Accelerating Cleanup of the Defense Nuclear Legacy

Quarterly Technical Progress Report
for the period
April 1, 2007 – June 30, 2007

Dr. Roger King, Interim Principal Investigator

Report No. 07040R02

Institute for Clean Energy Technology
Mississippi State University
205 Research Boulevard
Starkville, MS 39759

icet@icet.msstate.edu
www.icet.msstate.edu

Notice
This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed or represents that its use would not infringe privately-owned rights. 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 Unites States Government or any agency thereof. The views and opinions of authors expressed therein do not necessarily state or reflect those of the United States Government or any agency thereof.

Table of Contents

List of Figures

List of Tables

Task 2. Support of Hanford Single Shell Tank Waste Disposition

In-tank/At-tank Characterization for Closure of Hanford Tanks

During this quarter, the ICET Fourier Transform Profilometry (FTP) effort has continued its effort to test and improve the stitching algorithm. A decision was made to immediately address technical challenges not yet solved so that, to the extent possible, there would be greater uniformity of the FTP system used for the different FTP Performance Evaluation Stages. The high-precision laboratory pan and tilt system for Stage 2 was successfully tested. Efforts were expended in determining how to cope with the loss of two of the seven ICET FTP team members due to the retroactive budget recision.

During this reporting period, progress on the ICET Stereovision effort was significantly slowed by the unexpected departure in December of the graduate student working on this effort. Because of the retroactive budget recision, it was not possible to replace the graduate student.

Process Chemistry and Operations Planning for Hanford Waste Alternatives

Development of a neural network to augment the chemistry in HTWOS, specifically for the C tank farm retrieval was begun. The input molecular stream limits for the chemistry calculations were developed from the BBI data, charge balance with minimum mass change. Work on implementing batch mode processing of the ESP program to generate the neural net training set data was begun.

Additional data on the gibbsite to boehmite transition was obtained under different experimental conditions and at temperatures as low as 100 $^{\circ}$C. Attempts to quantify the transition at temperatures of 50 and 80°C revealed no change in the starting gibbsite material up to 540 hours at constant temperature. Factors that might affect the transition, including water vapor pressure and caustic loading had little or no impact on the change of gibbsite as a function of time. The primary parameter controlling the transition was determined as the sample temperature. Validation of the TGA method was accomplished through x-ray diffraction (XRD) on specific samples. A sample heated at 120°C for 240 hours was determined to be approximately 50% gibbsite and 50% boehmite from XRD. The corresponding result from the TGA measurement was 55% gibbsite, in good agreement with the semi-quantitative XRD analysis.

Porting of the V7DBLSLT private database, developed at ICET, to the MSE (Mixed Solvent Electrolyte) framework was initiated. In collaboration with OLI Systems, Inc., the incorporation of solubility measurements performed at ICET into the MSE framework will allow use of these data in modeling efforts in support of Hanford and SRS. Within the MSE framework, it is possible to represent behaviors from the dilute aqueous solution regime to the fused salt limit, and offers some advantages in modeling and simulation of waste retrieval activities at the DOE sites.

Task 3. Disposition of Idaho HLW Calcine

Support of the CH2M-WG Idaho Calcine Disposition Project

CH2M Hill-Washington Group International (CH2M-WG Idaho) at the Idaho National Laboratory (INL) Site is currently gathering information to make decisions about the disposition of the calcined HLW in the bin sets. ICET has been conducting research on stabilized waste forms to assist the site in making those decisions.

The goal is to provide decision quality data and documentation to the Calcine Disposition Project located at the INL Site under management of CH2M-WG Idaho that will lead to an acceptable waste form for stabilized high-level waste calcine. Waste forms were produced, analyzed, and tested in collaboration with CH2M-WG Idaho scientists and engineers. The appropriate physical and chemical performance characteristics (as per the waste acceptance requirements) have been determined for three simulated calcine waste forms. (These data are being provided under a quality program compatible with DOE/RW-0333P as directed by CH2M-WG Idaho.) Based on the data developed during these tests, grout cement has been down-selected as the preferred calcine waste form for follow-on mock-up testing.

Task 4. Support of SRS Salt Disposition and Other SRS Alternatives

Modeling and Experimental Support for High-Level SRS Salt Disposition Alternatives

Modeling of the Tank 51 HM sludge batch 5 simulant was investigated using ESP V7.0 and employing several databanks. Model predictions were in good agreement with SRS Tank 51 inventories. Current site plans call for leaching of the sludge batch 5 with 50wt% caustic for aluminum removal. Modeling of this procedure using varying amounts of caustic showed at least 140,000 gallons of caustic would be required to dissolve all of the aluminum at a temperature of 50°C. Upon cooling of this leached stream to 30°C, some aluminum solids re-precipitation is predicted to occur.

Process Improvements for the Defense Waste Processing Facility (DWPF)

Work on evaluating LIBS for on-line analysis of the Pu residue feeds during the immobilization of Pu waste in the form of a Lanthanum borosilicate (LaBS) glass continued. Different optical fiber designs for long-term LIBS measurements have been tested. In addition to the standard solid core optical fiber, a hollow-core fiber to deliver the nanosecond Nd:YAG laser pulse has been tested. Efforts were also designed for preparing die sample press for LIBS experiments. Different sizes of the dies have been tested and the optimum pressure to hold the surrogate powder together without any binder has been determined. Pellets from various amounts of surrogate powder have been made to determine the minimum weight of powder required for reproducible results.

Process Improvements for the Defense Waste Processing Facility (DWPF)
Task 2 – Improvement of Waste Throughput

This effort will assist the acceleration of the DWPF mission by allowing the DWPF melter to produce glasses with higher waste loadings without negatively impacting waste throughput. Waste loadings that are desired are higher than previously demonstrated in the DWPF melter system (approximately 40%). This suggests that a better understanding of melt chemistry (a function of frit composition, sludge composition, and waste loading) and enhanced melter control may be required in order to reliably produce glasses with higher waste loading.

This project builds on several previous ICET efforts – the development of high temperature monitoring systems for the glass industry and for the Tennessee Valley Authority (TVA), the development of glass formulations for Atomic Energy of Canada, Ltd. (AECL), and for the Radioactive Isolation Consortium, LLC, (RIC). ICET's work enabled the RIC to reliably produce glassy waste forms with over 50 wt% waste loading.

Task 5. Support of DOE Headquarters

HEPA and Regenerable Filter Performance Assurance

The HEPA Filter Performance Assurance task provides data needed to address issues related to the performance of high efficiency particulate air (HEPA) and regenerable sintered metal and ceramic membrane filters. In the second quarter of 2007, further progress was made in the study of the performance and regenerable nature of CeraMem ceramic membrane filters. Work this quarter primarily was centered on optimization of the air back pulse filter cleaning system; and it was determined that the time needed to load filters should be shortened. Therefore, the regenerable filter test bed was modified to accommodate this.

Bio-availability studies of mercury and other heavy metal contaminants in ecosystems of selected DOE sites

In this quarter, the experiments on the effects of naturally occurred minerals on mercury release from Oak Ridge soil contaminated with HgS. Fe_3O_4, Fe_2O_3 and $MnCO_3$ have been tested. The preliminary results showed that iron oxides triggered the release of Hg, while $MnCO_3$ did not affect the release of Hg from HgS minerals in Oak Ridge soils. The concentration of Hg released from HgS mineral in contaminated soils was linearly correlated to that of dissolved Fe in extracts, but negatively correlated with concentrations of sulfate. In addition, the manuscript entitled "Stability and Bioavailability of HgS in Oak Ridge soils" was prepared. The paper on "Bioavailability and Stability of Mercury Sulfide in Tennessee (USA) Soil" was published in the Proceedings of the 11th International Conference on Environmental Remediation and Radioactive Waste Manage, 2007, Belgium.

Phytoremediation and Long-Term Monitoring of Heavy Metal Contaminants

During this reporting period, researchers continued mercury phytoremediation experiments with sunlit chambers. Chinese brake fern (*P. vittata*) was grown on clean soil, but the plant shoot was enclosed into a chamber that containing mercury contaminated soil but with no direct contact to the plant. Two mercury sources (mercury chloride and mercury sulfide) have been tested.

Task 6. Technology Development

Development of new technologies for DOE site applications

In this quarter, the newly designed ringdown optical bench with a multiplex of two near-infrared (NIR) laser diodes was extensively tested. Each of the laser diodes has been individually tested by measuring NIR spectra and the multiplexed laser diodes have also been tested by simultaneously measuring C-H overtone spectra in the two NIR spectral regions. The result shows that the laser diode-multiplexing is a success and is suitable for detection of multiple species. To the best of our knowledge, this is the first reported effort of multiplexing two laser diodes in the NIR for a portable ringdown system. This design will significantly reduce instrument costs and enhance the capability of measuring multiple compounds. By replacing different laser diodes, the ringdown optical bench can be used for detection of a variety of chemical compounds.

Support of Oak Ridge Site Closure

Characterization of Corrosion for Closure of Oak Ridge Research Reactor

David L. Monts, Ping-Rey Jang, Yi Su, Jeffrey S. Lindner

The U.S. Department of Energy reduced the FY 07 funding from $5M to $4M dollars for the Institute for Clean Energy Technology. With the reduction in funding, MSU management had to make hard decisions as to which tasks to continue. After a thorough examination of several factors, it was determined that Task 1 Support of Oak Ridge Site Closure would be removed from the scope of work. This information has been conveyed to DOE. Should additional funding and customer support become available, this work may continue.

Support of Hanford Single Shell Tank Waste Disposition

In-tank/At-tank Characterization for Closure of Hanford Tanks

David L. Monts, Ping-Rey Jang, Yi Su, Chuji Wang

INTRODUCTION

The goal of this project is to develop and deploy in-tank waste characterization tools for use at the Hanford Site. These will be used to reduce uncertainties and risks associated with waste processing and closure activities. Some of the systems developed for this effort are also applicable to other DOE sites, such as Savannah River.

After as much waste as practical has been removed from the tank, analyses of remaining deposits will be needed to determine the long-term risk associated with the residual waste and to determine the appropriate steps required for closure. These needs are described in Hanford Technical Challenges WT-115, Technology to Support Post-Retrieval Evaluation of SSTs.

ICET will assemble and test the following systems for potential deployment for nondestructive, *in situ* imaging means of quantitatively determining the volume and height of waste (including that deposited on tank walls, and the volume and depth of sediments), based on Fourier-transform profilometry (FTP) and stereovision (SV). FTP images are obtained by using a white light source to project a fringe pattern onto the object of interest and using a camera to record the resulting distortions of the fringe pattern due to reflection from non-flat surfaces. A software package has been developed by ICET that automatically processes the FTP image to yield quantitative measurements and renderings of the object. In some cases, tank solids are covered by a layer of pipeline flush water, following the completion of retrieval. Quantitative mapping of tank sediments would enable a more accurate determination of the volume of residual tank wastes. Sediment mapping is not feasible with currently deployed instrumentation. FTP will evaluate the feasibility of sediment mapping under a variety of conditions. Stereovision also provides 3-D topographical reconstruction of target surfaces by using images simultaneously recorded by two or more cameras from different viewpoints.

During CA06, the Fourier transform profilometry (FTP) probe effort initiated a series of FTP performance evaluation tests under simulated Hanford waste tank conditions. The purpose of these tests is to test and document the accuracy, precision, and operational performance using blind testing techniques. Nondescript targets have been created and their volumes determined by traditional methods, but the values of the volumes were not known to those ICET personnel who

used FTP to quantitatively determine their volumes. The first stage of this testing involved simulating objects on the bottom of a flat C200-series Hanford waste tank and analyzing the volume of individual objects from single FTP images. The second stage involves using new non-descript targets and determining the total volume present by "stitching" the results of individual images together. These tests will demonstrate the performance of the FTP system prior to demonstration in Hanford's Cold Test Facility (CTF). In order to test the durability and reliability of components comprising the FTP system, a series of tests have begun subjecting selected components to gamma-ray radiation. All FTP tests are being conducted with frequent consultation with our Hanford collaborators.

The Stereovision effort has developed and improved the ICET Stereovision system with better cameras, and has also evaluated a variety of algorithms for stereomatching. Our results show that performance (accuracy and computer analysis time) of a stereomatching algorithm often varied with specific test images. The stereovision system and algorithms have been tested with images of selected targets at different working distances. For Hanford tank inspection, parallel implementation of stereomatching algorithms is necessary because large image size and disparity search range are inevitable.

WORK ACCOMPLISHED:

STEREOVISION

Progress on the Stereovision effort was significantly slowed this quarter by the unexpected departure in December of the graduate student working on this effort. Because of the retroactive CA07 budget recision, it was not possible to replace the graduate student.

FOURIER TRANSFORM PROFILOMETRY

This quarter, ICET's Fourier Transform Profilometry (FTP) efforts were directed towards the goal of validating ICET stitching software for FTP Performance Evaluation Stage 2 using synthetic images and further development of the capabilities of the FTP image simulator. Multiple images will be required to survey the residual wastes remaining in the Hanford waste tanks. Therefore, it is necessary to stitch together the volume determinations from single images to obtain an accurate overall volume determination. A variety of tilt angles was simulated and the stitching results compared. A software error was discovered and corrected. The influence of FTP phase unwrapping procedures on the ability to obtain unsupervised volume determinations was reviewed.

During the last quarter, a "pan" and "tilt" apparatus was constructed with the goal of achieving angle measurements on the order of 0.02°. This quarter, the apparatus was utilized for obtaining multiple adjacent images where only the "pan" angle was varied. These images were subsequently analyzed and it has been demonstrated that the reconstruction of these images can be achieved with sufficient accuracy to meet ICET data quality objective. The manipulation of the "tilt" angle did not proceed at this point due to an unanticipated coupling of the "pan" and "tilt" adjustment means. A correction procedure was developed to enable calculation of the

adjustment settings necessary to manipulate the "pan" and "tilt" at any desired combination. Further testing of the "tilt" manipulation is necessary to verify its precision.

Multiple members of the research team were trained in the use of the FTP image simulator. Previously, only the author/developer of the simulator was adequately knowledgeable in its use and simulations of the FTP system had to be planned and scheduled in advance. This caused delays in the turnaround time between the initial identification of potential problems with the FTP procedure and the analysis/presentation of simulator results.

At the beginning of May, the ICET Fourier Transform Profilometry (FTP) effort learned that the employment of two of the seven members of the FTP development team was being terminated at the end of May due to the retroactive recision of 20% of the ICET CA07 budget. Those terminated are a Ph.D. mechanical engineer who has had responsibility for a comprehensive investigation of all factors relating to determination of uncertainty with regard to the FTP technique and instrumentation, and a technician whose duties have included fabrication and volume determination of the non-descript targets used in the multi-stage FTP Performance Evaluation testing. Some time was spent evaluating how these changes are going to affect the FTP effort in terms of both manpower and budget.

Based upon the 20% retroactive recision of the CA07 budget, a revised CA07 workscope was developed and provided to Hanford collaborators for their comments/suggestions. At the request of Hanford collaborators, a PowerPoint overview of the status of the Fourier Transform Profilometry (FTP) effort was prepared and discussed with Hanford collaborators during a bi-weekly conference call.

The ICET FTP effort is performing a multi-stage performance evaluation of the FTP technique in order to document the capabilities of this technique under simulated Hanford waste tank conditions; each stage imposes increasingly realistic conditions. As originally envisioned, the progressive stages were to be used to sequentially incorporate improvements/increased capabilities into the FTP software and instrumentation. One consequence of this approach is that a different FTP system would, in effect, be utilized for each of the stages, making comparison among the stages difficult. Therefore, the ICET FTP team decided it would be better (to the extent possible) to address immediately the technical challenges that had not yet been solved so that there would be more uniformity with regard to the FTP system used for the different evaluation stages. This approach was inaugurated by addressing questions relating to how FTP handles curved (non-perpendicular) background surfaces (such as a curved waste tank bottom).

WORK PLANNED

STEREOVISION

Progress will remain slow until the graduate student can be replaced; a graduate research assistant will be hired as soon as funds are available. The Stereovision effort will then continue to optimize the experimental setup and software for deployment into the Hanford waste tanks. A

series of experiments at large distances was previously performed. At that time, analysis of the acquired images will continue, with an emphasis on improving the disparity match.

FOURIER TRANSFORM PROFILOMETRY

During the next reporting period, the FTP effort expects to continue its efforts to immediately address technical challenges that have not yet been solved so that there will (to the extent possible) be more uniformity with regard to the FTP system used for the different Performance Evaluation Stages. Preparation for Performance Evaluation Stage 2 is expected to be completed. The report for Performance Evaluation Stage 1 will be completed and submitted to Hanford collaborators. Work will also continue on study of phase unwrapping algorithms[1, 2] for target areas that have large height discontinuities and/or surface isolations. Research on image quality improvement algorithms[3, 4] is on-going.

REFERENCES

1. D. C. Ghiglia and M. D. Pritt, *Two-Dimensional Phase Unwrapping* (John Wiley & Sons, New York, 1998).
2. Yosuke Takahashi, Mitsuo Takeda, Masaya Kinoshita, Quan Gu, and Hideaki Takai, "Frequency-Multiplex Fourier-Transform Profilometry: a Single Shot Three-Dimensional Shape Measurement of Objects with Large Height Discontinuities and/or Surface Isolations", *Applied Optics* **36** (22) 5347-5354 (1997).
3. Chang Wen Chen and Ya-Qin Zhang, *Visual Information Representation, Communication, and Image Processing*, (Marcel Dekker, New York, 1999).
4. Bahram Janidi, *Image Recognition and Classification – Algorithms, Systems, and Applications* (Marcel Dekker, New York, 2002).

ACRONYMS

CTF	Cold Test Facility
FTP	Fourier transform profilometry
ICET	Institute for Clean Energy Technology
SV	stereovision

Process Chemistry and Operations Planning for Hanford Waste Alternatives

Jeff S. Lindner, John C. Luthe, Laura T. Smith, Valerie Phillips, Rebecca K. Toghiani

INTRODUCTION

Evaluation of the potential difficulties associated with meeting regulatory milestones for cleanup of the Hanford site tank wastes has indicated that tank farm operations are limited by the lack of available space in the existing double shell tank (DST) system. Whereas additional efforts are currently being evaluated for alternative processing of the low activity waste (LAW) such as bulk vitrification and fractional crystallization, the shear volume of waste, the capacities of the treatment facilities, and the lack of storage space dictate the single shell tank retrieval schedule.

Part of the difficulty in controlling the available space lies in the underlying chemistry associated with salt cake and sludge retrievals. A number of salts present in the waste, including sodium oxalate and natrophosphate ($Na_7F(PO_4)_2 \cdot 19H_2O$, require considerable water for dissolution, thereby increasing the available volume needed. Sludge retrievals typically employ sluicing. Owing to the limited solubilities of metal hydroxides and oxides, only minimal dissolution is expected during sludge retrievals. Here, however, the resulting slurry feed must meet specific requirements such as percent solids by weight, and the ability to effectively blend the waste with that already present in the DST.

Salt cake chemistries have been studied in these laboratories for some time. Initial efforts centered on thermodynamic modeling using the Environmental Simulation Program (ESP, OLI Systems Inc.) of salt core dissolution experiments conducted by Herting [1]. Comparison of the experimental results with model predictions identified data gaps for a number of double salt systems present in the waste. A subsequent effort was then developed to measure solubility data in these laboratories [2, 3]. The data obtained were later evaluated with respect to available literature data and then developed into a database for use in the ESP software. The DBLSLTDB database was initially directed for use in ESP version 6.5 [4]. The database relies upon some of the fundamental data contained in the default Public database that is always called by the program. OLI Inc. eventually upgraded the ESP code to version 6.7 and then version 7.0. This mandated the re-fitting of the DBLSLTDB compilation. The current version has been denoted as V7DBLSLT and has been extensively employed for salt processing simulations associated with both Hanford and the Savannah River Site.

The behavior of salt wastes has been further evaluated based upon laboratory and pilot-scale experiments. The later have been conducted at the Applied Research Center (ARC) at Florida International University (FIU). Detailed comparisons between the experimental results and model predictions have been reported [5]. The database was also used in simulations applicable to the retrieval of salt cake from SRS tank 41H [6]. Present deficiencies within the thermodynamic data are expected to be associated with some of the sludge constituents. The overriding goal for the current work is to improve the understanding of the thermodynamics of sludge components and to perform research on the possibility of associated models in support of

Hanford waste alternatives. Additional efforts are also described wherein the existing V7DBLSLT database will become integral to the vendor supplied model.

The current project is divided into three sub-tasks.

Task 1 Research on Neural Networks: The work proposed for the coming year is directed at the development of a more-restricted network, specific to either the C tank farm or 242-A evaporator operations. Current retrieval scheduling indicates that processing of the C farm waste will continue for 4-5 years. Thus, development of a network for use within the HTWOS model is expected to provide insight into the retrieval process and in the mixing of the waste within the DST system. Alternately, one means for reducing waste volume is to evaporate water. Previous efforts in these laboratories have demonstrated that the salt representation developed in connection with the DBLSLTDB database is capable of reproducing 222-S laboratory boil-down experiments. Results have also been compared with waste reduction factors obtained during actual campaigns and found to agree as well.

Discussions with site engineers will be used to select the network target. Development of the network will then begin based on BBI data and process operations.

Task 2 Aluminum Chemistry Evaluations: The gibbsite to boehmite transition will be evaluated using caustic compositions at different temperatures. Solutions will be prepared and heated in a low-temperature furnace and analyzed using thermogravimetric analysis. To evaluate the rate at which the transition occurs, measurements will be made as a function of time. Select end products will be evaluated by x-ray diffraction to correlate the weight loss data from the TGA with an absolute method.

Task 3 Database Distribution and Development: Although not mentioned directly above, the need to maintain the DBLSLTDB database in light of changes made at the vendor has taken considerable effort. Ideally, the database should be portable from one version of the software to another; however, vendor changes in some of the underlying thermodynamic data make this impossible. Thus, efforts in FY'06 were first made in porting the database to the version 6.7 software, followed by migrating to version 7.0 after the short-lived 6.7 version was shelved. Owing to these difficulties, it is considered necessary that the database be formally incorporated by the vendor.

OLI Inc. offers 2 different thermodynamic formalisms. The original framework is based on the Bromley model and has been used in ESP versions through 7.0. The second format is based on their mixed solvent electrolyte (MSE) model. Discussions with OLI personnel indicate the MSE model is the model of the future. The three options, as far as the DBLSLTDB compilations is concerned, involve 1) continue to maintain and update the database when OLI upgrades to new versions, 2) port the database and/or the original data sets to OLI for them to incorporate the work into the ESP Public database, or 3) port the collection to OLI for incorporation in the MSE framework.

For reasons described above, the first option is not appealing. Whereas ICET would maintain direct control and distribution rights to the database, subtle changes brought on by changing the ESP Public database can lead, as noted, to a significant effort to requiring significantly more time and effort through updating data regressions. Option 2 is similar to option 1 in that the framework would still be the standard electrolyte model; however, one benefit is that the pedigree of the database would now be adopted by OLI. This approach has the benefit of distribution from a commercial entity, thereby implying a formal QA/QC program. The third approach is attractive both in that the majority of work at OLI Inc. is now concerned with the MSE and that the QA/QC has been noted as being rigorously controlled. In adopting the third approach, it is also noted that the MSE framework is expected to be supported for many years to come, thereby providing a permanent home for V7DBLSLT.

The goal then is to provide a modest subcontract (on the order of $25-$30K) to OLI for porting V7DBLSLT to the MSE formalism. During this work, personnel from MSU\ICET will travel to OLI to learn the MSE regression procedures and concepts. This later activity will be necessary as additional data on, for example Al, Cs, and K solubilities have been or are being obtained and will need to be included in the database. Delays in porting the database have led to delays in incorporating these additional data.

WORK ACCOMPLISHED

Task 1 Research on Neural Networks:

The development of a neural network for use within the HTWOS model requires an extensive training set. The training set will be the results from ESP simulations (using the V7DBLSLT database) for a range of input streams. The input molecular streams will cover the range of the contents of the C tank farm as given in the Best Basis Inventory (BBI). In order to generate valid input for ESP the BBI data must be charge balanced for neutral input streams. The charge can be balanced with a minimal change in the total tank mass by splitting the charge imbalance difference equally between the anions and cations. The overall amount of the anions and cations is adjusted, and apportioned over all the contributing species, to match the difference. For the C tank farm, the total mass change is 1.4%, ranging from -3.2% to 2.2% for individual C-100 tanks. The total mass change for all 175 tanks is 0.7%. The input streams for ESP simulations consist of the stable molecular compounds, the charge balanced ionic species are converted to the analyte compounds, typically as mole fractions. The ranges of mole fraction values for the tank constituent compounds for the all 175 tanks is shown in Figure 1, and the contents of the C-100 tanks is shown in Figure 2
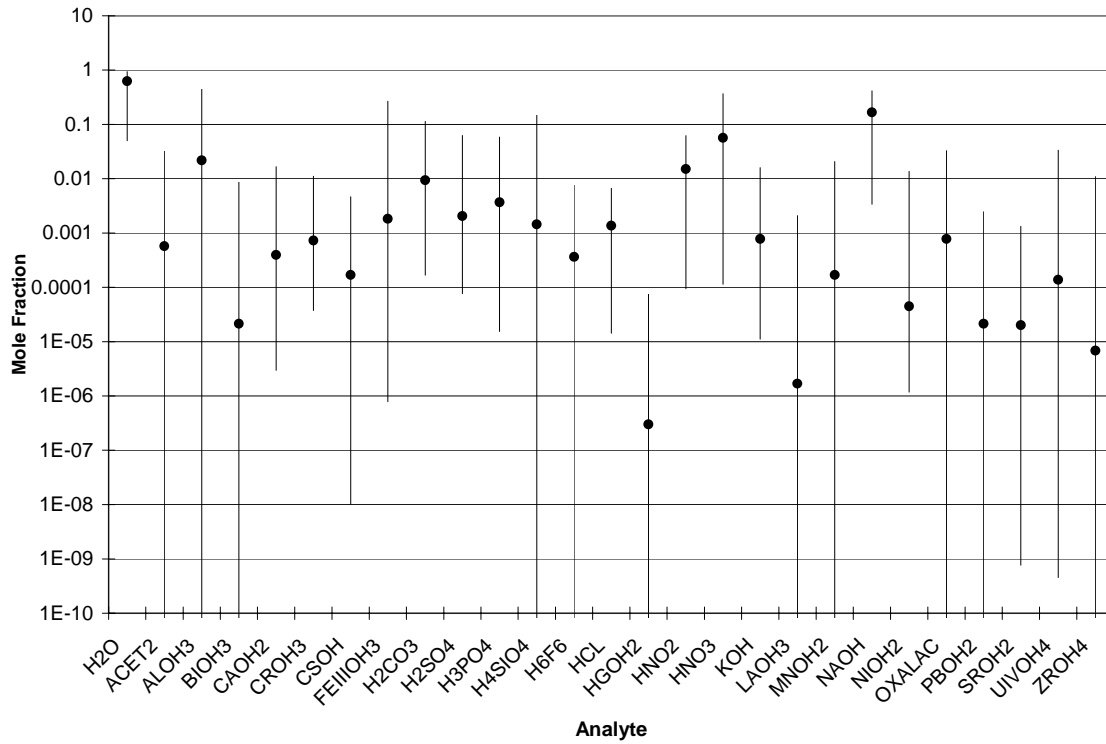
Figure 1 Ranges of the tank contents as mole fraction for the entire tank farm.
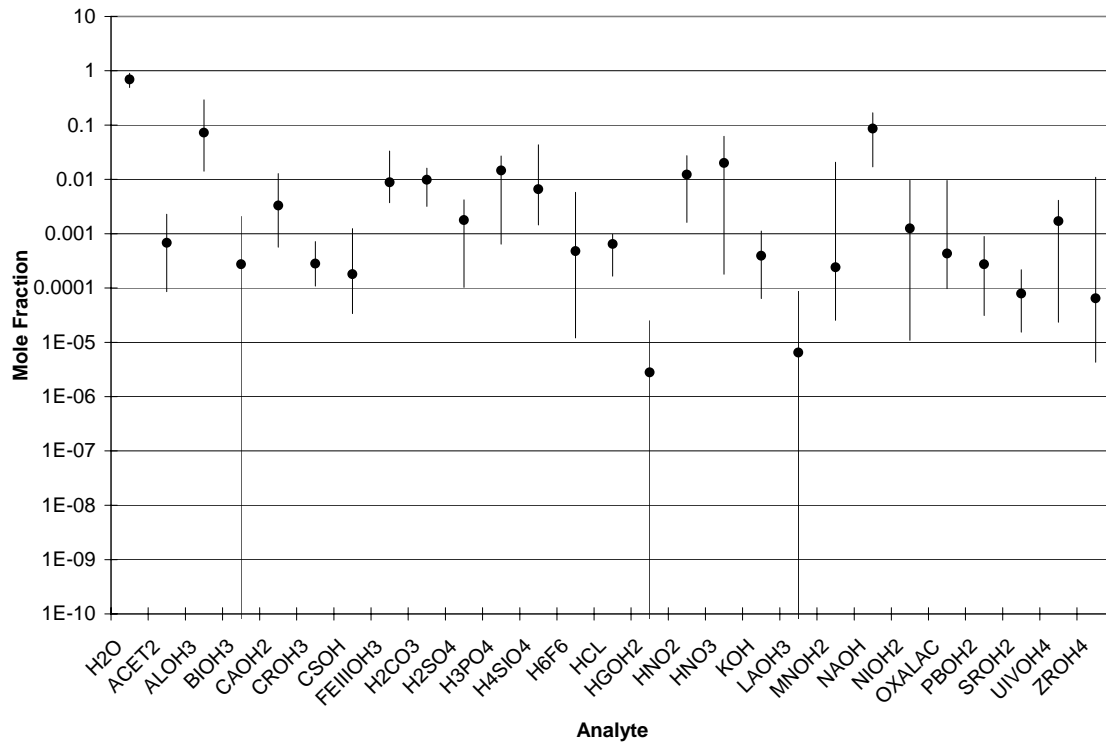
Figure 2 Ranges of the tank contents as mole fraction for the C-100 tanks.

The neural networks generated previously were trained from data sets calculated using OLI Systems, Inc. StreamAnalyzer. The data sets were built up from step-wise dilutions of representative tank contents. However, for this task an ESP simulation model of the tank recovery process will be constructed. This model will approximate the corresponding section of HTWOS where the neural network will be used. Such a general simulation model requires the use of ESP rather than StreamAnalyzer. In order to build a comprehensive training set that covers the ranges of tank constituents many ESP simulations will have to be performed. The automation of such tasks, which require preprocessing of input files and post processing of output files, is done with a scripting language such as Perl (Practical Extraction and Reporting Language). Perl is platform independent and freely available. The script routines will replace the ESP user input interface program, which constructs the model parameter input files and invokes the ESP computation program. The details of the user input – computation program interaction are not yet completed.

Task 2 Aluminum Chemistry Evaluations: Details of the importance of determining the form of aluminum in the Hanford wastes along with preliminary experiments evaluating the gibbsite to boehmite transition were described in the previous report [7]. Results indicated that boehmite formation can occur, under low water vapor conditions, at temperatures as low as 120 ^{o}C. This work was expanded to consider lower temperatures, high water vapor conditions, and the effect of 3m NaOH as opposed to 1.5m NaOH.

A number of measurements were attempted at 50, 80, and 100 ^{o}C. No changes were observed at the lower temperatures up to 540 hours. Small conversions of the Almatis gibbsite were found at 100 ^{o}C, Figure 3. Known mass standards were used to determine the accuracy of the TGA balance. A 5 mg sample was found to weight 4.95 mg and a 20 mg standard resulted in a mass of 19.7 mg. These result in 1 and 1.4% errors respectively. After 240 hours at 100°C the amount of gibbsite in a sample was 93.9%, which is outside of experimental error.
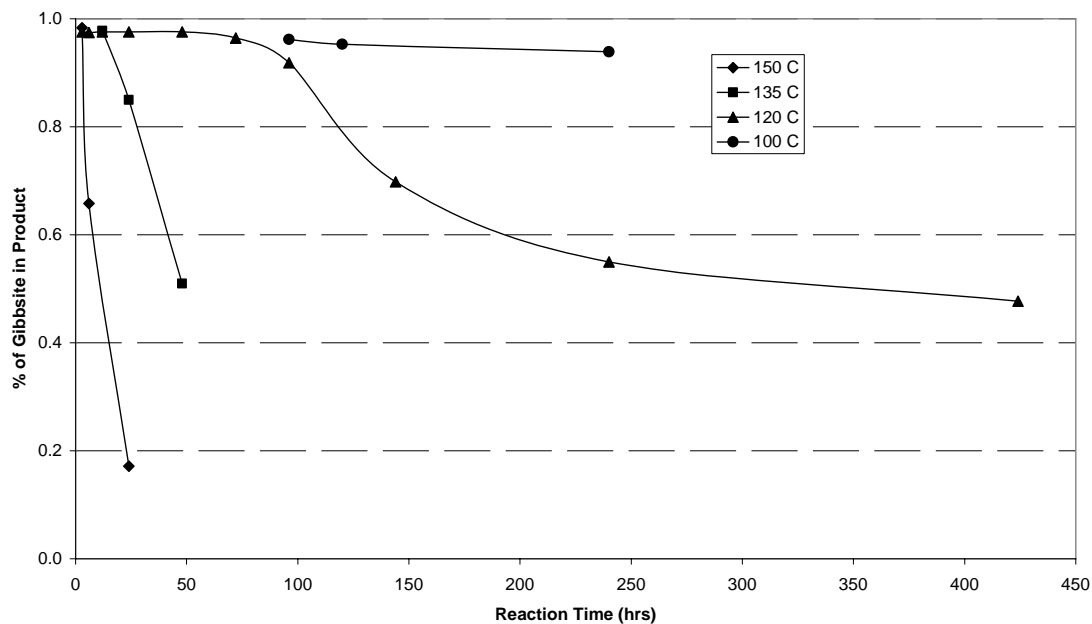
Figure 3 Data obtained for the low water vapor conditions examined for the gibbsite to boehmite transition. All of the samples were prepared in 1.5 m NaOH.

Figure-1 Data obtained for the low water vapor conditions examined for the gibbsite to boehmite transition. All of the samples were prepared in 1.5 m NaOH.

Confirmation of the accuracy of the TGA method was obtained on selected samples using semi-quantitative x-ray diffraction (XRD) performed by Evans Analytical Group, Round Rock, TX.. Figure 4 is a trace obtained for the sample that was heated at 120 $^{\circ}$C for a period of 240 hours.
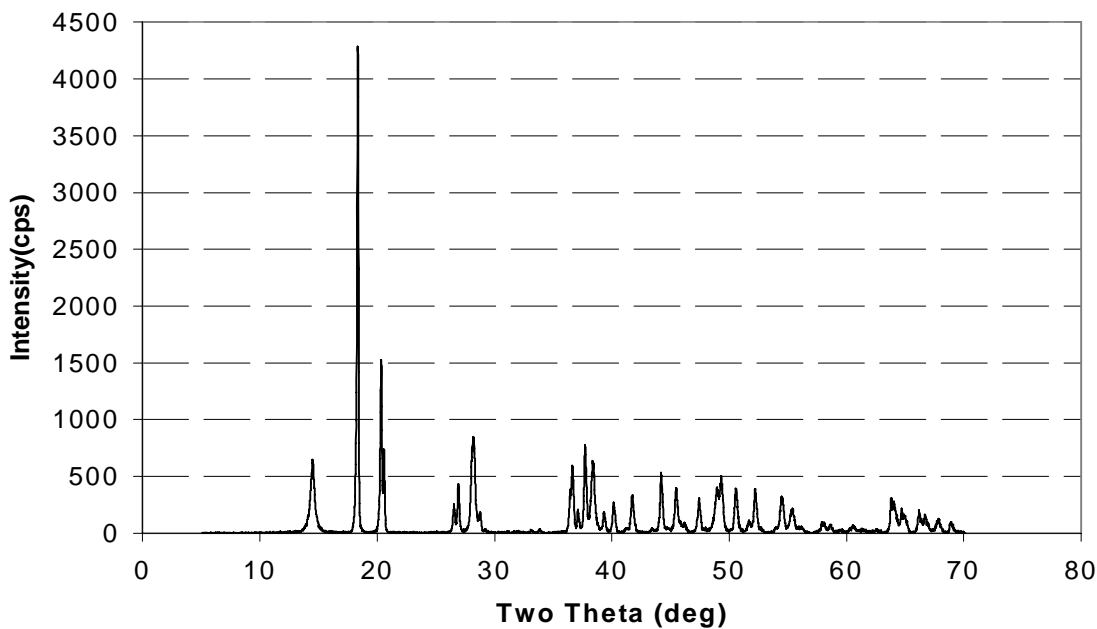
Figure 4 XRD pattern for a sample heated at 120 $^{\circ}$C for 240 hours.

Comparison of the pattern with traces for gibbsite (Figure 5) and boehmite (Figure 6) revealed that the sample was approximately 50% gibbsite and 50% boehmite in close agreement with the TGA results given in Figure-1 [8, 9].
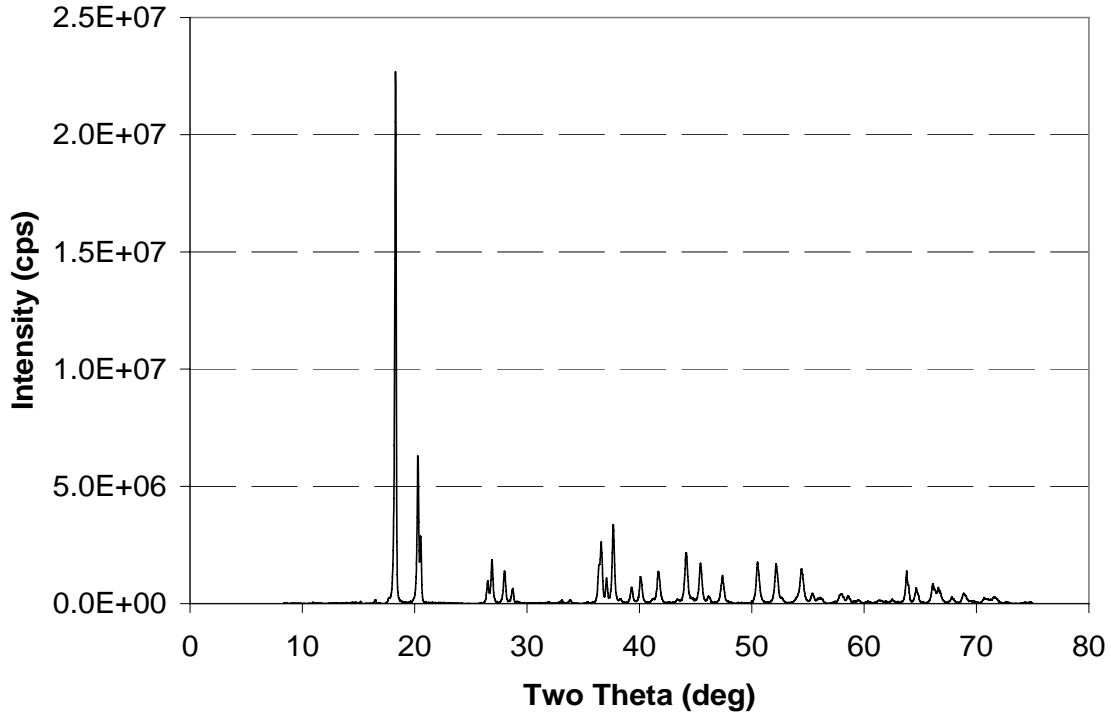
Figure 5 XRD pattern for the Almatis gibbsite. Computer comparison using the Inorganic Crystal Structure Database (ICSD) did not reveal any other constituents [10].
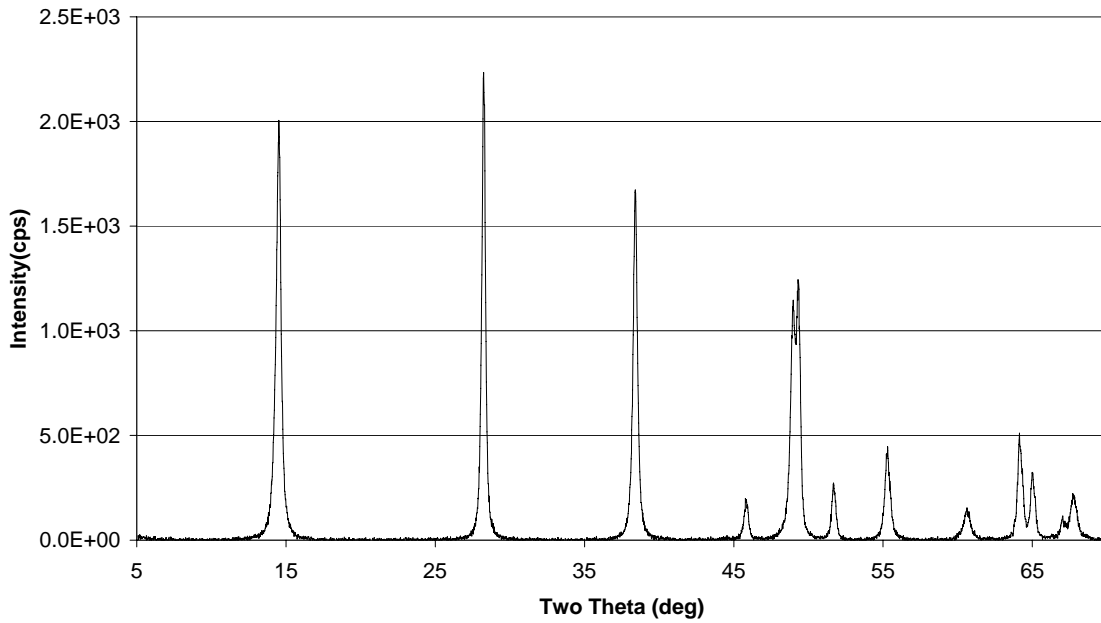
Figure 6 XRD trace of pure boehmite.

No significant differences were observed for the transitions evaluated under low water vapor (dry) and high water vapor (wet) conditions, Figure 7.
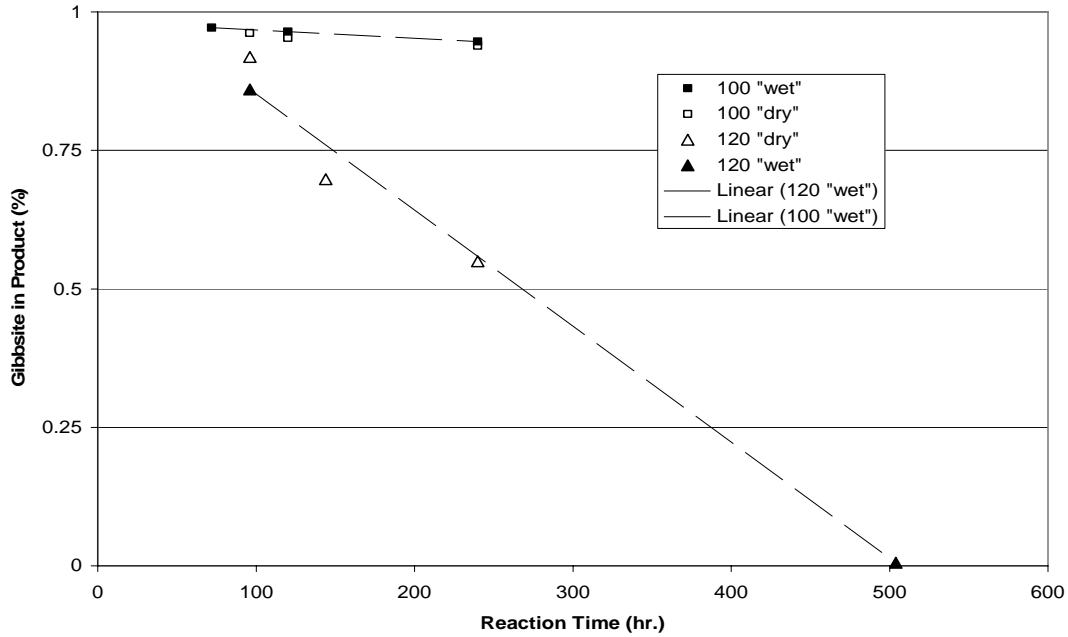
Figure 7 Comparison of the mass percentage of gibbsite remaining under low and high water vapor conditions.

This indicates that the primary parameter affecting the transition is temperature as opposed to the moisture content within the tank waste. One other parameter that was investigated was the effect of caustic loading (1.5 and 3m). The data in Figure 8 shows that the change in gibbsite percentage as a function of time is the same at both 150 and 120 $^{\circ}$C once the transition begins.
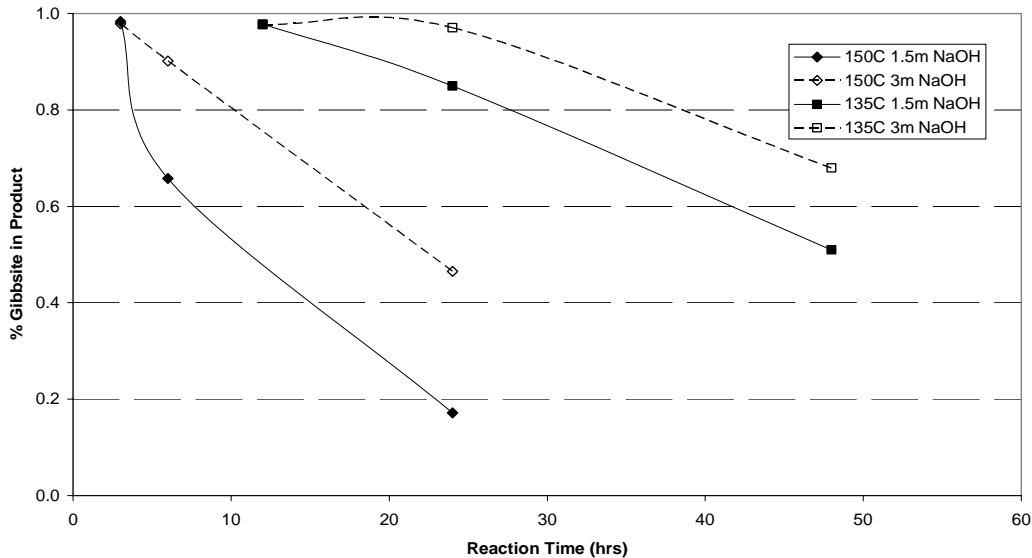
Figure 8 Effect of caustic loading on the gibbsite to boehmite transition.

Of those factors investigate, the primary parameter affecting the conversion of gibbsite to boehmite was temperature.

Further analysis of the data is in progress to determine reaction rates and the activation energy. Data for the transition can then be compared with historic Hanford waste temperature records [11]. An estimate of the fraction of boehmite contained in specific tanks will be possible through knowledge of the waste temperature and loading of aluminum in a specific tank.

Task 3 Database Distribution and Development:

Further negotiations with OLI Systems Inc. resulted in the development of a subcontract that was issued from Mississippi State University. The number of systems that will be initially incorporated into the mixed solvent electrolyte database had to be limited owing to subcontract cost limitations. The revised listing is collected in Table-2. The primary system not listed is that for Na_2SO_4-Na_2CO_3. This will have to be added in a subsequent budget period. Solubility data on cesium and potassium have been obtained in support of SRS. These will likely be added in the next subcontracting period (FY'08).

Table 1 Systems from the V7DBLSLT database that will be ported to the mixed solvent electrolyte database.

Missing Pure Components	Binary Systems	Verification of Predictions
$NaNO_2$	$NaOH$-$NaNO_3$	NaF-Na_2SO_4
HNO_2	NaF-$NaOH$	$NaOH$-Na_2SO_4
	NaF-Na_3PO_4	$NaNO_3$-Na_2SO_4
	NaF-$NaNO_3$	$NaNO_3$-Na_2CO_3
	Na_3PO_4-$NaNO_3$	
	$NaNO_2$-Na_2CO_3	
	$NaNO_2$-Na_2SO_4	
	$NaNO_2$-$NaOH$	
	$NaOH$-Na_2CO_3	

ICET's responsibilities within the subcontract to OLI Systems, Inc., include the identification and retrieval of literature data, compilation of said data combined with laboratory measurements made at ICET on the specific system, preparation of the necessary regression input files, preliminary regression of these data for parameterization of necessary interactions within the aqueous-based framework, along with preliminary predictions of the solubility envelopes. For each system listed in Table 2, the various items listed above have been or are being gathered. The effort has been divided into 7 groupings for transfer to OLI. These are detailed in Table 3.

Table 2 Data transfer to OLI Systems, Inc.

Grouping #	System(s) Included
1	NaF-$NaNO_3$-$NaOH$; NaF-$NaOH$; $NaNO_3$-$NaOH$
2	$NaNO_2$-$NaOH$
3	Na_3PO_4-$NaNO_3$-$NaOH$; Na_3PO_4-$NaOH$
4	NaF-Na_2SO_4-$NaOH$; Na_2SO_4-$NaOH$
5	$NaNO_3$-Na_2SO_4-$NaOH$; $NaNO_2$-Na_2SO_4-$NaOH$
6	NaF-Na_3PO_4-$NaOH$; NaF-Na_3PO_4-$NaNO_3$-$NaOH$
7	$NaNO_3$-Na_2CO_3-$NaOH$; $NaNO_2$-Na_2CO_3-$NaOH$; Na_2CO_3-$NaOH$

During this quarter, the necessary data files and literature sources for groupings 1, 2, and 3 were transmitted to OLI Systems, Inc.

WORK FORECAST

The details of the ESP program operation have to be determined in order to develop batch scripting in place of the interactive program interface.

Evaluation of the kinetics of the gibbsite to boehmite transition will be performed along with a summary evaluation of the maximum waste temperatures recorded in the Hanford tank farms.

Transfer of necessary files/information to OLI Systems, Inc., for chemical groupings 4 and 5 will be accomplished during the next quarter.

CONCLUSIONS

The preparation and development for batch production of ESP simulations of the C tank retrievals to be used as neural net training sets is underway.

Further evaluation of the gibbsite to boehmite transition has validated the use of the thermogravimetric method through associated XRD analysis and has indicated that, of the parameters investigated, water vapor pressure, caustic loading, and temperature, that the later is the only significant driver for the reaction. Results obtained under different water vapor pressures were, within, experimental error, the same. Slight changes were observed at 3m NaOH as opposed to the 1,5m condition. These typically amounted to longer solvent evaporation periods with little change in the corresponding mass percentage of gibbsite remaining in the sample as a function of time.

Initial efforts are underway to transfer the information content within V7DBLSLT to a more permanent repository, maintained by OLI Systems, Inc. Incorporation into the Mixed Solvent Electrolyte model will provide for improved modeling and predictive capabilities with regards to waste retrieval activities at the Hanford and SRS sites.

REFERENCES

1. Toghiani, R.K., and Lindner, J.S., *Saltcake Dissolution Modeling, FY 2000 Status Report*, DIAL-40395-TR00-1, Diagnostic Instrumentation and Analysis Laboratory, Mississippi State University, MS(1999), **http://vax.icet.msstate.edu/~lindner/FY2000 Saltcake Dissolution Report/**
2. Toghiani, R. K., Phillips, V. A., and Lindner, J. S., "Solubility of Na-F-SO$_4$ in Water and in Sodium Hydroxide Solutions," Journal of Chemical and Engineering Data 50(5), 1615, (2005).

3. Selvaraj, D. K., (2003), Solubility Studies in the Na-F-PO$_4$ System in Sodium   Nitrate and in Sodium Hydroxide Solutions, MS Thesis, Chemical Engineering, Mississippi State University, Mississippi State, MS.

4. Toghiani, R. K., et al., "Improved Process Chemistry for Legacy Nuclear Waste Remediation: Development of DBLSLTDB," presented at the 14th Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, TN (2005).

5. Toghiani, R. K., Smith, L. T., Lindner, J. S., Tachiev, G. L., and G. Yarri, "Modeling of Pilot-Scale Saltcake Dissolution," WM'06 Conference, February, 2006, Tucson AZ.

6. L. T. Smith, J. S. Lindner, V. Phillips, A. Antonyraj, and R. K. Toghiani, "Modeling and Experiments for the SRS Low-Curie Salt Process." Separation Science and Technology, 41(11), 2341-2360 (2006).

7. Lindner, J. S., Luthe, J. C., Smith, L. T., and R. K. Toghiani, "Process Chemistry and Operations Planning for Hanford Waste Alternatives," ICET Quarterly Technical   Progress Report for the period January-March 2007.

8. Saalfeld, H., Neues Jahrb Mineral., Abh., v95 p1 (1961).

9. Farkas, L., Gado, P., Werner, P.E., Mater. Res. Bull., v12 p1213 (1977

10. http://www.icsd-usergroup.net/index.html

11. Flanagan, B. D., "Maximum Surface Level and Temperature Histories for Hanford Waste Tanks," WHC-SD-WM-TI-591 ,rev. 0, Westinghouse Hanford Corporation, Richland WA (1994).

Disposition of Idaho HLW Calcine

Support of the CH2M-WG Idaho Calcine Disposition Project

Ronald A. Palmer

INTRODUCTION

Since September 2003, ICET has been assisting the Calcine Disposition Project to develop a stabilized form for about 4400 m^3 of mixed high-level radioactive calcined waste stored at the INL Site. The Calcine Disposition Project is developing process designs for retrieval and packaging "as is" in a canister or for stabilization and packaging of the calcine, with a record of decision on the packaging process planned for September 2009. The Calcine Disposition Project baseline assumption is that the HLW calcine can be removed from the hazardous waste category via regulatory negotiations and/or by developing a stabilized calcine waste form, which would meet the Toxicity Characteristic Leaching Procedure (TCLP).

The ICET effort has yielded the data necessary for CH2M-WG Idaho to evaluate waste forms produced via three different stabilization methods versus the appropriate repository waste acceptance standards. The candidate stabilization methods tested by ICET were iron phosphate ceramic, hydroceramic grout, and grout cement. Waste form properties were researched and documented, and the ability of each waste form to comply with the Waste Acceptance Product Specifications (WAPS) was evaluated.

The ICET data will be considered an integral and traceable part of the Calcine Disposition Project that can be used to verify the preferred stabilization method via the quality assurance requirements of DOE/RW-0333P. ICET researchers have worked in the field of stabilization of radioactive waste for many years, and have the expertise and equipment necessary for handling, producing, and testing all stabilization alternatives proposed for the calcine waste.

Grout cement was selected in July 2005 by CH2M-WG Idaho as the best of the three candidate processes for continued bench scale development and mock-up studies. The down selection was based on how well the candidate met the performance parameters based on the experimental data that had been collected by ICET since September 2004 per the test plan (ICET/ICP-SP3-TP-001).

The tasks for CY2007 include mock-up tests on key components and process control monitors are planned. The purpose of this phase of testing would be to replace manual steps and small laboratory equipment used in the bench scale tests with prototype components and automated process control steps. Particular attention would be given to the simplicity, remote operability,

reliability, and recovery from failure exhibited by the key components and process control monitors.

The key components to be mocked-up and tested include the calcine, stabilizer and water batch vessels, the mixer, the small diameter neck (i.e., 3-6 inches in diameter) of the waste canister, and methods to sample the calcine feed to the mixer and product feed to the canister.

Key process monitoring steps include:
a) rate of calcine, stabilizer, and liquid delivery to the mixer,
b) inventory of ingredients in the mixer during ingredient addition,
c) torque load and RPM on mixer paddle and viscosity of the stabilizer while mixing,
d) any build up of residual in the mixer, and
e) fill level of the canister while pouring.

Specific activities to be completed over this reporting period include:
- Conduct mock-up runs on non-hazardous and mixed calcine simulant,
- Conduct mock-up runs on major calcine types,
- Conduct confirmatory mock-up runs,
- Test some of the stabilized waste for compression strength and ability to meet leach limits in the TCLP and PCT, and
- Test some of the stabilized waste for the effects of high temperature exposure (200-350⁰C) on the compression strength and the ability to meet leach limits in the TCLP and PCT.

WORK ACCOMPLISHED

Non-hazardous Calcine Simulant
Two 55-gallon drums of calcine simulant (non-hazardous) shipped from INL were received in good order. Samples were taken from one drum of the calcine simulant for chemical analysis and fabrication of test cubes. The chemical analysis is reported in Table 3.

Analyte	Wt.%
Aluminum	30.4
Boron	0.700
Calcium	3.11
Magnesium	1.74
Sodium	5.02

Table 3 Chemical analysis of non-hazardous calcine simulant.

Two sets of cubes were made, one at 17% and one at 34% waste loading, from the calcine simulant to test for mechanical strength. No anomalies were observed during mixing, however, neither set appeared to cure as quickly as before. The sets were aged for a total of 37 days and then subjected to compression testing. The results (Table 4) show that both formulations are sufficiently strong after the 37 day period.

Sample	Breaking Stress (psi)	Cure Time (days)
G17A	739	37
G17B	912	37
G17C	853	37
G34A	1326	37
G34B	1211	37

Table 4 Compressive strength of cubes made from the non-hazardous calcine simulant (first batch)

A larger batch with this simulant was also prepared (with the hopes that scaling up will give better results). After seven days, only the 34% cubes had cured; the compression strength is not quite good enough. After curing 36 days, the strength is sufficient. (See Table 5.)

Sample	Breaking Stress (psi)	Cure Time (days)
G34A	426	7
G34C	465	7
G34E	388	7
G34B	478	36
G34D	597	36
G34F	640	36

Table 5 Compressive strength of cubes made from the non-hazardous calcine simulant. (second, larger batch)

Pilot Facility Construction and Check-out

On the ICET hardstand, a test platform was built to allow the installation of feeders, mixers, and control equipment above grade so that pouring the grout could be done from the bottom of the mixing tank. The mixing tank is a 55-gallon drum with a drain in the center of the bottom. Figure 9 is a photograph of the mock up system.

A safety review of the assembled feeders, mixers, and control equipment was first completed then a small test batch consisting of only sand was used to check the operation of the feeders. No problems were encountered.

The first shakedown test was run by mixing the powders and then adding the water. (Table 4 provides the details of the four pilot-scale tests.) This was not particularly successful as the solids mostly stayed in the bottom of the mixer, but the feeders, mixers, and control equipment functioned well. (A blank test plan that is used for each run of the mock up system is attached.)

A second run was completed using the same amounts of raw materials. However, for this run, the water was put in the mixing tank before adding the powders. The sodium sulfide was added to the water and stirred prior to the addition of the other raw materials. As the raw materials were fed into the mixing tank, the mixer was operating continuously. In addition, the one-inch bottom drain was replaced with a two-inch drain.

Three samples (2-inch cubes) were taken at the beginning, middle, and end of this run. After 7 days, the compressive strength testing of one sample was 150psi. The other two were tested at 35 days and had strengths of 415psi and 685psi.

For the third run, the size of the batch was increased to about 15 gallons and the mixing process was altered so that mixing was continuous as the materials are being added. Again, three samples were taken at the beginning, middle, and end of the run. After 14 days, the compressive strength testing of one sample was 371psi. The other two were tested at 40 days and had strengths of 340psi and 290psi.

Batch	Amounts (pounds)			
Components	Pilot #1	Pilot #2	Pilot #3	Pilot #4
Fly ash	6.25	6.25	12.5	37.5
Slag	6.25	6.25	12.5	37.5
Portland cement	12.5	12.5	25	75
Simulant	25	25	50	150
Water	25	25	50	135
Sodium Sulfide	0.75	0.75	1.50	4.56

Table 6 Details of make-up for pilot batches.

The fourth run was designed to have about 10% less water in the batch in an attempt to increase the compressive strength. This was the largest batch tested so far. Feeding time for the powders was approximately 30 minutes. The mixing time (held constant over all four runs) was 20 minutes.

Nine samples were taken, 3 at the beginning (1A, 1B, and 1C), 3 in the middle (2A, 2B, and 2C), and 3 at the end (3A, 3B, and 3C). Results of the compression strength testing are given in Table 7. Acceptable strengths are starting to be reached after aging for about a month.

Sample	Breaking Stress (psi)	Cure Time (days)
1A	375	14
2A	344	14
3A	375	14
1B	360	32
1C	298	32
2B	413	32
2C	548	32
3B	725	32
3C	455	32

Table 7 Compressive strength of cubes made during Pilot #4.

WORK FORECAST

Two more pilot tests at larger batch sizes are planned in order to get a better sense of the times required for feeding, mixing, and emptying the mix tank.

CONCLUSION

The equipment is operating in a satisfying manner.

Figure 9 Pilot facility setup.

ATTACHMENT

Test Plan Number DOE-RP-INL-070001, Rev. 1

Date _____

Issued by _____ CTE

Approved by _____ PI

_____ Health and Safety Officer

_____ Waste Management and Environment Officer

Test Plan for ICET – MSU testing on the calcine waste formulation.

Test number **DOE-RP -INL -070005**

Test begin date _____

1. Prepare a mixture comprising 25% ash, 25% slag and 50% Portland cement.

    Fly ash added _____ lbs

    Slag added _____ lbs

    Portland cement added _____ lbs

2. Run this mixture through the V-blender for a period of at least 2 hours.

    Blending start time _____

    Blending end time _____

    Total time blended _____ hours

3. Prepare an equal weight of calcine surrogate for the test

    Surrogate ready for the tests _____ lbs

Performed by _____

Time _____   **Date** _____

4. Prepare an equal weight of water for the tests.

5. Water ready for the tests _____ lbs

Pre-test equipment preparation

6. Is the pressure washer ready for the test   Yes _____   No _____

7. Are the feeders ready for the test   Yes _____   No _____

8. Is the mixer ready for the test Yes _____   No _____

9. Air connected to the mixer Yes _____   No _____

10. Variable frequency drives for the mixer and feeders turned on Yes ___No___

11. Computer ready for the tests Yes _____   No _____

Loading the water and powders

12. Move the mixer lifting air valve to the lift position from the middle position and then go around and press the pedal to elevate the mixer top all the way and slide out the drum. Examine the stirrer and the drum and determine if they are both clean. Stirrer/drum clean? Yes _____   No _____

13. Slide the drum back into the mixer and tighten the belt that holds the drum in place

14. Add the water to the mixing drum
     Water added _____ lbs.

15. Add any other dry compounds into the drum, i.e. sodium sulfide, etc.

     Sodium Sulfide added _____ g

                    Added _____ g

16. Turn the air valve on the mixer to the LOWER position and go around and lower the feeder

17. Turn the mixer on for at least 10 minutes so that the Sodium Sulfide will dissolve in the water in the tank.
    Time start _____ Time end _____

Performed by _____

Time _____   **Date** _____

18. Reset the weights on the feeders.

       Feeder no 1   Total weight _____ lbs
                     Tare weight _____ lbs
                     Fed weight   _____ lbs

       Feeder no 2   Total weight _____ lbs
                     Tare weight _____ lbs
                     Fed weight   _____ lbs

19. Set the mixer drive frequency controller to 60 Hz and stir the mixture.
    Time started _____   Time ended _____

20. Load the **ash/slag/cement** mix into the hopper on **feeder no 1**

21. Load the **calcine** into **feeder no 2**

Performed by _____

Time _____   **Date** _____

22. Tare the weights

Feeder no 1   Total weight _____ lbs
              Tare weight _____ lbs
              Fed weight   _____ lbs

Feeder no 2   Total weight _____ lbs
              Tare weight _____ lbs
              Fed weight   _____ lbs

23. Set the variable frequency drives to 25 Hz on the feeders.

24. Set the variable frequency drives to 25 Hz on the feeders.

25. Turn on feeder no 1 and allow all the particulates to empty into the mixer drum. After it is all fed, note down the weights fed from the computer screen

Feeder no 1   Total weight   _____ lbs
Total weight   _____ lbs
Tare weight   _____ lbs
Fed weight   _____ lbs

26. Turn on feeder no 2 and allow all the particulates to empty into the mixer drum. After it is all fed, note down the weights fed from the computer screen

Feeder no 2
Total weight   _____ lbs
Tare weight   _____ lbs
Fed weight   _____ lbs

Performed by _____

Time _____   **Date** _____

27. Continue stirring the mixture for 20 minutes

28. Stirring started at _____   Stirring complete at _____

Drain the system
29. Open the drain valve on the mixer drum and drain into the drain tank,
Sample   _____   taken at   _____
Sample   _____   taken at   _____
Sample   _____   taken at   _____
Sample   _____   taken at   _____
Sample   _____   taken at   _____
Sample   _____   taken at   _____

Take as many samples as requested (time of sampling may not be feasible since the drain rate may be too fast.

30. Determine the amount of water to wash the drum

Water used to drain the system   _____ gallons

Performed by _____

Time _____   **Date** _____

Support of SRS Salt Disposition and Other SRS Alternatives

Modeling and Experimental Support for High-Level SRS Salt Disposition Alternatives

Jeff Lindner, Laura T. Smith, and Rebecca K. Toghiani

INTRODUCTION

High-level nuclear wastes contained at the Savannah River and Hanford sites exhibit large variation in constituents and concentrations. Consequently, different processing scenarios will be associated with these locations. Specific chemical information has not previously been available for a number of waste stream components. Formally identifying data gaps in relation to existing models and databases, followed by experimentation and data analysis provides an underlying scientific basis for understanding the behavior of the wastes.

The overall goal of this project is to augment the existing thermodynamic data and models associated with high caustic chemistries. The work includes solubility experiments on binary and ternary systems along with more complicated experiments based upon simulants of the tank wastes. In this way, the fundamental chemistry of the wastes is captured and second order effects are also ascertained.

Extensive experimental and modeling work has been performed in these laboratories for several salt waste simulants [1-3]. Experiments performed in FY06 included preparation of a SRS 8F sludge simulant and subsequent incorporation into a 38H salt simulant for two small column experiments in order to determine how the sludge affects transfers, ion compositions, and dissolution times. Past experiments have shown these column experiments to take approximately two weeks to achieve greater than 70% dissolution by weight. With the addition of the sludge a significant increase in time, six weeks, was noted for the same dissolutions by weight. Work on identifying the solids within the sludge composition and the solids remaining from both experiments using XRD analysis is currently underway.

An extensive literature search was undertaken on potassium and cesium complexes and compared to the ESP model. Little or no information was found on several of these components in caustic. Model predictions (using the Public and DBLSLTDB databanks) were used to design several solubility experiments and data were collected on these systems. Preliminary analytical results show discrepancies in model predictions.

Based on other evaluations, little modeling has been performed on sludge components. As mentioned previously, this laboratory has prepared the SRS 8F sludge simulant and performed aluminum solubility experiments in support of the Hanford site. The thermodynamic model was used to follow the sludge preparation.

This project is divided into two tasks.

Task 1 Laboratory scale experiments and modeling of salt cake simulants: Dissolve, deliquify and adjust (DDA) experiments will be performed on one or two tank simulant compositions based on current core analysis studies for Tanks 25 and 28. One question regarding the SRS waste compositions concerns the tank to tank heterogeneity of the waste. Previous studies have provided differing results for DDA experiments and associated thermodynamic modeling for wastes contained in 31, 37, 38, and 41H tanks. Large variation in constituent compositions may signify that different retrieval scenarios be considered. Laboratory-scale experiments under controlled conditions and associated modeling will provide for further validation of the model and an assessment of retrieval options.

Task 2 Impacts of sludge leaching on downstream processing: Current SRS site plans call for the preparation of sludge batch 5, derived from HM sludge, for feed to DWPF. The base sludge is approximately 30% by weight aluminum with a much smaller iron loading than the 8F sludge. Reducing the aluminum loading in the sludge through caustic leaching is expected to result in waste minimization through an increase in the waste loading in the glass and an associated reduction in the number of glass canisters.

One possibility for processing the secondary wash stream is blending with low activity streams obtained from later stages of the DDA process and subsequent conversion to saltstone. This task will model the blending process. Simulant compositions (as well as data from earlier DDA experiments and model predictions) are available for the following H-farm tanks; 37, 38, and 41. A simulant for the HM sludge was previously reported by Hobbs and was also used in a study on the possible use of oxalic acid [4, 5]. The ESP model will be used to evaluate stream blending with final comparison to the saltstone waste acceptance criteria [6]. An envelope will be developed which will establish the waste stream volumes that can be successfully combined on order to process the secondary waste stream as saltstone [7].

WORK ACCOMPLISHED

Modeling and results
Following discussions with site personnel on proposed plans to remove excess aluminum from sludge batch 5 (Tank 51) via caustic leaching, flow sheets were examined to model the sludge before and after the caustic strike for identification of the resulting leachate stream components and the viability of blending this aluminum-rich stream with other potential streams such as DDA (dissolve, deliquify, and adjust) fractions from tanks such as 41H, the DWPF recycle stream, or ETF streams. Figure 10 contains an overview of the flow sheet design currently under investigation by the site.
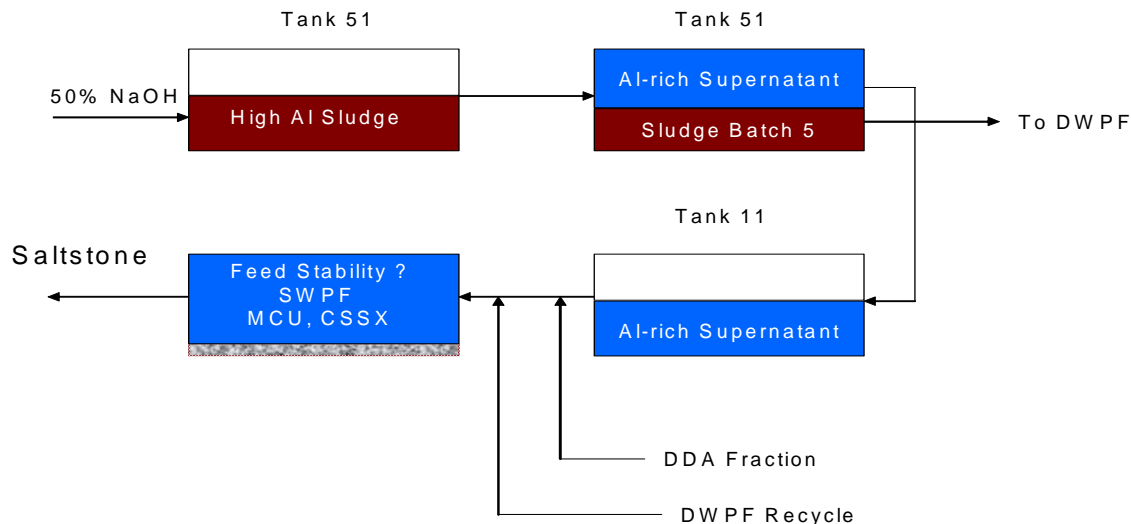
Figure 10 Current SRS flow sheet under review for aluminum removal from batch 5 sludge.

Stream blending can be complicated due to potential solids re-precipitation, thereby causing additional diluent such as caustic or water to be added to the processing cycle, and requiring additional tank space. Previous studies performed in this laboratory [1] have shown solids re-precipitation may occur due to changes in pH, ionic strength, and/or temperature when two or more fractions are blended. In addition, solids such as sodium aluminosilicate may form when specific ions (i.e. Al, Si) are present in equimolar amounts in the presence of sodium, hydroxide, nitrate, and/or carbonate [1,8]. Modeling of these streams can assist in obtaining details for the determination of the factors involved in solids re-precipitation.

Preliminary modeling of the Tank 51 HM sludge batch 5 simulant [4,5] was performed using ESP V7.0 and employing the V7DBLSLT, Corrosion, JEFF(setting the temperature for boehmite from 30-200°C), Zeolite, and Public databases. Results were then tuned to the aluminum value (29% by weight) and density obtained from communications with site engineers [9]. Table 8 contains a comparison of initial tank inventory and model predictions. The model predictions are in good agreement with SRS Tank 51 inventories.

Table 8 SRS characterization of Tank 51 and model results.

Stream Information	SRS Data	ESP Predictions
Total Volume, gal	492,000	484,000
wt% Insoluble solids	9.3%	9.14%
Total Mass, kg	2,018,000	2,030,000
Aqueous Phase		
Volume, gal	471,000	471,000
SpG	1.026	1.040
Mass aqueous, kg	1,830,000	1,850,000
Al, kg	1,000	1029
Concentration (M)		

Na$^+$	1.08	1.064
NO$_2^{-1}$	0.46	0.466
NO$_3^{-1}$	0.24	0.297
OH$^-$("free")	0.100	0.142
Cl$^-$	0.0007	0.006
SO$_4^{-2}$	0.023	0.024
F$^-$	0.0020	0.002
CO$_3^{-2}$	0.12	0.037
AlO$_2^-$	0.021	0.021
C$_2$O$_4^{-2}$	0.0045	0.005
PO$_4^{-3}$	0.0009	0.001
K$^+$	0.0031	0.003
Solid Phase		
Volume, gal	20,700	13,400
SpG	2.40	3669.95
Mass Insoluble solids, kg	188,000	186,000
Wt% Al in solids	25.3%	25.29%
Al, kg (as elemental)	47,500	47,000
Other components, kg	140,000	139,000

Step two of the modeling included varying the volumes of 50 wt% caustic added to the sludge simulant. Figure 11 shows the predicted dependence of the mass of aluminum in solution and solid phases in addition to the mass of insoluble solids at 100-150,000 gallon additions of 50 wt% caustic held at 50°C. For additions of 140,000 gallons of caustic or greater, the model predictions indicate that all of the aluminum present initially in the solid phase is found in the aqueous phase after treatment.
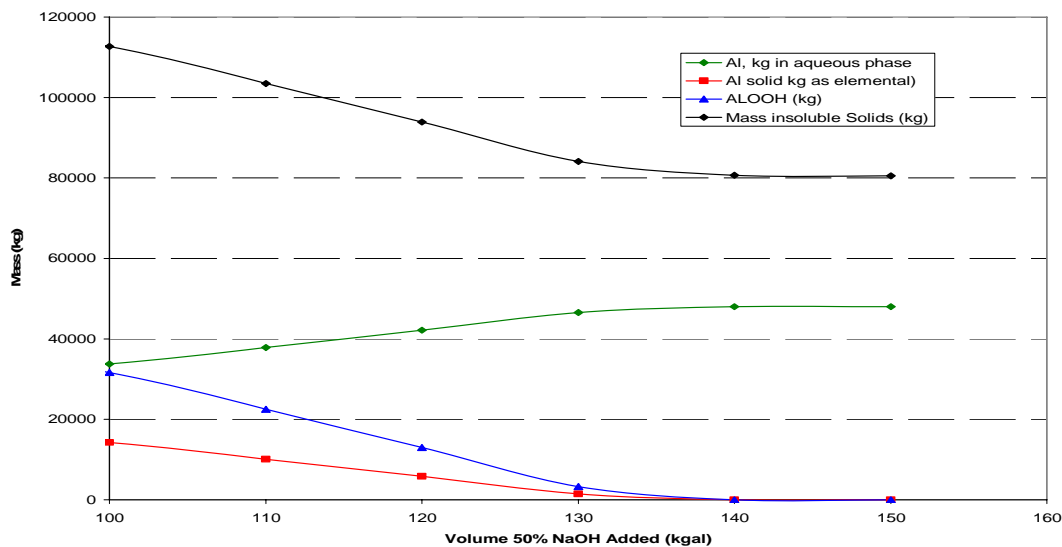

Figure 11 Solid/aqueous aluminum as well as insoluble solids species at differing volumes of 50wt% caustic additions.

Plans currently being investigated call for approximately 128,000 gallons of 50 wt% caustic to be added to Tank 51 and the temperature to be maintained at 65°C for a set period of time, followed by transfer of a portion of the aluminum supernatant to another tank. Table 9 includes model predictions of the major ion and solids data for the 50 wt% caustic additions.

Table 9 Model predictions for additions of 10,000 gallon increments (50 wt% caustic) at 50°C to Tank 51 HM sludge simulant.

Vol (gal)50 wt% NaOH	100,000	110,000	120,000	130,000	140,000	150,000
Stream Information						
Aqueous Phase						
Volume, gal	570000	581000	592000	602000	612000	621000
SpG	1.15	1.16	1.17	1.18	1.18	1.19
Mass aqueous, kg	2490000	2550000	2620000	2680000	2740000	2800000
Al, kg	33,760	37,879	42,134	46,520	47,994	47,994
Concentration (M)						
Na^+	4.15	4.39	4.63	4.86	5.09	5.31
NO_2^{-1}	0.384	0.377	0.370	0.364	0.358	0.353
NO_3^{-1}	0.245	0.241	0.236	0.232	0.228	0.225
OH^-("free")	2.83	3.02	3.21	3.39	3.62	3.86
SO_4^{-2}	0.0196	0.0193	0.0189	0.0186	0.0183	0.0180
CO_3^{-2}	0.0302	0.0296	0.0291	0.0286	0.0281	0.0277
AlO_2^-	0.580	0.638	0.697	0.756	0.768	0.756
$C_2O_4^{-2}$	0.0007	0.0007	0.0006	0.0006	0.0006	0.0006
Solid Phase						
Volume, gal	7090	6300	5480	4630	4340	4330
SpG	4.20	4.34	4.539	4.80	4.91	4.91
Mass Insoluble solids, kg	112,719	103,490	93,944	84,089	80,676	80,508
Wt% Al in solids	12.63%	9.77%	6.23%	1.75%	0	0
Al, kg (as elemental)	14,234	10,115	5,861	1474	0	0
wt% Insoluble solids	4.34%	3.90%	3.47%	3.04%	2.85%	2.79%

When the caustic addition is complete, the temperature of the resulting dissolution will be allowed to return to ambient conditions. Modeling of the leachate stream at these reduced temperatures resulted in solids re-precipitation. Figure 12 follows the solids re-precipitation when the 140,000 and 150,000 gallon caustic aqueous streams are cooled from 65 to 25°C. At 30°C, the total solids loading is 0.63 percent by weight and the predominant solid was predicted to be gibbsite.
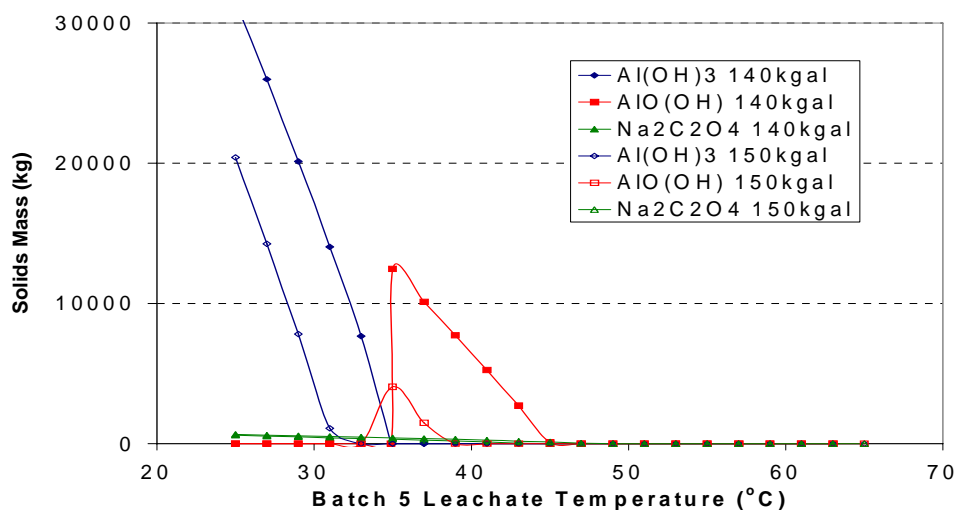
Figure 12 Plot of solids re-precipitation predicted as the 140,000 and 150,000 gallon caustic leach streams are cooled from 65 to 25°C.

The predicted aqueous phases for Tank 51 were also compared to tank corrosion requirements [10]. At temperatures of less than 75°C and a concentration of nitrate ion less than or equal to 1.0 M, three variables must be considered. The hydroxide ion concentration must fall within the range $0.01 \text{ M} \leq [OH^-] \leq 8.0 \text{ M}$. The nitrite ion concentration must fall within the range of $0.011 \leq [NO_2^-] \leq 5.5 \text{ M}$ and finally, all three ion concentrations must fit within the equation $[NO_3^-]/([OH^-] + [NO_2^-]) < 2.5$. All resulting leach streams at 50°C meet these technical safety requirements.

WORK FORECAST

Modeling on actual stream information amounts with blending of streams from DWPF and /or DDA fractions from Tank 41 dissolution will be performed. Experiments designed to mimic these streams and the blending processes will also commence. The aluminum data within the V7 Public database is not compatible with data within the Zeolite database. Formation of sodium aluminosilicates due to blending of streams containing differing amounts of silicon and aluminum demonstrates the need for upgrading of the SRS Zeolite database so that it is compatible with the latest ESP release (V7.0).

CONCLUSIONS

Modeling of the SRS Tank 51 sludge batch 5 and the proposed caustic strike has been investigated. Good agreement was found between the model and actual sludge simulant although the type and percentage of aluminum complex (gibbsite, boehmite) may affect the total dissolution. Model predictions demonstrated total aluminum dissolution using 50 wt% caustic would require at least 140,000 gallons. Solids formation (0.63 % by weight) from the leached stream at lower temperatures was within acceptable processing requirements.

REFERENCES

1. L. T. Smith, J. S. Lindner, V. Phillips, A. Antonyraj, and R. K. Toghiani, "Modeling and Experiments for the SRS Low-Curie Salt Process." Separation Science and Technology, 41(11), 2341-2360 (2006).
2. Toghiani, R.K., and Lindner, J.S., Saltcake Dissolution Modeling, FY 2000 Status Report, DIAL-40395-TR00-1, Diagnostic Instrumentation and Analysis Laboratory, Mississippi State University, MS 1999), **http://vax.dial.msstate.edu/~lindner/fy2000rep/**
3. Toghiani, R. K., Smith, L. T., Lindner, J. S., Tachiev, G. L., and G. Yarri, "Modeling of Pilot-Scale Saltcake Dissolution," WM'06 Conference, February, 2006, Tucson AZ.
4. Hobbs, D. T., Stallings, M. E., and B. J. Wiersma, "Dissolution of simulated and radioactive Savannah River site high level waste sludge with oxalic acid and citric acid solutions," WSRC-TR-2004-00043, Westinghouse Savannah River Co, Aiken, South Carolina, (2004).
5. Ketusky, E. T., "Use of an equilibrium model to forecast dissolution effectiveness, safety impacts, and downstream processability from oxalic acid aided sludge removal in Savannah River site high level waste tanks 1-15," M. Tech. Thesis, University of South Africa, (2005).
6. Langton, C. A., "Direct Grout Stabilization of High Cesium Salt Waste: Salt Alternative Phase III Feasibility Study," WSTC-TR-98-0337, Westinghouse Savannah River Company, Aiken, SC (1998).
7. Smith, L. T., Toghiani, R. K., and Lindner, J. S., (2005), "Support of Alternatives Disposition of High Level SRS Waste" in "Characterization and Cleanup of the Defense Nuclear Legacy," DIAL Quarterly Technical Progress Report for the period July 1,-September 31, 2005, Report Number 07029R02 U. S. Department of Energy Agreement Number DE-FC01-05EW-07029, Mississippi State, MS.
8. Smith, L. T., Toghiani, R. K., and Lindner, J. S., (2004), "Support of Alternatives Disposition of High Level SRS Waste" in "Characterization and Cleanup of the Defense Nuclear Legacy," DIAL Quarterly Technical Progress Report for the period October 1, -December 31, 2004, Report Number 54600R05 U. S. Department of Energy Agreement Number DE-FC01-04EW-54600, Mississippi State, MS.
9. Pike, J.A. and Gillam, J.M. "Flowsheet for Aluminum Removal from Sludge Batch 5." LWO-PIT-2007-0042, rev. 1, Washington Savannah River Company, Aiken, SC (2007).
10. Banning, D.L. "Double-shell Tanks Chemistry Control Data Quality Objectives." RPP-8532-Rev. 3, CH2M Hill Hanford Group, Inc. September, 2001.

Process Improvements for the Defense Waste Processing Facility (DWPF)

J.P. Singh

INTRODUCTION

Direct analysis of dried sludge or glass in shielded cell facilities will significantly increase the analytical throughput and reduce waste generation in radiological analytical facilities. In this subtask, the feasibility of using laser induced breakdown spectroscopy (LIBS) as an analytical tool for reducing waste and turnaround time for the plutonium residue vitrification processing facility (PRVPF) will be evaluated. For improved, on-line waste loading determination, LIBS on-line real-time capability to determine the ratio of Li to Fe from the pour stream can be used. LIBS uses a high pulse energy laser beams to produces a micro plasma to vaporize, dissociate, excite, or ionize species on material surfaces. The study of the atomic emission from the micro plasma provides information about the composition of the material. LIBS is a powerful analytical tool which is suitable for quick and on-line elemental analysis of any phase of material.[1-3] The laser light and emitted signal can be delivered via optical fiber so it is useful for hazardous situations. LIBS can provide an accuracy of 3-5% for elements with concentration >1% and an accuracy of 5-10% or better for minor elements in solid samples.

WORK PERFORMED

To evaluate a fiber optic LIBS system that can deliver the laser pulse to a sample surface for the Plutonium Disposition Project (PDP), different fiber optic configurations have been tested. The main difficulty on coupling the laser beam to the optical fiber is to transmit high-peak-power laser with good coupling efficiency without damaging the fiber. Initial parametric tests using a homemade optical fiber (see Figure 13) have been performed. It has been found that the damage on the input surface of the fiber degraded the fiber transmission efficiency significantly. With a fused silica core fiber, a coupling efficiency of ~60-70% has been achieved and the fiber end was found damaged at 20 mJ in 10 minutes. An Axicon lens was also evaluated for focusing the laser beam at a longer focal depth to avoid fiber damage. However, it was difficult to couple the backward signal to the second fiber with the current experimental configuration when this optics was used.

Literature citations show hollow-core fibers have better capability to deliver a high peak power pulse as compared to solid core optical fibers. Therefore, the hollow-core fiber (HCF) for delivery of the 532-nm laser beam for long-term operation was evaluated.[5] To couple light into a hollow core optical fiber is very similar to couple light into a standard solid core optical fiber; however, to minimize the optical loss, the focused input beam should have a beam diameter at the entry to the HCF at around 65% to 70% of the HCF bore size. When the light is reasonably well centered in the surface of the HCF, it leads to the best transmission characteristics and will avoid the beam hitting the front edge of the fiber. In order to minimize the loss through the fiber, the numerical aperture (NA) of the focused laser beam should be kept very low. High NA can

cause the light to propagate down the HCF being absorbed and causing localized heating. Therefore, it is important to keep the lowest beam input NA and correctly fills the HCF bore when coupling light into fiber.

With these facts in-mind, two one-meter, hollow-core fibers were evaluated. The first hollow-core fiber (HWCA7501200) is optimized for CO_2 laser. A focal lens of 30-cm was used to focus the laser beam into this fiber. A lens combination of 20-cm and 5-cm focal lens was used to collimate the beam and focus the beam from the fiber on the sample surface. The laser transmission efficiency was tested and it that ~ 50% transmission efficiency was obtained up to 40 mJ/pulse for 532-nm laser beam from the Nd:YAG laser. The transmission efficiency is relatively low as compared with previous data obtained using a standard solid core optical fiber with a 532-nm laser. The second hollow core fiber (HWEA7501200) had optimized transmission for a Er:YAG laser. This fiber was expected to have better transmission efficiency for 532-nm excitation wavelength. The fiber has been purchased and its transmission efficiency will be tested and reported.

For implementing LIBS in a glove box at SRNL, a press will be used to make a solid surface of the sample powder and will remain in the holder/container that during the experiment. The sample press will be mounted on a rotating plate during LIBS measurement. Different sizes of the dies (height and diameter) have been tested. A typical die is shown in Figure 14. Different pressures were applied on the die to determine the minimum pressure needed to hold the sample together without any binders. A pressure of 3000 psi was found to be necessary to make a solid surface pellet. In addition, pellets from various amounts of surrogate powder were made to determine the minimum weight of powder required for reproducible results. LIBS data were recorded with different laser energies and gate delay. Figure 15 shows the comparison of LIBS signal at different gate delay time for a pulse laser energy of 5mJ for a 5g sample press. The preliminary study shows that minimum weight of the powder for a 1" die that can produce reproducible results is 5g.

A new composition of surrogate feed material which contains Mg, K, Na, Ca, Fe, Ni, F, Al, Cr, Si, W, Zn, Ta was received. A new batch containing the above elements was prepared. LIBS data of the sample made from the new powder batch were prepared. Experimental data were collected under different laser energy, detection window, and lens-to-sample distance. The reported limits of detection for Cl, F are relatively poor with LIBS comparing to other elements. The best experimental condition to detect these two elements needs to be determined.

WORK FORECAST

Work will continue on the evaluation of optical fiber LIBS for PDP. LIBS data of the new batch will be recorded. The optimum condition for Cl and F lines will be determined.

REFERENCES

1. D.A. Cremers and L.J. Radziemski, "Laser Plasmas for chemical analysis" in laser spectroscopy and its applications, chapter 5, L.J.Radziemski, R.W. Solarz and J.A. Paisner, eds (Marcel Dekker, New York, 1987).
2. Fang-Yu Yueh, Jagdish P. Singh and Hansheng Zhang, "Laser-induced breakdown spectroscopy-elemental analysis", in *Encyclopedia of Analytical Chemistry,* R.A.Meyers, ed. (Wiley, New York, 2000).
3. Israel Schechter, "Laser induced plasma spectroscopy, a review of recent advances," Rev. Anal. Chem. **16,** 173-298 (1997).
4. Bansi Lal, Hongbo Zheng, Fang-Yu Yueh, and Jagdish P. Singh. Parametric study of pellets for elemental analysis with laser-induced breakdown spectroscopy. *Applied Optics* 43: 2792 (2004).
5. A.P. Yalin, M. DeFoort, and B. Wilson, Y. Matsuura and M. Miyagi, "Use of hollow-core fibers to deliver nanosecond Nd:YAG laser pulses to form sparks in gas", Opt. Lett. 30: 2083 (2005).

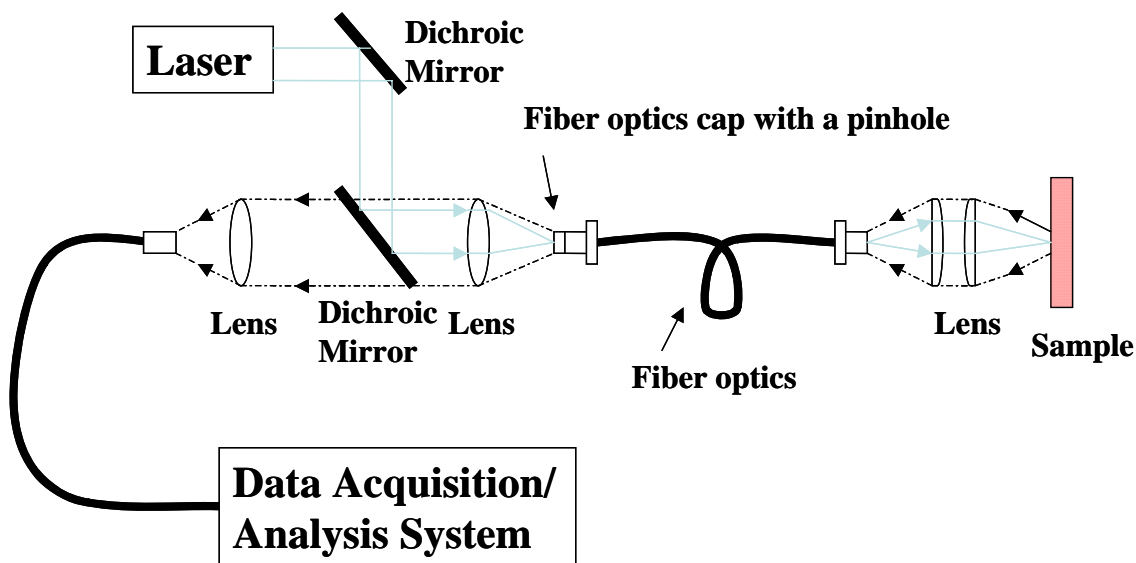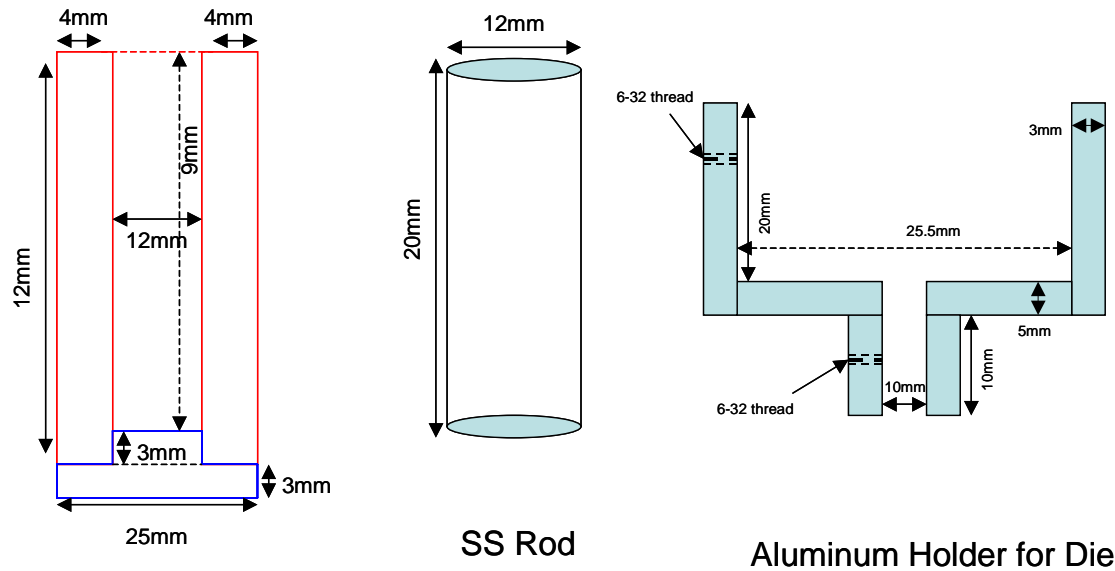**Figure 13 Schematic of Optical Fiber LIBS**

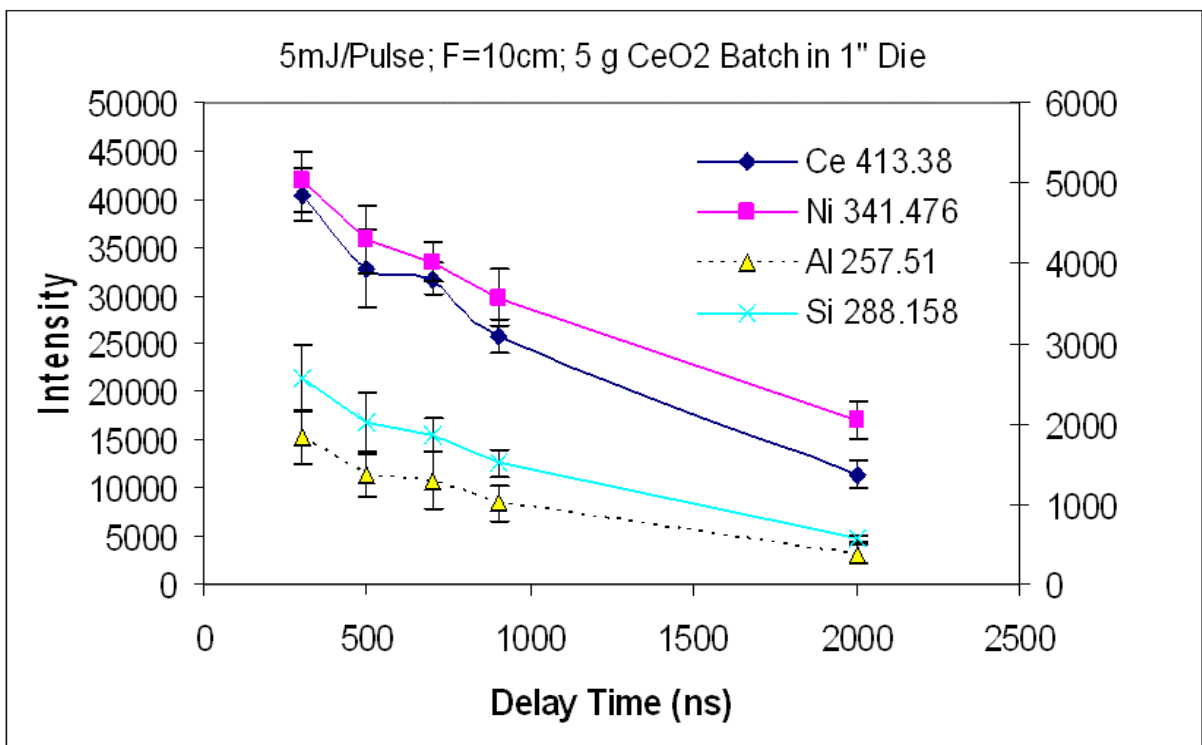**Figure 14   Schematic Diagrams of Stainless Steel (SS) Die for Simulated Plutonium Oxide Reside Sample.**

Figure 15 LIBS signal of 5g sample press at different gate delay time.

Process Improvements for the Defense Waste Processing Facility (DWPF) Task 2 – Improvement of Waste Throughput

R. A. Palmer

INTRODUCTION

This effort will improve the ability of the DWPF to process high Al_2O_3 containing streams (i.e., SB4) at relatively high waste loadings and/or melt rates so overall attainment is not negatively impacted.

Melt Chemistry Experiments

ICET will carry out a series of experiments to better understand the reactions between the frit and the waste simulant and the dynamics and chemistry of the cold cap, a floating structure of not-yet-dissolved material specific to glasses as a function of waste loading. These experiments will utilize both off line techniques such as optical and scanning electron microscopy (SEM) and real-time instrumentation to determine the chemistry of the reactions occurring during melting of high level waste glasses, both in the melting feed and in the gas phase.

The specific frits and feed materials to be studied will be Frit 418 and Frit 503 and SRAT product representing sludge batch 4 (SB4), which is relatively high in aluminum oxide.

The steps to be followed include:
1. Studying the physical interaction of the frit with the sludge, paying particular attention to phenomena such as sequestration, and to the reaction dynamics at the interface between the cold cap and the melt.
2. Identifying, as a function of temperature, the chemical reactions and phase changes occurring within the cold cap.

WORK ACCOMPLISHED

A series of crucible-scale melts has been run examining the behavior of mixtures of materials for Sludge Batch 4. These materials include:
Frit 418
Frit 503
SB4 SRAT Product
SB4 SME Product + Frit 418
SB4 SME Product + Frit 503

The SME Product mixtures were made up with a waste loading of 35%. The materials were dried in an oven at 110C then 20g-sized melts were heated for two hours at 700C, 750C, 800C, 850C, and 900C. The object was to compare the behavior of the two frit compositions.

Some observations
1. Both frits raise to about the same height in the crucible during the melting process.
2. Frit 503 has fewer/bigger bubbles than Frit 418 at 750°C.
3. Frit 503 seems to have consolidated more than Frit 418 at 80°0C.
4. Frit 418 has more bubbles than Frit 503 all the way up to 900°C.
5. Frit 503 has almost no bubbles at 900°C.

The presence of bigger bubbles and more rapid consolidation seems to indicate that Frit 503 would be less likely to foam. That could translate into a faster melting rate.

A second series of crucible-scale melts has been started examining the behavior of mixtures of materials for Sludge Batch 4 (SRAT Product and Frits 418 and 503) at higher waste loadings (40 wt% and 45 wt%).

First impressions of the results appear to lead to the conclusion that higher waste loadings would be possible with these frits with this waste simulant. Further analysis will be done and a report evaluating both sets of experiments will be issued.

A new series of crucible-scale melts is being designed to study Sludge Batch 5. Six plastic jars of SB5-2 SRAT Product (approximately 3600g) to be used as the waste simulant were received.

The waste simulant will be mixed with four different frit compositions (see Table 10):

Frit ID	B_2O_3	CaO	Li_2O	Na_2O	SiO_2	Total
503	14	0	8	4	74	100
517	17	0	10	3	70	100
519	20	0	9	3	68	100
521	10	1	8	6	75	100

Table 10 Frit compositions

Four different waste loadings, 35, 38, 41,and 44 wt%, will be studied. Frit 503 is already available from previous experiments, the other three will have to be prepared.

WORK FORECAST

The three frits for Sludge Batch 5 will be prepared in one of the ICET laboratory using the following raw materials:
Glass sand, SiO_2
Sodium Carbonate, Na_2CO_3
Calcium Carbonate, $CaCO_3$
Lithium Carbonate, Li_2CO_3
Boric Acid, H_3BO_3

The powdered simulant and frits will be mixed to provide waste loading of 35, 38, 41, and 44 wt%. The mixtures will be placed in 50mL alumina crucibles heated for two hours at five temperatures (700, 750, 800, 850, and 900 ^{o}C) to study the series of reactions.

Support of DOE Headquarters

Support of DOE Headquarter

Roger King, Charles Waggoner, Jeff Lindner, Yi Su

During the second quarter of 2007, the Institute for Clean Energy Technology (ICET) took necessary steps to reduce its DOE cooperative agreement scope of work in order to adjust to a reduction in funding level from $5 million to $4 million. Extensive networking with the DOE sites and Headquarters was required to accomplish this task. Information in the DOE Roadmap document was used as the guiding principles for reducing the scope of work commensurate with the funding reduction and for directing the balance of activities for 2007. Information included in the April version of the Roadmap document was discussed in several executive staff meetings and in an ICET-wide seminar. All ICET efforts were instructed to emphasize activities that would reduce technical uncertainty and risk and conform to the objectives put forth in the Roadmap.

Remote Sensing and Long-Term Monitoring of Surface/Subsurface Contaminants Workshop

Yi Su

This workshop has been rescheduled for early summer 2008.

HEPA and Regenerable Filter Performance Assurance

Steven Alderman

INTRODUCTION

The U.S. Department of Energy (DOE) currently employs High Efficiency Particulate Air (HEPA) filters in a variety of applications that range from particulate matter removal from ventilation air to treatment of off-gasses from storage or treatment of mixed wastes. This project will provide data needed to address issues related to the performance of both standard glass fiber HEPA filters and regenerable (sintered metal and ceramic) filters. The objective of the proposed effort will be to provide a more complete set of descriptors to the process used in design of air and off-gas treatment systems. Recommendations will also be made to the ASME AG-1 Committee concerning Sections FC and FI, for traditional glass fiber media and metal media filters, respectively, to influence future modifications to these codes. The results of this work will be beneficial for the development of qualification testing techniques for metal media filters, which are currently subject to the same testing techniques as traditional glass fiber HEPA media.

A significant part of the proposed scope of work will center on utilizing the vast amounts of data generated over the course of filter evaluations to revise modeling of filter mass loading rates, mass loading capacities, filtering efficiencies, the filter most penetrating particle size. This updated and enhanced set of tools will be very useful in the future design of nuclear air filtration systems.

Worked to be completed during FY 2007 can be grouped under two Sub-Tasks, which are presented below:

Sub-Task 1 – Glass Fiber HEPA Media Velocity Testing

Media velocity testing for AG-1 filters conducted in FYs 2005 and 2006 will be expanded upon. An initial set of data for this series of tests was generated in 2005 using a set (12) of AG-1 filters from Flanders. Filters obtained from Camfil Farr were evaluated in 2006, with final testing taking place in 2007.

This series of media velocity tests is also in support of standard developments currently under way by the Committee on Nuclear Air and Gas Treatment (CONAGT). A Test Plan has been developed and reviewed by the AG-1 committee in order to ensure appropriateness of data type and quality. Filters will be tested at media velocities ranging from 2.0-4.5 cm/s. Data generated by this testing will produce initial values for filter efficiency and most penetrating particle size. Lifetime testing for each filter will demonstrate changes in both filter efficiency and most penetrating particle size as a function of filter loading as monitored by differential pressure.

Detailed models of filter loading will be developed utilizing the most current and widely accepted theoretical models. Complementary to this will be activities in which filters are

"autopsied" to gather information to reveal filter loading patterns and the degree of surface loading vs. depth loading. This will be accomplished through the use of optical techniques and scanning electron microscopy.

Information gathered in this series of activities will be used to revise and enhance existing models describing filter loading parameters with respect to both media velocity and particle size distribution of the aerosol challenge. These data will also be provided to filter manufacturers and to the ASME Filtration Subcommittee AG-1 Standard and engineering data to be used in the development of new air filtration systems.

Sub-Task 2 – Evaluation of Regenerable Filter Media

ICET larger test stand will be modified to facilitate studies addressing the regenerability of ceramic filters utilizing an air back pulse. This testing will be conducted in a configuration in which the regenerable media serves as a pre-filter for an upstream glass fiber HEPA filter. The lack of an AG-1 standard for regenerable filters coupled with general concerns about HEPA filters voiced by stakeholders has resulted in cleanable filters being considered as pre-filters in applications too aggressive for conventional units. This allows use of cleanable filters that can withstand higher loading rates, high moisture content, and high temperatures to protect the AG-1 HEPA filters and reduce the rate at which they must be changed out. However, it is necessary to confirm the ability of such filter media to be repeatedly cleaned and retain function.

WORK ACCOMPLISHED

Air back-pulse cleaning studies using large CeraMem filters were continued. A set of three filters was loaded to 2 in. w.c. above baseline ΔP and back-pulsed at 25, 50, 75 ,and 100 psi. This was done in an effort to find a back-pulse pressure that resulted in the most efficient filter cleaning. It was discovered that varying the air back-pulse pressure had negligible effect on filter cleaning efficiency. This observation suggested that the filters should be loaded to a greater extent prior to cleaning. Therefore, a change in the testing process was needed. It was decided that modifications to the test stand were in order that would allow the test volumetric flow rate to be increased 7 scfm to 14 scfm. This modification permits loading more aerosol on the filters per unit time, and may increase the level of ΔP recovered after the back pulse cleaning cycle. These modifications were performed in June, which included incorporating into the system 1-100 in. w.c. differential pressure gauges and re-scaling the venturi flow meter used to calculate the flow rate through the filter.

After completing this task, another series of tests was performed to determine the optimum back pulse pressure for maximum ΔP recovery. This set of tests was performed at 100 and 75 psi. It was determined that the 100 psi back pulse resulted in the recovery of more differential pressure, thus more effectively cleaned the filter. The back-pulse testing consisted of a total of 12 tests. It should be noted that the relative humidity probe was sent back to the manufacturer for repairs, which delayed testing for 2 weeks.

Additional testing included monitoring residual water in the aerosol stream to determine what effect it had on the mass concentration measured by the SMPS and APS. A KCl aerosol was generated by varying the flow rate of the gear pump to see what effect that had on the particle size distribution measured by the SMPS and APS upstream of the filter.

The manuscript "Load-Wash Testing of Regenerable Sintered Metal and Ceramic Membrane Filter Media"[1] was accepted for publication in *Environmental Engineering Science*.

WORK FORECAST AND CONCLUSIONS

During the first half of FY 2007, the regenerable filter test bed and associated accessories were developed and optimized to facilitate studies addressing the regenerable nature of CeraMem ceramic membrane filters. Work will be performed in the following quarter that will provide this needed information.

REFERENCES

1. Alderman, S.L.; Nagel, B.A.; Parsons, M.S.; Hogancamp, K.U.; Waggoner, C.A. "Load-Wash Testing of Regenerable Sintered Metal and Ceramic Membrane Filter Media" *Env. Eng. Sci.* 2007, *24*, 1135

Bio-availability studies of mercury and other heavy metal contaminants in ecosystems of selected DOE sites

Fengxiang Han, Yi Su, David Monts, and Charlie Waggoner

INTRODUCTION

The goal of these experiments is to unveil the mechanisms governing biogeochemical processes for the most recent increase in concentrations of mercury in fish and water of lower East Fork Poplar Creek (LEFPC) of Oak Ridge.

WORK ACCOMPLISHED

In this quarter, experiments on the effects of naturally occurred minerals on mercury release from Oak Ridge soil contaminated with HgS were conducted. Fe_3O_4, Fe_2O_3, and $MnCO_3$ have been tested. The preliminary results showed that iron oxides triggered the release of Hg, while $MnCO_3$ did not affect the release of Hg from HgS minerals. The concentration of Hg released from HgS mineral in contaminated soils was linearly correlated to that of dissolved Fe in extracts.

The manuscript entitled "Stability and Bioavailability of HgS in Oak Ridge soils" was prepared. The paper on "Bioavailability and Stability of Mercury Sulfide in Tennessee (USA) Soil" was published in the Proceedings of the 11th International Conference on Environmental Remediation and Radioactive Waste Manage, 2007, Belgium.

WORK FORECAST

The extractability of mercury in mercury sulfide contaminated Oak Ridge soils with various reagents will be studied. The reagents include 4 M nitric acids, 12 M nitric acids, oxalate solution, hydroxylamine hydrochloride, ammonia nitrate, hydrogen peroxide, and EDTA.

CONCLUSIONS

The preliminary study indicates that iron oxides triggered the release of Hg, while $MnCO_3$ did not affect the release of Hg from HgS minerals in Oak Ridge soils. The concentration of Hg released from HgS contaminated soils was linearly correlated to that of dissolved Fe in extracts, while was negatively correlated with that of sulfate.

REFERENCES

1. Fengxiang X. Han, Safwan Shiyab, Jian Chen, Yi Su, David L. Monts, Charles A. Waggoner, and Frank B. Matta. 2007. Bioavailability and Stability of Mercury Sulfide in Tennessee (USA) Soil, the Proceedings of the 11th International Conference on Environmental Remediation and Radioactive Waste Manage, 2007, Belgium.

Phytoremediation and Long-Term Monitoring of Heavy Metal Contaminants

Yi Su, Fengxiang Han, David Monts

INTRODUCTION

The objective of this work is to investigate the possible leaf uptake of mercury vapor from ambient air immediately above the contaminated soil.

WORK ACCOMPLISHED

A phytoremediation experiment with mercury contaminated soils and Chinese brake fern (*P. vittata*) that started during the previous reporting period was completed. The experiment was designed to study the plant leaf uptake of mercury from ambient air immediately above contaminated soil. Plant and soil samples were collected for chemical analysis. Meanwhile, some of the plant tissue (both shoots and roots) and soil samples from previous experiments were analyzed. In addition, data have been processed and manuscripts for publication are being prepared.

CONCLUSIONS

Conclusions on the possible leaf uptake of mercury vapor from ambient air immediately above the contaminated soil by Chinese brake fern (*P. vittata*) are expected following completion of the experiments.

REFERENCES

1. B. B. Maruthi Sridhar, F. X. Han, D. L. Monts, S. V. Diehl, Yi Su, "Spectral Reflectance and Leaf Internal Structure Changes of Barley Plants Due to Phytoextraction of Zinc and Cadmium", *International Journal of Remote Sensing*, 28**:**1041-1054 (2007).

2. B. B.Maruthi Sridhar, F. X. Han, S. V. Diehl, D. L. Monts and Yi Su, "Monitoring the effects of arsenic- and chromium- accumulation in Chinese brake fern (*pteris vittata*)", *International Journal of Remote Sensing*, 28**:**1055-1067 (2007).

Technology Development

Development of new technologies for DOE site applications

Chuji Wang

INTRODUCTION

The development of innovative measuring and monitoring techniques for trace volatile organic compounds (VOCs) and semi-VOCs would be of significant benefit for many DOE site applications. Currently, these analyses must be done through remote sampling, followed by shipment of samples to a laboratory capable of performing the needed analyses. Such measurements are typically performed with GC-MS. A GC-MS system can cost several hundred thousand dollars and cannot be deployed for real field use due to the operational requirements of the instruments.

The cw-CRDS technique has been developed in ICET and measured more than 10 VOCs and gases, such as acetone, formaldehyde, benzene, chlorobenzene, 1,2-dichlorobenzene, toluene, 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene), 2,3-dimethyl-1,3-butadiene, CH_4, CO_2, CO, etc. This technique can be adapted and further developed for real-time characterization of a variety of tank organic compounds with required sensitivity and high accuracy. This technique will potentially displace the aforementioned conventional technique in diverse DOE site applications and will help address the issues of real-time, cost-effective, and field-readable measuring and monitoring techniques.

The goal of this project is to develop and deliver real-time, site-deployable, high sensitivity spectroscopic techniques, which are currently not available yet needed to address issues in DOE sites applications: measuring, monitoring, and characterization of multiple tank VOCs and toxic gases.

WORK ACCOMPLISHED

The development goal of the project in this quarter is to multiplex two NIR diode lasers using optical fiber splitters and combiners. Since the portable ringdown platform was designed to measure multiple species simultaneously, switching among different measuring wavelengths must be realized by an optical-electrical switch, so that the system will be able to operate automatically for detection of different species in different wavelengths. A 1 X 2 optical splitter with a 50%/50% splitting ratio was procured and tested with two laser diodes operating at 1596 and 1650 nm. The optical switching function was tested in the laboratory ringdown system through scanning NIR spectra of methane and carbon dioxide individually. Due to optical loss in the fiber splitter, the ringdown signal intensities at the two wavelengths were lower, thus a worse signal-to-noise ratio; however, this problem was solved by raising the laser diode operating currents to 100 mA and using a photodetector with a built-in preamplifier. This significant

accomplishment allows for future development effort to be focused on assembly of the system and evaluation of the system's performance.

For the measurements of toxic trace elements, the experimental emphasis during the second quarter changed from the detection of uranium atoms generated in an ICP with diode laser-CRDS to the detection of mercury naturally evaporating out of contaminated soils and solutions. The optical parameters were vigorously examined and the laboratory background interference was thoroughly surveyed.

WORK FORECAST

The planned activities in the 3rd quarter include 1) optimize an instrument fame which will house the optical bench and the associated ringdown electro-optical control parts, so that the system will be standalone, site-deployable, 2) assemble the system, and 3) perform initial testing on the system integration.

CONCLUSION

Multiplexing diode lasers was completed in this quarter. This achievement demonstrated the technological feasibility of measuring multiple species using a single ringdown optical platform (or optical bench). To our knowledge, two laser diodes coupled with one optical isolator for detection of multiple species at different wavelength regions through automatically switching the laser wavelengths has not been reported thus far.

Development of Fiber Optic Sensor Technologies for DOE Site Applications

DOE reduced the FY 07 funding from $5M to $4M dollars for the Institute for Clean Energy Technology. With the reduction in funding, MSU management had to make hard decisions as to which tasks to continue. After a thorough examination of several factors it was determined that Task 6.2 Optical Sensors would be removed from the scope of work. This information has been conveyed to DOE