

FY 2000 Saltcake Dissolution and Feed Stability Workshop

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Tanks
Focus
Area

FY 2000 Saltcake Dissolution and Feed Stability Workshop

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LETTER REPORT

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PROGRAMMATIC OVERVIEW

The Tanks Focus Area (TFA) continues to work closely with the Office of River Protection (ORP) to better understand the chemistry involved with the retrieval, transport, and pretreatment of nuclear wastes at Hanford. Since a private contractor is currently responsible for the pretreatment and immobilization activities in this remediation effort, the TFA has concentrated on saltcake dissolution and waste transport at the request of the ORP. Researchers at Hanford have performed a series of dissolution experiments on actual saltcake samples. Staff members at Mississippi State University (MSU) continue to model the dissolution results with the Environmental Simulation Program (ESP), which is used extensively by ORP personnel. Several ways to improve the predictive capabilities of the ESP were identified. Since several transfer lines at Hanford have become plugged, TFA tasks at AEA Technologies, Florida International University (FIU), MSU, and Oak Ridge National Laboratory (ORNL) are investigating the behavior of the supernatants and slurries during transport. A combination of experimental and theoretical techniques is used to study the transport chemistry. This effort is expected to develop process control tools for waste transfer. The results from these TFA tasks were presented to ORP personnel during the FY 2000 Saltcake Dissolution and Feed Stability Workshop, which was held on May 16–17 in Richland, Washington. The minutes from this workshop are provided in this report.

With the anticipated changes in the privatization effort at Hanford, the ORP is expected to rely more heavily on the TFA for technology development. In addition, discussions during and after the workshop confirmed the need for three new starts for FY 2001. The first initiative, which is already in the program plan for FY 2001, involves the development of methods to remove pipeline plugs. The other two initiatives will require modifications to the pretreatment plans for FY 2001. These new starts are the radionuclide partitioning during saltcake dissolution and the addition of the Pitzer model to the ESP code.

The workshop also evaluated the ability of the TFA to respond to the needs and requirements of the ORP. During last year's workshop (FY 1999), participants identified several action items for the saltcake dissolution team. The status of each of these action items is listed below. Considerable progress has been made on nearly all of the action items.

- Integration between the two pretreatment tasks (Saltcake Dissolution and Feed Preparation) and the retrieval task (Pipeline Plugs) is required.

Progress: The principal investigators for both pretreatment tasks participated in the same weekly conference calls, and a joint workshop was held. The Retrieval Technology Integration Manager also participated in the conference calls and in the workshop.

- The TFA researchers need to work more closely with the process engineers. The TFA products must be in a format that can be easily used by the process engineers.

Progress: Interaction between the ORP and TFA staff members has increased significantly through conference calls and kickoff meetings. TFA test plans were provided to the ORP personnel for their review and comment.

- The chemical forms that are selected by the ESP must be physically possible.

Progress: The TFA researchers continued to identify compounds and conditions that are problematic. In addition, several discrepancies in the ESP data bases were identified.

- When additional characterization information on a Hanford waste is needed for the modeling effort, the user should be contacted so that he or she can make the appropriate request to the Hanford Characterization Organization.

Progress: Due to limited funds, the Hanford Characterization Organization cannot respond to all of the requests. Whenever possible, the TFA staff performed the necessary chemical analyses.

- The data base for the double salts should be improved.

Progress: Solubility results for key double salts continued to be acquired.

- Input for the user guide on the ESP model and for the test cases to validate the new version of the ESP model was requested by ORP personnel.

Progress: Unfortunately, other ORP priorities severely limited progress on the user guide.

- Future ESP results should include the data base, the selected options, and the composition of the final feed.

Progress: The TFA researchers have been requested to include this information in their reports.

- Users should verify whether key assumptions in the TFA research are reasonable.

Progress: ORP personnel were routinely asked to provide input on test conditions.

AGENDA

SALTCAKE DISSOLUTION AND FEED STABILITY WORKSHOP

The Conference Center in Richland, Washington

May 16–17, 2000

Tuesday, May 16, 2000

- 8:00 a.m. *Introduction*
Phil McGinnis and Joe Cruz
- 8:15 a.m. *Review of FY 1999 Workshop (Path Forward and Action Items)*
Chuck Weber
- 8:30 a.m. *Single-Shell Tank Retrieval and Waste Feed Delivery Program*
Warren Thompson and Randy Kirkbride
- 10:00 a.m. *Saltcake Dissolution Tests and Modeling*
Dan Herting and Becky Toghiani
- 1:00 p.m. *Solubility Tests to Improve the ESP Data Base*
Becky Toghiani and Jeff Lindner
- 1:30 p.m. *Comparison of Calculations by ESP, SOLGASMIX, and Moonis Ally's Model*
Becky Toghiani and Chuck Weber
- 2:00 p.m. *Status and Planning of Hanford Data Base Reconstruction and Hanford Waste Speciation Prediction Code Using OLI Software*
Albert Hu
- 2:30 p.m. *Identification of Future Tests and Benefits*
Becky Toghiani
- 3:00 p.m. *River Protection Project: Status of Waste Transfers, Criteria, and Plugs*
Dan Reynolds
- 3:45 p.m. *Retrieval Tasks on Waste Transfers and Plugs*
Pete Gibbons
- 4:30 p.m. *Overview of the Feed Stability Tasks*
Tim Welch

Wednesday, May 17, 2000

- 8:00 a.m. *Saltwell Pumping/Pipeline Plugging*
Jeff Lindner
- 8:45 a.m. *Model Development for the Waste Transfers*
Hani Al Habbash and Jeff Lindner
- 9:45 a.m. *Pipeline Transfers at Florida International University*
Ruben Lopez and Rajiv Srivastava
- 10:45 a.m. *Identification of Future Tests and Benefits*
Tim Welch
- 11:00 a.m. *Program Outlook and Path Forward for Saltcake Dissolution and Feed Stability*
Phil McGinnis and Randy Kirkbride

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ADDITIONAL COMMENTS

Introduction

Phil McGinnis

- Due to problems with the privatization contract, the TFA and the ORP will explore the need for additional technology development tasks to treat the nuclear waste at Hanford.
- The TFA and the ORP must take an integrated approach to solving the waste remediation problems at Hanford. Randy Kirkbride and Jim Jewett of the ORP continue to play key roles in the development and implementation of the TFA pretreatment tasks for Hanford.
- The TFA has considerable experimental and theoretical resources, which continue to support the needs of the ORP.
- The TFA is currently scheduled to fund several research tasks for FY 2001. These tasks can be divided into three groups: saltcake dissolution, feed stability, and sludge processing.

Joe Cruz

- While the problems with the privatization plan clearly indicate that changes are needed, the design effort for the pretreatment and vitrification facilities will continue as originally planned.
- A new milestone will be added to the salt well pumping task. This milestone will involve the development of a request for proposal to replace the current privatization contract.
- The remediation effort at the Hanford site is now under a consent decree. Therefore, a court will be involved with any missed milestones.

Review of Saltcake Dissolution Workshop Held May 18-19, 1999

Chuck Weber

- The Saltcake Dissolution Workshop focused on the following five major areas: the Hanford requirements, the use of the ESP code, the experimental efforts, the need for more communication between the TFA and the ORP, and the TFA program status.
- The Hanford Tank Waste Operations Simulator (HTWOS) and the ESP are the primary models used by ORP personnel. The HTWOS model is used to predict the effects of the waste transfer and to determine if the new waste meets the contract specification.

- At the moment, the ORP is more concerned with physical constraints such as space and equipment availability than with waste compatibility.
- The ESP is used to determine if the proposed transfer will cause a problem based on the chemistries of the wastes.
- During FYs 1998 and 1999, the initial remediation of Tank SY-101 became a high priority. After this effort was completed, the ESP was used to model the results from the saltcake dissolution experiments on Tanks A-101, BY-102, and S-102.
- Unresolved issues may impact confidence in the ESP predictions. These issues include the various methods for charge reconciliation, the discrepancies in predictions between different versions of ESP, and the lack of solubility data for key chemical systems.
- Experimental results and other code calculations continue to be obtained in an effort to validate the ESP.

Single-Shell Tank Retrieval and Waste Feed Delivery Program

Randy Kirkbride

- The ORP has the details on the BNFL, Inc., flow sheets and has received some of the flow sheets, which contain a limited amount of experimental results.
- The HTWOS is a dynamic model for waste transfers. The model includes a mass balance and takes approximately 2 h per simulation.
- Experimental results and model predictions are used to develop tank-specific flow sheets.
- Due to the changes in privatization, the ORP needs to develop an integrated model for waste transfers and pretreatment, and operating envelopes for waste transfers may change.
- The ORP also needs a model that can predict the physical properties of slurries.
- The models are needed to support the limited experimental results.
- Tank AN-104 will be retrieved first due to concerns with flammable gases. The salts in Tank AN-104 contain high concentrations of sulfate, so several transfers may be needed.
- Tanks AN-102 and AN-107 may be caustic deficient, which can lead to corrosion.
- During saltcake dissolution, the ORP needs to know if precipitation will occur after the wash solutions are combined and if preferential dissolution will take place.

- The entrained solids from saltcake dissolution will be sent to a double-shell tank.
- The latest version of the Tank Waste Remediation System's Operations and Utilization Plan (TWRSO&UP II) is now available.

Warren Thompson

- The cost of retrieving the waste in Tank C-106 was over \$1 million. It may be possible to close Tank C-106. Data collection to support "operational closure" was initiated.
- FY 2000 plans include a 3-year acceleration of the retrieval schedule for the sludge in Tank C-104. Preliminary engineering will be initiated this year.
- Alternative retrieval technologies will be evaluated as appropriate. The crawler technology will be tested after the operators have been trained.
- Fifty-eight of the 149 single-shell tanks contain 90% of the long-term radionuclides, which do not include cesium. Forty-two of the 58 tanks are considered to be sound.
- One possible processing scenario is to demonstrate the retrieval process in a sound tank and then proceed to a leaking tank.

Saltcake Dissolution Tests and Modeling

Dan Herting

- Dissolution experiments were performed on five saltcake samples, and the chemical composition of the saltcakes varied considerably.
- The saltcake sample from Tank S-102, which will be the first saltcake tank to be retrieved, was almost pure sodium nitrate and contained very little water.
- The dissolution results at 25 and 50°C were comparable.
- When the water washes were combined in the receiver jar, solids formed due to reduced solubility of certain components as the ionic strength was increased.
- The initial saltcake sample from Tank A-101 contains the sodium sulfate carbonate double salt. After the saltcake dissolution process, undissolved solids were primarily sodium carbonate.
- For Tank AN-104, ESP predicts that the sulfate will not reprecipitate when the supernatant and dissolved saltcake are recombined.

- The saltcake from Tank TX-113 contained the sodium nitrate sulfate double salt, and no sodium nitrate was observed. The needle crystals were due to sodium phosphate or sodium carbonate.
- A compilation of optical data on all potentially relevant salts is under way to assist in the identification process. This information will be made available to TFA and ORP staff members.
- The sludge in the saltcake hinders the identification of the solids in the initial samples.

Becky Toghiani

- ESP calculations on the saltcakes from Tanks BY-102 and TX-113 indicated the need for special data bases. For Tank BY-102, the TRONA data base was needed for the high carbonate. The Na_2SO_4 data base was required for the high sulfate in Tank TX-113.
- The recommended practices for the ESP include the proration method of charge balancing and the preprocessing of important data. The ESP code encounters significant problems with saltcake samples that contain very little water.
- The ESP predictions encountered a problem with fluoride and sulfate. This difficulty may be due to the presence of a sodium fluoride sulfate double salt, which is not included in any of the ESP data bases.
- The ESP was used to predict solids that would form when the different wash solutions from a saltcake dissolution experiment were combined. The ESP predictions and the experimental results were in reasonable agreement. The ESP predicts the formation of gibbsite, which was not observed in the actual tests. However, the kinetics for gibbsite formation can be very slow.
- ESP also overestimates the formation of dawsonite, which is not stable at a pH above 9.

Andy Felmy

- The modeling of dilution experiments is a trivial exercise. A rigorous validation of the ESP code requires chemical conditions where species are in two different phases.
- A systematic approach is needed to validate ESP. The phase diagrams for small groups of key constituents should be compared with ESP predictions.

Dan Reynolds

- Problems with ESP increase as the temperature of the chemical system increases. Improvements to the data bases may reduce these problems.

Solubility Tests to Improve the ESP Data Base

Jeff Lindner

- The solubility tests on the fluoride and phosphate system were conducted in water, 1 *m* sodium hydroxide, and 3 *m* sodium hydroxide. Temperatures of 25, 35, and 50°C were used, and the minimum equilibration period was 2 weeks.
- ESP can use a temperature fit expression (KFIT) or the Gibbs free energy of formation to predict the equilibrium species distributions.
- The ESP consistently underestimated the solubility of sodium fluoride as compared with the SOLGASMIX code.
- For natrophosphate, the solubility increased slightly as the temperature was raised from 25 to 35°C.
- With the current arrangement, OLI Corporation is able to fit the solubility results.
- A study on the solubility on the sodium fluoride sulfate double salt was initiated.
- Very limited information on the extent of hydrate formation for sodium carbonate, sodium phosphate, and sodium sulfate at elevated ionic strength is available.
- The solubility of sodium carbonate decreases as the ionic strength increases.

Randy Kirkbride

- The maximum processing temperatures for the saltcakes are the temperatures in the tanks. In contrast, the temperature of the sludges may be increased during sludge processing.

Comparison of Calculations by ESP, SOLGASMIX, and Moonis Ally's Model

Becky Toghiani

- The SOLGASMIX code models equilibria using Gibbs energy minimization and the Pitzer model, while Moonis Ally's model is a lattice model.
- The ESP predictions for sodium fluoride are dependent on the mode of calculation, which can be either KFIT or Gibbs free energy of formation.
- Solubility data from Hanford on the sodium, fluoride, and phosphate system was incorporated into the data base for ESP.
- The discrepancies between the ESP predictions and the experimental results for the sodium, fluoride, and sulfate system increase as the pH increases.

- The predictions of the ESP and Moonis Ally's model are in good agreement at 25°C. Deviations between ESP and the model increase at 100 and 125°C.

Randy Kirkbride

- When ESP was selected, it was the only commercially available software that provided a robust engineering tool. The ESP is not just a program to calculate chemical equilibria.

Graham MacLean

- At the time of the selection of ESP, CHEMSAGE, which is a commercial version of the SOLGASMIX code, was the only alternative. Although ASPEN can handle Pitzer parameter, this ability is not one of its strengths.

Status and Planning of Hanford Data Base Reconstruction and Hanford Waste Speciation Prediction Code Using OLI Software

Albert Hu

- Inconsistencies between ESP predictions and analytical results increase as the concentrations in the waste increase. The limitations of the ESP for extreme waste conditions must be validated.
- It would normally take a day for ESP to complete its waste speciation predictions for a single tank.
- The stream analyzer in ESP is not robust enough for the Hanford waste. Development of a window-based code is needed to automate the modeling efforts and to increase the speed of the calculations.
- Water, nitrate, sodium, hydroxide, and nitrite account for nearly 88% of the Hanford waste. The ORP should establish the parameters of the binary electrolyte in this multicomponent system. Then, secondary components such as sodium carbonate, sodium fluoride, sodium phosphate, and sodium sulfate should be added.
- Equilibrium constant, ESP parameters, and solubility of sodium nitrate were determined using the OLI-modified Bromley electrolyte model of ESP.
- At temperatures below 50°C, the new $K_{eq}(ppt)$ agreed better with the public data base; above 50°C, the new $K_{eq}(ppt)$ was closer to the Hanford data base.
- Errors in the $K_{eq}(aq)$ can lead to errors in the ionic strength, which can change all of the speciation calculations.
- The public data base for the ESP needs to be customized systematically to meet the ORP requirements.

Additional ESP Studies at the Hanford Site

Don Geniesse

- A sensitivity study using the ESP is under way to determine the solubility of solids as a function of temperature and dilution. The results of this effort will be used by the ORP in flow sheet development.
- The ESP is known to have a problem with chromium chemistry.

Identification of Future Tests and Benefits for Saltcake Dissolution

Becky Toghiani

- The deficiencies in the ESP data bases should be addressed.
- The best way to treat saltcake with low water content needs to be determined.
- Sludge processing should be added to the current modeling effort on saltcake dissolution.
- Aluminum and chromium chemistry must be analyzed, and the results must be added to the ESP data bases.

Andy Felmy

- The ESP should be modified so it can accept Pitzer parameters.

River Protection Project: Status of Waste Transfers, Criteria, and Plugs

Dan Reynolds

- ESP has been used at the Hanford site since 1982.
- The maximum specific gravity for liquids and slurries to be transferred is 1.41 g/mL. Currently, the ORP is transferring 1 million gal of liquid waste per year from the single-shell tanks.
- The criteria for the transfers can be found in several semiofficial documents.
- In the past five years, three pipeline plugs have occurred during transfers from saltcake tanks. In each case, the transfer of the waste was suspended, and the pipeline was not flushed with water. The line from Tank BY-103 was abandoned. A hot water flush broke the plug from Tank SX-104, while a jumper was pulled to break the U-103 plug.
- Temperature can dramatically affect the weight percent of solids. For Tank SY-101, a sample contained 70% liquid at 65°C. However, when the sample was cooled to 25°C, it contained no free liquid.

- No plug has ever been recovered and analyzed. Most plugs were probably due to sodium phosphate. The length of a sodium phosphate crystal and its density cannot be measured.
- During transfers, the needle crystals of sodium phosphate present a more significant problem than the round crystals of natrophosphate.
- Carbonate may have been responsible for the plug from Tank BY-103. No evidence for a plugged pipeline due to aluminum has been observed.
- The diameters of the slurry and supernatant transfer lines are 2 and 3 in., respectively. The new transfer lines are not heat traced and are designed for very high pressures.

Jim Jewett

- The cost of replacing a transfer line depends on length, location, and many other factors.

Retrieval Tasks on Waste Transfers and Plugs

Pete Gibbons

- At the Savannah River Site (SRS), the heel in Tank 19 is an equal mixture of sludge and zeolites.
- In the retrieval task for the SRS, the particle size ranged from 5 to 20 μm .
- Potentially high-level waste sludges were discovered at Idaho.

Overview of the Feed Stability Tasks

Tim Welch

- The retrieval program of the TFA has focused on physical aspects of waste transfers, while the pretreatment program will examine fluid dynamics, thermodynamics, viscosity, precipitation, and crystallization.
- An on-line viscometer will be added to the pipeline system at FIU.
- One of the objectives is to define and validate better waste transfer criteria.

Harry Babad

- The sum of limitations for pipeline transfers can be found in the authorization basis.
- Future transfer tests should focus on waste that can lead to pipeline plugs.
- A transfer could encounter three phases: gas, liquid, and solid.
- Aging may influence the morphology of the solids.

Jim Jewett

- The document for the authorization basis covers the hazards to workers, the public, and the environment; it does not cover hazards to the program or to the equipment. The consequences of plugging generally fall into the latter category.

Wally Schultz

- Future pipeline tests need to examine recovery methods.

Randy Kirkbride

- Hanford engineers have limited process controls over the transfers. Options include the temperature, pump rate, and amount of dilution water.

Don Geniesse

- OLI Corporation has a kinetics program for precipitation and crystallization.

Yasuo Onishi

- The only requirement for the chemical portion of the transport model is to accurately predict the viscosity of the waste.

Saltwell Pumping/Pipeline Plugging

Jeff Lindner

- Variation in the chemical compositions in the simulant for Tank SX-104 can lead to gel formation, solid deposition, or both. Different plug mechanisms may be possible.
- Plugging from gel formation should result in a pressure drop different from plugging due to gradual particle deposition.
- For the waste transfer from Tank C-104, approximately 260,000 gal of diluent must be added to achieve a solids loading of 20 weight percent. The retrieved waste should conform to the storage criteria requirements.
- The gel is not covalently bonded.

Randy Kirkbride

- A thorough understanding of past problems can be used to prevent future problems.
- The results from saltwell pumping can be used during the retrieval of the saltcake tanks.

Model Development for the Waste Transfers

Hani Al Habbash

- The current plan is to use the ESP and a commercial computational fluid dynamics (CFD) code.
- The CFD code must have multiphase capability. Fluid properties such as flow rates, pressure, and viscosity and particle properties such as size, shape, and growth kinetics are expected to be key variables.
- Four commercial CFD codes—CFD 2000, Fluent, Pheonics, and Tempest—were evaluated. Pheonics was selected due to its open source code, its pre- and post-processing capabilities, and its comprehensive physical models.

Yasuo Onishi

- It is very difficult to model a pipeline transfer. Empirical models usually provide better predictions. Any transfer model must emphasize the chemistry of the waste.
- In Tempest simulations, nearly 90% of the computational time may be used by the chemistry module.

Randy Kirkbride

- The pipeline plugs occur when the temperature of a saturated solution drops. The ORP needs a tool to identify potential problems.

Harry Babad

- Models for the transfers of brine solutions may be useful in this effort.

Jim Jewett

- The cost of removing the most recent plug was between \$700,000 and \$800,000.

Pipeline Transfers at Florida International University

Rajiv Srivastava

- The ORP has proposed the transfer of slurries from Tanks AN-103 and C-104.
- The pipeline system at FIU will be used to simulate these proposed transfers. If a plug occurs, recovery methods will be tested.
- The flow rates in the FIU system will range from 2 to 8 ft/s, while the typical flow rate of a slurry transfer at Hanford is 6 ft/s.
- The pressure drop will be determined as a function of bulk viscosity and solids formation.

Dan Reynolds

- The addition of fluoride to prevent the formation of sodium phosphate crystals is not an option.
- The use of steam will interfere with leak detection. However, the line can be preheated with hot water.

Joe Cruz

- Two major concerns for the ORP are pipeline plugs and tank space. Efforts to reduce the potential for pipeline plugs must be balanced with the limited amount of tank space.

Identification of Future Tests and Benefits

Randy Kirkbride

- Pipeline plugs during the Phase I transfers are unlikely. The FIU tests should confirm this conclusion.

Dan Reynolds

- Future tests should focus on recovery methods from full and partial plugs.
- The conditions that lead to phosphate or carbonate plugs should be evaluated further. The waste that was responsible for the last cross-site line plug contained very little phosphate and a considerable amount of carbonate.
- A chemical analysis of a sample before it is transferred is critical.
- In addition to pipeline plugs, feed stability should also focus on waste compatibility, criticality, and flammable gases.

Jim Jewett

- The chemical composition of the waste should be included in the transfer criteria.

Program Outlook and Path Forward for Saltcake Dissolution and Feed Stability

Phil McGinnis

- This workshop has identified two additional needs that should be addressed by the TFA. These needs are the partitioning of radionuclides during saltcake dissolution and the addition of Pitzer parameters to the ESP. The effort to include these new tasks in the TFA program plan for FY 2001 was initiated.

Randy Kirkbride

- ESP in its current form is important and heavily used.
- The TFA should continue to improve the ESP model and its data bases.
- The TFA should support Onishi's need for chemistry during waste transfers.
- The ORP supports the proposed modifications to the TFA work scopes for FY 2001.
- The ORP should decide on the best way to handle the various ESP data bases.
- The ORP should determine if the preferential dissolution of salts offers any significant advantages.
- Potential users of the TFA results need to make themselves known and be identified.

Appendix A

TANKS FOCUS AREA PRESENTATIONS

Review of FY 1999 Workshop

Charles F. Weber

Presented at the FY 2000
Saltcake Dissolution and Feed
Stability Workshop
May 16-17, 2000

Review of FY 1999 Workshop

- Hanford requirements
- Use of ESP code
- Experimental efforts
- Communication
- TFA Program Status

Hanford Processing Operations Require Modeling Support

- Modeling and simulation tools
 - ◆ Hanford Tank Waste Operations Simulator (HTWOS)
 - ◆ ESP
- Problem areas
 - ◆ Remediation of tank SY-101
 - ◆ Evaluations of other tanks (S-102, A-101, BY-102)
- Ability to match dissolution experiments

ESP Is an Important Analytical Tool

- Minimize need for actual experiments
- Establish parameters for tank farm operations
- Improvements needed
 - ◆ Avoid excess conservatism in operations
 - ◆ Match all experiments

Unresolved Issues May Affect Confidence in ESP Predictions

- Method of charge reconciliation
- Discrepancies with certain experimental results
- Validation needed
 - ◆ Previous versions of ESP
 - ◆ Other code calculations
 - ◆ Experimental data
- Need for improvement in OLI data bases

Experiments in Support of Code Validation and Modeling

- Effects of dilution, viscosity
- Saltcake dissolution tests (Herting)
- Solubility of Na-F-PO₄ and other double salts
- Isopiestic measurements

Communication Is Essential

- TFA researchers and users
- Integration between different tasks
- Validation of ESP
 - ◆ Test cases relevant to users
 - ◆ Comparison with other code calculations
 - ◆ Better explanations of input and data sets
 - ◆ Collaboration with OLI to improve data sets

Saltcake Workshop 2000

Richland, May 16, 2000

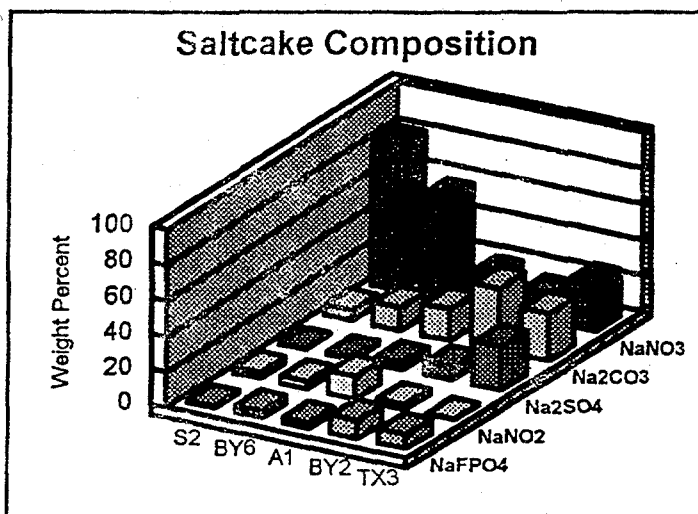
Hanford Laboratory Program

TTP No. RL-08-WT-41

D. L. Herting, PI

Hanford FY2000 Tasks

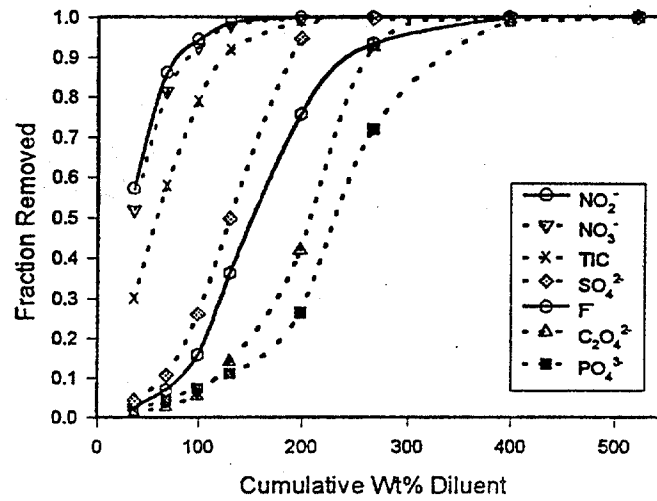
- Task A - Feed Stability (5 tanks)
 - stepwise dissolution to model retrieval
- Task B - Batch Dissolution (TX-113)
 - sequential dissolution to determine composition
 - series dissolution to measure trends
- Task C - Solids Analysis/Identification
 - PLM, SEM/EDS, XRD



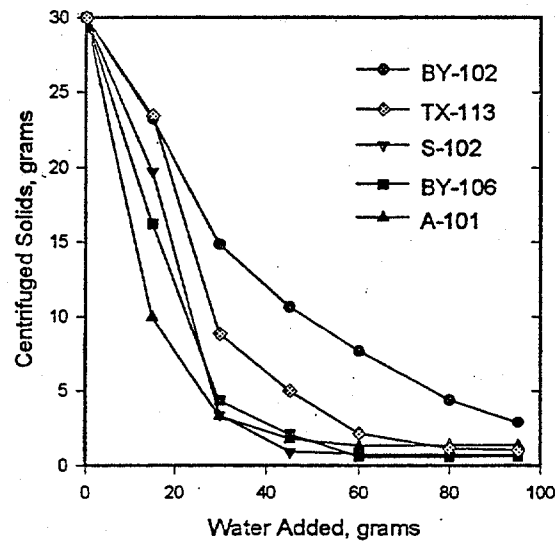
Feed Stability Procedure

1. Start with "source tank" and "receiver"
2. Add 30 g saltcake to "source tank"
3. Add 15 g H₂O, mix, centrifuge
4. Decant liquid to "receiver", weigh solids
5. Repeat steps 3 & 4 total of 10 contacts
6. Identify solids that form in "receiver"

Tank BY-102 Dissolution Profile, FY99 Test



Saltcake Dissolution Progress



Solids Formed in Receiver

(no solids formed in S-102)

Contact	BY2	BY6	A101	TX3
2	S, FS, FP			S, FS
3	FS, Ox, FP	Ox	Ox	FP
4		Ox		FP
5	FP			
6	FP, Ox			

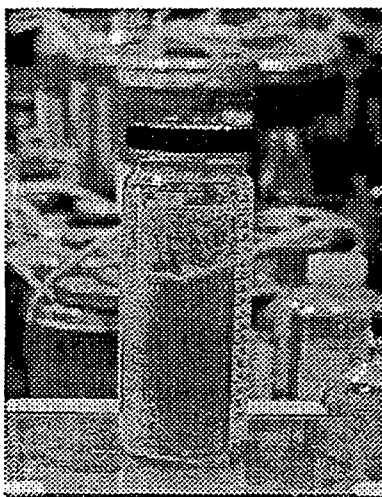
Conclusions

- Salts dissolved in tank A re-form in tank B
- Quickly reach point of diminishing return
- Plan retrieval carefully

Task B - Batch Dissolution, TX-113

- Sequential Dissolution (ESP Input)
 - 30 g saltcake + 30 g H_2O , mix, decant Wash #1
 - Add 30 g H_2O , mix, decant Wash #2
 - Analyze Washes 1 & 2 + residual solids
- Series Dissolution (ESP Output)
 - X g saltcake + nX g H_2O , where
n = 0.5, 1.0, 1.5, 2.0, 2.5, 3.0
 - Analyze liquid phase

Tank TX-113 Composite Sample

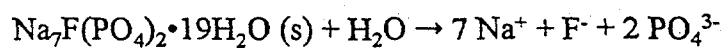


TX-113 PLM, Original Sample

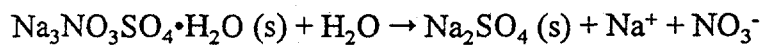


2 Types of Double Salts

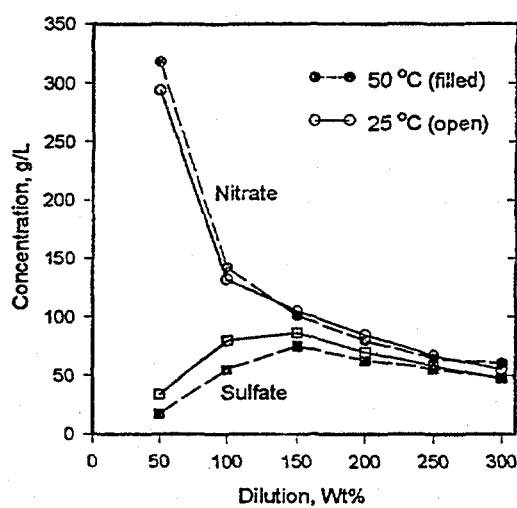
- Congruent:



- Incongruent:



TX-113 Series Dissolution



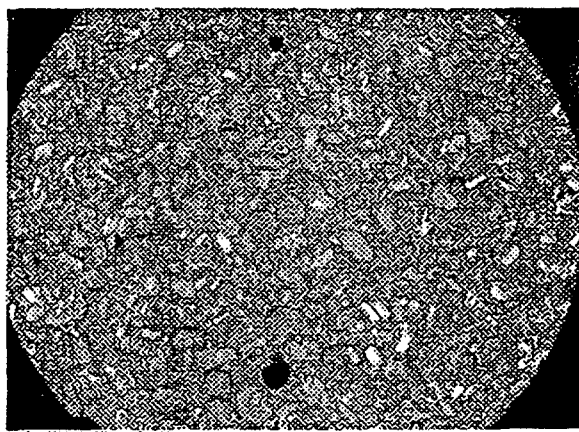
Task C - Solids Identification

- PLM - polarized light microscopy
- SEM/EDS - scanning electron microscopy
+ x-ray fluorescence
- XRD - x-ray diffraction
- Example: Na_3FSO_4

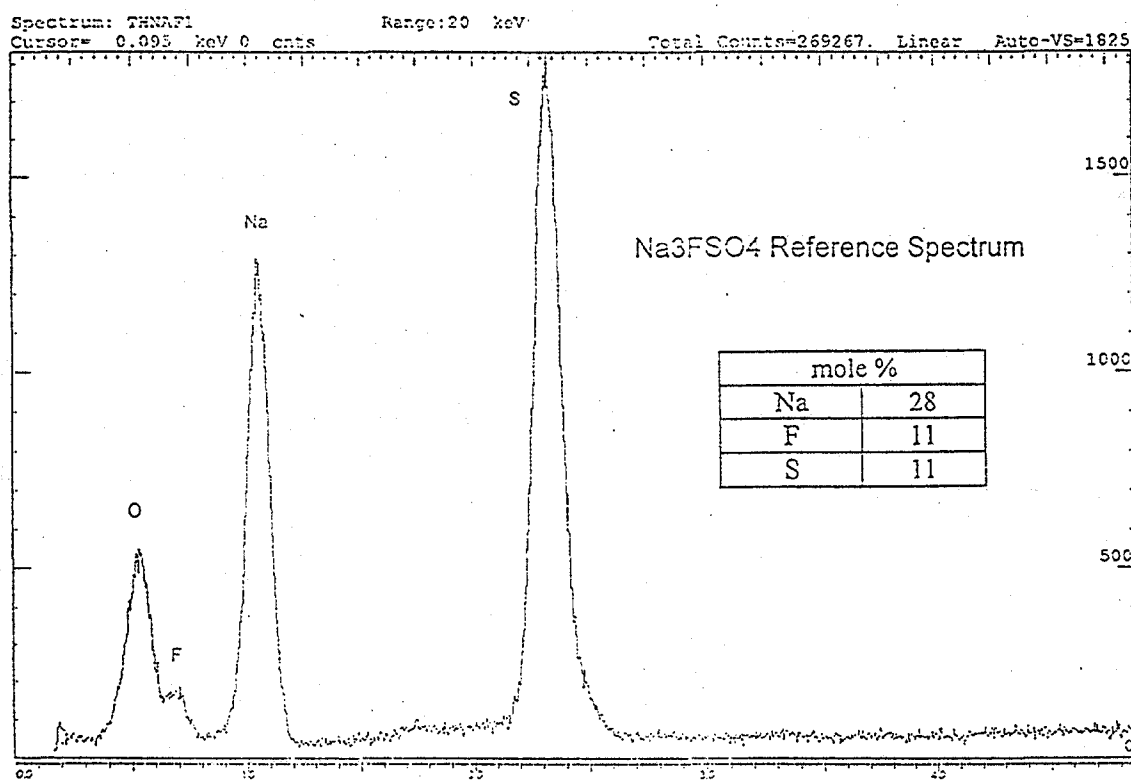
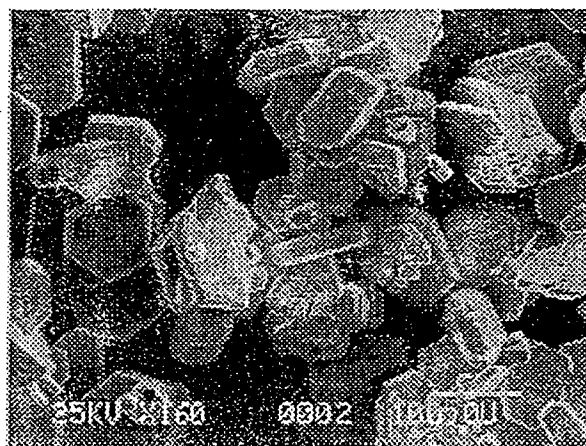
Na_3FSO_4 Optical Data

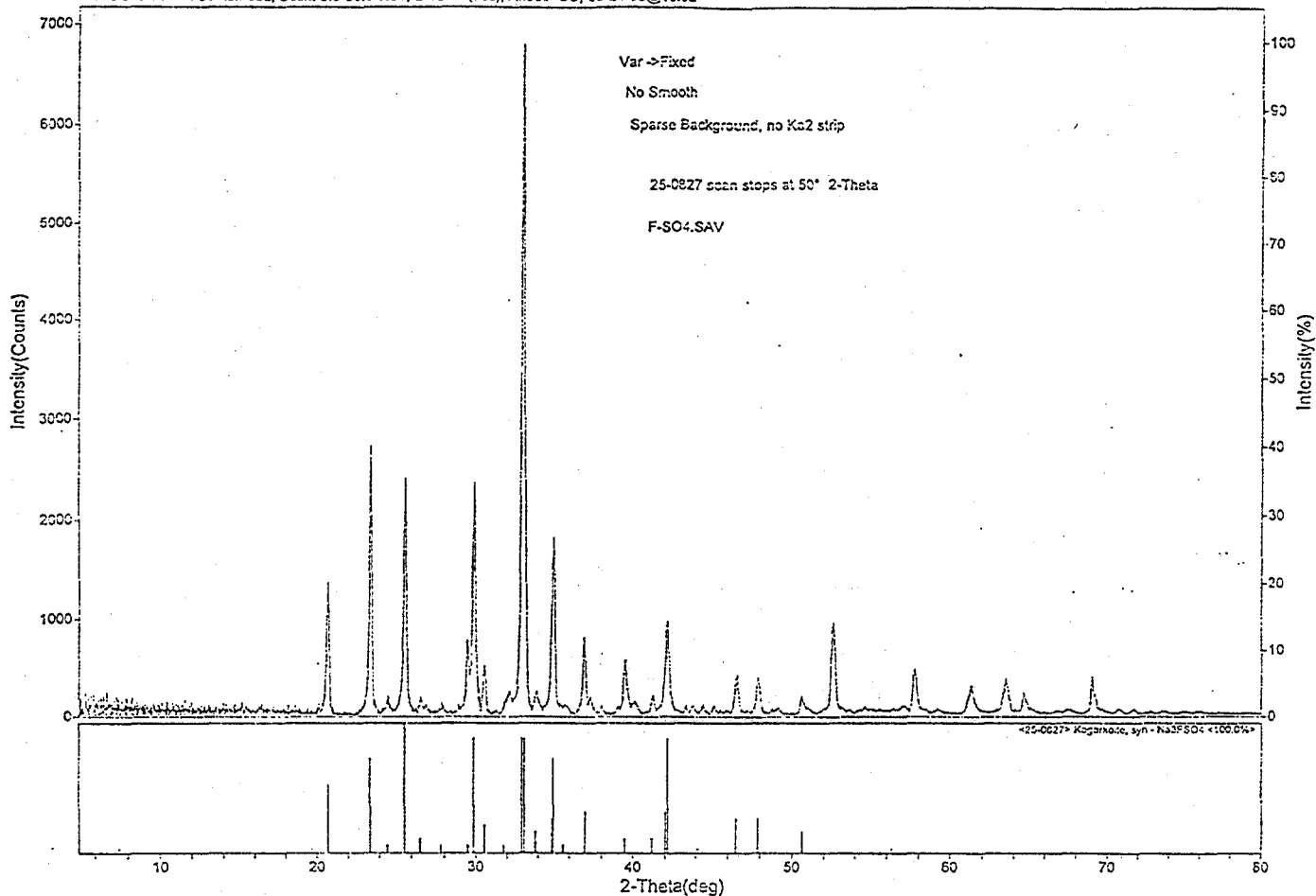
- Crystal system: hexagonal
- Habit: basal tablets or rhombohedra
- Polarization info:
 - uniaxial positive
 - birefringence = 0.003 (very low)
 - $n_o = 1.426$; $n_e = 1.429$

PLM Photo of Na_3FSO_4



SEM Photo of Na₃FSO₄





Plans for FY2001

- one more tank (tbd) for ESP
- continue solids analysis development
- expand feed stability to mixed tanks?
- identify solids that don't dissolve?
- determine ^{99}Tc distribution?
- expand and dovetail simulant testing for "physical" parameters

Saltcake Dissolution Modeling

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Progress to Date

- Modeling of Saltcake Dissolution Experiments
 - 5 tanks; diverse saltcake compositions
 - Identified need for proper database selection
 - Examination of supernate composition; solids speciation
- Modeling of Feed Stability Experiments
 - Staged retrieval
 - Examination of cumulative supernate to identify potential solids formation

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Saltcake Compositions (wt. %)

	BY-102	BY-106	A-101	S-101	TX-113
H ₂ O	26.5	14.7	31.2	(5.0)	10
Al	1.65	1.59	2.39	0.67	0.3
Cr	0.2	0.11	0.17	0.12	0.04
Fe	0.05	0.02	0.02	0.03	0.03
K	0.1	0.24	0.31	0.07	?
Na	27.8	25.0	21.2	23.0	27
F ⁻	1.17	0.62	0.07	<0.02	0.7
Cl ⁻	0.11	0.16	0.41	0.16	0.07
NO ₃ ⁻	1.85	2.71	7.43	2.04	0.2
NO ₂ ⁻	10.9	40.5	12.6	53.7	29
PO ₄ ³⁻	0.60	0.34	0.39	0.52	3
SO ₄ ²⁻	5.12	1.16	2.44	0.32	13
C ₂ O ₄ ²⁻	1.99	1.26	1.35	0.17	?
CO ₃ ²⁻	20.6	7.15	9.04	2.94	14
OH ⁻	1.09	1.14	2.1	0.42	?

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Summary of FY99 Tasks

- ESP Input Data Pre-processing Issues
 - Processing of experimental data
 - Charge reconciliation method
 - Adjustment of input density
- Comparison with Experimental Data
 - Revised ESP predictions for BY-102, BY-106
 - Solids Identification for BY-102
 - ESP Predictions for A-101, S-102

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FY00 Workscope – ESP Efforts

- ESP Prediction of TX-113
- Feed Stability Studies
- ESP Predictions – Comparison with Other Models
 - NaNO₃/H₂O at high ionic strength
 - Na-F-SO₄ double salt as function of ionic strength and temperature

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Charge Reconciliation – Recommended Practices

- Proration method
- Pre-processing of data important
- Tuning of density to provide experimentally measured % water
- Practices implemented for all 5 tanks examined
 - Difficulties encountered for low-water content saltcakes (S-102, TX-113)

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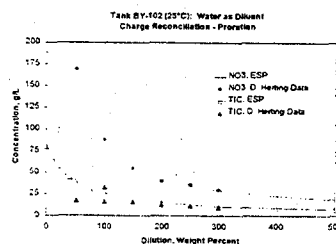
DIAL

ESP Public Database

- Deficiencies in the database identified through saltcake dissolution simulations
 - Representation of carbonate behavior
 - Representation of sulfate behavior
- Deficiencies in the database identified through comparative calculations with other codes
 - Representation of double salts
 - Pure component solubility for NaF

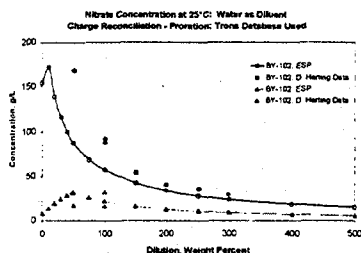
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Carbonate & Nitrate Behavior Public Database



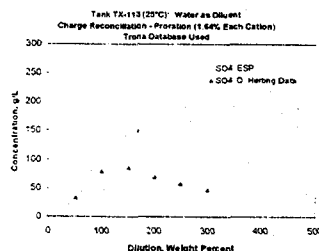
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Carbonate & Nitrate Behavior Trona Database



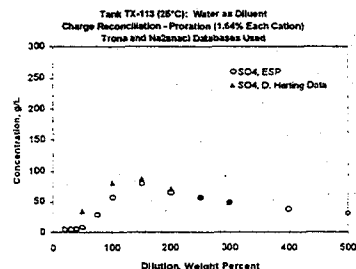
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Sulfate Behavior – TX113



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Sulfate Behavior – TX113 Special Sulfate Database



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Database Selection

- Critical in development of ESP as a routine process operations tool
- Database(s) used must properly model known behavior of species at high ionic strength
- Identified need for specialized databases only through comparison with saltcake dissolution experiments

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TX113 Saltcake Dissolution

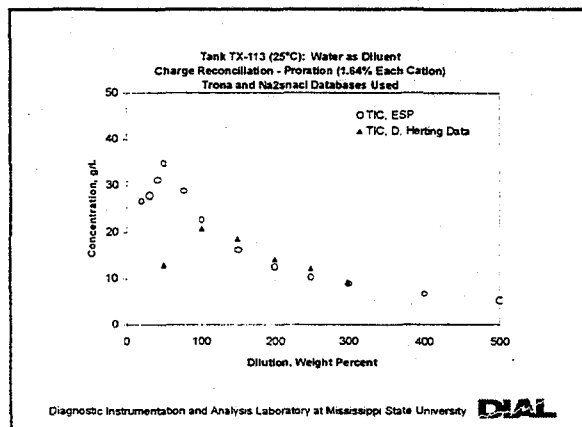
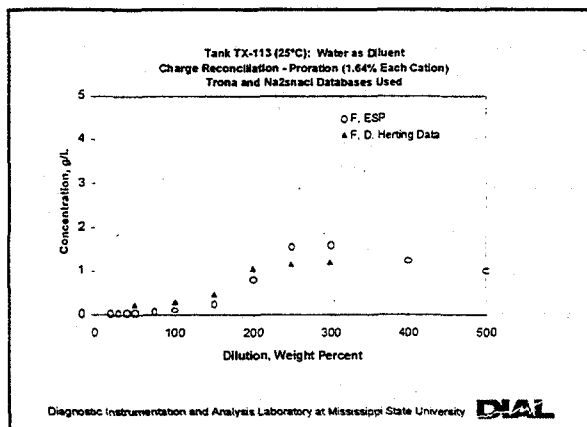
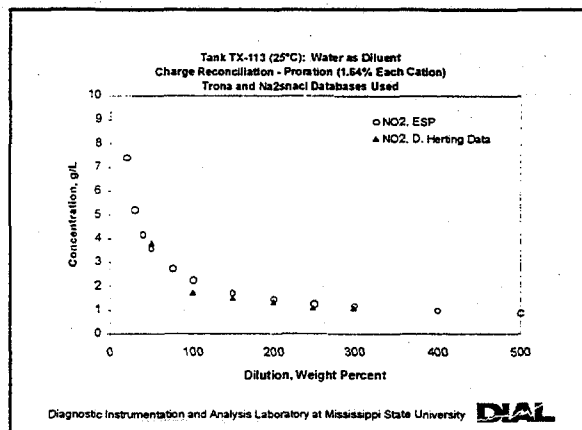
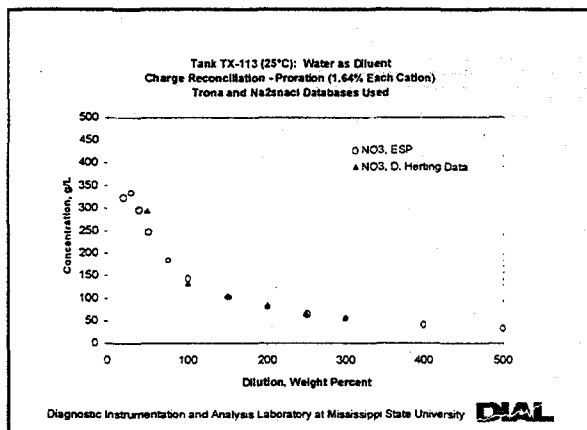
- Recommended practices for data pre-processing and charge reconciliation used
- Water input was adjusted so that generated molecular stream contained sufficient water for equilibration calculations (20 g H₂O/100 g saltcake added)

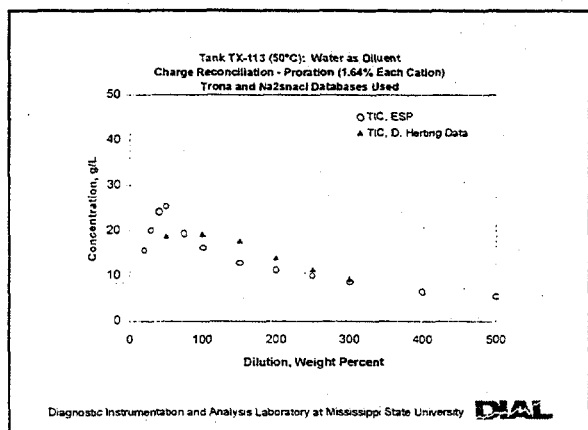
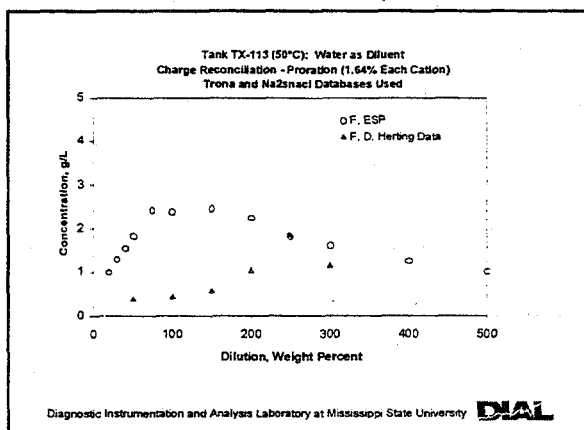
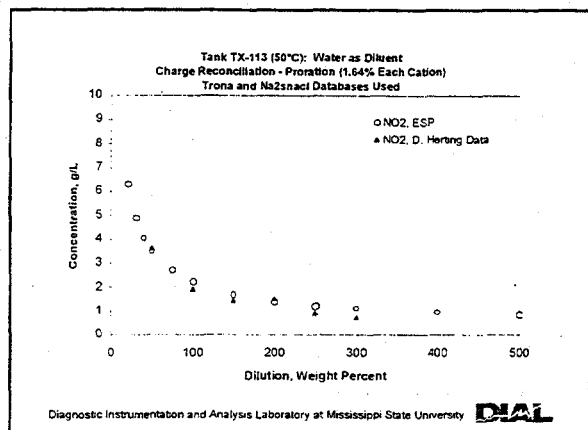
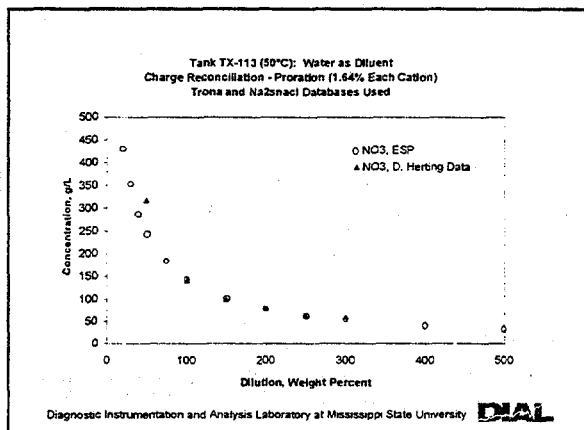
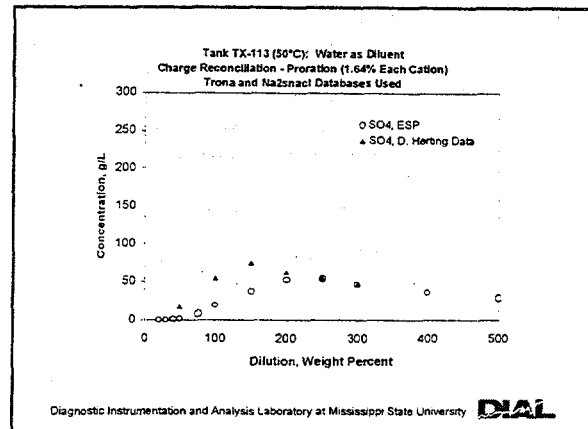
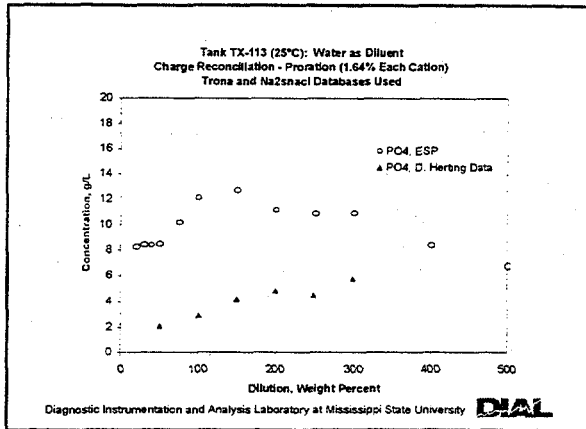
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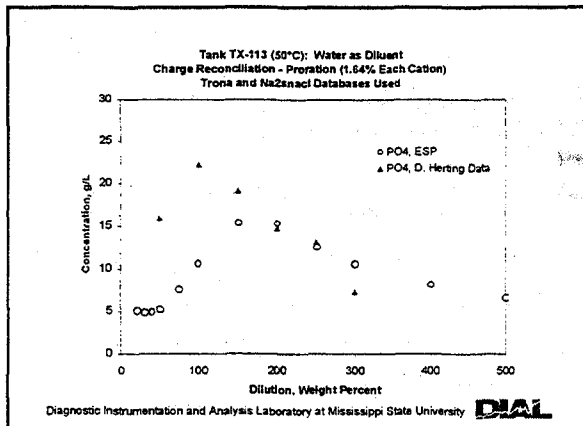
TX113 Saltcake Dissolution

- Trona & Special Sulfate databases used
- Inhibited water as diluent
- Dilution level range: 20 to 500% dilution by weight
- Temperatures of 25°C and 50°C

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ESP Predictions of TX113

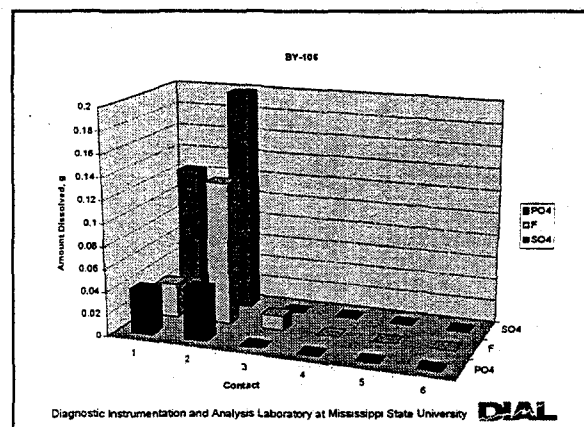
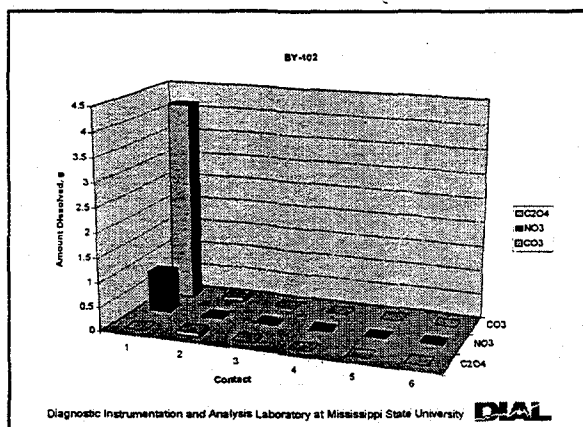
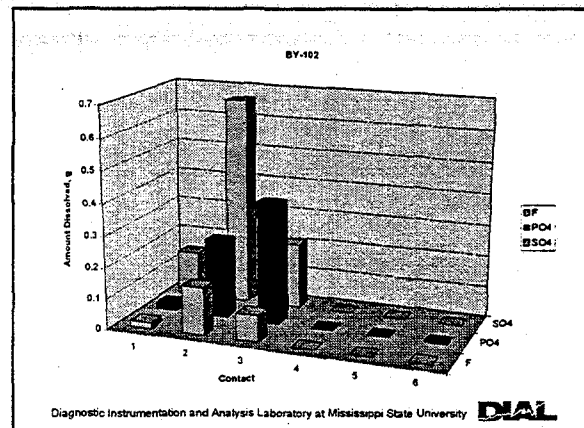
- Major trends exhibited by experimental data are reproduced
- Discrepancies at low dilution levels still apparent for select anions
- Results reinforce the need for solubility data for sulfate-(carbonate, fluoride, nitrate) double salts
- Double salts are predicted to be present until high levels of dilution

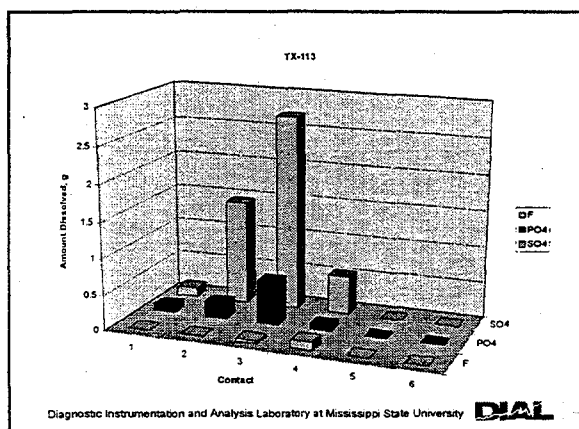
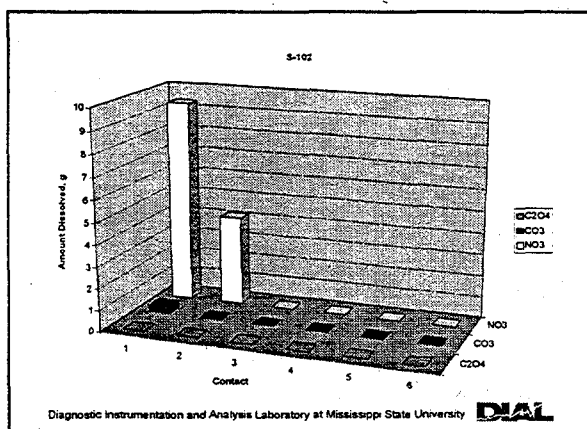
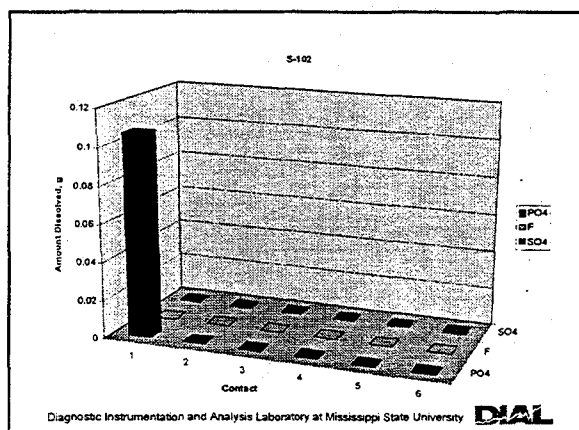
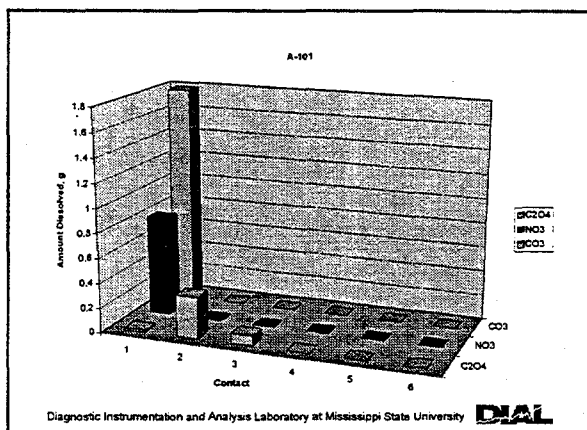
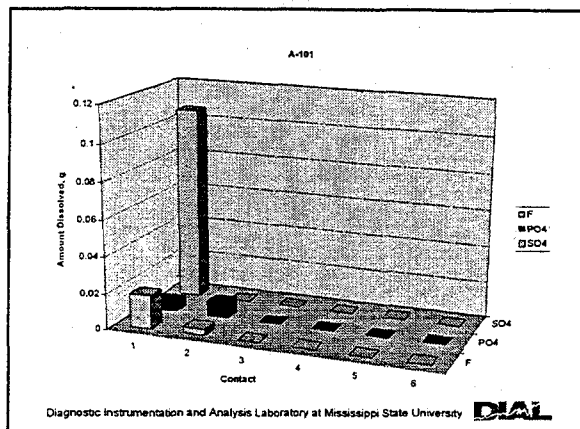
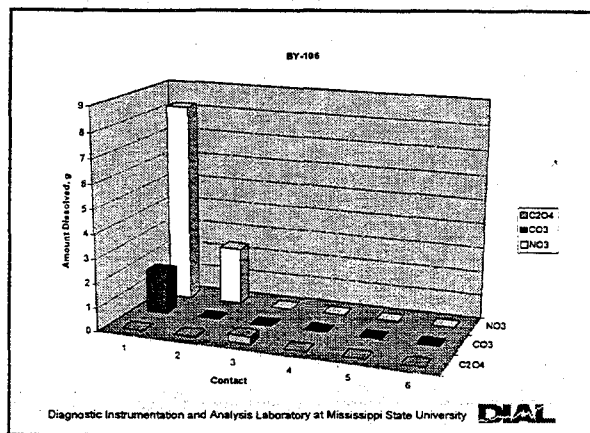
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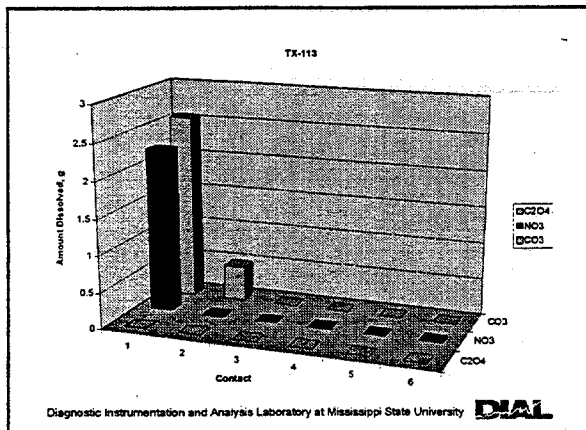
Feed Stability Studies

- Simulate experimental test plan
- Purpose – examine potential solids formation when supernates obtained at different stages of retrieval are remixed
- Molecular streams generated during FY99 used as input for ESP model calculations

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Solids Formation in Cumulative Supernate

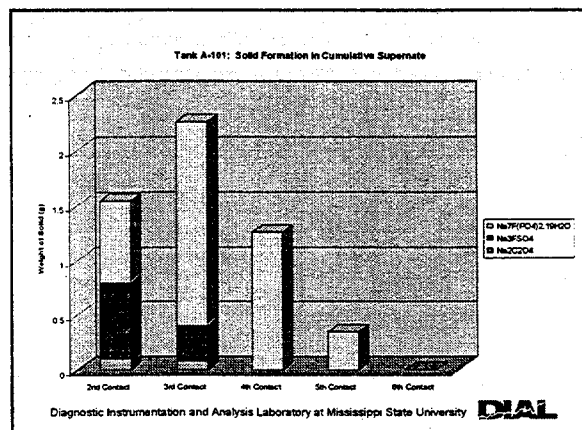
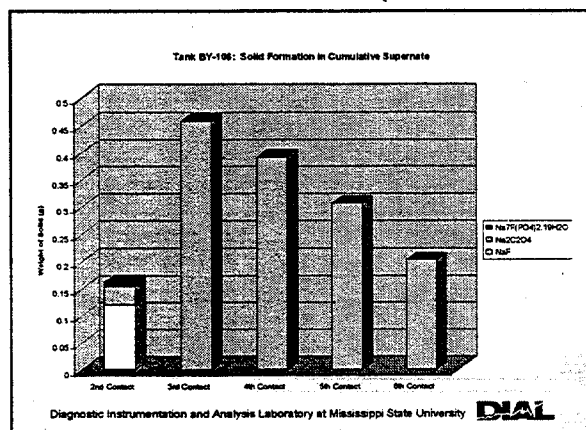
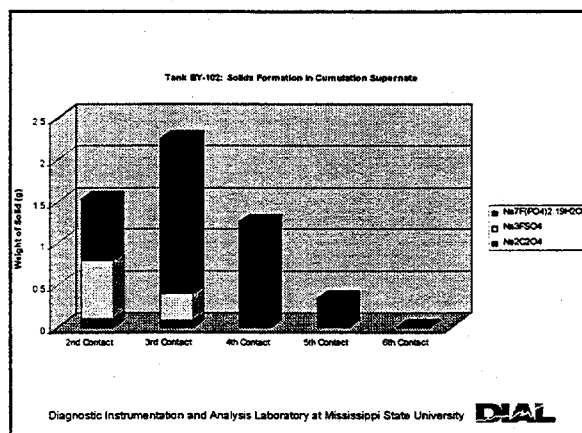
- As supernate obtained from different contacts is accumulated, potential for solids formation exists
- Double salts will reprecipitate and then go into solution as more supernate is accumulated and ionic strength of the cumulative supernate drops
- Major trends found in experimental data exhibited by model predictions

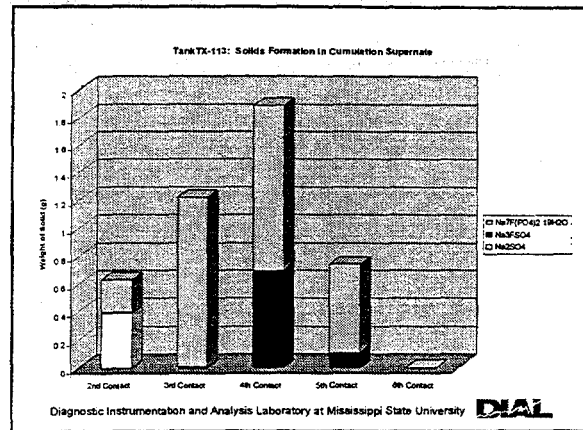
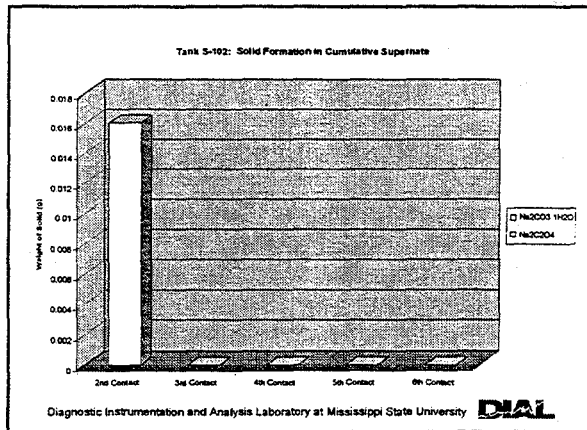
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Solids Predicted to Form in Receiver

Contact	BY-102	BY-106	A-101	S-102	TX-113
2	FP, FS, Ox	F, Ox, FP	FP, FS, Ox	Ox	S, FP, FS
3	FP, FS, Ox	Ox	FP, FS, Ox		FP, FS
4	FP	Ox	FP		FP, FS
5	FP	Ox	FP		FP, FS
6		Ox			

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ESP Comparison Studies

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Progress to Date

- Sodium/Fluoride/Phosphate System
 - comparison with SOLGASMIX calculations
 - behavior as function of ionic strength at 25 C
- Sodium/Fluoride/Sulfate System
 - comparison with SOLGASMIX calculations
 - behavior as function of ionic strength at 25 C
 - ESP database combinations examined
- Sodium Nitrate/Water System
 - comparison with M. Ally model

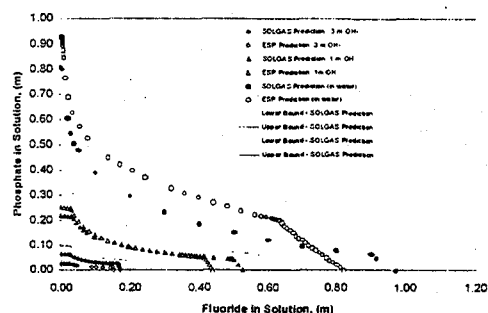
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Na-F-PO₄ System

- Discrepancies noted between ESP and SOLGASMIX
- Pure component solubility for sodium fluoride
- Solubility dependence on [OH⁻] different between ESP and SOLGASMIX models

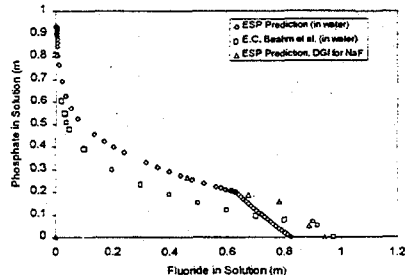
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Solubility Envelope for Sodium-Phosphate-Fluoride System



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Na-F-PO₄ System at 25°C

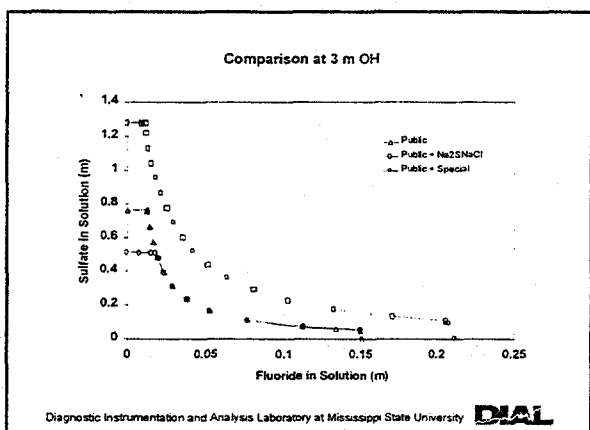
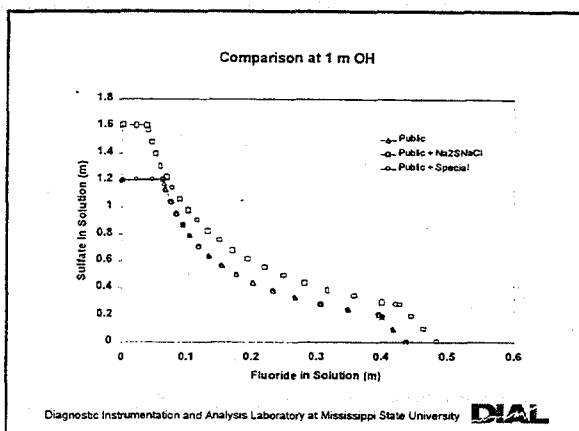
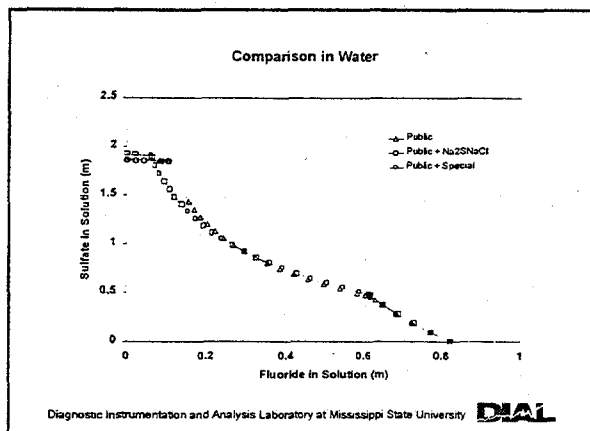


Diagnostic Instrumentation and Analysis Laboratory at Mississippi State University **DIAL**

Na-F-SO₄ System

- Preliminary examination of ESP predictions for sodium-fluoride-sulfate double salt
- Examined at 25°C as function of [OH⁻]

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Na-F-SO₄ Predictions

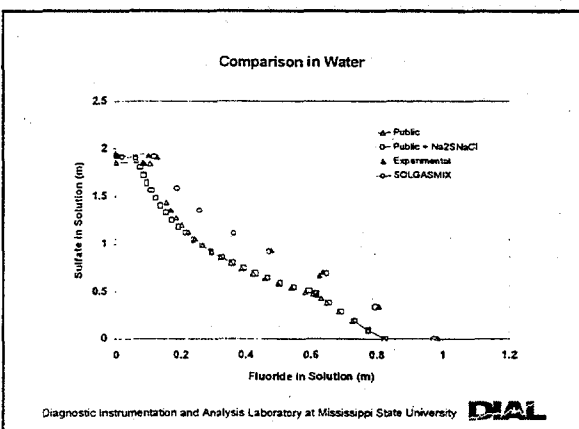
- Different database combinations examined
 - ESP Public database
 - ESP Public + Na₂SNaCl (supplied by OLI for sodium sulfate system at higher ionic strength)
 - ESP Public + Special (developed by G. Maclean)
- Discrepancies evident - higher solubility in solution at elevated ionic strength predicted by Na₂SNaCl database - as ionic strength increases, gap between predictions grows

Diagnostic Instrumentation and Analysis Laboratory at Mississippi State University **DIAL**

ESP and SOLGASMIX

- Comparison in water at 25°C
- ESP Public + Na₂SNaCl database used
- SOLGASMIX predicts higher solubility compared to ESP
- Comparisons as function of [OH⁻] and temperature are planned

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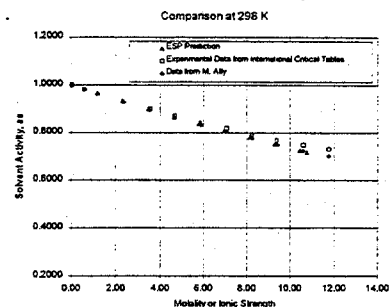


Comparison with Work of Ally

- Objective - to investigate validity of ESP and models of electrolyte solution behavior at high ionic strength
- Reasonable agreement at 25°C
- Deviations between ESP predictions and Ally's predictions at 100°C and 125 °C

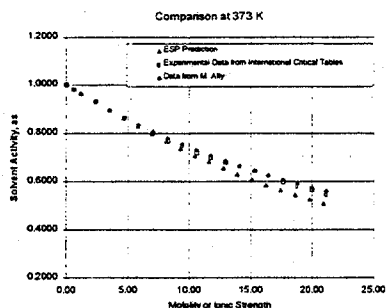
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Sodium Nitrate/Water System - 25°C



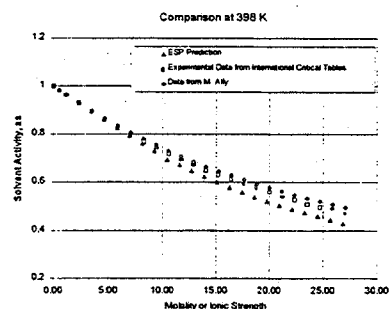
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Sodium Nitrate/Water System at 100°C



Diagnostic Instrumentation and Analysis Laboratory at Mississippi State University **DIAL**

Sodium Nitrate/Water System at 125°C



Diagnostic Instrumentation and Analysis Laboratory at Mississippi State University **DIAL**

Conclusions

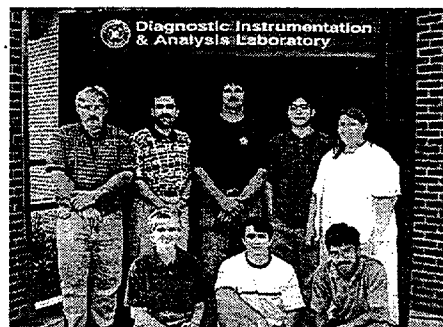
- ESP models/methods appear to provide good prediction at elevated ionic strength for simple single salt system (sodium nitrate)
- Comparisons for double salts validate need for experimental effort measuring SLE as function of ionic strength and temperature
- Discrepancy for NaF pure component solubility should be discussed with OLI personnel to determine a means of resolution

Diagnostic Instrumentation and Analysis Laboratory at Mississippi State University **DIAL**

Solubility Tests to Improve the ESP Database

- Craig Barfield, Mong Tan
 - MS Students Chemical Engineering
- Sam Nicholason
 - BS Chemical Engineering (MSU Dec'99)
 - Med School (Aug'00)
- Valerie Phillips
 - MS Analytical Chemistry (MSU 1988)
- Becky Toghiani, Jeff Lindner

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Acknowledgements

- Tanks Focus Area
 - Phil McGinnis (TIM) Tim Welch (ORNL)
 - Tom Brouns (visit to DIAL)
- DOE University Programs
 - DIAL Cooperative Agreement
 - Tom Brown, Contract manager
- Rodney Hunt, Chuck Weber (ORNL)
- Dan Herting,

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Accomplishments FY'98

- Comparison of thermodynamic parameters in ESP Public Database with Compilations from NIST and NEA
- Simulations on Saltcakes from 2 tanks
- Calculations for Remediation Operations for 241-SY-101
- Equilibrium Comparison calculations for the Na-F-PO₄-OH System

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Accomplishments FY'99

- Completion of SY-101 calculations
- Studies on electroneutrality reconciliation
- Dissolution Modeling extended to Saltcakes from 4 Tanks
- Na-F-PO₄-OH Solubility Experiments

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Work in Progress FY'00

- Revised dissolution calculations and predictions for TX-113
- Feed Stability simulations
- ESP Calculations for NaNO₃ at high ionic strength
- Continued Solubility Experiments
 - Na-F-SO₄-OH
 - Na₂CO₃·xH₂O
 - Na₃PO₄·xH₂O

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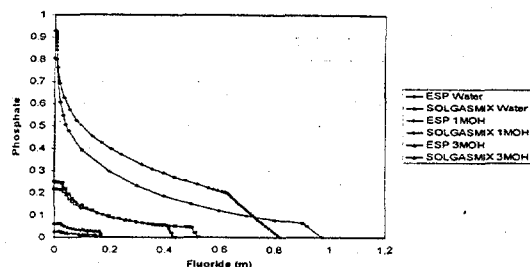


Equilibrium Chemistry Experiments

- A number of double salts are predicted by ESP to exist and have been observed in Hanford waste
- Data for these systems is sparse and improvement of model predictions is only possible through improved and additional measurements

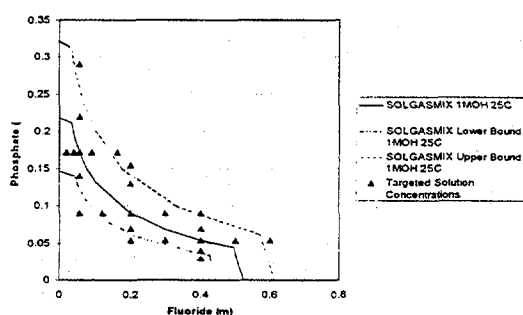
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Solubility Studies on the Na-F-PO₄-OH System ESP and SOLGASMIX Model Predictions



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Selection of Initial Concentrations



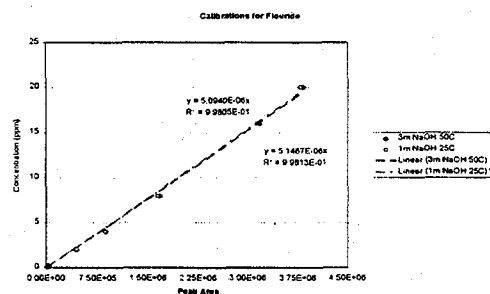
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Experimental Summary

- Solutions prepared in water, 1m and 3m OH
- Temperatures of 25,35, and 50°C
- Allowed to dissolve at elevated temperature
- Equilibrated with occasional shaking for a period of not less than two weeks
- Liquid phase characterization using IC
- Solids by PLM

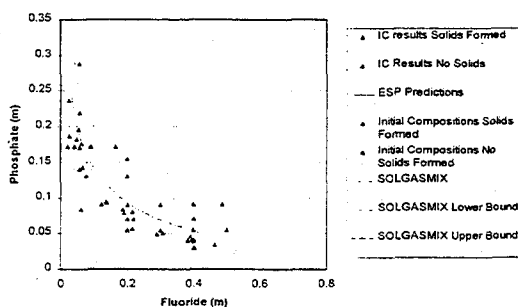
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Typical IC Calibration for Fluoride Anion



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Data and Predictions for 1m OH at 25°C



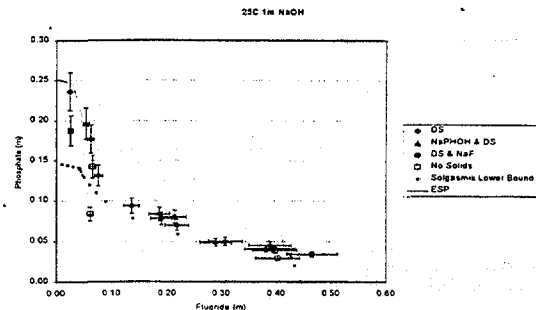
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PLM Image of natrophosphate (10x)



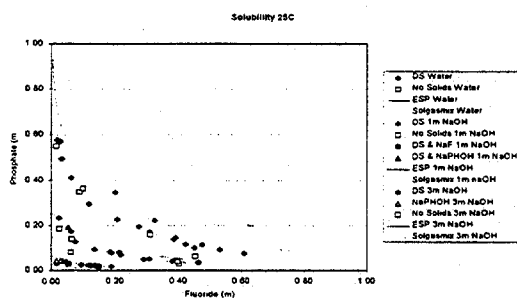
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Solids ID with Conservative IC Errors



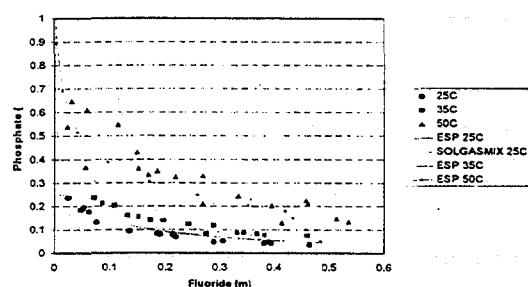
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Solubility Data for 25°C



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Results for 1mOH at Different Temperatures



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ESP Calculations for Pure Components

- ESP predictions consistently underestimate NaF solubility as compared to SOLGASMIX
- ESP employs a temperature fit expression (KFIT) to predict the equilibrium constant
- If a KFIT expression is not available ESP will revert to the Gibbs energy of formation
- Becky requested a special database for NaF and $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O} \cdot 0.25\text{NaOH}$ containing the free energies then compared the results to the KFIT expression and to the SOLGASMIX results

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Pure Component Solubilities from ESP (2 calculation options) and SOLGASMIX

NaF

	ESP-KFIT	ESP-ΔG _f	SOLGASMIX	SOLGASMIX (Lower Bound)	SOLGASMIX (Upper Bound)
Water	0.8235	0.9425	0.974	0.87091	1.0885
1 m OH	0.4366	0.5287	0.524	0.4451	0.6147
3 m OH	0.1506	0.1899	0.1693	0.139	0.206

$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O} \cdot 0.25\text{NaOH}$

	ESP-KFIT	ESP-ΔG _f	SOLGASMIX	SOLGASMIX (Lower Bound)	SOLGASMIX (Upper Bound)
Water	0.9294	0.9159	0.8069	0.6083	1.1695
1 m OH	0.2526	0.2403	0.2184	0.1471	0.3213
3 m OH	0.0263	0.0246	0.0224	0.0094	0.0973

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Summary of Pure Component Solubility Modeling

- In water and 1m OH the difference between the ESP and SOLGASMIX predictions are within the range of the SOLGASMIX calculation bounds
- In 3m OH the pure component solubility predicted by ESP is approximately 1/3 that calculated from SOLGASMIX

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Summary of Solubility Experiments for natrophosphate

- Experimental results are in qualitative prediction with model calculations
- Only a small increase in solubility is observed in going from 25 to 35°C
- Model Prediction in 1m OH are in good agreement with the SOLGASMIX calculations
- Pure component solubility can depend on the calculation mode in ESP

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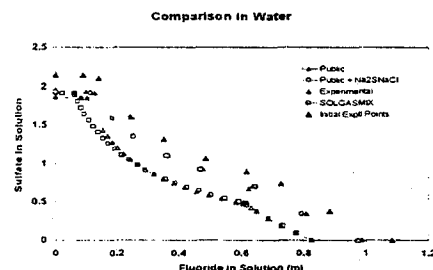
Initial Studies on Na_3FSO_4

- ESP and SOLGASMIX calculations at 25°C
- Preparation of Solutions
- Work Planned at 25 and 50°C in water and 1m, 3m OH
- Previous experimental data
- Foote, H. W., and Schairer, J. F., JACS, 52, 4202 (1930)

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Model Calculations and Solution Preparation for Na-F-SO_4



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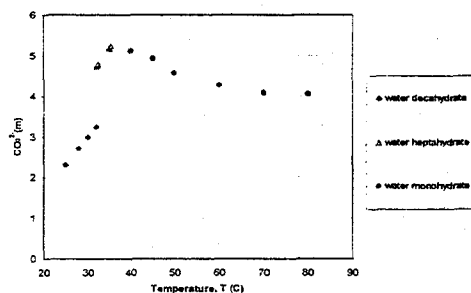
Equilibrium Experiments - Hydrates

- Proposed by Dan Herting
- Little Information is available on the extent of hydrate formation for Na_2CO_3 , Na_3PO_4 , and Na_2SO_4 at elevated ionic strength
- Initial focus on Na_2CO_3

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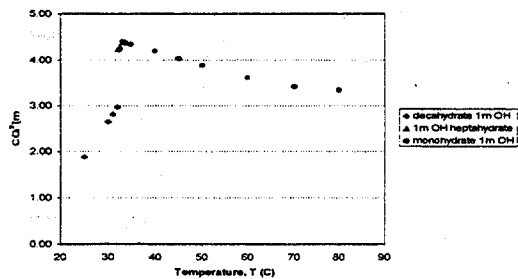
ESP Equilibrium Calculations for $\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$



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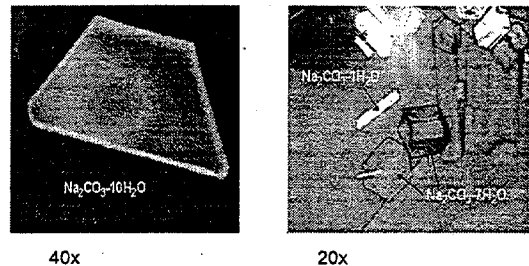
DIAL

ESP Predicted Solubility for $\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$ 1m OH



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PLM Images for $\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$



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Summary Sodium Carbonate Equilibrium Experiments

- Solubility decreases with increasing ionic strength
- Formation of the heptahydrate occurs over a narrow temperature range, crystal form not predicted in 7m OH
- Preliminary PLM images predict that the monohydrate and heptahydrate can coexist in contrast to the ESP calculations

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Path Forward

- Data for the natrophosphate system will be transferred to OLI Inc. to develop a revised database, equilibrium calculations will be re-run to confirm with the existing experimental data
- Equilibrium Calculations (SOLGASMIX and ESP) have been performed on the Na-F-SO₄-OH system and experiments have commenced

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Path Forward

- Calculations and experiments are in progress for the Na_2CO_3 system. ESP predicts distinct crystal types whereas PLM images indicate that different crystal forms can coexist
- Studies on Na-SO₄-NO₃-OH are planned

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Overview Of The TFA Feed Stability Tasks

Tim Welch
Oak Ridge National Laboratory

Salt Dissolution and Feed Stability
Workshop

Richland, Washington
May 16-17, 2000

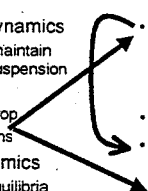
Some Recent and Ongoing Work Related To Feed Preparation and Transport

- Defining waste acceptance criteria and technical risk for feed delivery (PNNL et al)
- Modeling of tank mixing (with chemical reaction) for retrieval (Onishi et al, PNNL)
- Retrieval and pipeline unplugging demonstrations (TFA retrieval)
- Waste phase equilibrium, solubility, ESP (Hanford: Herting, Maclean, Hu, Felmy, et al; MSU: Lindner, Toghiani; ORNL: Beahm, Hunt, Weber)
- Viscosity (RPP, ORNL, PNNL)
- Precipitation kinetics and precipitate properties (AEA)
- Saltcake dissolution (RPP, MSU)

Why address waste stability?

- To prevent pipeline plugging and maintain stable waste flow
 - Cross-site transfer lines plugged
 - Plugging during saltwell pumping of SX-104 and U-103
- To prevent process disruptions (e.g., evaporator shutdown at SRS)
- To deliver feed within specifications (solids content)
- To improve processes
 - Minimize water additions during saltwell pumping
 - Increase availability
- To understand and prevent catastrophic events—Avoid those changes in conditions that can result in dramatic change in chemical state, physical properties, or flow patterns

Factors That Effect Pipeline Plugging

- Slurry fluid dynamics
 - Velocity to maintain particle in suspension
 - Viscosity
 - Pressure drop
 - Flow patterns
 - Thermodynamics
 - Chemical equilibria
 - Solubility
 - Precipitation /Crystallization
 - Nucleation and growth kinetics
 - Particle agglomeration and breakup
 - Temperature-heat transfer
 - Viscosity
 - Chemistry of continuous phase
 - Solids fraction
 - Particle size distribution
 - Particle shape
 - Temperature
- 

The objectives of the feed stability tasks include:

- To model waste transfer operations coupling chemical reaction/precipitation and flow.
- To conduct tests to validate models and determine parameters for transfer without plugging.

Waste Transfer Stability Tasks

- Slurry transport tests
 - AN-103, C-104
- Precipitation kinetics and precipitate properties
 - SX-104, AN-103
- Modeling of pipeline flow with precipitation
- Saltwell pumping tests
 - SX-104, U-103

Composition of Simulated Wastes

	Composition of Simulated Wastes (M)			
	Saltwell Pumping (MSU)		Pipeline Slurry Transport (FIU)	
	SX-104* U-103	X1	X2	AN103* C-104
Aluminate	1	1.6		2
Aluminum				
Nitrate	-	-		1
Nitrate** 7	7.4		7	2
Hydroxide	2	1.7	3	3
Phosphate	0.2	0.15	0.6	0.03
Carbonate	0.4	0.3		.7
Fluoride		0.2		0.6
Sulfate				0.045
Silicate				0.03
Sodium				

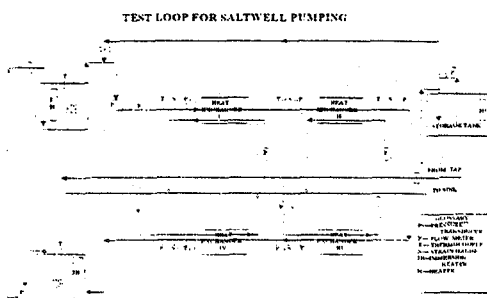
*Growth kinetics and precipitate property studies at AEA.

**This is the sum of nitrate and nitrite in actual wastes.

Objectives of the Saltwell Pumping Tests

- Identify plugging potential of specific wastes
- Provide data and model to evaluate saltwell pumping operations
- Improve saltwell pumping operations

Laboratory-Scale Salt Well Pumping Apparatus



Salt Well Pumping System Test Matrix

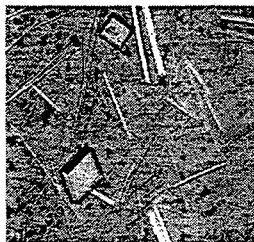
Simulant	Simulant NaCl Concentration %	Cooling Water Temperature °C	Simulant Flow Rate GPM (R)	Cooling Water Flow Rate GPM (all in the test section)			
				40	45	50	55
Water	50	20	4 (180)				
Simulant 1 SX-104	50	20	4 (180)				
Simulant 2 U-103	50	20	4 (180)				

NOTE 1: Reynolds number calculations are based on a 0.25 inch inner diameter tube.

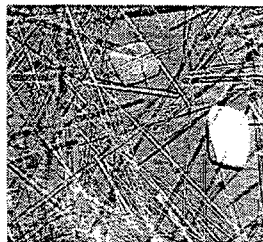
NOTE 2: Completing the matrix for all conditions may not be necessary. Decision will be made as results and significant effects are obtained.

PLM Image of Solids at Room Temperature (10x)

Rodney 2



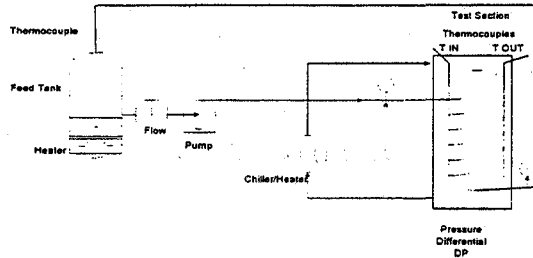
Sample 8



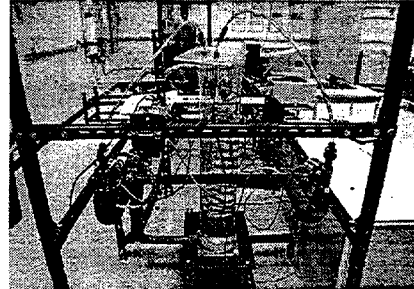
Objectives of the Slurry Transport Tests

- Evaluate the pipeline transport of specific waste slurries
- Provide data to support slurry transport modelling
- Develop a better understanding of plugging mechanisms
 - Physical
 - Chemical
 - Flow

FIU Bench-Scale Pipeline Test Flowsheet



Test Section Used for Scoping Tests at FIU



Test Matrix

- Feed tank temperature:
 - 50°C
- Test section temperatures:
 - 15°C, 40°C, 50°C
- Flow rates
 - Laminar, $Re < 2,300$
 - Transition, $Re < 10,000$
 - Turbulent, $Re > 10,000$

FIU Test Section Tubing Plugged by Hydroxide-Phosphate-Fluoride Simulant



FIU Test Section Partially Plugged by Hydroxide-Phosphate-Fluoride Simulant



Objectives and Requirements of Waste Transport Model

- Develop practical engineering tools to support data evaluation, waste transfer planning and waste transfer operations
- Must predict operating parameters (pressure, flowrate) during waste transfers
- Must predict plug formation, time to plug, and location
- Must be in terms of measurable and controllable variables

Initial Transport Modeling Approach

- 3D fluid mechanics
- Solid-liquid flow, solids suspension
- Chemical reaction / precipitation
- Solids population balance
 - Nucleation and growth
 - Particle agglomeration and breakup
- Viscosity (chemistry, volume fraction, particle shape, temperature)
- Temperature effects (heat transfer)

Waste Transport Model Development Phases

- Build complete model
 - Start with CFD–Slurries
 - Chemical reactions
 - Population balance
 - Crystal nucleation and growth kinetics
 - Particle agglomeration and breakup
 - Viscosity (chemistry, solids fraction, shape, PSD)
 - Heat transfer, conductivity
 - Validate with data from simulated waste tests
- Test and reduce
 - Simplify where appropriate
 - Validate with data from simulated waste and actual waste tests
- Apply
 - Validate with pilot tests
 - Apply to operations

Tomorrow's Feed Stability Presentations

- Saltwell pumping tests (MSU)
- Slurry transport modeling (MSU)
- ESP (equilibrium) modeling of simulated tank wastes to be used at FIU and MSU
- Slurry transport tests (FIU)

Salt Well Pumping/Pipeline Plugging Model Development for Waste Transfers

- Vijay Kumar
 - MS Student, Chemical Engineering
- Sam Nicholson
 - BS Chemical Engineering (MSU Dec'99) Med School (Aug'00)
- Johri Andol, Research Assistant I
- Hani Al Habbash, Jeff Lindner, Becky Toghiani

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Salt Well Pumping

- Recent plugs from SX-104 and U-103 supernates
- Need for Laboratory Test Loop
 - evaluate plug mechanisms
 - support model development
 - confirm and/or enhance operations, dilution, flushing

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Pipeline Plugging

- New CSTL only available route for delivery of waste to the vitrification contractor
- Other CSTL's are plugged, leak or do not meet current environmental regulations
- Development of a validated Engineering Tool will allow Farm Operators to confirm existing models and criteria

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DIAL Program Activities

- Development of a Salt Well Pumping Test Loop and Testing with Waste Simulants
- Engineering Tool Development and Validation
 - slurry transfers and salt well pumping
 - ORNL surrogate compositions, viscosities
 - FIU slurry transport experiments
 - AEA surrogate particle growth, size

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Gantt Charts (2)

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ESP Supporting Calculations

- Obtain insight into phase equilibrium behavior and surrogate chemistry and properties
- Salt Well Pumping Experiments
 - SX-104
 - U-103
- Support of FIU Slurry Transport Experiments
 - AZ-101 AN-103 C-104

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SX-104 Surrogate Studies

Anion ORNL^(a) Sample 5 Sample 8

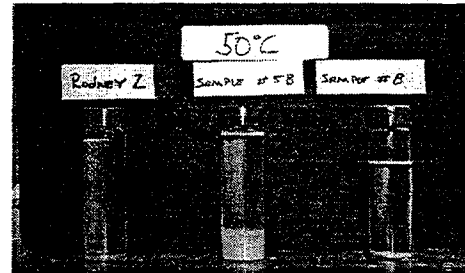
Aluminate	1	1	1
Nitrate	7	7	7
Hydroxide	2	2	2
Phosphate	0.2	0.3	0.3
Carbonate	0.4	0.4	0.1

Sodium cation

(a) recipe revised in an attempt to separate plug formation mechanisms

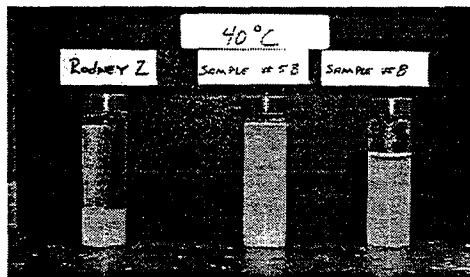
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SX-104 Surrogates following Initial Prep at 70°C and Cooling to 50°C



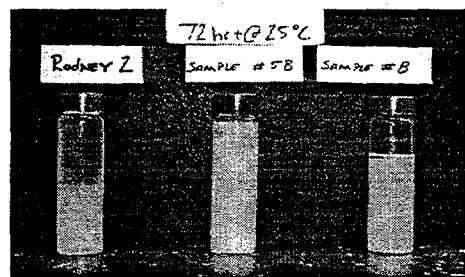
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SX-104 Surrogates on Cooling to 40°C



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SX-104 Surrogate on Cooling to 25°C after 3 days

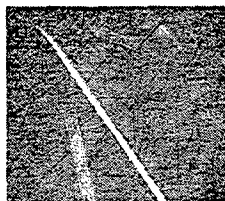
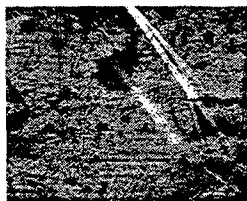


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PLM Images of Solids at 40°C (10x)

Rodney 2

Sample 8

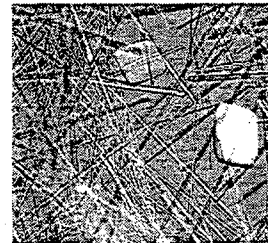
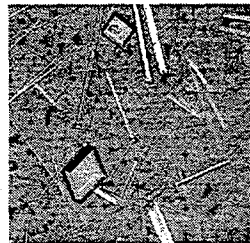


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PLM Image of Solids at Room Temperature (10x)

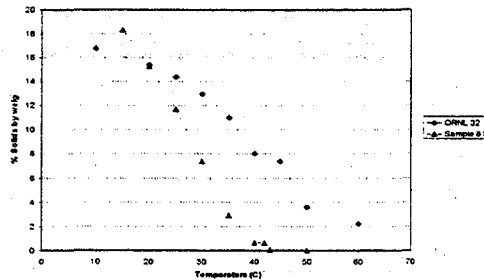
Rodney 2

Sample 8



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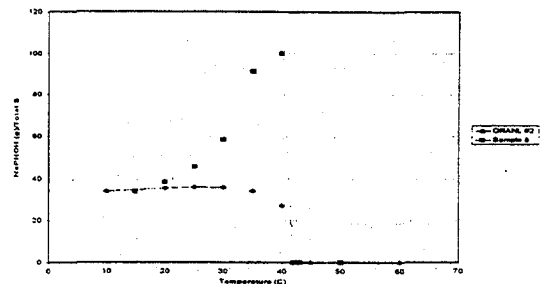
Predicted Solids Loading at Different Temperatures



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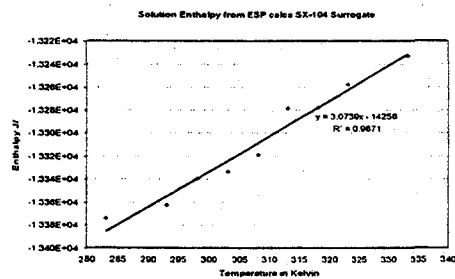
Weight Fraction of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O} \cdot 0.25\text{NaOH}$ in Surrogate Predicted by ESP



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Heat Capacity Calculation Based on ESP Results



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Summary of Surrogate Studies

- Different plug mechanism may be possible
- Gel formation is from $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O} \cdot 0.25\text{NaOH}$
- Separation of Plug Formation due to gelation can be accomplished using the sample 8 formulation
- The 80% of non-gel forming solids predicted with the ORNL surrogate can be used to isolate particle deposition mechanisms
- It is anticipated that plugging from gel formation will result in a different pressure drop than from gradual particle deposition

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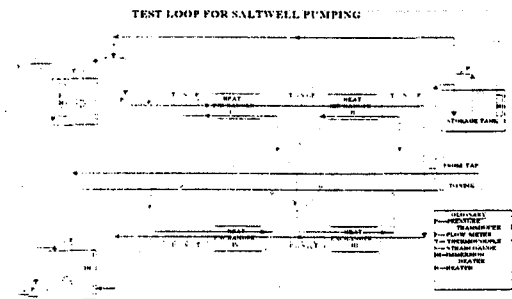
Salt Well Pumping Test Loop

- Heat transfer calculations
- Scoping Experiments
- Component Selection
- Acquisition
- Construction
- Testing
- Surrogate experiments

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Laboratory-Scale Salt Well Pumping Apparatus



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Salt Well Pumping System Test Matrix

Surrogate	Simulant Stream Temperature, °C	Existing Water Temperature, °C	Surrogate Flow Rate, Gal/hr (Re)	Existing Water Flow Rate, Gal/hr (all in the turbulent flow regime to enhance heat transfer)
Water	30	20	4 (180)	40 45 50 55
Hanford 1 SX-104	30	20	4 (180)	40 45 50 55
Hanford 2 U-105	30	20	4 (180)	40 45 50 55

Note 1: Reynolds number calculations are based on a 1/2 inch inner diameter tube.
 Note 2: Completing the matrix for all conditions may not be necessary. Decision will be made as results and significant effects are obtained.

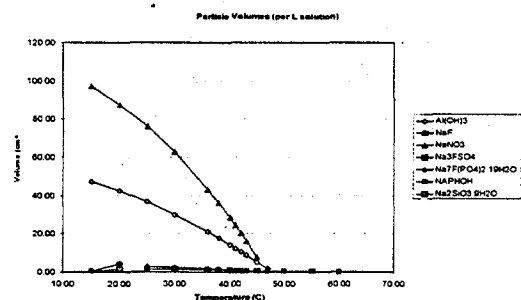
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ESP Simulations for Slurry Transport

- ORNL Surrogates for AZ-101 and AN-103
- AN-103 slurry measurements have been performed by FIU
- AZ-101 solids loading << 5% wt. few problems expected
- Search for a second surrogate, C-104 recommended by J. Jewett, et al.

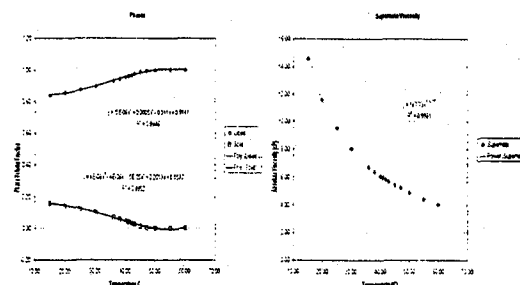
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ESP Predictions of Particle Volumes ORNL AN-103 Surrogate



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Model Input Correlations for AN-103 Surrogate



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Stream Compositions Predicted for the AN-103 Surrogate (1-L basis)

Temperature, °C	15.00	20.00	30.00	36.00	40.00	45.00	50.00	60.00
Total Stream								
Total g	1415.31	1415.31	1415.30	1415.30	1415.30	1415.32	1415.30	1415.31
Volume, L	0.91	0.92	0.94	0.95	0.96	0.98	0.99	1.00
Density, g/L	1561.36	1544.16	1506.96	1483.87	1467.65	1445.90	1430.45	1415.30
% Solids by wt	24.42	21.90	15.68	10.94	7.30	2.11	0.03	0.02
% Solids by vol	15.98	14.19	10.24	7.03	4.63	1.31	0.02	0.01
% Water by wt	43.68	43.88	43.90	43.95	44.01	44.06	44.06	44.06

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ESP Simulations for C-104 & AY-101, Development of Surrogate (ORNL) to Replace AZ-101

- Jewett, J. R. personal comm. 4/21/00
 - Phase 1 HLW
 - O'Rourke, J. F., "Results of Retrieval Studies with Waste from Tank 241-C-104," RPP-5798, Fluor Hanford, Feb 8, 2000
 - High Solids Loading ~37% by wt.
 - Tom Crawford, C-104 fails to meet tank farm storage requirements

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Tank Farm Storage Requirements

- For Temperatures less than or equal to 100°C and for $[\text{NO}_3^-] < 1.0$

$$[\text{OH}^-] \quad 0.010\text{M} < [\text{OH}^-] < 5.0\text{M}$$

$$[\text{NO}_2^-] \quad 0.011\text{M} < [\text{NO}_2^-] < 5.5\text{M}$$

$$[\text{NO}_3^-]/([\text{OH}^-] + [\text{NO}_2^-]) < 2.5 \text{ for DST}$$

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Equilibrium Simulation Goals

- Determination of diluent required to achieve 20% solids by weight
- What Diluent composition (caustic addition) is required to make C-104 or AY-101 correspond to storage requirements

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ESP Parameters

- BBI
- ESP Lab, Trona, Public Databases
- Proration in Water Analyzer
- Large Model

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Solids Distribution

	C-104 Base	+ 1E6 L Water	+ 1E6 L 2m NaOH	+ 1E6 L 4m NaOH	AY-101	C-104 + AY-101	C-104 + AY-101	C-104 + AY-101	C-104 + AY-101
Temperature, C	30.5	30.5	30.5	30.5	33.0	31.1	31.3	31.6391	31.6391
Solids									
ALOH3	2.44E+05	2.62E+05	2.37E+05	2.12E+05	2.92E+04	2.92E+05	2.69E+05	2.40E+05	
CaSO4H2					1.57E+03				
CaF2	6.20E+03	6.56E+03	6.59E+03	6.59E+03		7.74E+03	7.74E+03	7.74E+03	
CaOH2									
CRON3	2.30E+03	2.73E+03	2.23E+03	1.70E+03	4.71E+02	3.23E+03	2.82E+03	2.34E+03	
Fe(OH)3	5.60E+04	5.67E+04	5.60E+04	5.71E+04	5.27E+03	6.40E+04	6.33E+04	6.24E+04	
MNOH2	1.23E+04	1.26E+04	1.26E+04	1.22E+04	7.34E+02	1.35E+04	1.34E+04	1.32E+04	
Na2CO3	1.41E+04	1.12E+04	1.20E+04	1.30E+04		1.08E+04	1.30E+04	1.41E+04	
NaF	7.51E+04	5.59E+04	6.19E+04	7.31E+04		4.55E+04	5.28E+04	5.77E+04	
Na2PO4.10H2O	1.81E+04	6.62E+03	1.30E+04	1.56E+04		5.81E+03	1.48E+04	1.87E+04	
NOH2	4.67E+03	4.65E+03	4.65E+03	4.67E+03	9.35E+01	4.78E+03	4.77E+03	4.77E+03	
UO2OH2	7.32E+04	6.93E+04	7.50E+04	7.61E+04		6.73E+04	7.37E+04	7.58E+04	
ZrO2	9.86E+04	9.86E+04	9.86E+04	9.86E+04	1.73E+01	9.86E+04	9.86E+04	9.86E+04	

Diagnostic Instrumentation and Analysis Laboratory at Mississippi State University **DIAL**

Stream Totals Predicted for C-104, dilution of C-104, AY-101 and addition of diluted C-104 stream to AY-101

	C-104 Base	+ 1E6 L Water	+ 1E6 L 2m NaOH	+ 1E6 L 4m NaOH	AY-101	C-104 + AY-101	C-104 + AY-101	C-104 + AY-101	C-104 + AY-101
Temperature, C	30.5	30.5	30.5	30.5	33.0	31.1	31.3	31.6391	31.6391
Stream Totals									
Total	1.723E+06	2.722E+06	2.783E+06	2.740E+06	6.321E+05	3.354E+06	3.426E+06	3.489E+06	
Total Vol	1.006E+06	2.006E+06	2.010E+06	1.932E+06	5.641E+05	2.566E+06	2.582E+06	2.594E+06	
Target Dilution g/L	5.961E+02	2.944E+02	2.889E+02	2.955E+02	8.615E+01	2.380E+02	2.376E+02	2.384E+02	
% H2O by wt	40.67	62.57	60.51	57.62	34.19	66.66	64.93	63.30	
% Solids by wt	35.48	21.67	20.87	20.83	5.91	18.28	17.90	17.06	
% Solids by Volume	19.55	9.58	9.33	9.54	2.57	7.87	7.79	7.48	
Stream Density	1580.01	1359.78	1383.81	1418.62	1120.57	1307.43	1327.20	1345.25	

Diagnostic Instrumentation and Analysis Laboratory at Mississippi State University **DIAL**

Anion Molarities

	C-104 Base	+ 1E6 L Water	+ 1E6 L 2m NaOH	+ 1E6 L 4m NaOH	AY-101	C-104 + AY-101	C-104 + AY-101	C-104 + AY-101	C-104 + AY-101
Temperature, C	30.5	30.5	30.5	30.5	33.0	31.1	31.3	31.6391	31.6391
OHON	2.18	1.34	2.13	2.38	0.97	1.20	1.82	2.40	
NO2ON	0.84	0.43	0.43	0.47	0.37	1.13	1.12	1.12	
NO3ON	0.33	0.17	0.17	0.18	0.17	0.62	0.61	0.61	

$[\text{NO}_3^-] < 1.0\text{M}$ $T < 100^\circ\text{C}$
 $[\text{OH}^-] > 0.010\text{M} < 5.0\text{M}$
 $[\text{NO}_2^-] > 0.011\text{M} < 5.5\text{M}$
 $[\text{NO}_3^-]/([\text{OH}^-] + [\text{NO}_2^-])$ is < 2.5 for DST

Diagnostic Instrumentation and Analysis Laboratory at Mississippi State University **DIAL**

Preliminary Results C-104 Calculations

- Around 1×10^6 L (260 kgal.) of diluent will be required to achieve a 20% solids loading by weight
- Initial results indicate that the waste conforms to the storage criteria requirements

Diagnostic Instrumentation and Analysis Laboratory at Mississippi State University **DIAL**

Slurry Transport and Salt Well Pumping Model Objectives

- Capable of predicting plug formation in a waste transfer line
- Location and time needed to form the plug
- Values of variables that are used by the Tank Farm Operators (Pressures, Flow Rates..)
- Ultimate Model must be practical, easy to use, reliable, validated
- Modular Approach

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Modeling Requirements: Initial Starting Point

- Number of species and concentrations
- Conservation (mass, momentum, energy)
- Fluid properties (flow rates, pressure, density, viscosity)
- Particle size, shape, density, growth kinetics
- Population balance
- Chemical reactions
- Phase equilibria
- Sedimentation and deposition behavior

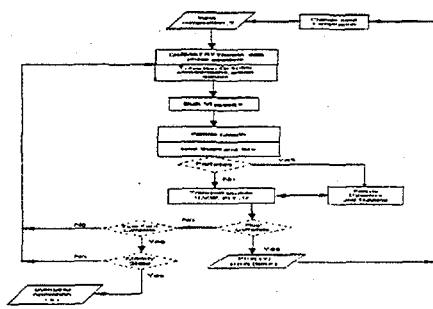
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Modeling Approach

- General Purpose CFD Code
- Multi-phase formalism
- Chemistry
 - correlations
 - calls to existing models
- Particle growth, dynamics,
- Bulk viscosity
- Pre and post-processing capabilities

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Model Flowchart



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Down-Selection of Transport Module Criteria for Selection

- Cost, User Support
- Open Source Coding
- Built-in Capabilities
- Availability
- Ease of Use

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- Fluent (25K/yr, comprehensive capabilities)
- CFD 2000 (low cost, limited capabilities, company undergoing mergers)
- Pheonics (3.5K/yr software and support, open source code, pre and post processing capabilities, comprehensive physical models)
- Tempest (2 versions, good capabilities, public version limited model)

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- Water w/o particles
- Drift Flux Multi-Phase Flow Model
- Turbulence
- Simulation Objectives
 - Evaluate Code
 - grid generation
 - initial and boundary condition specifications
 - conversion criteria
 - post-processing capabilities

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- Carrier fluid 20°C, 70% by volume
- Particles
 - 200 micron, 400 Micron, 15% by volume each
- Pipe dimensions 0.3 x12m cast iron
- Transient simulation
- Input velocity and simulation period
 - 1m/s 12 s
 - 0.5 10 s
 - 0.1 6 s
 - 1 steady state

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- Panel Plots
- Velocity, Carrier, Particle 1, Particle 2
- An initial time of 12 seconds was not sufficient to achieve steady state, flow is in moving bed regime
- Lowering the input velocity results in increased deposition, maximum deposition at 0.1 m/s
- Increasing flow to 1 m/s clears out the deposition and restores a moving bed flow

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1.1. The name of the organization: "The National Aeronautics and Space Administration" (NASA).

1.2. The title of the document: "The National Aeronautics and Space Administration's Policy on the Use of the English Language in the Publication of Technical Reports and Documents." (NASA's Policy on the Use of the English Language in the Publication of Technical Reports and Documents).

1.3. The date of the document: "1964".

1.4. The author of the document: "The National Aeronautics and Space Administration".

1.5. The subject of the document: "The National Aeronautics and Space Administration's Policy on the Use of the English Language in the Publication of Technical Reports and Documents." (NASA's Policy on the Use of the English Language in the Publication of Technical Reports and Documents).

2. The second part of the document is a table of contents section containing the following information:

2.1. The title of the section: "Table of Contents".

2.2. The page number of the section: "1".

2.3. The page number of the first section: "1".

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Path Forward

- Develop correlations based on the results of other team members
- Start simulation work for FIU AN-103 Studies
 - geometry and grid generation
 - code modifications
 - module development
 - results validation
- Begin Salt Well Pumping Model

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Solids Formation and Feed Stability During Waste Slurry Transfer



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Objective

- ♦ To investigate the effect of temperature and chemical reactions on the slurry transport and stability
- ♦ To test the plugging potential of pipelines due to precipitation and crystallization
- ♦ To study ways to unplug transfer lines

SALTCAKE DISSOLUTION AND FEED STABILITY WORKSHOP

MAY 16-17, 2000

FY00 Task Execution Plan

- ♦ Bench-scale
 - Experimental setup
 - Scoping tests
- ♦ Pilot-scale
 - Mockup setup
 - Experiments

SALTCAKE DISSOLUTION AND FEED STABILITY WORKSHOP

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Bench-scale Unit

- Slurry composition
- Slurry conditioning
 - ♦ Feed tank with two electrical heaters
- Slurry transfer in 3/8-inch (ID) tubing
 - ♦ Moyno pump
- Plug monitoring
 - ♦ Time-lapse video recorder
- Process conditions monitoring
 - ♦ Temperature, flow rate, pressure drop

SALTCAKE DISSOLUTION AND FEED STABILITY WORKSHOP

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Bench-scale Unit



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Simulants Tested

- ♦ Hydroxide-phosphate-fluoride system
 - X1
 - ♦ 3M NaOH + 0.6M Na₃PO₄ + 0.2M NaF
 - X2
 - ♦ 3M NaOH + 0.6M Na₃PO₄ + 0.2M NaF + 7M NaNO₃
- ♦ AN 103
 - ♦ 1.982M NaAlO₂ + 1.103M Al(NO₃)₃ · 9H₂O + 0.148M NaCl + 0.692M Na₂CO₃ + 0.061M NaF + 2.016M NaNO₃ + 6.744M NaOH + 0.031M Na₃PO₄ + 0.028M Na₂SiO₃ · 5H₂O + 0.045M Na₂SO₄ + 49.113M H₂O

SALTCAKE DISSOLUTION AND FEED STABILITY WORKSHOP

MAY 16-17, 2000

Test Matrix

- ♦ Feed tank temperature
 - 50°C
- ♦ Test section temperatures
 - 15°C, 40°C
- ♦ Flow rates
 - Laminar, $Re < 2,300$
 - Transition, $2,300 < Re < 10,000$
 - Turbulent, $Re > 10,000$

SALTCAKE DISSOLUTION AND FEED STABILITY WORKSHOP

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Experimental Results

- ♦ X1 simulant plugging
 - Total plugging at 15°C and $v < 2.1$ ft/s
 - Plugs manually removed
 - Partial plugging at 40°C
 - System kept running at lower flow rate
- ♦ X2 simulant
 - Similar to X1, except needle like crystals
 - Unplugging achieved by heating system and increasing pump power
- ♦ AN 103
 - Similar to X2

SALTCAKE DISSOLUTION AND FEED STABILITY WORKSHOP

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Experimental Observations (X1)

Simulant	Feed Tank Temperature, °C	Flow rate, GPM (Re)	Comments	
			Temperature at test section, 15°C	Temperature at test section, 40°C
X1 (3M NaOH, 1.6M Na ₂ PO ₄ , 0.2M NaF)	50	0.26 (2201) 0.8 ft/s	Complete plugging. No flow after plugging. Pump speed was increased to maximum power to try to unplug the system, but this procedure was unsuccessful, the system did not unplug. Plugs were manually removed after pump shut down.	Partial plugging. Crystals formation after cooling samples obtained from loop.
	50	0.57 (4826) 1.7 ft/s	Partial plugging. Solids formation.	No plugging. Solids formation. Normal flow conditions.
	50	0.72 (6096) 2.1 ft/s	No plugging. Some solids formation. Normal flowing conditions.	No plugging. Normal flowing conditions.
	50	0.91 (7705) 2.7 ft/s	No plugging. Solids observed. Normal flow.	Normal flowing conditions. Some solids.

SALTCAKE DISSOLUTION AND FEED STABILITY WORKSHOP

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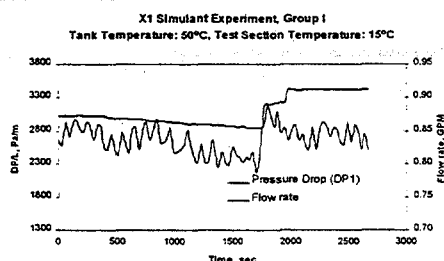
Experimental Observations (X2)

Simulant	Feed Tank Temperature, °C	Flow rate, GPM (Re)	Comments	
			Temperature at test section, 15°C	Temperature at test section, 40°C
X2 (3M NaOH, 0.63M Na ₂ PO ₄ , 0.2M NaF, 75M NaNO ₃)	50	0.26 (2201) 0.8 ft/s	Plugging observed with significant solids formation. Unplugging of the system was attained when increasing pump power and temperature. System was successfully flushed after unplugging. Any remaining solids were manually removed after pump shutdown.	Partial plugging. Solids formation. Needle-like crystals observed in samples.
	50	0.57 (4826) 1.7 ft/s	Abnormal flow. Partial plugging. Solids formation increased.	No plugging. Some solids formation. Normal flow conditions.
	50	0.72 (6096) 2.1 ft/s	No plugging. Some solids formation. Normal flowing conditions.	No plugging. Normal flowing conditions. Few solids observed.
	50	0.91 (7705) 2.7 ft/s	No plugging. Solids observed. Normal flow.	Normal flowing conditions. Very few solids.

SALTCAKE DISSOLUTION AND FEED STABILITY WORKSHOP

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X1 Pressure Drop Data



SALTCAKE DISSOLUTION AND FEED STABILITY WORKSHOP

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X1 and X2 plugging



Partial

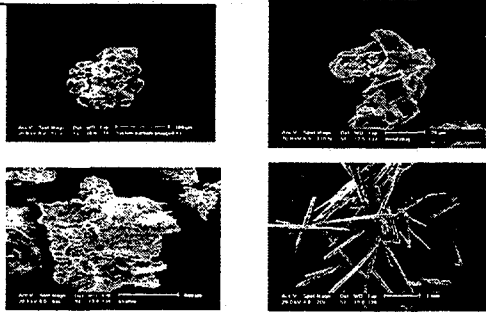


Total

SALTCAKE DISSOLUTION AND FEED STABILITY WORKSHOP

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Plug Samples



SALTCAKE DISSOLUTION AND FEED STABILITY WORKSHOP

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Pilot-scale Unit

- ♦ C104 – AY101
- ♦ Valve pit 241-SY-A
- ♦ Miter bends, Hanford connectors, dips, gradients, expansion, etc.

SALTCAKE DISSOLUTION AND FEED STABILITY WORKSHOP

MAY 16-17, 2000

Acknowledgments

- ♦ Hosae Melbourne, Ronnie Belle, and Andre Elie, John Acquaah
- ♦ Phil McGinnis, Tim Welch, Rodney Hunt, and Jim Jewett
- ♦ Pete Gibbons

SALTCAKE DISSOLUTION AND FEED STABILITY WORKSHOP

MAY 16-17, 2000

Identification of Future Tests and Benefits

Tim Welch
Oak Ridge National Laboratory

Salt Dissolution and Feed Stability
Workshop

Richland, Washington
May 16-17, 2000

Objective: Maintain Feed Stability —Prevent Pipeline Plugs

- Model waste transfer operations (coupling chemical reaction/precipitation and flow)
- Conduct tests to validate models and determine parameters for transfer without plugging.

Feed Preparation and Transport Tasks

- Solids Formation—Solids formation and dissolution, waste property data and predictive methods
 - Chemical and physical conditions leading to solids precipitation and gel formation
 - Viscosity of slurries
 - Chemical methods to remove pipeline plugs (Hanford and SRS)
 - Precipitation kinetics and precipitate properties
 - Confirm operating envelopes with Hanford wastes (New, RFP)
 - (Solubility and viscosity tests with actual wastes)
- Feed Stability
 - Pipeline slurry transport tests with simulated Hanford waste
 - Engineering modeling of slurry transport and saltwell pumping
 - Saltwell pumping tests with simulated wastes
 - Development of simulated waste recipes
 - Stability of supernatant mixtures (New, RFP)

Feed Preparation and Transport Tasks (continued)

- Sludge Settling
 - Effect of shear on settling rates and sediment properties of actual wastes
- Saltcake Dissolution Testing and Solids Characterization
 - Lab tests with actual saltcake
- ESP code development and validation
 - Comparison of ESP with literature data
 - Comparison of ESP predictions with saltcake dissolution tests
 - Expand ESP database to address Hanford saltcake

Solids Formation Ensure Thermodynamic Stability—Avoid Supersaturation of Major Components

- Determine chemical operating envelopes for Hanford pipeline transfers
- Includes phosphates, fluoride, nitrate, nitrite, and carbonate
- Measure simulated waste viscosities
- Identify and characterize solids (PLM, SEM, XRD)

Feed Stability/Waste Transport Chemistry Ensure that Saltcakes and Slurries Can Be Pumped

- Pipeline tests with simulated wastes to determine acceptable ranges of chemical and transport parameters to prevent pipeline plugging
- Bench-scale tests with simulated wastes to improve saltwell pumping; reduce plugging and increase availability
- Measure precipitation kinetics and precipitate properties (size, shape, density).
- Model transport of slurries and saltcakes using computational fluid dynamics code with chemical reaction, population balance.
- Evaluate data and transport model results to understand plugging mechanisms and determine stable regions of chemical-physical-transport parameters.
- Study solids formation in receiving tank from mixed saltcakes

Benefits From The Feed Stability Tasks

- Identify potential problems transferring specific wastes
- Provide data and tools to plan and evaluate waste transfers
- Develop a better understanding of plugging mechanisms
 - Physical
 - Chemical
 - Flow
- Improve waste transfer criteria
- Support waste staging
- Support waste transfer operations
- Identify and test improvements in saltwell pumping operations
- Improve understanding of plugging mechanisms
- Improve measurement and control requirements specifications
- Collaboration on modeling, data development, and evaluation

Topics For Further Discussion

- Slurry flow-loop tests at FIU
 - Transfer criteria
 - Solids fraction
 - Velocity
 - Reynolds no
 - Test Design
 - Candidate tanks
 - Pipe and jumper geometry/layout
- Modeling
 - Viscosity models for "needles"
- Recovery/restart from partial plug

Appendix B

OFFICE OF RIVER PROTECTION PRESENTATIONS

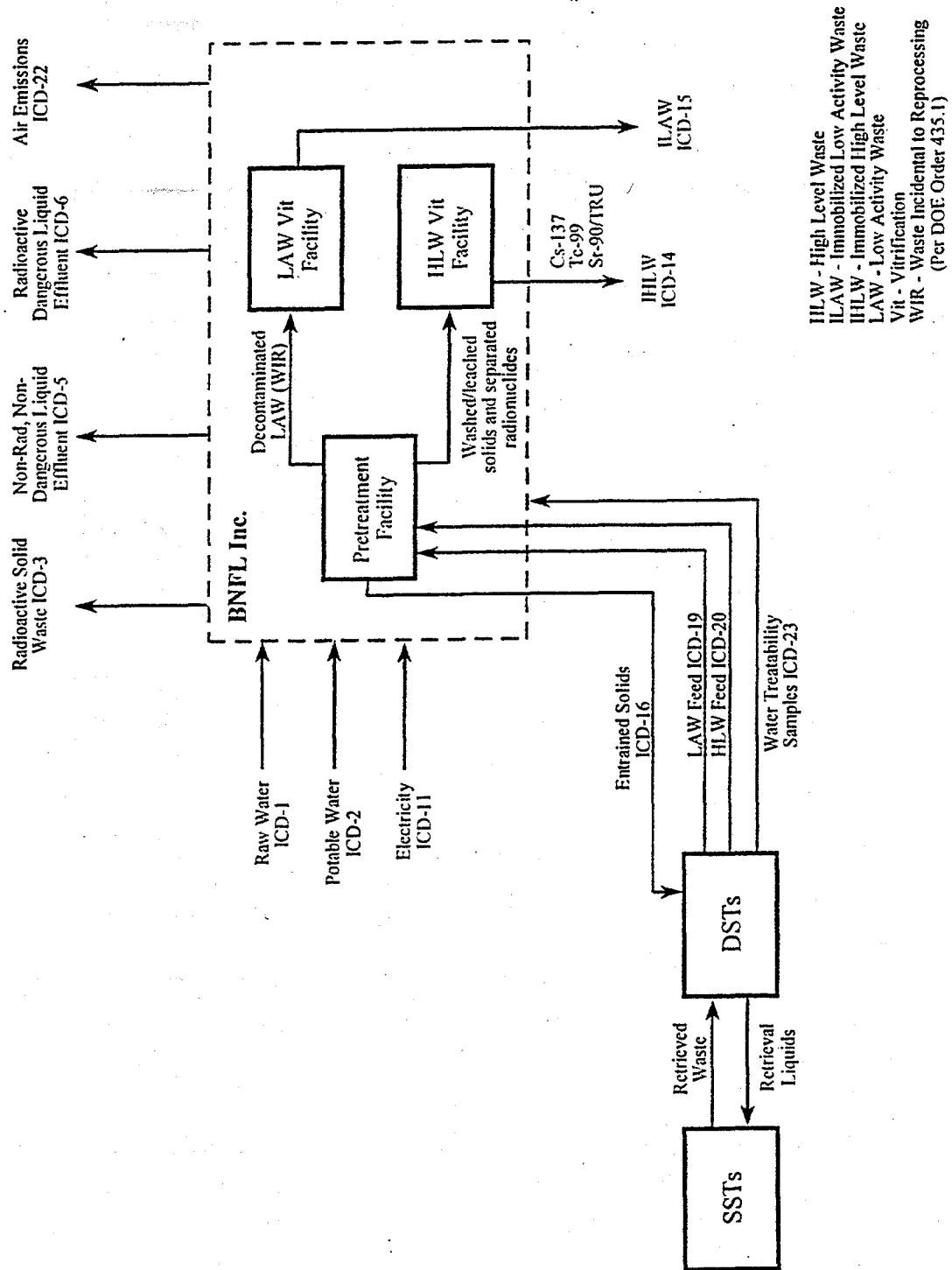
Overview of Privatization Waste Feed Delivery

By Randy Kirkbride

May 15, 2000

For the Saltcake Dissolution and Feed
Stability Workshop

Phase 1 Process Interfaces



LOW-ACTIVITY WASTE FEED STAGING SEQUENCE CASE 356 PHASE I

ENVELOPE	SOURCE TANK	STAGING TANK	BATCH
A	AP-101	1	
A		AZ-101, AZ-102 SUPERNATE	2
		PRETREAT B' WASTE	
C	AN-102	SUPERNATE	3
		SUPERNATE	4
A	AN-104	DISSOLVED SOLIDS	5
		SUPERNATE	6
C	AN-107	SUPERNATE	7
		SUPERNATE	8
A	AN-105	DISSOLVED SOLIDS	9
		SUPERNATE	10
A	SY-101	SUPERNATE	11
		SUPERNATE	12
A	AN-103	DISSOLVED SOLIDS	13
		SUPERNATE	14
A	AW-101	DISSOLVED SOLIDS	15
		SUPERNATE	16
A	AW-104 (SWL)	SUPERNATE	17
		SUPERNATE	18
A	SY-103	SUPERNATE	19
		SUPERNATE	20
C	AP-106 (SWL)	SUPERNATE	21
		SUPERNATE	22
C	S-102 (S-103, S-105)	SALTCAKE DISSOLUTION	23
		SALTCAKE DISSOLUTION	24
C	S-105 (S-106, S-108)	SALTCAKE DISSOLUTION	25
		SALTCAKE DISSOLUTION	26
A	AP-105 (SWL)	SUPERNATE	27
		SUPERNATE	28
A	AP-108	SUPERNATE	29

BNFL INC. TREATMENT FACILITIES

MINIMUM ORDER EXTENDED

*PO IS OUT OF SPEC
SWL - SALTWELL LIQUOR
(S-103, S-105) - WASTE FROM TANKS S-103 & S-105 ARE INCLUDED

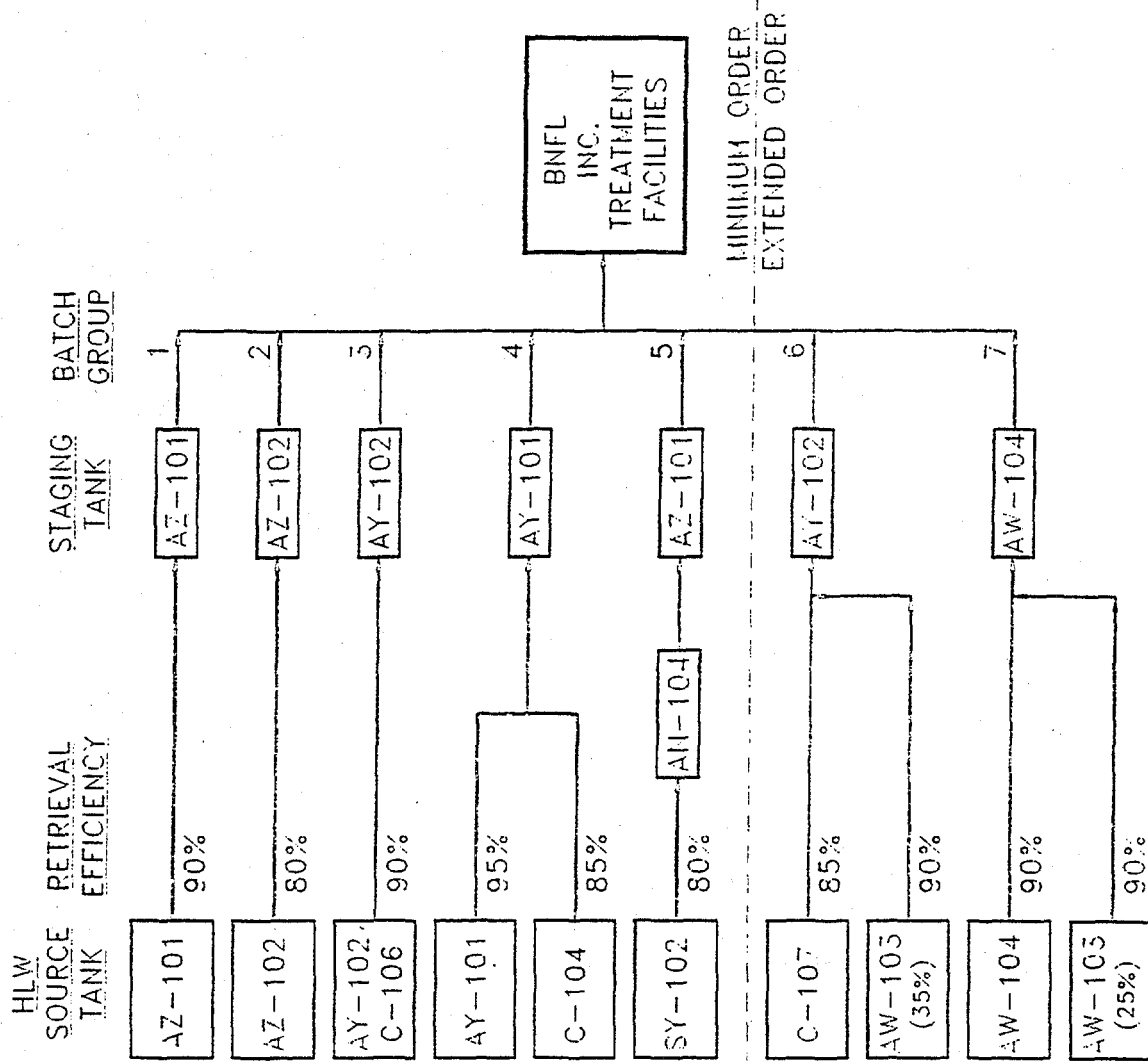


TABLE 10-1

Saltcake Chemistry and Feed Stability

- Need better understanding of chemistry for:
 - AN-104 dissolved salts “sulfate problem”
 - AN-102/AN-107 residual solids
 - HLW slurry compositions
 - SST waste blending
 - Tank farm system operation

**Single-Shell Tank Program
Single-Shell Tank Waste Retrieval Project**

**Carolyn Haass
Warren Thompson**

SALTCAKE DISSOLUTION AND FEED STABILITY WORKSHOP

**The Conference Center
Richland, Washington
May 16, 2000**

Mission Scope

- Retrieve waste from initial SSTs to provide waste feed for the treatment (vitrification) system during Phase 1 Privatization (4 tanks by 2018, first tank by 2007)
- Retrieve waste from SSTs to backfill DSTs during Phase 1 Privatization (approximately 15 tanks by 2018, first tank by 2009)
- Select and demonstrate cost-effective and efficient technologies for waste retrieval, leak detection and response, etc. to support SST waste retrieval
- Implement retrieval processes that allow for SST closure
- Develop the engineering and management foundation to support programmatic and regulatory decisions needed to plan and complete SST waste retrieval (e.g., cost of waste retrieval by tank, risk reduction resulting from waste retrieval, implication of tank waste remaining in tanks)

SST Current Status

- Of all tank waste, SSTs contain ~65% mass, ~70% long-term radionuclides. 67 of 149 SSTs are known or are suspected to have leaked.
- Other than Interim Stabilization and C-106, no recent retrieval of SST waste.
- Proposed work via modified FY 2000 work planning provides solid planning basis; initiates retrieval of SST waste by 2007 (demonstration of salt cake retrieval earlier).

Proposed Work Targets Key Tanks

- 58 SSTs contain ~90% long term radionuclides and ~75% (26 Mgals) waste
 - FY 2000 replanning (BCRs 00-32 and 00-36) initiates retrieval of this key SST waste.
- 52 SSTs contain less than ~1% long term radionuclides and ~10% (4 Mgals) waste
 - FY 2000 replanning (BCR 00-25) initiates interim closure activities potentially applicable to these tanks.
- SST baseline is updated accomplishing the above work.

Drivers for SST Waste Retrieval

- SSTs are planned as part of Phase 1 Waste Feed Requirements
 - 4 SSTs (241-C-104, C-107, S-102, and S-105)
 - 1 SSTs will be used for technology demonstrations (241-S-103)
- SST retrieval must proceed as soon as DST space becomes available (~FY 2009) to address public concerns on SST waste
- Satisfy RCRA/CERCLA requirements and Tri-Party Agreement commitments for SST waste retrieval and tank farm closure (Major Milestone M-45-00)
- Build credibility to attain the necessary funding commitment and regulatory support to begin and complete the SST waste retrieval and closure mission
 - Credibility of Phase 1 will be influenced by Phase 2 planning and agreement on mission requirements and end points

Technical Foundation

- In the next few years, ORP needs sound engineering and management foundation for a compliant regulatory path to conduct and complete SST waste retrieval and closure activities which
 - Address and reduce program uncertainties
 - Allow SST waste retrieval to safely and cost-effectively proceed
 - Establish a path for completing the ORP Mission
- Initial engineering must start immediately for SST retrieval for Phase 1 and DST backfill
 - Alternatives to Past Practice Sluicing have promise for cost reduction and will be demonstrated prior to deployment

Technical Approach

- Retrieve waste from SSTs on a fixed schedule and in sufficient quantity to feed privatized waste immobilization facilities
- Perform tank retrieval with one retrieval campaign -reentering for closure to be avoided - achieve closure requirements with single retrieval effort
- Select and demonstrate SST waste retrieval technologies in time to support design and construction of waste retrieval systems (solutions to the SST waste retrieval problem will require additional technology deployments)
- Implications (health and environmental threat) of tank waste releases to the environment will be an important factor in the development of requirements for SST waste retrieval and tank farm closure activities

SST Waste Retrieval is Segregated into Three Distinct Phases

- Phase 1 waste feed requirements
- Backfill of DSTs that are retrieved to provide waste feed during Phase 1 with SST waste
(this waste will be used during the initial years of Phase 2 to meet waste feed requirements.)
- Long-term SST waste retrieval (balance of mission)

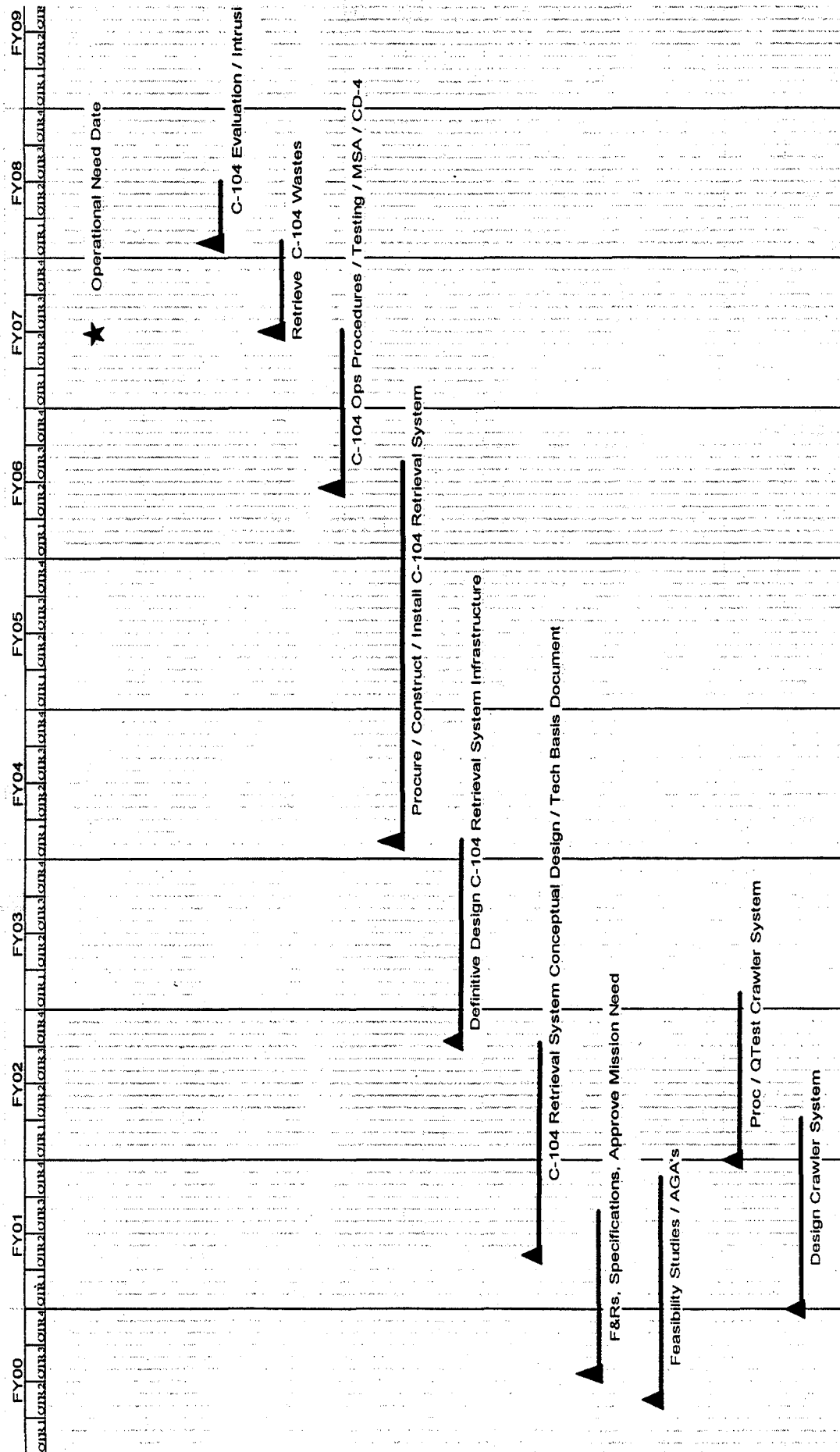
Goals for SST Waste Retrieval

- Meet Phase 1 waste feed requirements to retrieve SST waste by 2007 by assuming:
 - Accelerate retrieval of Tank 241-C-104 into Phase 1 Minimum Order (~4 years)
 - Use of past-practice sluicing until alternate technologies are available
 - Retrieval of 85% of the waste from each SST retrieved during Phase 1,
 - goal is to achieve closure requirements
 - Retrieval leak protection based on graded risk strategy developed under the Retrieval Performance Evaluation (RPE) process and described in the LDMM strategy document
- Plan for SST retrieval to meet balance of mission requirements by:
 - Establishing credibility for the life-cycle of the SST Program (technical, cost, and schedule)
 - Retrieving waste for Phase II (completion of the balance of mission)
 - Linking waste retrieval to tank farm closure activities, including groundwater/vadose zone activities

Replanning FY 2000 Proposed Work

- BCR 00-32: Accelerates C-104 sludge (Phase 1 feed material) retrieval 3 years. Initiates preliminary engineering this year.
- BCR 00-25: Initiates C-106 data collection to support “operational closure”. Performs SST degradation studies to support SST retrieval planning and prioritization.
- BCR 00-36: Deploys salt cake dissolution technology in SST, readies crawler for Operations training and deployment (both systems required for Phase 1 feed material and DST backfill).

Conceptual Schedule for SST Retrieval



Planned Accomplishments Through FY06

- Completed S-103 Saltcake Dissolution Retrieval
- Completed Construction of C-104 Retrieval Systems
- Initiated Construction of C-107 Retrieval Systems
- Attained C-106 Interim Closure Status
- In-Process for Interim Closure for Nine Additional SSTs
- Procured and Tested a Crawler Based Retrieval System
- Initiated Conceptual Engineering for S Farm Retrievals
- Initiated Testing for Remaining Systems Configurations

Expected Results/Outcomes

- Technologies for SST waste retrieval are available and demonstrated
- Technologies for closure and mitigation of subsurface contamination are known and feasible
- End point requirements are known and bounded
- A credible, defensible and traceable technical, cost, and schedule foundation

Single-Shell Tank Characteristics and Proposed Work

Single Shell Tanks	Long Term Radionuclide (LTR) Inventory	Tank Integrity	Waste Type	BCR Proposed Work	DST Backfill and Phase I Feed
149 Single-Shell Tanks	58 Tanks Contain 90% LTR in 25.7 Mgals	42 Sound Tanks Contain 71% LTR	24 Saltcake tanks, 42% LTR, 11 Mgal	BCR#36: initiates S-103 retrieval preliminary engineering. BCR#25: see below	11 tanks
			14 Mixed tanks, 26% LTR, 6 Mgal	BCR-032 & BCR#36: depending on outcomes in C-104 retrieval and crawler testing, apply best technology to these type of tanks. BCR#25: see below	4 tanks
			4 Sludge tanks, 3% LTR, 1 Mgal	BCR-032: C-104 retrieval preliminary engineering. BCR#25: see below	2 tanks
			15 Tanks which leaked <8000 gals contain 19% LTR	9 Saltcake tanks, 12% LTR, 5 Mgal 4 Mixed tanks, 5% LTR, ~2 Mgal 2 Sludge tanks, 2% LTR, <1 Mgal	BCR#36: low water volume methods - saltcake dissolution and crawler apply to leaking and potentially leaking tanks BCR#25: see below
		1 Saltcake Tank which leaked >8000 gals contains ~1% LTR		Cost data developed in retrieving the 58 tanks containing 90% LTR will help define "economically and technically achievable" for these tanks BCR#25: see below	2 tanks
	39 Tanks Contain 9% LTR in 5.6 Mgals (includes 21 past leaking tanks)				
	52 Tanks Contain 1% LTR in 4.1 Mgals (includes 30 past leaking tanks)			BCR-025: data collection from C-106 supports interim closure investigations for tanks with little waste. See below.	1 tank

BCR#25 funds assessments on SST initial conditions, applicable to the deployment of all retrieval technologies. BCR#25 also funds assessments of SST retrieval delays and the impact that has on selection of retrieval methods.

Status on Improving Hanford Waste Speciation Modeling Using OLI Software

Albert Hu

CH2M Hill Hanford Group Inc.

Steve Sandra and Brian Li

OLI Systems, Inc.

**Tank Focus Area Workshop on Saltcake Dissolution and Feed Stability
May 16, 2000 at Richland Conference Center, Washington**

Status on Current ESP modeling

- Application of ESP at Hanford Waste:
 - 1) Calculate the tank waste species at equilibrium;
 - 2) Simulate the waste process.
- Evaluations of ESP for Hanford application indicate that there are inconsistencies between the model predictions and observed analytical results, especially for undiluted waste.
- To perform the tank waste speciation prediction normally takes a day for one tank. Thus it takes over half year continuously to run one calculation for 177 tanks.

Improve the Accuracy and Efficiency on Hanford Waste Speciation Modeling

Accuracy:

Systematically reconstruct the database to model Hanford waste using the OLI regression utility and validate the limitations of the ESP model for extreme waste conditions.

Efficiency:

Develop a window-based code “Hanford Waste Speciation Prediction” that interfaces with the OLI software to customize and automate the modeling efforts.

Characteristics of Hanford Waste

Global Tank Waste Inventory				
Temperature range: 12 - 77 °C				
Density: 1.1 - 1.9 g/mL				
pH: 11.4 - 14.8				
Analytes	Total (Kg)	wt%	Cumulative wt%	M(mole/L)
Water	1.33E+08	43.67%	43.67%	36.45
NO ₃ ⁻¹	5.19E+07	17.08%	60.75%	4.14
Na ⁺¹	4.77E+07	15.70%	76.45%	10.26
OH(TOTAL)	2.25E+07	7.40%	83.86%	6.54
NO ₂ ⁻¹	1.24E+07	4.07%	87.93%	1.33
TIC(CO ₃ ⁻²)	9.50E+06	3.13%	91.05%	0.78
Al ⁺³	8.10E+06	2.66%	93.72%	1.48
PO ₄ ⁻³	5.69E+06	1.87%	95.59%	0.30
SO ₄ ⁻²	3.21E+06	1.05%	96.64%	0.16
TOC	1.50E+06	0.49%	97.14%	0.62
Fe ⁺³	1.33E+06	0.44%	97.58%	0.12
Si ⁺⁴	1.16E+06	0.38%	97.96%	0.20
F ⁻¹	1.14E+06	0.37%	98.33%	0.30

Customized Database

- **Strategy:** to study the major species of Hanford Waste such as NaNO_3 , NaNO_2 , Na_2CO_3 , NaOH , then add secondary species like NaPO_4 , NaSO_4 , NaF into databank. Then work on the minor/trace species such as Cr, Cs, Sr, which were identified to be important to waste operations.
- **Methodology:** to first establish parameters of the binary electrolyte in the multicomponent, $\text{Na-NO}_3\text{-NO}_2\text{-CO}_3\text{-OH-Al-PO}_4\text{-SO}_4\text{-F-Cr-H}_2\text{O}$, chemical system using OLI-modified Bromley electrolyte model ESP, then construct the new parameters for ternary or higher order systems. The newly constructed database will be validated with waste data stage-by-stage.

Major subsystems: $\text{Na-NO}_3\text{-NO}_2\text{-OH-H}_2\text{O}$

- For example, the major subsystem $\text{Na-NO}_3\text{-NO}_2\text{-OH-H}_2\text{O}$, the following binary and higher order electrolytes will be studied,
- Binary: $\text{NaNO}_3\text{-H}_2\text{O}$, $\text{NaNO}_2\text{-H}_2\text{O}$, $\text{NaOH-H}_2\text{O}$,
- Ternary: $\text{NaNO}_3\text{-NaOH-H}_2\text{O}$,
- $\text{NaNO}_2\text{-NaOH-H}_2\text{O}$,
- $\text{NaNO}_3\text{-NaNO}_2\text{-H}_2\text{O}$
- Quaternary: $\text{NaNO}_3\text{-NaNO}_2\text{-NaOH-H}_2\text{O}$,

Data Regression On $\text{NaNO}_3\text{-H}_2\text{O}$

- Experimental Data (195 data points):

Osmotic Coeff., water activity, and solubility data

Temperature: 0 to 118 °C

Concentrations: 0.1 m to 22 m

- Determine the Equilibrium constant for



- Determine ESP Parameters for
Na (ion) and NO_3 (ion) interaction.

ESP Activity Coeff. Parameters for Na and NO₃ Interaction

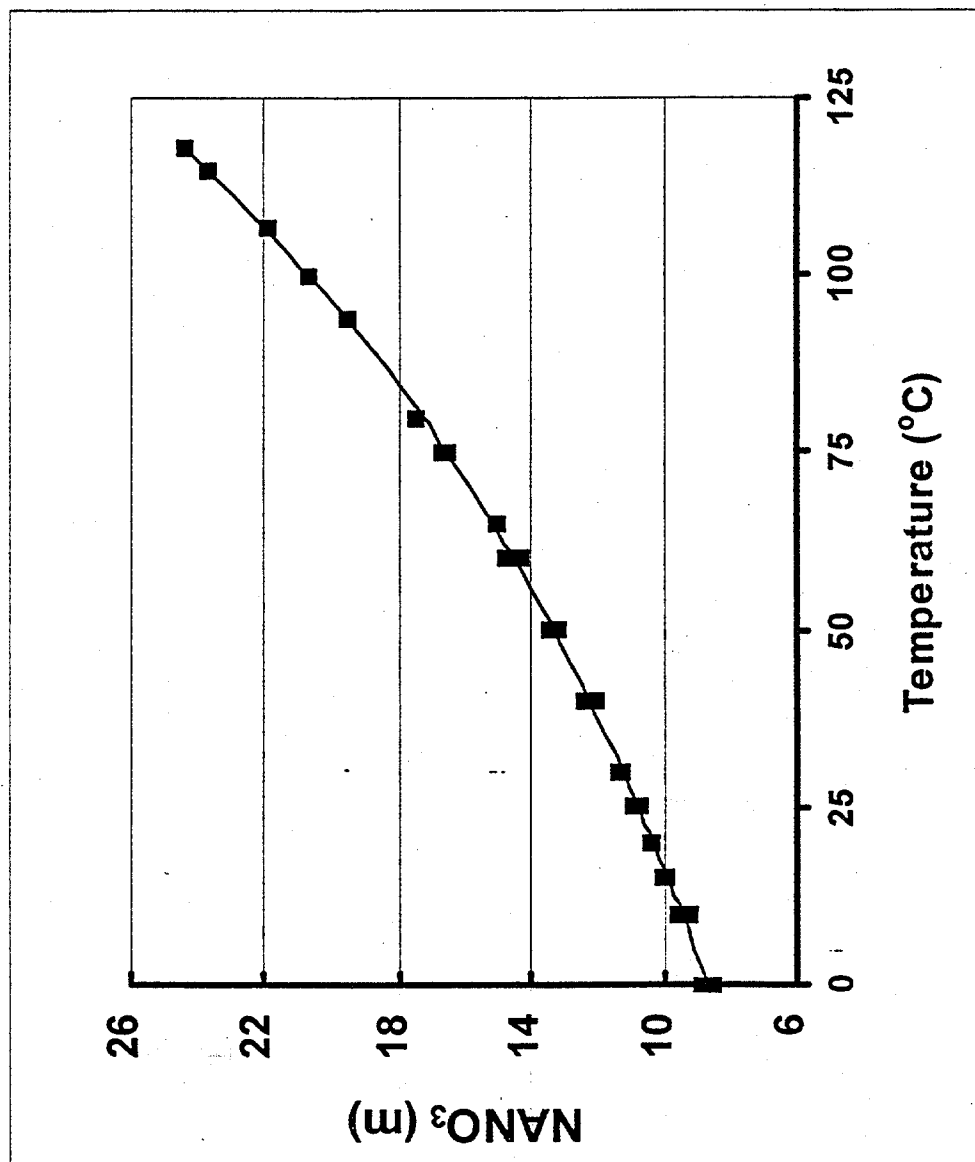
- Activity = Activity Coeff. X Concentration
 - Activity Coeff.
- = Long Range (z, I) + Short Range (... , b_{ij}, c_{ij} I, d_{ij} I², ...)
- where $x_{ij} = x_1 + x_2 T + x_3 T^2$ (x= b, c, and d)
- and ionic strength $I = 1/2$ Summation ($m_i z_i^2$)

Bromley Parameters for Na and NO ₃ interaction	
This work	Stern et al (1996)
b1 = 4.98E-3	b1 = 1.39E-3
b2 = 6.07E-4	b2 = 8.38E-4
c1 = -1.97E-3	c1 = -4.95E-3
	c2 = -1.81E-5
	d1 = 4.19E-4

$K_{eq}(\text{ppt})$ of NaNO_3

KFIT Parameters For K_{NaNO_3} (Solid)			
Coeff. ¹	This work	Public ²	Hanford ³
a	5.616	1.996	4.251
b	-814.48	-359.78	-941.95
c	-8.94E-03	4.87E-02	0.0
d	1.13E-05	4.82E-06	0.0
Note: ¹ The temperature dependent coefficient in $\log K = a + b/T + c T + d T^2$			
² The ESP databank			
³ Hanford databank based on Sterner et. al., 1996, PNWD-SA-4436, PNNL			
K-value for $\text{NaNO}_3(\text{ppt}) = \text{Na}^+ + \text{NO}_3^-$			
Temp.	This work	Public*	Sterner
0 °C	10.81	10.97	6.34
25 °C	16.66	16.66	12.34
50 °C	24.26	27.07	21.66
75 °C	34.03	41.07	35.08
100 °C	46.63	61.49	53.24
Note: *The data is out of the temperature range for this application			

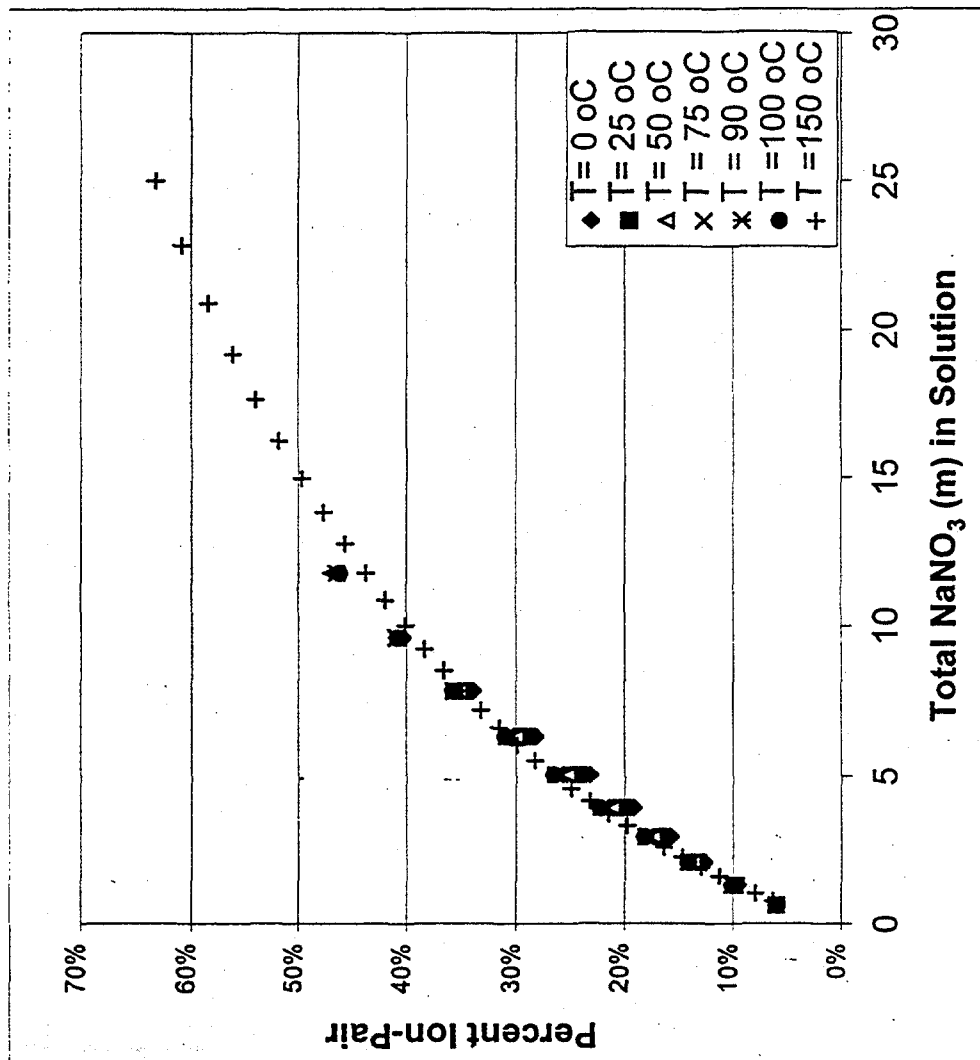
NaNO_3 Solubility in Water from 0 - 118 °C



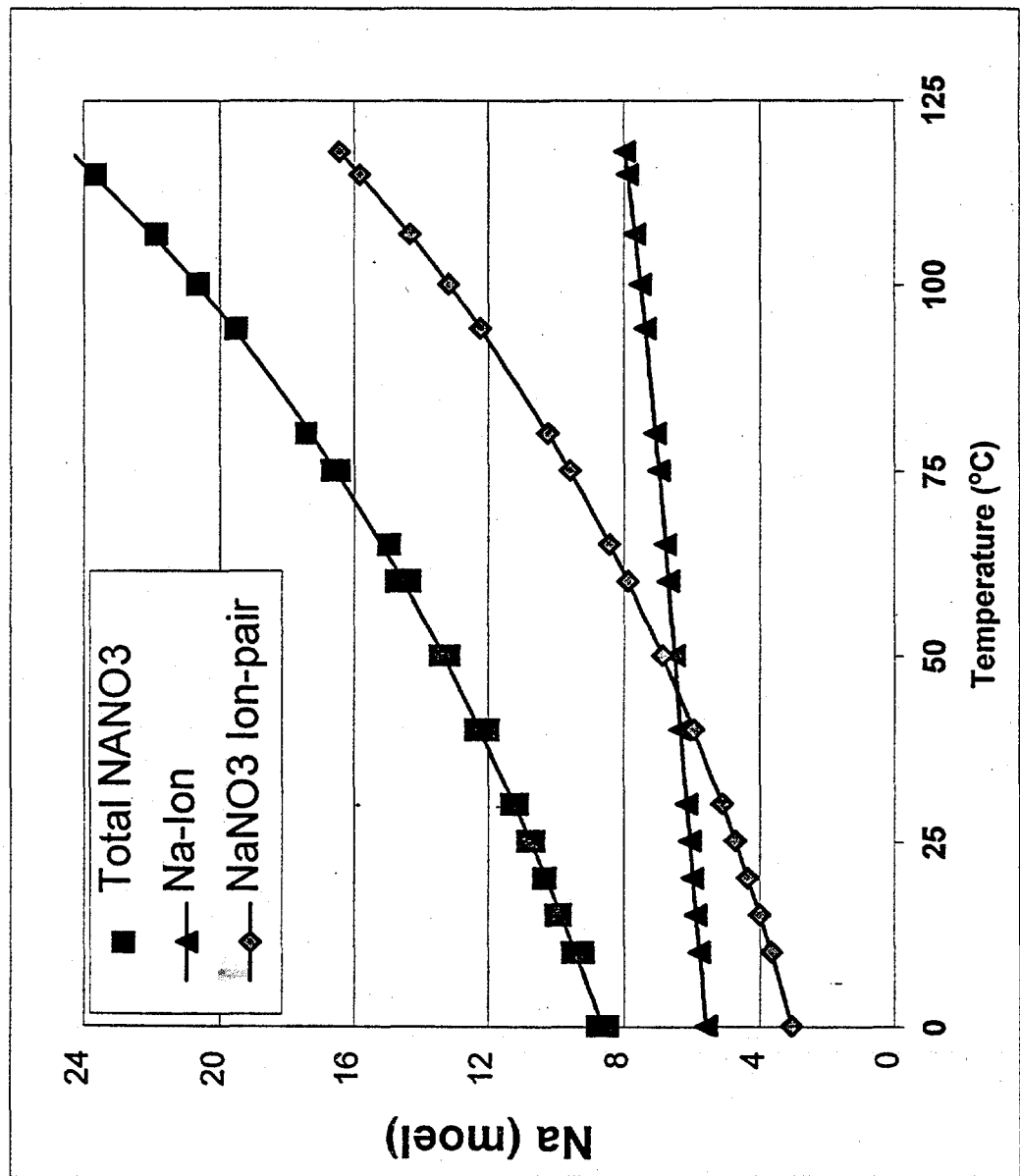
Keq (Aqueous) of NaNO_3

KFIT Parameters For K_{NaNO_3} (aqueous)				
Coeff. ¹	This work	ESP-Public ²	Sterner ³	Justice
a	0.579	1.903	0.588	NA
b	0.0	-56.98	0.0	NA
c	0.0	-5.96E-03	0.0	NA
d	0.0	4.53E-05	0.0	NA
Note: ¹ The temperature dependent coefficient in $\log K = a + b/T + c/T + d/T^2$				
² The ESP databank				
³ Hanford databank based on Sterner et al., 1997, PNWD-SA-4436, PNNL				
K-value for $\text{NaNO}_3(\text{aq}) = \text{Na}^+ + \text{NO}_3^-$				
Temp.	This work	ESP-Public ¹	Sterner	Justice ²
0 °C	3.79	51.52	3.88	NA
25 °C	3.79	54.25	3.88	3.55
50 °C	3.79	56.85	3.88	NA
75 °C	3.79	59.36	3.88	NA
100 °C	3.79	61.82	3.88	NA
Note: ¹ The data indicate the application out of temperature range				
² Justice, M.C. et al, Electrochim Acta, 1971, 16, 687.				

Percent NaNO_3 Ion-pair vs Total NaNO_3 in Water at Various Temperature



Distribution of Na ion and NaNO_3 ion-pair



Summary and Discussion of $\text{NaNO}_3\text{-H}_2\text{O}$

- This study generated a new set of interaction parameters and equilibrium constants using OLI software, and compared them with the data in Public and Hanford databank.
- In general, the $K_{eq}(\text{ppt})$ agree better with Public for $T < 50^\circ\text{C}$, and with Hanford for $T > 50^\circ\text{C}$
- The $K_{eq}(\text{aq})$ agree with Hanford and Literature value, while the value is 15 times smaller than Public databank
 - The large $K_{eq}(\text{aq})$ value in Public will predict most NaNO_3 in water is dissociated and overestimates ionic strength, which will change whole speciation calculations.
 - This work shows that NaNO_3 in water will only partially dissociate between 5.5 to 7.5 molal at saturate condition from 0 to 100°C .

Thoughts: Hydration of NaNO_3

- Aqueous data such as vapor pressure will reflect whether the NaNO_3 in water is associated or dissociated because for dissociation the charged ions will trap the polar molecule like H_2O .
- Hydration theory may explain the regression results quantitatively.
 - Hydration: an ion in aqueous solution is surrounded by H_2O .
 - Hydrated radii (Harris, 1996): 4.5 Å for Na^+ , 3 Å for NO_3^- , NO_2^- , Cl^-
 - Robinson (1948): the hydration number is 3.5 for each Na and Cl ion.
 - Since NO_3^- , NO_2^- , and Cl^- have the same hydrated radii, it is logic to set hydration number as 3.5 to each Na and NO_3^- ions. From the regressions, the ratio of moles water to dissociated Na and NO_3^- ion per liter is about 4.2 in this work and 4.0 for Sterner et al (1996), which is close to the hydration number of Na and NO_3^- .
- Possible experiment: FTIR in Aqueous Solution

On-going and Near Future Work

- To continue the regression work on $\text{Na-NO}_3\text{-NO}_2\text{-OH-H}_2\text{O}$ system
- To study $\text{Na-Al-OH-H}_2\text{O}$ system and the system with NaNO_3 and NaNO_2 salts.
 - Dan Herting's (FDH) data
 - Jun Liu's (PNNL) data
 - Literature data
- To study the system of $\text{Na-PO}_4\text{-OH-H}_2\text{O}$ and $\text{Na-SO}_4\text{-OH-H}_2\text{O}$.
- The newly established parameters will be reviewed by OLI, validated with waste data continuously, and documented.

General Comments on Existing Databanks

- **ESP Public databank need to be customized systematically to characterize Hanford waste.**
- **Efforts in the Hanford databank (Stern et al. 1996) provide a good start and guidelines to better characterize the parameters for the databank reconstruction.**
- **Special databank (MacLean) and other available databank contains information of species identified in Hanford waste but not available in Public and can be evaluated and consolidated to reconstruct the databank.**

Hanford Waste Speciation Prediction (HWSP) Code

- HWSP is a customized code to speed-up and automate the efforts for modeling Hanford Waste using OLI software
- HWSP code developed in Visual-Basic within MS Excel provides front-end capability to interface OLI thermodynamic code and can be bridged to other engineering calculations such as HTWO modeling.
- Phase I development focused on automating the speciation modeling of the tank waste inventory. The code incorporates all the required user interactive procedures and possible logic/iterations of modeling efforts to get the speciation results in one-keystroke.
- Phase II development will automate process simulations like dilution or leaching.

Current Status of HWSP

- The code predicts the species directly with input tank waste inventory, and it can handle five tanks at one time and takes about half hour per tank.
- It provides the choice to reconcile the input data and the choice to optimize the input data to match the Cr, TOC, pH, and wt% water data in liquid phase.
- Needs more polishing, feature-adding and validation to work properly and easily. It also requires a better database to understand the issues while developing the logic to automate the simulation.

Acknowledge

- Thanks to CHG Retrieval Engineering/Process Development for providing funding.
- Thanks to Graham MacLean, Randy Kirkbride, Ron Orme, James Jewett, Jim Person, Dan Reynolds and Kent Hodgson for their input and useful discussion.
- Thanks to Andy Felmy for providing the experimental raw data and useful discussion.

STATUS OF WASTE TRANSFERS, CRITERIA, AND PLUGS

By
D. A. Reynolds
CH2M-Hill Hanford Group

CH2M-HILL
SERIAL 13

INTRODUCTION

- Hanford has 53.7 millions of gallons of waste – all has to be moved.
- The solids will be dissolved or slurried to move.
- Currently are removing liquid waste from single-shell tanks (about 1 million gallons per year.)

CH2M-HILL
SERIAL 13

Topics of Discussion

- Official Criteria
- Recent Pipeline Plugs
- Chemistry of these plugs
- Successful Process Parameters
- Where To Go From Here

CH2M-HILL
SERIAL 13

Current "Official" Criteria

- Waste Compatibility Program has limits for liquids and slurries of 1.41 specific gravity.
- Cross-site Transfer System has limits for liquids and wt% solids. Currently only transferring liquids.
- Liquids must stay below 1.35 SPG with less than 30 wt% solids.

CH2M-HILL
SERIAL 13

Recent Plugs

- There has been three plugs in the last 5 years.
- BY-103
- SX-104
- U-103

CH2M HILL
Engineering & Construction

BY-103

- Was let pumping without dilution and told to shut off without flushing due to flammable gas concern.
- Some months later the plug was discovered.
- Could move plug about 400 feet from either end.
- Could not attack with chemicals.
- Abandoned the pipeline.

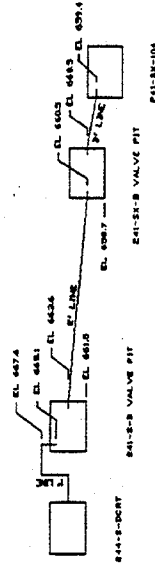
CH2M HILL
Engineering & Construction

SX-104

- Pumping with ineffective dilution.
- Stopped for a while. Plug formed in unheated jumper on restart.
- Eventually unplugged with hot water flush.
- Improved dilution scheme.

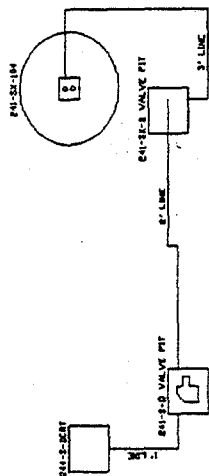
CH2M HILL
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SX-104 Pipeline



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SX-104 Pipeline



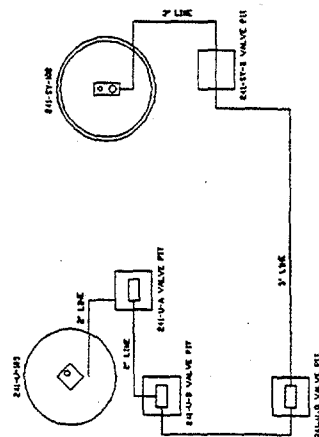
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U-103

- Pump stopped. No flush for over 24 hours.
- On restart, a plug formed in non-heat traced jumper.
- Jumper pulled to break plug.
- Currently using the line.

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U-103 Pipeline



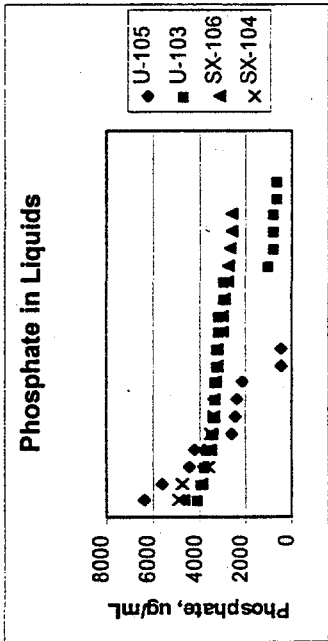
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Chemistry of Plugs

- Liquid from salt cake is at saturation and often warm.
- Sodium phosphate is special problem due to crystal habit, low solubility, and high temperature dependency.

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Phosphate Composition of SX and U Farm Tanks



Phosphate Phase Diagram Showing Temperature Dependency

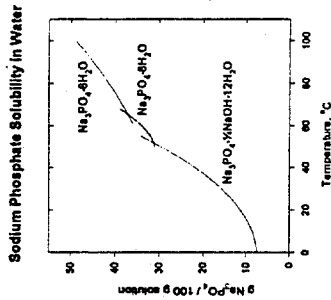


Photo of Sodium Phosphate



Photo of Sodium Fluoride Phosphate



BY-103 Liquid Composition

• Sodium	9.35 M
• Nitrate	2.7 M
• Nitrite	1.17M
• Hydroxide	2.21 M
• Aluminum	1.54 M
• TIC	0.31M
• Phosphate	0.009M
• %H2O	59%
• Density	1.29g/mL

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SX-104 Liquid Composition

• Sodium	10.0M
• Nitrate	4.68M
• Nitrite	2.12M
• Hydroxide	1.40M
• Aluminum	0.96M
• TIC	0.19M
• Phosphate	0.0715M
• %H2O	51%
• Density	1.48g/mL

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U-103 Liquid Composition

• Sodium	10.5M
• Nitrate	2.8M
• Nitrite	2.8M
• Hydroxide	2M
• Aluminum	1.4M
• TIC	0.3M
• Phosphate	0.017M
• %H2O	50%
• Density	1.43g/mL

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Successful Dilution Strategies and Flushing

- 1:1 has worked for dilution
- 1:1 up to 2 gpm of water, then 2 gpm water max
- Flush with 1 line volume
- Flush when pump down for > 2 hours
- Flush every week
- Currently, flush every 21 days
- Clock reset every time flush
- Assuring heat trace is functional

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Where To Go From Here

- Adding dilution and flush water increases the volume of waste.
- Stopping to flush increases operating time.
- Need to dilute lowers the rate waste is removed from tanks.
- Optimizing dilution to minimize cost and schedule is desirable.
- Not much literature on flushing lines to avoid plugging.

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