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# Accelerating Cleanup of the Defense Nuclear Legacy

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# Table of Contents

<b>EXECUTIVE SUMMARY</b> .....	<b>1</b>
<b>Task 2. Support of Hanford Single Shell Tank Waste Disposition</b> .....	<b>1</b>
<b>Task 3. Disposition of Idaho HLW Calcine</b> .....	<b>2</b>
<b>Task 4. Support of SRS Salt Disposition and Other SRS Alternatives</b> .....	<b>2</b>
<b>Task 5. Support of DOE Headquarters</b> .....	<b>3</b>
<b>Task 6. Technology Development</b> .....	<b>4</b>
<b>Task 1. Support of Oak Ridge Site Closure</b> .....	<b>10</b>
<b>Task 2. Support of Hanford Single Shell Tank Waste Disposition</b> .....	<b>11</b>
In-tank/At-tank Characterization for Closure of Hanford Tanks.....	11
Process Chemistry and Operations Planning for Hanford Waste Alternatives.....	16
<b>Task 3. Disposition of Idaho HLW Calcine</b> .....	<b>26</b>
Support of the CH2M-WG Idaho Calcine Disposition Project .....	26
<b>Task 4. Support of SRS Salt Disposition and Other SRS Alternatives</b> .....	<b>29</b>
Modeling and Experimental Support for High-Level SRS Salt Disposition Alternatives.....	29
Process Improvements for the Defense Waste Processing Facility (DWPF) .....	37
Process Improvements for the Defense Waste Processing Facility (DWPF) Task 2 – Improvement of Waste Throughput.....	39
<b>Task 5. Support of DOE Headquarters</b> .....	<b>41</b>
Support of DOE Headquarter .....	41
Remote Sensing and Long-Term Monitoring of Surface/Subsurface Contaminants Workshop .....	42
HEPA and Regenerable Filter Performance Assurance .....	43
Bio-availability studies of mercury and other heavy metal contaminants in ecosystems of selected DOE sites.....	48
Phytoremediation and Long-Term Monitoring of Heavy Metal Contaminants .....	50
<b>Task 6. Technology Development</b> .....	<b>52</b>
Development of new technologies for DOE site applications .....	52
Development of Fiber Optic Sensor Technologies for DOE Site Applications .....	54

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## List of Figures

Figure 1. Table-top “sine-bar” apparatus for determination of pan and tilt angles to within 0.02° .....	13
Figure 2. TGA trace for the Almatris Gibbsite.....	21
Figure 3. Percent of gibbsite in the product for different heating durations at temperatures of 120, 135, and 150 °C .....	22
Figure 4. K <sup>+</sup> or Cs <sup>+</sup> ion concentration in ppms at weekly sample intervals.....	31
Figure 5. Solubility envelope for K and Na (as a function of NO <sub>3</sub> ) concentration in water at 25°C.....	32
Figure 6. Experimental and model predictions for the solubility envelope of K and Na (as a function of NO <sub>3</sub> ) concentration in water, 1 & 3 molal caustic at 25°C. ....	32
Figure 7. Literature values and ESP v 6.7model predictions for K and Na (from NO <sub>3</sub> ) concentrations in water at 50°C.....	33
Figure 8. Literature values and ESP v 6.7model predictions for K and Na (from NO <sub>3</sub> ) concentrations in 1 molal caustic at 50°C. ....	33
Figure 9. Experimental and model predictions for the solubility envelope of K and Na (as a function of NO <sub>3</sub> ) concentration in water, 1 and 3 molal caustic at 50°C. ....	34
Figure 10. Experimental results and model predictions for cesium solubility (from CsNO <sub>3</sub> ) as a function of temperature.....	34
Figure 11. Experimental and model predictions for the solubility envelope of Cs and Na (as a function of NO <sub>3</sub> ) concentration in water, 1 and 3 molal caustic at 25°C. ....	35
Figure 12. Experimental and model predictions for the solubility envelope of Cs and Na (as a function of NO <sub>3</sub> ) concentration in water, 1 and 3 molal caustic at 50°C. ....	35
Figure 13. Filter Housing (left) and inlet face of CeraMem ceramic membrane filter. ....	45
Figure 14. Filter efficiency as a function of differential pressure for the first four loading/backpulse cleaning cycles. ....	46
Figure 15. Downstream geometric count mean diameter as a function of filter differential pressure for the first and fourth loading cycle. ....	47
Figure 16. Kinetics of mercury release from HgS contaminated Oak Ridge soil by iron oxide (Fe <sub>3</sub> O <sub>4</sub> ).....	48
Figure 17. Kinetics of mercury release from HgS contaminated Oak Ridge soil by EDTA .....	49
Figure 18. Setup of the sunlit chamber study on mercury uptake by fern. Fern was planted in a pot containing clean soil under the chamber.....	50
Figure 19. Sunlit chamber study setup .....	51

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## List of Tables

<i>Table 1. Work Plan for HTWOS Model Tank Waste Chemistry Neural Network.....</i>	<i>18</i>
<i>Table 2. Systems where solubility measurements have been completed in the ICET laboratories.....</i>	<i>23</i>
<i>Table 3. Systems examined in subcontract .....</i>	<i>23</i>
<i>Table 4. Major cations (weight %) present in the calcine simulant .....</i>	<i>27</i>
<i>Table 5. Results of compression testing for waste forms with different waste loadings and curing times .....</i>	<i>28</i>

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## EXECUTIVE SUMMARY

### **Task 2. Support of Hanford Single Shell Tank Waste Disposition**

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

During this reporting period, the ICET Fourier Transform Profilometry (FTP) effort has concentrated upon extensive testing and improvement of the performance of the FTP data analysis software for stitching. 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. Preparation for FTP Performance Evaluation Stage 2 (stitching of results of objects on simulated flat tank bottom) has included construction of laboratory apparatus to determine pan and tilt angles to within 0.02°.

This quarter, progress on the ICET Stereovision effort was significantly slowed by the unexpected departure in December of the graduate student working on this effort. Efforts to replace the graduate student have not yet been successful.

#### **Process Chemistry and Operations Planning for Hanford Waste Alternatives**

Efforts are presented regarding progress in association with the development of neural networks, studies on the transition of gibbsite to boehmite, and transfer of the ICET double salt database (V7DBLSLT) to OLI Systems, Inc., for inclusion in their mixed solvent electrolyte (MSE) database. Current work associated with neural networks has been aimed at the development of a work plan for continuing the studies. The plan delineates the responsibilities of ICET and CH2M Hill Hanford Group employees with regard to specific tasks. Evaluation of the gibbsite to boehmite transition is of interest with regard to high and low level waste separations. Gibbsite is soluble in caustic, whereas dissolution of boehmite takes from between 600-700 times longer. The amount of boehmite contained in the waste at Hanford is unknown; consequently, the overall effectiveness of caustic leaching to enable the separation is also unknown. Previous experiments have indicated that the transition from gibbsite to boehmite can occur at temperatures of 150 °C. The current work has extended this result to 120 °C. It is well known that some of the wastes at the site exceeded this lower temperature. Determination of kinetic information (pre-factors and activation energies) along with historical data associated with waste temperatures will allow for an estimation of the extent of boehmite in particular tanks and associated farms. From these data, the caustic leaching process can be tailored to specific waste, thereby reducing the amount of aluminum destined for the high level waste melter. An initial discussion is also given regarding the transfer of the ICET V7DBLSLT database to OLI Systems, Inc., for incorporation in the mixed solvent electrolyte (MSE) database. The systems included in V7DBLSLT have been identified and negotiations with OLI are on-going with regard to letting a subcontract from Mississippi State University.

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### **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 are being 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. The information has been used to down-select grout cement 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**

Results are presented for thermodynamic calculations performed for potassium and cesium salt systems. Literature values, when available, were compared with the model predictions and discrepancies were identified. Initial tests were performed on the pure components to determine equilibration times. A series of solubility experiments were performed and analyzed for the systems: (K,Na)-NO<sub>3</sub> and (Na,Cs)-NO<sub>3</sub> in 0, 1 and 3 m NaOH at 25 and 50°C. Model predictions were previously obtained using ESP version 6.7 using either the Public or MSU/ICET DBLSLTDB databases and detailed in a letter report to the site. There were little or no literature data available for these systems in caustic solutions. Modeling of the experimental data was executed in ESP V7.0, using both the Public and V7DBLSLT databases. A comparison of model predictions to experimental data reveals that solubilities are underestimated by the model for both systems.

#### **Process Improvements for the Defense Waste Processing Facility (DWPF)**

During this reporting period, work concentrated 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. Cerium (Ce) has been used as a surrogate for Pu oxide residue surrogate in the preliminary investigation. The plutonium residue vitrification processing facility (PRVPF) expressed an interest in using a fiber optics LIBS system with the sample in pellet form (without added binder) in practical environment. Therefore, researchers are focusing on developing a fiber optics system for long-terms operation in the test facility and on designing a sample container for this application. The study of pellet samples without binder is underway to obtain

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the optimum experimental condition for this type of sample. Different optical fiber designs have been tested. The possibility to use a hollow-core fiber to deliver the nanosecond Nd:YAG laser pulse for long-term operation was also explored.

## **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. One significant task to be performed in FY 2007 is a performance evaluation of ceramic membrane filters undergoing repeated aerosol challenge/air back pulse cleaning cycles. During the first quarter of FY 2007, essential tasks required before filter testing could move forward were completed. These tasks included: 1) design and assembly of a regenerable filter test bed and filter housing; 2) modification of an existing large HEPA filter test stand in a manner that allowed a slip stream of aerosol challenge to be diverted into the aforementioned test bed; 3) verification of the proper function of aerosol measurement instrumentation when sampling from the regenerable test bed; 4) installation of differential pressure transducers and venturi flow meters; 5) interfacing process control parameters to existing data logging software; 6) air back pulse cleaning system construction and implementation; 7) collection of preliminary data to include filter efficiency (FE), differential pressure drop ( $\Delta P$ ), and challenge aerosol mass loading rate and particle size distribution (PSD). Other activities conducted during the first quarter of FY 2007 included analysis of data collected in FY 2006 and writing/editing peer-reviewed manuscripts.

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

Mercury contamination is ubiquitous in the Y-12 Watershed of Oak Ridge, TN and has been identified as a key contaminant in soil, sediment, surface water, groundwater, buildings, drains, and sumps. An estimated 128,370 kg (283,000 lb) has been transported out of the area. Additionally, more than 70 US DOE sites have Hg-contaminated wastes and hence potentially have mercury in their ecosystems. The goal of these experiments is to unveil the mechanisms governing biogeochemical processes for the most recent increase in concentrations of total mercury in fish and water of lower East Fork Poplar Creek (LEFPC) of Oak Ridge. In this quarter, a series of new experiments on stability and bioavailability of HgS-contaminated Oak Ridge soils have been conducted. The experiments include the reaction kinetics of soil HgS with iron/manganese oxides, which are widely present in soils and sediments. The release kinetics of mercury from soil HgS by complexing agents such as EDTA and oxalate acids, which are present in rhizosphere soils were also studied.

## **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, efforts were continued in the development of a portable cavity ringdown spectroscopic technique, so that the system can be eventually site-deployable for tank vapor characterization. NIR spectra of three small atmospheric molecules around 1596 and 1567 nm wavelength regions using a newly developed, compact ringdown optical platform have been measured. These molecules have been measured previously in a laboratory-ringdown system. The purpose of the measurements was to evaluate the system accuracy, robustness, and portability. These development efforts will be used as a base for the further packaging of a site-deployable ringdown system. The needed spectroscopic validation was successfully done

**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

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## **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 tools 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 locations, such as the Savannah River Site.

After as much waste as practical has been removed from the tank, an analysis 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 Fourier-transform profilometry (FTP) and stereovision (SV) for potential deployment for nondestructive, *in situ* imaging for quantitatively determining the volume and height of waste (including that deposited on tank walls, and the volume and depth of sediments). 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

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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 with better cameras, and has evaluated a variety of algorithms for stereomatching. Results have indicated 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. Efforts to replace the graduate student have not yet been successful.

### **FOURIER TRANSFORM PROFILOMETRY**

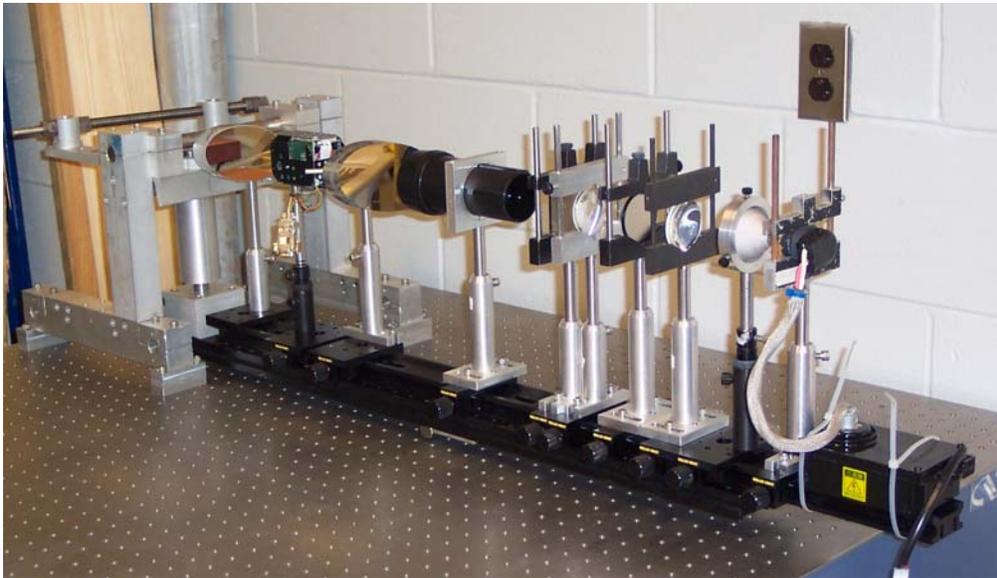
During this quarter, the Fourier Transform Profilometry (FTP) effort continued to validate performance by use of synthetic images generated analytically. These synthetic images, which simulate target surfaces at a distance of 20 feet from camera, were subsequently processed with the FTP analysis software. This analysis of synthetic images where the target object is fully contained with a single image resulted in errors of less than 1% of the actual volume of the target surface. The target object was a right circular cone with radius and height of 15 cm and thus a volume of 3534 cm<sup>3</sup>. This initial use of our FTP simulator mimics measurement conditions where the tank floor is directly under the tank riser used for camera access. In this area of the tank, the tank surface is mostly perpendicular to the camera optical axis and has insignificant curvature.

Using the simulator, researchers were also able to identify a problem with the software code used for stitching volume contributions of target object portions contained in separate, but overlapping images. The effort spent on developing this capability to simulate the FTP instrument should prove its anticipated usefulness for verifying FTP data quality in the future.

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Some effort was also spent to measure the shape of the full-scale “prop” surface that was constructed to allow target objects to be measured on surface such as will be encountered in the “heel” area of the S-100 series tanks. The prop surface has very good precision in the tangential direction, but lack of incorporated reference data made determination of accuracy of the surface in the radial direction more difficult than originally anticipated.

The effort to enhance our fundamental understanding of how real-world obstacles limit the ability of the FTP technique to obtain surface profile data with sufficient accuracy for determination of Hanford tank residual waste volumes was considerably expanded. The previously proposed “Stage II” series of FTP performance evaluation experiments were designed to determine the FTP technique’s ability to stitch together volume contributions from tank regions that fall in adjacent and overlapping images. Preliminary experiments were performed to identify unanticipated problem areas in the proposed stitching procedure. Through these experiments, a couple of limitations in the proposed stitching procedure were identified. First, it was determined that it is preferable not to have the stitching boundary extend to the edge of an image, but that it is better to have the boundary fall approximately halfway into the overlap region. This avoids anomalies that occur in the transform procedure near the image edges. The second limitation is the ability to accurately determine the relative image positions and thus accurately predict the geometry of the image overlap regions. This depends on the ability to determine the “pan” and “tilt” angles with adequate resolution. An estimate of the waste volume uncertainty due to errors in “pan” and “tilt” has been obtained for the S-100 series tank. Assuming angle measurement uncertainties of  $\sim 0.02^\circ$ , a waste volume uncertainty of  $\sim 2-2.5\%$  is obtained. Preliminary preparations were made to setup the current full-scale FTP optical configuration on an optical table whereby the camera and grid projector can be independently manipulated in the “pan” and “tilt” directions. Previous “stitching” had made obvious the need for significant improvement (two orders of magnitude) in the determination of pan and tilt angles. To meet this angle-resolution requirement, a “sine bar”-type apparatus was designed and constructed (shown in Fig. 1) that is expected to meet the required angle measurement resolution of  $0.02^\circ$ .



**Figure 1. Table-top “sine-bar” apparatus for determination of pan and tilt angles to within  $0.02^\circ$**

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Preparations for the start of the “Stage II” series of experiments underway also included synthetic generation of overlapping FTP images and subsequent FTP profile and volume analysis. The use of synthetic images enables us to investigate the inherent performance of the current FTP analysis software with ideal data. Initially researchers were puzzled as to why stitching along one of four image boundary scenarios had yielded what appeared to be significantly higher error (-6.7 % vs. -2.9 % for the other cases) when the error was reported as relative error. Upon closer examination of the input conditions, it was noted that the test target was very small when compared to waste objects that are currently being encountered by Hanford post-retrieval. The test targets consisted of two right circular cones situated along the image boundary with each cone having a base of 10.0 cm and a height of 4.0 cm (true volume of 104.7 cm<sup>3</sup>). The camera-to-surface distance utilized was 6.1 meter (20 ft). When reported as an absolute error, the error is only 7 cm<sup>3</sup>. Considering the analyzed image size and the anticipated average waste deposit height, ~2.5 cm, this compares very favorably to the expected average tank volume contribution for that image, ~1350 cm<sup>3</sup> (< 0.52%).

## **WORK PLANNED**

### **STEREOVISION**

During the next quarter, the graduate student will be replaced. The Stereovision effort will continue to optimize the experimental setup and software for deployment into the Hanford waste tanks. Researchers have previously performed a series of experiments at distances up to 60 feet. 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 complete its preparation for Performance Evaluation Stage 2 and to conduct and complete that stage. The report for Performance Evaluation Stage 1 will be completed and submitted to our Hanford collaborators. Work will also continue on study of phase unwrapping algorithms<sup>1, 2</sup> for target areas that have large height discontinuities and/or surface isolations. Research on image quality improvement algorithms<sup>3, 4</sup> is on-going.

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## **ACRONYMS**

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

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## 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 sheer 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 ( $\text{Na}_7\text{F}(\text{PO}_4)_2 \cdot 19\text{H}_2\text{O}$ ), 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 with waste 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

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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: Efforts this quarter were aimed at developing a path for further calculations and network development. Results of previous calculations were evaluated. Towards this end, additional Best Basis Inventory data was obtained along with a document regarding HTWOS model inventory preparation.

In conjunction with CH2M Hill Hanford engineers, a work plan was developed describing the tasks necessary for further development of neural network representations, Table-1. Specific requirements needed to make the use of a neural network a reality are delineated. Work on developing networks for either 242-A evaporator operation of C-farm retrievals will commence following additional discussions with CH2M Hill Hanford personnel.

**Table 1. Work Plan for HTWOS Model Tank Waste Chemistry Neural Network.**

<b>Work Activity</b>	<b>Description</b>	<b>Organization</b>
Develop Initial Tank Waste Chemistry Neural Network Model for Waste Dissolution	Perform ESP calculations to predict the compositions in the serial dilution of wastes from six SSTs. This has been completed and is listed for information about the effort.	ICET/MSU
Program the HTWOS to use Neural Network models of tank waste chemistry	Write code within the HTWOS model to perform tasks and calculations using the Neural Network Model. 2. Debug the code by performing various tests.	CH2M HILL
Test the chemistry predictions made by the Initial Tank Waste Chemistry Neural	Test the waste chemistry predictions made by the Initial Tank Waste Chemistry Neural Network Model for Waste Dissolution Test the neural network using other input stream	CH2M HILL ICET/MSU

<b>Work Activity</b>	<b>Description</b>	<b>Organization</b>
Network Model for Waste Dissolution	data (for simple systems such as NaNO <sub>3</sub> , or from the inventory data for other tanks) to see if the predictions are consistent with the current understanding of Hanford tank waste chemistry.	
Revise the Initial Tank Waste Chemistry Neural Network Model for Waste Dissolution	Revise the Initial Tank Waste Chemistry Neural Network Model for Waste Dissolution to improve the network's ability to predict the chemistry associated with the water dissolution of Hanford tank waste during retrieval.	ICET/MSU
Develop additional neural network models.	Develop the training data and train a neural network model for predicting solids formation during the concentration of Hanford tank waste liquids in the 242-A Evaporator. (Note: This effort may start by evaluating the chemistry of liquids recently processed through the 242-A Evaporator and expand to include projected compositions of evaporator feed streams.) Develop other neural network chemistry models as needed and identified through the interaction between the Hanford site and the DOE University Programs.	ICET/MSU
Test the chemistry predictions made by the additional neural network models.	Test the implementation of and predictions made by new neural network models.	CH2M HILL and ICET/MSU

Task 2 Aluminum Chemistry Evaluations: As noted above, the particular form of aluminum in the waste has implications on sludge washing and leaching. In essence, the sludge leaching process has been developed to solubilize the aluminum (and, potentially chromium) using NaOH, thereby providing a separation [7]. The resulting sludge will contain the majority of the actinides and other radionuclides that are best vitrified. The aluminum leachate can, however, be mixed and processed as LAW, thereby reducing the volume of waste destined for the glass plant.

Different aluminum compounds such as gibbsite, Al(OH)<sub>3</sub>, and boehmite, AlOOH, are known to exhibit different solubilities in caustic solutions with AlOOH being comparatively insoluble.[8, 9]. The kinetics of dissolution have also been studied [10]. Here it has been shown that the dissolution of gibbsite is approximately 600-700 times faster than for boehmite. Consequently, the sludge leaching process is expected to be more efficient if the aluminum present in the waste is in the form of gibbsite.

Aluminum, like sodium, can also act as a diluent in the production of glass. With regard to the wastes contained at Hanford, Al is the most prevalent cation with the exception of sodium [11]. It is therefore of importance to limit the amount of aluminum destined for the vitrification plant.

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A reduction in the number of canisters that need to be made will result in significant cost savings.

In order to tailor the caustic leaching process, it becomes important to understand the form of aluminum within the tank farms. Earlier work by Gong et al. indicated that a temperature of 150 °C was sufficient for converting the gibbsite crystal to boehmite by the elimination of water [12]. Experiments were performed in open and in sealed containers, providing for low water vapor and high water vapor conditions. Data analysis was performed using quantitative x-ray diffraction. These workers indicated that partial conversion could be obtained in as little as 3.5 hours. No differences were observed between the conversions with high and low water vapor pressures.

A number of questions resulted from this work including the potential for lower temperature transitions and whether added components such as sodium nitrate might affect the results. Efforts in these laboratories were then begun to further examine the transition.

Experimental: Gibbsite (99.5% purity) was provided by Almatix (product number C-333). Multiple solutions were prepared in either Nalgene Teflon vials or Parr stainless steel general purpose pressure vessels with TFE gaskets. All of the solutions were made to 6.61 m Al in 1.5 or 3m NaOH and subsequently heated in either a Precision Thelco Laboratory Oven ( $\pm 1.0$  °C) or Thermolyne model 48000 Furnace (stability of  $\pm 0.2$  °C at a maximum temperature of 1000 °C with a uniformity of  $\pm 3.6$  °C). Temperatures of 50, 100, 120, 135, and 150 °C were investigated. Following some period of time, the solution was removed from the oven and filtered (high vapor pressure conditions) or the solid was ground (low vapor pressure- complete evaporation). The collected solids were copiously washed so as to remove any impurities present in the system. The samples were then allowed to dry at room temperature.

Conversion of the remaining gibbsite in the recovered solids was evaluated using thermogravimetric analysis (Perkin Elmer Pyris Diamond TG/DTA 6300). A small mass sample (typically 20-30 mg) was placed in the oven and a temperature program was developed to provide for heating rate control. Initially the sample was heated to 150 °C and then held for a period of around 30 minutes. Interstitial water was evolved at this temperature and the new weight became the actual starting mass for the analysis. The sample was then heated from 150 to greater than 600 °C at 10°C/minute. This allowed for the transition of gibbsite to boehmite and finally to alumina based on the following reactions.



The theoretical weight loss from reaction 1 is 23.1% while the corresponding mass change from reaction 2 is 15%. Taken together, a sample of pure (100%) gibbsite would result in a mass loss of 34.64%.

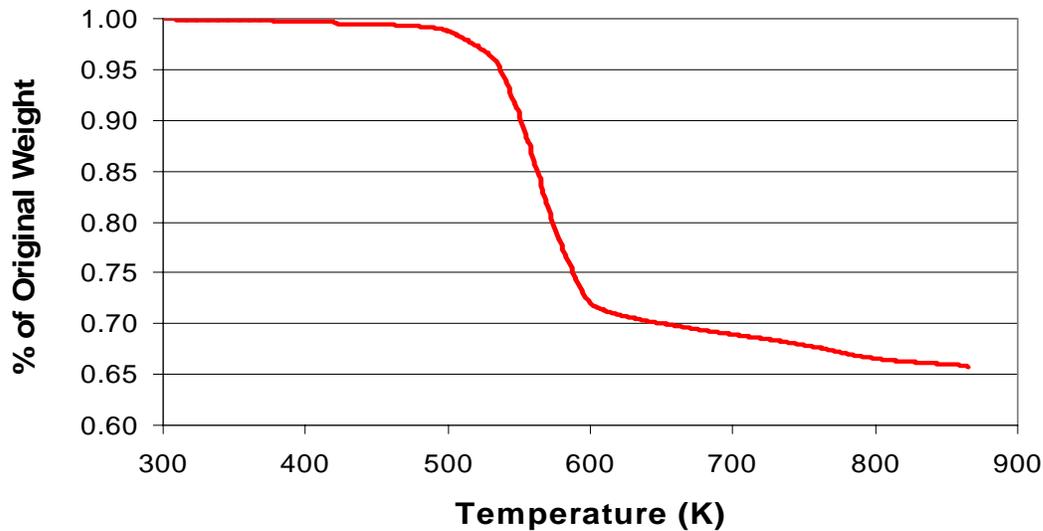
The mass fraction of boehmite ( $x_{\text{boehmite}}$ ) in the prepared sample can be calculated based on Equation 1.

$$x_{boehmite} = \frac{w_i - \left[ \frac{(w_f - w_i) MW_{gibb}}{MW_{H_2O}} \right]}{w_i} \quad (3)$$

Here,  $w_i$  and  $w_f$  are the initial and final weights. It is known that the initial treated solids are only composed of gibbsite and/or boehmite and that eventually all of the boehmite in the TGA experiment is converted to alumina. Under these conditions, the mass fraction of gibbsite can be obtained based on the overall stoichiometry of the transitions.

$$x_{Al(OH)_3} = \frac{\left[ \frac{w_i - w_f}{w_i} - \frac{1}{2} \frac{MW_{H_2O}}{MW_{boeh}} \right]}{\left[ \frac{3}{2} \frac{MW_{H_2O}}{MW_{gibb}} - \frac{1}{2} \frac{MW_{H_2O}}{MW_{boeh}} \right]} \quad (4)$$

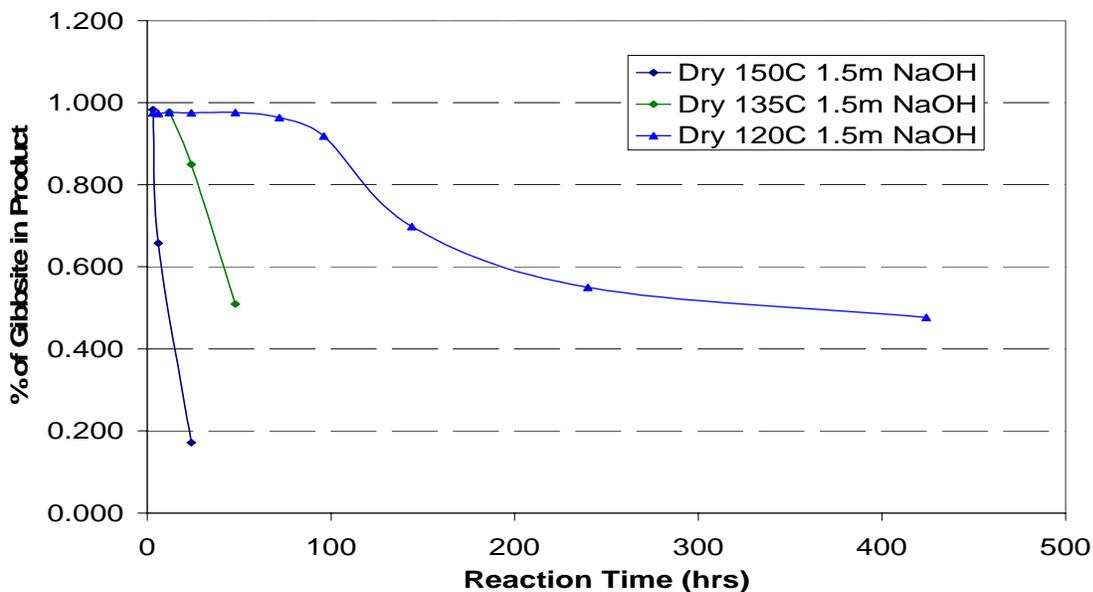
**Preliminary Results:** The thermogram for the Almatris gibbsite is presented in Figure 2. The initial drop in mass at 423 K (150 °C) corresponds to a small amount of interstitial water remaining in the sample. The primary gibbsite to boehmite transition begins shy of 500 K and continues to 600 K. The second transition to  $Al_2O_3$  continues to around 870 K.



**Figure 2. TGA trace for the Almatris Gibbsite.**

Analysis of the trace in Figure 2 according to Equation 4 indicates a total mass loss of 34.6%. This value should be compared to the theoretical weight loss of 34.64% based upon the transition reactions (Equations 1 and 2). The knowledge that the starting material was nearly pure gibbsite

allowed confidence in the TGA method and a number of experiments were conducted (low vapor pressure configuration) at 120, 135, and 150 °C, Figure 3.



**Figure 3. Percent of gibbsite in the product for different heating durations at temperatures of 120, 135, and 150 °C**

Rapid conversion of gibbsite to boehmite was observed at 135 and 150 °C. An initial plateau is observed at 120 °C. This corresponds to evaporation of the caustic in those samples, thereafter the conversion begins. The data at the highest temperature are similar to that obtained by Gong et al. indicating that rapid conversion is possible at 150 °C [12].

The data in Figure 3 indicate that the conversion of gibbsite to boehmite can occur at temperatures as low as 120 °C.

Additional experiments are planned to extend the investigations to lower temperatures and to evaluate the effect of caustic loading on the results. Experiments in the sealed containers are also planned so as to determine if water vapor pressure has an effect on the reaction.

Task 3: Database Distribution and Development: A list was compiled of the major salt cake systems for which solubilities have been measured in the ICET laboratories, Table 2. Measurements were made at ion loadings from 0 m to saturation; consequently, the ternary systems listed in Table 1 contain data for the associated binary systems. For example at 0 m F, the Na-F-NO<sub>3</sub> system reverts to the Na-NO<sub>3</sub> system. All determinations of solubility were performed in pure water and also at various loadings of OH, typically 1 and 3 m.

**Table 2. Systems where solubility measurements have been completed in the ICET laboratories.**

Na-F-NO <sub>3</sub>	Na-NO <sub>2</sub> -CO <sub>3</sub>	Na-SO <sub>4</sub> -PO <sub>4</sub>
Na-F-SO <sub>4</sub>	Na-NO <sub>3</sub> -CO <sub>3</sub>	
Na-F-PO <sub>4</sub>	Na-NO <sub>2</sub> -SO <sub>4</sub>	Na-Al-NO <sub>3</sub>
Na-PO <sub>4</sub> -NO <sub>3</sub>	Na-NO <sub>3</sub> -SO <sub>4</sub>	K-NO <sub>3</sub>
Na-F-PO <sub>4</sub> -NO <sub>3</sub>	Na-SO <sub>4</sub> -CO <sub>3</sub>	Cs-NO <sub>3</sub>

Solubilities for the Na-Al-NO<sub>3</sub> system were recently determined and have not yet been incorporated into V7DBLSLT. Measurements on the K and Cs-NO<sub>3</sub> systems are being performed in support of SRS and will be considered for incorporation into the MSE database in the future.

The systems in Table 2 can be reduced to the systems given in Table 3. These formed the initial basis for development of the workscope for the subcontract to be let to OLI Systems, Inc. Details of the work required to complete the regressions are also contained within the Table. Data for the pure components, NaNO<sub>2</sub> and HNO<sub>2</sub>, have not yet been incorporated into the MSE Public database. Since many of the solubility measurements were performed with added nitrite (Table 2), the fundamental data for these systems are required. Some binary systems, involving either NaOH and a sodium salt or two sodium salts, must be incorporated through regression of available data into the MSE framework. Other binary systems are currently contained in the MSE framework, and predictions using this MSE basis will be compared to laboratory data for these systems obtained at ICET in caustic solutions.

The list of systems was transmitted to OLI Systems, Inc., for an initial price quote. The preliminary value came back considerably higher than the projected subcontract value. Further discussions indicated that some cost-savings were possible through performing much of the background literature review and preliminary fitting of the data here. Negotiations continue to attain the planned cost of the subcontract.

**Table 3. Systems examined in subcontract**

Missing Pure Components	Binary Systems	Verification of Predictions
NaNO <sub>2</sub>	NaOH-NaNO <sub>3</sub>	NaF-Na <sub>2</sub> SO <sub>4</sub>
HNO <sub>2</sub>	NaF-NaOH	NaOH-Na <sub>2</sub> SO <sub>4</sub>
	NaF-Na <sub>3</sub> PO <sub>4</sub>	NaNO <sub>3</sub> -Na <sub>2</sub> SO <sub>4</sub>
	NaF-NaNO <sub>3</sub>	NaNO <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub>
	Na <sub>3</sub> PO <sub>4</sub> -NaNO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub> -Na <sub>2</sub> SO <sub>4</sub>
	NaNO <sub>2</sub> -Na <sub>2</sub> CO <sub>3</sub>	
	NaNO <sub>2</sub> -Na <sub>2</sub> SO <sub>4</sub>	
	NaNO <sub>2</sub> -NaOH	
	NaOH-Na <sub>2</sub> CO <sub>3</sub>	

## WORK FORECAST

Discussions will be held with CH2M Hill Hanford Group engineers to decide the target (242-A evaporator operation or C-farm retrieval) for the neural network calculations. Thereafter, the data from the BBI will be analyzed and reconciled followed by conversion into a molecular stream for input into the ESP model. Flowsheets will be developed and tested. Automation of

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the software is expected to allow the generation of a large number of streams from which training of the neural network will proceed.

Studies on the gibbsite to boehmite transition will continue with the evaluation of data at a second caustic loading and at lower temperatures. Data will be analyzed to establish the kinetic parameters (pre-factor and activation energy) associated with the reaction.

Discussions with OLI Systems, Inc., will continue with the goal of letting the subcontract during the next reporting period.

## CONCLUSIONS

A path forward for continuing the development of neural networks associated with Hanford waste operations has been developed. The plan outlines the associated responsibilities for workers at ICET and at the site. Evaluation of the gibbsite to boehmite transition indicated that the reaction can occur at temperatures as low as 120 °C. This finding potentially places a large portion of the aluminum waste contained in the single-shell tank farms at the site as boehmite. Discussions have begun with personnel at OLI Systems, Inc., for transferring the V7DBLSLT database to the MSE thermodynamic framework. Current efforts center on selecting the initial systems to port to the database and the associated cost for the subcontract.

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# Disposition of Idaho HLW Calcine

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## 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<sup>3</sup> of mixed high-level radioactive calcine 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.

CH2M-WG Idaho has provided the Stabilization Lead role for the down-select process and the decision authority for waste form production and testing. The Calcine Disposition Project has collaborated with ICET by providing calcine simulants, down-selecting the three alternatives for testing, co-authoring a test plan with performance specifications (“DIAL/MSU Test Plan to Develop Stabilizers for High Level Waste Calcine”, DIAL/ICP-SP3-TP-001, June 3, 2004), observing tests, reviewing test data and results, reviewing traceability of data and documentation, and eliminating iron phosphate ceramic and hydroceramic grout as two of the three candidate processes based on their inability to meet performance objectives laid out in the test plan.

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ICET is responsible for simulated waste form production, data collection, and application of a quality program for data and document acceptability. For each of the three alternatives, waste forms have been prepared and tested to evaluate stabilizer composition and waste loading on the performance parameters of compression strength, TCLP, and PCT (Product Consistency Test). The performance of the stabilized waste forms with regards to meeting the TCLP test and PCT has been compared to each other and to that of the raw calcine to show the improvement due to the stabilization treatment.

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).

During 2006, the following tasks were completed:

- Waste loading of the waste form was optimized,
- The effects of calcine compositional variability on the waste loading and waste form performance parameters were examined,
- A final report on the results of the tests conducted per the ICET Test Plan was issued in March 2006,
- A Mock-up Test Plan was issued,
- Mock-up components procurement initiated and the test stand will be constructed in November 2006, and
- An Annual Report, including the results of bench scales tests and the current status of the mock-up test stand and shake down testing was issued in December 2006.

## WORK ACCOMPLISHED DURING THIS QUARTER

Two 55-gallon drums of calcine simulant (non-hazardous) shipped from INL have been 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 given in Table 4 below.

Analyte	Result
Aluminum	30.4
Boron	0.700
Calcium	3.11
Magnesium	1.74
Sodium	5.02

**Table 4. Major cations (weight %) present in the calcine simulant**

Two sets of cubes (17% and 34%) to test for mechanical strength were made in December. No anomalies were observed during mixing, however, neither set appears to be curing as before. The sets were aged for a total of 37 days and then tested in compression. Results, Table 5, show that both formulations are sufficiently strong after that period of time.

A larger batch with this simulatant was also prepared (with the hopes that scaling up will give better results). After seven days, only the 34% cubes had cured; the compression tests are given below. They are not quite strong enough at this point.

Sample	Maximum (lbs)	Load	Breaking (psi)	Stress	Curing time (days)
12G34A	5302		1326		37
12G34B	4843		1211		37
G17A	2954		739		37
G17B	3648		912		37
G17C	3413		853		37
G34A	1704		426		7
G34C	1858		465		7
G34E	1550		388		7

**Table 5. Results of compression testing for waste forms with different waste loadings and curing times**

The feeders, mixers, and control equipment have been installed on the test stand for the mock up system. A small test batch consisting of sand was used to check the operation of the feeders. No problems were encountered.

A safety review of the assembled feeders, mixers, and control equipment has been completed. The first shakedown test was run by mixing the powders and then adding the water. This was not particularly successful as the solids mostly stayed in the bottom of the mixer. The next test will be run differently, perhaps by having the water already in the mixer as the powders are added.

## **WORK FORECAST**

A second run will be scheduled with the main difference being that the water was already in the mixer as the powders are added. In addition, the one-inch bottom drain will be replaced with a two-inch drain.

Further runs will be scheduled in an attempt to increase the volume of material to be produced, and the process method will be adjusted appropriately, as the behavior of the equipment is learned.

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# Support of SRS Salt Disposition and Other SRS Alternatives

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## **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 variations 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 select 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 that these column experiments require 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 required to achieve the same extent of dissolution by weight. Current efforts focus on solids identification within the sludge composition and the solids remaining from both experiments using XRD analysis.

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 solutions. Model predictions (using the Public and DBLSLTDB databanks) were used to design several solubility experiments and solubility data were collected for these systems. Preliminary analytical results show discrepancies with 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

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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 in order to process the secondary waste stream as saltstone [7].

## **WORK ACCOMPLISHED**

An extensive literature search was performed for solubilities of potassium and cesium salts in order to determine where gaps between the published experimental data and model predictions may exist. A letter report was compiled that included recommendations for solubility experiments and sent to the site. The recommended systems included the following:

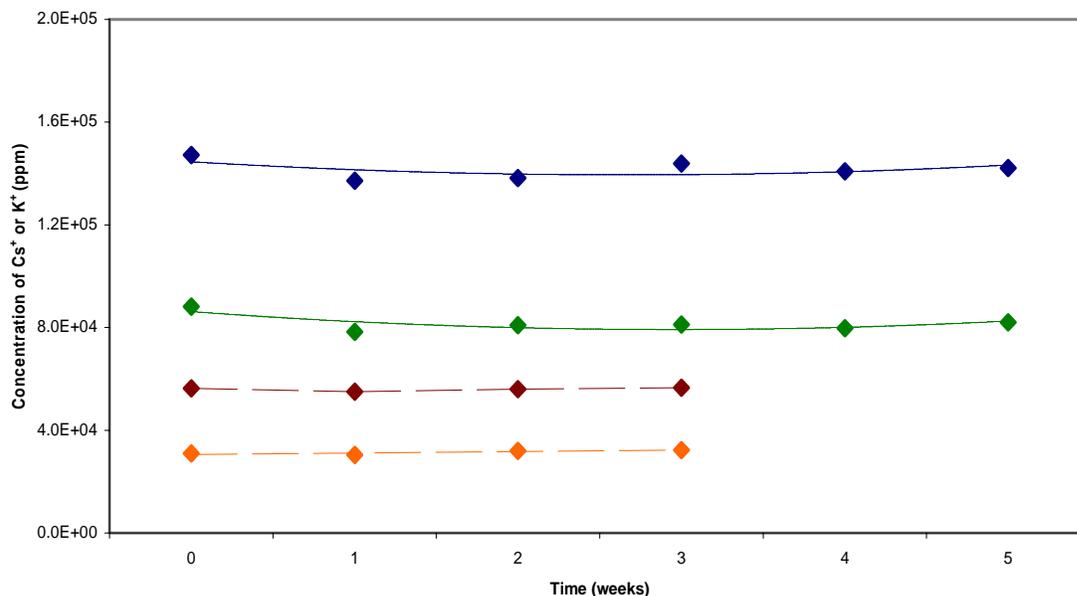
KNO<sub>3</sub>, CsNO<sub>3</sub> in 0-7 m NaOH at 25,50°C  
KNO<sub>3</sub>-NaNO<sub>3</sub> in 0,1, & 3 m NaOH at 25,50°C  
CsNO<sub>3</sub>-NaNO<sub>3</sub> in 0,1, & 3 m NaOH at 25,50°C

Results and model comparisons using ESP version 6.7 with either the Public or MSU/ICET DBLSLTDB databases for the KNO<sub>3</sub> and CsNO<sub>3</sub> in 0-7 m NaOH at 25°C were reported

previously and demonstrated good agreement with both databases [7]. The remaining systems have been completed and are detailed below.

### Experimental

A series of the pure component salts,  $\text{KNO}_3$  and  $\text{CsNO}_3$ , in water, 1m and 3m  $\text{NaOH}$  were prepared and sampled weekly until there was no apparent change in ion concentration in order to obtain equilibrium times. Figure 4 is a plot of the  $\text{K}^+$  or  $\text{Cs}^+$  ion concentration (ppm) for samples taken at weekly intervals. Little or subtle change appeared to occur in either ion concentration after one week equilibration time.



**Figure 4.  $\text{K}^+$  or  $\text{Cs}^+$  ion concentration in ppms at weekly sample intervals.**

Solutions of  $\text{KNO}_3$ - $\text{NaNO}_3$  and  $\text{CsNO}_3$ - $\text{NaNO}_3$  in 0, 1m, & 3 m  $\text{NaOH}$  at 25 & 50°C were then prepared based upon earlier model predictions. For all solutions (except pure components) in both temperatures, no solids formation was observed. New solutions were then prepared using the maximum concentration (obtained from the pure component solubility results) for either  $\text{KNO}_3$  or  $\text{CsNO}_3$  and varying the amount of  $\text{NaNO}_3$  added. Figure 5 contains the earlier model predictions for  $\text{KNO}_3$ - $\text{NaNO}_3$ -Water at 25°C. There is a significant difference between the Public and DBLSLTDB predictions owing to the pure sodium nitrate solubilities, but both databases suggest lowered  $\text{KNO}_3$  solubility as the  $\text{NaNO}_3$  concentration increases. The limited published experimental data [8] appears to go against the trend.

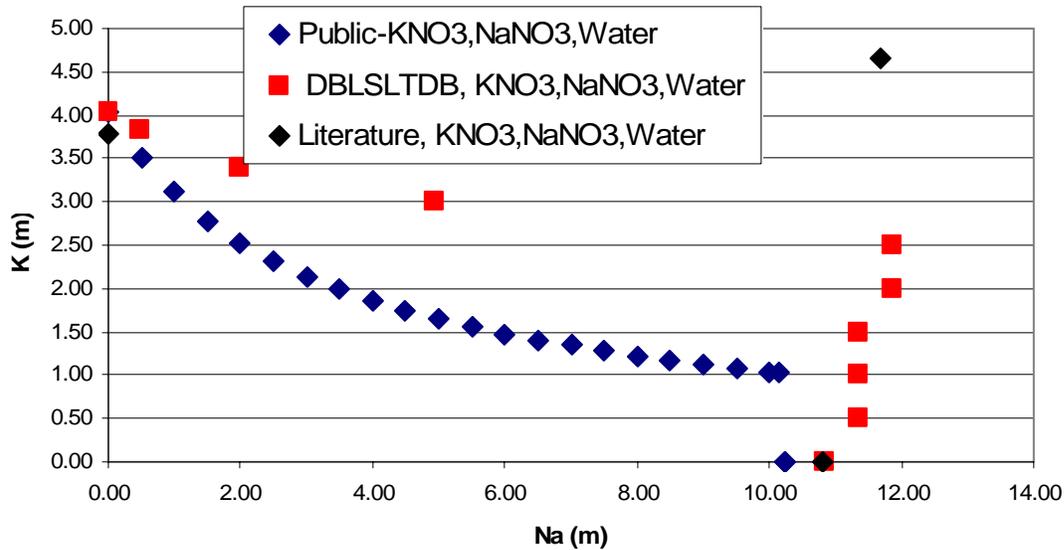


Figure 5. Solubility envelope for K and Na (as a function of  $\text{NO}_3$ ) concentration in water at  $25^\circ\text{C}$ .

Experimental results obtained from the  $\text{KNO}_3$ - $\text{NaNO}_3$  in 0, 1, & 3 m NaOH at  $25^\circ\text{C}$  were compared to ESP V7 (using both Public and V7DBLSLT databases) model predictions and are shown in Figure 6. The experimental results obtained by this laboratory follow the Linke data, with an increased solubility as the  $\text{NaNO}_3$  concentration increases with a maximum combined  $\text{NO}_3$  ion concentration above the pure component solubilities added together. These maximum concentrations are not included on the plot due to the lack of solids formation in this region for each solvent. Experimental results for the pure component  $\text{KNO}_3$  (3.503 molal) is somewhat higher than the model prediction and the published values (3.175 and 3.149 molal) [8, 9].

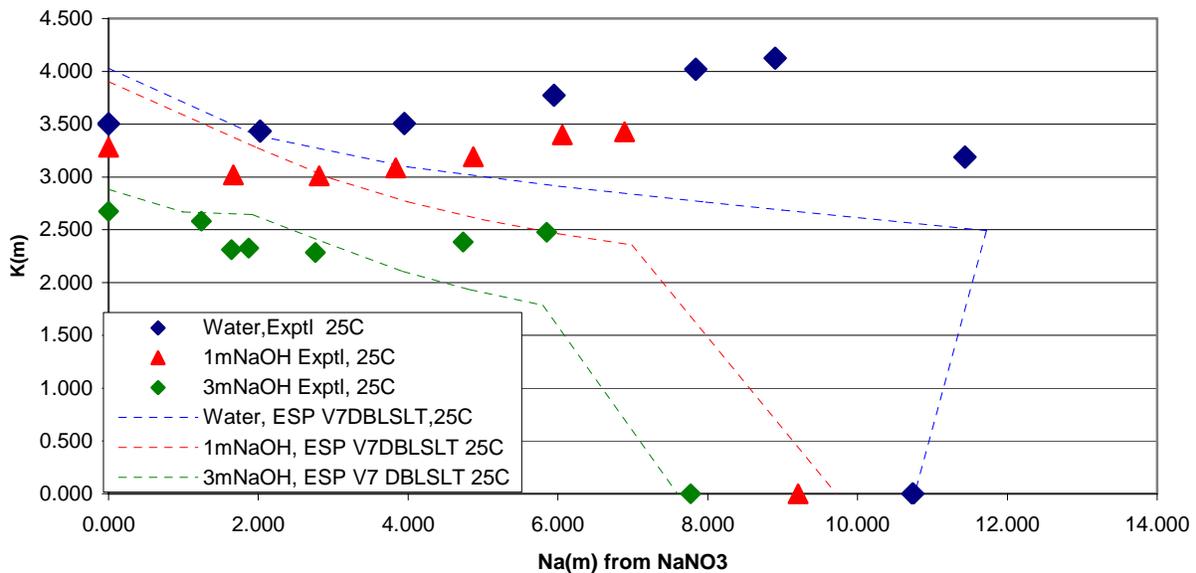


Figure 6. Experimental and model predictions for the solubility envelope of K and Na (as a function of  $\text{NO}_3$ ) concentration in water, 1 & 3 molal caustic at  $25^\circ\text{C}$ .

At 50°C, the system follows a similar trend of increasing  $\text{KNO}_3$  concentration as the  $\text{NaNO}_3$  concentration increases. Figures 7 and 8 contain comparisons of literature values to early model predictions in water and 1molal caustic. Again, the issues lie with differences between databases and with published results. Figure 9 includes our experimental data with comparisons to ESP v7 and V7DBLSLT model predictions.

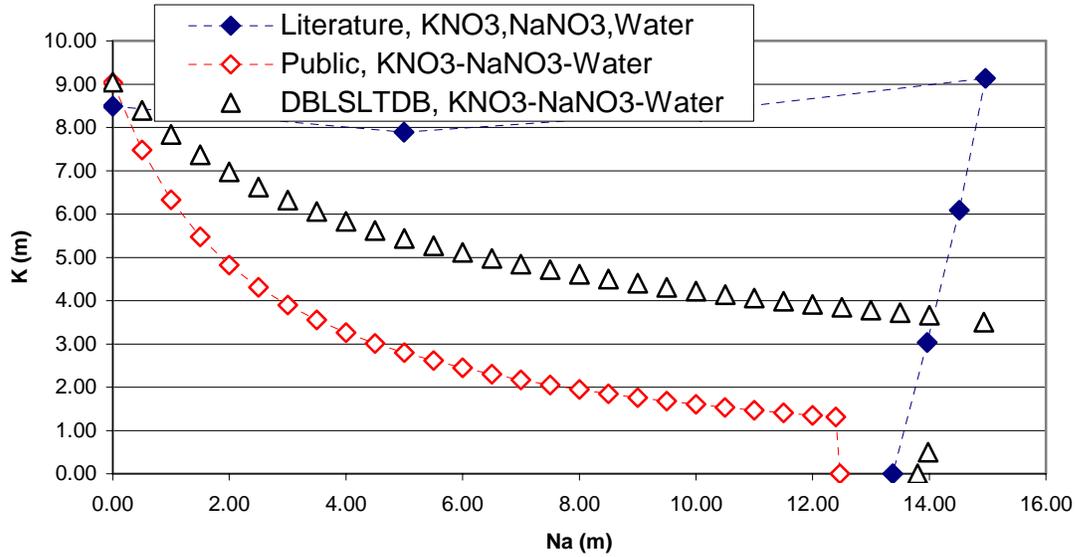


Figure 7. Literature values and ESP v 6.7 model predictions for K and Na (from  $\text{NO}_3$ ) concentrations in water at 50°C.

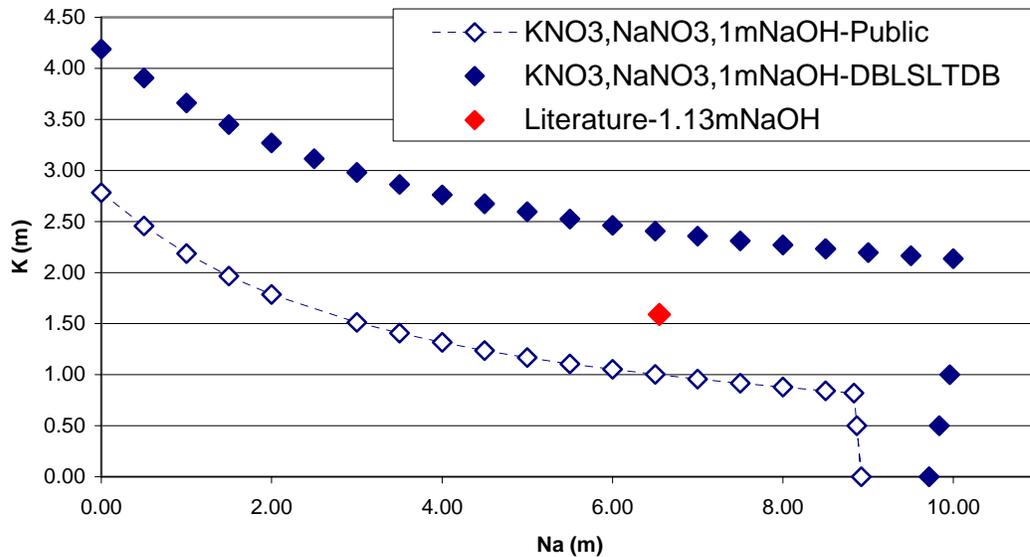
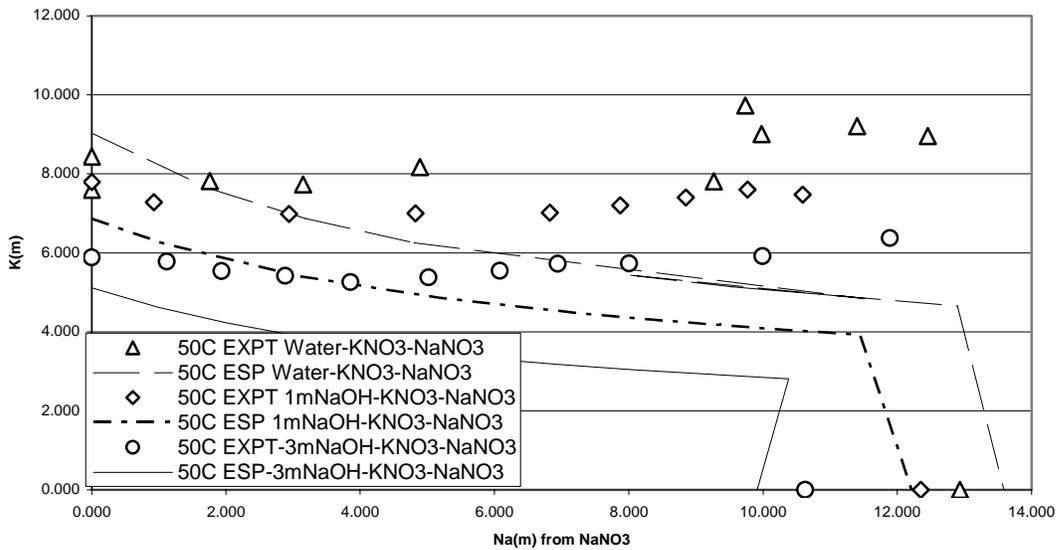


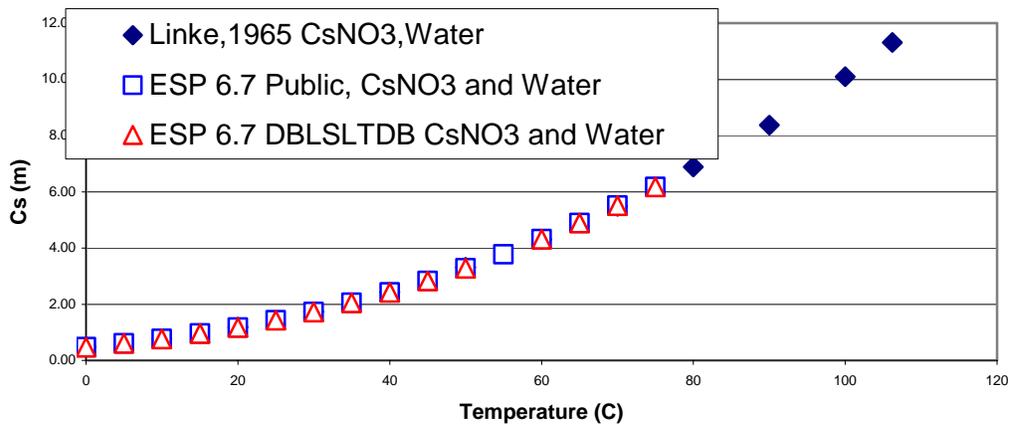
Figure 8. Literature values and ESP v 6.7 model predictions for K and Na (from  $\text{NO}_3$ ) concentrations in 1 molal caustic at 50°C.



**Figure 9. Experimental and model predictions for the solubility envelope of K and Na (as a function of  $\text{NO}_3$  concentration in water, 1 and 3 molal caustic at  $50^\circ\text{C}$ .**

The  $\text{CsNO}_3\text{-NaNO}_3$  experimental systems in 0, 1, & 3 m NaOH at  $25^\circ\text{C}$  follow the potassium system's trend of increasing solubility with increasing  $\text{NaNO}_3$  concentrations.

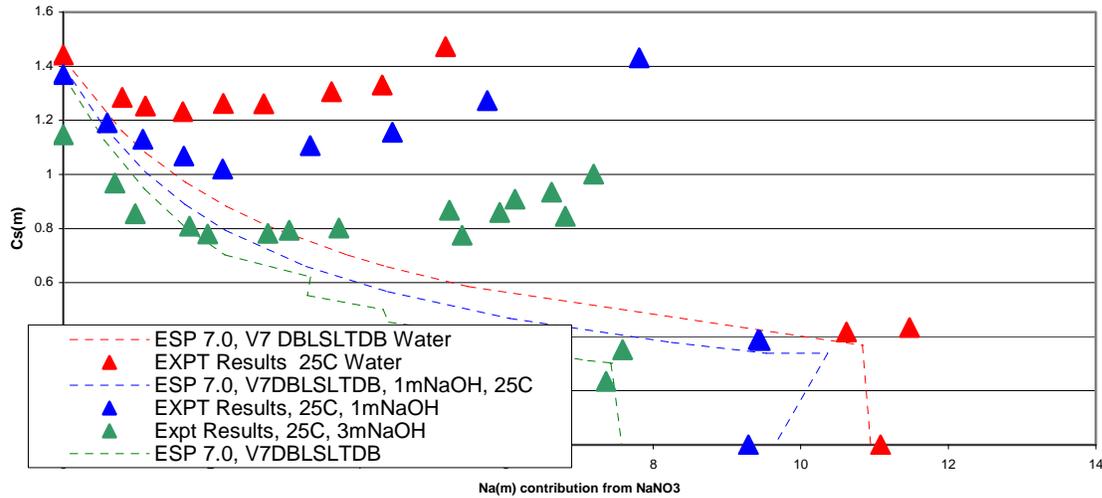
The binary system,  $\text{CsNO}_3\text{-H}_2\text{O}$ , includes the largest percentage of literature data available. Figure 10 captures the excellent agreement between published values and earlier model predictions with increasing temperatures. There were no published values in caustic at either 25 or  $50^\circ\text{C}$  for this system.



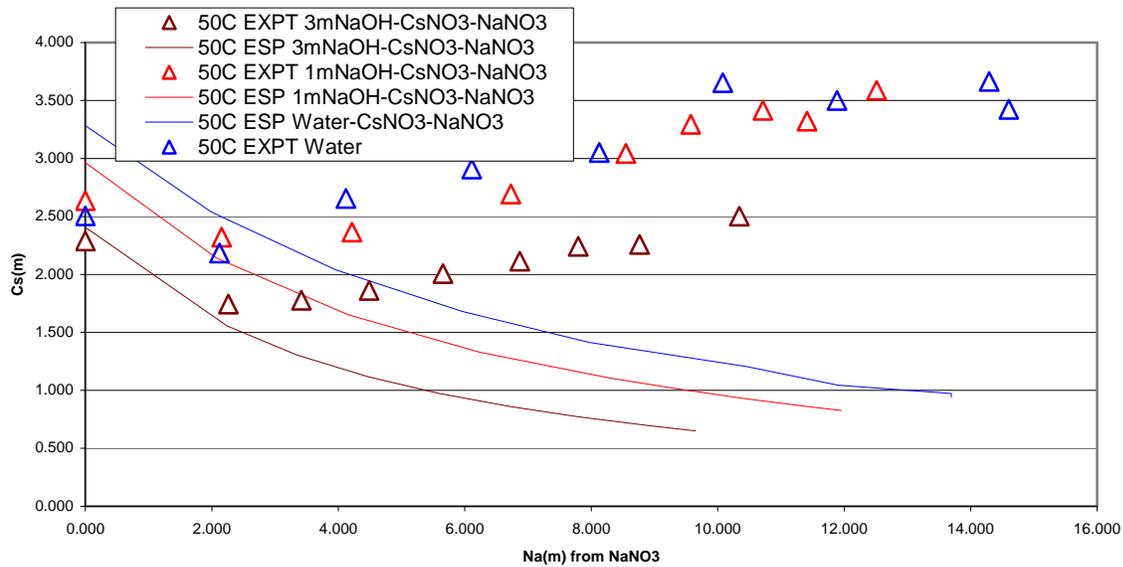
**Figure 10. Experimental results and model predictions for cesium solubility (from  $\text{CsNO}_3$ ) as a function of temperature.**

Figure 11 contains the comparisons between experimental data and current model predictions. For the pure component concentrations, there is good agreement between the published values (1.43 and 1.427 molal)[8, 10] and this work (1.44 molal). As with the potassium systems, the

maximum concentrations were not included due to the absence of solids formation. Figure 12 includes the experimental data from this study with current model comparisons. Pure component  $\text{NaNO}_3$  solubility was not duplicated for this study. The experimental data point for the pure component in water was deemed unreliable in that some of the  $\text{CsNO}_3$  fell out of solution during the filtration process. Literature values (3.28 and 3.282 molal) are in good agreement with the current databases (3.283 molal).



**Figure 11. Experimental and model predictions for the solubility envelope of Cs and Na (as a function of  $\text{NO}_3$ ) concentration in water, 1 and 3 molal caustic at 25°C.**



**Figure 12. Experimental and model predictions for the solubility envelope of Cs and Na (as a function of  $\text{NO}_3$ ) concentration in water, 1 and 3 molal caustic at 50°C.**

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## WORK FORECAST

Work continues on developing sludge blending streams in addition to caustic leaching simulations. Simulant recipes are in progress for stability studies and further DDA experiments with sludge inclusion.

## CONCLUSIONS

Solubility studies of two systems,  $\text{KNO}_3\text{-NaNO}_3$  in 0, 1, & 3 m NaOH at 25 and 50°C and  $\text{CsNO}_3\text{-NaNO}_3$  in 0, 1, & 3 m NaOH at 25 and 50°C are now complete. Results are compared to model predictions, obtained using ESP. Porting of these data into the MSE platform for a permanent repository is being considered for 2008.

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## 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 (PRVFP) is being evaluated. LIBS offers on-line real-time capability to determine the ratio of Li to Fe from the pour stream.

LIBS uses a high pulse energy laser beam to produce 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.<sup>1-3</sup> 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

In previous work, LIBS spectra of different sample forms (i.e. pellet with binder, pellet without binder, and powder on tape) of surrogate for plutonium oxide was compared. Although the sample of pellet with binder gave the best analytical figure of merit, due to the consideration of practical operation in the test facility, the PRVFP prefers to use samples of pellet without binder. This sample form requires less preparation. Since the sample will be kept inside the glovebox in the test facility while the LIBS system will be outside of the glovebox, a fiber optic LIBS system that can deliver the laser pulse to sample surface is the preferable experimental configuration for the PRVFP. To design a fiber optics system for long-terms operation, the ranges of laser energy that can be delivered by optical fiber to produce breakdown in sample surface but without damaging the fiber need to be determined. Different optical designs have been tested. Various lenses that are needed to expand the laser beam and focus the laser beam are being ordered. To reduce the cost in the initial parametric study, homemade optical fibers were used in the initial test. Since the Nd:YAG laser can be focused to a very small spot size, the pulse intensity is relatively high and can cause damage on the input surface of the fused silica fiber. Researchers are testing various optical configurations to avoid the damage on the input surface of the fiber and are working on improving the fiber transmission efficiency. The possibility to use a hollow-core fiber to deliver the nanosecond Nd:YAG laser pulse for long-term operation was also explored. Initial testing of a one-meter hollow-core fiber for transmitting high pulse energy laser is in progress. To date, 40mJ, 532-nm laser beam through this fiber with 50% efficiency has been achieved. To improve the coupling efficiency, another hollow fiber for visible light (i.e. 532nm) is being evaluated.

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Due to the practical consideration, the sample in the test facility will be in pellet form and retain in its press container. Evaluation of the LIBS system with a sample similar to the one used in the test facility requires a pellet container that can be used to press the sample. A holder was designed and fabricated. To prepare the surrogate feed material for LIBS test, the needed chemicals were ordered. Effects of laser energy, lens-to-sample distance, and pressure applied to the sample to form the pellet are being studied.

## **WORK FORECAST**

Work will continue on the evaluation of LIBS for on-line analysis of the Pu residue powder. More parametric study on LIBS application to Pu residue will be performed.

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## **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<sub>2</sub>O<sub>3</sub> 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:

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.

Identifying, as a function of temperature, the chemical reactions and phase changes occurring within the cold cap.

### **WORK ACCOMPLISHED DURING THIS QUARTER**

X-ray Diffraction (XRD) experiments on SB4 simulant with Frits 418 and 503 were begun this quarter. Materials heated to 600C, 700C, and 800C are being examined. It is clear that there are new phases appearing as other phases disappear with increased temperature. The most interesting appearing/disappearing phases are two major phases of silica, cristobalite, and tridymite. There may also be lithium silicate and lithium disilicate. The changes of these phases in these melts could provide insight to the overall melting behavior.

### **WORK FORECAST**

In order to confirm the presence of the lithium silicate and disilicate, glass compositions will be prepared and crystallized. XRD patterns and thermal behavior will then be obtained by differential scanning calorimetry (DSC).

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A series of crucible-scale melts will be made in order to examine 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 will be made up with a waste loading of 35%. The materials will be dried in an oven at 110°C then 20g-sized melts will be heated for two hours at 700, 750, 800, 850, and 900°C. The object is to compare the behavior of the two frit compositions.

# Support of DOE Headquarters

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## **Support of DOE Headquarter**

*Roger King, Charles Waggoner, Jeff Lindner, Yi Su*

ICET took part in the EM-20 Roadmapping workshop in October 2006 and during the first quarter of 2007 continued participation by reviewing and providing feedback on drafts of the Roadmap document. Drafts of the Roadmap were circulated within ICET to lead researchers and its organizational structure/objectives were topics of discussion at several of our staff meetings.

During the first quarter of 2007, the scope of ICET's efforts had to be reduced to match a 20% reduction in budget. This revision in scope was conducted with the objectives of reducing technical risk and uncertainty in mind.

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

*Yi Su*

This workshop has been rescheduled for early summer 2008.

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## HEPA and Regenerable Filter Performance Assurance

*Steven Alderman*

### INTRODUCTION

The 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 group 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 CONAGT (Committee on Nuclear Air and Gas Treatment). 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

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“autopsied” to gather information to reveal filter loading patterns and the degree of surface loading vs. depth loading. This will be accomplished by using 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.

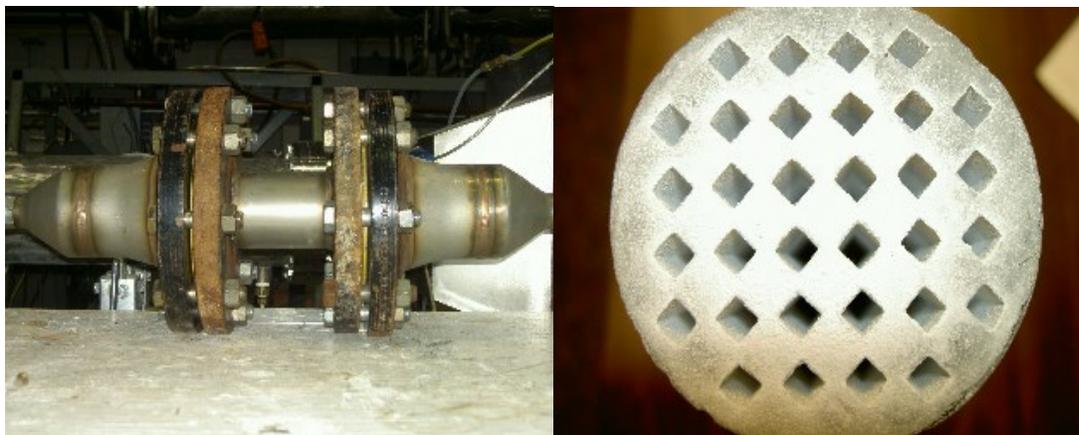
### Sub-Task 2 – Evaluation of Regenerable Filter Media

The 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**

Work accomplished during the first quarter of FY 2007 dealt primarily with Sub-Task 2 - Evaluation of Regenerable Filter Media. During January, a filter housing designed to hold the CeraMem ceramic membrane filter during loading with an aerosol challenge and during an air back pulse cleaning cycle was assembled. The filter housing inlet consists of a 10 cm slip-on flange to which a 10 cm to 2.5 cm bell reducer was welded. The filter housing measures 62 cm from end to end. The filter housing body consists of a 10 cm blind flange on both ends machined to fit 7 cm diameter stainless steel tubing 22 cm long. The filter housing outlet has the same make up as the inlet. The filter is held in place by rubber gaskets on both ends of the filter. The filter housing is sealed by tightening the flanges together. The filter housing is shown in Figure 13.

The ceramic membrane filters to be tested, supplied from CeraMem, consist of a porous ceramic support coated with a filtration membrane composed of metal oxide ceramics. The filter coupons tested were 20 cm in length and consisted of 32 parallel passageways extending the length of the filter. Each aerosol passageway entrance was 5 mm by 5 mm. Every other passageway is plugged on the inlet side to a depth of a 5 mm to prevent flow entrance. The remaining passages are plugged on the outlet side to prevent the flow from exiting. Consequently, the aerosol (gaseous fluid and particulate) must flow through the filtration membrane and ceramic support to exit the filter. The inlet face of a test filter is shown in Figure 1. The filtration surface area was determined to be 1705 cm<sup>2</sup>. Filter evaluations were made at media velocities of 1.95 cm/s and 3.9 cm/s.



**Figure 13. Filter Housing (left) and inlet face of CeraMem ceramic membrane filter.**

The test bed was also constructed and assembled in the month of January. Minor modifications were made to the HEPA filter test stand to setup the regenerable filter test bed. Aerosol challenge for the large CeraMem filters is pulled as a slip stream from the main HEPA filter test stand. The upstream section of the regenerable filter test bed consists of 2.5 cm non-conductive tubing and 2.5 cm stainless steel pipe fittings and pipe with two particulate sampling locations. The downstream section consists of 2.5 cm stainless steel pipe fittings and pipe and a venturi meter as well as three particulate sampling locations.

Preliminary testing was performed to ensure that our aerosol measurement instrumentation could sample against the negative pressure environment of the regenerable filter test bed. The upstream measurement section has two sampling locations separated by six inches. Instrumentation typically utilized to sample upstream of the filter are a TSI Scanning Mobility Particle Sizer and a TSI Aerodynamic Particle Sizer. The sampling probes are 0.32 cm diameter tubing. The downstream measurement section has three sampling locations separated by six inches each. The instruments sampling downstream of the filter are a TSI Condensation Particle Counter (CPC) for determination of total downstream particle concentrations and a Particle Measuring Systems Laser Particle Counter for determination of downstream particle size distributions. The sampling probe for the CPC is 0.32 cm diameter tubing and 0.48 cm diameter tubing for the laser particle counter. The first and third sampling locations are used to avoid interference between the instruments.

In February, the control system was automated and interfaced to existing data logging software. An initial test was performed to detect any problems with the system. Although the primary method of regeneration for these filters will be air-back pulse, an apparatus that will facilitate aqueous regeneration was constructed. Flow through the test stand is measured by a venturi meter. The flow rate is controlled manually with a ball valve. The data acquisition program records the pressure difference measured by the venturi meter. This pressure difference is then converted from differential pressure into volumetric flow rate units. The pressure drop across the filter housing and the static pressure in the test-bed are also measured and recorded by the data acquisition program.

In March, initial testing of the large CeraMem regenerable filters began. Experiments were conducted to determine the initial filtering efficiency, initial pressure drop, and approximate mass loading rate. These data were needed in order to devise a test plan for actual testing to be conducted during April. Additionally, the air back-pulse regeneration system was constructed and implemented.

Potassium chloride test aerosol was generated by evaporation of an aqueous 30 % (w/w) solution that was introduced to an aerosol generation chamber via an air atomizing nozzle. The geometric count mean diameter of the aerosol challenge was on the order of 180 nm with a geometric standard deviation of approximately 2.2. Mass loading rates were on the order of 50 mg/m<sup>3</sup> and particle concentrations were approximately 1x10<sup>5</sup>/cm<sup>3</sup>.

Figure 14 illustrates filter efficiency as a function of differential pressure for four load/back-pulse cycles. For the data shown, the filtration media velocity was maintained at 1.95 cm/s and the filter was back-pulsed with 3 times with a 20 PSI burst of air between loading cycles.

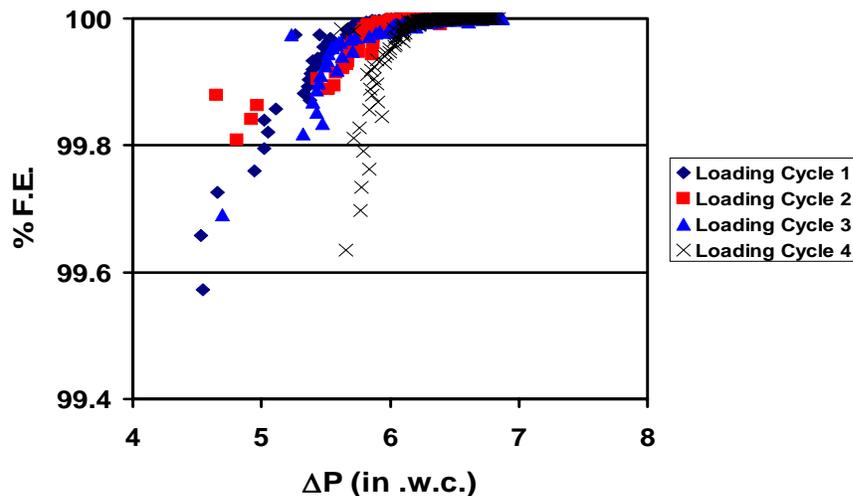


Figure 14. Filter efficiency as a function of differential pressure for the first four loading/backpulse cleaning cycles.

Here, an initial filter efficiency near 99.6 % was observed, which converged to approximately 100% after approximately a 1 in. w.c. increase in ΔP due to loading of the filter. However, note that the ΔP starting point for subsequent loading cycles is at increasing higher values relative to the starting point of loading cycle 1. This indicates that the filter was not being fully cleared of deposited particles during the back pulse procedure.

The downstream geometric count mean diameter was computed for the first and fourth loading cycles as a function of differential pressure, as shown in Figure 15. Note that as the filter loads, the downstream particle size distribution is shifted to smaller size.

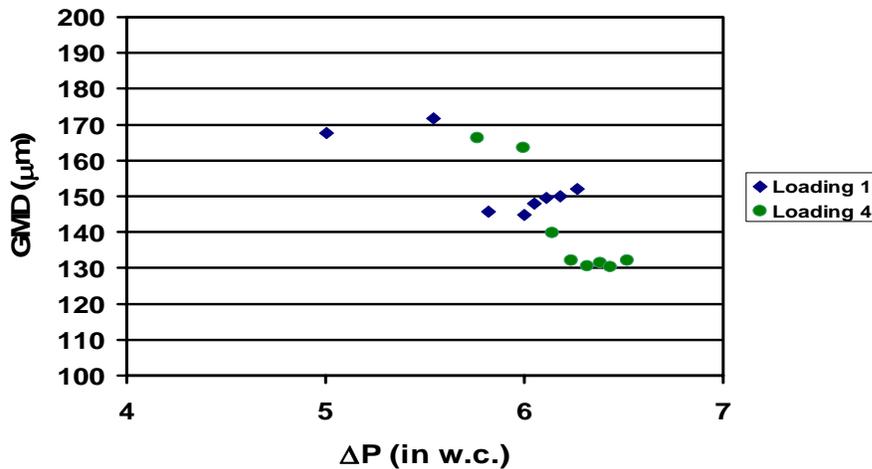


Figure 15. Downstream geometric count mean diameter as a function of filter differential pressure for the first and fourth loading cycle.

In order to determine if the air back-pulse pressure had an effect on  $\Delta P$  recovery, a series of tests was performed in which the filter was loaded and back-pulse cleaning was conducted at 25, 50, 75, and 100 PSI. This was done initially at a filtration media velocity of 1.9 cm/s and the filter was loaded 1-1.5 in. w.c. beyond the initial  $\Delta P$  value. The results of this study revealed that the back-pulse pressure had little effect on the extent to which  $\Delta P$  was recovered. It was hypothesized that not loading enough material on the filter was the cause for not seeing sufficient  $\Delta P$  recovery as a function of back-pulse pressure. Therefore, in order to capture more mass of aerosol challenge per unit time, a similar study was performed which entailed loading the filter at 2 times the previous media velocity, (3.9 cm/s). The results indicated that back-pulsing at 100 PSI was most efficient for  $\Delta P$  recovery. Therefore, future filter evaluations at a media velocity of 3.9 cm/s, with a back-pulse pressure of 100 PSI will be performed.

The manuscript "Load-Wash Testing of Regenerable Sintered Metal and Ceramic Membrane Filter Media" was revised based on the comments of three reviewers. The manuscript was re-submitted to Environmental Engineering Science.

Analysis of the vast amounts of data compiled during FY 2006 HEPA filter media velocity testing was continued and a manuscript is in development.

## WORK FORECAST AND CONCLUSIONS

Infrastructure was put in place to begin testing of CeraMem ceramic membrane regenerable filters during the first quarter of 2007. The aerosol challenge was characterized with respect to particle size distribution and mass loading rate. Preliminary results indicate that the experimental methods are sound and a complete battery of tests is scheduled.

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## 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 both total mercury and methylmercury in fish and water of lower East Fork Poplar Creek (LEFPC) of Oak Ridge.

### WORK ACCOMPLISHED

In this quarter, a series of new experiments on stability and bioavailability of HgS-contaminated Oak Ridge soils have been conducted. The experiments include the reaction kinetics of soil HgS with iron/manganese oxides, which are widely present in soils and sediments (Figure 16). The release kinetics of mercury from soil HgS by complexing agents such as EDTA (Figure 17) and oxalate acids, which are present in rhizosphere soils, were also studied. The extractability of pure chemical HgS and soil HgS was compared. Both the effects of time and concentrations of iron oxides have been examined.

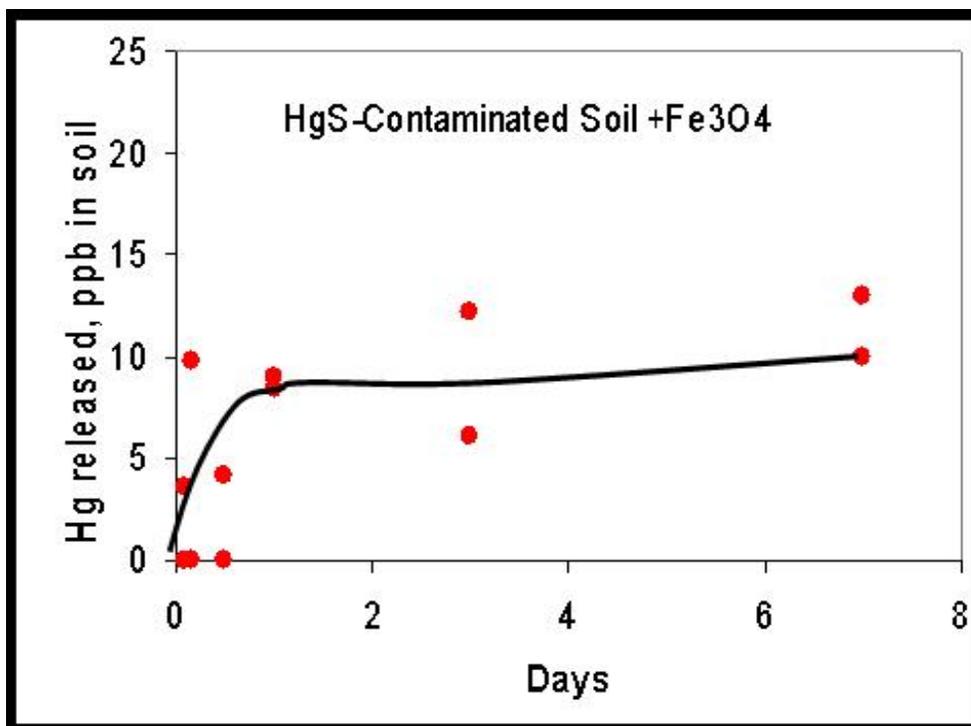


Figure 16. Kinetics of mercury release from HgS contaminated Oak Ridge soil by iron oxide (Fe<sub>3</sub>O<sub>4</sub>)

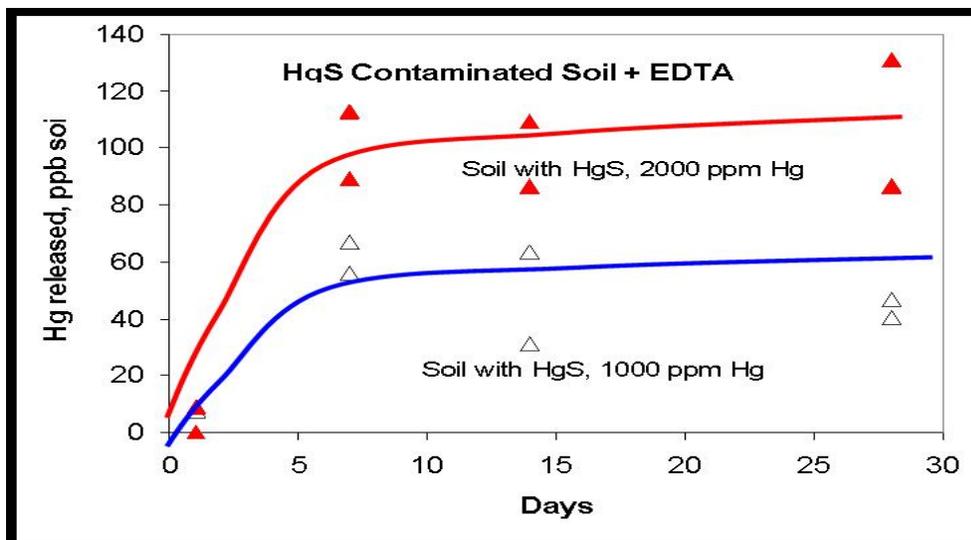


Figure 17. Kinetics of mercury release from HgS contaminated Oak Ridge soil by EDTA

## WORK FORECAST

In the next quarter, we will continue to study the kinetics of mercury release from Oak Ridge soil by iron oxides and manganese minerals. We are going to look at the relationships between concentrations of sulfate and dissolved iron and mercury.

## CONCLUSIONS

The results showed that chelate EDTA solubilizes soil HgS from contaminated Oak Ridge soil (Fig. 2) with the peak concentrations of mercury after one week reaction, while extractability of pure chemical HgS by EDTA was much less than that of soil HgS. The mercury release rate by iron oxides could be as high as around 10 ppb with the peak concentrations at one day of reaction (Fig. 1).

## REFERENCES

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2. Han, F.X., W.D. Patterson, Y. Xia, B.B.M. Sridhar, and Y. Su. 2006. Rapid determination of mercury in plant and soil samples using inductively coupled plasma atomic emission spectroscopy, a comparative study. *Water, Air and Soil Pollution* 170: 161-171.

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# 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

During this quarter, mercury phytoremediation experiments were continued with in-house built sunlit chambers. Chinese brake fern (*P. vittata*) was grown on clean soil, but the plant shoot was enclosed into a chamber containing mercury contaminated soil (Figure 18). The mercury source was  $Hg^0$  in the air of the chamber from contaminated soil spread at the bottom of the chamber. The shoots of the fern had no direct contact with the contaminated soil. The purpose of this setup was to study the shoots uptake of mercury from the air. Two mercury sources (mercury chloride and mercury sulfide) have been tested. Meanwhile, samples and data from previous experiments have been analyzed.



**Figure 18. Setup of the sunlit chamber study on mercury uptake by fern. Fern was planted in a pot containing clean soil under the chamber.**



**Figure 19. Sunlit chamber study setup**

Also during this quarter, two papers were published in International Journal of Remote Sensing.

## **WORK FORECAST**

The experiment was expected to finish in April.

## **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**

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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

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## Development of new technologies for DOE site applications

*Chuji Wang*

### INTRODUCTION

The development of innovative measuring and monitoring techniques for radionuclides, trace metals, and volatile organic compounds (VOCs) and semi-VOCs would be of significant benefit for many DOE site applications, including real-time *in situ* concentration measurement of trace radioactive analytes, such as alpha emitters (U, Pu, Am, etc.), heavy metals in subsurface waste streams and groundwater, and VOCs and semi-VOCs in/at tank. Prior to and during processing of tank waste, tank farm workers will have to perform limited analyses to ensure that waste can be retrieved and processed, and that it meets acceptance criteria. Currently, these analyses must be done through sampling, followed by shipment of samples to a laboratory capable of performing the needed analyses. Such measurements are typically performed with either ICP-MS or alpha scintillation counting (ASC) or GC-MS. ICP-MS or GC-MS systems are expensive and cannot be deployed for real field use due to the operational requirements of the instruments, such as high power, high gas flow rates, vacuum pump, etc. Furthermore, these methods, including ASC, require rather tedious sample preparation and long data processing time.

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 contaminants either in- or at-tank. Technologies and methods to be developed in this project will provide the required measurements either inside the tank or at the tank. The new techniques will potentially reduce costs, improve operating efficiency, and minimize technical risks (sensitivity and accuracy) by eliminating a lengthy sample-transport-analyze-report regimen.

### WORK ACCOMPLISHED

The research efforts in this quarter were focused on the measurements of C-H overtone spectra of methane and spectra of carbon dioxide using two near-infrared diode lasers with the newly developed ringdown optical platform. The purpose of the research development is to evaluate the measurement sensitivity and accuracy. Both carbon dioxide and methane have been measured in the laboratory ringdown system and the portable ringdown optical platform. In terms of measurement accuracy, which is characterized by the ringdown baseline stability, both systems have similarly measurement accuracy, less 4% of the full-scale readings. The sensitivities are 1.0 ppm for methane and 200 ppm for carbon dioxide for the ringdown platform,

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which has a cavity of 28 cm in length. The robustness of the optical platform has been tested through moving around the optical bench, and through installation and uninstallation of the ringdown platform from an instrument case. This quarter also consisted of optimization of the detection of uranium utilizing a blue diode laser. Efforts were concentrated on optimizing the plasma parameters as well as the detection electronics and triggering mechanism.

## **WORK FORECAST**

The planned activities for the second quarter include 1) multiplexing of multiple laser diodes for multiple species detections, 2) Testing and optimizing optical feedback of the novel optical module (two laser diodes sharing one optical isolator), 3) measuring C-H overtone spectra to evaluate the efficiency and ruggedness of the laser multiplexing, and 4) Emphasis for the second quarter will shift to studies of mercury naturally evaporating from spiked solution and soil samples.

## **CONCLUSION**

The newly developed ringdown optical platform has been tested to be robust. The system design and optical configuration can be adopted for the development of a site-deployable technique for tank characterization. The measurement accuracy of the portable optical platform is compared with the one from the laboratory ringdown system. Due to the shorter cavity length, 28 cm, used in the optical platform, the detection sensitivity is two-fold lower than that from the laboratory system; however, its sensitivity is sufficient for the measurements of tank related chemical species. This work allows the further development in the second quarter to be focused on wavelength multiplexing.

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## **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