Report on Qualitative Validation Experiments Using Lithium-Aluminum Layered Double-Hydroxides for the Reduction of Aluminum from the Waste Treatment Plant Feedstock

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List of Terms

Abbreviations

ARF	Aluminum Removal Facility
ATL	Advanced Technologies and Laboratories, Intl.
BSE	Back Scattered Electron
D.I.	De-ionized
DST	Double-Shell Tank
EDS	Energy Dispersive Spectrometry
IC	Ion Chromatography
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma – Mass Spectroscopy
LiHT	Lithium Hydrotalcite
PLM	Polarized Light Microscopy
SEM	Scanning Electron Microscopy
SST	Single-Shell Tank
TIC/TOC	Total Inorganic Carbon/Total Organic Carbon
TGA	Thermal Gravimetric Analysis
WTP	Waste Treatment and Immobilization Plant
XRD	X-ray Diffraction

Units

g	Gram
M	Molar
µg	Microgram
L	Liter
mL	Milliliter
NTU	Nephelometric Turbidity Unit

1.0 EXECUTIVE SUMMARY

- A process for removing aluminum from tank waste simulants by adding lithium and precipitating Li-Al-dihydroxide (Lithiumhydrotalcite, $[\text{LiAl}_2(\text{OH})_6]^+\text{X}^-$) has been verified. The tests involved a double-shell tank (DST) simulant and a single-shell tank (SST) simulant. In the case of the DST simulant, the product was the anticipated Li-hydrotalcite. For the SST simulant, the product formed was primarily Li-phosphate. However, adding excess Li to the solution did result in the formation of traces of Li-hydrotalcite.
- The Li-hydrotalcite from the DST supernate was an easily filterable solid. After four water washes the filter cake was a fluffy white material made of $<100\ \mu\text{m}$ particles made of smaller spheres. These spheres are agglomerates of $\sim 5\ \mu\text{m}$ diameter platelets with $< 1\ \mu\text{m}$ thickness. Chemical and mineralogical analyses of the filtrate, filter cake, and wash waters indicate a removal of 90+ wt% of the dissolved Al for the DST simulant.
- For the SST simulant, the main competing reaction to the formation of lithium hydrotalcite appears to be the formation of lithium phosphate. In case of the DST simulant, phosphorus co-precipitated with the hydrotalcite. This would imply the added benefit of the removal of phosphorus along with aluminum in the pre-treatment part of the waste treatment and immobilization plant (WTP).
- For this endeavor to be successful, a serious effort toward process parameter optimization is necessary. Among the major issues to be addressed are the dependency of the reaction yield on the solution chemistry, as well as residence times, temperatures, and an understanding of particle growth.

2.0 INTRODUCTION

The reduction of aluminum would benefit the operations of the WTP by both a substantial reduction in the volume of glass produced and a reduction in the duration of operations. The recently published *River Protection Project System Plan* Rev. 4 (ORP-11242) includes a proposal for an aluminum removal facility (ARF). The ARF would reduce the amount of aluminum in the feed to the WTP by 5,900 MT¹ via the formation of insoluble Lithium-Hydrotalcite (LiHT²) and has the potential to recycle sodium hydroxide to the sludge leaching process.

As indicated in the general reaction in Equation 2-1, lithium combines with the aluminate ion to form the Li-Al-dihydroxide complex with intercalated anions and water molecules. The excess sodium hydroxide generated by the reaction could be recycled for caustic leaching of aluminum-bearing solids from tank farm sludges to increase the amount of sodium aluminate [NaAl(OH)₄] in the supernate.

The schematic drawing in Figure 1 addresses the structure with examples of CO₃, NO₃, and OH ions dispersed. Of these anions, carbonate is the most likely to be intercalated ([LiAl₂(OH)₆]₂CO₃).

Figure 1. Lithium-Hydrotalcite Schematic.

¹ Based on Figure 5-1 in the System Plan R4 this amount can be calculated: {23,900 MT Li-hydrotalcite / 440 g/mol (mol. wt. Li-hydrotalcite)} x 4 (Al per Li-hydrotalcite) x 27 g/mol (mol. wt. Al) = 5,866 MT Al.

² The mineralogically appropriate term would be Lithium-Aluminum Layered Double-Hydroxide Hydrate. Hydrotalcite is defined as the substance Mg-Al-Double-Hydroxide. However, the term Li-hydrotalcite was coined in the literature over the last 50 years and will be used henceforth in this report.

The 222-S Laboratory at US Department of Energy Hanford Site was tasked to verify the precipitation of aluminum using lithium hydroxide as proposed by AREVA Corporation³. AREVA has applied for an international patent⁴ on the application of this process to remove aluminum from aqueous solutions. The basic reaction of precipitating Li-Al-dihydroxide from a caustic Li-Al-bearing solution can be traced back to a publication entitled “The Action of Caustic Hydroxides on Aluminum” (Allen and Rodgers 1900). Recent industrial applications of this process were aimed toward producing nano-scale surface layers or to use hydrotalcites as drug delivery systems; therefore, although the chemistry of lithium hydrotalcite is well studied, reaction conditions in the literature are not directly adaptable to the removal of aluminum from tank waste.

To challenge the process, two Hanford tank simulants were used: one simulant representing DST chemistry and one representing SST chemistry. The tests were primarily designed to qualitatively verify the process’ potential for the Hanford WTP, and to identify the areas of improvement.

A prior draft version of this report (LA-RPT-09-00003) and a presentation at the Office of River Protection educational forum contained preliminary chemical data. Any results and conclusions are superseded by this report presenting the Quality Control-verified chemical analyses. Appendix A contains the sample breakdown diagrams including the sample numbers. Appendix B is a compilation of the chemical data provided by the analytical laboratory.

³ AREVA is a registered trademark of the Societe des Participations du Commissariat a l'Energie Atomique CORPORATION FRANCE, Paris, France.

⁴ International Application No. PCT/US2008/076589 (*A Process for Removal of Aluminum Oxides from Aqueous Media*).

3.0 TEST DESCRIPTION

The tests were performed as described in the associated test plan LAB-PLAN-09-00003, *Validation of Initial Laboratory Experiments Using Lithium-Aluminum Layered Double-Hydroxides for the Reduction of Alumina from the Waste Treatment Plant Feedstock*. All data and observations during the experiments were recorded in the controlled laboratory notebook HNF-N-586-2.

The general flow chart of the process is shown in Figure 2. It contains all steps including gibbsite leaching, crystal ripening at 90 °C (for 4 hours), filtration, and final wash steps. This procedure was applied to all test runs with slight modifications described in the individual chapters.

Figure 2. Flow Chart for Preparation of Lithium Hydrotalcite.

The SST and DST simulants were prepared according to the recipes in the test plan, with slight modifications. The original compositions were based on the descriptions of the SST early feed simulant and the DST simulant in CH2M-0403873, *Preparation of Simulated Waste Samples for EM-21 Project*. The DST simulant was prepared as a 5-M sodium version. The intent of the SST approach was to identify the boundaries of the process in terms of ionic strength and saturation of some anions. Therefore, the SST simulant was prepared with the original sodium molarity (8.5 M).

For each test, a glass beaker on a hot plate with a stir bar and thermocouple temperature controller was used. The glass reactor originally planned for these tests was not deliverable on short notice. Since the primary objective of these test runs was to qualitatively confirm the process, the approach using glass beakers was sufficient.

Samples for chemical analyses were taken from the wash water of each of the four washing steps, as well as from an aliquot of the filter cake. All samples were submitted to Advanced Technologies and Laboratories, Intl. (ATL) for analyses on Li, Al, Cs, P, S, anions, total inorganic carbon/total organic carbon (TIC/TOC), free hydroxide, and percent water (using, e.g., inductively coupled plasma-atomic emission spectroscopy (ICP-AES), inductively coupled plasma-mass spectroscopy (ICP-MS), Ion Chromatography (IC), and thermal gravimetric analysis (TGA)). From the remaining filter cake, samples were taken for physical characterization using polarized light microscopy (PLM), scanning electron microscopy (SEM), and X-ray diffraction (XRD).

3.1 DOUBLE-SHELL TANK SIMULANT

The 1-L DST simulant was prepared at 60 °C in a 2-L glass beaker. Table 1 shows the composition of the simulant.

Table 1. Double-Shell Tank Simulant Chemical Makeup (1-L Batch).

Reagent	MW	Weight [g]	Amount [mol]
NaOH	40.0	103.63	2.59
Na ₂ CO ₃	106.0	6.81	0.06
Na ₂ C ₂ O ₄	134.0	0.039	0.0003
KNO ₃	101.0	19.64	0.19
NaNO ₃	85.0	77.74	0.91
NaNO ₂	69.0	79.51	1.15
Na ₂ SO ₄	142.0	1.02	0.007
Na ₃ PO ₄ · 12H ₂ O · 0.25NaOH	390.1	2.81	0.007
NaCl	58.4	6.73	0.12
NaF	42.0	0.45	0.01
Na ₂ Cr ₂ O ₇ · 2H ₂ O	298.0	0.43	0.001
NaC ₂ H ₃ O ₂ · 3H ₂ O	136.1	5.44	0.04
CsNO ₃ ^a	211	0.101	0.0005
Al(OH) ₃ ^b	78	62.4	0.80

^a Cs-nitrate was added as an aqueous solution of 210 mg Cs-nitrate salt in 250 mL water.

^b Gibbsite was heat leached into the solution at 105 °C for 1 hour.

The 1-L simulant was heated to 105 °C for the gibbsite leaching for 1 hour and then the simulant was filtered using a Whatman^{®5} 1.0-μm glass fiber filter. A sample of the filtrate was taken for

⁵ Whatman is a registered trademark of the Whatman Paper Limited Company, Kent, England.

chemical analyses. The filtrate was kept at 90 °C, and 17.30 g of Li-hydroxide monohydrate was added as a 10 wt% solution⁶. After 4 hours, the solution was cooled to 65 °C and filtered again using a Whatman® 1.0-µm glass fiber filter. The 1 L of filtrate was a clear yellow solution and was sampled for chemical analyses. The filter cake was washed four times with 1 L of de-ionized (D.I.) water per wash (1:1 ratio filtrate to wash water), and then weighed.

3.2 SINGLE-SHELL TANK SIMULANT – INITIAL TEST

The second test run involved the SST simulant, which was prepared as shown in Table 2.

Table 2. Single-Shell Tank Simulant Chemical Makeup (1-L Batch).

Reagent	MW	Weight [g]	Amount [mol]
NaOH	40.0	85.27	2.13
Na ₂ CO ₃	106.0	61.48	0.58
Na ₂ C ₂ O ₄	134.0	1.34	0.01
KNO ₃	101.0	3.03	0.03
NaNO ₃	85.0	328.95	3.87
NaNO ₂	69.0	56.58	0.82
Na ₂ SO ₄	142.0	19.88	0.14
Na ₃ PO ₄ · 12H ₂ O · 0.25NaOH	390.1	15.60	0.04
NaCl	58.4	4.67	0.08
NaF	42.0	0.63	0.02
Na ₂ Cr ₂ O ₇ · 2H ₂ O	298.0	11.92	0.04
CsNO ₃ ^a	211.0	0.021	0.0001
Al(OH) ₃ ^b	78.0	31.2	0.40

^a Cs-nitrate was added as an aqueous solution of 210 mg Cs-nitrate salt in 250 mL water.

^b Gibbsite was heat leached into the solution at 105 °C for 1 hour.

The SST simulant was prepared in the same way as the DST simulant, accounting for the formulation differences. The test was run according to the flow chart in Figure 2. After addition of 6.79 g of Li-hydroxide (0.16 mol), the solution was kept at 90 °C. Due to time constraints, filtration was performed after 2 hours of ripening (instead of 4 hours as in the DST test) and produced 850 mL of filtrate. For each water wash, 850 mL D.I. water (1:1 ratio of filtrate to wash water) was used.

⁶ 172.01 mL of LiOH solution {25.15 g LiOH·H₂O (mol. weight 41.96 g/mol) in 250 mL water} = 0.41 mol Li.

3.3 SINGLE-SHELL TANK SIMULANT - RETEST

Due to the unexpected results of the initial SST test (see section 4.2), the decision was made to run an additional test with the SST simulant. The SST retest was designed to address the Lithium demand for producing Li-hydrotalcite.

The test matrix for the retests was set for adding the equivalents of 0.2 M, 0.3 M, and 0.4 M Li to 330 mL aliquots; this corresponds to a Li:Al ratio of 1:2, 3:4, and 1:1 respectively. The three solutions will henceforth be referred to as 0.2-M Li, 0.3-M Li, and 0.4-M Li.

Another 1-L batch of the SST simulant was prepared as described in chapter 3.2 (see Table 2), and 31.21 g (0.40 mol) of gibbsite heat was leached into the solution. Three aliquots of 300 mL of the supernate were staged in three 500-mL beakers. Li-hydroxide was added⁷ and the solution was stirred at 90 °C for 4 hours. After 30 minutes, the products were filtered and a sample of each filter cake was taken for SEM analysis. Since the amount of filterable material after 30 minutes was very low, the samples were insufficient for an XRD preparation. After 4 hours, the products were filtered again and the three filter cakes were washed four times each with 330 mL of D.I. water. The filtration and water washes were performed in a Millipore⁸ filter holder with clamp, using a 1.0- μ m Whatman[®] glass fiber filter, thus allowing much easier removal of the filter cake afterwards. The washed filter cakes were weighed.

Due to limited funding at the time of the retest experiments, no samples of the filter cake were submitted for chemical analyses for the SST rerun. Physical analyses of the solids were performed using XRD and SEM. Any variations in product quality (size, optical appearance, chemical composition) caused by ripening time could be traced with the SEM results.

⁷ '0.2 M Li': 2.63 g LiOH.H₂O => 321 mL supernate + LiOH solution (0.20 M Li); '0.3 M Li': 3.94 g LiOH.H₂O => 332 mL solution (0.28 M Li); '0.4 M Li': 5.26 g LiOH.H₂O => 342 mL solution (0.37 M Li).

⁸ Millipore is a registered trademark of the Millipore Filter Corporation, Bedford, Massachusetts.

4.0 RESULTS AND DISCUSSION

The results are presented in the order outlined in Section 3. Appendix B contains the compilation of final analytical results. In order to verify the amounts of PO_4 and SO_4 from the IC analyses, phosphorous and sulfur were added to the list of analytes in a rerun of ICP-AES analysis.

4.1 DOUBLE-SHELL TANK SIMULANT

Filtration of the gibbsite leach produced a clear yellow supernate. The comparison of the mixed supernate and the analysis of the actual supernate is shown in Table 3. The increase in carbonate is most likely due to the one hour heat leaching of the gibbsite. The reduction in hydroxide can be attributed to the OH used by the dissolution of gibbsite to the $\text{Al}(\text{OH})_4$ -ion.

Table 3. Comparison of Amounts Used in Supernate Preparation and Amounts Analyzed After Gibbsite Leaching and Filtration.

DST	Added [mol]	Analyzed [mol]	Difference [mol]
Al	0.80	0.91	-0.11
Cs	0.0005	0.0006	-0.0001
NO3	1.11	1.03	0.07
NO2	1.15	1.08	0.07
Ox	0.0003	n.d.	-
CO3	0.06	1.79	-1.73
OH	2.20	1.69	0.52
F	0.01	0.01	0.002
Cl	0.12	0.11	0.005
P	0.01	0.01	0.00
PO4	0.01	0.02	-0.01
S	0.01	0.01	0.00
SO4	0.01	0.01	0.00

Added = amounts from Table 1; Analyzed = amounts based on results in Appendix B.

n.a. ... not analyzed; n.d. ... not determined (below detection limit)

Addition of Li-hydroxide caused a reaction in less than 2 minutes with white particulate flocculating in the beaker. During the 4 hours of crystal ripening at 90 °C, the solution turned milky white (see Figure 3). The solution filtered quickly (~ 1 min) and produced an off-white filter cake. Four washing steps of the filter cake produced a bright white fluffy product of highly crystalline material (see Figure 4).

The filtrate was clear and showed no visible signs of unfiltered solids. A compilation of aliquots of the filtrate and four washes from the DST experiment is displayed in Figure 5. The most important observation in Figure 5 is the lack of coloration in the 2nd to 4th water washes.

Figure 3. Double-Shell Tank Simulant Product after Four Hours of Ripening and Unwashed Filter Cake.

Figure 4. Final Water-Washed Filter Cake from Double-Shell Tank Simulant.

Figure 5. Comparison of Aliquots of the Filtrate and Wash Filtrates from Double-Shell Tank Simulant Filter Cake.

(left to right: filtrate after 4 hours reaction time, 1st to 4th water wash)

The wet filtercake mass was 130.6 g. Based on the TGA analysis of 66.2 wt% water in the filter cake, this is equivalent to a calculated dry weight of 44.1 g. However, as described in the summary section, the actual dry weight is more likely to be 114.6 g (containing 102 of Li-hydrotalcite), suggesting that the TGA analyses also included the release of intercalated carbonate.

Table 4. Comparison of Selected Analytes in Filtrates and Wash Filtrates of Double-Shell Tank Supernate.

[mol%] ^a	Al	Li	TIC	P	NO ₃	NO ₂	OH ^c	S	¹³³ Cs
Filtrate	5.72	4.08	0.08	3.59	79.2	78.0	87.7	100	76.8
Wash 1	2.07	2.05	0.03	<0.4	6.38	6.56	8.14	5.93	6.40
Wash 2	0.11	0.26	0.01	0.06	0.06	0.05	0.16	<0.01	0.05
Wash 3	0.04	0.15	0.01	0.06	0.04	0.04	0.08	0.39	0.02
Wash 4	0.04	0.15	<0.01	0.77	0.03	0.03	0.08	0.54	0.02
Filter Cake ^b	92.0	93.3	99.9	95.5	14.3	15.3	3.86	n.r.	16.7

^a Mol% are normalized to supernate composition; calculations were based on analytical data in Appendix B; amount of filtrate was 650 mL, washes 1 to 4 were 1000 mL each.

^b The quantities of filter cake were calculated from the difference between the supernate (= “Analyzed” in Table 3) and the sum of filtrate (after Li-addition) plus washes 1 to 4; in case the calculated amount was negative, ‘n.r.’ (= not retained) was used as classifier.

^c Takes the OH-contribution from the LiOH-addition into account.

Table 4 and Figures 6 and 7 compare the amounts of ions in the filtrate and in the water washes. All data are normalized to the supernate (i.e., simulant recipe plus gibbsite leaching). After the 1st water wash, <1 mol% of the removable ions were left on the filter cake.

Figure 6. Comparison of Mol% of Selected Analytes in Filtrates from Double-Shell Tank Simulant.

The phosphorus distribution showed an interesting increase for the 4th wash. Before drawing any conclusions on the retention of phosphorus in the hydrotalcite, the results need to be closely examined. There is no trend established, since the results of the filtrate, wash 2, and wash 3 are estimated values indicating the data were within the 10 times (defined as the limit of quantification) of the detection limit. As previously mentioned, phosphate was additionally measured using the IC. In this case, the results for the filtrate, wash 1, and wash 2 were below the detection limit, and wash 4 was about 5 times larger than wash 3. In summary, the reason for the increase of the phosphorus concentration in the final wash cannot be derived from these analyses.

Figure 7. Comparison of Mol% of Selected Analytes in Filtrates from Double-Shell Tank Simulant.

One of the concerns about the precipitation of the hydrotalcite is whether or not radionuclides within Hanford waste would co-precipitate and could be removed by washing the filter cake. The test runs included ^{133}Cs in the simulant composition. In order to avoid issues with the detection limit of cesium, the amount was approximately 100-fold the concentration of ^{137}Cs found in the tanks.

From the ease with which the cesium was able to be washed from the product, the cesium appears not to be incorporated into the structure of the hydrotalcite; however, ~17 mol% of Cs is retained in the filter cake. At the calculated retained molarity (see Table 4), and two orders of magnitude increased concentration versus actual DST supernate, the mass of ^{133}Cs retained in the filter cake would be 0.124 mg. Assuming that the ^{133}Cs would behave as ^{137}Cs and the specific activity of ^{137}Cs is 87 Ci/g, then 10.8 mCi Cs is retained in the filter cake. With a mass of 102 g for the Li-hydrotalcite⁹, the input of ^{137}Cs would yield 106 $\mu\text{Ci/g}$ in the dry Li-hydrotalcite.

⁹ See calculation in chapter "Summary and Recommendations."

Subsamples of the filtercake were used for the physical analyses, by PLM, SEM, and XRD to identify the mineralogy and chemistry of the cake product. The PLM image in Figure 8 shows clusters of material. Due to the preparation of the slide with a cover slip, any spherical agglomerates are flattened. However, the individual crystallites are clearly visible. This indicates that the product is stable, but soft and easily compactable.

Figure 8. Polarized Light Microscopy Image of Double-Shell Tank Simulated Filter Cake.

Typical agglomerates found in the DST LiHT product are displayed in the Back Scattered Electron (BSE) images of Figures 9 and 10. The agglomerates reach about 50 μm in diameter and are made of very thin platelets (~1 μm) of about 5-10 μm diameter. This structure is in agreement with the theoretical structure shown in Figure 1. The overview in Figure 10 (top left image) shows the size distribution of particles on the SEM preparation slide. The particle in close-up is one of the larger specimens. The Energy Dispersive Spectrometry (EDS) spectra of the platelets in Figures 9 and 10 identify an Al-rich phase with a minor P-peak, which is consistent with Li-hydrotalcite¹⁰.

¹⁰ The atomic number of lithium is too low to be detected in an EDS. The C peak is not indicative for carbonate since it is primarily due to the carbon coating applied during the SEM specimen preparation. Whether the phosphorus is intercalated in the Li-hydrotalcite or surficially attached could not be determined.

Figure 9. Back Scattered Electron Image and Energy Dispersive Spectrometry Spectrum of Double-Shell Tank Filter Cake Product.

Figure 10. Back Scattered Electron Image and Energy Dispersive Spectrometry Spectrum of Double-Shell Tank Simulant Filter Cake.

Based on the appearance in Figures 9 and 10, a three-step formation seems to be likely. First the platelets form, then the primary spherical objects, and finally the particulates as found in the filter cake. Whether these stages are distinctly separate from each other or a continuous formation takes place is not known to date. However, for future investigations this aspect might be a crucial step, since all that is necessary for the process to work is a filterable product (i.e., the formation of the platelets).

The XRD spectrum in Figure 11 reveals the structural nature and composition of the particulates. Comparison to the reference spectra shows the filter cake is entirely made of Li-hydroxalcalite in the carbonate form. Only traces of sodium nitrate (NaNO_3) were found as an additional phase.

Thermo-gravimetric analysis was used to determine the percentage water of the filter cake (Figure 12). The inflection point in the spectrum at 110 °C (in a duplicate analysis at 120 °C) is indicative of the release of the intercalated water.

Figure 11. X-Ray Diffractogram of Double-Shell Tank Simulant Filter Cake. **Figure 12. Thermal Gravimetric Analysis Spectrum of Double-Shell Tank Simulant Filter Cake.**

4.2 SINGLE-SHELL TANK SIMULANT – INITIAL TEST

The comparison between the simulant composition (before gibbsite leaching) and the supernate composition (“analyzed” = after gibbsite leaching) is shown in Table 5. After Li-hydroxide addition, an instantaneous reaction was observed with a white product flocculating in the beaker. Within 1 minute, the beaker was entirely opaque. Over the next 2 hours of crystal ripening, the general appearance did not change much. The product after 2 hours of crystal ripening is shown in Figure 13.

Table 5. Comparison of Amounts Used in Supernate Preparation and Amounts Analyzed After Gibbsite Leaching and Filtration.

SST	Added [mol]	Analyzed [mol]	Difference [mol]
Al	0.40	0.36	0.04
Cs	0.0001	0.0001	0.0000
NO3	3.90	3.08	0.82
NO2	0.82	0.63	0.19
Ox	0.010	0.009	0.001
CO3	0.58	0.10	0.48
OH	1.89	1.29	0.60
F	0.02	0.02	-0.0008
Cl	0.08	0.06	0.02
P	0.04	0.05	-0.01
PO4	0.04	0.05	-0.01
S	0.14	0.11	0.03
SO4	0.14	0.14	0.00

Added = amounts from Table 1; analyzed = amounts based on results in Appendix B.
n.a. ... not analyzed; n.d. ... not determined (below detection limit)

Figure 13. Single-Shell Tank Simulant Product after Two Hours of Ripening and Washed Filter Cake.

The washed filter cake consisted of white crystals. The wet mass was 7.84 g (dry mass 3.87 g, based on TGA analysis). The product filtered quickly and produced an optically very clear filtrate. Turbidity measurements were not performed on this run, but were performed on the subsequent SST retests (see section 4.3). The setup in Figure 14 shows Erlenmeyer flasks with an aliquot of the filtrate and the four water washes. The extreme color change between filtrate, wash water 1, and wash water 2 indicates that most of the Cr is washed out in the first step. As with the DST product, the wash processes released most of the water soluble ions in the first water wash.

Figure 14. Comparison of Aliquots of the Filtrate and Wash Filtrates from Single-Shell Tank Simulant Filter Cake.

(left to right: filtrate after 4 hours reaction time, 1st to 4th water wash)

Table 6 and Figures 15 and 16 show the retention of analytes in the filtercake during the filtration and subsequent wash cycles for the SST supernate. In this case, all of the nitrate, nitrite, hydroxide sulfur, cesium, and most of the carbonate were found in the filtrate. Lithium formed Li_3PO_4 but not entirely; only ~ 87 mol% of the available Li precipitated, of which 10 mol% were water soluble during the washes.

Table 6. Comparison of Selected Analytes in Filtrates and Wash Filtrates of Single-Shell Tank Supernate.

[mol%] ^a	Al	Li	TIC	P	NO ₃	NO ₂	OH ^c	S	¹³³ Cs
Filtrate	91.7	14.2	96.3	8.98	104	102	103	101	101
Wash 1	0.34	4.37	1.5	6.76	0.32	0.32	0.93	3.32	0.32
Wash 2	0.008	1.98	0.2	2.92	0.002	<0.01	0.31	0.02	0.002
Wash 3	0.004	1.18	0.1	1.73	0.001	<0.01	<0.01	0.01	0.001
Wash 4	0.003	1.01	0.2	1.28	0.001	<0.01	<0.01	0.44	0.001
Filtercake ^b	7.91	77.3	1.7	78.3	n.r.	n.r.	n.r.	n.r.	n.r.

^a Mol% are normalized to supernate composition; calculations were based on analytical data in Appendix B; amounts of filtrate and wash 1 to wash 4 were 850 mL.

^b Filter cake was calculated as the difference between supernate (= “Analyzed” in Table 5) and the sum of filtrate (after Li-addition) plus washes 1 to 4; in case the calculated amount was negative, ‘n.r.’ (= not retained) was used as classifier.

^c Takes the OH-contribution from the LiOH-addition into account.

Figure 15. Comparison of Mol% of Selected Analytes in Filtrates from Single-Shell Tank Supernate.

Figure 16. Comparison of Mol% of Selected Analytes in Filtrates from Single-Shell Tank Supernate.

The white crystallites of the filter cake were analyzed with SEM, XRD and PLM to identify the phases involved. Special emphasis was placed on whether there was any evidence that Li-hydroxalcalite formed.

PLM analysis of the filter cake shows 1-2 μm -sized crystals, round- to hexagon-shaped, but no large agglomerates are visible (Figure 17).

Figure 17. Polarized Light Microscopy Image of the Single-Shell Tank Simulant Filter Cake.

The BSE image and EDS spectrum in Figure 18 reveal the nature of the filter cake product. The crystals have a mixed composition of a P-rich phase and some Na-Al-silicate. However, no sign of hydrotalcite could be observed, i.e., an aluminum-rich phase.

Figure 18. Back Scattered Electron Image and Energy Dispersive Spectrometry Spectrum of the Single-Shell Tank Simulant Filter Cake.

This result is further clarified by the XRD pattern shown in Figure 19. The two phases identified were Li-phosphate and the minor phase hydroxy cancrinite (Na-Al-silicate); the latter is most likely an artifact from the dissolution of Si out of the glass beaker. No traces of hydrotalcite could be determined.

Figure 19. X-Ray Diffractogram of the Single-Shell Tank Filter Cake Product.

4.3 SINGLE-SHELL TANK SIMULANT - RETEST

Addition of the different amounts of Li showed slight visual differences in reaction kinetics. The 0.2-M Li-containing beaker immediately formed white crystallites as in the previous SST run. However, the reaction in the other two beakers was delayed by about 15 to 20 seconds. After 4 hours of crystal ripening, the three beakers had the same appearance (see Figure 20).

Figure 20. Single-Shell Tank Simulant Retest Product after Four Hours of Ripening.

The three different products behaved differently during filtration: the 0.2-M Li-product stuck to the sidewalls of the beaker but filtered rapidly. The 0.3-M Li product had no material sticking to the sides, the filter cake had a smoother look, and the filtrate started foaming during the

filtration. The 0.4-M Li-product behaved like the 0.3-M Li; however, the filtrate was much clearer.

In Table 7, the significantly different amounts of filter cake and associated filtrate turbidities are compared to the actual amounts of Li, Al, and P added to each beaker. It can be seen that the excess Li reaction (0.4 M Li) produced the largest amount of filter cake and the clearest filtrate (Table 7 NTU values). In contrast, the 0.2-M Li filter cake had the lowest mass, even lower than the SST original experiment¹¹. No explanation has been found to date, although one possibility may be that the extended reaction time in the SST retest (4 hours versus 2 hours) caused the product breakdown. Figure 21 shows the filter cakes after the four wash cycles for each case.

Table 7. Comparison of Yield and Turbidity with Lithium, Aluminum and Phosphorus Concentrations for the Single-Shell Tank Simulant Retests.

Sample	0.2 M Li	0.3 M Li	0.4 M Li
Li [mol] ^a	0.063	0.094	0.125
Al [mol] ^a	0.12	0.12	0.12
P [mol] ^a	0.012	0.012	0.012
Filtrate turbidity [NTU] ^b	6.0	3.1	0.6
Filter cake weight [g]	0.24	3.33	3.47

^a Actual moles added to each of the 300 mL aliquots.

^b Compared to distilled water with a turbidity measurement of 0.8 NTU.

Figure 21. Images of the Single-Shell Tank Simulant Retest Filter Cake for the Three Different Li-Loadings after Four Hours.

In Figures 22 and 23 the SEM results for the filter cakes after 30 minutes and after 4 hours are compared. Figure 22 shows the 30-minute filter cake samples analyzed with the SEM. The needle-shaped phase in the BSE image on the right of Figure 22 is most likely a piece of the glass fiber filter – hence the huge Si, Ca, and Al peaks. The precipitated particles have the same composition as in case of 0.3-M Li.

¹¹ 0.2 M Li SST retest: 0.24 g (wet weight)*(1000/300) = 0.19 g (recalculated to 1-L) => 5 wt% of SST original (7.84 g).

Figure 22. Back Scattered Electron Images and Energy Dispersive Spectrometry Spectra of Single-Shell Tank Simulant Retest Filter Cake after 30 Minutes.

In Figure 23, the analytical results of samples of the filter cakes from the three different Li-loadings after 4 hours are shown. No substantial changes between the products were identifiable by SEM and EDS. Some of the spheres show a loss of the central portion. This could be due to leaching in the water wash steps or to loss during the 4 hours of ripening. Despite the reduced integrity of the spheres, the filter cake samples after 4 hours have a more complex look to them (more overgrowth) than the 30-minute samples.

Figure 24 shows the XRD spectrum for the 0.4-M Li (Li:Al=1) - for comparison, check the 0.2-M Li product XRD spectrum in Figure 19. The 0.4-M Li XRD spectrum shows Li-phosphate still as the major component, with minor amounts of cancrinite.

However, a trace of the Li-hydrocalcite could be identified. Even at the small angle of 11.5° 2θ {representing the (100) plane}, a clear peak is visible. This shows that adding twice the assumed Li-demand may be the threshold of the concentration needed to start the precipitation of Li-hydrocalcite for the SST simulant.

Figure 23. Back Scattered Electron Images and Energy Dispersive Spectrometry Spectra of Single-Shell Tank Simulant Retest Filter Cake after Four Hours.

Figure 24. X-Ray Diffraction Spectrum of 0.4 M-Li Single-Shell Tank Simulant Retest Filter Cake after Four Hours.

5.0 SUMMARY AND RECOMMENDATIONS

A summary of the test results is presented in Table 8. For the DST simulant, the amount of aluminum and lithium retained in the filter cake is in the 90+ mol% range. This product is composed primarily of lithium-aluminum-carbonate-hydroxide hydrate (i.e., Li-hydrotalcite). The Li-hydrotalcite that formed contains primarily carbonate (TIC) as the intercalated anion. It is unlikely that the nitrate and nitrite retained in the filter cake could be intercalated; however, the XRD results indicated sodium nitrate, NaNO_3 , as the minor phase.

Table 8. Amounts of Assorted Analytes Retained in the Washed Filter Cakes.

Analyte	DST Filtercake		SST Filtercake (Initial Test)	
	[mol]	[mol %]	[mol]	[mol %]
Aluminum	0.84	92	0.030	7.9
Lithium	0.508	93	0.165	77.3
TIC	1.8	99.9	0.002	1.8
Phosphorus	0.0069	95.5	0.038	78.3
Nitrate	0.148	14	n.r.	n.r.
Nitrite	0.165	15	n.r.	n.r.
Hydroxide	0.122	3.86	n.r.	n.r.
Fluoride	0.003	32.5	n.r.	n.r.
Sulfur	n.r.	n.r.	n.r.	n.r.
Cs-133	0.0001	16.7	n.r.	n.r.

Amount retained is calculated as the difference between the filtrate after gibbsite leaching (supernate) and the sum of the post-Li-addition filtrate plus all of the water washes (for analytical results see Appendix B).

n.r. not retained.

Based on the values shown in Table 8, the following calculations can be made for the DST test: the filter cake contained ~0.23 mol carbonate Li-hydrotalcite¹² ($[\text{LiAl}_2(\text{OH})_6]_2\text{CO}_3 \cdot 3 \text{H}_2\text{O}$) with a molecular weight of 439.9 g/mol. This would refer to 102 g of Li-hydrotalcite in the filter cake. The calculated amount of sodium nitrate based on Table 6 would be 13 g. The wet filter cake weighed 130.6 g; thus, the wet filter cake only contained 16 g (12 wt%) moisture. The dry weight based on this result is 114.6 g. The question of which phase contained the rest of the carbonate (1.8 mol TIC – 0.23 mol in LiHT = 1.6 mol) remains unanswered.

In the case of the SST simulant, very little aluminum is retained (~8 mol%), but ~75 mol% of the lithium and phosphorus precipitated as lithium phosphate. The reason why 25 mol% of the lithium did not precipitate could not be identified. The aluminum in the SST supernate generally did not react at all. Some formed cancrinite (NaAl -silicate) with silicon leached from the glass beaker.

The SST retest with variable amounts of lithium ($\text{Li}:\text{Al} = 0.5 - 1$) showed that a certain lithium concentration does produce Li-hydrotalcite beside the omnipresent Li-phosphate. However,

¹² Each mol LiHT is made of 4 mol Al and 2 mol Li => $\frac{1}{4}$ of the mole Al ($0.84 / 4 = 0.21$) and $\frac{1}{2}$ of the mole Li ($0.508 / 2 = 0.254$), on average 0.23 mol LiHT.

even in the case of Li:Al=1, only trace amounts of Li-hydrotalcite were observed. In order to remove the misleading contribution of Si from the glass beakers, the SST test should be rerun using Teflon¹³ reaction vessels and increasing Li:Al ratios to determine when the maximum production of hydrotalcite occurs.

Besides the formation of Li-phosphate, no other competing reactions were evident within this effort. Theoretically, the formation of Li-fluoride and Li-carbonate are potential reactions to interfere with the precipitation of the Li-hydrotalcite. As shown in Table 9, the solubility of the individual lithium salts is highly variable (CRC¹⁴ *Handbook of Chemistry and Physics*, 90th Edition). One of the unknowns to date is the solubility of the LiHT within the conditions of the SST stimulant.

Table 9. Solubility Products and Solubilities for Different Lithium Compounds.

Compound	K _{sp} (at 25 °C) ^a	Solubility in Water ^b (g/L)
LiNO ₃	Not Reported	1020 (25°C)
Li ₂ SO ₄	Not Reported	342 (25°C)
Li ₂ CO ₃	8.15E-04	13.0 (25°C)
LiF	1.84E-03	1.34 (25°C)
Li ₃ PO ₄	2.37E-11	0.27 (25°C)
LiOH	Not Reported	125 (25C)

^a CRC® 90th Ed., page 8-128

^b CRC® 90th Ed., pages 4-71 to 4-72

From the observations during the SST retest, the following can be derived: The first precipitate was Li-phosphate. Even in the slightly elevated Li:Al = 3:4 case (0.3-M Li), no clear sign of Li-hydrotalcite was observed. In the case of the Li:Al = 1, the carbonate Li-hydrotalcite could be identified with XRD; thus, at least 5% of the crystals were Li-hydrotalcite. This implies that the solubility of the Li-hydrotalcite is higher than Li-phosphate, but lower than Li-carbonate and Li-fluoride. Although the amount of fluoride in the stimulant is insufficient to be detected by XRD even if all of it precipitated as Li-fluoride, Table 8 shows that none of the fluoride was retained in the filter cake.

In summary the authors make the following recommendations (not to be construed as an all-inclusive list):

¹³ Teflon is a trademark of the E. I. DuPont De Nemours and Company, Wilmington, Delaware.

¹⁴ CRC is a registered trademark of the CR Press, Inc., Corporation, Boca Raton, Florida

- Optimize reaction and crystal ripening time. Identify the particle-size phases.
- Optimize the heating and cooling cycles of the filtrate.
- Monitor anions to identify the limiting factors for precipitation. Determine whether or not an increase in release of certain anions and cations during the later stages of washes are real or an analytical artifact.
- Investigate the effect of filter cake washes (chemistries, pH, types, and number) on the product. Place special focus on up-flow bed expansion versus down-flow.
- Select reactors with appropriate materials of construction (Teflon, stainless steel) for the SST tests.
- Determine the threshold lithium concentrations for various waste types based upon the lithium demand in the waste. Identify the boundaries of the effects of different ionic strength solutions.
- Obtain XRD and Raman spectra of each potential species of LiHT under the WTP conditions with the anions present in most of the tanks at Hanford site.

6.0 REFERENCES

ORP-11242, 2009, *River Protection Project System Plan*, Rev. 4, Washington River Protection Solutions, LLC, Richland, WA.

CH2M-0403873, 2004, *Preparation of Simulated Waste Samples for EM-21 Project*, CH2M HILL Hanford Group, Richland, WA.

LAB-PLAN-09-00003, 2009, *Validation of Initial Laboratory Experiments Using Lithium Aluminum Layered Double Hydroxides for the Reduction of Alumina from the Waste Treatment Plant Feedstock*, Washington River Protection Solutions, LLC, Richland, WA.

CRC Press, 2000, *Handbook of Chemistry and Physics*, D. R. Lide, Editor in Chief, New York, 90th Edition.

E.F. Allen and H.F. Rodgers, 1900, *The Action of Caustic Hydroxides on Aluminum*, American Chemical Journal 24, pp. 304-318.

APPENDIX A

Sample Breakdown Diagrams

Sample Breakdown Diagrams

Customer: RESEARCH
Project: Hydrotalcite Test
Group: 20090884
Due: January 15, 2010

Hydrotalcite Test - DST

Customer: RESEARCH
Project: Hydrotalcite Test
Group: 20090884
Due: January 15, 2010

Hydrotalcite Test - SST

Customer: RESEARCH
Project: Hydrotalcite Test
Group: 20090884
Due: January 15, 2010

Hydrotalcite Test - SST, Run 2

APPENDIX B

Data Summary of Chemical Analyses as Provided by Advanced Technologies and Laboratories International, Inc. (ATL)

Data Summary of Chemical Analyses as Provided by Advanced Technologies and Laboratories International, Inc. (ATL)

Note: "Filtrate 1" is referred to as "Supernate" in the text; "Filtrate 2" as "Filtrate."

10-feb-2010 11:51:03
Hydrotalcite Test
Data Summary of All Results

ID		SAMPLE	ANALYTE	UNIT	RESULT	DUP.	AVE.	RPD	QA
DST Simulant	Filter Cake	S09R000673	Percent water	%	67.8	64.6	66.2	4.77	
DST Simulant	Filter Cake	S09R000673	Total organic carbon	ug/g	<169	207	n/a	n/a	U
DST Simulant	Filter Cake	S09R000673	Total inorganic carbon	ug/g	5.81E+03	5.98E+03	5.90E+03	2.88	
DST Simulant	Filter Cake	S09R000675	Hydroxide	ug/g	<1.66E+03	n/a	n/a	n/a	U
DST Simulant	Filter Cake	S09R000677	Aluminum	ug/g	8.57E+04	8.72E+04	8.64E+04	1.74	
DST Simulant	Filter Cake	S09R000677	Lithium	ug/g	1.11E+04	1.19E+04	1.15E+04	7.29	
DST Simulant	Filter Cake	S09R000677	Phosphorus	ug/g	1.56E+03	1.55E+03	1.56E+03	0.921	
DST Simulant	Filter Cake	S09R000677	Sulfur	ug/g	<77.0	<76.8	n/a	n/a	U
DST Simulant	Filter Cake	S09R000677	Silicon	ug/g	233	229	231	1.36	
DST Simulant	Filter Cake	S09R000677	Cesium-133	ug/g	2.70	2.73	2.72	0.89	
DST Simulant	Filtrate 1	S09R000661	Fluoride	ug/mL	191	n/a	n/a	n/a	
DST Simulant	Filtrate 1	S09R000661	Chloride	ug/mL	4.43E+03	n/a	n/a	n/a	
DST Simulant	Filtrate 1	S09R000661	Nitrite	ug/mL	5.65E+04	n/a	n/a	n/a	
DST Simulant	Filtrate 1	S09R000661	Bromide	ug/mL	<26.3	n/a	n/a	n/a	U
DST Simulant	Filtrate 1	S09R000661	Nitrate	ug/mL	7.29E+04	n/a	n/a	n/a	
DST Simulant	Filtrate 1	S09R000661	Phosphate	ug/mL	1.48E+03	n/a	n/a	n/a	
DST Simulant	Filtrate 1	S09R000661	Sulfate	ug/mL	1.01E+03	n/a	n/a	n/a	
DST Simulant	Filtrate 1	S09R000661	Oxalate	ug/mL	<117	n/a	n/a	n/a	U
DST Simulant	Filtrate 1	S09R000661	Aluminum	ug/mL	2.80E+04	n/a	n/a	n/a	
DST Simulant	Filtrate 1	S09R000661	Lithium	ug/mL	<0.600	n/a	n/a	n/a	U
DST Simulant	Filtrate 1	S09R000661	Phosphorus	ug/mL	253	n/a	n/a	n/a	
DST Simulant	Filtrate 1	S09R000661	Sulfur	ug/mL	207	n/a	n/a	n/a	
DST Simulant	Filtrate 1	S09R000661	Silicon	ug/mL	54.6	n/a	n/a	n/a	J
DST Simulant	Filtrate 1	S09R000661	Cesium-133	ug/mL	84.0	84.6	84.3	0.71	
DST Simulant	Filtrate 1	S09R000661	Hydroxide	ug/mL	3.25E+04	3.27E+04	3.26E+04	0.72	
DST Simulant	Filtrate 1	S09R000661	Total inorganic carbon	ug/mL	1.22E+05	n/a	n/a	n/a	
DST Simulant	Filtrate 1	S09R000661	Total organic carbon	ug/mL	1.42E+03	n/a	n/a	n/a	c
DST Simulant	Filtrate 2	S09R000662	Fluoride	ug/mL	167	166	166	0.19	
DST Simulant	Filtrate 2	S09R000662	Chloride	ug/mL	4.53E+03	4.51E+03	4.52E+03	0.44	
DST Simulant	Filtrate 2	S09R000662	Nitrite	ug/mL	5.97E+04	6.00E+04	5.99E+04	0.64	
DST Simulant	Filtrate 2	S09R000662	Bromide	ug/mL	<26.3	<26.3	n/a	n/a	U
DST Simulant	Filtrate 2	S09R000662	Nitrate	ug/mL	7.82E+04	7.79E+04	7.81E+04	0.45	
DST Simulant	Filtrate 2	S09R000662	Phosphate	ug/mL	<42.3	<42.3	n/a	n/a	U
DST Simulant	Filtrate 2	S09R000662	Sulfate	ug/mL	768	787	777	2.45	
DST Simulant	Filtrate 2	S09R000662	Oxalate	ug/mL	<117	<117	n/a	n/a	U
DST Simulant	Filtrate 2	S09R000662	Aluminum	ug/mL	2.17E+03	n/a	n/a	n/a	
DST Simulant	Filtrate 2	S09R000662	Lithium	ug/mL	238	n/a	n/a	n/a	
DST Simulant	Filtrate 2	S09R000662	Phosphorus	ug/mL	12.3	n/a	n/a	n/a	J
DST Simulant	Filtrate 2	S09R000662	Sulfur	ug/mL	281	n/a	n/a	n/a	
DST Simulant	Filtrate 2	S09R000662	Silicon	ug/mL	72.3	n/a	n/a	n/a	

ID		SAMPLE	ANALYTE	UNIT	RESULT	DUP.	AVE.	RPD	QA
DST Simulant	Filtrate 2	S09R000662	Cesium-133	ug/mL	87.6	n/a	n/a	n/a	
DST Simulant	Filtrate 2	S09R000662	Hydroxide	ug/mL	5.05E+04	n/a	n/a	n/a	
DST Simulant	Filtrate 2	S09R000662	Total inorganic carbon	ug/mL	138	n/a	n/a	n/a	
DST Simulant	Filtrate 2	S09R000662	Total organic carbon	ug/mL	1.34E+03	n/a	n/a	n/a	c
DST Simulant	Wash 1	S09R000665	Fluoride	ug/mL	4.37	n/a	n/a	n/a	
DST Simulant	Wash 1	S09R000665	Chloride	ug/mL	245	n/a	n/a	n/a	
DST Simulant	Wash 1	S09R000665	Nitrite	ug/mL	3.26E+03	n/a	n/a	n/a	
DST Simulant	Wash 1	S09R000665	Bromide	ug/mL	<0.261	n/a	n/a	n/a	U
DST Simulant	Wash 1	S09R000665	Nitrate	ug/mL	4.09E+03	n/a	n/a	n/a	
DST Simulant	Wash 1	S09R000665	Phosphate	ug/mL	<0.419	n/a	n/a	n/a	U
DST Simulant	Wash 1	S09R000665	Sulfate	ug/mL	31.7	n/a	n/a	n/a	
DST Simulant	Wash 1	S09R000665	Oxalate	ug/mL	<1.16	n/a	n/a	n/a	U
DST Simulant	Wash 1	S09R000665	Aluminum	ug/mL	509	n/a	n/a	n/a	
DST Simulant	Wash 1	S09R000665	Lithium	ug/mL	77.8	n/a	n/a	n/a	
DST Simulant	Wash 1	S09R000665	Phosphorus	ug/mL	<1.00	n/a	n/a	n/a	U
DST Simulant	Wash 1	S09R000665	Sulfur	ug/mL	10.8	n/a	n/a	n/a	J
DST Simulant	Wash 1	S09R000665	Silicon	ug/mL	3.06	n/a	n/a	n/a	J
DST Simulant	Wash 1	S09R000665	Cesium-133	ug/mL	4.75	n/a	n/a	n/a	
DST Simulant	Wash 1	S09R000665	Hydroxide	ug/mL	2.89E+03	n/a	n/a	n/a	
DST Simulant	Wash 1	S09R000665	Total inorganic carbon	ug/mL	33.6	n/a	n/a	n/a	J
DST Simulant	Wash 1	S09R000665	Total organic carbon	ug/mL	143	n/a	n/a	n/a	J
DST Simulant	Wash 2	S09R000666	Fluoride	ug/mL	<0.622	n/a	n/a	n/a	U
DST Simulant	Wash 2	S09R000666	Chloride	ug/mL	<0.313	n/a	n/a	n/a	U
DST Simulant	Wash 2	S09R000666	Nitrite	ug/mL	25.8	n/a	n/a	n/a	
DST Simulant	Wash 2	S09R000666	Bromide	ug/mL	<2.39	n/a	n/a	n/a	U
DST Simulant	Wash 2	S09R000666	Nitrate	ug/mL	41.4	n/a	n/a	n/a	
DST Simulant	Wash 2	S09R000666	Phosphate	ug/mL	<3.85	n/a	n/a	n/a	U
DST Simulant	Wash 2	S09R000666	Sulfate	ug/mL	<2.21	n/a	n/a	n/a	U
DST Simulant	Wash 2	S09R000666	Oxalate	ug/mL	<10.6	n/a	n/a	n/a	U
DST Simulant	Wash 2	S09R000666	Aluminum	ug/mL	25.9	n/a	n/a	n/a	
DST Simulant	Wash 2	S09R000666	Lithium	ug/mL	9.67	n/a	n/a	n/a	
DST Simulant	Wash 2	S09R000666	Phosphorus	ug/mL	0.129	n/a	n/a	n/a	J
DST Simulant	Wash 2	S09R000666	Sulfur	ug/mL	<0.100	n/a	n/a	n/a	U
DST Simulant	Wash 2	S09R000666	Silicon	ug/mL	0.0793	n/a	n/a	n/a	JY
DST Simulant	Wash 2	S09R000666	Cesium-133	ug/mL	0.0354	n/a	n/a	n/a	
DST Simulant	Wash 2	S09R000666	Hydroxide	ug/mL	35.2	n/a	n/a	n/a	
DST Simulant	Wash 2	S09R000666	Total inorganic carbon	ug/mL	8.00	n/a	n/a	n/a	J
DST Simulant	Wash 2	S09R000666	Total organic carbon	ug/mL	24.0	n/a	n/a	n/a	J
DST Simulant	Wash 3	S09R000667	Fluoride	ug/mL	0.271	n/a	n/a	n/a	
DST Simulant	Wash 3	S09R000667	Chloride	ug/mL	1.47	n/a	n/a	n/a	
DST Simulant	Wash 3	S09R000667	Nitrite	ug/mL	18.5	n/a	n/a	n/a	
DST Simulant	Wash 3	S09R000667	Bromide	ug/mL	<0.0237	n/a	n/a	n/a	U
DST Simulant	Wash 3	S09R000667	Nitrate	ug/mL	22.5	n/a	n/a	n/a	
DST Simulant	Wash 3	S09R000667	Phosphate	ug/mL	1.06	n/a	n/a	n/a	
DST Simulant	Wash 3	S09R000667	Sulfate	ug/mL	2.13	n/a	n/a	n/a	
DST Simulant	Wash 3	S09R000667	Oxalate	ug/mL	<0.105	n/a	n/a	n/a	U
DST Simulant	Wash 3	S09R000667	Aluminum	ug/mL	10.1	n/a	n/a	n/a	
DST Simulant	Wash 3	S09R000667	Lithium	ug/mL	5.58	n/a	n/a	n/a	

ID		SAMPLE	ANALYTE	UNIT	RESULT	DUP.	AVE.	RPD	QA
DST Simulant	Wash 3	S09R000667	Phosphorus	ug/mL	0.129	n/a	n/a	n/a	J
DST Simulant	Wash 3	S09R000667	Sulfur	ug/mL	0.715	n/a	n/a	n/a	J
DST Simulant	Wash 3	S09R000667	Silicon	ug/mL	0.461	n/a	n/a	n/a	
DST Simulant	Wash 3	S09R000667	Cesium-133	ug/mL	0.0175	n/a	n/a	n/a	
DST Simulant	Wash 3	S09R000667	Hydroxide	ug/mL	15.3	n/a	n/a	n/a	
DST Simulant	Wash 3	S09R000667	Total inorganic carbon	ug/mL	10.5	n/a	n/a	n/a	J
DST Simulant	Wash 3	S09R000667	Total organic carbon	ug/mL	18.0	n/a	n/a	n/a	J
DST Simulant	Wash 4	S09R000668	Fluoride	ug/mL	0.325	n/a	n/a	n/a	
DST Simulant	Wash 4	S09R000668	Chloride	ug/mL	1.14	n/a	n/a	n/a	
DST Simulant	Wash 4	S09R000668	Nitrite	ug/mL	16.9	n/a	n/a	n/a	
DST Simulant	Wash 4	S09R000668	Bromide	ug/mL	<0.0237	n/a	n/a	n/a	U
DST Simulant	Wash 4	S09R000668	Nitrate	ug/mL	20.4	n/a	n/a	n/a	
DST Simulant	Wash 4	S09R000668	Phosphate	ug/mL	5.42	n/a	n/a	n/a	
DST Simulant	Wash 4	S09R000668	Sulfate	ug/mL	2.98	n/a	n/a	n/a	
DST Simulant	Wash 4	S09R000668	Oxalate	ug/mL	<0.105	n/a	n/a	n/a	U
DST Simulant	Wash 4	S09R000668	Aluminum	ug/mL	10.7	n/a	n/a	n/a	
DST Simulant	Wash 4	S09R000668	Lithium	ug/mL	5.87	n/a	n/a	n/a	
DST Simulant	Wash 4	S09R000668	Phosphorus	ug/mL	1.72	n/a	n/a	n/a	
DST Simulant	Wash 4	S09R000668	Sulfur	ug/mL	0.992	n/a	n/a	n/a	J
DST Simulant	Wash 4	S09R000668	Silicon	ug/mL	0.853	n/a	n/a	n/a	
DST Simulant	Wash 4	S09R000668	Cesium-133	ug/mL	0.0147	n/a	n/a	n/a	
DST Simulant	Wash 4	S09R000668	Hydroxide	ug/mL	15.9	n/a	n/a	n/a	J
DST Simulant	Wash 4	S09R000668	Total inorganic carbon	ug/mL	<7.00	n/a	n/a	n/a	U
DST Simulant	Wash 4	S09R000668	Total organic carbon	ug/mL	<15.0	n/a	n/a	n/a	U
SST Simulant	Filter Cake	S09R000674	Percent water	%	2.76	n/a	n/a	n/a	
SST Simulant	Filter Cake	S09R000674	Total organic carbon	ug/g	<301	n/a	n/a	n/a	U
SST Simulant	Filter Cake	S09R000674	Total inorganic carbon	ug/g	2.31E+04	n/a	n/a	n/a	
SST Simulant	Filter Cake	S09R000676	Hydroxide	ug/g	2.19E+04	n/a	n/a	n/a	
SST Simulant	Filter Cake	S09R000678	Aluminum	ug/g	1.29E+04	n/a	n/a	n/a	
SST Simulant	Filter Cake	S09R000678	Lithium	ug/g	1.15E+05	n/a	n/a	n/a	
SST Simulant	Filter Cake	S09R000678	Phosphorus	ug/g	1.73E+05	n/a	n/a	n/a	
SST Simulant	Filter Cake	S09R000678	Sulfur	ug/g	1.03E+03	n/a	n/a	n/a	
SST Simulant	Filter Cake	S09R000678	Silicon	ug/g	1.11E+03	n/a	n/a	n/a	
SST Simulant	Filter Cake	S09R000678	Cesium-133	ug/g	0.901	n/a	n/a	n/a	J
SST Simulant	Filtrate 1	S09R000663	Fluoride	ug/mL	372	n/a	n/a	n/a	
SST Simulant	Filtrate 1	S09R000663	Chloride	ug/mL	2.79E+03	n/a	n/a	n/a	
SST Simulant	Filtrate 1	S09R000663	Nitrite	ug/mL	3.55E+04	n/a	n/a	n/a	
SST Simulant	Filtrate 1	S09R000663	Bromide	ug/mL	<26.3	n/a	n/a	n/a	U
SST Simulant	Filtrate 1	S09R000663	Nitrate	ug/mL	2.36E+05	n/a	n/a	n/a	
SST Simulant	Filtrate 1	S09R000663	Phosphate	ug/mL	5.03E+03	n/a	n/a	n/a	
SST Simulant	Filtrate 1	S09R000663	Sulfate	ug/mL	1.37E+04	n/a	n/a	n/a	
SST Simulant	Filtrate 1	S09R000663	Oxalate	ug/mL	995	n/a	n/a	n/a	
SST Simulant	Filtrate 1	S09R000663	Aluminum	ug/mL	1.21E+04	n/a	n/a	n/a	
SST Simulant	Filtrate 1	S09R000663	Lithium	ug/mL	<0.600	n/a	n/a	n/a	U
SST Simulant	Filtrate 1	S09R000663	Phosphorus	ug/mL	1.76E+03	n/a	n/a	n/a	
SST Simulant	Filtrate 1	S09R000663	Sulfur	ug/mL	4.46E+03	n/a	n/a	n/a	
SST Simulant	Filtrate 1	S09R000663	Silicon	ug/mL	105	n/a	n/a	n/a	
SST Simulant	Filtrate 1	S09R000663	Cesium-133	ug/mL	15.5	n/a	n/a	n/a	

ID		SAMPLE	ANALYTE	UNIT	RESULT	DUP.	AVE.	RPD	QA
SST Simulant	Filtrate 1	S09R000663	Hydroxide	ug/mL	2.71E+04	n/a	n/a	n/a	
SST Simulant	Filtrate 1	S09R000663	Total inorganic carbon	ug/mL	7.50E+03	6.63E+03	7.06E+03	12.3	
SST Simulant	Filtrate 1	S09R000663	Total organic carbon	ug/mL	378	474	426	22.5	c
SST Simulant	Filtrate 2	S09R000664	Fluoride	ug/mL	1.44E+03	n/a	n/a	n/a	
SST Simulant	Filtrate 2	S09R000664	Chloride	ug/mL	2.77E+03	n/a	n/a	n/a	
SST Simulant	Filtrate 2	S09R000664	Nitrite	ug/mL	3.62E+04	n/a	n/a	n/a	
SST Simulant	Filtrate 2	S09R000664	Bromide	ug/mL	<26.3	n/a	n/a	n/a	U
SST Simulant	Filtrate 2	S09R000664	Nitrate	ug/mL	2.45E+05	n/a	n/a	n/a	
SST Simulant	Filtrate 2	S09R000664	Phosphate	ug/mL	767	n/a	n/a	n/a	
SST Simulant	Filtrate 2	S09R000664	Sulfate	ug/mL	1.32E+04	n/a	n/a	n/a	
SST Simulant	Filtrate 2	S09R000664	Oxalate	ug/mL	1.07E+03	n/a	n/a	n/a	
SST Simulant	Filtrate 2	S09R000664	Aluminum	ug/mL	1.11E+04	n/a	n/a	n/a	
SST Simulant	Filtrate 2	S09R000664	Lithium	ug/mL	248	n/a	n/a	n/a	
SST Simulant	Filtrate 2	S09R000664	Phosphorus	ug/mL	158	n/a	n/a	n/a	
SST Simulant	Filtrate 2	S09R000664	Sulfur	ug/mL	4.49E+03	n/a	n/a	n/a	
SST Simulant	Filtrate 2	S09R000664	Silicon	ug/mL	84.2	n/a	n/a	n/a	
SST Simulant	Filtrate 2	S09R000664	Cesium-133	ug/mL	15.7	n/a	n/a	n/a	
SST Simulant	Filtrate 2	S09R000664	Hydroxide	ug/mL	3.17E+04	n/a	n/a	n/a	
SST Simulant	Filtrate 2	S09R000664	Total inorganic carbon	ug/mL	7.22E+03	n/a	n/a	n/a	
SST Simulant	Filtrate 2	S09R000664	Total organic carbon	ug/mL	390	n/a	n/a	n/a	c
SST Simulant	Wash 1	S09R000669	Fluoride	ug/mL	5.70	n/a	n/a	n/a	
SST Simulant	Wash 1	S09R000669	Chloride	ug/mL	10.5	n/a	n/a	n/a	
SST Simulant	Wash 1	S09R000669	Nitrite	ug/mL	112	n/a	n/a	n/a	
SST Simulant	Wash 1	S09R000669	Bromide	ug/mL	<2.39	n/a	n/a	n/a	U
SST Simulant	Wash 1	S09R000669	Nitrate	ug/mL	758	n/a	n/a	n/a	
SST Simulant	Wash 1	S09R000669	Phosphate	ug/mL	334	n/a	n/a	n/a	
SST Simulant	Wash 1	S09R000669	Sulfate	ug/mL	431	n/a	n/a	n/a	
SST Simulant	Wash 1	S09R000669	Oxalate	ug/mL	<10.6	n/a	n/a	n/a	U
SST Simulant	Wash 1	S09R000669	Aluminum	ug/mL	41.5	41.0	41.3	1.12	
SST Simulant	Wash 1	S09R000669	Lithium	ug/mL	76.4	75.7	76.1	0.89	
SST Simulant	Wash 1	S09R000669	Phosphorus	ug/mL	119	117	118	1.77	
SST Simulant	Wash 1	S09R000669	Sulfur	ug/mL	148	146	147	1.43	
SST Simulant	Wash 1	S09R000669	Silicon	ug/mL	1.59	1.59	1.59	0.25	
SST Simulant	Wash 1	S09R000669	Cesium-133	ug/mL	0.0492	n/a	n/a	n/a	J
SST Simulant	Wash 1	S09R000669	Hydroxide	ug/mL	106	n/a	n/a	n/a	
SST Simulant	Wash 1	S09R000669	Total inorganic carbon	ug/mL	110	n/a	n/a	n/a	
SST Simulant	Wash 1	S09R000669	Total organic carbon	ug/mL	129	n/a	n/a	n/a	J
SST Simulant	Wash 2	S09R000670	Fluoride	ug/mL	4.23	n/a	n/a	n/a	
SST Simulant	Wash 2	S09R000670	Chloride	ug/mL	<0.0341	n/a	n/a	n/a	U
SST Simulant	Wash 2	S09R000670	Nitrite	ug/mL	0.510	n/a	n/a	n/a	J
SST Simulant	Wash 2	S09R000670	Bromide	ug/mL	<0.261	n/a	n/a	n/a	U
SST Simulant	Wash 2	S09R000670	Nitrate	ug/mL	4.42	n/a	n/a	n/a	
SST Simulant	Wash 2	S09R000670	Phosphate	ug/mL	142	n/a	n/a	n/a	
SST Simulant	Wash 2	S09R000670	Sulfate	ug/mL	2.10	n/a	n/a	n/a	J
SST Simulant	Wash 2	S09R000670	Oxalate	ug/mL	<1.16	n/a	n/a	n/a	U
SST Simulant	Wash 2	S09R000670	Aluminum	ug/mL	1.01	n/a	n/a	n/a	
SST Simulant	Wash 2	S09R000670	Lithium	ug/mL	34.7	n/a	n/a	n/a	
SST Simulant	Wash 2	S09R000670	Phosphorus	ug/mL	51.4	n/a	n/a	n/a	

ID		SAMPLE	ANALYTE	UNIT	RESULT	DUP.	AVE.	RPD	QA
SST Simulant	Wash 2	S09R000670	Sulfur	ug/mL	0.742	n/a	n/a	n/a	J
SST Simulant	Wash 2	S09R000670	Silicon	ug/mL	0.523	n/a	n/a	n/a	Y
SST Simulant	Wash 2	S09R000670	Cesium-133	ug/mL	3.83E-04	n/a	n/a	n/a	
SST Simulant	Wash 2	S09R000670	Hydroxide	ug/mL	11.5	n/a	n/a	n/a	J
SST Simulant	Wash 2	S09R000670	Total inorganic carbon	ug/mL	14.0	n/a	n/a	n/a	J
SST Simulant	Wash 2	S09R000670	Total organic carbon	ug/mL	31.5	n/a	n/a	n/a	J
SST Simulant	Wash 3	S09R000671	Fluoride	ug/mL	1.03	n/a	n/a	n/a	
SST Simulant	Wash 3	S09R000671	Chloride	ug/mL	<0.0341	n/a	n/a	n/a	U
SST Simulant	Wash 3	S09R000671	Nitrite	ug/mL	<0.440	n/a	n/a	n/a	U
SST Simulant	Wash 3	S09R000671	Bromide	ug/mL	<0.261	n/a	n/a	n/a	U
SST Simulant	Wash 3	S09R000671	Nitrate	ug/mL	1.93	n/a	n/a	n/a	J
SST Simulant	Wash 3	S09R000671	Phosphate	ug/mL	83.4	n/a	n/a	n/a	
SST Simulant	Wash 3	S09R000671	Sulfate	ug/mL	0.915	n/a	n/a	n/a	J
SST Simulant	Wash 3	S09R000671	Oxalate	ug/mL	<1.16	n/a	n/a	n/a	U
SST Simulant	Wash 3	S09R000671	Aluminum	ug/mL	0.534	n/a	n/a	n/a	
SST Simulant	Wash 3	S09R000671	Lithium	ug/mL	20.7	n/a	n/a	n/a	
SST Simulant	Wash 3	S09R000671	Phosphorus	ug/mL	30.5	n/a	n/a	n/a	
SST Simulant	Wash 3	S09R000671	Sulfur	ug/mL	0.382	n/a	n/a	n/a	J
SST Simulant	Wash 3	S09R000671	Silicon	ug/mL	0.323	n/a	n/a	n/a	Y
SST Simulant	Wash 3	S09R000671	Cesium-133	ug/mL	1.68E-04	n/a	n/a	n/a	
SST Simulant	Wash 3	S09R000671	Hydroxide	ug/mL	<9.22	n/a	n/a	n/a	U
SST Simulant	Wash 3	S09R000671	Total inorganic carbon	ug/mL	10.1	n/a	n/a	n/a	J
SST Simulant	Wash 3	S09R000671	Total organic carbon	ug/mL	21.0	n/a	n/a	n/a	J
SST Simulant	Wash 4	S09R000672	Fluoride	ug/mL	0.683	n/a	n/a	n/a	
SST Simulant	Wash 4	S09R000672	Chloride	ug/mL	<0.0341	n/a	n/a	n/a	U
SST Simulant	Wash 4	S09R000672	Nitrite	ug/mL	<0.440	n/a	n/a	n/a	U
SST Simulant	Wash 4	S09R000672	Bromide	ug/mL	<0.261	n/a	n/a	n/a	U
SST Simulant	Wash 4	S09R000672	Nitrate	ug/mL	1.54	n/a	n/a	n/a	J
SST Simulant	Wash 4	S09R000672	Phosphate	ug/mL	60.4	n/a	n/a	n/a	
SST Simulant	Wash 4	S09R000672	Sulfate	ug/mL	54.5	n/a	n/a	n/a	
SST Simulant	Wash 4	S09R000672	Oxalate	ug/mL	<1.16	n/a	n/a	n/a	U
SST Simulant	Wash 4	S09R000672	Aluminum	ug/mL	0.388	n/a	n/a	n/a	
SST Simulant	Wash 4	S09R000672	Lithium	ug/mL	17.6	n/a	n/a	n/a	
SST Simulant	Wash 4	S09R000672	Phosphorus	ug/mL	22.5	n/a	n/a	n/a	
SST Simulant	Wash 4	S09R000672	Sulfur	ug/mL	19.7	n/a	n/a	n/a	
SST Simulant	Wash 4	S09R000672	Silicon	ug/mL	0.264	n/a	n/a	n/a	JY
SST Simulant	Wash 4	S09R000672	Cesium-133	ug/mL	9.64E-05	n/a	n/a	n/a	J
SST Simulant	Wash 4	S09R000672	Hydroxide	ug/mL	<9.22	n/a	n/a	n/a	U
SST Simulant	Wash 4	S09R000672	Total inorganic carbon	ug/mL	14.0	n/a	n/a	n/a	J
SST Simulant	Wash 4	S09R000672	Total organic carbon	ug/mL	18.0	n/a	n/a	n/a	J

n/a = Not Analyzed, ND = Not Detected

Qualifiers:

J - Estimated

U - Less Than Detection Limit

Y - Comment

c - RPD Outside Range

Electronically Approved by:

UserName: Duncan, James (h0079048)

Title: APD Chemist

Date: Thursday, 08 April 2010, 01:01 PM Pacific Daylight Time

Meaning: Approved by the author or delegate

=====

UserName: Cooke, Gary (h0410221)

Title: APD Chemist

Date: Thursday, 08 April 2010, 03:28 PM Pacific Daylight Time

Meaning: Additional approval obtained

=====

UserName: Sams, Terry (h0068391)

Title:

Date: Thursday, 08 April 2010, 04:28 PM Pacific Daylight Time

Meaning: Approved by the customer or delegate

=====

UserName: Seidel, Cary (h0009079)

Title: APD Manager

Date: Friday, 09 April 2010, 07:30 AM Pacific Daylight Time

Meaning: Approved by the APD Manager or delegate

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