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Alternative Sodium Recovery Technology

by High Hydroxide Leaching

Pacific Northwest NATIONAL LABORATORY

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Problem Statement & Study Goals

- The U.S. Department of Energy (DOE) is responsible for environmental remediation at the Hanford Site in Washington State.
- Retrieving, processing, immobilizing, and disposing of the 2.2 × 10^5 m^3 of radioactive wastes stored in the Hanford underground storage tanks dominates the overall environmental remediation effort at Hanford.
- The Hanford Tank Waste Treatment and Immobilization Plant (WTP) is the cornerstone of the tank waste remediation effort.
- Capacity of the WTP for treating and immobilizing the Hanford tank wastes is such that completion of the mission in the time framed required by the Tri-Party Agreement is questionable.
- One waste component of particular concern is aluminum. To keep Al in solution during the caustic leach, sodium hydroxide concentrations must be kept elevated or large leachate/Al ratios must be used. Using the baseline conditions of 5 M Na,100°C, this will require large additional amounts of sodium to be added to the LLW stream (bad) or leaving enhanced amounts of Al in the HLW solids (also bad).
- In addition, when Al is present in the HLW in the form of boehmite, the rate of reaction under plausible leaching conditions of 5 M Na, 100°C, and a 16 hr contact time, may be insufficient kinetically to dissolve significant portions of the boehmite in high Al solids.
- However, the solubility curve for Al as a function of hydroxide is sharply concave up to 10-12 M as shown in Figure 1 below, which may provide for a more efficient use of sodium both to keep dissolved Al in solution and to enhance slowly dissolving phases of Al, even under milder reaction conditions.
- The goals of this work are to:

1) Examine the rate of boehmite dissolution as a function of initial Al concentration, initial [OH] and temperature.
2) Develop a model for the dissolution of boehmite under alkaline conditions.
3) Using the model, evaluate the efficiency of Na use with respect to enhancing Al dissolution.

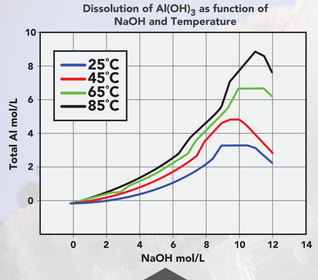


Figure 1.

Calculated Thermodynamic Solubility of Al Hydroxide as a function of NaOH and temperature (Calculated using ESP OLI Analyzer version 3.1, Mixed Solvent Electrolyte (MSE) database).

Experimental Design

- Reaction vessel is a 1-L polymethylpentene vessel as shown in Figure 2.
- Gibbsite (Almatis C333) dissolved into target initial hydroxide concentration with stirring at 120 rpm and heating to achieve target initial [Al].
- Sodium molybdate added as an internal standard to account for evaporative losses during the experiment.
- System equilibrated at the target temperature and verify gibbsite dissolution visually, and sample.
- Target amount of boehmite (APYRAL AOH 20) added to start leaching kinetic examination.
- Test solution sampled at 4, 8, 24, 30, and 48 hrs in all cases, 1 and 2 hr sampling for 85°C tests; 54 hrs also sampled in the 25°C and 60°C tests.
- Sampling involved taking a 7-mL supernatant sample and filtering it through a 0.45 micron Nylon® syringe filter before analysis.
- Solution analyzed for metal content (by ICP-OES), density (by weight using 2-mL volumetric glassware), and free hydroxide by titration. XRD analysis of washed and dried solids performed on selected samples.

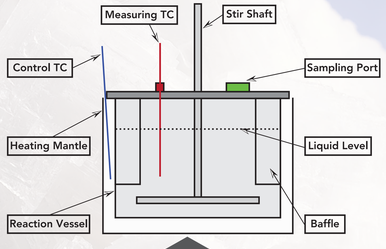
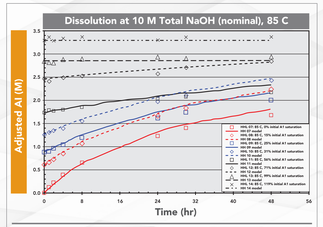


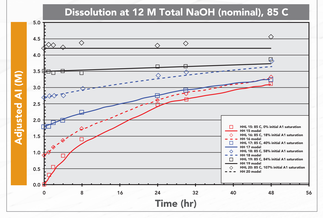
Figure 2.

Schematic Drawing of the Caustic Leaching Test Setup

Data Analysis

Best fit to date: B=2/3, k=0.00563, Ea=115 kJ/mol, OH=1.51, and A=0.47





The rate equation used was of the form

$$\frac{d}{dt}\left(\frac{n_{bo}}{n_{bo,0}}\right) = -k e^{\frac{E_a}{R}\left(\frac{1}{373}-\frac{1}{T}\right)} \left(\frac{n_{bo}}{n_{bo,0}}\right)^{B} \left(C_{OH,L}\right)^{H} \left(1-\frac{C_{Al,L,0}}{C_{Al^*,L,0}}\right)^{A} \left(1-\frac{C_{Al,L}}{C_{Al^*,L,0}}\right)$$

where
- n_{bo} = moles of boehmite
- $n_{bo,0}$ = initial moles of boehmite
- k = pre-exponential rate constant (/hr /(M^H)), obtained by fitting
- E_a = activation energy (J/mol), obtained by fitting
- R = ideal gas constant (J/mol K)
- T = absolute temperature (K)
- $C_{OH,L}$ = molarity of free OH at time t, adjusted to a constant-volume basis
- H = exponent of hydroxide concentration, obtained by fitting
- B = exponent of unreacted boehmite fraction, obtained by fitting
- $C_{Al,L,0}$ = molarity of dissolved Al at time = 0, adjusted to a constant-volume basis
- $C_{Al^*,L,0}$ = molarity of dissolved Al if the saturated concentration for boehmite at that temperature and total OH concentration were present; calculated from Panias et al. (2001) correlation, as in WTP-RPT-186 Rev. 1, based on $C_{OH,L,0}$
- A = exponent of dissolved Al subsaturation, obtained by fitting
- $C_{Al,L}$ = molarity of dissolved Al at time t, adjusted to a constant-volume basis

The concentrations of free hydroxide and aluminate are calculated at each point in time from mass balances on the species:

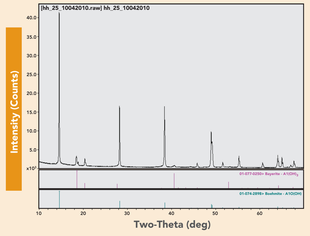
$$C_{Al,L} = C_{Al,L,0} + \frac{n_{bo,0}}{V_L}$$

$$C_{OH,L} = C_{OH,L,0} - C_{Al,L}$$

where
- $C_{OH,L,0}$ = molarity of total OH at time = 0; should be the same at all times, based on the assumption of constant liquid volume V_L; calculated as the average of all measurements of (free OH plus dissolved Al) in molarity adjusted to a constant-volume basis to offset volume changes during the test
- V_L = liquid volume, assumed constant through test

Experimental Results – XRD analysis of Initial and Residual Solids

Sample XRD of Residual Solids



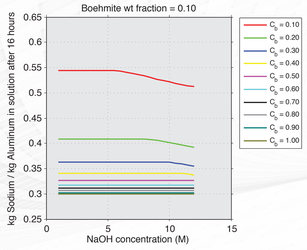
Summary of XRD Analysis of Residual Solids

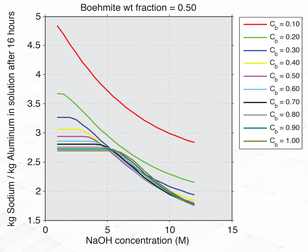
Sample	2 theta	FWHM	Composition (%) based on a full refinement			
			Gibbsite	Bayerite	Boehmite	Refinement agreement (%)
AOH	14.516	0.085	0	0	100	30
C333	18.338	0.066	100	0	0	15
HHL1	14.559	0.095	0	5	95	10
HHL20	14.625	0.126	0	8	92	10
HHL21	14.643	0.092	0	7	93	9
HHL25	14.641	0.093	0	12	88	11
HHL29	14.473	0.078	0	0	100	10

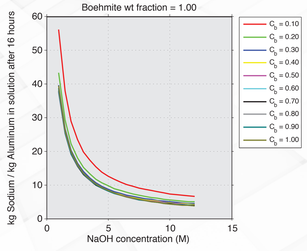
Conclusion from XRD study:

Unleached solids composed of boehmite; bayerite likely formed from Al in interstitial liquid during post-leach operations (solids washing and drying)

Evaluation of Efficiency of Sodium Use in Boehmite Dissolution (16 Hours Leach Time, 85°C); C_b = initial boehmite concentration (in M)







Conclusions:

- Large data set(a-b) allows kinetic evaluation of boehmite dissolution.
- Use of a Multi-Variable Fit to a Shrinking Core Model(c-d) to fit data yields:
  - B=2/3, k=0.00563, Ea=115 kJ/mol, OH=1.51, and A=0.47
- Evaluation of efficiency of Na in dissolving Al shows more efficient use of Na with high Al, high boehmite solid leaching

Future Studies

- Addition of 1 M NaOH Al Dissolution Data(a) to Model
- Further Data Analysis to Test Alternative Dissolution Models
- Repeat experimental design using PEP simulant waste (including Cr)
- Perform validation testing using high Al Hanford Tank Waste solids
- Quantitative evaluation of Caustic demand for equivalent Al removal under standard versus high caustic leaching scenarios.

Acknowledgements

- Donita Neiner for XRD analysis
- Don Rinehart for Lab Assistance
- Cynthia Niver for free hydroxide titrations

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