

Lithium Hydrotalcite Method for Alumina Removal from Hanford Waste - 10234

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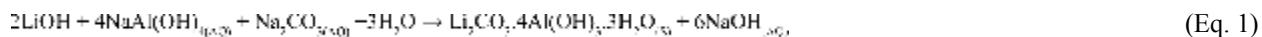
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ABSTRACT

The waste stored in the Hanford Tank Farms contains a high volume of alumina sludge, which poses significant processing challenges. Alumina sludge is difficult to filter because the fine particles rapidly blind filter surfaces causing frequent filter backwashing and chemical cleanings. Alumina sludge forms high-viscosity mixtures which compromise Pulse Jet Mixer (PJM) performance. Additionally, alumina forms amorphous solids which can plug process equipment and pipelines. Finally, alumina sludge retains hydrogen gas which can cause flammable conditions in Waste Treatment Plant (WTP) operations.

The traditional approach to managing the alumina is to add sodium hydroxide, which then leaches the alumina sludge and maintains its solubility throughout processing, but at the cost of significant additional volume of waste to be vitrified. The current projection of sodium hydroxide required to manage the alumina sludge will increase the mass of low-activity waste (LAW) by an estimated 80%. The large volume of sodium hydroxide is required to maintain alumina solubility at 5M Na and 25°C for WTP process operations. This increase impacts the quantity of immobilized low-activity waste (ILAW) glass and waste processing schedule over the baseline proportionally.

An alternative approach has been discovered by AREVA Federal Services that shows significant promise. Alumina may be removed from Hanford waste by reaction with lithium hydroxide to produce lithium hydrotalcite (LiHT) by the following reaction:



By this reaction, soluble sodium aluminate ($\text{NaAl}(\text{OH})_4$) is precipitated as lithium hydrotalcite ($\text{Li}_2\text{CO}_3 \cdot 4\text{Al}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$) and sodium hydroxide (NaOH) is regenerated for additional alumina sludge leaching. The amount of lithium required (1,000 MT) for this reaction is much less than the amount of sodium hydroxide (50,000 MT Na or 90,000 MT NaOH) required to maintain alumina solubility in WTP operations. Regeneration of sodium hydroxide by the LiHT reaction eliminates or substantially reduces the amount of sodium hydroxide to be imported for alumina sludge leaching.

The lithium hydrotalcite forms large (50 μm) particles that are easily separated by conventional filtration and decontaminated of cesium-137 by water washing. The clean, dried lithium hydrotalcite may bypass the WTP pretreatment unit and be used as a glass former in ILAW glass or be disposed in another approved waste form. The amount of lithium used in producing lithium hydrotalcite is less than one-half the amount used in the LAW glass formulation. Therefore, the use of LiHT as a glass former does not increase the volume of LAW glass, and the reduction of sodium hydroxide substantially reduces the amount of LAW glass, WTP processing time, and lifecycle cost.

The lithium hydrotalcite process was initially discovered by AREVA Federal Services using thermodynamic simulation and then tested in one-liter laboratory experiments using DST simulants at Georgia Tech during winter 2007. The tests confirmed that the reaction occurs spontaneously and the product filters rapidly. Analytical results indicate high alumina yield (>95%) and high cesium decontamination ($\text{DF} > 2,000$). These experiments completed "proof-of-concept" validation to attain an estimated Technology Readiness Level of Three (TRL-3).

Keywords: Hanford waste, lithium hydrotalcite, alumina leaching, alumina removal, sodium hydroxide

INTRODUCTION

Removal of alumina from Hanford waste sludge is of critical importance to minimize the required amount of high-level waste (HLW) glass and the associated waste processing time/disposal cost in the Waste Treatment Plant (WTP). Alumina sludge forms high-viscosity mixtures and amorphous solids which compromise filter and Pulse Jet Mixer (PJM) performance. Also, alumina sludge retains hydrogen gas which can cause flammable conditions in WTP operations.

In the WTP flowsheet, sodium hydroxide is used for alumina dissolution. The amount of sodium hydroxide required to leach alumina sludge and maintain its solubility through WTP operations is estimated to increase the total Hanford waste sodium by 50,000 MT Na or more. This increases the processing schedule and mass of low-activity waste (LAW) glass over the baseline by ~330,000 MT immobilized low-activity waste (ILAW) glass. The large volume of additional sodium hydroxide is required because alumina has very low solubility in WTP processing conditions (0.25 M Al @ 2M NaOH). Thus, a large mass of additional sodium (50,000 MT Na or 90,000 MT NaOH) is required to dissolve and maintain solubility of alumina (8,710 MT Al) through WTP operations.

The LiHT process is proposed to remove the alumina from the waste prior to WTP processing. A block flow diagram of the proposed process is shown below.

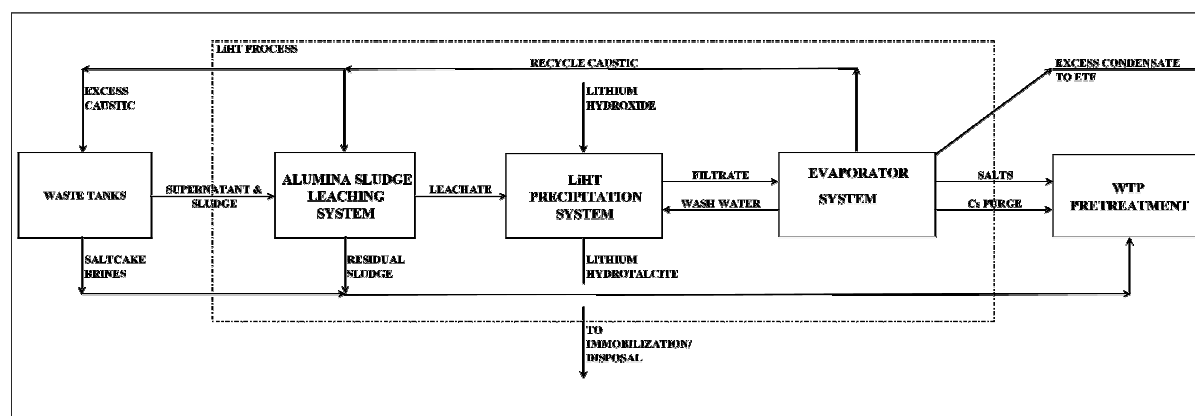


Fig. 1. Flow diagram of the proposed LiHT process.

Saltcake brines, low in sodium hydroxide and alumina sludge, bypass the LiHT process and are fed directly to the WTP. Sludge and supernatant, high in alumina and sodium hydroxide are heat leached using native and recycled sodium hydroxide. After leaching, the residual sludge (which is low in alumina) is fed to the WTP. Leachate, containing dissolved sodium aluminate, is filtered and reacted with lithium hydroxide. The resulting LiHT precipitate (containing the alumina) is separated, washed, and dried and transferred to immobilization and/or direct disposal. Filtrate from the LiHT process is concentrated by evaporation to distill and recycle wash water. Concentrated sodium hydroxide is recycled to alumina sludge leaching; excess caustic is returned to waste tanks or partially purged to WTP. Excess distilled water is exported to the Effluent Treatment Facility (ETF), and sodium salts are transferred to the WTP.

The LiHT reaction has been demonstrated with Hanford single-shell tank (SST) and double-shell tank (DST) simulants in one-liter bench-scale experiments. Analytical results of proof-of-principal LiHT experiments concur with literature reports and thermodynamic models of the method. The technology readiness level (TRL) of the process is estimated to be TRL-3 as defined by the *DOE EM Technology Readiness Assessment/Technology Maturity Plan Process Guide*, March 2008.

Because the LiHT process has the potential to dramatically reduce the alumina sludge mass to be processed through WTP, the sodium hydroxide demand for leaching and maintaining alumina solubility, and the lifecycle cost of Hanford waste treatment, the process development and demonstration effort will be accelerated to expedite implementation. Development efforts of laboratory validation, chemical research, process development, unit operations testing, and pilot plant integration will be advanced rapidly by using the accomplishments of prior

research, the consultation with subject-matter experts, and utilization of proven technologies for nuclear service. The proposed multi-phased development path will provide a sound basis for performing system design for a full-scale process operating in a radioactive environment. Supporting engineering analyses and flowsheet development work will clearly define the process conditions and interfaces within the overall Hanford site waste treatment facilities.

BACKGROUND

Hanford waste contains abundant alumina (8,710 MT Al) from plutonium production operations. Currently, less than 30% of total alumina is dissolved as sodium aluminate ($\text{NaAl}(\text{OH})_4$). Upon cooling and/or dilution to 25°C and 5 M Na (WTP processing requirements), most (>90%) of the alumina in Hanford waste will precipitate as sludge, amorphous gels, or mineral scale. To prevent precipitation of alumina during WTP operations, sufficient sodium hydroxide must be added to the waste to dissolve and maintain alumina solubility through WTP operations. However, addition of sodium hydroxide may cause sodium phosphate and sodium oxalate to precipitate in WTP operations.

To understand the large sodium hydroxide demand, the following analysis illustrates the relationship between ionic strength and hydroxide concentration on alumina solubility. For the alumina dissolution reaction



The solubility product is

$$K_{sp} = [\text{Al}(\text{OH})_4^-][\text{OH}^-] \quad (\text{Eq. 3})$$

A plot of $1/K_{sp}$ vs. Ionic Strength of experimental data at 25°C is shown in Fig. 2.

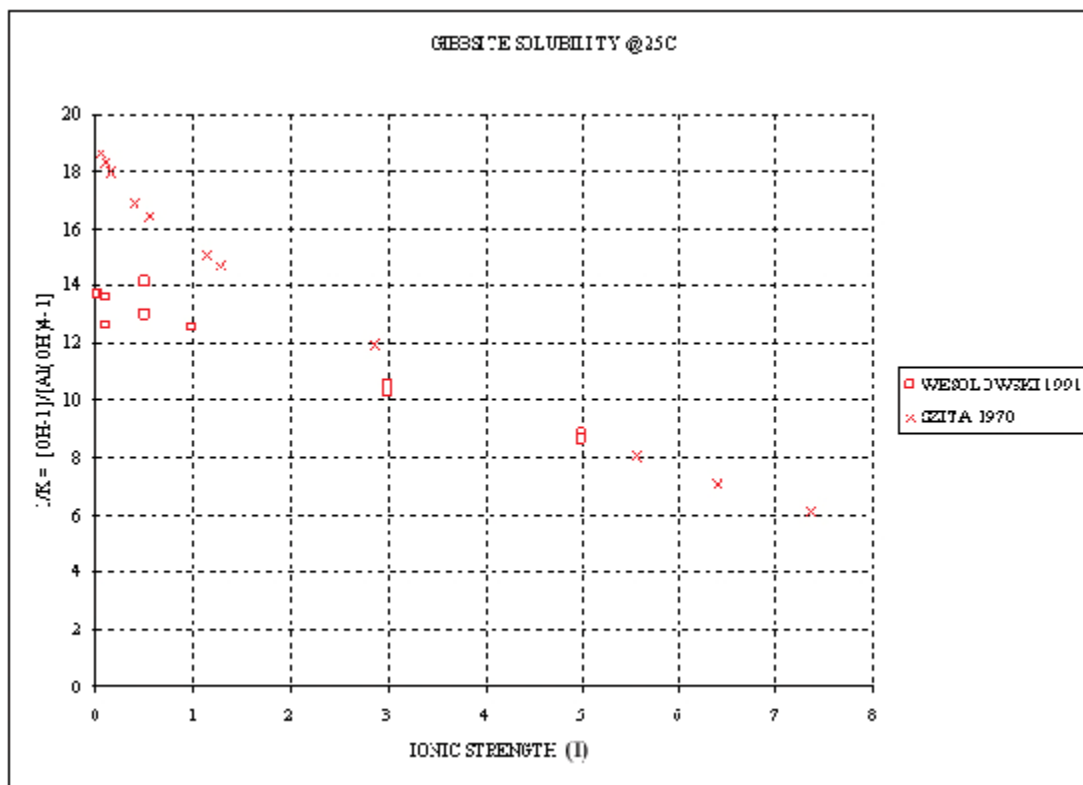


Fig. 2. Alumina solubility as a function of ionic strength.

The experimental data indicates that the amount of sodium hydroxide to dissolve alumina decreases with increasing ionic strength (the concentration of dissolved species). Thus adding non-hydroxide salts to a saturated alumina solution increases alumina solubility. The “enhanced alumina solubility” due to the “salt effect” has been measured in Hanford waste in high ionic strength of concentrated (>5M Na) supernatants. For example, the solubility of alumina in a 3M NaOH solution may be increased by ~80% by adding 5M of NaNO₃ salt.

Unfortunately, the “salt effect”, as applied to Hanford waste processing, is often misunderstood. To process Hanford waste, the total sodium concentration must be diluted to less than 5M Na to dissolve all sodium salts (e.g. NaNO₂, NaNO₃, Na₂CO₃, Na₂SO₄, Na₃PO₄). By doing this, the “salt effect” works against alumina solubility. Maximum alumina solubility occurs when the total sodium is only sodium hydroxide. For example, at 5 M Na, maximum alumina solubility occurs at 5M NaOH (0.675M Al). At constant 5M Na, other anions dilute hydroxide and lower alumina solubility (e.g. 4M NaOH + 1M NaNO₃ has lower alumina solubility than 5M NaOH). Theoretically 5M NaNO₃ + 0 NaOH has near zero (1E-8 M) alumina solubility. Thus, dilution with non-hydroxide salts (aka “salt effect”) lowers alumina solubility when the waste is diluted to 5M Na. Large amounts of sodium hydroxide must be added to displace non-hydroxide salts in 5M Na solution to dissolve alumina sludge. To solubilize all alumina sludge, enough sodium hydroxide must be added to increase the sodium hydroxide from 20% to 40% of total sodium salts.

At a concentration of 5M NaOH, I ~ 5.8, and from Fig. 2.

$$1/K_{sp} = 8 \quad \text{(Eq. 4)}$$

Thus, 8 moles of OH⁻¹ are required to maintain the solubility of 1 mole of alumina in equilibrium at 25°C and 5M NaOH. From this analysis, the sodium hydroxide demand for Hanford alumina solubility may be estimated:

$$8,710 \times 0.9 \times 8 \times 23/27 \times 0.89 = 47,545 \text{ MT Na} \quad \text{(Eq. 5)}$$

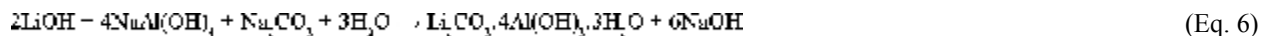
Where:

- 8,710 = MT Al in Hanford inventory
- 0.9 = fraction of alumina that is precipitated after dilution to 5M Na
- 8 = 1/K_{sp} = [OH⁻¹]/[Al(OH)₄⁻¹]
- 23/27 = Na/Al Atomic weight ratio
- 0.89 = Fraction of leachable alumina (11% as aluminosilicates)

The sodium hydroxide demand (47,500 MT Na) for alumina solubility at 5M Na & 25°C is approximately equal to the total sodium in Hanford waste (48,800 MT Na). Other factors, such as the existing NaOH inventory and the reduced alumina solubility in 2M OH, offset each other so that the net sodium hydroxide demand roughly doubles the waste Na inventory. Thus sodium hydroxide leaching of alumina sludge is a highly inefficient process; to leach <10,000 MT Al requires doubling the waste mass, processing time and cost. In addition, alumina, in its present form, is prone to precipitate as an amorphous gel or mineral scale. For these reason, the LiHT process was developed to remove alumina and recycle sodium hydroxide to conserve the mass of Hanford waste and ease waste processing.

LABORATORY EXPERIMENTS

The potential method for using a lithium salt to remove alumina and regenerating sodium hydroxide was discovered by AREVA Federal Services by a literature search of alumina precipitation methods. The reaction of lithium hydroxide with alumina results in precipitation of lithium hydrotalcite ($\text{Li}_2\text{CO}_3 \cdot 4\text{Al}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$) and regeneration of sodium hydroxide:



To determine the extent and selectivity of the LiHT reaction, thermodynamic models were developed for hydrotalcite reactions in Hanford waste. Several waste types were simulated, and mass balances were generated to guide experimental work. In each case, the hydrotalcite precipitation was energetically favored and the extent of reaction was near-complete.

To demonstrate the viability of the hydrotalcite precipitation process using soluble lithium salts, a two-phase laboratory program was privately funded and conducted by AREVA at Georgia Institute of Technology (Georgia Tech). Phase One experiments were conducted during the summer of 2007. The experiments were planned to test the temperature and pH ranges of the LiHT reaction. It was determined that high alumina yield (>93%) was obtained at high temperature (100°C) and high pH (>14). From those results, it was concluded that the reaction can be performed directly in concentrated caustic waste without dilution or partial neutralization and at elevated temperature to maximize the rate of reaction and alumina yield. Also, carbonate does not limit yield; other anions which are abundant in Hanford waste (e.g. PO_4^{-3} , OH^{-1} , NO_3^{-1} , NO_2^{-1}) may substitute in a carbonate depleted feedstock.

The Phase Two experimental matrix was designed to test the sensitivity of the Li/Al mole ratio, the lithium reagent (LiNO_3 & LiOH), the reaction period, solid/liquid separability, and the amount of wash water for cesium decontamination. The reactions were conducted near the boiling point of the solution (~100°C) where alumina has the highest solubility in caustic solution at atmospheric pressure. The separations (slurry filtration and product washing) were performed at 60°C.

For each experiment, one liter of DST simulant (7.2M Na, 3.1 M free OH^{-1}) was heated to 90°C , then fortified with solid $\text{Al}(\text{OH})_3$ to simulate heat leaching of alumina sludge into hot supernatant (Photo A, Fig. 3). A total of 128 grams/liter of alumina (1.6 M Al) were heat leached into the DST simulant using native sodium hydroxide. In these experiments, aqueous solutions of lithium hydroxide or nitrate were used as the reagents. A total of 19.5 grams of lithium hydroxide or 56.1 grams of lithium nitrate (0.8 M Li) was used.

Based upon observation of reaction progress, nucleation and growth of lithium hydroxalcite appeared spontaneous and slightly exothermic ($\Delta T = 5^{\circ}\text{C}$) as indicated by the suspended LiHT particles (Photo B, Fig. 3). Reaction times for the experiments ranged from 15 minutes to one hour.

The slurries were deliquored and washed using a büchner funnel (Photo C, Fig. 3) with fine frit media. The slurries dewatered rapidly (~ 100 ml/min) on the filter indicating high cake permeabilities. Within 10 minutes, the cakes were drained of free liquid. Each filter cake was re-pulped and dispersed in 1-liter of deionized (DI) water and re-filtered. The washing procedure was repeated two to four times for each experiment. (Photo D, Fig. 3). Based on observation, residual chromium (seen as yellow) in the product cake and spent wash, the extent of decontamination was near complete after 2 one-liter washes. (Photo E, Fig. 3). After cooling to ambient temperature and settling for one day, the filtrates did not produce settled solids, thus indicating that the LiHT reaction was complete before filtration.

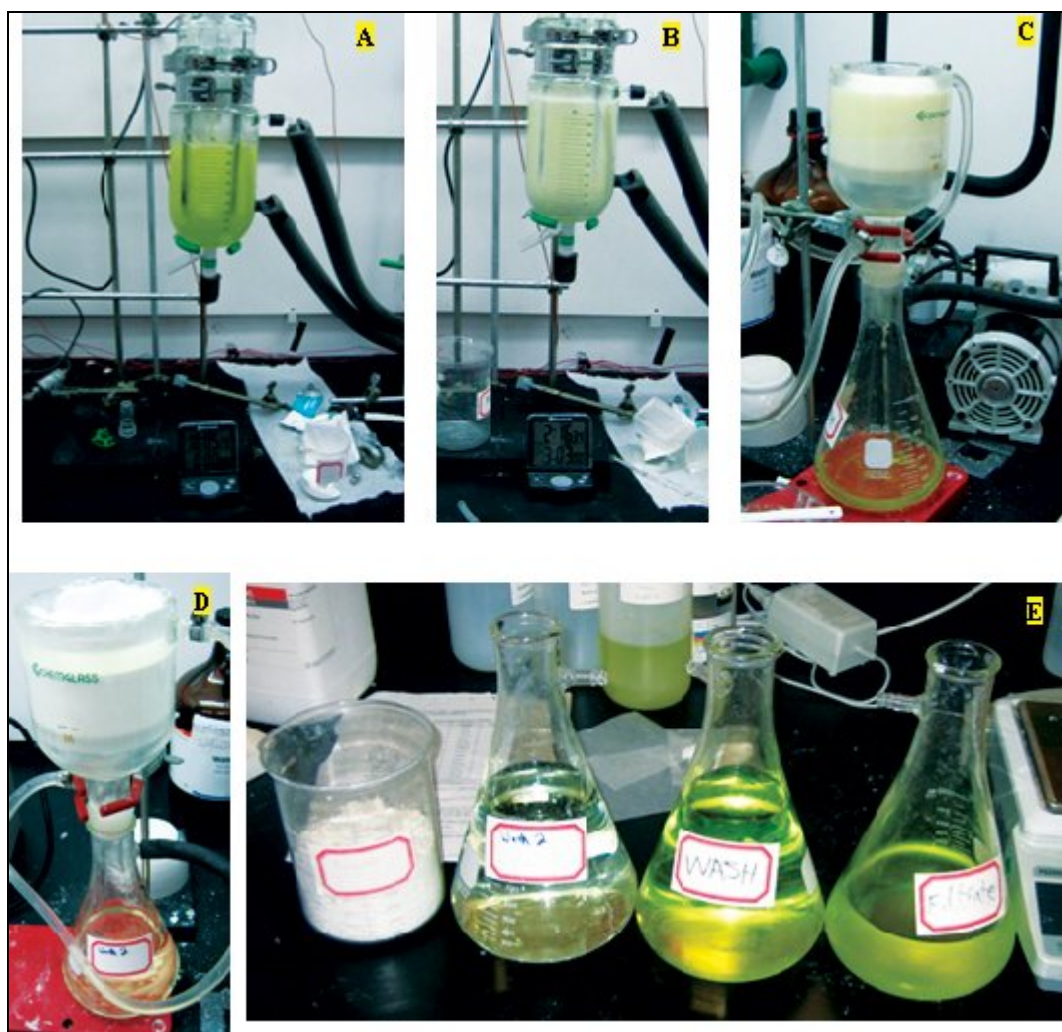


Fig. 3. Experimental sequence photographs at Georgia Tech.

The filter cake drained rapidly, and the texture resembled soft clay (Fig. 4). The products were oven-dried at 90°C to remove residual filter cake moisture. The dried product is a free-flowing, hygroscopic bright white powder. The products were sampled for analysis.



Fig. 4. Photograph of filter cake texture.

EXPERIMENTAL RESULTS

Results of X-Ray Photoelectron Spectroscopy (XPS) analysis of the LiHT product are shown in Fig. 5.

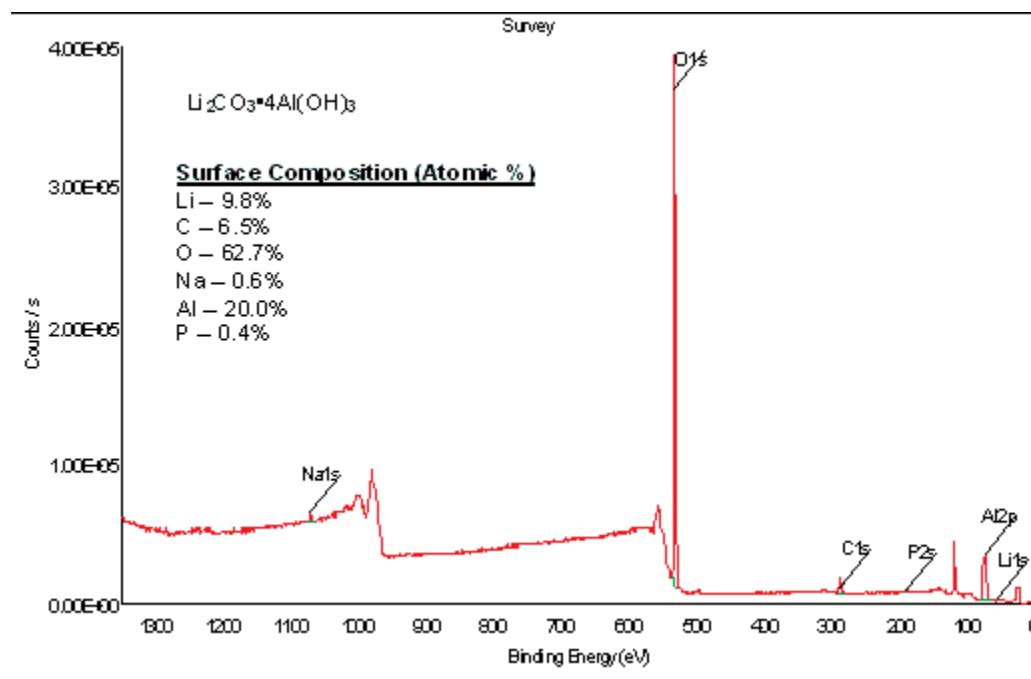


Fig. 5. XPS Analysis of Anhydrous Lithium Hydroxalcite.

The XPS analysis identified the dried product as anhydrous Lithium Carbonate Hydroxalcite with an approximate formula of $\text{Li}_2\text{CO}_3 \cdot 4\text{Al}(\text{OH})_3$ with a 1:2 Li/Al atomic ratio. The XPS survey indicated that the major surface elements were lithium, carbon, oxygen, and aluminum. In addition, trace amounts of sodium and phosphorous were detected. The surface concentrations of the detected elements are very close to the theoretical values (ignoring hydrogen which cannot be detected by XPS).

Results of mass spectroscopy analysis of LiHT are shown in Table I.

Table I. - Phase Two Product MS Analytical Results

SAMPLE #		2	6	9	11
RUN #		1	2	3	3
FEED Li/Al		1	0.5	0.5	0.5
WASHES		2	2	2	4
	MW	mg/kg	mg/kg	mg/kg	mg/kg
Cl	35.45	85	150	150	7.8
N	14.01	740	620	1,000	28
Al	26.89	320,000	460,000	490,000	340,000
Cs*	132.91	0.37	0.65	0.74	0.085
Li	6.94	35,000	52,000	54,000	36,000
Na	22.99	5,200	11,000	14,000	1,300
TOTAL		361,025	523,771	559,151	377,336
Li/Al		0.424	0.438	0.427	0.410
Cs DF		461	377	353	2,131
Na DF		457	310	260	1,941
Cs Ci/m ³		40	71	81	9

*below quantitation limit

Although the lithium dose was higher in Run #1, the MS results indicated an average Li/Al of 0.42. Increasing lithium above stoichiometric (1:2 Li/Al) as in Run 1 did not increase lithium in the product.

There appears to be no direct correlation between run time and product quality. Run #3 was done rapidly (LiOH addition < 30 minutes) and produced equivalent yield to the other runs. This result indicates that the reaction rate at 90°C is rapid and long retention time is not necessary to complete the reaction.

The extent of decontamination for each experiment was directly proportional to the dilution and displacement of soluble species by wash water. Cesium measurements were below the analytical quantitation limit, and the cesium decontamination factor (DF) exceeded the sodium DF in all cases. Both Na and Cs decontamination were very high (DF~2,000) after four one-liter re-pulp washes. This result indicates Cs and Na were not measurably included in the hydrocalcite crystal structure and are extracted from interstitial liquor by water washing.

Based on a Cs-137/Cs-133 ratio of 0.5 (typical for Hanford DST waste), total radioactivity ranges from 9 to 81 Ci/m³ in the dried powder product. At the highest value, this loading is 1.7% of the Class C disposal limit (4,600 Ci/m³). After four one-liter washes, Sample #4 had a cesium concentration (Cs = 9 Ci/m³) less than the Class B disposal limit (44 Ci/m³).

Product drying results are shown in Fig. 6.

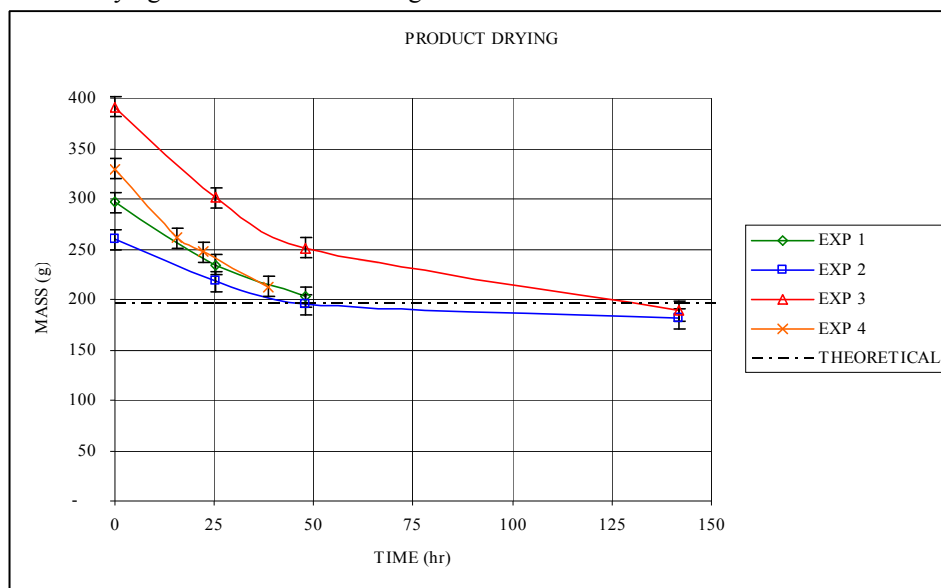


Fig. 6. Product drying results.

The products were dried in an oven at 90°C for several days to remove residual cake moisture. The graph indicates the moisture loss during the drying process. Although there was a wide variation in initial wet cake mass (260 to 390 g), the final dried masses were within 93% of the theoretical yield. Theoretical yield for this experiment, shown as the dotted line in Fig. 10, was 197.2 grams.

Particle size distribution for dried product from Run #3 is shown in Fig. 7. The particle size distribution was measured by dry screening of the product.

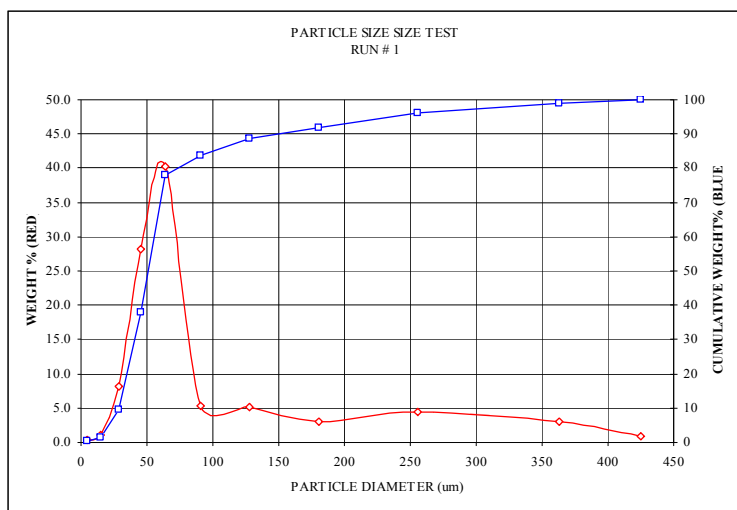


Fig. 7. Product particle size distribution.

Mass-averaged particle size was 50µm, with few (0.43%) particles below 5 µm. The uniform particle size improves permeability and enhances solid/liquid separation by creating a uniform void distribution within the filter cake. By this method, clean wash water can remove interstitial contamination by dilution and displacement from the filter cake.

Scanning light microscopy (SEM) showed that the particles are comprised of 5 µm LiHT crystallites aggregated into 50 µm spheroidal particles. It is expected that the aggregates are shear sensitive. Literature sources indicate that

high shear may disintegrate hydrotalcite aggregates into individual 5 μm LiHT crystallites; low shear may re-aggregate the particles into large spheres. High shear may be used to remove residual trapped contaminants from the aggregates and low shear may be used to reassemble the particles into large aggregates for solid/liquid separation.

During fractional crystallization pilot testing at SRNL in July 2008, a sample of SST simulant was heated to $\sim 80^\circ\text{C}$ and solid lithium nitrate was added in a 1:2 mole ratio of Li/Al. The resulting LiHT slurry was filtered and washed. An XRD analysis of the filter cake is shown in Fig. 8 below. The analysis identified lithium carbonate hydrotalcite ($\text{Li}_2\text{CO}_3 \cdot 4\text{Al}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$) and lithium carbonate (Li_2CO_3).

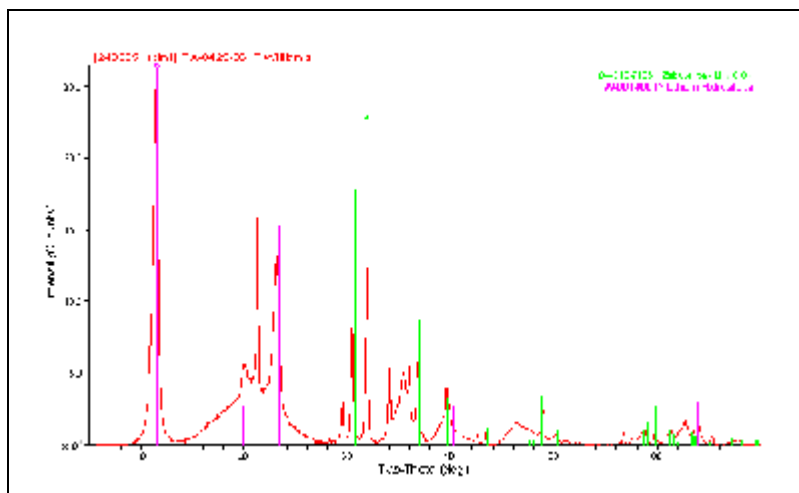


Fig. 8. XRD of LiHT precipitated from SST stimulant.

Analytical results of proof-of-principal lithium hydrotalcite experiments concur with literature reports and thermodynamic models of the method. From experimental results, it may be concluded that aqueous sodium aluminate can be rapidly precipitated, separated, and decontaminated in high yield from SST and DST simulants by the addition of soluble lithium salts and precipitation of lithium hydrotalcite. LiHT forms $\sim 5 \mu\text{m}$ crystallites and large (50 μm) aggregates which filter rapidly and decontaminate with water washing. The reaction regenerates sodium hydroxide for recycle to leach alumina sludge. The TRL of the LiHT process is estimated to be TRL-3 as defined by the *DOE EM Technology Readiness Assessment/Technology Maturity Plan Process Guide*, March 2008 “Analytical and experimental critical function and/or characteristic proof-of-concept”.

FUTURE DEVELOPMENT WORK

Because the lithium hydrotalcite process has the potential to dramatically reduce the alumina sludge mass to be processed through WTP, the sodium hydroxide demand for maintaining alumina solubility, and the lifecycle cost of Hanford waste treatment, the process development and demonstration effort will be accelerated to expedite implementation. Development efforts of laboratory validation, chemical research, process development, unit operations testing, pilot plant integration, will be advanced rapidly by using the accomplishments of prior research, the consultation with subject-matter experts, and utilization of proven technologies for nuclear service.

The scope of the proposed LiHT development program is detailed in report LiHT-3002038 *Test Program for Alumina Removal and Sodium Hydroxide Regeneration from Hanford Waste by Lithium Hydrotalcite Precipitation*. Phase 1 of the LiHT development program is designed to achieve a TRL of four (TRL-4) “Component and/or system validation in a laboratory environment.” Initially, previous LiHT experiments using DST and SST simulants will be repeated to independently validate prior results of product yield and purity. The product will be analyzed by several techniques to determine the selectivity of the reaction and the expected byproducts and contaminant concentrations. After the initial tests, parametric tests will be performed on several simulants to test a wide range of waste compositions.

In parallel, physicochemical research of lithium compounds will be performed to develop fundamental thermodynamic data of the stability of lithium compounds in multi-component Hanford waste. Results of this research will allow computer prediction of product yield and purity under a wide range of conditions and concentrations under equilibrium conditions. Parametric computer and laboratory tests will be performed on a variety of simulants with actual and expected waste compositions. These tests will be used to determine the best methods to harvest alumina from the waste, conserve sodium hydroxide, and accelerate waste treatment.

In addition to thermodynamic research, kinetic studies will be performed to determine the rates of dissolution of alumina sludge and precipitation of LiHT as a function of temperature and reagent concentration. These studies will determine the size of equipment for pilot- and full-scale applications. These experiments will use instrumentation for real-time measurement of chemical and physical properties to allow *in situ* observation and measurement of particle morphology, size distribution, growth, and dissolution rates during the leaching, LiHT precipitation, and evaporation experiments.

After several simulant parametric tests, actual waste tests will be performed on a graduated basis. These tests will be performed in a hot cell under controlled conditions. The initial tests will mimic the simulant tests using filtered DST and SST supernatants to leach fresh gibbsite and precipitate LiHT and use the cold work methods to re-pulp and wash the product. Upon successful completion of hot supernatant experiments, HLW sludge will be leached with DST and SST supernatants. Leaching experiments will follow the protocol of previous HLW sludge leaching experiments and use the specific conditions of the LiHT process to determine alumina yield and residual concentrations of HLW contaminants in the product. The purpose of these tests is to validate prior results and develop efficient techniques to leach alumina sludge and minimize radionuclide inclusion in the LiHT product.

A parallel research effort will be made in waste characterization and immobilization technologies. LiHT product from simulant and actual waste experiments will be tested for waste loading and regulatory compliance of potential waste forms. For the methods that meet disposal regulatory requirements, disposal paths will be researched in parallel to the LiHT process development effort.

Phase Two of the LiHT development program is designed to achieve a TRL of five (TRL-5) “The basic technical components are integrated so that the system configuration matches the final application in all respects.” Phase Two testing will be performed on a 100-liter “pre-pilot” scale using prototypical reactor/separators systems and simulant chemistry.

The goal of Phase Two is to determine the equipment type and configuration for the three basic functions (reaction, filtration, re-pulp washing) of the LiHT process. In addition, the supplementary processes of alumina leaching and fractional crystallization will be performed. Once the fundamental properties of dissolution, reaction, crystallization, and filtration rates are determined, the leaching, LiHT precipitation, fractional crystallization, and filtration operations will be performed by dedicated units in batch operation mode. At the pilot scale, dedicated equipment will be used in a sequential manner to allow continuous operation and recycles of process streams.

On a 100-liter scale, sufficient quantities of LiHT will be produced for testing of the primary unit operations of continuous elutriation, batch filtration, and fractional crystallization. The extent of product decontamination will be studied on a larger scale, and methods of re-pulp washing and product drying will be evaluated for efficacy. Filtrate and spent wash from the LiHT process will be evaporated and partially crystallized to recycle water, concentrate the sodium hydroxide liquor for recycle, and crystallize sodium salts. This method of pre-pilot development reduces the amount of waste produced and allows study of the effects of recycle streams on product yield and purity.

Results from the 100-liter tests will be used to specify process equipment for the pilot-scale facility. It is expected that the pilot-scale LiHT process will mimic the 100-liter operations of batch reaction, separation, and decontamination so that information gathered from the 100-liter scale will be transferable to the pilot system.

Phase Three of the LiHT development program is designed to achieve a TRL of six (TRL-6): “Engineering scale models or prototypes are tested in a relevant environment.” The purpose of pilot-scale testing is to demonstrate operation of the integrated LiHT process in a system that is approximately one-fifth (1/5) of a full-scale system. The size of the pilot system (10,000 – 50,000 liters) will depend upon the required capacity for full-scale implementation.

The required full-scale capacity will be defined by system planning of tank waste retrieval and the anticipated treatment methods. The LiHT process may treat waste prior to or during WTP operations and it may also support a separate parallel supplemental treatment facility. In each case, the fundamental process steps are the same: alumina leaching, LiHT precipitation, and spent wash evaporation and sodium salt crystallization. The integrated pilot plant will contain all three systems to allow continuous LiHT production and sodium hydroxide recycle.

The integrated pilot system will contain all unit operations and instrumentation expected to be used in the actual application. Pilot scale LiHT unit operations (e.g. reactor, filter) will be specified during the Phase Two pre-pilot studies. The pilot plant will be constructed with sufficient instrumentation and controls to allow fully automatic operation, emergency shutdown, and upset recovery situations. The pilot plant will run continuously for several weeks to provide sufficient information on system stability, product purity and yield. The system will be studied for the actual radioactive waste application. Process shielding requirements will be assessed, and equipment, instruments, and control systems will be evaluated for remote operation, reliability, maintenance, and replacement. Methods to clean and decontaminate vessels, pipelines, and instruments for maintenance and/or replacement will be developed and tested on the pilot scale.

The continuous production of LiHT will allow continuous product immobilization. Depending upon the results of waste characterization and research of immobilization technologies, processes of calcination, vitrification, and/or cementation may be used to process the LiHT into an immobilized waste form during pilot plant operations. The immobilization process may be integrated with the LiHT pilot unit or operate separately depending upon the desired end product.

Results of the Phase Three activities will be compared to laboratory and pre-pilot results, thermodynamic models, and to regulatory requirements for immobilization and final disposal. Information such as equipment capacity, system stability, and on-stream availability generated from pilot plant studies will be used to develop and design the full-scale modular process systems for the actual Hanford applications.

CONCLUSIONS

The proposed lithium hydrotalcite process has been demonstrated using Hanford SST & DST simulants on a one-liter scale. Results indicate that a high alumina yield (~95%) may be obtained in less than one hour by reaction with a soluble lithium salt. Analytical results identified the products as lithium carbonate hydrotalcite trihydrate ($\text{Li}_2\text{CO}_3 \cdot 4\text{Al}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$). The LiHT products were decontaminated of soluble species in direct proportion to the amount of wash water applied to the filter cake. Sodium hydroxide was regenerated by the reaction for recycle to leach alumina sludge.

Additional testing and expert reviews are planned to validate prior results and to develop process data required for scale up to pilot plant operations. The proposed multi-phased development path will provide a sound basis for performing system design for a full-scale process operating in a radioactive environment. Supporting engineering analyses and flowsheet development work will clearly define the process conditions and interfaces within the overall Hanford site waste treatment facilities.

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