitric/hydrofluoric acid.

The CANRES solids seemed to become visually less gritty with leaching. Like the ACRES tests, no bubbling occurred and no obvious colored fumes were produced in the CANRES tests.

3.2 Composition of the Starting Materials

Results of radiochemical analyses of KECDVSR24H-2, the starting material for the present leaching tests, and KEACRESID1, the starting material from the prior residue leaching tests (Carlson et al. 1998), are presented in Table 2. Also given in Table 2 are the radionuclide quantities for each test aliquot, based on measured concentrations plus the weights provided in Table 1.

Table 2. Radiochemical Concentrations and Quantities in the Starting Materials

	Concentration in Solid					
Solid	^{137}Cs, µCi/g	U, µg/g	^{239,240}Pu, nCi/g	^{241}Am, nCi/g	^{238}Pu/^{241}Am, nCi/g	Total Alpha, nCi/g
KEACRESID1	4.65	120	274	35.6	85.9	359.9
KECDVSR24H-2	33.6	6470	4650	1250	1830	6830
	Quantity in Test					
Test	^{137}Cs, µCi	U, µg	^{239,240}Pu, nCi	^{241}Am, nCi	^{238}Pu/^{241}Am, nCi	Total Alpha, nCi
ACRES 5	0.713	18.40	42.00	5.46	13.17	55.17
ACRES 6	1.036	26.74	61.05	7.93	19.14	80.19
CANRES1	4.86	936	673	181	265	988
CANRES2	4.54	875	629	169	247	923

The canister sludge residue, KECDVSR24H-2, is distinctly higher in radionuclide contamination than the composite floor and Weasel Pit sludge residue, KEACRESID1. The canister sludge residue ^{137}Cs concentration is ~7 times higher, the uranium concentration about 46 times higher, the ^{239,240}Pu concentration ~17 times higher, the ^{241}Am concentration ~35 times higher, and the total alpha concentration ~19 times higher than the KE area composite residue.

The ERDF limit for uranium is 0.0026 g/mL (which is 0.0013 g U/g, assuming a solids bulk density of 2 g/mL). The concentration of uranium in KECDVSR24H-2, 6470 µg/g (0.0065 g U/g), is about a factor of 5 above the ERDF criterion. The ^{137}Cs concentration is about a factor of 2 above the ERDF limit of 16 µCi/g (32 µCi/mL at a density of 2 g/mL).

The total alpha concentration for KECDVSR24H-2 is derived as the sum of the ^{239,240}Pu, ^{238}Pu/^{241}Am, and ^{243,244}Cm AEA measurements. The starting material exceeds the TRU limit of 100 nCi/g by about 70-fold based on these total alpha results.

The ^{239}Pu and ^{240}Pu each have 29 nCi/mL ERDF disposal limits. Because ^{239}Pu constitutes about 2/3 of the ^{239,240}Pu activity in K Basin materials, the ^{239}Pu limit is more restrictive than the ^{240}Pu limit. The ^{239,240}Pu concentration of 4650 nCi/g in KECDVSR24H-2 thus represents about 3100 nCi ^{239}Pu/g or 6200 nCi ^{239}Pu/mL, exceeding the ERDF criterion by a factor of about 200. The ^{241}Am concentration of 1250 nCi/g (2500 nCi/mL) exceeds the 50 nCi/mL ERDF criterion by about 50-fold. The actinides, particularly plutonium, thus are of most concern in decontaminating the KECDVSR24H-2 to meet ERDF acceptability.

3.3 Leachate Analyses

The concentrations of radioelements found in the combined water transfer solutions, leachates, and rinses from nitric/hydrofluoric acid leaching of the KEACRESID1 (ACRES 5 and ACRES 6) and KECDVSR24H-2 (CANRES1 and CANRES2) solids are presented in Table 3. The concentration data in the replicate tests compare well in light of the small quantities of starting material. As shown at the bottom of Table 3, ^{241}Am solution concentrations were obtained by deducting the contribution of ^{238}Pu to the ^{238}Pu/^{241}Am AEA peak. The measurement uncertainties in the GEA of ^{241}Am ranged from 9% to 10% compared with 2% to 3% in the AEA.

Table 3. Radiochemical Concentrations in Combined Test Solutions, Leachates, and Rinses

Test	Leachate Concentrations					
	^{137}Cs, μCi/mL	U, μg/mL	^{239,240}Pu, nCi/mL	^{241}Am, nCi/mL*	^{238}Pu/^{241}Am, nCi/mL	Total Alpha, nCi/mL**
ACRES 5	0.0430	1.28	3.61	0.532	1.11	4.74
ACRES 6	0.0675	2.22	5.26	0.908	1.75	7.05
CANRES1	0.339	78.0	86.1	18.44	29.2	118
CANRES2	0.348	73.1	74.6	17.08	26.4	104

* To decrease measurement variability, ^{241}Am concentrations were not obtained by GEA but were derived by deducting the contribution of ^{238}Pu to the ^{238}Pu/^{241}Am AEA peak. To determine the ^{238}Pu contribution for the ACRES samples, the ^{238}Pu/^{239,240}Pu activity ratio of 0.16 ± 0.01 was applied to the ^{239,240}Pu AEA peak. The ^{238}Pu/^{239,240}Pu ratio was taken to be the average of the ratios found in characterization samples from the KE Basin floor and Weasel Pit (Welsh et al. 1996). The ^{238}Pu/^{239,240}Pu ratio for the CANRES samples, 0.125, was derived from the GEA and AEA counting data of the present tests.

** Total alpha is the calculated sum of the ^{239,240}Pu, ^{241}Am, and ^{243,244}Cm (not presented) activities.

3.4 Leach Residue Analyses

The radiochemical concentrations in the leach residues are given in Table 4. The solids fractional weight losses resulting from the leach treatments also are presented. The concentration data agree well within the duplicate samples. The weight losses caused by leaching are 10% to 30%. This leachant is aggressive towards silicates. As shown in Figure 1, both starting materials, KEACRESID1 and KECDVSR24H-2, are high in silica and have comparable chemical compositions (Carlson et al. 1998 for KEACRESID1).

The composite canister sludge residue evidently is more susceptible to nitric/hydrofluoric acid, as shown by its higher weight loss upon leaching.

Table 4. Radiochemical Concentrations in Test Residues

Test	Concentration						Fractional Weight Loss
	^{137}Cs, µCi/g	U, µg/g	^{239,240}Pu, nCi/g	^{241}Am, nCi/g*	^{238}Pu/^{241}Am, nCi/g	Total Alpha, nCi/g**	
ACRES 5	1.49	12.3	37.0	2.67	8.59	45.7	0.149
ACRES 6	1.85	10.5	33.4	2.43	7.77	41.3	0.094
CANRES1	7.49	580	186	80.0	103.2	290	0.207
CANRES2	6.82	381	179	74.9	97.3	278	0.290

* To decrease measurement variability, ^{241}Am concentrations were not obtained by GEA but were derived by deducting the contribution of ^{238}Pu to the ^{238}Pu/^{241}Am AEA peak. To determine the ^{238}Pu contribution for the ACRES samples, the ^{238}Pu/^{239,240}Pu activity ratio of 0.16 ± 0.01 was applied to the ^{239,240}Pu AEA peak. The ^{238}Pu/^{239,240}Pu ratio was taken to be the average of the ratios found in characterization samples from the KE Basin floor and Weasel Pit (Welsh et al. 1996). The ^{238}Pu/^{239,240}Pu ratio for the CANRES samples, 0.125, was derived from the GEA and AEA counting data of the present tests.

** Total alpha is the calculated sum of the ^{239,240}Pu, ^{241}Am, and ^{243,244}Cm (not presented) activities. High dissolved solids caused self-shielding in the total alpha analysis of the direct-mounted digestate, compromising the results.

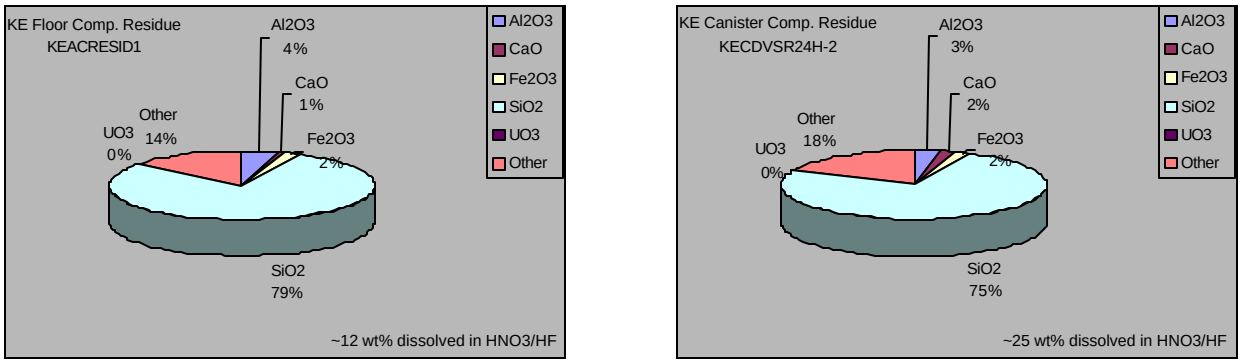

Figure 1. Chemical Compositions of Starting Residues from the Composite KE Floor and Weasel Pit and the Composite KE Canister Sludges.

The ^{137}Cs concentration in the composite KE canister residue KECDVSR24H-2 was approximately two times ERDF limit at ~34 µCi/g and decreased by a factor of ~5 to less than half the ERDF limit. Uranium concentrations in the initial solids were a factor of ~5 above the ERDF criterion and, with HNO_3/HF leaching, decreased to ~0.0005 g U/g, less than half the ERDF criterion.

The TRU (total alpha) concentrations in the KECDVSR24H-2 starting material are ~70 times the ERDF criterion, whereas the residues from leaching are approximately three times the ERDF criterion of 100 nCi/g. The initial KECDVSR24H-2 solid is ~6200 nCi ^{239}Pu/mL. The concentration in the HNO_3/HF acid-leached residue decreased by a factor of ~25 to ~240 nCi ^{239}Pu/mL, approximately eight times the ERDF criterion for this isotope. The ^{241}Am concentration decreased ~16-fold by HNO_3/HF acid treatment leaving a 80 nCi/g residue, exceeding the 50 nCi ^{241}Am/mL ERDF criterion by a factor of ~3.

3.5 Material Balances

The radiochemical material balances for the leach tests for ^{137}Cs, U, ^{239,240}Pu, ^{241}Am, ^{238}Pu/^{241}Am, and total alpha are given in Tables 5 through 10, respectively. The material balances compare the quantities of radiochemicals found in the weighed amounts of starting KEACRESID1 and KECDVSR24H-2 materials with the sum of the quantities found in the leach test fractions (solids residue and leachate). The ratios of the sum to the amount in the starting material, expressed as % recovery, also are given in Tables 5 through 10. The material balances show reasonable recoveries ranging from 90% to 130%.

Table 5. Leach Testing Material Balance for ^{137}Cs

Test	^{137}Cs, µCi				
	Start	Residue	Leachate	Sum	% Recovery
ACRES 5	0.57	0.194	0.456	0.650	114.9
ACRES 6	0.82	0.373	0.709	1.082	131.6
CANRES1	4.86	0.859	3.560	4.419	90.9
CANRES2	4.54	0.655	3.550	4.204	92.6

Table 6. Leach Testing Material Balance for Uranium

Test	Uranium, µg				
	Start	Residue	Leachate	Sum	% Recovery
ACRES 5	18.40	1.60	13.57	15.17	82.5
ACRES 6	26.74	2.12	23.31	25.43	95.1
CANRES1	936	66.6	820	886	94.6
CANRES2	875	36.6	746	782	89.4

Table 7. Leach Testing Material Balance for ^{239,240}Pu

Test	^{239,240}Pu, nCi				
	Start	Residue	Leachate	Sum	% Recovery
ACRES 5	34.65	4.82	38.27	43.09	124.4
ACRES 6	50.35	6.74	55.23	61.97	123.1
CANRES1	673	21.3	904	925	137.5
CANRES2	629	17.2	761	778	123.8

Table 8. Leach Testing Material Balance for ^{241}Am

Test	^{241}Am, nCi				
	Start	Residue	Leachate	Sum	% Recovery
ACRES 5	6.13	0.35	5.64	5.99	97.7
ACRES 6	8.91	0.49	9.54	10.03	112.5
CANRES1	181	9.17	181	190	105.0
CANRES2	169	7.19	185	192	113.6

Table 9. Leach Testing Material Balance for $^{238}Pu/^{241}Am$

Test	$^{238}Pu/^{241}Am$, nCi				
	Start	Residue	Leachate	Sum	% Recovery
ACRES 5	11.90	1.12	11.77	12.89	108.3
ACRES 6	17.29	1.57	18.38	19.94	115.3
CANRES1	265	11.84	307	318	120.3
CANRES2	247	9.34	269	279	112.6

Table 10. Leach Testing Material Balance for Total Alpha

Test	Total Alpha, nCi				
	Start	Residue	Leachate	Sum	% Recovery
ACRES 5	46.5	5.96	50.2	56.2	120.8
ACRES 6	67.6	8.33	74.0	82.4	121.8
CANRES1	988	33.2	1239	1272	128.7
CANRES2	923	26.7	1061	1087	117.8

3.6 Decontamination Factors

The solids decontamination factors (DFs), based on dry solids weights, are shown in Table 11. Because relatively little solids dissolved, even with nitric/hydrofluoric acid, these DFs represent true leaching and not solubilization caused by dissolution of the matrix. However, dissolution of the silicate matrix must be key to the relative success of the HNO_3/HF leaching compared with the other nitric acid based leachants.

Table 11. Decontamination Factors for Solids

Test	^{137}Cs	Uranium	$^{239,240}Pu$	^{241}Am	$^{238}Pu/^{241}Am$	Total Alpha
ACRES 5	2.8	8.0	7.6	14.6	9.8	8.0
ACRES 6	2.6	10.9	8.3	18.6	11.5	9.0
CANRES1	4.1	10.5	34.4	16.4	21.3	30.3
CANRES2	5.1	17.0	35.9	21.1	23.6	32.3

The decontamination requirements for residual solids from K Basin sludge dissolution are most pressing, in terms of meeting the ERDF disposal criteria, for the transuranium constituents (^{239}Pu, ^{241}Am, and TRU). These analytes are quantified in the $^{239,240}Pu$, ^{241}Am, $^{238}Pu/^{241}Am$, and total alpha results. The DF data in Table 11 show, encouragingly, that the nitric/hydrofluoric acid leachant gave higher DFs from the transuranium constituents for the more contaminated canister sludge residue (KECDVSR24H-2) than for the area composite sludge residue (KEACRESID1). The DFs from ^{137}Cs and from uranium also were moderately higher for the canister sludge residue (CANRES) than for the area composite sludge residue (ACRES).

3.7 Dissolution Coefficients

The fractions of analyte dissolved in the HF/HNO_3 leach treatment are given in Table 12. The fraction is calculated by dividing the quantity reporting to solution (in the leachate) by the total quantity present in the leach test (leachate plus residue). These quantities, given in Tables 5 through 10 for ^{137}Cs, U, $^{239,240}Pu$, ^{241}Am, $^{238}Pu/^{241}Am$, and total alpha, respectively, were used to calculate the dissolution coefficients.

Table 12. Dissolution Coefficients

Test	^{137}Cs	Uranium	^{239,240}Pu	^{241}Am	^{238}Pu/^{241}Am	Total Alpha
ACRES 5	0.701	0.894	0.888	0.942	0.913	0.894
ACRES 6	0.655	0.917	0.891	0.951	0.921	0.899
CANRES1	0.806	0.925	0.977	0.952	0.963	0.974
CANRES2	0.844	0.953	0.978	0.963	0.966	0.975

Significantly, from 95% to 98% of the transuranic constituents dissolved from the canister sludge residue (compared with 89% to 95% for the area composite sludge residue). Uranium and ^{137}Cs dissolutions, about 94% and 82%, respectively, also were higher for the canister sludge residue than for the area composite.

4.0 References

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