
Characterization and Cleanup of the Defense Nuclear Legacy

**Quarterly Technical Progress Report
for the period
July 1, 2004 - September 30, 2004**

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Table of Contents

	Executive Summary	1
	Task 1. Support of Closure Sites	2
	Task 2. Support of Hanford Single Shell Tank Waste Disposition	2
	Task 3. Disposition of Idaho HLW Calcine	6
	Task 4. Support of SRS Salt Disposition and Other SRS Alternatives	6
	Task 5. HEPA Filter Performance Assurance.	6
Task 1	Support of Closure Sites	7
	Fernald Silos Project Monitoring and Control Integration.	7
	Accelerating Phytoremediation by Monitoring Plant Status	13
Task 2	Support of Hanford Single Shell Tank Waste Disposition	15
	In-tank/At-tank Characterization for Closure of Hanford Tanks	15
	Diffuse Reflectance Spectroscopy, Laser- induced Fluorescence Imaging, Spectral Imaging and Stereovision.	19
	Information Sifting	19
	Fiber Optic Sensors	20
	Fourier Transform Profilometry	20
	Microwave-induced Plasma-ringdown Spectroscopy	22

Table of Contents

	Process Chemistry and Operations Planning for Hanford Waste Alternatives	27
	Flexible Scintillating Optical Fiber Sensor for Determination of Liquid Level.	44
	Tank Leak Detection and Monitoring System	46
Task 3	Disposition of Idaho HLW Calcine.	47
	Support for the INEEL Calcine Disposition Project	47
Task 4	Support of SRS Salt Disposition and Other SRS Alternatives	50
	Support of SRS Salt Disposition and Other SRS Alternatives	50
	On-line Analysis for the Defense Waste Processing Facility.	56
Task 5	HEPA Filter Performance Assurance	61
	Regenerable HEPA Filter Performance Testing	61

List of Figures

Figure 1	Paper cone target and reconstructed 1D profile of cone peak	22
Figure 2	2D and 3D profiles of cone reconstructed from FTP data	22
Figure 3	Apparent aluminum concentrations measured as a function of time	32
Figure 4	Apparent aluminum concentrations measured as a function of time for a higher initial aluminate loading series	33
Figure 5	Pretreatment alternatives system concept – fractional crystallization	35
Figure 6	Solids predicted to form from processing the “late” salt feed.	38
Figure 7	Spectral line shape of Li 610	57
Figure 8	Calibration curve for Li/Fe in glass sample	58

List of Tables

Table 1	Results of FTP measurements under simulated conditions	21
Table 2	Minimum acceptable requirements and desired targets for pretreatment process	36
Table 3	Projected feed compositions for the dissolved salt streams	37
Table 4	ESP model results for the porosity (aqueous phase entrainment) studies for evaporative processing and solid liquid separation of the “late” dissolved salt stream	39
Table 5	Parameters for the projected streams from evaporation of the “early” feed to low activity and high activity remediation processes.	41
Table 6	The reproducibility of glass measurement at different lens-to-sample distances.	58
Table 7	Comparison of the accuracy and precision of LIBS measurement of pellet and glass samples.	59

Executive Summary

The DOE/Office of Environmental Management's technology development and deployment investments are focused on high payoff site closure and remediation problems. The investments are either directed toward accelerating closure or examining high-risk alternatives with the potential to provide step changes in either costs or schedule.

DIAL's Cooperative Agreement has been aligned with those twin foci. This agreement consists of eleven projects, grouped into five tasks. The first task is specifically focused on closure issues. The other four are focused on looking at alternatives that provide step improvements in either costs or schedule, or both.

Each of the projects has been developed through direct contacts with DOE site personnel. DIAL is working with the DOE sites to maximize the relevance of each of the projects, and to ensure that each project will meet the site's identified needs.

The Cooperative Agreement has three major objectives:

Task 1. Support of Closure Sites

- to provide “decision-quality” data so that site personnel have the best possible information available to make technical decisions relating to either closure or acceleration;
- to facilitate beneficial interactions between technology developer, users, and stakeholders (particularly regulators); and
- to provide rapid response to emerging needs at DOE sites.

Task 1. Support of Closure Sites**Fernald Silos Project Monitoring and Control Integration**

Progress on this task is summarized in the Task 1 chapter.

Accelerating Phytoremediation by Monitoring Plant Status

Progress on this task is summarized in the Task 1 chapter.

Task 2. Support of Hanford Single Shell Tank Waste Disposition**In-tank/At-tank Characterization for Closure of Hanford Tanks**

DIAL researchers participated in a conference call with Hanford on September 2 in order to report our progress to date and discuss our future efforts. As a result of this exchange, Hanford has provided DIAL with information about the Hanford waste tanks that will help us in preparing our systems for deployment at Hanford.

During this reporting period, the stereovision effort has been investigating the effect on stereovision performance of different parameters, such as distance between the cameras, working distance between cameras and objects of interest, window size for disparity map computation, etc. We also investigated the possibility of utilizing Pulnix cameras rather than Sony block cameras.

The laser-induced fluorescence–spectral imaging effort has received and tested the repaired charge-coupled device (CCD) camera detector from the manufacturer. We have set-up the equipment to collect laser-induced fluorescence spectra of selected simple uranium and thorium compounds and have begun optimization of the apparatus using surrogate samples.

During this quarter, the information sifting effort completed implementation of all the design features of the spectral identification tool. The spectral identification software was successfully installed on a Windows-based computer in order to be evaluated by users other than the software developer. The results of this evaluation will be used to improve the utilization of the software by non-experts and will allow us to determine how best to integrate the use of this software with the diffuse reflectance spectroscopy systems.

The fiber optic sensor effort's work during this reporting period was divided to two parts. First, sol-gel materials doped with ZnS have been prepared by adding ZnCl_2 and Na_2S solution to a TMOS sol solution. The silica materials obtained have been examined using the fluorescence technique. Second, a literature research has been conducted in order to establish techniques to synthesis metal sulfide quantum dots and incorporate the quantum dot material into a transparent polymer in order to produce an alpha particle sensor.

Design and fabrication of the two plates required to center the Fourier transform profilometry (FTP) probe have been completed. A prototype of the FTP probe cable management system for electrical

cables has been constructed. Design details for keying of the telescoping sections of the FTP probe have been completed. A 3-ft prototype telescoping FTP probe was fabricated and assembled utilizing the WVNS' FTP-instrument elbow and an existing support tower. Movie files were recorded to show the current status of work and illustrate the probe's computer-controlled movements. Work continued on development of the probe control system and the probe support tower. Using our current FTP probe one-meter elbow optical setup, FTP measurements were obtained at simulated target distances of 15 ft, 21 ft, and 27 ft. Further simulation measurements/analyses are underway.

The plasma source used for atomization has a large bearing on the sensitivity and performance of a plasma-cavity ringdown spectroscopy (PCRDS) system. During this quarter, several different configurations of the new tube-shape plasma sources have been incorporated into the PCRDS system for testing. PCRDS measurements of mercury under atmospheric conditions were performed for the first time. The results show that different plasma torch configurations yield different detection sensitivities for mercury. With the same laser beam path length in the plasma, the detection sensitivity of mercury obtained with the tube-shape microwave-induced plasma (MIP) torch is approximately three orders of magnitude better (lower) than the one obtained with the candle-shape MIP torch. Abundant experimental data has been processed. A manuscript is being prepared for submission to a peer-reviewed journal.

Process Chemistry and Operations Planning for Hanford Waste Alternatives

Results are presented on the equilibration of aluminum – phosphate solutions. These experiments are being performed to provide additional data on aluminum solubility that is not currently available in the literature. The data is needed to provide a better description of the Hanford waste chemistry using the ESP model. Equilibration

times approaching and exceeding five months have been observed. The approach of the aluminum ion concentration to a constant value is represented by a decay curve. The solutions are currently being analyzed and following that the results will be used to develop an aluminum chemistry database.

Additional calculations on the fractional crystallization process are presented. Model simulations were performed on two dissolved salt solutions, one from an early portion of the retrieval and therefore containing some interstitial liquor with cesium and nitrite and the second for a late portion of a retrieval containing smaller quantities of cesium and nitrite. The simulations were conducted at typical evaporator operating conditions and indicated that fractional crystallization can be used to selectively precipitate sodium sulfate and carbonate solids. Calculations were performed as a function of entrained mother liquor in the recrystallized solids and indicated that activity separations will be possible assuming that the effective liquid entrainment is less than 45%. The ability to control the formation of the sodium sulfate carbonate double salt also has bearing on waste fractions that will be routed to the waste treatment plant. Simulation results indicated that sulfate concentrations in the streams routed to the WTP were acceptable for producing glass. The calculations indicate that recycling through the evaporator provides the best means for controlling the pretreatment process.

Flexible Scintillating Optical Fiber Sensor for Determination of Liquid Level

Progress on this task will be reported at a later date.

Tank Leak Detection and Monitoring System

Progress on this task will be reported at a later date.

Task 3. Disposition of Idaho HLW Calcine

Support of the INEEL Calcine Disposition Project

Progress on this task is summarized in the Task 3 chapter.

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

Support for SRS Salt Disposition Alternatives

Progress on this task will be reported at a later date.

On-line Analysis for the Defense Waste Processing Facility

Progress on this task is summarized in the Task 4 chapter.

Support of Production of High Waste Loading Glasses in the DWPF

Progress on this task is summarized in the Task 4 chapter.

Task 5. HEPA Filter Performance Assurance

Regenerable HEPA Filter Performance Testing

Progress on this task is summarized in the Task 5 chapter.

**Fernald Silos Project Monitoring and Control
Integration**

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INTRODUCTION

The Silos 1 and 2 material, known as K-65, will be removed from the silos, transferred to and temporarily stored at the Transfer Tank Area (TTA) prior to final treatment. The K-65 will be retrieved from the TTA tanks as thin slurry and dewatered to increase the waste loading of the treated material. The solids content of the slurry from the TTA is unknown but is expected to be variable and in the range of 5 to 30-weight percent. Fifteen-weight percent is currently being used in the design basis. The 15-weight percent slurry is expected to be dewatered using a clarifier, wherein the solids concentration will be increased to approximately 40-weight percent. The de-watered K-65

will then be mixed with stabilization chemicals to form a solid that meets the waste acceptance criteria of the disposal facility and the requirements imposed by the Department of Transportation. A general stabilization formulation was developed at the University of Cincinnati (UC) to treat Fernald Silos K-65 waste to meet TCLP, disposal and transportation requirements. The UC team demonstrated that this formulation will meet all the requirements by subjecting treated K-65 samples to TCLP and a series of tests designed to simulate the transportation conditions including thermal cycling and vibration tests. Most of these verification tests were, however, performed on samples that were cured for five days. The selection of this curing time was based on a process baseline that assumed a five-day holding period between waste mixing and shipping the containerized treated waste. This baseline has changed, and if possible, waste will be shipped between 24 and 48 hours after mixing. If a formulation cannot be developed that meets the 24 set time criteria, then the minimum grout set time must be determined.

The primary waste acceptance criterion established by the Nevada Test Site (NTS) is that the treated material must contain no free water. However, stakeholders, including the Ohio EPA, have requested that the final grout formulations meet TCLP requirements. Therefore, the final grout formulas must contain between 8% and 12% cement by weight. Grout formulations with cement concentrations in this range have been demonstrated by UC to pass the TCLP. The UC testing also demonstrated that grout formulations with a minimum total solids concentration of 65% by weight contained no bleed water after a five-day set time.

In addition to the disposal requirements, operational requirements must also be met. The freshly mixed grout will be discharged from the mixer into a disposal container and it must fill the entire container unaided by vibration or other mechanical leveling techniques. Therefore, the grout must be free flowing and self-leveling. Also, any additives must be in liquid form or must be readily converted to a liquid

form. Addition of dry additives would require that they be pre-blended with the cement or fly ash. The facility does not have a mechanism to introduce additional dry treatment agents. Pre-blending the cement or fly ash with chemical additives should therefore be considered if all other options have been exhausted.

The present studies are an extension of previous work and will focus on reducing the time required for the grout mix to set and characterizing the rheologic properties of the mix as a function of percent solids and different chemical additives. The services of MSU-DIAL will be used to define the parameters and practical conditions that the K-65 stabilization formulation must satisfy in order to enable shipping the containerized treated waste 24 to 48 hours after mixing without risk of water separation.

In addition to formulation testing, the Fernald Closure Project has requested that MSU-DIAL perform testing to determine the amount of radium and lead that will leach from K-65 during the slurry transfer operations. The Fernald wastewater treatment plant has a limit on the levels of dissolved radium and lead that can be processed. A Wastewater Equilibration Study (WES) has been designed to mimic the slurry transfer operation of the full-scale facility. The WES will determine the levels of radium and lead that leach out of the Silos material. Water from the WES samples will be decanted and treated to identify the best means of precipitating radium and lead from the wastewater.

WORK ACCOMPLISHED

Waste Stabilization Formulation Development

The formulation testing continued. Some baseline formulations were developed using cement, fly ash, slag and Advacast. However, the Fernald Closure Project process group indicated that a supplier of blended cement and slag could not be found in the greater Cincinnati

area. The consequence is that only two dry stabilization agents can be used in the grout formulations, given that there are only two dry storage silos available in the processing facility. Therefore, only cement and fly ash are to be used for the grout formulation development work.

During August, the primary goal of the grout testing was to develop baseline formulations and determine the operating envelope for various waste loading and total solids content values. Following the baseline development testing, grout formulations were prepared that will be employed in the event that a given grout mixture is too stiff for handling and transfer operations. These grout formulas use Advacast 500, a super plasticizing agent. Testing with Advacast has demonstrated that its use is sensitive to the total water content of the grout mixture. Addition of too much Advacast 500 results in the formation of free water on the treated material.

During September, the primary goal of the grout testing was to develop formulations using a super plasticizing agent on formulas that proved to be overly stiff and hence, unacceptable from an operational standpoint.

Two final tests need to be performed on all acceptable grout formulations, freeze/thaw and shaker tests. The freeze/thaw test is designed to simulate climactic changes during storage and transportation. The shaker test is designed to approximate the vibration and bump characteristics of transport by truck.

Wastewater Equilibration Study

The Wastewater Equilibration Study (WES) continued through July. Four additional treatment samples were prepared with K-65 solids to water ratios of 1:5. The samples were agitated for seven days in order to bring the suspended and dissolved species into equilibrium. Following the seven-day agitation, two of the samples were allowed

to settle for approximately 48 hours, and the remaining two samples were allowed to settle for approximately two weeks. These four WES samples were filtered through a 0.45-micron filter and buffered with calcium hydroxide to varying pH levels, ranging from a pH of 10.5 to a pH 11.5. Radium-226 levels were measured before and after the samples are buffered.

The Wastewater Equilibration Study (WES) was concluded in August. Follow-up activities are being planned in order to determine treatment methods that will be employed during full-scale operations. The wastewater generated during silos mining operations must meet water requirements of the Fernald Advanced Waste-Water Treatment facility.

The Wastewater Equilibration Study (WES) was concluded in August. Follow-up activities are being planned in order to determine treatment methods that will be employed during full-scale operations. The wastewater generated during silos mining operations must meet water requirements of the Fernald Advanced Waste-Water Treatment facility.

Settling Tests

Currently, the silos mining strategy involves the hydraulic removal of K-65 from the existing silos and transfer to four temporary storage tanks. After the slurried material is pumped into a storage tank, current operating plans are to let it settle for approximately 8 to 24 hours. The supernatant will then be pumped back to the mining equipment and used to remove more material from the existing silos. Observations made during the WES testing revealed that the K-65 material does not settle into a clear supernatant as expected. In addition, Ra-226 activities in the supernatant are much higher than expected.

During September, settling tests were performed for three settling durations. At each settling duration, the settling characteristics of three different slurry concentrations were evaluated. The resulting supernatant and settled solids component for each sample was analyzed for percent solids, radium concentration, and density. The tests were performed for settling time intervals 8, 24 and 48 hours at slurry concentrations of 5%, 10% and 15% solids.

WORK PLANNED

The following activities are planned for the upcoming months:

- Continue formulation testing with K-65;
- Perform settling tests with increased salt concentrations;
- Plan and perform settling tests using a flocculating agent;
- Perform TCLP on baseline grout samples;
- Participate in the full-scale surrogate testing of the Silos processing facility.

Accelerating Phytoremediation by Monitoring Plant Status

Dr. Yi Su

Dr. David Monts

INTRODUCTION

Phytoremediation is a technology that uses various plants to degrade, extract, contain, or immobilize contaminants from soil and water. The current project is specifically focused on mercury removal from the Oak Ridge site. Our long-term objectives include phytoremediation of other heavy metals and radionuclides of interest to DOE. Phytoremediation provides a cost-effective alternative to traditional remediation strategies for mercury and other heavy metal contaminants. In particular, phytoextraction is the uptake of contaminants by plant roots and translocation within the plants to shoots or leaves. Contaminants are generally removed by harvesting the plants. Since no natural mercury hyperaccumulator has been found, we will screen and select the best suitable plant species for mercury phytoextraction at the chosen Oak Ridge site. Through this project, a methodology for acceleration of mercury phytoremediation will be developed. Acceleration will be achieved through expedited harvesting of metal accumulating plants, thereby allowing multiple crops during each growing season. This ground-level study will also help to determine whether physiological reflectance signals are stronger than disturbances introduced by factors such as the position of the sun, heterogeneity of the landscape, or atmospheric interference. The resulting information will be essential to determine whether remote sensing technology can be used for long-term monitoring of the spread of heavy metal and other pollutants at selected DOE sites.

Previous studies conducted at our laboratory have yielded spectral indices (signatures) that indicate the impact and the content of certain heavy metals in the leaves and canopies of live plants. The results

suggest that diffuse reflectance spectra in the near infrared from live plant canopies may be used as indicators for certain metal contaminants in plants and soil. By means of monitoring the leaf and canopy spectral reflectance, we can improve the capabilities for characterizing the physical, chemical and biological properties of the subsurface and improve capabilities for measuring contaminant migration and system properties that control contaminant movement. If the physiological reflectance signals resulting from mercury or other contaminants are strong enough for remote sensing application, it will indicate the potential for significant reductions in the costs of long-term monitoring at selected DOE closure sites, such as Fernald, the DOE complex for clean-up, closure, and monitoring applications.

WORK ACCOMPLISHED

During this reporting period, we finished a mercury phytoremediation experiment with brake fern. The experiment began in May. Mercury was provided as HgCl_2 , HgS and $\text{Hg}(\text{NO}_3)_2$. Plants and soil samples from different treatment groups were collected for chemical analysis. Sample and data analyses have begun and are expected to be completed in the next reporting period.

We have examined the solution/liquid phase speciation of mercury in spiked soils without plants and also after a growing season with brake fern plants. Redistribution and transformation of solid-phase mercury species in spiked soil were also investigated. The effects of plants and incubation time on bioavailability and chemical stability (especially of mercury sulfide) have been examined as well. The preliminary results are very promising and encouraging.

Meanwhile, We have been writing and revising papers based on earlier experiments.

Support of Hanford Single Shell Tank Waste Disposition

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

Dr. David L. Monts

Ping-Rey Jang

Dr. Yi Su

Dr. Shiquan Tao

Dr. Chuji Wang

INTRODUCTION

This project provides tools for characterization of tank waste either in- or at-tank. Prior and during processing of Hanford tank waste, the tank farm operator will have to perform limited analyses to ensure that waste can be retrieved, and that it meets acceptance criteria for the Hanford Waste Treatment Plant. Currently, this must be done through remote sampling, followed by shipment of samples to a laboratory capable of performing the needed analyses. Tools that can provide the required measurements either inside the tank, or at the tank (e.g., in the tank's riser or possibly in the retrieval line output

from the transfer pump going to the receiver tank) potentially could reduce costs and accelerate waste processing by eliminating a lengthy sample-transport-analyze-report regimen.

Similarly, 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 (primarily due to technetium and uranium), and to determine the appropriate manner to stabilize the residual waste. These needs are described in Hanford Technical Challenges WT-102, Post-retrieval Evaluation: *In Situ* Characterization, and WT-115, Technology to Support Post-retrieval Evaluation of SSTs.

DIAL will assemble and test the following systems for potential deployment:

- Nondestructive, in situ means of determining the spatial extent of species of concern, such as gibbsite (a-aluminum hydroxide) and uranium deposits, based on a combination of spectral imaging (SI) and diffuse reflectance spectroscopy (DRS). When water is added to a waste tank to dissolve condensed species, gibbsite may form. Since the porosity of gibbsite is low, a layer of gibbsite on the tank surface would significantly inhibit the ability to dissolve and remove condensates from a tank. This has, in fact, been observed in previous Hanford salt dissolution studies at DIAL. The formation of gibbsite can be inhibited by addition of NaOH, but the pH inside most Hanford tanks is already greater than 15 so it is desirable to avoid complications associated with further addition of caustic. Thus a means of in-tank monitoring of the existence and spatial distribution of gibbsite would facilitate removal of wastes from the tanks. Uranium deposits are also of concern. Spectral resolution is achieved by illuminating an area of interest with an appropriate light source and placing a narrow-bandpass filter in front of the camera. The resulting image contains information on the spatial distribution of species that absorb/emit light in that wavelength region. Confirmation can be obtained from the

diffuse reflectance spectrum, which is obtained by collecting the light reflected by a surface, using a spectrometer to wavelength-resolve the reflected light, and using a photodetector to record the resulting diffuse reflectance spectrum.

- Nondestructive, *in situ* fiber-optic sensor for activity level to address criticality issues. The cost for collecting, storing and processing radioactive waste depends on the level of radioactivity of the waste. The waste has precipitated during the decades that the wastes have been stored in the Hanford tanks. The composition of the precipitant is changing with time. Therefore, it can be expected that the distribution of the radioactivity in the solid waste is inhomogeneous. Therefore, a sensor that senses in real time the radioactivity of the sludge in which it is immersed can address criticality issues. During the current Cooperative Agreement period, we are developing a sol-gel silica scintillation fiber doped with anthracene to monitor beta particles. As a continuation of our effort for sensing radioactivity inside waste tanks, scintillation fiber sensors for monitoring gamma-ray and alpha radioactivity will be developed during the next year. Development of an optical fiber sensor for detection of neutrons is also planned after completion of the development of the alpha and gamma sensors.
- 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 DIAL 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 determina-

tion 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 cameras from different viewpoints.

- A compact, real-time, on-line analyzer is needed to determine elemental and isotopic concentrations of species of concern in the processing of tank waste retrieval, *in situ* characterization, and post-retrieval evaluation. DIAL's plasma-cavity ringdown spectroscopy (plasma-CRDS) has been demonstrated to be a powerful technique for sensitive elemental and isotopic measurements. Several elements (Pb, Hg, Mn, Cr, Al, Fe, Ca, Ni, Am, Cs, *etc.*), including uranium and its isotopes, have been measured in a laboratory plasma-CRDS system with the capability of measuring uranium isotopes (U-235/U-238) in the natural abundance ratio. All these elements are generated through plasma dissociation of their chemical compounds injected into the plasma. Detection sensitivity of elements is as low as hundreds of parts-per-trillion (ppt) (e.g., 200 ppt for Pb and 70 ppb for U-235 and U-238). During this Cooperative Agreement period, a compact plasma-CRDS system will be developed using a compact microwave plasma source with diode lasers to provide the capability for both elemental analysis and determination of isotopic concentrations. The system will have low operating costs and no generation of new wastes.

WORK ACCOMPLISHED

DIAL researchers participated in a conference call with Hanford on September 2 in order to report our progress to date and discuss our future efforts. As a result of this exchange, Hanford has provided DIAL with information about the Hanford waste tanks that will help us in preparing our systems for deployment at Hanford.

Diffuse Reflectance Spectroscopy, Laser-induced Fluorescence Imaging, Spectral Imaging and Stereovision

During this reporting period, the stereovision effort has been investigating the effect on stereovision performance of different parameters, such as distance between the cameras, working distance between cameras and objects of interest, window size for disparity map computation, etc. We also investigated the possibility of utilizing Pulnix cameras rather than Sony block cameras. The Pulnix cameras were found to produce better quality images and hence better disparity maps. However, the Pulnix cameras do not have computer-controlled zoom capability (as the Sony block cameras do); for application in the Hanford waste tanks, the ability to zoom is expected to be essential. For other applications, the Pulnix cameras might be a better choice.

The laser-induced fluorescence–spectral imaging effort has received and tested the repaired charge-coupled device (CCD) camera detector from the manufacturer. During May, the CCD camera detector on the spectrometer was diagnosed as malfunctioning and was sent to the manufacturer for repair and was received back from the manufacturer in late May. Subsequent testing in June revealed that the CCD detector was still not functioning properly and in late June was once again shipped to the manufacturer for repair. During July, the manufacturer did repair the CCD system and shipped it back to us in late July. During August, we tested the CCD system and verified that it is working properly. We have set-up the equipment to collect laser-induced fluorescence spectra of selected simple uranium and thorium compounds and have begun optimization of the apparatus using surrogate samples.

Information Sifting

During this quarter, the information sifting effort completed implementation of all the design features of the spectral identification

tool. The spectral identification software was successfully installed on a Windows-based computer in order to be evaluated by users other than the software developer. The results of this evaluation will be used to improve the utilization of the software by non-experts and will allow us to determine how best to integrate the use of this software with the diffuse reflectance spectroscopy systems. The graduate student programmer working on this effort has graduated and left the effort; because of temporary budgetary concerns, the graduate student will not be replaced until January 2005.

Fiber Optic Sensors

Our work during this reporting period was divided to two parts. First, sol-gel materials doped with ZnS have been prepared by adding ZnCl₂ and Na₂S solution to a TMOS sol solution. The silica materials obtained have been examined using the fluorescence technique. Second, a literature research has been conducted in order to establish techniques to synthesis metal sulfide quantum dots and incorporate the quantum dot material into a transparent polymer in order to produce an alpha particle sensor. ZnS, CdS and CdSe quantum dots have recently been synthesized.^{1,2} These quantum dot materials are highly fluorescent and have potential applications in chemical/biochemical sensing, laser design, and optoelectronics.³ These nanometer-size semiconductor particles can be incorporated into polymers through different approaches.^{4,5} In a recent report,⁶ a CdSe/ZnS core/shell (CdSe@ZnS) quantum dot has been incorporated in silica powder using a sol-gel process. This quantum dot incorporated silica material was irradiated with alpha particles from a Po-210 alpha source; the resulting scintillating pulse from the material was recorded as an indication of the presence of alpha particles.

Fourier Transform Profilometry

Design and fabrication of the two plates required to center the Fourier transform profilometry (FTP) probe have been completed. A

prototype of the FTP probe cable management system for electrical cables has been constructed. Design details for keying of the telescoping sections of the FTP probe have been completed. A 3-ft prototype telescoping FTP probe was fabricated and assembled utilizing the WVNS' FTP-instrument elbow and an existing support tower. Movie files were recorded to show the current status of work and illustrate the probe's computer-controlled movements. Work continued on development of the probe control system and the probe support tower. Using our current FTP probe one-meter elbow optical setup, FTP measurements were obtained at simulated target distances. For these FTP measurements, the target was a paper cone with the following dimensions: (1) base diameter = 26.7 cm; (2) peak height = 10.4 cm; and (3) volume = 1941.00 cm³. Measurement results are listed in Table 1 for three camera-to-target distances: ~15 ft (455.3 cm), ~21 ft (640.2 cm), and ~27 ft (828.3 cm).

TABLE 1. Results of FTP measurements under simulated conditions.

Camera-to-Target (L) (cm)	Camera-to-Projector (d) (cm)	Measured Peak Height (cm)	Error (%)	Measured Volume (cm ³)	Error (%)
455.3	20.96	10.31	0.9	1962.73	1.1
640.2	26.67	10.25	1.4	1034.31	0.3
828.3	27.15	10.44	0.4	1960.11	1.0

Typical results of target analysis and reconstruction are illustrated in Figures 1 and 2. Further optimization of the optical parameter settings to improve the accuracy and repeatability of the FTP determinations is under way.

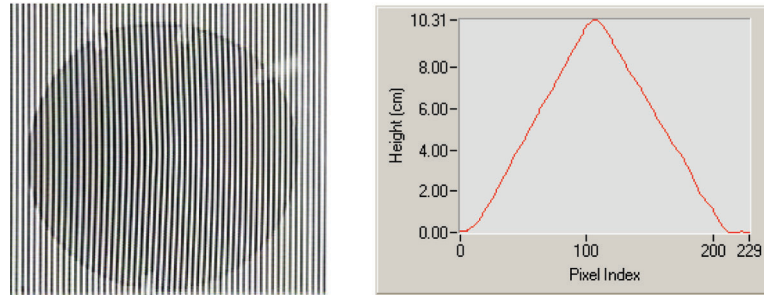


FIGURE 1. Paper cone target and reconstructed 1D profile of cone peak.

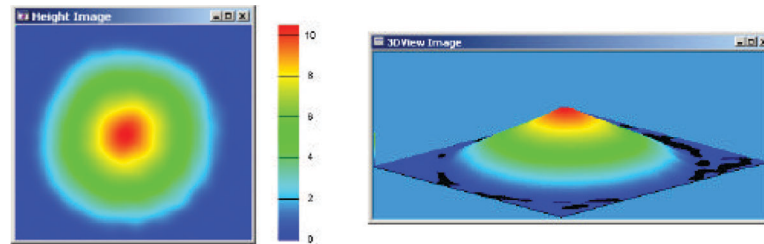


FIGURE 2. 2D and 3D profiles of cone reconstructed from FTP data.

Microwave-induced Plasma–ringdown Spectroscopy

The plasma source used for atomization has a large bearing on the sensitivity and performance of a plasma-cavity ringdown spectroscopy (PCRDS) system. An ideal plasma source for ringdown measurements of elements and isotopes must have a stable plasma plume, low gas flow rates, low plasma power, and a long laser beam path length inside the plasma. So far, an array of tube-shape plasma torches have been designed, fabricated, and tested. These new plasma sources effectively generate atoms and ions. Their performance has been evaluated by recording the emission spectra of a variety of elements. During this quarter, these new tube-shape plasma sources have been incorporated into the plasma-cavity ringdown system to conduct ringdown measurements. Plasma torches with several different con-

figurations have been separately incorporated into the plasma-ring-down system for testing. Plasma-ringdown measurements of mercury under atmospheric conditions were performed for the first time. The results show that different plasma torch configurations yield different detection sensitivities for mercury. Compared with the candle-shape microwave-induced plasma (MIP) torch, this new tube-shape MIP torch has much lower (better) detection sensitivity. With the same laser beam path length in the plasma, the detection sensitivity of mercury obtained with the tube-shape MIP torch is approximately three orders of magnitude better than the one obtained with the candle-shape MIP torch. Mercury hyperfine structures were also observed. Abundant experimental data has been processed. A manuscript is being prepared for submission to a peer-reviewed journal.

WORK PLANNED

Diffuse Reflectance Spectroscopy, Laser-induced Fluorescence Imaging, Spectral Imaging and Stereovision

During the next quarter, the stereovision effort will continue its investigation of the effects on stereovision performance of selected parameters, including working distance between cameras and objects of interest, window size for disparity map computation, distance between cameras, etc. Issues related to design of the deployable instrumentation package will also be addressed.

During the next reporting period, we will complete optimization and begin acquisition of laser-induced fluorescence spectra from selected simple uranium and thorium compounds. These LIF spectra will be used to select excitation and observation wavelengths. The diffuse reflectance spectroscopy (DRS) effort will record DRS spectra of selected simple thorium compounds so that the spectral identification tool developed by the information sifting effort can be tested to evaluate the selectivity and reliability of our spectral identification determinations.

Information Sifting

The spectral identification software will be evaluated by non-experts in order to determine how to improve its utilization and how best to integrate the use of this software with the diffuse reflectance spectroscopy systems. A graduate student programmer will be sought to join this effort in January 2005.

Fiber Optic Sensors

Our next step for this project is developing chemical processes to synthesis CdSe@ZnS semiconductor quantum dots, dope the semiconductor quantum dots into a polymer, and coat the quantum dot-doped polymer onto a tubular waveguide in order to make a scintillation fiber optic sensor for alpha particles.

Fourier Transform Profilometry

Work will continue on the FTP insertion probe engineering work, on the detachable elbow section of the insertion probe, and on correction for non-perpendicular FTP surface measurements. Study of phase unwrapping algorithms^{7,8} for target area that have large height discontinuities and/or surface isolations will continue. Research on image quality improvement algorithms^{9,10} will be on-going. Camera and material radiation tolerance tests will continue. Efforts for solution of problems associated with distortion that is caused by non-perpendicular target surface FTP measurement are underway.

Microwave-induced Plasma-cavity Ringdown Spectroscopy

Future efforts will include down-selection of plasma torch configuration, characterization of the chosen plasma torch, and improvement of system performance. Additionally, a new external cavity blue diode laser will be tested and used for ringdown measurements of uranium.

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ACRONYMNS

CCD	charge coupled device
CdS	cadmium sulfide
CdSe	cadmium selenide
DRS	diffuse reflectance spectroscopy
FTP	Fourier transform Profilometry
IS	information sifting
LIF	laser-induced fluorescence
MIP	microwave-induced plasma
Na ₂ S	sodium sulfide
PCRDS	plasma-cavity ringdown spectroscopy
Po-210	polonium 210
SI	spectral imaging
SV	stereovision
TMOS	tetramethylorthosilicate
UV	ultraviolet
WVNS	West Valley Nuclear Services
ZnCl ₂	zinc chloride
ZnS	zinc sulfide

Process Chemistry and Operations Planning for Hanford Waste Alternatives

Dr. Jeff Lindner

Dr. Rebecca Toghiani

INTRODUCTION

Previous work in these laboratories has resulted in a number of findings that support the implementation of alternative waste processing operations at the Hanford site. Considerable efforts have been devoted to upgrading the quality of ESP calculations. These studies have included the testing of the model against core salt cake dissolution studies from a number (13) of single-shell tanks. Thermodynamic data for various double salts including $\text{Na}_7\text{F}(\text{PO}_4)_2 \cdot 19\text{H}_2\text{O}$, Na_3FSO_4 , $\text{Na}_6(\text{SO}_4)_2\text{CO}_3$, and the nitrate-sulfate double salt have been obtained along with pure component solubilities. These results were analyzed using regression with the coefficients developed into a special database denoted as DBLSLTDB. The data library has been subsequently used in predicting laboratory-scale salt cake dissolution experiments and in evaluating the chemistry occurring in the 242-A evaporator/crystallizer.

Additional solubility measurements were begun with the aim of improving model predictions for aluminum containing systems. Previous work by Reynolds at the site resulted in the development of the Weslow database. Testing in these laboratories indicated much improved predictions of aluminum partitioning using this database as compared to the default Public database; however, some differences were still noted in connection with salt cake dissolution studies. Thus experiments were begun to include additional systems such as carbonate, sulfate, nitrate, and nitrite. These data are being evaluated along the same lines as that obtained earlier for the double salts. Part of the proposed work scope is the development of an additional data-

base wherein the partitioning of aluminum between gibbsite and the aqueous phase species AlO_2^{-1} and $\text{Al}(\text{OH})_4^{-1}$ are improved.

Further calculations are also needed with respect to supporting HNF evaporator operations. To date simulations have been performed on the waste streams expected from dissolution and retrieval of the salt waste in tank S-112. Other tanks scheduled for retrieval will be evaluated with the aim of developing a quick reference diagram for solids crystallization based on the input stream composition and on the predicted performance of the 242-A evaporator/crystallizer and on receiving tank temperatures.

This project consists of two tasks: ESP Database Development and Application of ESP to Hanford Waste Processing Alternatives.

Task 1. ESP Database Enhancements

This task will focus on the completion and distribution of Version 5 of the DBLSLTDB database, the determination of the solubilities for aluminum and the subsequent development of a special database that accurately describes the aqueous phase thermodynamics of aluminum systems at typical Hanford waste conditions.

Sub-task 1-1. Distribution of the DBLSLTDB Database

Work is continuing on the completion of the DBLSLTDB library. This work is expected to end early in the calendar year and involves additional fitting for the sulfate-phosphate system. Details of the solubility measurements and the fitting results will be published. Compilation of the solubility measurements revealed the need to examine the impact of nitrate on the solubility envelope in the $\text{Na-SO}_4\text{-CO}_3$ system. The impact of nitrate on natrophosphate $[\text{Na}_7\text{F}(\text{PO}_4)\cdot 19\text{H}_2\text{O}]$ was determined to be significant through experimental measurements in our laboratory. The interactions of nitrate with sulfate and with carbonate have previously been measured in our laboratory. Solubility

measurements for the Na-SO₄-CO₃-OH system revealed the formation of burkeite [Na₆(SO₄)₂CO₃] in 1-m OH solution at 25°C. Its formation at this lower temperature has not previously been reported and the ESP Public database does not predict its formation (due to temperature limit restrictions). Thus, measurement of the solubility envelope in the Na-SO₄-CO₃ system in the presence of nitrate (1 and 3 m) will provide additional information regarding the formation of burkeite in wastes of high ionic strength.

Sub-task 1-2. Solubility Studies on Aluminum Systems

Literature studies on aluminum solubilities and comparisons of reported data with ESP predictions using the Public and the Weslow databases were performed in FY 2003. These results and laboratory scale salt cake dissolution experiments indicated that the presence of additional anions significantly influence aluminum partitioning. Solubility envelopes for the aluminum system with nitrate and with carbonate, the later to investigate the formation of Dawsonite (NaAlCO₃(OH)₂), Owing to the complexity of aluminum systems additional experiments are needed along to assess the influence of other major anions, specifically nitrite and phosphate, that are present in the Hanford waste. The obtained data will be used in Sub-task 1-3 for upgrading the model predictions for aluminum.

Sub-task 1-3. Aluminum Database Development and Distribution

The solubility data obtained in Sub-task 1-2 will be analyzed within the Bromley framework to determine the dependence of aluminum solubility on temperature, hydroxide loading, and double salt (Dawsonite) k-fit parameters. Data for the systems will be incorporated with a special aluminum database and will be routed to engineers at Hanford for evaluation and use. A full statistical analysis of the quality of the regression results will, similar to that employed for the DBLSLTDB, be performed.

Task 2. Application of ESP to Hanford Waste Operations

Volume limitations within the Hanford DST system are expected to have a pronounced impact on the rate at which salt cake waste can be processed either using vitrification or alternative process technologies. Efficient evaporator operations provide a means for significantly reducing the volume of the waste and are expected to lead to the potential for separating solids based on the operating conditions within the 242-A unit and the receiving tank temperature. For example, in processing the anticipated salt waste from the retrieval of tank S-112 simulations predicted that the sulfate can be separated from nitrate solids at temperatures of between 40 and 50°C. Such a separation would allow for the development of mixing strategies that could effectively eliminate or reduce the amount of sulfate containing waste routed to vitrification.

The current effort will extend the evaporator studies to include projected streams from other salt waste containing tanks. Specific efforts will be centered on S-102 and S-109. The primary compositions from these streams will be compared to assess the ability of various separation processes using the evaporator and final waste temperature. Waste from other SSTs will then be evaluated to develop a composition map that will be correlated to evaporator performance and separations. As in the work from S-112, the ability to recycle aqueous streams obtained following solids separation will be investigated.

WORK ACCOMPLISHED

Task 1. ESP Database Enhancements

Sub-Task 1-1. Distribution of the DBLSLTDB Database

A revised version of the DBLSLTDB was distributed in August. The new release contained improved fits for carbonate and sulfate.

Sub-Task 1-2. Solubility Studies on Aluminum System

Solid-liquid equilibrium studies on the aluminum-phosphate system continued. The solutions were made from technical grade sodium aluminate, sodium phosphate dodecahydrate, and water. The sodium aluminate loading was held constant and the phosphate concentration varied.

Samples of the technical grade NaAlO_2 were dissolved and then subjected to ICP analysis to determine the actual formula of the material. NaAlO_2 is prepared from the addition of caustic to aluminum hydroxide. The average of repetitive measurements provided a mass percentage for aluminum of $27.03 \pm 0.15\%$ and for sodium of $28.8 \pm 0.2\%$. For pure sodium aluminate these percentages would be 32.9% for Al and 28% for Na. The sample was therefore deficient in aluminum as compared to the pure material and a series of calculations were performed considering the reactants (NaOH and $\text{Al}(\text{OH})_3$) and products (NaAlO_2 and H_2O). Based on the original percentages of the material, a TGA analysis of the water in the solid, and the molecular weights of the reactants and products the technical grade aluminate was determined to have the formula $0.5785 \text{ NaAlO}_2 \cdot 0.0484 \text{ Al}(\text{OH})_3 \cdot 0.207 \text{ NaOH} \cdot 0.17 \text{ H}_2\text{O}$ with a molecular weight of 62.477 g/mol. The amount of gibbsite remaining in the product amounts to 8% if the original gibbsite that is reacted leading to a reaction conversion of 92%.

Solutions were prepared at four different aluminate loadings with varying phosphate concentration. Approximately 100 g of each solution was prepared and then split into two roughly equal fractions. One portion of the solution was sampled at different times and analyzed for aluminum using the ICP. This allowed the approach to equilibrium to be followed. Once equilibrium is attained the solution that had not been sampled will be analyzed. Solids expected in the studies at 25°C are gibbsite and the sodium phosphate dodecahydrate.

Examples of the time approach to equilibrium for two of the four series are given in Figures 3 and 4. The aluminum concentrations are noted as apparent values. The Al molality, m, (mol/kg H₂O) is based on the mass of water in the system and the total amount of water has not been corrected for hydrated water contained in any Na₃PO₄·12H₂O·0.25NaOH solids that form.

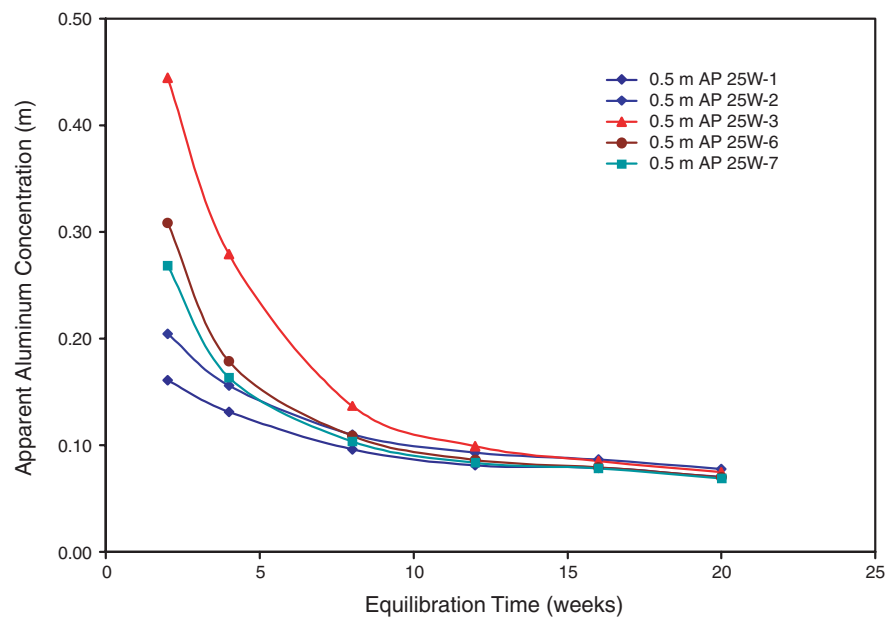


FIGURE 3. Apparent aluminum concentrations measured as a function of time.

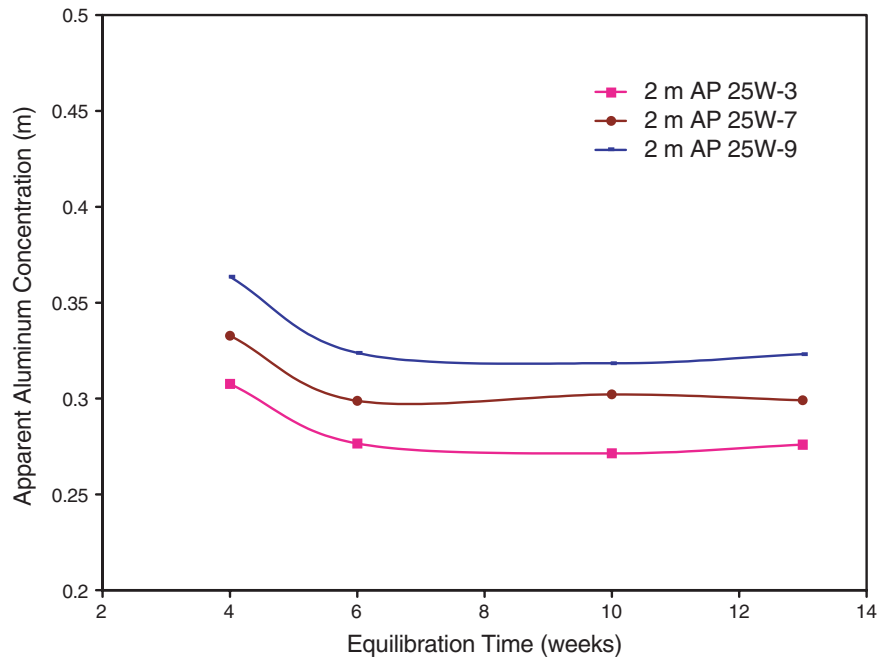


FIGURE 4. Apparent aluminum concentrations measured as a function of time for a higher initial aluminate loading series.

The generic trend for the apparent aluminum concentrations for both series indicate a decrease in concentration with increasing time. Times of up to 20 weeks (5 months) are required to achieve equilibration.

Similar equilibration durations have also been observed for the aluminum-nitrate system. Currently all of the equilibrated systems are undergoing solid-liquid separation, aluminum analysis and phosphate (nitrate) analysis using ion chromatography. Solids are being identified using the polarizing light microscope. Once these studies are completed the data necessary for the development of the aluminum database will be available.

Sub-Task 1-3. Aluminum Database Development and Distribution

This task will commence following the characterization of the aluminum-phosphate and aluminum-nitrate systems as described above.

Task 2. Application of ESP to Hanford Waste Operations

ESP Simulations in Support of Evaporator Operations

Earlier work regarding the application of the Environmental Simulation Program to evaporative processing of many Hanford wastes has been reported in this sequence previously.^{11,12} Recently CH2M Hill issued a request for proposal that was aimed at developing a fractional crystallization process for separating low and medium curie wastes based on activity and routing the lower activity wastes to the developing bulk vitrification facility.¹³ The remaining high activity wastes are expected to be routed to the waste treatment plant (WTP). By routing the low activity waste to bulk vitrification an overall mission time savings is expected.

DIAL's efforts to secure funding for this initiative were ineffective. Still, considerable effort was expended into proof of concept calculations for a prospective flowsheet. There being no other venue for publication of the results it was decided to present a summary of the calculations here.

The generic concept is shown in Figure 5. Dissolved salt solution or slurry is fed from one of the million gallon tanks at a minimum of 10 gallons-per-minute (gpm). The process will operate a fractional crystallizer to promote the crystallization of the less soluble salts (such as the fluorosulfate, sulfate carbonate double salt, oxalate, etc.) that also have limited solubility in the WTP low activity waste glass. Crystallization has been used for many years in the commercial chemical industry to produce refined sodium salts (e.g., sodium nitrate). Solid liquid separation is performed and the cesium-rich

stream is sent to the WTP. The wet solids may require washing to remove residual cesium in the interstitial liquid. The washed solids are dissolved and sent to supplemental treatment.

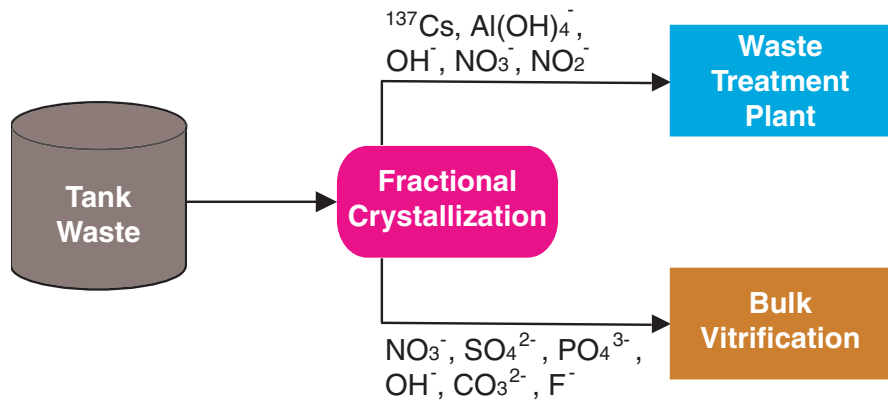


FIGURE 5. Pretreatment alternatives system concept – fractional crystallization.

An initial flowsheet was developed drawing on previous chemical equilibrium calculations performed to assess the performance of the 242-A evaporator, on additional calculations for the target streams provided and on previous experience with salt waste processing. The Environmental Simulation Program (ESP) was employed for the calculations.

The primary difference between the proposed process and typical operation of the 242-A evaporator is that a solid-liquid separation unit will be required downstream of the evaporator. Critical portions of the flowsheet include: the ability to selectively recrystallize solids, the need to efficiently and effectively separate the resulting high activity supernatant from the precipitated solids, and the subsequent dissolu-

tion of the solid fraction. The desired requirements for the process are given in Table 2.

TABLE 2. Minimum acceptable requirements and desired targets for pretreatment process.¹³

Pretreatment Output Stream	Criterion	Minimum Acceptable Requirement	Desired Target
Bulk Vitrification Feed	¹³⁷ Cs activity	< 0.05 Ci/L	< 0.0012 Ci/L
	Na ⁺ concentration	5 M (± 20%)	5 M (± 10%)
	Na ⁺ split	Contain at least 50% of the Na ⁺ in the input stream	Contain at least 90% of the Na ⁺ in the input stream
	Contaminants of concern ^a	TRU concentration must be less than 100 nCi/g	TRU concentration must be less than 100 nCi/g
WTP Feed	Sulfate: sodium mole ratio	< 0.01	≤ 0.0022
	DST storage	Must meet DST storage requirements and pipeline transfer requirements	Must meet DST storage requirements and pipeline transfer requirements

^a Contaminants of concern include (for this application): ¹³⁷Cs, ¹²⁹I, ⁹⁹Tc, ⁹⁰Sr, ⁷⁹Se, ¹⁴C, total uranium, total alpha isotopes, Cr(VI), nitrate, nitrite, sulfate, and phosphate.

The process is expected to be applicable to salt streams generated at different extents of dilution and to double shell slurry feeds con-

tained in many of the tanks. Model calculations are presented for the “late” and “early” dissolved salt streams (Table 3).

TABLE 3. Projected feed compositions for the dissolved salt streams.¹³

Ion	Early Feed moles/L	Early Feed mg/L	Late Feed moles/L	Late Feed mg/L
Al ⁺³	0.48	1.30E+04	0.04	1.08E+03
C ₂ O ₄ ⁻²	0.01	8.80E+02	0.02	1.76E+03
Cl ⁻	0.08	2.84E+03	0.01	3.55E+02
CO ₃ ⁻²	0.92	5.52E+04	0.27	1.62E+04
Cs ⁺		1.14E+00		1.14E-01
F ⁻	0.03	5.70E+02	0.1	1.90E+03
K ⁺	0.03	1.17E+03	0.01	3.91E+02
Na ⁺	8.7	2.00E+05	2.9	6.67E+04
NO ₂ ⁻	0.59	2.71E+04	0.07	3.22E+03
NO ₃ ⁻	3.9	2.42E+05	1.6	9.92E+04
OH ⁻	1.5	2.55E+04	0.01	1.70E+02
PO ₄ ⁻³	0.04	3.80E+03	0.05	4.75E+03
SO ₄ ⁻²	0.14	1.34E+04	0.17	1.63E+04

As projected and seen in our earlier calculations of salt cake dissolution the initial fractions are high in hydroxide, nitrite, and cesium from dilution of the interstitial liquor. As dilution proceeds less of the interstitial liquid remains within the waste and subsequent ion concentrations decrease.

Figure 6 shows the use of the DBLSLTDB and OLI ESP applied to the “late” feed waste streams to show how evaporation might be operated to promote crystallization of various double salts. The figure provides a plot of the solids that are predicted to form at different waste volume reduction factors (WVRF). Lower WVRF’s correlate to

lower extents of evaporation and it can be seen that some solids separation for the “late” feed is possible. Initially, the sulfate containing double salts Na_3FSO_4 and $\text{Na}_6(\text{SO}_4)_2\text{CO}_3$ are predicted to form along with natrophosphate ($\text{Na}_7\text{F}(\text{PO}_4)_2 \cdot 19\text{H}_2\text{O}$) and sodium oxalate. At a WVRF of around 70% the simulation predicts the formation of the sodium carbonate monohydrate and at a still higher extent of evaporation, solid sodium nitrate is expected.

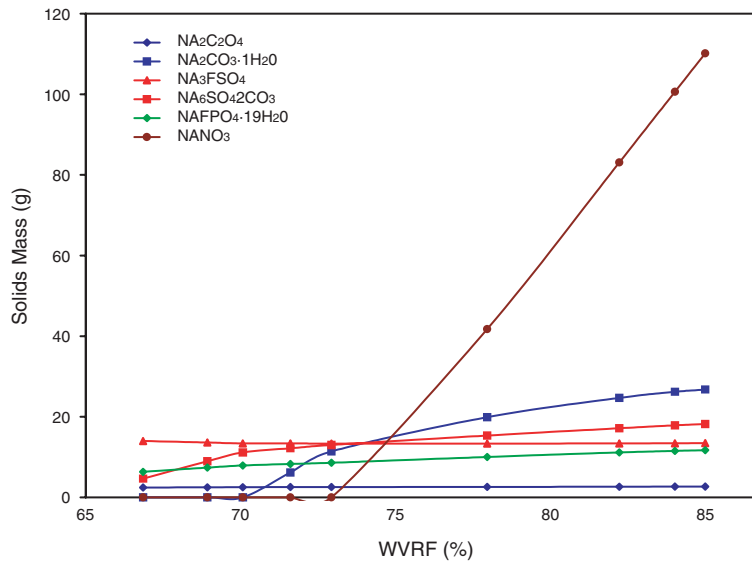


FIGURE 6. Solids predicted to form from processing the “late” salt feed.

The data provide for the development of evaporator operating scenarios where multiple passes can be used to tailor the selective removal of a particular crystal. For example, by running the evaporation to a 70% WVRF then separating the formed crystals a large portion of the sulfate carbonate double salt would be expected to be removed while still leaving nitrate at a concentration below saturation.

Calculations were performed as a function of the mass of entrained evaporated liquid/mass of recrystallized solids. The extent of entrainment is similar to the concept of porosity. A decrease in porosity corresponds to less of the high activity aqueous phase being routed to the bulk vitrification facility, which is related in the decreasing cesium activities and the slightly reduced sodium loadings calculated. The initial results indicate that the process requirements can be achieved provided that the porosity of the solids is below 42%; such a value being considerably larger than those typically observed (30%) for salt cakes comprised of 80% sodium nitrate (by weight). The calculated cesium activities at porosities of 28 and 33%, meet the minimum targets for the bulk vitrification feed.

ESP model calculations were performed by evaporating the given feed stream and separating the resulting phases. The volume of the solid phase was determined and then used with the assumed porosity to determine the volume of interstitial liquid that would be retained in the pores of the solid matrix. The volume of liquid was then converted to mass, and along with the total solids mass, used to determine the mass of entrained liquid per gram of solid. By varying the assumed porosity of the resulting solids, it is possible to more fully examine the solids filtration step of the proposed flowsheet and set some limits on the actual ability to perform the separation. Simulation results are collected on Table 4.

TABLE 4. ESP model results for the porosity (aqueous phase entrainment) studies for evaporative processing and solid liquid separation of the “late” dissolved salt stream.

Porosity (%)	WAC	28	33	38	42
Bulk Vitrification Specifications					
Cs ¹³⁷ activity (Ci/L)	< 5.0E-02	8.60E-03	1.10E-02	1.33E-02	1.54E-02
Na ⁺ concentration (M)	5 M	4.98	5.03	5.08	5.13
⁽¹⁾ Requirements for other nitrate loadings are available.					

TABLE 4. ESP model results for the porosity (aqueous phase entrainment) studies for evaporative processing and solid liquid separation of the “late” dissolved salt stream.

Porosity (%)	WAC	28	33	38	42
Na ⁺ split	> 50% Na from input stream	81.08	83.05	85.16	87.21
WTP Feed					
[SO ₄ ⁻²] / [Na ⁺]	< 0.01	7.89E-03	7.89E-03	7.89E-03	7.89E-03
TSR Corrosion					
[NO ₃] > 3M ⁽¹⁾		6.91	6.91	6.91	6.91
[NO ₂ ⁻] + [OH ⁻] > 1.2(M)		2.46	2.46	2.46	2.46
⁽¹⁾ Requirements for other nitrate loadings are available.					

The sulfate to sodium molar ratio is driven by the recrystallization of the sodium double salts. The high activity stream, projected to become WTP feed, was calculated to have a sulfate to sodium molar ratio of 0.008, which is considerably less than the minimum acceptable requirement for the process and also meets the desired target requirements. The other entry given in Table 4 relates to corrosion limits as set for the DST farm.^{14,15} Calculations for all processed streams resulting from the “late” feed indicated that the nitrate anion concentration was always greater than 3 M. The 6.91 M concentration is, in fact, greater than the 5.5 M limit of the corrosion WAC. Dilution of the stream, intended for processing in the WTP, by 30% will still result in a combined nitrite (NO₂⁻) and hydroxide (OH⁻) loading of 1.9M.

Other waste transfer/acceptance requirements for the double shell tank system include limits based on criticality, organic and energetic reactions, flammable gas generation, and emissions.^{14,15} All of the feeds targeted for pretreatment are not believed to contain a sufficient concentration of organics so as to pose an unresolved safety question (USQ). The stream routed to the DST systems will be a supernatant

and not slurry; thereby rendering the possibility of additional gas generation within the receiving tank unlikely. The possibility of direct emissions from the proposed process is also considered unlikely based on the need for secondary containment of the processing units.

Calculations similar to those described above were also performed on the “early” waste feed stream. As in previous ESP calculations performed on earlier 242-A evaporator campaigns, the “early” waste feed was diluted to reduce the initial aqueous phase density.^{11,12} The stream was then processed in a manner similar to the “late” feed calculations, with different values of the porosity assumed. Table 5 provides the ultimate results for comparison to the WAC requirements for the “early” feed stream destined for bulk vitrification and to the waste treatment plant. Cesium activities are somewhat larger than those values expected for the “late” feed. The initially higher loading of sodium in the “early” feed gives rise to a lower percentage of sodium routed to bulk vitrification.

TABLE 5. Parameters for the projected streams from evaporation of the “early” feed to low activity and high activity remediation processes.

Porosity (%)	WAC	28	35	45
Bulk Vitrification Specifications				
Cs ¹³⁷ activity (Ci/L)	< 5.0E-02	1.16E-02	1.52E-02	2.18E-02
Na ⁺ Concentration (M)	5M	5.07	5.15	5.29
Na ⁺ Split	> 50% Na from input stream	57.02	58.91	62.53
WTP Feed				
[SO ₄ ⁻²] / [Na ⁺]	< 0.01	9.59E-04	9.59E-04	9.59E-04
TSR Corrosion				
[NO ₃ ⁻] > 3M ⁽¹⁾		3.97	3.97	3.97
[NO ₂ ⁻] + [OH ⁻] > 1.2(M)		6.50	6.50	6.50
⁽¹⁾ requirements for other nitrate loadings are available				

The results of the calculations for both the “late” and “early” waste feed streams indicate that a sufficient portion of the high activity aqueous phase can be accommodated in the separation units downstream from the evaporator. It is believed, but not definitively known at this time, that the porosities of the recrystallized salts will likely be less than 30% (based on previous work on salt cake wastes). If this is the case, the cesium inclusion in the trapped interstitial liquid would not seem to be of major concern.

In practice, it may also be necessary to wash the crystals. The initial results indicate that the process requirements can be achieved provided that the porosity of the solids is below 45%. The necessity of crystal washing will need to be determined by experimental measurements.

CONCLUSIONS

Durations as long as five months have been needed in order to attain thermodynamic equilibrium for the aluminum – phosphate system. Evaluation of projected streams for evaporative processing of dissolved HNF salt solutions has indicated that it will be possible to achieve some separation based on the fractional crystallization of specific solids. A main benefit of the process will be a large decrease in the sulfur to sodium ratio of the streams routed to the waste treatment plant.

WORK FORECAST

Most all of the aluminum – phosphate and aluminum – nitrate solubility samples have reached or are very close to equilibrium conditions. Analyses of these solutions are in progress and the results will be used to develop a new database specific to aluminum chemistry. Simulations on the pilot-scale salt cake dissolution experiments being

conducted at FIU are also in progress and will be continued into the next fiscal year.

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Flexible Scintillating Optical Fiber Sensor for Determination of Liquid Level

Dr. Shiquan Tao

INTRODUCTION

At the Hanford site, radioactive wastes have been stored in underground tanks since the 1940s. It is highly desirable to continuously monitor the moisture level within the tanks in order to optimize tank closure efforts. Previous periodic monitoring of the Hanford tanks has revealed a direct correlation between the Cs-137 level and the water level (as determined by neutron probe) within the tanks. Thus, the level of water within the Hanford tanks can be inferred by monitoring gamma-ray radiation from Cs-137.

Current methods of liquid level monitoring are cumbersome, and do not provide rapid feedback to the operator. On a monthly basis, a neutron probe is lowered into the tank to determine the neutron signature of the tank (assumed to provide a measure of the water level). After removal of the neutron probe, a gamma probe is inserted to determine the Cs-137 level as a function of height in the tank. These readings are then compared with previous readings to determine whether a change has occurred. During waste processing, this will be overly tedious and will not provide continuous real-time indication of water level.

Scintillating techniques have long been used to detect/monitor high-energy particles emitted from radioactive materials. Several classes of compounds, including inorganic salts (ZnS(Ag), NaI, etc.) and polyaromatic hydrocarbons (anthracene, stilbene, etc.), have been used to detect/monitor alpha, beta and gamma particles. These compounds emit electromagnetic radiation when exposed to high-energy particles. The emitted light can be coupled into a photodetector and detected. In conventional scintillating techniques, a large crystal of

the scintillating agent, which is expensive and hard to handle, is required. In this work, an optical fiber coated with a layer of silica doped with a scintillating agent will be used as a sensor. The silica coating will be produced by sol-gel techniques that will produce a waveguide that can monitor the depth of gamma-emitting Cs-137 within the waste tanks. It is currently envisioned that the sensor system will contain a bundle of such fibers, so that continuous feedback can be provided on gamma (and hence moisture level) with minimal operator action required.

WORK ACCOMPLISHED

Progress on this task will be reported at a later date.

Tank Leak Detection and Monitoring System

Dr. Chuji Wang

INTRODUCTION

Large volumes of hazardous liquids are stored underground tanks at DOE sites. Frequently, these tanks are found to leak, thereby resulting in not only a loss of stored inventory, but more importantly, contamination to soil and groundwater. During processing of the waste removal and treatment, there are two methods of detecting leakage from tanks: monitoring the liquid level of waste in the tanks and monitoring the soil under the tanks for leaks. Liquid level sensors can signal a leak but provide no information about the leak location or distribution of the resulting plume. Methods and technologies for tank waste leak detection, monitoring, and mitigation (LDMM) have been investigated about ten years. Various methods and techniques have been proposed for LDMM, which include the mass balance method, gamma and neutron moisture method, tracer gas method, bore hole seismic method, and electrical resistivity method. All of these methods have their significant limitations in real site applications (see **previous quarterly reports**). Cavity ringdown-based tank leak detection system (TLPS) is proposed as an alternative approach for tank LDMM.

WORK ACCOMPLISHED

Progress on this task will be reported at a later date.

Disposition of Idaho HLW Calcine

Support for the INEEL Calcine Disposition Project

*Dr. W. G. Ramsey
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INTRODUCTION

The proposed DIAL work will assist the Calcine Disposition Project to develop a stabilized form for the high-level radioactive calcine waste stored at the Idaho National Engineering and Environmental Laboratory (INEEL).

About 4400 m³ of mixed high-level radioactive calcine waste is stored in Calcine Solids Storage Facilities at the INEEL. The Calcine Disposition Project is developing process designs for retrieval, stabilization, and packaging of the calcine, with full-scale hot start-up of these processes planned for 2019. The Calcine Disposition Project baseline assumption is that the calcine can be removed from the haz-

ardous waste category via regulatory negotiations and/or by developing a stabilized calcine waste form, which would meet the toxicity characteristics leaching procedure (TCLP).

Based on current guidance from DOE/HQ, stabilization via vitrification is not an option. The preferred option is to package the calcine as is or to use a stabilization method other than vitrification.

The DIAL effort will yield the data necessary for INEEL researchers to evaluate three waste forms produced via three different stabilization methods versus the appropriate repository waste acceptance standards. Potential candidate stabilization methods for consideration include, but are not limited to, polystyrene encapsulation, Sn encapsulation, grout, and phosphate ceramics. Waste form properties will be researched and documented, and the ability of each waste form to comply with the waste acceptance production specifications (WAPS) will be evaluated. If it is determined that a waste form cannot be tested by a WAPS criteria - specifically, if a waste form's physical or chemical properties are incompatible with a particular test method - this will be denoted with appropriate documentation.

INEEL will provide the stabilization lead role for the down-select process and the decision authority for waste form production and testing. The INEEL Calcine Disposition Project will collaborate with DIAL by providing calcine simulants, down-selecting the three alternatives for testing, drafting an outline of the test plan and performance specifications, observing tests, reviewing test data and results, reviewing traceability of data and documentation, and co-approving documentation leading to the down-selection of a preferred stabilization alternative for hot testing.

The DIAL data will be considered an integral and traceable part of the Calcine Disposition Project that can be used to verify the preferred stabilization method via the quality assurance requirements of DOE/RW-0333P.

DIAL will be responsible for waste form production, data collection, and application of a quality program for data and document acceptability. DIAL will develop a cold bench test plan with procedures, test matrix, and performance objectives for making and testing stabilized calcine waste forms. For each of the three alternatives a small set of waste forms to evaluate bounding conditions (e.g., RCRA metals content, waste loading, calcine type) is the expected test matrix. The performance of the stabilized waste forms with regards to meeting the TCLP test and PCT will be compared to that of the raw calcine to show the improvement due to the stabilization treatment. It is anticipated that a successful effort will lead to additional work, including pilot testing and formal acceptance protocol evaluations.

WORK ACCOMPLISHED

Progress on this task was reported to the Idaho National Engineering and Environmental Laboratory (INEEL) in a report entitled *DIAL/MSU Development of Stabilizers for High Level Waste Calcine*.¹⁶

REFERENCE

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TASK 4

Support of SRS Salt Disposition and Other SRS Alternatives

**Support of SRS Salt Disposition and Other SRS
Alternatives**

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Dr. Laura T. Smith
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INTRODUCTION

Previous DIAL efforts have focused on the salt cake waste contained within the Hanford single-shell tanks. Work centered on the evaluation, application, and improvement of the Environmental Simulation Program (ESP).¹⁷ This effort involved comparing the data called by the software with other thermodynamic compilations, contrasting model predictions with those of other programs, and determining discrepancies predicted by the model when evaluated against salt cake dissolution experiments on tank core samples. The work was extended to include solubility studies on specific systems and the

subsequent development of a database specific to double salts chemistry.

The purpose of the present program is to investigate alternatives for processing the salt waste at the Savannah River Site (SRS). Salt cakes at SRS share many similarities to the Hanford waste. Specifically tanks at both facilities contain large amounts of nitrate, nitrite, carbonate, and aluminum. As opposed to Hanford salt; however, the SRS waste contains only small amounts of fluoride. Average SRS phosphate loadings are also well below those at Hanford. These differences tend to severely impact Hanford salt cake dissolution through the formation of a number of hard to dissolve or otherwise problematic solids, such as $\text{Na}_7\text{F}(\text{PO}_4)_2 \cdot 19\text{H}_2\text{O}$, Na_3FSO_4 , and $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O} \cdot 0.25\text{NaOH}$.¹⁸

Thus, significant portions of the previous work with the ESP model are directly applicable to processes under investigation at SRS. Additional site constraints must also be considered with respect to the routing and eventual disposition of dissolved salt streams. Engineers at SRS have initiated the Low-Curie Salt Process.¹⁹ This process is aimed at initially retrieving the high cesium loaded interstitial liquor within the salt matrix, followed by the addition of diluent. Dissolution is then allowed to proceed followed by retrieval of the resulting supernatant. The process is commonly referred to as drain, add, sit, and remove (DASR).

Extraction of the cesium in this way is expected to result in a coarse separation that will allow the interstitial liquid to be processed as high activity waste and the resulting dissolved salt stream to be routed to the SRS Saltstone (grouting) facility.

A number of potential factors can influence the proposed concept. First, the total volume of the original salt cake liquor removed must be sufficient such that the dissolved salt stream does not achieve activities that exceed the acceptance criteria for waste sent to the Salt-

stone facility.²⁰ Similar comments apply to the sodium loading of the resulting stream. Second, the ability to successfully grout the waste will depend on the solids loading in the feed stream. Inadvertent solids formation, either within a staging tank or in transfer piping can have serious repercussions on the eventual retrieval and transfer of the waste. Previous salt cake dissolution work has shown that solids re-precipitation can occur when different dissolution fractions are mixed together.²¹ The propensity for additional solids precipitation, should other streams be considered within the total process, is not known, but is likely to depend on the composition, ionic strength, and volume of the streams being mixed.

Previous column dissolution experiments in these laboratories have revealed that solid re-precipitation can occur on top of the actual salt matrix.²² For the experiment cited it was found that gibbsite ($\text{Al}(\text{OH})_3$) formed a layer upon the addition of water to a Hanford salt cake simulant. The use of 1 or 3-m NaOH as the diluent did not result in gibbsite formation. The impact on the dissolution process with water was noted as an increase, by a factor of three, in the time needed to complete the experiment. This implied that a significant change occurred in the permeability of the salt matrix. Recovery from such an event occurring within an actual waste tank is expected to be difficult and expensive.

In 1999, the SRS 242-16H evaporator became completely inoperable due to aluminosilicate ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) scale deposits. In addition to the scale deposits, an insoluble sodium diuranate ($\text{Na}_2\text{U}_2\text{O}_7$) had accumulated on top of the scale thereby becoming a criticality hazard. A property database was modified to include several sodium aluminosilicates and NASgel solubilities in high caustic and high sodium molarities.²³ Evaluation and comparison of this database using ESP is of interest for potential use in evaporator processes. This database enhancement would be updated using current literature values on the solubilities of the NAS compounds located within the

NAS database and also include other NAS compounds of interest that may predict co-precipitation of the insoluble uranium compounds.

The SRS FY 2003/4 work at DIAL involves a stepwise investigation of DASR, along with model calculations and experimental studies aimed at understanding downstream solids precipitation and the potential for gibbsite lenses to form within the SRS tanks and evaluation of the sodium aluminosilicate (NAS) database for potential use in evaporator processes. The work is divided into two tasks that are briefly described below and serve as a framework for the Work Accomplished/Results section of these reports.

Task 1. Improved, Selective Salt-Cake Dissolution Technologies

A number of experiments have been conducted on simulated salt cakes in these labs. In addition, recent dissolution experiments conducted at SRTC have indicated a somewhat wider variability in waste composition than was expected. It is not known, *a priori*, if the porosities and permeabilities of revised surrogates will be similar to, or radically different from, the simulants already examined. One case in point is the silicon concentration within tank 37H, which was noted as greater than 1000x the loading found in SRS tank 31H. Additional determinations of the physical properties of the salt cakes are necessary in connection with the DASR process and to assess if other dissolution options, such as sluicing, will be required. Flow through and DASR column experiments will be conducted on simulated salt cakes for SRS tanks 38H, and 37H. Dissolved salt streams will be examined for solids re-precipitation and the waste dilutions necessary to satisfy both saltstone and corrosion waste acceptance criteria will be established.

Task 2. Database Development

Previous solid-liquid equilibria calculations for SRS waste evaporator operation have relied on the Geochemists Workbench program.

Upgrading the ESP software with an associated NAS database would enhance the value of the code and permit the seamless evaluation of process operations within the tank farms. This sub-task will obtain all of the necessary thermodynamic data and then develop the database. Fitting will be performed based on the existing Bromley formalism employed in ESP and fit quality will be assessed based on residuals and standard deviation errors. Previous simulations performed will be compared to the revised ESP calculations. The product database will be delivered to the customer in the form of a letter report citing the data used and the results of the regression analyses.

WORK ACCOMPLISHED

Progress on this task will be reported at a later date.

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On-line Analysis for the Defense Waste Processing Facility

Dr. Jagdish P. Singh
Fang-Yu Yueh

INTRODUCTION

Direct analysis of dried sludge or glass in shielded cell facilities will significantly increase the analytical throughput and reduce waste generation in radiological analytical facilities. In this subtask, we will evaluate the feasibility of using laser-induced breakdown spectroscopy (LIBS) as an analytical tool for reducing waste and turnaround time for the defense waste processing facility (DWPF). For improved, on-line waste loading determination, we can use the LIBS on-line real-time capability to determine the ratio of Li to Fe from the pour stream.

LIBS uses a high pulse energy laser beam to produce a micro plasma to vaporize, dissociate, excite or ionize species on material surfaces. The study of the atomic emission from the micro plasma provides information about the composition of the material. LIBS is a powerful analytical tool which is suitable for quick and on-line elemental analysis of any phase of material.²⁴⁻²⁶ 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 5 - 10% or better for minor elements in solid samples.

WORK PERFORMED

To obtain the calibration data for the glass samples, four glass samples with different Li-to-Fe ratios (i.e. $[\text{Li}_2\text{CO}_3/\text{Fe}_2\text{O}_3] = 0.5, 1.2, 1.8, 2.5$) were made. Some technical problems with making the glass samples from our furnace system were initially encountered but

solved after a few tests to determine the optimum experimental parameters. We have recorded LIBS data with those glass samples under different experimental setups. The data recorded under different laser energies and gate delay times were analyzed with different Li and Fe analyte lines. We found that the higher laser energy and longer gate delay time results in a serious saturation effect for high Li/Fe ratio. Also, we only need half of the laser energy used in pellet sample measurement for glass measurement to achieve the same detection sensitivity as with the pellet sample. The data recorded with 12.5 mJ and 1-microsecond gate delay time shows a linear calibration for many pairs of the Li and Fe lines. Among all the tested Li and Fe lines, we found that Li 610.4 nm and Fe 430.08 nm gives best relative precision (better than 7%) from all four glass samples. The lens to sample distance (LTSD) is another important parameter which can affect LIBS measurement accuracy. Figure 7 shows the spectral shape of Li 610.4-nm line obtained with different LTSD. It clearly shows the spectral shape of Li 610.4-nm line suffered from self-absorption for LTSD close to the focal length of the lens. Table 6 shows the calculated relative standard deviation for two Li/Fe pairs. The best precision was found from the data recorded with the focus point at 1 mm inside the glass surface.

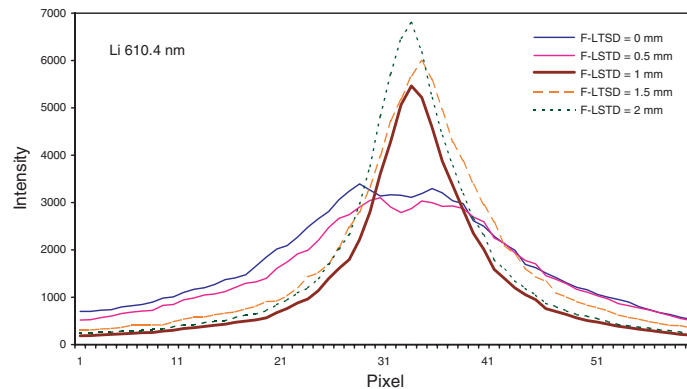


FIGURE 7. Spectral line shape of Li 610

TABLE 6. The reproducibility of glass measurement at different lens-to-sample distances.

F - LSTD (mm)	Li 610.4 nm/ Fe430.08 nm	Li 323.3 nm/ Fe 430.08 nm
2	0.34	0.46
1.5	0.12	0.10
1	0.02	0.10
0.5	0.08	0.07
0	0.09	0.15

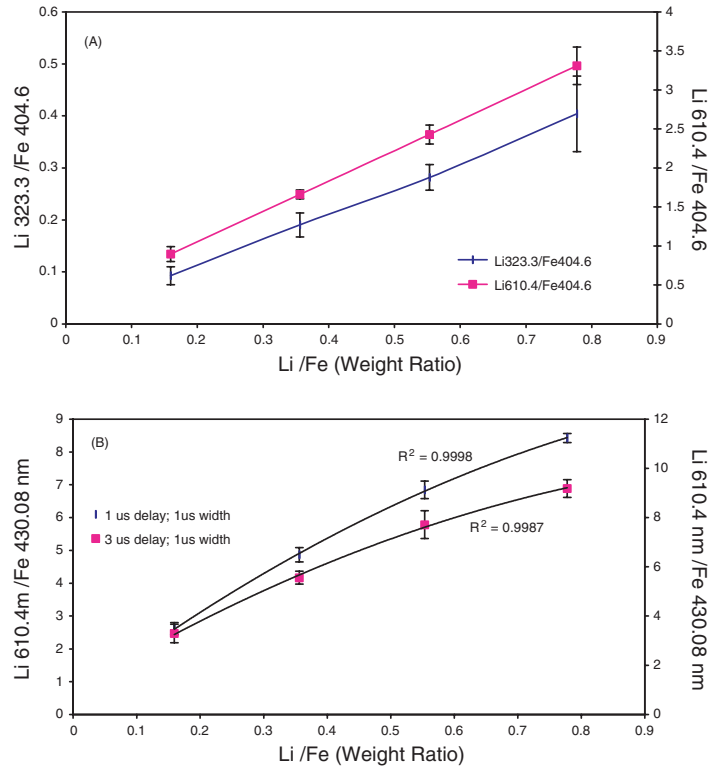


FIGURE 8. Calibration curve for Li/Fe in glass sample: (A) calibration data for two Li lines (610.4 and Li 323.3 nm) recorded with 1- μ m delay and 10- μ m gate width; (B) calibration data for Li 610.4-nm line recorded with 1- μ m and 3- μ m gate delay times and 10- μ m gate width.

The calibration data for glass were then collected using 12.5 mJ laser energy; the laser was focused 1 mm inside the glass surface. We have recorded the data with both 1- μ s and 3- μ s gate delays and 10- μ s gate width. Figure 8A shows the calibration curve for Li 610.4 nm/Fe 404.6 nm and Li 323.3 nm/Fe 404.6 nm recorded with 1- μ s gate delay. The calibration curves plotted for two delay times for Li 610.4 nm/Fe 404.6 nm are shown in Figure 8B. It shows that the calibration curve obtained using 1- μ s delay and 10- μ s gate width gives better detection precision than with 3- μ s delay and 10- μ s gate width.

The detailed analysis also shows that the RSTD of the LIBS glass measurement is better than 6% for all the major elements. The analytical figures of merit of the pellet and glass measurement based on the calibration data recorded at its optimum condition were compared and shown in Table 7. The LIBS measurement of glass and pellet samples give comparable accuracy and precision.

TABLE 7. Comparison of the accuracy and precision of LIBS measurement of pellet and glass samples.

Composition Ratio [Li ₂ CO ₃ /Fe ₂ O ₃]	Pellet		Glass	
	RA	RSTD	RA	RSTD
0.5	0.09	0.11	0.08	0.07
1.2	0.03	0.02	0.02	0.04
1.8	0.06	0.02	0.03	0.04
2.5	0.03	0.05	0.04	0.02

The initial investigation of sludge samples has started, and various experimental geometries are being tested to obtain the proper signal level of the analytical lines of interest.

WORK FORECAST

The study of the sludge samples from DWPF will continue. A sampling system for the sludge sample will be designed.

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HEPA Filter Performance Assurance

Regenerable HEPA Filter Performance Testing

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INTRODUCTION

The DOE currently employs HEPA filters in a variety of applications that range from particulate matter removal from ventilation air to treatment of off-gases from storage or treatment of mixed wastes. All of the applications are subject to permitting under the clean air act. It is clear that the PM emission rate downstream of these filters is extremely low, however, inability to demonstrate filtering efficiency on an ongoing basis causes variability in operating conditions for HEPA filters to come under heightened scrutiny. This is particularly true in applications where challenge conditions are not ideal for filter

life or performance such as exposure to moisture, excessive heat, or high loading rates.

Expediting processes involved in cleanup and closure of sites often produces challenge conditions capable of blinding HEPA filters within a matter of days. Operating experience at DOE facilities indicates that the HEPA filters must be changed out on a significantly more frequent basis when waste processing rates are increased, tanks are mixed, etc. Frequent changing of filters in operating processes is expensive in terms of filters, manpower, and disposal costs. In instances where there are redundant banks of HEPA filters, changing out units is even more problematic.

Public acceptance of metal or ceramic HEPA filters used in DOE facilities dated May 1999 identifies five areas of concern because of their potential for inducing failure:

- high particulate loading from smoke,
- excessive heat,
- wetting,
- filter strength from factors such as aging or shelf life, and
- air leaks.

A national technical working group (TWG) provided oversight guidance for development of a test plan to evaluate mass emission rates of PM downstream of HEPA filters. This test plan was the subject of two ASME Type II peer reviews and DIAL scientists and engineers are currently in the process of completing the activities outlined in this plan.

The current testing consists of three areas of activity:

- calibration of test stands and measurement instrumentation and establishment of standard testing conditions;
- evaluation of the PM emission rates as HEPA filters are challenged to failure by moisture, heat, seal deformation, smoke, and pin holes/tears in the filter media; and
- evaluation of the PM emission rates as the nature of challenge conditions changes. The full scope of work described in the test plan is to be completed by the end of the fiscal year (November 2003).

Work proposed for the coming fiscal year will provide necessary information to decide the utility of metallic or ceramic cleanable HEPA filters in a variety of DOE applications. Additionally, a more functional method of measuring emissions for HEPA filtered processes will be finalized.

WORK ACCOMPLISHED

A variety of testing was completed during the third quarter of 2004. This testing included challenging filters manufactured by the Ceramem Corporation and Porvair. Preparation work for a presentation and two posters was completed. The title of the presentation was "Evaluation of Emissions from HEPA Filters as a Function of Challenge Conditions." The posters were titled "Design and Evaluation of a Large Scale Particle Generator for DIAL HEPA Filter Facility" and "A HEPA Filter/Diagnostics Test Facility at DIAL-MSU. The presentation and posters will be presented at the American Association for Aerosol Research 2004 Conference in Atlanta, Georgia. Preliminary work on a soot inhalation project was also completed.

The filter penetration tests were completed and testing with a variety of cleanable filters was initiated. The first cleanable filters

tested were ceramic filters with a membrane coating manufactured by CeraMem Corporation. These filters were challenged with potassium chloride (KCl) and ferric oxide (Fe_2O_3). The two sizes of these filters tested were 3 x 3 (15-centimeters length) and 4 x 4 (1-inch length).

The 3 x 3 refers to three openings by three openings on the ends and likewise for the 4 x 4. The test plan for the 3 x 3 filters consisted of loading and washing alternately three times. This was done for two filters. One 3 x 3 filter was washed with a dilute acid solution of 0.016 M HNO_3 and 0.012 M HCl with a pH of 1.64. The second 3 x 3 filter was washed with a concentrated acid solution of 10% HNO_3 with a pH of 0.14. Both of these filters were challenged with ferric oxide (Fe^{+3}). Both these filters were cut and examined using the scanning electron microscope (SEM) on the campus of Mississippi State University.

The test plan for the 4 x 4 filters consisted of loading and washing once. DIAL tested four 4 x 4 filters. One filter was challenged with KCl, but not washed. This filter was cut and examined by the SEM. Another 4 x 4 filter was challenged with ferric oxide, but not washed. This filter was then cut and examined by the SEM. The final two 4 x 4 filters were loaded with ferric oxide and washed once. One 4 x 4 was washed with a dilute acid solution of 0.016 M HNO_3 and 0.012 M HCl with a pH of 1.64. The second 3 x 3 filter was washed with a concentrated acid solution of 10% HNO_3 with a pH of 0.14. These two filters were cut and examined by SEM also.

The second type of cleanable filter tested was the Porvair cleanable filter. The Porvair cleanable filter is a sintered metal filter. These filters were challenged with both potassium chloride and iron aerosols. The Porvair filters are 47-mm diameter. The potassium chloride (KCl) used testing was 30% by weight KCl dissolved in de-ionized water. The iron aerosol was 30% by weight FeSO_4 solution dissolved in de-ionized water. The Porvair filters were washed with acid and loaded with particulate alternately three times each. Method 5i mea-

surements were performed during testing also. These filters were loaded at low relative humidity and high relative humidity in the HEPA filter test stand. These filters loaded much more slowly at high relative humidity (55 - 60%) than at low relative humidity. Another way of stating this is that the differential pressure on the filters increased much more slowly at high relative humidity.

The HEPA team focused on a joint project with the Department of Biological Sciences involving soot inhalation by rats as well. A Lexan enclosure, 2 x 1.5 x 3 feet, was constructed to house the animal cages. Because the target particle size distribution included only smaller, respirable particles, several cyclones were built to collect the larger particles before introduction into the cage. The two cyclones made for the project were reproductions of cyclones III and V from the SRI 5-stage cyclone sampler. These cyclones have cut-points of 2 and 0.3 micrometers, respectively, for particles with a specific gravity of two at a flow rate of 1 cfm. Test runs were conducted with soot and potassium chloride (KCl) to verify the operation of the cyclones.

The dilution system used to reduce the number concentration was also developed. The first approach was to construct an educator that would be placed immediately before the cyclones, but the back pressure on the cyclones diminished the suction to unworkable levels. Instead, two Dekati ejector diluters (intended for use with the ELPI) will be allowed to aspirate from the soot-laden air exiting the cyclones. These diluters should reduce the concentration by a factor of approximately 100; make-up air will be added to the output until the intended flow rate through the cage (about 100 L/min) is achieved.