Aluminum Solids Dissolution Kinetic Studies

AL Pajunen
Polestar Applied Technology, Inc.

Technical Exchange on Aluminum and Chromium Leaching Workshop

January 23-24, 2007

POLESTAR APPLIED TECHNOLOGY, INC.

Introduction

- Dissolution studies were completed by Polestar Applied Technology for the Washington Savannah River Company to support evaluating mitigation of waste tank aluminum inventory uncertainties
- Mitigation approach considered aluminum dissolution from Tank 12, 13, 15, 32, 35, and 39 sludge, followed by managing supernate to avoid transferring aluminum solids to DWPF feed tanks
- Study efforts resulted in:
  - LWO-PIT-2006-00006, *Evaluation of Boehmite Dissolution Kinetics in Tank Waste*
  - LWO-PIT-2006-00011, *Salt Waste Handling of Aluminum Bearing Supernates Topical Report*
  - LWO-PIT-2006-00057, *Preliminary Aluminum Dissolution Parameters*
  - Material balance spreadsheet for describing alternative dissolution configurations
- This presentation summarizes kinetic and dissolution parameter evaluations

Boehmite Dissolution Evaluation

- Tank waste solids contain both gibbsite and boehmite
- Literature indicates boehmite dissolution in caustic slower than gibbsite
- Objective is to estimate time to dissolve aluminum solids assuming boehmite is dominant form in sludge

General Mineral Dissolution Rate Equation

$$\frac{dm}{dt} = -(S)\left(Ae^{-\frac{E}{RT}}\right)f(a_i)\,g(\Delta G_r)$$

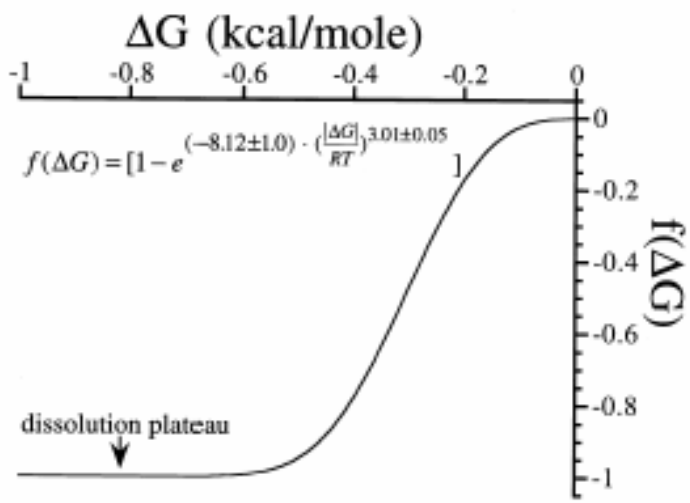
where:

dm/dt =	Dissolution rate, gmol solid/hr
S =	Solids surface area, m^2
A =	Dissolution reaction pre-exponential factor, gmol solid/m^2-hr
E =	Dissolution reaction activation energy, cal/gmol
T =	Absolute temperature, K
R =	Gas constant, cal/gmol-K
$f(a_i)$ =	Reactant concentration function, dimensionless
$g(\Delta G_r)$ =	Function describing impact of approach to solubility limit on solids dissolution rate, dimensionless

POLESTAR APPLIED TECHNOLOGY, INC.

General Rate Equation Simplifications

- Solids surface area decreases linearly with mass of solid remaining
- Dissolution rate variation with temperature from literature [dm/dt~exp(-14,800/T)]
- Dissolution rate variation with liquid phase composition from literature [dm/dt~$(a_{NaOH})^{1/2}$ for concentrations less than 6.8 M NaOH]
- Dissolution endpoint does not approach solubility limit



POLESTAR APPLIED TECHNOLOGY, INC.

Integrated Rate Equation

- Integrated Rate Equation based on transient material balance for the liquid phase

$$t = \frac{\alpha F(wf, \alpha)}{(\eta^0 \gamma_{\pm}^{1/2} A)\sqrt{C_{OH}^0}} e^{\frac{14800}{T}}$$

where :

t = Dissolution time, hr

$$F(wf, \alpha) = \frac{1}{\sqrt{\alpha(\alpha - 1)}} \mathrm{Ln}\left|\frac{(\sqrt{\alpha} - \sqrt{\alpha - 1})(\sqrt{\alpha - 1 + wf} + \sqrt{\alpha - 1})}{(\sqrt{\alpha} + \sqrt{\alpha - 1})(\sqrt{\alpha - 1 + wf} - \sqrt{\alpha - 1})}\right|$$

α = Mole ratio at initial conditions of free OH ion in the liquid phase relative to Al in the solid phase, dimensionless

C_{OH}^0 = Initial liquid phase concentration of free OH ion in molal units, gmol/kg water

T = Dissolution operating temperature, K

wf = Weight fraction of initial Al remaining in solids at the conclusion of the dissolution process, dimensionless

$(\eta^0 \gamma_{\pm}^{1/2} A)$ = Constant grouping determined from test data, hr^{-1}-(gmol OH/kg water)$^{-1/2}$

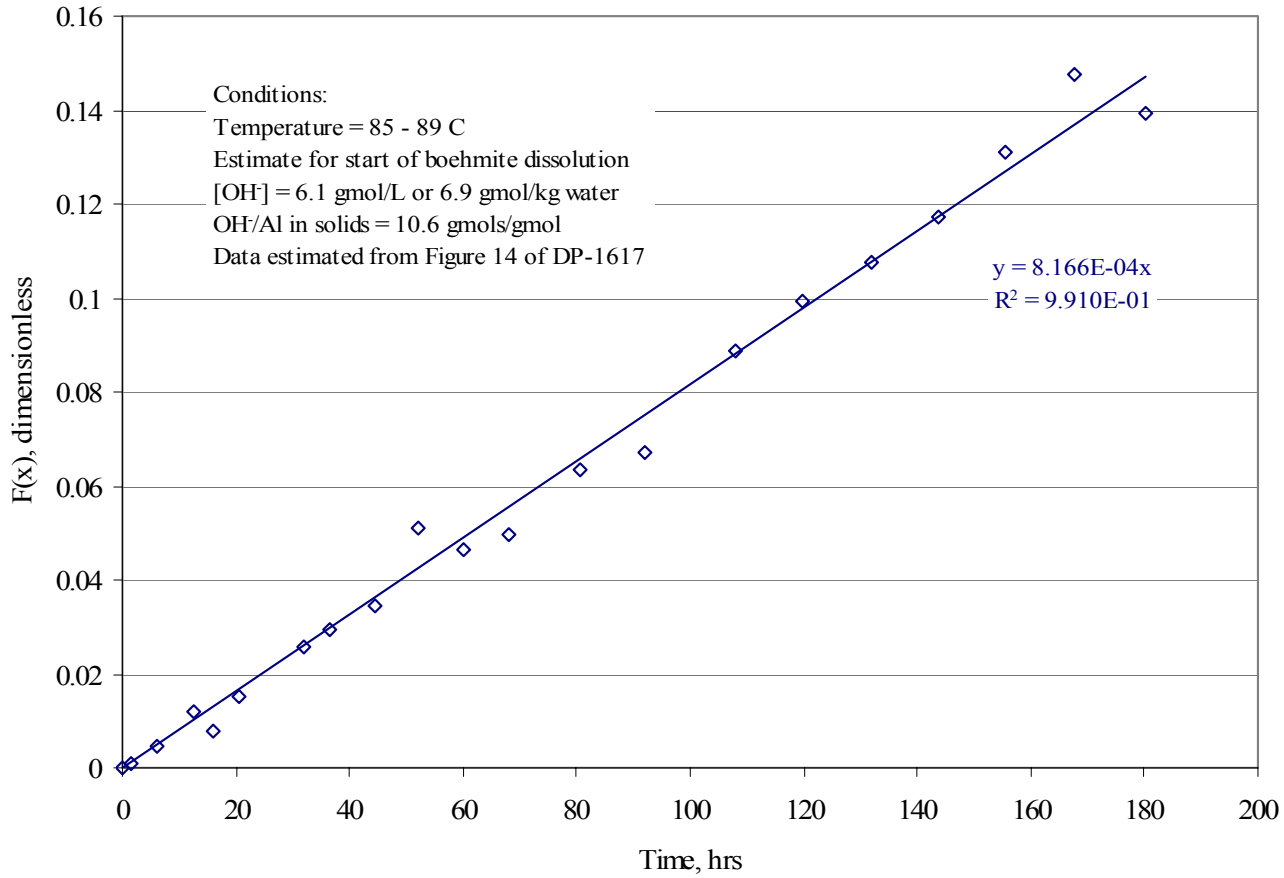
POLESTAR APPLIED TECHNOLOGY, INC.

Estimates of Rate Constants from Experimental Data

Estimate Basis		Estimated Value of ($\eta^0 \gamma_{\pm}^{1/2} A$), hr^{-1}-(gmol OH/kg water)$^{-1/2}$
Test Scale	Solid Material Source	
Laboratory Scale Tests	Cold Chemical Boehmite	4.8×10^{15}
	Cold Chemical Boehmite + Sand	4.6×10^{15}
	Cold Chemical Boehmite	8.0×10^{15}
	Estimated Boehmite Fraction of Actual Tank 12 Sludge (Archived Sample)	1.6×10^{15}
Pilot Scale Test	Boehmite Fraction of Synthetic Tank 11 Sludge	2.4×10^{15}
Full Scale Demonstration	Estimated Boehmite Fraction of Actual Tank 15 Sludge	2.8×10^{15}

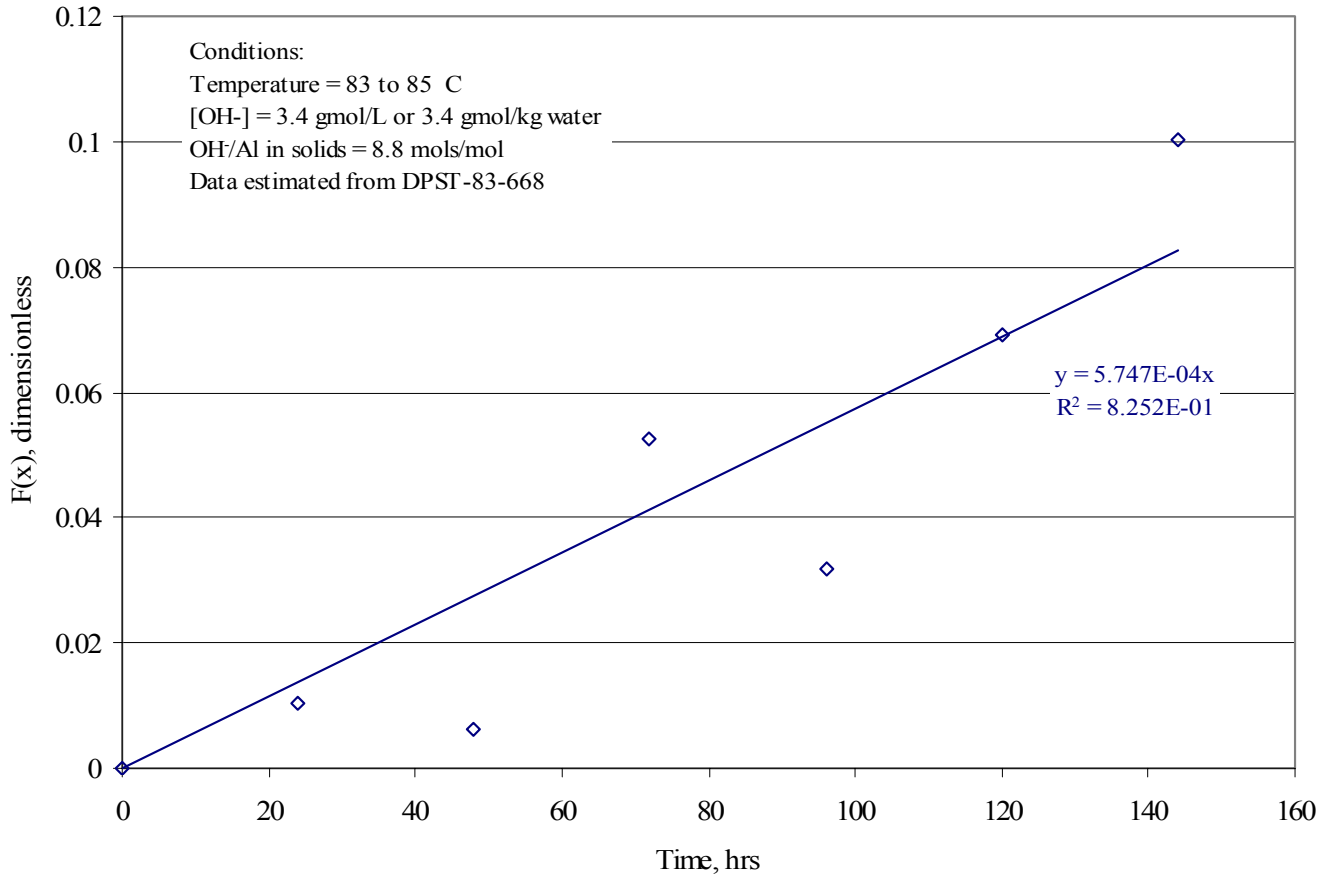
Rate Constant Evaluation from Pilot-Scale Data

(Synthetic Tank 11 Sludge)



POLESTAR APPLIED TECHNOLOGY, INC.

Rate Constant Evaluation from Full-Scale Demonstration Data



POLESTAR APPLIED TECHNOLOGY, INC.

Dissolution Model Limitations

- Solids Composition
  - Limited to predicting dissolution times based on solids as boehmite
- Operating Conditions
  - Temperature is constant
  - All liquid phase additions complete
  - Adequate phase mixing provided
- Solution Composition
  - Limited to aqueous phase concentrations < 5 gmol OH/kg water or modest changes in free hydroxide concentration over the dissolution when > 5 gmol OH/kg water
  - Limited to $\alpha > 1$
- Approach to Solubility Limit
  - Limited to liquid phase compositions that do not approach solubility limit
  - Documentation provides quantitative estimates for applicable liquid phase compositions
  - Large region at 85°C, decreasing as dissolution temperature is decreased

Boehmite Dissolution Parametric Study Results

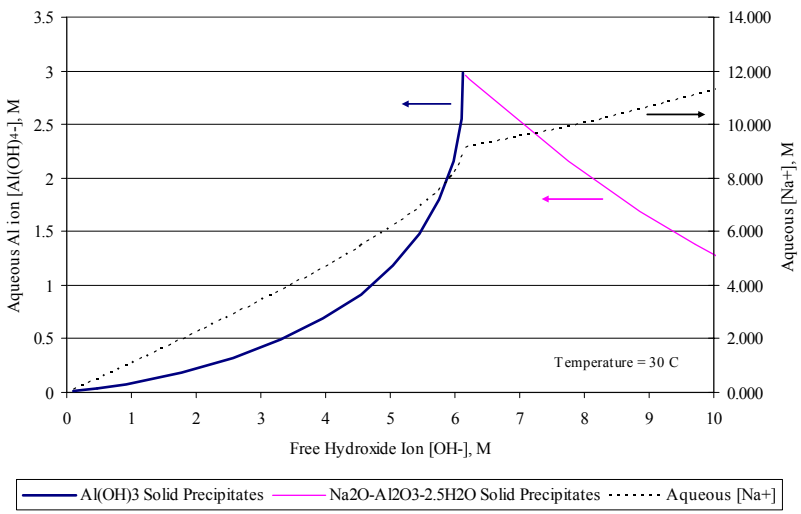
- Integrated rate equation used to perform parametric studies of dissolution time
- Dissolution time is dependent on:
  - Constant grouping
  - Fraction of initial aluminum solids to be dissolved
  - Liquid phase free hydroxide to solid phase aluminum mole ratio at initial conditions
  - Initial liquid phase free hydroxide ion concentration, and
  - Temperature
- Dissolution time most sensitive to fraction of initial aluminum solids to dissolve and temperature
- Dissolution time less sensitive to liquid phase free hydroxide to solid phase aluminum mole ratio at initial conditions and initial liquid phase free hydroxide ion concentration
- Temperature of 80°C to 90°C required to dissolve 75% of boehmite solids in less than 25 days

Dissolution Parameter Evaluation

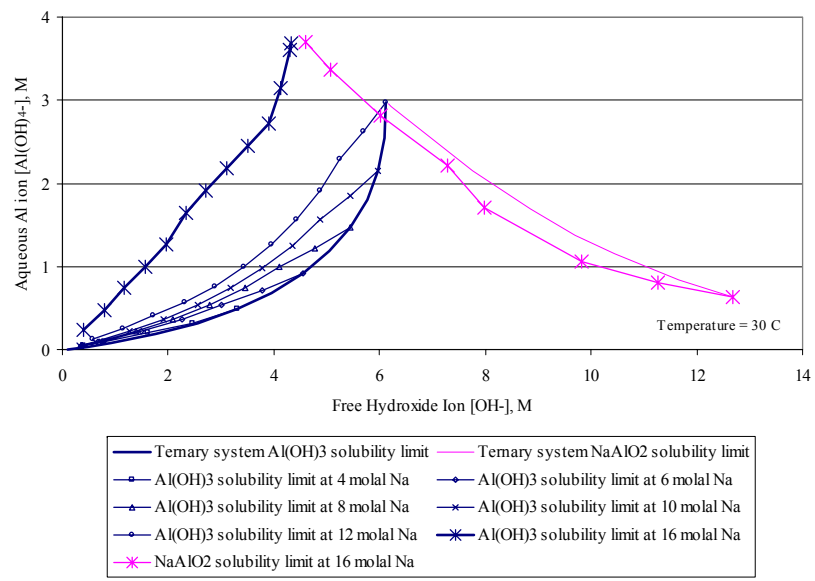
- General alternatives for implementing Al dissolution from tank sludge
  - Dissolve Al from sludge and avoid Al solids precipitation during interim supernate storage
  - Dissolve Al from sludge and allow Al solids precipitation during interim supernate storage. Re-dissolve any Al precipitate prior to salt waste processing
- Basis for dissolution parameters developed based on:
  - Avoid Al precipitation during interim supernate storage at a minimum storage temperature of 30°C
  - Remove 75% of aluminum from Tanks 12, 13, 15, 32, 35, and 39
  - Supernate stored without concentration
  - Minimize supernate volume and total sodium added
- Evaluation indicates factors that influence selection of dissolution conditions

Conservative Estimate of Aluminum Solubility

- ESP predictions indicate ternary system (Al_2O_3-Na_2O-H_2O) is conservative estimate of aluminum solubility



Predicted ternary system solubility at 30°C

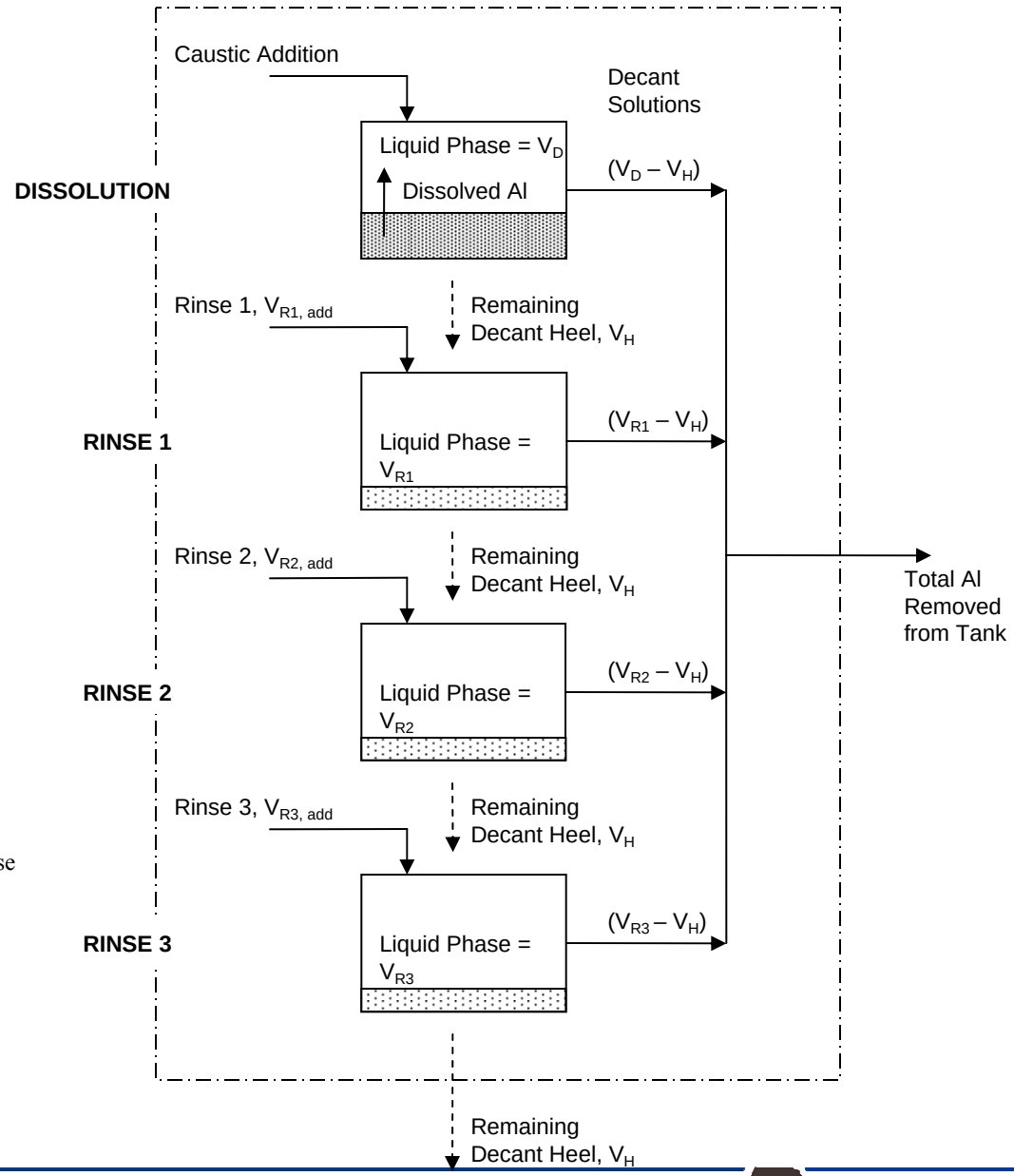


Predicted aluminum solubility variation at 30°C with ionic strength

POLESTAR APPLIED TECHNOLOGY, INC.

Simplified Block Diagram of Dissolution Steps

- Decant heel volume, post-dissolution rinse volume, and number of rinses influence the fraction of aluminum solids that must be dissolved



$$f = \frac{\{\text{Fraction of Al Inventory Removed from Tank}\}}{\left[(1-\gamma) + \gamma\left(\frac{1-\beta}{\beta}\right)\sum_{j=1}^{N}\beta^{j}\right]}$$

where :

f = mole fraction of aluminum dissolved from solid to liquid phase

$$\gamma = \frac{\{\text{Liquid phase volume in tank heel after decanting}\}}{\{\text{Liquid phase volume in tank during dissolution step}\}}$$

$$\beta = \frac{\{\text{Liquid phase volume in tank heel after decanting}\}}{\{\text{Liquid phase volume in tank during rinse step}\}}$$

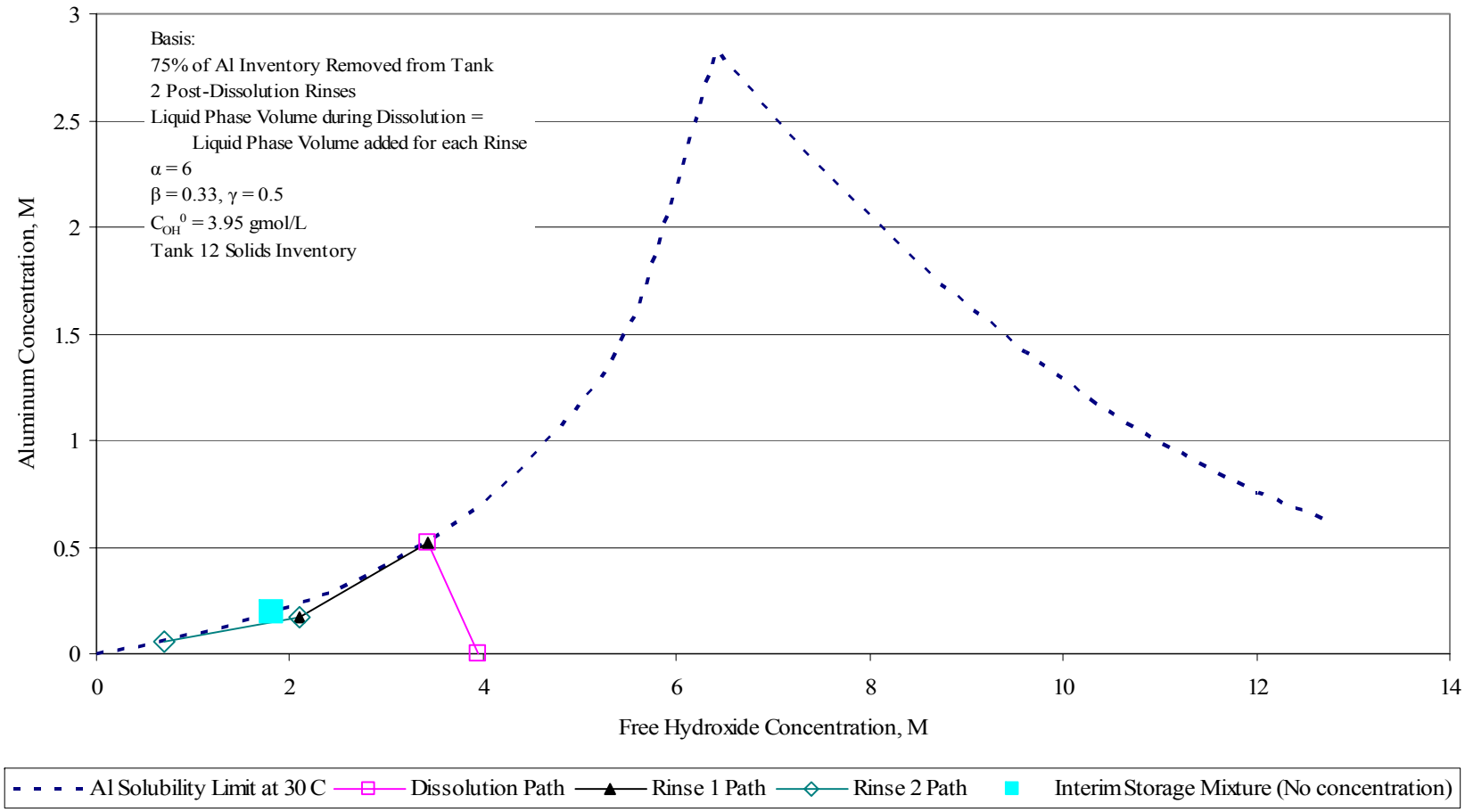
N = the number of post - dissolution rinse steps performed

POLESTAR APPLIED TECHNOLOGY, INC.

Comparison of Dissolution Endpoint to Aluminum Solubility

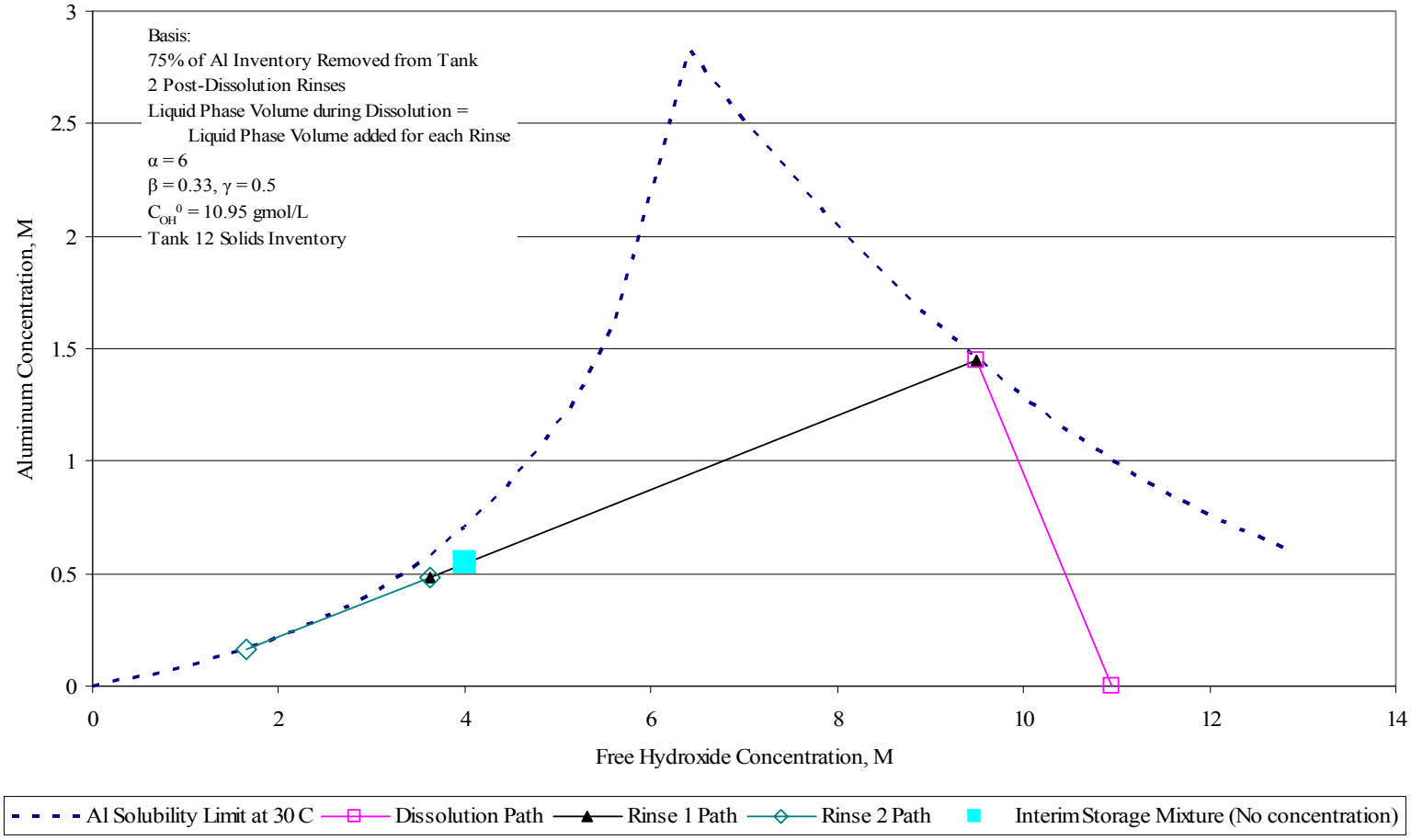
- Post-dissolution rinse selection:
  - Assumed 50% of liquid phase can be decanted after dissolution, each rinse volume added equals liquid phase volume during dissolution, and all heel volumes are equal
  - For 75% aluminum removal, Al solids to dissolve: 1 rinse = 90%, 2 rinses = 79%, and 3 rinses = 76%
  - Selected 2 post-dissolution rinses for further evaluation
- Determined variation of supernate volume and total sodium additions with dissolution conditions (initial caustic concentration and α) that avoid aluminum precipitation in supernate

Example Operating Diagram for Tank 12 Waste at minimum initial NaOH Concentration



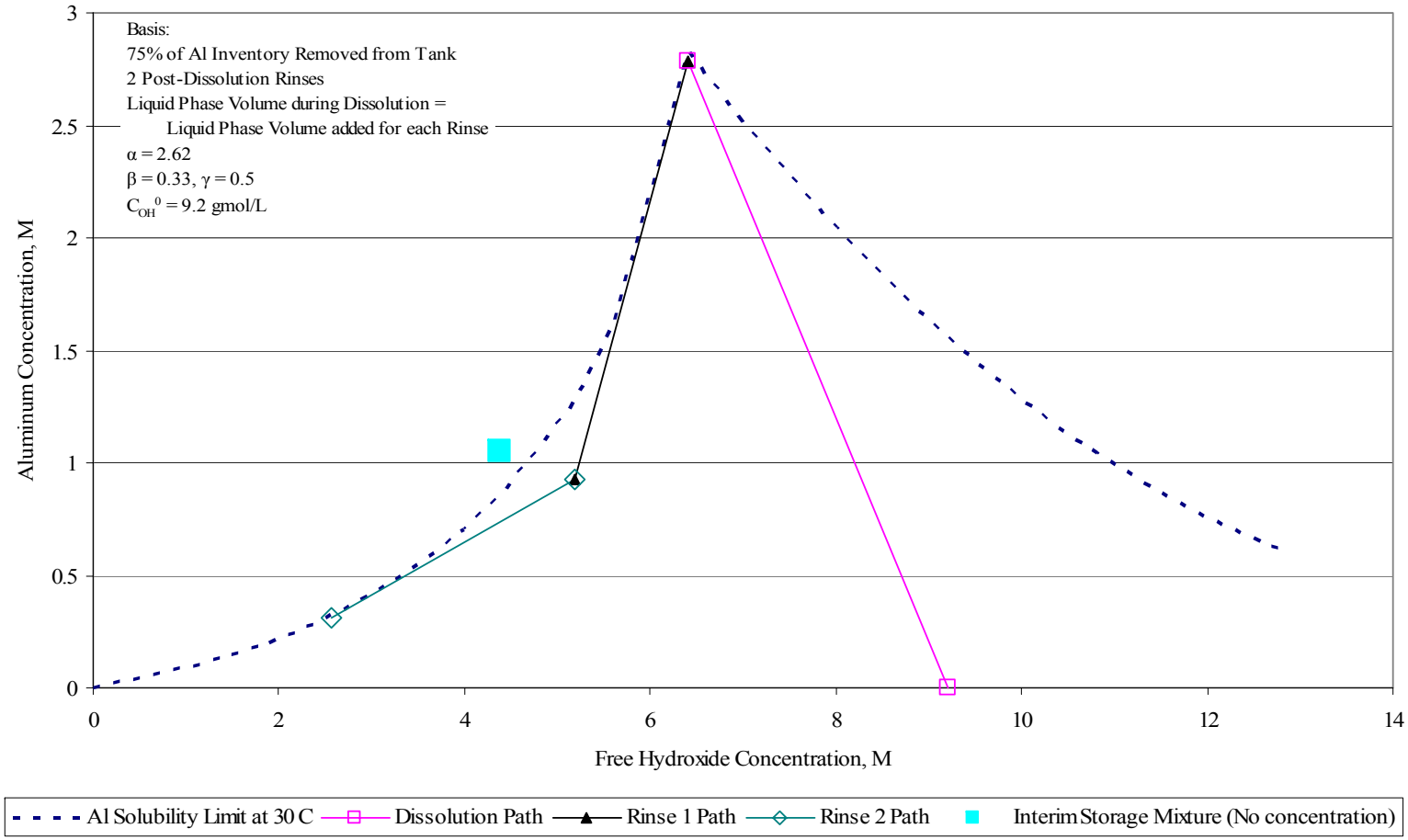
POLESTAR APPLIED TECHNOLOGY, INC.

Example Operating Diagram for Tank 12 Waste at maximum initial NaOH Concentration



POLESTAR APPLIED TECHNOLOGY, INC.

Example Operating Diagram for Tank 12 Waste producing minimum Supernate volume

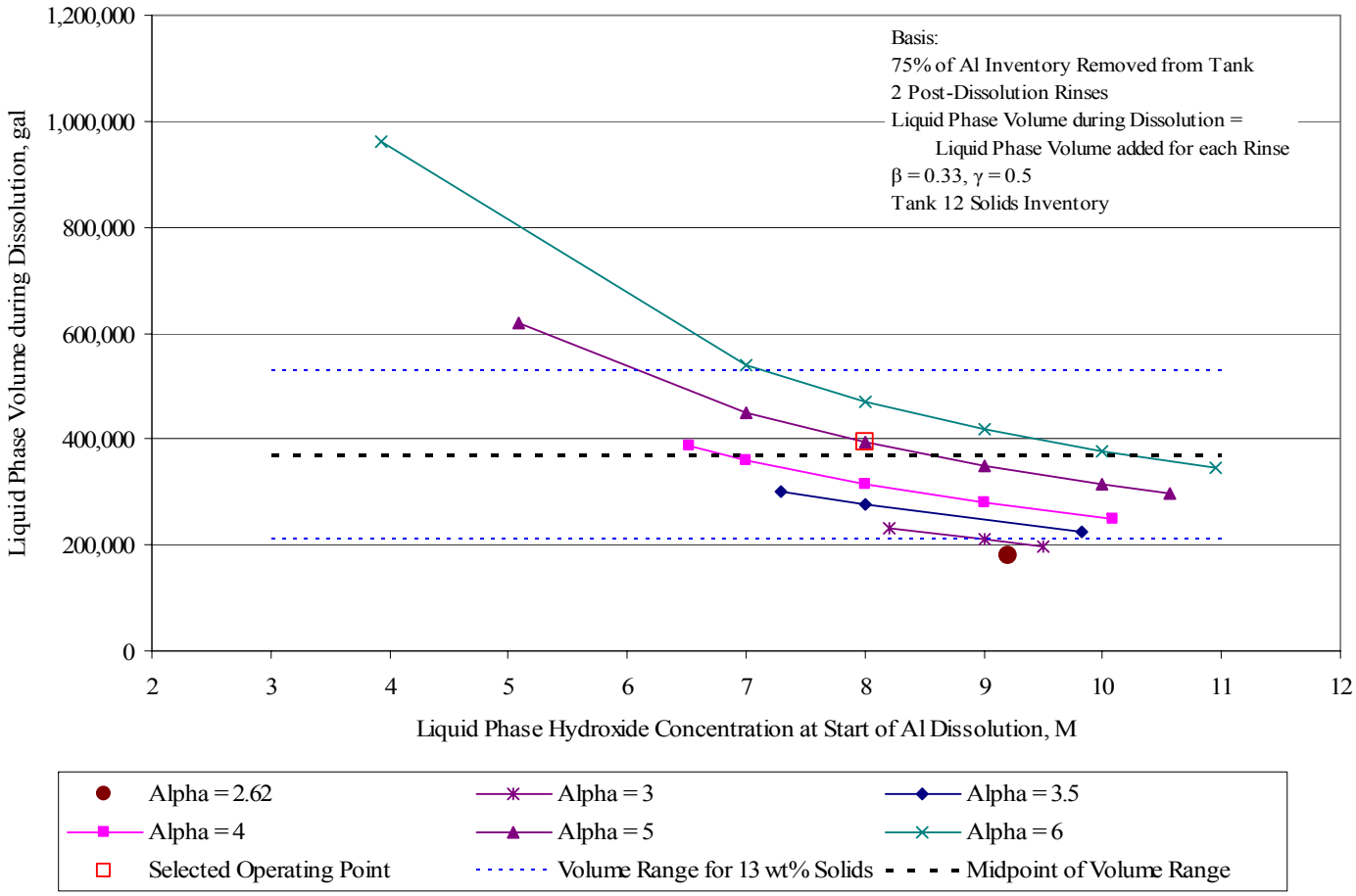


POLESTAR APPLIED TECHNOLOGY, INC.

Minimum Supernate Volume from Aluminum Dissolution and Post-Dissolution Rinse for Tanks 12, 13, 15, 32, 35, and 39

Tank	12	13	15	32	35	39	Total
Minimum Liquid Phase Volume during Aluminum Dissolution, gal	179,200	159,200	205,600	167,200	108,400	149,200	---
Minimum Interim Storage Volume, gal	448,000	398,000	514,000	418,000	271,000	373,000	2,422,000
Nominal Solids Content of Slurry Dissolution Step at Minimum Volume Condition	23 wt%	47 wt%	17 wt%	24 wt%	25 wt%	20 wt%	---

Influence of Phase Mixing on Selecting Dissolution Conditions



POLESTAR APPLIED TECHNOLOGY, INC.

Impact of Limiting Solid Phase to 13 wt% on Dissolution Conditions

Tank	12	13	15	32	35	39	Total
Molar ratio of free hydroxide ion in liquid phase to aluminum in solid phase at start of dissolution (α)	5	9	4	5	5	4	---
Liquid phase free hydroxide concentration at start of dissolution (C_{OH}^{0}, gmol/L)	8	5	9	8	8	8	---
Liquid Phase Volume during Dissolution, gal	390,000	1,000,000	320,000	370,000	240,000	260,000	---
Interim Storage Volume of Supernates from Aluminum Dissolution, gal	980,000	2,500,000	800,000	920,000	600,000	660,000	6,500,000

POLESTAR APPLIED TECHNOLOGY, INC.

Conclusions from Dissolution Parameter Evaluation

- Selection of aluminum dissolution parameters is influenced by:
  - Liquid phase heel volume remaining after decant, post-dissolution rinse volume, and number of post-dissolution rinses
  - Quantity of inert solids in sludge and solid phase loading that can be adequately mixed during dissolution and post-dissolution rinses
- In this study, approximately 80% of initial aluminum solids dissolved to remove 75% of aluminum
- Rinse solutions must contain caustic to avoid potential to precipitate aluminum
- The minimum total supernate volume generated from Tanks 12, 13, 15, 32, 35, and 39 is estimated at 2.4 million gal
- Demonstrated mixing capabilities increase the projected supernate volume to approximately 6.5 million gal