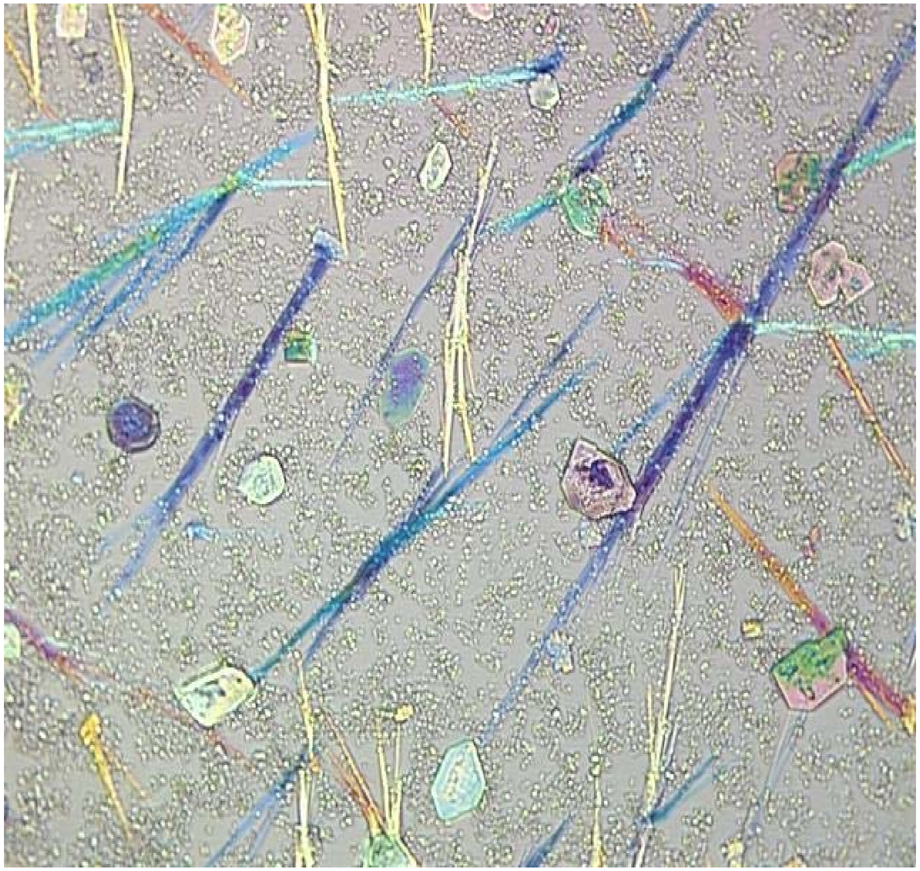
# Aluminum Solubility



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# Overview

- Aluminum Solubility
- Leaching of aluminum from SRS 8F simulated sludge
- Gibbsite to boehmite transition

# ICET Waste Chemistry Solubility Efforts

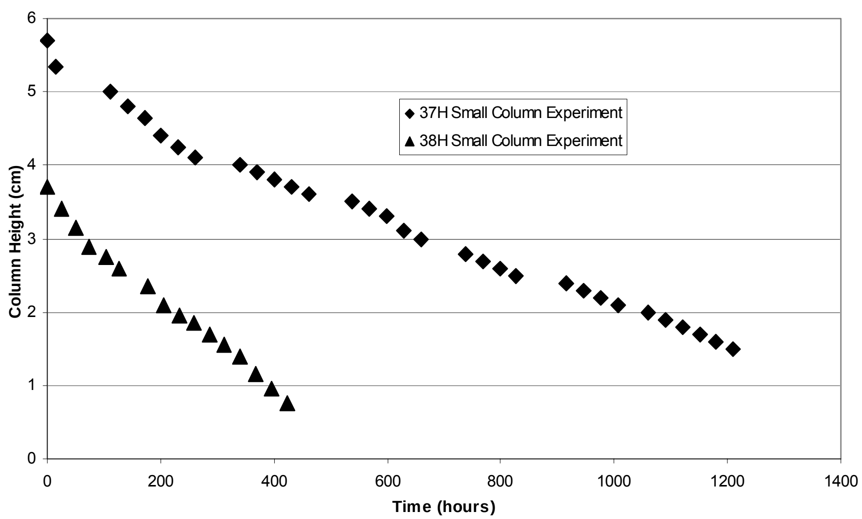
- Initially tasked with the development of improved salt cake chemistry representations for use in the Environmental Simulation Program (ESP, OLI Systems Inc.)
- Solubility studies
- Data fitting
- Database development
  - DBLSLTDB ESP 6.5
  - V7DBLSLTDB ESP 7.0
- FY'07 Porting to Mixed Solvent Electrolyte (MSE) model

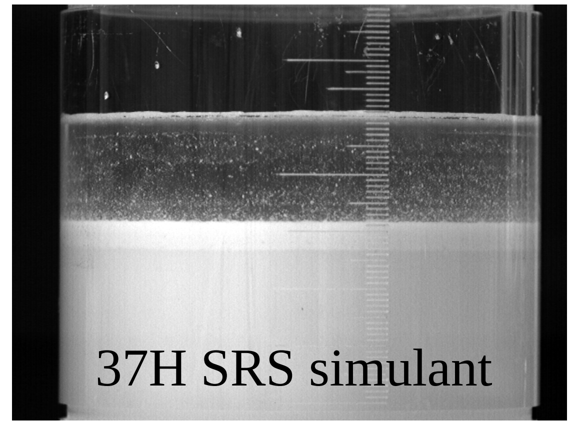
# Status of Solubility Experiments (25, 50°C, NaOH) Fits needed in blue, current experiments in red

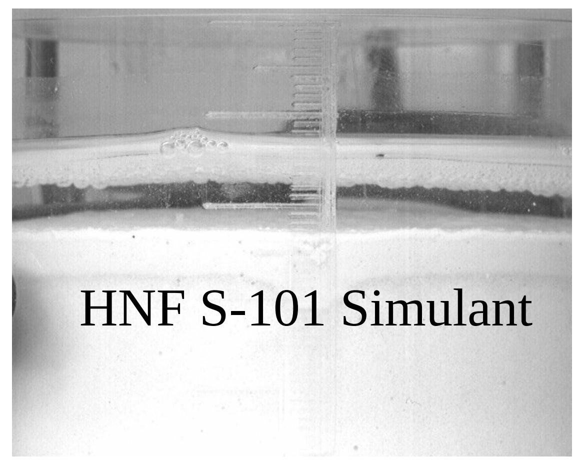
- Na-F-$NO_3$-OH
- Na-F-$SO_4$-OH
- Na-F-$PO_4$-OH
- Na-F-$PO_4$-$NO_3$-OH
- Na-$PO_4$-$NO_3$-OH
- Na-$NO_2$-$CO_3$-OH
- Na-$NO_3$-$CO_3$-OH
- Na-$SO_4$-$CO_3$-OH
- Na-$SO_4$-$PO_4$-OH
- Na-$SO_4$-$NO_2$-OH
- Na-$SO_4$-$NO_3$-OH
- K-$NO_3$-OH
- Cs-$NO_3$-OH
- Na-Al-$NO_3$-OH
- Na-F-$PO_4$-OH(15,20°C)
- Na-Cs,K-$NO_3$-OH

# Effects of Aluminum on Salt Cake Dissolution

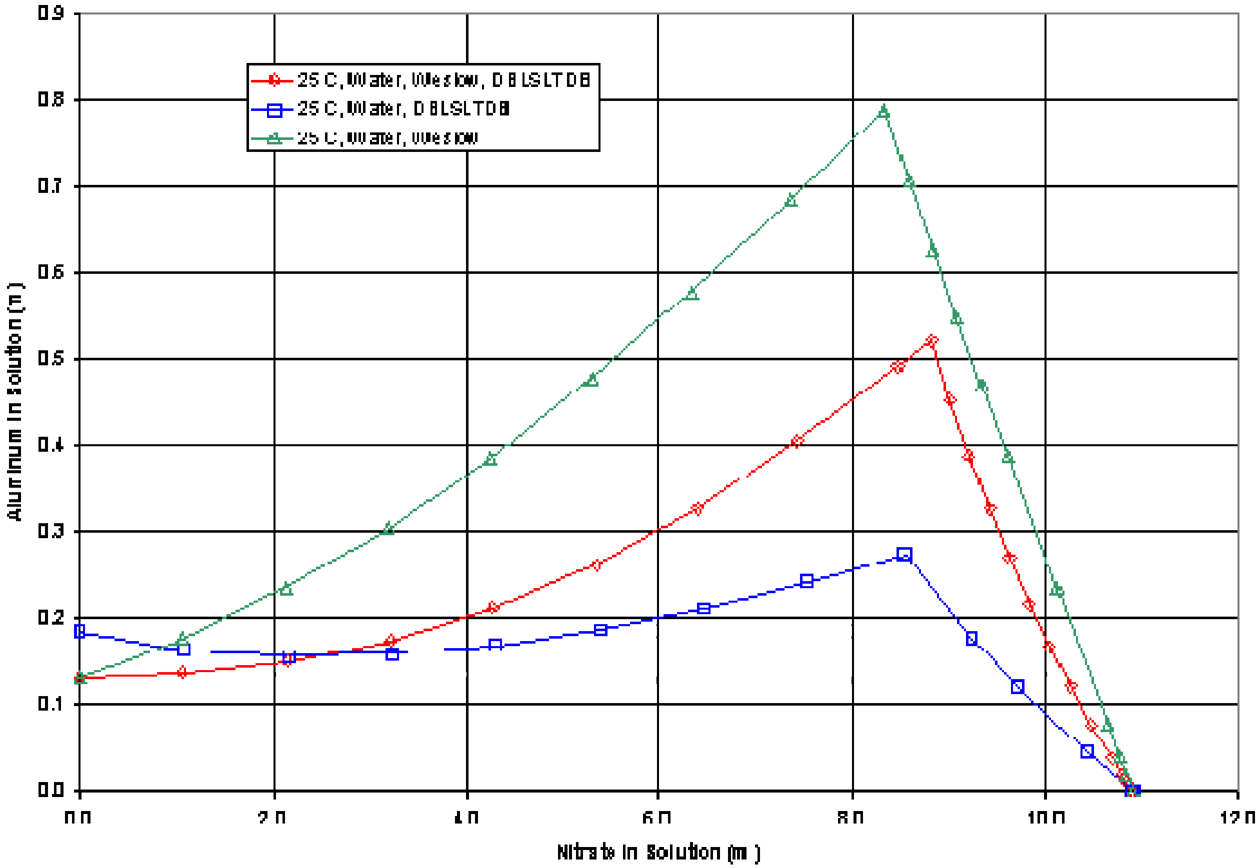
- During the dissolution portion of several small column salt cake simulant experiments, $Al(OH_3)$ or cancrinite layers have been formed.
- The presence of these layers delays the dissolution process.



# ESP v6.5 calculations indicate enhanced solubility in nitrate, large variation in predictions using different databases

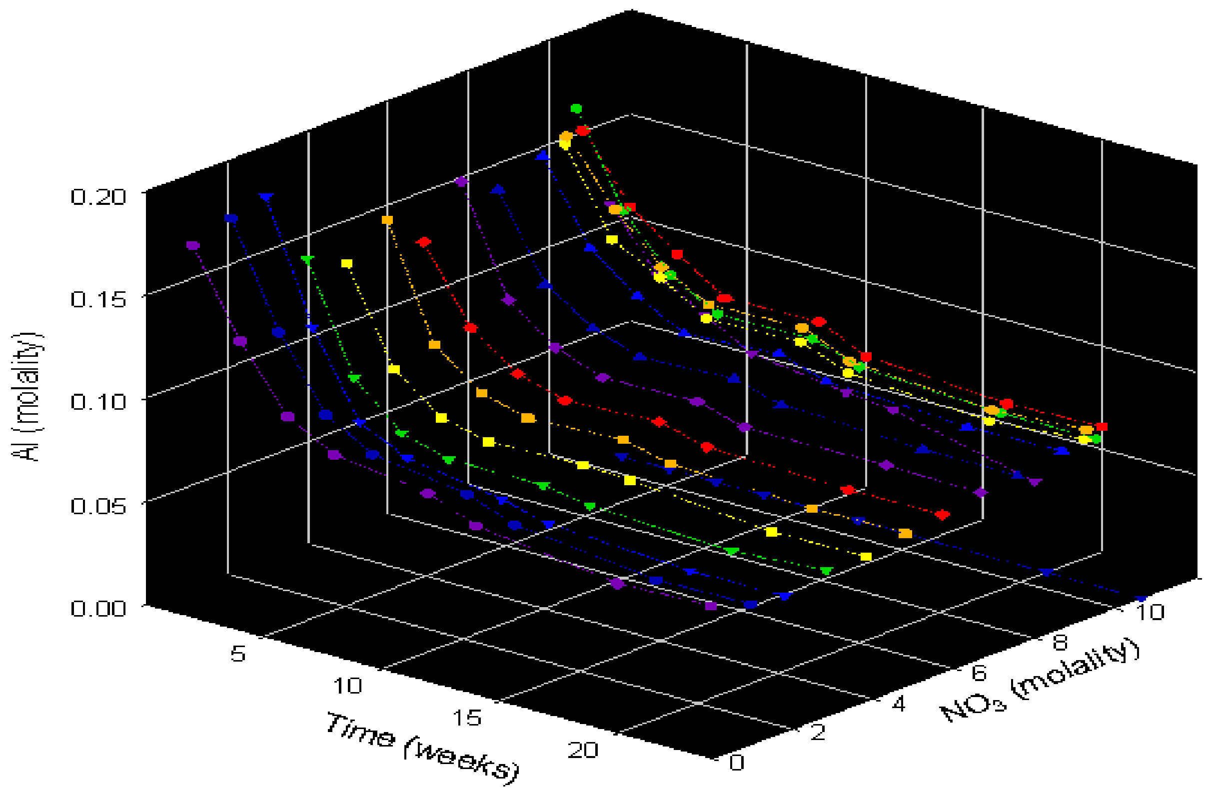


Commercial grade sodium aluminate solutions were evaluated at 25 and 50°C. $NaAlO_2 \cdot 2.5H_2O$ [63.1045g/mol]

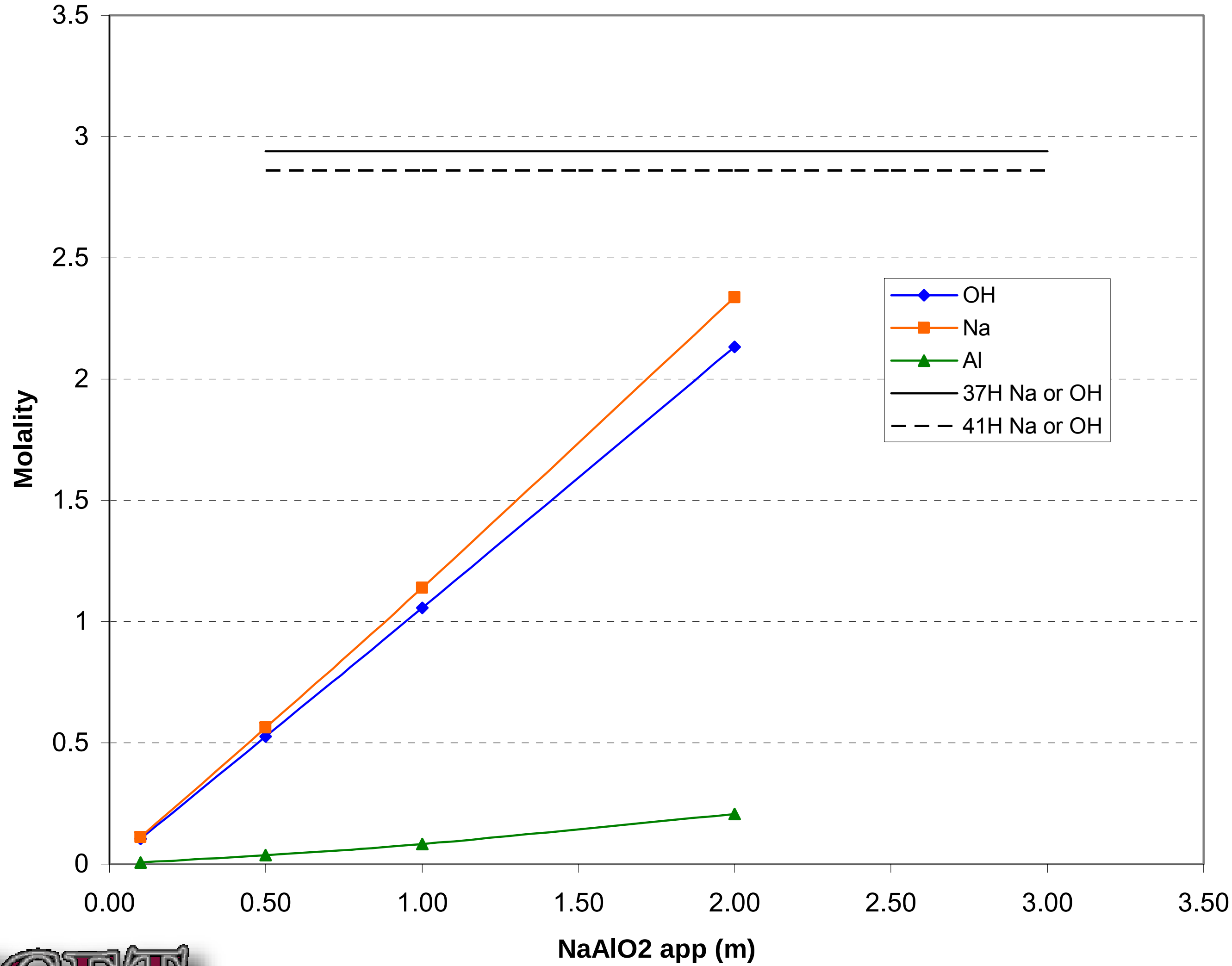
[0.5785 $NaAlO_2 \cdot$ 0.0484 $Al(OH)_3 \cdot$ 0.2071 $NaOH \cdot$ 0.17 $H_2O$]

0.1, 0.5, 1.0, 2.0 m $NaAlO_2$-$NaNO_3$-water

Systems exhibited equilibration times up to 5 months



# Initial solubility studies using commercial grade sodium aluminate provided restricted results



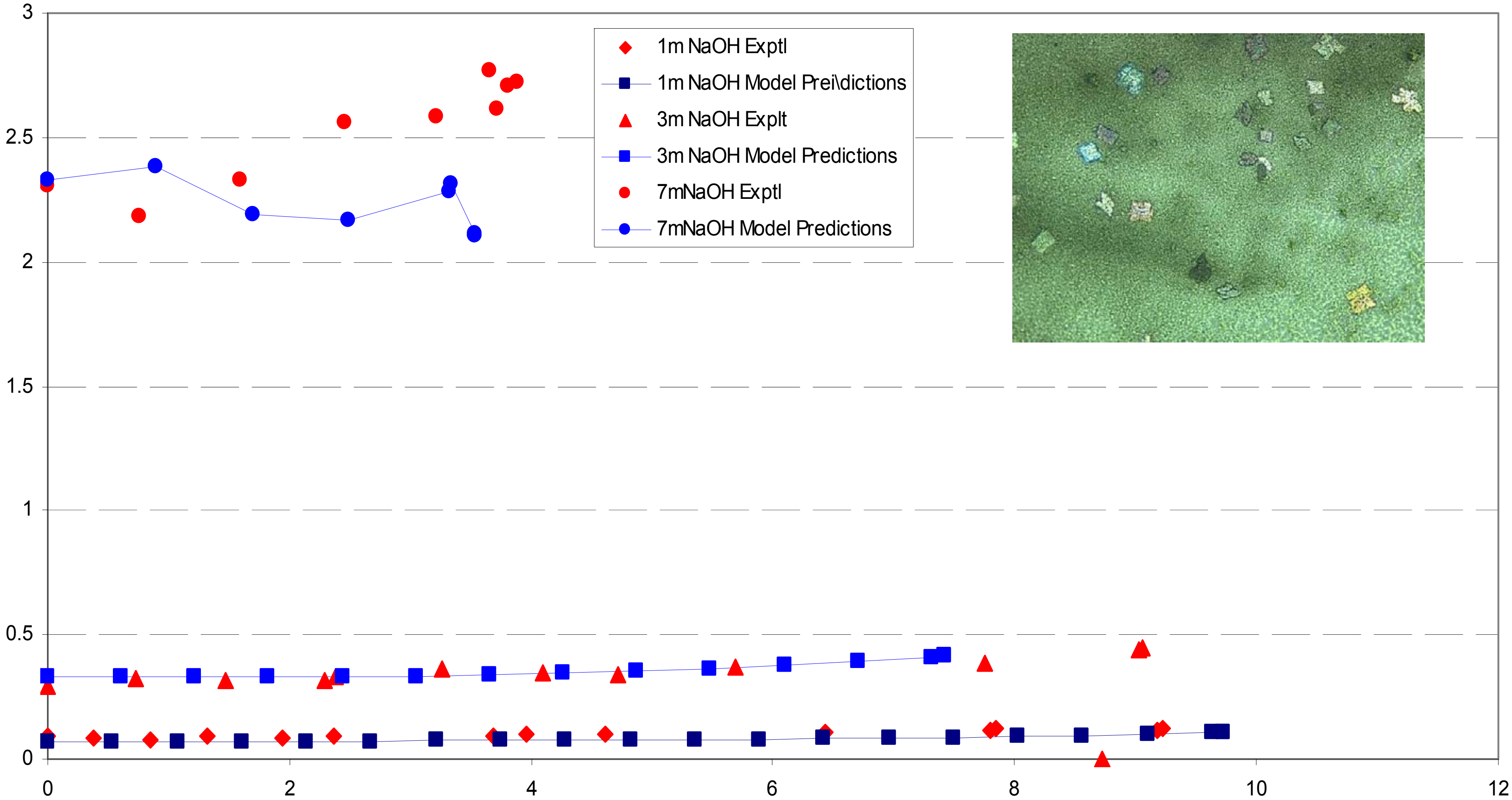
# Aluminum Wire Experiments

- Solutions were prepared in 1,3,5, and 7m NaOH, varying the amount of sodium nitrate
- Test solutions were monitored biweekly until aluminum equilibrium was established
- Solids were identified through PLM, Al using ICP and $NO_3^-$ IC

# Al Wire/Caustic Equilibrium Preparation

Glenn Hefter, et al. Heat Capacities of Concentrated Aqueous Alkaline Aluminate solutions at 25°C, *J. Chem. Eng. Data* **2002**, *47*, 960.

# Experimental and Model Al/$NO_3$ comparison for 1, 3, and 7m NaOH solutions

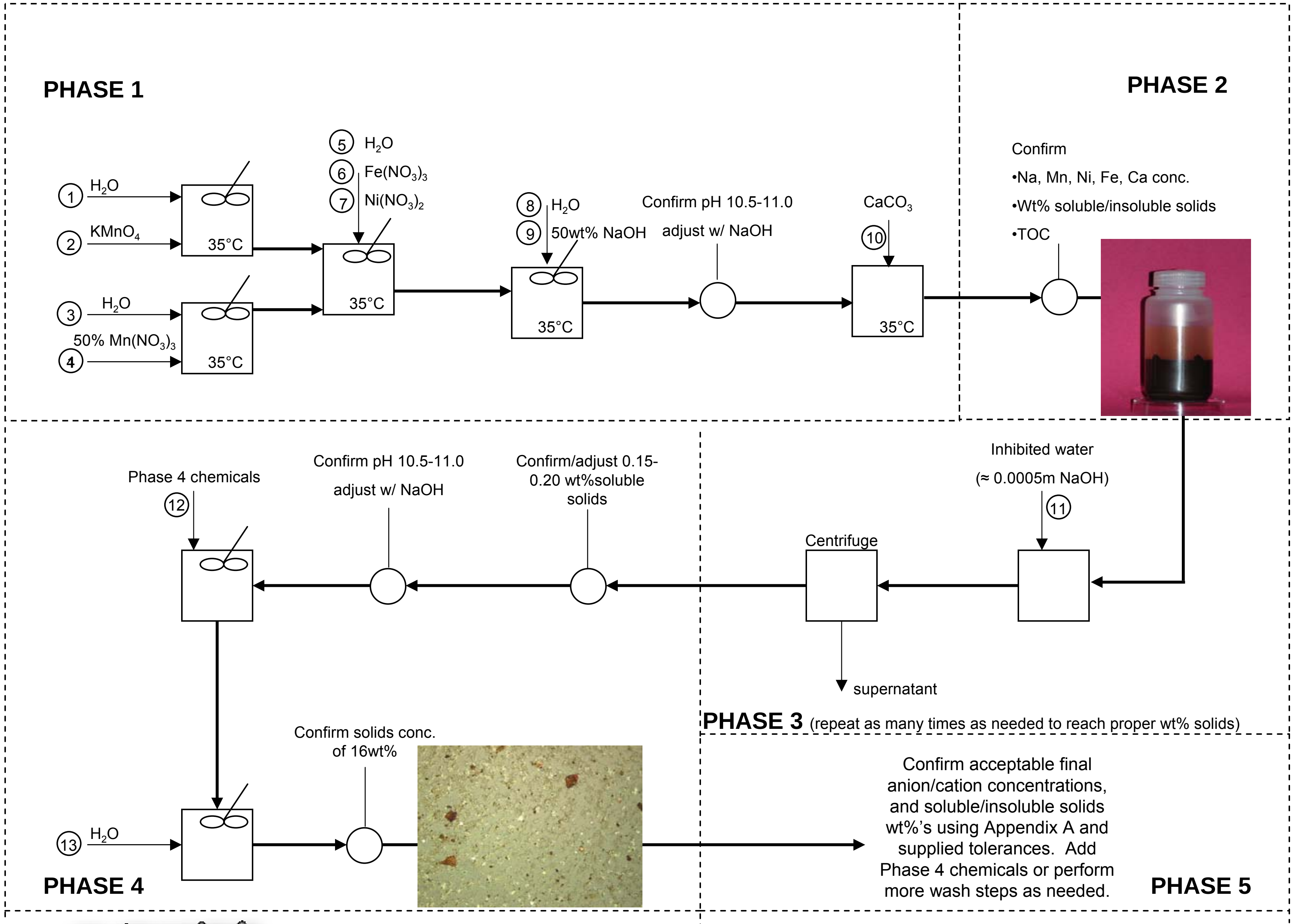


# 8F SRS sludge simulant preparation

- 1L of sludge simulant prepared following procedure of Poirier

  Poirier, Michael R., (2005), *Recipe for Simulated Tank 8F Sludge Containing No RCRA Metals or Halides*, WSRC-TR-2005-00045, Rev. 0, Westinghouse Savannah River Company, Aiken SC.

- Analysis performed after each step
- ESP modeling of procedure upon completion

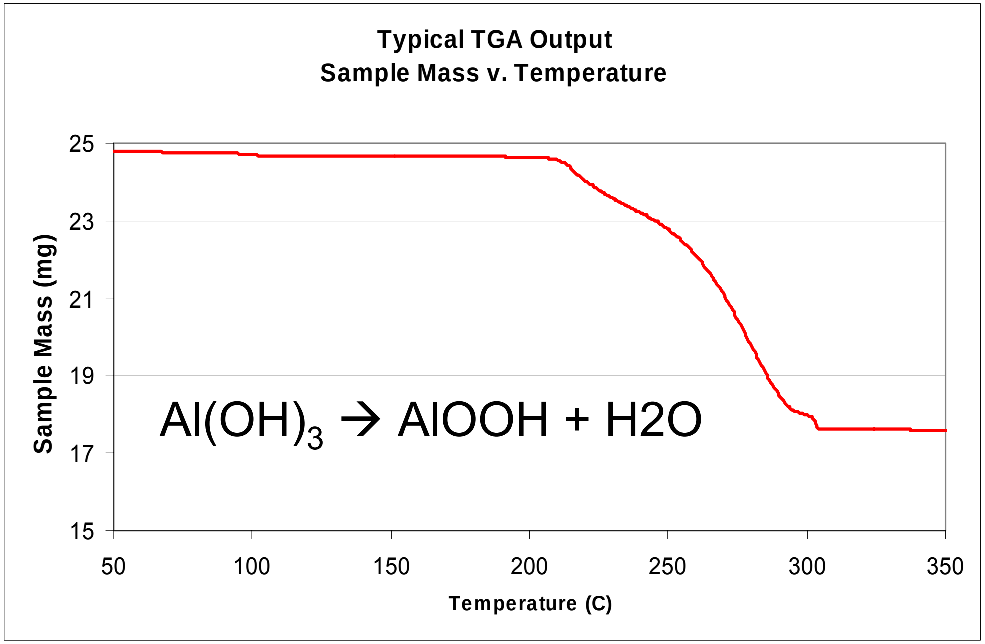

PHASE 1
1 $H_2O$
2 $KMnO_4$
35°C
3 $H_2O$
50% $Mn(NO_3)_3$
4
35°C
5 $H_2O$
6 $Fe(NO_3)_3$
7 $Ni(NO_3)_2$
35°C
8 $H_2O$
9 50wt% NaOH
35°C
Confirm pH 10.5-11.0
adjust w/ NaOH
$CaCO_3$
10
35°C
PHASE 2
Confirm
•Na, Mn, Ni, Fe, Ca conc.
•Wt% soluble/insoluble solids
•TOC
Inhibited water
(≈ 0.0005m NaOH)
11
Centrifuge
supernatant
PHASE 3 (repeat as many times as needed to reach proper wt% solids)
Confirm/adjust 0.15-0.20 wt%soluble solids
Confirm pH 10.5-11.0
adjust w/ NaOH
Phase 4 chemicals
12
13 $H_2O$
Confirm solids conc. of 16wt%
PHASE 4
Confirm acceptable final anion/cation concentrations, and soluble/insoluble solids wt%'s using Appendix A and supplied tolerances. Add Phase 4 chemicals or perform more wash steps as needed.
PHASE 5

# Model predictions using V7 ESP and DBLSLTDB indicate differences in Mg and Si loadings

| Predicted Solids | Wt% dry (Model) | Cations | Wt% dry (Expt) |
|---|---|---|---|
| $Al(OH)_3$ | 27.79 | Al | 29.96 |
| $Fe_2O_3$ | 45.89 | Fe | 48.63 |
| $MnO_2$ | 10.24 | Mn | 5.34 |
| $Ni_3O_4$ | 5.26 | Ni | 5.12 |
| $CaCO_3$ | 6.89 | Ca | 7.34 |
| CuO | 0.17 | Cu | 0.25 |
| $SrCO_3$ | 0.15 | Sr | 0.21 |
| ZnO | 0.35 | Zn | 0.47 |
| $Ca_5(OH)(PO4)_3$ | 0.26 | Si | 2.68 |
| $NaAl(CO_3)(OH)_2$ | 1.62 | Mg | 1.22 |
| Quartz | 0.68 | | |
| Amesite 14A | 0.71 | | |

# Gibbsite to boehmite transition

- The speciation of Al solids contained within the sludge is of concern. Gibbsite [$Al(OH)_3$] is relatively soluble in NaOH making its removal easy; boehmite [AlO(OH)] is quite insoluble.
- Thus, it is important to know the gibbsite-boehmite fractions in tanks.
- Gibbsite converts to boehmite at 190-210°C and brings about a 23% weight loss as water is liberated.



# Gibbsite-to-Boehmite Transition Kinetics

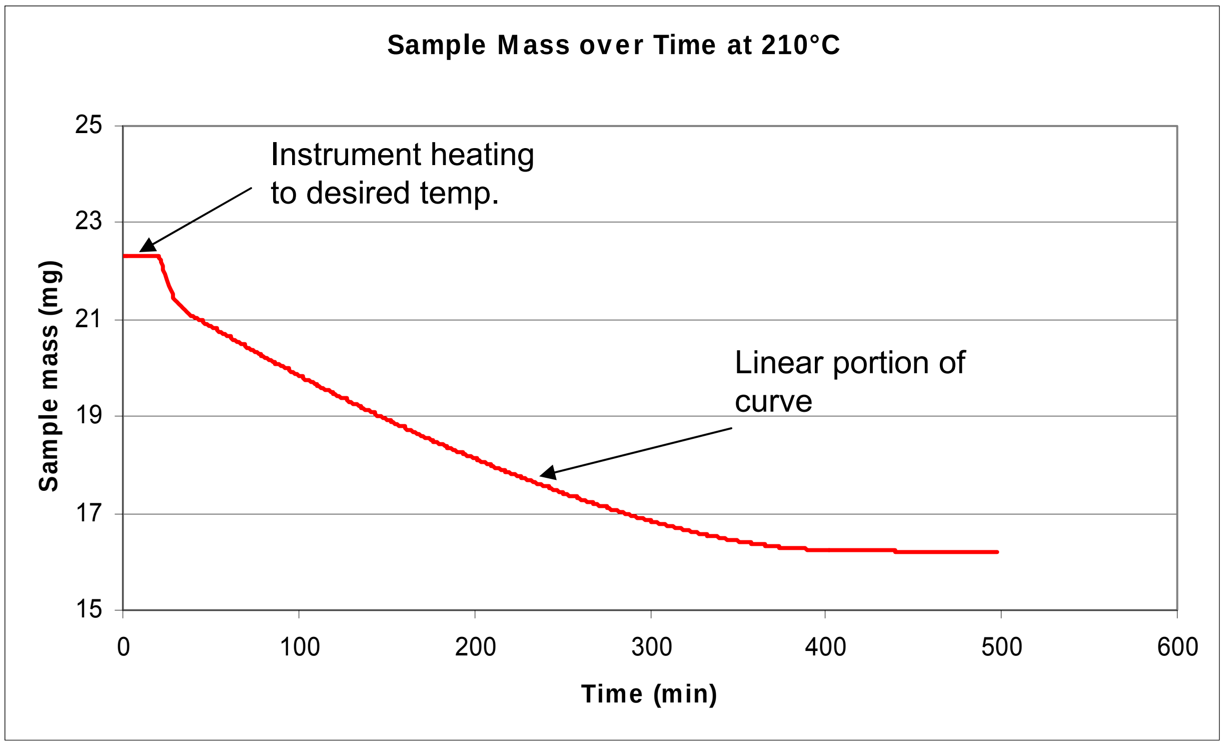
•Constant temperature analyses was performed at 200°C and 210°C.

•Extraction of a first order rate constant from the linear portion of each plot was performed. k(200°C)=0.0027mol/min, k(210°C)=0.0062mol/min

•Arrhenius' equation predicts an activation energy ($E_A$) of 158 kJ/mol using the two rate constants.

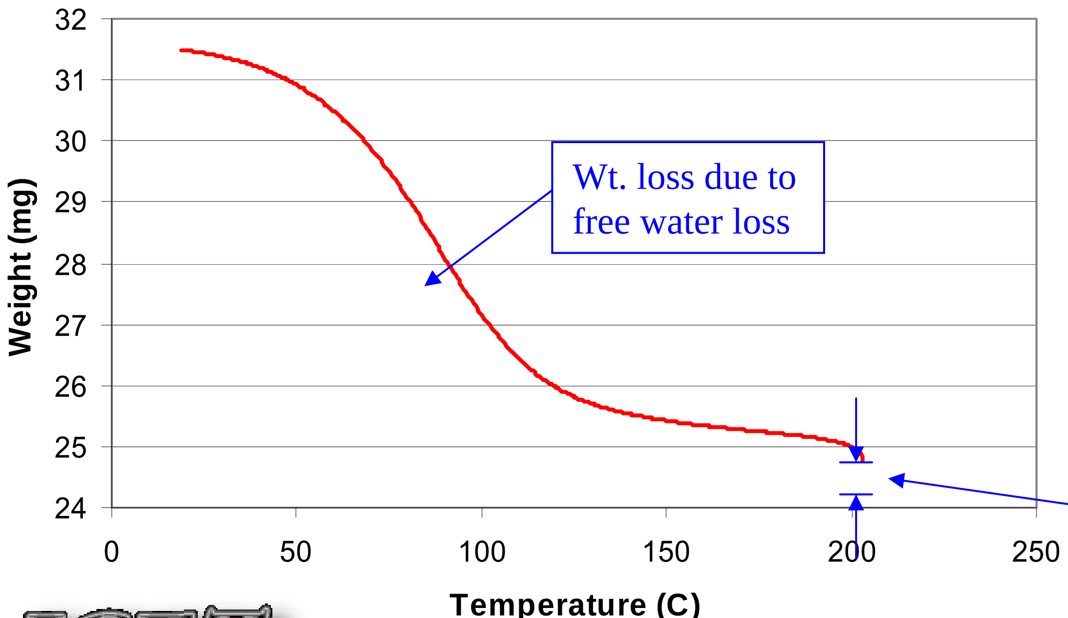
•This lies just above the published value of $E_A$=142 kJ/mol.

[L.Candela and D.Perlmutter, Kinetics of Boehmite Formation by Thermal Decomposition of Gibbsite, *Ind. Eng. Chem. Res.* **1992**, *31*,694.]



# Transition at Lower Temperatures

- Transition was observed at 150°C in 1.5m NaOH solutions
  [David T. Hobbs, et al. Gibbsite to Boehmite Transformation in Strongly Caustic and Nitrate Environments, *Ind. Eng. Chem. Res*., **2003**, *42*, 2163.]
- Attempt to verify that boehmite can be formed at even lower temperatures in caustic solutions.
- Gibbsite exposure to 120°C in 1.5m caustic – findings…




Small wt. loss due to transition of remaining gibbsite to boehmite.

… After 24h exposure, isolated solid is about 95% boehmite.

# Conclusions

- Initial aluminum predictions using ESP V6.5 demonstrated wide variances when using differing databases such as Weslow and DBLSLTDB. Better agreement was observed using ESP 7.0 with the modified preparation (Al wire).
- Preliminary experimental results on preparation of the 8F sludge simulant indicate good agreement with experimental results and the ESP model with the exception of Mg and Si. This aids in identifying further experiments needed to bolster sludge chemistry representations.
- High temperature kinetic experiments of the gibbsite to boehmite transition are in agreement with earlier literature studies.
- In caustic solutions the transition is occurring at temperatures less than 150$^{o}$C. Additional experiments and temperature histories can be used to identify wastes rich in boehmite that may be difficult to retrieve.

# Acknowledgements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