


ORISE
 OAK RIDGE INSTITUTE FOR SCIENCE AND EDUCATION

February 23, 2004

Ms. Christianne Ridge
 Mail Stop TWFN 7J8
 U.S. Nuclear Regulatory Commission
 11545 Rockville Pike
 Rockville, MD 20852

SUBJECT: REPORT FOR ANALYSIS OF READILY AND SLOWLY AVAILABLE URANIUM IN ASH SAMPLES FROM THE KISKI VALLEY ASH LAGOON, LEECHBURGH, PENNSYLVANIA [RFTA 04-001]

Dear Ms. Ridge:

The Environmental Survey and Site Assessment Program (ESSAP) of the Oak Ridge Institute for Science and Education (ORISE) was requested to perform a study on the Readily Available Uranium (RAU) and the Slowly Available Uranium (SAU) in five ash samples collected in December 1994 at the Kiski Valley Ash Lagoon, Leechburgh, Pennsylvania. The experimental design used was a modification of NUREG/CR-6232 which you provided to ESSAP via a facsimile on December 15, 2003. Two separate tests were conducted on the five ash samples. The first test used dilute acetic acid for the RAU portion of the procedure. The second test used deionized water that was pre-equilibrated with a low-level ash sample for 18 hours for the RAU portion of the procedure. Both tests used dilute sodium bicarbonate for the SAU portion of the procedure. A detailed procedure and some general comments on the analytical process are presented in the enclosed case narrative. Table 1 presents gamma spectroscopy data for the five ash samples. The results of test one and test two are presented in Tables 2 and 3, respectively.

ESSAP's Quality Control (QC) requirements were met for these analyses. The QC files are available for your review upon request.

Please contact me at (865) 241-3242 or Wade Ivey at (865) 576-9184 should you have any questions.

Sincerely,

Dale Condra

Dale Condra
 Laboratory Manager
 Environmental Survey and
 Site Assessment Program

RDC:WPI:ar

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 File/897

Distribution approval and concurrence:	Initials	Date
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NMSS 21
 Add:
 A. Christianne Ridge

CASE NARRATIVE
2/23/04

KISKI VALLEY ASH SAMPLES

ESSAP performed two individual tests on five ash samples from the Kiski Valley Ash Lagoon, Leechburgh, PA. Both tests were modeled after a procedure for Readily Available Uranium (RAU) and Slowly Available Uranium (SAU) from NUREG/CR-6232. This case narrative presents NUREG/CR-6232 procedural modifications. The modifications were discussed with Ms. Ridge of the Nuclear Regulatory Commission (NRC) who subsequently approved the changes.

The following are the procedural changes ESSAP made, the corresponding procedure section reference in NUREG/CR-6232 for the RAU and SAU tests, and some general observations.

1. Step C.12.3.1 deviation: ESSAP did not have field moist samples and therefore, the samples used were dry.
2. Step C.12.3.4 deviation: ESSAP did not use a rotary agitation device, but instead used a magnetic stirring plate with a magnetic stir bar inside the sample container.
3. Step C.12.3.5 deviation: ESSAP acidified the sample to a pH of one with hydrochloric acid (HCl) instead of nitric acid (HNO₃). HCl was used to facilitate ESSAP's analytical procedure for isotopic uranium.
4. Step C.12.4.2 deviation: ESSAP did not use a shaking water device. Instead, a magnetic stir bar/magnetic stirrer was substituted.
5. Step C.12.4.5 deviation: ESSAP acidified the SAU leachate to a pH of one with HCl instead of HNO₃. Again, HCl was used to facilitate ESSAP's analytical procedure for isotopic uranium.

Each sample was subjected to four individual 18 hour leachings for the RAU portion and one six hour leaching for the SAU portion of each test, as prescribed in NUREG/CR-6232. Each leachate was analyzed for isotopic uranium.

The pH of the acetic acid (HAc) for the RAU portion before the leaching process was 2.9. After the leaching process the solution pH increased to a range of 3.44 to 4.12. The pH of the sodium bicarbonate solution for the SAU portion before the leaching process was 8.3. After the leaching process, the solution pH change was minimal.

The second test was identical to the first except that the leaching material for the RAU was deionized water that had been pre-equilibrated with an ash sample that had little uranium activity. The deionized water was added to the low activity ash sample and stirred on a stirring plate for 18 hours. The solid portion was removed from the water by

filtering it through a 0.65 μm filtering membrane. The pH of the pre-equilibrated water was approximately 6 and the pH did not change significantly after each RAU leach. The pre-equilibrated water was analyzed for isotopic uranium via alpha spectrometry and was found not to contain any uranium above ESSAP's minimum detectable concentration. One final comment is that ESSAP inadvertently used a 0.45 μm filter instead of the 0.65 μm filter for the separation of the sodium bicarbonate from the solid fraction for the SAU portion for the second test. There is no evidence to indicate that using a 0.45 μm filter instead of a 0.65 μm filter would cause any significant changes to the presented data. Below is a detailed, step by step procedure ESSAP used for these two tests.

The following procedure is a variation of a procedure taken from NUREG/CR-6232, pages 73-74 and ESSAP Laboratory Procedure AP11, Revision 2. Per agreement with Ms. Ridge, routine ESSAP Quality Control (QC) samples and the associated QC requirements were applied.

Readily Available Uranium (RAU) and Slowly Available Uranium (SAU) Leaching Procedure

1. Weigh 5-10 grams of dried sample. Record the mass and transfer the sample to an appropriate size polyethylene bottle. Add a stir bar to the bottle.
2. Add an amount of 0.1 M acetic acid (for the first test) (HAc; pH=2.9) or pre-equilibrated deionized water (for the second test) such that the ratio of solution volume (in mL) to sample mass (in g) is 20:1. For example, if 10 grams of sample were used, add 200 mL of the 0.1 M HAc or water.
3. Cap the bottle and shake the suspension. Loosen the cap to relieve any pressure that may have developed. Note on the assignment sheet which samples had considerable pressure build-up.
4. Recap the bottle and place on a stir plate. Stir the suspension at a fast enough speed such that the solid material remains in suspension. Do not stir too fast. Stir the sample for 18 ± 2 hours at room temperature.
5. At the end of the agitation period, centrifuge the sample to remove the solids. Decant the solution into an 800 mL beaker. Measure the pH of the filtrate and record. Filter the filtrate through a 0.65 μm filter membrane. To the filtrate, add a known amount of U-232 tracer. Record the amount of U-232 used on the assignment sheet. For the filtrate portion, proceed to Step 1 of Separation and Determination of Uranium. For the soil portion, continue with step 6 below.
6. Using the soil residue remaining after decanting the filtrate from step 5 above, repeat steps 2 through 5 three more times. Analyze each solution fraction for uranium. After the fourth RAU leach, continue with step 7 below.

7. After the final leaching of the sample for RAU, transfer the soil residue needed for the SAU analysis into a 250 mL polyethylene bottle. Add 200 mL 0.1 M NaHCO_3 (pH=8.3). Add a stir bar to the bottle. Add 1 mL 35% H_2O_2 . Cap the bottle loosely and place bottle on a stir plate.
8. Stir the suspension for 3 hours. Stir the suspension at a fast enough speed such that the solid material remains in suspension. Add 1 mL 35% H_2O_2 and stir for another 3 hours.
9. Centrifuge the sample and discard the solid fraction. Filter the solution through a 0.65 μm filter membrane and pour the solution into an 800 mL beaker.
10. Record the pH of the solution.
11. Add a known amount of U-232 tracer and record on the assignment sheet.
12. Acidify the sample to a pH of about 1 with 3 M HCl (do not use HNO_3 , as the uranium will not be able to be reduced during the BaSO_4 precipitation).
13. Add 5 mL of fusion solution and take to dryness on a hot plate. Proceed to Separation and Determination of Uranium.

Separation and Determination of Uranium

1. Adjust the volume to approximately 350 mL by either evaporating the solution or adding deionized water.
2. Add 25 mL concentrated HCl .
3. Add 5 g Na_2SO_4 and 10 g K_2SO_4 .
4. Add a stir bar and place on a stir plate. Heat solution to boiling with constant stirring.
5. Carefully add 3 g $\text{K}_2\text{S}_2\text{O}_5$ and 1 mL 25% $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$. Boil for 15 minutes.
6. Add five 3 mL portions of 0.45% BaCl_2 . The precipitate that is formed is BaSO_4 and will contain all of the actinides, except uranium.
7. Filter the solution through a 0.45 μm filter membrane. Save the supernatant and put into a clean 800 mL beaker for the uranium. Discard the BaSO_4 precipitate into the Ba waste stream.
8. Heat the solution to boiling with stirring. Add 4 drops 1% Safranin-O indicator and 20% TiCl_3 dropwise until the solution becomes colorless.

9. Add four 3 mL portions of 0.45% BaCl₂. The precipitate that is formed is BaSO₄ and will contain uranium.
10. Filter the solution through a 0.45 μm filter membrane and transfer the filter to a 50 mL centrifuge tube.
11. Add 20 mL 0.05 M KEDTA and 3 drops 10 M KOH. Vortex the centrifuge tube and place in a boiling water bath to dissolve the BaSO₄.
12. Remove the filter paper. Add 4 drops 20% TiCl₃ and 2 mL 10 M KOH. Vortex and heat in a hot water bath for 10 minutes.
13. Centrifuge the sample and decant and discard the supernatant
14. Dissolve the precipitate with 10 mL 3 M HCl. Heat if necessary.
15. Filter the sample into a clean centrifuge tube through a 0.45 μm filter membrane. Discard the filter paper.
16. To the solution, carefully (and in a hood), add 50 μL Ce carrier and 2 mL concentrated HF. Mix.
17. After 15 minutes, filter the solution through a 0.1 μm filter membrane. Place the filter on a counting disc and submit the sample to the count room.

ORISE TABLE 1

**SELECTED GAMMA EMITTING RADIONUCLIDE CONCENTRATIONS
IN SOIL SAMPLES
BY GAMMA SPECTROSCOPY
CP1, REVISION 13
KISKI VALLEY
LEECHBURG, PENNSYLVANIA**

ESSAP Sample ID	NRC Sample ID	Radionuclide Concentrations ^a (pCi/g dry weight)	
		U-238 by Th-234	U-235
897S001	25N 35E, 200-215 cm	40.3 ± 3.4 ^b	7.78 ± 0.62
897S002	30N 15E, 160-175 cm	135 ± 10	29.0 ± 1.7
897S003	30N 15E, 200-215 cm	73.1 ± 6.8	15.6 ± 1.3
897S004	30N 25E, 100-115 cm	10.9 ± 3.1	2.75 ± 0.78
897S005	35N 5E, 100-115 cm	114.1 ± 9.0	22.9 ± 1.5

^aThe average MDC for a 15 minute count of soil in a 0.5L Marinelli is 3.1 pCi/g for U-238 by Th-234 and 0.79 pCi/g for U-235.

^bUncertainties represent the 95% confidence level, based on total propagated uncertainties.

ORISE TABLE 2

CONCENTRATIONS OF URANIUM ISOTOPES
 BY READILY AVAILABLE URANIUM (RAU) USING ACETIC ACID
 AND SLOWLY AVAILABLE URANIUM (SAU)
 IN ASH SAMPLES
 BY ALPHA SPECTROMETRY AP11, REVISION 2; CP2, REVISION 11
 KISKI VALLEY
 LEECHBURG, PENNSYLVANIA

ESSAP Sample ID	NRC Sample ID	Radionuclide Concentrations (pCi/g dry weight)											
		RAU #1		RAU #2		RAU #3		RAU #4		SUM RAU		SAU	
		U-234	U-238	U-234	U-238	U-234	U-238	U-234	U-238	U-234	U-238	U-234	U-238
897S001	25N 35E, 200-215 cm	0.77 ± 0.06 ^a	0.15 ± 0.02	0.60 ± 0.05	0.13 ± 0.02	1.13 ± 0.08	0.23 ± 0.02	0.68 ± 0.05	0.14 ± 0.02	3.18 ± 0.12	0.65 ± 0.04	38.7 ± 5.5	7.0 ± 1.1
897S002	30N 15E, 160-175 cm	9.53 ± 0.63	1.74 ± 0.12	9.04 ± 0.91	1.61 ± 0.20	6.29 ± 0.42	1.21 ± 0.09	4.02 ± 0.27	0.75 ± 0.06	28.9 ± 1.2	5.31 ± 0.26	173 ± 26	32.7 ± 5.0
897S003	30N 15E, 200-215 cm	7.26 ± 0.50	1.39 ± 0.10	4.02 ± 0.30	0.71 ± 0.07	4.21 ± 0.29	0.81 ± 0.07	2.94 ± 0.21	0.55 ± 0.05	18.43 ± 0.68	3.46 ± 0.15	113 ± 16	22.1 ± 3.3
897S004	30N 25E, 100-115 cm	0.05 ± 0.01	0.00 ^b ± 0.00	0.04 ± 0.01	0.00 ± 0.00	0.08 ± 0.01	0.02 ± 0.01	0.12 ± 0.02	0.03 ± 0.01	0.29 ± 0.03	0.05 ± 0.01	4.40 ± 0.68	1.08 ± 0.22
897S005	35N 5E, 100-115 cm	6.48 ± 0.45	1.28 ± 0.10	3.65 ± 0.26	0.69 ± 0.06	3.83 ± 0.27	0.74 ± 0.06	3.81 ± 0.27	0.71 ± 0.06	17.77 ± 0.64	3.42 ± 0.14	121 ± 17	24.2 ± 3.5

^aUncertainties represent the 95% confidence level, based on total propagated uncertainties.

^bZero value due to rounding.

ORISE TABLE 3

CONCENTRATIONS OF URANIUM ISOTOPES
 BY READILY AVAILABLE URANIUM (RAU) USING WATER
 AND SLOWLY AVAILABLE URANIUM (SAU)
 IN ASH SAMPLES
 BY ALPHA SPECTROMETRY AP11, REVISION 2; CP2, REVISION 11
 KISKI VALLEY
 LEECHBURG, PENNSYLVANIA

ESSAP Sample ID	NRC Sample ID	Radionuclide Concentrations (pCi/g dry weight)											
		RAU #1		RAU #2		RAU #3		RAU #4		SUM RAU		SAU	
		U-234	U-238	U-234	U-238	U-234	U-238	U-234	U-238	U-234	U-238	U-234	U-238
897S001	25N 35E, 200-215 cm	0.03 ± 0.01 ^a	0.00 ^b ± 0.00	0.06 ± 0.01	0.01 ± 0.01	0.03 ± 0.01	0.00 ± 0.00	0.13 ± 0.02	0.02 ± 0.01	0.25 ± 0.04	0.03 ± 0.01	5.66 ± 0.63	1.18 ± 0.17
897S002	30N 15E, 160-175 cm	0.38 ± 0.04	0.08 ± 0.01	0.20 ± 0.02	0.04 ± 0.01	0.18 ± 0.02	0.04 ± 0.01	0.71 ± 0.06	0.14 ± 0.02	1.47 ± 0.08	0.30 ± 0.03	14.3 ± 1.6	2.79 ± 0.37
897S003	30N 15E, 200-215 cm	1.18 ± 0.10	0.24 ± 0.03	0.39 ± 0.04	0.08 ± 0.01	0.25 ± 0.03	0.06 ± 0.01	0.74 ± 0.06	0.15 ± 0.02	2.56 ± 0.13	0.53 ± 0.04	23.0 ± 2.4	4.51 ± 0.52
897S004	30N 25E, 100-115 cm	0.00 ± 0.00	0.00 ± 0.00	0.04 ± 0.01	0.00 ± 0.00	0.03 ± 0.01	0.00 ± 0.00	0.59 ± 0.05	0.13 ± 0.02	0.66 ± 0.05	0.13 ± 0.02	1.71 ± 0.23	0.36 ± 0.08
897S005	35N 5E, 100-115 cm	0.41 ± 0.04	0.09 ± 0.01	0.20 ± 0.02	0.04 ± 0.01	0.18 ± 0.02	0.04 ± 0.01	0.04 ± 0.01	0.00 ± 0.00	0.83 ± 0.05	0.17 ± 0.02	19.0 ± 2.0	3.82 ± 0.44

^aUncertainties represent the 95% confidence level, based on total propagated uncertainties.

^bZero value due to rounding.