Process Chemistry and Operations Planning for Hanford Waste Alternatives

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Introduction

The stability of waste streams containing aluminate is a significant factor relating to unit operations (ion exchange) within the Waste Treatment Plant (WTP). At an operational cost of $500M/yr for the WTP, a loss of one day of operation would amount to $1.37M. The overall recovery cost will be a function of the amount of gibbsite ($Al(OH_3)$) that forms. For small loadings where additional caustic leaching at elevated temperature will restore operation, the time delay may be five days. At significant precipitation where 50% or more of the interstitial volume within the ion exchange (IX) column is blocked, options will include re-insertion of new resin or extended leaching. A conservative estimate would then be from $6.6-41M/year.

Test Plan

A test plan was written, designed, and reviewed in 2009 to address the possible influences of sodium, hydroxide, major anion components, and how, if any, these influences would change as a function of temperature on the aluminum solubility. Due to the long equilibration periods for these solutions at 25°C, testing will continue over a span of two years. Solution concentration limits taken from max/min values of Ultra Filtration Process (UFP) leaching streams (*1*).

Analyte	UFP-1 Leaching		UFP-2 Leaching		Overall Range	
	mol/kg H_2O	mol/kg H_2O	mol/kg H_2O	mol/kg H_2O	mol/kg H_2O	mol/kg H_2O
	min	max	Min	max	Min	max
Na	8.10E-01	6.20E+00	1.92E+00	6.74E+00	8.10E-01	6.74E+00
$Al(OH)_4$	3.60E-02	7.04E-01	1.26E-01	4.86E-01	3.60E-02	7.04E-01
OH	4.33E-01	5.46E+00	1.45E+00	4.40E+00	4.33E-01	5.46E+00
NO_2	4.78E-09	7.96E-01	1.18E-02	6.60E-01	4.78E-09	7.96E-01
NO_3	4.28E-03	1.81E+00	1.86E-01	1.64E+00	4.28E-03	1.81E+00
CO_3	2.95E-09	5.20E-01	6.32E-05	2.31E-01	2.95E-09	5.20E-01
PO_4	3.18E-03	1.63E-01	1.13E-02	1.29E-01	3.18E-03	1.63E-01
SO_4	1.82E-03	9.98E-02	1.17E-02	1.60E-01	1.82E-03	1.60E-01

Test #	NO_3^-	NO_2^-	CO_3^{2-}
1	M	L	L
2	L	M	L
3	L	H	M
4	M	H	H
5	L	L	H
6	H	L	M
7	M	M	M
8	H	M	H
9	H	H	L
10	H	H	H
11	L	L	L

[mol/kg H_2O]	NO_3^-	NO_2^-	CO_3^{2-}
High (H)	3.0	1.5	0.5
Medium (M)	1.5	0.75	0.25
Low (L)	0.0	0.0	0.0

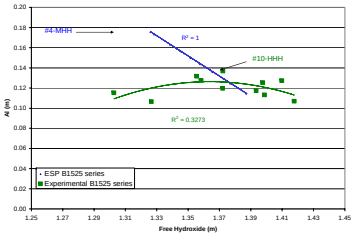
- *Aluminum: added as wire or gibbsite*
- *four caustic loadings: 0.5,1.5,3.5,and 5.5 molal*
- *three temperatures: 25,40 and 55°C*

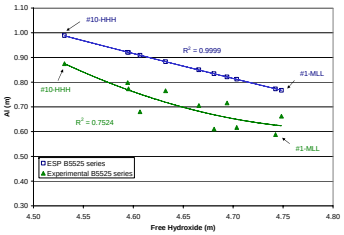
Test matrix was developed using existing literature data and anticipated WTP solution conditions (1) and the Taguchi statistical method (JMP software).

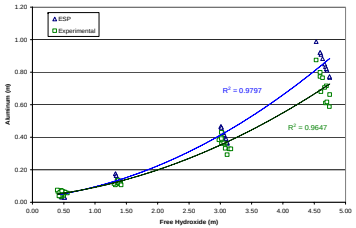
Experimental

Sodium hydroxide solutions were prepared at four selected loadings and aluminum wire was added following literature procedures (*2*). Once the redox was completed, the solution was then separated into test vessels and salts are added. Two sets of solutions have been prepared for each sample, one tested as a function of time while the second remains undisturbed for analysis of the equilibrated solution. Additional solutions approaching SLE from below have been prepared using gibbsite as the aluminum starting material. ESP modeling of the solutions were performed and compared to the data.

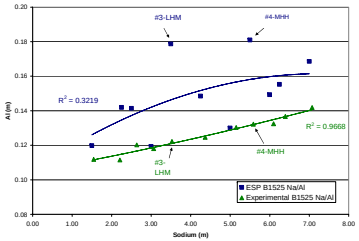
Results

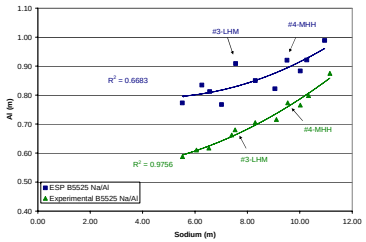




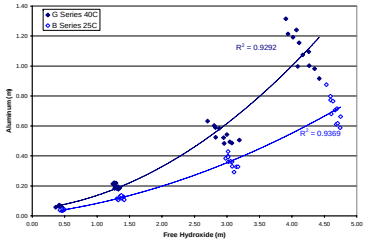


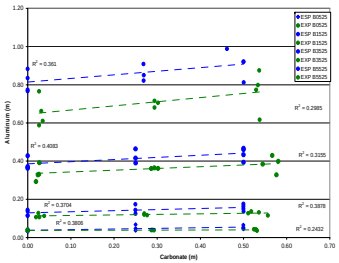
All 25°C gibbsite data and 0.5mNaOH wire solutions were examined for evidence of correlation and results indicate strong correlation for the aluminum and free hydroxide concentrations. The correlation appears to be consistent when the 40°C results are included as demonstrated in the plot below.

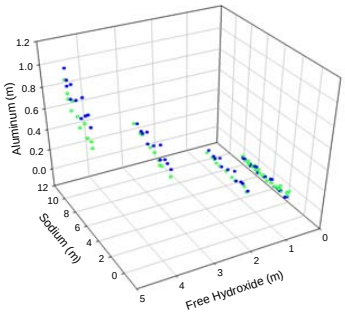




Experimental and Model Prediction Comparison Plots of Aluminum Concentrations with Free Hydroxide or Sodium Concentrations at 25°C. The model predicts higher aluminum concentrations for solutions having high values of nitrite though the experimental results do not appear to be in agreement.







Little influence between the carbonate and aluminum concentrations is apparent whereas the aluminum concentration increases as sodium increases and free hydroxide decreases as shown in the plots above.

Path Forward

Solutions at 25°C in 3.5 and 5.5 molal caustic have not reached SLE after many months at constant temperature and shaking. All test solutions at 40°C have been prepared and gibbsite test solutions have been analyzed. All solutions will undergo IC, TIC, ICP, titrations for free OH-, solids identification, and density measurements. Test solution preparations at 55°C have begun and upon completion, all data will undergo regressions and be transferred to a permanent repository.

Acknowledgements

This effort was funded by the U.S. Department of Energy's Office of Environmental Management through Cooperative Agreement DE-FC30-06EW07040.
ICET DOE Program Manager: John Shultz
ORP-DOE : Billie Mauss, RL-DOE: Julie Reddick
Hanford: Terry Sams, Dan Herting, Heinz Huber, Jacob K. McCoskey

(1) Personal communication, Draft Sodium Assessment Report, J. Reddick, Hanford.
(2) Sipos, P., Hefter, G., and May, P.M. "A Hydrogen Electrode Study of Concentrated Alkaline Aluminate Solutions", Aust. J. Chem, 1998, 51, 445.

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