AUSTRALIAN NUCLEAR SCIENCE
AND TECHNOLOGY ORGANISATION
LUCAS HEIGHTS SCIENCE AND TECHNOLOGY CENTRE

A REPORT TO ILUKA RESOURCES LTD

on

SECULAR EQUILIBRIUM & SOLIDS WASTE LEACHABILITY
DOUGLAS MINE – PHASE 2

by

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EXECUTIVE SUMMARY

ANSTO Minerals has completed a Solids Waste Leachability Study of materials from the Hamilton [redacted] heavy mineral sands plants. The work program presented in this report constitutes Phase 2 of that program. The objectives of the Phase 2 work were to determine:

- secular equilibrium in [redacted] acidic leach residues from the Phase 1 program of work;
- uranium and thorium (full decay chains) leachability of [redacted] additional samples from the Phase 1 program of work for both acidic (pH 5.0) and alkaline (pH 9.2) leaching fluids using the Australian Standard Leaching Procedure (ASLP) [2];
- [redacted]

The samples studied in the Phase 2 program were:

- Hamilton FPC Sand Tailings;
- [redacted]
- Hamilton Cleaning Circuit Mags [redacted];
- Hamilton Gypsum Filter Cake;
- [redacted]
- [redacted]

[redacted]

[redacted]

Leaching of radium from the solids is related to mineralogy and/or chemistry and was independent of the initial concentration of radium in the solid.

The physical state of the Hamilton Gypsum Filter Cake (wet versus dry) did not influence the leaching characteristics of the solid. There was no significant difference in leachate concentrations using either the acetate and borate leach liquors when comparing the Phase 1 (wet) and Phase 2 (dry) results.

[redacted]

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TABLE OF CONTENTS

APPENDICES

1. INTRODUCTION

[redacted]

ANSTO Minerals (AM) recently completed Phase 1 of the project [redacted]. A limited number of the samples were leached and none of the leach residues were assayed. Phase 2 of the program of work involved the leaching of further samples from the Phase 1 program and the analysis of several leach residues from the Phase 1 program. All samples are currently held in storage at AM. A flowsheet for the Phase 2 work program is given in **Appendix A**.

The work was conducted on samples which arrived at ANSTO Minerals in April 2013 and on leach test residues generated during the Phase 1 program of work.

[redacted].

[redacted]

2. OBJECTIVES

The objectives of the Phase 2 work were to determine the following:

- secular equilibrium in [redacted] acidic leach residues from the Phase 1 program of work;
- uranium and thorium (full decay chains) leachability of [redacted] additional samples from the Phase 1 program of work for both acidic (pH 5.0) and alkaline (pH 9.2) leaching fluids using the Australian Standard Leaching Procedure (ASLP) [2];
- [redacted]

[redacted]

3. SAMPLE PREPARATION

[redacted] samples supplied by Iluka on 22 April 2013 were retrieved from storage at AM. The samples are listed in **Table 1**. The sample numbers used in this study are the same as those used in the Phase 1 program of work. The gypsum filter cake was dried at 110°C and crushed to a free flowing powder before leaching. [redacted]

The [redacted] dry, acidic leach residues produced from the pH 5.0 ASLP leach tests carried out in Phase 1 (samples 2, 6 and 11 – see **Table 1**) were pulverised prior to radiochemical assaying.

TABLE 1
Sample Characteristics

Sample No.	Description	Weight Loss on Drying %
	Samples Supplied by Iluka in April 2013	
1	Hamilton FPC Sand Tailings	4.6
[redacted]	[redacted]	[redacted]
5	Hamilton Cleaning Circuit Mags [redacted]	< 0.1
6	Hamilton Gypsum Filter Cake	39.5
[redacted]	[redacted]	[redacted]
	Dry pH 5.0 ASLP Leach Residues from Phase 1	
2	Hamilton WRP Slimes	-
[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]

4. SAMPLE ASSAYS

Leachate samples were analysed for elemental content using inductively coupled plasma optical emission spectrometry (ICPOES) and inductively coupled plasma mass spectrometry (ICPMS). The analytical results are presented in the leach test worksheets, which are provided in **Appendix B**.

Leach residues from the Phase 1 program of work and leachate samples from this study were assayed for radionuclide content using the following techniques:

- Gamma spectrometry[1] for Th-232 and U-238 decay chain progeny, together with U-235 and its decay chain progeny, in solids and liquors.
- Neutron activation analysis (NAA) for parent Th-232 in solids.
- Delayed neutron activation (DNA) analysis for parent U-238 in solids.
- Alpha spectrometry for Po-210 in solids and liquors.
- ICPMS for parent Th-232 and parent U-238 in liquors.

A summary of Th and U results for the Phase 1 leach residues and the corresponding sample solids is given in **Table 2**. [redacted]

[1] Detection limits in gamma spectrometry vary depending on peak energy, peak abundance, detector efficiency, detector background and sample matrix and are calculated using the GammaVision software.

TABLE 2
Thorium and Uranium Concentrations in Sample Solids and Leach Residues (ppm)

Sample No.	2		6		[redacted]	
Sample Description	Hamilton WRP Slimes		Hamilton Gypsum Filter Cake		[redacted]	
	Solid	Leach Residue	Solid	Leach Residue	[redacted]	[redacted]
Th	820	780	290	410	[redacted]	[redacted]
U	116	118	29	42	[redacted]	[redacted]

5. ASLP LEACHING

The bottle leaching procedure is designed to assess the potential for solid wastes, sediments and sludges to contaminate groundwater in a variety of disposal to land scenarios. The reagents that were added to the leaching fluids covered the range of pH values that would be observed in groundwater in such scenarios. The wide range is capable of detecting any significant solubility.

Two leachability tests were carried out on each of [redacted] samples [redacted] in accordance with ASLP 4439.3-1997 [2]. The leaching fluids were an acetate buffer chosen using the prescribed preliminary tests and a tetraborate buffer of pH 9.2. The samples were leached without any particle size reduction to meet the P_{100} requirement of 2.4 mm. The samples (50 g, as-received for samples 1, 4 and 5; 50 g dried material for sample 6) were leached, to produce approximately 1 L of leachate. No duplicates or blank leaches were performed, because AM previous experience has found that radionuclides are not detected in the reagents used.

For the [redacted] alkaline leaches, the alkaline leaching fluid had an initial pH of 9.2 and contained 38.2 g/L of sodium tetraborate. The solution density was 1.022 g/mL.

Preliminary tests to determine the acid neutralising capacity of the solids were conducted to select the initial pH for the acetic acid leaching fluid. The results are given in **Table 3.** The pH of a 5% slurry in water was found to be less than 5.0 for the [redacted] ilmenite samples, [redacted] The low pH values indicate that the solids had minimal acid neutralising capacity. The pH of the 5% slurry of FPC Sand Tailings (sample 1) rapidly decreased when the specified amount of hydrochloric acid was added, which indicated that the pH 5.0 fluid should be used. [redacted] The solution contained 5.7 mL of glacial acetic acid and 64.3 mL of 1 mole/L sodium hydroxide per L of water. The dried gypsum cake was acid neutralising and therefore, the more acidic leaching fluid, pH 2.9, was chosen for sample 6 (5.7 mL of glacial acetic acid per L of water).

The leaching tests were carried out using a liquid to solid mass ratio of 20:1 in end-over-end rolled bottle leach tests (see **Figure 1**) at ambient temperature for 16-20 hours. In accordance with the standard method, the mass of the leaching fluid was 20x the mass of the wet pressure filter cake. The dry solids (g) to leach liquor (mL) ratio was calculated in each leach test worksheet, as shown in **Appendix B**.

TABLE 3
Selection of the Acidic Leaching Fluid

Sample	Description	pH of 5% Slurry	pH of slurry after HCl[#]	pH of Selected Leaching Fluid
1	Hamilton FPC Sand Tailings	6.6	1.6	5.0
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
5	Hamilton Cleaning Circuit Mags[redacted]	4.6	nr	5.0
6	Dried Hamilton Gypsum Filter Cake	8.7	6.6	2.9

specified HCl addition of 3.5 mL of 1 M HCl / 100 mL of 5% slurry
nr - not required as slurry pH was < 5

FIGURE 1 End-over-end Bottle Roll Test Rig

The definitions in the standard [2], which have been used in this work, are:

- **Test sample** - a sample prepared from the laboratory sample and from which test portions will be taken.
- **Leaching fluid** - the solution produced in the laboratory to be used for the leaching of the test sample.
- **Percentage solids** - that amount of a test portion remaining after all liquids have been expelled by pressure filtration under a pressure of 350 kPa, expressed as a percentage.
- **Sample liquid** - the liquid which is separated from a test sample by pressure filtration.
- **Solids leachate** - the liquid produced by treatment of the solids with the leaching fluid and subsequent filtration.

5.2 Results of Leach Tests

Details of the leach test conditions and elemental deportment are provided in **Appendix B**. A summary of the leach test results, together with results for U, Th and Ra, are given in **Table 4**. Sodium was not monitored, as it was a constituent of the leaching fluids.

The fraction of each element extracted was calculated from the amounts in the final leachate and the initial solids. The mass of a moist sample was converted to a dry weight and divided by the total leach fluid volume to produce the "g dry solids/L leach fluid". The volume of moisture in the sample was added to the leaching fluid volume. Although the standard method specifies a mass ratio of 20:1, the g dry solids/L ratio was never exactly 50 due to the density of the leaching fluids

The extractions were then calculated as follows:

$$\% \text{ Extracted} = \frac{\text{mg/L in leachate} \times 100 \times 1000}{\text{mg/dry kg in solids} \times (\text{g dry solid/L})}$$

Indicated "less than" extractions (see **Appendix B**) are dependent on the assays of the feed solids and the detection limits for the assays of the leach solutions.

[redacted]

TABLE 4
Summary of the Leach Test Results

Sample No. Sample Description		1 FPC Sand Tailings	[redacted]	5 Cleaning Circuit Mags [redacted]	6 Gypsum Filter Cake (dry)	[redacted]
Iluka Sample Solids	U (mg/dry kg)	< 10		625	30	
	Th (mg/dry kg)	53		7070	291	
	Ra-226 (Bq/g)	0.15		9.3	0.14	
	Ra-228 (Bq/g)	0.23		35	0.65	
Acetate Leachate	pH	5.0		4.9	6.5	
	U (mg/L)	< 0.01		< 0.01	0.1	
	Th (mg/L)	< 0.01		< 0.01	< 0.01	
	Ag (mg/L)	< 0.01		< 0.01	< 0.01	
	Ca (mg/L)	11		2	2090	
	Cr (mg/L)	0.04		0.03	0.32	
	Mg (mg/L)	2		< 1	221	
	S (mg/L)	< 10		13	500	
	Ra-226 Bq/L)	0.98		0.9	0.52	
	Ra-228 (Bq/L)	0.63		3.4	1.1	
Borate Leachate	pH	9.3		9.3	8.8	
	U (mg/L)	< 0.01		< 0.01	< 0.01	
	Th (mg/L)	< 0.01		< 0.01	0.09	
	Ag (mg/L)	< 0.01		0.02	< 0.01	
	Ca (mg/L)	4.5		< 1	774	
	Cr (mg/L)	0.02		0.02	0.04	
	Mg (mg/L)	1.2		< 1	7	
	S (mg/L)	< 10		14	3310	
	Ra-226 Bq/L)	< 0.34		0.9	0.44	
	Ra-228 (Bq/L)	< 0.55		0.73	< 0.30	

[redacted]

6.1 Radionuclide Analysis

The [redacted] solid samples used in the leaching testwork were analysed for their radionuclide content as part of a separate study of the radioactivity content of Iluka wastes [1]. The [redacted] acetate buffer (i.e. acidic) leach residues from the Phase 1 program were also analysed for radionuclide content as part of this study. [redacted]

The radionuclide results for the acidic leach residues are given in **Table 8**, together with the total contained activities. The results show that no radionuclides had been leached from any of the [redacted] solids, Hamilton WRP Slimes (sample 2), Hamilton Gypsum Filter Cake (sample 6) [redacted] which is commensurate with the leachate assay results from the Phase 1 study.

The acetate and borate leachates from the bottle leaching tests [redacted] were assayed to determine the concentrations of naturally occurring radioactivity. The radionuclide results are given in **Table 9**. The total contained activities (total alpha, total beta and total alpha + beta[2]) have been calculated for all radionuclides in the Th-232, U-238 and U-235 decay chains from the measured results for the long-lived radionuclides in each of the respective decay chains. The total contained activities are also given in **Table 9**. For ease of comparison, the Phase 1 leaching results for the Hamilton Gypsum Filter Cake (sample 6) [redacted] have been included in **Table 9**.

[2] Gross alpha and gross beta counting are screening techniques only. The total contained activity provided in this study is an accurate assessment of the contribution of ALL individual radionuclides in a sample.

[redacted]

TABLE 8

Radionuclide Results (Bq/g) – Iluka Waste Solids and Leach Residues

(DNA, NAA ± 3%, Gamma and Alpha Spectrometry ± 10%)

Sample	Hamilton WRP Slimes		Hamilton Gypsum Filter Cake		[redacted]
AM Identification	ILU-220413-2		ILU-220413-6		
	Solid	Leach Residue	Solid	Leach Residue	
Th-232 Decay Chain					
Th-232	3.3	3.2	1.1	1.5	
Ra-228	4.5	4.5	0.65	0.91	
Th-228	3.1	3.3	0.62	0.86	
U-238 Decay Chain					
U-238	1.6	1.5	0.36	0.52	
Th-230	1.4	1.7	0.44	0.71	
Ra-226	1.8	1.8	0.14	0.18	
Pb-210	1.3	1.5	0.28	0.40	
Po-210	0.87	0.87	0.09	0.23	
U-235 Decay Chain					
U-235	0.074	0.069	0.017	0.024	
Pa-231	< 0.14	< 0.14	< 0.098	< 0.084	
Ac-227	na	0.078	na	0.060	
Th-227	0.11	0.078	0.047	0.060	
K-40	0.24	0.43	< 0.056	0.10	
Total Alpha	32	33	5.8	8.8	
Total Beta	25	26	4.3	6.0	
Total Alpha + Beta	57	59	10	15	

TABLE 9
Radionuclide Analysis of the Solids and Leachates

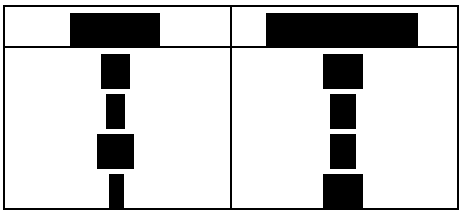
Sample	Hamilton FPC Sand Tailings			[redacted]	Hamilton Cleaning Circuit Mags (CL Ilmenite)			Hamilton Gypsum Filter Cake				
								dry sample this work			wet sample Phase 1	
AM Identification	ILU-220413-1				ILU-220413-5			ILU-220413-6			ILU-220413-6	
	Solid Bq/g	Acetate Bq/L	Borate Bq/L		Solid Bq/g	Acetate Bq/L	Borate Bq/L	Solid Bq/g	Acetate Bq/L	Borate Bq/L	Acetate Bq/L	Borate Bq/L
Th-232 Decay Chain												
Th-232	0.24	< 0.04	< 0.04		38	< 0.04	0.07	1.1	< 0.04	< 0.04	< 0.04	< 0.04
Ra-228	0.23	0.63	< 0.55		35	3.3	0.73	0.65	1.1	< 0.30	1.5	< 0.42
Th-228	0.24	0.35	< 0.19		38	< 0.13	0.54	0.62	< 0.14	< 0.11	0.20	< 0.12
U-238 Decay Chain												
U-238	0.16	< 0.12	< 0.12		11	< 0.12	< 0.12	0.36	1.3	< 0.12	0.87	< 0.12
Th-230	< 0.20	< 4.1	< 9.5		10	< 5.7	< 6.8	0.44	< 4.5	< 5.2	< 13	< 8.2
Ra-226	0.15	0.72	< 0.34		9.3	0.89	0.75	0.14	0.52	0.32	1.1	0.54
Pb-210	0.15	< 1.4	< 2.3		9.3	< 1.6	< 1.3	0.28	< 1.6	< 1.2	< 2.9	< 2.5
Po-210*	0.17	0.14	< 0.10		1.8	0.045	0.10	0.09	0.10	0.12	0.11	0.29
U-235 Decay Chain												
U-235^	0.007	< 0.66	< 0.81		0.51	< 0.81	< 0.69	0.017	0.060	< 0.64	0.040	< 0.006
Pa-231	< 0.055	< 1.2	< 3.5		< 0.30	< 1.8	< 1.2	< 0.098	< 2.1	< 1.1	< 2.2	< 2.4
Ac-227	< 0.013	< 0.27	< 0.45		< 0.66	< 0.38	< 0.32	na	< 0.39	< 0.32	na	na
Th-227	< 0.013	< 0.27	< 0.45		< 0.66	< 0.38	< 0.32	0.047	< 0.39	< 0.32	< 0.42	< 0.41
K-40	0.060	< 2.4	< 4.1		< 0.087	< 2.8	< 2.4	< 0.056	< 2.9	< 2.4	< 5.4	< 5.3
Total Alpha[#]	2.5	4.8	0		299	3.6	5.9	6.3	4.8	1.4	7.3	2.5
Total Beta[#]	1.9	3.4	0.0		206	8.4	4.0	4.3	5.9	0.64	7.4	1.1
Total Alpha + Beta[#]	4.5	8.2	0		505	12	10	11	11	2.0	14.7	3.5

* Po-210 concentration on date of alpha counting.

^ Calculated from U-238 concentration.

[#] Less than values assume zero concentration for those particular radionuclides in solids and solutions.

[redacted]



8. CONCLUSIONS

[redacted]

9. ACKNOWLEDGMENTS

Specialised analyses were carried out by Patrick Yee, Chris Chipeta, Ariunaa Altantsetseg, Isabella Naletilic and Gordon McOrist.

10. REFERENCES

[1] Emett M. *et al* [2013] Solids Waste Leachability - Phase 1, ANSTO Report C1331 to Iluka Resources, June.

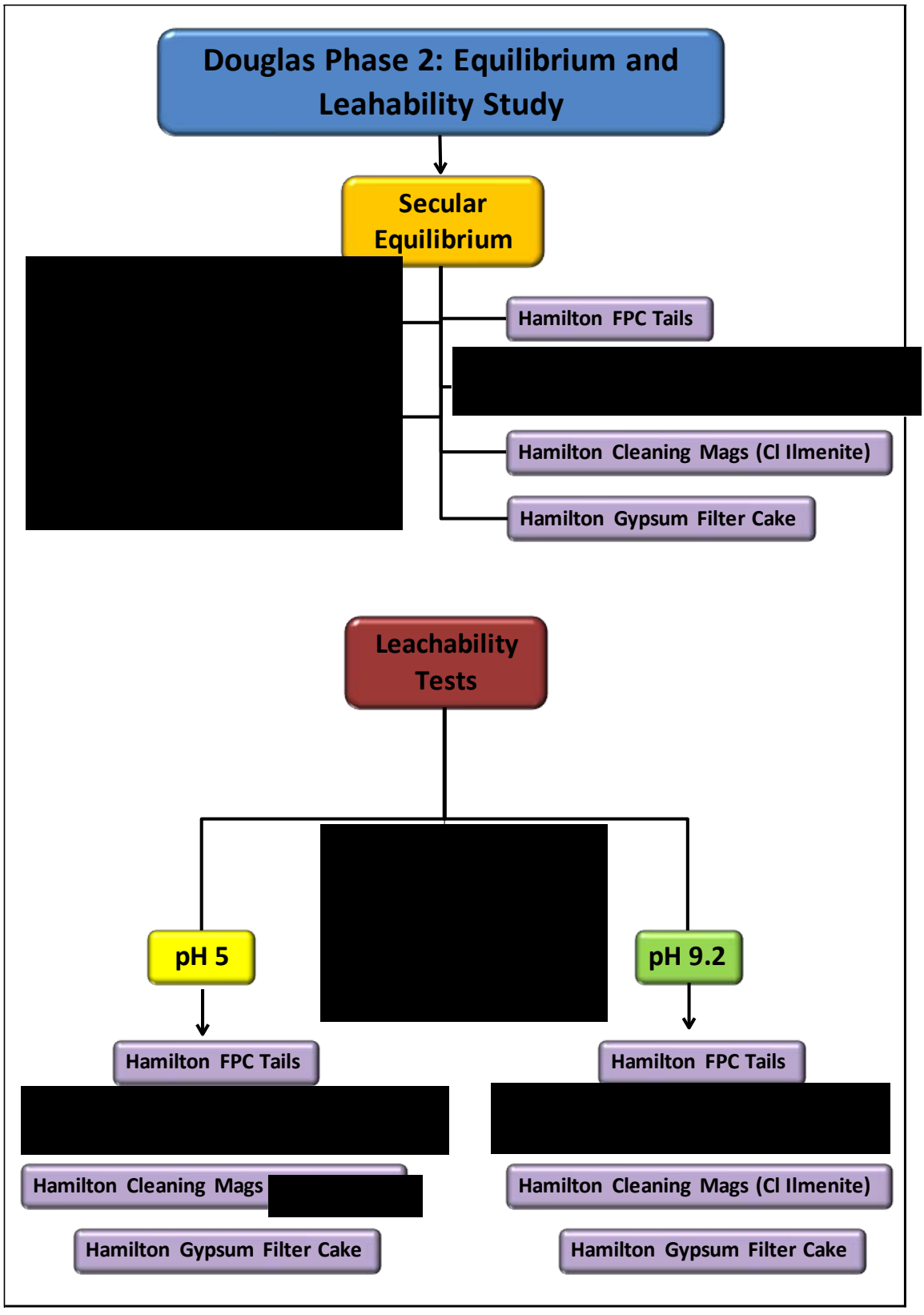
[2] AS 4439.3-1997, Wastes, sediments and contaminated soils, Part 3, Preparation of leachates - Bottle leaching procedure.

[3] CEN/TS 14997:2006 Characterization of Waste – Leaching Behaviour Tests – Influence of pH on Leaching with Continuous pH-control.

[redacted]

APPENDIX A

Sample Source and Study Program (from Client)



APPENDIX B Leach

Test Logsheets

Sample :	1
Description :	FPC Sand Tailings
Loss on Drying (wt%) :	4.60
Acid Leach Fluid Selection	
pH of 5% slurry:	6.61
pH of 5% slurry + HCl:	1.62
Acetate Leaching Fluid pH:	5.0

	Sample Solids	Solids Leachate Acetate	Extraction	Solids Leachate Borate	Extraction
Dry Solids/Leach Fluid	g/L	47.7		48.7	
Final Leachate pH		5.0		9.3	
	mg/dry kg	mg/L	%	mg/L	%
Ag	<10	<0.01	un	<0.01	un
Al	47599	<1	< 0.04	<1	< 0.04
As	<100	<0.1	un	<0.1	un
Ba	382	<1	< 5	0.54	2.9
Ca	2717	11	8.4	4.5	3.5
Cd	<10	<0.01	un	<0.01	un
Cr	2033	0.04	0.044	0.02	0.016
Fe	49773	<1	< 0.04	<1	< 0.04
K	1028	<10	< 20	<10	< 20
Mg	6067	2.0	0.70	1.2	0.40
Mn	1822	<1	< 1	<1	< 1
Mo	<10	<0.01	un	<0.01	un
Ni	82	<0.02	< 0.5	<0.02	< 0.5
Pb	70	<0.01	< 0.3	<0.01	< 0.3
S	<1000	<10	un	<10	un
Se	<100	<0.1	un	<0.1	un
Th	53	<0.01	< 0.4	<0.01	< 0.4
U	<10	<0.01	un	<0.01	un
V	498	<0.01	< 0.04	0.090	0.38
Zn	266	0.08	0.67	0.03	0.20
Zr	2736	<0.01	< 0.01	0.018	< 0.01
	Bq/g	Bq/L	%	Bq/L	%
Ra-228(Th-232 decay chain)	0.23	0.63	5.7	< 0.55	< 5.0
Ra-226(U-238 decay chain)	0.15	0.98	14	< 0.34	< 4.8

un = unknown because complete leaching of the low concentration elements from the solids would have produced element concentrations in the leachate which were below the detection limit

Sample :	6dry
Description :	Gypsum Filter Cake
Loss on Drying (wt%) :	39.5
Acid Leach Fluid Selection	
pH of 5% slurry:	8.67
pH of 5% slurry + HCl:	6.65
Acetate Leaching Fluid pH:	2.9

	Sample Solids	Solids Leachate Acetate	Extraction	Solids Leachate Borate	Extraction
Dry Solids/Leach Fluid	g/L	50.0		50.0	
Final Leachate pH		6.5		8.8	
	mg/dry kg	mg/L	%	mg/L	%
Ag	<10	<0.01	un	<0.01	un
Al	7950	<1	< 0.3	<1	< 0.3
As	<10	<0.1	un	<0.1	un
Ba	72	<1	< 28	0.22	6.2
Ca	221000	2088	19	774.3	7.0
Cd	<10	<0.01	un	<0.01	un
Cr	297	0.32	2.1	0.04	0.30
Fe	46900	<1	< 0.04	<1	< 0.04
K	340	<10	< 59	13	< 76
Mg	7010	221	63	7	2
Mn	100	<1	< 20	<1	< 20
Mo	<10	<0.01	un	<0.01	un
Ni	-	0.049	un	0.038	un
Pb	18	<0.01	< 1	<0.01	< 1
S	110000	500	9.1	3311	60
Se	<100	<0.1	un	<0.1	un
Th	291	<0.01	< 0.1	0.09	0.65
U	30	0.10	7	<0.01	< 0.7
V	223	<0.01	< 0.09	0.093	0.84
Zn	100	0.02	0.44	0.03	0.54
Zr	3500	<0.01	< 0.006	0.041	0.02
	Bq/g	Bq/L	%	Bq/L	%
Ra-228(Th-232 decay chain)	0.65	1.1	3.4	< 0.30	< 0.9
Ra-226(U-238 decay chain)	0.14	0.52	7.4	0.44	6.3

un = unknown because complete leaching of the low concentration elements from the solids would have produced element concentrations in the leachate which were below the detection limit