washington river protection solutions

Aluminum Dissolution Work at 222-S and ICET

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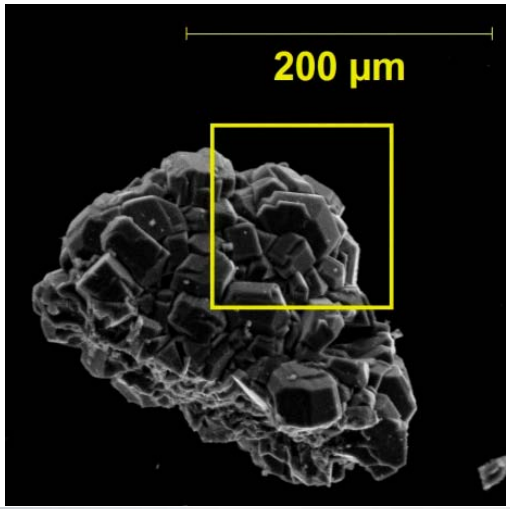
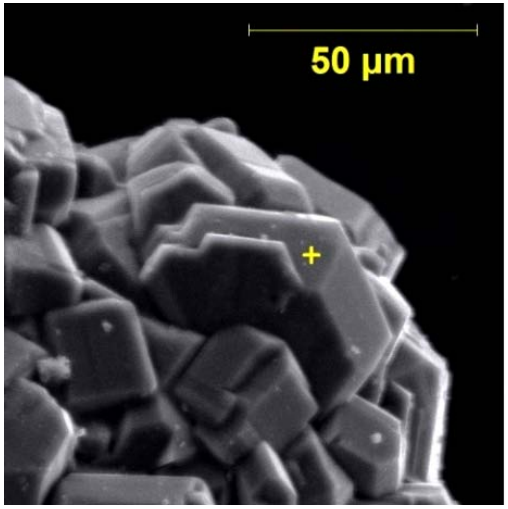




Agenda

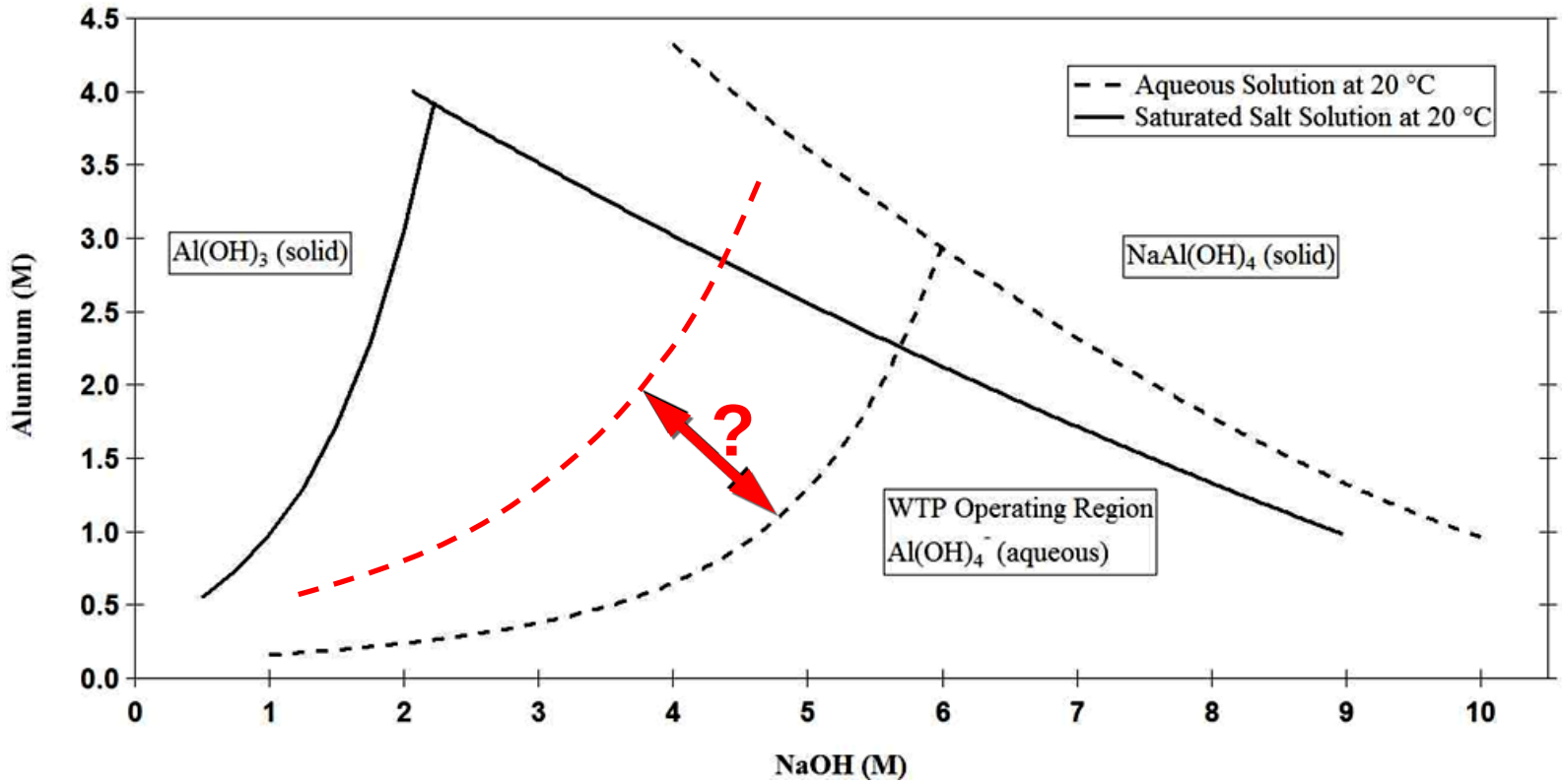
- Work Scope Mississippi State University, Institute for Clean Energy Technology (ICET)
- Work Scope Washington River Protection Solutions LLC (WRPS), 222-S

The ICET related Project is funded by U.S. Department of Energy, Office of Waste Processing, EM-21

- Current dissolution studies at 222-S (not directly related to ICET work)
  - Oxalic acid dissolution of gibbsite heel
  - Large Scale gibbsite dissolution

Aluminum dissolution experiment at ICET

- **Questions addressed at ICET**
  - What is the influence of ionic strength on gibbsite solubility (esp., for Na, OH, NO_3, NO_2 and/or CO_3)?
  - How do these influences change as a function of temperature?



Result: revised algorithm for NaOH requirement to keep Al in solution

Aluminum dissolution experiment at ICET

- **Experimental Approach**
  - Leaching Experiment
    - Heat the electrolyte solution containing the aluminum sample to ~ 80 °C for 4 hours.
    - Cool the solution to a controlled temperature (25, 40, or 50°C).
    - Periodically sample the leachate until the solid and liquid phases aluminum equilibrium is achieved.
  - Bottom Up Experiment
    - Add gibbsite to the electrolyte solution and approach the aluminum liquid/solid phase equilibrium from below the aqueous saturation point at a controlled temperature.

Aluminum dissolution experiment at ICET

- Electrolyte solution description
  - Al is added as wire.
  - Three temperature settings – 25, 40, and 50°C.
  - Four caustic loadings – 0.5, 1.5, 3.5, and 5.5 molal.
  - A three level Taguchi statistical approach for addition of the nitrate, nitrite, and carbonate ions was chosen.

The three levels of concentration were based on upper and lower limits for the feed vessels of WTP.

[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 dissolution experiment at ICET

Result of the Taguchi approach = Test matrix

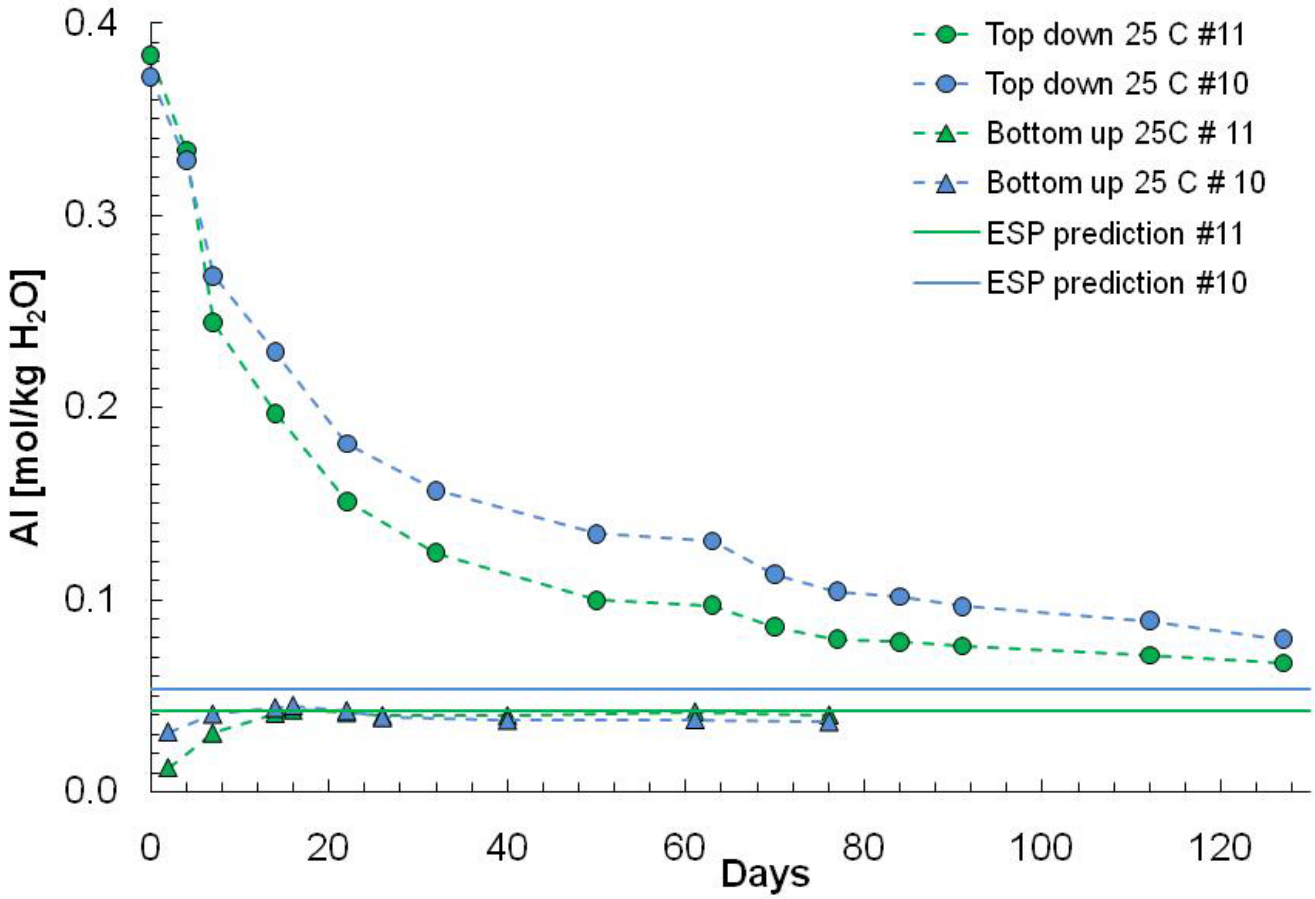
Test #	NO_3^-	NO_2^-	CO_3^{2-}
1	M	L	L
2	L	M	L
3	L	H	M
4	M	H	H
5	L	L	H
6	H	L	M
7	M	M	M
8	H	M	H
9	H	H	L
10	H	H	H
11	L	L	L

Aluminum dissolution experiment at ICET

- Preliminary Results 1

  Influence of the carbonate concentration

  = comparison of run # 10 (HHH) and # 11 (LLL) at 25°C

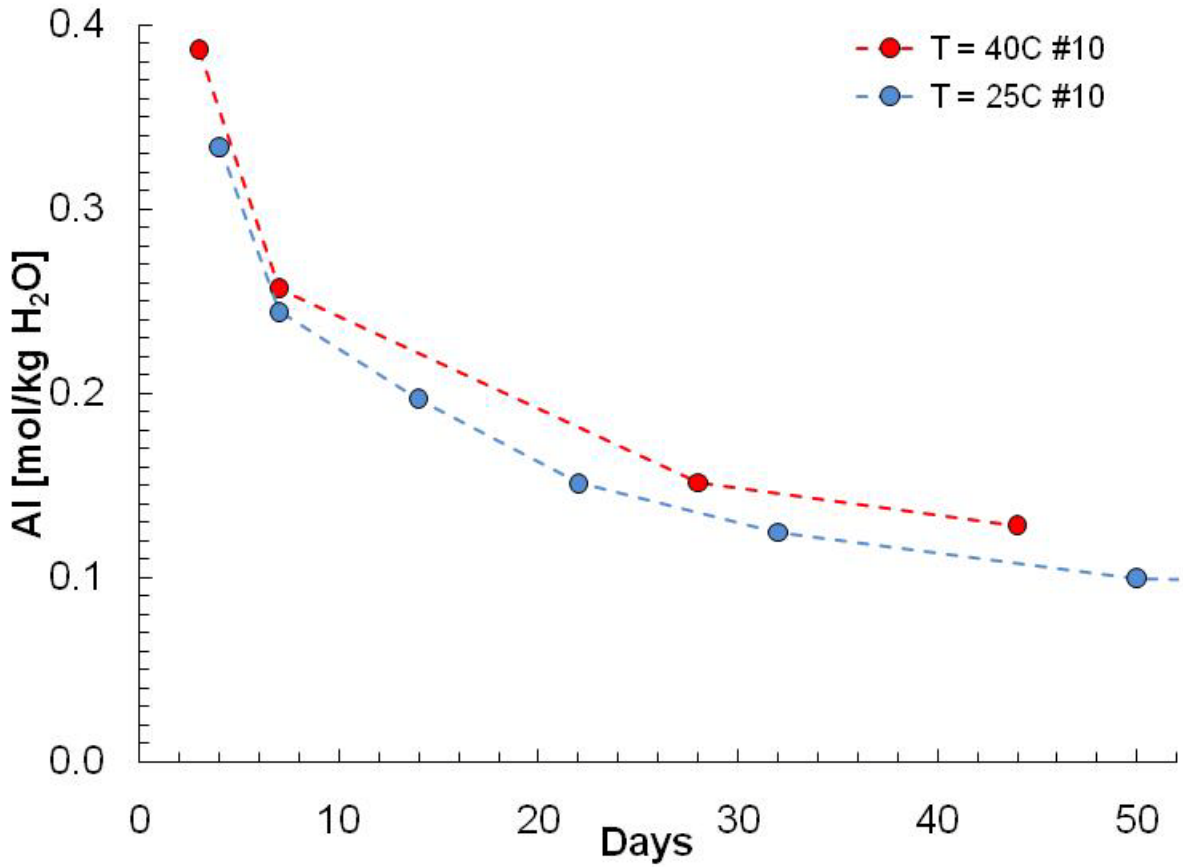


Aluminum dissolution experiment at ICET

- Preliminary Results 2

  Temperature Influence on run #10 (HHH)

  = comparison of 25°C and 40°C



222-S Aluminum Dissolution Experiment

- **Purpose**
  - To validate the results of the ICET testing with actual tank waste samples.
  - Compare the dissolution of aluminum wire in a simple caustic electrolyte solution against the dissolution of gibbsite and boehmite in a caustic solution containing actual tank sludge.

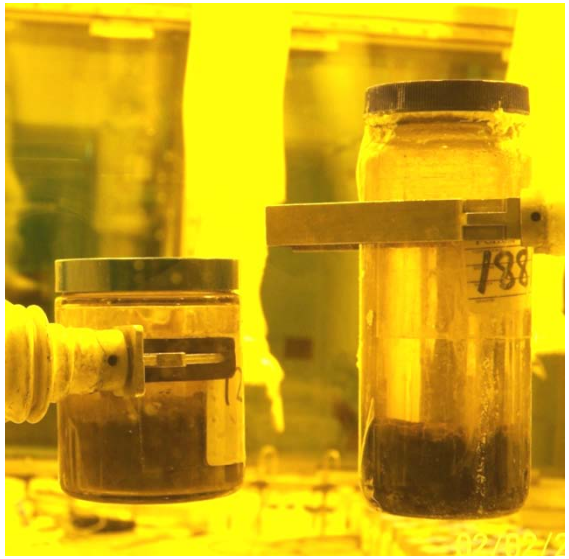
- **Experimental Approach**
  - Caustic loadings of 0.5, 1.5, 3.5, 5.5 m.
  - 4 archived tank samples were selected as good representations of the following categories
    - Cladding Waste
    - Phosphate-Bismuth
    - Gibbsite bearing
    - Boehmite bearing

222-S Aluminum Dissolution Experiment

- Leaching Experiment
  - Leach the caustic slurry at ~ 80 °C (comparable to WTP condition).
  - Periodically sample the supernate during the subsequent cooling period until the aluminum solid/liquid phase equilibrium is achieved.
- Bottom Up Experiment
  - Add gibbsite to a composite of archived actual supernate and approach the aluminum liquid/solid phase equilibrium from below the aqueous aluminum saturation point.

222-S Aluminum Dissolution Experiment

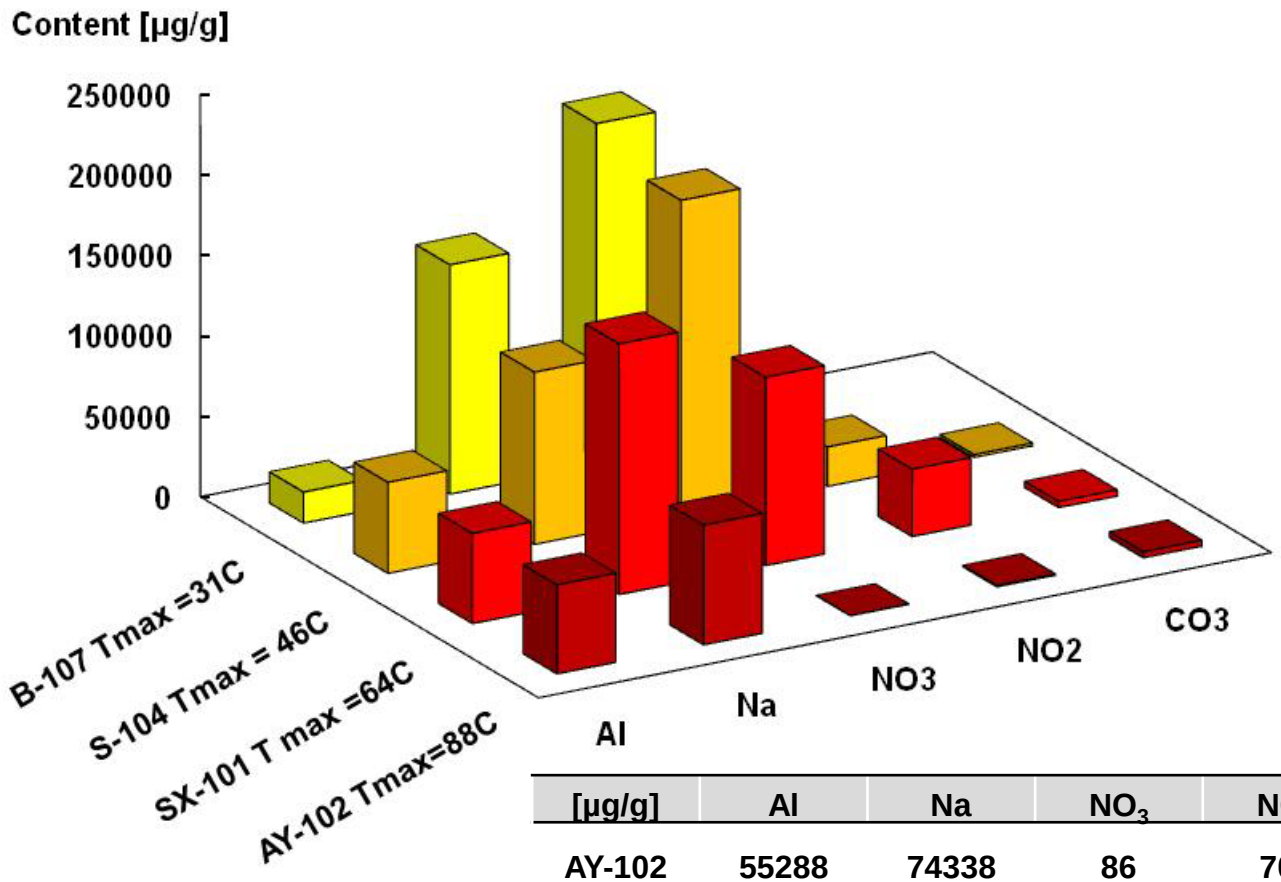
- Sample selection
  - $BiPO_4$: B-107
    - Core 217, Seg. #2 contains first cycle decontamination waste from the BiPO4 process and cladding waste from the PUREX process
  - Cladding Waste: S-104
    - Composite contains cladding waste from REDOX, REDOX waste and REDOX salt cake
  - Gibbsite bearing: SX-101
    - Core 225, Seg. 2 contains REDOX waste and REDOX salt cake
  - Boehmite bearing: AY-102
    - Core 290, Composite contains PUREX low level waste, B plant low level waste and decontamination waste



S-104 (left) and AY-102 (right)

222-S Aluminum Dissolution Experiment

- Sample selection – chemical composition (TWINS based)



[µg/g]	Al	Na	NO_3	NO_2	CO_3	T [°C]
AY-102	55288	74338	86	706	3703	88
B-107	19250	142500	212325	4326		31
SX-101	55950	155750	117000	41865	3785	64
S-104	56497	106958	195750	24450	1693	46

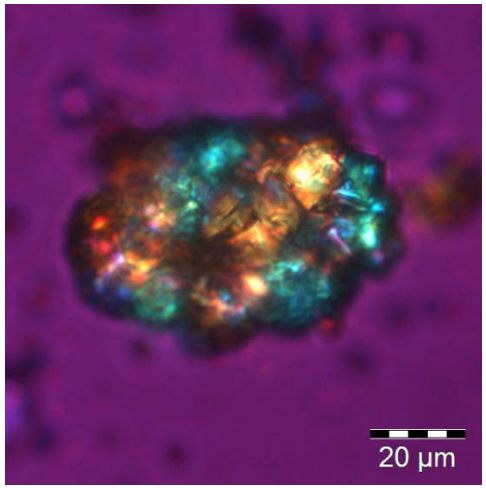
Current State of Experiments

- Mississippi State ICET
  - Completed the 25°C runs.
  - Currently conducting the 40°C experiments.

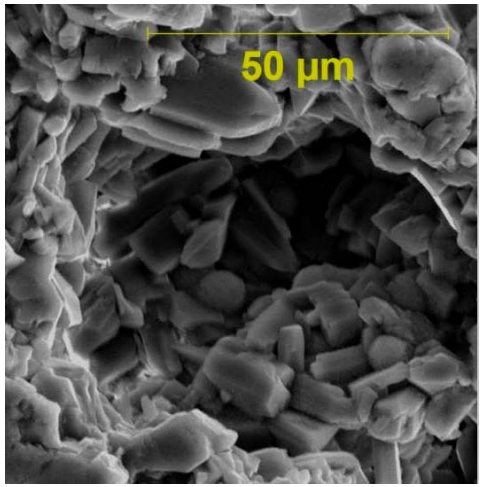
- Hanford 222-S
  - Test plan is issued.
  - Samples are staged.
  - Test procedure for cold tests is in final approval steps.
  - Expected start of cold tests in Mid-February.

Other current dissolution projects at 222-S

- **Oxalic acid dissolution of gibbsite heel**
  - Commercial gibbsite consists of ~5 µm particulates but forming ~100 µm agglomerates.



Almatis C-33 commercial gibbsite



C-103 heel: SEM-BSE image of gibbsite

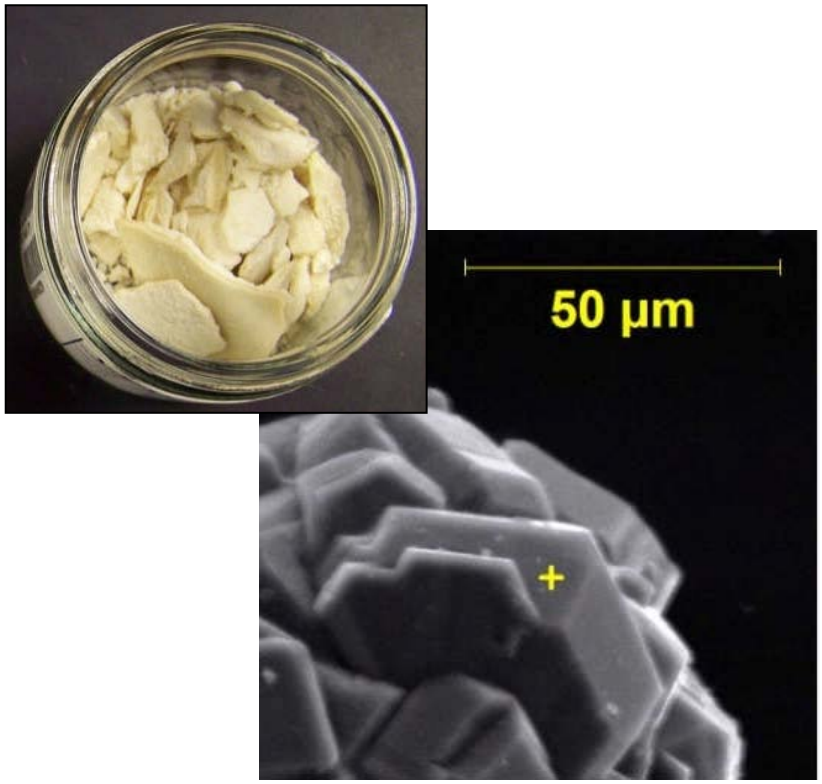
C-103 heel: gibbsite 2.5 cm diameter

  - Tank waste contains individual particles of up to 100 µm. In the heel of tank C-103 and C-108 gibbsite agglomerates of up to 2 inches were found.

Other current dissolution projects at 222-S

- **Oxalic acid dissolution of gibbsite heel**

In 2009 a process to produce gibbsite heels in a kg-scale was developed at 222-S. 50 kg of heel were produced by Center for Laboratory Sciences, Pasco, WA.



SEM-BSE image of gibbsite heel from process experiments

Gibbsite heel samples (diameter ~ 30 cm)

Other current dissolution projects at 222-S

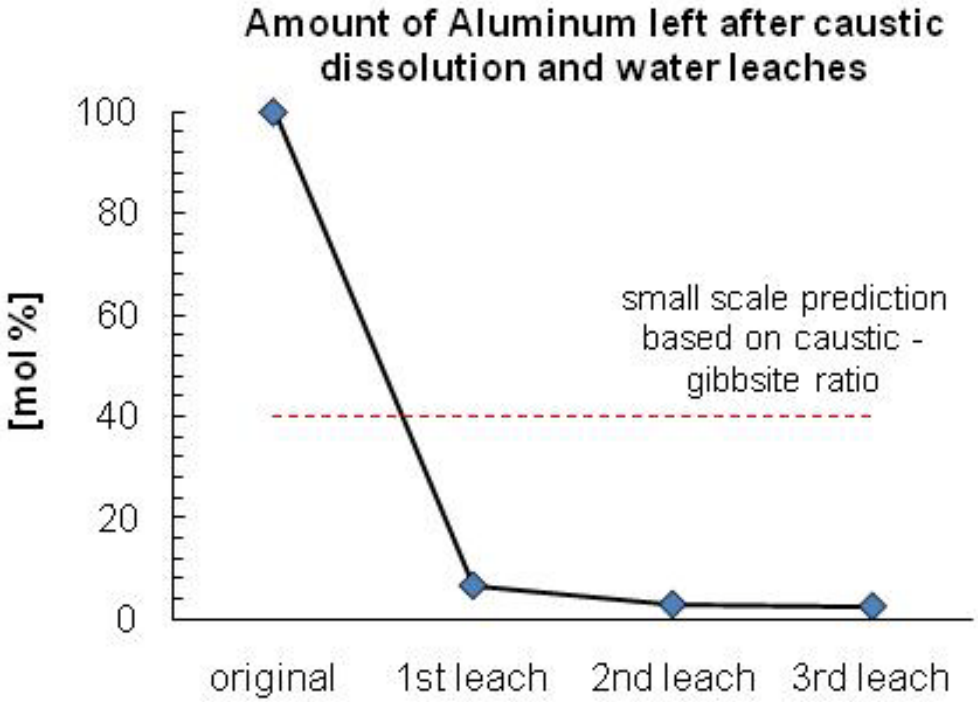
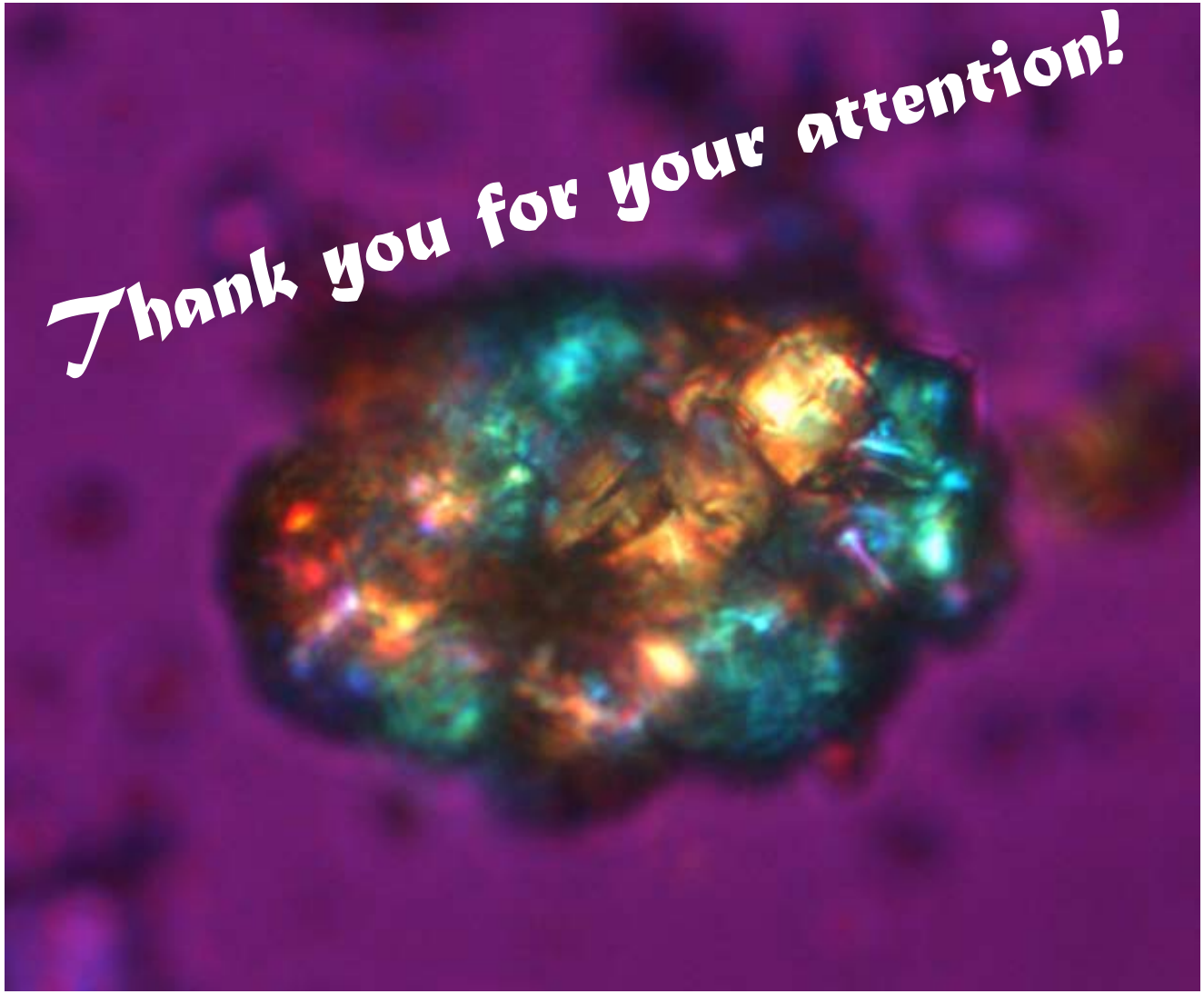
- **Oxalic acid dissolution of gibbsite heel**

Dissolution tests using oxalic acid with varying conditions are ongoing. Examples of the differences in molarities are shown below

(1 M oxalic acid added left; 0.1 M acid added right)

Other current dissolution projects at 222-S

- **Large scale gibbsite dissolution:**
  - Compared dissolution rates for bucket-size to mL-size in previous dissolution studies (3.4 kg of gibbsite in 5.1 L 19.4 M NaOH solution).
  - Compared dissolution rates for
    - (a) adding all the caustic at once or
    - (b) adding it in two batches with wash step in-between.
  - Results show
    - an increased amount of dissolved gibbsite compared to the predicted value of 60 mol.% (>90 mol%).
    - a decline in dissolution rate from 90+ mol.% to 70+ mol.% for splitting the addition of caustic .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