EM Waste Processing Technical Exchange

Thermodynamic Modeling of Waste Processing

8:00 November 18, 2010

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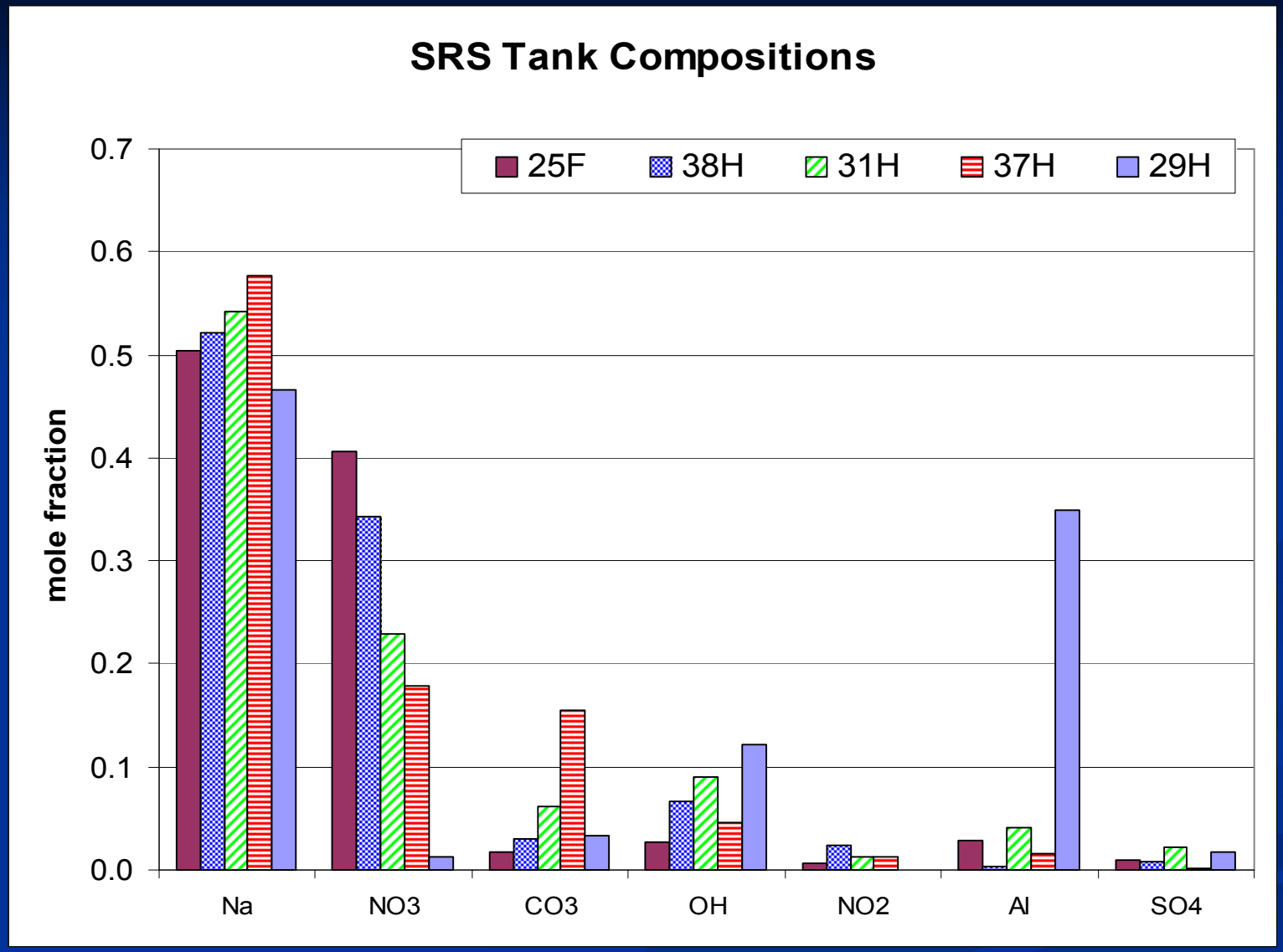
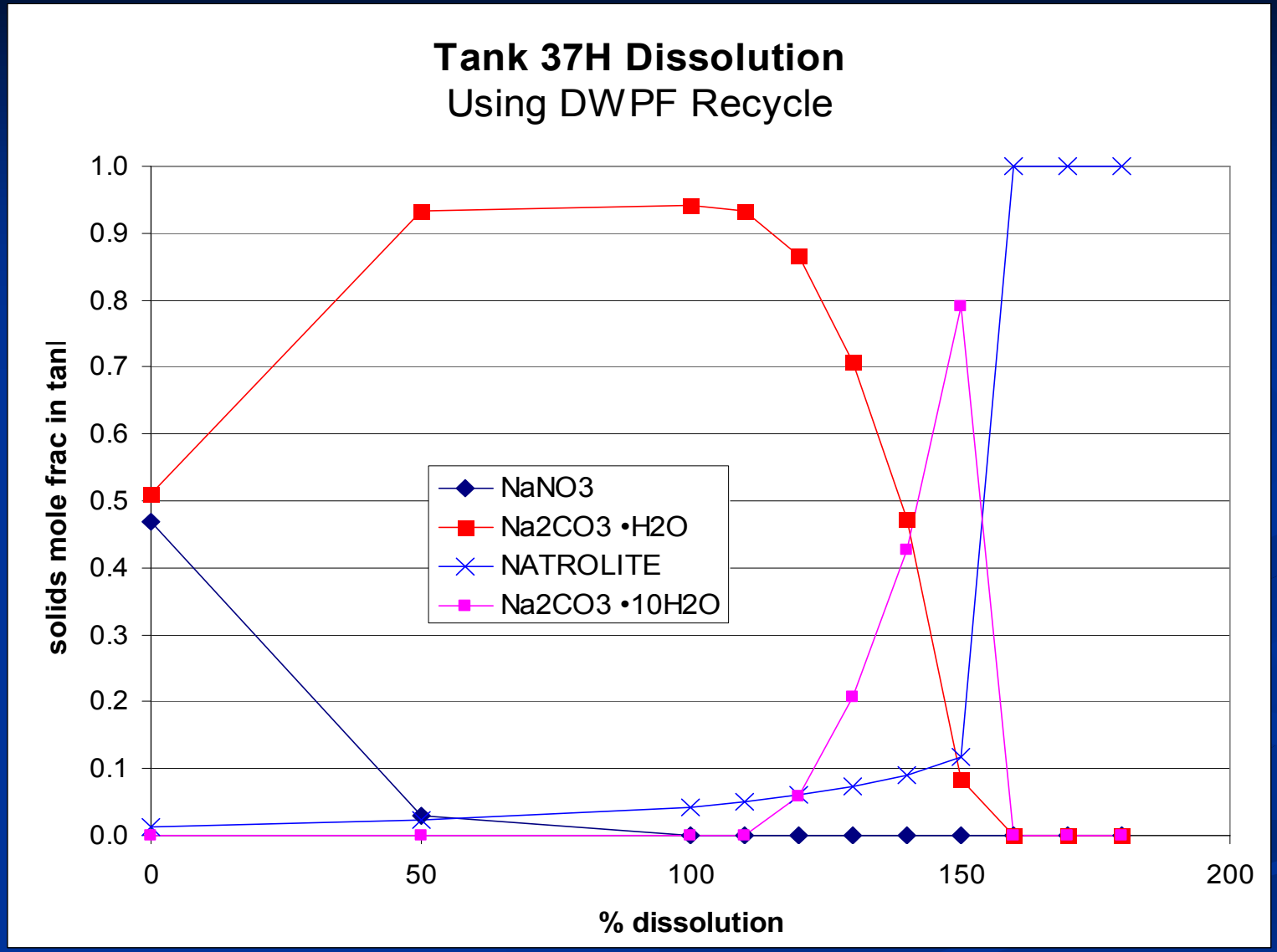
SRS Saltcake Waste Modeling

- Environmental Simulation Program (OLI Systems Inc)
  - Version 8.0.58
  - Built-in Public database
  - Corrosion and V7DBLSLT (ICET developed) databases
- ESP Modeling
  - Saltcake dissolution using DWPF recycle
  - Corrosion control of dissolution streams with leachate from Batch 5 sludge processing
  - Waste carryover into CSSX scrub and strip solutions
- Prediction of Solids Formation
- Comparison of ESP predictions with experimental results


SRS Tank Compositions
25F
38H
31H
37H
29H
mole fraction
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Na
NO3
CO3
OH
NO2
Al
SO4



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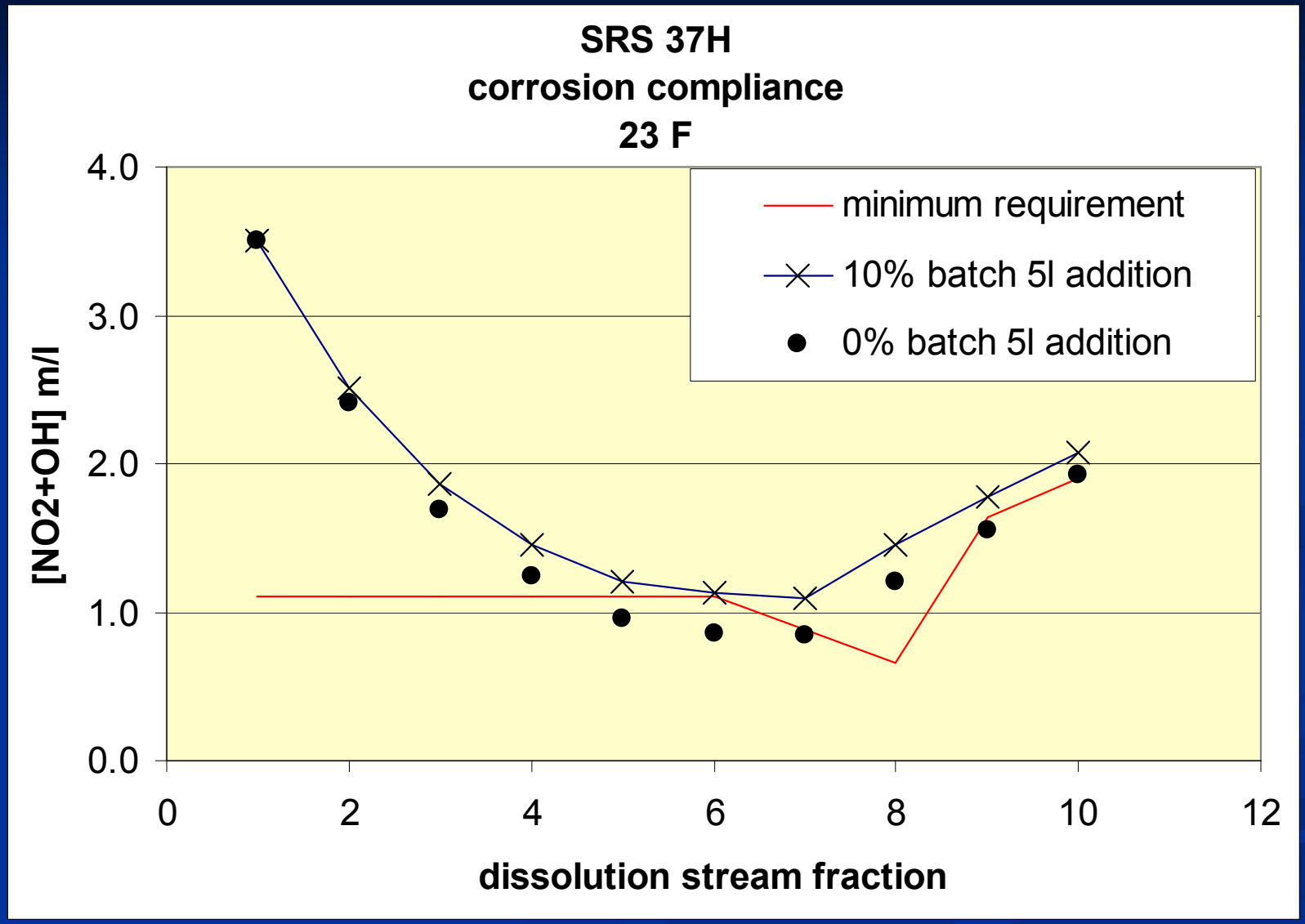
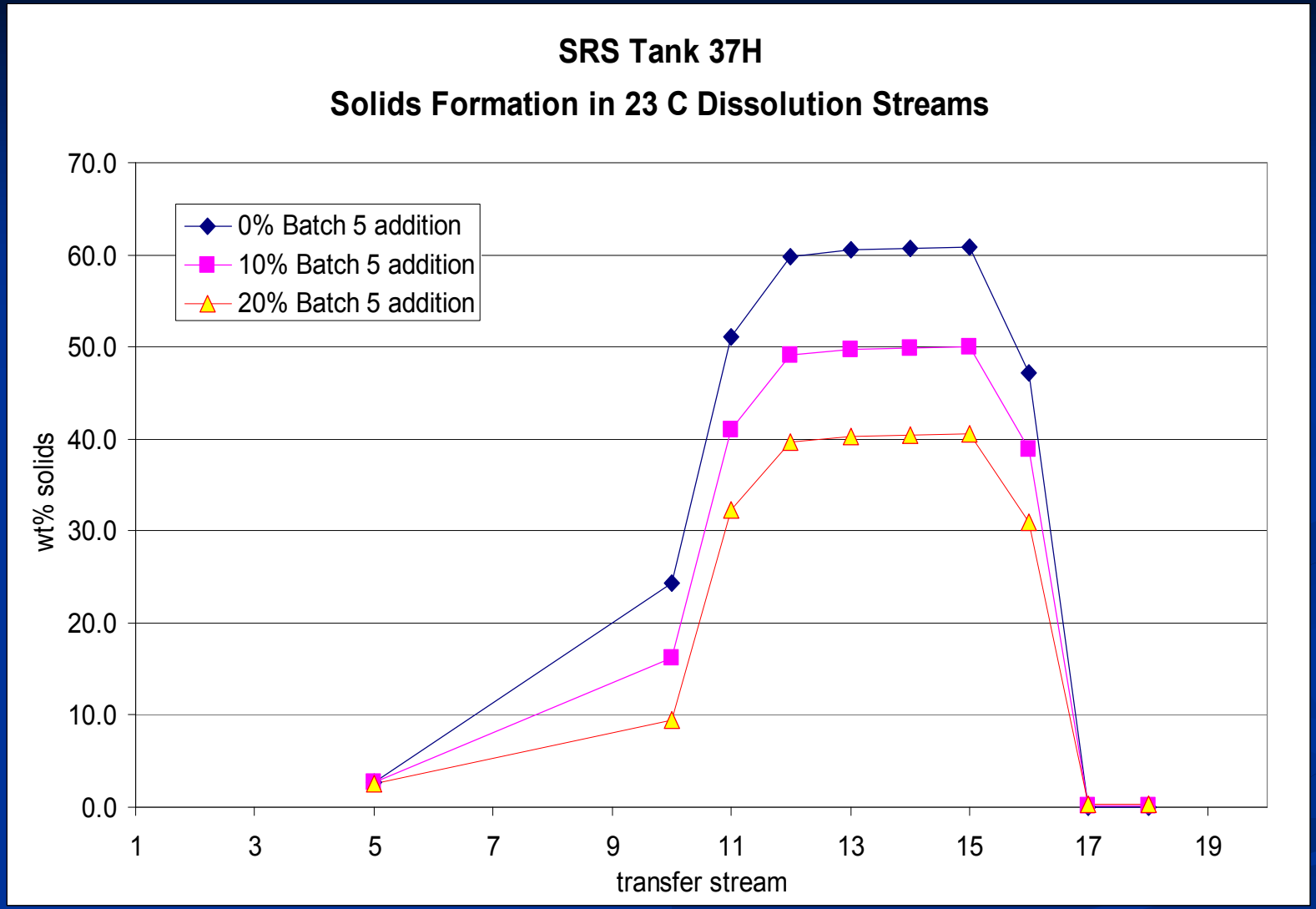

SRS 37H
corrosion compliance
23 F
4.0
3.0
2.0
1.0
0.0
[NO2+OH] m/l
0
2
4
6
8
10
12
dissolution stream fraction
minimum requirement
10% batch 5l addition
0% batch 5l addition



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SRS Tank 37H
140% Dissolution Stream Simulant

- Right Sample Simulant kept at 30º

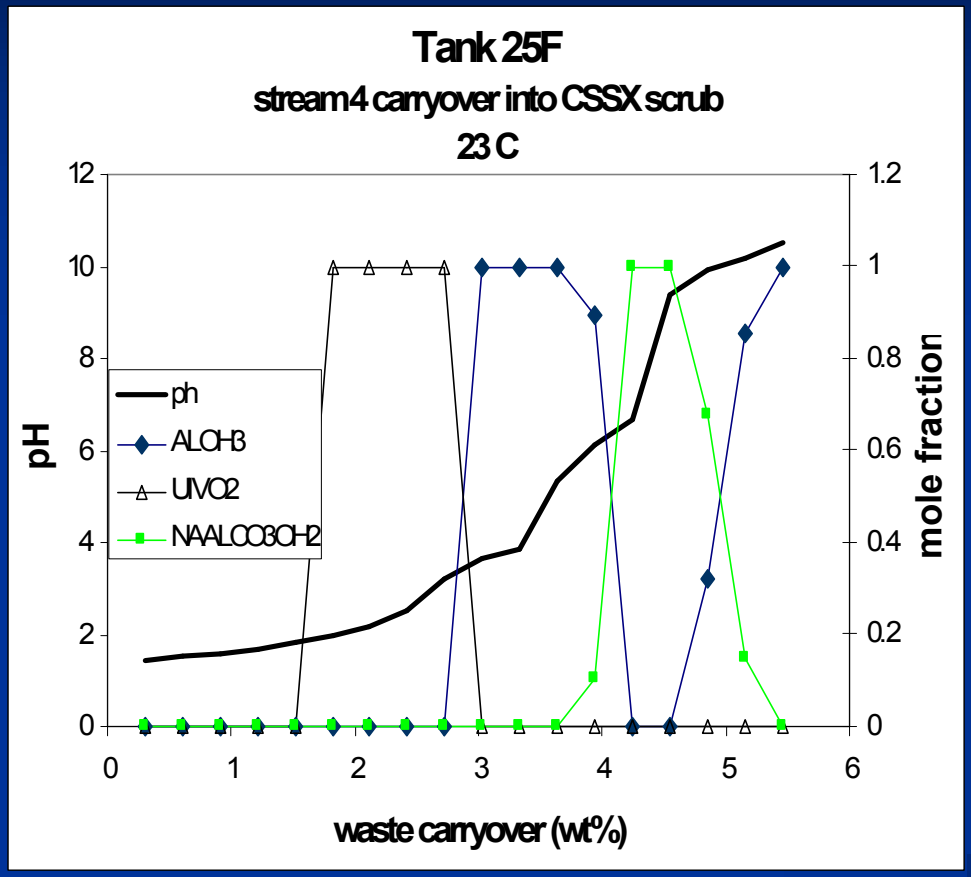
- Left Sample Simulant cooled to 23ºC

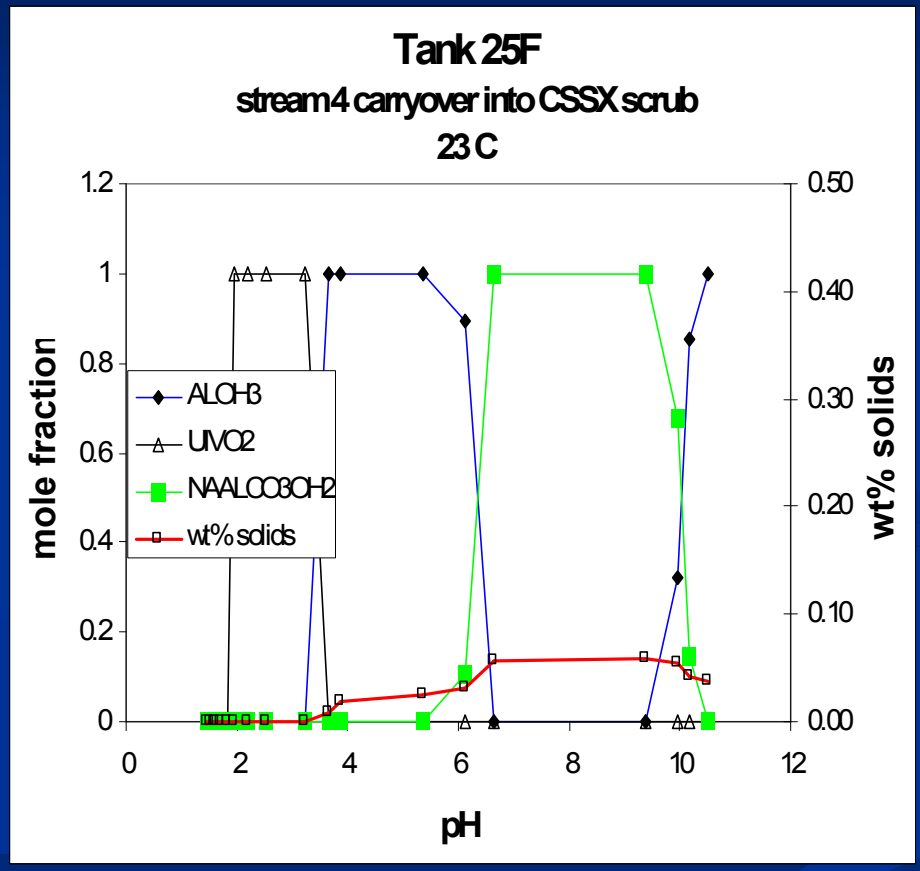
TGA of crystals showed 66%(wt) water which indicates $Na_2CO3 \cdot 10H_2O$ as Predicted by ESP

Caustic Side Solvent Extraction Process

- Comprised of 4 steps
  - Extraction of cesium into solvent
  - Scrubbing of loaded solvent to remove co-extracted sodium and potassium
  - Stripping to transfer cesium out of solvent
  - Washing of stripped solvent for recycle
- Precipitation of solids observed during scrubbing process

Waste Carryover into Scrub Liquid





Experimental Approach

- Experiments designed to examine solids formation during scrubbing operation
- Three streams examined, each representative of a stream composition encountered at different stages of retrieval from Tank 25F
- Precipitation may occur when small amounts of the aqueous solution is carried over into the scrub solution, 0.05 M nitric acid

Simulant/Sample Preparation

- Simulants representing retrieval streams with 10% diluent addition, 40 % diluent addition and 50% diluent addition developed.
- Each simulant was prepared in the laboratory.
- Aliquot of liquid phase removed daily from each simulant, analyzed for aluminum and sodium concentration, pH also monitored
- Equilibrated simulant established by aluminum and sodium concentrations remaining constant over period of several consecutive days
- Solutions visually inspected daily for evidence of solids formation

Simulant Recipe

Chemical	Stream 1 10% Dilution (g)	Stream 4 40% Dilution (g)	Stream 5 50% Dilution (g)
Water	590.28	559.56	563.98
Aluminum Hydroxide	18.61	5.60	5.54
Sodium Nitrate	286.52	350.37	344.06
Sodium Nitrite	14.81	14.86	15.96
Sodium Carbonate Monohydrate	30.66	19.37	15.88
Sodium Sulfate	7.85	21.40	23.63
Sodium Fluoride	0.26	0.15	0.138
Sodium Chloride		0.064	0.062
Sodium Hydroxide	49.30	27.93	29.59
Potassium Hydroxide		0.12	0.34
Sodium Oxalate	0.23	0.51	0.46
Sodium Phosphate Dodecahydrate	0.003	0.01	0.013
Sodium Metasilicate Nonahydrate		0.052	0.31
Ferric Nitrate Nonahydrate	1.48		
Cesium Chloride			0.043

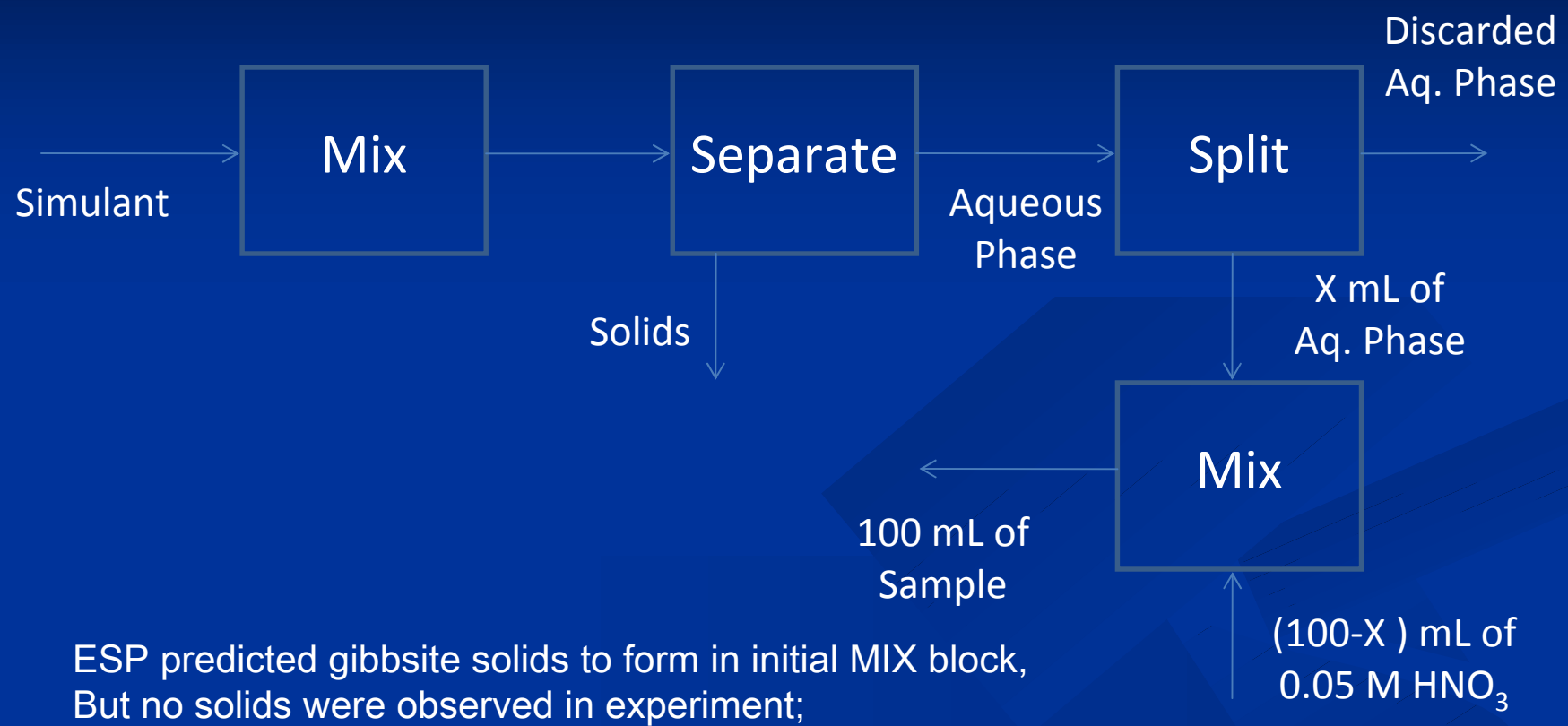
Mixing Experiments

- Purpose: to determine those combinations of simulant and 0.05 M nitric acid that will give rise to precipitated solids
- X mL of simulant mixed with (100-X) mL 0.05 M nitric acid; X is defined as % carryover by volume
- Samples representing 2 to 10 % carryover by volume prepared for each simulant, allowed to equilibrate
- 1 mL aliquots removed daily from each sample, aluminum concentration determined

Mixing Experiments (continued)

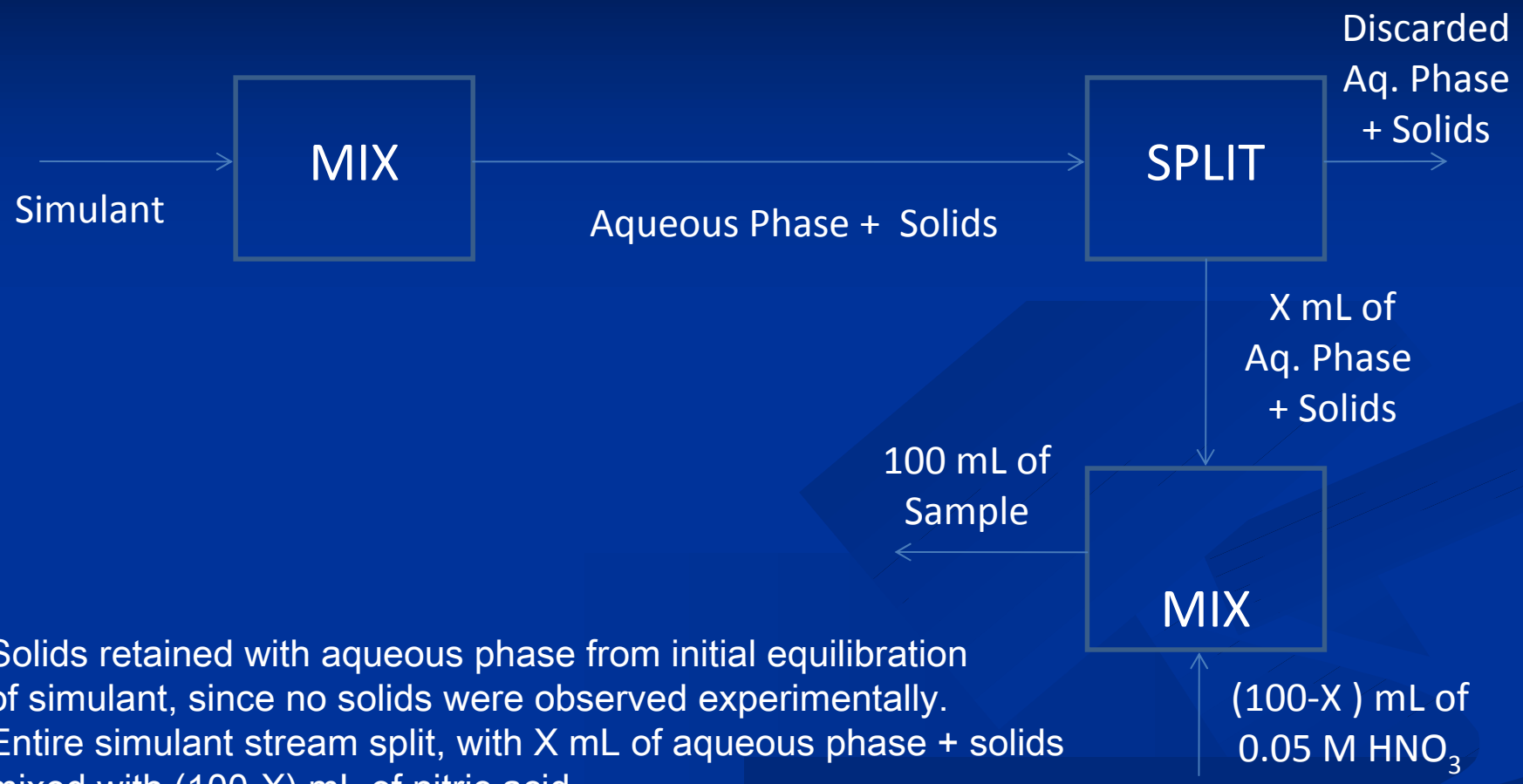
- Once aluminum concentration remained constant for several consecutive days, solution was filtered for solids recovery
- Isolated solid dried at 50 °C, ground and washed for analysis
- Solids analyzed using XRD and PLM
- Not all prepared samples gave rise to solids

Initial Modeling Approach



ESP predicted gibbsite solids to form in initial MIX block,
But no solids were observed in experiment;
Solids removed, leaving only small portion of aluminum available in the aqueous phase feeding the split
Aluminum concentrations predicted by ESP were significantly lower than observed experimental concentrations

Refined Modeling Approach

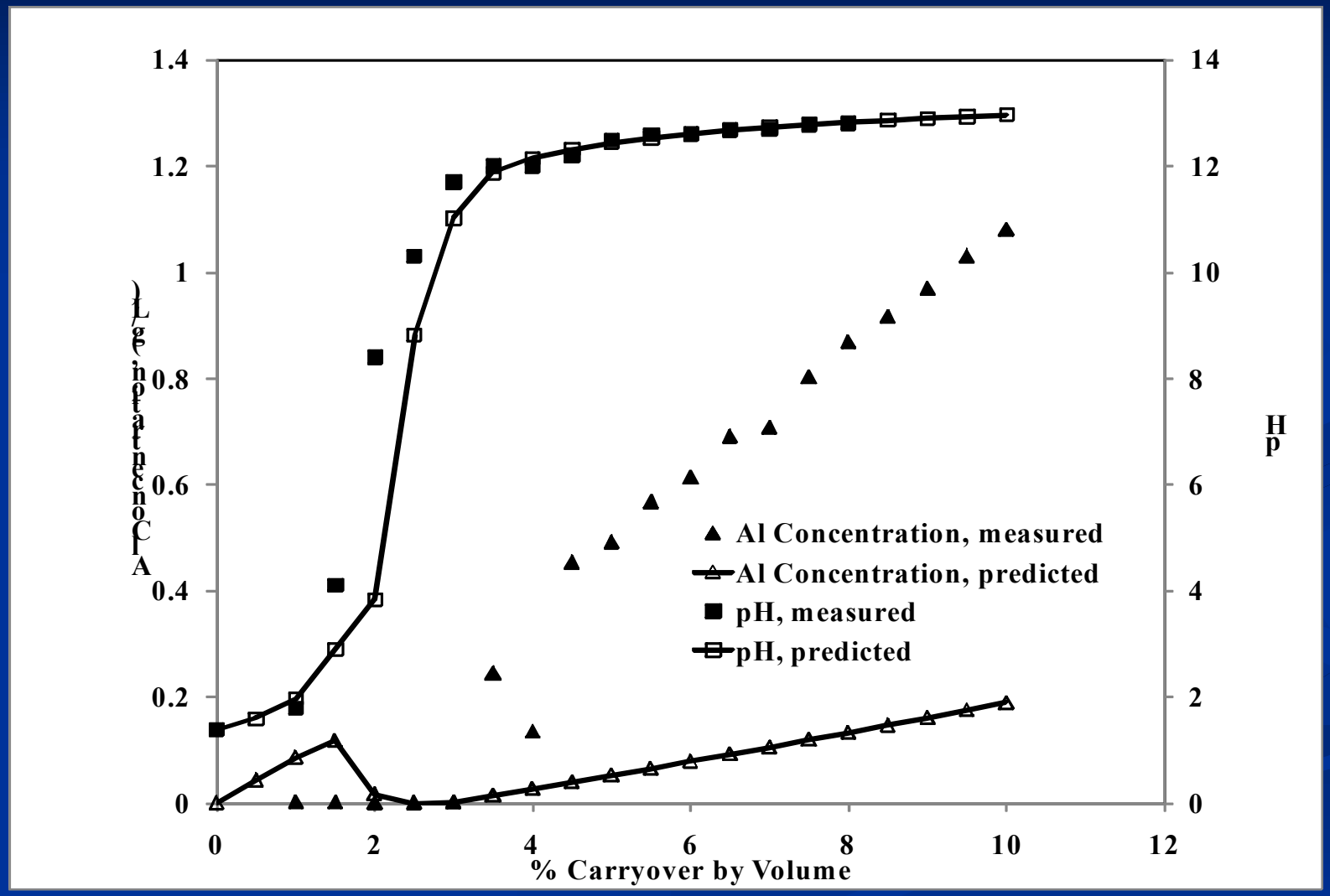


Solids retained with aqueous phase from initial equilibration of simulant, since no solids were observed experimentally.
Entire simulant stream split, with X mL of aqueous phase + solids mixed with (100-X) mL of nitric acid.
Aluminum concentrations predicted by ESP were same order of magnitude as experimentally observed

Overview of Experimental Results and Model Predictions

- Solids were observed to form in a limited number of samples for each of the streams examined. For each stream, % carryover by volume range corresponded to the region where pH was rapidly changing
- Experimental and predicted pH in excellent agreement
- Dawsonite. in addition to gibbsite, was predicted to form over this same range for each stream.
- Experimentally observed aluminum concentrations were greater than those predicted by ESP for majority of samples

Experimental Results – Stream 1



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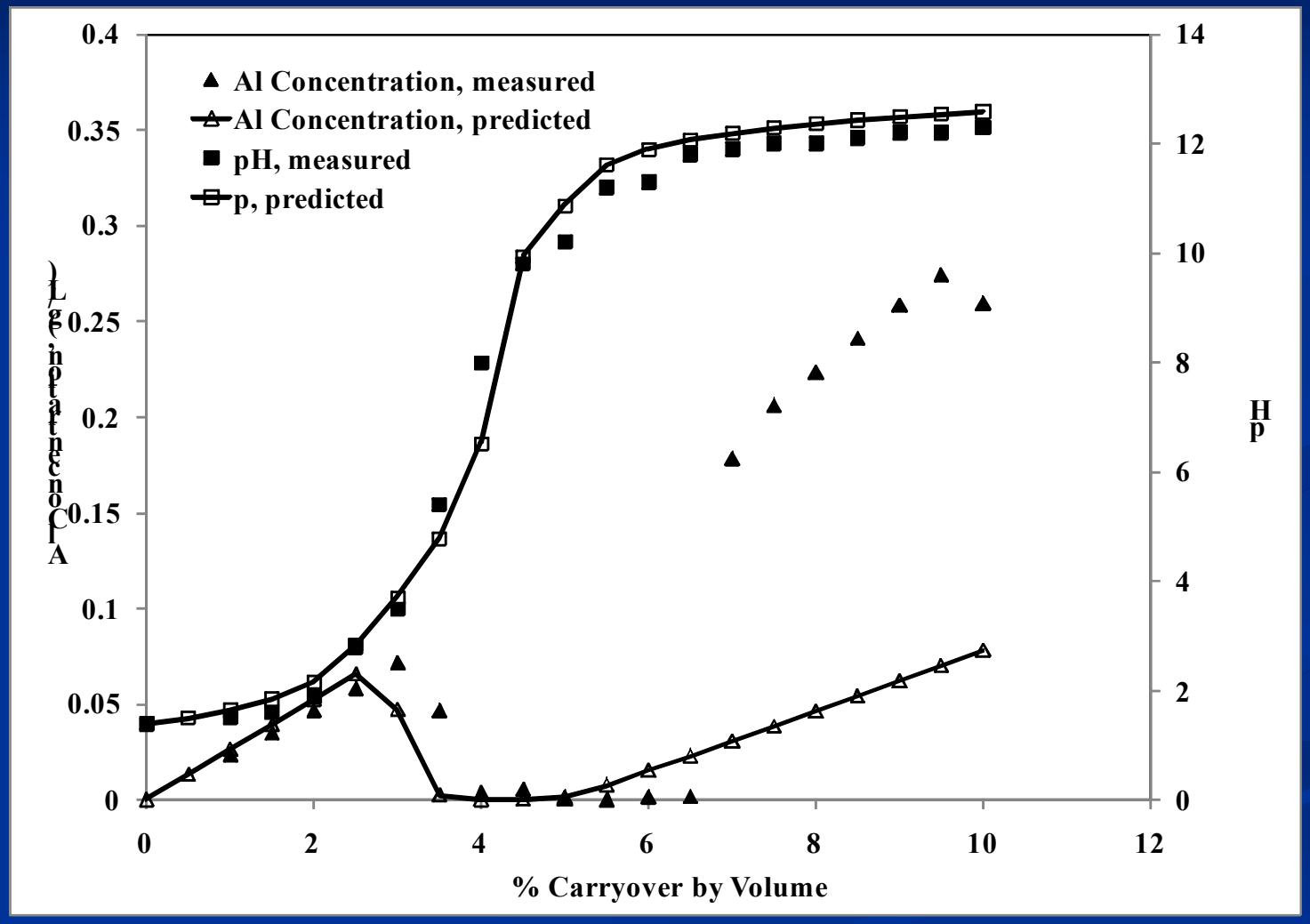
Experimental Results – Stream 4



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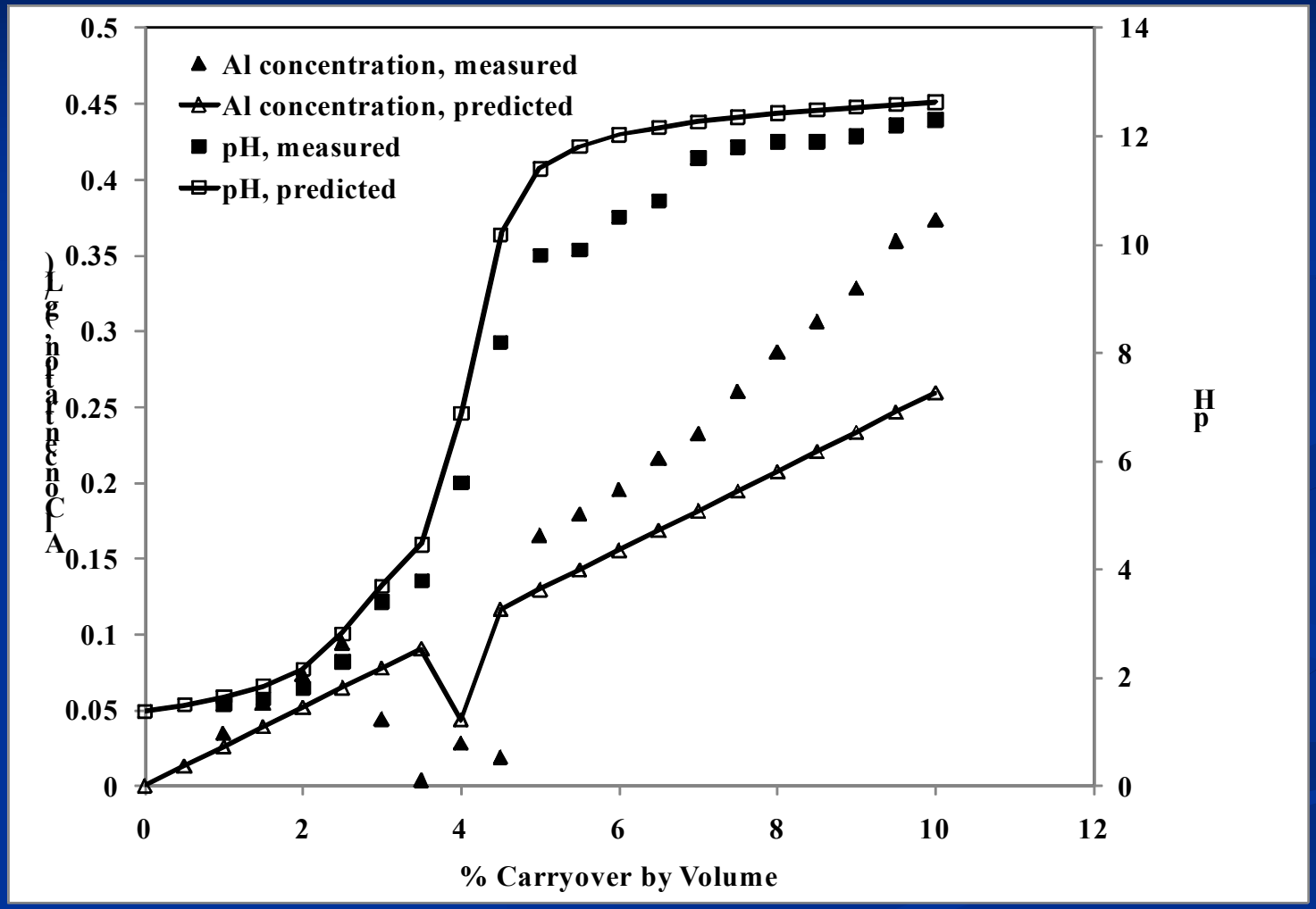
Experimental Results – Stream 5



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Solids Formation

- Observed for Stream 1 for 2 % to 4 % carryover by volume
- Observed for Streams 4 and 5 for 4 to 6 % carryover by volume
- Experimental matrix developed to examine precipitation kinetics in these solutions

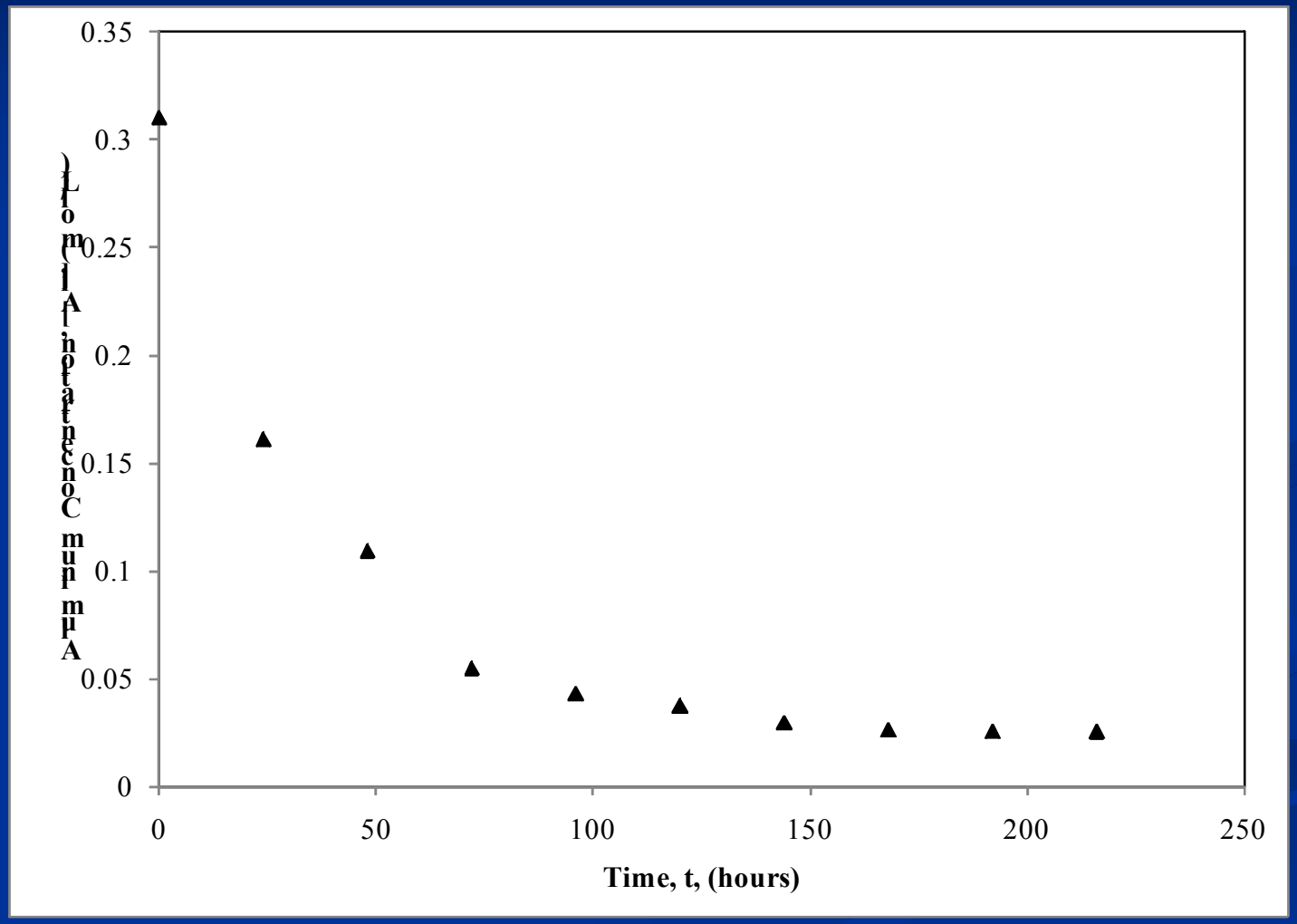
Kinetics – Experimental Matrix

Tank	Transfer Stream	Simulant (ml)	0.05M HNO_3 (ml)	Carryover (Volume %)
25F	1	2.0 3.0 4.0	98.0 97.0 96.0	2.0 3.0 4.0
25F	4	4.0 5.0 5.5 6.0	96.0 95.0 94.5 94.0	4.0 5.0 5.5 6.0
25F	5	4.0 5.0 5.5 6.0	96.0 95.0 94.5 94.0	4.0 5.0 5.5 6.0

Kinetics Experimental Procedure

- Simulant/nitric acid sample prepared as for mixing experiments
- Small aliquot of liquid removed daily and aluminum concentration measured
- Daily monitoring continued until visual observation of solids in sample

Typical Aluminum Concentration Profile Stream 1, 2% Carryover



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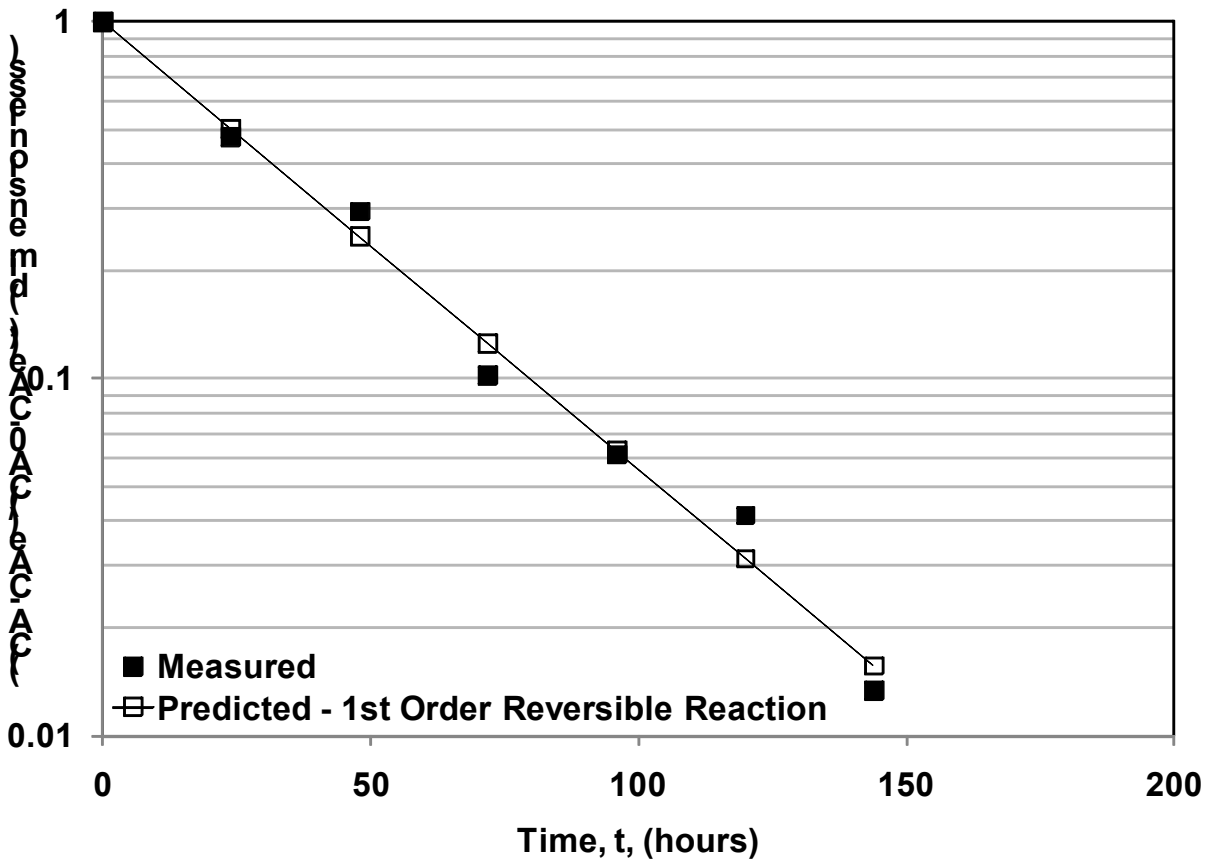
Kinetic Data - Analysis

- Experimental aluminum concentrations fit to a first order reversible rate law.
- Last 3 to 4 data points used to establish aluminum equilibrium concentration [C_{Ae}], and equilibrium conversion, X_{Ae}
- Use of standard batch reactor design equation with proposed rate law results in:

$$\ln\left[\frac{C_A(t) - C_{Ae}}{C_{A0} - C_{Ae}}\right] = \frac{-k_f}{X_{Ae}} t$$

Kinetic Analysis – Stream 1, 2% Carryover



Kinetic Rate Constants

Stream	% Carryover	Forward Specific Reaction Rate, k_f ($Hour^{-1}$)	Reverse Specific Reaction Rate, k_r ($Hour^{-1}$)	$[Al]_e$ (mol/L)
Stream 1	2	0.0265	0.0024	0.0254
	3	0.0194	0.0047	0.0612
	4	0.0114	0.0064	0.1120
Stream 4	4	0.0316	0.0015	0.0041
	5	0.0167	0.0035	0.0154
	5.5	0.0180	0.0023	0.0100
	6	0.0208	0.0022	0.0086
Stream 5	4	0.0162	0.0042	0.0179
	5	0.0144	0.0068	0.0278
	5.5	0.0165	0.0095	0.0320
	6	0.0071	0.0055	0.0379

Experimental Conclusions/Summary

- Solids formation was observed for a limited range of % carryover by volume for each of the transfer streams examined. Dawsonite was predicted to form in this region.

- Kinetic studies for these streams indicated specific reaction rates on the order of 0.007 to 0.032 hr-1 for the forward reaction, and 0.001 to 0.009 hr-1 for the reverse reaction.

Path Forward

- Examine tanks with higher aluminum (31H,29H) and higher carbonate (37H)
- Examine boric acid as scrub solution compared to nitric acid
- Both modeling and experimental studies are planned for FY11

Questions

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