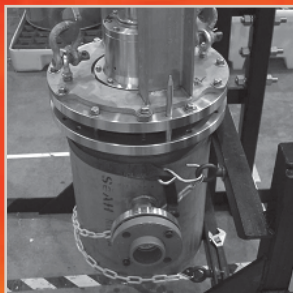


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Waste Processing Annual Technology Development Report 2007



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United States Department of Energy Waste Processing Annual Technology Development Report 2007

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TABLE OF CONTENTS

TABLE OF CONTENTS.....	2
LIST OF ACRONYMS AND ABBREVIATIONS	3
INTRODUCTION	5
1.1 IMPROVED WASTE STORAGE TECHNOLOGY	7
Chemical Process Alternatives for Radioactive Waste.....	7
In-Tank Characterization for Closure of Hanford Waste Tanks.....	11
Process Chemistry and Operations Planning for Hanford Waste Alternatives.....	13
HEPA and Regenerable Filter Performance Assurance.....	15
Demonstration Of A Fluidic Pipeline Unblocking System.....	18
1.2 RELIABLE AND EFFICIENT WASTE RETRIEVAL TECHNOLOGIES	20
Alternative Enhanced Chemical (Oxalic Acid) Cleaning of Waste Tanks.....	20
Design And Delivery Of A Fluidic Sampler For Tank 50 At The Savannah River Site	22
Design, Construction And Commissioning Of An Engineering Scale Test Tank Facility For Radioactive Waste Processing Facilities.....	24
1.3 ENHANCED TANK CLOSURE PROCESSES	26
Cementitious Barriers Partnership Project.....	26
Fluidic Jet Grouting Systems for Hanford 200 Series and Associated Tanks	28
Remediation Of Cooling Coils In Large Tanks	31
1.4 NEXT-GENERATION PRETREATMENT SOLUTIONS	34
Enhanced Monosodium Titanate	34
Hanford Medium/Low Curie Waste Pretreatment Alternative Project (Fractional Crystallization).....	37
Oxidative Leaching Studies	41
Development of Rotary Microfilter for Use at DOE Sites	43
Sludge Mass Reduction.....	45
Test Plan of Technology to Decompose Legacy Organics in Tank 48.....	48
Modeling and Experimental Support for High-Level SRS Salt Disposition Alternatives	51
Development of New Technologies for DOE Site Applications	53
Efficient Electrochemical Process to Recover Sodium from Radioactively Contaminated Alkaline Wastes.....	55
1.5 ENHANCED STABILIZATION TECHNOLOGIES.....	58
Fluidized Bed Steam Reforming (FBSR) Testing	58
Improved High Level Waste Glass Formulation	61
Test and Evaluate High Level Waste (HLW) Vitrification System Improvements 1 ..	64
Test and Evaluate High Level Waste (HLW) Vitrification System Improvements 2 ..	66
Enhanced LAW Glass Formulations	68
Support of the CH2M-WG Idaho Calcine Disposition Project	71
Process Improvements for the Defense Waste Processing Facility (DWPF): On-line Analysis.....	72
Process Improvements for the Defense Waste Processing Facility (DWPF): Melter Monitoring	74


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LIST OF ACRONYMS AND ABBREVIATIONS

C	Celsius
CBP	Cementitious Barriers Partnership
CEF	Cold Cap Evaluation Furnace
cpm	cycles per minute
CRADA	Cooperative Research and Development Agreement
CRESP	Consortium for Risk Evaluation with Stakeholder Participation
CSSX	Caustic-Side Solvent Extraction
CTC	Consolidated Tank Closure
CTF	Cold Test Facility
CUA	Catholic University of America
Cw-CRDS	continued wave-cavity ringdown spectroscopy
CY	calendar year
DNFSB	Defense Nuclear Facilities Safety Board
DOE	Department of Energy
DST	double shell tank
DWPF	Defense Waste Processing Facility
ECN	Energy Research Centre of The Netherlands
EM	Environmental Management
EMF	Electromotive Force
EPRR	Enhanced Processes for Radionuclide Removal
ESP	Environmental Simulation Program
FBSR	Fluidized Bed Steam Reforming
FC	Fractional Crystallization
FIU	Florida International University
fpm	feet per minute
ft	feet
FTP	Fourier transform profilometry
HEPA	high efficiency particulate air (filter)
HLW	high level waste
HM	high aluminum
HTWOS	Hanford Tank Waste Operations Simulator
ICET	Institute for Clean Energy Technology
INL	Idaho National Laboratory
LANS	large area NaSICON structures
LAW	low activity waste
LIBS	Laser Induced Breakdown Spectroscopy
LDRD	Laboratory Directed Research & Development
M	million
MOC	material-of-construction
MSE	Mixed Solvent Electrolyte
mMST	peroxide-modified monosodium titanate


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MST	monosodium titanate
MT	metric ton
NaSICON	Sodium Super Ionic Conductor membrane
NDAA	Ronald W. Reagan National Defense Authorization Act for Fiscal Year 2005
NIR	Near Infra Red
NIST	National Institute for Standards and Testing
NRC	US Nuclear Regulatory Commission
NVE	NuVision Engineering, Inc.
ORP	Office of River Protection
P-CRDS	compact plasma-cavity ringdown spectroscopy
PNNL	Pacific Northwest National Laboratory
ppt	parts per trillion
QA/QC	quality assurance/quality control
REDOX	REDuction/OXidation
RPP	River Protection Program
RTD	Remote Tool Deployment
SBW	Sodium-Bearing Waste
SLIM	Solid Liquid Interface Monitor
SME	Slurry Mix Evaporator
SNL	Sandia National Laboratory
SPF	Hanford Supplemental Pretreatment Facility
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
SV	stereovision
SWPF	Salt Waste Processing Facility
TCLP	Toxic Chemical Leach Procedure
TPB	tetraphenylborate
TRL	Technology Readiness Level
TTQAP	Task Technical and Quality Assurance Plan
VHT	Vapor Hydration Test
VMI	Virginia Military Institute
VOC	volatile organic compounds
VSL	Vitreous State Laboratory
VU	Vanderbilt University
WAO	Wet Air Oxidation
WG	Washington Group
WMT	Waste Management Technology
WSRC	Washington Savannah River Company
wt	weight
WTP	Hanford Tank Waste Treatment and Immobilization Plant

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INTRODUCTION

The Office of Environmental Management's (EM) Roadmap, *U.S. Department of Energy – Office of Environmental Management Engineering & Technology Roadmap* (Roadmap), defines the Department's intent to reduce the technical risk and uncertainty in its cleanup programs. The unique nature of many of the remaining facilities will require a strong and responsive engineering and technology program to improve worker and public safety, and reduce costs and environmental impacts while completing the cleanup program. The technical risks and uncertainties associated with cleanup program were identified through: 1) project risk assessments, 2) programmatic external technical reviews and technology readiness assessments, and 3) direct site input. In order to address these needs, the technical risks and uncertainties were compiled and divided into the program areas of: Waste Processing, Groundwater and Soil Remediation, and Deactivation and Decommissioning (D&D). Strategic initiatives were then developed within each program area to address the technical risks and uncertainties in that program area. These strategic initiatives were subsequently incorporated into the Roadmap, where they form the strategic framework of the EM Engineering & Technology Program.

The EM-21 Multi-Year Program Plan (MYPP) supports the goals and objectives of the Roadmap by providing direction for technology enhancement, development, and demonstrations that will lead to a reduction of technical uncertainties in EM waste processing activities. The current MYPP summarizes the strategic initiatives and the scope of the activities within each initiative that are proposed for the next five years (FY2008 – 2012) to improve safety and reduce costs and environmental impacts associated with waste processing; authorized budget levels will impact how much of the scope of activities can be executed, on a year-to-year basis.

As a result of the importance of reducing technical risk and uncertainty in the EM Waste Processing programs, EM-21 has focused considerable effort on identifying the key areas of risk in the Waste Processing programs. The resulting summary of technical risks and needs was captured in the Roadmap. The Roadmap identifies key Waste Processing initiative areas where technology development work should be focused. These areas are listed below, along with the Work Breakdown Structure (WBS) designation given to each initiative area. The WBS designations will be used throughout this document.

- Improved Waste Storage Technology (WBS 1.1)
 - Develop cost effective, real-time monitoring of tank integrity and waste volumes to ensure safe storage and maximum storage capacity.
 - Improve understanding of corrosion mechanisms and changing waste chemistry, including flammable gas generation, retention, release and behavior to establish appropriate assumptions in safety analyses.



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- Reliable and Efficient Waste Retrieval Technologies (WBS 1.2)
 - Develop optimization strategies and technologies for waste retrieval that lead to successful processing and tank closure.
 - Develop a suite of demonstrated cleaning technologies that can be readily deployed throughout the complex to achieve required levels of removal.
- Enhanced Tank Closure Processes (WBS 1.3)
 - Improve methods for characterization and stabilization of residual materials
 - Develop cost-effective and improved materials (e.g., grouts) and technologies to efficiently close complicated ancillary systems.
 - Perform integrated cleaning, closure, and capping demonstrations.
- Next-Generation Pretreatment Approaches (WBS 1.4)
 - Develop in- or at-tank separations solutions for varying tank compositions and configurations
 - Improve methods for separation to minimize the amount of waste processed as HLW.
- Enhanced Stabilization Technologies (WBS 1.5)
 - Develop next-generation stabilization technologies to facilitate improved operations and cost.
 - Develop advanced glass formulations that simultaneously maximize loading and throughput.
 - Develop supplemental treatment technologies.

This report compiles the technical progress on research and development activities associated with each of the MYPP Initiative areas that were completed during Calendar Year 2007. Reports from 28 technical tasks are included and represent significant accomplishments toward reducing the technical risk associated within the Waste Processing, EM-21, arena.

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1.1 IMPROVED WASTE STORAGE TECHNOLOGY

Chemical Process Alternatives for Radioactive Waste

Principal Investigator(s): David Roelant (FIU)

Collaborator(s): Erich Keszler (NVE)

Research Project Number: DE-FG01-05EW07033_1

Research Start Date: April 21, 2006 **Expected Research End Date:** February 2010

Research Objectives

This project supports the retrieval of high-level waste (HLW) from tanks at the Hanford and Savannah River sites. The project tasks focus on modeling based on data from pilot- and full-scale engineering studies on simulated wastes, and technology testing, evaluation and development to support critical issues related to HLW retrieval and processing. To accomplish these research objectives, four tasks were developed based on site needs:

- Unplugging Technology Qualification (Task 2) – qualify pipeline unplugging technologies for deployment at the DOE sites.
- Solid-Liquid Interface Monitor (Task 6) - design, develop, test, and deploy a solid-liquid interface monitor at Hanford.
- Mechanical & Chemical Cleaning of HLW Tanks (Task 7) - test & evaluate technologies for tank heel waste mobilization and retrieval from the HLW tanks.
- Engineering Studies of Innovative Technologies to Increase Tank Space (Task 8) - test & evaluate technologies and strategies that

directly impact limited waste storage space at Hanford.

Research Progress

In 2007 for Task 2, a test plan was developed in conjunction with engineers from Hanford and NuVision Engineering for the purpose of testing/qualifying NuVision's wave erosion technology. A heavily instrumented testbed was developed consisting of three testbed lengths; 285, 621 and 1797 ft. In addition, three types of plugs were developed for testing; kaolin clay, phosphate gel and aluminum gel. The kaolin clay plug has typical material properties of HLW at the sites and two chemical plugs are potential precipitates at the sites. A technology assessment of NuVision's wave erosion technology was performed on the three testbeds. The assessment showed that the technology is employing a water hammer technique as the primary mechanism for removal of the plug (Figure 1). Erosion rates were collected during the test trial. Additional analysis will continue into 2008.

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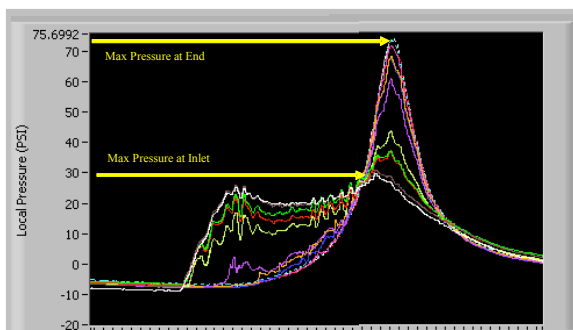


Figure 1. Amplification data from NuVision testing.

In 2007 for Task 6, The SLIM system was modified based on requirement changes by Hanford site personnel. A containment system was developed using a 48-foot tapered street pole and aluminum enclosure box. This allowed for the SLIM to be fully contained while parked inside the containment chamber. This pole required further structural analysis, which determined the need to increase the thickness of the enclosure box top plate and to add a vibration dampener to the system. In addition, support struts (Figure 2) were replaced with bridge jacks and a bellow, which placed all loads on the jacks and removed any from the tank riser.

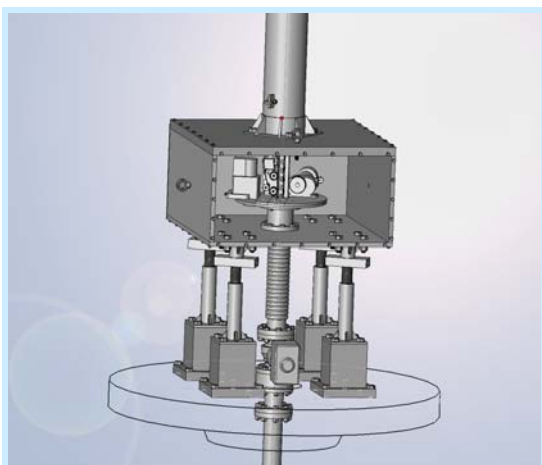


Figure 2. Front plate removed to show turntable and bolt pattern for support jacks.

Finally, due to a change in the site's tank riser availability, the SLIM system was moved from the original target riser to one that was below grade and provided a small concrete footing around the riser pit. This change required that a spacer be designed to be placed between the riser end and the ball valve. These changes finalized the design with the site and permitted initiation of fabrication and assembly of the enclosure component of the SLIM system. Completion of fabrication and in-house verification testing of SLIM will be complete near the end of Calendar Year 2008.

In 2007 for Task 7, experimental testing indicated that micro-hydrocyclones can enhance sludge removal due to their ability to separate fine simulant sludge particles of several microns in diameter from the main simulant waste stream. A significant increase in the insoluble solid content of the effluent underflow stream leaving the tank was achieved. This demonstrates the potential effectiveness of the new methodology in reducing the total volume of waste slurry being removed from waste tanks for the same amount of removed residual insoluble sludge. The findings also provide evidence of reduced necessary cleaning water to remove residual sludge from waste tanks.

For Task 8, FIU researchers are developing a 2-D axisymmetric numerical model of the tank to assist with the prediction of cesium (Cs) breakthrough curves in the resulting saltcake brine and to determine the displacement patterns of Cs. This predictive information is critical for scheduling and operational purposes.



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The concentration of cesium in the pumped liquid will follow elution patterns similar to the pilot-scale tall column saltcake tests performed during 2003-2005 at Florida International University. The 2-D axisymmetric model includes slow diffusion in a solid or stagnant pond, rapid transport in a void, and flow through pores in completely saturated and partial saturated media. Cs is a strong electrolyte, and it is assumed that advection and dispersion are the main two processes that affect its movement. The results of the selective dissolution model are analyzed and presented. During 2007, simulations showed that incremental addition (Figure 3) and drainage of the tank is more efficient compared to continuous addition of water and withdrawal of the salt solution. In order to remove 0.65 fractions of the total Cs, the continuous retrieval will use approximately 2.6 pore volumes of washing fluid, while the incremental retrieval will need 0.52 pore volumes of fluid to remove 0.59 fractions of the total Cs.

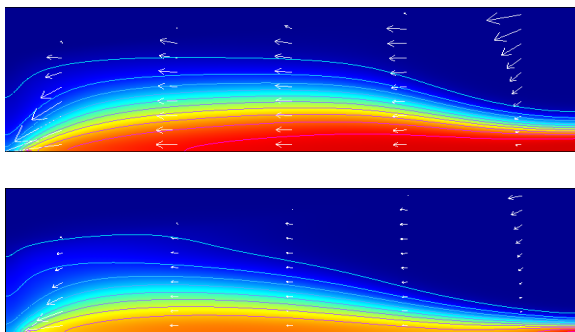


Figure 3. Distribution of Cs concentration within the tank after incremental retrieval at Resaturation-06 T= 7 days (top) and Resaturation-08 T= 7days (bottom).

Planned Activities

During the coming year, FIU-ARC engineers and researchers will work with HLW staff in the continuation of the several 2007 tasks, and in the execution of new proposed tasks. For Task 2, the project will look to prepare an in-depth technology assessment for the candidate pipeline unplugging technologies that Hanford is considering; specifically AIMMS technologies' Hydrokinetic system will be evaluated during 2008. Also, additional data analysis on the NuVision system will continue during the 2008 calendar year, culminating with a topical report on the research findings. These assessments will examine the fundamental principles at work, and parameters that can pipeline safety and system operation. The project will also execute the prototyping and verification testing of several tank waste monitoring systems for rapid deployment at the Hanford reservation. As a continuation of Task 6, the Solid Liquid Interface Monitor (SLIM) will undergo verification testing at FIU facilities during the fiscal year while potential deployment at Hanford in 2009 is planned. Also, a new Task 11 will evaluate the potential for an in-line weight percent solids monitor for waste transfer operations. The proposed system will undergo various test scenarios to determine its reliability for potential field deployment. Finally, as part of Task 8, the project will develop mathematical models to simulate alternative strategies for optimization of waste retrieval operations. The model developed will be expanded to simulate the possibility of using chemically unsaturated fluid for displacement of Cs



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and simultaneous dissolution of the saltcake. Task 7 has been completed during this calendar year.

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Weblinks

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1.1 IMPROVED WASTE STORAGE TECHNOLOGY

In-Tank Characterization for Closure of Hanford Waste Tanks

Principal Investigator(s): David L. Monts, Ping-Rey Jang, Yi Su (ICET)

Collaborator(s): Dennis Hamilton, Rick Raymond (CH2MHILL Hanford); Billie Mauss (DOE-ORP); Gary Josephson (PNNL)

Research Project Number: Task 2.1 ICET Cooperative Agreement DE-FC01-06EW-07040

Research Objectives

The goal of this project is to develop and deploy *in situ* quantitative imaging tools (based on Fourier transform profilometry, FTP, and stereovision, SV) for residual waste tank volume characterization at the Hanford Site to reduce uncertainties associated with closure activities. Systems developed are also applicable to other DOE sites, such as the Savannah River Site.

During 2007, the FTP effort conducted a multi-stage series of FTP performance evaluation tests under simulated Hanford waste tank conditions in order to document the accuracy, precision, and operational performance of FTP using blind testing techniques.

Future efforts include demonstration of a prototype FTP probe system initially at ICET and then at the Hanford Cold Test Facility (CTF).

Research Progress

During 2007, we successfully completed Stage 1 of a multi-stage series of Fourier transform profilometry (FTP) performance evaluation tests under simulated Hanford waste tank

conditions. These blind tests documented the accuracy, precision, and operational performance of FTP.

Successive stages impose increasing difficulty and increasingly more accurate approximations of in-tank environments.

Figure 1 shows the reconstruction of an object using the FTP system.

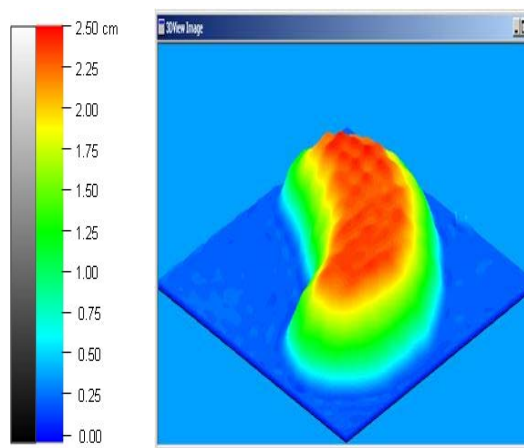


Figure 1. Reconstruction of Object Using the FTP System

An investigation of the dependence of FTP volume determination results on system operator found a relatively low dependence of results on personnel with varying levels of expertise. Good results



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were obtained even by previously inexperienced users.

The effect of prolonged gamma radiation exposure on the performance of FTP equipment was studied in order to understand how resulting image quality affects results.

The effect of higher camera resolution on FTP results was examined.

Planned Activities

A technical feasibility study is expected to be conducted during 2008.

During 2009, the multi-stage FTP performance evaluation testing will be completed, and a prototype FTP probe system will be demonstrated initially at ICET and then at the Hanford Cold Test Facility (CTF).

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1.1 IMPROVED WASTE STORAGE TECHNOLOGY

Process Chemistry and Operations Planning for Hanford Waste Alternatives

Principal Investigator(s): Jeff Lindner, Rebecca K. Toghiani, John Luthe (ICET)

Collaborator(s): Dennis Hamilton, Blain Barton, Randy Kirkbride (CH2MHill Hanford); Billie Mauss (DOE-ORP)

Research Project Number: Task 2.2 ICET Cooperative Agreement DE-FC01-06EW-07040

Research Objectives

Evaluation of the potential difficulties associated with meeting regulatory milestones for cleanup of the Hanford site tank wastes has indicated that tank farm operations are limited by the lack of available space in the double shell tank (DST) system. An overriding goal for the proposed work is to improve the understanding of the thermodynamics of waste components and to perform research on the possibility of associated models in support of Hanford waste alternatives. In this manner, models can be used to evaluate and develop process pretreatment and retrieval options. The use of validated models allows for reduced sampling and analytical costs.

Task 1 Research on Neural Networks: Efforts have been directed at evaluation of the applicability of a neural network model for use in the sites' Hanford Tank Waste Operations Simulator (HTWOS). Improvement of the chemistry representation, which currently relies on wash and leach factors, can be accomplished using a neural network.

Task 2 Aluminum Chemistry Evaluations: It is well-established that

gibbsite, $\text{Al}(\text{OH})_3$, is considerably more soluble than boehmite, AlOOH . The pretreatment and eventual retrieval of aluminum contained within the waste tanks will therefore depend on the form of the aluminum. Laboratory experiments were conducted to determine rate constants and the activation energy associated with the dehydration transition.

Task 3 Database Distribution and Development: Previous efforts have focused on the development of a double salt thermodynamic database that captured the properties of salt cake components. Following a number of version changes in the OLI Systems Inc Environmental Simulation Program (ESP) it was decided to transfer the database to OLI such that it would be available to future users while achieving the necessary QA/QC pedigree required by DOE facilities and site contractors.

Research Progress

Task 1 Research on Neural Networks focused on processing the data in the Hanford Best Basis Inventory to allow direct entry into the ESP software and on automating the software using the Perl



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computer language. Simulations associated with the retrieval of the wastes in the Hanford C-farm was initiated using two different (modified sluicing and mobile retrieval system) flowsheets.

Task 2 Aluminum Chemistry

Evaluations: Measurements of the transition of gibbsite to boehmite indicated that conversion occurs at temperatures as low as 100°C. Kinetic expressions were obtained and activation constant was determined. Correlation of these results with tank waste thermal histories is now possible allowing the tailoring of retrieval options for the insoluble boehmite.

Task 3 Database Distribution and Development:

A subcontract was issued to OLI Systems Inc. for incorporation of the ICET developed double salt database (V7DBLSLT) into the MSE formalism. The subcontract was completed and the database was recently released as part of the MSE Public Database allowing future use by site engineers and maintenance by OLI Systems Inc.

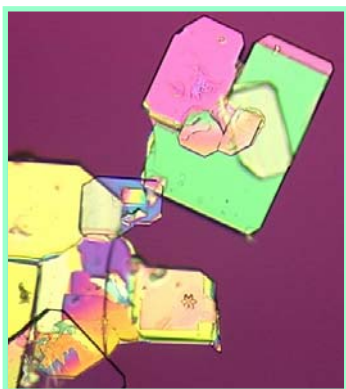


Figure 1. PLM Image of $\text{Na}_3\text{NO}_3\text{SO}_4$ Crystals

A polarized light microscope image of $\text{Na}_3\text{NO}_3\text{SO}_4$ crystals is shown in Figure

1, and the laboratory-scale saltcake dissolution experiment is shown in Figure 2.



Figure 2. Photograph of Laboratory Experiment

Planned Activities

Efforts are continuing on the development of the neural network for C-farm retrievals. The projected retrieval schedule has been obtained and ESP modeling continues. Automation of the ESP software is expected to allow for increased compositional coverage thereby resulting in more robust neural networks with improved predictions.

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1.1 IMPROVED WASTE STORAGE TECHNOLOGY

HEPA and Regenerable Filter Performance Assurance

Principal Investigator(s): Steven Alderman (ICET)

Collaborator(s): Duane Adamson (SRNL), Leader of AG-1 Section FI Working Group (High Efficiency Metal Media Filters); Jim Slawski, Editor of the Nuclear Air Cleaning Handbook; Jim Honeymann (CH2MHill Hanford); David Eaton (INEL); Pat Suggs (DOE-SR); Billie Mauss (DOE-ORP)

Research Project Number: Task 5.3 ICET Cooperative Agreement DE-FC01-06EW-07040

Research Objectives

The HEPA Filter Performance Assurance task provides data needed to address issues relating to the performance of high efficiency particulate air (HEPA) filters (Figure 1). Both the Defense Nuclear Facilities Safety Board and state regulators have questioned to what degree DOE can rely on the performance of HEPA filters to satisfy safety and regulatory controls in DOE facilities.

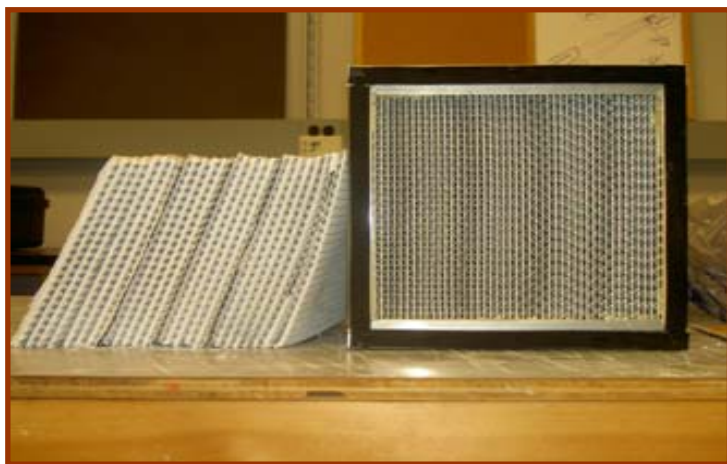


Figure 1. Photograph of HEPA Filter

The major objectives of this year's efforts were to: (1) complete the evaluation of effects of media velocity above 5 fpm on filter efficiency and most penetrating particle size for existing AG-1 HEPA filters, (2) develop engineering design data for new filtration systems with respect to loading rates as a function of media velocity and particle size distributions, and (3) assist in establishment of an AG-1 standard for metal media filters (Section FI of the AG-1 standard).

This activity has been a continuation of the previous year's efforts. Media velocity and lifetime studies were conducted with Camfil-Farr filters to compliment data for Flanders units. The proposed standard for metal media filters (Section FI) has been significantly revised twice during this year and has only one major issue remaining unresolved.

This set of activities has a cross-cutting impact on virtually all of DOE EM's activities. Potential impacts range from



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filters on glove boxes to waste tanks to waste processing units.

Research Progress

Media velocity and lifetime studies for Camfil-Farr filters, completed during the year, provided information useful to both AG-1 standard development and for incorporation into publications on design of new systems. The lifetime studies included media velocities ranging from less than 3 fpm to approximately 8 fpm in 1 fpm steps. This brackets the currently acceptable range of 4 to 5 fpm with sufficient additional data to draw conclusions on the effects of filtering efficiency, most penetrating particle size, and loading rates. Information gathered showed little effect of media velocity on most penetrating particle size or filtering efficiency. Differential pressures increase with an increase in media velocities tested, but remain within the Darcy regime.

Progress was made by the FI working group in development of a standard for metal media filters used in nuclear applications. This standard addresses filters used as prefilters, demisters, along with units with HEPA filter performance. Numerous DOE applications involve conditions outside the operating envelope of glass media HEPA filters because of temperature or humidity. Metal media filters, particularly sintered metal fiber media filters, have great utility in these applications. The only major issue that remains unresolved is the development of tables identifying typical sizes and performance characteristics for filters in different efficiency categories. Since

these units are currently specialty items, development of tables requires gaining a consensus among manufacturers that is requiring more effort than anticipated. It is hoped that a proposed standard will be ready for balloting before the end of 2008.

Planned Activities

A need exists to investigate how HEPA filters are affected by system upset conditions. A new series of investigations is being initiated to identify the range of upset conditions encountered by HEPA filters that would not automatically result in their replacement. This information will be used to develop a test plan to analytically evaluate lifetime performance of filters that have encountered excursions in humidity, temperature, sudden changes in differential pressure, and exposure to corrosive gases.

An additional set of activities will be undertaken this year to evaluate the patterns of buildup on the surface of filter media as a function of aerosol challenge conditions.

The testing to be conducted will require a larger test stand than the one currently operated by ICET. The existing test stand has been optimized to evaluate 1'x1'x1' filters and the next set of experiments will evaluate 2'x2'x1' units. Flow rates of the new stand will need to be increased to at least 2000 cfm.

References

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1.1 IMPROVED WASTE STORAGE TECHNOLOGY

Demonstration Of A Fluidic Pipeline Unblocking System

Principal Investigator(s): Erich Keszler, Laurie Judd (NVE)

Collaborator(s): FIU

Research Project Number: Hanford/Fluidic Pipeline Unblocking/01/V1

Start Date: Sept 2006

End Date: Ongoing

Research Objectives

Many of the DOE sites have processing facilities (such as the Waste Treatment Plant at Hanford) supplied by below-grade transfer lines that are susceptible to plugging during or between transfers due to a combination of factors including long line lengths, high solids content sludges, age, or cooling and crystallization.

The Initial scoping trials with the Fluidic Pipeline Unblocking System, which is pictured in Figure 1, have demonstrated the system's capability to provide a useful means of clearing blockages and obstructions that might limit transfer rates or transfer capability.

The purpose of this project is to design, build, and demonstrate the envelope of operation of a Fluidic Pipeline Unblocking system for the removal of pipeline blockages that may occur in the Hanford 200E/W cross site transfer line. The intention is to provide the end users with sufficient understanding and data to suitably envelope the operating characteristics of the system such that it could be confidently and rapidly deployed on site. The successful demonstration of a pipeline unblocking system is beneficial to all DOE sites

utilizing cross site transfer lines by offering an alternative blockage removal technique.



Figure 1. Fluidic Pipeline Unblocking System.



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Research Progress

NuVision Engineering designed, built and deployed the Field Test Prototype Unit at Florida International University (FIU) pictured in Figure 2. Field tests of the prototype unit were conducted in September and October of 2007 at FIU.



Figure 2. Pipeline Unblocking system (FIU field testing)

FIU constructed an outdoor, above ground pipeline (visible at left in Figure 2) as a test bed for this technology evaluation. The instrumented test bed was designed and constructed with the capability to evaluate the impact of a number of parameters on the technology effectiveness, including the distance to the plug; pipe layout (e.g. bends, expansions, reducers, etc.); and connection with limited accessibility (through a Hanford connector inside a pit).

Testing was conducted using 3 test bed lengths. The test bed lengths were selected based on the idea that testing

parameters (i.e., unplugging time, erosion rates, etc.) obtained at three different lengths could be used to predict the parameter at lengths up to 19,000 ft. The pressure and wave data from the testing was collected and is currently being analyzed at FIU and will be instrumental in assessing the technology and future work. However, initial indications are positive and it is likely that this approach will transition to a hot demonstration/deployment in either 2009 or 2010

Planned Activities

For 2008, NuVision Engineering Inc. plans to review the FIU report regarding 2007 work and assess the performance and identify any technical areas that need further development. NVE also plans on conducting a modified (abbreviated) technology maturity assessment to establish a current state and help establish a path forward for this technology. Any areas identified by the FIU report that indicate further development or testing work will be assessed and addressed in the 2008 scope of work. This scope will also consist of further development and testing to address any technical obstacles, with a goal of creating a field deployable system in 2009 / 2010.

References

Interim Reports are available upon request.



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1.2 RELIABLE AND EFFICIENT WASTE RETRIEVAL TECHNOLOGIES

Alternative Enhanced Chemical (Oxalic Acid) Cleaning of Waste Tanks

Principal Investigator(s): William D. King (SRNL)

Collaborator(s): Dan McCabe (SRNL)

Research Objectives

A test program will be conducted to identify alternatives to the baseline 8 wt. % oxalic acid chemical cleaning technology for sludge heel removal from Savannah River Site waste tanks and further understanding of the chemistry involved with the most promising tank cleaning methods.

As depicted in Figure 1, the EM-21 test plan takes a two-pronged approach: 1) identify, evaluate, and develop Alternative Enhanced Chemical Cleaning technologies, and 2) advance development and basic understanding of oxalic acid based technologies.

Due to changes in the requirements and expectations for tank chemical cleaning methods, there is a need to reevaluate the available technologies for sludge heel removal. The technologies considered in item #1 may include evaluation of acids other than oxalic as well as oxalic acid-based technologies not yet studied. The most promising technologies identified will be tested through scoping and optimization studies. Since oxalic acid based methods are currently the primary methods being utilized and considered for sludge heel removal, better basic understanding of the interactions of this acid with sludge materials and tank components is needed. The specific areas needing further study for oxalic

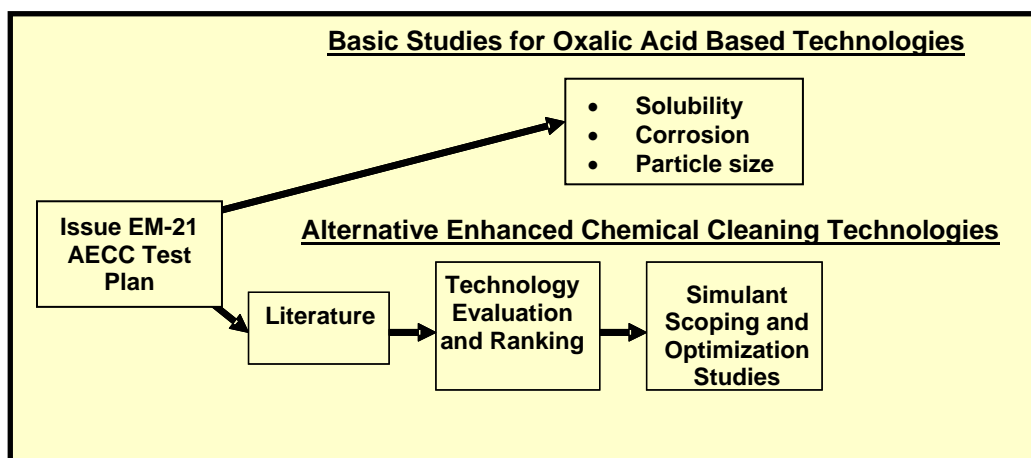


Figure 1. Task Plan Summary showing parallel paths for basic studies of OA based technologies and evaluations of AECC technologies.



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acid based technologies include criticality safety (solubility) and understanding of corrosion rates. This work will benefit the tank closure program for tanks not meeting current containment standards.

Research Progress

The Task Technical and Quality Assurance Plan for the Enhanced Chemical Cleaning program was drafted in 2007.

Planned Activities

Alternative Enhanced Chemical Cleaning technologies will be identified through literature reviews. The technologies will be evaluated and ranked and a select group will be chosen for study. Scoping studies will be conducted which will include simple solubility tests and limited evaluations of cleaning agent destruction methods. As needed, additional optimization tests and possibly corrosion tests will be conducted for the most promising technologies.

Test plans to advance basic understanding of the oxalic acid based technologies will include simulant solubility tests and corrosion evaluations varying the oxalic acid concentration and the temperature. The duration of the test program is approximately one year with key stages including the ranking and selection of alternative technologies for study and the identification of the most promising technologies based on the results. A report summarizing the results of basic oxalic acid and scoping and optimization studies and identifying

the most promising alternative technologies will be issued.

Planned activities for 2008 are outlined below:

Common Activities for Each Program Part

- Issue Task Plan*
- Write Report

Alternative Enhanced Chemical Cleaning Technologies

- Complete Literature Review**
- Evaluate/Rank Alternatives
- Conduct Modeling**
- Develop Final Testing Plans and Complete Hazards Analysis
- Conduct Scoping/Solubility Tests
- Complete Corrosion Evaluations
- Conduct Optimization Studies

Basic Studies of Oxalic Acid Based Technologies

- Conduct Modeling**
- Develop Final Testing Plans and Complete Hazards Analysis**
- Conduct Simulant Solubility and Corrosion Tests.

* indicates activities completed as of publication date

** indicates activities in progress

References

1. W. D. King, "Task Technical and Quality Assurance Plan for EM-21 Enhanced Chemical Cleaning Studies for Sludge Heel Removal," WSRC-RP-2008-00613, Rev. 0, May 2008.



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1.2 RELIABLE AND EFFICIENT WASTE RETRIEVAL TECHNOLOGIES

Design And Delivery Of A Fluidic Sampler For Tank 50 At The Savannah River Site

Principal Investigator(s): Erich Keszler, Laurie Judd, NuVision (NVE)

Collaborator(s): SRS and SRNL

Research Project Number: SRS/Samplers /01/v2

Start Date: July 2007

End Date: Ongoing

Research Objectives

At Savannah River and Hanford waste material is batched into large storage tanks prior to transfer to a treatment facility. The waste is collected, mixed, and sampled to ensure that it is within the acceptable predetermined envelope for the particular treatment plant. Once the sampling results have been confirmed by the site contractor, a small volume of the waste is transferred from the million gallon tank to the smaller treatment facility storage tanks where the waste is again mixed and sampled to ensure conformance with the process requirements. If the waste is found to be outside the acceptable envelope then it must be transferred back to the million gallon tank for conditioning, potentially causing the treatment facility to stop processing waste temporarily.

Sampling of high level waste tanks at DOE sites has traditionally been conducted by mixing the tanks for a long period, switching off the mixer pump nearest the sampling location, opening a tank riser, and manually collecting a sample from one location. This

technique has the inherent problem that once the mixer pump is switched off the material in the tank will start to settle or stratify and the sample from the one location may not be truly representative of all the tank contents.

NuVision Engineering has successfully developed and deployed Fluidic Single Point Samplers to collect samples of waste from High Level Waste Tanks in Nuclear Process Plants in the UK. The sampler design (Figure 1) has a number of distinct advantages over the baseline sampling method. The sampler is installed into the tank through available risers and becomes a permanent tank feature with no moving parts in the tank, consequently requiring no maintenance of the in-tank assembly. The dose to operators is negligible during sampling of the tank and the mixer pumps can be left running during the sampling operation.

Both Savannah River and Hanford have expressed an interest in the fluidic sampler to reduce the technical uncertainties and risk associated with



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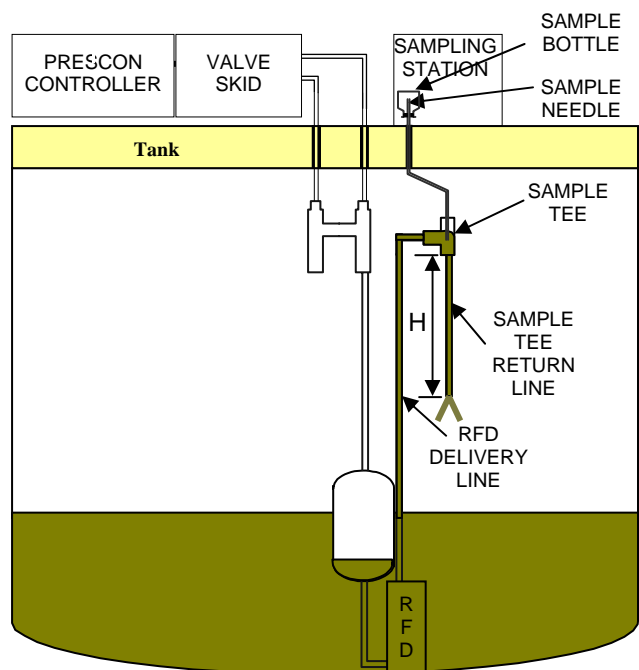


Figure 1. Schematic of Tank 50 Sampling System.

are working jointly on developing a technical specification that will allow progression into detailed design.

Planned Activities

NVE will continue to work with SRS to continue development of the technical specification, approval of current in-tank module design, and addressing any questions or concerns to this point. A 3-D animated version of the sample station will be presented to site in early July, 2008 for their approval. Detailed Design will begin after site approval. Fabrication and delivery will follow in late 2008 / early 2009.

high-level waste sampling. This project will start a phased approach to the design and fabrication of a unit for tank 50 at Savannah River.

Research Progress

Preliminary conceptual design of the sampling system is well advanced (90+% complete). Lessons learned from the previous sampler designs developed for SRS have been collected from site and will be incorporated into the current design. A revised conceptual design has been developed for the sample station, based on site feedback.

Dialogue has continued with the site to determine their requirements in terms of sample size, frequency and bottle materials. A list of technical questions has been developed and SRS and NVE



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1.2 RELIABLE AND EFFICIENT WASTE RETRIEVAL TECHNOLOGIES

Design, Construction And Commissioning Of An Engineering Scale Test Tank Facility For Radioactive Waste Processing Facilities

Principal Investigator(s): Erich Keszler, Laurie Judd (NVE)

Collaborator(s): None

Research Project Number: DOE/Engineering Scale Test Tank Facility/01/V1

Start Date: July 2007

End Date: Ongoing

Research Objectives

Retrieval and treatment of legacy radioactive wastes and tank closure activities across the DOE complex generally require the construction and operation of major new facilities with significant capital and operational cost. Risks associated with these facilities must be effectively identified and managed so that costs do not escalate and/or major operational inefficiencies or process failures do not occur. Risks are heightened when new or innovative technologies or applications are involved.

Significant investment in scale testing of processing and storage tank designs is going on in major projects at sites throughout the complex, such as the Salt Waste Processing Facility at Savannah River and the RPP Waste Treatment Plant at Hanford. This work is generally being done independently and at reduced scale, and technical risk and uncertainty in some cases is still substantial.

The overall objective of this project is to design, build and commission an

engineering scale test tank facility as a resource to use on projects across the DOE complex to develop and demonstrate tank mixing, pumping, retrieval, sampling and other equipment needed for waste storage, processing, and retrieval projects. Availability of a common engineering-scale test facility will allow testing of key systems to be carried out economically and at scales closer to full scale, thereby substantially reducing project risk.

Research Progress

The facility has been designed and subcontracts have been placed for its construction and fabrication. It has been designed to be as generic as possible in order to give maximum flexibility to the potential work to be conducted.

The facility will include a 20' diameter by 10', 15' or 20' high stainless steel tank (adjustable height) with available flat and dished bottoms, as shown in Figure 1.



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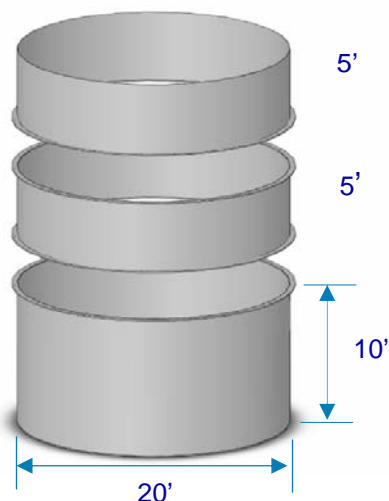


Figure 1. Schematic of Engineering-Scale Test Facility

The facility will be located in Mooresville, NC, where NuVision Engineering will supply services including, but not limited to, simulant preparation, limited fabrication, test rig assembly, engineering support, commissioning support, and test planning support.

The facility, when complete, will be used for a number of applications including tank mixing, bulk waste/heel retrieval, tank decontamination, robotic and remote applications, rapid response troubleshooting, system commissioning, operator training, and scalability verification.

Planned Activities

The facility is scheduled for completion in mid 2008 and will then be used to support the EM-21 program in key technical areas such as waste mixing, sludge and heel retrieval, improved sluicing and enhanced chemical cleaning.



Figure 2. Fabricated Engineering Scale Test Tank



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1.3 ENHANCED TANK CLOSURE PROCESSES

Cementitious Barriers Partnership Project

Principal Investigator(s): C. A. Langton (SRNL)

Collaborator(s): D. Kosson (VU)

Research Objectives

The objectives of this project were to

1. Document the current understanding and technical basis for the use of engineered cementitious barriers for radioactive waste disposal and containment and
2. Update progress made on waste tank closures in the DOE complex.

A Workshop on the Use of Cementitious Materials for Waste Treatment, Disposal, Remediation, and Decommissioning was held at SRNL, December 12-14, 2006. The objective of the workshop was to facilitate technical exchange among subject matter experts across the DOE complex, additional national and international experts, and representatives from local advisory groups and state and federal agencies with roles at DOE sites. One hundred and ten people attended the workshop in person while another 250 people participated either in full or in part via web cast.

The Cementitious Barriers Partnership (CBP) CRADA is a collaborative effort between Washington Savannah River Company, LLC (WSRC), acting through its applied research facility, the Savannah River National Laboratory (SRNL); Vanderbilt University (VU);

and the Consortium for Risk Evaluation with Stakeholder Participation (CRESP), the Energy Research Centre of The Netherlands (ECN), and SIMCO Technologies, Inc. The CBP was organized to conduct research to develop tools necessary to address performance of cementitious materials in the near surface low-level waste disposal environment.

In addition, during 2007, a paper (WSRC-STI-2007-00686) on the status of tank closures in the DOE complex was prepared and submitted to the 2008 Waste Management Symposia (WM08), Phoenix AZ.

Recommendations from the workshop formed the basis for the CBP Project Plan and for the formation of the CBP CRADA to carry out the project plan. Task descriptions for the CBP CRADA are identified in the 5-year CBP Project Plan, which was organized in Phases:

- Phase I is Documentation of the Current Status for Predicting Service Life of Cementitious Barriers for Performance Assessments
- Phase IIA is Model Development
- Phase IIB is Experimental Model Support
- Phase III is Advanced Processes, Demonstration and Validation.



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The paper submitted to WM08 on the status of DOE tank closures will be presented in 2008.

Research Progress

Several issues and gaps in current knowledge have been identified and recommendations are made in these areas:

- Standards of practice for use of cementitious materials in DOE-EM waste management missions, performance assessments, and test methods;
- Data bases and knowledge retention;
- Field monitoring and validation of performance and performance models, including sample archive programs, pilot-scale field tests, and monitoring programs;
- Defensibility and credibility, including independent review and knowledge exchange, stakeholder involvement, and independent funding, and
- Leveraging resources with initiatives by other federal agencies, national laboratories, international programs and university research. A multidisciplinary team from government (DOE, NRC, NIST), academia (Vanderbilt), and international partners (ECN, SIMCO) was assembled to develop the necessary tools.

The workshop proceedings including recommendations for future work were issued as WSRC-RP-2007-00210, March 28, 2007.

Planned Activities

The CBP CRADA will be set up during 2008 to implement a five year project plan to address long term prediction of engineered cementitious barriers for radioactive waste disposal and for radioactive containment in the DOE complex and commercial nuclear industry.

The report documenting the status of DOE waste tank closure activities will be updated periodically. The anticipated time frame is every five years.

References

1. WSRC-STI-2007-00686, "Recent Progress in DOE Waste Tank Closure," C. A. Langton and J. R. Cook.
2. WSRC-RP-2007-00210, March 28, 2007.

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1.3 ENHANCED TANK CLOSURE PROCESSES

Fluidic Jet Grouting Systems for Hanford 200 Series and Associated Tanks

Principal Investigator(s): Erich Keszler, Laurie Judd (NVE)

Collaborator(s): CH2M Hill Hanford Group

Research Project Number: Hanford/Jet Grouting/01/V1

Start Date: February 2007

End Date: December 2007

Research Objectives

There are four 55,000 gallon sludge tanks in the C-tank farm at Hanford that contain residual wastes that must be stabilized to support tank closure. To aid the closure process, the NuVision Engineering (NVE) Consolidated Tank Closure (CTC) System has been identified by site personnel as having the potential to produce an acceptable end state for each tank by evenly distributing and encapsulating the tank residuals in a grout matrix. In addition, there are a significant number of catch tanks (40+) and distribution pits that may require similar treatment.

The current baseline technology for treating the residual material calls for the addition of grout to the tank to stabilize the residuals. There is technical uncertainty regarding how well the grout encapsulates the waste during the grout addition. Insufficient mixing of the grout and residual material in the tank may result in pockets or layers of material remaining that are susceptible to leaching. This uncertainty could potentially be resolved by deploying a system capable of intimately mixing the heel with a suitably formulated grout.

The objectives of this work therefore were to evaluate the NVE CTC system for application to the C-200 area tanks (Figure 1) and catch tanks at the Hanford site and to assess the suitability of the currently proposed grout formulation for tank closure irrespective of method of application. This project addressed a technical uncertainty and risk associated with tank closure across the complex through project-specific system design evaluations.

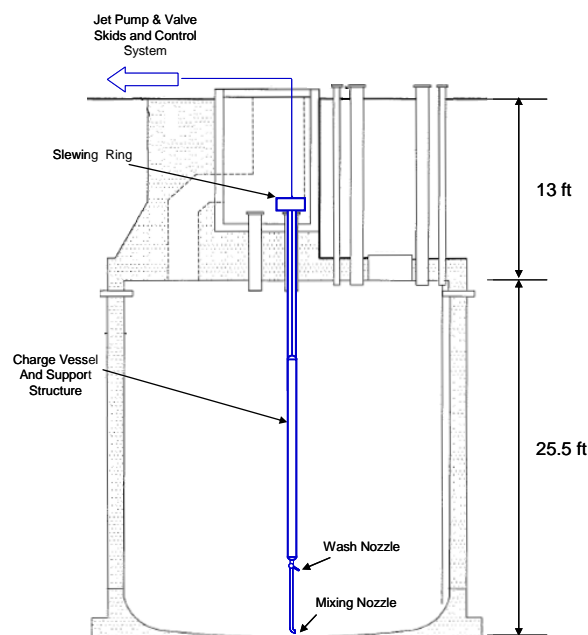


Figure 1. C200 Tank at Hanford



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Research Progress

In this project, NVE developed and successfully conducted proof-of-principle trials of a CTC system (Figure 2) that can not only mix and transfer liquid tank waste but also complete the final grouting stage for tank closure. The CTC was shown to be capable of distributing grout material within a tank heel while incorporating and ultimately encapsulating the waste materials into the cured grout. This process was shown to be more capable of encapsulating both solid and liquid phases of the tank heel material while producing minimal or zero bleed water.

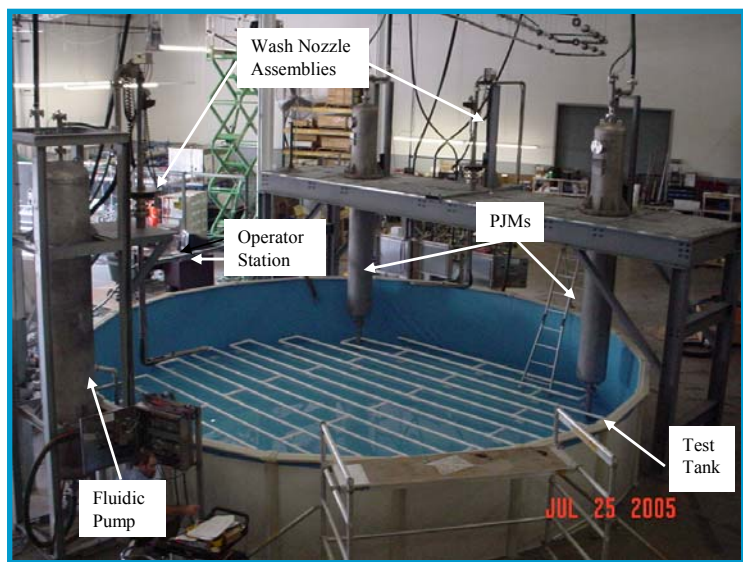


Figure 2. Consolidated Tank Closure System.

On the basis of this work, the CTC system has been identified as a potential candidate technology for the closure of tanks at the Hanford C-200 area and could also be applicable to other tanks, including four Series 200 tanks and sixteen catch tanks.

Some minor site concerns centered on the simple grout formulation that was adopted for the proof-of-principle trials were allayed through NVE's teaming partner Waste Management Technology (WMT). Their findings confirmed that the concerns from site were a function of the intentional simplicity of the chosen grout formulation and that they could be individually addressed during the formulation of a final grout formulation. They also generated a series of questions regarding the baseline Hanford grout formulation and suggested changes that should be considered before it is used, regardless of the technology to be adopted for individual tanks.

A report was issued which presents and discusses:

- The NVE Consolidated Tank Closure system
- NVE's assessment of available Hanford C-200 area Series 200 and catch tank information
- How the CTC system can be applied to the identified tanks
- WMT's assessment of tank operator's comments and their recommendations for the way forward.

The report concluded that

- The NVE CTC system should be considered for closure of all Hanford C-200 area Series 200 and catch tanks;
- Detailed assessment of the identified Series 200 and catch tanks should be conducted with an aim to tailor a CTC system to meet all requirements.



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- Further development and trials should be carried out to ensure that the final Hanford grout formulation meets the stated objectives and requirements, regardless of the grouting method to be used.

Planned Activities

Once the Hanford Tank Farm Operations Contract is awarded, it is anticipated that discussions will begin on how NVE's CTC system can be used to accelerate tank closure schedule at the site

References

The Final Report is available on request.



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1.3 ENHANCED TANK CLOSURE PROCESSES

Remediation Of Cooling Coils In Large Tanks

Principal Investigator(s): Erich Keszler, Laurie Judd (NVE)

Collaborator(s): SRS and SRNL

Research Project Number: SRS/Cooling Coils/01/v1

Start Date: February 2007

End Date: May 2008

Research Objectives

At DOE sites such as Savannah River and Hanford, large tanks (~1M gallons) have been used for storage of radioactive salts, sludge, and supernatant liquid. The Type I, II, and III tanks at SRS were built with internal carbon steel cooling coils used to remove the heat of radioactive decay from the stored waste. Each tank contains multiple cooling circuits up to 600 feet long (Figure 1).

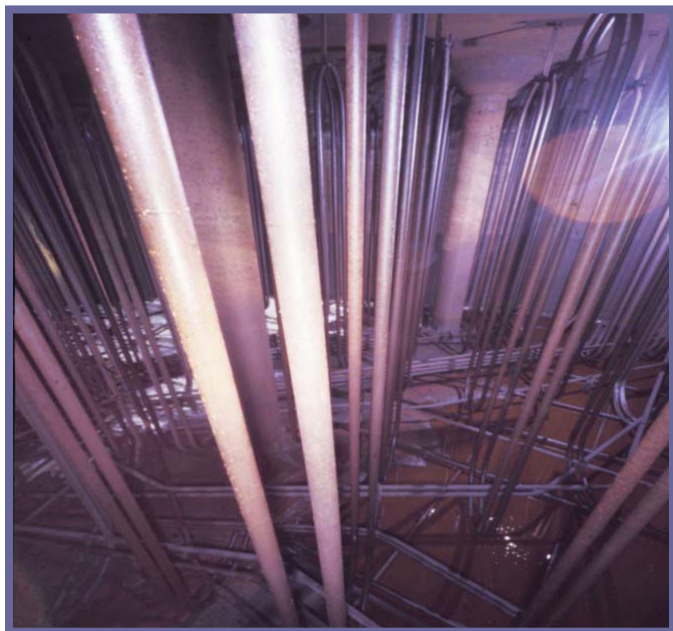


Figure 1. Type 1 Tank Cooling Coils (before waste additions to tank)

As this waste is being retrieved and the tanks are prepared for permanent closure, the cooling coils present a significant challenge to satisfying the closure requirements. The coils obstruct access to areas of the tank, thereby restricting waste removal. The tank cleaning process often causes the cooling coils to fail, allowing high level waste to internally contaminate the cooling system. Once the coils are breached, flushing is not completely effective and filling them with grout from the termination point traps residual radioactive material in the system. In addition, it is expected that the waste determination process prescribed by Section 3116 of the Ronald W. Reagan National Defense Authorization Act of Fiscal Year 2005 (NDAA) will require the elimination, or at least the reduction, of fast flow paths for infiltration water to travel through the closed, grouted tanks. If left intact, the cooling coils could allow water infiltration to migrate through the tank.

Many possibilities exist for the final end-state of large high level waste tanks with cooling coils installed in them. However, nearly every possibility will require some level of cooling coil management or closure to reach an acceptable tank end-state.



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The scope of work for this project was to document the problem definition, identify potential solutions, conduct research into available technologies, and recommend technology development to meet the anticipated need.

Research Progress

During 2007, NuVision Engineering (NVE) embarked on a project to conduct a feasibility study of alternative tank closure options for Type I tanks at the Savannah River Site. During this study, NVE worked closely with site representatives to better define the scope for the current problem related to the Type I tanks at the SRS site. The information required to better understand the complexity in removing these coil networks has been defined and documented in the final report titled "Remediation and Closure of Cooling Coils in Large Tanks". This report documented a number of possible alternatives for the removal of the complex cooling coil networks that heavily restrict access to these Type I Tanks at the SRS tank farm complex and pulled together some historical and relevant tank data to aid in refining the scope for the removal of these complex cooling coil networks in a safe and cost effective manner. The report also summarized a variety of possible off-the-shelf cutting technologies including some previously deployed in nuclear environments to provide cost effective cutting technology for remotely operated applications across the DOE complex.

The knowledge gained during the development of this report has helped to define different scope issues that will

need to be resolved before a comprehensive path forward can be developed. Many different technical issues raised in the report will need to be resolved and simulated to better understand the complete picture before moving forward. More simplistic things like the end state of the cut coils with open ends for flushing abilities, or closed or crimped end configurations to avoid possible material loss issues when removing the cut coils from the tanks, to the more challenging obstacles such as performance requirements of a Remote Tool Deployment (RTD) technology: All play important roles in developing the comprehensive path forward for the final remediation of these heavily congested tanks with complex cooling coil networks.

Planned Activities

NVE will be conducting a Phase II to the feasibility study of alternative tank closure options for the Type I tanks at the Savannah River Site for 2008. During this phase II study, NVE will further detail the total scope requirements to better understand the total cost, schedule and budget issues. These items will need to be better detailed to develop a cost effective and safe approach to this complex tank remediation challenge. Some preliminary concepts for tools to remediate cooling coils in Tank 1 waste tanks at SRS are depicted in Figure 2. Technologies to support tool deployment, cooling coil removal, site power, and video are just a few areas that need better definition in preparation for full scale tank operations.

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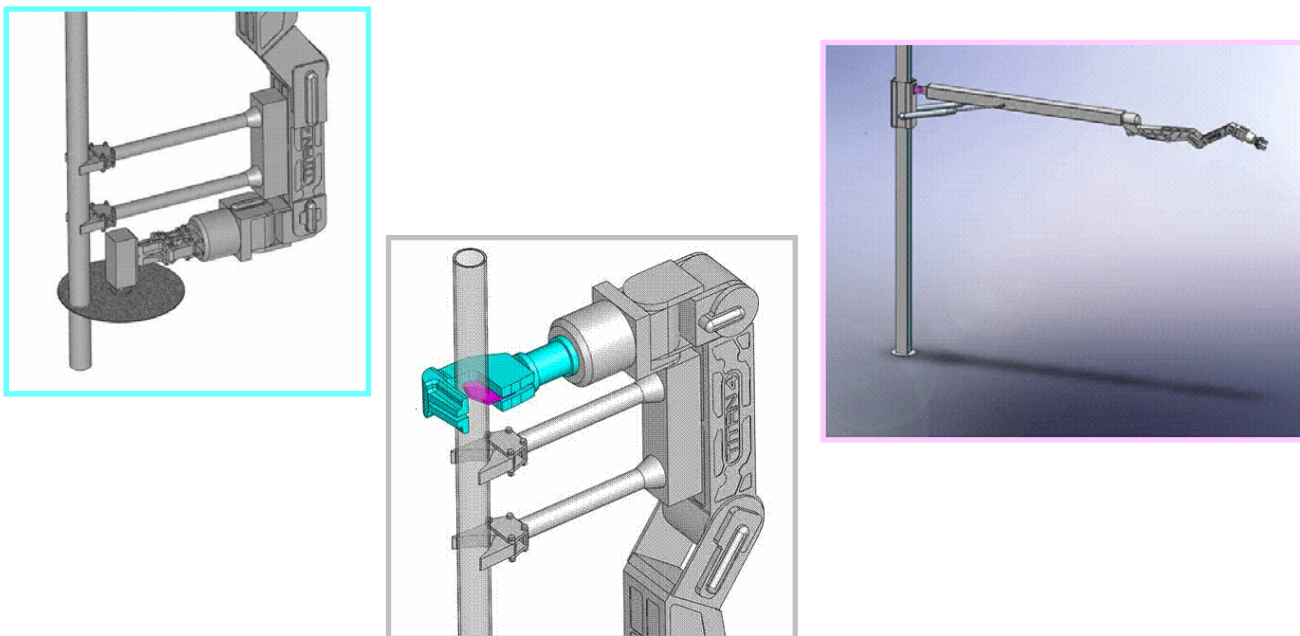


Figure 2. Preliminary Concepts for SRS Cooling Coil Remediation Tools

The Phase II scope will be based on progressive elaboration of the 2007 scope, utilizing site input, to aid in selecting two or three approaches and/or equipment solutions. The details of other ancillary equipment needs such as a remote tool deployment mask, debris retrieval system, and remote operations supports technologies needed to fulfill the requirements to embark on this challenging tank remediation campaign.

References

Reports are available on request.



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1.4 NEXT-GENERATION PRETREATMENT SOLUTIONS

Enhanced Monosodium Titanate

Principal Investigator(s): D. T. Hobbs (SRNL)

Collaborator(s): M. D. Nyman (SNL); T. B. Peters, M. R. Poirier, M. J. Barnes, M. E. Thompson, S. D. Fink (SRNL)

Research Objectives

This project seeks to develop an improved monosodium titanate (MST) sorbent for the cost effective removal of ^{90}Sr and alpha-emitting radionuclides from high-level nuclear waste solutions. During 2007 the project team completed Phase II activities associated with the development of the peroxide-modified MST material referred to as mMST. The major Phase II objectives included:

1. select preferred synthesis method;
2. scale-up synthesis method to the pilot-scale;
3. evaluate radionuclide removal performance and key material characteristics for use at SRS salt waste processing facilities and
4. issue final summary technical report of Phase II activities.

Synthesis method selection was based on strontium and actinide removal performance of bench-scale materials with simulated radioactive waste solutions. The selected method was scaled up approximately 50-fold in the laboratory. Performance of the larger bench-scale produced material was tested with both simulated and actual tank waste solutions. After successful demonstration of performance at the bench-scale, the project procured a pilot-

scale quantity of the enhanced MST and tested the performance and key characteristics of the enhanced MST material.

Research Progress

During 2007 we completed testing and issued a summary technical report of all Phase II activities (WSRC-STI-2007-00082, Rev. 0). Major findings from this activity included the following.

Testing evaluated three synthetic methods and eleven process parameters for the optimum synthesis conditions for the preparation of mMST. We selected the post synthesis method for continued development based on overall sorbate removal performance and successfully prepared three batches of the mMST at the 25-gram scale (Figure 1).

The laboratory- prepared modified MST exhibited increased sorption kinetics with simulated and actual waste solutions and similar filtration characteristics to the baseline MST. Testing indicated that the mMST exhibits reduced affinity for uranium compared to the baseline MST, reducing risk of fissile loading. Shelf-life testing indicated no change in strontium and actinide performance removal after the

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modified MST was stored for 12 months at ambient laboratory temperature.



Figure 1. Photograph of Bench-Scale Synthesis of Enhanced Monosodium Titanate (mMST)

Optima Chemical Group LLC prepared a 15-kilogram batch of the mMST and performance testing with simulated and actual waste solutions indicated that the material performs as well as or better than batches of mMST prepared at the laboratory-scale. Stirred-cell (i.e., dead-end) and crossflow filter testing revealed similar filtration rates relative to the baseline MST for both the laboratory and vendor-prepared mMST materials. Based on these findings we concluded that the mMST represents a much improved sorbent for the separation of strontium and actinides

from alkaline waste solutions and recommend continued development of the material as a replacement for the baseline MST for waste treatment facilities at the Savannah River Site. SRNL also completed supplemental testing beyond one year under laboratory controlled conditions and quantify the affinity of the mMST for uranium. Results indicated that the shelf-life of the mMST is a minimum of 30 months—as shown in Figure 2 for neptunium—and 17 months for the laboratory and vendor-prepared batches of mMST, respectively, when stored under controlled temperature conditions. Uranium affinity testing indicated that the mMST exhibits more than an order of magnitude lower sorption of uranium than the baseline MST. This is a significant characteristic in the processing of SRS tank wastes which contain highly enriched uranium. The decreased sorption of uranium by mMST reduces the nuclear criticality safety risk resulting from the accumulation of enriched uranium onto the MST sorbent. This property will allow more flexibility in processing wastes through SRS treatment facilities.

Planned Activities

2008 testing will focus on determining the influence of temperature and ionic strength on the strontium and actinide removal performance of the mMST. The effect of temperature will be evaluated over the range of 25 to 65 °C. The effect of ionic strength will be evaluated with simulated waste solutions spanning a range of between 4.5 and 6.5 M in sodium concentration.



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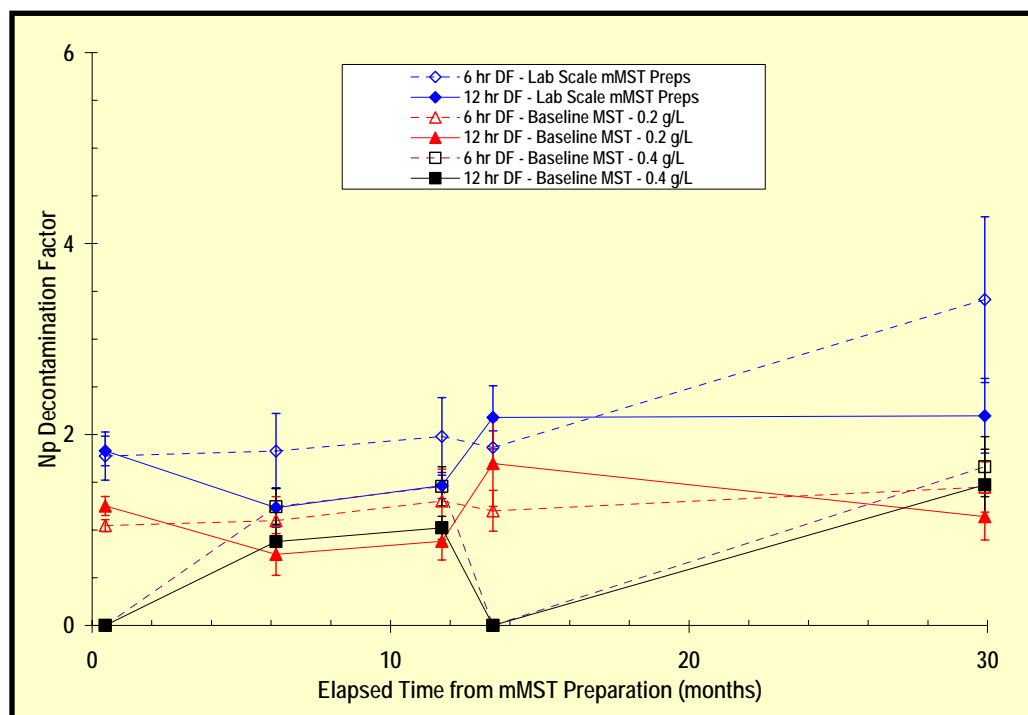


Figure 2. Neptunium Decontamination Factors versus Elapsed Time Since Laboratory Preparations of mMST

2008 testing will also investigate if the addition of a filtration step during synthesis of the mMST will reduce or eliminate the release of trapped gas from the mMST. Previously we observed that the freshly prepared mMST evolves oxygen, a by-product of the reaction between hydrogen peroxide and MST during the formation of the mMST. The rate of evolved oxygen rapidly decreases with time. However, if the gas evolution can be eliminated, it would eliminate the need for a vent on the mMST shipping and storage container.

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1.4 NEXT-GENERATION PRETREATMENT SOLUTIONS

Hanford Medium/Low Curie Waste Pretreatment Alternative Project (Fractional Crystallization)

Principal Investigator(s): Dennis W. Hamilton (CH2M HILL Hanford)

Collaborator(s): Dan Herting, Mike Johnson (CH2M HILL Hanford); Eric Nelson, Don Geniesse, Jack Zimmer (AREVA NC); Jim Majors (Swenson Technologies); Ron Rousseau, George (PJ) Dumont, Laurent Nassif (Georgia Institute of Technology); Alejandro Heredia-Langner (PNNL); Michael Restivo, Jack Zamecnik, Mike Williams, Dan Burns, Bill Giddings, Zafar H. Qureshi, Timothy Steeper, Mark Duignan (SRNL)

Research Project Number: RL041101

Research Start Date: December 2, 2004

Expected Research End Date: July 2008

Research Objectives

The primary focus of the Hanford Medium/Low Curie Waste Pretreatment Alternative Project is to investigate the feasibility of using Fractional Crystallization (FC) to perform pretreatment of Hanford waste. The specific objectives of the CH2M HILL FC program are

1. Define assumptions, uncertainties and risks associated with FC of Hanford tank waste;
2. Perform testing to validate assumptions, resolve uncertainties and mitigate risks such that FC can be considered as a potential pretreatment technology alternative during the conceptual design phase of the Hanford Supplemental Pretreatment Facility (SPF); and
3. Define design parameters necessary to develop a FC pretreatment plant conceptual design.

To support the validation of enabling assumptions, resolution of uncertainties,

and mitigation of risk associated with a FC of Hanford waste, a graduated testing and demonstration approach was developed. The approach has the following elements, and the overall schedule is shown in Figure 1.

Thermodynamic modeling using a commercial model, ESP by OLI

In multi-component Hanford waste, the solubility of components cannot be predicted from solubility diagrams or by hand calculation techniques because of the complexity of the chemistry. Solubility of components is a function of the water content, initial concentrations of the salts, free hydroxide, temperature, and ionic strength. To predict the solubility of components, the yield during crystallization, and the extent of decontamination, computational thermodynamic models are used. Environmental Simulation Program (ESP) software, leased from OLI Systems (Morris Plains, NJ), will be used to



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- Understand the FC as it applies to Hanford waste;
- Predict the process performance using a variety of waste compositions;
- Plan experiments and develop process flowsheets;
- Define lab, engineering, and pilot scale test parameters.

Laboratory experiments with simulants.
Laboratory experiments with simulants will be performed by two independent labs. The tests will range from simple, two-component batch crystallizations to multi-component semi-batch mixtures. The laboratory tests with simulant will be performed to

- Validate the computer model performance predictions;
Investigate ease of control and robustness.

Laboratory experiments with actual waste

Laboratory experiments with actual waste will be performed by the Hanford 222-S laboratory. The equipment and procedures used to perform the tests with actual waste will be the same as that used for the laboratory tests with simulants. The laboratory tests with actual waste will be performed to

- Verify that actual waste behaves like simulant;

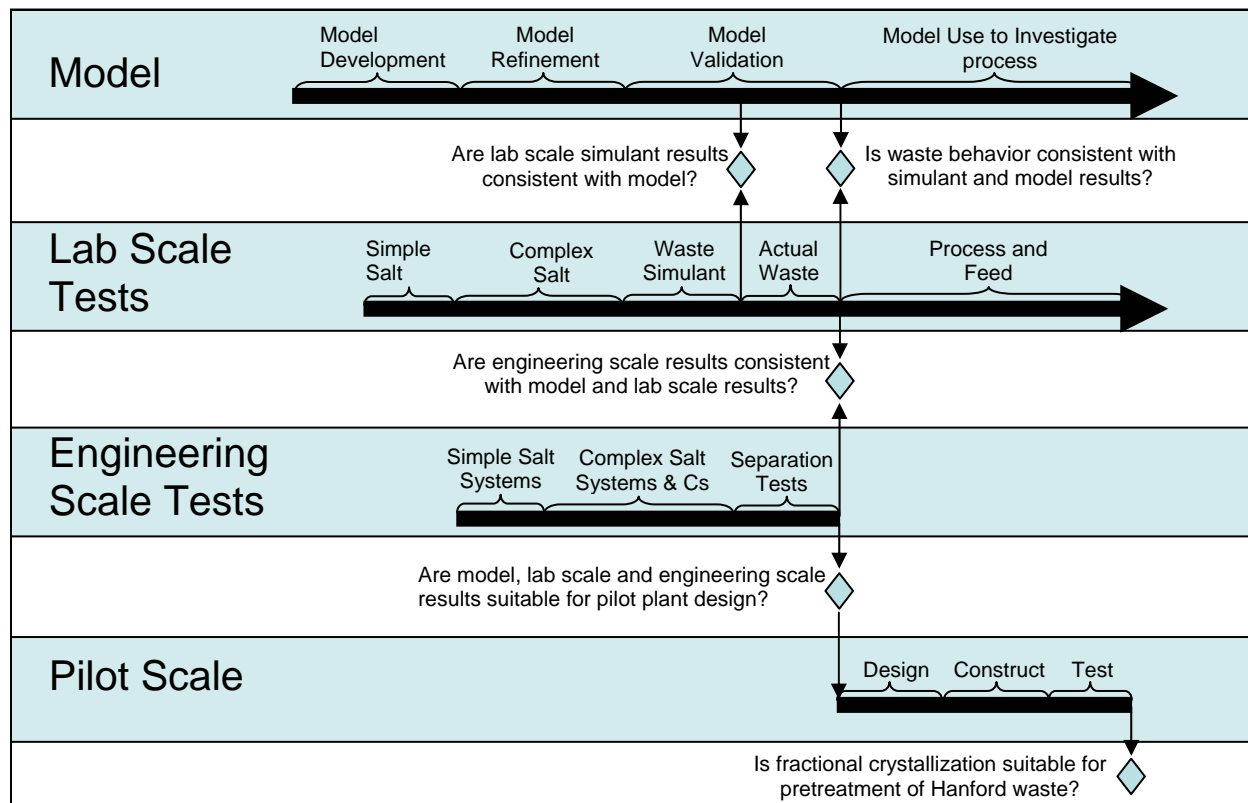


Figure 1. Relationships between the Elements of the Fractional Crystallization Testing Approach



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- Verify that the computer model predicts system performance with real waste at lab scale;
- Investigate co-precipitation, the formation of inclusions, and recrystallization.

Laboratory experiments with simulant and actual wastes.

Following early fractional crystallization laboratory tests, an expert technical review panel was convened to review test results to that point and recommend any additional testing that should be performed. Based on recommendations from the review panel, additional lab scale tests, using both simulant and actual waste will be performed to

- Define a feed envelop of a theoretical production scale fractional crystallization plant;
- Determine the impact of changing key fractional crystallization parameters such as temperature, pressure, evaporation rate, and residence time;
- Determine the effect of minor waste components such as organics and solids on the fractional crystallization process;
- Determine the extent to which Cs and other radio-nuclear waste components are incorporated into the product by co-precipitation and inclusions.

Engineering Scale tests performed with simulants.

Engineering scale tests with simulants will be performed by Swenson Technology, Inc., a world expert in the design, construction and operation of fractional crystallization plants. The tests will be performed at a Swenson test

facility, will duplicate the Georgia Tech results on a larger scale, and will use the same computer model and approach used by Georgia Tech. The tests will be performed to

- Investigate continuous mode operation with Hanford stimulant;
- Define pilot scale design parameters;
- Further investigate the effects of residence time and evaporation rate on product crystals.

Pilot Scale tests performed with simulants.

A graduated approach will be used during the pilot scale tests. Pilot scale tests will investigate: water only operation, complex salt systems, feed variability and off-normal ops. The pilot scale system and fractional crystallization components will be designed by Swenson Technologies. The pilot scale plant will be installed at Savannah River National Laboratory (SRNL) and operated by SRNL under the direction of AREVA and Swenson engineers (Figure 2). The pilot scale system will

- Verify that lab scale tests and the computer model can predict FC system performance at scales relevant to a production plant
- Use equipment that is prototypic of the equipment that would be used in a full scale production plant
- Allow testing to be performed under continuous operation conditions, rather than batch or semi-batch operation
- Allow testing to investigate potential impacts of process recycles
- Define parameters necessary for conceptual design of Hanford SPF.



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Research Progress

The project is progressing ahead of schedule and below budget. As of June 1, 2008, all activities had been



Figure 2. Control Room of Fractional Crystallization Pilot Scale Plant

completed, except for reporting associated with the recently completed pilot plant tests. Specifically:

- Thermodynamic modeling using a commercial model ESP by OLI is complete. The model predicts that FC can be successfully used to pretreat Hanford tank waste. (2008)
- Laboratory experiments with simulants are complete. Laboratory scale tests with simulant validated the thermodynamic modeling and indicated that Hanford tank waste simulants could be successfully pretreated by FC. (2008)
- Laboratory experiments with actual waste are complete. Laboratory scale tests with actual tank waste validated the thermodynamic modeling and demonstrated that actual Hanford tank waste could be pretreated by FC. Further, it demonstrated that actual Hanford tank waste behaved

in the same way as simulated waste during FC. (2007)

- Engineering Scale tests performed with simulants are complete. Engineering scale tests with simulant validated the thermodynamic modeling, defined parameters needed for design of larger FC facilities, and indicated that FC of Hanford waste was scalable and could be utilized at a production scale. (2006)
- Planned baseline Pilot Scale tests with simulants are complete. Pilot scale tests with simulated waste validated the thermodynamic modeling and demonstrated that the FC process was scalable and could be used to pretreat Hanford tank waste. (2008)

During all phases of testing all project cesium decontamination and sodium product yield goals were met:

- Cesium Decontamination (Goal > 50%): Actual decontamination factor > 150.
- Sodium Product Yield (Goal > 50%): For Hanford 200W single shell tank waste, the yield was 52% to 80%.

Further testing at all scales is recommended prior to preliminary design to allow for

- Optimization of design and operational parameters, and
- Testing of tank waste compositions that were not covered by the project baseline, including 200E double shell tank waste.

Planned Activities

The only activity to be completed is the preparation of the FC Pilot Plant Test Report. No other activities are planned.



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1.4 NEXT-GENERATION PRETREATMENT SOLUTIONS

Oxidative Leaching Studies

Principal Investigator(s): Jennifer E. Holland (JEH Consulting, Inc.)

Collaborator(s): Robert S. Reimers (Tulane University)

Research Project Number: 07RV14890.000

Research Objectives

The focus of this work is to evaluate a proprietary technology consisting of combinations of multiple oxidants in the refinement of the baseline oxidative leaching process to separation chromium from high level waste components in Hanford Site tank waste. The objective of the work in 2008 is to downselect several potential combinations of oxidants in identification of an optimal process. The goal of the work is to identify a process which oxidizes Hanford tank waste chromium species, especially those unaffected by the baseline permanganate oxidative leaching process, while minimizing the sodium addition (caustic addition) and processing time requirements.

As shown in Figure 1, combinations of oxidants are being applied in bench batch tests to a waste simulant which includes a recalcitrant form of chromium and a plutonium simulant in the presence of ionizing ultraviolet radiation (which simulates gamma radiation).

The oxidants tested include permanganate (MnO_4^-), ozonated water (O_3), hydrogen peroxide (H_2O_2), peroxyinitrite (ONOO^-) and, potentially, peroxyacetate ($\text{CH}_3\text{CO}(\text{O})\text{O}^-$). Bench experiments are currently in progress at



Figure 1: Vacuum Ultraviolet Lamps Used to Simulate Gamma Radiation

Tulane University with an expected completion date of September 30, 2008.

The Hanford Site Cleanup Project directly benefits from this work. Additional sites which require oxidative chemical processing technologies, such as other nuclear waste management sites and DNAPL remediation sites, may also benefit from this technology.

Research Progress

Scoping experiments completed in 2006 resulted in preliminary identification of promising combinations of oxidants, especially the use of ozonated water and irradiated nitrate. Previously unidentified synergisms between combinations of oxidants were observed (Figure 2).



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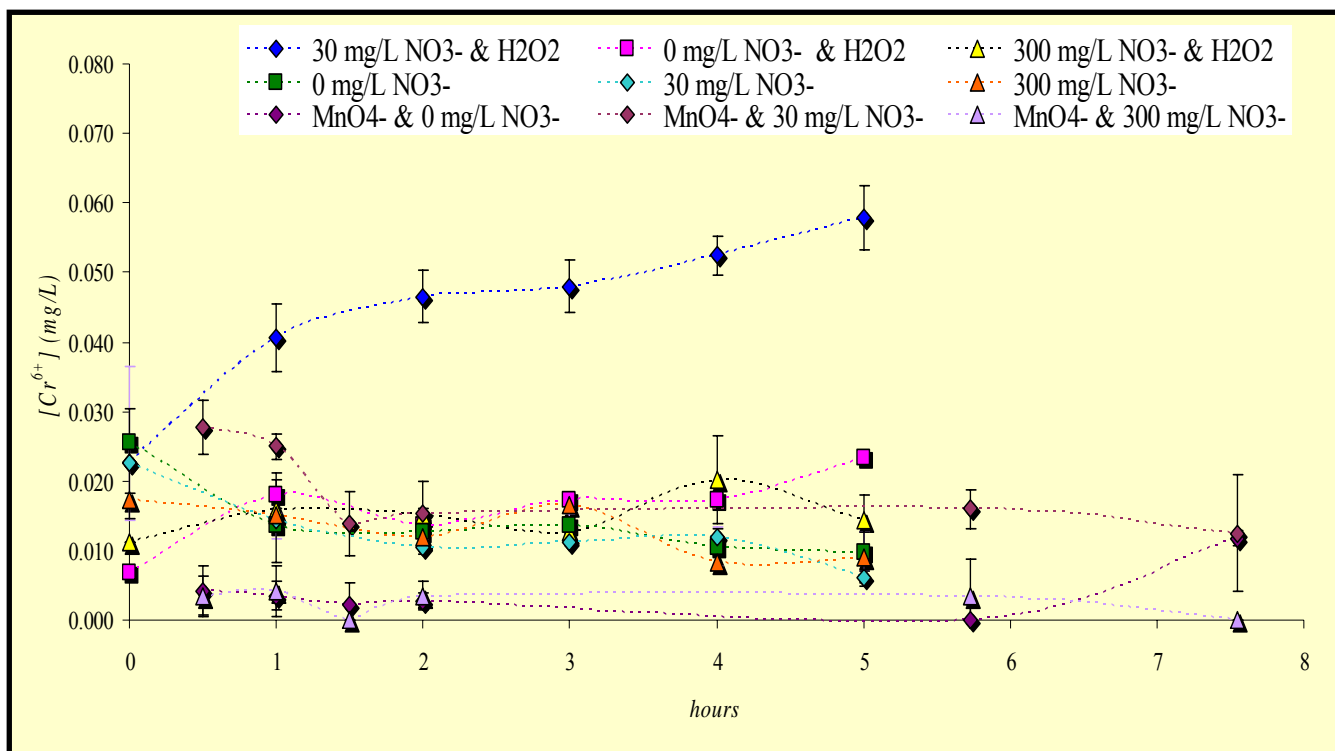


Figure 2: Scoping Experiments Results Indicate a Synergistic Effect of Select Concentrations of Irradiated Nitrate

Scoping experiments are being followed up by in-depth bench scale evaluation and down-selection during 2008. The current stage of critical evaluation for down-selection represents the second of three stages of planned experimentation.

Patent applications for the technology are currently under review at the U.S. Patent Office and select international patent offices. Results of scoping experiments were presented at the American Institute of Chemical Engineering Fall 2006 Annual Meeting and at the Savannah River Site Aluminum and Chromium Leaching Workshop in 2007. A review of oxidative processing technologies for chromium is being prepared for submittal to Chemical Reviews. Results of 2008 experiments will be submitted for presentation at appropriate conferences and will also be submitted

for publication in appropriate peer reviewed journals.

Planned Activities

The down-selection experiments currently underway will be completed during 2008. Further testing planned at pilot scale is included in the proposed 2009 budget.

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1.4 NEXT-GENERATION PRETREATMENT SOLUTIONS

Development of Rotary Microfilter for Use at DOE Sites

Principal Investigator(s): Michael R. Poirier (SRNL)

Collaborator(s): David T. Herman, Samuel D. Fink (SRNL)

Research Project Number: SRO-3-16-01

Research Objectives

The focus of this task is to continue the development of the rotary microfilter for waste treatment at DOE sites. The Savannah River Site (SRS) and Hanford are interested in the technology. SRS is interested in the technology for Enhanced Processes for Radionuclide Removal (EPRR) and for sludge washing. The Hanford site is interested in the technology for Supplemental Pretreatment and Bulk Vitrification.

This task will upgrade the existing rotary microfilter units (Figure 1) with air seals and silicon carbide bushings, test the upgraded units with simulated waste representing the expected feed for Hanford's Supplemental Pretreatment and SRS's EPRR. The testing will measure filter flux with those feeds and evaluate wear and reliability of the air seal and bushing. In parallel to the testing, the researchers will procure an upgraded demonstration unit with an air seal, silicon carbide bushing, and tighter manufacturing tolerances. They will test that unit with a simulated SRS or Hanford waste.

Finally, the program will evaluate alternative filter media to improve

throughput, develop filter cleaning strategies, and develop a 50-disk unit, which will allow more filter area to be placed in a tank riser.

The work is expected to be complete in 2010.

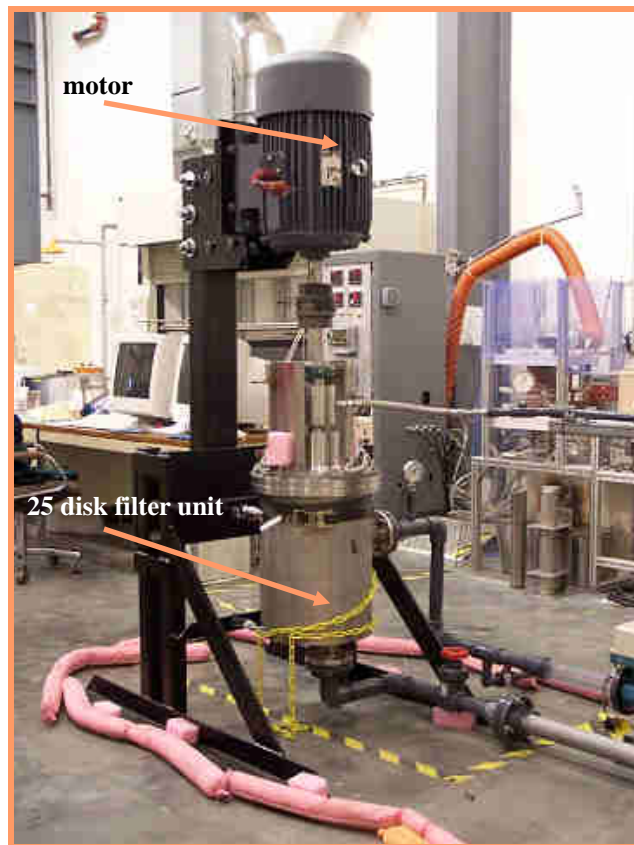


Figure 1. Full-Scale Rotary Filter at SRNL



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Research Progress

Previous work had identified the mechanical seal and bushing as two parts of the rotary microfilter that could be upgraded to increase the expected operating life of the filter in DOE site applications. The researchers upgraded the mechanical seal to an air seal and upgraded the bushing to a silicon carbide material. After making these changes, they tested the filter with a Hanford AN-105 simulant, operating it for more than 140 hours. Inspection of the seal after 140 hours showed minimal wear. Inspection of the bearing showed some wear. Testing with the Hanford simulant showed improved filtration rates over the crossflow filter.

Additional testing is planned with the improved seal and bearing (approximately 500 hours of operating time) to assess their reliability for DOE site applications.

In parallel with the testing, the researchers worked with SRS Liquid Waste personnel to define testing conditions to evaluate the rotary filter for the EPRR. These conditions include higher feed pressure and flow rate. They procured the equipment needed and modified the test apparatus to operate the filter at these conditions. The testing will occur in late 2008.

The testing involved full-scale rotary filter units with simulated Hanford waste.

Documentation of the work is in progress.

Planned Activities

In 2008, the researchers will test the filter at operating conditions expected for SRS's EPRR. These conditions include higher operating pressures and flow rates. The testing will operate the filter for approximately 300 hours to evaluate the reliability of the newly installed air seal and the upgraded silicon carbide bushing.

In parallel, the researchers will procure a new demonstration unit with an air seal, upgraded bushing, and tighter manufacturing tolerances. Once they receive the new unit, they will test it with simulated SRS waste to evaluate the improvements from these upgrades.

References

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1.4 NEXT-GENERATION PRETREATMENT SOLUTIONS

Sludge Mass Reduction

Principal Investigator(s): Chris Bannochie (SRNL)

Collaborator(s): Mike Hay, John Pareizs, David Peeler (SRNL)

Research Start Date: August 20, 2007 **Expected Research End Date:** September 2008

Research Objectives

The DOE has a significant volume of High Level Waste (HLW) that must be vitrified in borosilicate glass for disposal. Considerable costs are incurred each year for storing and treating the HLW, and additional costs are incurred with each waste canister produced for disposal. Therefore, technologies that could reduce the mass of HLW to be vitrified or increase the rate of treatment by either improved melter throughput or canister waste loading would be advantageous.

The sludge mass reduction task will focus on two methods for meeting this goal. The first will determine the feasibility of reducing the mass of sludge to be treated through low temperature aluminum (Al) dissolution. The removal is accomplished by adding caustic to sludge and heating the sludge for extended times at moderate temperatures. A demonstration of the technology will be performed, and the feed will be used to assess downstream impacts on the Tank Farm and Defense Waste Processing Facility (DWPF). The second task will focus on the glass formulation itself. Frits will be formulated to compensate for the removed Al and to try to optimize DWPF throughput with and without Al

dissolution. The Al dissolution process will be implemented at SRS in 2008.

Research Progress

A 3-L sample of high aluminum (HM) SRS HLW originally from Tank 11 was obtained for the low temperature Al dissolution demonstration. The demonstration assembly is pictured in Figure 1.

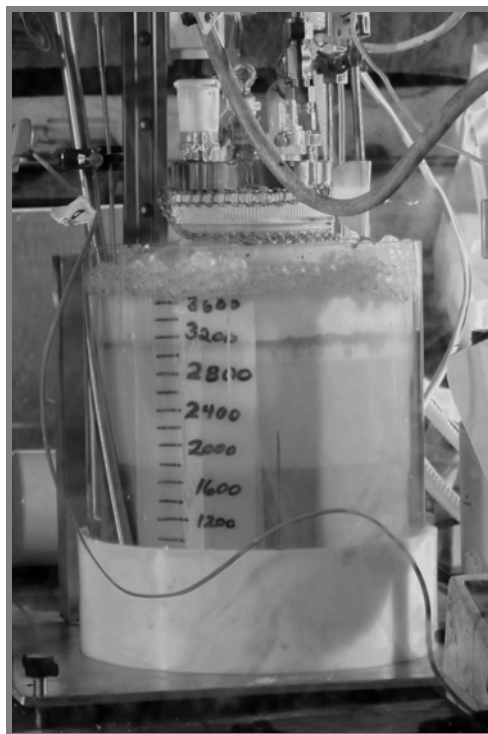


Figure 1. Aluminum Dissolution Experiment During Settling Phase



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Processing involved the addition of 50 wt% NaOH at a 5:1 molar (OH:Al) target ratio, heating to 55°C, mixing for 21 days, settling for 21 days, and decanting the available supernate. Small samples were taken throughout the process to understand the rate of dissolution. The process dissolved ~40% of the Al with ~20% removed through decanting. The results, including the performance of the other sludge components, are being documented in a technical report.

To better understand the potential downstream impacts of implementation of the process, demonstrations were performed of the typical SRS Tank Farm washing and DWPF feed preparation processes. Washing removed an additional ~20% of the aluminum and identified potential risks in the area of sludge settling and rheology behavior. Immediately after decanting the supernate, yield stress and consistency were very high and the sludge settling rate was very slow. These properties changed during washing with improved performance early in washing followed by a gradual decline in properties at the end of washing.

To assess DWPF processing, a demonstration of the Sludge Receipt and Adjustment Tank (SRAT) and Slurry Mix Evaporator (SME) cycles was completed. The processes are necessary to achieve the necessary chemical reactions (e.g. Hg removal) and to improve the feed rheological properties. The SRAT chemical reactions require acid addition and extended boiling under reflux conditions, while the SME

homogenizes the frit with the sludge and concentrates the feed. Hydroxide or total base is an input in DWPF's acid addition calculation, and the introduction of large quantities of NaOH presented a challenge for the measurement. This resulted in insufficient acid being added so the DWPF chemical reactions were not completed. This was identified as an area for further understanding in the SRS sludge mass reduction program. Results of this testing will be documented in 2008.

Glass formulation efforts for the program focused both on improved waste loading and melt rate for sludges with and without Al dissolution. For sludge batch 5, which is undergoing Al dissolution, SRNL fabricated glasses with Al₂O₃ concentrations of ~26 wt% and identified frits with reasonable waste loading windows for a range of Al concentrations (representing different levels of dissolution effectiveness). Assessments were then performed for all SRS future sludge batches with and without Al dissolution incorporated. More flexibility was found in frit selection for sludges without Al dissolution, which is partially driven by the fact that some minimal amounts of Al are necessary in the glass to maintain durability. However, reasonable operating windows were found for most systems.

In order to assess the impact of Al dissolution on melt rate for a DWPF type melter, average compositions representing with and without Al-dissolution "clusters" were developed using a statistical grouping routine since testing all sludge batches would have

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been time and resource intensive. The sludge clusters and selected frits will be fabricated and tested to determine the impact on melt rate in 2008.

Planned Activities

A technical report documenting the results of the low temperature Al dissolution demonstration on SRS HM sludge will be issued. After completing rheology measurements on the sludge, a separate report will be issued documenting the downstream impacts to the Tank Farm and DWPF.

Once the frits have been obtained from the vendor, melt rate testing will be performed with the two sludge clusters representing sludge with and without Al dissolution. A report will be issued discussing the impacts of Al dissolution on melt rate and the potential frit components that can influence melt rate for the two systems.

References

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1.4 NEXT-GENERATION PRETREATMENT SOLUTIONS

Test Plan of Technology to Decompose Legacy Organics in Tank 48

Principal Investigator(s): Kofi Adu-Wusu (SRNL)

Collaborator(s): William R. Wilmarth, Daniel J. McCabe (SRNL)

Research Start Date: August 20, 2007 **Expected Research End Date:** September 2008

Research Objectives

Returning Tank 48H to operational service is critical to the processing of high level waste at the Savannah River Site (SRS). Washington Savannah River Company (WSRC) management has the goal of returning Tank 48H to operational service by 2013 or as soon as practical.

Tank 48H currently holds legacy material containing organic tetraphenylborate (TPB) compounds from the operation of the In-Tank Precipitation process. This material is not compatible with the waste treatment processes at SRS and must be removed or undergo treatment to destroy the organic compounds before the tank can be returned to Tank Farm service. Tank 48H currently contains $\approx 240,000$ gallons of alkaline slurry with about 2 wt % potassium and cesium tetraphenylborate (KTPB and CsTPB). The main radioactive component in Tank 48H is ^{137}Cs .

Wet Air Oxidation (WAO) is one of two technologies currently under consideration for the treatment of TPB in Tank 48H. As depicted in Figure 1, WAO is an aqueous phase process in

which soluble and/or suspended waste components are oxidized using oxygen or oxygen in air. The process operates at elevated temperatures and pressures ranging from about 150 to 320°C and 7 to 210 atmospheres, respectively. The products of the reaction are carbon dioxide, water, and low molecular weight oxygenated organics (e.g. acetate, oxalate, etc.).

The objective of the WAO program is to develop test plans and execute the planned tests necessary to bring WAO to a Technology Readiness Level (TRL) of 6. A technology is deemed mature when it attains a TRL of 6.

The planned tests are as follows:

- (i) Integrated continuous-flow pilot-scale testing with Tank 48H simulant referred to as Phase I pilot-scale testing. It has a duration of about 9 months.
- (ii) Extended-duration batch bench-scale autoclave material-of-construction (MOC) testing with Tank 48H simulant. It will be done simultaneously with test (i) above.
- (iii) Batch bench-scale autoclave testing with actual (radioactive) Tank 48H waste. It has a duration of about 10 months.

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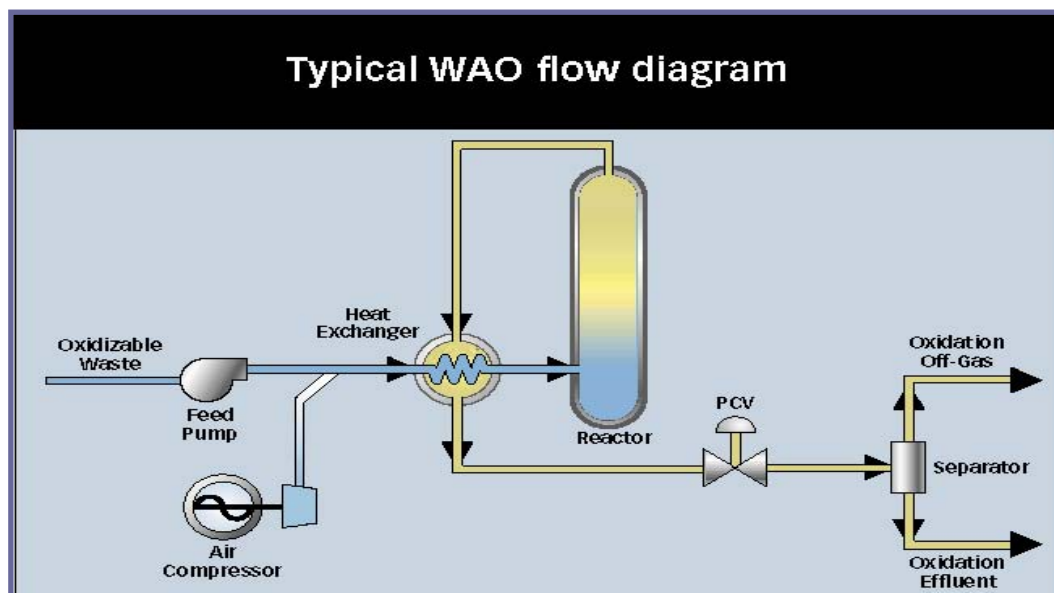


Figure 1. Wet Air Oxidation Process Schematic (Zimpro® WAO System)

- (iv) Integrated continuous-flow pilot-scale with prototypical off-gas treatment system and related equipment [e.g., high efficiency particulate air (HEPA) filters, blowers, etc.] testing using Tank 48H simulant referred to as Phase II pilot-scale testing. It has a duration of about 10 months.
- (v) Integrated continuous-flow engineering-scale (0.1 to 1.0 of full-scale) with prototypical off-gas treatment system/associated equipment testing using Tank 48H simulant. It has a duration of about 23 months.

Even though the work is specifically geared towards Tank 48H at SRS, it is broadly applicable to organic destruction in general and therefore may have potential complex-wide applications, e.g., residual oxalic acid used to dissolve sludges. In addition, it could be used to achieve faster dissolution rates of

aluminum in sludges in the Sludge Mass Reduction Program.

Research Progress

Schedules, cost estimates, and drafts of three test plans [referred to as Task Technical and Quality Assurance Plans (TTQAPs)] of the above five tests have been completed and are being reviewed. Anticipated completion date is January 31, 2008.

The first test plan deals with the Phases I and II pilot-scale testing and the extended-duration batch bench-scale autoclave MOC testing with Tank 48H simulant [items (i), (ii), and (iv) above]. The second test plan concerns batch bench-scale autoclave testing with actual (radioactive) Tank 48H waste [item (iii) above]. The third test plan deals with engineering-scale (0.1 to 1.0 of full-scale) testing with Tank 48H simulant [item (v) above].

Planned Activities



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The tests planned for 2008 are integrated continuous-flow pilot-scale testing and the extended-duration batch bench-scale autoclave MOC testing with Tank 48H simulant [items (i) and (ii) above].

It involves preparing a relatively large batch of Tank 48H simulant

The major activities of the tests are

1. Development and execution of procurement strategy for testing at a Vendor's facility;
2. Preparation of Tank 48H slurry simulant for the testing;
3. Integrated continuous-flow pilot-scale testing (Phases I) at a Vendor's facility;
4. MOC testing at a Vendor's facility;
5. Analytical measurements of samples taken during testing; and
6. Documentation of Vendor testing results in a technical report.

4. Weblink to Savannah River/Hanford/Idaho Technical Exchange, October 9-11, 2007:
<http://srnl.doe.gov/techex/> or
<http://srnl.doe.gov/techex/presentations2.htm> or
http://srnl.doe.gov/techex/PDFs/3b_3_Adu-Wusu.pdf

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1.4 NEXT-GENERATION PRETREATMENT SOLUTIONS

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

Principal Investigator(s): Jeff Lindner, Laura T. Smith, Rebecca K. Toghiani (ICET)

Collaborator(s): Jeff Pike (SRNL), Pat Suggs (DOE-SRS)

Research Project Number: Task 4.1 ICET Cooperative Agreement DE-FC01-06EW-07040

Research Objectives

A number of alternative processes are under investigation at the Savannah River Site for disposition of high-level salts and sludge. ICET is assisting the site through research on waste chemistry and potential flowsheeting associated with sludge leaching, saltcake dissolution, and subsequent blending operations with these streams and with the Defense Waste Processing Facility (DWPF) recycle stream. The primary goal of the work is to evaluate stream parameters that may be encountered and downstream processing effects and potentially find ways in which difficult streams (DWPF recycle) can be safely processed.

Earlier work in these laboratories has focused on laboratory-scale salt cake dissolution operations for a number of H-Area waste simulants. Associated thermodynamic calculations using the Environmental Simulation Program (ESP, OLI Systems Inc.) were used to evaluate the dissolution process and have been used to model the continuing large-scale retrieval from Tank 41H

Efforts in 2007 were aimed at evaluating the leaching of aluminum in Sludge Batch 5. In this process caustic was added to the sludge batch creating an aluminum-rich supernatant through dissolution of $\text{Al}(\text{OH})_3$. Calculations were performed to compare with other flowsheet calculations and to assess the ability of ESP to model aluminum chemistry. Preliminary calculations were performed in blending the resultant leachate with salt dissolution fractions from Tank 41H.

Solubility experiments were performed on CsNO_3 and on KNO_3 at 25 and 50°C in water, 1M NaOH and 3M NaOH. The goals of these experiments were to extend the solubility data available in the literature and to assess the ability of ESP to account for these systems at elevated loadings.

Research Progress

Studies centered on the primary factors that lead to solids formation and determination of optimal conditions to prevent solids formation. Simulations were performed using the ESP software and our double salt database for

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additions of from 100K to 150K gallon of 50 weight % caustic additions at tank operating temperatures. Results indicated 140K gallons of 50 wt% caustic would solubilize most of the aluminum at 50°C. Upon cooling the aqueous leachate stream to 30°C, the major solid predicted to form was $\text{Al}(\text{OH})_3$ at approximately 0.63% by weight. Blending of the aqueous stream with fractions from tank 41H predicted a slight increase of $\text{Al}(\text{OH})_3$ formed (0.65% by weight).

Model predictions for the KNO_3 -and CsNO_3 systems in NaOH were performed, and gaps between the model predictions and available literature data were identified and detailed in a letter report to the site. There were little literature data available for these systems in caustic solutions. A comparison of model predictions to experimental data reveals that solubilities are underestimated by the model for both systems.

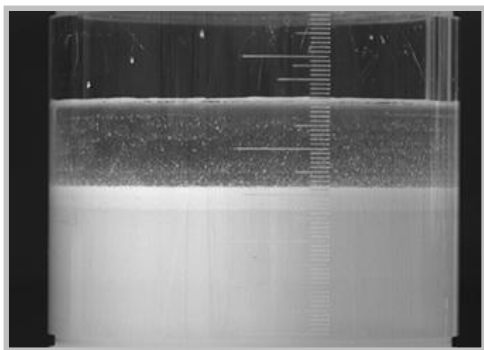


Figure 1. Photograph of Saltcake Dissolution Experiment

Figure 1, above, shows saltcake dissolution experiment showing the formation of an aluminosilicate layer for the simulant based on the waste in SRS tank 37H. Figure 2, below, shows a laser

confocal microscope image of saltcake simulant

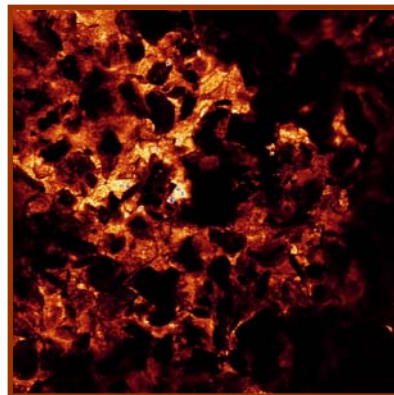


Figure 2. LCM Image of Saltcake Simulant

Planned Activities

Blending studies on dissolved salt fractions, the leachate from sludge batch 5 and the DWPF recycle system are continuing.

Additional work is aimed at evaluating simulant stability and solids formation for the caustic side solvent extraction process (CSSX). Samples from pilot-scale testing are being analyzed using x-ray diffraction and inductively coupled plasma emission spectroscopy.

References

1. Jeff S. Lindner, Rebecca K. Toghiani, L. T. Smith, and J. C. Luthe, "DOE Chemistry Studies." Presentation and poster given at the Hanford-Savannah River-Idaho Technology Exchange, Atlanta, GA., October, 2007.
2. Caleb Tash, Laura T. Smith, Rebecca K. Toghiani, and Jeff Lindner "Solubility Investigations of $(\text{K}^+, \text{Na}^+, \text{Cs}^+)-\text{OH}-\text{H}_2\text{O}$ Systems." Mississippi Academy of Sciences, February 2007.



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1.4 NEXT-GENERATION PRETREATMENT SOLUTIONS

Development of New Technologies for DOE Site Applications

Principal Investigator(s): Chuji Wang (ICET)

Collaborator(s): Christine E. Zeigler, Laurel Tovo (SRNL); Paula Kirk, George Southworth (ORNL)

Research Project Number: Task 6.0 ICET Cooperative Agreement DE-FC01-06EW-07040

Research Objectives

The development of innovative measuring and monitoring techniques for radionuclides, trace metals, and volatile organic compounds (VOCs) and semi-VOCs would be of significant benefit for many DOE site applications, including real-time *in situ* concentration measurement of trace radioactive analytes, such as alpha emitters (U, Pu, Am, etc.), heavy metals in subsurface waste streams and groundwater, and VOCs and semi-VOCs in/at tank.

The goal of this project is to develop and deliver real-time, site-deployable, high sensitivity spectroscopic techniques, which are currently not available yet needed to address issues in DOE site applications: measuring, monitoring, and characterization of multiple tank contaminants. The new techniques will potentially reduce costs, improve operating efficiency, and minimize technical risks (sensitivity and accuracy) by eliminating a lengthy sample transport, analyze, and report regimen.

ICET has developed and demonstrated two laser spectroscopic-based techniques:

1. compact plasma-cavity ringdown spectroscopy (P-CRDS) and
2. continued wave-cavity ringdown spectroscopy (cw-CRDS)

ICET's compact plasma-cavity ringdown spectroscopy has been demonstrated to be a powerful technique for real-time, sensitive elemental and isotopic measurements. Several elements (Pb, Hg, Mn, Sr, etc.), including uranium and its isotopes, have been measured using the P-CRDS technique with the capability of measuring uranium isotopes (U-235/U-238) in the natural abundance ratio. Detection limit of elements is as low as hundreds of parts-per-trillion (ppt), for instance, 200 ppt for Pb and 70 ppb for U-235 and U-238.

The cw-CRDS technique has been developed and measured for VOCs and gases. This technique can be adapted and further developed for real-time characterization of a variety of tank organic compounds with required sensitivity and high accuracy. These two techniques will potentially displace the

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aforementioned conventional techniques in diverse DOE site applications and will help address the issues of real-time, cost-effective, and field-readable measuring and monitoring techniques.

Research Progress

We have measured NIR spectra of a number of VOCs: acetone, formaldehyde, benzene, chlorobenzene, 1,2-dichlorobenzene, toluene, 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene), 2,3-dimethyl-1,3-butadiene, and three small atmospheric molecules, CH₄, CO₂, CO, around 1596 and 1567 nm wavelength regions using a newly developed, compact ringdown optical platform. The purpose of the measurements of these compounds in the compact ringdown platform was to evaluate the system accuracy, robustness, and portability.

The newly designed ringdown optical bench with a multiplex of two NIR laser diodes was extensively tested. The functionality of the portable ringdown has been tested and evaluated in the third quarter by measuring C-H overtone spectra of methane and carbon dioxide absorption in the near-infrared. The issue of potential mirror contamination due to the chemical deposition on the mirror surfaces was addressed. The portable, multiple species ringdown spectrometer is shown in Figure 1.

Planned Activities

1. Continue to measure absorption cross sections of tank-associated VOCs/gases.

2. Assembly of ringdown spectrometer for tank gas/vapor characterization.



Figure 1. Photograph of Portable Ringdown Spectrometer

References

1. Susan T. Scherrer, Chuji Wang, F-X. Han, Yixiang Duan, "Real-time Measurement of Elemental Mercury Naturally Evaporating from Contaminated Samples Using Cavity Ringdown Spectroscopy", The 34th FACSS Annual Meeting Memphis, TN, October 14 – 18 (2007).
2. Chuji Wang, Duan Yixiang and Dibble T. S., "Plasma Diagnostics Using Cavity Ringdown Spectroscopy Combined with Optical Emission Spectroscopy", 2007 IEEE International Plasma Science Conference, Albuquerque, NM, June 17-22 (2007).
3. Chuji Wang, Scherrer S. T.; Duan Yixiang and Winstead C. B. "Plasma Source Cavity Ringdown Spectroscopy for Environmental Applications: Detections of Elemental Mercury and its Stable Isotopes ", 2007 IEEE International Plasma Science Conference, Albuquerque, NM, June 17-22(2007)



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1.4 NEXT-GENERATION PRETREATMENT SOLUTIONS

Efficient Electrochemical Process to Recover Sodium from Radioactively Contaminated Alkaline Wastes

Principal Investigator(s): Shekar Balagopal (Ceramatec)

Collaborator(s): None

Research Project Number: DE-FG07-04ID14622

Research Start Date: June 2007

Research End Date: June 2008

Research Objectives

The objective of this research project is to identify an efficient electrochemical process to recover sodium from radioactively contaminated alkaline wastes. The NaSICON membrane concept is depicted in Figure 1.

Specific activities are

1. Establish operational reliability of NaSICON cells in AP104 simulant stream;
2. Develop process to make 2.4 inch

LANS membrane structure;

3. Design and validate LANS membrane-plastic scaffold seal;
4. Evaluate low cost electrodes as alternative to Pt on Ti Anode;
5. Establish operational stability of NaSICON membrane cell in AP104 and 50wt% caustic concentration;
6. Evaluate irradiation exposure of cell components (Plastics, electrode and NaSICON membrane) in presence of 50 wt % caustic;
7. Evaluate real waste at PNNL.

NaSICON Membrane
Na=Sodium
SI=Super Ionic
CON= Conductors

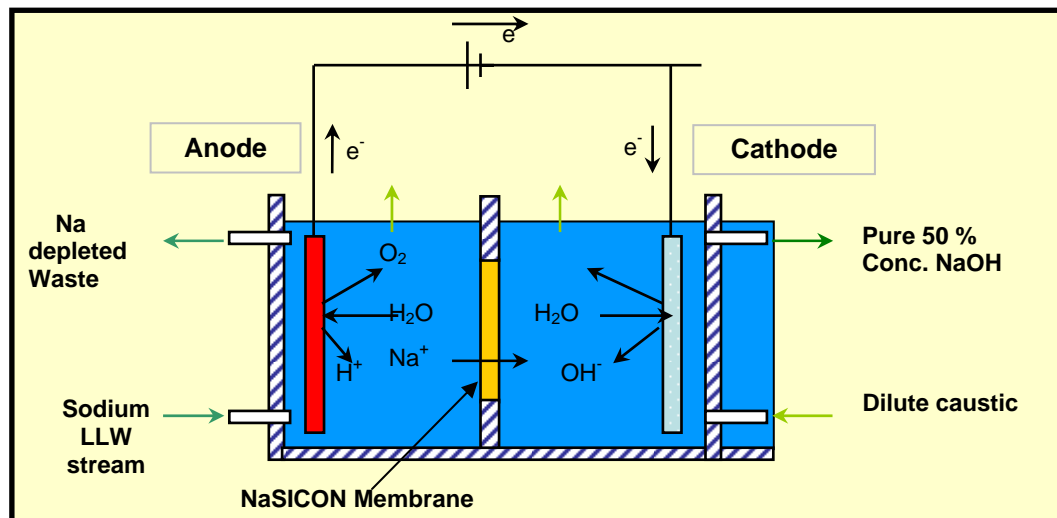


Figure 1. Electrolytic NaSICON Ceramic Membrane Concept for Caustic Recycling from LAW Stream



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Research Progress

Establish operational reliability of NaSICON cells in AP104 simulant stream

A series of laboratory size cells with 1.4 inch diameter membranes was evaluated to establish operational performance reliability in the AP104 simulant stream. The following cell variables were considered for the statistical performance evaluation:

- Kovar, Nickel and ICON electrodes
- Operation current density between 50 and 90 mA/cm²
- Cell voltage: 2.6-2.8-3.0 volts
- Two design configurations of LANS ceramic membrane.

Develop process to make 2.4 inch LANS membrane structure

A planar engineered NaSICON ceramic structure was developed with the objective to reduce the energy consumption for sodium transfer across the membrane and to establish reliability and robustness of ceramic membrane cells for caustic recycling. LANS refers to “large area NaSICON structures.” The tape casting process was perfected to make these advanced structures at 1.4 inch and 2.4 inch diameter. Down selection of a design was completed for final design and development.

Design and validation of LANS membrane-plastic scaffold seal

Sealing the LANS structure in plastic housing is an absolutely critical parameter for device design and to establish the safety and robustness requirements to apply and integrate

electrolytic caustic recycling technology at the WTP site is in progress

Evaluate low cost electrodes as alternative to Pt on Ti Anode

A critical milestone was achieved to select a series of low cost electrode materials which will require long term evaluation to meet performance requirements with good electro catalytic activity for AP104 type LAW simulant stream.

Operation stability of NaSICON membrane cell in AP104 and 50wt% caustic concentration

Tests were conducted to assess the stability of the NaSICON membrane to operate in AP104 and make 50wt % caustic. Membranes were operated in the range for 1500 to 2000 hours in continuous operation in a batch mode. Post analysis conducted on the membrane showed no evidence of corrosion and erosion of the membrane layer. Its pristine nature was confirmed by X-ray diffraction analysis and comparison with untested membrane. Six months of continuous operation milestone of a NaSICON cell in AP 104 simulant was achieved.

Planned Activities

Establish operational reliability of NaSICON cells in AP104 simulant stream

The results from the testing will be the basis to assess performance reliability to predict lifetime and operation characteristics of NaSICON membrane cells for recycling sodium to make caustic from the LAW stream. Additionally, the process information



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will be used in design of a prototype and a plan for conducting tests with simulant and real waste.

Irradiation exposure of cell components (Plastics, electrode and NaSICON membrane) in presence of 50 wt % caustic

Based on recommendation by the DOE assessment team, a preliminary test is being conducted to evaluate the stability of the cell components and NaSICON membrane as exposed to radiation and 50wt % caustic. This test will be conducted at PNNL for a long duration to get some initial results to support down selection of preferred plastic components for cell design.

Real waste evaluation at PNNL

A real waste test has been planned at PNNL for the month of August to evaluate the LANS ceramic cell with a potential low cost electrode system.



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1.5 ENHANCED STABILIZATION TECHNOLOGIES

Fluidized Bed Steam Reforming (FBSR) Testing

Principal Investigator(s): Carol M. Jantzen (SRNL)

Collaborator(s): James C. Marra, Charles L. Crawford, Paul R. Burket, John M. Pareizs (SRNL); Henry D. Schreiber (VMI)

Research Project Number: SR-04-12-01

Research Start Date: March 2004

Research End Date: December 2007

Research Objectives

The objectives of the Fluidized Bed Steam Reforming (FBSR) studies were to

1. demonstrate that the FBSR process could be performed and optimized on the laboratory scale;
2. demonstrate that these optimized parameters gave similar resulting mineralized waste form products during pilot scale testing; and
3. characterize the mineralized products produced on both the laboratory scale and the pilot scale.

To “optimize” the mineralized FBSR product, it is necessary to select appropriate additives, process temperatures, REDuction/OXidation conditions (REDOX), etc. FBSR testing included waste streams at INL, Hanford, and SRS.

The funding for this program began in 2004 and ended in 2007. As a result of the testing performed during the three year duration of this program, the FBSR technology is being pursued at the Idaho National Laboratory (INL) for remediation of their Sodium-Bearing Waste (SBW). The facility is in design and construction.

In addition, FBSR is being used to remediate Tank 48 wastes at SRS. This waste is contaminated with organics which are removed by the FBSR process by pyrolysis so that the Tank 48 wastes can be processed in the Defense Waste Processing Facility (DWPF) melter. Vendor selection for use of the FBSR process has just been completed at SRS.

In addition, the FBSR technology is being considered as a candidate for processing Hanford’s Low-Activity Waste (LAW). For the INL and Hanford LAW applications, clay is added as a co-reactant to the liquid waste in the steam reformer, and a mineral waste form is produced that effectively retains radionuclides and other hazardous constituents. The formation of sodalite-related minerals is especially desirable because these phases have “cage-like” structures that are well suited to immobilize the radionuclide and hazardous species. For the SRS application no co-reactant is used and a carbonate product that is compatible with melter processing is produced.

Research Progress



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During 2007 the last two objectives related to this task were accomplished:

1. definition of 12 REDOX couples as defined by an Electromotive Force (EMF) series and
2. determination of a clay based binder for the granular mineral waste form which would enable it to meet the compressive strength criteria for shallow land burial.

The EMF series was completed by Henry D. Schreiber of VMI (Figure 1) under subcontract to SRNL. Because the FBSR process is pyrolysis, the oxygen fugacity is low and the reactions occur at a reducing REDOX, i.e. log oxygen fugacities of -20 to -21 (Figure 1). By measuring the ($\text{Fe}^{\text{reduced}}/\text{Fe}^{\text{oxidized}}$) in the FBSR product, one can determine the log oxygen fugacity as indicated by the solid green lines in Figure 1. Once the oxygen fugacity of the product at the formation temperature is known, the oxidation state of the other multivalent elements can be determined (see dashed green lines for Cr REDOX and dashed blue lines for Re REDOX). The EMF series demonstrates that hazardous species such as Cr are predicted to be between 40-70% reduced to Cr^{+3} and thus sequestered into durable spinel phases formed from FBSR co-reactants during processing. Likewise the rhenium (Re is a surrogate for ^{99}Tc) at these oxygen fugacities is only predicted to be 2-6% reduced indicating that Re remains in the +7 state at these oxygen fugacities. Therefore, the Re or ^{99}Tc is predicted to be in the correct oxidation state to enter the sodalite structure as NaTcO_4 (Figure 1). Likewise, only 1-19% of the S will be reduced so S will remain oxidized as SO_4 to enter the

desired sodalite/nosean phase cage structures. Thus processing REDOX can be controlled to form the desired durable mineral phases.

Geopolymers were used as binders for FBSR granular product. The geopolymers are made from kaolin clay and sodium silicate. The geopolymers were determined to have a much higher compressive strength compared to other binders tested, i.e. cements, ceramicrete, and hydroceramics. The geopolymer binders did not deleteriously affect the durability of the FBSR granular mineral product. This work was co-supported by LDRD funding.

The FBSR process has a technical maturity level of 3 which is due to its application at INL for remediation of SBW wastes.

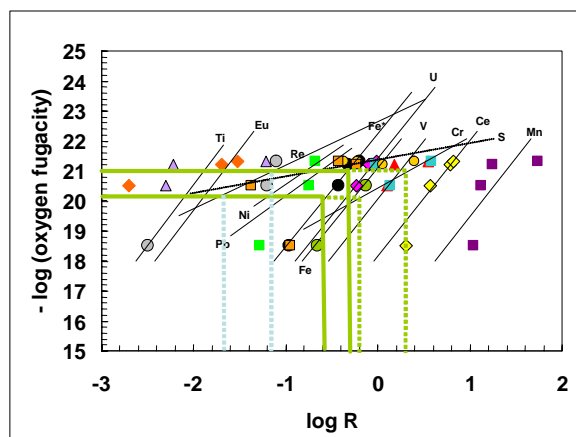


Figure 1. Electromotive Force (EMF) series developed by Schreiber for FBSR reactions. Log R is $\log (X^{\text{reduced}}/X^{\text{oxidized}})$.

Significant publications achieved during 2007 included

1. C.M. Jantzen, T.H. Lorier, J.M. Pareizs, and J.C. Marra, "Fluidized Bed Steam Reformed (FBSR)



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Mineral Waste Forms:

Characterization and Durability Testing,” Sci. Basis for Nucl. Waste Management XXX, D. Dunn (Ed.), 379-386 (2007) and

2. C.M. Jantzen, P.R. Burket, and C.L. Crawford, “Granular Thermal Treatment Residues and Waste Forms: Experiences with Various Monolithing Agents” US DOE Report WSRC-STI-2007-00523.

Planned Activities

There are no planned EM-21 activities for 2008.

References

1. Schreiber, H.D. "Redox State of Model Fluidized Bed Steam Reforming Systems Final Report Subcontract AC59529T," VMI Research Laboratories, VMI, Lexington, VA 24450 (December 2007).

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1.5 ENHANCED STABILIZATION TECHNOLOGIES

Improved High Level Waste Glass Formulation

Principal Investigator(s): J.D. Vienna (PNNL)

Collaborator(s): D.K. Peeler (SRNL); A.A. Kruger (ORP)

Research Start Date: August 1, 2007 **Expected Research End Date:** September 2010

Research Objectives

The primary objective of this research is to develop glass formulation methods to allow Hanford and Savannah River Sites to process waste glasses over a broader range of compositions, higher waste loadings, and faster rates. The work was divided into three tasks:

1. Develop a database and models for glass properties that cover a broader range of wastes and at significantly higher loading than the data currently available;
2. Develop a formulation approach to allow for processing of high-level waste (HLW) glasses with significant concentrations of crystals without increasing the risk of melter failure;
3. Study the impacts of melter feed concentration changes on processing rate to formulate glasses with higher processing rates in addition to higher loadings.

The first task is to be conducted in two phases. The first phase was completed in 2007, and the second phase will be completed in 2009.

The second task is a 3 year effort to be completed in 2009 in preparation for scaled melter testing.

The final task will take several smaller steps to accomplish and is aimed at completion in 2012.

This effort will significantly lower the cost and duration of HLW treatment at Hanford and Savannah River.

Research Progress

Task 1) A matrix of 60 glasses was developed to cover over 70 % of the HLW to be treated at Hanford and Savannah River [1]. The glasses were fabricated and tested for all necessary processing and product quality properties under the repository QA program. This database significantly increases the range of compositions to be used in formulation and model development. In particular, broader Al_2O_3 , Fe_2O_3 , Bi_2O_3 , CaO , Cr_2O_3 , Na_2O , and B_2O_3 concentration ranges were developed.

Task 2) Based on the Battelle internal investment of 2006, an approach to formulate glasses with higher crystal content without significant crystal accumulation was followed. A series of tests were performed on four test glasses based on Hanford tank AZ-101 – crystal equilibrium vs. temperature (as shown in Figure 1), viscosity vs. temperature, and concurrent spinel growth and settling kinetics (as shown in Figure 2).



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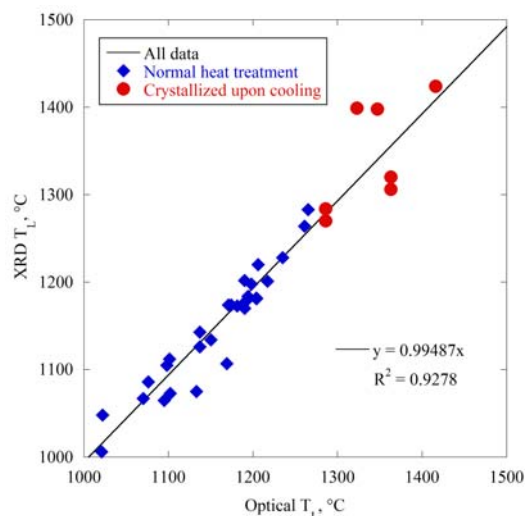


Figure 1. Plot of Crystal Formation as a Function of Optimal Liquidus Temperature

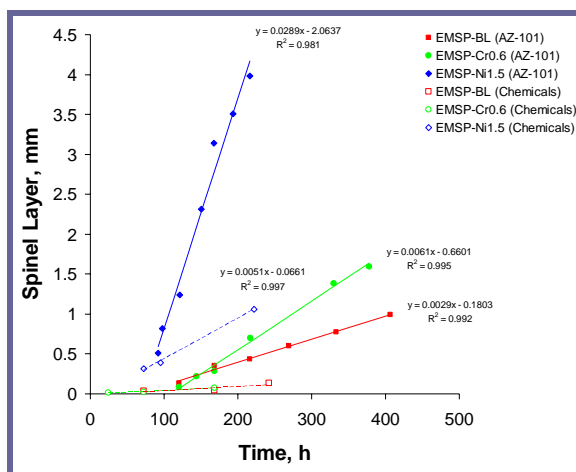


Figure 2. Plot of Crystal Growth Kinetics

These data are being incorporated into models that can predict crystal accumulation within the melter as a function of feed composition that will be used to formulate crystal tolerant glasses for higher waste loading. Preliminary estimates have suggested that such an approach would reduce glass volume at Hanford by over 40% from current estimates.

Task 3) Initial laboratory testing of simulated melter feed reactions began in

October 2007. Two feeds, previously tested in scaled melter tests at Catholic University of America were received. The reactions that lead from wet melter feed to a homogeneous silicate melt are being characterized to identify the rate limiting steps and how they are influenced by feed composition. Shown in Figure 3 is the intermediate crystalline phases grown from a simulated Defense Waste Processing Facility melter feed with temperature.

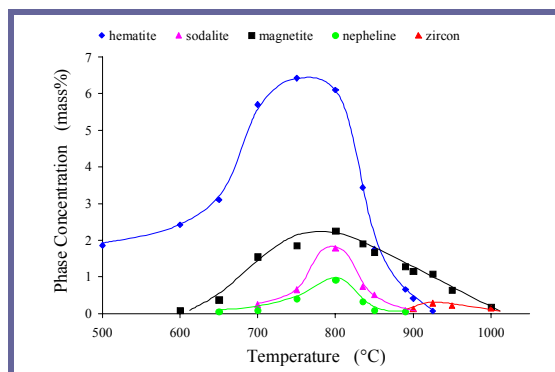


Figure 3. Plot of Formation of Crystalline Phases as a Function of Temperature

Planned Activities

Task 1) In 2008 efforts will focus on documenting the database. A joint EM-21 and CH2M Hill Hanford Group effort will take these data and develop broadly applicable models for application to Hanford HLW. In 2009 the second phase of testing and final model development activities will be performed.

Task 2) In 2008 and early 2009 the crystal accumulation data will be completed. Following the crystal accumulation data collection, models for formulation of high loaded glasses tolerant to crystals will be developed and demonstrated.

Task 3) Melting rate behavior tests will continue in 2008 through 2010 [2].



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Preliminary rate models will be developed starting in late 2010 and continuing through 2012 along with scaled melter tests and comparisons to actual rate data from DWPF.

References

1. D.S. Kim, P.R. Hrma. 2007. *Test Plan: EM-21 HLW Glass Studies – Glass Matrix Testing*, EMHLW-TP-07-01, Pacific Northwest National Laboratory, Richland, WA.
2. P.R. Hrma, M.J. Schweiger. 2007. *Test Plan: EM-21 HLW Glass Studies Melting Rate Enhancement Study*, EMHLW-TP-07-03, Pacific Northwest National Laboratory, Richland, WA.



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1.5 ENHANCED STABILIZATION TECHNOLOGIES

Test and Evaluate High Level Waste (HLW) Vitrification System Improvements 1

Principal Investigator(s): Ian L. Pegg, VSL

Collaborator(s): Innocent Joseph, Bradley W. Bowan (EnergySolutions); Albert A. Kruger (ORP)

Research Project Number: DE-AC27-06RV14790n

Research Start Date: April 21, 2006

Research End Date: April 16, 2007

Research Objectives

The principal objective of this work was to test and evaluate Hanford High Level Waste (HLW) glass compositions to determine the maximum waste loading that can be achieved while still producing a glass that has acceptable durability and processing characteristics.

Glass formulation development was based on four HLW waste compositions specified by The Office of River Protection (ORP) that have high concentrations of bismuth, chromium, aluminum, and aluminum in combination with sodium.

These objectives were addressed through a combination of crucible-scale tests and confirmation tests on the DM100 melter system installed at the Vitreous State Laboratory (VSL) at the Catholic University of America (CUA). All of the work is directly applicable to the Hanford site. In addition, however, high waste loading HLW glass formulations, and especially high aluminum compositions, are needed for the Savannah River site.

Research Progress

Glass formulation development and melter tests were completed in 2006. Fully compliant high waste loading glasses were developed for each of the four HLW streams specified by ORP. Subsequently, tests were conducted on the DM100 melter system to determine processing characteristics. Pictured in Figure 1, the DM100 is a joule heated ceramic melter that is a smaller version of the WTP HLW melters.



Figure 1. DM100 Joule Heated Ceramic Melter System.

During 2007, the final report for the Project was prepared and issued. The



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results from the work showed that substantial improvements in waste loading over the minimum WTP contract requirement are possible for all four of the HLW compositions. Waste loading improvements from this work demonstrated the potential to reduce HLW canister count by ~ 5000 – 6000. The HLW waste loading limiting components and the loadings achieved in this work are given below.

Waste Loading Limiting Component	WTP Contract Minimum Requirement	ORP/EM-21 Formulations From This Work (2007)
Cr ₂ O ₃ (with high SO ₃)	0.5 wt%	1.1 wt%
	Potential reduction in the amount of glass from Cr-limited HLW = 54%	
Bi ₂ O ₃	2.0 wt%	6.7 wt%
	Potential reduction in the amount of glass from Bi-limited HLW = 70%	
Al ₂ O ₃	11.0 wt%	24.0 wt%
	Potential reduction in the amount of glass from Al-limited HLW = 54%	
Al ₂ O ₃ + Na ₂ O	11.0 wt%	21.3 wt%
	Potential reduction in the amount of glass from Al + Na-limited HLW = 48%	

Several important issues were also identified in this work. Because of the high sulfur content, the waste loading in the Cr-limited HLW was limited by chromate/sulfate salt formation rather than by formation of chromium-containing crystals. In addition, even though high waste loadings were achieved for the Bi-limited HLW (50 wt%), the Al-limited HLW (54 wt%), and the Al + Na-limited HLW (48

wt%) streams, the processing rates measured in the DM100 melter tests under the nominal WTP processing conditions were lower than desired. However, various modifications of these conditions that were tested under a new contract in 2008 showed that substantial increases in melt rate are possible.

The results of this work clearly demonstrate the potential for improvements in waste loadings, resulting in significant reductions in the HLW canister count. Additional work is needed to improve the melt rates for some of the HLW streams investigated in this work. Larger scale testing is also needed to confirm processing rates and to provide confidence in the new formulations for HLW processing at Hanford. Since the tests were focused on Hanford HLW, the high aluminum glass formulation development and melter testing were conducted using glass former additive chemicals. To determine the applicability of this glass formulation approach to the Savannah River Site (SRS), melter tests need to be conducted with simulated SRS wastes and with glass frit instead of chemical additives.

Planned Activities

The contract work scope has been completed. However, ORP/EM-21 has initiated another contract to further optimize waste loading in Hanford HLW streams and to develop methods to improve processing rate of high aluminum HLW feeds.

References

1. "High Level Waste Vitrification System Improvements," VSL-07R1010-1, Rev. 0, 4/16/07.



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1.5 ENHANCED STABILIZATION TECHNOLOGIES

Test and Evaluate High Level Waste (HLW) Vitrification System Improvements 2

Principal Investigator(s): Ian L. Pegg, VSL

Collaborator(s): Innocent Joseph, Bradley W. Bowan (EnergySolutions); Albert A. Kruger (ORP)

Research Project Number: DE-AC27-06RV14884

Research Start Date: September 28, 2007

Expected Research End Date: December 2008

Research Objectives

The principal objectives of this work are

- Develop HLW glass formulations with high aluminum loadings that also show high melter processing rates.
- Investigate glass formulations that allow higher crystal content in order to develop higher waste loading glass compositions for HLW that contain high concentrations of Cr and other spinel forming components, and which do not cause processing issues in the melter.
- Determine the settling characteristics of various types of crystals in HLW glass melts.
- Develop higher waste loading glasses for four Hanford LAW streams specified by The Office of River Protection (ORP). These formulations will be designed without iron and titanium as glass former additives.
- Determine the effect of redox state on the behavior of vanadium in the glass. Foaming caused by vanadium can be a potential processing issue.

- Measure the high temperature density, specific heat, and thermal conductivity of two LAW and two HLW glasses.

The glass formulation development objectives will be addressed through a combination of crucible-scale tests, gradient furnace melt rate tests, and small-scale melter tests.

The processing rate of high-Al HLW feeds will be evaluated using DM100 melter tests (melt surface area of 0.108 m²) and confirmed on the HLW Pilot Melter (melt surface area of 1.20 m²) pictured in Figure 1.

LAW glass formulation development will be accomplished through a combination of crucible-scale tests and DM10 melter tests.

Tests using glass melts and physical models that mimic glass properties will be used to study settling of crystals in glass melts.

High temperature density and specific heat will be directly measured. Thermal



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Figure 1. HLW Pilot Melter System.

conductivity will be calculated from measured thermal diffusivity, density, and specific heat values.

All the work is directly applicable to the Hanford site. In addition, however, high waste loading HLW glass formulations, especially high aluminum compositions, are of great interest for the Savannah River Site.

Research Progress

During 2007, the Test Plan for development of high-Al HLW glass compositions with high processing rates was developed and issued for ORP review and approval. In addition, tests at the DM10 melter scale, and using a vertical gradient furnace system were developed to quickly screen glass compositions relative to their processing rates. Glass compositions with high aluminum loadings that were developed in earlier work for ORP/DOE-EM-21

were selected as the starting point on which to base modifications directed towards increased processing rates.

Planned Activities

These activities are planned for 2008:

- Complete formulation development, four DM100 melter tests, and one HLW Pilot Melter test with HLW glasses with high aluminum loadings and improved processing rates. Issue report on development and testing of these HLW glass formulations.
- Issue Test Plan for HLW glass formulation development and testing for glasses with higher crystal content; investigate crystal settling, and measure high temperature properties. Complete glass formulation development and melter testing, crystal settling studies, and property measurements. Issue final report documenting results of work.
- Issue Test Plan for LAW glass formulation development and testing; investigate the effect of redox state on the behavior of vanadium in LAW glasses, and measure high temperature properties. Complete glass formulation development and melter testing, study of the effect of redox state on behavior of vanadium in LAW glasses, and high temperature property measurements. Issue final report documenting the results of the work.

References

The experimental work will be completed and reports issued in 2008.



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1.5 ENHANCED STABILIZATION TECHNOLOGIES

Enhanced LAW Glass Formulations

Principal Investigator(s): Ian L. Pegg, VSL

Collaborator(s): Innocent Joseph, Bradley W. Bowan (EnergySolutions); Albert A. Kruger (ORP)

Research Project Number: DE-AC27-03RV14539

Research Start Date: July 15, 2003

Research End Date: October 5, 2007

Research Objectives

The objective of the work was to develop high waste loading glass compositions for five Hanford Low Activity Waste (LAW) compositions that span the range of sodium and sulfur concentrations.

This was accomplished through a combination of crucible-scale tests and tests on the DM10 melter system installed at the Vitreous State Laboratory (VSL) at the Catholic University of America (CUA). Phase 1 of this work was started in 2003, and Phase 3 was completed in 2007.

The work is most directly beneficial to the Hanford site. The work is also of benefit to other sites (Idaho, Savannah River) that may have to deal with vitrification of waste streams with high concentrations of sodium and/or sulfur.

Research Progress

During 2007, high waste loading glass formulations that meet all processing and product quality requirements were developed for five Hanford LAW waste

streams that span the range of sodium and sulfur concentrations expected in Hanford LAW. Forty one crucible glass melts (Figure 1) were prepared and characterized to develop and identify suitable high waste loading glass compositions for each of the five Hanford LAW streams specified by The Office of River Protection (ORP).



Figure 1. Crucible Melt Preparation.

Glass formulation development followed an iterative approach, where characterization data from one set of



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crucible melts were used to guide the formulation of the next set. Once fully compliant glass formulations were identified for a particular waste stream, the best composition was selected in consultation with ORP for further tests on the DM10 melter.

Pictured in Figure 2, the DM10 melter system includes a continuously-fed, ceramic-lined, joule-heated melter that is a smaller version of the WTP LAW melters.



Figure 2. DM10 Joule Heated Ceramic Melter System.

During the melter tests, the sulfur concentration in the feed was increased in steps until a separate sulfate phase formed on the glass melt surface. In this manner, the maximum sulfur loading in the feed that will not lead to separate sulfate phase formation was identified. Five glass formulations were developed

and five DM10 melter tests were completed in 2007.

The factors that limited waste loading in high- Na_2O glasses are alteration rate on the Vapor Hydration Test (VHT), K-3 refractory corrosion, and secondary sulfate phase formation. In the high- SO_3 glasses, the major challenge was secondary sulfate phase formation, and to a lesser extent alteration rate on VHT and K-3 refractory corrosion.

The results from these tests combined with results from Phase 1 and Phase 2 LAW glass formulation development work for DOE-EM-21/ORP show the potential for an average Na_2O loading in Hanford LAW glasses of 20.6 wt% compared to the Hanford Tank Waste Treatment and Immobilization Plant (WTP) LAW baseline Na_2O loading of ~13 wt%. This is an overall relative increase in waste loading of 58%, which would result in a reduction in the total mass of LAW glass produced at Hanford by ~230,000 MT. The estimate in the reduction of LAW glass produced will change depending on assumptions about the fraction of LAW sent to supplemental treatment, and any increases in process sodium additions.

The Hanford LAW tank identifications and the waste loadings (in wt%) achieved in this work are given below.



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Hanford Tank ID	WTP Baseline Formulations (2001-2004)	ORP/EM-21 Formulations From This Work (2007)
AN-107	WL*: 16.2% Na ₂ O: 14.4% SO ₃ : 0.4%	WL: 26.2 % Na ₂ O: 24.0% SO ₃ : 0.9%
	Relative Improvement in WL = 62%	
AN-104	WL: 20.0% Na ₂ O: 14.6% SO ₃ : 0.4%	WL: 31.0 % Na ₂ O: 23.6% SO ₃ : 0.7%
	Relative Improvement in WL = 55%	
AN-102	WL: 14.0% Na ₂ O: 12.0% SO ₃ : 0.6%	WL: 24.9% Na ₂ O: 21.0% SO ₃ : 1.1%
	Relative Improvement in WL = 78%	
AZ-101	WL: 7.3% Na ₂ O: 5.5% SO ₃ : 0.7%	WL: 19.8% Na ₂ O: 16.0% SO ₃ : 1.5%
	Relative Improvement in WL = 171%	
AZ-102	WL: 3.7% Na ₂ O: 5.5% SO ₃ : 0.7%	WL: 11.9% Na ₂ O: 10.0% SO ₃ : 1.5%
	Relative Improvement in WL = 222%	

* WL – Waste loading

Some of the improvements from the ORP/DOE-EM-21 work have already been incorporated into the WTP Baseline LAW Correlation that will be used to calculate LAW glass formulations for waste processing at the WTP.

The glasses identified during the current work serve to define the likely limits of possible Na₂O and SO₃ loadings in

Hanford LAW glasses that are compliant with the current product quality and processing requirements. It should be noted, however, that these glasses were tested only at the crucible and DM10 melter scales. Additional testing at larger scales is required to confirm the results from smaller scale testing and the results of such testing may result in refinement of these limits. It should also be noted that because of the bounding nature of the formulations (they are deliberately close to the limits of the requirements), practically viable operating points would fall at somewhat lower waste loadings since nominal glass compositions selected for waste processing need to accommodate process variations without adverse effects on processing or product quality

Planned Activities

The contract work scope has been completed. However, ORP/EM-21 has initiated another contract to extend the glass formulation development to other Hanford LAW waste streams and to further optimize the LAW formulations. The new contract also includes support work to assess revisions to the WTP LAW correlation required to incorporate the recently developed high waste loading LAW glasses.

References

The final report for the Project was issued to ORP. The report reference is

1. "Enhanced LAW Glass Formulation Testing," VSL-07R1130-1, Rev. 0, 10/5/07.



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1.5 ENHANCED STABILIZATION TECHNOLOGIES

Support of the CH2M-WG Idaho Calcine Disposition Project

Principal Investigator(s): R. A. Palmer (ICET)

Collaborator(s): Alan Hurst (INL)

Research Project Number: Task 3.1 ICET Cooperative Agreement DE-FC01-06EW-07040

Research Objectives

The goal of this work was to provide decision quality data and documentation for the Calcine Disposition Project, located at the INL Site, which will lead to an acceptable waste form for stabilized high-level waste calcine. Waste forms were produced, analyzed, and tested in collaboration with CH2M-WG Idaho engineers. Physical and chemical performance qualities were determined for three simulated calcine waste forms. These data are being provided under a quality program compatible with DOE/RW-0333P.

The tasks for 2007 included mock-up tests on key components and process control monitors needed to replace manual steps and small laboratory equipment used in the bench scale tests with prototype components (as shown in Figure 1) and automated process control steps.

Research Progress

Laboratory studies and pilot-scale testing have led to the following:

- Lab scale testing of three low-temperature waste forms for the final

disposal of calcine (iron phosphate ceramic, hydroceramic grout and grout cement).

- The selection of grout cement as an acceptable candidate waste form based on TCLP performance and compressive strength characteristics at acceptable waste loadings.
- The demonstration of pilot-scale processing of the grout cement as an acceptable candidate waste form.



Figure 1. Photograph of Prototype Components

Planned Activities

This project is complete. The developed facility is expected to find use in studies of saltstone characteristics.



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1.5 ENHANCED STABILIZATION TECHNOLOGIES

Process Improvements for the Defense Waste Processing Facility (DWPF): On-line Analysis

Principal Investigator(s): Jagdish P. Singh (ICET)

Collaborator(s): David Peeler, Connie Herman, Kristine Zeigler, James Marra, Sharon Marra (SRNL); Patricia Suggs (DOE-SRS)

Research Project Number: Task 4.2 ICET Cooperative Agreement DE-FC01-06EW-07040

Research Objectives

The goal of this project is to assist the Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS) in accelerating melter operations through two approaches:

- The first is to provide a system for direct analysis of slurry in the analytical shielded cells. The capability of direct analysis will significantly increase analytical throughput and reduce waste generation, while providing analyses suitable for waste acceptance and production records.

- The second effort is evaluating plutonium (Pu) oxide residue compositions produced during the processing of the weapons grade material. The ability to quantify Pu residue feeds will provide assurance that appropriate lanthanide borosilicate (LaBS) glass feeds (and therefore compositions) are achieved.

The technique of Laser Induced Breakdown Spectroscopy (LIBS), illustrated in Figure 1, serves as the basis for both Tasks 1 and 2.

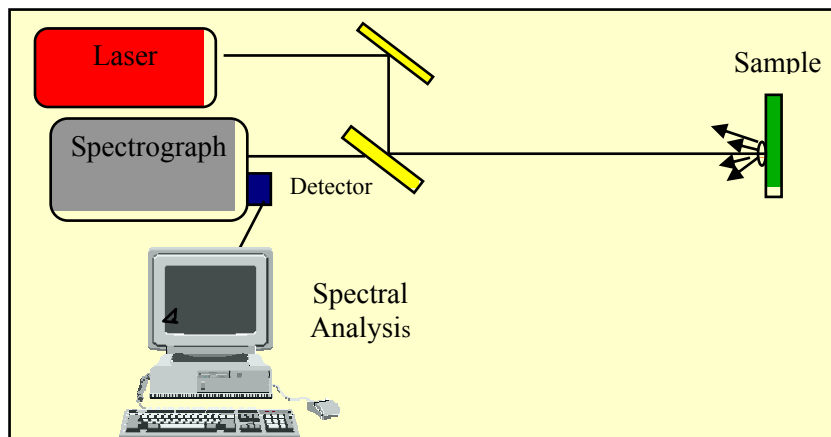


Figure 1. Laser-Induced Breakdown Spectroscopy (LIBS)



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Research Progress

Task 1: Work was concentrated on improving detection sensitivity and the accuracy of quantitative analysis. The use of an Echelle broadband detection system showed a high efficiency in simultaneous multi-element detection and determination of physical quantities. A signal processing technique, which normalizes the atomic emission with the whole plasma emission, significantly improved reproducibility. Still, higher detection sensitivity for minor species and measurement precision is needed for LIBS to be developed as a slurry composition monitor. One of the intrinsic challenges of slurries is particle sedimentation.

Task 2: The feasibility of LIBS application for *in situ* monitoring the composition of radioactive chemical Pu residue by using CeO₂ batch as a surrogate was successfully demonstrated. The major accomplishments in this task included development of a die system for preparing sample press for LIBS measurement; and optimizing LIBS experimental parameters. The accuracy and precision were determined to be 5% or better for major elements and 10% or better for the minor elements

Planned Activities

The planned work for the coming year includes:

1. Continued slurry sample analysis activities will focus on improving sampling, system sensitivity analysis using a double pulse laser excitation system and data analysis techniques;

2. Work on the analysis of surrogate PuO₂ will begin to develop the hardware necessary for interfacing a LIBS system to process facilities. A rotation mount for pellet samples with die will be designed and data will be obtained to determine precision and accuracy.

References

1. First North American Symposium on LIBS (NASLIBS) was organized by the Institute for Clean Energy Technology (ICET)/Mississippi State University (MSU) and held on October 8-10th, 2007 in New Orleans.
<http://www.icet.msstate.edu/naslibs2007/>
2. S. Y. Oh, T. Miller, F. Y. Yueh and J. P. Singh, (2007), "Comparative study of laser-induced breakdown spectroscopy measurement using two slurry circulation systems", *Applied Optics* 46, 4020-4025.
3. H. Zheng, F. Y. Yueh, and J. P. Singh, "Analysis of Surrogate of Plutonium Oxide Residue Using Laser Induced Breakdown Spectroscopy", *Materials Science and Technology Conference and Exhibition (MS&T' 07)*, September 16-20, 2007, Detroit, MI.
4. "Laser Induced Breakdown Spectroscopy" Editors, J.P. Singh and S. N. Thakur, Elsevier Press, Amsterdam, 2007

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1.5 ENHANCED STABILIZATION TECHNOLOGIES

Process Improvements for the Defense Waste Processing Facility (DWPF): Melter Monitoring

Principal Investigator(s): R. A. Palmer, R. Arunkumar (ICET)

Collaborator(s): David Peeler, Don Miller, Michael Smith (SRNL); Patricia Suggs (DOE-SRS)

Research Project Number: Task 4.4 ICET Cooperative Agreement DE-FC01-06EW-07040

Research Objectives

The goal was to assist SRNL in the operation of a new lab-scale melter. The Cold Cap Evaluation Furnace (CEF) was constructed to supplement existing melt rate tools currently with the primary goal of studying the feed flow and cold cap formation of different feeds. The secondary goal was to monitor off gas surges during the feeding process.

This objective was to be evaluated in future studies that would probably involve vessel top modifications and off gas equipment design. Comparing test results from different feeds might also provide an indication of relative melt rate. Continuous feeding and pouring is possible in the melter, but extended testing would require large amounts of feed.

Research Progress

The port assembly (shown in Figure 1), adaptor, installation/operation instructions, and system schematics were delivered to SRNL. The equipment should provide clear optical access for

imaging and other optical instruments during CEF operation.



Figure 1. Photograph of Port Assembly

The completed system includes a purge system for maintaining a clear view of the cold cap using nitrogen.

Planned Activities

This project is complete.



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