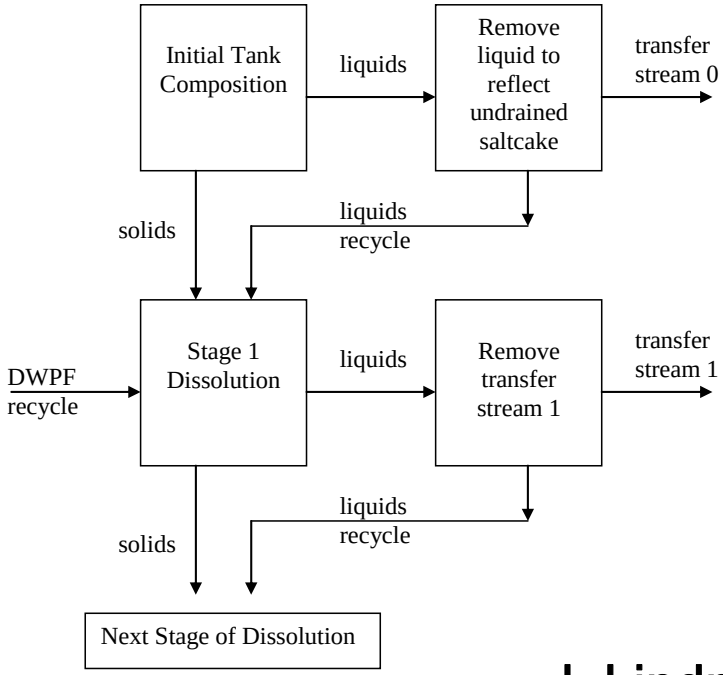
Thermodynamic Modeling Studies



J. Lindner, L. T. Smith, J. C. Luthe, L. Pearson.
R. K. Toghiani, Y. Xia, and P. Naik
Institute for Clean Energy Technology
Mississippi State University
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Overview of Presentation

- Database Activities and Needs
- C farm retrievals and neural network development
- Thermodynamic data and computational methods for liquid waste flowsheet modeling (SRS)
- Aluminum solubility studies

Database Activities and Needs

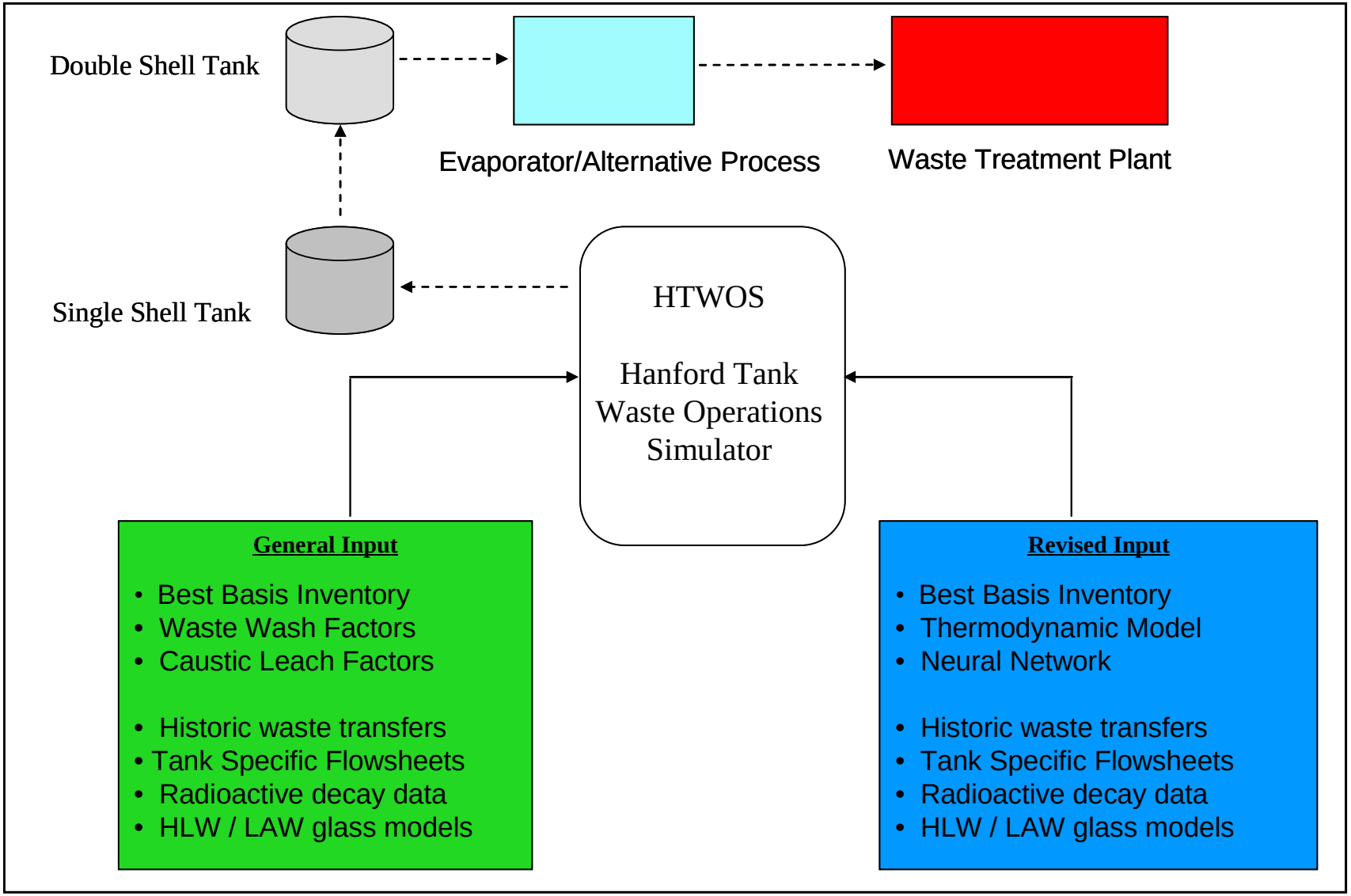
- Earlier a mid-term study addressed the solubility of a number of systems if interest to saltcake dissolution

$Na\text{-}F\text{-}NO_3$	$Na\text{-}NO_2\text{-}CO_3$	$Na\text{-}SO_4\text{-}PO_4$
$Na\text{-}F\text{-}NO_3$	$Na\text{-}NO_2\text{-}CO_3$	$Na\text{-}SO_4\text{-}CO_3$
$Na\text{-}F\text{-}PO_4$	$Na\text{-}NO_2\text{-}SO_4$	
$Na\text{-}PO_4\text{-}NO_3$	$Na\text{-}NO_3\text{-}SO_4$	
$Na\text{-}F\text{-}PO_4\text{-}NO_3$		

- The data were analyzed and fit resulting in the ESP double salt database (DBLSLTDB).
- In mid-2007 ICET entered into a subcontract with OLI Systems Inc to port the database to the mixed solvent electrolyte MSE formalism.
- OLI work was completed in early 2008.
- MSE does not yet contain some important systems, notably oxalate.
- Additional simulation in connection with SRS streams have indicated that the NAS chemistry is not completely represented in ESP or MSE.
- Previous work at SRNL resulted in the zeolite database and this compilation should eventually be incorporated into MSE.

C-farm retrievals and neural network development

- The Hanford Tank Waste Operations Simulator (HTWOS) uses wash/leach factors in place of thermodynamic data as a basis for its determinations.
- Accuracy of wash/leach factors is potentially an issue with difficult systems (Al, phosphate)
- Idea was to incorporate equilibrium chemistry in HTWOS
- Use ANN (Artificial Neural Network) model in place of explicit computations.
- Create ANN: train with the ESP transfer/mixing chemistry results.
- Target was C-farm retrievals

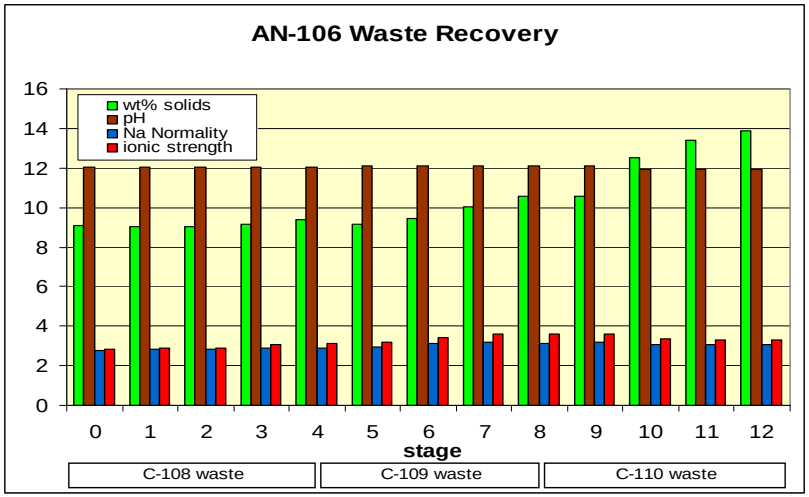

Double Shell Tank
Evaporator/Alternative Process
Waste Treatment Plant
Single Shell Tank
HTWOS
Hanford Tank Waste Operations Simulator
General Input
• Best Basis Inventory
• Waste Wash Factors
• Caustic Leach Factors
• Historic waste transfers
• Tank Specific Flowsheets
• Radioactive decay data
• HLW / LAW glass models
Revised Input
• Best Basis Inventory
• Thermodynamic Model
• Neural Network
• Historic waste transfers
• Tank Specific Flowsheets
• Radioactive decay data
• HLW / LAW glass models

Simulation results for AN-106

Equilibrium Model using ESP

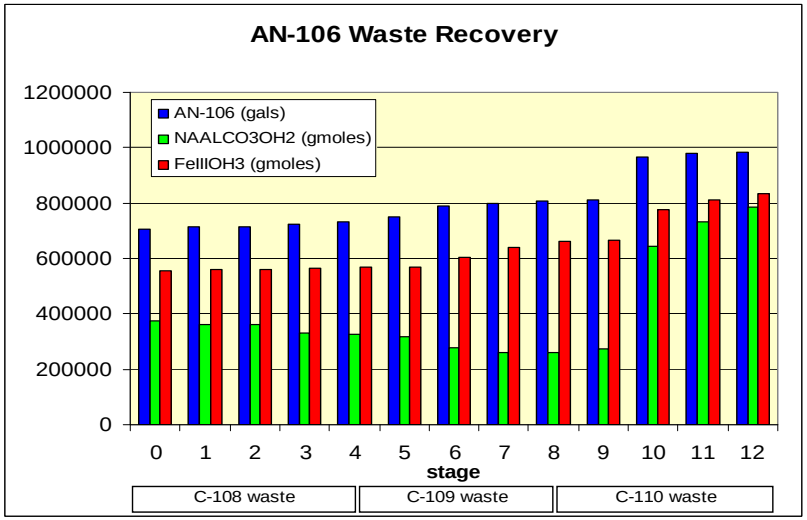
Stages based on:

- Retrieval Method.
  - Modified sluicing with recycle (MSwR)
  - Mobile retrieval system (MRS)
- The amount of waste retrieved.
- The percent of entrained solids attained.



Constraints (MSwR)

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



Status C-farm retrievals and neural network development

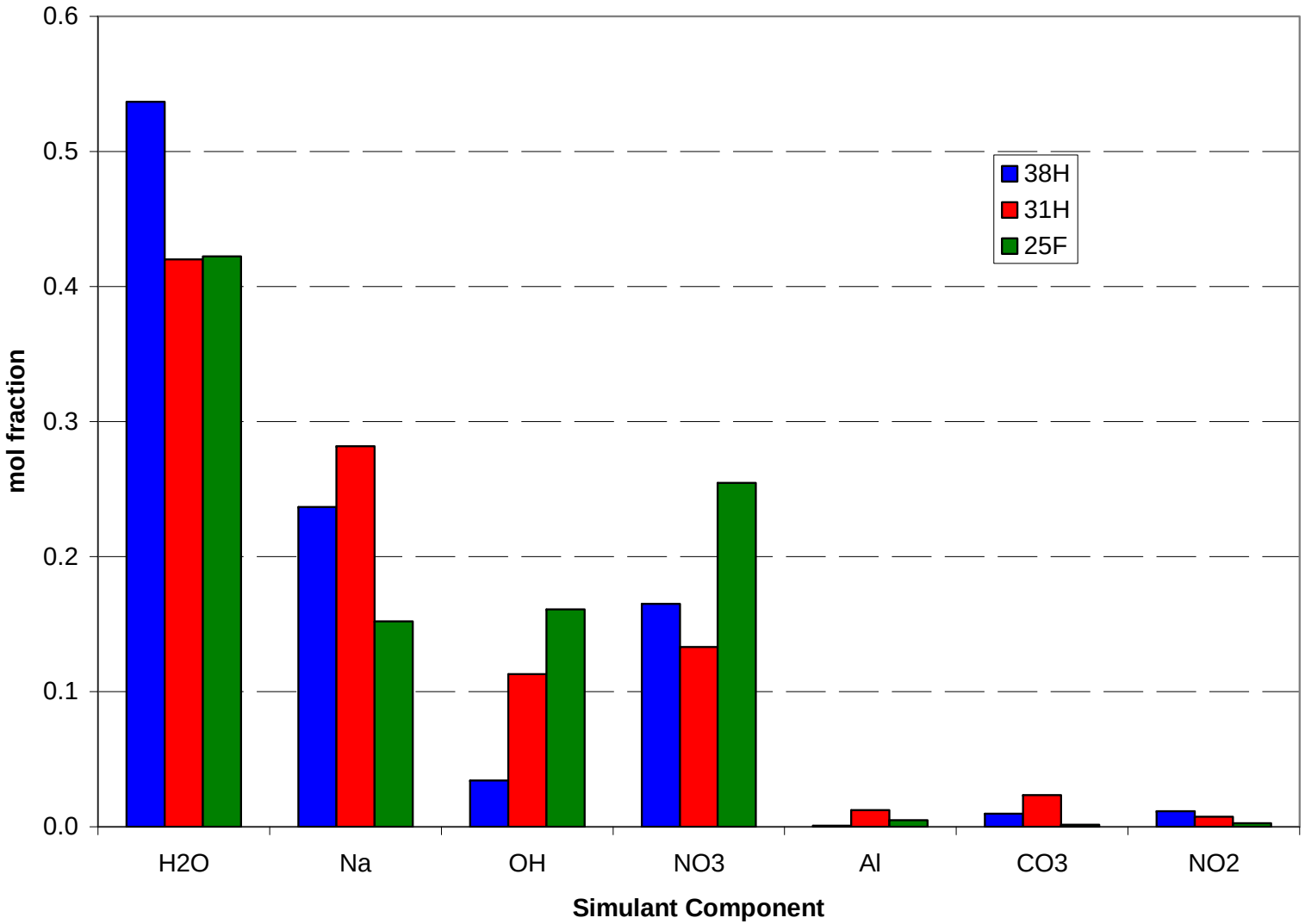
- Developed a thermodynamic model using ESP for MSwR and MRS retrievals.
- Simulated C-farm projected tank retrievals and generated tank and process stream parameters.
- C-101, C-102, C-104, C-105, C-107, C-108, C-109, C-110, C-111, C-112. routing into either AN-101, AN-106, AY-101, AZ-101.
- Modeling report in editing.
- Used the ESP simulation framework to develop ANN training sets for specific C-farm tanks.
- Adapted the standard interactive ESP program user interface for batch mode using a platform independent programming language (PERL).
- Developed the PERL program to loop through input stream ranges, construct ESP model input files, and collect ESP model output for input to the ANN.
- Building cases to populate ANN.

Thermodynamic data and computational methods for liquid waste flowsheet modeling (SRS)

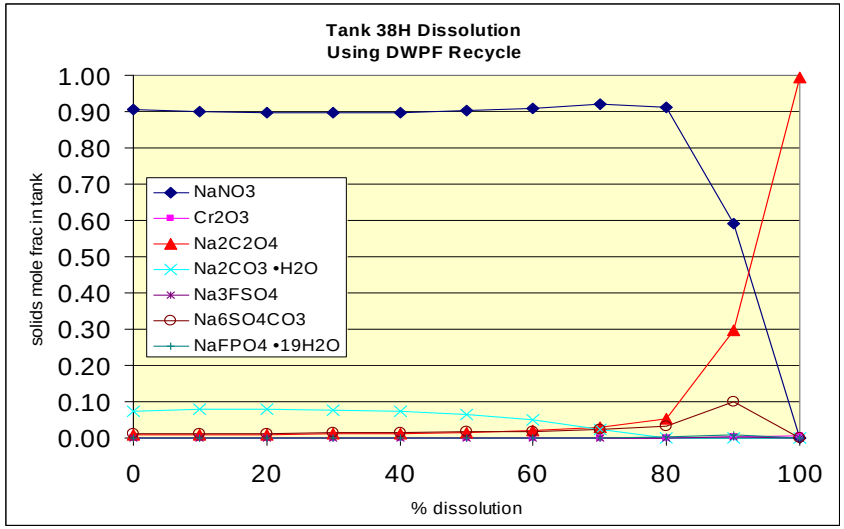
- Work has continued on the analysis of streams, blending, and associated process effects.
- Streams that are of interest are:
  - Dissolved salt solutions
  - High Al and OH streams from caustic leaching
  - High Si DWPF recycle stream

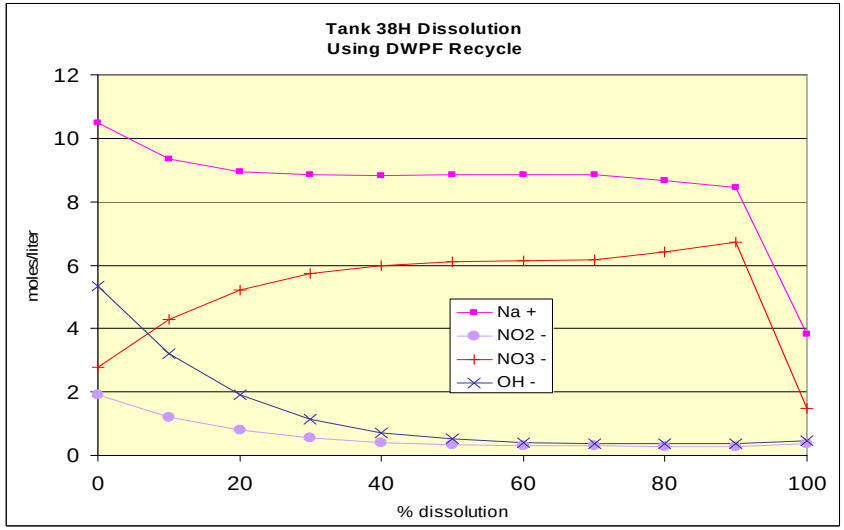
- Calculations have been performed on waste from three SRS tanks, 25F, 38H and 31H.
  - Saltcake dissolution using the DWPF recycle stream
  - Corrosion control using the Batch 5 leachate
  - Blending
  - Carry over into the 0.05M HNO_3 CSSX scrub solution

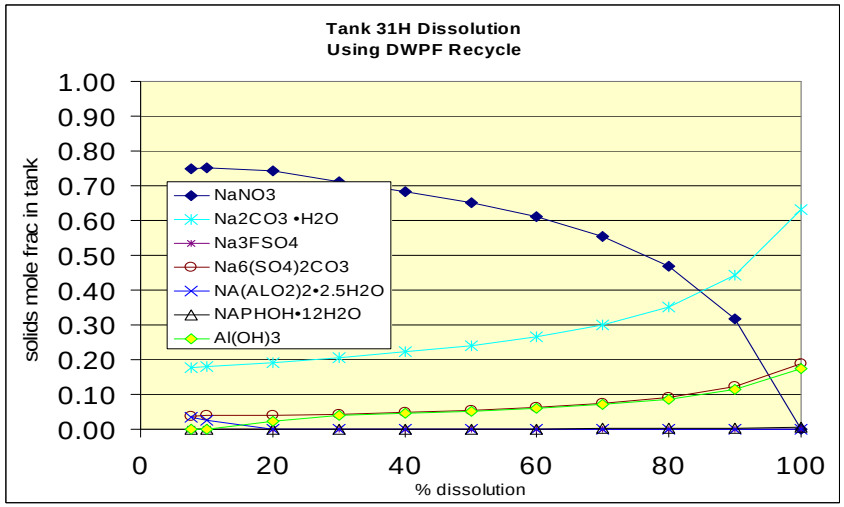
SRS Waste Comparison

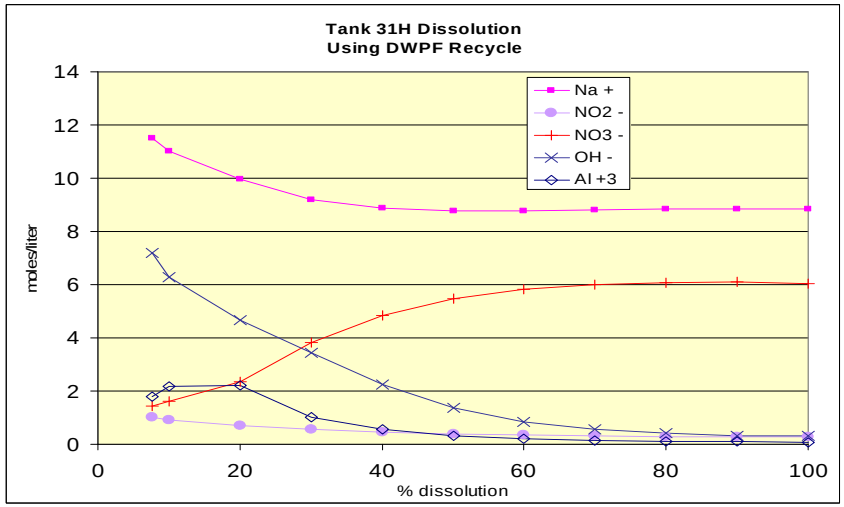


Tank Dissolutions 31H and 38H





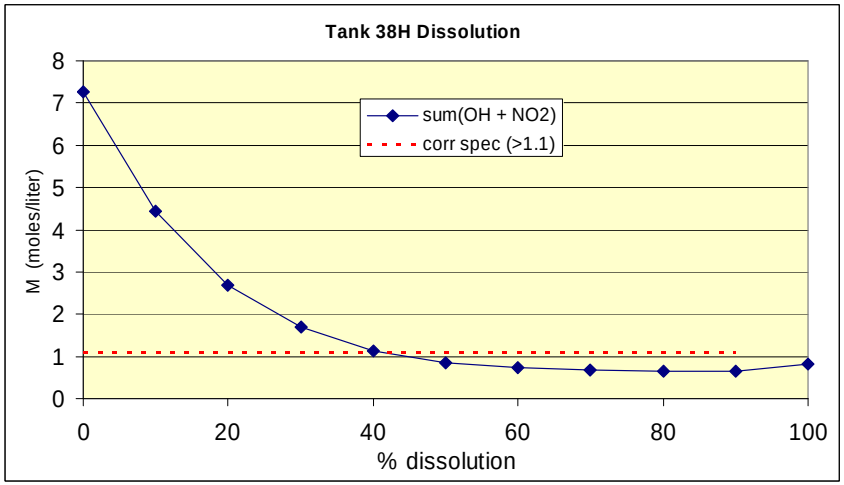


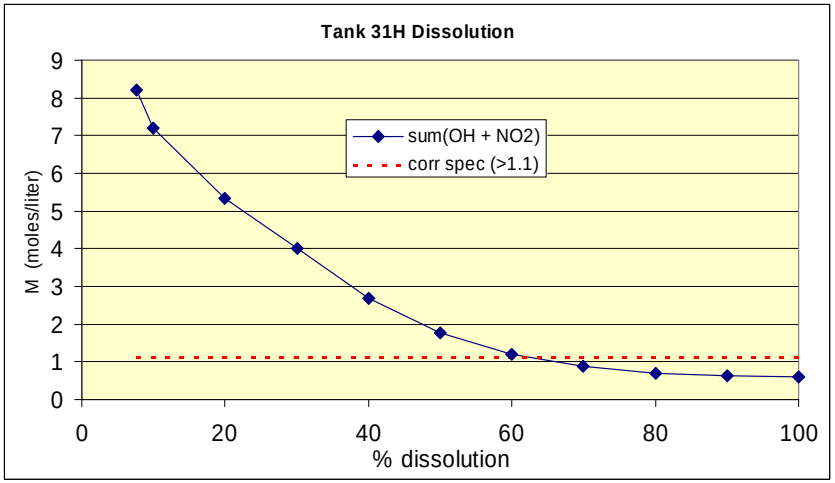


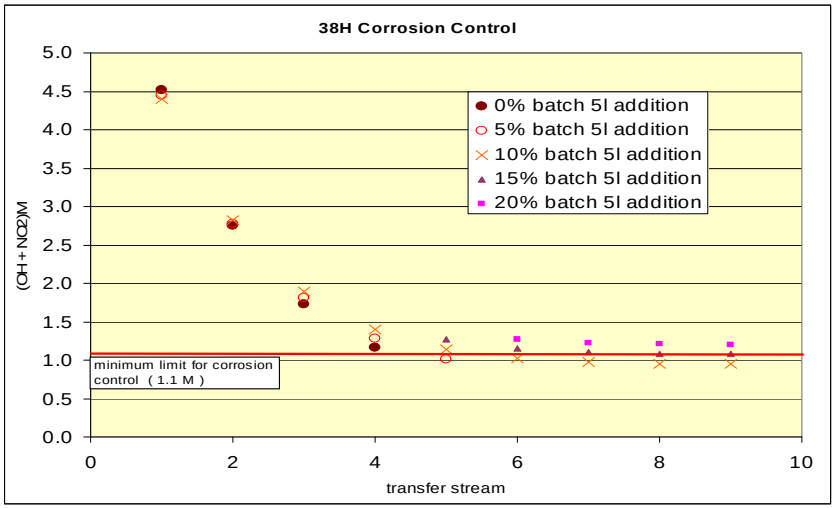
Solids speciation

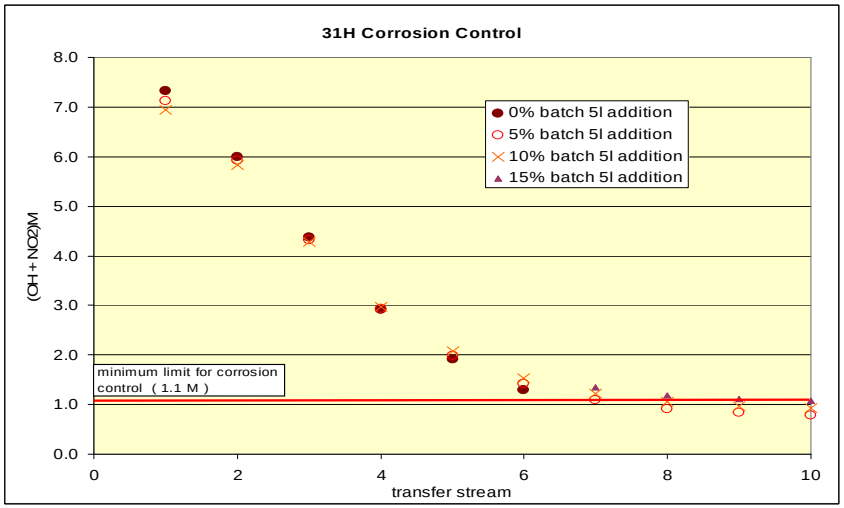
Aqueous phase composition

Data showing the attainment of corrosion inhibition through addition of the Batch 5 leachate

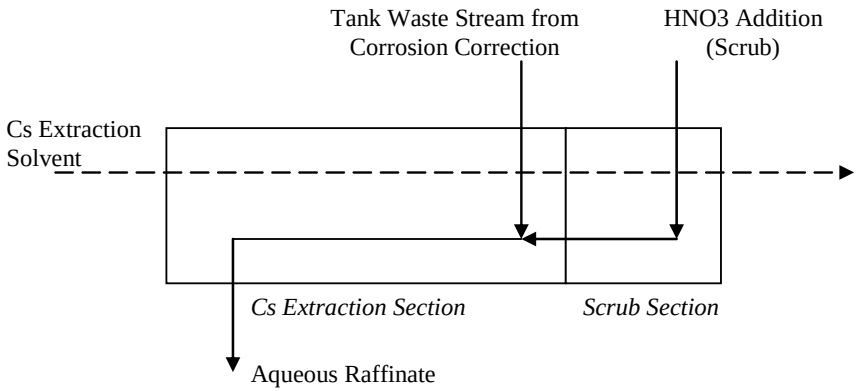


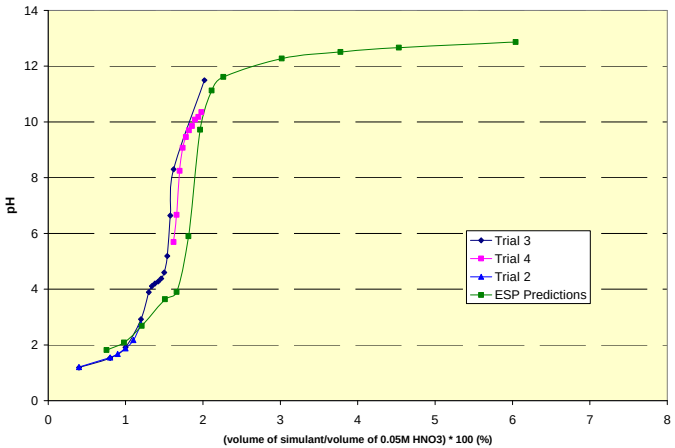


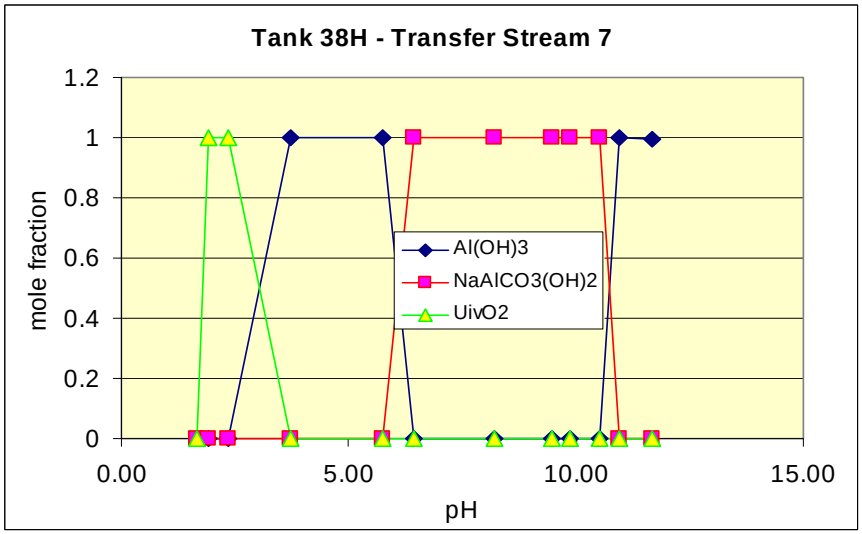


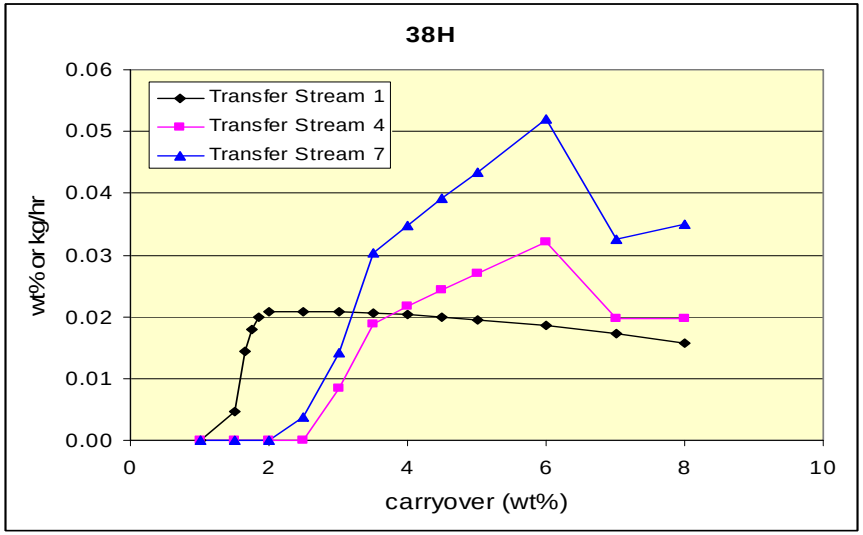


Solids formed in MCU process for 38H and ESP predictions for pH and % carry over compared to Parsons experiments

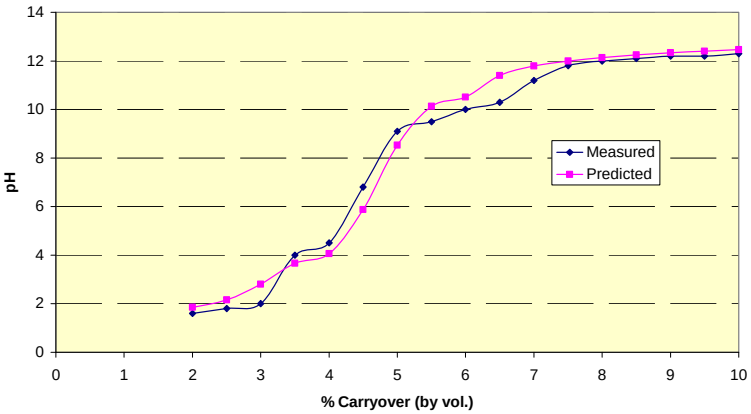


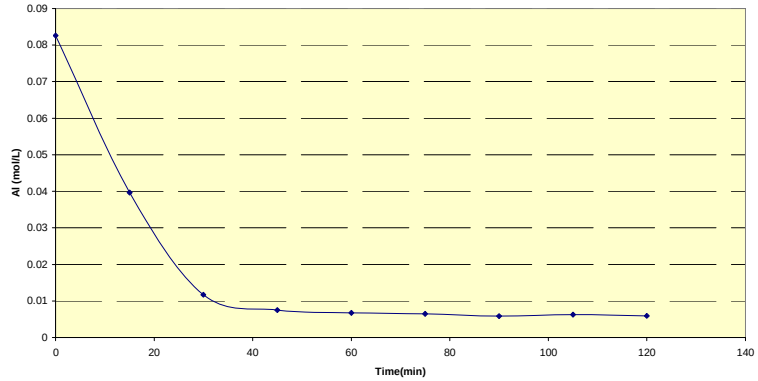






Initial results from experimental studies, simulant based on transfer stream 4 from 25F simulation





% Carryover	Solid Phase Observed
2	
2.5	
3	
3.5	
4	gel (within an hour)
4.5	gel like (1 week)
5	gel like (2 weeks)
5.5	solids (2-weeks)
6	solids (2-weeks)
6.5	
7	
7.5	
8	

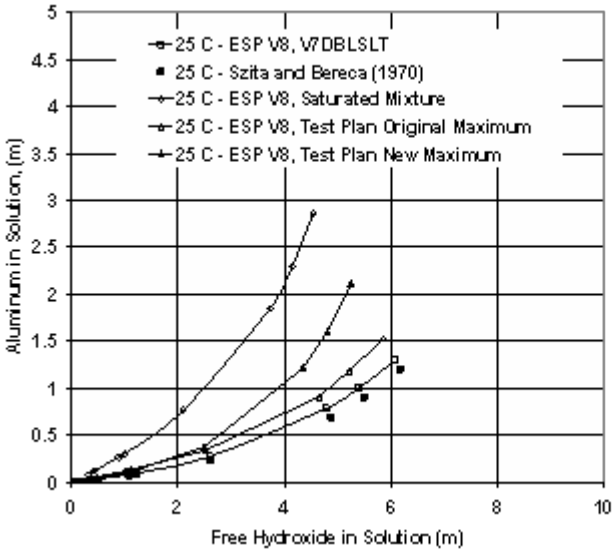
Kinetic Studies in Progress

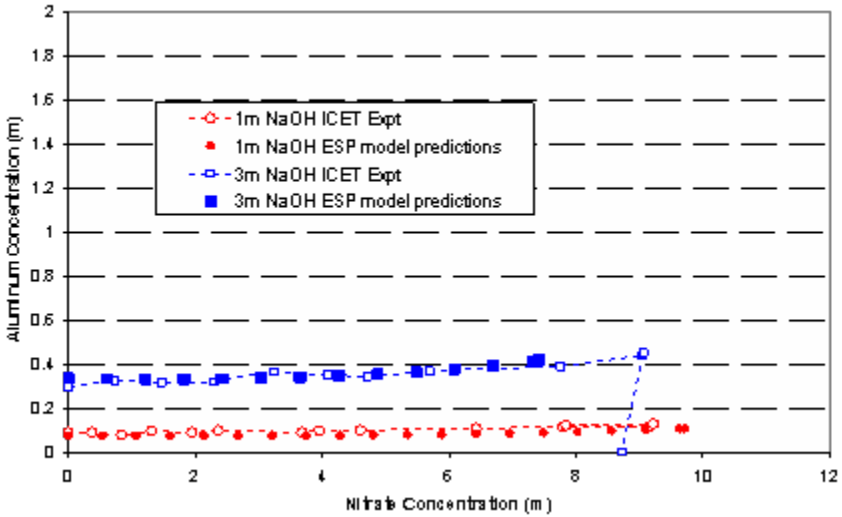
Status: Thermodynamic data and computational methods for liquid waste flowsheet modeling (SRS)

- Expected compositions from three SRS tanks, 25F, 31H and 38H, have been modeled.
- DWPF recycle stream can be used as a diluent for 25F and 38H, 31H showed re-precipitation carbonate solids.
- Batch 5 leachate is effective in adjusting OH^- and NO_3^- loadings to provide corrosion inhibition.
- Gibbsite and Dawsonite were predicted to form in the MCU process. The formation range for Dawsonite is between a pH of 5 and 10.
- Work begins on waste from SRS tank 37H (high Al, high Si)
- Experimental studies are in progress on mixing simulants with 0.05M HNO_3.

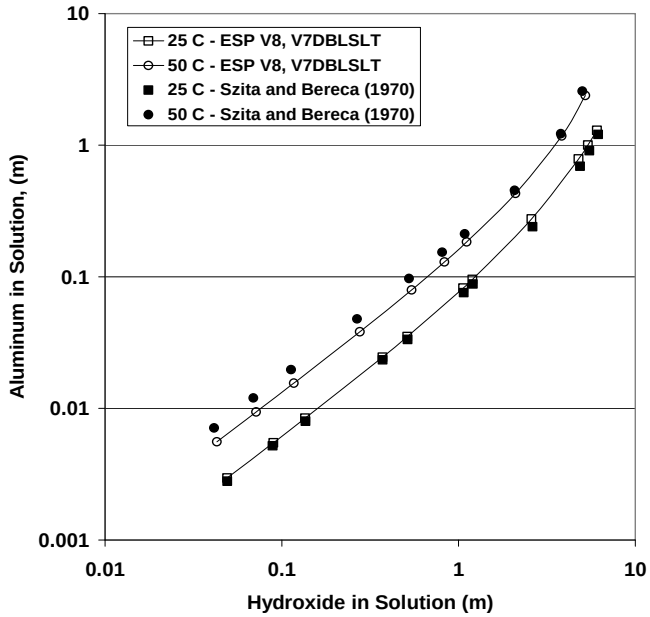
Aluminum Solubility Studies

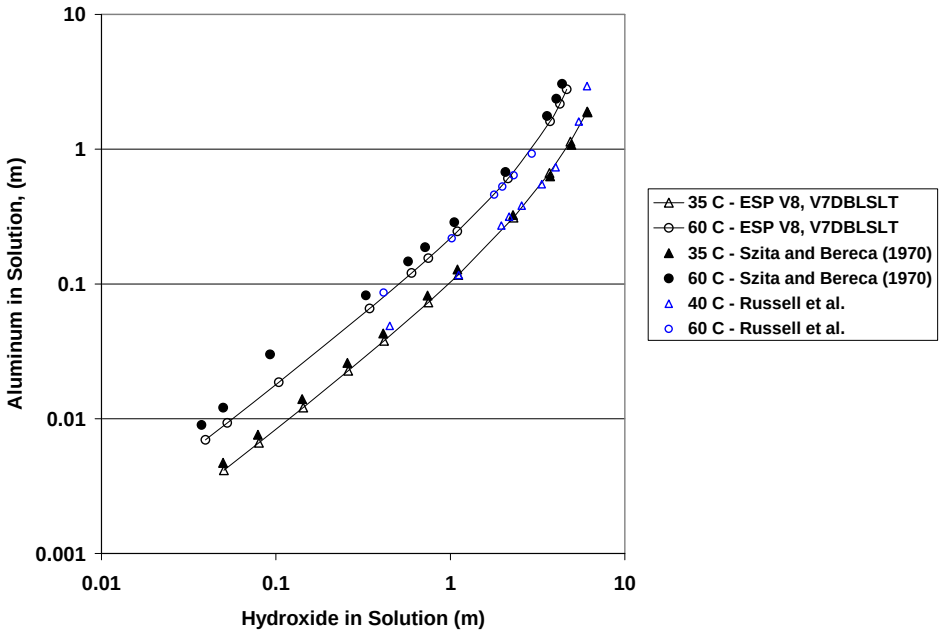
- Maintaining Al in the aqueous phase requires substantial caustic
  - aids in separating HLW from LAW, however.
  - results in LAW volume, cost, and schedule issues and may impact WTP through solids re-precipitation.
- Role of the interactions of other common species on Al solubility is not well understood
  - only limited data available and only for restricted $NaNO_3$ loadings.





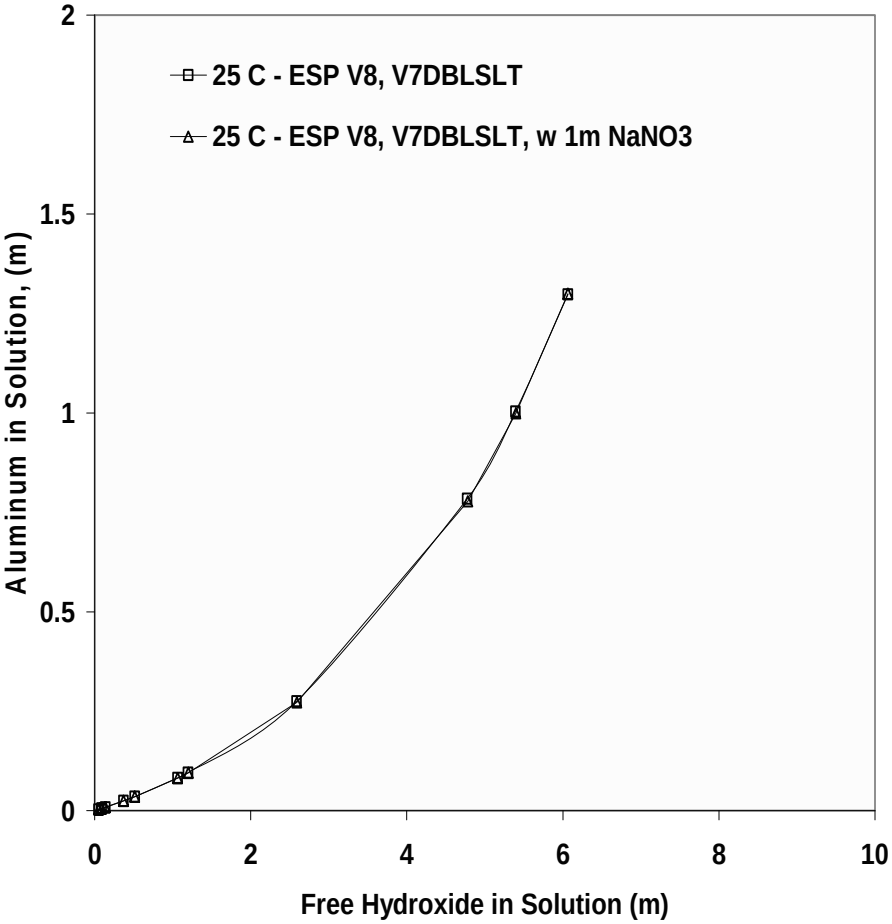
Comparison of ESP predictions (V8 and V7DBLSLT) to Literature Data at 25, 35, 40 and 60°C (Al-Na-OH system)

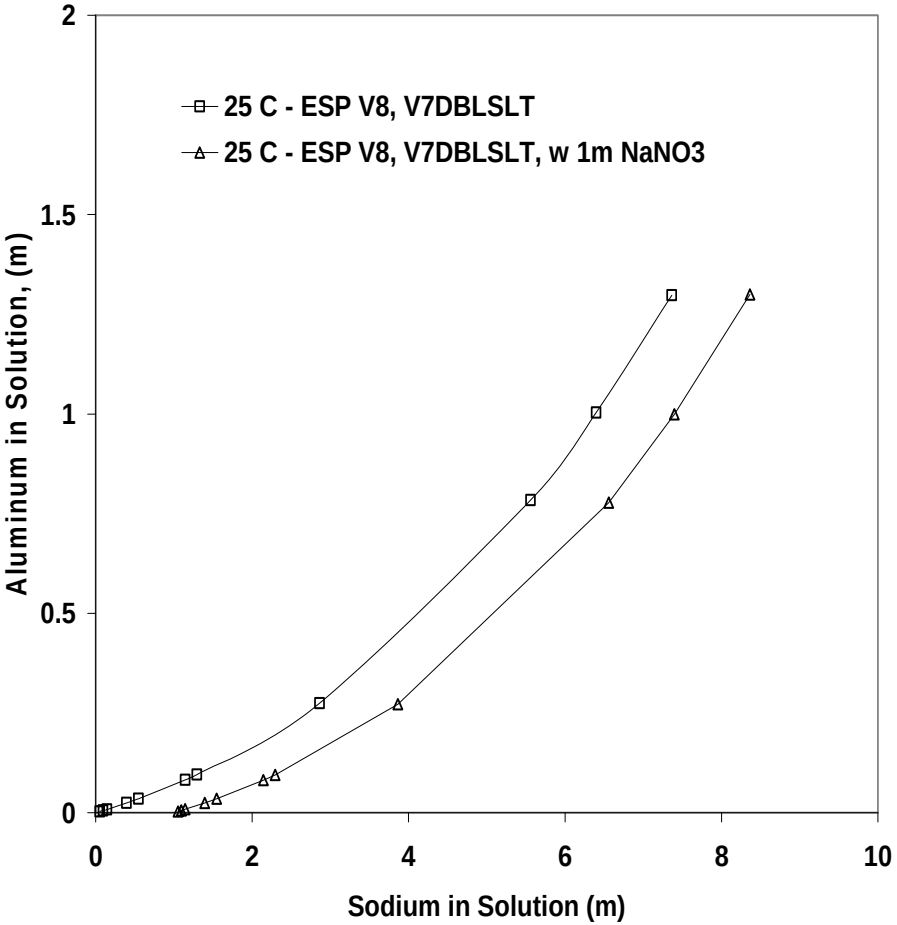




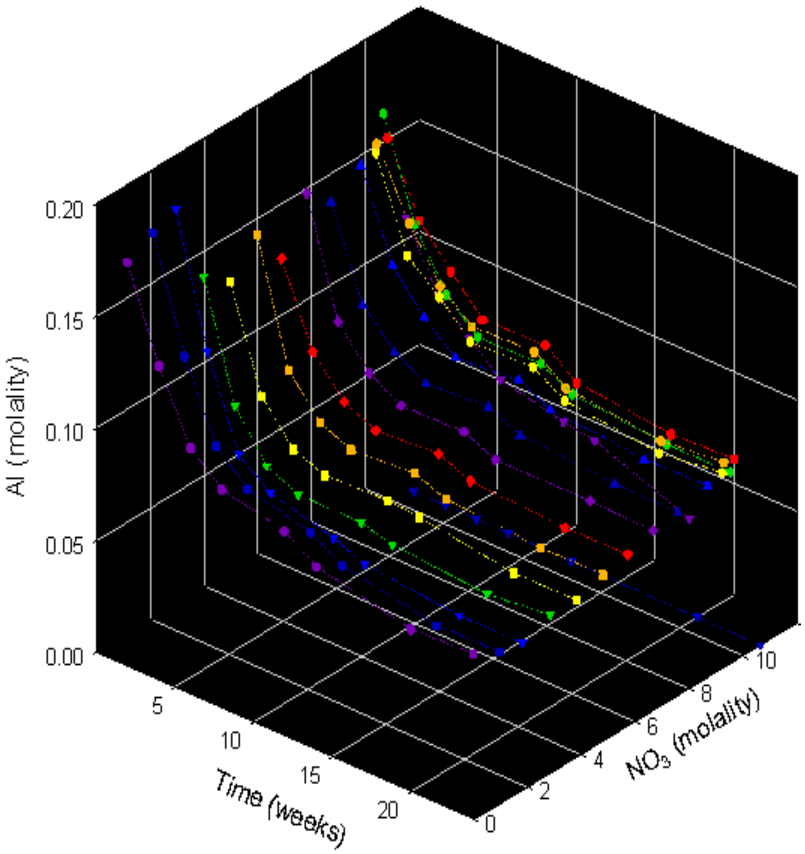
from Apps, J.A., Neil, J.M., Jun, C.H., "Thermochemical Properties of Gibbsite, Bayerite, Boehmite, Diaspore, and the Aluminate Ion between 0 and 350 °C", Technical Report, LBL-21482, August 1998.

Comparison of ESP predictions of gibbsite solubility in presence of 1 m $NaNO_3$





Previous ICET work:
Limited solubility studies at different [NaOH] and [$NaNO_3$]
Gibbsite to Boehmite transition



- Equilibration times of five months for sodium aluminate/nitrate systems
- Al wire experiments at 25°C demonstrated sodium nitrate had only a slight enhancement effect on the aluminum solubility
- Experiments with gibbsite to boehmite demonstrated transition could occur at lower temperatures (boehmite has lower solubility range)
- Ruff, T.J., Toghiani, R.K., Smith, L.T., Lindner, J.S., "Studies on the Gibbsite to Boehmite Transition," Separation Science and Technology, 43(9-10), 2887, (2008).

Test Plan for the Solubility Studies

- Primary issues that guided development include understanding the influence of
  - sodium and hydroxide on gibbsite solubility
  - other anions (nitrate, nitrite, carbonate, and/or sulfate) and
  - the effect of temperature
- Literature data and anticipated WTP solution (Julie Reddick) conditions formed the basis for developing the test matrix.

Analyte	UFP-1 Leaching		UFP-2 Leaching		Overall Range	
	mol/kg H_2O	mol/kg H_2O	mol/kg H_2O	mol/kg H_2O	mol/kg H_2O	mol/kg H_2O
	min	max	Min	max	Min	max
Na	8.10E-01	6.20E+00	1.92E+00	6.74E+00	8.10E-01	6.74E+00
$Al(OH)_4$	3.60E-02	7.04E-01	1.26E-01	4.86E-01	3.60E-02	7.04E-01
OH	4.33E-01	5.46E+00	1.45E+00	4.40E+00	4.33E-01	5.46E+00
NO_2	4.78E-09	7.96E-01	1.18E-02	6.60E-01	4.78E-09	7.96E-01
NO_3	4.28E-03	1.81E+00	1.86E-01	1.64E+00	4.28E-03	1.81E+00
CO_3	2.95E-09	5.20E-01	6.32E-05	2.31E-01	2.95E-09	5.20E-01
PO_4	3.18E-03	1.63E-01	1.13E-02	1.29E-01	3.18E-03	1.63E-01
SO_4	1.82E-03	9.98E-02	1.17E-02	1.60E-01	1.82E-03	1.60E-01

Establishment of Test conditions and number of experiments based upon concentration ranges obtained from site and statistical analysis using Taguchi method (JMP)

Pt no.	NO_3^-	NO_2^-	CO_3^{2-}
1	M	L	L
2	L	M	L
3	L	H	M
4	M	H	H
5	L	L	H
6	H	L	M
7	M	M	M
8	H	M	H
9	H	H	L
10	H	H	H

Values (mol/kg H_2O)	NO_3^-	NO_2^-	CO_3^{2-}
High (H)	3.0	1.5	0.5
Medium (M)	1.5	0.75	0.25
Low (L)	0.0	0.0	0.0

Test plan reviewed and refined; experiments commenced

- Temperatures selected are 25, 40, and 55°C
- NaOH solutions prepared
- Aluminum wire added, TGA analysis performed
- Salts added following completion of redox reaction
- Two sets of identical samples were prepared
  - one sampled as a function of time
  - second used for analysis of the equilibrated solution
- Analysis using ICP, TIC, IC, potentiometric titration, PLM, XRD
- Most experiments performed above saturations, some planned to approach the SLE from below.

Status Aluminum Solubility Studies

- Model calculations and evaluation of literature data was completed
- A test plan was developed and approved
- Experimental work on aluminum systems is ongoing, all 25°C samples have been prepared
- Solutions will be allowed to come to equilibrium and analyzed.
- Experiments will commence at the elevated temperatures
- Data will eventually be routed to OLI Systems Inc. for inclusion in the MSE database.

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- Parsons: Mark Brugh

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Questions

Contact Information
Jeff Lindner
Associate Director
ICET, MSU
lindner@icet.msstate.edu