

On the Formation and Treatment of Trisodium Phosphate Plugs

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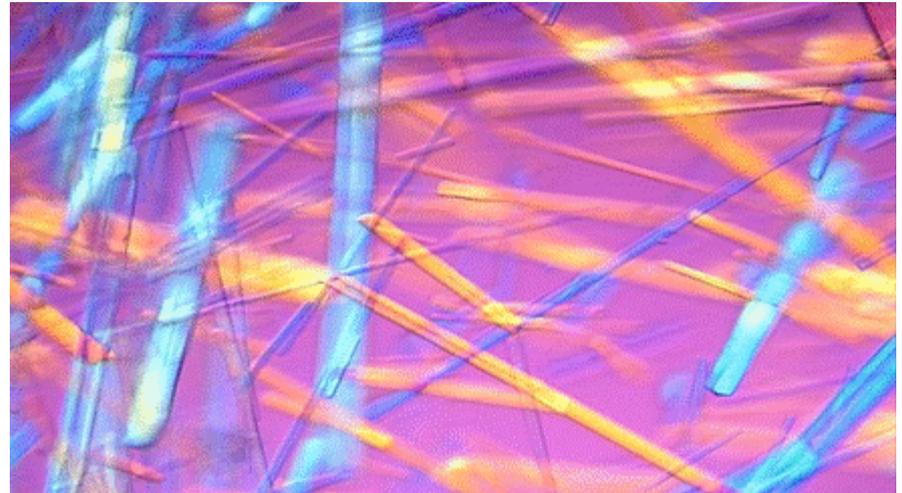


Background and Motivation

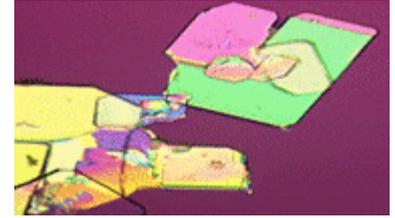
- Hanford Saltwell Supernatant Transfers
 - 0.4-5gpm 3 inch mild steel heat traced pipe
 - $Re=dV\rho/\mu = 180-1800$
 - Junction Boxes untraced
 - Plugs from SX-104, U-103, BY-102 \$2.4 million impact
- Actual SX-104 Supernatant Analysis
 - Herting PLM Cloudy at 25°C, Gel at 23°C
 - Steen $[PO_4] = 0.044M$

Background and Motivation

- Investigate Plug Formation SX-104 Surrogate
 - Construct Lab-Scale Flow Loop based on Re
 - Develop Operating Envelope, V , T , $[PO_4]$
- Examine unplugging options



Solubility Studies and Database Development



- Environmental Simulation Program (ESP, OLI Systems Inc.) - aqueous thermodynamic electrolyte model for solid-liquid equilibria (SLE)
- Selected at Hanford (and SRS) as a predictive engineering tool
 - reduce costs of analytical characterization
 - identification of compositions that could result in difficulties during pretreatment and retrieval operations
 - Flowsheet Development – Unit Operations
- Data gaps found for many chemical systems contained in Hanford wastes

Validation Issues

- Quality of the fundamental thermodynamic data
- Direct comparisons to experimental results
- Evaluation against other models
- Code will never be fully validated
 - interactions between all possible component combinations
- Focus on predominant systems

Development Path

- Comparison of simulation results to Hertings' core salt cake dissolution experiments
- Fundamental solubility experiments – Database Development
- Direct comparisons to other experimental results (FIU tall column experiments)
- Code will never be fully validated
 - interactions between all possible component combinations

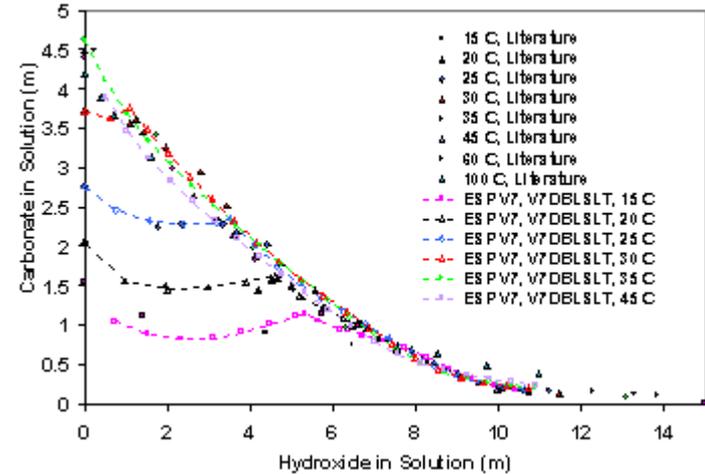


Regression Fits and Database Development

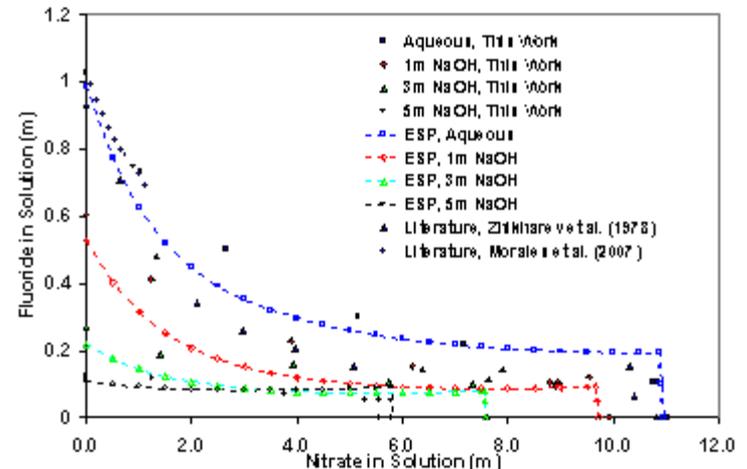
Na-F-NO ₃	Na-NO ₂ -CO ₃	Na-SO ₄ -PO ₄
Na-F-SO ₄	Na-NO ₃ -CO ₃	Na-Al-NO ₃
Na-F-PO ₄	Na-NO ₂ -SO ₄	KNO ₃
Na-PO ₄ -NO ₃	Na-NO ₃ -SO ₄	CsNO ₃
Na-F-PO ₄ -NO ₃	Na-SO ₄ -CO ₃	

- DBLSLTDB double salt database for use in ESP 6.5
- Attempted to port to ESP version 6.7
- Ported to ESP version 7.0 V7DBLSLT
- After fitting the data for 3 different versions of ESP initiated subcontract with OLI Systems Inc.
- Data will now be in a permanent repository
- Release from OLI Systems Inc., 1st Qtr 2008

Na-CO₃-OH System

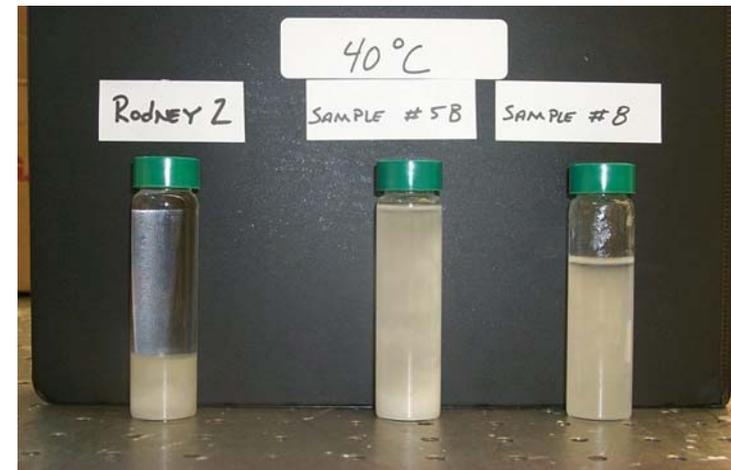


Na-F-NO₃ System



Development of Surrogate

SX-104 Supernatant Surrogate	ORNL	Sample 5	Sample 8
moles Sodium salt			
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
moles H ₂ O	55.51	55.51	55.51



Laboratory Scale Saltwell Pumping Flow Loop



Temperatures and Pressures Observed Following Activation of the Heat Exchanger

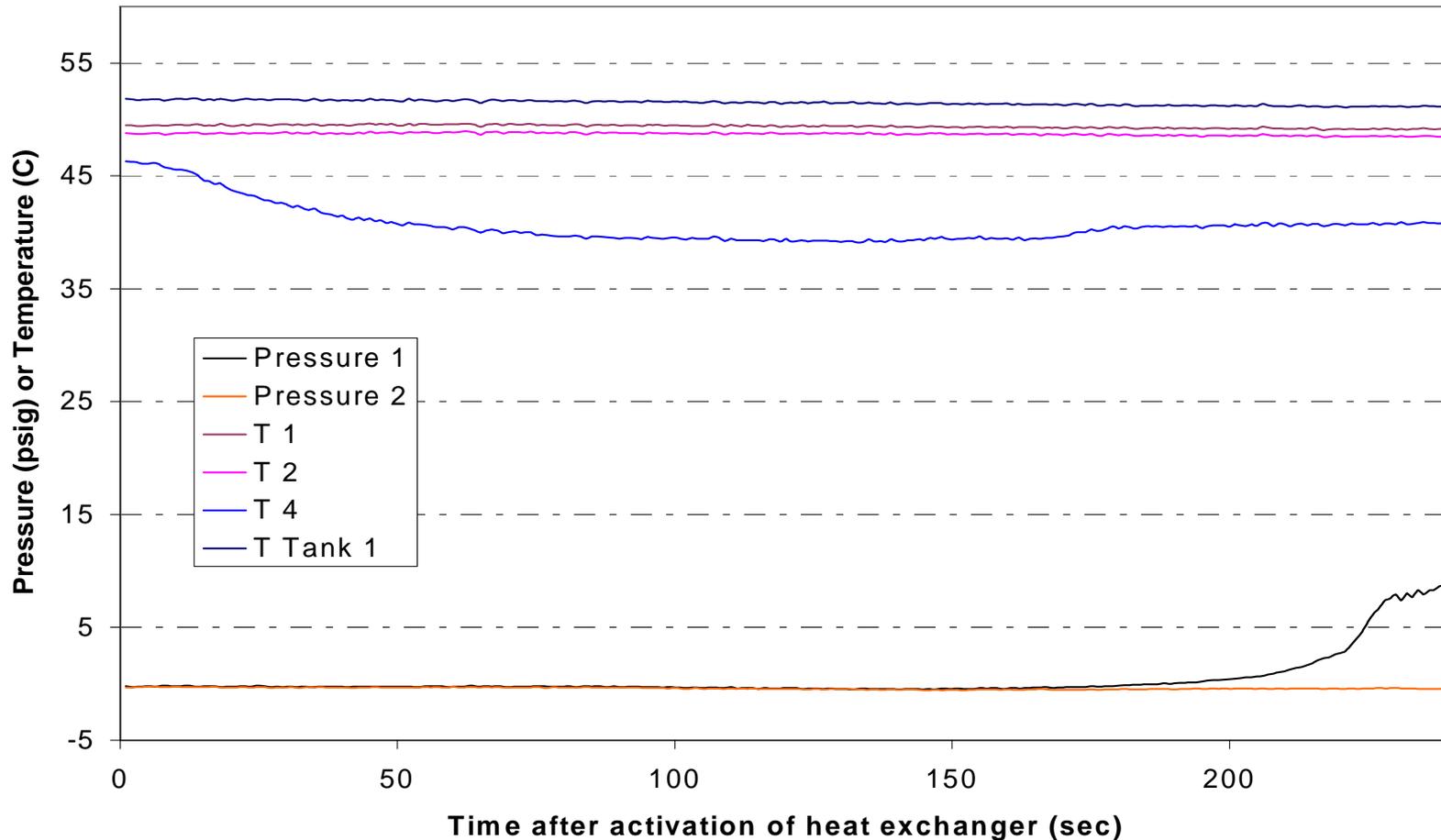
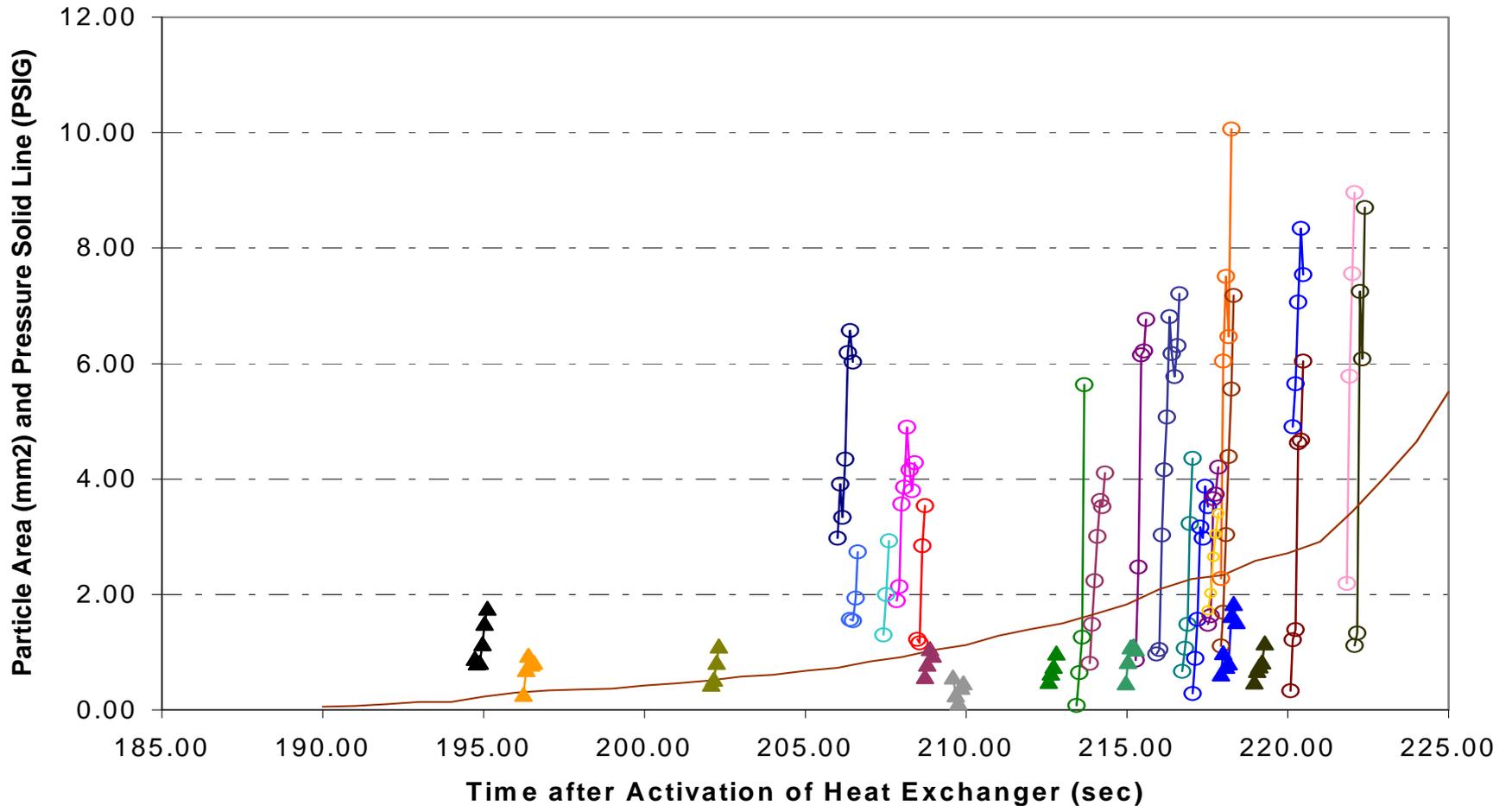


Image Sequence of Particle Growth

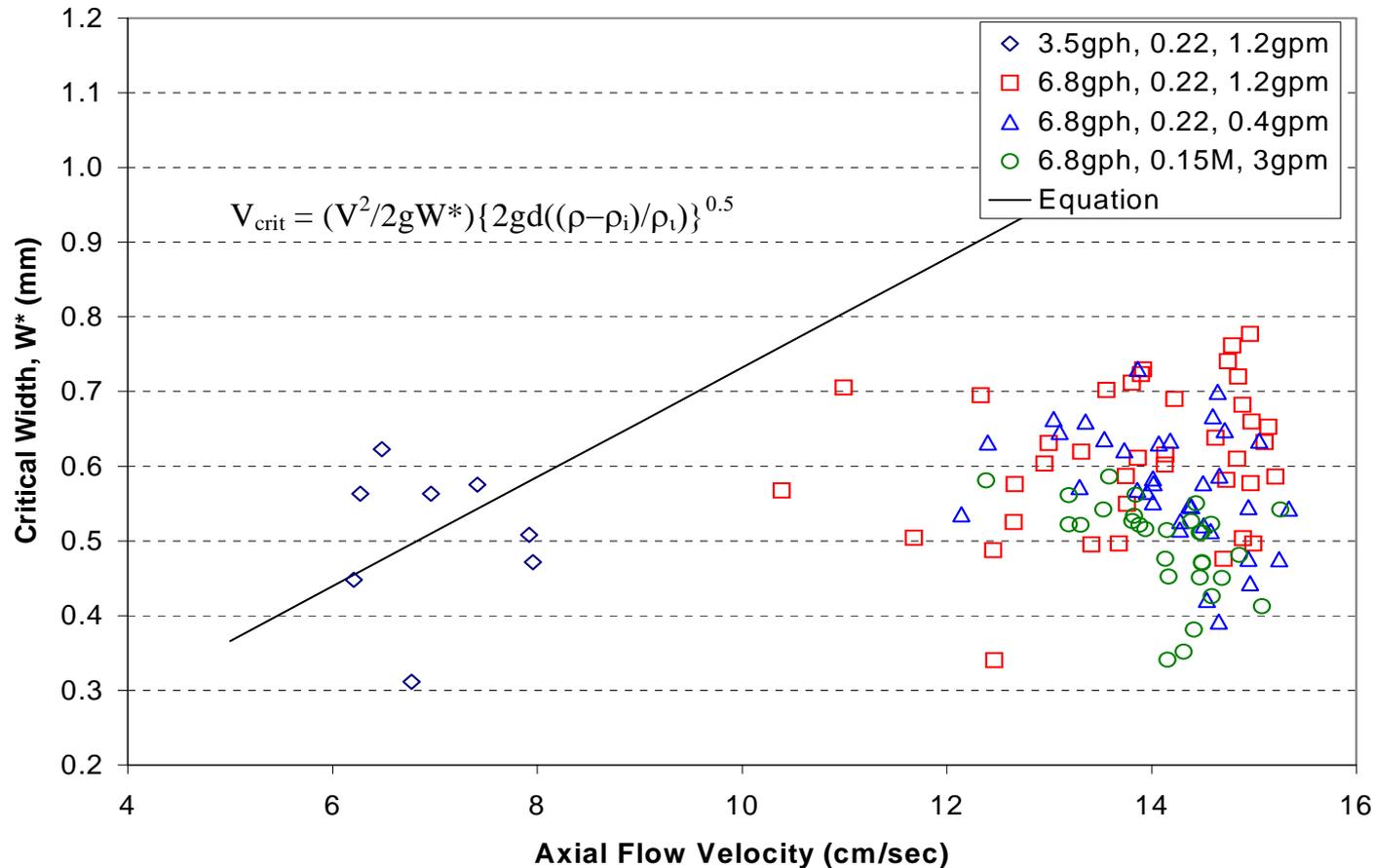


9 20 2

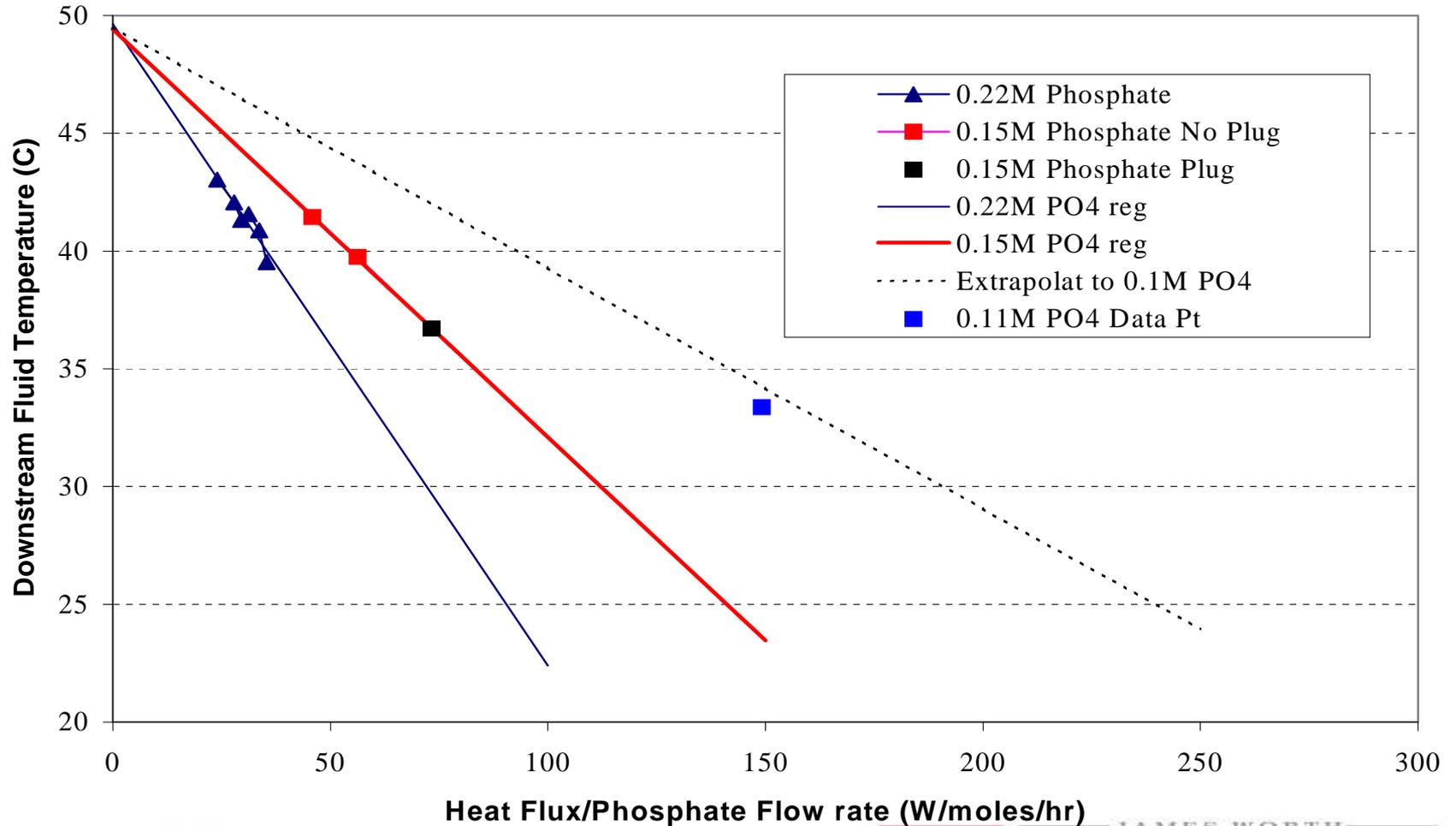
Single Particle (triangles) and Agglomerate (open circles) Areas and Growth



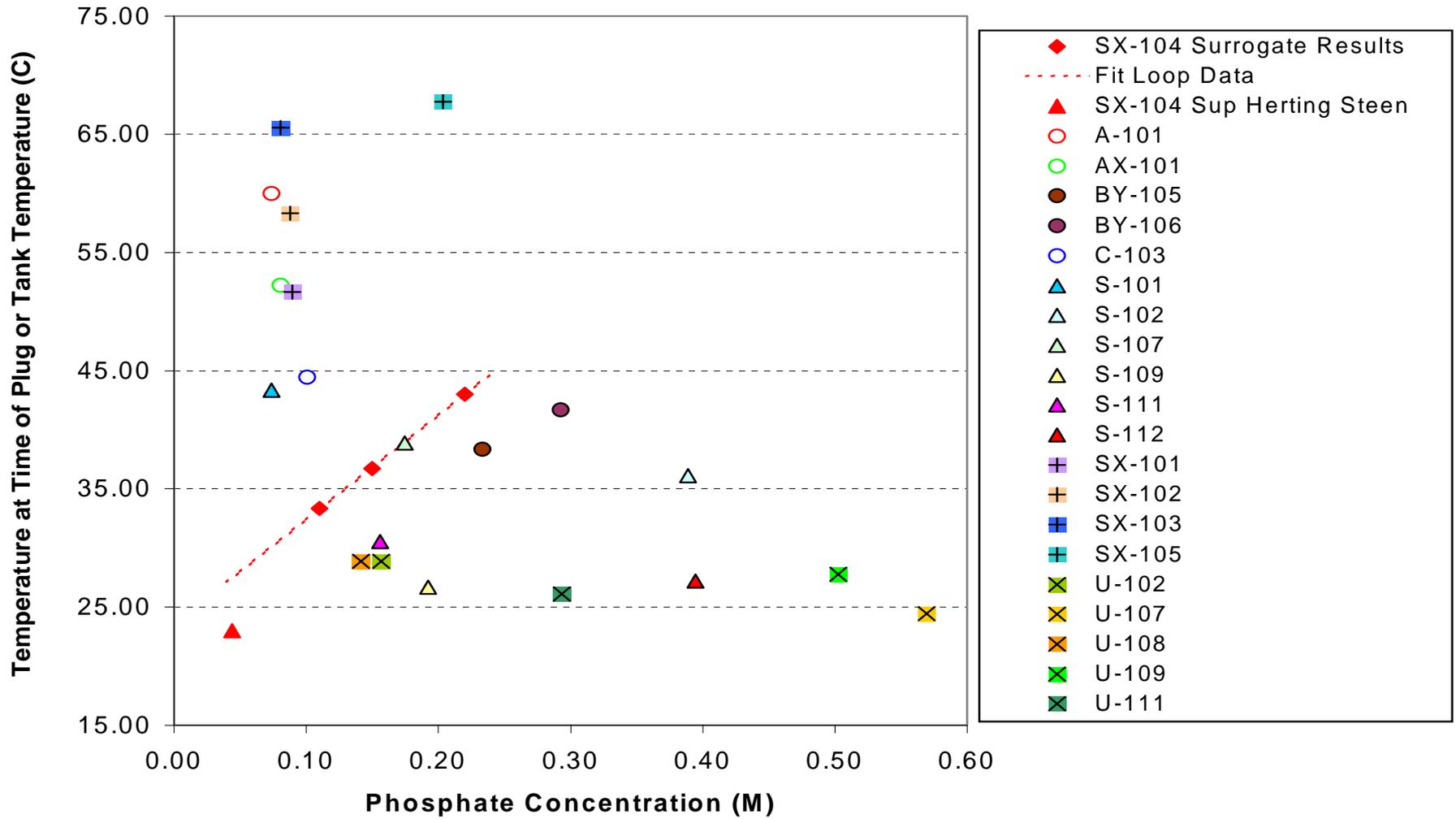
Measured Single Particle and Calculated Critical Deposition Widths



Plug Formation Depends on Phosphate Loading and Cooling Rate



Loop Data Extrapolated to Actual SX-104 SW Supernatant Non-Stabilized SST Waste Temperatures and [PO₄] (BBI)



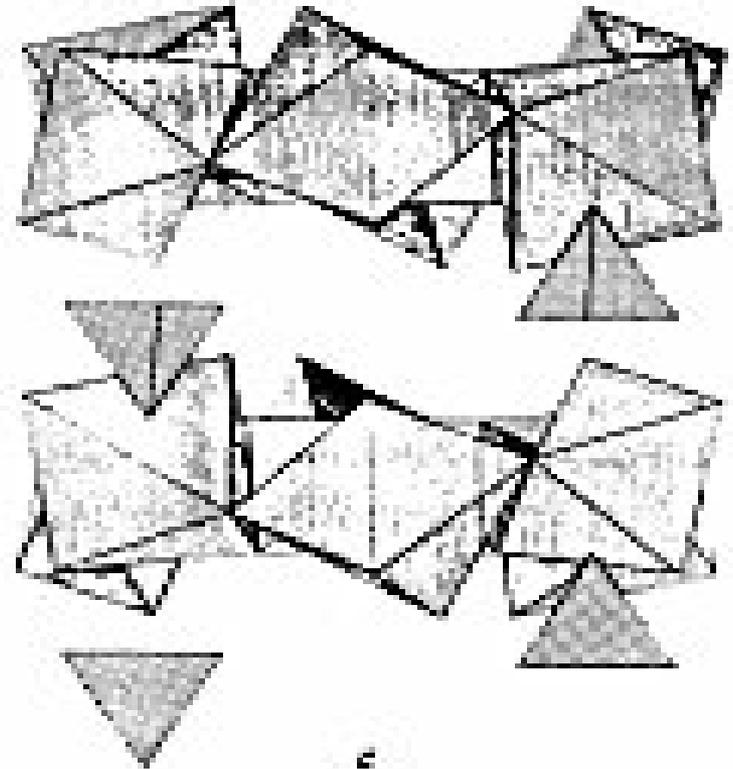
Key Findings for Interim Stabilization Transfers

- Growth Rates of single and agglomerate sodium phosphate dodecahydrate particles can approach 2 and 18mm²/sec respectively.
- Bed development commences when the particles or agglomerates exceed a critical size and settle.
- Plug formation can occur at temperatures as high as 43°C.
- An operating envelope for waste transfers based on the phosphate loadings in the tanks and temperature drops that may be encountered during routing has been advanced.

$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ Crystal Structure

Tillmans, E., & W. H. Baur, Inor. Chem, 9, 1957 (1970).

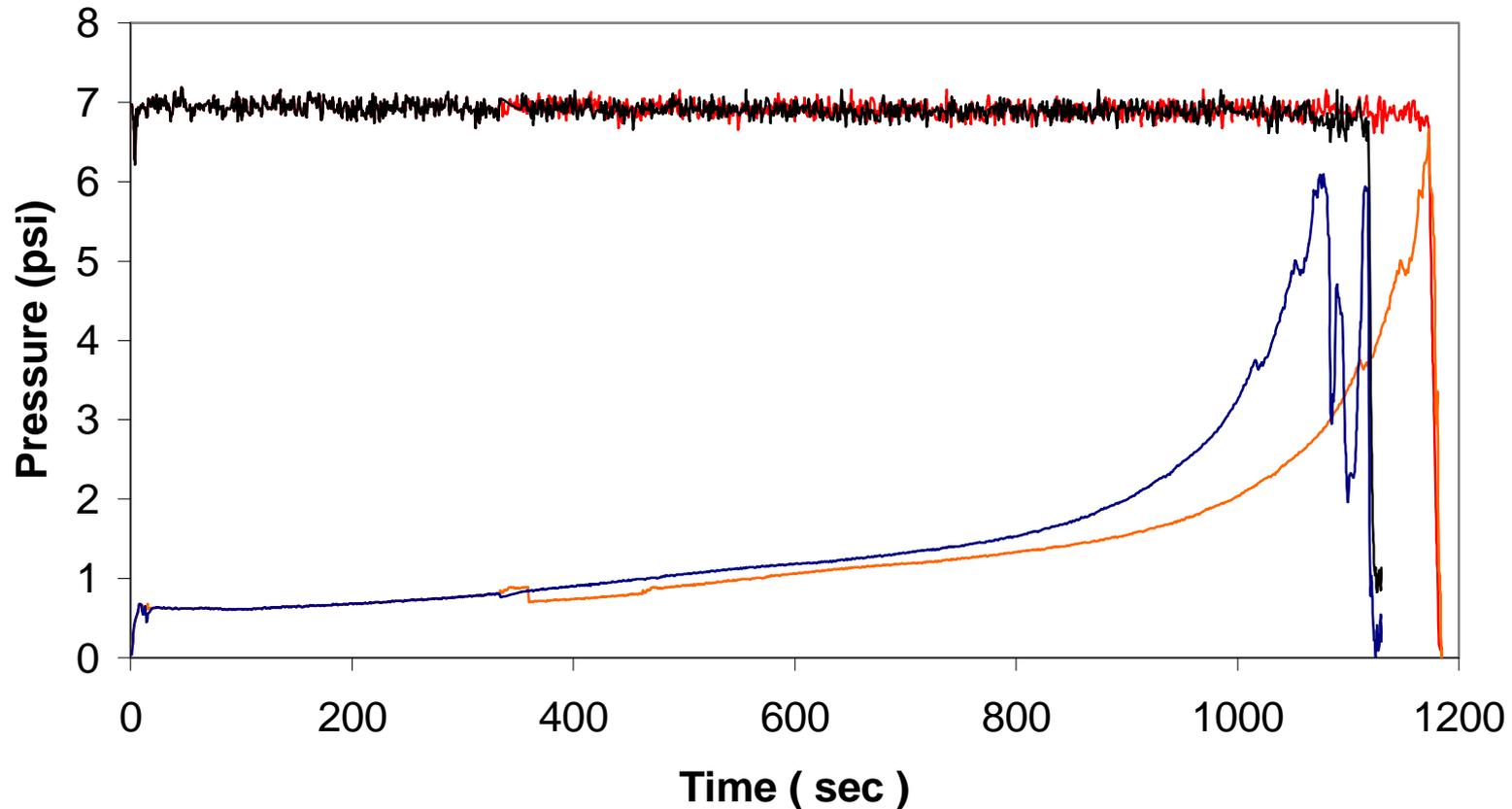
- Sheet with composition of $\text{Na}(\text{OH}_2)_4$ sharing corners to form rings with each ring connected to other rings by common edges
- Connections between sheets from hydrogen bonds from the water molecules to the phosphate groups located between the sheets
- Disrupt the hydrogen bonding fracture the structure



On the use of Carbonate Anion for Phosphate Plug Dissolution

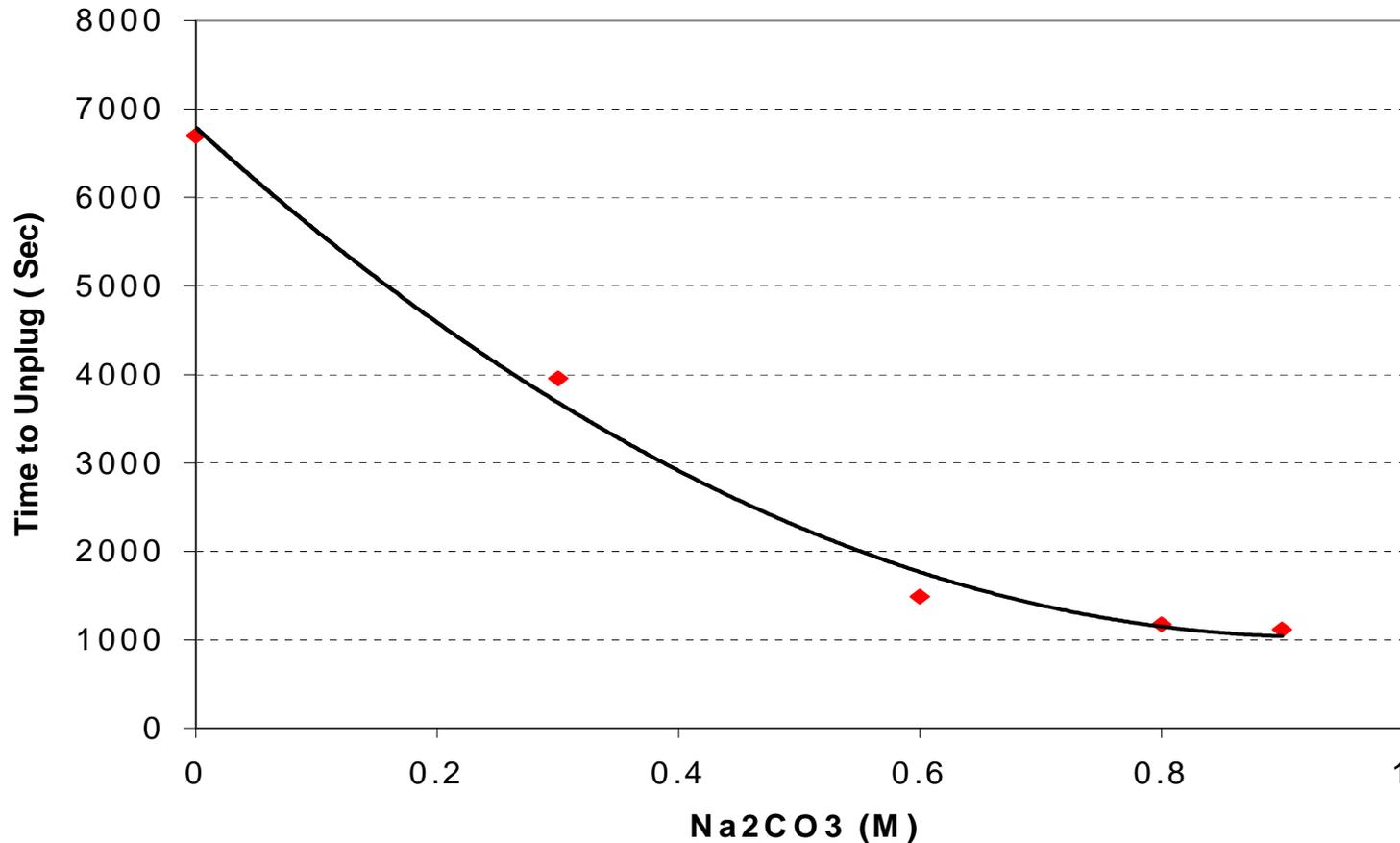
- Previous Work - “A novel reaction between carbon dioxide and trisodium orthophosphate dodecahydrate shown by photoelectron spectroscopy and X-ray diffraction,”
Belton, P. S. et al., J. Inor. Nucl. Chem., 43, 614 (1981).
- $\text{CO}_{2(g)} + \text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}_{(s)} \rightarrow \text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}_{(s)} + \text{NaHCO}_3_{(s)} + 4\text{H}_2\text{O}.$
- Unique reaction between a gas and a solid forming two solids.
- Phosphate plugs formed in test loop allowed same 2-hour residence time followed by addition of xM Na_2CO_3 solution.

Experimental Observation of Unplugging

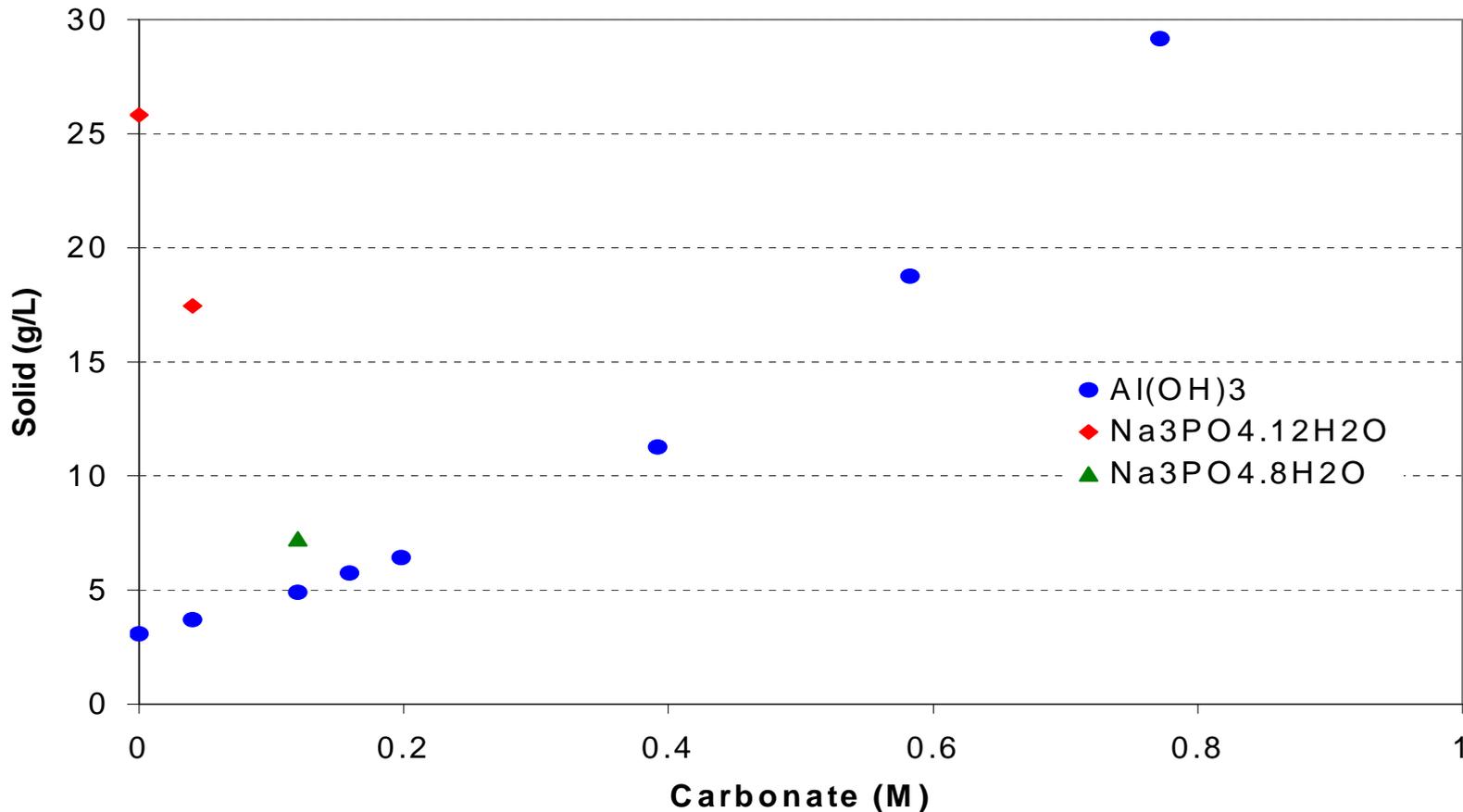


— pressure 0 at 0.8m Na₂CO₃ — pressure 3 at 0.8m Na₂CO₃
— Pressure 0 at 0.9m Na₂CO₃ — Pressure 3 at 0.9m Na₂CO₃

Reaction of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ with Na_2CO_3 solutions results in less time needed for unplugging than using water alone



Solids predicted by ESP for the reaction of $\text{CO}_{2(g)}$ with $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ in SX-104 surrogate



Observations regarding the use of CO_3^{-2} for destroying $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ Plugs

- Dissolution of a phosphate plug took approximately 1/7th the time with a 0.9M Na_2CO_3 solution compared to with water alone.
- The addition of carbonate causes reaction with the $\text{Na}(\text{OH}_2)_4$ sheet resulting in an increase in the NaCO_3^{-1} concentration and the destruction of hydrogen bonding.
- ESP simulations at carbonate concentrations less than ca. 0.1M indicate that the $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ converts to $\text{Na}_3\text{PO}_4 \cdot 8\text{H}_2\text{O}$. Further carbonate addition dissolves all phosphate solids.
- SpriteTM works.