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Radiochemical Analyses of the Filter Cake, Granular Activated Carbon, and Treated Ground Water from the DTSC Stringfellow Superfund Site Pretreatment Plant

Bradley K. Esser, William McConachie, Robert Fischer, Mark Sutton, Scott Szechenyi

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Disclaimer

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(1) Executive Summary

The Department of Toxic Substance Control (DTSC) requested that Lawrence Livermore National Laboratory (LLNL) evaluate the treatment process currently employed at the Department's Stringfellow Superfund Site Pretreatment Plant (PTP) site to determine if wastes originating from the site were properly managed with regards to their radioactivity. In order to evaluate the current management strategy, LLNL suggested that DTSC characterize the effluents from the waste treatment system for radionuclide content. A sampling plan was developed; samples were collected and analyzed for radioactive constituents. Following is brief summary of those results and what implications for waste characterization may be made.

1)   The sampling and analysis provides strong evidence that the radionuclides present are Naturally Occurring Radioactive Material (NORM).

2)   The greatest source of radioactivity in the samples was naturally occurring uranium. The sample results indicate that the uranium concentration in the filter cake is higher than the Granular Activated Carbon (GAC) samples. (11 -14 and 2-6 ppm respectively).

3)   No radiologic background for geologic materials has been established for the Stringfellow site, and comprehensive testing of the process stream has not been conducted. Without site-specific testing of geologic materials and waste process streams, it is not possible to conclude if filter cake and spent GAC samples contain radioactivity concentrated above natural background levels, or if radionuclides are being concentrated by the waste treatment process.

Recommendation: The regulation of Technologically Enhanced, Naturally Occurring Radioactive Materials (T-NORM) is complex. Since the results of this study do not conclusively demonstrate that natural radioactive materials have not been concentrated by the treatment process it is recommended that the DTSC consult with the Department of Health Services (DHS) Radiological Health Branch to determine if any further action is warranted. If it were deemed desirable to establish a background for the Stringfellow setting LLNL would recommend that additional samples be taken and analyzed by LLNL using the same methods presented in this report.

(2) Introduction

Background:

The Stringfellow Superfund Site pretreatment plant (PTP) treats contaminated groundwater from the site for metals and volatile organic compounds (VOCs). The source of the groundwater contamination was disposal of industrial waste in unlined acid pits from 1956 to 1972. During remediation, the pits were excavated and backfilled with clean soil. Contaminated groundwater is sequentially treated by lime flocculation to remove metals and then by GAC filtration to remove VOCs. Effluent from the process is discharged to the industrial wastewater line; the lime filter cake is sent to a Class 1 hazardous waste landfill; and the spent GAC is sent to the manufacturer's RCRA approved recycler.

In 1986, a DTSC report summarized all existing radiological characterization data for Stringfellow Site samples (including groundwater) and for community groundwaters samples. Two wells on the Stringfellow site, OW-1 and OW-2, produced water with high levels of gross alpha (up to 744 pCi/L), gross beta, uranium, and radium (DTSC, 1986). The majority of the radioactivity was due to uranium, and the source was suspected to be leaching of naturally occurring radionuclides from granitic aquifer materials by extremely acidic (pH 1.5-3.0) contaminated groundwater. No evidence exists that radioactive waste was disposed of at the site. After treatment, the effluent wastewater meets the 15 and 50 pCi/L discharge permit criteria for gross alpha and beta in drinking water. High levels of gross alpha-beta in waters contributing to the influent stream, and low levels of gross alpha-beta in the effluent stream raise the possibility that the waste treatment process concentrates radioactivity in lime cake and GAC waste. Neither the filter cake nor the GAC has been previously analyzed for radioactivity. High levels of radioactivity in GAC waste would require changes in how the waste is handled and disposed. Neither the landfill nor the GAC recycler is permitted to accept NRC-regulated radiological waste, and the discharge permit for industrial wastewater regulates gross alpha-beta activity levels based on drinking water standards. This study presents data for radionuclide content and source in Stringfellow PTP filter cake, spent GAC, and effluent, and discusses the implications of the findings on disposal of waste generated by the Stringfellow PTP.

The original 17 acres of the Stringfellow Superfund Site is the location of 45 extraction wells that produce metals- and VOC-contaminated groundwater. Water produced by these wells constitute the A-stream feed to the PTP metals treatment facility, where influent water is neutralized, lime is added, flocculated, and filtered, producing a "filter cake" that sequesters contaminant metals. The PTP operates in batch mode some 6-10 hours/day for 5 days/week generating 60-200 tons of filter cake/month. Effluent from the metals treatment process is mixed with VOC-contaminated groundwater from elsewhere on the site (the B, C, D, and F streams), and pumped to the VOC treatment facility where the mixed water is passed through a GAC sorbent and into the industrial wastewater line. The scale of the operation can be appreciated by looking at operations over a single month. In April 2003, total influent flux to the PTP was 3,076,260 gallons. Approximately 10% of this flux was from extraction wells feeding the A-stream (320,360 gallons for an average flow of 7.4 gpm), and 70 tons of filter cake were shipped to the Buttonwillow RCRA facility.

Flow chart for determination of regulatory status of Stringfellow waste with respect to radioactivity

Do waste treatment residues need to be managed in regard to radioactive content? (Filter Cake/GAC/Effluent)

Analysis Required

Filter cake (a, b, c) / Spent GAC (a, b, c) / GAC effluent (a, b, d)

→ Are the radionuclides present as NORM? — **No** → Consult DHS/RHB to determine regulatory status.

Yes ↓

- Unperturbed rock (a, b, c)
- Unperturbed groundwater (a, b, d)

→ Is NORM present in waste at levels above background? — **No** → Manage as hazardous waste.

Yes ↓

- Filter cake influent/ bulk contaminated groundwater: (a, b, d)
- Filter cake effluent/ GAC influent: (a, b, d)
- Impacted rock (a, b, c)
- Contaminated groundwater (a, b, d)
- Bulk hydrated lime (a, b, c)
- Lime flocculation agent (a, b, c)
- GAC (a, b, c)

→ Does the waste treatment process concentrate NORM?

Yes or No ↓

Consult with DHS/RHB. As T-NORM, is the waste regulated for its radioactivity? — **No** → Manage as hazardous waste.

Yes ↓

Dispose of as mixed waste

Analysis Key:
a - ICP-MS
b - Gross α, β
c - γ-Spec
d - Rn Emanation

Acronyms
NORM = Naturally Occurring Radioactive Material
T-NORM = Technologically Enhanced NORM
DHS/RHB = California Department of Health Services
　　　　　　Radiological Health Branch

Recommended Action Plan

Based on review of data from previous investigations and after conversations with DTSC, three questions were posed that required answers before the regulatory status of Stringfellow waste and waste residual could be determined. The questions were

- Is radioactivity in Stringfellow waste from natural or anthropogenic sources?
- Is radioactivity present in waste at levels above background?
- Does the waste treatment process concentrate radioactivity?

LLNL then recommended specific actions to answer these questions (see the "Flow chart for determination of regulatory status of Stringfellow waste with respect to radioactivity".)

This study specifically addresses the origin of the radioactivity in Stringfellow waste. To address this question, LLNL recommended determining the radionuclide content of waste samples using inductively-coupled plasma spectroscopy for determination of U isotopic composition, and gamma spectroscopy for determination of radioactive fission and activation products. Given that filter cake, spent GAC, and GAC effluent had never been analyzed for radioactivity, LLNL recommend characterization of these waste forms and waste residuals. More specifically, LLNL recommended that samples be concurrently collected three times over the course of three weeks to assess variability in the U and other alpha emitting radionuclide concentrations.

(3) Techniques

Three techniques were used to assay for radioactivity in Stringfellow process samples: radon emanation to determine ^{226}Ra activity in fluid effluent samples; gamma spectroscopy to determine gamma-emitting radionuclide activity (including ^{226}Ra) in solid filter cake and GAC samples; and isotope-dilution inductively-coupled plasma mass spectrometry (ICPMS) to determine U activity and isotopic composition in all samples.

Sample Collection

Filter cake and GAC effluent was collected three times over the course of three different weeks (12-11-2003, 12-18-2003, and 01-14-2004). Spent GAC was collected concurrently with filter cake and GAC effluent on one date (12-11-2004), and then separately on two other dates (04-03-2003 and 07-08-2004). All samples were stored in one-liter high-density polyethylene bottles. Each sample consisted of one liter of GAC effluent, one liter of wet filter cake, or three liters of wet spent GAC. Samples received by LLNL are tabulated in Table 1A.

Sample Preparation

Effluent samples: Received 1-L samples were filtered through 0.45 um high-capacity cartridge filters (Gelman, Inc). To reduce contamination, the sample was filtered using a peristaltic pump and Teflon-lined Tygon tubing, silicone tubing and Teflon connectors. All tubing and connectors

were acid cleaned, and rinsed with MQ water between filtrations. Each filter cartridge was only used once. One liter effluent samples were preserved after filtration by the addition of 1 mL of ultrapure concentrated nitric acid. The acidified solution was checked to insure that pH was less than 2. Approximately 9 mL of effluent sample was then adjusted to 2% concentrated nitric acid (by volume), spiked with a ^{233}U tracer, and run by ICPMS to determine U concentration and isotopic composition using isotope dilution. Approximately 400-500 mL of solution was used for determination of ^{226}Ra by radon emanation.

Filter cake samples: Approximately 30-50 g of sample was dried to constant weight by heating to 110° C for several days. Several small subsamples of 100 to 150 mg were taken, and individually dissolved in ultra high-purity grade nitric acid and spiked with a ^{233}U tracer, and diluted to 100 mL 2% concentrated nitric acid for determination of U concentration and isotopic concentration by isotope dilution ICPMS. Twenty grams of the remaining oven-dried sample was placed in a hermetically-sealed Prindle vial with spacers to eliminate any headspace, and allowed to sit for greater than 3 weeks for determination of gamma-emitting radionuclides by gamma spectroscopy, including determination of ^{226}Ra.

Granulated activated carbon samples: The GAC samples were taken to constant weight by oven drying at 110° C for several days. For gamma spectroscopy, 5-10 g samples were hermetically sealed in a Prindle vial, and short-lived daughters of ^{226}Ra were allowed to grow in over a period in excess of 3 weeks. For ICPMS, individual 1-g subsamples were taken and dry ashed at 1100° C for 4 hours (based on an ASTM method for determination of ash content in GAC). The ash was then dissolved in 50% concentrated nitric acid and brought up to 100 mL of 2% concentrated nitric acid for determination of U concentration and isotopic concentration by isotope dilution ICPMS.

Analytical methods

Radon emanation: The activity of ^{226}Ra in 400-500 mL effluent samples was determined in accordance with the radon emanation technique described in EPA Protocol 903.1 "Determination of Ra-226 in Drinking Water by Radon Emanation". Briefly, the radium-226 in the effluent sample was concentrated and separated by coprecipitation on barium sulfate. The precipitate was dissolved in EDTA reagent, placed in a sealed bubbler and stored for ingrowth of radon-222. After ingrowth, the gas was purged into a scintillation cell. After the short-lived radon-222 daughters had grown into equilibrium with the parent, the scintillation cell was counted for alpha activity. The absolute measurement of radium-226 was effected by calibrating the scintillation cell system with a standard solution of this nuclide.

Gamma Spectroscopy: Gamma spectroscopy can identify and quantify gamma-emitting isotopes in a sample, including ^{40}K and ^{87}Rb (naturally occurring radionuclides that may contribute significantly to gross beta activity), ^{226}Ra and ^{228}Ra (which are specifically regulated in drinking water and may contribute to gross alpha activity), ^{137}Cs (an anthropogenic radionuclide that was globally distributed during atmospheric testing of nuclear weapons), and short-lived fission and activation products (such as ^{60}Co and ^{152}Eu that would indicate local contamination). Sample preparation involves only aliquoting the sample into an appropriate hermetically-sealed container

such as a Prindle vial. The technique provides valuable information on the identity of radionuclides in the sample, information that is in important in attributing radioactivity to natural or anthropogenic sources. Some, such as tritium, ^{14}C, ^{32}P, ^{36}Cl, ^{63}Ni, and others, emit no gamma rays, and cannot be detected by gamma spectroscopy. Others, such as ^{60}Co, ^{137}Cs, and ^{226}Ra are easily detected by gamma spectroscopy. LLNL protocols are available upon request.

Inductively-Coupled Plasma Mass Spectrometry: ICPMS is an inorganic mass spectrometric technique that is widely used to determine trace metal concentrations; EPA protocols exist for trace metal analysis by ICPMS, which is commercially available for non-radioactive samples. ICPMS can also be used to determine the isotopic composition of radioactive elements (such as U); to detect ultra-trace levels of long-lived radionuclides (such as ^{99}Tc and ^{239}Pu); and to accurately determine metal concentrations (including U) using isotope dilution with isotopically enriched tracers. These types of analyses are generally not available commercially. For the Stringfellow site, LLNL determined the concentration (by isotope dilution) and the isotopic composition of U in Stringfellow filter cake, GAC and effluent. Sample preparation is described above; a detailed protocol for isotopic composition analyses is attached (Appendix 1).

(4) Results

LLNL results are tabulated in Table 1, including average values for replicate ICPMS analyses. Table 1A tabulates sample identification; sample form; and dates for sample collection, shipping and receival. Table 1B summarizes the gamma spectroscopy and radon emanation data. Table 1C summarizes averaged values of ICPMS analyses expressed as mass concentrations and as atom ratio isotopic compositions. Table 1D summarizes averaged values of ICPMS analyses expressed as activity concentrations and activity ratio isotopic composition. In ICPMS, mass concentrations and atom ratios are measured and must be converted to activities and activity ratios using invariant physical constants. Tabulation of U concentration and isotopic composition allows easy comparison to both regulatory limits and literature data.

For the ICPMS analyses, replicate analyses were done to assess heterogeneity. These data are tabulated in Table 2 along with ICPMS data for U standards. Table 2A tabulates sample identification and ICPMS analytical dates. Table2B summarizes individual values of ICPMS analyses expressed as mass concentrations and as atom ratio isotopic compositions. Table 2C summarizes averaged values of ICPMS analyses expressed as activity concentrations and activity ratio isotopic composition. Table 2D tabulates analyses of NIST-traceable uranium isotopic standards. Note that all activities and mass concentrations are normalized to dry weight (after drying to constant weight at 110 °C).

Radon emanation: Effluent samples had low levels of ^{226}Ra (0.4-0.5 pCi/L), far below regulatory or action limits for drinking water (Table 1B).

Gamma Spectroscopy: Filter cake and GAC samples had low or non-detectable levels of ^{226}Ra and ^{228}Ra, and nondetectable levels of ^{22}Na, ^{60}Co, ^{137}Cs and ^{241}Am (Table 1B).

Inductively-Coupled Plasma Mass Spectrometry:
Uranium concentrations in the effluent are uniform over the three weekly sampling events (9-10 pCi/L), and are below the drinking water standard (20 pCi/L) (Table 1D). Total U concentration is 11-14 mg/kg (ppm) in the filter cake, and 3-7 ppm in the GAC samples (Table 1C). Isotopic compositions do not provide evidence for nuclear fuel cycle uranium, i.e. uranium that has been enriched or depleted relative to natural uranium. The $^{235}U/^{238}U$ ratios are within error of the invariant natural ratio; ^{236}U, which does not occur naturally, is not detected; and the $^{234}U/^{238}U$ activity ratios are in the natural range.

The reproducibility of 2-5 replicate powder analyses (individual 100-150 mg samples taken from a 5 g sample of the filter cake, and 1 g samples of the GAC) for both concentration and isotopic composition demonstrate that heterogeneity is comparable or only slightly greater than the analytical precision of the technique (Table 2B and 2C). Analyses of U isotopic composition of NIST standards were within error of certified values (Table 2D). Process blanks were very low relative to sample concentrations, and no explicit blank corrections were made.

LLNL Data Summary of Stringfellow PTP Sample Analyses
TABLE 1A. Samples Received
Everett Guthrie and Richard Bibby, Environmental Monitoring Radiological Laboratory
Chemical Biology & Nuclear Science Division, CMS, LLNL

COC	ID	Sample	Plant	Week	Collected	Shipped	Delivered	Received	#	Container	Matrix
13673	74698	Filter cake-121103A	TO-58	Week #1	2003-12-11	2003-01-18	2003-12-19	2004-01-08	1	1-L bottle	lime
13673	74699	SP 523-121103A	TO-58	Week #1	2003-12-11	2003-01-18	2003-12-19	2004-01-08	1	1-L bottle	water
13673	74700	Spent GAC-121103A	TO-58	Week #1	2003-12-11	2003-01-18	2003-12-19	2004-01-08	3	1-L bottle	GAC
13674	74701	Filter cake-121803A	TO-58	Week #2	2003-12-18	2003-01-18	2003-12-19	2004-01-08	1	1-L bottle	lime
13674	74702	SP 523-121803A	TO-58	Week #2	2003-12-18	2003-01-18	2003-12-19	2004-01-08	1	1-L bottle	water
13675	74703	Filter Cake-011404A	TO-58	Week #3	2004-01-14	2004-01-16	2004-01-19	2004-01-21	1	1-L bottle	lime
13675	74704	SP 523-011404A	TO-58	Week #3	2004-01-14	2004-01-16	2004-01-19	2004-01-21	1	1-L bottle	water
13675	74705	Spent GAC-070803A	TO-58	Week #3	2003-04-03	2004-01-16	2004-01-19	2004-01-21	3	1-L bottle	GAC
	MEAA02735	Spent GAC-070804A	TO-58		2004-07-08		2004-07-22	2004-07-22	3	1-L bottle	GAC

LLNL Data Summary of Stringfellow PTP Sample Analyses
TABLE 1B. Radium-226 and Gamma-emmitting Radionuclides by Radon Emission and Gamma Spectrometry
Everett Guthrie and Richard Bibby, Environmental Monitoring Radiological Laboratory
Chemical Biology & Nuclear Science Division, CMS, LLNL

LLNL ID	DTSC ID	Plant	Week	Substrate	Method	Units	Na22			Co60			Cs137			Pb210			Ra226			Ra228			Th228			Am241		
							mean	2 sd	mda	mean	2 sd	mda	mean	2 sd	mda	mean	2 sd	mda	mean	2 sd	mda	mean	2 sd	mda	mean	2 sd	mda	mean	2 sd	mda
Effluent																														
74699	SP 523-121103A	TO-58	Week #1	Effluent	Radon (EPA 903.1)	pCi/L	-	-	-	-	-	-	-	-	-	-	-	-	0.39	0.02	0.02	-	-	-	-	-	-	-	-	-
74702	SP 523-121803A	TO-58	Week #2	Effluent	Radon (EPA 903.1)	pCi/L	-	-	-	-	-	-	-	-	-	-	-	-	0.46	0.05	0.05	-	-	-	-	-	-	-	-	-
74704	SP 523-011404A	TO-58	Week #3	Effluent	Radon (EPA 903.1)	pCi/L	-	-	-	-	-	-	-	-	-	-	-	-	0.43	0.04	0.04	-	-	-	-	-	-	-	-	-
Filter Cake																														
74698	Filter cake-121103A	TO-58	Week #1	Filter cake	Gamma spectroscopy	pCi/kg	nd		38	nd		34	nd		26	nd		185	nd		53	85	24	81	900	54	25	nd		23
74701	Filter cake-121803A	TO-58	Week #2	Filter cake	Gamma spectroscopy	pCi/kg	nd		218	nd		155	nd		1	nd		974	nd		226	nd		590	867	193	95	nd		102
74703	Filter Cake-011404A	TO-58	Week #3	Filter cake	Gamma spectroscopy	pCi/kg	nd		33	nd		28	nd		22	136	78	117	66	17	51	nd		103	791	46	24	nd		20
GAC																														
74700	Spent GAC-121103A	TO-58	Week #1	GAC	Gamma spectroscopy	pCi/kg	nd		29	nd		27	nd		21	394	69	204	333	36	48	170	26	83	86	10	19	nd		15
74705	Spent GAC-070803A	TO-58	Week #3	GAC	Gamma spectroscopy	pCi/kg	nd		29	nd		26	nd		19	307	270	405	324	21	42	151	41	70	125	21	20	nd		13
MEAA02735	Spent GAC-070804A	TO-58		GAC	Gamma spectroscopy	pCi/kg	-			nd		26	nd		21	348	66	208	268	23	43	195	75	75	282	17	17	nd		15

MDA = minimum detectable activity
- = not measured by radon emanation technique
nd = not detected

Radon = radon emanation
Gamma = gamma spectroscopy

LLNL Data Summary of Stringfellow PTP Sample Analyses
TABLE 1C. Uranium Isotopic Composition and Concentration by ICPMS (averaged values)

Brad Esser & Scott Szechenyi, Environmental Radioactivity ICPMS Facility
Chemical Biology & Nuclear Science Division, CMS, LLNL

LLNL ID	DTSC ID	Date	238U (ng/g)	235U/ 238U (atom ratio)	234U/ 238U (atom ratio)	236U/ 238U (atom ratio)	Total U (ng/mL)
Blk-EF-01	Effluent blank #1	EMRL	0.006 *0.004*	< 0.17105	< 0.175473	< 0.167461	0.006 *0.004*
74699	TO58 SP 523-121103	Week 1	11.30 *0.04*	0.00727 *0.00010*	0.000077 *0.000010*	< 0.000011	11.38 *0.04*
74702	TO58 SP 523-121803	Week 2	12.02 *0.03*	0.00721 *0.00008*	0.000075 *0.000011*	< 0.000015	12.11 *0.03*
74704	TO58 SP 523-011404	Week 3	11.40 *0.04*	0.00724 *0.00008*	0.000072 *0.000007*	< 0.000013	11.48 *0.04*
Sample Type	**DTSC ID**	**Week**	**238U (ng/g)**	**235U/ 238U (atom ratio)**	**234U/ 238U (atom ratio)**	**236U/ 238U (atom ratio)**	**Total U (ng/g)**
Blk-FC-01	Filter Cake Blank 1	EMRL	1.01 *0.07*	< 0.00688	< 0.013147	< 0.005504	1.01 *0.07*
Blk-FC-02	Filter Cake Blank 2	EMRL	0.76 *0.06*	< 0.02380	< 0.015146	< 0.010181	0.76 *0.06*
74698 ave	TO58 Filter cake-121103A	Week 1	13,302 *414*	0.00724 *0.00003*	0.000059 *0.000001*	< 0.000001	13,279 *78*
74701 ave	TO58 Filter cake-121803A	Week 2	11,202 *221*	0.00726 *0.00007*	0.000059 *0.000002*	< 0.000003	11,346 *66*
74703 ave	TO58 Filter Cake-011404A	Week 3	11,437 *521*	0.00726 *0.00003*	0.000059 *0.000004*	< 0.000019	11,659 *289*
Sample Type	**DTSC ID**	**Week**	**238U (ng/g)**	**235U/ 238U (atom ratio)**	**234U/ 238U (atom ratio)**	**236U/ 238U (atom ratio)**	**Total U (ng/g)**
74700 ave	TO58 Spent GAC-121103A	Week 1	3,229 *248*	0.00727 *0.00002*	0.000070 *0.000002*	< 0.000023	3,323 *158*
74705 ave	TO58 Spent GAC-070803A	Week 3	7,041 *60*	0.00724 *0.00005*	0.000069 *0.000001*	< 0.000006	7,071 *173*

Reported uncertainties are two-sigma
Reported detection limits are three-sigma
Filter cake and spent GAC values are averaged values of 2-5 replicates (see Table 2 for individual analyses)

LLNL Data Summary of Stringfellow PTP Sample Analyses
TABLE 1D. Uranium Activity by ICPMS (averaged values)
Brad Esser & Scott Szechenyi, Environmental Radioactivity ICPMS Facility
Chemical Biology & Nuclear Science Division, CMS, LLNL

LLNL ID	DTSC ID	Week	238U (pCi/L)	235U (pCi/L)	234U (pCi/L)	236U (pCi/L)	Total U (pCi/L)	234U/238U AR
Blk-EF-01	Effluent blank #1	EMRL	0.0020 *0.0012*	< 0.00222	< 6.6	< 0.06	0.0020 *0.0012*	
74699	TO58 SP 523-121103	Week 1	3.797 *0.014*	0.17752 *0.00247*	5.4 *0.7*	< 0.008	9.4 *0.7*	1.42 0.18
74702	TO58 SP 523-121803	Week 2	4.039 *0.011*	0.18736 *0.00224*	5.7 *0.8*	< 0.012	9.9 *0.8*	1.40 0.21
74704	TO58 SP 523-011404	Week 3	3.829 *0.013*	0.17836 *0.00212*	5.1 *0.5*	< 0.009	9.1 *0.5*	1.34 0.14
Sample Type	DTSC ID	Week	238U (pCi/kg)	235U (pCi/kg)	234U (pCi/kg)	236U (pCi/kg)	Total U (pCi/kg)	234U/238U AR
Blk-FC-01	Filter Cake Blank 1	EMRL	0.340 *0.023*	< 0.01504	< 83	< 0.4	0.34 *0.02*	
Blk-FC-02	Filter Cake Blank 2	EMRL	0.254 *0.021*	< 0.03890	< 71	< 0.5	0.25 *0.02*	
74698 ave	TO58 Filter cake-121103A	Week 1	4,469 *139*	208.2 *6.4*	4,863 *91*	< 0.6	9,499 *92*	1.09 0.03
74701 ave	TO58 Filter cake-121803A	Week 2	3,763 *74*	177.1 *1.1*	4,177 *162*	< 2.4	8,139 *163*	1.10 0.08
74703 ave	TO58 Filter Cake-011404A	Week 3	3,889 *97*	181.5 *3.3*	4,273 *311*	< 3.7	8,343 *312*	1.06 0.08
Sample Type	DTSC ID	Week	238U (pCi/kg)	235U (pCi/kg)	234U (pCi/kg)	236U (pCi/kg)	Total U (pCi/kg)	234U/238U AR
74700 ave	TO58 Spent GAC-121103A	Week 1	1,072 *88*	51.2 *1.7*	1,420 *40*	< 0.3	2,567 *74*	1.30 0.04
74705 ave	TO58 Spent GAC-070803A	Week 3	2,366 *20*	108.1 *4.6*	3,009 *79*	< 0.9	5,483 *72*	1.27 0.04

Reported uncertainties are two-sigma
Reported detection limits are three-sigma
Filter cake and spent GAC values are averaged values of 2-5 replicates (see Table 2 for individual analyses)

Activities were determined by converting measured mass concentrations
AR = activity ratio (pCi/pCi)

LLNL Data Summary of Stringfellow PTP Sample Analyses
TABLE 2A. ICPMS Samples (individual analyses)

Brad Esser & Scott Szechenyi, Environmental Radioactivity ICPMS Facility
Chemical Biology & Nuclear Science Division, CMS, LLNL

LLNL ID	DTSC ID	Date	Sample date	Rcvd date	Spike Date	ICPMS Date
Blk-EF-01	Effluent blank #1	EMRL			02/20/04	02/20/04
74699	TO58 SP 523-121103A	Week 1	12/11/03	01/08/04	02/20/04	02/20/04
74702	TO58 SP 523-121803A	Week 2	12/18/03	01/08/04	02/20/04	02/20/04
74704	TO58 SP 523-011404A	Week 3	01/14/04	01/21/04	02/20/04	02/20/04
Sample Type	**DTSC ID**	**Week**	**Sample date**	**Rcvd date**	**Spike Date**	**ICPMS Date**
Blk-FC-01	Filter Cake Blank 1	EMRL			04/01/04	04/07/04
Blk-FC-02	Filter Cake Blank 2	EMRL			04/01/04	04/07/04
74698-1A	TO58 Filter cake-121103A	Week 1	12/11/03	01/08/04	04/06/04	04/07/04
74698-1B	TO58 Filter cake-121103A	Week 1	12/11/03	01/08/04	04/06/04	04/07/04
74698-1C	TO58 Filter cake-121103A	Week 1	12/11/03	01/08/04	04/06/04	04/07/04
74701-1A	TO58 Filter cake-121803A	Week 2	12/18/03	01/08/04	04/06/04	04/07/04
74701-1B	TO58 Filter cake-121803A	Week 2	12/18/03	01/08/04	04/06/04	04/07/04
74701-1C	TO58 Filter cake-121803A	Week 2	12/18/03	01/08/04	04/06/04	04/07/04
74703-1A	TO58 Filter Cake-011404A	Week 3	01/14/04	01/21/04	03/30/04	04/01/04
74703-1B	TO58 Filter Cake-011404A	Week 3	01/14/04	01/21/04	04/06/04	04/07/04
74703-1C	TO58 Filter Cake-011404A	Week 3	01/14/04	01/21/04	04/06/04	04/07/04
Sample Type	**DTSC ID**	**Week**	**Sample date**	**Rcvd date**	**Spike Date**	**ICPMS Date**
74700-1A	TO58 Spent GAC-121103A	Week 1	12/11/03	01/08/04	03/30/04	04/01/04
74700-1B	TO58 Spent GAC-121103A	Week 1	12/11/03	01/08/04	03/30/04	04/01/04
74700-1C	TO58 Spent GAC-121103A	Week 1	12/11/03	01/08/04	04/01/04	04/07/04
74700-1D	TO58 Spent GAC-121103A	Week 1	12/11/03	01/08/04	04/01/04	04/07/04
74700-1D rep	TO58 Spent GAC-121103A	Week 1	12/11/03	01/08/04	04/01/04	04/07/04
74705-1A	TO58 Spent GAC-070803A	Week 3	04/03/03	01/21/04	03/30/04	04/01/04
74705-1B	TO58 Spent GAC-070803A	Week 3	04/03/03	01/21/04	04/01/04	04/07/04

LLNL Data Summary of Stringfellow PTP Sample Analyses
TABLE 2B. Uranium Isotopic Composition and Concentration by ICPMS (individual analyses)
Brad Esser & Scott Szechenyi, Environmental Radioactivity ICPMS Facilit
Chemical Biology & Nuclear Science Division, CMS, LLNl

LLNL ID	DTSC ID	Date	238U (ng/g)	235U/ 238U (atom ratio)	234U/ 238U (atom ratio)	236U/ 238U (atom ratio)	Total U (ng/mL)	Comments
Blk-EF-01	Effluent blank #1	EMRL	0.006 *0.004*	< 0.17105	< 0.175473	< 0.167461	0.006 *0.004*	
74699	TO58 SP 523-121103A	Week 1	11.30 *0.04*	0.00727 *0.00010*	0.000077 *0.000010*	< 0.000011	11.38 *0.04*	
74702	TO58 SP 523-121803A	Week 2	12.02 *0.03*	0.00721 *0.00008*	0.000075 *0.000011*	< 0.000015	12.11 *0.03*	
74704	TO58 SP 523-011404A	Week 3	11.40 *0.04*	0.00724 *0.00008*	0.000072 *0.000007*	< 0.000013	11.48 *0.04*	
LLNL ID	**DTSC ID**	**Date**	**238U (ng/g)**	**235U/ 238U (atom ratio)**	**234U/ 238U (atom ratio)**	**236U/ 238U (atom ratio)**	**Total U (ng/mL)**	
Blk-FC-01	Filter Cake Blank 1	EMRL	1.01 *0.07*	< 0.00688	< 0.013147	< 0.005504	1.01 *0.07*	
Blk-FC-02	Filter Cake Blank 2	EMRL	0.76 *0.06*	< 0.02380	< 0.015146	< 0.010181	0.76 *0.06*	
74698-1A	TO58 Filter cake-121103A	Week 1	13,539 *191*	0.00724 *0.00008*	0.000063 *0.000019*	< 0.000027	13,637 *191*	Not included in U234/U238 or Total U average
74698-1B	TO58 Filter cake-121103A	Week 1	13,157 *47*	0.00725 *0.00003*	0.000060 *0.000001*	< 0.000001	13,251 *47*	
74698-1C	TO58 Filter cake-121103A	Week 1	13,212 *88*	0.00724 *0.00003*	0.000059 *0.000002*	< 0.000001	13,307 *88*	
74701-1A	TO58 Filter cake-121803A	Week 2	11,077 *189*	0.00722 *0.00010*	0.000068 *0.000029*	< 0.000046	11,157 *189*	Not included in U234/U238 or Total U average
74701-1B	TO58 Filter cake-121803A	Week 2	11,241 *51*	0.00729 *0.00003*	0.000060 *0.000002*	< 0.000003	11,323 *51*	
74701-1C	TO58 Filter cake-121803A	Week 2	11,288 *83*	0.00727 *0.00004*	0.000059 *0.000004*	< 0.000006	11,369 *83*	
74703-1A	TO58 Filter Cake-011404A	Week 3	11,160 *139*	0.00726 *0.00004*	0.000053 *0.000012*	< 0.000019	11,240 *139*	Not included in U234/U238 or Total U average
74703-1B	TO58 Filter Cake-011404A	Week 3	11,473 *75*	0.00728 *0.00003*	0.000059 *0.000004*	< 0.000005	11,557 *75*	
74703-1C	TO58 Filter Cake-011404A	Week 3	11,677 *76*	0.00724 *0.00003*	0.000059 *0.000007*	< 0.000007	11,761 *76*	
LLNL ID	**DTSC ID**	**Date**	**238U (ng/g)**	**235U/ 238U (atom ratio)**	**234U/ 238U (atom ratio)**	**236U/ 238U (atom ratio)**	**Total U (ng/mL)**	
74700-1A	TO58 Spent GAC-121103A	Week 1	3,200 *38*	0.00719 *0.00006*	< 0.000091	< 0.000023	3,223 *38*	Not included in U234/U238 or Total U average
74700-1B	TO58 Spent GAC-121103A	Week 1	3,046 *42*	0.00728 *0.00005*	0.000070 *0.000013*	< 0.000016	3,068 *42*	Not included in U234/U238 or Total U average
74700-1C	TO58 Spent GAC-121103A	Week 1	3,218 *23*	0.00728 *0.00003*	0.000070 *0.000002*	< 0.000001	3,242 *23*	
74700-1D	TO58 Spent GAC-121103A	Week 1	3,304 *48*	0.00726 *0.00002*	0.000069 *0.000003*	< 0.000003	3,328 *48*	
74700-1D rep	TO58 Spent GAC-121103A	Week 1	3,375 *33*	0.00728 *0.00003*	0.000071 *0.000003*	< 0.000007	3,399 *33*	
74705-1A	TO58 Spent GAC-070803A	Week 3	7,020 *173*	0.00724 *0.00005*	0.000069 *0.000005*	< 0.000006	7,071 *173*	
74705-1B	TO58 Spent GAC-070803A	Week 3	7,063 *58*	0.00698 *0.00003*	0.000068 *0.000001*	< 0.000002	7,112 *58*	

All uncertainties are two sigma standard error of the mean. All detection limits are three sigma
Total U is the sum of all detectable U isotopes

LLNL Data Summary of Stringfellow PTP Sample Analyses
TABLE 2C. Uranium Activity by ICPMS (individual analyses)
Brad Esser & Scott Szechenyi, Environmental Radioactivity ICPMS Facility
Chemical Biology & Nuclear Science Division, CMS, LLNL

LLNL ID	DTSC ID	Week	238U (pCi/L)	235U (pCi/L)	234U (pCi/L)	236U (pCi/L)	Total U (pCi/L)	234U/238U AR	Comments
Blk-EF-01	Effluent blank #1	EMRL	0.0020 *0.0012*	< 0.00222	< 6.6	< 0.06	0.0020 *0.0012*		
74699	TO58 SP 523-121103A	Week 1	3.797 *0.014*	0.17752 *0.00247*	5.4 *0.7*	< 0.008	9.4 *0.7*	1.42 0.18	
74702	TO58 SP 523-121803A	Week 2	4.039 *0.011*	0.18736 *0.00224*	5.7 *0.8*	< 0.012	9.9 *0.8*	1.40 0.21	
74704	TO58 SP 523-011404A	Week 3	3.829 *0.013*	0.17836 *0.00212*	5.1 *0.5*	< 0.009	9.1 *0.5*	1.34 0.14	
LLNL ID	**DTSC ID**	**Week**	**238U (pCi/L)**	**235U (pCi/L)**	**234U (pCi/L)**	**236U (pCi/L)**	**Total U (pCi/L)**	**234U/238U AR**	
Blk-FC-01	Filter Cake Blank 1	EMRL	0.340 *0.023*	< 0.01504	< 83	< 0.4	0.34 *0.02*		
Blk-FC-02	Filter Cake Blank 2	EMRL	0.254 *0.021*	< 0.03890	< 71	< 0.5	0.25 *0.02*		
74698-1A	TO58 Filter cake-121103A	Week 1	4,549 *64*	211.9 *3.7*	5,324 *1,625*	< 23.2	10,085 *1,626*	1.11 0.02	Not included in U234, Total u or U234/238 AR averages
74698-1B	TO58 Filter cake-121103A	Week 1	4,420 *16*	206.0 *1.2*	4,895 *91*	< 0.6	9,521 *92*	1.09 0.03	
74698-1C	TO58 Filter cake-121103A	Week 1	4,439 *30*	206.8 *1.6*	4,832 *150*	< 0.7	9,477 *153*	1.09 0.03	
74701-1A	TO58 Filter cake-121803A	Week 2	3,722 *63*	172.8 *3.7*	4,684 *1,985*	< 33	8,578 *1,986*	1.11 0.04	Not included in U234, Total u or U234/238 AR averages
74701-1B	TO58 Filter cake-121803A	Week 2	3,777 *17*	177.0 *1.1*	4,178 *162*	< 2	8,132 *163*	1.10 0.08	
74701-1C	TO58 Filter cake-121803A	Week 2	3,792 *28*	177.2 *1.6*	4,176 *304*	< 4	8,146 *305*	1.10 0.08	
74703-1A	TO58 Filter Cake-011404A	Week 3	3,749 *47*	175.1 *2.4*	3,702 *868*	< 13	7,626 *869*	0.99 0.23	Not included in U234, Total u or U234/238 AR averages
74703-1B	TO58 Filter Cake-011404A	Week 3	3,855 *25*	180.3 *1.5*	4,251 *311*	< 4	8,286 *312*	1.10 0.08	
74703-1C	TO58 Filter cake-011404A	Week 3	3,923 *26*	182.7 *1.4*	4,294 *498*	< 5	8,400 *498*	1.09 0.13	
LLNL ID	**DTSC ID**	**Week**	**238U (pCi/L)**	**235U (pCi/L)**	**234U (pCi/L)**	**236U (pCi/L)**	**Total U (pCi/L)**	**234U/238U AR**	
74700-1A	TO58 Spent GAC-121103A	Week 1	1,075 *13*	49.7 *0.7*	< 1,810	< 5	1,125 *13*		Not included in U234, Total u or U234/238 AR averages
74700-1B	TO58 Spent GAC-121103A	Week 1	1,023 *14*	47.9 *0.7*	1,324 *254*	< 3	2,395 *254*	1.29 0.25	Not included in U234, Total u or U234/238 AR averages
74700-1C	TO58 Spent GAC-121103A	Week 1	1,081 *8*	50.6 *0.4*	1,409 *40*	< 0.3	2,541 *41*	1.30 0.04	
74700-1D	TO58 Spent GAC-121103A	Week 1	1,110 *16*	51.8 *0.8*	1,431 *62*	< 0.7	2,593 *64*	1.29 0.06	
74700-1D rep	TO58 Spent GAC-121103A	Week 1	1,134 *11*	53.1 *0.6*	1,491 *75*	< 1.4	2,677 *76*	1.31 0.07	
74705-1A	TO58 Spent GAC-070803A	Week 3	2,358 *58*	109.7 *2.8*	3,037 *230*	< 3	5,505 *237*	1.29 0.10	
74705-1B	TO58 Spent GAC-070803A	Week 3	2,373 *20*	106.5 *1.0*	2,981 *70*	< 0.9	5,460 *72*	1.26 0.03	

Reported uncertainties are two-sigma
Reported detection limits are three-sigma
Filter cake and spent GAC values are average values (see Table 2 for individual analyses)

Activities were determined by converting measured mass concentrations
AR = activity ratio (pCi/pCi)

LLNL Data Summary of Stringfellow PTP Sample Analyses
TABLE 2D. NRC Uranium Isotopic Standards
Brad Esser & Scott Szechenyi, Environmental Radioactivity ICPMS Facility
Chemical Biology & Nuclear Science Division, CMS, LLNL

Name	Date	Mass bias (%/amu)	235U/ 238U (atom ratio)	234U/ 238U (atom ratio)	236U/ 238U (atom ratio)
U005-50	Apr 6 2004 09:56 pm	0.31%	0.00492 0.00003	0.0000222 0.0000012	0.0000449 0.0000013
U005-50	Apr 6 2004 10:11 pm	0.31%	0.00493 0.00002	0.0000224 0.0000008	0.0000446 0.0000014
U005-50	Apr 7 2004 03:13 am	0.31%	0.00492 0.00002	0.0000221 0.0000007	0.0000444 0.0000007
U005-50	Apr 7 2004 03:28 am	0.31%	0.00492 0.00002	0.0000228 0.0000009	0.0000459 0.0000010
U005 measured	*average*		*0.004924 0.000006*	*0.0000224 0.0000007*	*0.0000450 0.0000013*
U005 certified	*certificate*		*0.004919 0.000005*	*0.0000219 0.0000004*	*0.0000468 0.0000005*
U010-50	Apr 6 2004 10:26 pm	0.31%	0.01013 0.00004	0.0000563 0.0000013	0.0000648 0.0000011
U010-50	Apr 6 2004 10:41 pm	0.31%	0.01011 0.00004	0.0000561 0.0000013	0.0000650 0.0000016
U010-50	Apr 7 2004 03:43 am	0.31%	0.01016 0.00005	0.0000561 0.0000013	0.0000652 0.0000015
U010-50	Apr 7 2004 03:58 am	0.31%	0.01015 0.00005	0.0000578 0.0000011	0.0000657 0.0000014
U010 measured	*average*		*0.010140 0.000045*	*0.0000566 0.0000016*	*0.0000652 0.0000007*
U005 certified	*certificate*		*0.010140 0.000010*	*0.0000547 0.0000005*	*0.0000688 0.0000007*

All uncertainties are two sigma standard error of the mean. All detection limits are three sigma.
Standards: U010 used to determine mass bias.

(5) Discussion

Are the radionuclides present in Stringfellow waste and waste residue from Naturally Occurring Radioactive Material (NORM)? The LLNL analyses provide strong evidence that the radionuclides present are Naturally Occurring Radioactive Material (NORM). Radionuclides associated with the nuclear fuel cycle or nuclear weapons testing (^{22}Na, ^{60}Co, ^{137}Cs or ^{241}Am) and U isotopic compositions associated with the nuclear fuel cycle are not present. The most diagnostic properties for distinguishing anthropogenic from natural U are the atomic abundance of ^{235}U, and the presence or absence of ^{236}U. Uranium-236 does not occur naturally, and the proportion of ^{235}U to ^{238}U is absolutely uniform in nature (Cowan and Adler, 1976; Steiger and Jager, 1977). Uranium used for military, nuclear or most commercial applications, however, is enriched or depleted in ^{235}U relative to the natural value, and typically contains ^{236}U . Enriched U is used in nuclear weapons and nuclear reactor fuels; depleted U is used as a hardener in military ordinance and armor, and in commerce. A ^{235}U /^{238}U atomic ratio measurably different from the natural ratio of .00725, and the presence of ^{236}U are both unambiguous indications of the presence of anthropogenic U. We do not detect ^{236}U and have measured ^{235}U/^{238}U ratios within error of the natural ratio in all cases (Figure 1).

A second line of evidence that the U present in Stringfellow process samples is natural in origin is the isotopic abundance of ^{234}U in the samples. The ^{234}U/^{238}U activity ratio (AR) increases systematically along the process path from the filter cake (1.08) to GAC (1.28) to effluent (1.39) (Figure 1). The filter cake AR will be representative of influent groundwater, since precipitation or sorption does not fractionate U isotopes, and is consistent with a single analysis by alpha spectrometry of groundwater U isotopes in OW-2, an on-site well feeding the A waste stream, which had an ^{234}U/^{238}U AR of 1.19 ± 0.07 (2 σ) (DTSC, 1986). The filter cake and influent groundwater ARs of slightly greater than one is consistent with values observed in natural groundwaters (Ivanovich and Harmon, 1992). Natural groundwaters often have an AR of greater than one due to preferential dissolution or recoil of ^{234}U from solid aquifer materials into groundwater. The systematic increase of ^{234}U/^{238}U AR along the process flow path is consistent with preferential dissolution or recoil of ^{234}U from the filter cake, followed by unfractionated sorption onto GAC, followed by preferential dissolution or recoil of ^{234}U from the GAC into the effluent. This pattern is geochemically consistent with a natural uranium origin and with very high distribution coefficients for U into filter cake, as modeled thermodynamically (discussed below and in Appendix 2), and observed in the concentrations of U in the filter cake and effluent.
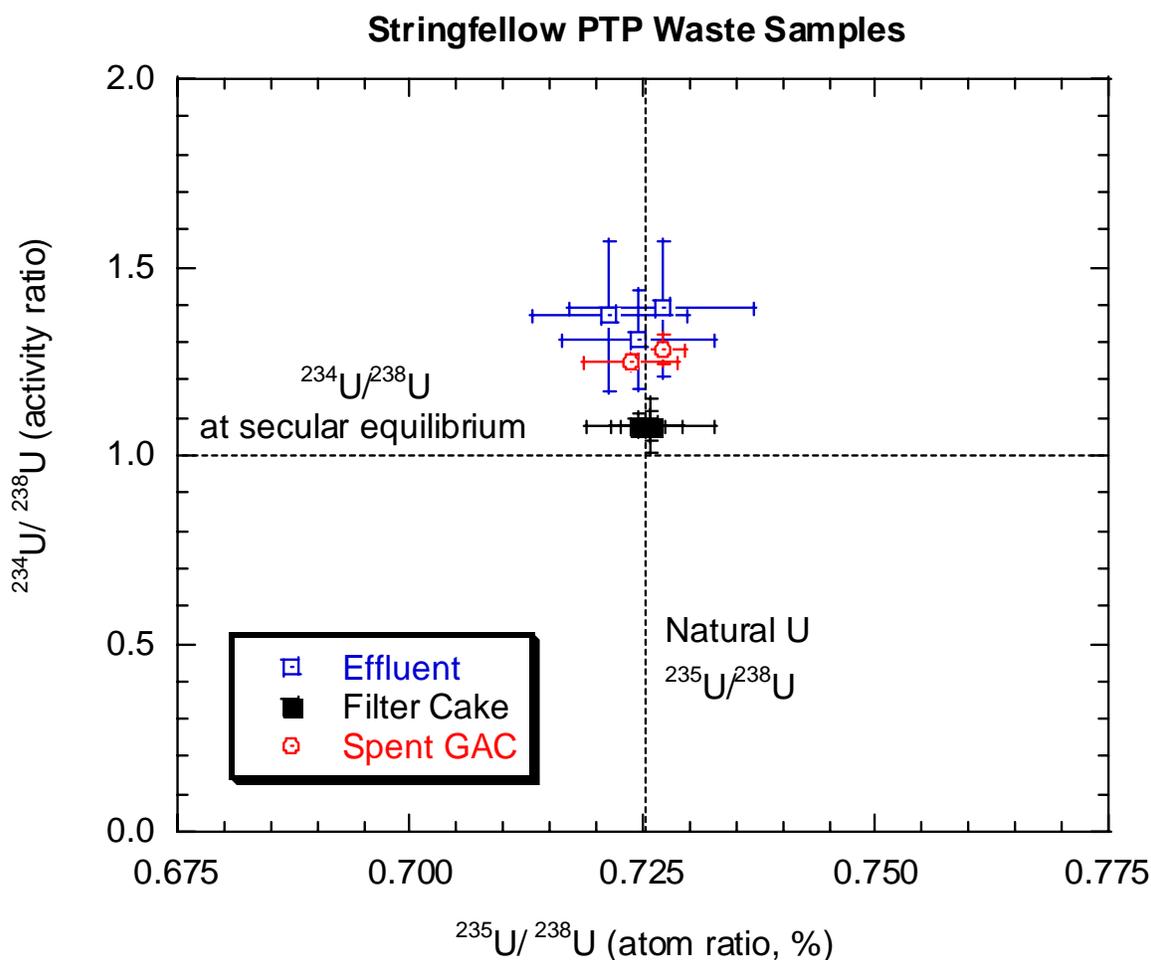
Figure 1. Uranium isotopic composition of Stringfellow PTP waste samples analyzed by LLNL. Data are averages of replicate runs with 2 σ reproducibility. Note that all samples are within error of the natural $^{235}U/^{238}U$ atom ratio of 0.007253, and have $^{234}U/^{238}U$ activity ratios of slightly greater than one, as is typical of natural groundwaters.

Is NORM present in Stringfellow waste and waste residue at levels above background?
In all sample matrices, the greatest source of radioactivity is uranium of natural isotopic composition. To determine if radionuclide levels in Stringfellow wastes samples are above background, they must be compared to the appropriate background samples. For GAC effluent samples, the appropriate comparison is with unperturbed groundwater. In GAC effluent samples, concentrations of both U and ^{226}Ra are below regulatory limits, and are well within the range of naturally occurring ground and surface waters. The uranium concentration of unperturbed upgradient groundwater at the Stringfellow site is not known. The 1986 DTSC report (DTSC, 1986) contains U data for on-site groundwaters as well as for groundwater from Glen Avon and surrounding communities. The report concludes that a small number of community groundwaters are elevated in uranium, and that the elevation is due to natural processes, not to Stringfellow

discharge. The report also presented data from a number of community wells that contained low levels of gross alpha radioactivity, and were therefore not tested for uranium, making it difficult to establish a background value for U. The GAC effluent samples tested in this study have U and ^{226}Ra activities that are below or in the same range as U and ^{226}Ra activities found in community groundwater.

Thermodynamic modeling (discussed in the next section and in Appendix 2) indicates that acidic groundwater produced by discharge from the Stringfellow acid pits could contain elevated levels of uranium. On-site wells (OW-1 and OW-2) have U activities of 169-774 pCi/L and Ra activities of 160-183 pCi/L (DTSC, 1986), considerably elevated relative to other groundwaters in the region, and consistent with enhanced leaching of U and Ra from geologic formations underlying the site. The GAC effluent samples tested in this study have U and ^{226}Ra activities that are significantly below U and ^{226}Ra activities found in groundwater from on-site wells OW-1 and OW-2.

For spent GAC and for filter cake, the appropriate background samples are unperturbed alluvium and bedrock underlying the Stringfellow site. The geologic setting of the Stringfellow site is discussed in a California DTSC report (DTSC, 1986). Although the geology is understood, no U concentrations are available for bedrock or alluvium at the site or in the basin. Granodiorite and quartz diorite and their metamorphic equivalents are significant in the bedrock of the basin, and are significant sources of alluvium found at the Stringfellow site. Literature compilations (see for example Table 3) indicate that granitic and metamorphic rocks of this type typically have U concentrations of 2-6 ppm.

Table 3. Typical U concentrations in common rock types

Rock Type:	U (ppm)	Source
Ultramafic rocks	0.014	Faure, 1986
Gabbro	0.84	
Basalt	0.43	
Andesite	2.4	
Nepheline syenite	8.2	
Granitic rocks	4.8	
Shale	3.2	
Sandstone	1.4	
Carbonate rocks	1.9	
Granitic gneiss	3.5	
Granulite	1.6	
Granites, granodiorites, rhyolites, dacites	2.2-6.1	Ivanovich and Harmon, 1992
Shales	2-4	
Black shales	3-1250	
Bauxite	11.4	
Phosphorites	50-300	
Coal	10-6,000	

Stringfellow filter cake samples have total U concentrations of 11-14 ppm, while Stringfellow spent GAC samples have total U concentrations of 3-7 ppm on a dry weight basis. The Stringfellow filter cake appears to have U concentrations on a dry weight basis that are slightly higher than typical for granitic rocks of similar composition to the bedrock at the Stringfellow site. No direct comparison is possible, however, and the filter cake values are within the range of acidic igneous rocks such nepheline syenites and tropical soils such as bauxites, and are lower than values typically found in some common sedimentary rocks (phosphorites, black shales and coal).

Does the waste treatment process at Stringfellow concentrate NORM? Naturally occurring radionuclides that are concentrated as the result of anthropogenic processes are referred to as Technologically Enhanced NORM (T-NORM). Preliminary thermodynamic modeling indicates that 1) acidic leachate from Stringfellow acid pits may enhance leaching of U, Th, and Ra from alluvium and bedrock underlying the Stringfellow site, and that contaminated groundwater from the site may contain above-background levels of U, Th and Ra, and 2) that treatment of contaminated groundwater with hydrated lime can cause these radioactive elements to be trapped in the filter cake (see Appendix 2). These model results indicate that lime precipitation from high-uranium groundwater may concentrate U and ^{226}Ra in filter cakes, resulting in filter cake having U and ^{226}Ra concentrations elevated above unperturbed alluvium and bedrock underlying the Stringfellow Site. Three observations suggest that this process may be occurring:

1) Filter cake U concentrations determined by LLNL are slightly higher than typical for granitic rocks of similar composition to the bedrock at the Stringfellow site.

2) GAC effluent samples analyzed by LLNL have U and ^{226}Ra activities considerably below activities determined for groundwaters from on-site wells OW-1 and OW-2, consistent with significant removal by treatment with lime and GAC.

3) The range of filter cake U concentrations calculated using a simple mass balance model is 8-20 ppm, and compares remarkably well to the range of measured filter cake U concentrations (11-14 ppm). The mass balance calculations assumed an A-stream influent with a U concentration of 450 pCi/L (which is typical of OW-1 and OW-2 well water measured in 1984), flow volumes and filter cake produced typical of values tabulated from July 2002 to April 2003, and quantitative removal of U from the influent to the filter cake.

These observations are suggestive, but by no means conclusive. The on-site well waters, for instance, were collected in 1984 and form only one component of the filter cake influent stream, while the influent flow volumes and filter cake masses are from 2003/2004. And neither unperturbed nor perturbed geologic samples from the Stringfellow site have been analyzed for U and ^{226}Ra activity, making determination of filter cake enrichment speculative.

In summary, neither the analytical nor the modeling results of the LLNL study conclusively demonstrate whether or not natural radioactive materials 1) are elevated above background levels, or 2) have been concentrated by the treatment process at the Stringfellow site.

Recommendations

1. The regulation of Technologically Enhanced, Naturally Occurring Radioactive Materials (T-NORM) is complex. Since the results of this study do not conclusively demonstrate whether natural radioactive materials have been concentrated by the treatment process, LLNL recommends that the DTSC consult with the DHS Radiological Health Branch to determine if any further action is warranted.

2. If DTSC deems it desirable to establish background radioactivity for the Stringfellow setting, LLNL recommends that additional samples be taken and analyzed by LLNL using the same methods presented in this report. For instance, to adequately assess whether or not radionuclides are concentrated in Stringfellow hydrated lime cake, further analyses of regional geologic samples would be necessary.

3. LLNL does not recommend further radiochemical analysis of Stringfellow samples to determine alpha-emitting radionuclides such as plutonium, since neither gamma spectroscopy nor ICPMS suggests that non-natural radionuclides are present in these samples.

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Acknowledgements

APPENDIX 1

DETERMINATION OF URANIUM CONCENTRATION AND ISOTOPIC COMPOSITION IN NATURAL WATERS BY SINGLE-COLLECTOR QUADRUPOLE INDUCTIVELY-COUPLED PLASMA MASS SPECTROMETRY

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September 20, 2004

REAGENTS AND EQUIPMENT

Instrumentation: Samples are run on a single-collector quadrupole inductively-coupled plasma mass spectrometer (ICPMS). LLNL has two Agilent Technologies HP4500's, which are benchtop instruments containing a 27.12 MHz crystal-controlled ICP source, turbo-pumped three-stage vacuum system, Omega lens ion optics, hyperbolic cross section molybdenum quadrupole mass analyzer with 3.0 MHz RF generator, and computer-controlled operation and data acquisition. Samples are introduced to the plasma with an autosampler, a Meinhard or Babington nebulizer, and a Peltier-cooled spray chamber.

Facilities: Sample chemistry (filtration, preservation, and preconcentration) and analysis takes place in a Class 100 or 1000 clean room under positive pressure with HEPA-filtered air.

Reagents: Deionized water (DI water) is produced by a large deionization and/or distillation system. Ultrapure 18 MΩ water (MQ water) is produced by a Millipore MQ system using DI water as a feedstock. Strong acids (nitric and hydrochloric) used for to clean Teflon labware are reagent-grade acids (Baker AR) diluted with DI water. Acid (nitric) used to preserve the samples and acids and bases (nitric acid and ammonium hydroxide) used in the sample chemistry are ultrapure trace metal grade from Seastar Chemicals diluted with MQ water. An Fe concentration standard (Spex or VHG Industries) is used in the iron hydroxide preconcentration chemistry.

Standards: NIST uranium isotopic standards (U-005, U-010, and U-500) are used to correct for deadtime and mass bias effects, and to provide quality control. A tracer isotopically enriched in ^{233}U is used to determined U concentration by isotope dilution. Uranium concentration standards (NIST 3164, Spex, and VHG) are used to calibrate the isotopically-enriched tracer, to tune the instrument, and to prepare standards for uranium concentration determination. All dilutions of these standards are prepared with MQ water and ultrapure concentrated nitric acid.

Filtration apparatus: Teflon-lined Tygon tubing, silicone peristaltic pump tubing, Teflon tubing connectors, and 2-way Teflon valves were cleaned by pumping MQ-water acidified to pH < 2 with ultrapure nitric acid through the sampling setup for several hours. Disposable high-capacity 0.45 micron polysulfone filter cartridges (Gelman).

Labware: A variety of labware is used in the sample chemistry and analysis, including Teflon jars and vials, polyethylene pipette tips and pippettors, and polypropylene centrifuge tubes. All

labware is cleaned using written protocols. New Teflonware is boiled sequentially in 50% HCl, DI water, aqua regia, DI water, 50% nitric acid, and MQ water. Used Teflonware is boiled sequentially in 50% nitric acid and MQ water. Other plastic labware is heated sequentially in 20% nitric acid and MQ water, and is only used once.

SAMPLE ANALYSIS

ICPMS Operation. The Agilent HP4500 used for the U isotopic analyses has met all manufacturer and LLNL performance specifications, as documented in the acceptance criteria. Each day, the instrument is operated for thirty minutes prior to optimization. This period allows the vacuum and electronic systems to stabilize. The instrument is optimized for mass calibration, mass sensitivity, and mass resolution using a 10 ng/mL multi-element tuning solution which spans the mass range from Li to U. A tune report recording tune settings and performance (sensitivity and precision, background, oxide and doubly charged ion formation, mass resolution) is generated after optimization and kept in a notebook. Other information (user, samples run, time on and off, etc.) is recorded in a log book. For uranium isotope ratio measurements, the ICP-MS is further optimized for U isotopes using a 10 ppb uranium solution (SPEX ICP-MS standards). Instrument sensitivity, mass calibration, and resolution are further tuned.

ICPMS Uranium Isotope Method. Data are acquired in isotopic analysis scan mode (1000 scans/repetition) on the central 3 channels (0.15 amu) of each mass. The mass spectrometer is set up to acquire 3 seconds/channel/repetition for masses 231, 234, 236 and 240; 1 second for mass 235; and 0.1 second for mass 238. Each analysis is set at 10 repetitions. The peristaltic pump program is set to 60 seconds of sample uptake (at 0.25 rps) and 60 seconds of signal stabilization (at 0.1 rps) before each analysis. A 15 second rinse (at 0.50 rps) and a 2-minute wash (at 0.25 rps), each in different 2% nitric acid solutions, follows each analysis. Total cycle time was less than 15 minutes; and less than 5 mL of sample is consumed.

Analyte mass count rates are corrected for nonspectral background. Background count rate is monitored at mass 231 and mass 240. The count rate at mass 240 is subtracted from count rates at masses 234, 235, 236 and 238 before ratio determination. Count rates at masses 231 and 240 are typically indistinguishable.

A second correction is made for instrumental mass bias. Isotope ratios measured with mass spectrometers deviate from absolute values. Mass bias effects observed with ICP-MS quadrupole mass spectrometers are due to several factors that are stable over hours. The deviation is typically within precision ($\leq 1\%$) of repeated measurements of a single solution. We measure NIST uranium standard U-500 to calculate mass bias for each analytical period. The NIST standard has equivalent ^{235}U to ^{238}U atom percent ($^{235}U/^{238}U = 0.9997$). The average $^{235}U/^{238}U$ ratio of the U-500 runs is used to determine the mass bias for the entire sequence. A simple linear law is used to correct for mass bias:

$$\text{Bias} = ((^{235}U/^{238}U)_{\text{certified NIST}}/(^{235}U/^{238}U)_{\text{measured NIST}} - 1)/(-3)$$

All measured U ratios in the submitted samples are then corrected for mass bias using:

$$(^{235}U/^{238}U)_{\text{corrected}} = (^{235}U/^{238}U)_{\text{measured}} * (1 + \Delta M * \text{Bias})$$

where ΔM = difference in amu (i.e., -3 for 235-238)

Reported error for measured ratios is two standard error of the mean of the ten repetitions, and are significant at the 95% confidence interval.

Uranium concentration by isotope dilution: An enriched [233]U tracer is added for quantitative concentration measurement by isotope dilution ICP-MS. The isotopic composition of the highly enriched tracer has been determined, and corrections for the contribution of tracer to analyte isotopic composition are made during data reduction. The [233]U concentration in the tracer solution has been determined by three independent techniques: alpha spectrometry, thermal ionization mass spectrometry, and ICP-MS. Results for these techniques agree within analytical uncertainty. Concentrations are reported as micrograms [238]U per gram sample. Uncertainty at the 95% confidence level is less than 1-2% for sample concentrations at the parts-per-billion level.

Quality Control: With every set of samples, a block of NIST standards is run before and after the sample run, and after every 10 samples. The block consists of the U-500 standard to monitor instrumental deadtime and mass bias, or a U-010 standard to monitor for mass bias, and a U-005 standard to monitor accuracy. The U-010 and U-005 standards have $^{235}U/^{238}U$ isotope ratios of 0.01014 and 0.004919 that bracket the natural ratio of 0.00725. Rinse and wash solutions of ultrapure 2% nitric acid are also run periodically to monitor memory at peaks of interest.

Isotopic data are not reported and samples are rerun if the internal precision at the 95% confidence level of the $^{235}U/^{238}U$ ratio exceeds 4%. The $^{234}U/^{238}U$ ratio is not reported if the two-sigma uncertainty (95% c.l.) exceeds 10%. These samples will be rerun if sample U concentration is greater than 5 ppb. The $^{236}U/^{238}U$ ratio is only reported if the ^{236}U signal exceeds the background-controlled detection limit (see below); otherwise the detection limit will be reported.

Demonstrated accuracy and precision: To assess the ability of single-collector quadrupole ICPMS to measure U concentrations and isotopic compositions, U solutions with NIST-certified isotopic compositions (U005, U3164, and U010) from depleted to enriched were run over a concentration range from 0.1 to 50 ng/mL. The relative abundances of ^{234}U, ^{235}U, ^{236}U and ^{238}U were determined in each solution. Detection limits for ^{236}U were also determined.

The concentration range was chosen to span U concentrations expected in analyte solutions from natural waters with and without 10 to 20-fold pre-concentration. The isotopic compositions of the standard solutions were chosen to bracket the isotopic composition of natural U. Standard SRM-3164 has a natural $^{235}U/^{238}U$ atomic ratio (0.00725); whereas standard U-005 is depleted (0.00492) and standard U-010 is enriched (0.01014) in fissionable ^{235}U. The U-500, with a $^{235}U/^{238}U$ ratio of close to one, or U-010 standard is used to correct for mass bias effects.

The average $^{235}U/^{238}U$ ratio of the six 10 ppb U-500 runs was used to determine the mass bias for the entire data set. The average measured $^{235}U/^{238}U$ ratio for the 10 ppb U-500 replicates was 1.0014 ± 0.0028 (2 s.e., n = 6), corresponding to a mass bias of 0.055%/amu. The average of all U-500 replicates was 1.0015 ± 0.0012 (2 s.e., n = 18).

Agreement between corrected ratios and certified values in all standards is excellent. Average $^{235}U/^{238}U$ ratios for 1, 10, and 50 ppb standards agree with certified values to better than 1% after correction for mass bias. Average $^{234}U/^{238}U$ and $^{236}U/^{238}U$ ratios for 1, 10 and 50 ppb standards agree with certified values to better than 2.5% after correction for mass bias and background (with the exception of $^{234}U/^{238}U$ for U-010 which is 5% lower than the certified value). Precision at the 95% c.l. is typically comparable to or better than accuracy.

The detection limit for ^{236}U was determined from the 3 sigma standard deviation on the 240/238 count ratio multiplied by the ^{238}U concentration in the sample. The instrumental detection limit for ^{236}U determined in this manner averages 20 fg/mL (i.e. 20 x 10^{-15} g/mL). Clean 2% nitric acid solutions have count rates at mass 236 which are indistinguishable from count rates at mass 240, indicating that the detection limit for ^{236}U is not limited by memory effects. No correction was made for a ^{235}U contribution (as a hydride or atomic ion) to the mass 236 peak. However, the uranium hydride ($^{238}U^1H$) at 239 amu is measurable. Measured 239/238 ratios ($^{238}U^1H/^{238}U$), after correction for non-spectral background, average 0.000016. For isotopic compositions close to natural U, the $^{235}U^1H$ signal at mass 236 would be equivalent to 1 fg/mL of ^{236}U in a 10 ppb U solution. Within the range of concentrations analyzed in this study, detection limits are limited by uncertainty in the background, and not by memory effects or by ^{235}U contributions to the mass 236 peak

Procedural and field U blanks for site groundwater sample analyses range from 0.1 to 1 ppt (pg/mL), and are insignificant for groundwater samples which typically contain > 1 ppb U (ng/mL).

APPENDIX 2

Thermodynamic Modeling of Uranium, Thorium and Radium Chemistry at the Stringfellow Site

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Chemical thermodynamics equilibrium modeling has been used for many years to understand and predict the chemistry, solubility and speciation of metals in the environment, especially in the field of hazardous and nuclear waste disposal, transport and fate. Using simple chemical thermodynamic MINTEQ code (Allison et al., 1998), we have examined the chemistry of uranium, thorium and radium leaching from the aquifer underlying the Stringfellow Site and their subsequent precipitation by hydrated lime filter cake formation.

Thermodynamic data was taken from the MINTEQ database and supported with data from the NIST Critical Stability Constant database (Motekaitis, 2001). No thermodynamic data for radium was available, and so barium was used as a chemical analog (Lide, 2002; Greenwood and Earnshaw, 1997; and Figure 1). However, the solubility of radium is expected to be higher than that of barium based on correlation of metal hydroxide solubility with metal ionic radius.
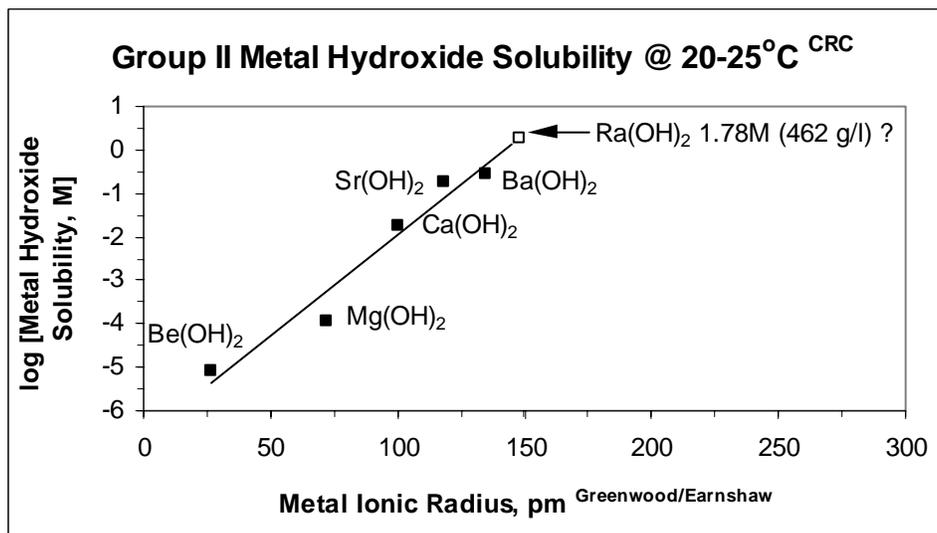

Figure 1: Prediction of radium hydroxide solubility based on metal ionic radius. Metals with measured hydroxide solubilities are represented by solid symbols. The solubility of radium hydroxide (open symbol) is extrapolated from the correlation between ionic metal ionic radius and metal hydroxide solubility. The question mark after the solubility of the radium salt emphasizes that this value has not been directly measured. Metal ionic radius data are from Greenwood and Earnshaw (1998); metal hydroxide solubility data are from Lide (2002).
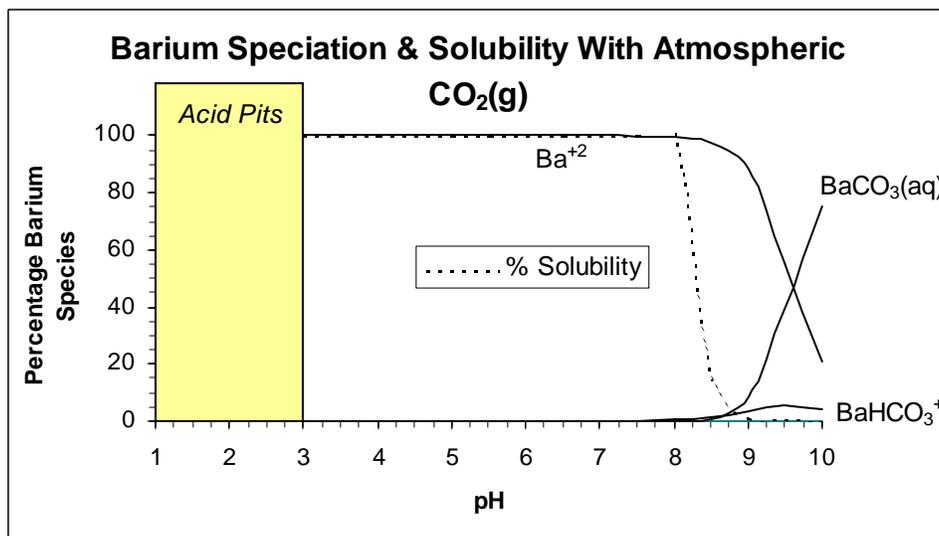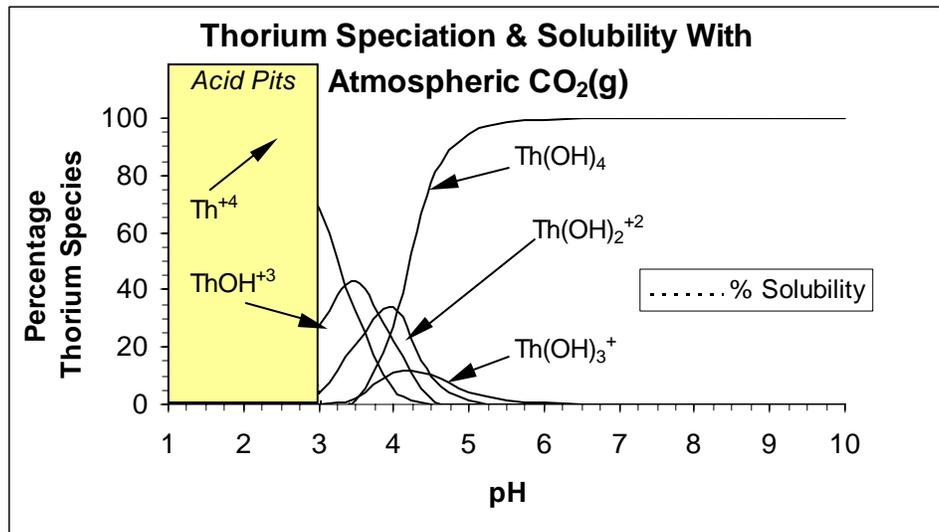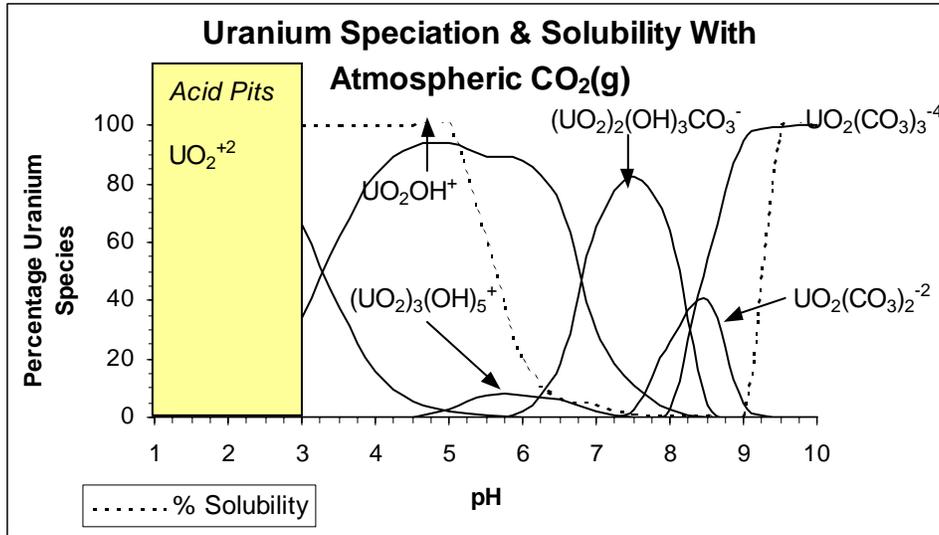
**Figure 2: Uranium, thorium and barium solubility as a function of pH.**
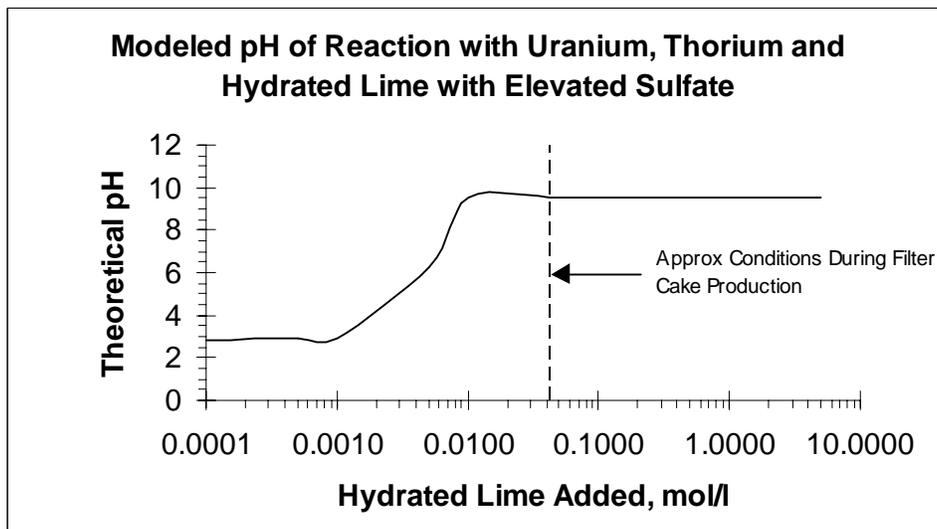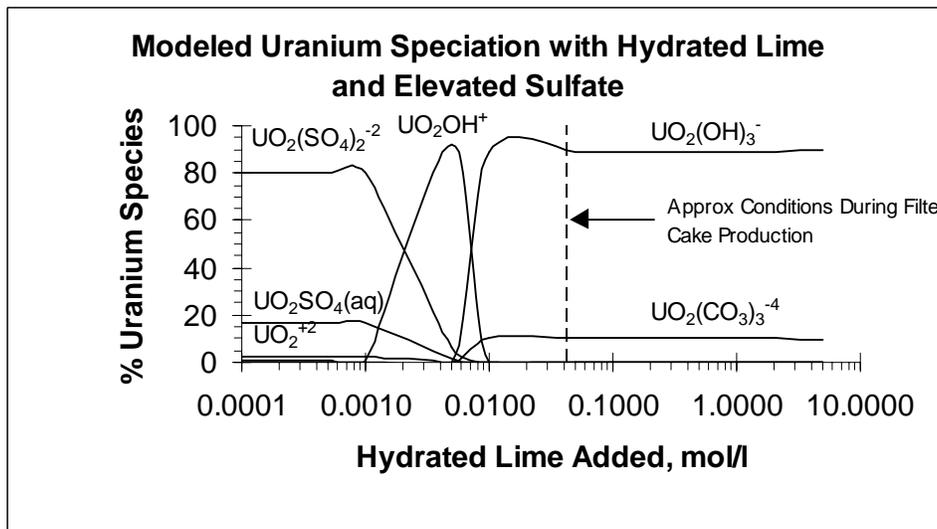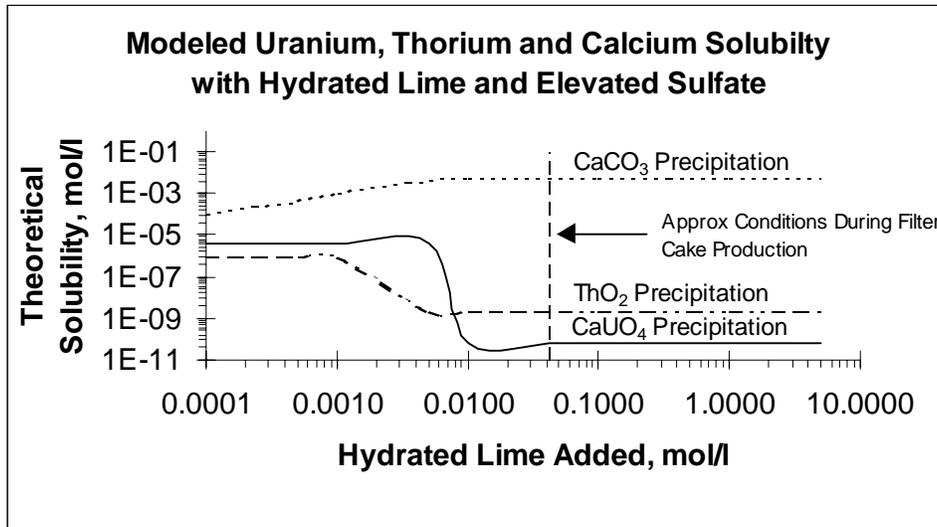
Figure 3: **The modeled effect of the addition of hydrated lime to waste stream A on the solubility of U, Th and Ca; on the speciation of U; and on pH.**

Thermodynamic models of U, Th, and Ba speciation in water equilibrated with atmospheric carbon dioxide indicate enhanced solubility under low pH conditions (Figure 2). The implication is that acidic leachate from Stringfellow acid pits enhance leaching of U, Th, and Ra from alluvium and bedrock underlying the Stringfellow site, and that contaminated groundwater from the site will contain above-background levels of U, Th and Ra.

The addition of hydrated lime to the waste stream allows the precipitation of metal hydroxides and (in the presence of air) carbonates (Figure 3). Subsequent modeling of the addition of hydrated lime and filter cake formation shows that uranium and thorium are likely to precipitate also as $CaUO_4$ (calcium uranate) and ThO_2. Radium is also expected to precipitate, but not specifically as a hydroxide or carbonate, rather as a co-precipitate.

Modeling of the sorption of radionuclides onto GAC is less constrained. The sorption of metals and radionuclides on GAC will be very sensitive to the point of zero charge (PZC) of the GAC used, solution pH, complexing agents, and solution contaminants that are present in high concentration and sorb strongly to GAC. Since the PZC of GAC materials ranges from 5.3 to 9.4 (Rivera-Utrilla and Sanchez-Polo, 2002), and the abundance of complexing agents and other sorbing species in the filter cake effluents are not known, sorption of U and Ra to GAC cannot be usefully modeled at this time.

To summarize, the results show that leaching of uranium, thorium and radium can indeed occur at the site due to the environmental conditions created by the waste, and that treatment with hydrated lime can cause these radioactive elements to be trapped in the filter cake. The presence of chelating, or solubility increasing components of the waste (e.g. EDTA, NTA, organics and inorganics) affect the solubility and speciation of each of the elements detailed. This in turn may lead to decreased levels of uranium, thorium and radium in the filter cake, and allow elevated levels to reach the GAC filtration stage of the pretreatment plant.

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