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United States Department of Energy
Office of Environmental Management

Waste Processing
Annual Technology Development Report
2008

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Unlimited (Release to Public)

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LIST OF ACRONYMS AND ABBREVIATIONS

ARP	Actinide Removal Process
CBP	Cementitious Barriers Partnership
CCIM	Cold Crucible Induction Melter
CEA	Commissariat à l'Énergie Atomique
CHPRC	CH2M Hill Plateau Remediation Company
CM	Challenging Materials
COTS	commercial off the shelf
CRADA	Cooperative Research and Development Agreement
CRESP	Consortium for Risk Evaluation with Stakeholder Participation
CSL	continuous sludge leaching
CSSX	Caustic-Side Solvent Extraction
CST	crystalline silicotitanate
CTF	Cold Test Facility
CUA	Catholic University of America
DBVS	Demonstration Bulk Vitrification System
DOE	Department of Energy
DoF	degrees of freedom
DST	double shell tank
DWPF	Defense Waste Processing Facility
ECC	Enhanced Chemical Cleaning
ECN	Energy Research Centre of The Netherlands
EM	Environmental Management
EPA	Environmental Protection Agency
EPRR	Enhanced Processes for Radionuclide Removal
ES	Energy Solutions
ESP	Environmental Simulation Program
FIU	Florida International University
FTP	Fourier transform profilometry
HEPA	high efficiency particulate air (filter)
HIP	hot isostatic pressing
HLW	high level waste
HTWOS	Hanford Tank Waste Operations Simulator
ICET	Institute for Clean Energy Technology
IDT	Initiative Development Team
ILSM	In-Line Solids Monitor
INEL	Idaho Engineering National Laboratory
INL	Idaho National Laboratory
ITSM	In-Tank Solids Monitor
IWTU	Integrated Waste Treatment Unit
JHM	Joule heated melter
LANL	Los Alamos National Laboratory
LANS	large area NaSICON structures
LAW	low activity waste
LIBS	Laser Induced Breakdown Spectroscopy
LMR	linear melt rate
MFC	Materials and Fuel Complex
MOC	material of construction
MOU	memorandum of understanding
MRF	melt rate furnace
MRI	melt rate indicator
mMST	peroxide-modified monosodium titanate
MRS	mobile retrieval system
MST	monosodium titanate

MSWR	modified sluicing with recycle
MTDS	Mast Tool Delivery System
MTHM	metric tons of heavy metal
NaSICON	Sodium Super Ionic Conductor
NDAA	Ronald W. Reagan National Defense Authorization Act for Fiscal Year 2005
NDE	non-destructive examination
NIST	National Institute for Standards and Testing
NNSA	National Nuclear Security Agency
NBO	non-bridging oxygen
NRC	US Nuclear Regulatory Commission
NSNFP	National Spend Nuclear Fuel Program
NTCR	near-tank cesium removal
NVE	NuVision Engineering, Inc.
ORNL	Oak Ridge National Laboratory
ORP	Office of River Protection
PA	performance assessment
PCCS	Process Composition Control System
PEP	Pretreatment Engineering Platform
PNNL	Pacific Northwest National Laboratory
PNTTS	pilot near-tank treatment system
QA/QC	quality assurance/quality control
RANS	Renolds-averaged Navier Stokes
RCRA	Resource Conservation and Recovery Act
REDOX	REDuction/OXidation
RF	resorcinol formaldehyde
RKC	Retrieval Knowledge Center
RTG	radioisotope thermal generator
SB	sludge batch
SEE	Systems Engineering Evaluation
SLIM	Solid Liquid Interface Monitor
SME	Slurry Mix Evaporator
SNF	Spent Nuclear Fuel
SNL	Sandia National Laboratory
SNM	Special Nuclear Material
SRAT	Sludge Receipt and Adjustment Tank
SRF	spherical resorcinol formaldehyde
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
SST	single-shell tank
SWPF	Salt Waste Processing Facility
TCLP	Toxic Chemical Leach Procedure
TPB	tetraphenylborate
TRL	Technology Readiness Level
TTP	Task Technical Plan
UTS	universal treatment standard
VSL	Vitreous State Laboratory
VU	Vanderbilt University
WAO	Wet Air Oxidation
WL	waste loading
WRPS	Washington River Protection Solutions
WSRC	Washington Savannah River Company
WTP	Hanford Tank Waste Treatment and Immobilization Plant
XRD	x-ray diffraction

INTRODUCTION

The Office of Waste Processing identifies and reduces engineering and technical risks and uncertainties of the waste processing programs and projects of the Department of Energy's Environmental Management (EM) mission through the timely development of solutions to technical issues. The risks, and actions taken to mitigate those risks, are determined through technology readiness assessments, program reviews, technology information exchanges, external technical reviews, technical assistance, and targeted technology development and deployment. The Office of Waste Processing works with other DOE Headquarters offices and project and field organizations to proactively evaluate technical needs, identify multi-site solutions, and improve the technology and engineering associated with project and contract management. Participants in this program are empowered with the authority, resources, and training to implement their defined priorities, roles, and responsibilities.

The Office of Waste Processing *Multi-Year Program Plan* (MYPP) supports the goals and objectives of the U.S. Department of Energy (DOE)– Office of Environmental Management *Engineering and Technology Roadmap* by providing direction for technology enhancement, development, and demonstration that will lead to a reduction of technical risks and uncertainties in EM waste processing activities. The MYPP summarizes the program areas and the scope of activities within each program area proposed for the next five years 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.

Waste Processing Program activities within the Roadmap and the MYPP are described in these seven program areas:

1. Improved Waste Storage Technology
2. Reliable and Efficient Waste Retrieval Technologies
3. Enhanced Tank Closure Processes
4. Next-Generation Pretreatment Solutions
5. Enhanced Stabilization Technologies
6. Spent Nuclear Fuel
7. Challenging Materials.

This report provides updates on 35 technology development tasks conducted during calendar year 2008 in the Roadmap and MYPP program areas.

IMPROVED WASTE STORAGE TECHNOLOGY PROGRAM AREA

Initiative Development Team Lead: Paul Bredt, Pacific Northwest National Laboratory (PNNL), paul.bredt@pnl.gov, 509-376-3777

Initiative Development Team: John Shultz, DOE EM Office of Waste Processing; Bruce Wiersma, Savannah River National Laboratory (SRNL); Rick Demmer, Idaho National Laboratory (INL); Rodney Hunt, Oak Ridge National Laboratory (ORNL).

Challenge

Both Hanford and Savannah River sites are limited in available tank space to support waste operations and tank retrieval. Many waste tanks are beyond their originally design life, and all will be by the end of the cleanup mission. It is difficult to determine the optimum measures to maximize the utility of the tanks and maintain their integrity. These factors have resulted in an overly conservative safety basis that further constrains available space and hinders tank farm operations.

Solutions

The initiatives in this area pertain to improved monitoring capabilities, improvements in tank integrity assessments, and improvements in understanding of waste tank chemistry and behavior. The goals of these initiatives are to develop technical approaches and tools that allow waste tank integrity to be more accurately assessed and tank storage capacity to be safely maximized. To achieve these goals, work is organized into three areas:

1. Increasing Waste Tank Capacity

This area encompasses development of advanced monitors integrated with new structural materials and methods to enable maximum utilization of existing tank space. Both Hanford and Savannah River sites are limited in available tank space to support waste operations and tank retrieval. This limitation is exacerbated by the inability to utilize single-shell tanks (SSTs) for active operations, the need for emergency tanks capacity, storage restrictions on cracked tanks, and inability to precisely measure sludge heights under a standing supernatant layer.

2. Improved Waste Tank Integrity Assessment

The waste storage tanks are critical national assets that must be maintained beyond their initial estimated design lives. However, it is difficult to determine the optimum measures to maximize the utility of the tanks and maintain their integrity due to incomplete understanding of the tank structural vulnerability and risk of liner corrosion. The goals in this area are to develop technical approaches and tools that allow waste tank integrity to be more accurately assessed such that tank storage capacity can be safely maximized.

3. Improved Understanding of Tank Waste Chemistry and Behavior

This initiative encompasses the chemical and physical behavior of tank waste affecting tank farm operations including safe storage and transport. Several issues must be addressed including:

- Continued reactions within the waste over time effecting its chemical properties as well as gas generation
- Physical and chemical properties of the waste effecting both storage and transfer operations.

Conservative assumptions in the tank farm safety basis relative the first of these issues limits waste storage capacity. Better understanding and control of the physical and chemical properties is needed to prevent and mitigate pipeline plugging, in addition to optimization of mixing, and blending.

Accomplishments

1. Increasing Waste Tank Capacity

During 2008, Florida International University completed work on the Solid-Liquid Interface Monitor (SLIM). This system will allow a much more accurate measurement of the sludge level in tanks under a standing supernatant layer. A more accurate measure removes uncertainty and will allow more sludge to be stored in existing tanks.

2. Improved Waste Tank Integrity Assessment

During 2008, the Office of Environmental Management oversaw the continued work of two External Technical Review Committees, Corrosion and SST Integrity. These committees are in the process of finalizing recommendations to EM.

3. Improved Understanding of Tank Waste Chemistry and Behavior

During 2008, Florida International University conducted detailed studies of two pipeline unplugging technologies and conducted further development of a probe for quantification of solids in transfer pipelines. In addition, Pacific Northwest National Laboratory, Savannah River National Laboratory, and Washington University conducted studies to modify the rheological properties of tank waste at high solids concentrations. All of these technologies will help the sites control their processes avoiding or mitigating the impact of maloperations and increasing processing throughput.

Plans

1. Increasing Waste Tank Capacity

During 2009, this initiative will begin work on reutilization of Hanford SSTs as well as technologies to repair cracked tanks at Hanford and Savannah River. This task will work with sites and regulators to determine what must be known and what technologies must be developed. This will likely include assessing the integrity of the tank liners, integrity of the concrete vaults, materials and technologies for secondary containment, necessary ancillary systems, as well as probes for real-time leak assessment

2. Improved Waste Tank Integrity Assessment

- During 2009, an independent review will be conducted to evaluate recent developments in non-destructive evaluation (NDE) equipment and how they might be applied to the unique conditions of high level waste tanks. The review will provide a forum for nationally and internationally recognized experts from academia and industry to provide recommendations for using state-of-the-art scientific capabilities to provide cost effective NDE of both the tank steel and the concrete materials. As well, vendors will be invited to make presentations of recent improvements to equipment.

- During 2009, this initiative will begin implementation of many of these committees' recommendations. These include developing the technical basis for more protective and less conservative corrosion standards at Hanford and Savannah River, examination of empty SSTs at Hanford to determine the effects of historic stresses on tank integrity, development of new leak detection methods, as well as new NDE technologies for the primary steel liners and concrete vaults.

3. Improved Understanding of Tank Waste Chemistry and Behavior

During 2009, this task will reexamine gas generation models to reduce conservatism, finalize a list of chemical additives that can be used to enable transfers and processing at much higher solids concentrations, develop new in-tank or near-tank probes to reduce risk and enable improved operations in the tank farms, and expand options for plug removal as well as defining control needed to prevent plugging.

IMPROVED WASTE STORAGE TECHNOLOGY

Solid-Liquid Interface Monitor (SLIM)

Principal Investigator: David Roelant, ROELANTD@FIU.EDU, 305-348-6625, and Dwayne McDaniel of Florida International University

Collaborators: Ruben Mendoza, Washington River Protection Solutions (WRPS), Paul Bredt, Pacific Northwest National Laboratory (PNNL)

Project Duration: 2004-2010

Waste Processing Challenge

As Hanford tank waste retrieval operations transfer waste between tanks, it is imperative that engineers have an accurate method of estimating tank waste volume. The inability to monitor the actual solid-liquid interface leads to conservative estimates of the actual amount of solids in the tank so as to prevent exceeding the safe maximum solids level due to gas generation. Hanford site personnel identified a critical need for such an interface monitor, which is capable of detecting the interface between the settled solids and the supernate liquid in a tank. Existing commercial off-the-shelf (COTS) technology for imaging the solids layer level are not suited to the highly radioactive and caustic environment inside these tanks.

SLIM will assist site engineers by providing an understanding of the interface location between the supernate and the settled solids during the transfer of tank waste between tanks. Knowing this location will improve uncertainty in the transfer of the supernate, reducing the likelihood of plugging in the pumps and transfer lines and preventing excess cost and schedule delays related to the plugging. In addition, having an accurate determination of the amount of solid waste will assist in reducing the risk of gas generation build up.

Research Objective

The focus of 2008 work was to complete the design based on additional Hanford-defined needs, and prepare it for deployment at Hanford's Cold Test Facility (CTF) in 2009. In addition, FIU would evaluate an alternative sonar system that could improve shortcomings associated with the sonar head, primarily relating to the onboard electronics.

Research Progress

Based on final requirements from Hanford, the SLIM system design was completed during 2008, while fabrication was started for cold test at the CTF. The containment system design was completed by performing a finite-element analysis of the enclosure loading, and the effect of that load on the support jacks. Laboratory testing validated that the support jacks would not hold the tension load associated with an 85 mph wind load. Based on this finding, the system was modified to use a machine table (Figure 1). The table was selected so that the table top oversized the dimensions of the bottom plate of the enclosure box. The figure below shows the stress distribution of the support table. The maximum stress was determined to be 9,018 psi concentrated at the upper area of the downwind legs, well below the yield strength of the material in use.

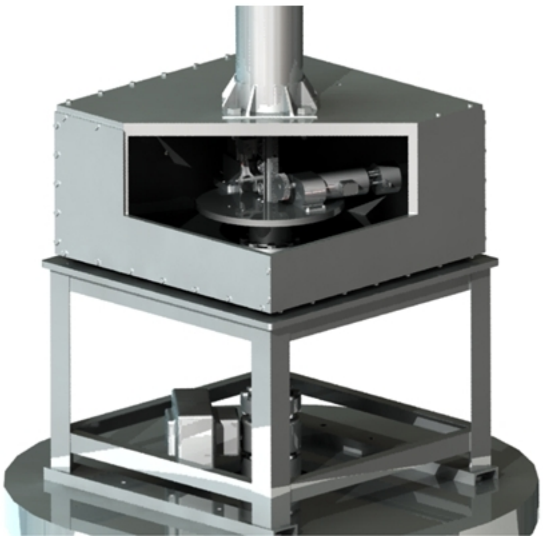

Figure 1. SLIM system with machine table

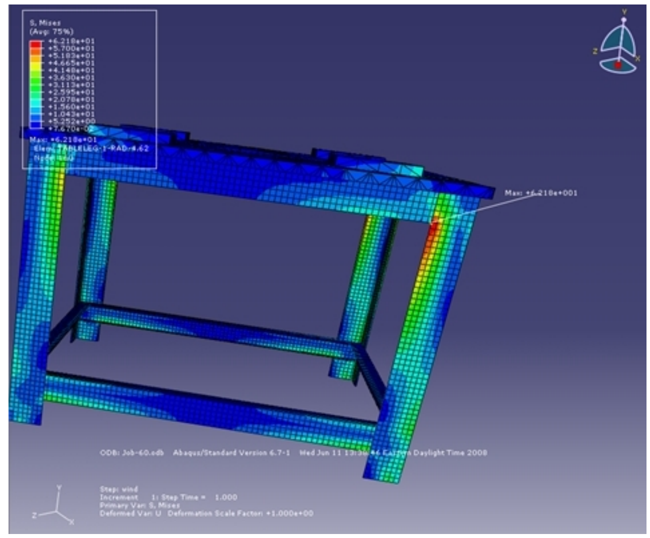

Figure 2. FEA of SLIM support table

At the initiation of 2008, FIU was informed by Hanford personnel that a lack of site funding would not allow the SLIM to be deployed at the CTF. Due to the costs and modifications required to perform cold testing at alternative facilities, FIU was forced to place cold testing on hold until Hanford's CTF could support such an effort. On a parallel task, FIU began to evaluate sonar systems that could reduce system complexity, address longevity issues with on-board electronics, and map with the resolution provided by the current side-scan sonar. Based on this search and evaluation, candidate sonar was selected. The modified system provides a 3D profile of the mapping area from 1 m to 20 m. The sonar operates at 1 MHz frequency, providing a 15 mm resolution at 1 m. All electronics are located in a NEMA 4X enclosure that can be located up to 30 m from the sonar head. The system has a 3.5 in diameter, leaving 0.25 in tolerance for maneuvering the riser into the tank. The housing is titanium with a polyurethane boot for signal propagation. The system includes a software package that can be used for volume estimation, individual depth readings, and control of the system. This alternative sonar was procured for integration into the current SLIM platform and modifications to the SLIM deployment platform were initiated to allow for integration with the new sonar system.

Planned Activities

The planned activity for 2009 will focus on completing the development of the SLIM utilizing the improved 3D profiling sonar; The system modifications as a result of the

3D profiling sonar will reduce areas of operational complexity by minimizing the control system to only include the reel motor, and minimize installation issues with the removal of the 48 ft streetlight pole. The 3D profiling sonar will greatly improve longevity of the system by removing any electronics from the sonar head. In addition, FIU will perform verification testing of the system at FIU, develop manuals and have technology ready for deployment when the opportunity arises.

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1. McDaniel, D., Awwad, A. Srivastava, R., Roelant, D., Varona, J., "Design and Testing of a Solid-Liquid Interface Monitor for High-Level Waste Tanks," Waste Management Symposia, February 2008.
2. Roelant, D., McDaniel, D., Awwad, A. Srivastava, R., Varona, J., Tachiev, G., "Chemical Process Alternatives for Radioactive Waste," Environmental Management Mid-Year Presentation, July 2008.

IMPROVED WASTE STORAGE TECHNOLOGY

Pipeline Unplugging Technology Qualification

Principal Investigator: David Roelant, ROELANTD@FIU.EDU, 305-348-6625, and Dwayne McDaniel of Florida International University (FIU)

Collaborators: Ruben Mendoza, Washington River Protection Solutions (WRPS); Paul Bredt, Pacific Northwest National Laboratory (PNNL); Erich Kezsler, NuVision Engineering (NVE); Dawn Wellman, PNNL; Adam Poloski, PNNL; Robb Burk, Bechtel

Project Duration: 2006-2011

Waste Processing Challenge

Availability of pipeline unplugging technology is critical to the effort of cross-site tank-waste transfers through pipelines. In the past, some of the pipelines have plugged resulting in schedule delays and increased costs. Currently, there are no unplugging technologies qualified to be deployed at the site should the plugging of a transfer line occur. In the past, a number of plug locating, and pipe unplugging technologies were demonstrated at FIU, which identified the most promising technologies with potential for deployment at the site. The current project will build upon results of these demonstrations by qualifying the effectiveness, efficiencies and costs for deploying the most promising pipeline unplugging technologies for use at Hanford and other DOE sites.

Plugged tank-waste pipelines can be expensive to repair, add to schedule delays and potentially expose the environment and site personnel to hazardous conditions. Having unplugging technologies qualified and readily available to assist site engineers when a blockage occurs could assist in minimizing these issues.

Research Objective

The overall objectives of this project are to identify the functions and requirements of unplugging technologies for deployment and to conduct technology qualification testing on the most promising technologies. In order to achieve this goal, novel unplugging methods will be set up at FIU and experimental and numerical techniques will be used to provide details on the governing physics.

Research Progress

During 2008, experimental data collected during the evaluation of NVE’s wave-erosion technique was completed. The operating principles of the wave-erosion method have been identified and the effects of various operating parameters such as drive time, suction and vent times and drive pressures on the unplugging effectiveness were investigated. A numerical model was developed to simulate the flow of the pressure transients in the pipelines with air trapped near the blockage. Results from the modeling were compared with the pressure distributions measured during the experiments with NVE.

In addition, a second pipeline unplugging method from AIMM Technologies was evaluated utilizing the FIU mock-up transfer pipeline with various unplugging scenarios. The pipeline at FIU was built in order to simulate the characteristics of tank-waste transfer lines and the total length of the pipeline was made adjustable (310 ft, 646 ft and 1822 ft) in order to understand the effects of plug distances on the technology parameters. Three different plugs were manufactured simulating clay and crystallized salt-type plugs. The plugs were made from Bentonite clay, potassium-magnesium-sulfate, sodium-aluminum-silicate and were placed in 4ft, 8ft and 12 ft pipe sections. The pipeline pressure distributions during the operation of the AIMM Technologies were recorded at 6 different locations at 1 kHz sampling rate using static and dynamic pressure sensors. In addition to this, internal fluid temperature and pipe wall vibration characteristics were also recorded. The experimental pipeline set up was able to investigate the effects of geometrical and configuration changes in pipelines such as constrictions, elbows and expansion joints. Results obtained after the analysis of the collected data during these experiments revealed crucial information on how the technology operates and what limitations and advantages it offers to site engineer

Figure 1. NVE's Wave-Erosion Method during Experiments at FIU in 2007

Figure 2. AIMM Technologies' Hydrokinetics Method during Experiments at FIU in 2008

Planned Activities

Future activities for 2009 will include completing the data analysis from the AIMM Technologies testing. Additionally, FIU will focus on evaluating alternative conceptual methodologies for pipeline unplugging. The task will initiate by defining the parameters for the additional concepts and conducting computer-aided modeling and simulations of the pipeline and plugged sections. The computational simulations will be used to evaluate if the new unplugging concepts offer improvements over commercially-available methods.

References

1. McDaniel, D., Gokaltun, S., Awwad, A. Srivastava, R., Roelant, D., Varona, J., "Qualification of Innovative Waste Pipeline Unplugging Technologies", Waste Management Symposia, February 2008.
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IMPROVED WASTE STORAGE TECHNOLOGY

Rheological Modifiers and Wetting Agents

Principal Investigator: Jaehun Chun, Pacific Northwest National Lab (PNNL),
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Collaborators: Erich Hansen, Savannah River National Laboratory (SRNL); John Berg, University of Washington

Project Duration: 2008-ongoing

Waste Processing Challenge

In the DOE complex, waste retrieval and processing operations require pipeline transport of solid/liquid slurries. Effective design of pipeline transport systems requires consideration of the minimum transport velocity needed to avoid deposition, calculating the required pressure drop to transport from location A to B, and sizing the pumps needed to facilitate the waste transport. All of these basic engineering calculations require knowledge of the fluid flow behavior, or rheological properties, of the slurry. Paramount among these properties is the so-called "yield-stress" of the slurry. This property is related to the amount of force needed to maintain the flow of the slurry in the pipe.

Efficient process design attempts to maximize the amount of solids flowing in the pipe and through the waste processing plant. Maximizing the solids content results in large yield stress values that become the bottleneck of plant throughput. In extreme situations, the slurry becomes too thick to pump with conventional pumps. The slurry must then be diluted to continue waste transport and processing. Waste throughput is then decreased due to dilution.

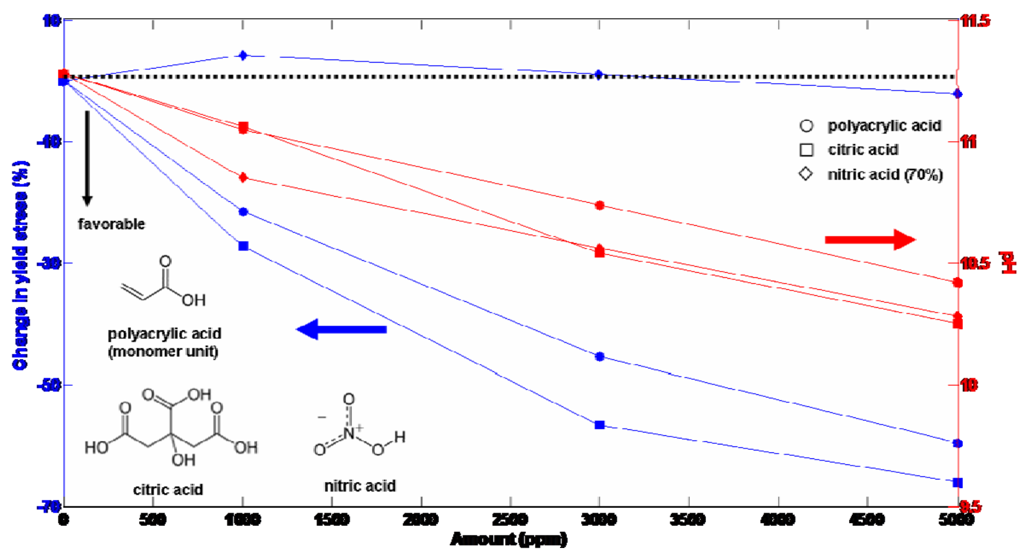
Research Objectives

DOE tank waste treatment plants, the Waste Treatment Plant (WTP) at Hanford and Defense Waste Processing Facility (DWPF) at Savannah River, are designed to vitrify radioactive waste slurries for long-term storage. Plant throughput is currently limited by the waste solids loading. To increase waste throughput rates in the plant, an increase in the slurry solids concentration (or conversely, a reduction in the mass fraction of water in the waste) is being considered. However, the present mechanical designs used to mix and transport theses slurries are limited by the rheological properties. This reduction of water results in an increase in rheological properties that challenge plant design and performance. To support this increase in throughput, there is a need to reduce the rheological properties of these waste slurries. The objective of this project is to determine a small set of well-performing and commercially available rheological modifiers that allow control rheological properties of various simulated and actual waste slurries and to understand the physical mechanisms that govern modification of waste rheology. It is estimated that processing at a higher solids concentration will reduce the operating life of these plants by one year for both facilities, representing roughly $1B in lifecycle cost savings. In addition, this research is potentially important to sustainable operations of both WTP and DWPF.

Research Progress

Preliminary scoping tests with a high-level waste (HLW) pretreated waste feed physical simulant have been performed to identify a set of possible rheological modifiers for further tests. The modifiers employed for tested were weak acids and surfactants. Based on types of repulsive colloidal interactions, rheological modifiers for colloidal slurries can be categorized into two types; binding agents strengthen an electrostatic repulsion and nonionic surfactants bring a steric repulsion. Preliminary results demonstrated the following key findings:

- Control of electrostatic repulsion via binding agents is more effective at reducing waste slurry yield stress than control of steric repulsion by nonionic surfactants.
- Nonionic surfactants do not facilitate an appreciable change in yield stress because of insufficient adsorption on the surface of the waste slurry particles.
- The decrease in yield stress facilitated by binding agents does not appear to be a direct effect of pH alone (see comparison of the weak citric acid to nitric acid in figure following).
- Among binding agents tested, citric acid was identified as the most effective rheological modifier for the HLW simulant.



Decreases in yield stress and pH for polyacrylic acid, citric acid, and nitric acid

Planned Activities

Tests will be performed to cover a wide range of waste types and process steps. Three representative Low Activity Waste (LAW) melter feed simulants will be selected. Corresponding melter feed simulants made by adding glass formers will be tested. Complex HLW simulants include 1) the HLW melter feed physical simulant, 2) an unmodified Pretreatment Engineering Platform (PEP) simulant, 3) a caustic-leached PEP waste simulant, and 4) the PEP simulant with added glass formers. SRNL has archived radioactive DWPF feed and DWPF melter feed samples that have been previously processed in the SRNL shielded cells. Select modifier(s) identified in the scoping studies will be tested with actual wastes. In addition, Dr. John Berg's research group at the University of Washington is performing detailed characterizations and studies on simple model systems such as Boehmite/water. These studies will shed a light on the fundamental mechanisms for rheological modification and allow for improved application of modifiers during tests of complex slurry systems at PNNL and SRNL.

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2. W.B. Russel, D.A. Saville, and W.R. Schowalter, "Colloidal Dispersions," Cambridge Univ. Press (1989).

IMPROVED WASTE STORAGE TECHNOLOGY

In-Line Solids Monitor

Principal Investigator: David Roelant, Florida International University (FIU), ROELANTD@FIU.EDU, 305-348-6625

Collaborators: Ruben Mendoza, Washington River Protection Solutions (WRPS), Paul Bredt, Pacific Northwest National Laboratory (PNNL)

Project Duration: 2008-2010

Waste Processing Challenge

During the past few decades there has been significant progress in moving two-phase tank waste from tank to tank within a single tank farm and across tank farms. At the DOE Hanford site some transfer lines have plugged as a result of these waste transfers. The chemical composition (phosphate levels), the amount of undissolved solids (percent by weight) and the ambient temperature (causing precipitation) have been identified as key plugging factors. To prevent further plugging problems, prior to removing waste from a tank, the composition is monitored and controlled. Heat tracing is added to new waste transfer lines to allow control of temperature during waste transfers. However, one critical parameter, the percent solids by weight entrained in a fluid, is missing because there are no commercial technologies able to measure this parameter.

The percent solids monitors will assist site engineers by providing more detailed characterization of the slurry prior to the transport of the tank waste than previously available. This additional information will reduce the risk of plugging in pumps and pipelines, reducing cost associated with repair and reducing the risk of hazardous exposure to site personnel and the environment. In addition, integrating the solids being transported will allow the site a more accurate and independent measurement of solids being transferred among tanks, across tank farms, and eventually to the WTP.

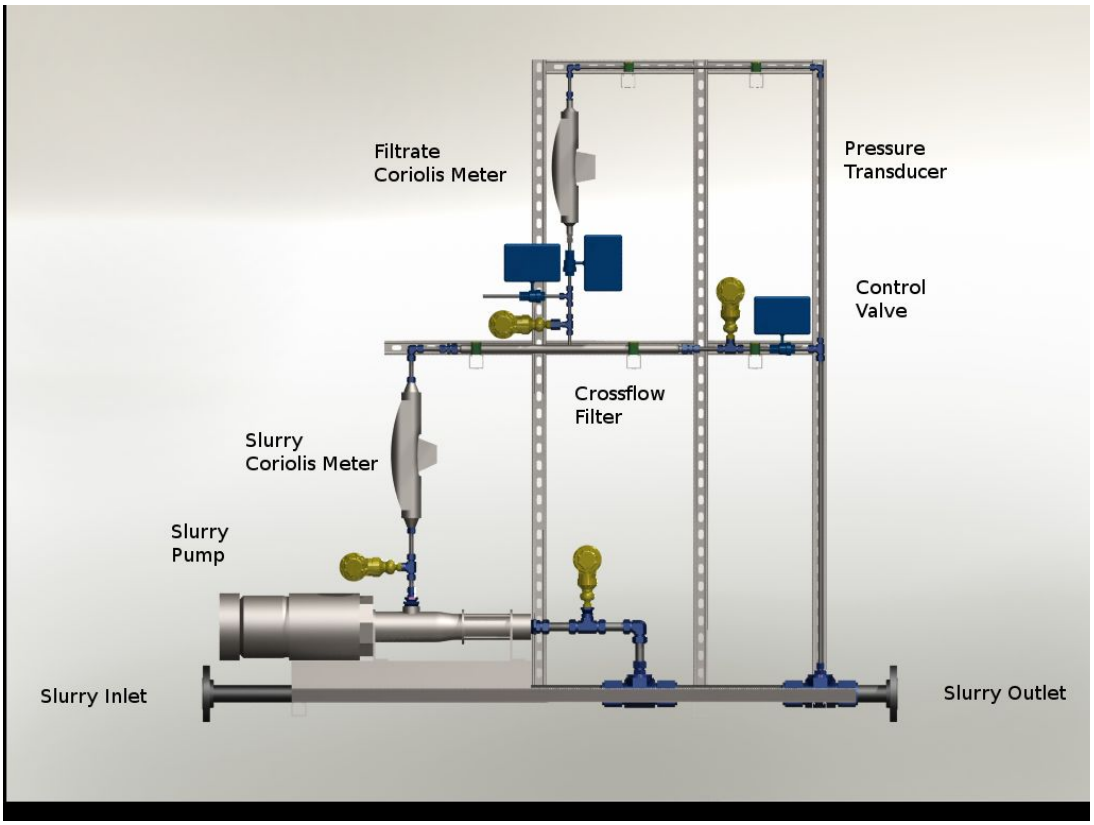
Research Objective

Florida International University with its expertise in tank waste composition and transport has developed a proprietary technology that allows for the direct measurement of percent solids entrained in two-phase fluids. In addition to preventing plugging, this technology can help monitor and calculate the total solids being transferred to the Waste Treatment Plant (WTP) for final treatment. The focus of the 2008 work in support of this project was to develop an In-line Solids Monitor (ILSM) design that integrates the proprietary technology into a system that can be installed within the tank-waste transfer lines. In 2009 the Hanford Site and the Savannah

River Site have both shown more interest in an in-tank solids monitor.

Research Progress

During 2008, transfer line properties were identified, including flow parameters, slurry properties and pipeline dimension and connections. After performing system flow calculations, the ILSM design was developed and the system components were identified. The ILSM consists of a progressive cavity pump, two Endress Hauser Coriolis meters capable of simultaneous measurement of flow (mass and volume flow), density, and temperature with an accuracy of ± 0.15%, a 0.5-micrometer Mott® cross-flow filter, four pressure transducers and three electronically controlled ball valves. All components are designed to withstand the harsh properties of the waste stream including; highly caustic (pH~14), high Gamma radiation, and an abrasive solids content.



In-line solids monitor

Planned Activities

Due to the site's recent interest in a system that can be deployed into the HLW tanks to determine the percent solids profile of the sludge within the tank, FIU will focus on taking the basic percent solids monitoring system developed at FIU and apply it to an in-tank monitor in 2009. Current site requirements call for the In-tank Solids

Monitor (ITSM) to be capable of deployment through an 8-inch diameter tank riser.

In addition, FIU will perform verification testing of the system at FIU, develop manuals and have technology ready for deployment when the opportunity arises.

Reference

Roelant, D., McDaniel, D., Awwad, A. Srivastava, R., Varona, J., Tachiev, G., “Chemical Process Alternatives for Radioactive Waste”, Environmental Management Mid-Year Presentation, July 2008.

RELIABLE AND EFFICIENT WASTE RETRIEVAL TECHNOLOGIES PROGRAM AREA

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Initiative Development Team: Gary Smith and Gary Peterson of DOE-EM Office of Waste Processing; Mike Rinker, Pacific Northwest National laboratory (PNNL); Rick Demmer, Idaho National Laboratory (INL); Mark Noakes, Oak Ridge National Laboratory (ORNL); Charlie Waggonner, Institute for Clean Energy Technology (ICET); Laurie Judd, NuVision Engineering (NVE)

Challenges

The Hanford and Savannah River Sites have over 200 waste tanks that have to be cleaned and closed. Current waste removal and retrieval operations are often limited in effectiveness by tank conditions and waste properties and can be costly. Complications include difficult-to-remove waste deposits, limited accessibility, in-tank debris, and tank obstructions. Bulk waste retrieval that leaves inhomogeneous (i.e. different size, shape, consistency) waste behind could lead to materials that are not acceptable for downstream processing due to size or composition. Additionally, a number of tanks are known or suspected to have leaked in the past, which may limit the use of current technologies that require the addition of significant volumes of water.

Efforts to improve the understanding of the capabilities and limitations of existing technologies will pay immediate benefits by ensuring that the most efficient technology available is selected. The improved definition of requirements and technology gaps will utilize the limited technology development budget in the most effective way possible to reduce the waste retrieval burden. Chemical retrieval technologies to reduce the source term of radioactive material in the waste tanks is an important step to tank closure.

Solutions

To efficiently solve the challenges of waste retrieval, two strategic initiative areas have been identified:

1. Develop a suite of residual-waste removal technologies.

This initiative will develop a “toolbox” of technology solutions to improve bulk waste removal operations and retrieval of residual waste in tanks with various configurations and ancillary systems in preparation for closure. This effort will include identifying and developing requirements and deployment strategies for adaptable concepts and technologies. Gaps in existing DOE and industrial technologies will be identified and used to further define technology needs. Other related activities include the development of adaptable sampling and characterization technologies and tools for use prior to and during residual waste retrieval. Understanding the properties of the material to be retrieved is critical to selecting the appropriate technology for efficient retrieval operations.

The approach in this initiative area involves development of a knowledge center that includes a searchable database of lessons learned and results from previous technology development and deployment across the complex. The requirements and deployment strategies will be developed using complex-wide expertise, and industry experience will be utilized as much as practical.

2. Develop options for chemically cleaning residual waste that cannot be removed with mechanical removal technologies.

Chemical cleaning is needed to dissolve and remove the final residual tank waste. Applying chemical cleaning technologies requires that consideration be given to tank integrity and the impact of residual chemicals on downstream processes. This initiative area focuses on the identification, development, and testing of technologies to be utilized for chemical cleaning while minimizing the impacts on downstream facilities and processes. Test activities will include simulants and real waste.

Accomplishments

The establishment of a Waste Retrieval Knowledge Center has been initiated. This effort is beginning with the development of a searchable database and the definition of retrieval requirements and deployment strategies. The basic requirements for a database have been identified, and development of the database and associated web page has been initiated. Initial brainstorming and technical meetings have been held with experts complex wide . Additionally, the collection and categorization of existing documents has been initiated. Additional details are provided in a following section of this report.

The enhanced chemical cleaning project has been initiated with the development and issuance of a technical task plan. A literature search for the identification of potential technologies for chemical cleaning has been completed. The results of this search are being evaluated to prioritize and define the next test steps. Detailed solubility and corrosion study test plans for oxalic-based technologies have been developed, and testing and modeling efforts initiated.

These enabling technologies pursued in 2008 are detailed in following sections of this report:

- Enhanced Chemical Cleaning
- Demonstration of Power Fluidic Mixing Technology to Enhance Chemical Cleaning Operations in Waste Tanks
- Demonstration of Articulated Nozzle for Improved Sluicing around Obstacles in Waste Tanks
- Large Scale Demonstration Testing of an Alternative Approach for the Retrieval of K-Basin Container Sludge Simulant
- Evaluation of HEPA Filter Performance under Upset Conditions.
- Engineering Studies of Innovative Technologies to Increase Tank Space.

Plans

Details are provided in following sections of this report.

RELIABLE AND EFFICIENT WASTE RETRIEVAL TECHNOLOGIES

Retrieval Knowledge Center

Principal Investigator: Andrew P. Fellinger, Savannah River National Laboratory (SRNL), a.fellinger @srnl.doe.gov, 803-725-5705, and Michael W. Rinker, Pacific Northwest National Laboratory (PNNL), mike.rinker@pnl.gov, 509-375-6623

Collaborators: Erich Keszler, NuVision Engineering (NVE)

Project Duration: 2008-ongoing

Waste Processing Challenge

Over the past several years, tank waste retrieval technologies have been deployed on a tank by tank basis across the Department of Energy's (DOE) complex with little synergy and sharing of information to assist with future retrieval activities. Furthermore, commercial technologies do not offer "off-the-shelf" deployable packages for waste tank retrieval. The Office of Waste Processing commissioned work in August 2008 to begin an initiative to develop a Retrieval Knowledge Center. The concept was to provide DOE, waste retrieval operators, and technology developers with a focused working-level forum to share knowledge, experience and expertise and provide a technical resource that could address technology challenges in waste retrieval across the DOE complex.

The Retrieval Knowledge Center will provide a simple, navigable, central location for retrieval documents and information pertinent to retrieval operations across the waste tank sites. The RKC task will also be used to help identify technical gaps in the retrieval programs based on the technical information made available through the database. The website and database are also expected to a valuable tool to help foster additional technical communications between users and serve as a clearinghouse for new retrieval technology ideas. The RKC also provides the venue to help advance potential retrieval technologies to expedite the insertion of promising technologies in tank cleaning and closure plans.

Research Objective

The objective of the Retrieval Knowledge Center (RKC) was to form an initial core team of complex-wide expertise in retrieval that could assess, gather and share information that would aide in addressing technical gaps in retrieval. The goal was for the RKC to provide a centralized location for sharing detailed technical information related to retrieval deployments at Hanford, Savannah River, Idaho and Oak Ridge. The RKC was also envisioned to facilitate information sharing through working meetings, workshops and through the development of a searchable database of waste retrieval technology information. Ultimately, the RKC would provide the venue for assembling information on new retrieval technologies and assessing state-of-the-art technologies applicable in to retrieval needs within the complex.

Research Progress

To encourage collaboration between DOE waste tank sites, the core RKC team was formed around co-leadership from SRNL and PNNL, and rounded out by NVE for their experience in providing the DOE with technologies to address specific waste tank needs.

Technical accomplishments in 2008 included SRNL and PNNL collaboration with NVE to develop a test version of the Retrieval Knowledge Center web site and database. NVE's subcontracted webpage design allowed provisions for users to submit technical information and reports, and includes a number of attributes attached to each entry (i.e. document) for an easy to use but fairly robust search engine (see figure following). The website also features a database that will import documents from the Retrieval Technology Guide that was previously developed but had not been maintained since 2002. The database may be used to research effective technology approaches for specific retrieval tasks and to take advantage of the lessons learned from previous operations. It is also expected to be effective tool for users to remain current with the state of the art in retrieval technologies and with ongoing technology development within the DOE complex. The core team completed two beta tests of the web site and database in 2008.

The RKC also hosted and facilitated two working meetings in the fall of 2008 designed to define top-level waste retrieval functional areas, exchange lessons learned, and develop a path forward to support a technical plan focused on addressing technology needs for retrieval. At Hanford, there have been several retrieval campaigns over the past several years, and the waste feed requirements for the Waste Treatment Plant are beginning to result in formidable flow down requirements to tank farm and treatment plant operations. At SRS, tank retrieval challenges could limit subsequent immobilization processing plants from reaching full capacity. The working meetings engaged tank farm operations and engineering personnel; national laboratory researchers; and commercial industry representatives (NVE). Those meetings resulted in technical challenges in each of the major high level retrieval functions. It also demonstrated the value of discussing the similarity of technology gaps between the sites, and provided recommendations on which of the technology gaps would hold the highest value when resolved.

Planned Activities

The team will issue a report documenting the retrieval challenges resulting from the two meetings in 2008. The team will also develop a roadmap(s) to tie potential technologies to the challenges and recommend areas of retrieval technology development and demonstration. The team will launch the RKC website and complete the collection of technical retrieval documents. The RKC will also work amongst the various retrieval technology development and deployment efforts (that involve private industry, national laboratory, and university work) to assist with developing a Community of Practice that will foster increased sharing of knowledge and experience in this technical area.

RELIABLE AND EFFICIENT WASTE RETRIEVAL TECHNOLOGIES

Alternative Enhanced Chemical Cleaning of Waste Tanks

Principal Investigator: William D. King, Savannah River National Laboratory (SRNL), william02.king@srnl.doe.gov, 803-725-7556

Collaborators: Michael S. Hay and Christopher J. Martino of SRNL

Project Duration: 2008-ongoing

Waste Processing Challenge

Mechanical cleaning often cannot remove remaining residual waste prior to tank closure. Baseline chemical cleaning technology utilizes high amounts of oxalic acid which causes downstream impacts. Alternative technology that utilizes less oxalic acid or alternative chemical must be identified

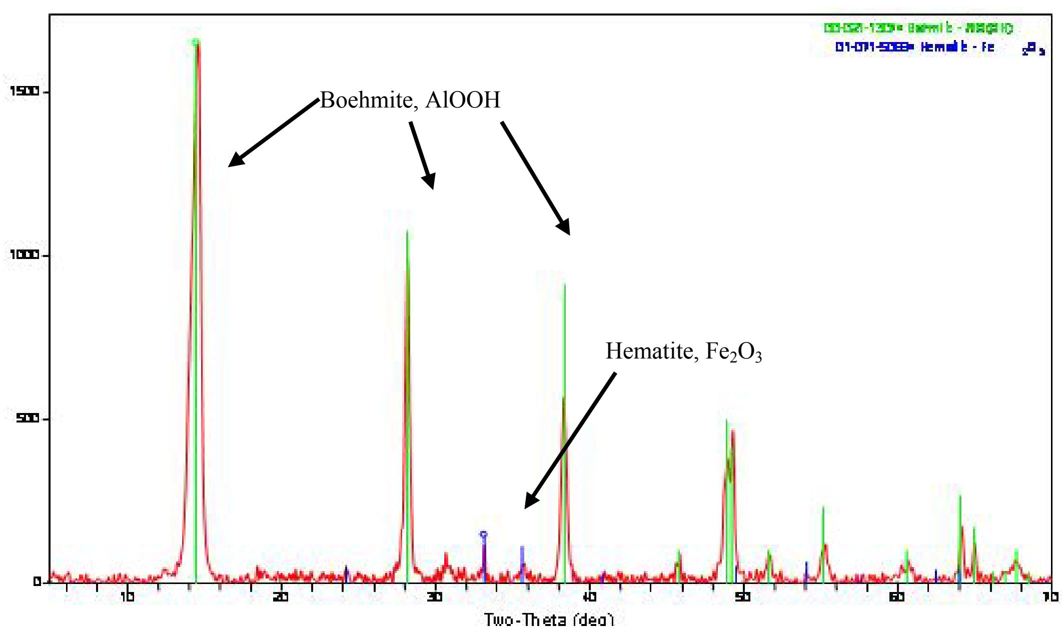
Research Objective

A test program is being conducted at the Savannah River National Laboratory which focuses on the removal of radioactive sludge slurry heels remaining in waste tanks at the completion of mechanical sludge removal campaigns. Nominally 5000 gallons of slurry remains distributed among a maze of cooling coils in Savannah River Site (SRS) waste tanks. Heel removal is required for tanks which are targeted for closure. The tank chemical cleaning concept involves the removal of these heels by chemical dissolution, although it is feasible that some suspended insoluble solids may also be removed in subsequent waste transfers. It is preferred that a technology be identified which is applicable to heel removal operations for waste tanks at both SRS and Hanford. Given the range of waste compositions existing in the tanks, however, it is unlikely that a single treatment technology can be used in all tanks. Rather, a suite of technologies will likely by needed with the preferred technology for a given tank depending upon the waste composition involved.

The focus of the Alternative Enhanced Chemical Cleaning Program is to identify and evaluate alternatives to the baseline SRS chemical cleaning technology (8 wt. % oxalic acid) and further understanding of the chemistry involved with the most promising methods. Oxalic acid is generally considered to be the cleaning agent of choice for the removal of tank heels, but oxalate ion has significant downstream processing impacts. Nonetheless, the baseline process has not been optimized to minimize the addition of oxalate to the tank farm. Oxalate minimization can occur by decreasing the amount of reagent added for dissolution or by destroying the oxalate prior to transfer to the receipt tank. Due to changes in the requirements and expectations for tank chemical cleaning methods and the desire to develop a number of tools for heel removal there was a need to reevaluate the alternative technologies. As a result, a Literature Review was conducted which built upon previous published reviews. Based upon the results of the review, a Systems Engineering Evaluation (SEE) was conducted to identify areas considered worthy of further study. Two separate rankings were performed in the SEE which focused on 1) alternative chemical cleaning technologies/reagents, and 2) organic oxidation technologies (primarily oxalate). Reports are currently being issued for the Literature Review and the SEE and plans are underway to initiate new testing programs based on SEE recommendations.

Research Progress

Solubility tests were initiated as part of a Basic Studies Program in parallel to the Literature Review and the SEE. Inconsistencies in historic testing results and recent observations in baseline SRS chemical cleaning operations with 8 wt. % oxalic acid revealed weakness in the basic understanding of the chemistry involved with oxalic acid cleaning. SEE recommendations validated this need as well as a need to evaluate other acids as a means to minimize oxalate usage. Solubility testing is being conducted with various combinations and concentrations of acids (including oxalic) in order to optimize and understand sludge dissolution chemistry with a focus on the primary sludge components, aluminum and iron. During this testing it was discovered that current sludge simulants have non-representative solubility characteristics due to the fact that acid solubility was not an evaluation criteria or requirement during simulant development. Furthermore, a review of historical x-ray diffraction (XRD) data on actual tank waste slurries revealed that only a limited number of aluminum and iron phases had been observed and these included some quite refractory phases. One of a handful of XRD analysis results obtained for actual waste samples is shown below.



XRD of SRS Tank 12 Actual Waste Sludge.

Testing in the Basic Studies Program has therefore focused on specific pure crystalline phases observed in tank heels. Results from these studies will be summarized in a report near the end of 2009. Additional XRD data on actual tank sludges is also being obtained through the Office of Waste Processing program in an effort to build the database of known phases present in SRS waste sludges. The development of sludge simulants with representative solubility properties is currently being funded by another program.

Planned Activities

Top recommendations for further study from the SEE include:

- Advanced oxidation processes for oxalate destruction (currently under development by SRS Liquid Waste Operations)
- Mn-catalyzed nitric acid for oxalate destruction
- Permanganate for oxalate destruction
- Combinations of oxalic with other acids or complexants to optimize dissolution and minimize added oxalate (already initiated as part of the Basic Studies Program).

RELIABLE AND EFFICIENT WASTE RETRIEVAL TECHNOLOGIES

Demonstration of Power Fluidic Mixing Technology to Enhance Chemical Cleaning Operations in Waste Tanks

Principal Investigator: Erich Keszler, keszler@nuvisioneng.com, 704-799-2707; Ethan King, and Laurie Judd of NuVision Engineering (NVE)

Collaborators: Sharon Marra, Savannah River National Laboratory (SRNL); Mark Mahoney, Washington Savannah River Company (WSRC); Leonel Lagos, Florida International University (FIU)

Project Duration: 2008-ongoing

Waste Processing Challenge

NVE is developing a Power Fluidic™ low level mixing system for application in the Enhanced Chemical Cleaning (ECC) operations planned for the Savannah River Site (SRS). Washington Savannah River Company (WSRC) is in the conceptual design phase for ECC for Tank 8, a 1M gallon waste tank. The baseline design for Tank 8 ECC includes Power Fluidic™ mixing systems.

The Enhanced Chemical Cleaning process aims to reduce oxalate loading and total volume of cleaning solution in comparison to previous methods. The key elements to the technology are dilute oxalic acid, low liquid levels, and circulation of the fluids. Circulation is required to promote a fresh boundary layer to the reacting materials and provide enough velocity to move particles away from the reaction site. This operational duty is technically challenging due to the low liquid levels and limitations posed by the tank geometry. Type I tanks like Tank 8 contain structural stanchions and grids of horizontal and vertical cooling coils that could obstruct fluid flow.

Research Objective:

The objective of this design/development project is to demonstrate Power Fluidics™ technology as a viable option for this mixing duty. The equipment will be designed, fabricated and tested at near full scale. A successful result will permit the detailed design of a deployable system and production of that system for Tank 8 operations.

Power Fluidics™ pulse jet mixers are maintenance-free nuclear equipment built around the principle of using one clean medium (air) to move radioactive fluids. A Power Fluidic™ system typically consists of a controller, a valve skid, a jet pump skid, a charge vessel, and an off-gas skid. The compressed air, acting across the jet pump, creates either a high pressure or a vacuum in the charge vessel. The charge vessel is filled with fluid and evacuated in cycles, creating the mixing action in the tank. A set of interconnecting pipebridges completes the set of equipment for the Power Fluidics™ pulse jet mixers. Two benefits of NVE's power fluidic systems are the potential for re-use of many of the original components for multiple tank cleaning campaigns (thus amortizing the initial capital outlay over a number of projects) and the maintenance-free reliability that results from few to no moving parts inside the tank.

Research Progress:

NVE has designed a Power Fluidic™ low level mixing system for application in ECC processes. This system is based on two fluidic pumps (two jet pump pairs, two charge vessels, and two discharge nozzles). The system is being fabricated and installed in NVE's near full scale Type I tank. This 80% scale, 60ft diameter tank was designed and constructed in the NVE facility for this demonstration project. The tank can be filled with two feet of water and contains simulated obstacles: horizontal cooling coils, stanchions, and vertical cooling coils (not pictured). NVE intends to demonstrate that this system is capable of generating the minimum required fluid velocity throughout the majority of the tank. The coordinated efforts of the two nozzles are expected to achieve if not maintain the required scalar fluid velocity in areas susceptible to mounds of waste.

80% scale, 60ft diameter tank designed and constructed in the NVE facility for this demonstration project

Planned Activities:

NVE will be hosting a stakeholder visit on July 22, 2009. Representatives from Office of Waste Processing, SRNL, and WSRC have been invited to witness a demonstration of the Power Fluidic™ low level mixing system in operation.

References:

Interim reports, test plans, and system profiles are available on request.

RELIABLE AND EFFICIENT WASTE RETRIEVAL TECHNOLOGIES

Demonstration of Articulated Nozzle for Improved Sluicing around Obstacles in Waste Tanks

Principal Investigator: Erich Keszler, keszler@nuvisioneng.com, 704-799-2707; Ethan King, and Laurie Judd of NuVision Engineering (NVE)

Collaborators: Sharon Marra, Savannah River National Laboratory (SRNL); Mark Mahoney, Washington Savannah River Company (WSRC)

Project Duration: 2008-ongoing

Waste Processing Challenge

Operators at the Savannah River Site attempted to perform sluicing operations in Type I waste tanks on several occasions. The equipment used in these operations ranged from straight hand-manipulated lances to improvised articulated equipment. These operations had limited success due to limited riser access and the highly obstructed nature of these tanks. NVE has deployed power fluidic technology in conjunction with articulated nozzles to accomplish tank sluicing with success. These 2-Degree-of-Freedom (DoF) nozzles are effective in tanks with open access but are not suitable for sluicing operations in waste tanks at the Savannah River Site. Waste tanks at Savannah River contain vertical obstructions including grids of cooling coils, instrument trees, in-tank equipment, and structural components. These obstacles will impose limits on the envelope of 2-DoF systems, where control of position and orientation are dependent. Obstacles inside the range of motion of the nozzle block the ability to aim in a particular direction. Obstacles closer to the target areas create shadow areas that the sluicing stream cannot reach. The use of a 2-DoF articulated sluicing system at SRS would result in more material left in the tank than is acceptable for tank closure.

Research Objective:

Effective sluicing operations in SRS waste tanks require development of improved articulation. The development of 4-DoF articulated nozzles would allow independent control of position and orientation (targeting) and reduce or avoid limitations posed by obstacles inside the range of motion. The improved system's extended range will allow the nozzle to reach down alleys between grids of cooling coils, target specific areas from different angles, and reduce the size of shadow areas. Figure 1 illustrates the potential range of a 4-DoF articulated nozzle.

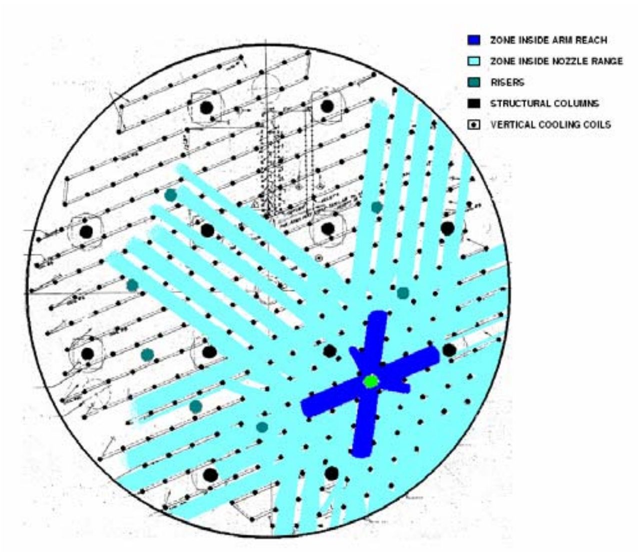


Figure 1. Potential range of a 4-DoF articulated nozzle.

The objective of this project is to design one or more articulated sluicing nozzles with improved capability. These nozzles will feature 4-DoF systems with increased lateral reach and independent control of position and targeting in order to facilitate sluicing among vertical cooling coils. NVE will then fabricate and demonstrate the capability of these designs in the new Engineering Scale Test Facility in Mooresville, NC. Successful demonstration will serve as the basis for including the technology in deployable equipment at Savannah River or other sites.

Research Progress:

NVE has developed five design concepts based on different technical approaches from a series of brainstorming and prototyping events. The five alternatives (Figure 2 below) include the baseline nozzle featured in past NVE deployments and an application of NVE's Artisan robotic arm. New designs include a gimbaled arm concept, a technology transfer of fire monitor devices, and a modular robotic concept based on Helac rotary hydraulic joints. For each concept, NVE has generated concept design data and assessed the technical feasibility and capability. NVE has estimated the effort and cost required to bring each concept to demonstration as well as the order of magnitude cost to bring to deployment.

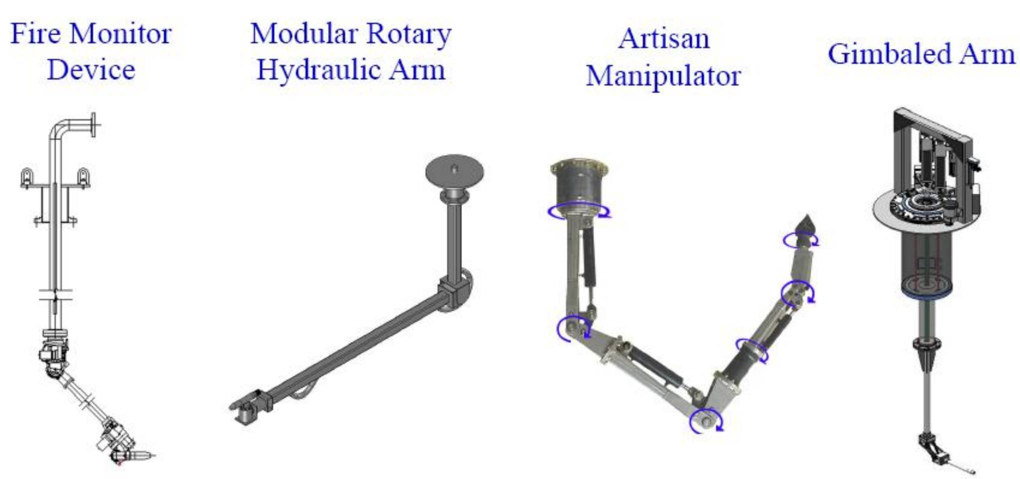


Figure 2. Illustrations of Technical Alternatives

Planned Activities:

NVE will conduct a down-selection analysis following the approach developed by UK consulting firm Cogentus. An external stakeholder criteria workshop will be held in April 2009 near the SRS site to create the selection criteria and establish criteria weights. NVE will score each alternative and input the data to a PROMAX decision analysis model.

A demonstration of the selected sluicing designs will be conducted in 2009.

RELIABLE AND EFFICIENT WASTE RETRIEVAL TECHNOLOGIES

Large Scale Demonstration Testing of an Alternative Approach for the Retrieval of K-Basin Container Sludge Simulant

Principal Investigator: Erich Keszler, keszler@nuvisioneng.com, 704-799-2707; Laurie Judd, and Paul Fallows of NuVision Engineering (NVE)

Collaborators: CH2M Hill Plateau Remediation Company (CHPRC)

Project Duration: 2008-2009

Waste Processing Challenge

As part of the continuing Hanford Site restoration, K-Basin sludges have been containerized prior to treatment and ultimate disposal. Each container consists of a number of chambers which slope to the base and an outlet connection. The baseline approach for sludge retrieval and transfer from these containers is to pump the sludge from a manifold arrangement which connects all of these outlets. Concerns regarding the technology maturity of this approach led to investigations into alternative methods for removing the sludge from these containers.

Research Objectives

The baseline approach to retrieval of sludge from the K Basin containers has been identified as being 'technically immature'. The proposed approach has been demonstrated to have the potential to provide DOE with a 'top retrieval' approach which is both more flexible and applicable to the requirements.

An alternative 'top retrieval' option was proposed by NVE in 2007 and resulted in proof of principle trials at facilities in the Richland area in 2008. These trials successfully demonstrated that the proposed approach was capable of mobilizing and transferring container sludge simulant. Success of the first phase of these demonstrations has led to the proposal of an extension of the trials into a second phase of activities to be conducted in Richland, WA, close to the Hanford site. The stated objective of this second phase of testing is to 'Characterize the retrieval of a representative Container simulant at 25 volume percent solids & 75 volume percent water and show that it can be transferred at a minimum of 5 volume percent, to a staging tank.

Research Progress

All testing has been completed. The unit under test (Figures 1 and 2) met or exceeded all stated test objectives, successfully transferring both Basin and Settler simulants from the test tank to the receiving tank.

Figure 1. Test Unit in Hopper Bottom Tank Prior to Testing

Figure 2. Test Personnel Inspecting Test Tank Contents after Retrieval

Planned Activities

The next phase of work will be to design a system in a prototypical configuration that could be tested prior to field deployment. This system must contain the operational features to enhance entry to the containers and operations in the basin. This prototypical unit will also be matched to the transfer system in terms of flows and pressures so that the entire system can be tested together.

RELIABLE AND EFFICIENT WASTE RETRIEVAL TECHNOLOGIES

Evaluation of HEPA Filter Performance under Upset Conditions

Principal Investigator: Charles A. Waggoner, Institute for Clean Energy Technology (ICET), waggoner@icet.msstate.edu, 662-325-7601

Collaborators: Steven L. Alderman and R. Arunkumar of ICET; Duane Adamson, Savannah River National Laboratory (SRNL), Leader of AG-1 Section FI Working Group (High Efficiency Metal Media Filters); Jim Slawski, Editor of the Nuclear Air Cleaning Handbook; Jim Honeyman (CH2MHill Hanford); David Eaton, Idaho National Engineering Laboratory (INEL); Pat Suggs, DOE Savannah River Operations Office (DOE-SR); Billie Mauss, DOE Office of River Protection (DOE-ORP)

Project Duration: 2008-2011

Waste Processing Challenge

Numerous applications exist within the waste treatment operations at DOE sites where temperature or moisture conditions exceed acceptable ranges for conventional fibrous glass HEPA filters. Sintered metal fiber media has emerged in the market place as a highly desirable substitute for fibrous glass media in these more aggressive environments. There is currently no standard covering use of such media in nuclear applications; however, Section FI Metal Media Filters of the AG-1 standard is under development.

Research Objective

Evaluate effects of media velocity on filter performance and loading capacity. These evaluations provide needed information for improved designs of new systems and operating strategies, updating AG-1 codes, and improving filter loading models.

Research Progress

Media velocity testing results were submitted for publication and appeared in the November, 2008 issue of Journal of Occupational and Environmental Health. Additional findings were reported at the 2008 Nuclear Air Cleaning Conference in Seattle, WA. These findings were based on studies involving 12”x12”x11.5” AG-1 HEPA filters challenged with two different particle size distributions of potassium chloride at media velocities ranging from four to eight feet per minute. Findings included determination of the variability of the most penetrating particle size over the test range for both of the particle size distributions tested. All filters tested had passed manufacturer conventional dioctyl phthalate (DOP) testing and had filtering efficiencies in excess of 99.97%. While numerous filters were tested at elevated media velocities without demonstrating leaks, ICET testing demonstrated excellent sensitivity in the detection of pinhole leaks not otherwise seen by conventional DOP testing. This testing demonstrates the sensitivity of polydisperse aerosol challenges to identify the presence of pinholes as opposed to elevated media velocities increasing leak rates through pinholes. Testing also demonstrated no effective change in the most penetrating particle size as a function of media velocity up to the maximum 8 feet per minute

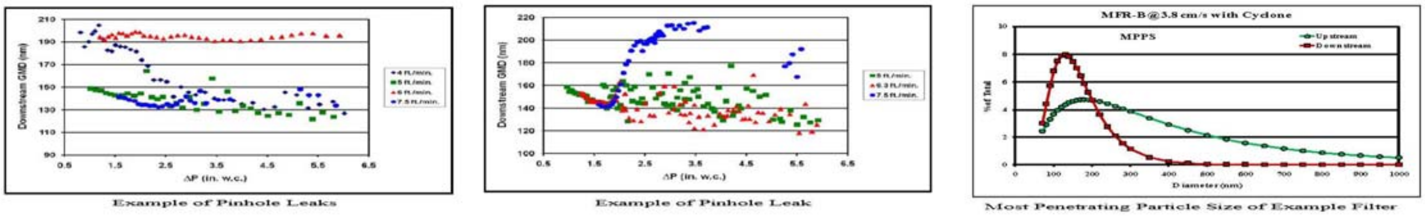


Figure 1 Media velocity text results

Autopsies were performed on all of the filters that were involved in media velocity testing conducted at ICET. Small coupons were excised from pleats representative of the filter media pack. These coupons were then utilized to determine the loading patterns of the individual pleats as well as the filter loading patterns from front-to-back and top-to-bottom for each media velocity tested. Selected samples were examined by electron microscopy to determine media depth loading.

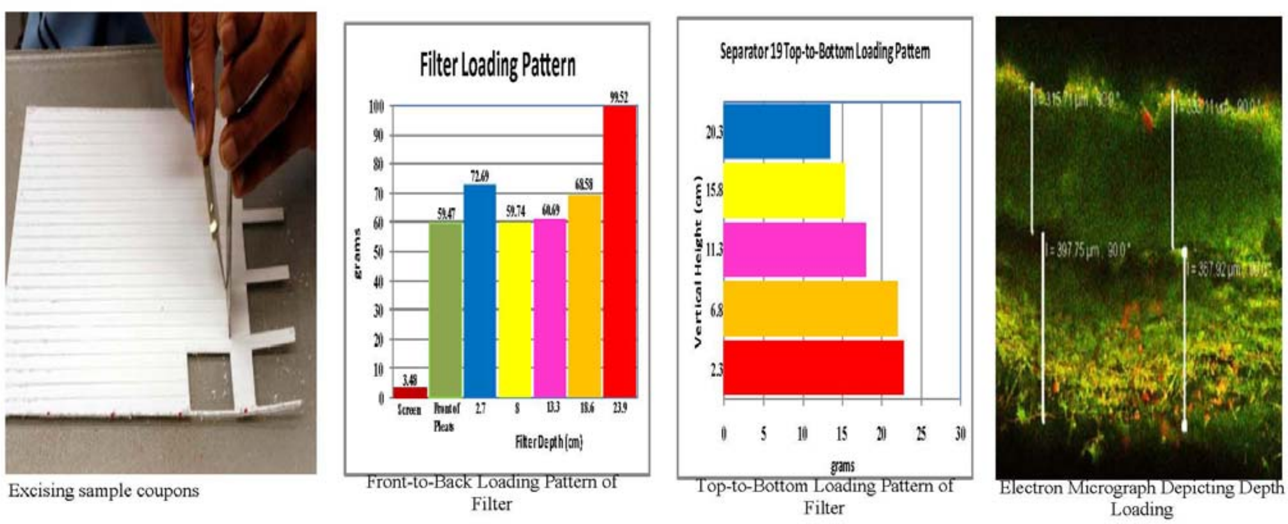


Figure 2. Filter autopsy results

Planned Activities

Collaborators: Elaine Diaz, DOE-ORP; Sharon Steele, National Nuclear Security Agency (NNSA)

ICET is developing a larger-scale HEPA filter test stand to evaluate the performance of one to four 1000 CFM (AG-1, Section FC) filters or up to two 2000 CFM (AG-1, Section FK) filters at rate flow velocities

and to differential pressure levels of 30 in w.g.
Activities to be conducted during 2009 include design and fabrication of new test stand, characterization of its performance and challenging AG-1 Section FK radial flow filters with carbon black. The test stand and auxiliary equipment will include the capability of challenging filters with smoke, soot, high moisture levels, and high temperatures. Test plans are currently under development through collaborations with representatives from Hanford ORP and from NNSA responsible for reviewing DOE-STD-1066-99 “Fire Protection Design Criteria”.

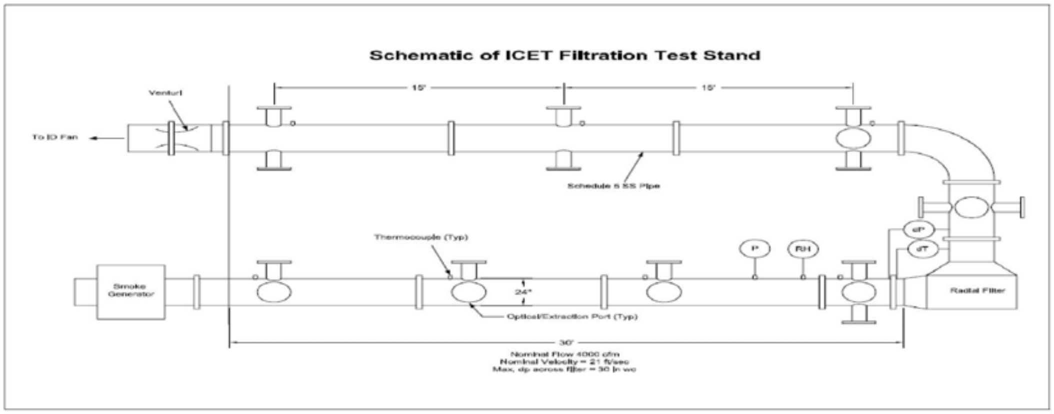


Figure 3. Schematic of New ICET Large-Scale HEPA Test Stand

References

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2. S.L. Alderman et al, “The Effects of Media Velocity and Particle Size Distribution on Most Penetrating Particle Size and Filter Loading Capacity of 12”x12”x11.5” AG-1 HEPA Filters”, Nuclear Air Cleaning Conference, Seattle, WA (2008).
3. Alderman, Steven L., Parsons, Michael S., Waggoner, Charles A., “Filter Autopsy for Evaluating Effects of Particle Size Distribution and Media Velocity on Loading Patterns”, Nuclear Air Cleaning Conference, Seattle, WA (2008).

RELIABLE AND EFFICIENT WASTE RETRIEVAL TECHNOLOGIES

Optimization of High Level Waste Retrieval Using Numerical Modeling

Principal Investigator: David Roelant, Florida International University (FIU), ROELANTD@FIU.EDU, 305-348-6625

Collaborators: Ruben Mendoza, Washington River Protection Solutions (WRPS), Paul Bredt, Pacific Northwest National Laboratory (PNNL), Blaine Barton, WRPS

Project Duration: 2007-2009

Waste Processing Challenge

The double-shell tanks (DSTs) in the Hanford site are used to temporarily store the waste retrieved from the single shell tanks (SSTs) before sending it to the Waste Treatment Plant. DST space is limited, and maximizing the utilization of DST space is the goal of the S-109 Partial Waste Retrieval Project that will provide waste feed to the Demonstration Bulk Vitrification System (DBVS). The waste liquid in S-109 contains significant amounts of cesium (0.32 Ci/L), enough that the S-109 retrieved waste must be pretreated prior to supplying feed to the DBVS to ensure compliance with the DBVS waste feed specification (<0.006 Ci/L). Pretreatment will be accomplished via selective washing and dissolution of the saltcake, which is 170 inches deep. A plan for pretreatment of S-109 is to add water to the top of the salt cake and pump liquids using a combination of three pumps installed at various depths inside the tank.

This study could potentially provide DOE site engineers with a technique for using significantly less water to effectively flush the water-soluble radionuclide from tanks, resulting in the most optimal and cost-efficient retrieval strategy.

Research Objective

Florida International University has developed a 2-D model of the tank to assist with the prediction of cesium breakthrough curves in the resulting salt cake brine. The 2-D model includes slow diffusion in a solid or stagnant pond, transport in void and flow through pores in completely saturated and partially saturated media. Cesium is a strong electrolyte, and it is assumed that advection and dispersion are the two main processes that affect its movement. The results of the selective dissolution model are analyzed and presented here. This predictive information is critical for scheduling and operational purposes; the results obtained from the simulation provide insight on the retrieval volumes as function of fraction of cesium retrieved for ten operating scenarios.

Research Progress

During 2008, 10 retrieval scenarios of cesium displacement were performed. The simulations were analyzed for two strategies: 1) addition of flushing liquid at the top of the tank, and 2) addition of flushing liquid at a side peripheral channel. Furthermore, the retrieval scenarios were analyzed for incremental retrieval (saturation of the tank with flushing liquid followed by complete drainage) and for continuous retrieval (water is continuously added at the top and retrieved at a central well). Additional analysis was provided for variable tank hydrology using a multilayer model; S-109 has 2 layers of considerably lower hydraulic conductivity compared to the remaining of the tank.

The comparison between various retrieval scenarios showed considerable advantage in using a series of cycles consisting of incremental addition of water and complete drainage. This method reduces the influence of dead zones in the tank. Modeling of the most effective removal of Cesium-137 (the radionuclide contributing most to the radioactivity of the tanks) in saltcake from tanks has shown that much less water can be used to effectively flush the water soluble radionuclide from the tank. Using less water in return requires less evaporation of the retrieved HLW and allows more rapid and effective waste retrieval. Addition of displacement fluid at the peripheral side channel demonstrates best performance for a homogeneous porous media; however, for a multilayer system with considerably lower permeability of some of the layers, the retrieval rates are slower compared to uniform addition at the top of the tank.

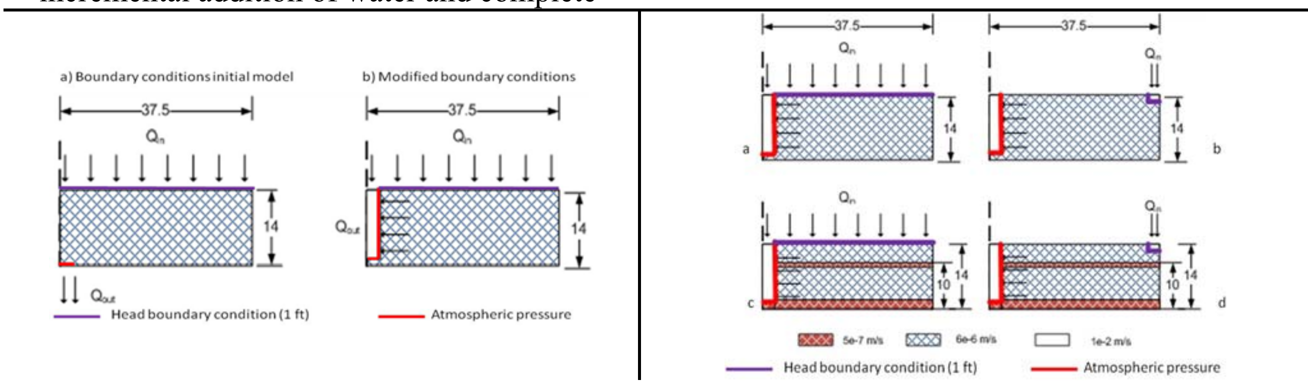


Figure 1. Numerical model boundary conditions for continuous (left) and side & incremental retrieval (right)

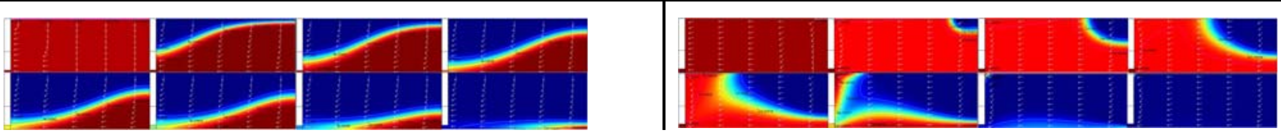


Figure 2. Continuous retrieval (left), and incremental retrieval (right)

Planned Activity

The results of this study will be presented at the Waste Management Symposia in March 2009.

Reference

Roelant, D., McDaniel, D., Awwad, A. Srivastava, R., Varona, J., Tachiev, G., “Chemical Process Alternatives for Radioactive Waste”, Environmental Management Mid-Year Presentation, July 2008.

ENHANCED TANK CLOSURE PROCESSES PROGRAM AREA

Initiative Development Team Lead: Sharon Marra, Savannah River Nuclear Laboratory (SRNL), sharon.marra@srnl.doe.gov, 803-725-5891

Initiative Development Team: Gary Peterson and Steven Ross of DOE-EM Office of Waste Processing; Mike Rinker, Pacific Northwest National laboratory (PNNL); Rick Demmer, Idaho National Laboratory (INL); Mark Noakes, Oak Ridge National Laboratory (ORNL); Charlie Waggonner, Institute for Clean Energy Technology (ICET); Laurie Judd, NuVision Engineering (NVE)

Challenges

Over 200 waste tanks as well as hundreds of ancillary systems at the Savannah River Site and the Hanford site need to be closed. Several challenges make this a huge undertaking for the DOE complex:

- Residual material in difficult-to-reach locations, such as tanks with obstructions and ancillary systems such as transfer lines, will be difficult to characterize;
- Currently there is no well-defined system plan for the closure of ancillary systems;
- Grouts that can be deployed in difficult-to-access locations and that have the necessary chemical and physical properties will be difficult to formulate;
- A consistent set of tools to predict the performance of cementitious barriers over time does not exist.

Efforts to address tank closure processes will pay huge dividends. The DOE Complex has yet to realize all of the challenges associated with this effort. The sheer number of tanks and ancillary systems make the closure effort immense, but uncertain and changing regulatory drivers add to the challenge. The sharing of data and information across the complex will reduce uncertainty and duplication of effort. Although regulatory requirements may be different, opportunity still exists for efficiency. An example of this may be the development of closure materials that can be deployed at more than one site. Other examples include deployment methods and methodologies. An industry-wide technical basis for evaluation among stakeholders can provide large benefit to all sites.

Solutions

The solutions to those technical challenges will require

- Utilization of industrial capabilities, where practical, particularly in the area of characterization
- Utilization of complex-wide expertise and lessons learned
- Common understanding of the similarities and differences in regulatory requirements at the various sites and the sharing of information in order to gain as much efficiency as possible even with varying regulatory requirements.

Accomplishments

A Cementitious Barriers Partnership has been formed with national and international partners. The objective of this partnership is to develop a reasonable and credible set of tools to predict the structural, hydraulic, and chemical performance of cement barriers used in nuclear applications over extended time frames. A Memorandum of Understanding (MOU) and a Cooperative Research and Development Agreement (CRADA) have been established. Current state-of-the-art information is being documented, and model development has been initiated.

Additional detail is provided in a following section of this report.

An effort has been initiated to define the state of technology and planning for closure of ancillary systems. Some work previously has been performed to document the state of tank closure, and that effort will continue for tanks and address ancillary systems. Results from Oak Ridge and Idaho will be included in addition to the efforts at Savannah River Site and Hanford.

These enabling technologies pursued in 2008 are detailed in following sections of this report:

- Design and Delivery of a Fluidic Sampler for Tank 50 at the Savannah River Site
- Strategy for Handling Closure of Ancillary Systems
- Remediation of Cooling Coils in Large Tanks
- In-Tank Characterization for Closure of Hanford Waste Tanks (Fourier Transform Profilometry).

Plans

Details are provided in following sections of this report.

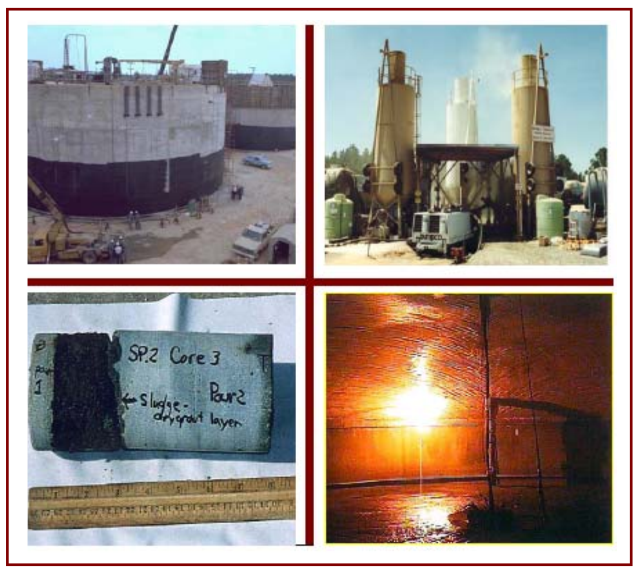
ENHANCED TANK CLOSURE PROCESSES

Partnership for the Development of Next-Generation Simulation Tools to Evaluate Cementitious Barriers and Materials Used in Nuclear Applications (Cementitious Barriers Partnership Project)

Principal Investigator: C. Langton, Savannah River National Laboratory (SRNL), christine.langton@srnl.doe.gov, 803-725-5806

Collaborators: A. Baione, U.S. Department of Energy, Office of Environmental Management (DOE-EM); D. Esh, M. Fuhrmann, J. Philip, U.S. Nuclear Regulatory Commission (NRC); D. Kosson, S. Mahadevan, A. Garrabrants, Consortium for Risk Evaluation with Stakeholder Participation (CRESP)/Vanderbilt University; H. van der Sloot, R. Comans, J. C. L. Meeussen, P. F. A. B. Seignette, Energy Research Centre of The Netherlands (ECN); E. Garboczi, K. Snyder, National Institute of Standards and Technology (NIST); E. Samson, J. Marchand, SIMCO, Inc.; R. Dimenna, SRNL

Project Duration: 2008-2013



Waste Processing Challenge

The US DOE has been and plans to continue using engineered cementitious barriers to enhance the performance of low-level radioactive waste (LLW) disposal sites located in the near-surface environment.

Research Objective

The US DOE intends to support this practice by funding a project that is expected to result in improving performance of engineered cementitious barriers and also in predicting the performance of the barriers over long periods of time.

There are several key impacts:

- Reduced uncertainty and improved consistency for performance assessments
- Updated guidance documents (assessment tools, test methods, data)
- Industry-wide technical basis for evaluation amongst stakeholders
- Improved technology foundation and integration of existing and new scope.

Research Progress

During 2008, the Cementitious Barriers Partnership (CBP) was formed with partners from government (DOE, NRC, and NIST), academia (CRESP/Vanderbilt), and international entities (ECN, SIMCO). The objective of the partnership is to develop a reasonable and credible set of tools to predict the structural, hydraulic, and chemical performance of cement barriers used in nuclear applications over extended time frames (up to 10,000 years) in the DOE complex and in commercial nuclear industry. A Memorandum of Understanding (MOU) and a Cooperative Research and Development Agreement (CRADA) were developed, and an Expert Advisory Panel was chartered.

The 5-year CBP Project Plan was issued. The plan is organized into Phases, each containing multiple tasks:

- 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.

Technical work has started; current state-of-the-art information is being documented, and model development has been initiated.

Planned Activities

During 2009, the partnership is scheduled to begin issuing documentation addressing tasks in both Phase I and Phase II as well as to address CBP topics in national and international symposia:

MISCELLANEOUS TASKS
- Establish and Implement CBP QA Plan

PHASE 1

Task 1: Current Performance Assessment Modeling Approaches
- Report: Summary of DOE and NRC PA Approaches
- Report: DOE PA Uncertainty Needs and Methods Roadmap
- Present paper at WM09: Summary of DOE and NRC PA Approaches and DOE PA Uncertainty Needs and Methods.

Task 2: Review State-of-the-Art Mechanistic and Process Understanding and Approaches
- Report: Current Understanding of the Parameters that Influence Hydraulic and Leaching Properties and Uncertainty Analysis of Cementitious Barriers (multiple chapters)
- Report: Description of the Candidate Software and Integrating Platform for the CBP Project (multiple chapters)

PHASE 2
- Task 6: Prototype Reference Cases
- Task 7: Demonstrate Software on Prototype Case(s)

EVENTS
- DOE Waste Management Symposium, February 2009, Phoenix AZ
- Team Meeting at Vanderbilt University, February 2009, Nashville TN
- International Workshop on Long-term Performance of Cementitious Barriers and Reinforced Concrete in Nuclear Power Plants and Waste Management, March 2009, Cadarache, France
- 33rd International Symposium: "Scientific Basis for Nuclear Waste Management", May 2009, St. Petersburg, Russia
- The 12th International Conference on Environmental Remediation and

Radioactive Waste Management,
October 2009, Liverpool, UK

Reference

Project Plan for the Partnership for the Development of Next Generation Simulation Tools to Evaluate Cementitious Barriers and Materials Used in Nuclear Applications (Cement Barriers Partnership) WSRC-SRNL-PR-008-001-01.

ENHANCED TANK CLOSURE PROCESSES

Design and Delivery of a Fluidic Sampler for Tank 50 at the Savannah River Site

Principal Investigators: Erich Keszler, keszler@nuvisioneng.com, 704-799-2707, Laurie Judd, and Paul Fallows of NuVision Engineering (NVE)

Collaborators: Savannah River Site (SRS) and Savannah River National Laboratory (SRNL)

Project Duration: 2007-ongoing

Waste Processing Challenge

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 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.

Research Objective

NVE has successfully developed and deployed Fluidic Single Point Samplers to collect samples of waste from waste tanks in nuclear process plants in the United Kingdom (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 tank-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

Definitive design of the sampling system is nearing completion. The design work (3-D model) was created in Solidworks and drawings were generated directly from that model (see Figure 2). The design incorporates valuable input from SRS and will soon be ready for Design Review and HAZOP by SRS.

Planned Activities

NVE will complete the detailed design and submit it for Design Review and final HAZOP. Once all comments have been received, resolved, incorporated and closed, the final design package will be sent to SRS for approval. When the design is approved it will be released for bid by fabricators. Following selection of the fabricator, then fabrication and construction of the first unit for field deployment will begin.

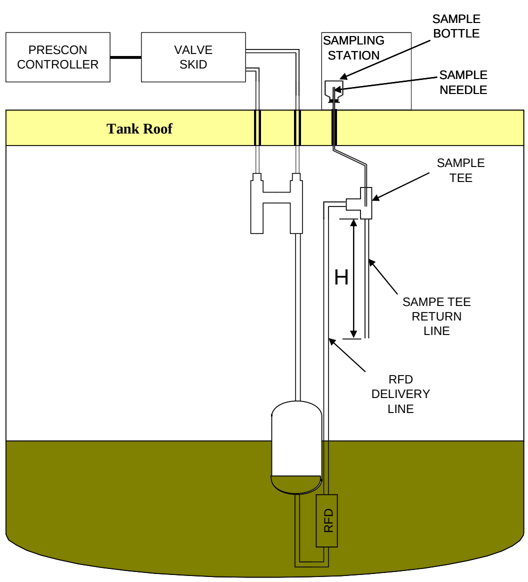


Figure 1. Schematic of Sampler System

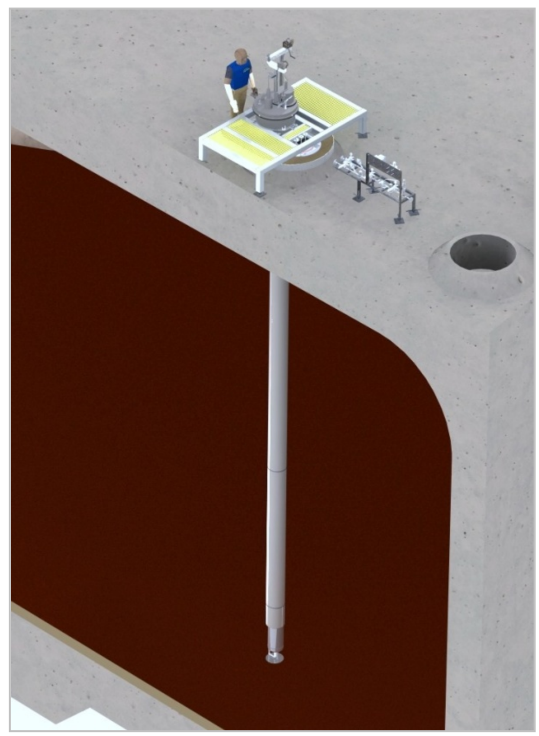


Figure 2. Rendering of 3-D model used to generate drawings

ENHANCED TANK CLOSURE PROCESSES

Strategy for Handling Closure of Ancillary Systems

Principal Investigator: H. Holmes Burns, Savannah River National Laboratory (SRNL), heather.holmes@srnl.doe.gov, 803-819-8469

Collaborator: A. P. Fellinger, SRNL

Project Duration: 2008-2009

Waste Processing Challenge

Gaps exist in both technology and material applications for removal of residual waste from, and closure of, ancillary systems such as cooling coils, transfer piping, tank top, annulus, and ventilation system. The overall effort is huge and has not yet been addressed in a systematic manner. A 2001 report documents the "state of art" for tank closure across the complex. The results in this report need to be expanded to all ancillary systems that will need to be closed along with the empty waste tanks.

Research Objectives

The Waste Processing Division of the Office of Engineering and Technology requested an assessment of the current state of closure of ancillary systems to the DOE waste tanks. The objective in conducting this effort was to identify gaps in both technology and material application for the closure of ancillary systems that include the tank annulus space, cooling coils, transfer piping, pump/valve pits and other miscellaneous tank farm structures (Figures 1 and 2). Information was assessed from several sources including Hanford and SRS waste retrieval workshops, subject matter experts, and literature to:

1. Document the current state of knowledge regarding tank ancillary system closure,
2. Identify technology needs (i.e., information gaps); and

Figure 1. Tank Annulus Space in SRS Waste Tank

Figure 2. Cooling Coils in SRS Waste Tank

3. Provide recommendations for technical programs to improve the closure programs for waste-tank ancillary systems. The bases for recommendations include: reducing project cost and schedule, improving the technical bases for design, construction, operation, and performance predictions, and facilitating stakeholder understanding and acceptance.

Research Progress:

A report was prepared and issued (SRNL-STI-2009-00243, Rev. 0) to document the results of this effort to assess the status of tank ancillary system closures in the DOE complex. Several issues and gaps in current knowledge were identified and recommendations for technology programs were made. The report documents:

- "Best Practices" used in ancillary system closure,
- 20 Significant Challenges identified in ancillary system closure, and
- 5 Recommended Programs to mitigate the technical and regulatory risks

The report concluded that, due to the nature of the identified risks and uncertainties, five programs are needed / recommended to mitigate these challenges:

- Ancillary System Technology Transfer Program - The Retrieval Knowledge Center should be expanded to include ancillary system closure initiatives.
- Ancillary System Sampling and Characterization Program – Regulatory agencies have recognized the need to characterize the difficult-to-access ancillary systems with actual waste characterization data. Therefore, technology programs are needed to focus on the development of sampling tools and non-intrusive methodologies, locating sensors, and analogues to aid in the accurate characterization of waste in ancillary systems.
- Ancillary System Waste Retrieval Program – Programs are needed to improve both the chemical and mechanical cleaning strategies for ancillary systems which have the same regulatory requirements as tanks to remove waste to the "maximum extent practical". In addition, consideration of removing cooling coils and other tank obstructions should be evaluated to improve tank waste retrieval efforts.
- Ancillary System Stabilization Program – Programs are needed to develop and demonstrate improved grout design mixes and grouting tools/strategies that meet the unique requirements of the difficult-to-access ancillary systems. Test programs are also needed to confirm the assumptions in the performance assessment by evaluating the properties of grout and the evolution of these properties over time.
- Regulatory Program – The regulatory risk in tank/ancillary system closure that has stifled forward movement and will escalate costs is the "definition of success". When is removal of waste residuals sufficient enough to define the tank or system clean so that grouting, the final stage of closure, can commence? A Complex-wide

program is needed to answer these questions and provide definable criteria that demonstrate that waste retrieval has met the "maximum extent practical" requirement.

Planned Activities:

The Retrieval Knowledge Center (RKC) is recommended to be expanded to include the technologies that will address the risks associated with closure of ancillary systems. In addition, technical task plans (TTPs) are being developed by the IDTs (Initiative Development Teams) for the technology roadmap in the waste processing area to address ancillary system closure risks.

Reference

SRNL-STI-2009-00243, Rev. 0 "State of the Art Report on Closure of DOE Waste Tank Ancillary Systems and Recommended Path Forward for Future Test Programs (U)," H. Holmes Burns and A. P. Fellinger, Savannah River National Laboratory.

ENHANCED TANK CLOSURE PROCESSES

Remediation Of Cooling Coils In Large Tanks

Principal Investigators: Erich Keszler, keszler@nuvisioneng.com, 704-799-2707, and Laurie Judd of NuVision Engineering (NVE)

Collaborators: Savannah River Site (SRS) and Savannah River National Laboratory (SRNL)

Project Duration: 2008-2009

Waste Processing Challenge

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. 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 endstate of large high level Type I tanks with interior obstructions. However, nearly every possibility will require some level of cooling coil management or closure to reach an acceptable tank end-state.

Research Objective

The objective is to develop a cost effective approach for removing all the cooling coils from the Type I tanks, utilizing a rugged and reliable manipulator technology. The required capabilities consist of tight manipulations and complex kinematics required to position a cutting tool in order to cut and then remove the cooling coil segments.

Research Progress

Each of the technologies considered was analyzed to determine if the equipment could fit through the 23 inch diameter Type I tank risers through which the equipment will be deployed to access the inside of the tank.

Other evaluated capabilities were the technology's ability to perform the cutting operations and also to remove the cut segments of cooling coils from the tanks. The technologies satisfying those criteria were further evaluated to determine the most cost effective technology system.

Also, the project focused on developing a baseline cost estimate. The estimate for this feasibility study will include the hardware design/ fabrication costs, coil flushing and grouting, field operation/installation, riser jump estimates, additional riser additions, equipment demobilization and disposal, and removed coil handling and indefinite storage costs.

NVE conducted a survey of prior, similar, successful manipulator deployments across the DOE network. In order to minimize the equipment cost, and reduce the possibility of tank farm operational delays, while still providing an effective technology system, it was concluded that a system similar to the West Valley Mast Tool Delivery System (MTDS) offers the greatest operational flexibility and requires the least amount of tank top superstructure to execute the in-tank cutting and material removal operations.

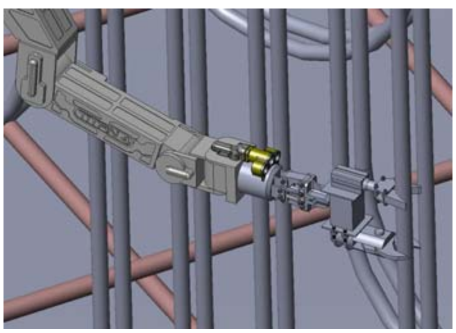


Figure 2. Dual function end effector

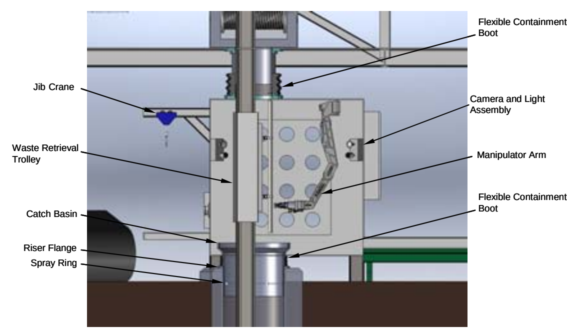


Figure 3. Material Removal Trolley

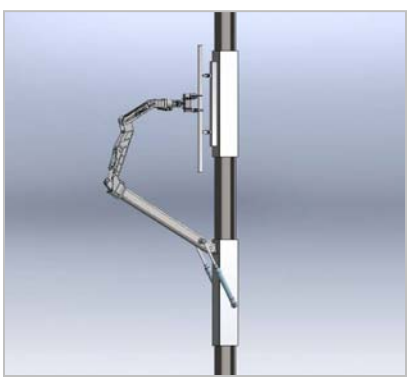


Figure 4. Dual Trolley System

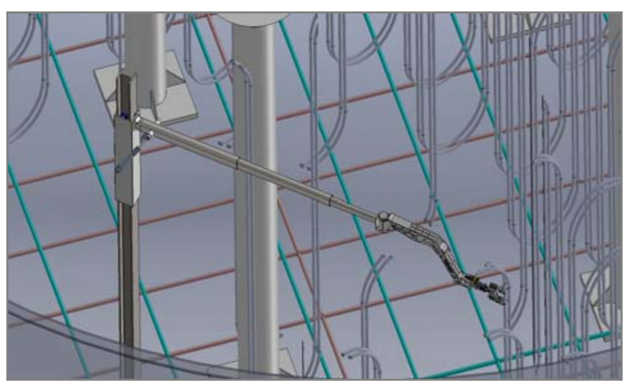


Figure 5. 20-ft coverage radius of Tool Delivery System

The West Valley MTDS can provide the required reach and kinematics needed to maneuver in the heavily congested environment of the Type I Tanks. Additionally, this system utilizes a floor supported mast which will minimize the tank top work structure needed to support the in-tank equipment. It will minimize the challenges of fitting a tank top supporting structure in the congested foot print of the Type I tanks. The West Valley technology provides acceptable capabilities for both the cooling coil cutting and removal of the cut coils from the tank's interior. The proposed NVE design is illustrated in Figures 2-5.

Planned Activities

The next steps are fabrication and demonstration of the proposed design.

ENHANCED TANK CLOSURE PROCESSES

In-Tank Characterization for Closure of Hanford Waste Tanks

Principal Investigator: David L. Monts, Institute for Clean Energy Technology (ICET), monts@icet.msstate.edu, 662-325-7389

Collaborators: Ping-Rey Jang, Yi Su, and Zhiling Long of ICET; Dennis Hamilton and Rick Raymond of CH2MHILL Hanford; Billie Mauss of DOE Office of River Protection (ORP)

Project Duration: 2007-2010

Waste Processing Challenge

Currently two techniques are used for assessing the amount of waste remaining within a tank following retrieval activities. The first technique is to photograph the waste tank from different locations and use objects of known size within the tanks to estimate the waste volume, and the second is to photograph the waste tank as a function of water volume displacement. The first approach often has large uncertainties associated with the waste volume estimates. The second approach is expected to increase risks associated with tank structures that have exceeded the design life. The ability to precisely determine residual waste volumes using non-intrusive diagnostic instrumentation will also allow for a more accurate measure and pinpoint specific locations within a waste tank where tailored grouts can be applied.

Research Objective

The goal of this project is to develop an in situ quantitative imaging tool based on Fourier transform profilometry (FTP) for residual waste volume characterization.

Fourier transform profilometry (FTP) is a non-contact, 3-D shape measurement technique. By projecting a fringe pattern onto a target surface and by using a camera to observe the fringe pattern's deformation due to surface irregularities, FTP is capable of determining the height (depth) distribution of the target surface, thus reproducing the profile of the target accurately. The steps of FTP image acquisition and analysis are under computer control.

Research Progress

During 2008, the prototype FTP system demonstrated the ability to reliably determine volumes under the most challenging conditions that are expected to occur within a Hanford waste tank. Assuming access to a Hanford waste tank through a 4" ID riser, the furthest part of the tank will be about 53' away when the FTP instrument arm is 25' above the floor. Under these conditions, the system was able to determine the volume of small non-descript targets with an average volume error of about 5-10%.

Figure 1 shows an FTP image of a non-descript target under simulated most challenging tank conditions and the resulting 3-D reconstruction of the object. Figure 2 shows a similar image and reconstruction at a distance of 25 feet. Here the average volume error for a number of different targets was 5-10%.

A technical feasibility study to characterize and document factors (both inherent and instrumental) that affect the accuracy, precision, and operational performance of the FTP system was initiated. Increasing the camera-to-projector distance was found to reduce the measurement uncertainty. The effects of projected light field uniformity and intensity were examined. The ranges of the optimum camera parameters (such as zoom, f-number, shutter speed, etc.) were determined. The effects of and uncertainty introduced by warm-up by the FTP system were identified and characterized. The capabilities and limitations of the present imager are being compared with alternatives.

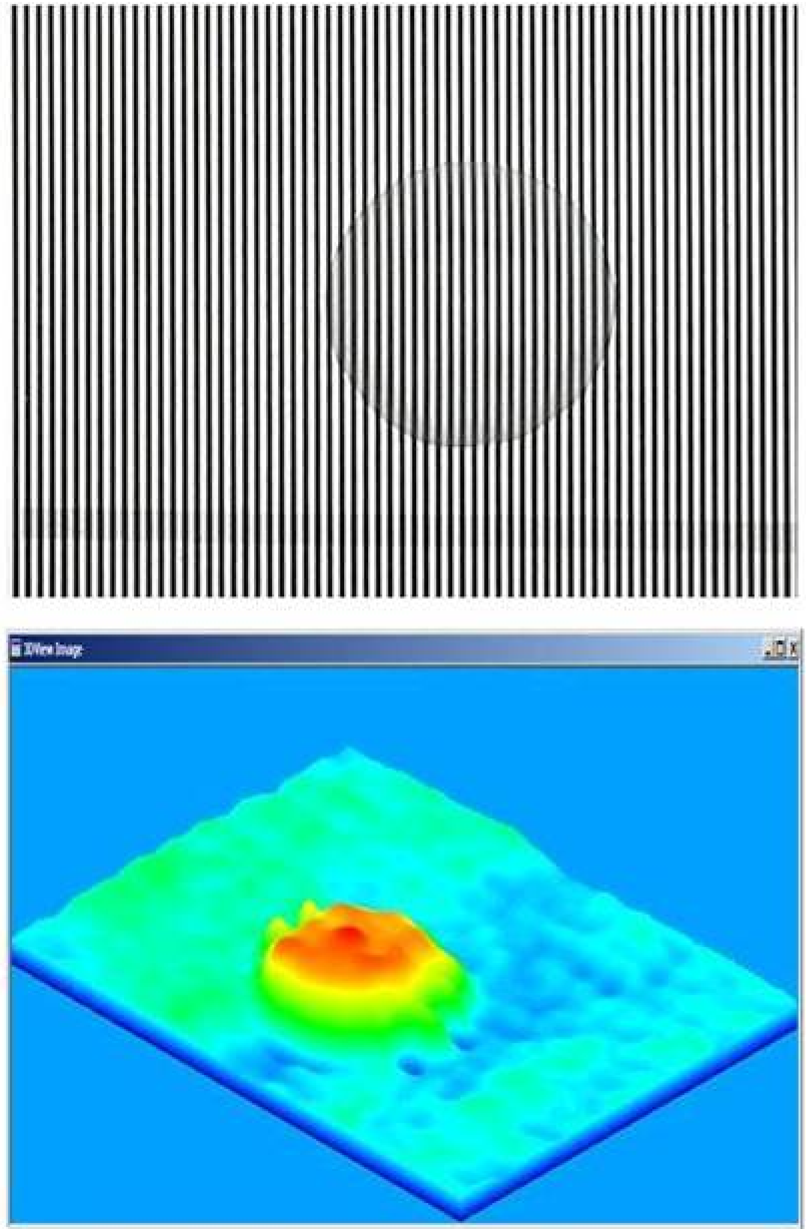


Figure 1. FTP image collected at a distance of 53 feet and 3-D reconstruction of non-descript object using the FTP system.

Planned Activities

The technical feasibility study will be completed during 2009. Items that remain to be completed are a comparison of the present imager with alternatives; optimization of the FTP optics; characterization of the uncertainty introduced by the process of combining single-image volumes to obtain the total tank waste volume; and characterization of the uncertainty introduced by non-flat (curved) tank floors.

During 2010, a prototype FTP system will be demonstrated initially at ICET and then field tested. The FTP technology will be transferred to a commercial partner.

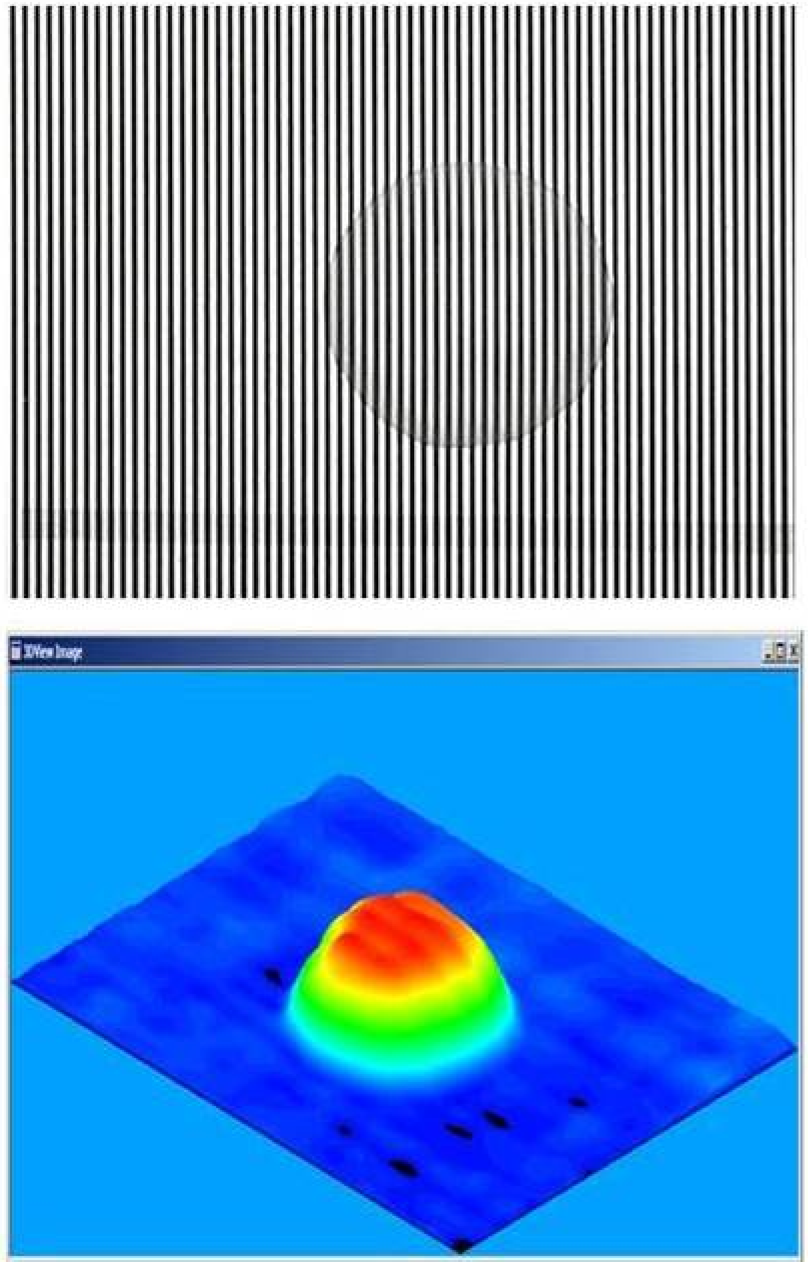


Figure 2. FTP image collected at a distance of 25 feet and 3-D reconstruction of non-descript object using the FTP system.

References

1. John A. Etheridge, Ping-Rey Jang, Teresa Leone, Zhiling Long, O. Perry Norton, Walter P. Okhuysen, David L. Monts, and Terry L. Coggins, "Evaluation of Fourier Transform Profilometry for Quantitative Waste Volume Determination under Simulated Hanford Waste Tank Conditions," Proceedings of 34th Waste Management Symposium (WM08), Phoenix, AZ, February 24-28, 2008, Paper No. 8106.
2. David L. Monts, Ping-Rey Jang, Zhiling Long, O. Perry Norton, Walter P. Okhuysen, Yi Su, and Charles A. Waggoner, "Technical Performance Capability of Fourier Transform Profilometry for Quantitative Waste Volume Determination under Hanford Waste Tank Conditions," Proceedings of 35th Waste Management Symposium (WM'09), March 1-5, 2009, Phoenix, AZ, Paper No. 9333.

NEXT-GENERATION PRETREATMENT SOLUTIONS PROGRAM AREA

Initiative Development Team Lead: Bill Wilmarth, Savannah River Nuclear Laboratory (SRNL), bill.wilmarth@srnl.doe.gov, 803-725-1727

Initiative Development Team: Nicholas Machara and John Shultz of DOE-EM Office of Waste Processing; Reid Peterson, Pacific Northwest National laboratory; Dan McCabe, SRNL

Challenges

The Next-Generation Pretreatment Solutions program area addresses two major sets of waste processing challenges:

1. There is too little tank space available at Hanford and Savannah River to enable recovery and closure of waste tanks as well as continued tank-farm operation. In addition, there is presently no alternative to processing opportunistic waste streams through Hanford's Waste Treatment Plant (WTP) and Savannah River's Salt Waste Processing Facility (SWPF), thus extending the time and cost of processing the primary waste streams intended for those facilities.

2. The long-term objectives of the proposed high-level waste (HLW) treatment systems at Hanford and Savannah River cannot be met without improving or supplementing the baseline technologies in place or under development.

The start-ups of the WTP and SWPF are still many years away, and the baseline operational schedules of those facilities extend until at least 2040. Technological advances will allow processing of tank wastes prior to start-up of those major facilities, thus reducing the overall lifecycle term, cost, and risk of HLW treatment and disposition.

If the above challenges can be met, the performance of the HLW treatment systems will be dramatically enhanced. Deployment of systems to create tank space will allow for accelerated closure of non-compliant tanks. This accelerated closure will reduce the long-term risk and liability associated with these tanks. In addition, treating more waste in the near term will dramatically reduce the eventual duration of Savannah River's Defense Waste Processing Facility (DWPF) and SWPF and Hanford's WTP. Likewise, by treating either problematic or opportunistic streams prior to receipt by these facilities, the amount of material to be processed and the time required to process the balance of material can be reduced significantly. These reductions in operating lifetime for these facilities translate directly into large cost savings.

Solutions

1. At-Tank or Near-Tank Processing

There are two primary objectives of this initiative: create tank space within the tank farms, and treat problematic or opportunistic waste prior to transfer to WTP or SWPF.

2. Improved Waste Separation to Minimize HLW

Three primary objectives of this initiative were pursued during 2008: provide incremental improvements to the planned pretreatment systems at SWPF and WTP; provide transformation changes to the sodium processing scheme at Hanford; and provide the technology development activities required to reduce the risk associated with the baseline activities.

Accomplishments

1. At-Tank or Near-Tank Processing

These enabling technologies pursued in 2008 are detailed in following sections of this report:

- *Transformational Technologies to Create Tank Space in the Near Term*
  - Develop small column ion exchange
  - Develop rotary microfilter
- *Transformational Technologies to Treat Problematic/ Opportunistic Streams Outside of Main Plant.*
  - Near-tank treatment system
  - Wet air oxidation of Tank 48 containing tetraphenylborate

2. Improved Waste Separation to Minimize HLW

These enabling technologies pursued in 2008 are detailed in following sections of this report:

- *Improve Performance of SWPF or WTP*
  - Advanced mixing models
  - Improved strontium and actinide separations
- *Transformational Technologies to Reduce Na Demand*
  - Ceramic membrane to separate NaOH from Hanford HLW stream
  - Aluminum solubility
- *Develop the Solutions that Reduce Risks of Baseline Pretreatment Processes*
  - Obtain thermodynamic data for waste processing flowsheets
  - C Tank Farm chemistry neural network development.

Plans

Details are provided in following sections of this report.

NEXT-GENERATION PRETREATMENT SOLUTIONS

Development of Rotary Microfilter for SRS/Hanford Deployment

Principal Investigator: Michael R. Poirier, Savannah River National Laboratory (SRNL), michael.poirier@srnl.doe.gov, 803-725-1611

Collaborators: David T. Herman and Samuel D. Fink of SRNL

Project Duration: 2002-2010

Waste Processing Challenge

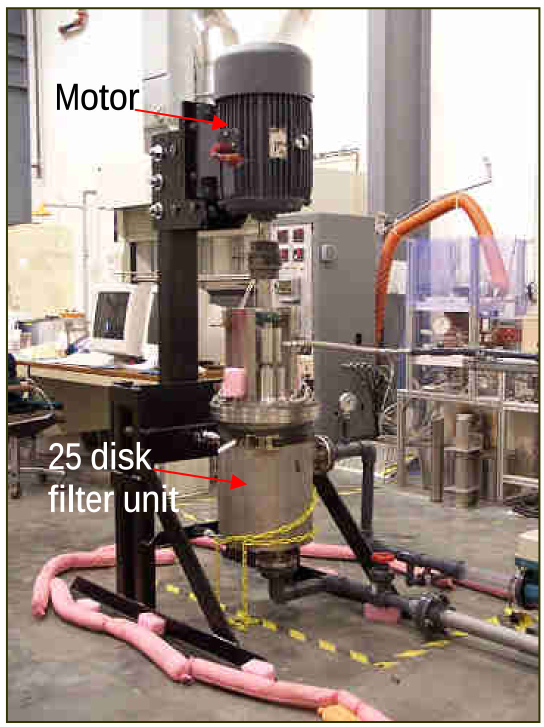
Solid-liquid separation is often the rate-limiting step of the processes to treat radioactive liquid waste at DOE's Savannah River and Hanford sites. Increasing the solid-liquid separation rate can increase the volume of waste treated and reduce the size and cost of the equipment needed. The rotary microfilter offers the potential to increase waste treatment processing rates and reduce waste treatment costs.

Research Objective

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. Hanford is interested in the technology for Supplemental Pretreatment and Bulk Vitrification.

Research Progress

Previous testing, conducted at bench-scale, pilot-scale, and full-scale, demonstrated higher processing rates than conventional crossflow filters with simulated waste and actual waste. In addition, the rotary filter requires a smaller volume than the crossflow filter, which decreases costs. Finally, the investigators developed a design to place two rotary filters in a tank riser, which uses the existing waste tank for shielding and eliminates the need to build a new shielded facility.



Full-Scale Rotary Filter

Planned Activities

The investigators are procuring a full-scale rotary microfilter with an air seal, an upgraded bushing, and improved tolerances. Once the unit is fabricated, they will conduct a 1000-hour test with simulated SRS sludge to evaluate the filter's reliability and performance. The feed composition will be similar to the feed composition expected in a sludge washing process. The testing will measure filter flux as a function of feed concentration and operating parameters. Following the testing, the investigators will measure wear and reliability of the air seal and bushing.

NEXT-GENERATION PRETREATMENT SOLUTIONS

In-Riser Cs Ion Exchange System – Small Column Ion Exchange

Principal Investigator: William D. King, Savannah River National Laboratory (SRNL), william02.king@srnl.doe.gov, 803-725-7556

Collaborators: Joseph F. Birdwell, Denise L. Schuh, and Paul A. Taylor of Oak Ridge National Laboratory (ORNL); Charles L. Nash, Mark R. Duignan, Sebastian E. Aleman, Larry L. Hamm, Frank G. Smith, Si Young Lee, and Kofi Adu-Wusu of SRNL

Project Duration: 2007-ongoing

Waste Processing Challenge

The critical path to closure of the Savannah River and Hanford waste tank farms is the processing of radioactive salt waste. Every tank grouping includes tanks containing salt waste, and there is currently limited ability to treat and dispose of salt waste and little tank-farm space to move the salt waste. Processing salt waste in advance of start-up of Savannah River's Salt Waste Processing Facility (SWPF) and Hanford's Waste Treatment Plant (WTP) will reduce the critical path and improve the life-cycle schedule and cost of tank-farm closure.

Research Objective

Oak Ridge and Savannah River National Laboratories are conducting a collaborative test program to support development of in-tank-riser ion exchange columns for removal of cesium from radioactive salt waste supernates at the Savannah River and Hanford sites.

The program builds upon efforts to develop a similar technology for utilization at the Savannah River Site (SRS) several years ago. An in-riser column was designed at Oak Ridge (partially through EM funding) for implementation at SRS based on crystalline silicotitanate (CST) ion exchange media. Since that time, an alternative and elutable ion exchange resin, a spherical form of resorcinol-formaldehyde (RF), has been developed and selected as the baseline media for the Hanford WTP. The focus of current Office of Waste Processing testing is on the development of RF resin for in-riser applications at both SRS and Hanford.

ORNL testing involves three major tasks: 1) testing to support isotherm model refinement, 2) radiolysis testing, and 3) hydraulic permeability testing.

SRNL testing and analysis includes: 1) SRS real waste testing, 2) study of non-acid RF eluates, and 3) in-riser column thermal analysis and design optimization.

Research Progress

In 2008, research teams at SRNL and ORNL, with input from SRS operations and Hanford, conducted research tasks addressing RF technology needs for both the large-scale WTP columns and the smaller in-riser columns at SRS and Hanford.

ORNL

Testing to support isotherm model refinement included measurement of cesium loading isotherms and determination of the RF resin titration curve.

ORNL radiolysis testing evaluated the performance impacts of resin radiolysis that would occur during column operations with real waste. Previous evaluations conducted to support the Hanford WTP had included resin exposure to 100 MRad. It was believed that RF resin used in riser columns at SRS would experience a significantly larger dose. Dose rates as high as 300 MRad were evaluated. SRNL assisted in that effort by conducting preliminary irradiation of some samples to 100 MRad to decrease the total dose time for the ORNL studies. The tests bounded the impacts of higher irradiation on RF cesium removal performance and the production of volatile and semi-volatile organics.

Tests were conducted with resin exposed to both radiation and oxygen to determine the impact on RF packed bed hydraulic permeability. Such evaluations had not been previously performed on irradiated resin. The tests measured the pressure drop across a 3-inch diameter packed bed of RF resin under dynamic fluid flow conditions. A photograph of the hydraulic permeability test equipment is shown below. To facilitate data comparisons, the equipment was designed and test conditions were selected to emulate previous WTP testing. The results would also be useful to evaluate hydraulic performance for in-riser column applications.

SRNL

RF hydraulic conductivity test loop.

SRNL

SRNL demonstrated cesium removal performance with RF columns using an SRS saltcake sample representative of the material requiring in-riser column treatment.

The study of non-acid RF eluates was conducted to prevent conversion of RF resin to hydrogen form during elution so as to prevent undesired volume changes and hydraulic issue and problems caused by introducing an acid eluate stream to tank farm systems based on caustic side chemistry.

Planned Activities

ORNL

Data from the testing to support isotherm model refinement will be used to refine and enhance the RF isotherm model previously developed at SRNL with a focus on low cesium concentrations. Performance at low cesium concentrations may significantly impact RF performance under assumed in-riser column operating conditions.

The hydraulic permeability test results will be evaluated for in-riser column applications.

SRNL

SRS radioactive waste will be tested with spherical RF resin. Analysis of spent RF resin after waste treatment is planned to assist in the determination of a resin disposal path.

Tests are planned at SRNL to study potential eluates for caustic side RF elution.

Also, as a follow-on to previous work conducted in support of SRS operations, thermal modeling of in-riser RF columns will be conducted to evaluate the potential to significantly simplify the design by removing the central cooling tube. This potential design simplification may be feasible because cesium loading on RF columns is significantly lower than is observed with CST. Thermal modeling will be used to determine the maximum acceptable column diameter under accident scenarios, which will maintain all portions of the column at or below the RF media temperature limit. This work will be primarily focused on in-riser column operations at Hanford but could potentially impact the column design utilized at either site.

Separate reports will be issued for the various test and analysis programs at ORNL and SRNL.

NEXT-GENERATION PRETREATMENT SOLUTIONS

Improved Strontium and Actinide Separations

Principal Investigator: David Hobbs, Savannah River National Laboratory (SRNL), david.hobbs@srnl.doe.gov, 803-725-2838

Collaborators: M. D. Nyman, Sandia National Laboratory (SNL), T. B. Peters, M. R. Poirier, M. J. Barnes, M. E. Thompson, S. D. Fink (SRNL)

Project Duration: 2007-2010

Waste Processing Challenge

SRS tank waste requires removal of Sr-90 and transuranics (Pu-238,Pu-239, Pu-240 and Np-237) to meet the waste acceptance criteria of the Saltstone Disposal Facility. Monosodium titanate (MST) serves as the baseline material for strontium and actinide separations in operating and planned salt-processing facilities, i.e., the Actinide Removal Process (ARP) and the Salt Waste Processing Facility (SWPF).

Though effective for that purpose, MST has some limitations:

- The rate of uptake of strontium and actinides limits facility throughput;
- Adsorption of uranium by MST is a nuclear criticality safety concern in salt processing facilities;
- The quantity of MST used in facilities can adversely impact glass production in the Defense Waste Processing Facility.

Research Objectives

This project seeks to develop an improved monosodium titanate (MST) sorbent for the cost-effective removal of Sr-90 and alpha-emitting radionuclides from high-level nuclear waste solutions.

Research Progress

During 2008 the project team completed initiated Phase III testing activities associated with the development of the peroxide-modified MST material referred to as mMST. The focus of the 2008 testing included the following:

1. Evaluate the effects of temperature and ionic strength on the performance of mMST for the removal of strontium and actinides
2. Evaluate the effectiveness of a low pH filtration step during the synthesis of the mMST to reduce post-synthesis gas release.

Testing indicated that increased temperature has no impact on the extent of plutonium removal and a small, but positive influence on the removal of strontium by mMST.

Testing also indicated no removal of uranium at any temperature, which is consistent with previous testing at 25 °C, that showed very little adsorption of uranium by the MST. The lack or only minor affects of temperature on strontium and actinide removal by mMST indicates that rigorous temperature control during a batch contact process is not required to achieve good adsorption of these sorbates. Overall, the rate of removal followed the order, Sr > Np > Pu.

Testing results indicated that an increase in the ionic strength of the simulated waste solutions resulted in a decrease in the removal of strontium and plutonium. Furthermore, the testing results indicated that neptunium removal by mMST did not change with changes in the ionic strength of the solution. Lastly, the influence of ionic strength on uranium removal proved indeterminate given the low affinity of mMST for uranium.

Test results indicated that incorporating a lower pH filtration and brief air drying period (1.25 hours) during the synthesis of the mMST provided only a minor change on the gas release rate.

Photographs of Monosodium Titanate (top) and Modified Monosodium Titanate (bottom)

Planned Activities

2009 testing will focus on determining the settling and suspension characteristics, sorbate desorption, strontium and actinide removal performance at reduced mixing conditions, and gas release at an elevated storage temperature of mMST. We will also evaluate the performance of filter cartridges in which the filter membrane is imbedded with MST and crystalline silicotitanate (CST) powders. This would extend the application of these materials to other wastewaters such as contaminated cooling basin waters.

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NEXT-GENERATION PRETREATMENT SOLUTIONS

Wet Air Oxidation of Tank 48 Waste Containing Tetraphenylborate

Principal Investigator: Caroline Atseff, Savannah River Remediation (SRR), caroline.atseff@srs.gov, 803-208-8793

Collaborators: Earl Brass, SRR; Kofi Adu-Wusu and Chris Martino of Savannah River National Laboratory (SRNL)

Project Duration: 2006-2009

Waste Processing Challenge

Returning Tank 48 to operational service is critical to the processing of tank waste at the Savannah River Site (SRS). Tank 48 contains tetraphenylborate (TPB) from the operation of the In-Tank Precipitation process, which used NaTBP to precipitate CsTPB. TPB is not compatible with the SRS waste treatment program and needs to be removed or destroyed before Tank 48 can be returned to service.

Research Objective

The objective of this research is to determine the effectiveness of wet-air oxidation (WAO) in destroying TPB so as to make Tank 48 available to support Salt Waste Processing Facility (SWPF) operations when the SWPF comes online in about 2013.

A unit of up to 5-gpm would fit in the facility dedicated for the Tank 48 treatment project. 1, 3 and 5-gpm units with 75% operational time at 1:1 feed dilution could treat Tank 48 Waste (250,000 gal) in about 15, 5 and 3 months respectively. Lower dilutions would result in even shorter treatment times.

Research Progress

Three test plans necessary to bring WAO to a technical readiness level of 6 as well as associated schedule and cost estimates have been developed:

1. Bench-scale simulant testing will be performed to demonstrate destruction of TPB (< 2 mg/L). A short-duration (100-hour) material-of-construction (MOC) test will follow.
2. Pilot-scale simulant testing will be conducted to determine off-gas composition and to demonstrate stable and safe steady-state operations. Extended (1000-hour) MOC testing will follow. Design data for 3 and 5-gpm full-scale systems including the evaluation of process economics will be provided.
3. Bench-scale radioactive waste testing will be conducted to confirm destruction efficiencies and rates using a batch autoclave unit.

Preparation of components to make the Tank 48 simulant is complete. Award of contract for the WAO Phase I pilot-scale/MOC testing is complete.

Planned Activities

Plans are underway for the batch bench-scale radioactive waste testing.

Reactor used for pilot testing in Rothschild, WI.

NEXT-GENERATION PRETREATMENT SOLUTIONS

Thermodynamic Data and Computational Methods for Liquid Waste Flowsheet Modeling

Principal Investigator: Larry Pearson, Institute for Clean Energy Technology (ICET), pearson@icet.msstate.edu, 662-325-7626

Collaborators: Jeff Lindner, ICET; Quy Nguyen, Savannah River Remediation (SRR)

Project Duration: 2007-2010

Waste Processing Challenge

A major challenge in the SRS tank farms is the separation of actinides and cesium from salt wastes to permit the processing of the high activity waste fraction in the Defense Waste Processing Facility (DWPF) and stabilization of the lower activity waste as saltstone.

Research Objective

Towards this end, efforts are currently underway for the development of the Salt Waste Processing Facility (SWPF) containing the Actinide Removal Process (ARP) and Caustic Side Solvent Extraction Unit (CSSX). Any stream blending will be performed upstream of the SWPF. ICET is assisting the site through research aimed at assessing stream stability for blended compositions arising from potential tank farm operations. The primary streams of concern are the DWPF Recycle stream, which consists of DWPF overheads and is routed to the tank farm, high aluminum concentration streams from sludge leaching operations (Batch 5 leachate) and dissolved salt streams originating from saltcake dissolution. Previous ICET efforts have focused on laboratory-scale salt cake dissolution operations and modeling to determine factors leading to solids formation during stream blending. Simulations were performed using the ESP software and our double salt database

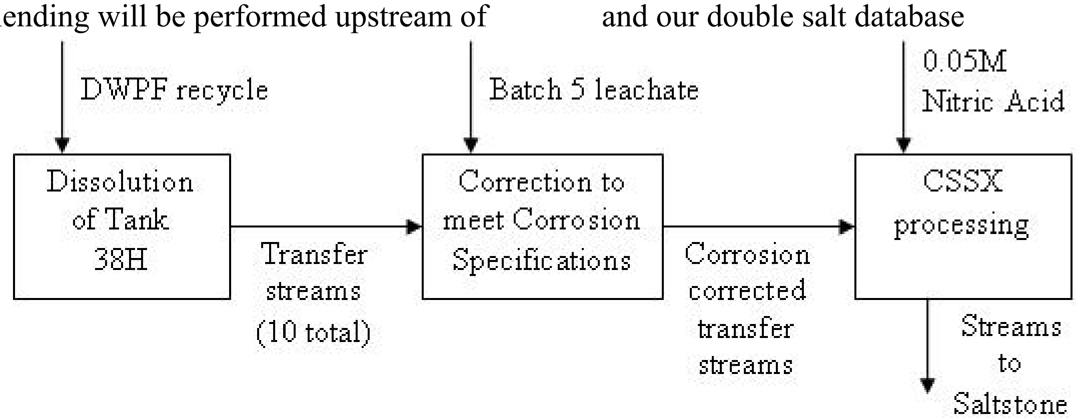

Figure 1. Simplified Diagram of ESP Model

Research Progress

During 2008, simulation of the salt cake dissolution process was performed using an ESP model. The simulation, Figure 1, was constructed to evaluate stream parameters during the process operations of saltcake dissolution, blending for corrosion control, and introduction into the CSSX process. Saltcake dissolution was simulated using the DWPF recycle stream as diluent. The resulting dissolved salt streams were cooled and evaluated for solids formation and adherence to corrosion specifications, Figure 2. Calculations were performed evaluating the effectiveness of using the Batch 5 leachate for corrosion control of non-compliant streams. Finally, the introduction of the corrosion compliant dissolved salt fractions into the CSSX process was modeled to determine the effect of waste stream carryover into the 0.05M HNO_3 CSSX scrub solution. In particular, solids formation was evaluated versus waste stream carryover.

Preliminary results from simulation of SRS Tank 25F and 38H support the use of DWPF recycle as a diluent in the salt cake dissolution process. In addition, the blending of the dissolved salt streams with the Batch 5 leachate appears to be an effective option for adjusting OH^- and NO_3^- loadings to provide corrosion inhibition. The ESP model was also used to predict the type and amount of solids formation due to waste carryover in the CSSX process. Additional ESP simulation evaluations are necessary to confirm these preliminary results.

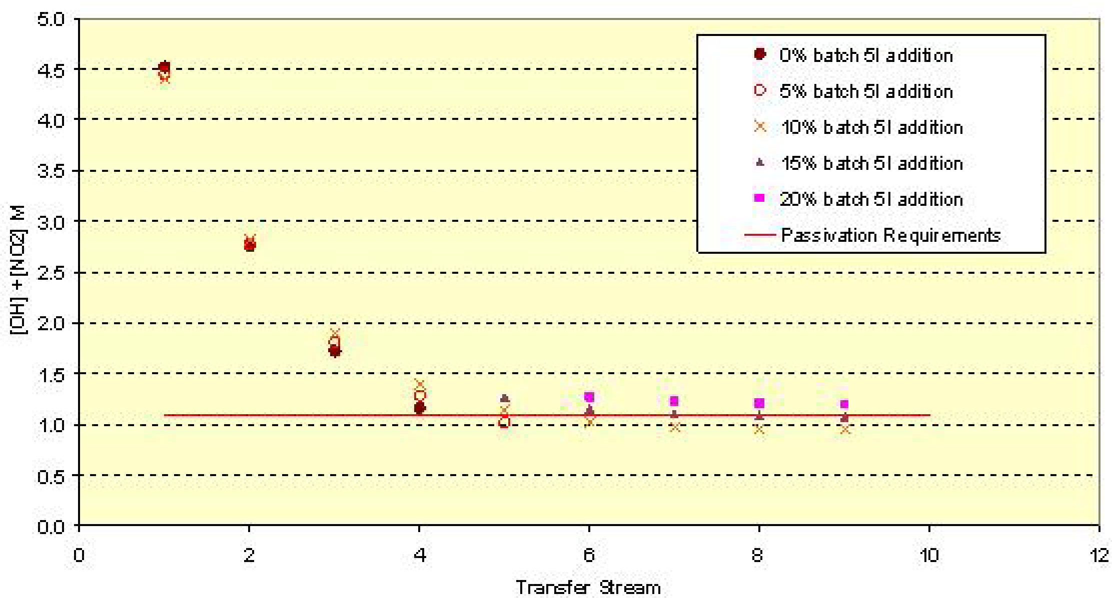

Figure 2. Addition of the DWPF Batch 5 leachate (high aluminum and high hydroxide) allows for achieving passivation requirements for storage of liquid waste. Larger transfer stream numbers correspond to salt dissolution at higher percent dilution by weight.

Planned Activities

ESP modeling and laboratory studies are planned to confirm the preliminary results obtained for SRS Tanks 25F and 38H. In addition, SRS Tanks 31H and 37H will be evaluated using the developed ESP simulation model. Work will continue to determine stream parameter relationships which affect corrosion compliance and solids formation which could negatively impact dissolution and CSSX operations.

Reference

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NEXT-GENERATION PRETREATMENT SOLUTIONS

Aluminum Solubility

Principal Investigator: L. T. Smith, Institute for Clean Energy Technology (ICET), lsmith@icet.msstate.edu, 662-325-0499

Collaborators: R. K. Toghiani and J. L. Lindner of ICET; Dan Herting, Heinz Huber, and Blaine Barton of Washington River Protection Solutions; Billie Mauss, DOE Office of River Protection (ORP)

Project Duration: 2008-20109

Waste Processing Challenge

Aluminum is a major component in Hanford tank wastes accounting for 1.3 % by weight of the total mass. Current plans call for the addition of large amounts of sodium hydroxide to dissolve solid phase aluminum and to maintain aluminum in the aqueous phase during downstream processing. An increase in the sodium content has implications on the generation and processing of additional low activity waste and on unit operations associated with the Waste Treatment Plant (WTP). High sodium concentrations interfere with the separation of ^{137}Cs in the ion exchange process. Dilution of the wastes prior to ion exchange will alter the thermodynamics of aluminum and could result in unwanted solids re-precipitation.

Research Objective

Knowledge of the solubility of aluminum under typical process conditions is needed to determine the need for additional processing capacity and for developing waste composition envelopes for ion exchange.

Research Progress

Initial efforts centered on thermodynamic modeling of aluminum using the Environmental Simulation Program (ESP, OLI Systems Inc.). Figure 1 provides comparisons of current model predictions with experimental solubility data of Szita and Berecz taken from Apps et al (1988) for aluminum in sodium hydroxide. At the lowest temperature (25 °C), ESP predictions are in excellent agreement with the experimental data over the sodium molality range. However, at 50°C, the predictions are slightly lower than the experimental data, with a greater difference observed for the lower end of the sodium molality range.

Predictions were also performed to examine the impact of sodium nitrate on the gibbsite solubility. Shown in Figures 2 and 3 are the predictions at 25 °C. In Figure 2, the horizontal axis is sodium in solution (m), while in Figure 3, the horizontal axis is free hydroxide in solution. The presence of sodium nitrate in solution at 1m concentration essentially shifts the curve along the sodium axis, but when the data are plotted using free hydroxide along the horizontal axis, the predictions fundamentally fall on the same curve. There appears to be no significant difference in the predicted gibbsite solubility in the presence of 1m sodium nitrate in solution versus no sodium nitrate.

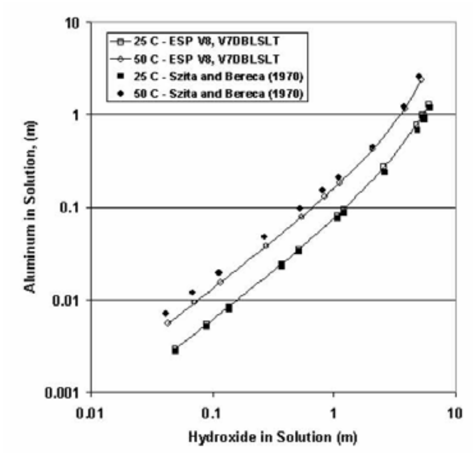

Figure 1. Comparison of ESP (V8 and V7DBLSLT database) predictions to literature data.

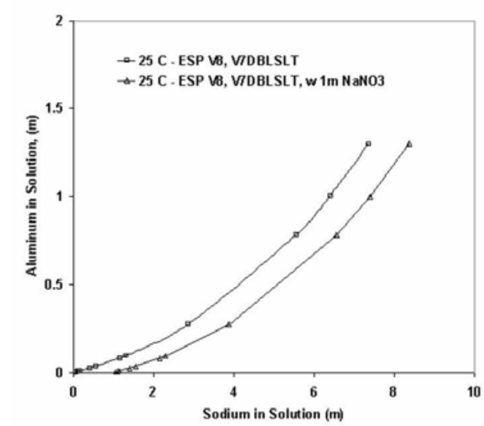

Figure 2. Comparison of ESP Predictions of aluminum solubility in presence of sodium nitrate (horizontal axis is sodium molality in solution).

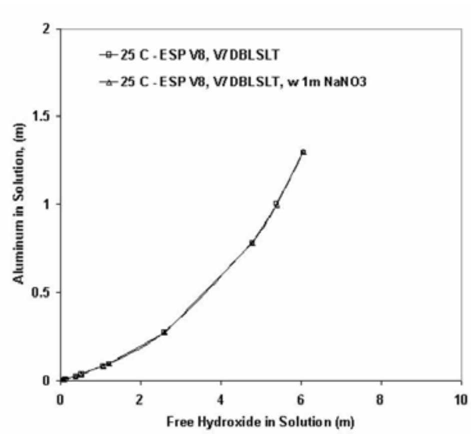

Figure 3. Comparison of ESP Predictions of aluminum solubility in the presence or absence of sodium nitrate (horizontal axis is free hydroxide molality in solution).

Values for sodium salts anticipated in Hanford waste streams for WTP processing were obtained and development of a test plan was begun. Experiments have been designed to obtain an understanding of the effects of sodium and hydroxide as well as major anions such as nitrate, nitrite and carbonate, on aluminum solubility at the processing temperature ranges of interest. Statistical methods (Taguchi) will be used to populate the test matrix.

Planned Activities

Completion and approval by site personnel of the aluminum test plan and all necessary equipment will be obtained. Previous work with aluminum systems has shown extended equilibrium times up to 6 months, however, some options exist for decreasing the equilibration time and these will be investigated. Solubility data, along with existing data in the literature will be subjected to analysis such that revisions and omissions in currently available thermodynamic databases will be corrected. The results of this study will then be available for workers in the future.

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NEXT-GENERATION PRETREATMENT SOLUTIONS

C Tank Farm Chemistry Neural Network Development

Principal Investigator: Larry Pearson, pearson@icet.msstate.edu, 662-325-7626, and John Luthe of Institute for Clean Energy Technology (ICET)

Collaborators: Jeff Lindner, ICET; Blaine Barton and Randy Kirkbride of Washington River Protection Solutions (WRPS)

Project Duration: 2007-2009

Waste Processing Challenge

Primary concerns associated with cleanup of the Hanford site tank wastes are the lack of available space in the existing double-shell tank (DST) system and the lack of an efficient means to predict and avoid solids formation within the waste retrieval transfer system.

Research Objective

The goal of this work is to improve the understanding of the thermodynamics of waste components through the use of equilibrium models. These models could then be used to evaluate and develop process pretreatment and retrieval options which address the Hanford site tank waste retrieval concerns. In addition, data generated from modeling of the retrieval process is being used to generate a neural network to replace or compliment the wash and leach factors currently used in the Hanford Tank Waste Operations Simulator (HTWOS).

Research Progress

Modified Sluicing with Recycle (MSwR) and the Mobile Retrieval System (MRS) are the technologies currently proposed for recovery of C Farm Tank wastes. Modeling of these technologies required the development of a simulation based on the constraints imposed and solids recovery predicted by Hanford personnel from prior waste retrievals. The model uses the OLI Systems Inc. Environmental Simulation Program (ESP) structured as a batch process for each stage of retrieval processing and delivers outputs relating thermodynamically predicted compositions. A basis for the calculations performed in the ESP modeling centers upon the initial compositions of both the receiver DSTs and the C Farm single shell waste tanks to be recovered. Work conducted by ICET during 2007 and 2008 also included research on the development of a neural network for use within the Hanford Tank Waste Operations Simulator (HTWOS) model, specifically for C farm tank retrievals. The use of a neural network based on thermodynamic data would provide waste stream compositions based on solution chemistry as predicted by a validated model. Improvements in chemical predictions are expected.

Efforts at ICET have led to the development of an ESP equilibrium-based model for use in the simulation of Hanford C Farm Tank retrievals. This model was used to predict tank and stream parameters, including waste solids volume and species, for each waste retrieval according to the current schedule and constraints. Results confirm that equilibrium-based modeling in the evaluation and planning of retrieval options can help address Hanford C Farm Tank cleanup concerns. The benefit of using ESP models to predict process parameters during waste retrievals can be seen in Figure 1. Results from the modeling of the sequential retrieval of C108, C-109, and C-110 into AN-106 indicate the total receiver tank volume required, as well as, the amount and species of solids generated during each stage of the recovery

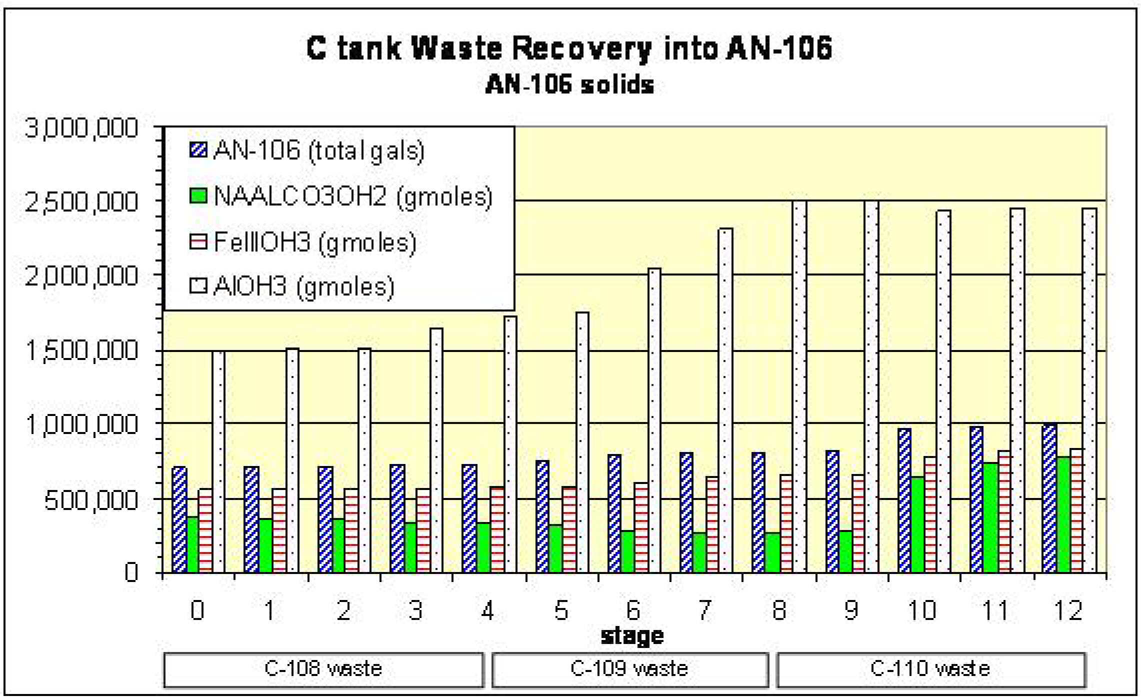

Figure 1 – Waste Retrieval Summary (C-108, C-109, C-110 into AN-106)

Results from the ESP model were then used to generate training set data for a prototype neural network. The equilibrium calculation results from each stage of the multi-step retrieval scheme for each of the ten C-farm tanks are included in the training set. In this manner, a significant number of training sets were generated allowing large coverage of the compositions of the important chemical species and associated physical properties. Predicted neural network results for AN-106 solid components during the recovery of C-109 compare with actual ESP generated values, as shown in Figure 2. This demonstrates the potential for neural network improvement of HTWOS in Hanford tank operations and campaign planning.

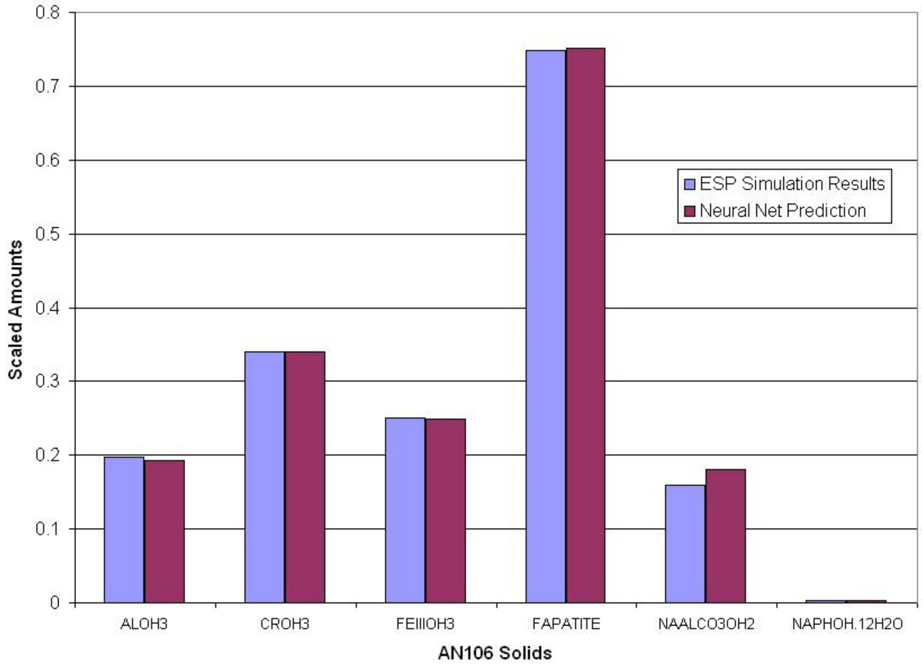

Figure 2 – Neural network for C-109 transfer into AN-106

Planned Activities

A report on the development of the ESP equilibrium-based model and neural net representation of the model will be completed. A data package is being prepared to route to workers at Hanford for eventual incorporation into HTWOS.

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NEXT-GENERATION PRETREATMENT SOLUTIONS

Advanced Mixing Models

Principal Investigator: Richard A. Dimenna, Savannah River National Laboratory (SRNL), Richard.dimenna@srnl.doe.gov, 803-725-8203

Collaborators: David A. Tamburello, SRNL; Si Young Lee and David R. Rector of Pacific Northwest National Laboratory (PNNL)

Project Duration: 2008-ongoing

Waste Processing Challenge

Pump mixing times in the large waste tanks at the Savannah River Site (SRS) are based largely upon custom established over the years. Operational cautiousness may have made those values overly conservative. Operational considerations include potential down-stream impacts of inadequate mixing and possibly unrepresentative tank waste samples resulting from tank configurations that limit access to most of the tank.

More reliably quantifying the mixing time required to suspend sludge particles in waste tanks could reduce operating time and maintenance (including replacement) costs of the mixer pumps because of significantly reduced mixing time requirements. Safety improvements related to reduced operating and maintenance times also could be achieved through reduced exposure to operating and maintenance personnel.

Research Objective

The objective of this research is to quantify the mixing time required to suspend sludge particles with the mixer pumps in an SRS waste tank by establishing a reliable, computational mixing criterion.

Implementing objectives include determining the state of mixing technology and developing an interim report on current methodologies and developing a computational indicator for mixing performance in large tanks.

Research Progress

Accomplishments to date include:

- Identified a widely accepted and appropriate mixing correlation in the mixing literature, the Grenville-Tilton correlation [1, 2].
- Identified candidate computational parameters, turbulent kinetic energy, turbulent kinetic energy dissipation rate, and turbulent eddy viscosity to use as measures of mixing.
- Completed initial calculations showing qualitatively good agreement between these computational parameters and the Grenville-Tilton correlation. Figure 1 shows induced velocity profiles from a jet mixer in a tank, and Figure 2 shows contours of constant turbulent kinetic energy dissipation rate showing lowest values near the bottom of the tank. This indicates that this is the slowest region to mix.

- Initiated additional calculations with an outside contractor (Clemson University) to evaluate computational results, sensitivities, boundary conditions, etc.
- Proposed and tested an additional mixing criterion, the Taylor Reynolds number, and found qualitatively acceptable comparisons with Grenville-Tilton results.

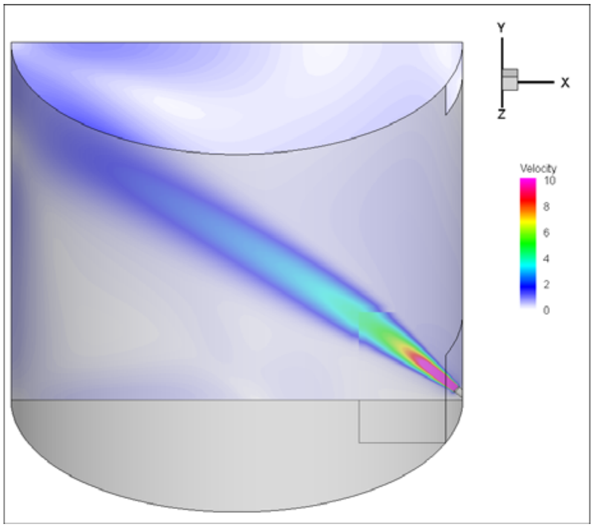

Figure 1. Induced velocity profiles from a jet mixer in a tank.

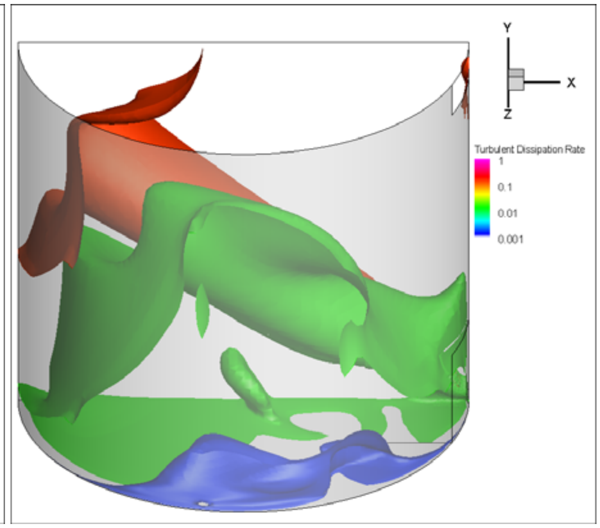

Figure 2. Contours of constant turbulent kinetic energy dissipation rate showing lowest values near the bottom of the tank.

Planned Activities

Several activities are ongoing or planned to evaluate the usefulness of the Taylor Reynolds number as a threshold indicator of a mixed condition. These include:

- Grid and time-step sensitivity calculations to evaluate computational convergence.
- Grid sensitivity to evaluate the kinetic energy and energy dissipation rates from a coarse-grid model to similar values calculated with a fine-grid model.
- Boundary condition sensitivity calculations to ensure the jet mixer is being properly calculated.
- Determination and comparison of a threshold value of the Taylor Reynolds number for comparison with the Grenville-Tilton correlation.
- Comparison of the Reynolds-averaged Navier Stokes (RANS) approach to a large-eddy simulation (LES) for a representative geometry.
- Application of the RANS approach to a Savannah River waste tank for a single-phase mixing condition.

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NEXT-GENERATION PRETREATMENT SOLUTIONS

Pilot Near-Tank Treatment System

Principal Investigator: Terry Sams, Washington River Protection Solutions (WRPS), Terry_L_Sams@rl.gov, 509-376-4653

Collaborators: Reid Peterson, Renee Russell, Dean Kurath, and David Blanchard of Battelle

Project Duration: 2006-2012

Waste Processing Challenge

The Near-Tank Treatment System should provide a modular, integrated system that minimizes the addition of sodium into the waste tanks while removing the aluminum and the cesium from the waste.

Research Objective

The technical approach for the Pilot Near-Tank Treatment System is to combine the two previous Advanced Remediation Technologies, Continuous Sludge Leaching (CSL) and Near Tank Cesium Removal (NTCR), into a single integrated demonstration system. The demonstration system will also integrate suitable technologies to minimize the addition of further sodium into the waste tanks. The CSL would utilize a suitable Hanford simulant containing Boehmite, Gibbsite, sludge and supernate and would be operated to leach the Boehmite and Gibbsite with the caustic leaching process. The clarified liquid would be routed to the ion exchange process for cesium (Cs) removal, NTCR. The cesium decontaminated effluent would then be sent to the caustic recycle process for recovery of the caustic which would be reused in another cycle of caustic leaching in the CSL. This integrated system forms the basis for the Pilot Near-Tank Treatment System (PNTTS).

Continuous Sludge Leaching

Research Objectives

The primary objective of this work was to validate the design assumptions used in the development of the CSL process. The primary assumption was that > 90% conversion of boehmite could be achieved with a 300 hour residence time in the reaction vessel. A secondary objective was to provide data to allow potential optimization of the process to either reduce the caustic demand or improve the process throughput.

Research Progress

Bench-scale simulant tests were performed to evaluate varying ratios of caustic to explore trade-offs in optimizing the reactor size and caustic requirements. Tests involved operating with continuous feed and examining the impact of changing reactor conditions such as residence time and caustic concentration on conversion.

The target dissolution (90+%) was achieved. The results from the model used indicate that there is a significant increase in performance in boehmite dissolution from 0 to 100 hours, then incremental increases from 100 to 300 hours in reaction vessel residence time.

It was found that there is little impact of sodium molarity on reaction kinetics. This suggests that the hydroxide ion concentration is not directly involved in the rate limiting step for this dissolution reaction. This was the expected behavior based on prior batch testing. Therefore, a significant impact of changing the hydroxide concentration was not expected.

Results indicate that a relatively small amount of CrOOH has dissolved. However, recent actual waste tests have indicated that 50% of the Cr from high boehmite wastes is removed by batch caustic leaching – but more importantly, that there is insufficient Cr in this type of waste to require significant Cr removal – due to the presence of relatively higher concentrations of U (there is roughly 30 times more U in leached REDOX sludge than there is Cr).

These results provide the necessary basis for proceeding with pilot plant testing. The conditions required to achieve 90% dissolution of boehmite have been identified and are within the expected operating conditions of the CSL process. Initial pilot plant operations should employ a 300 hour residence time with a target boehmite solubility of 0.5.

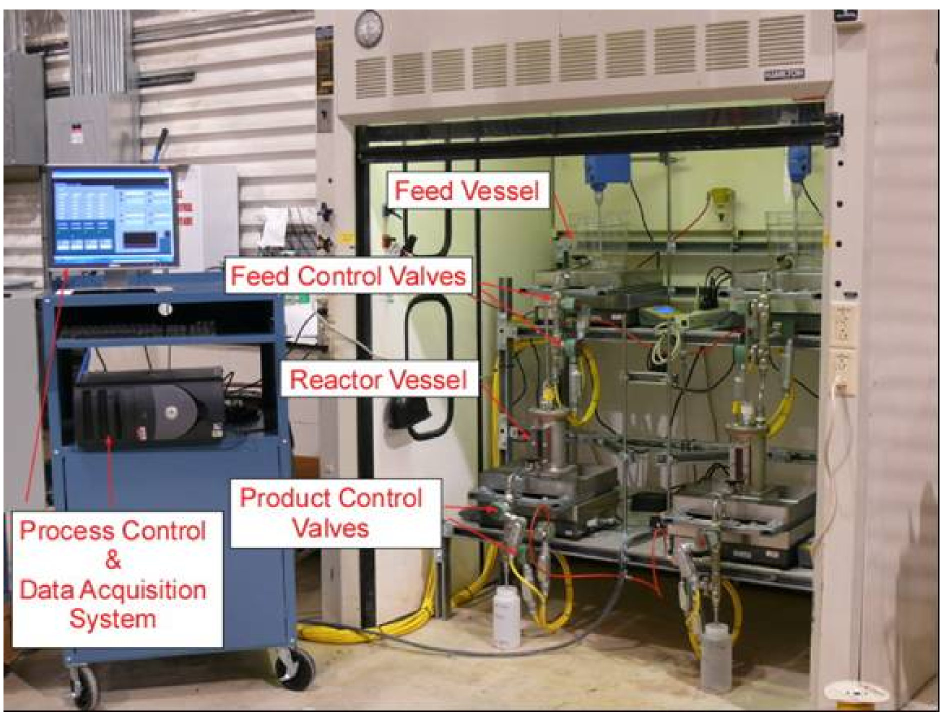

Figure 1. Picture of the CSL Testing Setup

Near Tank Cesium Removal

Research Objectives

The overall objective of the Near Tank Treatment Demonstration is to provide an effective system to separate glass limiting aluminum (Al) and cesium (Cs) from Hanford tank wastes, while minimizing added sodium (Na), using one or more modular shielded systems that can be easily deployed near Hanford tanks. The system will be comprised of three components: a Continuous Sludge Leaching (CSL) module, a Near Tank Cesium Removal (NTCR) module, and a Sodium Recycle module.

The primary objective of the NTCR testing in 2008 was to demonstrate the NTCR process chemistry and provide initial optimization and characterization to provide the basis for pilot scale testing. NTCR uses an elutable ion exchange system based on the Spherical Resorcinol Formaldehyde (SRF) resin. Testing was focused in two areas, SRF resin dissolution/destruction and SRF ion exchange process testing. Temperature and acid concentration were varied in bench scale testing of resin dissolution/destruction to demonstrate the feasibility of the process and provide initial optimization of conditions. Preliminary characterization of off-gas and dissolved resin liquor was conducted for initial assessment of disposal requirements and options. Small column ion exchange tests were conducted to assess the effect of abbreviated processing conditions on ion exchange performance, evaluate the impact of feed variability, and assess the effect of lower-than-ambient temperature on elution performance.

Research Progress

Minimum conditions for SRF resin dissolution and initial destruction and more vigorous conditions for additional SRF resin destruction were demonstrated. In-column resin destruction was found difficult to control. Instead a two step process is recommended in which mild conditions (3M – 5M nitric acid, 50ºC – 70ºC) are used to begin dissolution/destruction and flush the resin from the column to a digester vessel, and higher temperature and/or acid concentration (up to 7 M acid and 90ºC) are used for more complete destruction (up to 70%). The organic carbon remaining in solution is small compared to the amount of sugar that will be added to control the redox potential of the glass melt at the melter. Addition of caustic solutions, used in the ion exchange process tests, to the acidic dissolved resin liquor resulted in neutralization with no adverse reactions such as precipitation or gas generation. The off-gas contains a significant amount of NOx (~35%) of which NO is the principal component. Analysis of a number of dissolved resin liquor samples for semi-volatile organic compounds (SVOCs) showed that none of 66 SVOCs of interest were detected. The results collected in this set of tests provides the necessary basis for pilot plant tests of resin dissolution/ destruction and neutralization for addition to the Cs-decontaminated LAW stream if this is selected as the resin disposal option for NTCR.

The small column ion exchange testing was comprised of six single-column SRF ion exchange tests and one dual-column SRF ion exchange test. Five tank waste simulants were used for the tests. Feed processing (Cs loading), feed displacement, elution, and regeneration ion exchange steps were tested. Two of the elutions were run at reduced temperature (10°C and 15°C). In all but one test, a short (15 BV) second load cycle was run to assess elution and regeneration performance. Samples were collected during all steps and analyzed to determine the concentration of Cs in the process streams as a function of the processed volume to assess performance for each step.

The small column ion exchange testing objectives were met, and additional results pertinent to the NTCR process conditions were documented . The major results and conclusions are:

- Satisfactory Cs decontamination of at least 100 BV of three tank waste simulants was demonstrated. The simulants cover the range of the expected K and Cs concentrations in the target Hanford tank waste feeds.
- An abbreviated LAW displacement, short upflow elution, and upflow resin regeneration using a dense regenerant were successfully demonstrated. Some adjustments to the proposed process operations parameters were required.
- The impact of feed variability was assessed— performance for the expected waste feeds is within the NTCR design basis.
- Reduced temperature elution was successfully demonstrated – no adverse impact to the elution performance was observed at the two lower temperatures (Figure 2).

Ion exchange processing conditions were recommended for pilot plant testing based on the small column ion exchange test results.

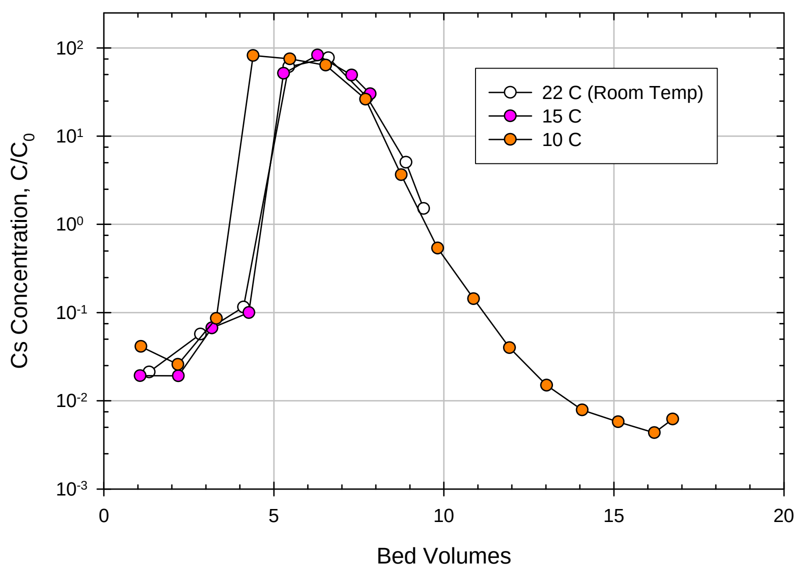

Figure 2. Effect of Reduced Temperature on Elution of Cs from SRF Resin.

Planned Activities for the Pilot Near-Tank Treatment System

The project's objectives for Phase II, Task 2 are to develop and test a portable, modular integrated pilot scale demonstration unit that would treat a waste tank simulant containing high concentrations of recalcitrant aluminum solids (boehmite). The demonstration will dissolve and separate aluminum for potential disposition as low activity waste by removing key radionuclides (e.g. cesium) from this stream, per the objectives of the two unit operations (CSL and NTCR).

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NEXT-GENERATION PRETREATMENT SOLUTIONS

Enhanced Sodium Recycling Processes

Principal Investigator: Shekar Balagopal, Ceramatec, Inc., Shekar@ceramatec.com, 801-978-2142

Collaborators: Gary Savigny and Mathew Fountain of Pacific Northwest National Laboratory (PNNL)

Project Duration: 2005-2008

Waste Processing Challenge

The Department of Energy's (DOE) Office of River Protection (ORP) is chartered to provide safe storage, retrieval, treatment and disposal of over 53 million gallons of radioactive mixed waste in 177 underground storage tanks at the DOE's Hanford site near Richland, Washington. Within Hanford's Waste Treatment Plant, the high-level waste (HLW) stream will require removal of non-radioactive hydrated aluminum oxides in the form of either Gibbsite or Boehmite sludge. The sludge is removed from the HLW by a leaching process that utilizes large amounts of sodium hydroxide. As the amount of sodium added in the form of sodium hydroxide approaches the base sodium in the HLW inventory, a technological need to develop methods to allow for recovery and recycling of the available caustic inventory to reduce the overall sodium load to the low-activity waste (LAW) feed is necessary.

Research Objectives

The overall research objective is to demonstrate an electrochemical process to recycle sodium from the LAW stream.

Ceramatec's process employs a sodium (Na) super ionic conductor membrane (NaSICON) to selectively remove sodium from LAW and supplemental waste streams under the influence of an electric field across the membrane. This allows for recycling of the caustic used to remove aluminum during sludge washing as a pretreatment step in the vitrification of radioactive waste and will allow reduction of the LAW waste volume by as much as 40%. This technology will potentially reduce the handling and processing of waste and the time schedule at DOE sites. Potential cost savings in billions of dollars for waste cleanup may be realized by lowering the volume of waste.

Implementing objectives include evaluating the technology benefits of tubular and planar membrane design configuration based on site process-flow requirements, robustness, and device reliability for application at Hanford's Waste Treatment Plan (WTP) and developing a low-cost electrode.

Research Progress

Ceramatec is developing electrochemical cells for the separation of sodium from radioactive waste, which will allow the recycling of caustic and removal of sodium from waste prior to vitrification of the LAW. The feasibility of Ceramatec's technology over the years was demonstrated in tests at the Savannah River Site with PNNL using radioactive/ contaminated sodium containing solutions (i.e., not simulant solutions). The results of these tests demonstrated the utility of this technology for meeting the strategic goals of the DOE. The research program continues this research and development program to mature the technology with several key objectives to be completed. The major objectives for 2008 are as follows:

1. Evaluate performance of NaSICON membranes in radioactive simulant chemistries; both chemistries have higher potassium concentration levels (1) AP-101 (Na/K ratio of 7:1) and (2) typical Hanford blend (Na/K ratio of 50:1);
2. Design a bench-scale electrochemical system with engineering scale up features, and operate the unit to demonstrate the maturity of the process to recycle sodium from AP104 type stimulant.;
3. Conduct overall process economics by Ceramatec and PNNL for implementation of NaSICON-membrane technology for a full-scale system at the waste treatment plant, and validate the performance targets for sodium separation from low-level wastes.

Accomplishments include:

- The powder production process was developed for large volume production of NaSICON ceramic membranes. Quality assurance and quality control tools were applied to manufacture planar NaSICON membrane.
- Energy efficient Large Area NaSICON Structures (LANS) was developed. The thin functional layer of NaSICON membrane (250 microns thickness) on a ribbed structural support made from the same material was fabricated by using the advanced tape casting method. The LANS membrane has reduced the energy required by up to 50% to recycle sodium from waste simulant chemistries
- Successfully demonstrated with single membrane cells the ability to produce up to 50 wt % of sodium hydroxide product from recycling sodium from AP104 simulant in continuous cell operations for 7.35 months (> 5300 hours)
- Statistical significance performance of membrane cells to remove sodium in AP104 simulant were successfully tested in 10's of thousands of hours of evaluation to establish the statistical performance reliability of the electrochemical membrane process. The sodium removal efficiency of the membrane based cell to separate sodium is nearly 100%.
- A bench scale size cell with multiple membrane stacks, 53 times larger than the laboratory size single membrane cell (See Figure) was operated to demonstrate the maturity of the planar modular configuration to handle large processing throughput of waste feed. The cell stack performance was evaluated at an operating temperature of 45^{o}C with 55 gallon simulant waste tank

sizes in continuous mode operation to recycle sodium.

- Sodium from 40 % to 75 % percent can be recycled with the electrochemical membrane process depending on the type of waste chemistries at Hanford before solid precipitation occurs in the feed stream
- Two actual waste tests were successfully completed at PNNL under a sub-contract from Ceramatec, Inc. to efficiently separate sodium, and results were nearly identical to the results achieved with simulants at Ceramatec (Report # PNNL18216, PNNL18333- DE-AC05-76RL01830). There was no Alumina precipitation observed in samples obtained at saturation ratios up to 8.9 after 4 months from completing the AP104 waste test.
- The NaSICON membrane in the LANS configuration was electrochemically tested in a in a single membrane scale apparatus with Group 5 and 6 tank waste in a batch mode test to determine the membrane performance when actively transporting Na for approximately 5 days (PNNL18333- DE-AC05-76RL01830)
- Economic Feasibility of Electrochemical Caustic Recycling at the Hanford Site was completed by PNNL through a subcontract from Ceramatec (PNNL-18265, Contract # DE_AC05-76RL01830). The economics for caustic recycling from LAW for re-use on site showed considerable savings to DOE on processing schedule and good return on investment with large cost savings associated with procurement of caustic
- The planar technology design is matured to scale up to pilot demonstration to recycle sodium from Hanford waste streams. The safety and reliability factor to recover cells in case of gelling and precipitation of solids to meet the down

Bench-scale custom-designed cell containing three scaffolds, each with eight 2.4" NaSICON membranes.

stream process requirements at site is in progress.

Planned Activities

A detailed final technical report will be submitted to DOE-EM Office of Waste Processing Contract's Office to cover the project progress for the period of April 2005 to April 2009. The current technology development and demonstration phase that commenced in August 2008 should be concluded by December 2009

ENHANCED STABILIZATION TECHNOLOGIES PROGRAM AREA

Initiative Development Team Lead: John Vienna, Pacific Northwest National Laboratory (PNNL), john.vienna@pnl.gov, 509-372-2807

Initiative Development Team: Kurt Gerdes, DOE-EM Office of Waste Processing; Innocent Joseph, Energy Solutions (ES); David Peeler, Savannah River National Laboratory (SRNL); Jay Roach, Idaho National Laboratory (INL); Joe Westsik, PNNL

Challenge

The challenge addressed by this initiative is enabling the effective immobilization of the wide variety of tank and bin related wastes stored at U.S. DOE sites including Hanford, Idaho, Oak Ridge, and Savannah River.

Solutions

1. Develop Next-Generation Melter Technology

This initiative is to permit higher melter throughput and/or increased waste loading by developing the next generation of melter technologies. Waste glass melter throughput is determined by a number of interdependent parameters. To increase melter throughput, these parameters must be considered and optimized specifically for the waste and facility to enable higher glass production rates. The loading of waste in glass is controlled in part by the melter processing related parameters. Certain incremental melter design changes could yield improved loading of Savannah River high-level waste (HLW) in glass, Hanford HLW in glass, and Hanford low-activity waste (LAW) in glass, while completely new melter designs may yield greater improvements in waste immobilization within the U.S.

2. Develop Advanced Glass Formulations

This initiative is to improved glass formulations to reduce treatment time and waste form management costs. In addition, this initiative will develop predictive models for glass properties, processing rate, and waste form qualification. Although currently listed as “glass formulation,” “waste form formulation” is more descriptive as waste forms other than glass may be developed under this initiative.

3. Develop Supplemental Treatment Technologies

This initiative is to develop and demonstrate technology for the immobilization of secondary waste streams from the major EM sites. Several streams are to be considered, including:

- excess pretreated LAW from Hanford
- pretreated salt wastes from SRS
- secondary wastes from tank farm and vitrification plant operations at SRS Hanford, INL, and ORNL
- calcine and sodium bearing wastes at INL. It is critical to address these waste streams as possible inability to safely dispose of these streams can limit the deployment and/or utility of the primary waste treatment processes that they support.

Accomplishments

1. Develop Next-Generation Melter Technology

- In 2008 work focused on incremental improvements in existing melter technologies. Testing was performed to evaluate production rate and waste loading improvements for Hanford HLW glass by melting at incrementally higher temperatures of 1175°C and 1200°C compared to the baseline 1150°C. The results of this testing showed marked increase in production rate for high-alumina, high loaded glass. Specifically, there was a 42% increase in production rate (1500 kg/m^2/d) compared to higher melting high alumina glass at 1150°C (1050 kg/m^2/d) or a 2.5× increased rate compared to the low melting glass from 2007 (600 kg/m^2/d).
- In 2008 engineering tests were performed on cold-crucible induction melter technology for application to SRS wastes. This technology shows promise for treating HLW slurries using frit as an additive.

2. Develop Advanced Glass Formulations

  - CY08 efforts included the development of data and models for predicting glass properties over broader, higher waste loaded glasses at Hanford and SRS. Interim models for use in predicting the impacts of waste composition and process variation on HLW were developed as a joint EM-21 and Hanford Tank Farm Contract effort. High waste loaded glasses were formulated for selected wastes at Hanford (4 LAW wastes with higher sodium and sulfur, and one HLW glass) and SRS (one high alumina stream). A revolutionary approach to formulating glasses with significant crystallinity was developed. By this approach, the accumulation of crystals in a melter can be predicted as a function of melter feed composition. Significantly higher waste loading can result from such an approach and the need for chromium removal from Hanford HLW is significantly diminished.

3. Develop Supplemental Treatment Technologies

  - Fluidized bed steam reforming (FBSR) pilot plant demonstrations were successfully completed in 2008 on both simulated LAW and WTP secondary waste streams. The safe, long-term (>100hr) operation of the THOR® process for each simulated waste stream was demonstrated. Future research will focus on the FBSR treatment of Hanford secondary wastes and breaking the Hanford LAW off-gas recycle.
  - Direct hot isostatic pressing (HIP) of the INL alumina and zirconia calcine, without treatment additives, confirmed the significant economic and environmental advantages that HIPing offers compared to direct disposal. Vast volume reductions of between 50% and 70% compared to as stored calcine, for zirconia and alumina calcines respectively, have been demonstrated.

Plans

1. Develop Next-Generation Melter Technology

In the future, the next-generation melter initiative will begin to develop transformation melter technologies for tank and/or calcine waste vitrification. This initiative will consider induction heating or hybrid heating methods to obtain step function increases in loading and throughput rates.

2. Develop Advanced Glass Formulations

- Future efforts will focus on allowing for the prediction of nepheline formation in high alumina waste glasses.
- Future efforts will continue to develop high loaded glasses for a broader range of waste compositions and demonstrate these glasses in scale melter tests.
- Future efforts are required to complete and validate the crystal accumulation model at laboratory scale, scale up melter testing to demonstrate the concept, and glass formulation using the models to take advantage of this advance in glass formulation technology.
- Future efforts are being planned to develop phosphate based glasses for higher loading of selected DOE tank and bin wastes.
- Future efforts are also being planned to study the corrosion of glass in water to develop new test methods that more directly correlate LAW glass response to performance assessment. This is expected to significantly improve the loading of LAW in glass.

3. Develop Supplemental Treatment Technologies

- Future research will focus on the FBSR treatment of Hanford secondary wastes and breaking the Hanford LAW off-gas recycle.
- Future work will focus on applying HIP to other waste streams.

ENHANCED STABILIZATION TECHNOLOGIES

Cold Crucible Induction Melter

Principal Investigator: Eric Tchemitcheff, AREVA Federal Services LLC,
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Collaborators: Sharon Marra, Savannah River National Laboratory (SRNL); Jay Roach, Idaho National Laboratory (INL); Christophe Girold, Commissariat à l'Énergie Atomique (CEA); Laurent David, SGN

Project Duration: 2007-2012

Waste Processing Challenge

Cold Crucible Induction Melter (CCIM), co-developed by AREVA and the French Atomic Energy Commission (CEA), is an alternative vitrification technology that, when successfully deployed, could accelerate the high-level waste vitrification program schedule, reduce lifecycle cost, and mitigate technical risks at selected sites of the DOE complex.

Research Objective

CCIM technology has the potential to be retrofitted into the Defense Waste Processing Facility (DWPF) at Savannah River, replacing the existing Joule-heated Melter (JHM) technology currently installed there. Such a retrofit is the focus of the ART CCIM Phase II-A project effort.

The principal objectives of this 21-month project are

1. Perform laboratory studies and testing activities at SRNL and at CEA Marcoule to design a glass matrix which allows waste loading of the order of 50wt% with a Sludge Batch 4 (SB4)-type waste composition (versus the current DWPF process capability for this feed at about 33wt%).
2. Run pilot-scale demonstrations under representative conditions on existing CCIM research platforms at INL and at CEA Marcoule to validate the promising waste loading rates which are expected when processing in the 1,250-1,300°C melt pool temperature range.
3. Perform specific engineering studies of key technical issues identified in Phase I of the ART CCIM project that validate the feasibility of retrofitting CCIM technology into the existing DWPF Melter Cell.
4. Develop a comprehensive plan (including cost and schedule) for laboratory-testing, pilot- and large-scale demonstrations, and engineering activities to be performed during Phase II-B of the project.

Research Progress

In early project work, technical discussions were held among contributors regarding the simulated waste to be used for laboratory studies and demonstration runs. Sludge Batch 4 (SB4) was selected due to the high aluminum content which proved to limit waste loading in previous DWPF operations.

Phase II-A Laboratory Work

A glass composition development effort was completed to identify and recommend a frit composition and SB4 simulant waste loading target for subsequent demonstration testing. The lab-scale development effort was aimed at developing a glass composition (glass frit composition and waste loading) where both glass durability and liquidus temperature were deemed acceptable. It was recommended that the Frit 503-R6 composition be utilized for the demonstrations. Furthermore, a waste loading of 46wt% should be targeted. The recommended frit and waste loading would produce a glass with acceptable durability with a liquidus temperature adequately below the 1250°C nominal CCIM operating temperature selected for vitrifying the SB4 waste type. Further laboratory testing concluded that the demonstrations should be conducted using the REDOX control strategy developed for DWPF operations at 1,150°C. A REDOX ratio of 0.06 to 0.10 Fe^{2+}/total Fe should be targeted for the demonstrations. A sludge simulant recipe was then developed by SRNL to represent the chemical and physical characteristics of the actual SB4 sludge waste, including chemical precipitation steps and sludge washing steps to provide a melter feed that would be prototypic of the current DWPF flowsheet.

Figure 1. General view of the pilot-scale CCIM demonstration platform – CEA Marcoule

Figure 2. 650 mm diameter pilot-scale CCIM – CEA Marcoule

Phase II-A Demonstration Runs

After refinement of objectives, the project team decided that two runs - one initial run for system set-up and one extended-duration run at a single defined operating temperature of 1250°C - would be performed at CEA's 650 mm diameter CCIM in Marcoule (completed in 2009). Meanwhile, INL's demonstration at its 267 mm diameter engineering scale CCIM was to focus on characterizing the off-gas stream which results from processing at the higher temperatures employed by the CCIM process.

INL demonstrations were performed using the engineering-scale CCIM platform in two discrete sessions. The initial session was performed during the week of December 15, 2008 and consisted of a parametric evaluation of operating conditions within ranges defined by process and test objectives. INL operated the CCIM with the generator energized for a total of about 30 hours. Operators were able to observe the temperature of the melt, cold cap behavior, and power level changes while varying the feed rate from a minimum of about 1 kg/hr to a maximum of about 6 kg/hr.

Phase II-A Engineering Studies

The engineering scope of work was to conduct mechanical engineering studies regarding the feasibility to install and maintain a CCIM in the DWPF Melter Cell, and process studies to define the Process Data Flow Sheet for such a CCIM retrofit. Under the topic of mechanical engineering studies, SGN defined the CCIM layout configuration within the Melter Cell, designed the CCIM frame, and selected the preferred maintenance strategy among the three approaches defined in ART CCIM Phase I studies.

The results of this assessment found that maintenance of the CCIM within the melt cell is achievable by all three strategies considered, but that the strategy which relies on robot(s) mounted on the CCIM frame, is the preferred alternative (offers the most flexibility for CCIM operations, minimizes the duration of operating and maintenance tasks, and does not require any significant modification to the Melter Cell).

In addition, modeling studies were performed by CEA to directly supplement these mechanical engineering studies: assessment of the preferred configuration of mechanical stirrer(s) to be fitted to the CCIM envisioned for retrofit at DWPF, and identification of electromagnetic parameters for an eventual full-scale production CCIM.

Planned Activities

- Second session of Off-gas System Evaluation testing at INL (Jan 2009)
- CEA pilot-scale demonstration runs on the 650 mm diameter CCIM at Marcoule (March and April 2009) and submittal of corresponding report
- Development/submittal of CCIM process flowsheet (June 2009)
- Development/submittal of proposal for ART CCIM Phase II-B (June 2009)

ENHANCED STABILIZATION TECHNOLOGIES

Broader Hanford High-Level Waste Glass Formulations

Principal Investigator: Ian L. Pegg, Vitreous State Laboratory (VSL), The Catholic University of America (CUA), pegg@cua.edu, 202-319-6700

Collaborators: Innocent Joseph and Bradley W. Bowan of EnergySolutions; Albert A. Kruger, Office of River Protection (ORP)

Project Duration: 2007-2009

Waste Processing Challenge

Methods to increase waste loadings and processing rates for high-level waste (HLW) glass formulations offer great potential for cost and schedule reductions at DOE's HLW treatment facilities that employ or plan to employ vitrification. This work addresses these needs, specifically for Hanford HLW and low activity waste (LAW) treatment, with results that are broadly applicable to other facilities.

Research Objectives

1. Develop advanced HLW glass formulations that have high aluminum loadings and that also show high processing rates;
2. Investigate the application of the approaches developed for Hanford HLW to Savannah River high-aluminum wastes;
3. Investigate the effects of alternative aluminum forms and alternative reductants on processing rate;
4. Investigate glass formulations that allow higher crystal content in order to develop higher waste loading glass compositions for HLW streams that contain high concentrations of Cr and other spinel-forming components. Determine the settling characteristics of various types of crystals in HLW glass melts and their impacts on melt rheology;
5. Develop higher waste loading glasses for four Hanford LAW streams that incorporate higher levels of sodium and sulfur;
6. Measure the high temperature density, specific heat, and thermal diffusivity of representative Hanford HLW and LAW glasses to collect data to support facility heat load estimates, the results of which can be throughput limiting.

Research Progress

The objectives were addressed through a combination of crucible-scale tests, melt rate screening tests, and small- and pilot-scale melter tests. This work built on our earlier work that demonstrated fully compliant HLW glasses with Al2O3 loadings of 24 wt%, an 85% increase over the present WTP baseline maximum loading for Al-limited HLW. In the present work, two types of small-scale melt rate screening tests were employed to successfully develop improved formulations that exhibit increased melt rates while retaining high waste loadings. Enhanced processing rates were then demonstrated in a series of continuous melter tests on a DM100 vitrification system (melt surface area of 0.11 m2). Further testing was performed on the DM1200 vitrification system installed at VSL, which is a one-third scale (1.20 m2) pilot melter for the WTP HLW melters and which is fitted with a fully prototypical off-gas treatment system as shown in the figure.

DM1200 WTP HLW Pilot Melter.

Melt rates that exceed the requirements for WTP HLW vitrification by up to 88% were successfully demonstrated, highlighting the potential for a transformational improvement in WTP performance. Ongoing testing in this area is evaluating the prospects for further increases in waste loading and processing rate, and the effects of the various chemical forms of aluminum in the HLW streams, alternative reductants, and use of LAW as a potential sodium source.

The effects of increased crystal content as means to increase waste loadings of other HLW streams (e.g., spinel- or Cr-limited) have been investigated through a series of small-scale tests to investigate settling rates and impacts on melt rheology. Based on these results, five runs were successfully performed on the DM100 vitrification system with high crystal content formulations, followed by extended idling. The results serve to substantiate the potential of this approach but longer-term melter tests are needed. Measurements of high temperature density, specific heat, and thermal diffusivity were completed on representative WTP HLW and LAW glass formulations, which together permit the calculation of the thermal conductivity. Despite the importance of these properties, these are the first such measurements on WTP glasses. Finally, further progress was made on increased loading in WTP LAW glasses, supported by extensive melter testing on the DM10 vitrification system (0.02 m2). All of this work is directly applicable to Hanford tank waste. In addition, however, high waste loading HLW glass formulations, especially high aluminum compositions, are also relevant for the Savannah River site (SRS).

Planned Activities

- Complete the balance of a series of twelve DM100 melter tests and four DM1200 tests with HLW glasses with high aluminum loadings and enhanced processing rates.
- Develop new glass formulations for SRS high-aluminum HLW, specify and procure waste simulants and new glass frit, and complete DM100 melter testing with and without bubbling.
- Perform an engineering study to evaluate the retrofit of bubblers into the DWPF melter to increase processing rates.
- Develop Test Plans for high magnesium WTP LAW glasses to assess alternative Al leaching concepts being considered by ORP and for work with WTP high bismuth HLW streams.

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ENHANCED STABILIZATION TECHNOLOGIES

Enhanced DOE High-Level Waste Melter Throughput Studies

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Project Duration: 2007-2012

Waste Processing Challenge

High-level waste (HLW) throughput (i.e., the amount of waste processed per unit time) is a function of two critical parameters: waste loading (WL) and melt rate. For the Waste Treatment and Immobilization Plant (WTP) at the Hanford Site and the Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS), increasing HLW throughput would significantly reduce the overall mission life cycle costs for the Department of Energy (DOE).

Research Objective

The objective of this study was to generate supplemental validation data that could be used to determine the applicability of the current liquidus temperature (TL) model to expanded DWPF glass composition regions of interest based on higher WLs. Two specific flowsheets were used in this study to provide such insight:
1. Higher WL glasses (45 and 50%) based on future sludge batches that have (and have not) undergone the Al-dissolution process.
2. Coupled operations supported by the Salt Waste Processing Facility (SWPF), which increase the TiO_2 concentration in glass to greater than 2 wt%.

Glasses were also selected to address technical issues associated with Al_2O_3 solubility, nepheline formation, and homogeneity issues for coupled operations.

Research Progress

A test matrix of 28 glass compositions was developed to provide insight into the issues discussed in the previous section. The glasses were fabricated and characterized using chemical composition analysis, X-ray Diffraction (XRD), liquidus temperature (T_L) measurement (lowest temperature at which crystals do not form in the glass) and the Product Consistency Test (PCT).

The results of this study are summarized below:
1. TiO_2 concentrations up to ~ 3.5 wt% were retained in DWPF type glasses, where retention is defined as the absence of crystalline TiO_2 (i.e., unreacted or undissolved) in the as-fabricated glasses. Although this TiO_2 content does not bound the projected SWPF high output flowsheet (up to 6 wt% TiO_2 may be required in glass), these data demonstrate the potential for increasing the TiO_2 limit in glass above the current limit of 2 wt% (based strictly on retention or solubility).

2. For those study glasses that had very close compositional overlap with the model development and/or model validation ranges of the current DWPF TL model (except TiO_2 and MgO concentrations), there was very little difference in the predicted and measured T_L values. Even though the TiO_2 concentrations were above the 2 wt% upper limit, the results indicate that the current T_L model is applicable in this compositional region with TiO_2 contents up to approximately 3.5 wt%.

3. As the target glass compositions diverge from the model development and validation ranges, the T_L data suggest that the model under-predicted the measured values. These discrepancies imply that there are individual oxides or oxide combinations that need to be accounted for in the model. These oxides include B_2O_3, SiO_2, MnO, TiO_2 and/or their combinations, More data would be required to fill in these anticipated DWPF compositional regions for higher WL glasses so that the model coefficients could be refit to account for these differences.

Planned Activities

Using the data generated in 2007, 2008 and historical data, compositional gaps will be identified and additional HLW glasses will be fabricated and characterized. Should the development of alternative models or refinements to existing models be necessary, the 2009 effort may not yield enough data.

Development of the 2009 glass compositional region will be based on three primary inputs:
1. projected sludge batch compositions (i.e., the range of the primary sludge oxides);
2. higher waste loading targets (i.e., between 40 and 55%);
3. frit compositions of interest.

With respect to the projected sludge composition, the latest revision of the High Level Waste Systems Plan will be utilized. The glass compositional region will be defined based on the projected sludge compositions over waste loadings of interest as well as anticipated contributions from the four primary frit components (Na_2O, Li_2O, B_2O_3, and SiO_2). Since specific frits for each sludge batch will not be developed, a general glass compositional region (in terms of minimum and maximum values for each major oxide) will be defined based on these three inputs. Statistical algorithms will then be used to design the 2009 test matrix using a series of imposed constraints. Glasses will be selected to intentionally challenge various property constraints based on model predictions and associated limits defined for the compositional region of interest.

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ENHANCED STABILIZATION TECHNOLOGIES

Develop Predictive Models for Hanford and SRS High Waste Loading Glasses

Principal Investigators: John Vienna, john.vienna.peeler@pnl.gov, 509-372-2807, Mike Schweiger, and John McCloy of Pacific Northwest National Laboratory (PNNL)

Collaborator(s): David Peeler, Fabienne Raszewski, and Kevin Fox of Savannah River National Laboratory (SRNL)

Project Duration: 2007-2012

Waste Processing Challenge

With current technology, the amount of high-level waste (HLW) glass to be produced at Hanford and the Savannah River Site (SRS) significantly exceeds DOE plans. The technology challenges that most impact HLW glass volume in the Defense Waste Processing Facility (DWPF) at SRS and the Waste Treatment Plant (WTP) at Hanford include: 1) solids accumulation in the melter that may limit melter life (e.g., spinel); 2) crystallization of slow cooled glasses that cause decrease in waste form durability (e.g., nepheline); and 3) data and models for processing and qualification of high-loaded HLW glasses. The challenge is to develop the technology that will allow DOE-EM to reduce the amount of HLW glass produced and thereby reduce the life-cycle costs to below those currently estimated.

Research Objective

Due to the life-cycle costs associated with long-term storage of vitrified high-level nuclear waste (HLW), it is desirable to maximize the waste loading to decrease the overall volume of vitrified waste for storage and disposal. One of the significant limitations to waste loading is the aluminum component for which elaborate separation steps have been devised to lower its concentration in waste feed to vitrification. It would thus be very beneficial to understand limitations of high-aluminum glasses and be able to predict crystallization and processing properties.

The goal of this project is to develop new models and refine existing ones for high- waste loading HLW glasses for Hanford and Savannah River. A focus was made on high aluminum waste compositions, rather than high iron or bismuth, because about 50% of Hanford wastes and 30% of Savannah River wastes are high aluminum. To achieve this we took two approaches. One-component-at-a-time composition variations were evaluated and a few additional glasses were made to fill in gaps in the compositional space created by these higher loadings in glass.

Research Progress

A data set of 60 new glasses generated in 2008 was combined with data from previous studies into a modeling database of 3406 glasses. Key properties of these 3406 glasses were fitted to empirical models of this form:

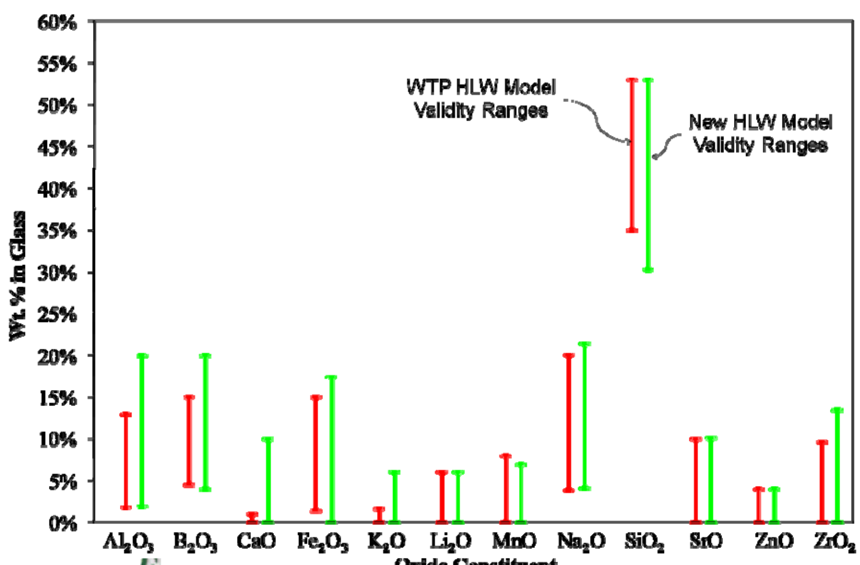
$$g_\alpha(p_\alpha) = \sum_{i=1}^{N} b_{\alpha i} x_i + \text{Selected}\left\{ \sum_{i=1}^{N} b_{\alpha ii}(x_i)^2 + \sum_{i}^{N-1} \sum_{<\ j}^{N} b_{\alpha ij} x_i x_j \right\}$$

g_α = α^{th} predicted transformed property
p_α = α^{th} property
N = number of coefficients or terms in the model
$b_{\alpha i}$ = the i-th component coefficient for the g_α transformed property
x_i = the i-th component mass fraction in glass.

Models for viscosity and electrical conductivity as functions of temperature, product consistency test results for normalized boron, sodium, and lithium, normalized toxicity characteristic leaching procedure response, specific volume, and liquidus temperature for spinel and zircon primary phases. These models have significantly increased the range of model validity as shown in the figure below. Primary among the changes is the expansion of Al2O3 upper bound from 13 to 20 wt% in glass, which will allow for calculation of high-loaded, high-alumina glasses. The increases in B2O3 and CaO which will allow for the use of boria and lime in reducing nepheline precipitation. The increase in K2O will allow for its use as a glass former to reduce spinel precipitation. The expansion of the ranges for CaO, Fe2O3, Na2O, SiO2, and ZrO2 will all help to increase waste loading

Planned Activities

Further data collection is necessary to model the formation of nepheline in high alumina glasses and to extend the glass property models to a broader range of Hanford HLWs. Upon completion of additional data collection, another phase of modeling will be required in order to increase waste loadings and predict HLW glass volumes to be produced at Hanford and SRS.



Comparison of Composition Regions of HLW Property Models Planned Activities

ENHANCED STABILIZATION TECHNOLOGIES

Predictive Model for Glass Production or Melt Rate

Principal Investigator: A. S. Choi, Savannah River National Laboratory (SRNL), alexander.choi@srnl.doe.gov, 803-725-5094

Project Duration: 2007-2010

Waste Processing Challenge

Completing tank closure activities at SRS and Hanford by their respective schedules requires increases in the nominal or current high-level waste (HLW) production rate. The SRS reference case calls for an increase in loading to 50 wt% and an increase in production rate to 250 canisters per year, while at Hanford, the reference case assumes 7.5 MT of glass produced per day and a total canister count reduction to ~12,500. These projections require increased processing rate at the same time as increased loading of waste in glass. This is particularly challenging since increased loading typically decreases melting rate

Research Objective

The primary objective of this task is to develop a predictive model of relative, not absolute, melt rates of different HLW batches based on their ever-changing chemistry. The underlying premise of the model is simple; melt rate would increase as the final melt becomes thermodynamically more stable, i.e., lower free energy, or the rate of calcine gas generation is lower. This approach was shown to work for the Melt Rate Furnace (MRF) data obtained with simulated Defense Waste Processing Facility (DWPF) feeds but for a limited compositional range. The 2008 scope consisted of the following tasks:

1. Merging of the two existing melt rate criteria, i.e., the free energy of melt and the rate of calcine gas generation, into a single Melt Rate Indicator (MRI).
2. Validation of the model premise with feeds of a wider compositional range, particularly high in aluminum and boron.
3. Development of theoretical bases for the model in terms of feed chemistry vs. melt structure.
4. Bench- and pilot-scale melter tests to collect data that reflect the composite effects of feed chemistry, rheology and bubbling rate on melt rate.

Task #1 involved an empirical fitting of MRF data using the free energy output of the 4-stage cold cap model. Task #2 involved utilization of existing MRF linear melt rate (LMR) data from 2001 (Batch 2) and 2007 data (Batch 4) for continued validation of the model premise. Task #3 involved an in-depth literature review of the alkali alumino-borosilicate glass chemistry to account for the impact of increasing boron used in frits to counter increasing aluminum in the feeds. Finally, Task #4 is yet to be initiated; it will form the last phase of the 3-4 year modeling effort.

Research Progress

Task #1: It was discovered early on that the free energy of a melt and the rate of calcine gas generation could not be used as robust-enough melt rate indicators, since they did not always trend in the same direction and no weighting factors were defined for them. It was therefore necessary to develop a single Melt Rate Indicator (MRI) using the free energy output from the 4-stage cold cap model; the first MRI developed is shown in Eq. (1). The need for an empirical fitting of MRI arises partly due to the fact that the free energy database currently being used has not been fully optimized, particularly for the systems containing B2O3.

$$MRI = \frac{\left[\Delta G_{f,m}(sludge\ Na - Al - B) * \Delta G_{f,m}(frit\ Na - Al - B)\right]^{0.2} \left(mole\ \%\ sludge\ Na_2O\ in\ glass\right)^{0.5}}{\left[\Delta G_{f,m}(Al + B)\right]^{1.5}\ \Delta G_{f,cg}} \quad (1)$$

Task #2: Validation of the model premise continued using Eq. (1) against SB2/3/4 data; the results are plotted in Figure 1. It is clear that Eq. (1) severely over-predicted more than 60% of SB2 data, while it under-predicted SB4 data, meaning that the applicability of the existing MRI cannot be extended to the SB2/SB4 glasses that are high in either boron or aluminum.

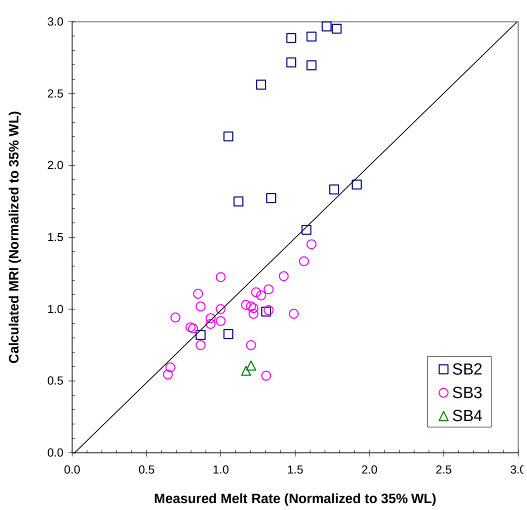


Figure 1. Normalized LMR vs. MRI (Eq. 1).

Task #3: An additional premise was added to the model; melt rate decreases with increasing rigidity of the network. Alkali ions create non-bridging oxygen (NBO) upon dissolution into the network, thus help melt rate. However, Al+3 and B+3 dissolve into the network as AlO4/2- and BO4/2-, respectively, consuming one NBO each in the process. Thus, melt rate should decrease with increasing presence of 4-coordinated Al and B. Complexities arise, however, since the B coordination number decreases back to 3 upon further increase in boron.

The MRI was next revised as the product of the relative measures of how easily the frit melts, MRIfrit, and of how well the waste components dissolve into the melt, MRIglass.2 As in Eq. (1), the latter is still based on the free energy output of the cold cap model with additional terms such as sulfate, while the former is defined as:

$$MRI_{frit} = R'/K \quad where \qquad (2)$$
$$R' = ([Na_2O] + 0.7[Li_2O] - [Al_2O_3])/[B_2O_3]$$
$$K = [SiO_2]/[B_2O_3]$$

Compared to Figure 1, the revised MRI is shown in Figure 2 to predict most MRF data more closely.

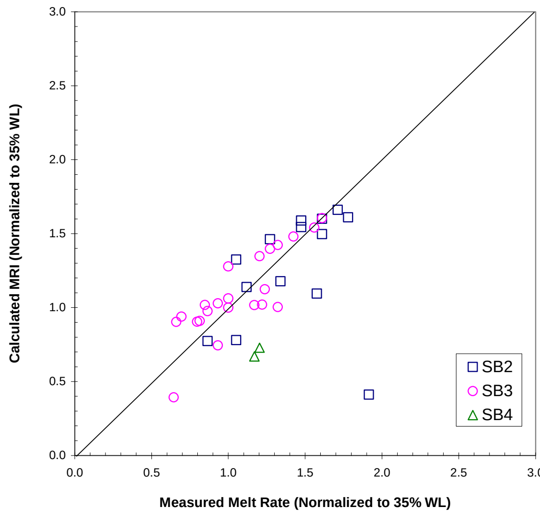


Figure 2. Normalized LMR vs. Revised MRI.

Planned Activities

Work will continue to better reflect the impact of boron chemistry on melt rate both theoretically and experimentally.

The melt rate database will be expanded by including the WTP pilot melter data.

Frit-only MRF runs will be run to provide the necessary data to fine tune MRIfrit. Glass samples will be analyzed using an X-ray scanning technique for more accurate quantitative determination of melt rate.

Further validate the MRI’s predictability against 2008 SB5/6 data.

ENHANCED STABILIZATION TECHNOLOGIES

Development of Crystal-Tolerant High-Level Waste Glasses

Principal Investigator: J. Matyas, Pacific Northwest National Laboratory (PNNL), Josef.Matyas@pnl.gov, 509-376-5740

Project Duration: 2007-2010.

Waste Processing Challenge

The loading of high-level waste (HLW) into borosilicate glass is limited by crystallinity constraints to prevent crystal accumulation on the bottom and in the glass discharge riser of HLW glass melter during extended idling periods. The deposited layer may disrupt electric current and obstruct the discharge of molten glass. The constraints significantly limit the waste loading, which is reflected in a high volume of waste glass, and thus result in high capital, production, and disposal costs.

Research Objective

The objective of this research is to develop crystal-tolerant HLW glasses for higher waste loading through the use of experimental models. By keeping the spinel crystals small and therefore limiting spinel deposition in the melter, these glasses will allow high waste loading without decreasing melter lifetime.

Research Progress:

Settling of Spinel Crystals in Simulated HLW Glasses

The crystal accumulation in the glass discharge riser of HLW melter was simulated for each of twelve designed glasses made of AZ-101 simulant and additives (e.g., B_2O_3, Li_2O, Na_2O, and SiO_2) using the laboratory-scale and bench-scale tests. The addition of ~1 wt% of NiO to baseline glass resulted in formation of big spinel crystals (~ 100 µm after 200 h at 850°C) and the highest accumulation rate of all tested glasses (~252.5 mm/year). Addition of ~5 wt% of Fe_2O_3 to baseline glass significantly increased the number density of crystals (700-850 crystals/mm^2) and decreased the size of spinel crystals (<10 µm). The small crystals did not settle and remained suspended in the bulk glass even after 27 days at 850°C.

A series of tests was performed on designed glasses to determine the kinetics of crystallization (crystal growth/dissolution and spinel crystal equilibrium vs. temperature). Processing properties of glasses such as the viscosity and liquidus temperature were measured and evaluated. Resulting experimental data are being incorporated into models that can predict crystal accumulation within the melter as a function of feed composition. Developed models will help formulate crystal tolerant glasses for higher waste loading.

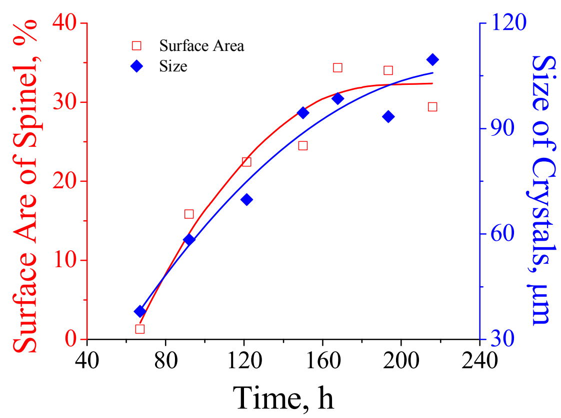


Figure 1. Measured surface area and size of spinel crystals in deposited layer for EMSP-Ni1.5 (AZ-101) glass heat-treated at 850°C for different times.

Physical Modeling of Particle Settling

The settling of single particles of different sizes and the motion of hindered settling front of different particle volume fraction suspensions were studied in stagnant, transparent-silicone oils at room temperature to access the shape factor and hindered settling coefficient of spinel crystals in the modified Stokes equation, to enable prediction of the spinel settling behavior in the glass discharge riser of HLW melter.

The dimensions and terminal settling velocities of single particles (spherical glass beads and octahedral spinel crystals) were obtained with an optical particle-dynamics-analyzer. The experimental shape factor of glass beads 0.2206 was only 0.73% lower compared to the theoretical shape factor 2/9 of a perfect sphere. The shape factor acquired for the spinel crystals 0.1599 was lower than that of the glass beads because of the larger drag force caused by the larger surface area to volume ratio of the octahedral crystals, and matched the theoretically predicted value for isometric octahedron to within 23%. This difference was attributed to shape divergence of tested spinel crystals from the shape of isometric octahedron as well as surface defects and orientation of crystals during free settling. Polydisperse suspensions of spinel crystals formed a smooth concentration gradient. Selected volume fraction, corresponding to approximately constant average crystal size, was followed and used to define the position of the settling front. The experimental hindered settling coefficient of spinel crystals decreased with increased volume fraction of crystals as predicted by the Richardson-Zaki equation $k_h=(1-C)^{4.5}$.

Preliminary estimates have indicated that the glass volume at Hanford can be reduced by over 40% from current estimates.

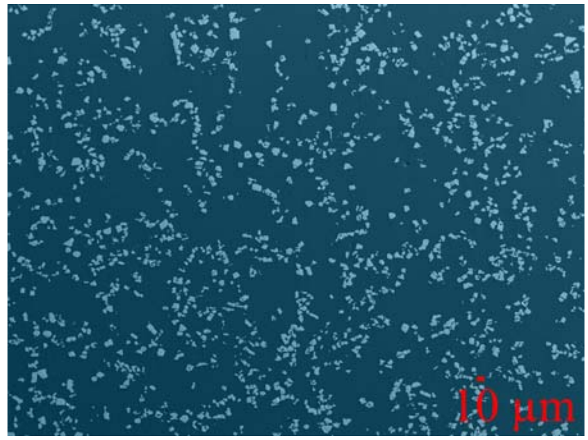


Figure 2. SEM image of EMSP-Fe20 (AZ-101) glass heat-treated at 850°C for 27 days.

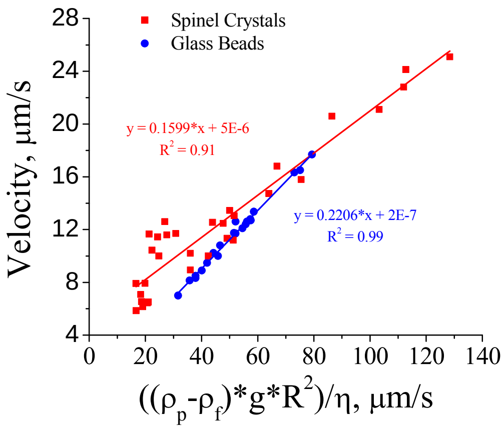


Figure 3. Measured terminal settling velocities as a function of $(\rho_p-\rho_f)*g*R^2/\eta$ for single glass beads and spinel crystals. The slopes of fitted lines correspond to experimentally determined shape factors.

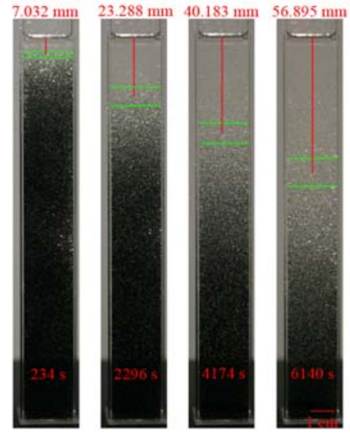


Figure 4. Hindered settling of 1.5 vol% spinel crystals (ρ = 5.3 g/cm^3, R ~ 149-212 μm) in 4.84 Pa.s silicone oil.

Planned Activities:

We will continue to study the crystal accumulation including kinetics of spinel crystallization with different experimental tests. The glass matrix will be expanded to evaluate the effect of different concentration of spinel forming components, noble metals and alumina on size and concentration of crystals, and on accumulation rate. The experimental data will be integrated into models that can predict crystal accumulation as a function of feed composition. Next activity was prompted by the need to understand and control particle agglomeration. We will investigate the impact of agglomeration on settling of solids in HLW glass melters. Without noble metals, spinel crystals are more or less evenly distributed within the melt, depending on the feed homogeneity and the impact of the velocity and temperature fields on their distribution. Therefore, spinel usually settles as individual crystals. However, noble metals are generally present in radioactive wastes in concentrations sufficient to nucleate spinel and form large agglomerates that combine, e.g. RuO_2 and spinel. Such agglomerates are expected to settle rapidly, forming a thick sludge layer over a short period of time. This sludge layer can also be electrically conductive and distort the electric field within the melt. Therefore, we will measure the electric conductivity for spinel sludge or sludge that combines RuO_2 and spinel,

ENHANCED STABILIZATION TECHNOLOGIES

Steam Reforming for the Treatment of Hanford Waste Treatment Plant Secondary Liquid Waste Recycle Streams

Principal Investigator: Leo Thompson, THOR Treatment Technologies, LLC,
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Collaborator: C.M. Jantzen, Savannah River National Laboratory (SRNL)

Project Duration 2007-2010

Waste Processing Challenge

Low-activity waste (LAW) at the Hanford site will be treated by the LAW vitrification facility, which is part of the Waste Treatment Plant. Supplemental treatment may be required to achieve timely and cost-effective treatment of the LAW.

The LAW vitrification facility off-gas treatment system is projected to generate 1.28 million gallons of secondary liquid waste per year with the stream containing significant concentrations of 99-Tc, 129-I, CrO_4, halides, sulfates and nitrates. The current WTP baseline requires this stream to be returned to the WTP Pretreatment facility and recycled back through the LAW vitrification facility. Because certain problematic species in the recycle stream are not effectively destroyed or retained in the LAW glass, a large fraction of these species is released again to the off-gas treatment system, perpetuating the recycle loop. The recycle process adds considerably to the volume to be treated by the LAW melters and reintroduces (recycles) species that can affect the performance of the LAW vitrification facility, including limiting waste loading in the glass and increasing the risk of corrosion to the melter.

Research Objective

The project's objective is to evaluate the effectiveness of the THOR® fluid bed steam reforming process as a supplemental treatment of LAW and WTP secondary liquid wastes. Current emphasis is being directed to the secondary liquid waste stream.

Research Progress

Pilot plant demonstrations were successfully completed in 2008 on both simulated LAW and WTP secondary waste streams. The safe, long-term (>100hr) operation of the THOR® process for each simulated waste stream was demonstrated. The NOx destruction efficiency of 91-94% readily met test objectives. Cesium and rhenium (surrogate for 99-Tc) were captured in the mineralized product with system removal efficiencies of >99.9%. Halides (chloride, fluoride and iodine) and sulfates were captured in the mineralized product. The Principal Organic Hazardous Constituent, benzene, was destroyed in the process at an average of 99.999% for all tests; a factor of 10x below the US Environmental Protection Agency's (EPA's) Maximum Achievable Control Technology (MACT) requirement of 99.99%. The durability and leach performance of the mineral products were determined to be superior to Low Activity Reference (LRM) glass standard for sodium and silicon. Starting in 2008, SRNL initiated a test program to evaluate several potential binders for use in producing a monolithic waste form of the mineral product. This testing is continuing into 2009. A photograph of one of the monolith samples is provided in the figure below.

A monolithic sample of mineral product evaluated by SRNL

Planned Activities

In 2009, the monolith testing by SRNL will be completed. In addition, a radioactive bench scale steam reforming test program will be initiated in 2009 using a sample of actual secondary liquid waste from the Defense Waste Processing Facility. The sample will be chemically altered to reflect the composition of WTP secondary waste.

SRNL has carried out similar bench scale testing on other radioactive waste streams. Therefore, potential project risks are considered acceptable. The development and full-scale application of the THOR® process for the WTP secondary liquid waste stream is considered appropriate with limited risk given the successful pilot plant tests, positive development history for other DOE waste streams, and routine commercial operations of the THOR® process of other waste streams.

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ENHANCED STABILIZATION TECHNOLOGIES

Demonstrate HIP Process for INL Calcine Waste and DOE Legacy Waste

Principal Investigator: Ken Bateman, Idaho National Laboratory (INL), ken.bateman@inl.gov, 208-533-7061

Collaborators: Bruce Begg, Sam Moricca, ANSTO Inc.

Project Duration: 2008-Ongoing

Waste Processing Challenge

Idaho calcine is derived from calcining first cycle-raffinate from reprocessed spent fuel. It is classified as mixed high-level waste and consists of 4400m3 of heterogenous granular material in six bin-sets. The calcine contains varying quantities of heavy metals regulated under the Resource Conservation Recovery Act (RCRA).

Research Objective

The objective of this research is to demonstrate the benefits that tailored waste forms and flexible hot-isostatic pressing (HIP) technology can provide to either the treatment or super-compaction of Idaho calcines.

The process of HIPing radioactive wastes involves a can being filled with the calcined feed (with or without treatment additives). The can is evacuated and sealed, then placed into the HIP furnace and the vessel closed, heated and pressurized. Pressure is applied isostatically via argon gas. The combined effect of heat and pressure consolidates and immobilizes the waste into a dense monolithic block sealed within the can. The chemical durability of the resulting waste form is driven by the nature of the additives included in the process. There are no off-gas emissions during the high-temperature processing. The process can be applied to a wide range of legacy waste streams.

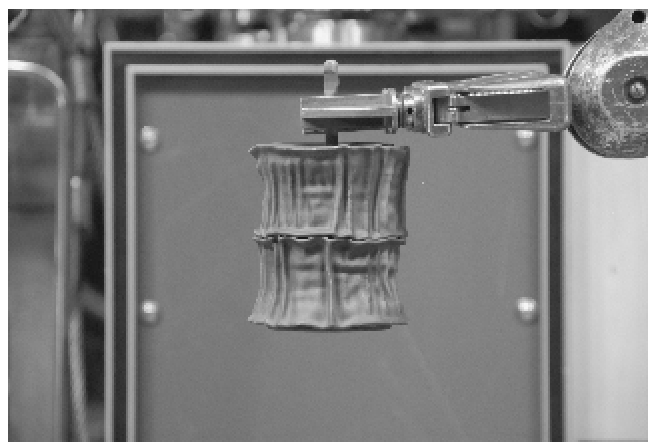
Research Progress

Simulated alumina and zirconia calcine, containing full RCRA heavy metal components, was produced in a pilot-scale fluidized bed calciner. Calcine liquid feed compositions were based on historical process model data, provided by CWI (Idaho cleanup contractor), and reflect actual calcination runs. To account for significant differences noted in the key RCRA components, specifically mercury in the alumina calcine and cadmium in the zirconia calcine, three separate RCRA variants of each calcine composition were prepared. The concentrations of mercury and cadmium were varied from a baseline average, through a transition to a maximum concentration for the alumina and zirconia calcine respectively. All other RCRA components were kept constant and at maximum concentrations.

Chemical analysis of the resulting solid calcine simulant was found to be in good agreement with data available on actual calcine, representing baseline chemical durability for direct disposal of calcine. Toxic characteristic leaching procedure (TCLP) tests on those calcine simulants indicated that all failed to meet the universal treatment standard (UTS) for multiple elements.

However, direct HIPing of the alumina and zirconia calcine, without treatment additives, confirmed the significant economic, environmental, and regulatory advantages that HIPing offers compared to direct disposal.

Vast volume reductions of between 50% and 70% compared to as stored calcine, for zirconia and alumina calcines respectively, have been demonstrated. Volume reduction calculations have been conservatively calculated based on the maximum cylindrical envelope volume of the final HIPed can. This equates to a multibillion-dollar repository cost saving compared to direct disposal (based on a geologic repository disposal cost of $620,000 per canister). In addition, the conversion of the loose granular calcine into a dense monolithic solid without treatment additives, also significantly enhances the chemical durability of the disposal product. This was most pronounced for the alumina calcine, where the direct HIPed maximum RCRA sample completely met the UTS requirement.



Direct HIPed alumina calcine showing a 69% volume reduction (left), and post-HIPed treated zirconia calcine inside the INL's Materials and Fuel Complex (MFC) hot-cell HIP facility (right).

Four independent treatment trials of the baseline RCRA zirconia calcine have been performed. These samples each had an 80wt% waste loading, and exhibited on average a 39% volume reduction compared to the as-stored calcine. Volume reductions compared to alternative treatment technologies would be very much larger. In addition to this very significant volume reduction, the chemical durability of this treated sample exceeded the regulatory UTS and environmental assessment (EA) requirements. The feasibility of HIPing calcine samples in a hot-cell has also been confirmed. Two trials conducted to date within the Idaho National Laboratory Hot Fuel Examination Facility HIP hot-cell, have verified the results obtained by ANSTO.

Industrial scale maturity of HIP technology has also been confirmed. Over thirty HIP units are in production operation in the US that have capacity up to twice that proposed for calcine disposition. These units remotely process work pieces between 10,000 lbs and 18,000 lbs at temperatures and pressures exceeding those proposed for calcine treatment. Many of these industrial HIP units have been in operation for over 30 years in a production environment.

An engineering conceptual outline for a HIP production facility for calcine disposition has been developed and costed. The facility is designed to be co-located to the Idaho Integrated Waste Treatment Unit (IWTU) and consists of a dual interchangeable process line. The dry mechanical process, in which calcine is processed inside sealed HIP cans offers significant advantages and minimizes process risks. In particular the enhanced contamination control measures and the absence of off-gas emissions during hot consolidation significantly simplify process design and implementation. In addition, as waste never comes into contact with the HIP process vessel, final decontamination costs are minimized.

The engineering feasibility together with the technical demonstration trials are confirming that flexible HIP technology can mitigate the current regulatory uncertainty regarding final calcine disposition pathway and deliver multi-billion dollar repository cost savings irrespective of whether direct disposal or treatment is required.

Planned Activities

Further demonstration trials are ongoing to examine performance for transition and maximum RCRA containing calcine. Calcine mixtures and treatment of surrogate calcine spiked with radioactive components are also planned, as is a 100-fold scale demonstration. Proof-of-concept demonstrations highlighting the benefits HIP tailored waste forms can provide to a wide range of other problematic legacy wastes are to be conducted in 2009.

ENHANCED STABILIZATION TECHNOLOGIES

Direct Analysis of Slurry Receipt and Adjustment Tank Contents

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Collaborators: Fang Yu Yueh, ICET; Kristine Zeigler and James Marra of Savannah River National Laboratory (SRNL)

Project Duration: 2006-2008

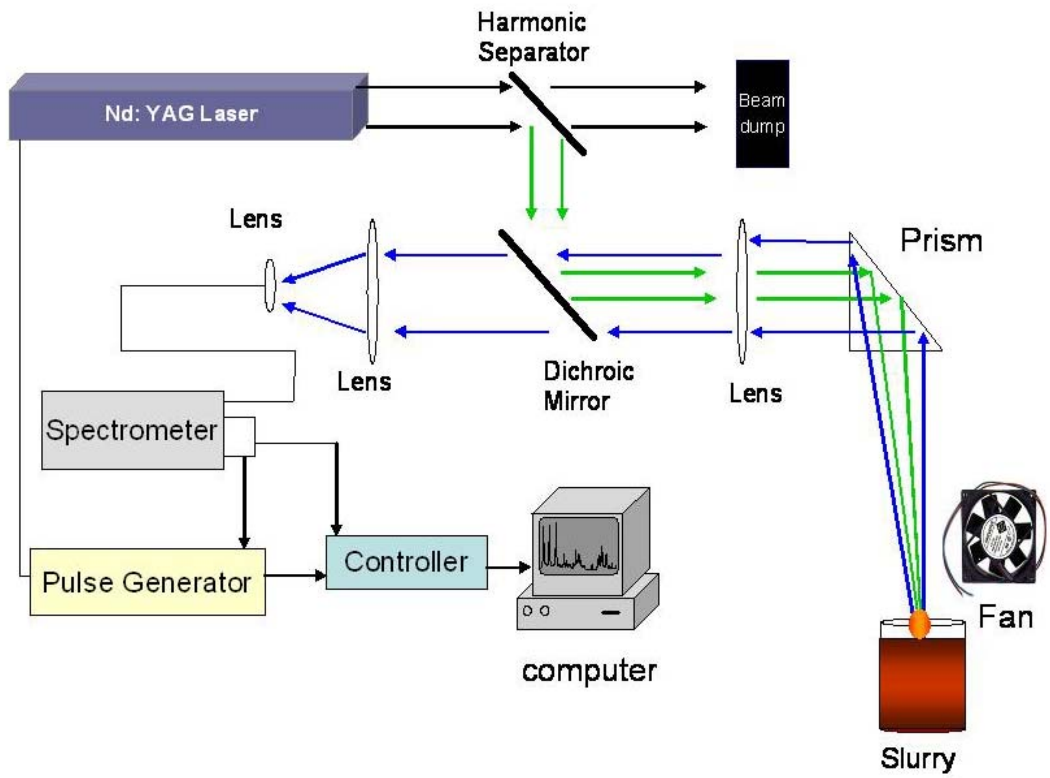

Figure 1. Experimental setup for slurry measurement

Waste Processing Challenge

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

Research Objective

The first task of this project was to provide a system for direct slurry analysis in the DWPF's shielded cells. Availability of this capability could significantly increase analytical throughput, reduce waste generation in radiological analytical facilities, and provide data suitable for waste acceptance and production records.

Laser Induced Breakdown Spectroscopy (LIBS) was selected as the system for direct analysis of DWPF Sludge Receipt and Adjustment Tank (SRAT) sludge slurry product. The analytical results will be used to support the determination of the appropriate amount of frit to be combined with the sludge in the melter. LIBS will also be used to provide the analytical data to support Slurry Mix Evaporator (SME) (slurry containing both the sludge + frit) acceptability decisions within the Process Composition Control System (PCCS). The SME product is also referred to as the melter feed material.

Research Progress

Previous work had demonstrated that LIBS measurement in some solid samples has an accuracy of 3-6% for elements with a concentration greater than 1 wt% and an accuracy of 5-10% or better for minor elements depending on their concentration (based on statistical confidence). The accuracy has been poorer in the case of slurry analysis due to the short lifetime of the laser-induced plasma and sedimentation and turbulence on the slurry surface owing to the laser induced shock wave. The major research efforts are in improving the performance of LIBS measurement with slurry sample. LIBS experiments of DWPF slurry continued by direct sampling the slurry in a small beaker (see Fig.1). Experiments were performed with different laser frequencies and it was found that a laser frequency of 1Hz gives a more stable emission spectrum with reduced splashing. However, splashing is still a problem for maintaining clean optics for long-term system operation. Different experimental configurations to minimize this problem were evaluated. To minimize the slurry sedimentation problem for long-term operation, experiments were performed with two methods. First, the slurry sample in a beaker was placed on a rotation stage to maintain constant motion. Second, magnetic stirrer was placed inside the slurry container to stir the sample during the measurement. The measurement results show that the data using a magnetic stirrer has better reproducibility for an over 30-minute test (see Figure 2).

Planned Activities

In the first quarter of 2009, efforts will continue to investigate the feasibility of using LIBS for quantification of key constituents in slurries. The effect of water loading on emission spectra and the use of different substrates, upon which a sample of slurry can be placed and interrogated, will be evaluated. Working in conjunction with ICET chemists a series of four sludges will be tested to establish secondary calibration. The calibration will be evaluated using unknowns and the results of the work will be disseminated.

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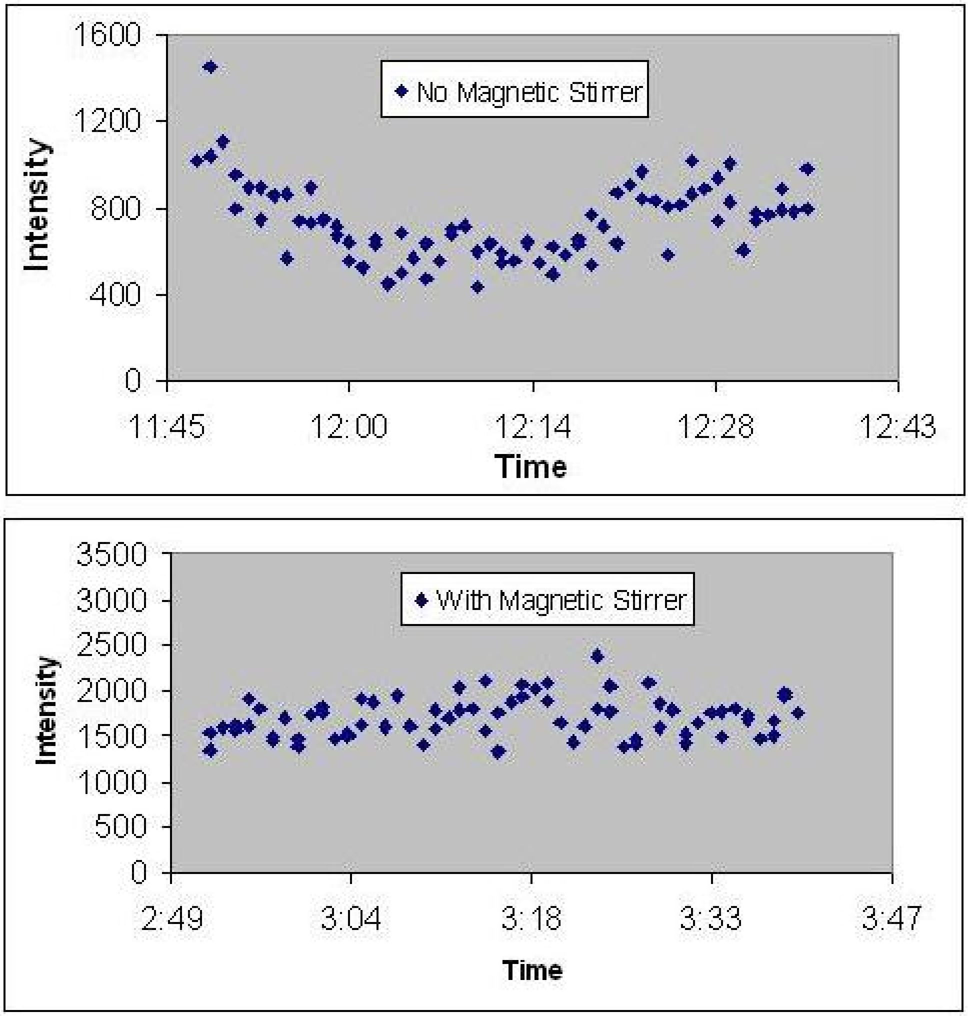

Figure 2. Slurry LIBS data taken with no magnetic stirrer and with magnetic stirrer

SPENT NUCLEAR FUEL PROGRAM AREA

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Challenge

Spent nuclear fuel (SNF) is fuel that has been permanently withdrawn from a nuclear reactor following irradiation, the constituent elements of which have not been separated by reprocessing. Some irradiated targets are also managed as SNF due to their close similarity to reactor fuels and to their planned disposition in a geologic repository. The United States stopped reprocessing the Department of Energy's (DOE) SNF for production purposes in 1992. A mission of the DOE Office of Environmental Management (EM) is to safely and efficiently manage their SNF inventory during interim storage and to prepare it for final disposition.

The DOE currently manages about 2,450 metric tons of heavy metal (MTHM) of SNF (owned by the DOE) at four sites: Hanford, Idaho, Savannah River, and Fort St. Vrain. An additional 30 MTHM is expected to be received into inventory over the next 35 years, primarily from domestic and foreign research reactors.

The DOE's current inventory comes from: its test and materials production reactors; non-DOE U.S. Government reactors; U.S. university research reactors; foreign research reactors; and DOE-owned commercial SNF. There are over 250 different fuel types that have different enrichment, fissile materials, cladding, and geometry. The SNF Strategic Plan shows quantities at the interim storage sites.

Solutions

DOE EM-owned SNF must be stabilized, packaged for interim storage, and prepared for anticipated disposal in a geologic repository. The path forward for disposal of DOE-managed SNF is described in the 2008 draft *DOE-owned Spent Nuclear Program Strategic Plan*.

Several major technical risks and uncertainties associated with SNF must be addressed:

1. Spent Fuel Storage

Current SNF storage environments and fuels are subject to continued environmental deterioration. As disposition end states are extended, DOE must develop technologies to predict performance of storage systems ensuring overall safe management of the SNF.

2. Spent Fuel Stabilization

Present facilities and methods are not designed for processing all SNF types.

3. Disposal Packaging Preparation

Current disposal requirements include packaging SNF into welded canisters containing materials for criticality control over long timeframes. New technologies for performing this packaging are required.

Accomplishment

In 2008, a SNF Initiative Development Team (IDT) was created as part of the overall Office of Waste Processing technology portfolio to address implementation of the DOE Engineering and Technology Roadmap. The SNF IDT will support the implementation of DOE's Office of Nuclear Materials Disposition strategic plan for dispositioning the DOE's SNF. This is currently coordinated through the National Spent Nuclear Fuel Program (NSNFP).

Plans

The Initiative Development Team (IDT) will comprise both DOE-EM federal and contractor personnel responsible for SNF management (subject matter experts), and national laboratory personnel. The DOE-EM lead will be jointly represented by the Office of Waste Processing and the Office of Nuclear Materials Disposition. SNF subject matter experts will be routinely engaged as their expertise is needed.

The IDT will coordinate with the NSNFP in this effort with primary emphasis on interim storage issues, including providing the technical bases for safe extended storage.

CHALLENGING MATERIALS PROGRAM AREA

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Challenge

Miscellaneous nuclear materials exist throughout the DOE complex that cannot be dispositioned for a variety of reasons, and as such are considered "orphan" materials. They include accountable special nuclear materials (SNM); mixed waste streams (i.e. radioactive and hazardous constituents) that require remote/special handling; classified components; activated metals; sealed sources; radioisotope thermal generators (RTGs); and other unique materials. This diverse inventory is collectively referred to as Challenging Materials (CM). Four primary groups of material types have been initially identified due to similarities of the waste streams. They include SNM, Fission Products, Activated Metals, and Miscellaneous Materials. As more comprehensive inventory data are developed, these categories may be modified.

Solution

The overall scope of the CM Initiative is to develop and implement an integrated program that addresses the national needs associated with management and disposition of challenging nuclear materials. This is a new initiative.

Accomplishment

The Challenging Materials Initiative Development Team (IDT) has been established and comprises both DOE-EM and National Laboratory personnel. Subject matter experts from these and other national laboratories will be routinely engaged as their expertise is needed. Specific projects are now being identified based on site needs.

Plans

The basic approach proposed for this initiative is as follows:

1. Identify and maintain the complete inventory of orphan nuclear materials, to the extent the information is available. The objective of this effort is to be able to conduct a comprehensive gap analysis to determine which of the materials can be dispositioned, what the barriers are restricting disposition, what type of actions are required to enable disposition (i.e. packaging, conditioning, regulatory compliance, reuse, etc.) and the impacts

(i.e. cost, schedule, risk reduction benefits) of taking specific action to effect disposition versus continuing the current management strategy for the inventory.

2. As specific potential technology and solution options are identified by the sites, this initiative will focus on determining the technical risks, uncertainties, and data gaps that must be addressed to enable the disposition strategy. Subsequently, directed technology development, testing, and validation efforts will be implemented to resolve the risks and uncertainties associated with the final end-state.
3. Provide technical expertise to support determining the required facility designs, including investigation of existing infrastructure for applicability, such that the most appropriate option for implementation of the defined process flowsheet can be determined. The final recommendation would be based on determining the optimal balance between key criteria such as cost, risk, schedule, environmental safety, and security.