# ICET 2008 SOW
# Review of Tasks
# Status and Progress Report

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# Presentation Outline

- **Contract In Place on 6/1/08**
- **Five Active EM-21 Tasks**
  - ➢ **SRS Tank Chemistry**
  - ➢ **Hanford C-Farm Tank Chemistry**
  - ➢ **HEPA Filtration**
  - ➢ **LIBS Monitor for DWPF**
  - ➢ **SRS Saltstone**
- **Project Status and CY 08 Effort**

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

- This project supports efforts associated with the SRS SWPF and with upstream blending of saltcake dissolution fractions, high concentration aluminum streams arising from sludge batch leaching and potential disposition of the DWPF recycle stream. Other customer requests involving chemical cleaning with oxalic acid are being examined.

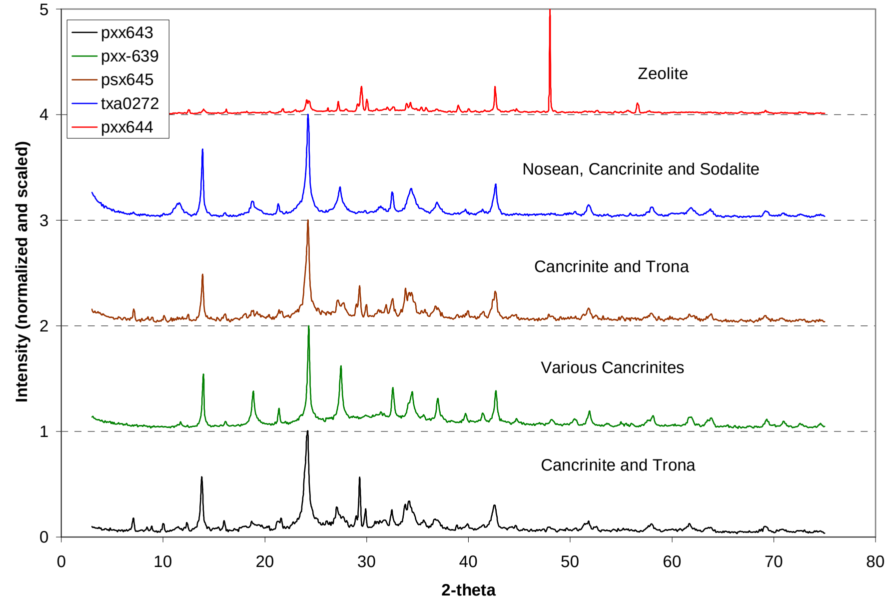
- One significant issue associated with SRS waste streams is formation of sodium aluminosilicates (NAS) sometimes accompanied with co-precipitation of uranium.  Such materials have been previously observed in evaporators and may also be found in SWPF unit operations. These cement-like materials will form with an Al/Si ratio of 1. Proper blending of the waste streams could control the Al/Si ratio thereby minimizing or eliminating NAS formation

# Project Description – Technical Strategy/Approach

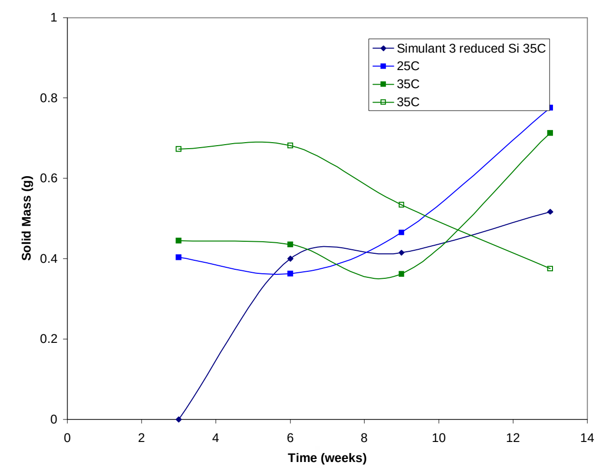
- The work centers on the application of the Environmental Simulation Program (ESP, OLI Systems Inc.) and associated laboratory experiments on simulants and customer samples.
- Task 1.1 Thermodynamic evaluations of CSSX processing operations 7 samples were received from Barnwell and are being analyzed using xrd and ICP. Simulants have been prepared and are being used to evaluate solids formation at different temperatures and durations.
- Task 1.2 Impacts of sludge leaching on downstream processing The ESP model is being used with streams from saltcake dissolution, from the leaching of sludge batch 5 and the DWPF recycle. The model was also used in evaluating the chemical cleaning of Tank 5 using oxalic acid.

# Technical Status and Results

- XRD analysis of scale samples from the CSSX contactors indicated NAS formation.
- Simulants prepared with different Si loadings.
- Solids formation studied at 15,25,& 35°C for extended times.
- XRD and ICP analysis in progress
- Predominant solid is $Al(OH)_3$



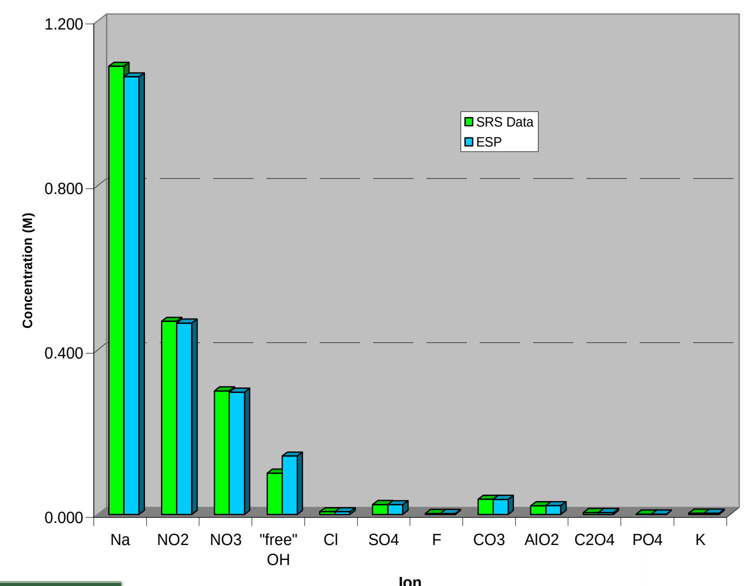

| Chemical Name | Chemical Formula | Simulant 1 g for 1L |
|---|---|---|
| Aluminum nitrate nonahydrate | Al(NO3)3 · 9H2O | 1.05E+02 |
| Cesium chloride | CsCl | 7.24E-02 |
| Copper sulfate pentahydrate | CuSO4 ?· 5H2O | 5.55E-03 |
| Iron nitrate nonahydrate | Fe(NO3)3 ?· 9H2O | 1.03E-02 |
| Potassium nitrate | KNO3 | 1.52E+00 |
| Sodium carbonate monohydrate | Na2CO3 · H2O | 1.86E+01 |
| Sodium chloride | NaCl | 1.40E+00 |
| Sodium fluoride | NaF | 1.18E+00 |
| Sodium hydroxide | NaOH | 1.27E+02 |
| Sodium meta-silicate nonahydrate | Na2SiO3 · 9H2O | 8.53E+00 |
| Sodium molybdate dihydrate | Na2MoO4 · 2H2O | 1.90E-02 |
| Sodium nitrate | NaNO3 | 9.98E+01 |
| Sodium nitrite | NaNO2 | 3.45E+01 |
| Sodium oxalate | Na2C2O4 | 1.07E+00 |
| Sodium phosphate heptahydrate | Na2HPO4 · 7H2O | 1.88E+00 |
| Sodium sulfate | Na2SO4 | 1.99E+01 |
| Zinc nitrate hexahydrate | Zn(NO3)2 ?· 6H2O | 3.70E-02 |
| Tin chloride dihydride | SnCl2 ?· 2H2O | 4.49E-03 |
| Water | H2O | 8.37E+02 |



# Technical Status and Results

- Batch 5 Leaching
- Started with HM sludge stimulant – Ketusky, E., “High Level Waste System Impacts from Acid Dissolution of Sludge” CBU-PIT-2005-00260R1, Westinghouse Savannah River Company, Aiken, SC (2005).
- Tuned to attain approximate 29% by weight Al, Set density
- Added 130kgal 50% NaOH at 50$^{o}$C

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



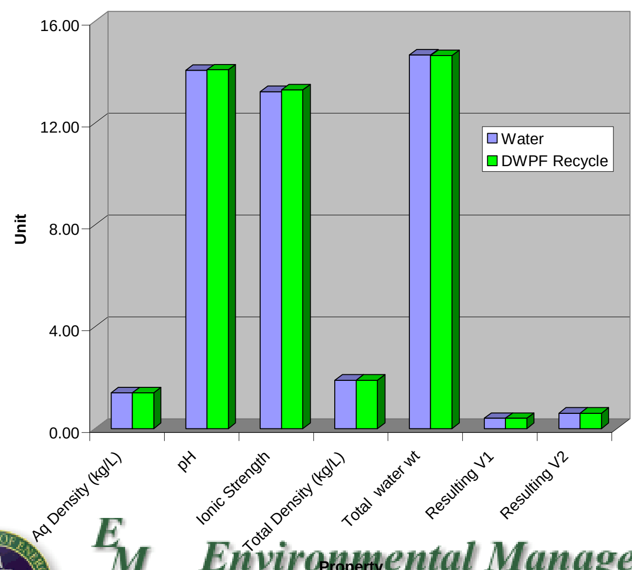
# Technical Status and Results

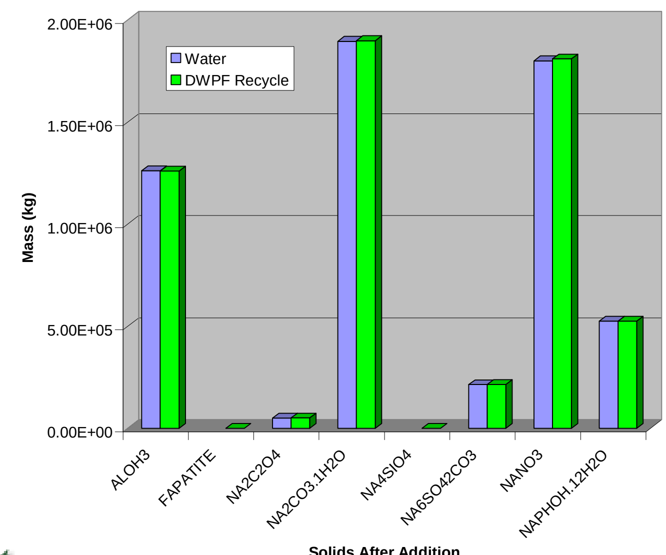
- DWPF Recycle Stream
- Acidic composition from Stone, M. E., “DWPF Recycle Evaporator Simulant Tests,” WSRC-TR-2005-00142, Rev. 0.
- The acid composition was then neutralized with NaOH akin to tank farm operations.
- The dilute stream is predicted to contain ~1.2 x10$^{-3}$ M Si and has an SpG of 1.05.

| Aq. | | Solids (dust) | | Total Stream | |
|---|---|---|---|---|---|
| H2O | 7.85E+02 | CACO3.H2O | 1.54E-02 | | |
| | | FEIII2O3 | 6.37E-01 | | |
| Mass (g) | 8.36E+05 | HGO | 6.60E-02 | Mass (g) | 8.38E+05 |
| Volume (L) | 7.98E+02 | LAOH3 | 5.68E-04 | Volume (L) | 7.98E+02 |
| Density (g/L) | 1047.70 | MGOH2 | 8.65E-02 | Density (g/L) | 1050.00 |
| pH | 13.65 | MNOH2 | 7.94E-02 | % water wt | 93.73 |
| Ionic Strength | 1.27 | NIFE2O4 | 3.32E-02 | % solids wt | 0.17 |
| | | PUIVOH4 | 2.81E-04 | | |
| | | UIVO2 | 8.17E-02 | | |

# Technical Status and Results

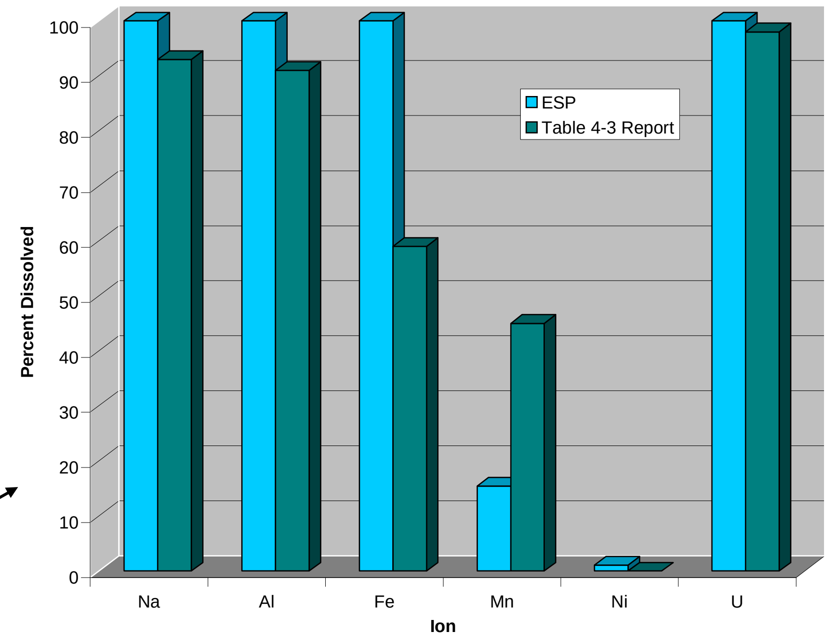
- The remaining streams for blending considerations arise from the DDA process.
- Extensive experimental and modeling work has been earlier performed on 41H, 37H, 38H, and 31H.
- Some experiments indicated the possibility for using the DWPF recycle stream as the diluent in the saltcake dissolution process.
- Additional calculations were performed. Same volume of either water or recycle stream 175 kgal added to dissolved salt fraction from 41H.



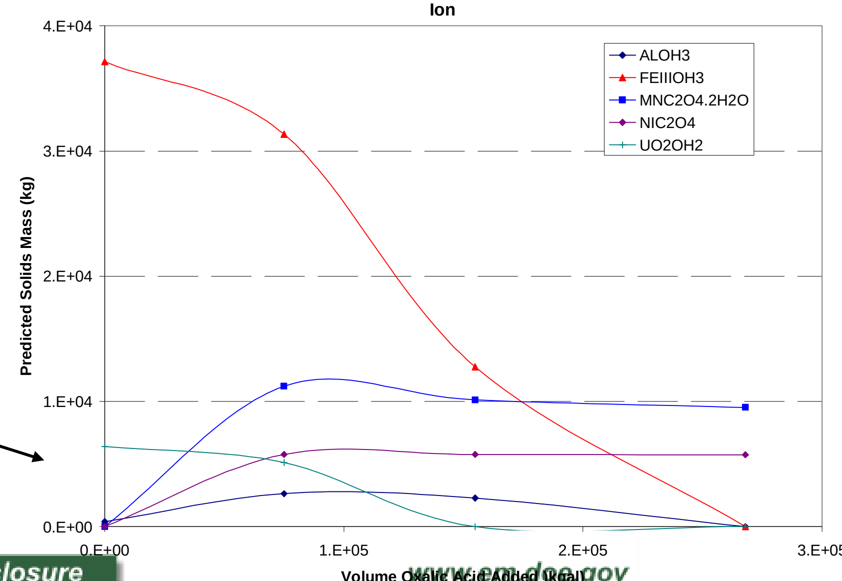



# Technical Status and Results

- Modeling support for cleaning of Tank 5F using 8% (wt.) oxalic acid.
- Earlier SRNL studies Hay, M. S. et al., “Characterization and actual waste tests with Tank 5F Samples,” WSRC-ST1-2007-00192, Rev 1.
- Compositions from report.
- Simulations of lab experiments – semi-quantitative agreement differences thought to reflect kinetics.




- Full-scale simulations indicate that $Fe(OH)_3$ $Al(OH)_3$ and $UO_2(OH_2)$ dissolve upon further addition of oxalic acid while Ni and Mn oxalates form.



# Project Impact

- Evaluation of simulants and samples for the CSSX process is of value in that the formation of scale on the contactor surfaces is best avoided. One potential mechanism for scaling may be an imposed concentration gradient resulting from extraction of the Cs and the 20,000g force.
- Proper blending of the incoming waste is expected to allow for some feed composition control. The order of the blending has not formally been established and it may be that use of the DWPF recycle stream will be restricted to certain tank composition. Using the Perl software approach, blending studies can be expanded to cover additional mixing scenarios.
- As additional simulations are performed the value of using the ESP software has become apparent. In most all cases and using the ICET developed double salt database, the data compared within a few percent to laboratory measurements reported by workers at SRNL.

# Process Chemistry and Operations Planning for Hanford Waste Alternatives - Research on Neural Networks Hanford Tank Retrieval/Closure

- Incorporate equilibrium chemistry in HTWOS (Hanford Tank Waste Operations Simulator) for C-tank transfers, in place of wash/leach factors, to predict process stream parameters, e.g. solid formation.
- Use ANN (Artificial Neural Network) model in place of explicit computations.
- Develop ESP simulation model of the tank recovery process to approximate the process chemistry streams in the sections of HTWOS where ANN will be used.
- Create ANN: train with transfer/mixing chemistry results.

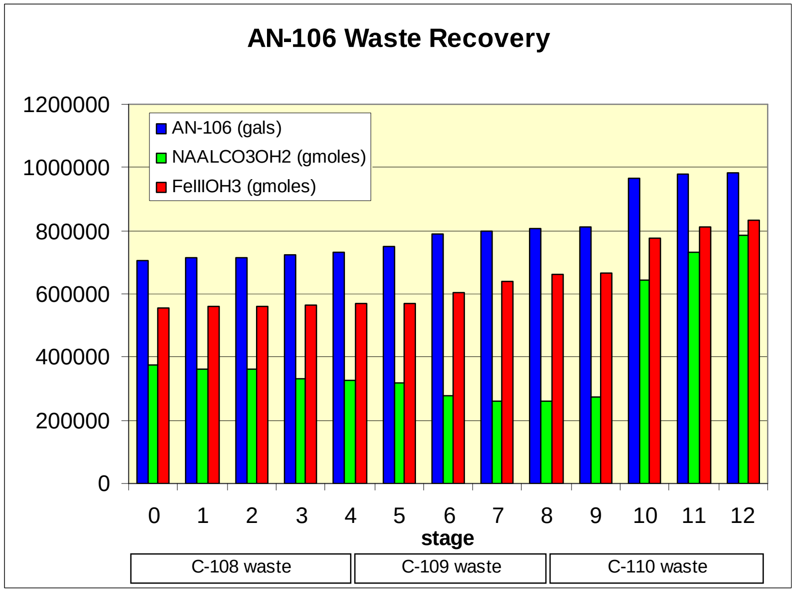
# Process Chemistry and Operations Planning for Hanford Waste Alternatives - Research on Neural Networks Hanford Tank Retrieval/Closure

- C-Farm retrievals to be done using the modified sluicing with recycle (MSwR) method of waste retrieval and mobile retrieval system (MRS).
- MSwR consists of four basic stages based on 1) the amount of waste retrieved and 2) the percent of entrained solids attained.

| Sim | Source Tank | Receiver Tank | Technology |
|---|---|---|---|
| x | C-108 | AN-106 | MSwR |
| x | C-109 | AN-106 | MSwR |
| x | C-104 | AN-101 | MSwR |
| | C-107 | AY-101 | MSwR |
| x | C-110 | AN-106 | MSwR |
| | C-112 | AN-101 | MSwR |
| x | C-101 | AY-101 | MRS |
| | C-105 | AY-101 | MRS |
| | C-102 | AZ-101 | MSwR |
| | C-111 | AN-101 | MRS |

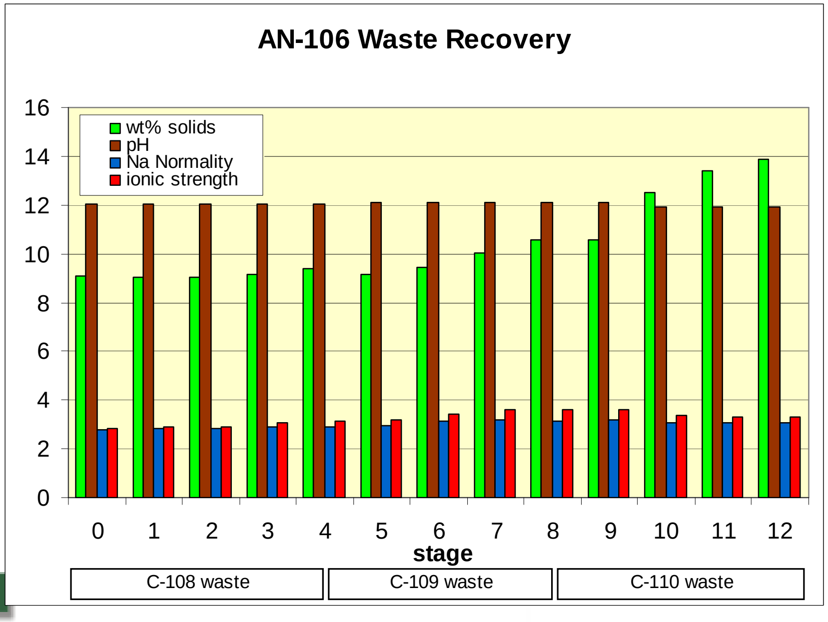
| Stage | Ending tank waste volume (gal) | Retrieved waste volume (gal) | Solids entrainment (vol%) |
|---|---|---|---|
| 1 | | 5400 | 1.0 |
| 2 | 20,000 | | 6.0 |
| 3 | 8,000 | | 2.0 |
| 4 | 2,693 | | 0.5 |

# Process Chemistry and Operations Planning for Hanford Waste Alternatives - Research on Neural Networks Hanford Tank Retrieval/Closure




Additional retrieval constraints:

1) 5,400 gallons of waste retrieved per week.
2) Maximum Na concentration per stream of 5 moles/liter.
3) Maximum insoluble solids concentration per stream 10% (wt).
4) Maximum water usage of 70,000 gallons per retrieval (must fulfill 2 & 3).
5) Maximum specific gravity per stream of 1.3.




*Environmental Management*

safety ❖ performance ❖ cleanup ❖ closure

# Process Chemistry and Operations Planning for Hanford Waste Alternatives - Research on Neural Networks Hanford Tank Retrieval/Closure

- Using ESP simulation framework neural network training sets consisting of input stream values and the ESP computation output have been built.
- Expanded training sets will contain the simulation results for a range of input streams, covering the C-Farm inventory.
- Each input stream variation requires an execution of the ESP program.
- Standard interactive ESP user input replaced with script, programmed in Perl (a freely available, platform independent programming language).
- Scripts written to loop through input stream ranges, construct ESP input files, and parse ESP output for the neural network training set.

# Project Impact

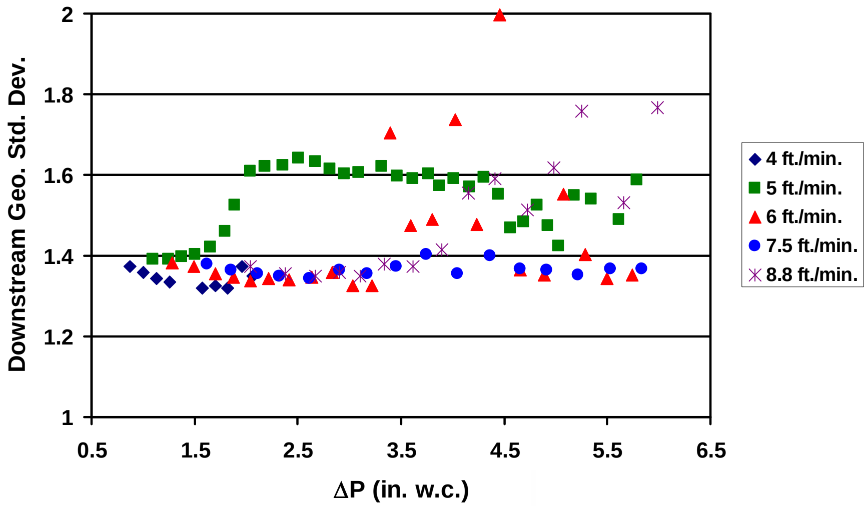
- Simulation results have been transferred to CH2M Hill Hanford engineers.
- An evaluation of the retrieval schedule, including source and destination tanks is expected from the ANN.
  - Allow for different retrieval scenarios.
  - Schedule optimization.
  - Straightforward approach for evaluating the use of ANN's in the HTWOS model as chemistry is not as complex as saltcake retrieval or evaporation.

# HEPA Filtration

- HEPA Filters Ubiquitous in DOE Complex Vital Safety Systems
- Nuclear Grade Filters Conform to AG-1 Standard
- Literature Limited with Respect to Lifetime Testing
- System Design Considerations
- Maximum Media Velocity Imposed by Standard

# Project Description – Technical Strategy/Approach

- Three Areas of Activity
  - ➢ Establishment of Future Testing Limits
  - ➢ Work on Standards Development
  - ➢ Publication of Findings
- Autopsy of Loaded Filters
- Develop Test Bed for Larger Filters
- Compile Data Set of DOE Process Excursions




EM Environmental Management

safety ❖ performance ❖ cleanup ❖ closure

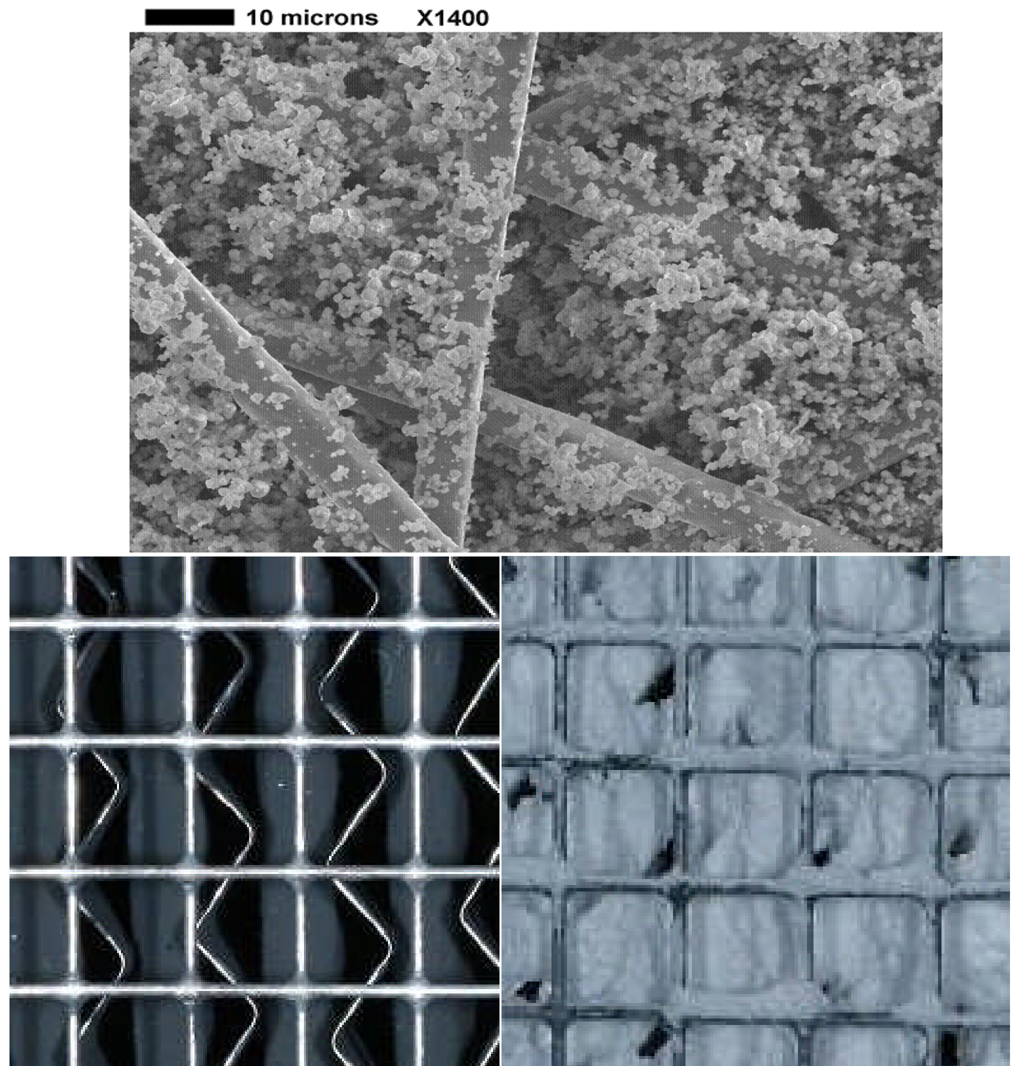
www.em.doe.gov

# Technical Status and Results

- Collect Data on Conditions Experienced by HEPA Filters Across the Complex Under Abnormal Operating Conditions but Less Than Safety Basis
- Standards Development
  - AG-1 FC Subcommittee – Media Velocity Study
  - AG-1 FI Subcommittee – Metal Medial Standard Almost Ready for Balloting
- Publications – Peer Reviewed and Air Cleaning Conf
- Specifications for Larger Scale Test Stand

# Project Impact

- Enhanced Guidelines for Filtration System Design and Operation
- Assist Establishment of AG-1 Standard for Metal Media Filters
- Develop Test Plan for Upset Conditions Effect on HEPA Filters



# Pilot-scale Studies of Saltstone Process

- DWPF Batch 5 contains higher loadings of Al than previous batches.
- Caustic leaching of the sludge will generate a stream rich in Al which is to be processed as saltstone.
- This has raised concerns about excess heat of hydration which may create problems for the processing and storage of the waste form.
- Different formulations are under investigation.

# Pilot-scale Studies of Saltstone Process

- Establish protocol for making small (lab-scale) batches
- Establish heat of hydration method ASTM C186 (or similar method)
- Measure heat of hydration of reference Saltstone and new formulations
- Select new formulations for pilot-scale tests
- Perform pilot-scale experiments (55-gallon drums)
- Transfer of data package to SRS

# Technical Status and Results

- Collaboration with SRNL on Saltstone
- This is a new project growing out of our successful demonstration of making a grout waste form for INL calcine

# Project Impact

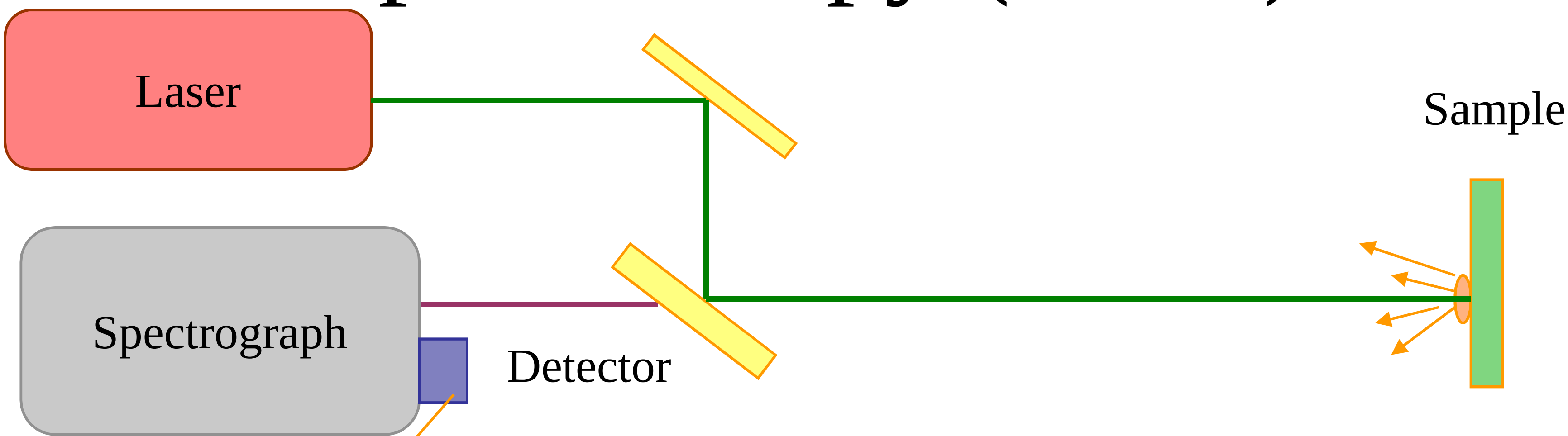
- Pilot-scale testing of new formulations is designed to alleviate concerns about excess heat of hydration which may create problems for the processing and storage of the Saltstone waste form.
- Testing will provide validation of thermal models and expectations of lab-scale tests.
- Project will lead to the selection of a formulation that can be safely stored in the current facilities.

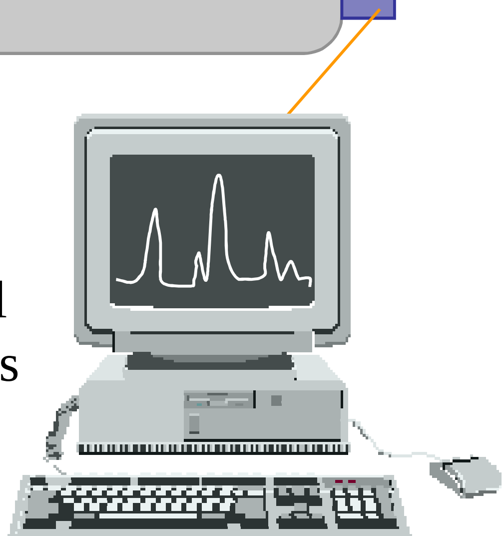
# Project Description

## On-line Analysis for the Defense Waste Processing Facility (DWPF): LIBS

The goal of this project is to assist the Defense Waste Processing Facility (DWPF) in accelerating melter operations through two approaches. The first is to provide a system for direct analysis of slurry in the analytical shielded cells. The capability of direct analysis will significantly increase analytical throughput and reduce waste generation, while providing analyses suitable for waste acceptance and production records. The second effort is evaluating plutonium (Pu) oxide residue compositions produced during the processing of the weapons grade material.

# Laser-induced breakdown spectroscopy (LIBS)




**LIBS Advantages**

1. Minimal sample preparation
2. Simple, easily remotable
3. Fast response
4. Simultaneous analysis of many species

# Technical Status and Results

- Work are concentrated on improving detection sensitivity and the accuracy of quantitative analysis. A signal processing technique, which normalizes the atomic emission with the whole plasma emission, significantly improved reproducibility. One of the main factors currently being addressed is the intrinsic challenge of slurry particle sedimentation.
- The feasibility of LIBS application for *in situ* monitoring the composition of radioactive chemical Pu residue by using $CeO_2$ batch as a surrogate was successfully demonstrated. The accuracy and precision were determined to be 5% or better for major elements and 10% or better for the minor elements.

# Project Impact

This project develop a rapid analysis system to accelerate waste processing.

- Reduce analysis cycle time from 40 hours to 2 hours

- Reduce the cost of the analysis from $4,000/ sample to $800/ sample

- A typical saving of ~$1 M / month for DWPF