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# Accelerating Cleanup of the Defense Nuclear Legacy

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

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

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

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

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

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

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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 were produced, analyzed, and tested in collaboration with CH2M-WG Idaho scientists and engineers. The appropriate physical and chemical performance characteristics (as per the waste acceptance requirements) have been determined for three simulated calcine waste forms. (These data are being provided under a quality program compatible with DOE/RW-0333P as directed by CH2M-WG Idaho.) Based on the data developed during these tests, grout cement has been down-selected as the preferred calcine waste form for follow-on mock-up testing.

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

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

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

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

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

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

### **Task 2 – Improvement of Waste Throughput**

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

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

## **Task 5. Support of DOE Headquarters**

### **HEPA and Regenerable Filter Performance Assurance**

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

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

In this quarter, the experiments on the effects of naturally occurred minerals on mercury release from Oak Ridge soil contaminated with HgS.  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{MnCO}_3$  have been tested. The preliminary results showed that iron oxides triggered the release of Hg, while  $\text{MnCO}_3$  did not affect the release of Hg from HgS minerals in Oak Ridge soils. The concentration of Hg released from HgS mineral in contaminated soils was linearly correlated to that of dissolved Fe in extracts, but negatively correlated with concentrations of sulfate. In addition, the manuscript entitled "Stability and Bioavailability of HgS in Oak Ridge soils" was prepared. The paper on "Bioavailability and Stability of Mercury Sulfide in Tennessee (USA) Soil" was published in the Proceedings of the 11<sup>th</sup> International Conference on Environmental Remediation and Radioactive Waste Manage, 2007, Belgium.

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## **Phytoremediation and Long-Term Monitoring of Heavy Metal Contaminants**

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

## **Task 6. Technology Development**

### **Development of new technologies for DOE site applications**

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

**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 will be used to reduce uncertainties and risks associated with waste processing and closure activities. Some of the systems developed for this effort are also applicable to other DOE sites, such as Savannah River.

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

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

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

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

## **WORK ACCOMPLISHED:**

### **STEREOVISION**

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

### **FOURIER TRANSFORM PROFILOMETRY**

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

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

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

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

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

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

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

## **WORK PLANNED**

### **STEREOVISION**

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

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

### **FOURIER TRANSFORM PROFILOMETRY**

During the next reporting period, the FTP effort expects to continue its efforts to immediately address technical challenges that have not yet been solved so that there will (to the extent possible) be more uniformity with regard to the FTP system used for the different Performance Evaluation Stages. Preparation for Performance Evaluation Stage 2 is expected to be completed. The report for Performance Evaluation Stage 1 will be completed and submitted to Hanford collaborators. Work will also continue on study of phase unwrapping algorithms<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.

### **REFERENCES**

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

### **ACRONYMS**

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

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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 the waste with that already present in the DST.

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

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

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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.

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

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

## **WORK ACCOMPLISHED**

### Task 1 Research on Neural Networks:

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

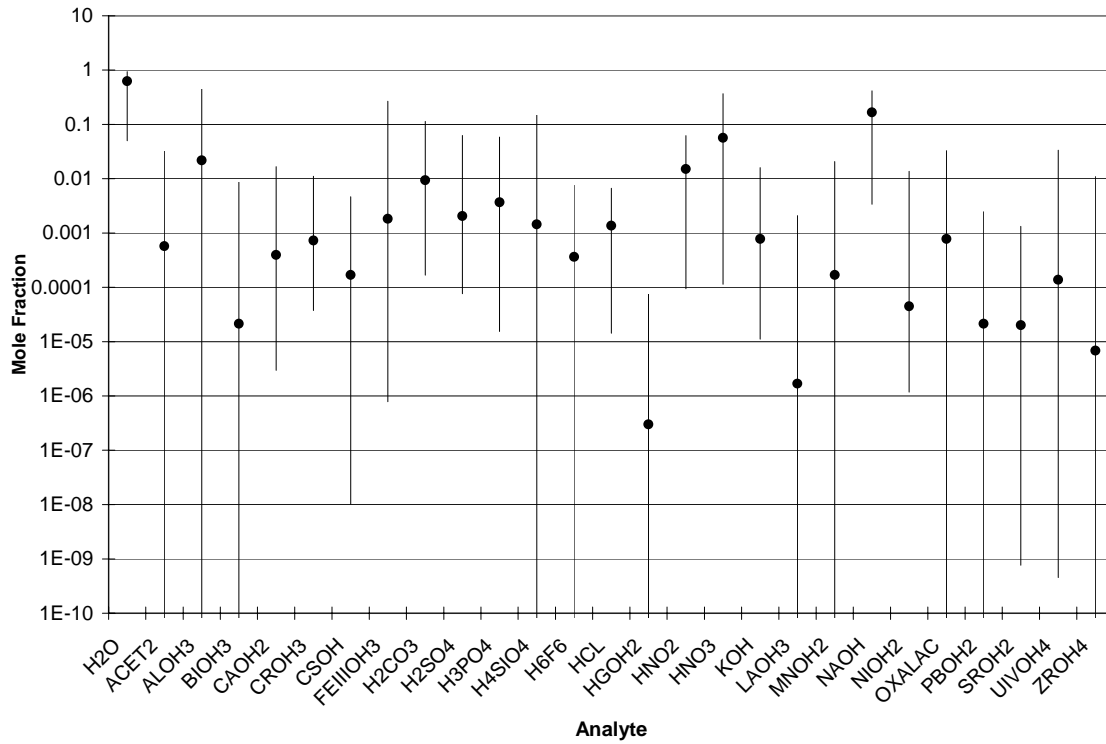


Figure 1 Ranges of the tank contents as mole fraction for the entire tank farm.

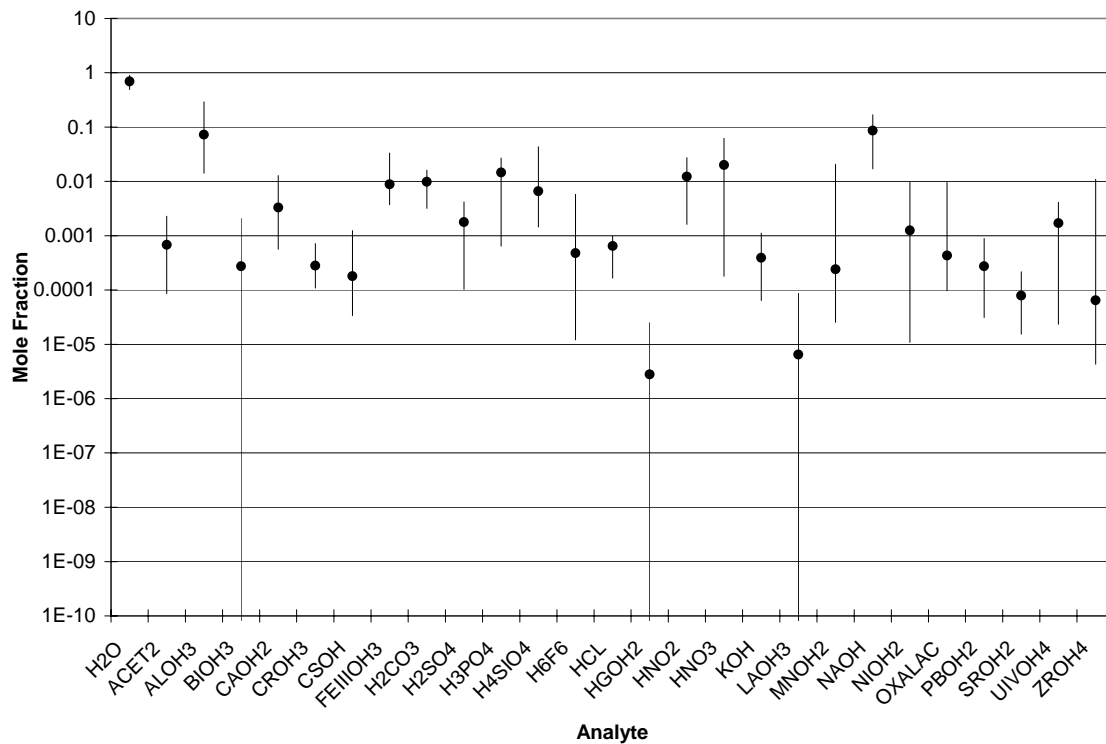


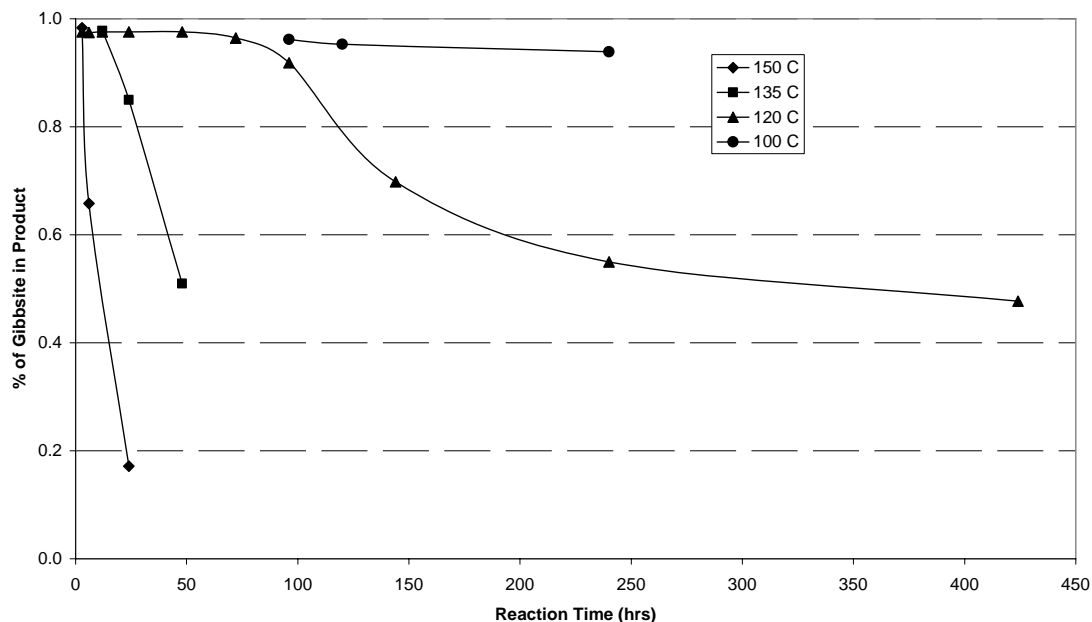
Figure 2 Ranges of the tank contents as mole fraction for the C-100 tanks.

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

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

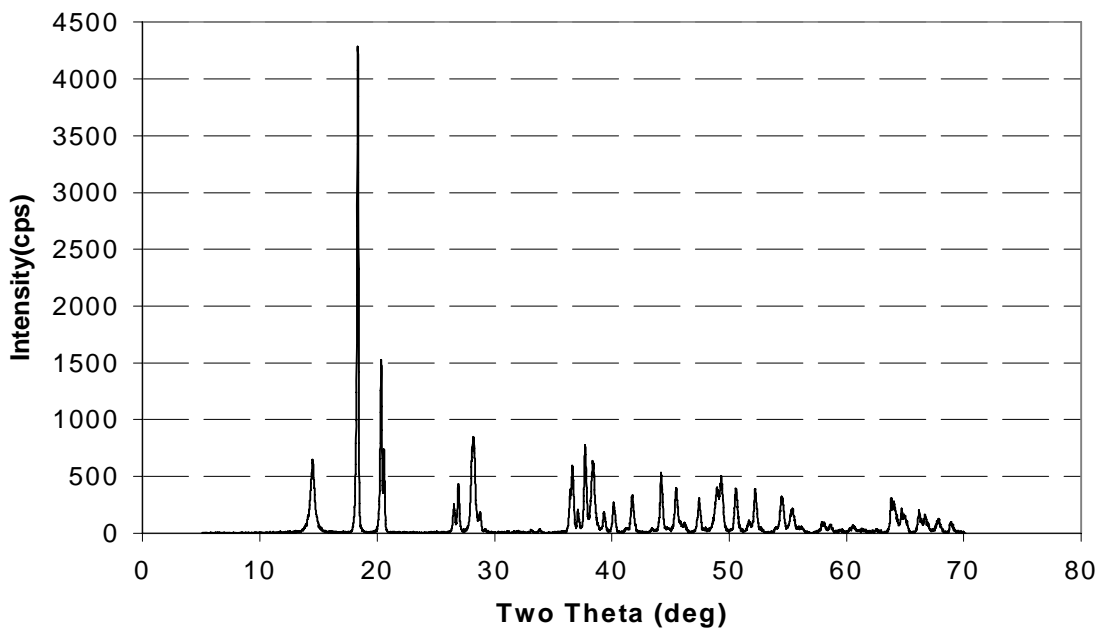
A number of measurements were attempted at 50, 80, and 100 °C. No changes were observed at the lower temperatures up to 540 hours. Small conversions of the Almatris gibbsite were found at 100 °C, Figure 3. Known mass standards were used to determine the accuracy of the TGA balance. A 5 mg sample was found to weight 4.95 mg and a 20 mg standard resulted in a mass of 19.7 mg. These result in 1 and 1.4% errors respectively. After 240 hours at 100°C the amount of gibbsite in a sample was 93.9%, which is outside of experimental error.



**Figure 3** Data obtained for the low water vapor conditions examined for the gibbsite to boehmite transition. All of the samples were prepared in 1.5 m NaOH.

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

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



**Figure 4** XRD pattern for a sample heated at 120 °C for 240 hours.









































































