Accelerating Cleanup of the Defense Nuclear Legacy

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Table of Contents

EXECUTIVE SUMMARY *4*

Task 1. Modeling and Experimental Support for High-Level SRS Salt Disposition Alternatives . **8**

Task 2. Process Improvements of the Defense Waste Processing Facility (DWPF) **16**

Task 3. High Efficiency Particulate Air (HEPA) **20**

Task 4. Support of Hanford Single Shell Tank Waste Disposition **23**

Task 5. Long-Term Monitoring of Selected Heavy Metal and Radionuclide Contaminants and Application of Phytoremediation **28**

Task 6 . SRS Saltstone Process Studies **29**

Task 7 . Bioavailability studies of mercury and other heavy metal contaminants in ecosystems of selected DOE sites **31**

Task 8. Hanford Tank Inspection **32**

List of Tables

Table 1. .CSSX simulant compositions for kinetic studies 9

Table 2. Solids weight & weight percent for Simulants 1 and 2 tri-weekly samples 10

Table 3. Base composition of the Batch 5 sludge 11

Table 4. Effects of caustic addition on the Batch 5 sludge 11

Table 5. Principal aqueous phase parameters for the DWPF recycle stream 13

Table 6. Instrument information for three different LIBS systems 18

Table 7. Comparison of FTP analysis of images acquired from analog and digital cameras using similar fields-of-view. The target is nondescript target #6 (true volume 647 cm^3) from the Stage 1 FTP Performance Evaluation study 34

Table 8. Comparison of FTP analysis of images acquired from analog and digital cameras using similar fields-of-view. The target is nondescript target #3 (true volume 19547 cm^3)and nondescript #6 (true volume 647 $cm^{3)}$ from the Stage 1 FTP Performance Evaluation study 35

List of Figures

Figure 1. Solids formation in simulants one and two over time in weeks 10

Figure 2. Ion concentrations resulting from addition of 50% NaOH to the Batch 5 sludge 12

Figure 3. Effect of temperature on Batch 5 sludge with 140 kgal of 50% caustic added 13

Figure 4. Scheatic diagram of LIBS measurement apparatus 19

Figure 5. LIBS SPECTRA OF Sludge Receipt and Adjustment Tank slurry around 386 nm. The spectra of dashed line and solid line are recorded by Czerny-Tuner & Echelle spectrometers, respectively 19

Figure 6. Trends in Initial Filter Efficiency as a Function of Media Velocity 21

Figure 7. Trends in Downstream Particle Count as a Function of Media Velocity 21

Figure 8. Trends in Downstream Count Median Diameter as a Function of Media Velocity 22

Figure 9. Flush Volume for C Tank Recovery into AN-106 25

Figure 10. C-108 Waste Retrieval Summary 26

Figure 11. C-108 Waste Retrieval Summary – AN-106 Solids 26

Task 1. Modeling and Experimental Support for High-Level SRS Salt Disposition Alternatives

Two CSSX simulants were prepared for kinetic studies of solids formation. Early results indicate after nine weeks both simulants at 15°C appear to have similar slow rates for solids formation but at 35°C in the lower silicon simulant two, solids appear almost three times faster than ambient. Studies are ongoing for solids identification for these simulants. Blending calculations using the DWPF recycle stream to dissolve saltcake in Tank 25 and then adding Batch 5 leachate streams were initiated. Modeling results indicate the later dissolution streams (~ > 30 % dilution by weight) as being out of compliance for tank corrosion requirements. Model predictions using small volumes of the Batch 5 leachate stream can bring the DDA streams within tank corrosion acceptance values.

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Task 2. Process Improvements for the Defense Waste Processing Facility (DWPF)

Laser induced breakdown spectroscopy (LIBS) is a diagnostic technique that can measure the concentrations of various elements in a test sample. This project evaluates LIBS as an on-line, simultaneous multi-species analysis of the Defense Waste Processing Facility slurry sample. During this work period, we have evaluated two detection systems for slurry analysis. The boradband Echelle spectrometer evaluated gives better spectral resolution as compared to the Czerny-Turner detection system. Different laser frequencies and sample stirring methods were tested for LIBS experiments of slurry sample to determine the best experimental configuration. To improve LIBS analytical performance, a double-pulse laser system was ordered. Double-pulse LIBS system was under tested with aluminum sample.

Task 3. High Efficiency Particulate Air

The 2007 scope of work for the HEPA filter-testing task was a continuation of previous year's activities. The objectives for 2007 included providing additional information to the ASME Committee on Nuclear Air and Gas Treatment (CONAGT) for their standards making activities in two important areas: development of a standard for metal media filters (Section FI) and modification of the current AG-1 standard for the maximum media velocity for fibrous glass filters (Section FC). These objectives included the conduction of testing of nuclear grade HEPA filters for performance at various media velocities above and below the current maximum media velocity of five feet per minute. Additionally, significant effort was put forth to place as much of the ICET HEPA filter testing data as possible in the refereed literature.

ICET researchers completed media velocity testing with Flanders AG-1 nuclear grade HEPA filters during 2007. A series of 12x12x11.5 inch AG-1 HEPA filters were loaded from initial differential pressures (approximately one inch) to 6 inches of water column using a set of solid KCl aerosols at media velocities ranging from 4 to approximately 8 feet per minute. The two-aerosol challenge conditions were established by either including or removing a cyclone (d50 cut point of 3 micrometers) from the aerosol generation process. Test data were collected continuously as the filters were loaded and trends were recorded to report the effects of media velocity on filter efficiency and most penetrating particle size as a function of both particle size distribution and differential pressure as the filters load.

Results of this initial series of media velocity tests were compiled and reported to the full CONAGT committee and to the FC subcommittee at the winter meeting in February 2007. The method of testing with solid aerosols was discussed Camfil Farr agreed to provide ICET with another set of filters for testing. DOE currently uses AG-1 filters from only three US manufacturers: Flanders, Camfil Farr, and American Air Filters. Camfil Farr units do not have the same amount of media in their filters or the same number of pleats. Testing and comparing these units to the Flanders filters will provide a better representation of the impact that a change in allowable media velocities would have on DOE operations. Filters from Camfil Farr were obtained during 2007 and media velocity testing of those units was initiated in a manner equivalent to that for the Flanders filters.

ICET played a significant in efforts during 2007 to complete development of Section FI for metal media filters. The FI working group is comprised of representatives of all three of the major manufacturers of metal media filters: Mott, Porvair, and Pall. Also populating the committee are consultants, the API filter testing facility, and engineering representatives from one of the DOE sites. ICET's location in the Bagley College of Engineering at Mississippi State University provides it credibility as an unbiased mediator to resolve issues arising among factions representing manufacturers or between manufacturers and users. ICET also presented a status report for the development of Section FI to both the FC subcommittee and full committee during the summer meeting of CONAGT.

Task 4. Support of Handford Single Shell Tank Waste Disposition

Development of a neural network to augment the chemistry in HTWOS, specifically for the C tank farm retrieval continued. An ESP program process model using the Modified Sluicing Method was used to simulate the sequential retrieval of waste from C-108, C-109, and C-110 into AN-106. Programs for ESP program batch mode processing have been tested with the generation of a test neural net training set.

Task 5. Long-Term Monitoring of Selected Heavy Metal and Radionuclide Contaminants and Application of Phytoremediation

During this quarter, we have finished two sets of experiments with the homemade chambers. The experiments were designed to investigate mercury uptake by leaves of Chinese brake fern and Indian mustard from ambient atmosphere above Hg contaminated soil.

Meanwhile, sample and data studies from previous greenhouse studies on oxidative stress of Indian mustard by Hg were analyzed and summarized. Two common varieties, Florida Broadleaf and Longstanding were used. Results show that antioxidant enzymes (catalase, CAT; peroxidase, POD; and superoxide dismutase, SOD) were the most sensitive indices of mercury-induced oxidative response of Indian mustard plants. Indian mustard effectively generated an enzymatic antioxidant defense system (especially CAT) to scavenge H_2O_2, resulting in lower H_2O_2 in shoots with higher mercury concentrations. These two cultivars of Indian mustard demonstrated an efficient metabolic defense and adaptation system to mercury-induced oxidative stress. In addition, majority of Hg was accumulated in the roots and low translocations of Hg from roots to shoots were found in two cultivars of Indian mustard. The reports were prepared as a manuscript for publication.

Task 6. Saltsone

This project is designed to assist the Savannah River Site (SRS) in the production of the Saltstone waste form from low-level tank waste. The expectation of increased aluminum content in the next batch has raised concerns about an excess heat of hydration which may create problems for the storage of the waste form. The facility also relies on vault temperature modeling to protect vault temperature limits. These studies are designed to examine the effects of the heat created by the reactions and to discover methods for either dealing with the excess heat or preventing it from occurring in the first place.

Task 7. Bioavailability studies of mercury and other heavy metal contaminants in ecosystems of selected DOE sites

During this quarter, the design and initial preparation for a comprehensive test bed were started. Meanwhile, we continued to analyze previous experiments on oxidation kinetics of pure HgS and HgS contaminated Oak Ridge soils by two common iron oxides (Fe_2O_3 and Fe_3O_4), which are in presence of the subsurface of Oak Ridge site. The results show that oxidation rate of HgS in contaminated Oak Ridge soil was initially fast and keep increasing until the 30 min mark, then followed by a plateau. 80-90% of S in the reaction system was SO_4 with a small amount of other intermediate S species.

Task 8. Hanford Tank Inspection

Based upon Hanford's interest in utilizing higher-resolution cameras for future tank deployments, ICET performed preliminary experiments to compare the FTP performance of a digital camera and the current analog camera. The ICET FTP group made substantial progress in its efforts to address questions relating to how FTP handles curved (non-perpendicular) background surfaces (such as a curved waste tank bottom). Since regions of bare tank bottom ("zero height") may be separated by distances greater than a single image, ICET continued its investigation of procedures for how to best propagate height across stitched image boundaries so as to minimize measurement uncertainty.

During this reporting period, the ICET Stereovision effort completed a literature review of recent advances in stereovision, including color stereovision. The use of color in stereovision may reduce errors in disparity matching, a critical step in analysis of stereovision images. The feasibility of utilizing color stereovision for waste tank characterization is being evaluated.

At end of this quarter, ICET was informed that because of the downward revision of the ICET Cooperative Agreement CA08 budget, that there are no funds to support the Hanford in-tank characterization effort for the current Cooperative Agreement year. ICET administrators subsequently issued a stop-work order. The bi-weekly conference calls with our Hanford collaborators were suspended. At this time, no further efforts are planned until funding becomes available.

Task 1

Support of SRS Salt Disposition

Jeffrey S. Lindner and Laura T. Smith

INTRODUCTION

Major needs in the SRS tank farms are dictated by the desire to separate actinides and cesium from salt wastes permitting the processing of the high activity waste fraction in the Defense Waste Processing Facility (DWPF) and stabilization of the lower activity waste as saltstone. Towards this end, efforts are currently underway for the development of the Salt Waste Processing Facility (SWPF) containing the Actinide Removal Process (ARP) and Caustic Side Solvent Extraction Unit (CSSX).[1-3] Current progress involves the pilot-scale testing of the CSSX process wherein solids re-precipitation and emulsions formation has been observed within the contactors and in wash and scrub liquors.

In addition the processing of sludge (caustic addition to Batch 5) to reduce the fraction of aluminum routed to the DWPF is scheduled for FY'08. [4-6] It is expected that aluminum-rich supernatants will be processed in the same manner as salt waste. Here, however, the downstream implications of mixing the aluminum-rich supernatant with DDA fractions from salt waste retrieval and other streams such as the DWPF recycle are unknown. The silicon concentration within the DWPF recycle stream along with the high aluminum loading in the Batch 5 (and potentially other sludge batches) leachate may indicate the formation of intractable aluminosilicates which will create a downstream problem owing to negligible solubility and the propensity for co-precipitation of uranium.

This project is divided into 2 Tasks. Task 1.1 is aimed at evaluation of the CSSX process through experiments and thermodynamic modeling. In collaboration with Parsons Engineering, the analysis of solids and scales observed in various portions of the process, including contactors, filters and solids formed in drain tanks. These solids will be analyzed using x-ray diffraction and inductively coupled plasma emission spectroscopy. Laboratory kinetic experiments are also planned to examine the stability of simulants to be used in pilot-scale testing at Parsons.

Task 1.2 is aimed at assessing stream stability for blended compositions arising from potential tank farm operations. Any stream blending will be performed upstream of the SWPF. The primary streams of concern are the DWPF Recycle stream, which consists of DWPF overheads and is routed to the tank farm, high aluminum concentration streams from sludge leaching operations (50% NaOH) and dissolved salt streams originating from saltcake dissolution. Predicted compositions will be assessed through calculated parameters such as percent solids by weight, aqueous phase density, adherence to corrosion waste acceptance criteria, [7] and ionic strength. Initial examination of blending along with the results from Task 1.1 allow for a starting point for SWPF waste acceptance criteria. [8]

WORK ACCOMPLISHED

Task 1.1 Previous modeling [9] of the CSSX simulant to be employed for pilot scale studies demonstrated aluminum species as the major solids formed during the simulant preparation. Aluminum solubility experiments from this lab [10] have shown extensive equilibrium times are needed thereby leaving the possibility of solids formation long after the simulant is prepared and filtered and includes the possibility of sodium aluminum silicate formation. Studies on the kinetics of solids formation for this simulant and for a second simulant prepared using a reduced amount of silicon began. The two simulant compositions are shown in Table 1.

Table 1 CSSX simulant compositions for kinetic studies.

Chemical	Formula	Molecular Wt. (g/mol)	Simulant 1 amount (g)	Simulant 2 amount (g)
Potassium nitrate	KNO_3	101.3	1.5191	1.5208
Cesium chloride	CsCl	168.37	0.0717	0.0707
Sodium hydroxide	NaOH	40	127.4588	127.4581
Sodium nitrate	$NaNO_2$	84.99	99.7591	99.848
Sodium nitrite	$NaNO_3$	69	35.4504	34.47
Aluminum nitrate nonahydrate	$Al(NO_3)_3 \cdot 9H_2O$	375.14	105.0417	105.0254
Sodium carbonate monohydrate	$Na_2CO_3 \cdot H_2O$	124.01	18.5941	18.5949
Sodium sulfate	Na_2SO_4	142.04	19.8333	19.8342
Sodium chloride	NaCl	58.44	1.4022	1.4022
Sodium fluoride	NaF	41.99	1.1736	1.1762
Sodium phosphate heptahydrate	$Na_2HPO_4 \cdot 7H_2O$	268.09	1.8719	1.8827
Sodium oxalate	$Na_2C_2O_4$	134	1.0713	1.0721
Sodium meta-silicate nonahydrate	$Na_2SiO_3 \cdot 9H_2O$	284.2	8.5277	5.328
Sodium molybdate dihydrate	$Na_2MoO_4 \cdot 2H_2O$	241.95	0.0201	0.0193
Copper sulfate pentahydrate	$CuSO_4 \cdot 5H_2O$	249.68	0.0049	0.0059
Zinc nitrate hexahydrate	$Zn(NO_3)_2 \cdot 6H_2O$	297.47	0.0391	0.0419
Iron nitrate nonahydrate	$Fe(NO3)_3 \cdot 9H_2O$	404	0.0166	0.0121
Tin chloride dihydride	$SnCl_2 \cdot 2H_2O$	225.63	0.005	0.0042
Water	H_2O	18.015	837.0175	836.9899
Total solution weight (g)			1258.8781	1254.7566

One component, di-n-butyl phosphate, was not included in this study. Both simulants were prepared adding each component as described in previous literature. [11] The simulants were allowed to equilibrate overnight and then filtered. Only simulant 1 contained visible solids. Each simulant was then equally separated into several HDPE bottles and placed in one of three temperature controlled appliances set at 15, 25 or 35°C. An initial aqueous sample was removed for baseline analysis. Every three weeks one bottle was removed, filtered, and an aqueous aliquot sent for analysis. The filtered solutions were then weighed and placed back at temperature. The weighed solids were kept for further analysis. Table 2 provides the weight and weight percent of solids formed initially and for samples through nine weeks.

Table 2. Solids weight and weight percent for Simulants 1 and 2 tri-weekly samples.

Sample	Sim 1 grams, wt% 15°C	Sim 1 grams, wt% 25°C	Sim 1 grams, wt% 35°C	Sim 2 grams, wt% 15°C	Sim 2 grams, wt% 35°C
Initial	0.000	9.1190(0.72)	0.000	0.000	0.000
3 weeks	0.000	0.4033(0.14)	0.4445(0.28)	0.000	0.6726(0.43)
6 weeks	0.4800(0.31)	0.3630(0.12)	0.4353(0.27)	0.3997(0.27)	0.6814(0.44)
9 weeks	0.4697(0.30)	0.4653(0.16)	0.3623(0.28)	0.4150(0.27)	0.5343(0.36)

A comparison plot of the temperature results for solids shown in Figure 1 indicate that at lower temperatures, solids formation for both simulants occurs at a slower time frame but catch up after six weeks when compared to ambient conditions. At the higher temperature of 35°C, solids occur at twice the rate of ambient conditions for simulant one while solids formation in simulant two is three times faster. Further analysis of the solids is underway. Complete analysis of all samples will include additional solids formed in the filtered solutions and will be reported later.

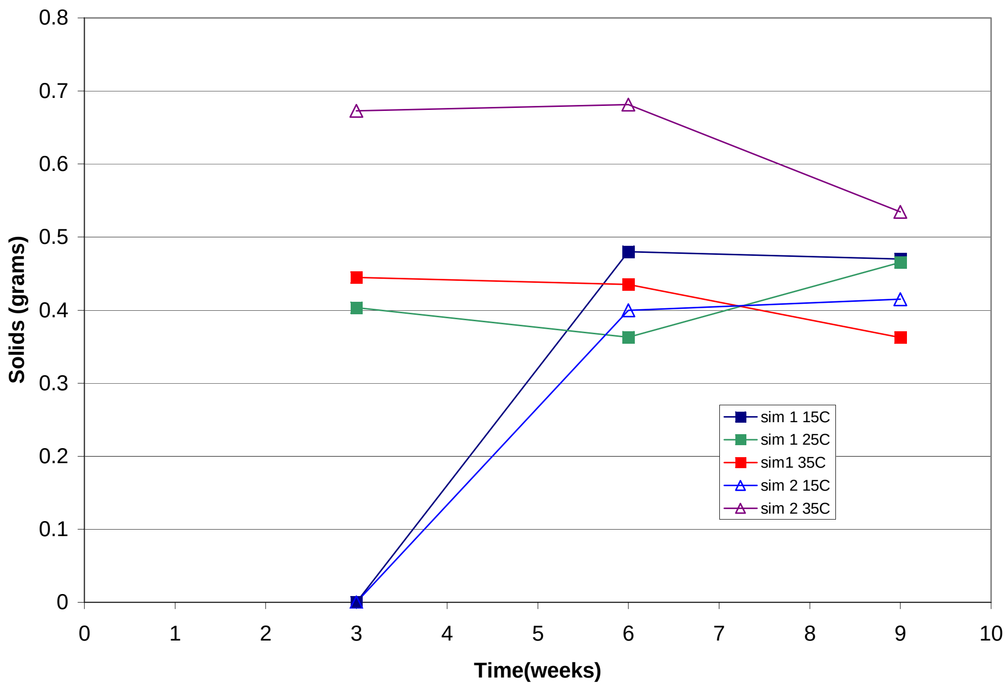

Figure 1. Solids formation in simulants one and two over time in weeks.

Task 1.2 The initial concept was to examine streams from the DWPF recycle, from caustic leaching of sludge batches destined for DWPF and from salt fraction arising from saltcake dissolution. Earlier experiments in these laboratories indicated that a simulant for the DWPF recycle stream could be used to dissolve saltcake [12]. Additional calculations have been performed on the recycle stream with saltcakes from SRS tanks 41H and 25F. Since it is desired to blend all of the streams prior to the SWPF, one main approach was to use the leachate from Batch 5 for blending with the dissolved salt fraction. This would allow for the disposition of all streams provided that significant solids would not form and corrosion control waste acceptance criteria could be maintained.

DWPF Batch 5 Leachate

Results of Environmental Simulation Program (ESP, OLI Systems Inc.) simulations of the initial DWPF Batch 5 sludge composition are given in Table-3. The base recipe for the HM sludge simulant was taken from Ketusky [6]. The ESP predictions are in good agreement with the results from SRS.

Table-3 Base composition of the Batch 5 sludge.

	SRS Data	ESP
Aqueous Phase		
Volume, gal	4.68E+05	4.71E+05
Sp G	1.03	1.04
Mass Aq, kg	1.83E+06	1.85E+06
Al, kg	1000	1029
pH		12.33
Ionic Strength		1.10
Solid Phase		
Volume, gal	2.07E+04	1.34E+04
Sp G	2.40	3669.95
Mass Insol solids, kg	1.88E+05	1.86E+05
wt% Al in solids	25.30	25.29
Al kg as elemental)	4.75E+04	4.70E+04
Other Components, kg	1.40E+05	1.39E+05
Total Tank		
Total Volume, gal	4.89E+05	4.84E+05
wt% insoluble solids	9.30	9.14
Total Mass, kg	2.02E+06	2.03E+06

Sludge leaching simulations were done with 50% NaOH at 50^{o}C as a function of added volume, Table-4. Of main interest are the pH, ionic strength, and aqueous phase densities. Important ion concentrations are plotted against the volume of caustic added in Figure-2. Aluminum increases and then eventually reaches a plateau around a value of 0.7M.

Table-4 Effect of caustic addition on the Batch 5 sludge.

50% NaOH added (kgal)	0, ESP	100	110	120	130	140	150

Aqueous Phase							
Mass (kg)	1.85E+06	2.49E+06	2.55E+06	2.62E+06	2.68E+06	2.74E+06	2.80E+06
Volume (gal.)	4.71E+05	5.70E+05	5.81E+05	5.92E+05	6.02E+05	6.12E+05	6.21E+05
Density (kg/L)	1.04	1.15	1.16	1.17	1.18	1.18	1.19
Al (kg)	1029	33760	37879	42134	46520	47994	47994
pH	12.33	13.87	13.93	13.98	14.03	14.09	14.14
Ionic Strength	1.10	4.57	4.86	5.15	5.43	5.70	5.96
Total Stream							
Mass (kg)	2.03E+06	2.60E+06	2.65E+06	2.71E+06	2.77E+06	2.82E+06	2.88E+06
Volume (gal.)	4.84E+05	5.77E+05	5.87E+05	5.97E+05	6.07E+05	6.17E+05	6.26E+05
wt% insoluble solids	9.14	4.34	3.90	3.47	3.04	2.86	2.79

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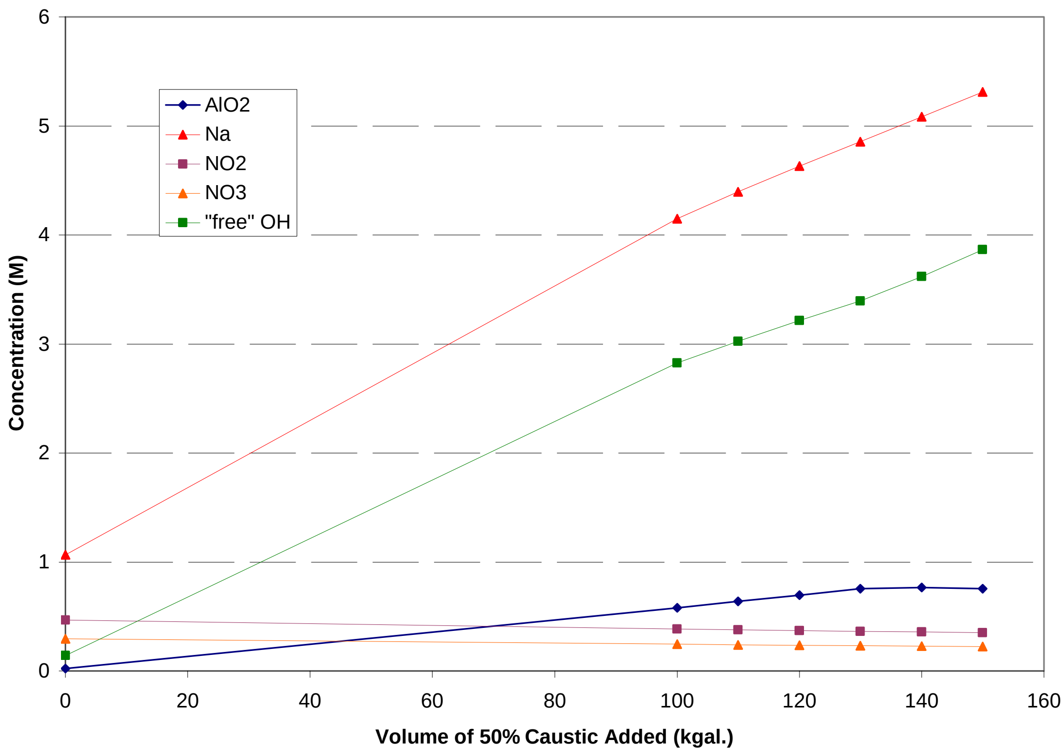

Figure-2 Ion concentrations resulting from addition of 50% NaOH to the Batch 5 sludge.

The actual leaching operation was carried out with 140 kgal added at a temperature slightly higher than 50°C. Figure-3 shows the effect of cooling the leached stream down. Initially Boehmite (AlOOH) is formed followed by Gibbsite ($Al(OH)_3$)

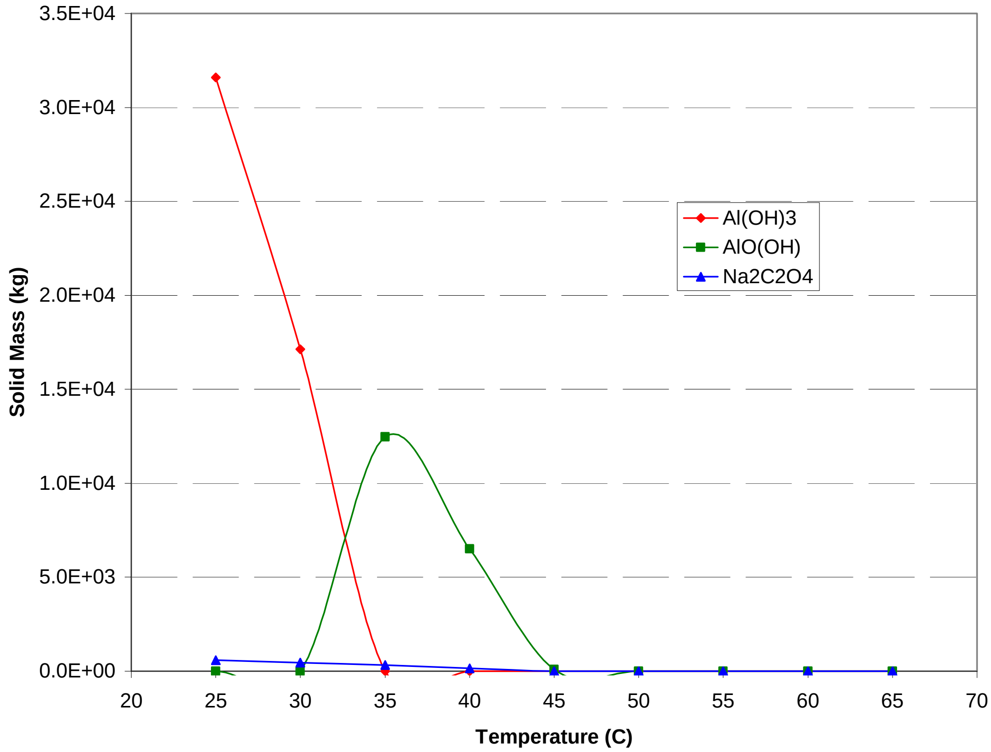

Figure-3 Effect of temperature on Batch 5 sludge with 140 kgal of 50% caustic added.

For the initial blending calculations, the leachate stream with 140 kgal of 50% caustic added was then cooled to 30°C and the aqueous phase was separated from the solids. This process corresponds to decanting the aluminum rich stream away from the sludge. The resulting supernatant had an aqueous phase density of 1.18 kg/L with a calculated pH of 14.7 and an ionic strength of 5.37. The percent water (by weight) was calculated to be 77.4. The high pH and associated hydroxide loading may be of use in maintaining aluminum from saltcake dissolution operations in the aqueous phase.

DWPF Recycle Stream

As opposed to relying upon a simulant used in studies previously it was decided to re-examine the composition of the actual stream that had been analyzed at SRNL [13]. Results from the simulation of the acid-side DWPF recycle stream and after caustic addition are given in Table-5.

Table-5 Principal aqueous phase parameters for the DWPF recycle stream.

Stream	acid stream	with NaOH addition
Aqueous		
Total g/hr	7.55E+05	8.36E+05
Volume, L/hr	7.56E+02	7.98E+02
Density, g/L	999.22	1047.46
pH	1.48	13.65
Ionic Strength	0.06	1.27

A small amount of solids was formed (0.2%) upon addition of the caustic. These were omitted from subsequent simulations using a separation block within ESP. The pH adjusted DWPF stream contained approximately $1.2x10^{-3}$ M Si.

The initial blending studies can consider the addition of the recycle stream to the leachate from Batch 5 or to aqueous fractions from salt cake dissolution. Waste compositions from a number of tanks including 41, 31, 37 and 38 (all H-farm tank) have been examined in these laboratories previously [9, 12].

WORK FORECAST

Seven samples from Parsons were received and will be analyzed for solids identification. A letter report will be released on the solids analysis this summer. Additional simulants are being prepared with varying amounts of the silicon component to identify conditions for prevention of aluminosilicate compounds formation.

Blending calculations will begin using a simulant from 41H and the DWPF recycle stream. Options for adding the Batch 5 leachate stream will then be considered. Assuming that the streams can be successfully mixed laboratory experiments will be necessary to confirm the thermodynamic predictions.

CONCLUSIONS

Studies with the CSSX simulant were started and preliminary results show delayed solids formation at 15°C when compared to ambient while at 35°C solids formed over twice as fast as ambient. Solids and solution analysis are underway. Several new simulants have been prepared varying the silicon component amount. Seven samples were received from Parsons full scale tests for solids identification.

Modeling of DWPF recycle, Tank 25F saltcake, and Batch 5 leachate streams for blending studies were investigated. Beginning studies used the DWPF stream as diluent for the 25F salt dissolution process. Early DDA streams demonstrated compliance for tank corrosion requirements but blending a portion of the high caustic, high aluminum leachate stream can bring later stage dilution streams into compliance.

REFERENCES

1. Dimenna, R.A.; Elder, H.H.; Foweler, J.R.; Fowler, R.C.; Gregory, M.V.; Hang, T.; Jacobs, R.A.; Paul, R.K.; Pike, J.A.; Rutland, P.L.; Smith, F.G.; Subosits, S.G.; Taylor, G.A.; Campbell, S.G.; Washburn, F.A. "Bases, Assumptions, and Results of the Flowsheet Calculations for the Decision Phase Salt Disposition Alternatives" WSRC-RP-99-00006, Rev. 3, Westinghouse Savannah River Company, Aiken, SC (2001).
2. Leonard, R.A.; Aase, S.B.; Arafat, H.; Conner, A.C.; Chamberlain, D.B.; Falkenberg, J.R.; Regalbutto, M.C.; Vandergrift, G.F. "Experimental Verification of Caustic-Side Solvent Extraction for Removal of Cesium from Tank Waste" *Sol. Extr. and Ion Exch*. **21(4)**, *2003*, 505.

3. Campbell, S.G.; Geeting, M.W.; Kennell, C.W.; Law, J.D.; Leonard, R.A.; Walker, D.D. "Demonstration of Caustic-Side Solvent Extraction with Savannah River Site High Level Waste" WSRC-TR-2001-00223, Rev.1, Westinghouse Savannah River Company, Aiken, SC (2001).
4. Weber, E.J. "Aluminum Hydroxide Dissolution in Synthetic Sludges" DP-1617, 1982.
5. Hay, M.S.; Pareizs, J.M.; Bannochie, C.J.; Stone, M.E.; Click, D.R.; McCabe, D.J. "Preliminary Data from the 3L Tank 51H Aluminum Dissolution Test" SRNL-CST-2007-00102, Savannah River National Lab, Aiken, SC (2007)
6. Ketusky, E., "High Level Waste System Impacts from Acid Dissolution of Sludge" CBU-PIT-2005-00260R1, Westinghouse Savannah River Company, Aiken, SC (2005).
7. Tank Farm Corrosion Program, WSRC-IM-2003-00010.
8. Waste Acceptance Criteria for Aqueous Waste sent to the Z-Area Saltstone Production Facility (U). X-SD-Z-00001, Rev. 2, 2004.
9. L. T. Smith, J. S. Lindner, V. Phillips, A. Antonyraj, and R. K. Toghiani, "Modeling and Experiments for the SRS Low-Curie Salt Process." Separation Science and Technology, 41(11), 2341-2360 (2006).
10. Smith, L. T., Toghiani, R. K., and Lindner, J. S., (2007), "Modeling and Experimental Support for High-Level SRS Salt Disposition Alternatives" in "Characterization and Cleanup of the Defense Nuclear Legacy," ICET Quarterly Technical Progress Report for the period October 1, - December 31, 2007, Report Number 070409R04 U. S. Department of Energy Agreement Number DE-FC01-06EW-07040, Mississippi State, MS.
11. Peterson, R.A., "Preparation of Simulated Waste Solutions for Solvent Extraction Testing" WSRC-RP-2000-00361, Rev.0, Westinghouse Savannah River Company, Aiken, SC (2000).
12. Lindner, J. S., Toghiani, R. K., Hill, P., Smith, L., and Antonyraj, A. (2002), "Modeling and Experimental Support for High-Level SRS Salt Disposition Alternatives" in "Characterization and Cleanup of the Defense Nuclear Legacy," ICET Quarterly Technical Progress Report for the period October 1, - December 31, 2002, Report Number 40395R18 U. S. Department of Energy Agreement Number DE-FC26-98FT-40395, Mississippi State, MS.
13. Stone, M. E. et al,, "DWPF Recycle Evaporator Simulant Tests," WSRC-TR-2005-00142, Rev. 0. Westinghouse Savannah River Company, Aiken, SC (2005).

Task 2

Process Improvements for the Defense Processing Facility (DWPF)

Jagdish P. Singh

INTRODUCTION

An on-line, real-time analysis of Defense Waste Processing Facility **(**DWPF) samples will significantly increase analytical throughput and will reduce waste generation in radiological analytical facilities. The goal of this Task is to develop system for rapid analysis of DWPF samples to accelerate waste processing using laser-induced breakdown spectroscopy (LIBS).

The first subtask of this project will provide a system for direct analysis of slurry in the DWPF's analytical shielded cells. The capability of direct analysis of slurry will significantly increase analytical throughput and will reduce waste generation in radiological analytical facilities, providing analyses suitable for waste acceptance and production records. The second subtask is to provide compositional data for plutonium residue feeds before being processed into glass.

LIBS uses a high pulse energy laser beams to produces a micro plasma to vaporize, dissociate, excite, or ionize species on material surfaces. The study of the atomic emission from the micro plasma provides information about the composition of the material. LIBS is a powerful analytical tool which is suitable for quick and on-line elemental analysis of any phase of material.[1-3] The laser light and emitted signal can be delivered via optical fiber so it is useful for hazardous situations. LIBS can provide an accuracy of 3-5% for elements with concentration >1% and an accuracy of 5-10% or better for minor elements in solid samples.

WORK PERFORMED

Work continue on improving the system performance of LIBS for slurry sample. To determine the detection system that can provide best LIBS analytical performance, we have evaluated two detection systems. Figure 1 shows a general schematic diagram of the experimental setup used for recording LIBS spectra of DWPF slurry. A frequency-doubled, Q-switched Nd:YAG laser was incorporated into the LIBS system as an excitation source. The 532-nm laser light is focused onto the sample surface using an ultraviolet grade quartz lens of 500 mm focal length. Atomic emission from the laser-induced plasma was collected by an optical fiber bundle using a UV-grade quartz lens. The two detection system used are a Czerny-Turner spectrometer fitted with a 1024-element intensified diode array detector and a Echelle spectrograph with 1024×1024 element intensified charge coupled device (see Table 1). A pulse generator is used to trigger and synchronize the detector with laser operation to provide the desired gate delay and width for detection. Although the Czerny-Turner detection system provide good sensitivity and fast data acquisition as compared to the Echelle detection system, Echelle detection system providing broadband with high resolution is more suitable for detecting the multiple elements. Figure 2 shows the LIBS spectra of DWPF slurry recorded by both detection systems. It is clear that the Czerny-Turner detection system is not sufficient to resolve the multiple spectral emission lines in the line-rich spectral region. The Echelle detection system gives the linear dispersion per pixel between the minimum of 5 pm/pixel at 200 nm to the maximum of 19 pm/pixel at 780 nm. Due to the capability of simultaneous detection between 200-800nm and better spectral resolution, we decide to continue the slurry with the Echelle detection system.

LIBS experiments of DWPF slurry were performed with different laser frequencies. We found that the laser frequency of 1Hz gives more stable LIBS signal and fewer splashes. However, the splash of the slurry is still a problem for maintaining clean optics for long term LIBS operation. Different experimental configurations to minimize this problem are being evaluated. To minimize the slurry sedimentation problem for long term operation, LIBS experiments of simulated DWPF slurry were performed with two methods. First, the slurry sample in a beaker was placed on a rotation stage to maintain constant rotation during LIBS experiment. Second, magnetic stirrer was placed inside the slurry container to stir the sample during the measurement. The measurement results show that the data with magnetic stirrer has better reproducibility for an over 30-minute test.

LIBS can provide real-time elemental analysis with almost all sample types. As compared to the solid analysis, it is a more challenge work for LIBS in liquid analysis. This is because in liquid analysis with either bulk or liquid surface, The laser induced shockwave caused splashing, surface ripples which results high signal variation from laser shot to shot. Also water can cause LIBS signal the extinction and a shorter plasma life time which results poorer limit of detection. Recently, the fundamental improvement of LIBS detection limit was obtained by means of the Double-Pulse (DP) technique are reported from both the experimental and theoretical point of view. To improve the analytical performance of our LIBS system, a laser system which can fire two laser pulses in an interval of few microsecond was ordered. In this work period, we have concentrated on testing the new dual pulsed laser system. Dual pulsed laser system was external trigger separately with a pulse generator to achieve the desired inter pulse delay between the two lasers. The optimum inter pulse delay between the two lasers need to be determined to achieve the best LIBS analytical performance. Preliminary test of the dual pulse LIBS experiment with this laser system was performed with aluminum sample and an enhancement of 2-5 times was observed as compared with single laser with the same total laser energy.

WORK FORECAST

Work will continue on improving the analytical performance of slurry measurement. More study on the effect of inter-pulse delay on double pulse LIBS signal will be conducted with pellet samples

CONCLUSION

Spectroscopic analysis using the Echelle detection system is more efficient for simultaneous multi-element detection as compared to the Czerny-Turner detection. We have evaluated the effect of laser frequency to slurry measurement and found 1Hz give more stable LIBS signal and fewer splashes. To minimize the slurry sedimentation problem for long term operation, we decide to stir the sample with magnetic stirrer during the measurement. We have setup and tested the new double pulse laser system in our laboratory. We will perform double LIBS experiments with solid sample to optimum the system. This system will later be used for slurry measurement.

REFERENCES

1. J. P. Singh and S. N. Thakur, Laser- Induced Breakdown Spectroscopy, Elesvier Science B. V., Amsterdam, The Netherlands, 2007.
2. A. Miziolek, V. Palleschi and I. Schechter, Laser- Induced Breakdown Spectroscopy (LIBS): Fundamentals and Applications, Cambridge University Press, 2006.
3. Fang-Yu Yueh, Jagdish P. Singh and Hansheng Zhang, "Laser-induced breakdown spectroscopy-elemental analysis", in *Encyclopedia of Analytical Chemistry,* R.A.Meyers, ed. (Wiley, New York, 2000).

Table 6. Instrument information for three different LIBS systems

Detection System	Czerny-Tuner	Echelle
Spectrometer Model	Spex 500M	ESA 3000 LLA
Spectral Coverage	0-750 nm	200-780nm
Simultaneous Spectral range	~20nm	~580nm
Grating	2400 lines/mm	
Pulse Generator	Princeton Inst. PG-10	Fast pulse generator (Model 3000 FP)
ICCD or IDPA	EG&E PARC Model 4456 IDAD	KAF-1000 Kodak ICCD

Data Acquisition Software	OMAVISION	ESAWIN

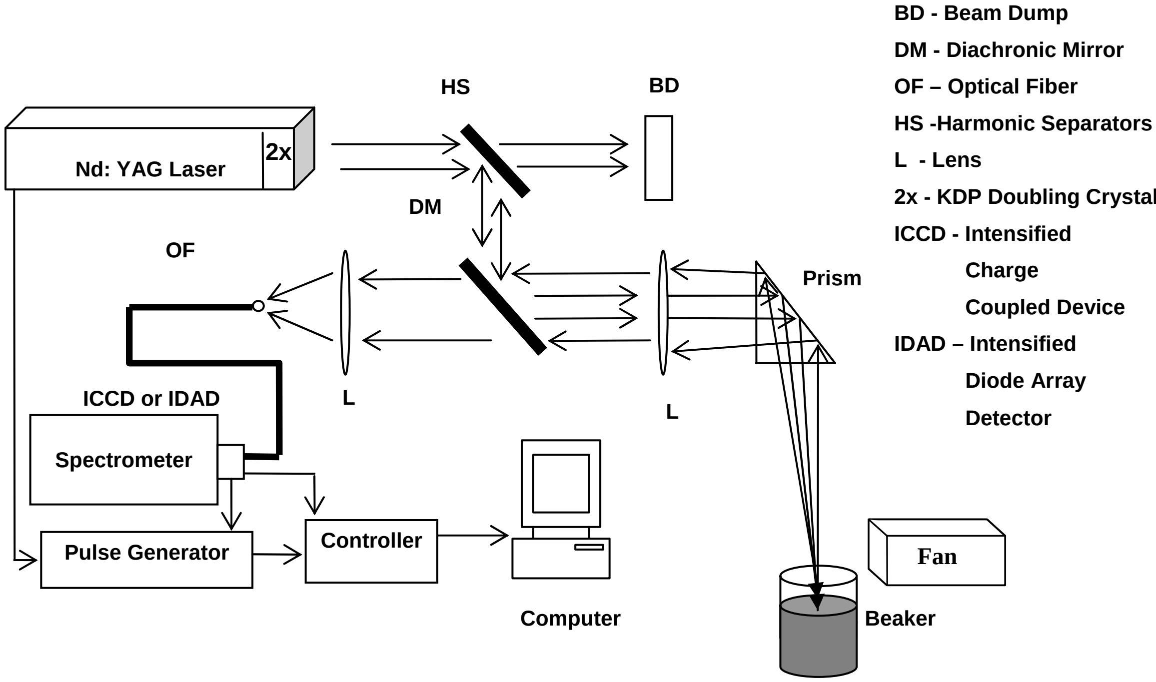

Figure 4 Schematic diagram of LIBS measurement apparatus.

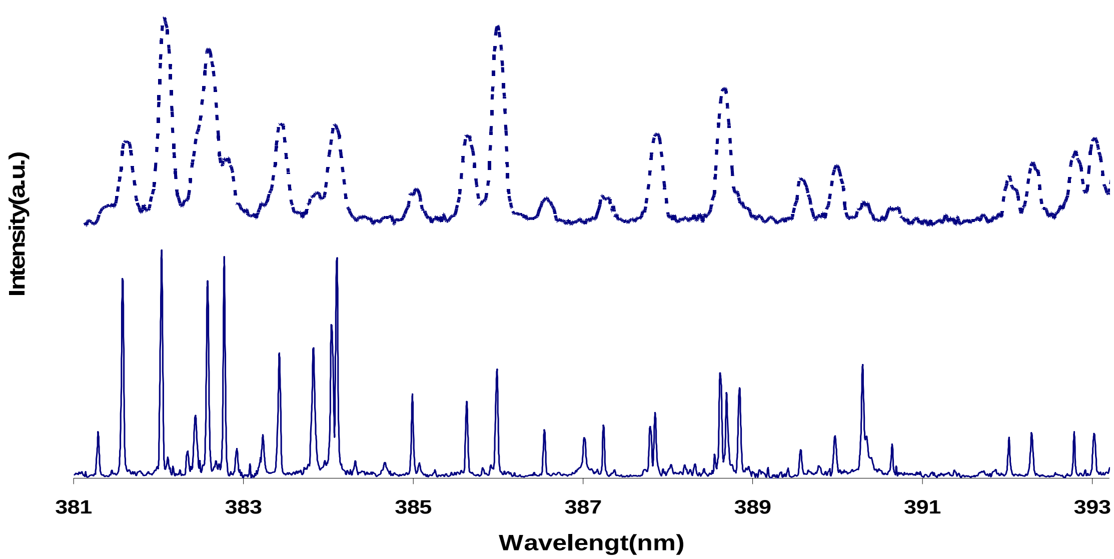

Figure 5 LIBS spectra of Sludge Receipt and Adjustment Tank slurry around 386 nm. The spectra of dashed line and solid line are recorded by Czerny-Tuner and Echelle spectrometers, respectively.

Task 3

High Efficiency Particulate Air (HEPA)

Rangaswami Arunkumar and Charles A. Waggoner

INTRODUCTION

Several activities and accomplishments are to be reported during the first quarter of 2008 for the HEPA Filter Task. ICET researchers completed media velocity testing of the Camfil Farr filters during this performance period. A series of 12x12x11.5 inch AG-1 HEPA filters were loaded from initial differential pressures to 6 inches of water column using a set of solid KCl aerosols at media velocities ranging from 4 to approximately 8 feet per minute. Test data were collected continuously as the filters were loaded and trends related to the effects of media velocity on filter efficiency and most penetrating particle size as a function of both particle size distribution and differential pressure as the filters load were observed. Figures 6-8 illustrate trends in initial filter efficiency, downstream particle count, and count media diameter, respectively, as a function of media velocity.

WORK ACCOMPLISHED DURING THIS QUARTER

ICET researchers worked with the metal media working group of the Committee on Nuclear Air and Gas Treatment (CONAGT) to resolve issues in Section FI of the AG-1 Standard. ICET researchers also collected various versions and comments on Section FI and compiled an updated version for review at an upcoming meeting of the CONAGT.

ICET researchers submitted a paper with respect to HEPA filter media velocity studies for publication to the Journal of Environmental and Occupational Hygiene (JOEH) in late 2007. ICET authors of this paper collected and responded to editorial comments on the manuscript during the 1st quarter of 2008.

WORK FORECAST

ICET will also serve as a session organizer for Waste Management ’09 (WM09) conference. This will include development of sessions, both presentation and poster in format, on gas and liquid filtration.

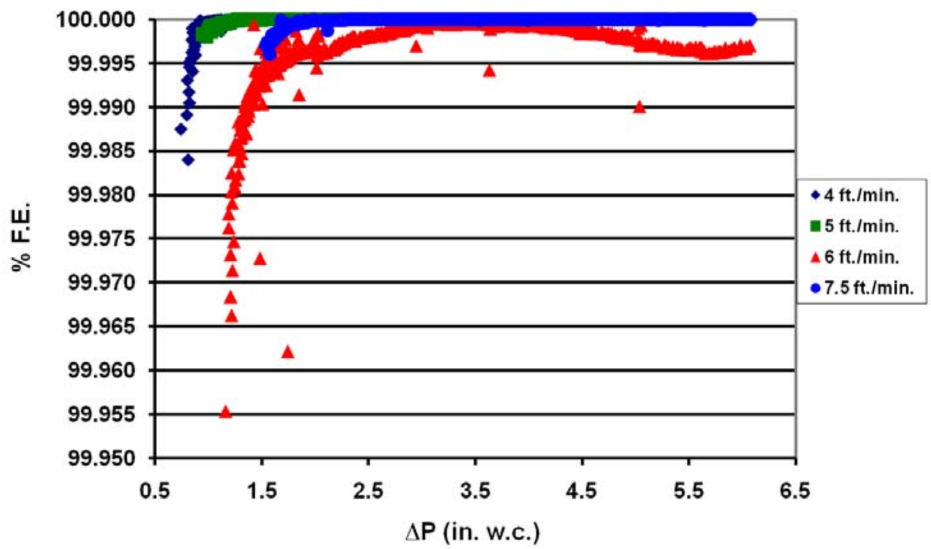

Figure 6. Trends in Initial Filter Efficiency as a Function of Media Velocity.

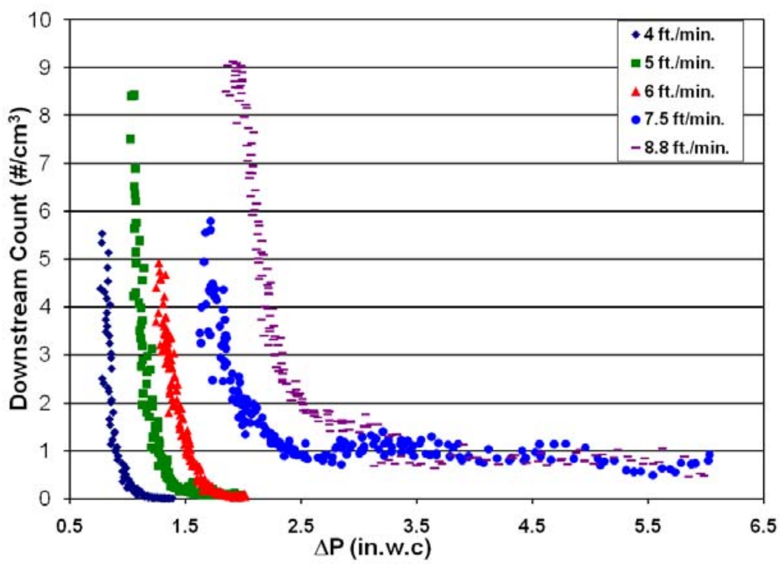

Figure 7. Trends in Downstream Particle Count as a Function of Media Velocity.

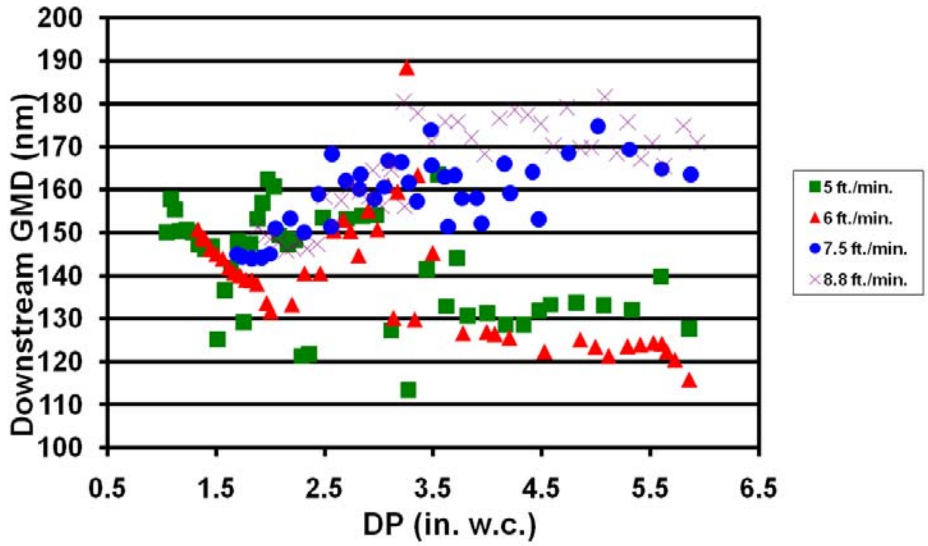

Figure 8. Trends in Downstream Count Median Diameter as a Function of Media Velocity.

Figure 6 demonstrates the rapid increase in filtering efficiency for filters, regardless of media velocity. Figure 7 demonstrates the downstream concentration of aerosol particles as a function of media velocity and filter loading. Finally, Figure 8 shows the effect of media velocity on the median particle size downstream of the filter as the filter loads. The increase range of these values is due to counting statistics for such a small number of particles.

Task 4

Support of Hanford Single Shell Tank Waste Disposition

Jeffrey Lindner, John Luthe, Larry Pearson, Laura Smith, Rebecca Toghiani

INTRODUCTION

Knowledge of the chemistry associated with the wastes contained in the Hanford tank farms has bearings on waste pretreatment, retrieval, vitrification, alternative processing, and tank closure operations. Much of the work conducted at ICET has focused on developing an understanding of the salt chemistry found in these tanks. A number of experiments have been performed and have led to the development of the V7DBLSLT thermodynamic database for use in the OLI Systems Inc. Environmental Simulation Program (ESP). This work consisted of extensive solubility measurements of specific sodium salt systems at the temperatures and pH values typical of the site waste [1,2]. Additional efforts were directed at aluminum chemistry and with development of a neural network model based on a framework of ESP simulations for use in conjunction with the Hanford H2 (overall campaign flowsheeting) simulator.

The Hanford Tank Waste Operations Simulator (HTWOS) is used for scheduling the entire retrieval campaign and includes model representations for vitrification and low activity waste processes. Chemistry representations used in the (HTWOS) rely on wash and leach factors as opposed to direct, solid-liquid equilibrium thermodynamic calculations. Site engineers have previously requested an evaluation of the feasibility of upgrading the chemistry representation to include ESP. Having a proper chemistry representation within HTWOS will reduce the uncertainties associated with wash and leach factors. Earlier work identified the use of a neural network as a preferred option due to the large number of calculations needed during a HTWOS campaign run. As an initial evaluation of this approach, site engineers requested the application of the process to the retrieval of C farm tanks.

The development of a neural network for use within the HTWOS model requires an extensive set of training data. To generate this data, ICET constructed an ESP program process model of the retrieval of C tank waste based on the procedures and constraints followed in the Modified Sluicing Method [3] of waste retrieval. With this ESP simulation framework, a neural network training set consisting of the input stream values and the ESP computation output can be built. Construction of the training set to cover the ranges of possible input streams requires an execution of the ESP program for each case. Since ESP is an interactive program, a batch mode processing routine is necessary to replace the ESP user interface. Perl [4], a freely available platform independent programming language was used to provide this batch mode processing. The retrieval of C-108 waste using flush liquid from AN-106 was simulated with the ESP program process model and Perl to provide the initial neural net training data. Simulations of each of the remaining C farm tanks, using this model, will provide the data necessary for the generation of an expanded neural network training set applicable across the entire range of C farm tank compositions. This expanded neural network will allow an evaluation of the retrieval schedule including different combinations of source and destination tanks. Since the neural network utilizes equilibrium chemistry as its basis, the potential result is a more accurate, as well as, timely method for Hanford campaign simulation.

WORK ACCOMPLISHED

The retrieval of waste from C-108, C-109, and C-110 using the Modified Sluicing Method [5]and flush liquid from AN-106 has been modeled using the OLI ESP equilibrium program. This is a continuation of the initial simulation involving the retrieval of C-108 into AN-106. The ESP simulations were performed sequentially in the order: C-108, C-109, C-110. This follows the current projected sequence of C farm waste retrievals and completes the planned retrievals which utilize AN-106. The ESP model simulations were performed using identical procedures and constraints as reported previously [3].

Figure 9 shows the amount of water and AN-106 flush liquid that are necessary to retrieve the C tank solids per stage. The simulations represented allow water addition only to meet the requirement that transfer streams not exceed a Na molarity of 5.0. AN-106 liquid is used to meet the remaining constraints: 1) a maximum solids concentration of 10.0 %(wt) for any transfer stream and 2) a maximum specific gravity of 1.3 for any transfer stream. Figure 1, therefore, should demonstrate the minimum amount of water required for the retrieval of C-108, C-109, and C-110 into AN-106.

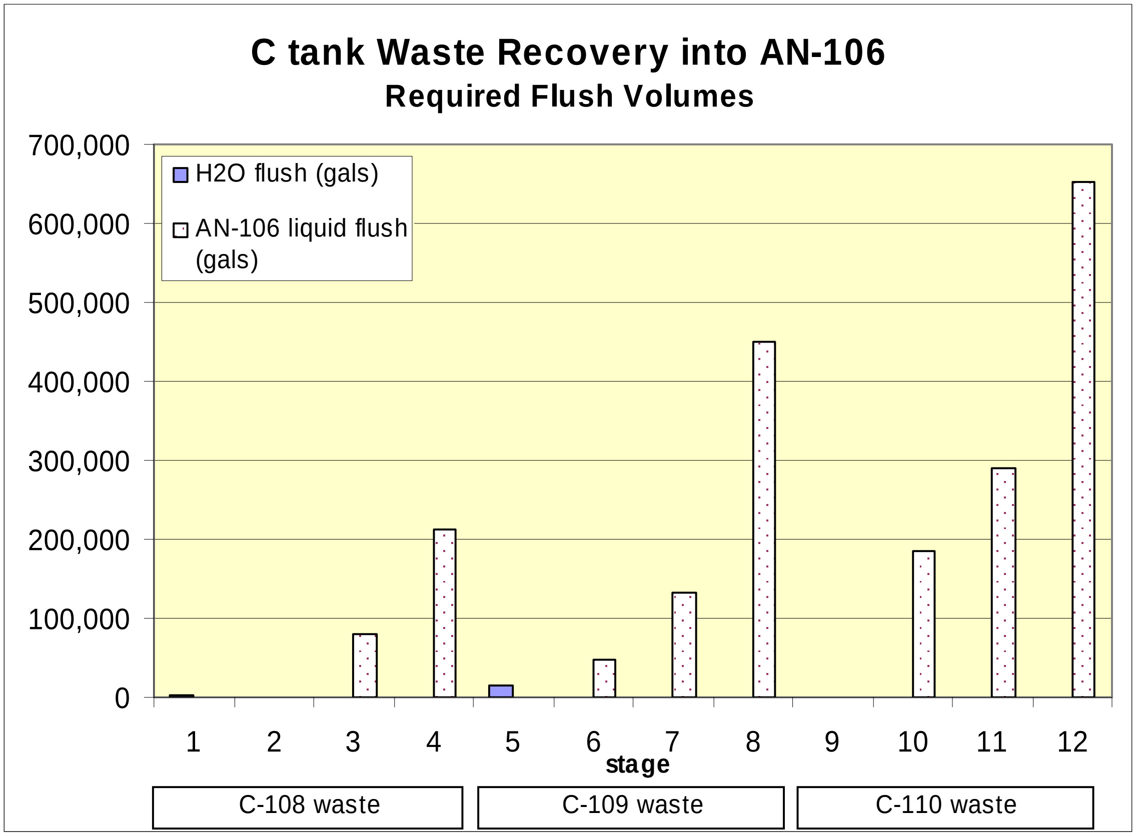

Figure 9 Flush Volumes for C tank Recovery into AN-106

Figure 10 displays several parameters of interest for the AN-106 tank. The data represents the initial conditions (stage 0) followed by the conditions present at the end of each stage of the waste transfer process. As each tank is processed sequentially, one can observe the accumulation of solids, as well as, the variation in parameters such as pH, etc… Figure 11 shows the amount of solids (gram moles) for selected compounds which are present in AN-106 as the C tanks are retrieved.

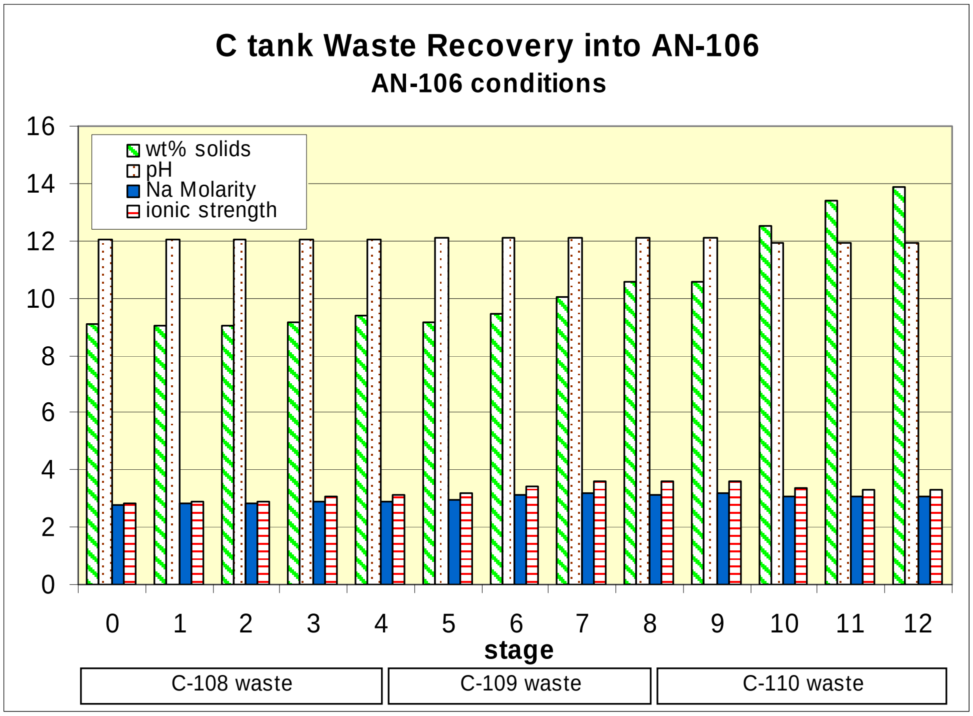

Figure 10 C-108 Waste Retrieval Summary

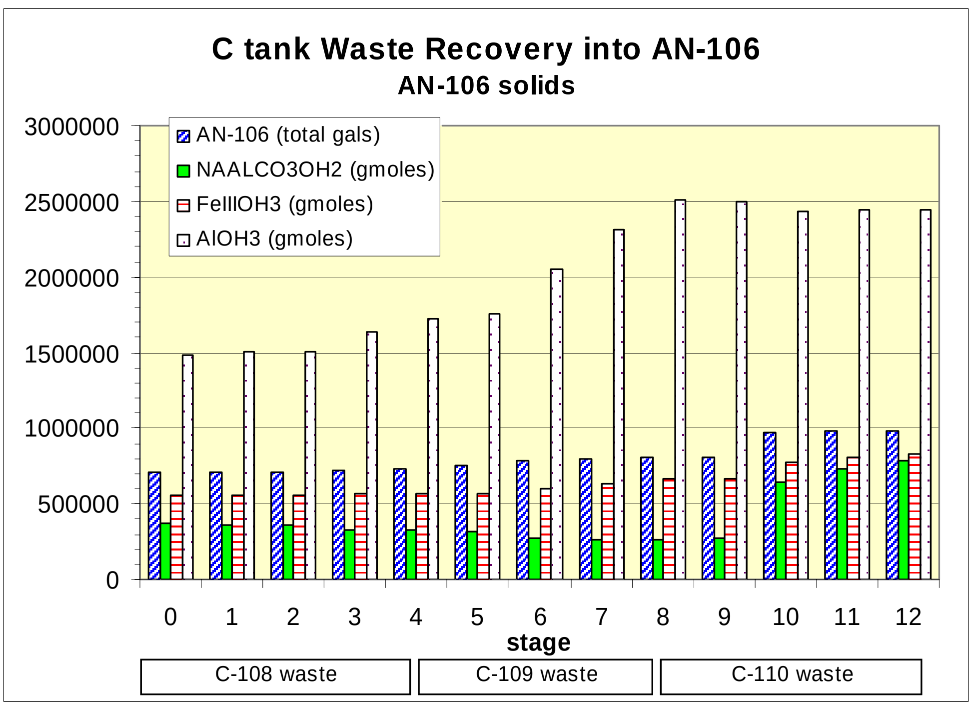

Figure 11 C-108 Waste Retrieval Summary – AN-106 Solids

The earlier single tank version of this ESP simulation framework, detailed in a previous report [3], was used to build a test neural network training set. The training set contained the stage input stream values for the C-108 retrieval into AN-106, with the corresponding ESP computation results. This was a test of the batch scripting of the ESP program. The resulting training set, while containing several thousand points, covered a very narrow region of the constituent compound range. The training set was built by varying the AN-106 flush and fresh water flush volumes. A more interesting and useful training set will be built from the multiple tank retrieval detailed above.

To build a training set that covers the ranges of possible input streams requires an execution of the ESP program for each case. The normal use of the ESP program is as an interactive program, however it is possible to write programs to replace the ESP user input program and execute the ESP computation program in a non-interactive batch mode. The first version of a batch mode processing program, written in Perl (a freely available, platform independent programming language) was used for the single tank retrieval simulation. The batch script looped over the range of AN-106 flush volume, up to 80,000 liters, and the water flush volume, up to 7500 liters, as input values to the ESP parameter input file for the ESP computation program. The routine then filed the ESP output for the neural network training set. Additional routines are being developed to combine all the generated ESP results into the input file format for NeurOn-Line Studio, the neural network development tool.

WORK FORECAST

Additional ESP process simulations will be developed for the other C tank retrievals. In particular, the ESP simulation model will be adapted to evaluate the mobile retrieval system (MRS) [5] which is projected for use with several of the C tank retrievals. Neural network training set data will be generated using the expanded ESP process simulations. Additional batch scripting modules for the ESP program will be developed for stages of the process simulations, as needed to build the neural network training sets.

CONCLUSIONS

An ESP process simulation model, which approximates the C tank farm Modified Sluicing Method, has been used to evaluate the sequential waste retrieval of C-108, C-109, and C-110 into AN-106. A test neural network training set was built based on a single tank, C-108, retrieval into AN-106. A Perl batch mode processing program was utilized to vary ESP input parameters over specified ranges. The construction of this test neural network served as a test of the batch scripting of the ESP program execution.

Task 5

Phytoremediation and Long-Term Monitoring of Heavy Metal Contaminants

Yi Su, Fengxiang Han, and David Monts

INTRODUCTION

Mercury, a potent neurotoxin, is released to the environment in significant amounts by both natural processes and anthropogenic activities. No natural hyperaccumulator plant has been reported for mercury phytoremediation. Few studies have been conducted on the physiological responses of Indian mustard, a higher biomass plant with faster growth rates, to mercury pollution as well as Hg uptake from ambient air.

WORK ACCOMPLISHED

Three studies with homemade chambers on mercury uptake by leaves of Chinese brake fern and Indian mustard have been conducted. Meanwhile, analysis of previous samples and data of mercury-induced oxidative stress show that mercury uptake induced a strong antioxidative response in the two cultivars of Indian mustard. Antioxidant enzymes are one of the most sensitive indexes for the adaptation and responses of Indian mustard plants to mercury stress. The two cultivars of Indian mustard showed an efficient metabolic defense and adaptation system to mercury-induced oxidative stress. Indian mustard effectively generated enzymatic antioxidant defense system to scavenge H_2O_2, resulting in lower H_2O_2 in shoots, especially for higher mercury concentrations. Majority of Hg was accumulated in the roots and low translocations of Hg from roots to shoots were found in two cultivars of Indian mustard.

CONCLUSIONS

Based on oxidative response of Indian mustard to Hg, Indian mustard might be a potential candidate plant for phytofiltration/phytostabilization of mercury contaminated waters.

WORK PLANNED FOR NEXT QUARTER

Continue the chamber studies and investigate the effects of Hg on structural and other physiological status changes of Indian mustard.

Task 6

SRS Saltstone Process Studies

Ronald Palmer, R. Arunkumar and Walter Okhuysen

INTRODUCTION

This project is comprised of two subtasks. The first consists of laboratory scale experiments designed to examine the thermal properties of new saltstone formulations. The second consists of Pilot Scale studies.

Laboratory Scale Experiments

Small batches prepared in the laboratory must be done prior to designing the pilot scale tests. Lab methods will be set up for measuring the heat of hydration for various saltstone formulations.

Mixers capable of providing batches from as small as several 10s of grams to more than one kilogram are available in the ICET laboratory. A standard protocol for making these small batches will be developed.

An adiabatic calorimeter will designed and built to measure the heat of hydration of the saltstone formulations. This device will provide basic thermal property measurements. These data are important contributions to new revisions of the Performance Assessment documentation.

Pilot Scale Studies

Small batches prepared in the laboratory can only provide preliminary information. A pilot-scale facility, capable of producing 55-gallon drum sized product, is available at the ICET laboratories. Drums can be appropriately instrumented to examine the heat generation of Saltstone formulations on an intermediate scale between the laboratory and actual Saltstone production facility.

Using these same waste simulant recipes, various formulations of saltstone will be produced at our pilot-scale facility. The laboratory scale work provides the basis for determining which formulations to study further. The results of this work will provide the confidence necessary for full scale production at the saltstone production facility.

WORK ACCOMPLISHED

Discussions were held with representatives of Savannah River regarding the scope of this project. Specific tasks and material formulations have yet to be finalized.

[Funding for this project is expected to be available later in this calendar year.]

WORK FORECAST

After funding approval is obtained, the details of the scope of work for this project will be worked out.

REFERENCES

1. Steimke, J. L. and M. D. Fowley, “Measurement of Thermal Properties of Saltstone,” WSRC TR-97-00357, Westinghouse Savannah River Company, Aiken, SC, 1997.
2. Harbour, J. R. et al., “Characterization of Slag, Fly Ash and Portland Cement for Saltstone,” WSRC-TR-2006-00067, Revision 0, Savannah River National Laboratory, Aiken, SC, 2006.
3. Harbour, J. R. et al., “Heat of Hydration of Saltstone Mixes – Measurement by Isothermal Calorimetry,” WSRC-STI-2007-00263, Revision 0, Savannah River National Laboratory, Aiken, SC, 2007.

Task 7

Bioavailability Studies of Mercury and other Heavy Metal Contaminants in Ecosystems of Selected DOE Sights

Fengxiang X. Han, Yi Su, David L. Monts, and Charles A. Waggoner

INTRODUCTION

The majority of Hg in the floodplain soils of East Fork Poplar Creek, TN has been reported to be in the form of HgS. Most recently the Hg levels in both water and fish were found to have increased. The effects of Fe/Mn minerals on bioavailability and stability of HgS is important to better understand the mechanisms and reasons for the increase.

WORK ACCOMPLISHED

The previous studies on oxidation kinetics of both pure HgS and Oak Ridge contaminated soils with Fe_2O_3 and Fe_3O_4 were analyzed. Sulfate quantity produced by the reactions was used to represent the oxidation rate. Different S species in the reaction system was also identified (SO_4 and other intermediate S species).

CONCLUSIONS

Further studies are needed to draw conclusion.

WORK PLANNED FOR NEXT QUARTER

Due to the ICET funding cuts, this project was temporarily suspended.

IN-TANK CHARACTERIZATION FOR CLOSURE OF HANFORD WASTE TANKS

David L. Monts

EXECUTIVE SUMMARY:

Based upon Hanford's interest in utilizing higher-resolution cameras for future tank deployments, ICET performed preliminary experiments to compare the FTP performance of a digital camera and the current analog camera. The ICET FTP group made substantial progress in its efforts to address questions relating to how FTP handles curved (non-perpendicular) background surfaces (such as a curved waste tank bottom). Since regions of bare tank bottom ("zero height") may be separated by distances greater than a single image, ICET continued its investigation of procedures for how to best propagate height across stitched image boundaries so as to minimize measurement uncertainty.

During this reporting period, the ICET Stereovision effort completed a literature review of recent advances in stereovision, including color stereovision. The use of color in stereovision may reduce errors in disparity matching, a critical step in analysis of stereovision images. The feasibility of utilizing color stereovision for waste tank characterization is being evaluated.

At end of this quarter, ICET was informed that because of the downward revision of the ICET Cooperative Agreement CA08 budget, that there are no funds to support the Hanford in-tank characterization effort for the current Cooperative Agreement year. ICET administrators subsequently issued a stop-work order. The bi-weekly conference calls with our Hanford collaborators were suspended. At this time, no further efforts are planned until funding becomes available.

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 the Savannah River Site.

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 and also in DOE-EM Engineering & Technology Roadmap, Improve Residual Waste Tank Characterization and Stabilization.

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 CA07, ICET's efforts for this task are to include:

- During CA06, the Fourier transform profilometry (FTP) probe effort initiated a series of FTP performance evaluation tests under simulated Hanford waste tank conditions. The purpose of these tests is to test and document the accuracy, precision, and operational performance using blind testing techniques. Nondescript targets have been created and their volumes determined by traditional methods, but the values of the volumes were not known to those ICET personnel who used FTP to quantitatively determine their volumes. The first stage of this testing involved simulating objects on the bottom of a flat C200-series Hanford waste tank and analyzing the volume of individual objects from single FTP images. The second stage involves using new non-descript targets and determining the total volume present by "stitching" the results of individual images together. These tests will demonstrate the performance of the FTP system prior to demonstration in Hanford's Cold Test Facility (CTF). In order to test the durability and reliability of components comprising the FTP system, a series of tests have begun subjecting selected components to gamma-ray radiation. All FTP tests are being conducted with frequent consultation with our Hanford collaborators.

- The Stereovision effort has developed and improved the ICET Stereovision system with better cameras, and has also evaluated a variety of algorithms for stereomatching. Our results show that performance (accuracy and computer analysis time) of a stereomatching algorithm often varied with specific test images. The stereovision system and algorithms have been tested with images of selected targets at different working distances. For

Hanford tank inspection, parallel implementation of stereomatching algorithms is necessary because large image size and disparity search range are inevitable.

WORK ACCOMPLISHED:

STEREOVISION

The literature review of recent advances in stereovision, including color stereovision was completed. The use of color in stereovision may reduce errors in disparity matching, a critical step in analysis of stereovision images. The feasibility of utilizing color stereovision for waste tank characterization is being evaluated.

FOURIER TRANSFORM PROFILOMETRY

The ICET Fourier Transform Profilometry (FTP) effort collected preliminary data to compare FTP volume determinations using the current analog camera and a compact digital camera. This effort is in response to Hanford's interest in converting its tank inspection efforts from analog to digital cameras. The cameras used for this comparison are the analog Sony 78B (640 x 480 resolution, 0.3 Megapixels, x25 optical zoom) and the digital Cannon PowerShot G9 (12 Megapixels, x6 optical zoom). The Cannon G9 digital camera was chosen because it can fit through a 4" ID riser. When a comparison is made using similar fields-of-view for both cameras, the volume measurement errors were comparable for the two cameras and for different resolutions, as shown in Table 1 below. However when using the maximum field-of-views for the two cameras (Table 2), the results from the analog camera are better than those of the digital camera because the analog camera images are of higher quality (higher contrast) than those of the digital camera. On the other hand since the digital camera has a larger field-of-view, its use would reduce the number of images required to be recorded and analyzed for tank characterization. Because the analog camera has a higher optical zoom (x25) than the digital camera (x6), this analog camera is capable of recording images that show more detail than this digital camera. Another difference between these analog and digital cameras is that the digital camera is controlled by manufacturer-provided software that is not as useful and flexible as the control software developed by ICET for the analog camera; currently, the software development kit (SDK) for developing similar control software is not available from the digital camera's manufacturer. A more extensive comparison should be made using pattern-generating filters (Ronchi filters) with higher frequencies and at larger target distances (such as 50-60 ft). The higher resolution digital camera is expected to be able to resolve fringe patterns that the analog camera is not able

Table 7. Comparison of FTP analysis of images acquired from analog and digital cameras using similar fields-of-view. The target is nondescript target # 6 (true volume 647 cm^3) from the Stage 1 FTP Performance Evaluation study.

Camera	**Analog**	**Digital**	**Digital**	**Digital**

Pixel Resolution	640 x 480	640 x 480	1600 x 1200	2592 x 1944
FOV Width (cm)	85.9	83.4	83.4	83.4
Measured Volume (cm^3)	692	678	685	689
Error (%)	+7.0	+4.8	+5.9	+6.5

Table 8. Comparison of FTP analysis of images acquired from analog and digital cameras using their maximum field-of-views. The targets are nondescript target # 3 (true volume 1954 cm^3) and nondescript target # 6 (true volume 647 cm^3) from the Stage 1 FTP Performance Evaluation study.

Camera	Analog	Digital	Digital
Resolution	640 x 480	1600 x 1200	2592 x 1944
FOV Width (cm)	58.6	83.7	83.7
S3 Measured Volume (cm^3)	1997	2223	2146
S3 Error (%)	+2.2	+13.8	+9.8
S6 Measured Volume (cm^3)	653	646	714
S6 Error (%)	+0.9	-0.2	+10.4

to resolve. Since FTP height resolution is inversely related to the fringe pattern frequency, the digital camera is expected to provide superior performance under these conditions.

We made substantial progress in our efforts to reduce errors associated with newly adopted corrections that address how FTP handles curved (non-perpendicular) background surfaces (such as a curved waste tank bottom). Curved tank bottom will not be encountered in the multi-stage performance evaluation until Stage 3, but in an effort to address all unresolved questions and to incorporate increased capabilities/improvements as soon as possible so that there is greater consistency in the FTP system utilized in the different Performance Evaluation Stages, this technical issue is being addressed now.-An error in the software code was found and corrected, reducing errors from 30% to less than 1%. Efforts on procedures for how to best propagate height across stitched image boundaries are continuing.

A conference paper on FTP evaluator dependence and preliminary radiation testing results for FTP cameras and optics was presented at the 2008 Waste Management Symposium.[1]

WORK PLANNED

At the end of March, ICET was informed that because of the downward revision of the ICET Cooperative Agreement CA08 budget, that there are no funds to support the Hanford in-tank characterization effort for the current Cooperative Agreement year. ICET administrators subsequently issued a stop-work order. The bi-weekly conference calls with our Hanford collaborators were suspended. At this time, no further efforts are planned until funding becomes available. Efforts have begun to seek funding for the FTP technical feasibility report requested by our Hanford collaborators.

REFERENCES

1. John A. Etheridge, Ping-Rey Jang, Teresa Leone, Zhiling Long, O. Perry Norton, Walter P. Okhuysen, David L. Monts, and Terry L. Coggins, "Evaluation of Fourier Transform Profilometry for Quantitative Waste Volume Determination under Simulated Hanford Waste Tank Conditions," *Proceedings of 34th Waste Management Symposium (WM08)*, Phoenix, AZ, February 24-28, 2008, Paper No. 8106.

ACRONYMNS

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

[1] Toghiani, R. K., Phillips, V. A., and Lindner, J. S., "Solubility of Na-F-SO_4 in Water and in Sodium Hydroxide Solutions," Journal of Chemical and Engineering Data 50(5), 1615, (2005).

[2] Selvaraj, D. K., (2003), Solubility Studies in the Na-F-PO_4 System in Sodium Nitrate and in Sodium Hydroxide Solutions, MS Thesis, Chemical Engineering, Mississippi State University, Mississippi State, MS.

[3] Lindner, J.S., Luthe, J.C., Pearson, L.E., Smith, L.T., Toghiani, R.K., (2007), "Process Chemistry and Operations Planning for Hanford Waste Alternatives" in "Accelerating Cleanup of the Defense Nuclear Legacy," ICET Quarterly Technical Progress Report for the period July 1, - September 31, 2007, Report Number 07040R03 U. S. Department of Energy Agreement Number DE-FC01-06EW-07040, Mississippi State, MS.

[4] Larry Wall, Tom Christiansen, Jon Orwant, "Programming Perl," Third Edition, O'Reilly, Sebastopol, CA 2000.

[5] R.A. Dodd, J.W. Cammann, "Progress in Retrieval and Closure of First High-Level Waste Tank at Hanford: Single-Shell Tank C-106," WM'05 Conference, February, 2005, Tucson AZ.