Technology Maturation Plan for Aluminum Removal and Sodium Hydroxide Regeneration from Hanford Waste by Lithium Hydrotalcite Precipitation

Sebastien Guillot (AREVA Federal Services LLC)
Washington River Protection Solutions
Richland, WA 99352
U.S. Department of Energy Contract DE-AC27-08RV14800

EDT/ECN:	DRF	UC:	
Cost Center:	2GB00	Charge Code:	20700
B&R Code:		Total Pages:	30

Key Words: Lithium Hydrotalcite (LiHT), Aluminum, Precipitation, Lithium Hydroxide, Technology Maturation Plan

Abstract: This Technology Maturation Plan schedules the development process that will bring the Lithium Hydrotalcite waste pretreatment process from its current estimated Technology Readiness Level of 3, to a level of 6. This maturation approach involves chemical and engineering research and development work, from laboratory scale to pilot scale testing, to incrementally make the process progress towards its integration in a fully qualified industrial system.

TRADEMARK DISCLAIMER. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors.

Nancy A Fouad
Release Approval

1/27/2011
Date

Approved For Public Release

TECHNOLOGY MATURATION PLAN FOR ALUMINUM REMOVAL AND SODIUM HYDROXIDE REGENERATION FROM HANFORD WASTE BY LITHIUM HYDROTALCITE PRECIPITATION

Sebastien Guillot
AREVA Federal Services LLC

Date Published
December 2010

P.O. Box 850
Richland, Washington 99352

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Contractor for the U.S. Department of Energy
Office of River Protection under Contract DE-AC27-08RV14800

ABSTRACT

This Technology Maturation Plan schedules the development process that will bring the Lithium Hydrotalcite waste pretreatment process from its current estimated Technology Readiness Level of 3, to a level of 6. This maturation approach involves chemical and engineering research and development work, from laboratory scale to pilot scale testing, to incrementally make the process progress towards its integration in a fully qualified industrial system.

KEY WORDS

Lithium Hydrotalcite (LiHT), Aluminum, Precipitation, Lithium Hydroxide, Technology Maturation Plan

EXECUTIVE SUMMARY

The U.S. Department of Energy (DOE), Office of River Protection, is constructing a Waste Treatment and Immobilization Plant (WTP) for the treatment and vitrification of the underground tank wastes stored at the Hanford site. The WTP will pre-treat the waste to separate high-level (HLW) and low-activity waste (LAW) fractions. Aluminum is a significant fraction of the Hanford waste and is to be leached with sodium hydroxide (caustic leaching) for processing in the WTP. To facilitate the leaching, a large quantity of new sodium hydroxide must be added to the waste. To reduce the amount of sodium hydroxide required and potentially ease processing of aluminum bearing sludge and supernates, AREVA has invented and patented the Lithium Hydrotalcite process (LiHT), for aluminum removal and sodium hydroxide regeneration from Hanford waste.

The LiHT process has been successfully demonstrated on a laboratory bench scale with several waste simulants.

The purpose of this Technology Maturation Plan is to describe the activities and schedules that will be used to bring the LiHT process from the current estimated technology readiness level (TRL) of “3”, as defined by the U.S. Department of Energy *Technology Readiness Assessment Guide*, to a TRL of “6”, which will indicate that the technology is ready for insertion into a detailed design for baseline performance at Critical Decision Point 2 (CD-2).

TABLE OF CONTENTS

1.0	Introduction	1
1.1	Purpose of the Lithium Hydrotalcite Pretreatment Planning Project.....	1
1.2	Purpose of the Technology Maturation Plan.....	2
1.3	DOE Technology Maturation Process	3
2.0	Technology Readiness Assessment of the project.....	5
2.1	Initial Assessment of the LiHT Process Technical Maturity Level	5
2.2	Technology Heritage.....	6
3.0	Process Technology Maturation Plan	7
3.1	Objective	7
3.2	Key Technology Addressed.....	7
3.3	Approach.....	8
3.4	Scope.....	9
3.4.1	Phase I – Achieve TRL-4.....	10
3.4.2	Phase II – Achieve TRL-5	12
3.4.3	Phase III – Achieve TRL-6.....	13
4.0	Technology Maturation Plan Schedule	14
5.0	Technology Maturation Plan Cost Summary	16
6.0	References	17

TABLE OF APPENDICES

APPENDIX A. TRL Criteria Planning	18
---	----

TABLE OF FIGURES

Figure 1. Schematic of DOE EM Technology Readiness Levels **	5
Figure 2. LiHT Process Simplified Block Flow Diagram	8

TABLE OF TABLES

Table 1. Descriptions of DOE EM Technology Readiness Levels	4
Table 2. Technical Performance Plan	15
Table 3. Technology Maturation Plan Cost Summary (\$k).....	16

LIST OF TERMS

Abbreviations and Acronyms

AFS	AREVA Federal Services LLC
CSL	Continuous Sludge Leaching
DST	Double Shell Tank
DOE	U.S. Department of Energy
ECR	Electro-chemical Caustic Recovery
ESP	Environmental Simulation Program
ETF	Effluent Treatment Facility
HLW	High Level Waste
ILAW	Immobilized Low Activity Waste
LAW	Low Activity Waste
LiHT	Lithium Hydrotalcite Precipitation
MSE	Mixed Solvent Electrolyte
ORP	Office of River Protection
PMP	Project Management Plan
RPP	River Protection Plan
RMF	Rotary Micro Filters
SST	Single Shell Tank
TMP	Technology Maturation Plan
TRA	Technology Readiness Assessment
TRL	Technology Readiness Level
WRPS	Washington River Protection Solutions, LLC
WTP	Waste Treatment and Immobilization Plant

1.0 INTRODUCTION

This Technology Maturation Plan (TMP) provides the planning for maturing the Lithium Hydrotalcite (LiHT) process to support removal of aluminum in Hanford tank wastes prior to their vitrification, and the recycling of sodium hydroxide for further tank sludge solubilization and retrieval activities. This TMP is organized in a manner consistent with the U.S. Department of Energy *Technology Readiness Assessment (TRA) Guide*, ref. DOE G 413.3-4.

1.1 PURPOSE OF THE LITHIUM HYDROTALCITE PRETREATMENT PLANNING PROJECT

The U.S. Department of Energy (DOE), Office of River Protection (ORP) is constructing a Waste Treatment and Immobilization Plant (WTP) for the treatment and vitrification of the ~57 million gallons of liquid waste and sludge stored in the underground single- and double-shell tanks (SSTs and DSTs) at the Hanford Site north of Richland, Washington. The WTP will pre-treat the waste retrieved and transferred from the tanks to separate it into two fractions, high level waste (HLW, predominantly a solid containing stream) and low-activity waste (LAW, a liquid stream), which will be each processed separately into glass. Under the current waste retrieval projects and WTP flowsheets, sludge leaching using sodium hydroxide is the baseline process for solubilizing the estimated 8,710 MT¹ of aluminum in the tank waste to obtain sodium aluminate $[\text{NaAl}(\text{OH})_4]_{(\text{aq})}$, a waste form that can be processed at the WTP.

However, the additional amount of sodium, in the form of sodium hydroxide (NaOH) that will be required to dissolve tank waste aluminum and maintain sodium aluminate in soluble form under planned operating procedures is expected to substantially increase the total sodium load of the Hanford waste delivered to the WTP. The increased sodium inventory will lead to proportional increases in WTP processing time and operational cost, and in the volumes of ILAW glass that will be produced for storage or disposal. In addition to the large increase in waste mass, treatability studies have shown that the high silica content of the waste, combined with the further addition of NaOH to maintain aluminum solubility has the potential to generate aluminosilicate gels that could cause moderate to severe operational problems for the WTP, conditions requiring extensive maintenance and equipment replacement.

Therefore, removal of aluminum from the tank waste upstream or prior to WTP operations would help to minimize the waste processing time and operational cost of the WTP, and in reducing the amount of LAW glass produced by the WTP.

AREVA Federal Services, LLC (AFS) has invented and patented² the LiHT process that would both remove aluminum and its negative operational consequences from the waste process stream, and would provide, as a by-product, recyclable sodium hydroxide to use to leach aluminum from

¹ Aluminum 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*

² PCT International Application PCT/US2008/076589

sludge in tank waste. The proposed LiHT process utilizes lithium hydroxide as an additive to the aluminum rich aqueous supernate to precipitate the soluble sodium aluminate as lithium hydrotalcite (LiHT). LiHT may be separated by filtration and decontaminated with water washing. After drying, the LiHT would be available for immobilization and disposal in an approved LLW form.

As a prime contractor to the U.S. DOE, Washington River Protection Solutions, LLC (WRPS) is in the process of preparing long term strategic planning options/evaluations to accomplish the mission of the River Protection Plan (RPP) including evaluation and development of supplemental pretreatment options for Hanford tank waste. The LiHT process is one option to be evaluated.

1.2 PURPOSE OF THE TECHNOLOGY MATURATION PLAN

The purpose of this TMP is to describe the activities and schedules that will be used to bring the LiHT process from the current estimated technology readiness level (TRL) of “3”, as defined by DOE G 413.3-4, to a TRL of “6”, which will indicate that the technology is ready for insertion into a detailed design for baseline performance at Critical Decision Point 2 (CD-2).

The TMP process is designed to minimize technological risk associated with developing technologies such as the LiHT process. This TMP will provide a basis to carry the development of the LiHT process through successive developmental stages while keeping project risks to a minimum.

This TMP describes a plan for maturing the AFS LiHT technology from laboratory scale validation testing, through engineering-scale testing, to the construction of a ~1/5 full-scale integrated LiHT process test platform for implementation under field conditions. These different steps may be combined to reduce the duration and overall costs of the development, depending on schedule constraints and risk status.

Neither the LiHT process nor a similar process has been implemented at the Hanford tank farms using Hanford wastes. Therefore, this TMP describes the general process, equipment, work activities, and procedural requirements to bring the LiHT process to maturity. The work activities were defined using AFS process-engineering experience in developing chemical processes and deploying them into a nuclear environment. These activities were also developed using the results of past testing of Hanford waste-treatment technologies, evaluations of the designs for the LiHT process, and technology readiness assessments as described in DOE G 413.3-4.

LiHT technology is expected to interface with other Hanford waste treatment systems that are at a higher maturity level or are currently under parallel development. For example:

- Continuous Sludge Leaching (CSL) may be used upstream of the LiHT process to leach aluminum sludge and separate leachate from residual waste sludge;
- A filtration process based on rotary microfilters (RMF) may be used upstream of the LiHT process as another way to feed it with filtered supernate,
- Electro-Chemical Caustic Recovery (ECR) may be used downstream of the LiHT process to utilize filtrate from the LiHT process to concentrate sodium hydroxide for recycling to leach sludge, and reduce tank waste volume.

However, this TMP is focused at presenting the activities necessary to bring the LiHT process to a higher level of technological maturity, recognizing that some of these other interface systems are already at a more advanced TRL, and would be a part of the overall LiHT process. They will be incorporated in integrated demonstrations in the future steps of the technology development process.

The schedule of the implementation of the proposed work activities is dependent on authorization by DOE. The schedule will be organized by time periods related to the developmental progression of the maturation of the LiHT process over a three year timeframe.

1.3 DOE TECHNOLOGY MATURATION PROCESS

This TMP is written in accordance with the guidance of the US DOE TRA guide, ref. DOE G 413.3-4. The DOE technology maturation process assesses hardware, process operations, and programmatic status of technologies, and identifies benchmarks to evaluate the progress of bringing technologies to a standard readiness of implementation. This TMP describes the activities and schedules that will be used to resolve technology maturity issues for the LiHT process. Appendix A contains the four tables that list the TRL Lines of Inquiry for TRL-4 through TRL-6 that have been used by the project to develop this TMP and the test Program (ref. 0). The specific actions planned to address TRL-3 through TRL-6 items will be detailed after the Project Management Plan is prepared and released, and in a logical fashion as information is developed at each TRL, for the following TRLs.

The technology maturation process is a formal process involving DOE experts as well as subject matter experts in the technologies being developed. The technology readiness levels (TRLs) defined in the DOE technology maturation process range from lowest to highest level of readiness and highest risk. The levels as shown on Table 1 are TRL-1 through TRL-9, with TRL-9 representing the highest level of maturity. Figure 1 graphically shows the relationships between the TRL levels. DOE has established that a technology is suitable (i.e. risk acceptable) for implementation before commissioning if it has achieved a readiness level of 6, which will indicate that the technology is ready for insertion into a detailed implementation design.

Table 1. Descriptions of DOE EM Technology Readiness Levels

TRL #	Definition *	Details *
9	System operated over the full range	Technology operational in final form implementation under full range of wastes and operating conditions
8	System completed and qualified via test and demonstration	Technology proven to work under expected hot waste conditions. End of system development
7	Full-scale similar – or prototype – system validation in relevant environment	Demonstration of system prototype in a relevant environment including full range of simulants. Final design complete
6	Engineering/pilot scale similar – or prototype – system validation in relevant environment	Engineering/pilot scale demonstration in relevant environment including full range of simulants. TRL-6 begins true engineering development and prototype capable of performing all operations of a functional system
5	Laboratory scale, similar system validation in relevant environment	Basic technology integration to ensure operational compatibility. Testing with full range of simulants and small scale actual waste
4	Component system and/or system validation in laboratory experiment	Establish technological components that will work together. First step in establishing system compatibility. Testing with full range simulants and small scale actual wastes
3	Analytical and experimental characteristic proof of concept	Initiate active research and development. Analytical and laboratory scale validation studies. Validate system components. Determine parameters of interest and compare to analytical predictions for critical subsystems
2	Formulate technology concept and/or application	Develop practical applications of basic principles. Assemble publications and corroborative work. Moving from pure to applied research
1	Basic principles observed and reported	Translate scientific research to applied development. Paper studies of basic properties of technology and observations

Note *: Source - DOE G 413.3-4.

Figure 1. Schematic of DOE EM Technology Readiness Levels **

Note **: Source - DOE EM TRA/TMP Process Guide - Page 5, March 2008.

2.0 TECHNOLOGY READINESS ASSESSMENT OF THE PROJECT

2.1 INITIAL ASSESSMENT OF THE LIHT PROCESS TECHNICAL MATURITY LEVEL

No formal DOE technology assessments have been completed for the LiHT precipitation process. However, a series of laboratory bench-scale experiments using non-radioactive Hanford Waste simulants, have been performed to demonstrate the viability of the LiHT process.

AFS conducted a first series of scoping tests in 2007 with the support of the Chemical Engineering Department of the Georgia Institute of Technology (Georgia Tech), and in 2010 with the support of the 222-S Laboratory at US Department of Energy Hanford Site. These experiments are described briefly in ref. RPP-48376.

Confirmatory tests were performed in 2010 with the support of RJ Lee Inc. at the Center for Laboratory Sciences in Pasco, and are described in ref. RPP-RPT 48380.

The analytical results of the experiments concur with literature reports (ref. ISSN 0081-5993) and thermodynamic models of the LiHT process. In addition, AFS formally patented the LiHT process (ref. PCT/US2008/076589) and continues modeling of the process.

AFS's evaluation of the LiHT process and the analytical results of AFS's experiments resulted in AFS's initial evaluation of a TRL of three for the overall LiHT process. This evaluation conducted internally in the spirit of the DOE EM TRA/TMP Process Guide is summarized in ref. RPP-48379.

2.2 TECHNOLOGY HERITAGE

The aluminum industry uses the Bayer Process to extract aluminum oxide from bauxite ore by treating the ore with sodium hydroxide. The insoluble impurities are separated from the aluminum hydroxide solution, which is cooled, and the resulting precipitate is then filtered, and the filtered precipitate is processed to recover aluminum. The separation and removal of the sodium aluminate contained in Hanford tank wastes using the LiHT process is quasi analogous situation in that both the ore and the aluminum in the tank wastes require leaching with sodium hydroxide to solubilize the aluminum so that it can be separated from the mother liquor. Theoretically, the Bayer Process could be used to remove aluminum and regenerate sodium hydroxide from tank waste leachate. However, laboratory experiments using DST waste simulants experiments showed that a strict application of the Bayer Process is very slow (~5 days), the per-pass yield is ~50%, and the process would require crystal seeding and a high recycle rate to obtain optimum yield.

AFS has invented and patented a modification of the Bayer Process that overcomes the disadvantages of the application of the Bayer Process for aluminum removal from tank waste, mainly the slow pace and per-pass yield of the reaction. This alternative method is the LiHT process, which is similar to processes used in industry to produce low-cost synthetic hydrotalcites³.

The LiHT process begins with a tank waste containing aqueous aluminum in the form of sodium aluminate ($\text{NaAl}(\text{OH})_{4(\text{AQ})}$) such as would be present in sodium hydroxide leached tank waste. A 10% aqueous solution of lithium hydroxide (LiOH) is reacted with aqueous sodium aluminate ($\text{NaAl}(\text{OH})_4$) and aqueous sodium carbonate (Na_2CO_3), which is also present in the tank waste stream, to produce solid lithium hydrotalcite $\text{Li}_2\text{CO}_3 \cdot 4\text{Al}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$, and to simultaneously generate aqueous sodium hydroxide according to the reaction:

The solid lithium hydrotalcite (LiHT) can be easily separated by filtration from the mother liquor, thus removing aluminum from the waste treatment system. The generated sodium hydroxide is then available to be recycled to leach additional aluminum sludge according to the reaction:

The recovered lithium hydrotalcite is water-washed to remove cesium contamination, and dried. It can then be used as a WTP LAW glass former, or disposed of as another approved Low Activity Waste form.

³ Handbook of Clay Science, F. Bergaya, p. 1027

3.0 PROCESS TECHNOLOGY MATURATION PLAN

3.1 OBJECTIVE

The objective of the LiHT process is to remove aluminum from Hanford sodium hydroxide leached tank waste as LiHT solid, and to regenerate sodium hydroxide that is recycled to leach aluminum sludge in tank waste.

3.2 KEY TECHNOLOGY ADDRESSED

The main functions of the LiHT Precipitation System are to:

1. Receive filtered feed high in dissolved aluminum. This may be from *in situ* tank leaching or from an *ex situ* Continuous Sludge Leaching (CSL) process or directly from the tanks.
2. Precipitate lithium hydrotalcite solid $\text{Li}_2\text{CO}_3 \cdot 4\text{Al}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ from actual Hanford tank waste.
3. Separate by filtration the solid LiHT from the aluminum depleted supernate containing regenerated sodium hydroxide.
4. Decontaminate the separated lithium hydrotalcite with wash water.
5. Make the decontaminated hydrotalcite available for LAW immobilization and disposal as an approved waste form (Optionally, the hydrotalcite could be dried and stored for later use as a LAW glass former).
6. Provide a waste feed meeting the WTP waste acceptance criteria.

A secondary process function of the LiHT process is to concentrate and recycle the mother liquor containing regenerated sodium hydroxide to the tank farms for further aluminum leaching.

Several deployment scenarios have been proposed to insert the LiHT process in the Waste treatment process. The different alternatives are presented in ref. RPP-RPT 48377.

Figure 2 is a simplified process flow diagram for an example of the LiHT process deployment configuration that shows the interfaces with the upstream and downstream waste treatment processes.

Figure 2. LiHT Process Simplified Block Flow Diagram

Sludge and supernatant retrieved from the Hanford underground tanks, which are high in aluminum and sodium hydroxide are heat leached using native and recycled sodium hydroxide. Saltcake brines, which are low in sodium hydroxide and aluminum sludge, bypass the LiHT process and are fed directly to the WTP. Residual sludge, which is low in aluminum, is fed to the WTP. The filtered leachate, containing dissolved sodium aluminate, is reacted with lithium hydroxide. The resulting LiHT precipitate, containing the aluminum, is precipitated, filtered, washed, dried, and transferred to an immobilization unit as LLW. Filtrate from the LiHT process which contains the regenerated sodium hydroxide is transferred to an electrochemical unit that concentrates a sodium hydroxide stream that is recycled to leach aluminum sludge. Excess caustic is returned to waste tanks or purged to the WTP. Excess distilled water is exported to the Effluent Treatment Facility (ETF).

3.3 APPROACH

The maturation approach for the LiHT process is organized into three specific successive phases of chemical and engineering research and development:

- Phase I – Laboratory-scale testing;
- Phase II - Pre-pilot-scale testing;
- Phase III - Pilot-scale testing.

Through these phases of the development program, the LiHT process will progress incrementally from the current estimated Technology Readiness Level of 3, with a proven feasibility, to

achieve a Technology Readiness Level of 6, with a full technology demonstration. This program will generate sufficient information to specify all process systems and conditions required for a full-scale process facility. A logic diagram that details the sequencing of the main testing activities is provided in Appendix B.

Phase I will involve laboratory tests that have the essential goal of expanding the scope of the previous validation tests, to a series of parametric tests using the full range of Hanford Waste simulants, and eventually actual waste samples in a hot cell environment. The parametric type testing will focus on identifying the factors that influence the Lithium Hydrotalcite precipitation reaction, and the characteristics of the precipitated solids. The parametric testing will determine the range of applicability for the process, and the acquired physical characteristics will provide engineering data for process equipment selection and development.

Because the LiHT process has the potential to dramatically reduce the mass of the Al containing sludge to be vitrified at WTP, the sodium hydroxide demand, and the lifecycle cost of Hanford waste treatment, the process development and demonstration effort could be accelerated to expedite implementation while meeting the intent of the US DOE TRA guide (DOE G 413.3-4). Development efforts for laboratory validation, unit operations testing, pilot plant integration and process development can be advanced concurrently as required. Formal evaluations of predecessor activities versus the assumed inputs for project tasks under progress will be conducted periodically for each TRL developed on parallel paths. Corrective actions will be defined immediately to minimize cost and schedule impacts.

Depending upon their respective capabilities and availability, the Hanford site laboratory (i.e. 222-S Laboratory), U.S. National Laboratories, or U.S. private laboratories will be contracted to perform selected parts of the overall modeling and testing program.

The multi-phased development path will provide a sound basis for a system design for a full-scale process operating in a radioactive environment. Supporting engineering analyses and flowsheet development work, and appropriate process hazard operations assessment and risk analyses will define the process conditions and interfaces within the overall Hanford site waste handling facilities.

3.4 SCOPE

The three phases of the TMP are organized in a graduated basis: from scientific research to development of integrated pilot-scale facilities. The defined activities may be performed sequentially or in parallel to accelerate implementation. Specific test plans for each activity will be developed to precisely define the key test objectives and success criteria, methods, measurements, and precautions to perform the experiments safely and to generate the necessary insight into the proposed tank waste treatment method.

3.4.1 Phase I –Achieve TRL-4

Phase I of the LiHT process TMP is designed to progress to a TRL of 4.

TRL 4	Definition : Component system and/or system validation in laboratory experiment	Objectives: Establish technological components that will work together. First step in establishing system compatibility. Testing with full range simulants and small scale actual wastes
-------	---	--

The scope of Phase I include the following main activities.

3.4.1.1 Bench Scale 1-Liter Parametric Experiments on Simulants

Bench scale 1-liter parametric experiments will be conducted, using a suitable extended range of non-radioactive simulant solutions, representing the range of Hanford single-shell and double-shell tank wastes.

Non-radioactive tests will replicate the one-liter LiHT process laboratory experiments performed for the process validation. These tests will use non radioactive simulants covering the full range of physical, and chemical properties of the supernatants and solubilized sludge anticipated for the WTP.

The tests will analyze and quantify the thermo-chemical parameters affecting the key performances of the LiHT process (yield, filterability, wash ability, and rate of sodium recovery), and measure and/or calculate the thermodynamic and physical properties of the products of the tests, especially lithium hydrotalcite.

The LiHT precipitation reaction will be analyzed under different conditions and applications than those considered in the initial process validation runs and parametric tests, in order to extend the applicability of those prior results to the broader range of Hanford Waste, and expected operating conditions.

These fundamental laboratory tasks are needed to lay the foundation for defining laboratory apparatus requirements and lab procedures, to be used for “hot” (i.e. radioactive) experiments with actual Hanford waste, and to implement the large scale demonstrations that will follow in phases II and III.

Phase I parametric experiments will include:

- Kinetic studies of the LiHT precipitation reaction rate as a function of time and temperature. The kinetic rate data will be used to determine the optimum reaction temperature achieving an acceptable balance between product yield and reaction rate, and to size process equipment.
- Physical studies of the LiHT product: A screening study will be conducted to determine the parameters and equipment that have the greatest influence on particle size, and to determine the nominal settling rate that can be used to size equipment. Particle size and settling rate influence both the process and the equipment. Small particles that do not separate or settle well may force equipment to be increased in size. Some reaction conditions may create larger particles and some equipment may shear particles. These studies will cover:
 - Effects of shear mixing on particle size.
 - Particle settling rate as a function of size.
 - Extent of cake dewatering as a function of particle size.
- Extent of LiHT decontamination as a function of wash volume, and temperature: The purpose of this study is to determine the optimum combination of de-liquoring, wash volume, and wash frequency to meet the required extent of decontamination of water soluble species.
- Study of crystal ripening for anion selectivity: Tests will be performed that will ripen the product in conditions that prefer carbonate, sulfate, phosphate, and /or nitrate over hydroxide or pertechnetate substitution in the LiHT structure.
- Extent of sodium hydroxide regeneration: The purpose of this study is to estimate the sodium hydroxide balance for the LiHT process.

3.4.1.2 Bench Scale 1-Liter Experiments on Actual Waste

Hot work experiments will be conducted on a graduated basis, to test LiHT chemistry and decontamination of the filtered LiHT product using actual Hanford radioactive tank waste samples (or composite samples). These experiments will cover a wide range of supernatant and sludge compositions.

3.4.1.3 LiHT Process Equipment Conceptual Design and Risk Analysis Update

The conceptual design analysis of the LiHT process will be reviewed in the light of the results of the bench-scale experiments, in order to affirm/adjust design as necessary. The alternative flow sheets proposed for the integration of the LiHT process in the overall waste treatment process will be reviewed and updated. For the reference option, emphasis will be placed on analysis of component capability, establishing process performance metrics, and development of process

controls and associated equipment needed to affirm the conceptual design applied to scale-up the LiHT process.

A Risk Analysis of the LiHT process will be conducted, especially considering future testing of the process using Hanford tank waste. The risk analysis will be accompanied by a Hazard Analysis to establish safe operational procedures and ensure worker safety, both for the bench- and pilot-scale tests and for anticipated full-scale deployment of the LiHT process technology. The LiHT Hazard Analysis will be designed to be revisited at each succeeding TRL level of maturation and for each step in proving and implementing the LiHT process.

3.4.1.4 LiHT Downstream Disposal Studies

This task will execute some research in decontaminated LiHT characterization, waste classification, and immobilization technologies (e.g. vitrification, grouting, calcination). LiHT produced from non-radioactive simulants and actual Hanford tank waste experiments will be analyzed with respect to waste loading and regulatory compliance. For the methods that meet disposal regulatory requirements, further studies of immobilization and disposal paths will be developed in parallel to the LiHT process development effort (continuing during Phase II and III).

3.4.1.5 LiHT Technology Readiness Assessment update

A Technology Readiness Assessment workshop will be held for the independent validation of TRL-4 based on results of Phase I laboratory and modeling activities.

3.4.2 Phase II – Achieve TRL-5

Phase II of the LiHT maturation plan is designed to achieve TRL-5.

TRL5	Definition: Laboratory scale, similar system validation in relevant environment	Objectives: Basic technology integration to ensure operational compatibility. Testing with full range of simulants and small scale actual waste
------	---	---

Phase II testing will be performed on a 100-Liter “Pre-Pilot” scale platform using a prototypical glass reaction vessel and separator systems, and simulant chemistry. Phase II will include the following main activities:

- Review results of Phase I testing to provide input to the engineering design of Phase II testing.
- Design equipment and process methodologies for 100-Liter scale LiHT process testing. A flowsheet analysis will provide specifications for the equipment for a high-fidelity Phase II test platform, as well as process protocols for conducting the testing with a range of representative Hanford single-shell and double-shell tank waste simulants. The test methodology will include review and update, if necessary, of the LiHT Hazard Analysis.

- Testing of key LiHT process components will include:
 - In line mixing.
 - Nutsche filter testing to examine solid-liquid separation.
 - Elutriation column testing (LiHT washing function).
- Design and run 100-Liter scale crystallization tests to examine LIHT filtrate concentrations.
- Perform detailed design of the ~1/5 full-scale pilot LiHT system to be used during Phase III, including the development of process flowsheets and P&IDs, detailed design drawings, and review of the LiHT Hazard Analysis. Some aspects of the CSL, RMF, and ECR processes, especially solid/liquid separation, will be studied for synergies with the LiHT process to simplify and/or improve the integrated pilot plant system.
- Hold a Technology Readiness Assessment workshop for the independent validation of TRL-5 based on the results of Phase II process and essential components testing.

3.4.3 Phase III – Achieve TRL-6

Phase III is designed to achieve TRL-6.

TRL6	Definition: Engineering/pilot scale similar – or prototype – system validation in relevant environment	Objectives: Engineering/pilot scale demonstration in relevant environment including full range of simulants. TRL-6 begins true engineering development and prototype capable of performing all operations of a functional system
------	--	--

The purpose of pilot-scale testing is to demonstrate operation of the integrated LiHT process in an integrated system that is approximately one-fifth (1/5) the size of a full-scale system. The size of the pilot system (10,000 – 50,000 liters) will depend upon the estimated required capacity for full-scale implementation. The pilot-scale system will contain all three systems to allow continuous LiHT production and sodium hydroxide recycling.

The main Phase III activities are the following:

- Complete equipment specifications for a ~1/5 full-scale integrated LiHT process test platform.
- Complete procurement activities for equipment and fabrication of the test platform.
- Construction of the ~1/5 full-scale integrated LiHT process test platform.

- Quality Assurance verification of equipment purchased and/or fabricated for Phase III testing to ensure design specifications have been met.
- Determination of the off-normal operating responses for $\sim 1/5$ full-scale test system.
- Commissioning of the $\sim 1/5$ full-scale integrated LiHT process test platform.
- Demonstration of the integrated LiHT process in the $\sim 1/5$ full-scale test system.
- Engineering design of the LiHT system for actual hot waste application including development of preliminary design drawings, determination of operating limits for the main process components, and definition of the system availability and reliability (RAMI). 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 integrated pilot system.
- Update Hazard Analysis for Phase III testing platform and procedures.
- Development of design documentation required for TRL-6. Results of the Phase III activities will be compared to Phase I laboratory-scale and Phase II pre-pilot results, thermodynamic models, and regulatory requirements for immobilization and final disposal. Information such as equipment capacity, system stability, and on-stream availability generated from the Phase III pilot plant studies will be used to develop and design the full-scale modular process systems for actual applications.
- Preparation of data package supporting determination of whether or not the LiHT process has met performance targets.
- Holding a Technology Readiness Assessment workshop for the independent validation of TRL-6 based on results of Phase III process and essential components testing.

4.0 TECHNOLOGY MATURATION PLAN SCHEDULE

The TMP for the LiHT process will be initiated upon approval from DOE. AREVA anticipates that TMP experiments and activities can be performed in a 3 year time frame.

Table 3 shows the LiHT Technical Performance Plan and describes the broad outline of the experiments/activities along with time milestones, performance targets, and TRL levels. These milestones and performance targets presume DOE approval to proceed with the LiHT Testing Program, and adequate funding. The specifics described in the Performance Plan will be finalized with the development of the proposed and DOE approved conceptual design and baseline plan.

In addition to DOE authorization and funding approval, the following elements may be critical to planning and scheduling of the LiHT Performance Plan:

- Finalization of functions and requirements of the testing tasks/phases.
- Approval of a Safety Plan and safety systems, including shielding for testing with Hanford tank wastes.
- Any formal DOE-mandated Technology Readiness Assessments.

Table 2. Technical Performance Plan

Time after Initiation of LiHT TMP	Milestone	Performance Targets	TRL Achieved
5 months	Additional non-radioactive simulant development and preparation for process sensitivity testing	Additional simulants ready for testing	TRL-4
12 months	Laboratory 1-Liter non-radioactive testing using extended simulant range	Complete process sensitivity testing	TRL-4
10 months	Laboratory 1-Liter radioactive testing using Hanford waste	LiHT chemistry and decontamination of the filtered LiHT product demonstrated using actual Hanford tank waste	TRL-4
17 months	Complete Laboratory-Scale Test Report	Document Task/Phase I Testing results. Complete Task/Phase I Testing	TRL-4
4 months	Pre-Pilot Engineering Scale 100 Liter Test Plan	Conceptual Task/Phase II test design, plan testing operations	TRL-5
12 months	100-Liter Testing using Tank Waste simulants	Complete Task/Phase II Testing	TRL-5
16 months	Complete Pre-pilot scale Test Report	Document Task/Phase II Testing results	TRL-5
22 months	Final Pilot-scale Test Plan	Conceptual Task/Phase III test design, plan testing operations	TRL-6
32 months	Integrated Pilot-scale Testing	Complete Task/Phase III Testing	TRL-6
34 months	Evaluate Pilot-scale Testing	Provide input to Full-scale Implementation	TRL-6
34 months	Complete Pilot-scale Test Report	Document Task/Phase III Testing results	TRL-6
35 months	Comprehensive LiHT Test Report	Complete comprehensive LiHT Test Report and Recommendation of TRL-7 implementation	

5.0 TECHNOLOGY MATURATION PLAN COST SUMMARY

The programmatic costs for the elements of the TMP are included only as estimated costs to be developed in more detail with project baseline planning. The detailed costs, including purchase of laboratory equipment, ordering/purchasing of long-lead time items, construction of testing platforms, and operational costs associated with each Task/Phase of the LiHT Performance Plan will be developed with approval to proceed with each Task/Phase. Specific cost estimates will be provided in tabular form for each element of the Work Breakdown Structure (WBS) after approval of the WBS.

Table 3 summarizes the broad outlines of the Tasks/Phases of the Technology Maturation Plan for the LiHT Process for the activities described in this TMP. Table 4 is a preliminary cost estimate and does not include programmatic and manufacturing maturation elements. More specific costs will be provided upon approval of the LiHT Testing Program as each Task/Phase of the program is approved to proceed and the detailed Test Plans are provided.

Table 3. Technology Maturation Plan Cost Summary (\$k)

Cost Element	Project Management & Documents	Thermodynamic modeling	Lab-scale Testing using simulants	Lab-scale Testing using actual waste	Pre-pilot scale Testing	Pilot (1/5)-scale Testing
Staffing, Hardware and Testing	1,703	720	2,367	3,785	1,756	26,762
Grand Total	37,093					

6.0 REFERENCES

- U.S. Department of Energy, 2009. *Technology Readiness Assessment (TRA) Guide*, DOE G 413.3-4.
- AREVA, 2008. *PCT International Application* PCT/US2008/076589.
- AREVA, 2010 - Test Program for Alumina Removal and Sodium Regeneration from Hanford Waste by Lithium Hydrotalcite Precipitation, RPP-43328, Rev. 0.
- AREVA, 2010 - Aluminum Removal and Sodium Regeneration from Hanford Waste by Lithium Hydrotalcite Precipitation, Summary of prior laboratory scale testing, RPP-48376, Rev. 0.
- AREVA, 2010 - Aluminum Removal and Sodium Regeneration from Hanford Waste by Lithium Hydrotalcite Precipitation, Laboratory Scale Validation on Waste Simulants, Test Report, RPP-RPT 48380, Rev. 0.
- AREVA, 2010, Aluminum Removal and Sodium Regeneration from Hanford Waste by Lithium Hydrotalcite Precipitation, Technology Readiness Evaluation, RPP-48379, Rev. 0.
- AREVA, 2010, Aluminum Removal and Sodium Regeneration from Hanford Waste by Lithium Hydrotalcite Precipitation, Process Model Flowsheet, RPP-RPT 48377, Rev. 0.
- Duan, X, and D.G. Evans, eds., 2005. *Layered Double Hydroxides, in Structure and Bonding*, Volume 119, Springer-Verlag, Berlin Heidelberg, ISSN 0081-5993.
- AREVA, 2010, Aluminum Removal and Sodium Regeneration from Hanford Waste by Lithium Hydrotalcite Precipitation, Alternative Process Deployment Scenarios, RPP-RPT 48378, Rev. 0.

APPENDIX A.

TRL Criteria Planning

Tables A.1 through A.4 list the TRL Lines of Inquiry for TRL-3 through TRL-6 criteria (DOE G 413.3-4, *Tables D.4, D.5, D.6, and D.7*).

Note (*): The planned effort to address all individual line of inquiry will be detailed at a later stage of the project after the Project Management Plan is prepared and issued. A logical process will be followed, building on information developed at each stage to identify or enhance the specific actions necessary to reach the next stage.

The first column in the tables below identifies the areas of readiness being evaluated: technical (T), programmatic (P), and manufacturing/quality requirements (M). A process is determined to have reached a given TRL if column 2 is judged to be 100% complete for all questions.

Table A.1
TRL-4 Items from DOE TRA Guide, 2009, DOE G 413.3-4

Scope Type T/P/M	Lines of Inquiry “Criteria”	Action Plan (*)
T	Key process variables/parameters have been fully identified	
M	Laboratory components tested are surrogates for system components	
T	Individual components tested in laboratory/ or by supplier	
T	Subsystems composed of multiple components tested at lab scale using simulants.	
T	Modeling & Simulation used to simulate some components and interfaces between components	
P	Overall system requirements for end user's application are <u>known</u>	
T	Overall system requirements for end user's application are <u>documented</u>	
P	System performance metrics measuring requirements have been established	
P	Laboratory testing requirements derived from system requirements are established	
M	Available components assembled into laboratory scale system.	
T	Laboratory experiments with available components show that they work together (lab kludge)	
T	Analysis completed to establish component compatibility (Do components work together)	
P	Science and Technology exit criteria established (S&T targets understood, documented, and agreed to by sponsor)	
T	Technology demonstrates basic functionality in simulated environment	
M	Scalable technology prototypes have been produced (Can components be made bigger than lab scale)	

Table A.1 (cont.)**TRL-4 Items from DOE TRA Guide, 2009, DOE G 413.3-4**

P	Draft conceptual designs have been documented	
M	Equipment scale-up relationships are understood/accounted for in technology development program	
T	Controlled laboratory environment used in testing	
P	Initial cost drivers identified	
M	Integration studies have been started	
P	Formal risk management program initiated	
M	Key manufacturing processes for equipment systems identified	
P	Scaling documents and designs of technology have been completed	
M	Key manufacturing processes assessed in laboratory	
P/T	Functional process description developed (Systems/subsystems identified)	
T	Low fidelity technology “system” integration and engineering completed in a lab environment	
M	Mitigation strategies identified to address manufacturability/producibility shortfalls	
T	Key physical and chemical properties have been characterized for a range of wastes	
T	A limited number of simulants have been developed that approximate the range of waste properties	
T	Laboratory scale tests on a limited range of simulants and real waste have been completed	
T	Process/parameter limits are being explored	
T	Test plan documents for prototypical lab scale tests completed	
P	Technology availability dates established	

Table A.2
TRL-5 Items from DOE TRA Guide, 2009, DOE G 413.3-4

Scope Type T/P/M	Lines of Inquiry “Criteria”	Action Plan (*)
T	The relationships between major system and sub-system parameters are understood on a laboratory scale	
T	Plant size components available for testing	
T	System interface requirements known (How would system be integrated into the plant?)	
P	Preliminary design engineering begins	
T	Requirements for technology verification established	
T	Interfaces between components/subsystems in testing are realistic (benchtop with realistic interfaces)	
M	Significant engineering and design changes	
M	Prototypes of equipment system components have been created (know how to make equipment)	
M	Tooling and machines demonstrated in lab for new manufacturing processes to make component	
T	High fidelity lab integration of system completed, ready for test in relevant environments	
M	Manufacturing techniques have been defined to the point where largest problems defined	
T	Lab scale similar system tested with range of simulants	
T	Fidelity of system mock-up improves from laboratory to bench scale testing	
M	Availability and reliability (RAMI) target levels identified	
M	Some special purpose components combined with available laboratory components for testing	
P	Three dimensional drawings and P&IDs for the prototypical engineering scale test facility have been prepared	
T	Laboratory environment for testing modified to approximate operational environment	
T	Component integration issues and requirements identified	
P	Detailed design drawings have been completed to support specification of engineering scale testing system	
T	Requirements definition with performance thresholds and objectives established for final plant design	
P	Preliminary technology feasibility engineering report completed	
T	Integration of modules/functions demonstrated in a laboratory/bench scale environment	
T	Formal control of all components to be used in final prototypical test system	
P	Configuration management plan in place	
T	The range of all relevant physical and chemical properties has been determined (to the extent possible)	

Table A.2 (cont.)**TRL-5 Items from DOE TRA Guide, 2009, DOE G 413.3-4**

T	Simulants have been developed that cover the full range of waste properties	
T	Testing has verified that the properties/performance of the simulants match the properties/performance of the actual wastes	
T	Laboratory scale tests on the full range of simulants using a prototypical system have been completed	
T	Laboratory scale tests on a limited range of real wastes using a prototypical system have been completed	
T	Test results for simulants and real waste are consistent	
T	Laboratory to engineering scale scale-up issues are understood and resolved	
T	Limits for all process variables/parameters are being refined	
P	Test plan for prototypical lab scale tests executed – results validate design	
P	Test plan documents for prototypical engineering scale tests completed	
P	Risk management plan documented	

Table A.3**TRL-6 Items from DOE TRA Guide, 2009, DOE G 413.3-4**

Scope Type T/P/M	Lines of Inquiry “Criteria”	Action Plan (*)
T	The relationships between system and subsystem parameters are understood at engineering scale allowing process/design variations and tradeoffs to be evaluated	
M	Availability and reliability (RAMI) levels established	
M	Frequent design changes occur	
P	Draft high level design drawings for final plant system are nearly complete	
T	Operating environment for final system known	
P	Collection of actual maintainability, reliability, and supportability data has been started	
P	Estimated cost of the system design is identified	
T	Operating limits for components determined (from design, safety and environmental compliance)	
P	Operational requirements document available	
P	Off-normal operating responses determined for engineering scale system	
T	System technical interfaces defined	
T	Component integration demonstrated at an engineering scale	
P	Scaling issues that remain are identified and understood. Supporting analysis is complete	

Table A.3 (cont.)**TRL-6 Items from DOE TRA Guide, 2009, DOE G 413.3-4**

P	Analysis of project timing ensures technology would be available when required	
P	Have begun to establish an interface control process	
P	Acquisition program milestones established for start of final design (CD-2)	
M	Critical manufacturing processes prototyped	
M	Most pre-production hardware is available to support fabrication of the system	
T	Engineering feasibility fully demonstrated (e.g. would it work)	
M	Materials, process, design, and integration methods have been employed (e.g. can design be produced?)	
P	Technology "system" design specification complete and ready for detailed design	
M	Components are functionally compatible with operational system	
T	Engineering scale system is high-fidelity functional prototype of operational system	
P	Formal configuration management program defined to control change process	
M	Integration demonstrations have been completed (e.g. construction of testing system)	
P	Final Technical Report on technology completed	
M	Process and tooling are mature to support fabrication of components/system	
T	Engineering scale tests on the full range of simulants using a prototypical system have been completed	
T	Engineering to full scale scale-up issues are understood and resolved	
T	Laboratory and engineering scale experiments are consistent	
T	Limits for all process variables/parameters are defined	
T	Plan for engineering scale testing executed - results validate design	
M	Production demonstrations are complete (at least one time)	

APPENDIX B.
Phased LiHT Process Maturation Approach – Logic Diagram