Aluminum Removal from Hanford Waste by Lithium Hydrotalcite Precipitation – Laboratory Scale Validation on Waste Simulants – Test Report

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Abstract: To reduce the additional sodium hydroxide and ease processing of aluminum bearing sludge, the lithium hydrotalcite (LiHT) process has been invented by AREVA and demonstrated on a laboratory scale to remove alumina and regenerate/recycle sodium hydroxide prior to processing in the WTP. The method uses lithium hydroxide (LiOH) to precipitate sodium aluminate ($\text{NaAl}(\text{OH})_4$) as lithium hydrotalcite ($\text{Li}_2\text{CO}_3 \cdot 4\text{Al}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$) while generating sodium hydroxide (NaOH). In addition, phosphate substitutes in the reaction to a high degree, also as a filterable solid. The sodium hydroxide enriched leachate is depleted in aluminum and phosphate, and is recycled to double-shell tanks (DSTs) to leach aluminum bearing sludges. This method eliminates importing sodium hydroxide to leach alumina sludge and eliminates a large fraction of the total sludge mass to be treated by the WTP. Plugging of process equipment is reduced by removal of both aluminum and phosphate in the tank wastes. Laboratory tests were conducted to verify the efficacy of the process and confirm the results of previous tests. These tests used both single-shell tank (SST) and DST simulants.

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ABSTRACT

To reduce the additional sodium hydroxide and ease processing of aluminum bearing sludge, the lithium hydrotalcite (LiHT) process has been invented¹ by AREVA and demonstrated on a laboratory scale to remove alumina and regenerate/recycle sodium hydroxide prior to processing in the WTP. The method uses lithium hydroxide (LiOH) to precipitate sodium aluminate ($\text{NaAl}(\text{OH})_4$) as lithium hydrotalcite ($\text{Li}_2\text{CO}_3 \cdot 4\text{Al}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$) while generating sodium hydroxide (NaOH). In addition, phosphate substitutes in the reaction to a high degree, also as a filterable solid. The sodium hydroxide enriched leachate is depleted in aluminum and phosphate, and is recycled to double-shell tanks (DSTs) to leach aluminum bearing sludges. This method eliminates importing sodium hydroxide to leach alumina sludge and eliminates a large fraction of the total sludge mass to be treated by the WTP. Plugging of process equipment is reduced by removal of both aluminum and phosphate in the tank wastes. Laboratory tests were conducted to verify the efficacy of the process and confirm the results of previous tests. These tests used both single-shell tank (SST) and DST simulants.

KEY WORDS

Lithium Hydrotalcite (LiHT), Aluminum, Precipitation, Lithium Hydroxide, Cesium, Decontamination, Phosphate

¹ PCT International Application PCT/US2008/076589

EXECUTIVE SUMMARY

Approximately 8,710 MT of aluminum bearing compounds² exist in Hanford waste, and comprises ~66wt% of waste sludge. Although a fraction (~30%) of the alumina compounds are currently soluble in waste supernatants, dilution to 5M Na must be performed to keep phosphate compounds in solution and to maintain corrosion control as required for Waste Treatment and Immobilization Plant (WTP) processing. Additional sodium hydroxide is required to dissolve and maintain the solubility of aluminum for WTP operations.

To reduce the additional sodium hydroxide and ease processing of aluminum bearing sludge, the lithium hydrotalcite (LiHT) process has been invented³ by AREVA and demonstrated on a laboratory scale to remove alumina and regenerate/recycle sodium hydroxide prior to processing in the WTP. The method uses lithium hydroxide (LiOH) to precipitate sodium aluminate ($\text{NaAl}(\text{OH})_4$) as lithium hydrotalcite ($\text{Li}_2\text{CO}_3 \cdot 4\text{Al}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$) while generating sodium hydroxide (NaOH). The carbonate form of LiHT is generated according to the equation:

By this reaction, soluble sodium aluminate is precipitated as a filterable solid and sodium hydroxide liquor is recovered in the filtrate. In addition, phosphate substitutes in the reaction to a high degree, also as a filterable solid. The sodium hydroxide enriched leachate is depleted in aluminum and phosphate, and is recycled to double-shell tanks (DSTs) to leach aluminum bearing sludges. This method eliminates importing sodium hydroxide to leach alumina sludge and eliminates a large fraction of the total sludge mass to be treated by the WTP. Plugging of process equipment is reduced by removal of both aluminum and phosphate in the tank wastes.

Laboratory tests were conducted to verify the efficacy of the process and confirm the results of previous tests. These tests used both single-shell tank (SST) and DST simulants and proved the following:

- The solids produced from both the DST and SST simulant tests were primarily LiHT.
- The solids were readily filtered using small pore size filter media in a Büchner funnel
- Aluminum removal efficiency ranged from 83% to 96% as a fraction of aluminum in the reaction slurry.
- The filter cakes were readily decontaminated, indicating the filter cakes could be disposed of as Class A waste (most restrictive) according to the Code of Federal Regulations (10CFR61.55, Table 2).
- Phosphate removal by the precipitation process was very effective and ranged from 75% to 99% as a fraction of the phosphate in the reaction slurry.
- The generation of hydroxide was inferred by the verification of the production of LiHT by XRD in the filter cake.

² Alumina and sodium inventories in Hanford waste is from HTWOS model run *SP4 Planning Case-3.0-8.4r0-2009-03-30-at-20-02-39*

³ PCT International Application PCT/US2008/076589

In general, the LiHT process performed as predicted by thermodynamic models and verified previous laboratory testing. Additional testing to further optimize the process should be conducted to advance the understanding of this very promising technology.

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LIST OF TERMS

Abbreviations and Acronyms

AFS	AREVA Federal Services LLC
ANN	Aluminum Nitrate Nonohydrate
ARF	Aluminum Removal Facility
DI	De-ionized water
DST	Double-Shell Tank
DOE	U.S. Department of Energy
HLW	High-Level Waste
IC	Ion Chromatography
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
LAW	Low-Activity Waste
LiHT	Lithium Hydrotalcite
MT	Metric Ton
PSD	Particle Size Distribution
PVDF	Poly Vinylidene Fluoride
SEM/EDS	Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscopy
SST	Single Shell Tank
TIC	Total Inorganic Carbon
TGA	Thermo Gravimetric Analysis
TRA	Technology Readiness Assessment
TRL	Technology Readiness Level
WRPS	Washington River Protection Solutions, LLC
WTP	Waste Treatment and Immobilization Plant
XRD	X-Ray Diffraction

1.0 INTRODUCTION

The U.S. Department of Energy (DOE) plans to vitrify both high-level waste (HLW) and low-activity waste (LAW) at the Hanford Site. Removal of aluminum from the waste is of importance to minimize the amount of HLW glass and allow processing flexibility to avoid precipitation and blockage issues, reduce total waste mass, and reduce costs associated with Waste Treatment and Immobilization Plant (WTP) processing.

By Lithium Hydrotalcite (LiHT) precipitation, sodium hydroxide is regenerated thus, eliminating a large mass of imported sodium hydroxide from the LAW waste mass. By reducing the masses of high- and low-activity wastes, processing times for mixing, filtering, separating, and vitrifying the wastes and the costs for long-term storage of the immobilized forms is minimized. The process has been demonstrated in one and two-liter laboratory scale experiments using Hanford waste simulants to remove alumina and regenerate sodium hydroxide. The method uses lithium hydroxide (LiOH) and waste sodium carbonate (Na_2CO_3) to precipitate sodium aluminate ($\text{NaAl}(\text{OH})_4$) as lithium hydrotalcite ($\text{Li}_2\text{CO}_3 \cdot 4\text{Al}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$) and regenerate sodium hydroxide (NaOH). In lieu of carbonate incorporation (intercalation) into the LiHT structure, more thermodynamically stable anionic forms of LiHT may form in the reaction (e.g. phosphate).

As indicated in the general reaction, 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 sludge to increase the amount of sodium aluminate [$\text{NaAl}(\text{OH})_4$] in the supernate.

Washington River Protection Solutions LLC (WRPS) River Protection System Plan Revision 5 includes an Aluminum Removal Facility (ARF) using the LiHT process to reduce mission duration, minimize waste generation, and reduce costs. Recent direction from the DOE, based on the immature technology status of the LiHT process, caused work on the ARF to be discontinued. Instead, alternative implementation scenarios are to be investigated.

Although the LiHT process was integral to the ARF, LiHT does not rely on the ARF. The ability to precipitate aluminum from Hanford waste and generate sodium hydroxide is an important chemical process that has the potential to be incorporated in alternative flow sheets being considered by WRPS. Therefore, AREVA was contracted by WRPS under the “Lithium Hydrotalcite Technology Readiness Confirmation and Closure Project,” to assemble the documentation package for advancing the LiHT demonstration documentation and testing to the point where a Technology Readiness Assessment (TRA) can be conducted.

The proposed laboratory-scale validation program included the following main activities:

- SST and DST (non-radioactive) simulants were prepared from SST and DST formulations developed during the Fractional Crystallization project. The simulant chemistry was based on analyses of actual tank waste samples. During Fractional Crystallization laboratory experiments, the simulants were determined to have the same chemical and physical properties as actual waste samples. Simulant chemistries of some tests were modified somewhat to ameliorate gibbsite dissolution issues.
- One- and two-liter laboratory tests of LiHT precipitation was performed to validate previous experiments using similar methodologies to previous testing.
- Solids washing was accomplished with a stir bar and Teflon beaker; filtration utilized a Büchner funnel and small pore filter media.
- Analysis of the filter cakes and filtrates was performed with:
 - ICP-AES and ICP-MS for metals.
 - IC, colorimetric analysis, and titrations for anions (including free hydroxide).
 - Particle Size Distribution (PSD) and TGA of final washed solids.
 - X-Ray Diffraction (XRD) of initial and final washed cakes.
 - Total Inorganic Carbon (TIC) for carbonate determination.
 - SEM/EDS of final washed solids.

2.0 APPARATUS

The reactor utilized in the experiments was a Chemglass (Vineland, NJ) two-liter jacketed vessel, model number CG-1950, with variable speed agitator, digital temperature indicator, condenser, and stand. Ancillary equipment included a chiller for the condenser, silicon oil heater/controller for the reactor jacket, and micro-peristaltic pump with micro bore tubing for LiOH additions. The system is shown in Figure 1.

Figure 1. Lithium Hydrotalcite Reactor System.

3.0 TEST DESCRIPTION

The tests were performed as described in the *Lithium Hydrotalcite Precipitation Development Planning – Single-Shell Tank Supernatant Tests* (RPP-PLAN-48090), and *Lithium Hydrotalcite Precipitation Development Planning – Double-Shell Tank Supernatant Tests* (RPP-PLAN-48091).

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 general test sequence was followed for all test runs with modifications described in the individual sections.

Figure 2. General 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 also as noted in the individual sections. The original compositions were based on the formulations of the SST early feed simulant and the DST simulant in *CH2M-0403873, Preparation of Simulated Waste Samples for EM-21 Project*. These one-liter recipes are normalized to a sodium concentration of 5 M Na. The test procedure specified the leaching of aluminum from gibbsite ($\text{Al}(\text{OH})_3$) rather than aluminum being added to the simulant as $\text{NaAlO}_2 \cdot 2\text{H}_2\text{O}$, due to unknown impurity and quantification issues with the Technical Grade Sodium Aluminate. At this time, there is no commercially-available reagent grade Sodium Aluminate.

For the first DST test, the specified gibbsite leaching protocol was followed; however, some gibbsite remained in the reactor, as a suspended solid, after the specified leaching time had elapsed. Extended leaching time did not alleviate the remaining turbidity of the solution, and the test continued in spite of this. This likely affected the product yield in the first DST test. Due to the leaching issue, a decision was made to adjust the simulant recipes and utilize Aluminum

Nitrate nonahydrate, (ANN, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), as an aluminum source as much as practicable, with stoichiometrically correct ratios for hydroxide and nitrate maintained.

For the SST simulant, the entire mass of aluminum to be added was in the form of ANN, while the DST simulant still needed a relatively small amount of leached gibbsite to obtain correct mole ratios due to the lower sodium nitrate quantity added to the DST simulant. The gibbsite leaching was facilitated by a $[\text{OH}^-]$ to $[\text{Al}]$ ratio of 6:1 using the ANN recipe, vs. a 3:1 ratio with the original chemical constituents.

For each test, simulant chemicals were weighed on a four place balance and transferred to the 2-liter reactor through a port in the lid. Agitation was initiated, and dissolution steps commenced. After simulant make up and heating to 90°C , 10% LiOH solution was introduced to the reactor and precipitation of LiHT followed. After the four-hour ripening period, the product was transferred out to the filtration system. Samples for chemical analyses were taken from the initial filtrate (Mother Liquor), wash water of each of the four washing steps, as well as from an aliquot of each of the filter cakes after each sequential wash. All samples were submitted to RJ Lee Group of Pasco, WA. Figure 3 provides details of the Sample Schedule followed for each of the four individual tests.

1.	Liquid Samples
1.	Mother liquor after first filtration
a.	ICP- AES for: Li, Al, Na, P, S, K
b.	ICP/MS for Cs, Cr
c.	Alkalinity for free hydroxide by titration
d.	Anions by IC for NO_3 , NO_2 , SO_4 , F, PO_4
e.	CO_3 by TIC
2.	Each wash
f.	ICP- AES for: Li, Al, Na, P, S, K
g.	ICP/MS for Cs, Cr
h.	Alkalinity for free hydroxide by titration
i.	Anions by IC for NO_3 , NO_2 , SO_4 , F, PO_4 , CO_3
2.	Filter cake samples
1.	Initial filter cake from LiOH reaction
a.	ICP- AES for: Li, Al, Na, P, S, F, K
b.	ICP/MS for Cs, Cr
2.	First three filter cakes after washes
a.	ICP- AES for: Li, Al, Na, P, S, F, K
b.	ICP/MS for Cs, Cr
3.	Dried filter cake ONE SAMPLE PER TEST
a.	ICP- AES for: Li, Al, Na, P, S, F, K
b.	ICP/MS for Cs, Cr
c.	CO_3 (TIC)
d.	XRD
e.	SEM/EDS
f.	TGA
g.	Re-suspension of cake for liquid (slurry) phase PSD

Figure 3. LiHT Testing Sample Schedule.

The solids washing steps entailed washing the filtered solids with four consecutive 1-liter DI water washes (ambient temperature) in a beaker with magnetic stir bar. Washing in the beaker was performed with a high agitation rate to provide continuous contact between the wash water and solids. After 30 minutes of washing, the slurry was again filtered through a 0.45 μm pore filter with vacuum filtration through a Büchner funnel.

Analysis methodologies and equipment for the individual methods:

- **Particle Size Analysis**

Particle size distribution analysis (volume based and number based) was conducted using a Horiba LA-910 Light Scattering Particle Size Distribution Analyzer. Laser diffraction particle size distribution analyzers report results in volume distribution but the number distribution can be calculated by the data acquisition software. Number distribution should only be used to compare to microscopy data. A small portion of the samples was dispersed in approximately 125 ml of DIUF water. Approximately 100 ml of the dispersed sample was added to the sample reservoir (which contained between 150-315 ml DIUF water) and was analyzed.

- **TGA Analysis**

The instrument used for the analysis of the sample was a simultaneous TGA/DSC (Q600 SDT). The specific experimental conditions used are as follows:

Sample size: see plots

Heating rate: 20 $^{\circ}\text{C}/\text{min}$

Data sampling interval: 0.5 sec/point

Temperature range: $\sim\text{RT} - 1000^{\circ}\text{C}$

Nitrogen: 100 ml/min

The Universal Analysis 2000 Software (Version 4.1D, TA Instruments) was used for the processing of the data. The samples showed a weight loss of in the range of ~ 65 to 80%. Samples were in duplicate.

- **X-ray diffraction (XRD) for crystalline phases**

A portion of the samples was ground and mounted into a standard XRD holder for analysis. The samples were run on a PANalytical X'Pert Pro diffractometer using copper radiation. The resulting diffraction pattern was then analyzed using the X'Pert HighScore program utilizing the ICDD database

- **SEM/EDS Analysis**

A representative portion of each sample was dry deposited on a carbon adhesive tab for SEM analysis. The samples were coated with a thin layer of platinum via sputter deposition. The samples were analyzed in a Hitachi S-5500 ultra-high resolution field-emission SEM (FESEM) using a 2kV accelerating voltage. Furthermore to verify the presence of P (phosphorous) a representative portion of the sample was dry deposited on a carbon adhesive tab for SEM analysis. The sample was analyzed in an RJ Lee Instruments Personal SEM (PSEM) Model 75 using a 20kV accelerative voltage. Analysis was performed in low vacuum mode in order to prevent charge buildup on the surface without the use of a conductive coating layer.

4.0 RESULTS AND DISCUSSION

In general, the testing proceeded as planned. The major exception was the use of ANN for simulant make up due to issues associated with gibbsite leaching. In addition, for two of the tests, in order to capture additional LiHT, an overnight ripening period at ambient temperatures was utilized in DST #2 and the SST test.

The results are presented in the order of the second DST test (DST #2), the third DST test (DST #3), followed by the SST test. The first DST test (DST #1) results are presented in Appendix A as some of the results were inconclusive, likely due to incomplete leaching of the gibbsite. Appendix B contains the compilation of final analytical results.

In order to verify the amounts of PO_4 from the IC and ICP-AES analysis, colorimetric total phosphate was also determined; however, the IC and total phosphate results both proved to be less reliable than the ICP-AES and were not used in calculations. They are, however, presented in the summary tables of Appendix B.

Free hydroxide is generated in the LiHT reaction by stripping carbonate and/or phosphate anions from its respective sodium salt. The reaction generates two moles of sodium hydroxide for every mole of LiHT product. Total alkalinity analysis by titration was performed for determination of carbonate and hydroxide concentrations, and TIC was used for determination of carbonate. The difference between the two yields the free hydroxide concentration. Unfortunately, the expected results for hydroxide generation were not able to be verified by the analysis methods that were selected. Qualitatively, the generation of hydroxide can be inferred from the fact that LiHT was actually generated in the reaction (as verified by XRD) and by the reaction stoichiometry.

4.1 DST TEST #2

Several modifications to the testing protocol were made to facilitate this test:

- Partial use of ANN for simulant make up instead of all gibbsite. To accomplish this, the nitrate source was changed from sodium nitrate to ANN. To balance the hydroxide, the total sodium hydroxide was increased stoichiometrically. For the purpose of improving the leaching process for the balance of the aluminum (from gibbsite), the entire quantity of NaOH was used, resulting in a caustic to gibbsite ratio of 3 to 1, rather than 6 to 1 as in the original recipe. When the leachate was combined with the remainder of the chemicals in the simulant, the integrity of the original recipe was maintained. The DST #2 recipe is shown in Table 1.
- Overnight ripening at ambient conditions to capture excess slow forming precipitates as noted in DST Test #1
- Previous testing indicated that lithium phosphate (Li_3PO_4) preferentially precipitates over LiHT. In order to ensure that adequate lithium ion was present for complete conversion of aluminum to LiHT, the total lithium added was determined by first

satisfying the stoichiometric aluminum demand, then the stoichiometric phosphate demand, and adding 10% excess.

Table 1. DST Test #2 Simulant Chemical Makeup (1-L Batch)

Reagent	MW	Target Molarity	Target Weight or Volume	Actual Weight or Volume
NaOH	40	3.51	140.26 g	140.250 g
Na ₂ CO ₃	106	0.06	6.86 g	6.862 g
Na ₂ C ₂ O ₄	134	0.003	0.38 g	0.384 g
KNO ₃	101	0.19	19.68 g	19.688 g
NaNO ₃	85	N/A	N/A	N/A
NaNO ₂	69	1.15	79.44 g	79.443 g
Na ₂ SO ₄	142	0.007	1.02 g	1.019 g
Na ₃ PO ₄ · 12H ₂ O	380.1	0.007	2.74 g	2.740 g
NaCl	58.4	0.12	6.73 g	6.732 g
NaF	42	0.011	0.46 g	0.461 g
Na ₂ Cr ₂ O ₇ · 2H ₂ O	298	0.001	0.43 g	0.432 g
NaC ₂ H ₃ O ₂ · 3H ₂ O	136.1	0.04	5.48 g	5.483 g
CsNO ₃ solution	NA	1.05E-05	2.43 mL	2.43 mL
Al(OH) ₃	78	0.577	45.01 g	45.02 g
Al(NO ₃) ₃ · 9H ₂ O	375.1	0.305	114.41 g	114.38 g
LiOH · H ₂ O	42	0.509	21.37 g	21.37 g

Note: CsNO₃ solution is prepared by dissolving 210 mg reagent CsNO₃ salt in 250 mL water.

For the second DST test, the leaching protocol employed for the reduced quantity of gibbsite was to add water, caustic, and gibbsite for extended, agitated leaching at 100°C in a Teflon beaker. Use of the Teflon beaker eliminated the silica that was produced from the caustic etching of the glass reactor during the leach process. This, in combination with the higher caustic-to-aluminum ratio, produced a clear leachate in about 45 minutes.

10wt% LiOH was added to the reactor at a predetermined rate that would ensure a one-hour addition period. Approximately 15 minutes after the start of the LiOH addition, a sudden formation of precipitate occurred, likely due to a slow increase to super saturated conditions. The white precipitate continued to gradually form through the remainder of the LiOH addition, as well as the 4-hour ripening period. Reactor contents were cooled to 50°C after the ripening period and the product slurry (935 ml) was transferred to a polypropylene container for overnight ripening at ambient conditions. The test sequence for DST #2 is indicated in the flowchart as shown in Figure 4.

Figure 4. Experiment Flow Chart for DST Test #2.

Time lapse photographs of the DST Test #2 reaction progression are presented in Figure 5. As indicated, the LiHT reaction is characterized by the rapid onset of precipitation at about 25 minutes after the start of LiOH addition. Using the black thermocouple as a reference, the accumulation of solids as the reaction progresses can be seen (Figure 5). Scaling on the reactor walls is responsible for some of the indicated lack of clarity, but reaction precipitates are the primary cause.

Figure 5. DST #2 Reaction Progressions and Elapsed Time from Start of Lithium Hydroxide Addition.

After approximately 21 hours of crystal ripening at ambient temperatures, the slurry was filtered using a Büchner funnel and 0.45 μm PVDF filter paper. Samples of the filtrate and solids were taken for analysis as noted in the Test Procedure. The cake produced was an off-white color due to the presence of sodium dichromate and resembled soft clay. The product filtered readily and

was easily removed from the Büchner funnel. All filtrates were clear and showed no signs of unfiltered solids.

The XRD spectra of the unwashed solids compared to the reference spectra indicates LiHT in the carbonate form as the major species, with only trace unknowns (Figure 6).

Phase	Composition	Concentration	PDF Number
Lithium Aluminum Carbonate Hydroxide Hydrate	$(\text{Al}_2\text{Li}(\text{OH})_6)_2\text{CO}_3 \cdot x\text{H}_2\text{O}$	Major	00-042-0729
Unknown(s)	-	Trace

Figure 6. X-Ray Diffraction Pattern of Sample “DST #2 Initial Filter Cake” in red, and the reference pattern 00-042-0729 in blue with Degrees 2 θ Along the X-Axis and Intensity (Counts) Along the Y-Axis.

4.1.1 DST TEST #2 SOLIDS WASHING

The same solids washing steps were followed as in the previous run. Samples of both the filtrate and the filter cake were taken for analysis after each filtration step. Appendix B contains the analysis results. The final washed cake was a white, fluffy, highly crystalline material. The second through the fourth wash filtrates were water clear, indicating the majority of residual dichromate was washed out in the first wash (Figure 7). This is verified by analytical results showing the dichromate readily washes from the cake.

Figure 7. Filtrate and Cake Samples from DST #2 Test.
(Left to Right: Mother Liquor and Initial Cake, 1st, 2nd, 3rd, 4th Wash Filtrates and Filter Cake Samples)

XRD analysis of the unwashed solids again indicates LiHT as the major species, with only trace unknowns (Figure 8).

Phase	Composition	Concentration	PDF Number
Lithium Aluminum Carbonate Hydroxide Hydrate	$(Al_2Li(OH)_6)_2CO_3 \cdot xH_2O$	Major	00-042-0729
Unknown(s)	-	Trace

Figure 8. X-Ray Diffraction Pattern of Sample "DST #2 Initial Filter Cake" 10130236, with Degrees 2θ Along with X-Axis and Intensity (Counts) Along the Y-Axis.

XRD analysis of the filter cake was performed on the cake after the fourth wash. The XRD pattern for the washed cake is provided in Figure 9. No change in the spectrum was noted after washing.

Phase	Composition	Concentration	PDF Number
Lithium Aluminum Carbonate Hydroxide Hydrate	$(\text{Al}_2\text{Li}(\text{OH})_6)_2\text{CO}_3 \cdot x\text{H}_2\text{O}$	Major	00-042-0729
Unknown(s)	-	Trace

Figure 9. X-Ray Diffraction Pattern of Sample “DST #2 4th Wash Filter Cake” 10130237, with Degrees 2θ Along with X-Axis and Intensity (Counts) Along the Y-Axis.

4.1.2 DST TEST #2 ALUMINUM REMOVAL

The initial damp filter cake weighed 146.16 grams. A portion of the cake was dried at 60°C overnight and indicates that the cake was 50.3% solids. In addition, reactor scale totaled

3.46 grams, dry basis. A small amount of precipitates formed in the mother liquor after the initial filtration and were determined to be the equivalent of 6.80 grams of dry cake in addition to the above. Net dry LiHT cake was 83.8 grams. The estimated gravimetric product yield is 86.4% based on a theoretical yield of 97.0 grams.

ICP-AES results show that for DST Test #2 the initial LiHT filter cake retained 93.8 mole% of the total aluminum in the initial product slurry. Slurry volume from the reactor was 985 ml. Initial filtrate (mother liquor) volume was 865 ml.

4.1.3 DST TEST #2 FILTER CAKE IMAGES

Final washed cake samples were imaged with SEM (Figure 10). In these images, as in other tests, it is evident that the LiHT “sand rose” crystal shape has been broken down by the washing process. Crystallite edge joining that is the hallmark of the LiHT structure is not apparent. Instead, the platelets have agglomerated into large spherical particles composed of small shards and pieces roughly $1\mu\text{m} \times 2\mu\text{m}$, with thickness 50nm to 100nm.

Figure 10. SEM Images of DST #2 4th Wash.

The EDS spectrums (Figure 11) for the sample indicates that carbon, sodium, oxygen, aluminum, silicon, and phosphorous are the major constituents. Lithium is too small to be seen with Energy Dispersive Spectroscopy and is, therefore, not indicated in the spectrum. The presence of phosphorous likely indicates what is believed to be the thermodynamically stable phosphate form of LiHT. The carbon peak indicates the carbonate form of LiHT is also present, as there is a stoichiometric deficit with respect to phosphorous.

Figure 11. Characteristic EDS Spectrum of Sample “DST #2 4th Wash Filter.

4.1.4 DST TEST #2 CESIUM DECONTAMINATION

Decontamination of the LiHT product will be necessary to eventually dispose of the cake derived from Hanford wastes as LAW. In order to test the ability to decontaminate the filter cakes, the test runs included ^{133}Cs in the simulant composition.

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.

DF is calculated by the following equation:

$$\text{Cesium DF} = \frac{\text{Mass Cs in/Mass Al in}}{\text{Mass Cs out/Mass Al out}}$$

Cesium DF is calculated for incremental (between washes) and cumulative cases and are presented in Table 2.

Table 2. DST #2 Incremental and Cumulative Filter Cake Cesium DF.

	Aluminum	Cesium	Incremental DF	Cumulative DF
Simulant (mg)	23796	2.04	N/A	N/A
Initial Cake (mg/kg)	197200	1.64		
1st wash Cake (mg/kg)	200400	0.079	21.1	217
2nd wash Cake (mg/kg)	116200	0.0028	16.4	3558
3rd wash Cake (mg/kg)	273300	0.0016	4.1	14644
4th wash Cake (mg/kg)	268800	0.001	1.6	23044

As can be seen from the data in the table above, the washing of the DST #2 solids were very effective with respect to cesium. The reasons(s) for this remarkably high decontamination compared to the other tests are unknown; however, it is apparent that LiHT does not retain alkali metals and is easily decontaminated.

4.1.5 DST TEST #2 PARTICLE SIZE DISTRIBUTION

Volume-based and number-based PSD curves and histograms are presented in Figures 12 and 13. The volume-based histogram indicates a bimodal distribution, with the primary population centered at 200 μm to 300 μm , and a large fraction of particles at 10 μm to 100 μm . The number-based distribution histogram indicate a large number of particles $\leq 1\mu\text{m}$, and are likely the cause of the increased filtration times as the washing progressed that is assumed to be caused by filter media fouling. This can be attributed to the effect of particle washing in the Teflon beaker with magnetic stir bar, as well as the effect of vacuum filtration, causing breakup of the LiHT crystal structure and re-agglomeration into large particles.

Figure 12. Sample “DST #2 4th Wash Filter” 10130237 Represented as a Number-Based Description.

Figure 13. Sample “DST #2 4th Wash Filter” 10130237 Represented as a Volume-Based Description.

4.1.6 DST TEST #2 THERMO GRAVIMETRIC ANALYSIS

The TGA analysis indicates approximately 57% LiHT solids (43% free water). This compares with oven dried samples (60 °C) that indicate 50.3% solids.

The analysis further indicates that 31% solids remains after calcining at 1000 °C. Degradation of the LiHT structure is likely at this temperature, and the resulting mineral forms are assumed to be Li_2O and Al_2O_3 . In future work, this should be confirmed with XRD analysis.

Figure 14. TGA Analysis of Sample “DST #2 4th Wash Filter.”

4.2 DST TEST #3

Several modifications to the testing protocol were made to facilitate this test:

- Partial use of ANN for simulant make up instead of all gibbsite. To accomplish this, the nitrate source was changed from sodium nitrate to ANN. To balance the hydroxide, the total sodium hydroxide was increased stoichiometrically. For the purpose of improving

the leaching process for the balance of the aluminum (from gibbsite), the entire quantity of NaOH was used, resulting in a caustic-to-gibbsite ratio of 3 to 1, rather than 6 to 1 as in the original recipe. When the leachate was combined with the remainder of the chemicals in the simulant, the integrity of the original recipe was maintained. The DST #3 recipe is shown in Table 3.

- Previous testing indicated that lithium phosphate (Li_3PO_4) preferentially precipitates over LiHT. In order to ensure that adequate lithium ion was present for complete conversion of aluminum to LiHT, the total lithium added was determined by first satisfying the stoichiometric aluminum demand, followed by the stoichiometric phosphate demand, and adding 10% excess.
- Rapid addition of the 10% LiOH solution to determine the effect on particle size distribution and yield.

Table 3. DST Test #3 Simulant Chemical Makeup (1-L Batch).

Reagent	MW	Target Molarity	Target Weight or Volume	Actual Weight or Volume
NaOH	40	3.51	140.26 g	140.305
Na_2CO_3	106	0.06	6.86 g	6.86
$\text{Na}_2\text{C}_2\text{O}_4$	134	0.003	0.38 g	0.381
KNO_3	101	0.19	19.68 g	19.861
NaNO_3	85	N/A	N/A	N/A
NaNO_2	69	1.15	79.44 g	79.441
Na_2SO_4	142	0.007	1.02 g	1.021
$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	380.1	0.007	2.74 g	2.81
NaCl	58.4	0.12	6.73 g	6.731
NaF	42	0.011	0.46 g	0.46
$\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	298	0.001	0.43 g	0.432
$\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$	136.1	0.04	5.48 g	5.481
CsNO ₃ solution	NA	1.05E-05	2.43 mL	2.43 mL
$\text{Al}(\text{OH})_3$	78	0.577	45.01 g	45.02
$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	375.1	0.305	114.41 g	114.38
$\text{LiOH} \cdot \text{H}_2\text{O}$	42	0.509	21.37 g	21.371

Note: CsNO₃ solution is prepared by dissolving 210 mg reagent CsNO₃ salt in 250 mL water

For the DST Test #3, the leaching protocol employed for the reduced quantity of gibbsite was to add water, caustic, and gibbsite for extended, agitated leaching at 105°C in a Teflon beaker. Use of the Teflon beaker eliminated the silica that was produced from the caustic etching of the glass reactor during the leach process. This, in combination with the higher caustic-to-aluminum ratio produced a clear leachate in about 45 minutes.

10wt% LiOH was rapidly added to the reactor over a 30 second period. LiHT formed with approximately 10 seconds after the start of the addition, and the precipitation was well underway at the end of the brief addition period. The white precipitate appeared to gradually form through a 4-hour ripening period. The test sequence for DST #3 is indicated in the flowchart as shown in Figure 15.

Figure 15. Experiment Flow Chart for DST Test #3.

Reactor contents were cooled to 50°C after the ripening period, and the product slurry (1000 ml) was filtered with a Büchner funnel and 0.45 µm pore size PVDF filter media samples of the filtrate and solids were taken for analysis as noted in the Sample Schedule (Figure 3). The cake produced was an off-white color due to the presence of sodium dichromate and resembled soft clay. The product filtered readily and was easily removed from the Büchner funnel. All filtrates were clear and showed no signs of unfiltered solids.

The XRD spectrum of the washed solids compared to the reference spectrum indicates LiHT in the carbonate form as the major species, with only trace unknowns (Figure 16).

Phase	Composition	Concentration	PDF Number
Lithium Aluminum Carbonate Hydroxide Hydrate	$(\text{Al}_2\text{Li}(\text{OH})_6)_2\text{CO}_3 \cdot x\text{H}_2\text{O}$	Major	00-042-0729
Unknown(s)	-	Trace

Figure 16. X-Ray Diffraction Pattern of Sample “DST #3 4th Wash Cake 10130251 with Degrees 2θ Along the X-Axis and Intensity (Counts) Along the Y-Axis.

4.2.1 DST TEST #3 ALUMINUM REMOVAL

The initial damp filter cake weighed 192.62 grams. A portion of the cake was dried at 60°C overnight and indicates that the cake was 60.01% solids. In addition, reactor scale totaled 5.34 grams, dry basis. A small amount of precipitates formed in the mother liquor after the initial filtration and was determined to be the equivalent of 11.63 grams of dry cake in addition to the above. Net dry LiHT cake was 132.6 grams.

ICP-AES results show that for DST Test #3 the initial LiHT filter cake retained 96 mole% of the total aluminum in the initial product slurry. Slurry volume from the reactor was 1000 ml. Initial filtrate (mother liquor) volume was 800 ml.

4.2.2 DST TEST #3 FILTER CAKE IMAGES

Final washed cake samples were taken and imaged with SEM (Figure 17). In these images, as in other tests, it is evident that the LiHT “sand rose” crystal shape has been broken down by the washing process. Crystallite edge joining that is the hallmark of the LiHT structure is not apparent. Instead, the platelets have agglomerated into large spherical particles composed of small shards and pieces roughly 1µm X 2µm, with thickness 50nm to 100nm.

Figure 17. SEM Images of Sample “DST #3 4th Wash Cake.”

The EDS spectrum for the sample indicates that carbon, sodium, oxygen, aluminum, silicon, and phosphorous are the major constituents (Figure 18). The silicon originates from the elevated temperature etching of the reactor vessel by sodium hydroxide, while the presence of phosphorous likely indicates the thermodynamically stable phosphate form of LiHT. The carbon peak indicates the carbonate form of LiHT is also present, as there is a stoichiometric deficit with respect to phosphorous.

Figure 18. Characteristic EDS Spectrum of Sample "DST #3 4th Wash Cake."

4.2.3 DST TEST #3 CESIUM DECONTAMINATION

Decontamination of the LiHT product will be necessary to eventually dispose of the cake derived from Hanford wastes as LAW. In order to test the ability to decontaminate the filter cakes, the test runs included ^{133}Cs in the simulant composition.

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.

DF is calculated by the following equation:

$$\text{Cesium DF} = \frac{\text{Mass Cs in/Mass Al in}}{\text{Mass Cs out/Mass Al out}}$$

Cesium DFs are calculated for incremental (between washes) and cumulative cases, and are presented in Table 4.

Table 4. DST Test #2 Filter Cake Cesium Decontamination

	Aluminum	Cesium	Incremental DF	Cumulative DF
Simulant (mg)	23796	1.40		
Initial Cake (mg/kg)	196000	1.97	5.8	6
1 st wash Cake (mg/kg)	241800	0.296	8.2	48
2 nd wash Cake (mg/kg)	202300	0.098	2.5	121
3 rd wash Cake (mg/kg)	260600	0.071	1.8	215
4 th wash Cake (mg/kg)	127800	0.027	1.3	278

As can be seen from the data in the table above, the washing of the DST #3 solids was very effective with respect to cesium. It is apparent that LiHT does not retain alkali metals and is easily decontaminated.

4.2.4 DST TEST #3 PARTICLE SIZE DISTRIBUTION

Volume-based and number-based PSD curves and histograms are presented in Figures 19 and 20. The volume based histogram indicates a normal distribution curve, centered around particle volume of 100 μm to 200 μm . The number based distribution histogram indicates a large

population of particles $\leq 1\mu\text{m}$ and are likely the cause of the increased filtration times as the washing progressed. This can be attributed to the effect of particle washing in the Teflon beaker with magnetic stir bar, as well as the effect of vacuum filtration, causing breakup of the LiHT crystal structure and re-agglomeration into large particles.

Figure 19. Sample "DST #3 4th Wash Cake" Represented as a Number-Based Distribution.

Figure 20. Sample "DST #3 4th Wash Cake" Represented as a Volume-Based Distribution.

4.2.5 DST TEST #3 THERMO GRAVIMETRIC ANALYSIS

The TGA analysis (Figure 21) indicates approximately 48% LiHT solids (52% free water). This compares with oven dried samples (60 °C) that indicate 60.01% solids. The discrepancy may be that decarboxylation or dehydration of the LiHT waters of hydration may take place at the TGA analysis conditions.

The analysis further indicates that 26.2% solids remains after calcining at 1000 °C. Degradation of the LiHT structure is likely at this temperature, and the resulting mineral forms are assumed to be Li_2O and Al_2O_3 . In future work, this should be confirmed with XRD analysis.

Figure 21. TGA Analysis of Sample “DST #3 4th Wash Cake.”

4.3 SST TEST

Several modifications to the testing protocol were made to facilitate this test:

- Full use of ANN for simulant make up instead of gibbsite. To accomplish this, the nitrate source was changed from sodium nitrate to ANN. To balance the hydroxide, the total sodium hydroxide was increased stoichiometrically. When the leachate was combined

with the remainder of the chemicals in the simulant, the integrity of the original recipe was maintained. The SST recipe is shown in Table 5.

- Overnight ripening at ambient conditions to capture excess slow forming precipitates as noted in DST Test #1.
- Previous testing indicated that lithium phosphate (Li_3PO_4) preferentially precipitates over LiHT. In order to ensure that adequate lithium ion was present for complete conversion of aluminum to LiHT, the total lithium to be added was determined by first satisfying the stoichiometric aluminum demand, followed by the stoichiometric phosphate demand, and finally adding 10% excess.
- The SST Test LiOH was added over a one hour period.

Table 5. SST Test Simulant Chemical Makeup (2 Liter Batch).

Reagent	MW	Target Molarity	Target Weight or Volume ⁽¹⁾	Actual Weight or Volume ⁽¹⁾
NaOH	40	2.57	205.4 g	205.41
Na_2CO_3	106	0.34	71.26 g	71.26
$\text{Na}_2\text{C}_2\text{O}_4$	134	0.01	1.56 g	1.561
KNO_3	101	0.02	3.54 g	3.541
NaNO_3	85	0.93	158.18 g	158.18
NaNO_2	69	0.48	65.82 g	65.82
Na_2SO_4	142	0.08	23.10 g	23.1
$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	380.1	0.02	17.74 g	17.74
NaCl	58.4	0.05	5.46 g	5.461
NaF	42	0.01	0.72 g	0.721
$\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	298	0.02	13.88 g	13.881
CsNO ₃ solution	N/A	1.05E-05	4.86 mL	4.86
$\text{Al}(\text{OH})_3$	78	N/A	N/A	N/A
$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	375.1	0.440	331.19 g	321.9 ⁽²⁾
$\text{LiOH} \cdot \text{H}_2\text{O}$	42	0.320	26.865 g ⁽³⁾	26.865

⁽¹⁾ Mass for 2 liter batch, rather than 1 liter batch

⁽²⁾ Available ANN supply was slightly less than the amount required

⁽³⁾ LiOH was added at 12.4% excess in the SST run, due to a slight shortage of ANN during the simulant make up

In order to produce enough filter cake for the extensive number of analyses requiring a sample, a two-liter batch of SST simulant was formulated.

As the 10wt% LiOH was dripped slowly into the reactor (one hour addition), a precipitate formed rapidly at the droplet location. The same phenomenon was observed in the DST tests, but to a much smaller degree. Since the SST simulant contained much higher levels of phosphate, this may indicate the rapid formation of lithium phosphate. The white precipitate

appeared to form continually during the 4-hour ripening period (Figure 22). Reactor contents were cooled to 50°C after the ripening period, and the product slurry (2205 ml) was filtered using a Büchner funnel and 0.45 µm PVDF filter medium. Total damp, unwashed cake produced during the initial filtration was 145.58 grams. A dried sample of the filter cake indicates that the cake was 42.3% solids. Filtrate (mother liquor) volume was 2110 ml. Samples of the filtrate and solids were taken for analysis, as noted in the Sample Schedule (Figure 3). The cake produced was a yellow color due to the presence of sodium dichromate and resembled soft clay. The product filtered readily and was easily removed from the Büchner funnel. All filtrates were clear and showed no signs of unfiltered solids. 10wt% LiOH was added to the reactor at a predetermined rate that would ensure a one-hour addition period.

The test sequence for the SST Test is indicated in the flowchart as shown in Figure 22.

Time lapse photographs of the SST simulant reaction progression are presented in Figure 23. The SST LiHT reaction is characterized by the rapid onset of precipitation as the LiOH droplets contacted the surface of the simulant. This may indicate the rapid precipitation of lithium phosphate. Using the black thermocouple as a reference, the accumulation of solids as the reaction progresses can be seen. Scaling on the reactor walls is responsible for some of the indicated lack of clarity, but reaction precipitates are the primary cause.

Figure 22. Flow Chart for SST Test.

Figure 23. SST Reaction Progression and Elapsed Time from Start of Lithium Hydroxide Addition.

4.3.1 SST TEST SOLIDS WASHING

The same solids washing steps were followed as in the previous runs. Samples of both the filtrate and the filter cake were taken for analysis after each filtration step (Figure 24). Appendix B contains the analysis results. The final washed cake was a white, fluffy, highly crystalline material. The third and fourth filtrates were water clear, indicating the majority of residual dichromate was washed out in the first two washes. This is verified by analytical results, showing the dichromate readily washes from the cake.

Figure 24. Filtrate and Cake Samples from SST Test.
(Left to right: Mother Liquor and initial cake, 1st, 2nd, 3rd, 4th wash filtrates and filter cake samples.)

XRD analysis of the unwashed cake indicates LiHT as the major species, with sodium carbonate as a minor component. Lithium phosphate is noted as a possible match to one of the unknown phases (Figure 25).

Phase	Composition	Concentration	PDF Number
Lithium Aluminum Carbonate Hydroxide Hydrate	$(\text{Al}_2\text{Li}(\text{OH})_6)_2\text{CO}_3 \cdot x\text{H}_2\text{O}$	Major	00-042-0729
Sodium Carbonate	Na_2CO_3	Minor	00-025-0815
Unknown(s)*	-	Trace	

*Lithium Phosphate (Li_3PO_4) (01-072-1963) is a possible match to one of the unknown phases. Further testing is necessary to confirm the phase.

Figure 25. X-Ray Diffraction Pattern of Sample “SST 4th Wash Filter Cake” with Degrees 2θ Along the X-Axis and Intensity (Counts) Along the Y-Axis.

4.3.2 SST TEST ALUMINUM REMOVAL

The initial damp filter cake weighed 145.58 grams. A portion of the cake was dried at 60°C overnight and indicates that the cake was 42.3% solids. A quantity of precipitates formed in the mother liquor after the initial filtration. This additional dried filter cake from continuing precipitation brought the total quantity of dried, unwashed cake to 123.1 grams.

ICP-AES results show that for the SST Test the initial LiHT filter cake retained 91.3 mole% of the total aluminum in the initial product slurry. Slurry volume from the reactor was 2205 ml. Initial filtrate (mother liquor) volume was 2110 ml.

4.3.3 SST TEST FILTER CAKE IMAGES

Final washed cake samples were taken and imaged with SEM (Figure 26). In these images, as in other tests, it is evident that the LiHT “sand rose” crystal shape has been broken down by the washing process. Crystallite edge joining that is the hallmark of the LiHT structure is not apparent. Instead, the platelets have agglomerated into large spherical particles (100-500 μm), composed of small shards and pieces roughly 1 μm X 2 μm , with thickness 50nm to 100nm. The EDS spectrum (Figure 27) for the sample indicates that carbon, sodium, oxygen, aluminum, and phosphorous are the major constituents. The presence of phosphorous indicates the thermodynamically stable phosphate form of LiHT. The carbon peak indicates the carbonate form of LiHT is also present, as there is a stoichiometric deficit with respect to phosphorous.

Figure 26. SEM Images of Sample “SST 4th Wash Filter Cake.”

Figure 27. Characteristic EDS Spectrum of Sample “SST 4th Wash Filter Cake.”

4.3.4 SST TEST CESIUM DECONTAMINATION

The SST test, as in the other tests, contained ^{133}Cs in the simulant composition as a surrogate for ^{137}Cs present in actual waste.

Cesium DF is calculated by the following equation:

$$\text{Cesium DF} = \frac{\text{Mass Cs in/Mass Al in}}{\text{Mass Cs out/Mass Al out}}$$

Cesium DFs for the SST tests are calculated for incremental (between washes) and cumulative cases and are presented in Table 6.

Table 6. SST Test Cesium Contamination.

	Aluminum	Cesium	Cesium Incremental DF	Cesium Cumulative DF
Simulant (mg)	23154	4.08		
Initial Cake (mg/kg)	140900	1.76	14.1	14
1 st wash Cake (mg/kg)	221000	0.107	25.8	364
2 nd wash Cake (mg/kg)	205700	0.04	2.5	906
3 rd wash Cake (mg/kg)	206500	0.02	2.0	1819
4 th wash Cake (mg/kg)	217600	0.017	1.2	2256

As can be seen from the data in the table above, the washing of the SST test solids was very effective with respect to cesium. LiHT does not retain alkali metals as part of the crystal structure and is easily decontaminated.

4.3.5 SST PARTICLE SIZE DISTRIBUTION

Volume-based and number-based PSD curves and histograms are presented in Figures 28 and 29. The volume-based histogram indicates the bulk of the particle mass/volume is 100 μm to 200 μm , with a substantial amount of particles down to 1 μm . Previous PSD curves of unwashed LiHT indicate a normal distribution should be expected. The difference between the curves can be attributed to the effect of particle washing in the Teflon beaker with magnetic stir bar, as well as the effect of vacuum filtration causing breakup of the LiHT crystal structure and re-agglomeration into large particles.

Figure 28. Sample “SST 4th Wash Filter Cake” 10130239 Represented as a Volume-Based Distribution.

Figure 29. Sample “SST 4th Wash Filter Cake” 10130239 Represented as a Number-Based Distribution.

4.3.5.1 SST Thermo Gravimetric Analysis

The TGA analysis indicates (Figure 30) approximately 36.2% LiHT solids (63.8% free water). This compares with oven dried samples (60°C) that indicate 42.3% solids. The discrepancy may be that decarboxylation or dehydration of the LiHT waters of hydration may take place at the TGA analysis conditions.

The analysis further indicates that 20.6% solids remains after calcining at 1000 °C. Degradation of the LiHT structure is likely at this temperature, and the resulting mineral forms are assumed to be Li₂O and Al₂O₃. In future work, this should be confirmed with XRD analysis.

Figure 30. TGA Analysis of Sample “SST 4th Wash Filter Cake” 10130239.

4.3.6 SST TEST FILTER CAKE SOLIDS SPECIATION

Phosphate analyses indicate that, following precipitation, nearly all of the phosphate remains in the filter cake. XRD analysis of the filter cake indicates the major component is the carbonate intercalated LiHT (LiHT-C; Li₂CO₃•4Al(OH)₃•3H₂O), with the possibility of lithium phosphate as one of the trace compounds. There is no existing XRD spectrum for the phosphate intercalated LiHT (LiHT-P; Li₃PO₄•6Al(OH)₃•nH₂O), and the potential exists for the actual phosphate containing compound to be LiHT-P, rather than lithium phosphate. In order to determine which

species is predominant, a simple mass balance considering each case can be performed utilizing analysis results.

The two cases considered are:

- Assuming all of the phosphorous in the cake is in the form LiHT-P, the cake would contain ~63 grams of LiHT-P and would also contain 0.6 mole of aluminum. The balance of the aluminum, 0.14 moles, is in the LiHT-C form. The carbonate demand for the 0.14 moles of LiHT-C is 0.035 moles, which balances very closely with the measured carbonate of 0.04 moles.
- Assuming all of the phosphorous is the lithium phosphate form, the cake would contain ~12 grams of lithium phosphate, leaving the entire balance of the aluminum, 0.74 moles, in the LiHT-C form. The carbonate demand for the 0.74 moles of LiHT-C is 0.184 moles, which is more than four times the quantity of carbonate in the cake analysis.

Since LiHT is known to be the major phase present in the cake from XRD analysis, it is clear from the two cases presented above that the filter cake phosphorous solids are in the LiHT-P form.

5.0 SUMMARY

A series of laboratory scale bench top tests were conducted to examine the ability of the LiHT precipitation process to remove aluminum from Hanford waste simulants. Three experiments utilizing a DST simulant, and one with a SST simulant were conducted. The results of these experiments proved that aluminum could be removed from the simulants with high efficiency, that the precipitate product was easily filterable, and that cesium was not integral to the precipitate and could be removed. In addition, phosphates present in the simulant were also retained in the LiHT solids (Table 7).

Table 7. Selected Initial Filter Cake Analytes.

Analyte	DST #1 Initial Cake (mole%)	DST #2 Initial Cake (mole%)	DST #3 Initial Cake (mole%)	SST Initial Cake
Al	82.7	93.8	95.8	91.3
Li	89.0	91.1	92.0	91.5
Na	7.7	13.6	21.6	8.6
Cs	9.1	15.0	25.7	9.0
P	97.5	98.3	99.2	99.8

Note: Values are calculated as a fraction of total ICP-AES results for the initial cake and mother liquor

The generation of sodium hydroxide could not be verified by the analytical techniques selected for the tests, but can be qualitatively inferred from the fact that LiHT was created in the process as indicated by XRD analysis and reaction stoichiometry.

Examples of the identification of the solids by XRD is shown in Figure 31 for two of the experimental runs.

Figure 31. Overlay of X-Ray Diffraction Patterns of Samples.
 “DST #2 Initial Filter Cake” (in pink), “DST #2 4th Wash Filter (in green), “SST Initial Filter Cake” (in blue), and “SST 4th Wash Filter Cake” (in red) with Degrees 2θ Along the X-Axis and Intensity (Counts) Along the Y-Axis.

5.1 ALUMINUM REMOVAL

Aluminum was removed with a high efficiency from the simulants and did not dissolve into the wash water during product decontamination (Figure 32).

Figure 32. Aluminum Concentration in Filter Cakes During Wash Progression.

Any residual aluminum in the filter cake interstitial liquid was readily washed out, as illustrated in Figure 33.

Figure 33. Aluminum Concentration in Filtrates During Wash Progression.

5.2 LIHT FILTRATION

The initial LiHT product slurry filtered rapidly through a 0.45 μm pore size PVDF filter medium. As the washing stages progressed, however, the filtration times increased substantially. This is likely due to the breakup of the well-ordered crystal structure into smaller platelets. The majority of the crystals re-agglomerated into large (100-500 μm) particles; however, a small portion of the product remained as submicron fragments (this is indicated by the bimodal distribution in some of the PSD histograms, and the large fraction of submicron particles in the number based distributions). These small particles are likely the cause of some degree of filter blinding, resulting in a gradual increase in filtration times to achieve a dewatered cake. In addition, the process of vacuum filtration in the Büchner funnel likely contributed to the fracturing of the crystallites. Figure 34 shows the filtration times required to remove free liquid from the DST #3 filter cake in the Büchner funnel during the wash progression. New filter papers were used for each wash iteration. The reduced dewatering time required for the final wash may be an indicator as to the extent of re-agglomeration of the crystallites.

Figure 34. DST Test #3 Filtration Times During Wash Progression.

A comparison of the PSD before washing (from previous Georgia Tech testing) to the final washed product from the SST Test illustrates the effect that the solids washing had on the particle sizes (Figures 35 and 36).

Figure 35. Unwashed Cake Particle Size Distribution from Georgia Tech Experiments.

Figure 36. Final Washed Cake from SST Test Particle Size Distribution (Volume Based).

5.2.1 CESIUM DECONTAMINATION

The filter cake solids were readily decontaminated by water washing. Figure 37 illustrates the effect of the ambient temperature water washing of the filter cakes. Again, the effect of the

crystallite breakup and re-agglomeration can be seen in the gradually decreasing decontamination efficiency as the washing stages progressed. Washing efficiency is a function of particle size and morphology as well as the salt concentration gradient between the wash liquid and the crystal interstitial liquid. The result is that larger particles with a more compact structure are less susceptible to the effects of the washing.

Figure 37. Filter Cake Cesium Decontamination During Wash Progression.

The exception to the general trend is DST Test #2, which indicates a very high level of Cs decontamination. What distinguishes the very high decontamination of DST #2 is the effectiveness of the second wash. For unknown reasons, the second wash in DST Test #2 achieved the same magnitude of decontamination as the first wash.

As a method to verify the validity of cesium removal for DST #2, both sodium and potassium reductions during the wash stages are plotted in Figure 38 along with cesium. This indicates that all alkali metals present in the simulant behave similarly, with the exception of lithium, which remains incorporated into the LiHT structure. Again, as the wash conditions for all of the tests were virtually identical, the reason(s) for the high removal efficiency are unknown. The results of this test do, however, demonstrate the potential to remove cesium to a high degree, even with the relatively crude washing method employed.

Figure 38. Alkali Metals from ICP in DST #2 Filter Cakes.

Waste classifications for disposal path determinations are located in 10CFR61.55, Table 2. For Class A waste, the cesium concentration must not exceed 1 curie per cubic meter. The stable isotope ^{133}Cs was used as a surrogate for ^{137}Cs in the LiHT tests, and the ICP-MS analytical results in mg/kg were converted to curies/ m^3 of ^{137}Cs . Calculated values in the final washed cakes from the four tests are presented in Table 8. Note that these calculations use the TWINS database ratio of ^{137}Cs to ^{133}Cs of ~20%. All final washed cakes indicate that they will meet Class A disposal requirements for ^{137}Cs , with the DST #2 filter cake meeting the limit by a wide margin. These calculations are inherently conservative, in that a LiHT particle density of 1.79 g/cm^3 was used in the calculations, rather than the bulk density.

Table 8. Analogous ^{137}Cs Concentrations in Final Washed Cakes.

	DST #1	DST #2	DST #3	SST
Final washed Cake (mg $^{133}\text{Cs/kg}$)	0.021	0.001	0.027	0.017
Final washed Cake (Ci $^{137}\text{Cs/m}^3$)	0.66	0.03	0.85	0.54

6.0 RECOMMENDATIONS

Additional laboratory scale testing is required to advance the LiHT process. Specific areas of investigation should include:

- Determine precipitation methods that increase yield while reducing cycle times. Examples of techniques that might be investigated to accomplish this include:
 - Reaction at higher temperatures.
 - Introduction of nucleation agents.
 - Use of ultrasound to increase crystallization rate.
 - Continuous precipitation with recycle.
 - Concentrate reactants during precipitation to increase super saturation.
 - Cooling reaction slurry after ripening.
 - Ripening at reduced temperatures.
- Determine solids washing methodologies that maintain the LiHT crystal structure, allowing further improvement to the already high degree of decontamination. Examples of techniques that might be investigated to accomplish this include:
 - Counter current solids washing.
 - Fluidized bed washing.
 - Elevated temperature washing.
- Verification of the formation of the phosphate intercalated LiHT compound, as well as other anionic species. Development of the XRD spectra for each of these species with the Rietveld refinement technique should be conducted to aid in the identification of the conditions leading to their formation.

APPENDIX A

DST TEST #1

This test was conducted with DST simulant components and protocol as specified in the Test Procedure. The specified gibbsite leaching protocol was followed; however, some undissolved gibbsite remained in the reactor after the specified leaching time had elapsed. Additional leaching time did not alleviate the remaining turbidity of the solution.

The test sequence for DST #1 is indicated in the flow chart as shown in Figure A-1. It contains all steps including gibbsite leaching, LiOH addition, crystal ripening at 90 °C (for 4 hours), filtration, and wash steps.

Table A-1. DST Test #1 Simulant Chemical Makeup (1-L Batch).

Reagent	MW	Target Molarity	Weight or Volume
NaOH	40	2.59	103.66 g
Na ₂ CO ₃	106	0.06	6.86 g
Na ₂ C ₂ O ₄	134	0.003	0.38 g
KNO ₃	101	0.19	19.68 g
NaNO ₃	85	0.91	77.76 g
NaNO ₂	69	1.15	79.44 g
Na ₂ SO ₄	142	0.007	1.02 g
Na ₃ PO ₄ · 12H ₂ O	380.1	0.007	2.81 g
NaCl	58.4	0.12	6.73 g
NaF	42	0.011	0.46 g
Na ₂ Cr ₂ O ₇ · 2H ₂ O	298	0.001	0.43 g
NaC ₂ H ₃ O ₂ · 3H ₂ O	136.1	0.04	5.48 g
CsNO ₃ solution	NA	1.05E-05	2.43 mL
Al(OH) ₃	78	0.882	68.80 g
LiOH · H ₂ O	42	0.441	18.52 g

Note: CsNO₃ solution is prepared by dissolving 210 mg reagent CsNO₃ salt in 250 mL water.

Figure A-1. Experiment Flow Chart for DST Test #1.

A.1 DST TEST #1 LiHT REACTION

In DST Test #1, the gibbsite leaching protocol employed was to add water, caustic, and gibbsite for extended, agitated leaching at 95°C. These conditions were maintained for 16 hours followed by one hour at 100 °C. At the end of this leach process, the solution was still not entirely clear, indicating that residual gibbsite remained in suspension (Figure A-2)

Figure A-2. DST Test #1 Simulant in the Reactor.

10wt% LiOH was added to the reactor at a predetermined rate to provide a one-hour addition period. Approximately 25 minutes after the start of the LiOH addition, a rapid formation of precipitate ensued, caused by the super saturated conditions in the reactor. The white precipitate continued to gradually form through the remainder of the LiOH addition, as well as the 4-hour ripening period.

Reactor contents were cooled to 60°C after the ripening period and the product slurry (1125 ml) was filtered through a 0.45 µm pore size PVDF filter, using vacuum filtration and a preheated Büchner funnel. Total damp, unwashed cake produced during this first run was 153 grams. Filtrate (mother liquor) volume was 940 ml. Samples of the filtrate and solids were taken for analysis as noted in the Test Procedure. The cake produced was yellowish in color due to the presence of sodium dichromate and physically resembled loose soft clay. The product filtered readily and was easily removed from the Büchner funnel. All filtrates were clear, with no indication of unfiltered solids. The XRD pattern of the solids indicates that the crystalline form of the material is LiHT, with only trace quantities of unknown compounds (Figure A-3).

Figure A-3. X-Ray Diffraction Pattern of Sample “DST Test #1” 10127924 with Degrees 2θ Along the X-Axis and Intensity (Counts) Along the Y-Axis.

A.2 DST TEST #1 SOLIDS WASHING

The solids filtered readily and were easily dewatered. Filtration time gradually increased during each successive wash cycle, likely due to the magnetic stir bar acting as a grinding media and abrading the LiHT product against the surface of the beaker. The final washed cake was a white, fluffy, highly crystalline material. The second through the fourth wash filtrates were water clear, indicating the majority of residual dichromate was washed out in the first wash (Figures A-4 and A-5). This is verified by analytical results showing the dichromate readily washes from the cake. Samples of both the filtrate and the filter cake were taken for analysis after each filtration step. Appendix B contains the analysis results.

Figure A-4. Filtration Apparatus, Washing Progression, and Final Washed Cake from DST #1.
 (Left to Right: Mother Liquor and Initial Cake, 1st, 2nd, 3rd, 4th wash filtrates and filter cakes,
 final washed filter cake close up.)

Figure A-5. Filtrate and Cake Samples from DST Test #1.
 (Left to Right: Mother Liquor and Initial Cake, 1st, 2nd, 3rd, 4th wash filtrates and filter cake
 samples.)

XRD and EDS analysis of the filter cake was performed on the filter cake after the fourth wash. Results for the initial filter cake are provided in Appendix B. No change in the spectra was noted after washing (Figure A-6).

Phase	Composition	Concentration	PDF Number
Lithium Aluminum Carbonate Hydroxide Hydrate	$(\text{Al}_2\text{Li}(\text{OH})_6)_2\text{CO}_3 \cdot x\text{H}_2\text{O}$	Major	00-042-0729
Unknown(s)	-	Trace

Figure A-6. X-Ray Diffraction Pattern of Sample “DST #1 4th Wash” 10127925 with Degrees 2θ Along the X-Axis and Intensity (Counts) Along the Y-Axis.

The XRD image indicates that the major constituent of the cake is LiHT with only trace unknowns.

A.3 DST TEST #1 ALUMINUM REMOVAL

The initial damp filter cake weighed 152.9 grams. A portion of the cake was dried at 60°C overnight and indicated that the cake was 46.3% solids. Net dry LiHT cake was 70.79 grams.

Theoretical yield is 96.80 grams dry cake (0.2205 mole LiHT), making actual yield, gravimetric basis of 73.1%. ICP-AES results show that for DST Test #1, the initial LiHT filter cake retained 78 mole % of the total aluminum in the initial product slurry.

The source of the relatively low aluminum removal stems from the continued precipitation in the mother liquor overnight. Visual observations indicate that the sample bottles contained approximately 50 vol% solids (Figure A-5), in what had been clear filtered liquid the day before. The reason for the incomplete precipitation at the completion of the ripening period is unknown. Since the large number of samples for the test required the utilization of all of the clarified mother liquor, it was not possible to quantify the solids in the sample bottles from DST Test #1 after precipitation occurred.

A.4 DST TEST #1 HYDROXIDE GENERATION

Free hydroxide is generated in the LiHT reaction by stripping carbonate and/or phosphate anions from its respective sodium salt. The reaction generates 2 moles of sodium hydroxide for every mole of LiHT product. Total alkalinity analysis by titration was performed for determination of carbonate and hydroxide concentrations, and TIC was used for determination of carbonate. The difference between the two yields the free hydroxide concentration.

The expected results for hydroxide generation were not able to be verified by the analysis methods that were selected. Qualitatively, the generation of hydroxide can be inferred from the fact that LiHT was actually generated in the reaction (as verified by XRD) and by the reaction stoichiometry.

A.5 DST TEST #1 FILTER CAKE IMAGES

Final washed cake samples were taken and imaged with SEM/EDS (Figure A-7). In these images, as in other tests, it is evident that the LiHT “sand rose” crystal shape has been broken down by the washing process. Crystallite edge joining that is the hallmark of the LiHT structure is not apparent. Instead, the platelets have agglomerated into large spherical particles composed of small shards and pieces roughly 1µm X 2µm, with thickness 50nm to 100nm. A side-by-side comparison of the effect of solids washing can be seen in Figure A-8.

The EDS spectrum for the sample indicates that carbon, sodium, oxygen, aluminum, silicon, and phosphorous are the major constituents. The silicon originates from the elevated temperature etching of the reactor vessel by sodium hydroxide, while the presence of phosphorous likely indicates what is believed to be the thermodynamically stable phosphate form of LiHT. The carbon peak indicates the carbonate form of LiHT is also present, as there is a stoichiometric deficit with respect to phosphorous.

Figure A-7. SEM Images and EDS Analysis of Sample "DST Test #1 4th Wash."

Figure A-8. SEM Images of LiHT Precipitate Before Solids Washing (Left) and After (Right).

A.6 DST TEST #1 CESIUM DECONTAMINATION

DF is calculated by the following equation:

$$\text{Cesium DF} = \frac{\text{Mass Cs in/Mass Al in}}{\text{Mass Cs out/Mass Al out}}$$

Cesium DFs were calculated for incremental (between washes) and cumulative cases and are presented in Table A-2.

Table A-2. DST #1 Incremental and Cumulative Filter Cake Cesium DF.

	Aluminum	Cesium	Incremental DF	Cumulative DF
Simulant (mg)	23800	2.04		
Initial Cake (mg/kg)	59760	1.08	4.7	5
1st wash Cake (mg/kg)	66530	0.154	7.8	37
2nd wash Cake (mg/kg)	38520	0.033	2.7	100
3rd wash Cake (mg/kg)	77000	0.024	2.7	275
4th wash Cake (mg/kg)	65440	0.021	1.0	267

These results indicate that cesium is readily removed from the LiHT solids. Optimization is needed to determine the methodology best suited to solids washing. Of particular note are the incremental results that indicate a gradual decrease in washing efficiency, which may be due to the breakup and re-agglomeration of crystallites into larger particles that could shield salt ions from the washing process.

A.7 DST TEST #1 PARTICLE SIZE DISTRIBUTION

Volume-based and number-based PSD curves and histograms are presented in Figures A-9 and A-10. A bimodal distribution is evident, indicating that there is a fraction of particles that are centered in the 10 μm range and a separate population of particles centered around 250 μm . PSD test results from prior testing of unwashed LiHT solids indicates that a normal distribution curve centered around 50 μm should be expected, which may confirm the effect of the washing steps on particle size.

Figure A-9. Sample “DST Test #1 4th Wash” Represented as a Number-Based Distribution.

Figure A-10. Sample “DST Test #1 4th Wash” PSD Represented as a Volume-Based Distribution.

A.8 DST TEST #1 THERMO GRAVIMETRIC ANALYSIS

The TGA analysis (Figure A-11) indicates approximately 38% LiHT solids (62% free water). This compares with oven dried samples (60°C) that indicate 45.3% solids. The discrepancy may be that decarboxylation or dehydration of the LiHT waters of hydration may take place at the TGA analysis conditions.

The analysis further indicates that 14.7% solids remains after calcining at 1000°C. Degradation of the LiHT structure is likely at this temperature and the resulting mineral forms are assumed to be Li₂O and Al₂O₃. In future work, this should be confirmed with XRD analysis.

Sample: TGA1133 10127925 D S T 4th Wash
Size: 13.5350 mg
Method: Ramp
Comment: TGA1133 10127925 D S T 4th Wash.001

DSC-TGA

File: ...TGA1133 10127925 D S T 4th Wash.001
Operator: rjk
Run Date: 2010-11-12 03:21
Instrument: SDT Q600 V8.0 Build 95

Figure A-11. Sample “DST Test #1 4th Wash” TGA Analysis.

APPENDIX B ANALYTICAL RESULTS SUMMARY FOR DST #1

Analyte	Al	Li	Na	F	K	Cs	Cr	P	PO4	PO4	S	SO4	Cl	TIC	Alkalinity mg/l as CaCO3	Nitrate	Nitrite	pH	Conductivity (uS/cm)
Method	ICP- AES	ICP- AES	ICP- AES	ICP- AES	ICP- AES	ICP-MS	ICP- MS	ICP- AES	Hach	IC	ICP- AES	IC	IC		Titration	IC	IC		
Initial Cake (mg/kg)	71400	776.38	71420	180	1330	1.08	154.1	5883	<24	<0.242	164	440	3100	1760	NA	9500	10000	NA	NA
1 st wash Cake (mg/kg)	66530	14672	11950	44	822	0.154	39.71	1437	170	<0.242	75	160	470	NA	NA	1700	1800	NA	NA
2 nd wash Cake (mg/kg)	38520	2830.3	3023	16	212	0.033	9.845	1509	220	<0.242	43	78	75	NA	NA	390	360	NA	NA
3 rd wash Cake (mg/kg)	77000	7521.1	2259	16	162	0.024	16.13	1691	230	<0.242	48	61	46	NA	NA	290	260	NA	NA
4 th wash Cake (mg/kg)	65440	8810.3	1917	13	140	0.021	14.19	1456	240	<0.242	24	37000	40	1560	NA	240	210	NA	NA
Initial Filtrate (mg/l)	1271	8.19	73060	4000	5108	1.012	55.92	12.53	<25		BQL	33000	64000	1190	134898	130000	140000	13.82	200
1 st wash Filtrate (mg/l)	126	37.5	6729	<0.10	507	0.1001	7.978	BQL	0.9142		12.99	34000	13000	NA	92003	14000	15000	13.58	51
2 nd wash Filtrate (mg/l)	33	18.84	821	<0.10	56	0.0118	2.219	BQL	0.2856		4.065	32000	8100	NA	1200	6600	5400	12.76	7.3
3 rd wash Filtrate (mg/l)	8.58	8.99	89.1	<0.10	6.06	0.0007	0.386	BQL	0.1261		BQL	32000	7400	NA	160	5000	<0.125	11.87	780
4 th wash Filtrate (mg/l)	4.49	5.2	23.09	<0.10	1.35	0.001	0.108	BQL	0.2612		BQL	36000	9000	<2	65	5600	<0.125	10.62	170

APPENDIX B (continued)
ANALYTICAL RESULTS SUMMARY FOR DST #2

Analyte	Al	Li	Na	F	K	Cs	Cr	P	PO4	PO4	S	SO4	Cl	TIC	Alkalinity	Nitrate	Nitrite	pH	Conductivity
Method	ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-MS	ICP-MS	ICP-AES	Hach	IC	ICP-AES	IC	IC		Titration	IC	IC		
Initial Cake (mg/kg)	197200	28340	114700	4.511	7669	1.64	180.5	2339	1.849	180	320	730	2500	3910	NA	16000	17000	NA	NA
1st wash Cake (mg/kg)	200400	28197	7553	16	495	0.079	124.4	3036	4.434	440	154	310	150	NA	NA	710	610	NA	NA
2nd wash Cake (mg/kg)	126700	10528	946	25	40	0.003	53	1659	2.425	240	134	190	40	NA	NA	55	46	NA	NA
3rd wash Cake (mg/kg)	273300	28392	734	15	20	0.002	74.9	2732	1.817	180	226	170	29	NA	NA	13	<13	NA	NA
4th wash Cake (mg/kg)	268800	23259	757	24	19	0.001	66.6	3099	2.882	290	204	130	25	5030	NA	<13	<13	NA	NA
Initial Filtrate (mg/l)	1499	315.48	83130	4300	5869	1.2470	71.77	4.677	110	<0.24	154.5	39000	44000	1010	142674	150000	160000	12.84	270
1st wash Filtrate (mg/l)	329	84.31	6932	<0.1	480	0.1060	7.16	BQL	<0.10	<0.24	BQL	33000	9800	NA	10000	15000	15000	13.16	52
2nd wash Filtrate (mg/l)	79.78	23.51	369	<0.1	25.68	0.0057	0.412	BQL	<0.10	<0.24	BQL	33000	7500	NA	700	5400	4600	12.07	3.4
3rd wash Filtrate (mg/l)	34.85	16.22	23.84	<0.1	0	0.0002	0.283	BQL	<0.10	<0.24	BQL	34000	17000	NA	190	5600	<0.125	11.64	540
4th wash Filtrate (mg/l)	29.41	13.48	4.33	<0.1	0	0.0000	0.649	BQL	<0.10	<0.24	0.7	39000	7300	<2	140	5600	<0.125	11.69	340

APPENDIX B
ANALYTICAL RESULTS SUMMARY FOR DST #3

Analyte	Al	Li	Na	F	K	Cs	Cr	P	PO4	PO4	S	SO4	Cl	TIC	Alkalinity	Nitrate	Nitrite	pH	Conductivity
Method	ICP-AES	ICP-MS Li	ICP-AES	ICP-AES	ICP-AES	ICP-MS	ICP-MS	ICP-AES	Hach	IC	ICP-AES	IC	IC		Titration	IC	IC		
Initial Cake (mg/kg)	196000	30922	147000	6	10450	1.97	263.8	2802	N/A	11	365	750	1900	7720	N/A	17000	18000	N/A	N/A
1 st wash Cake (mg/kg)	241800	20567	21390	25	1560	0.296	73	3481	N/A	2500	167	230	360	N/A	N/A	2300	2000	N/A	N/A
2 nd wash Cake (mg/kg)	202300	23994	6165	21	361	0.098	52.2	2777	N/A	1900	97	110	77	N/A	N/A	710	450	N/A	N/A
3 rd wash Cake (mg/kg)	260600	46545	3298	<10	112	0.071	47.1	2200	N/A	1100	115	52	25	N/A	N/A	77	27	N/A	N/A
4 th wash Cake (mg/kg)	195900	17067	1194	7.4	37	0.027	23.3	911.5	N/A	190	57	34	27	4700	N/A	50	16	N/A	N/A
Initial Filtrate (mg/l)	1334	429.66	84500	<0.1	6173	1.2160	71.612	3.428	<25	<0.242	154.6	<0.75	6600	1070	142674	19000	19000	12.62	250
1 st wash Filtrate (mg/l)	476	132.37	9972	<0.1	697	0.1380	10.664	BQL	3.475	<0.242	BQL	<0.75	2800	N/A	14000	4500	3900	13.2	70
2 nd wash Filtrate (mg/l)	39.5	49.25	835.3	<0.1	63.3	0.0127	1.121	31.18	39.5	<0.242	BQL	<0.75	2600	N/A	1500	<0.125	<0.125	12.24	7.9
3 rd wash Filtrate (mg/l)	8.63	47.98	186	<0.1	13.93	0.0019	0.657	39.65	46.55	<0.242	BQL	<0.75	2700	N/A	480	<0.125	<0.125	11.75	2.3
4 th wash Filtrate (mg/l)	3.02	24.69	21.25	<0.1	BQL	0.0000	0.0715	22.64	34.35	<0.242	BQL	<0.75	2700	<2	170	<0.125	<0.125	10.75	570

APPENDIX B ANALYTICAL RESULTS SUMMARY FOR SST TEST

Analyte	Al	Li	Na	F	K	Cs	Cr	P	PO4	P04	S	SO4	Cl	TIC	Alkalinity	Nitrate	Nitrite	pH	Conductivity
Method	ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-MS	ICP-MS	ICP-AES	Hach	IC	ICP-AES	IC	IC		Titration	IC	IC		
Initial Cake (mg/kg)	161400	31468	123300	200	971	1.76	4046	25030	131.6	130	3552	<75	730	3910	N/A	30000	6400	N/A	N/A
1 st wash Cake (mg/kg)	221000	22716	12380	330	65	0.107	472	38030	118.3	12000	449	710	22	N/A	N/A	1500	190	N/A	N/A
2 nd wash Cake (mg/kg)	205700	46368	6192	300	33	0.04	1457	42720	108.1	11000	298	450	11	N/A	N/A	960	88	N/A	N/A
3 rd wash Cake (mg/kg)	206500	40865	5483	280	25	0.02	84.4	49030	106	11000	256	280	1800	N/A	N/A	360	33	N/A	N/A
4 th wash Cake (mg/kg)	217600	42273	4992	280	23	0.017	8222	35000	105.4	11000	219	270	2100	5030	N/A	320	24	N/A	N/A
Initial Filtrate (mg/l)	895	170.32	76210	3700	484.9	1.03500	9.77	2.277	<25	<0.242	1281	91000	19000	2270	82474	27000	60000	12.71	200
1 st wash Filtrate (mg/l)	330	278.15	6119	<0.10	61.5	0.10220	#	97.9	79.25	<0.242	93.56	37000	8700	N/A	7800	28000	8900	12.92	39
2 nd wash Filtrate (mg/l)	7.52	67.26	278	<0.10	1.86	0.00383	6.426	124	110	<0.242	7.73	33000	7600	N/A	800	5500	4500	11.82	3
3 rd wash Filtrate (mg/l)	2.16	103.15	48.64	<0.10	0.47	0.00046	0.907	89.79	110	<0.242	0.91	34000	6600	N/A	560	6600	<0.125	11.37	1800
4 th wash Filtrate (mg/l)	1.79	74.74	20.82	<0.10	0	0.00014	0.507	130.1	120	<0.242	0.75	33000	8500	8	540	<0.125	<0.125	11.35	1700