Aluminum – What We Know and What We Need to Learn

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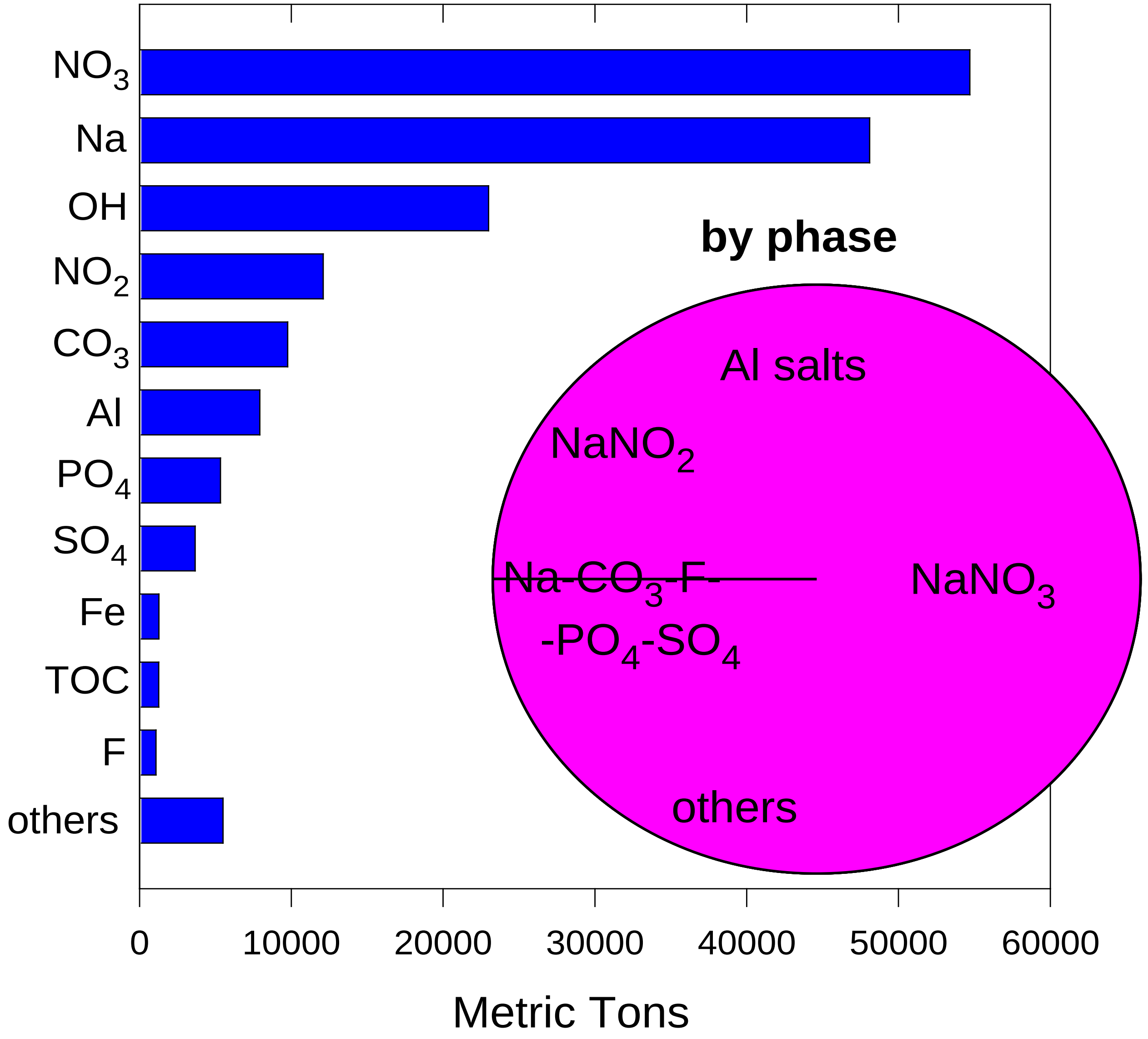
Aluminum in Hanford Tank Waste

- How much is there?
  - – 7,900 MT
- Where did it come from?
  - – Fuel cladding and reprocessing
- Where did it go?
  - – Sludge, supernate, saltcake
- Why do we care?
  - – $$$$ in disposal costs
- What are we going to do with it?
  - – Baseline vs. Options
- What do we need to learn?

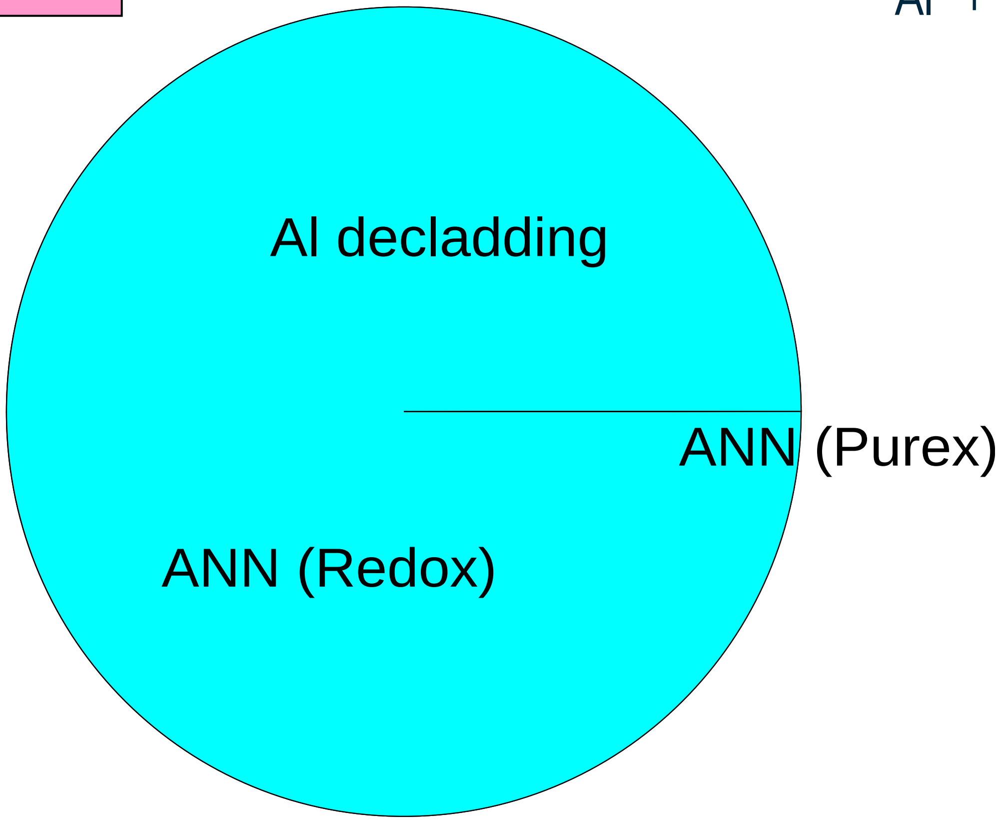
Tank Farm Chemical Inventory, Hanford Site



Aluminum – 7,900 MT

Al

Sources



Al decladding

$$Al^0 + NaOH + 3H_2O \rightarrow NaAl(OH)_4 + {}^3/_2H_2$$

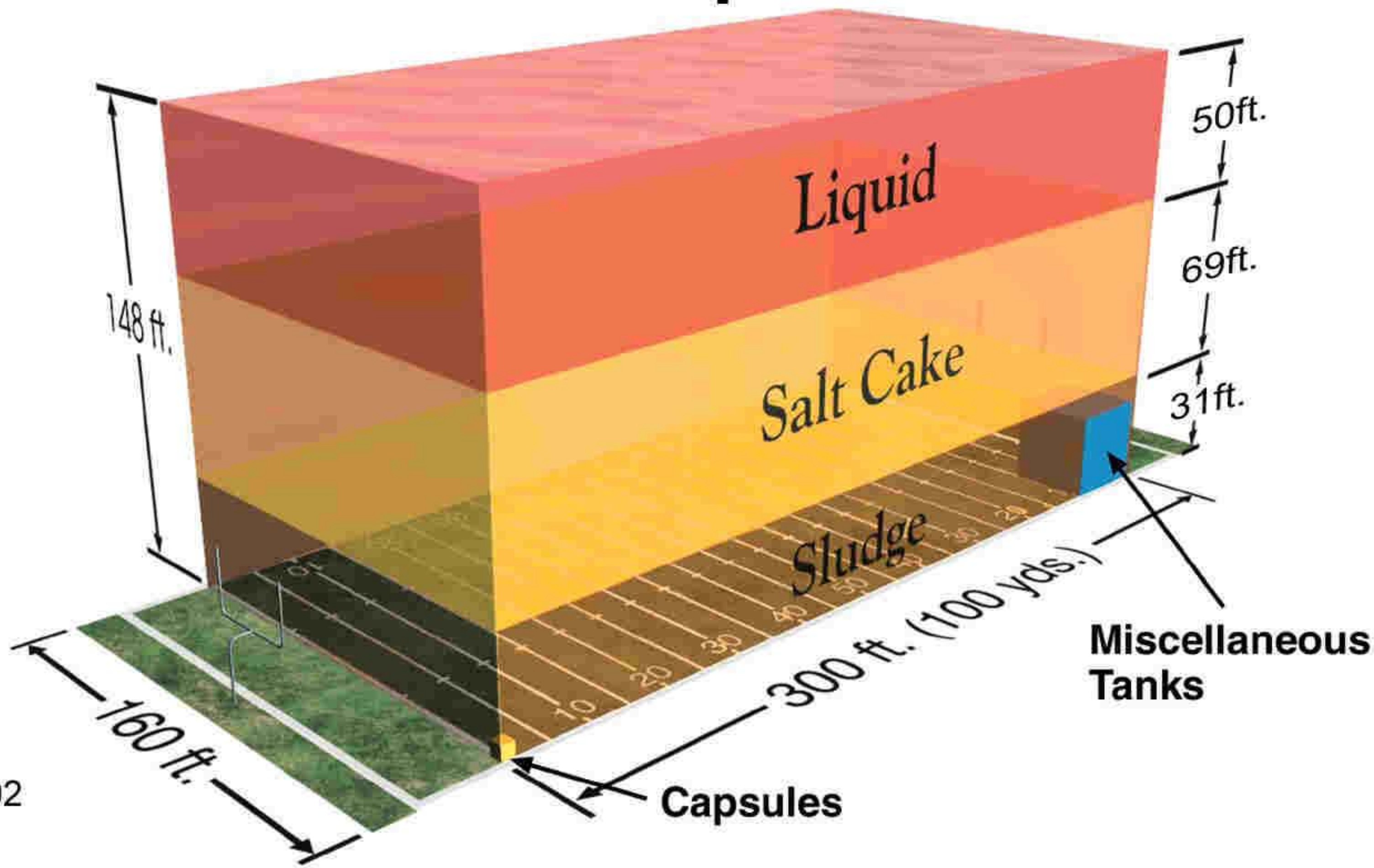
ANN (Redox)

$Al(NO_3)_3 \bullet 9H_2O$ used to increase ionic strength

ANN (Purex)

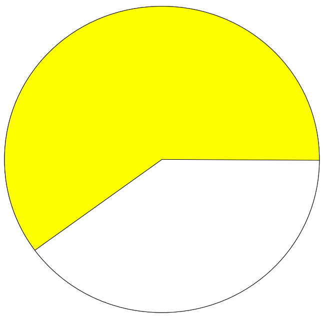
ANN used to complex fluoride

Hanford Tank Waste Would Cover a Football Field 150 Feet Deep



*As of April 2002
7/23/02

Where did it all go?



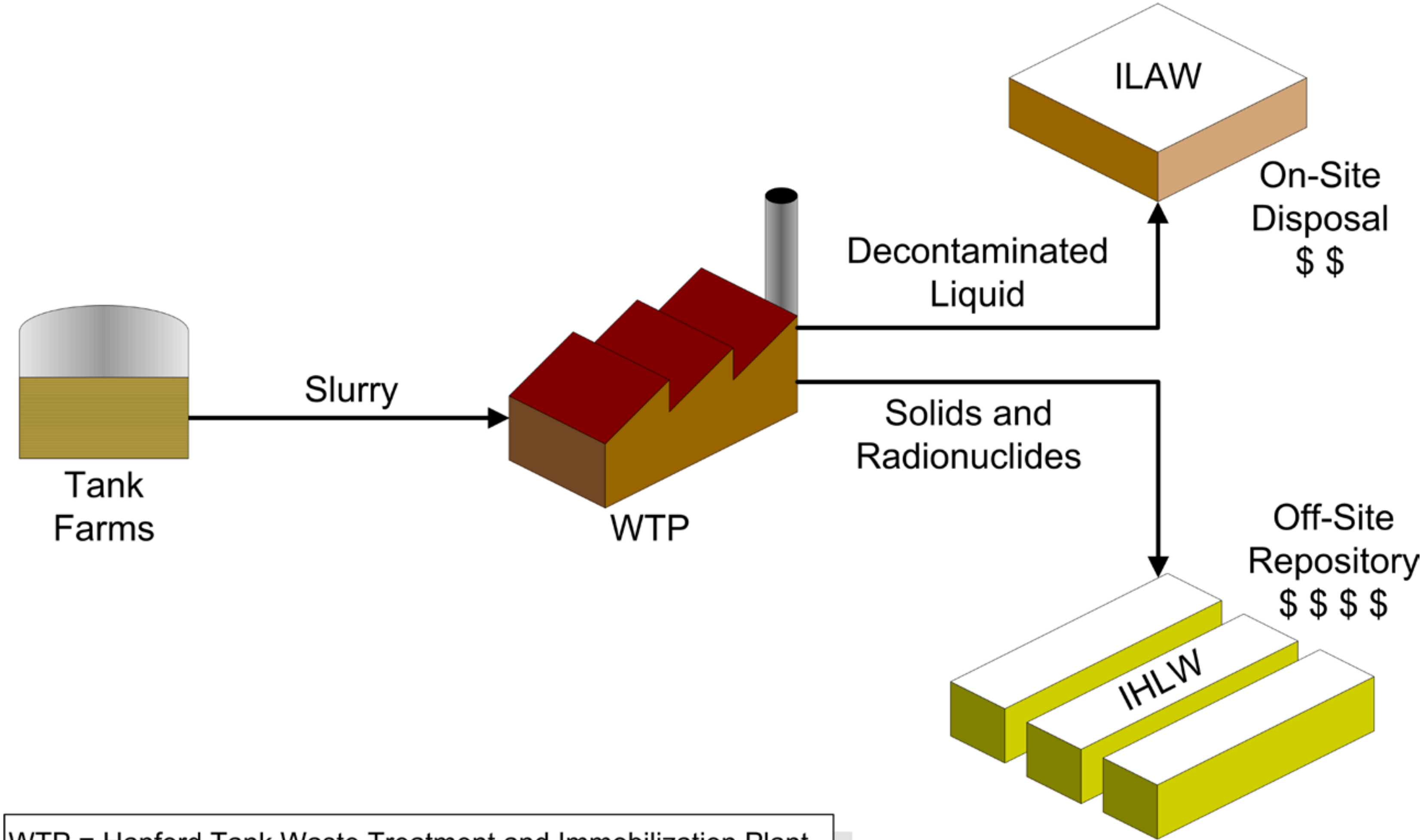
- **Sludge** (brown half of pie chart)
  - Hydroxides (gibbsite, boehmite, bayerite)
  - Aluminosilicates (cancrinite, sodalite, zeolite)
  - Dawsonite, $NaAlCO_3(OH)_2$
- **Saltcake** (white slice in pie chart)
  - Sodium aluminate, $NaAl(OH)_4$
  - Evaporators avoided precipitating aluminum
- **Supernatant liquid** (yellow part of pie chart)
  - Aluminate ion, $[Al(OH)_4]^-$, aka AlO_2^-

Estimated Hanford Sludge Composition[1]

Phase	Wt% of Sludge
Gibbsite, $Al(OH)_3$	50
Cancrinite, $NaAlSiO_4$-$NaNO_3$-H_2O	14
Boehmite, AlOOH	12
Dawsonite, $NaAlCO_3(OH)_2$	8
Ferrite, Fe_2O_3	8
Other (Ca, U, Cr, Zr, Bi, etc.)	8

[1]Wells, et al., WTP-RPT-153 Rev. 0, February 2007 (Battelle – Pacific Northwest Division).

Why Do We Care?

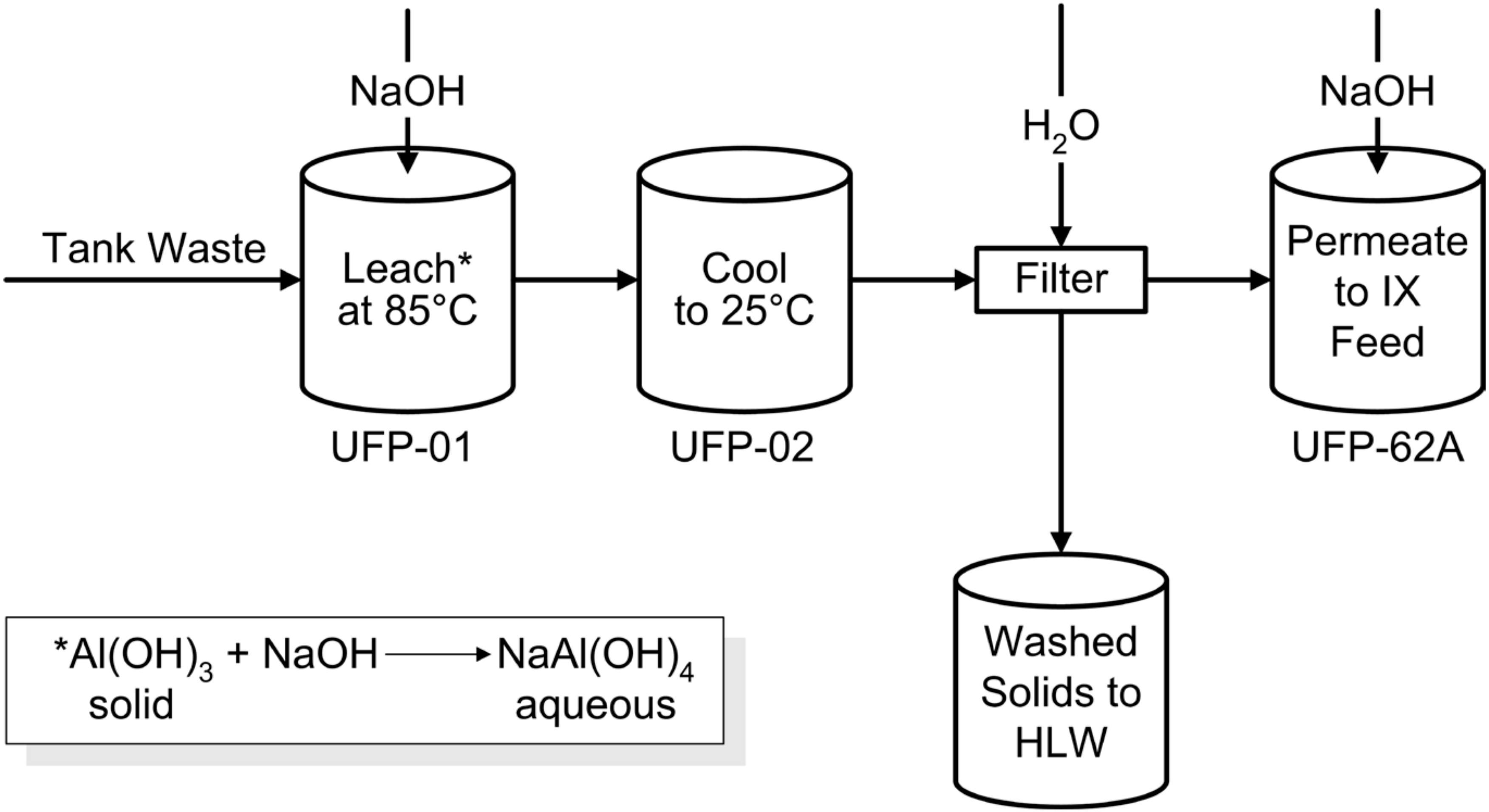


WTP = Hanford Tank Waste Treatment and Immobilization Plant
ILAW = Immobilized Low Activity Waste
IHLW = Immobilized High Level Waste

What Can We Do?

- Goal: minimize Al going to IHLW
- Baseline
  - Dissolve Al by leaching in WTP Pretreatment Facility
- Alternatives (or Additions)
  - Improve Al solubility correlations for WTP
  - Remove Al at Tank Farms (Aluminum Removal Facility)
    - Continuous leaching
    - Lithium hydrotalcite process
    - Leave gibbsite in tanks, grout in place with tank closure
  - Develop caustic (NaOH) recycle process
  - Improve glass loading

Al Leaching in WTP (simplified)



$$^{*}\underset{\text{solid}}{Al(OH)_3} + NaOH \longrightarrow \underset{\text{aqueous}}{NaAl(OH)_4}$$

WTP Leaching Pros and Cons

- Pros
  - Moves Al from solid to liquid phase
  - Decreases amount of $$$$ IHLW
- Cons
  - Adds Na to liquid phase
  - Increases amount of $$ ILAW
  - Increases complexity of WTP Pretreatment

WPT Leaching Trade-offs

Pretreatment	IHLW Cans	ILAW Cans	MT Na Added[1,2]
Don't Leach	22,300	65,000	1,200
Leach – current baseline	14,800	91,400	36,900
Leach – concept baseline	14,800	75,000	20,000

[1] Amount of Na added at WTP for leaching and other Pretreatment operations
[2] Na in WTP Feed = 36,000 MT

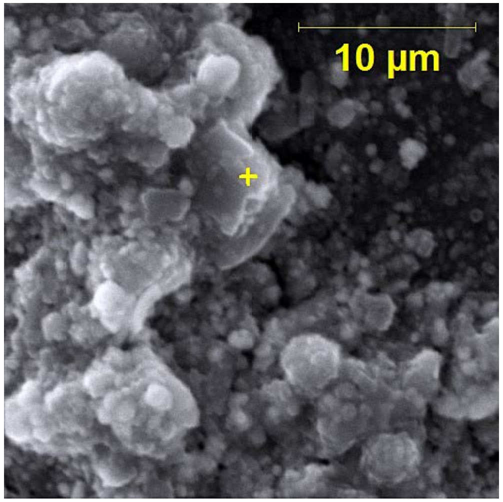
What Do We Know?

- How much Al is in the waste
  - 7,900 MT
- Which forms of Al are in the waste
  - Gibbsite, boehmite, sodium aluminate, dawsonite, aluminosilicates
- How various forms react with NaOH
  - Gibbsite and dawsonite dissolve rapidly, boehmite slowly, aluminosilicates not at all

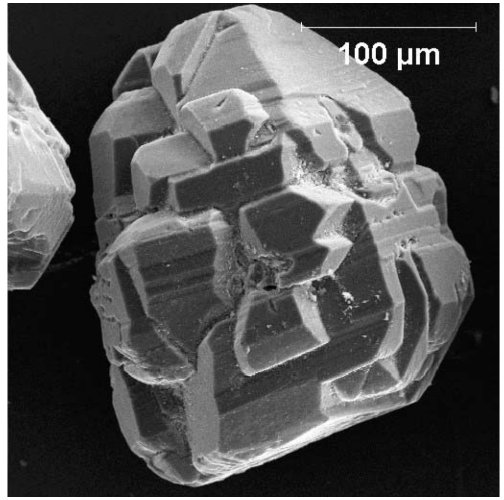
Hydroxides

- Gibbsite, $Al(OH)_3$
  - By far the dominant Al phase in sludges
  - Tends to dissolve readily in hot (80–90 ^oC) NaOH
- Other forms of $Al(OH)_3$
  - Bayerite, Nordstrandite rarely identified by XRD
  - Amorphous $Al(OH)_3$ and mixtures with other metals
- Boehmite, AlOOH [$Al(OH)_3 – H_2O$]
  - Major phase in REDOX boiling waste sludges
  - Tends to dissolve *slowly* in hot NaOH

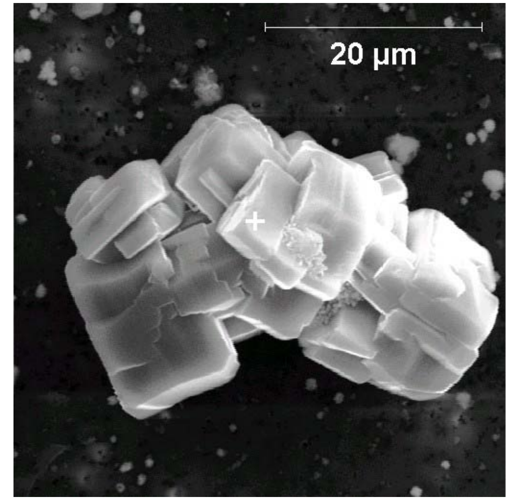
Gibbsite, $Al(OH)_3$



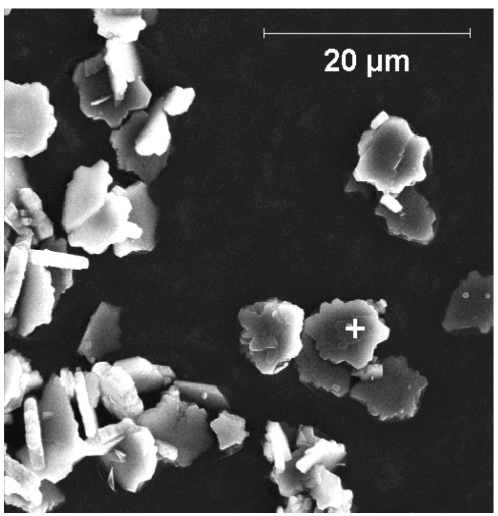
AY-102



S-102



C-103



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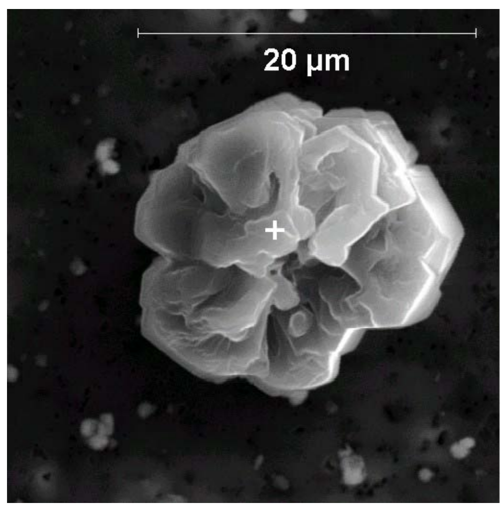

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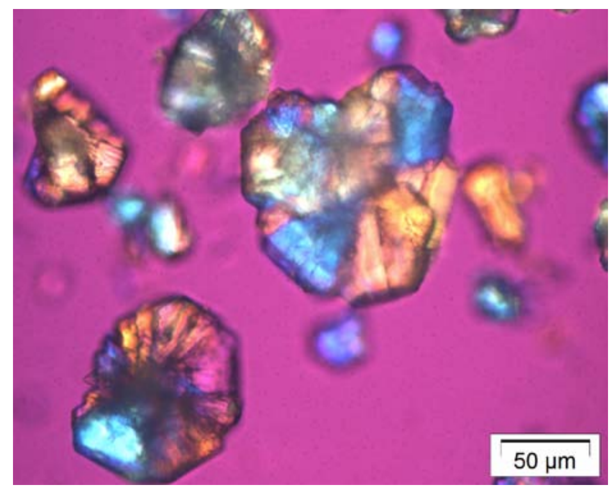
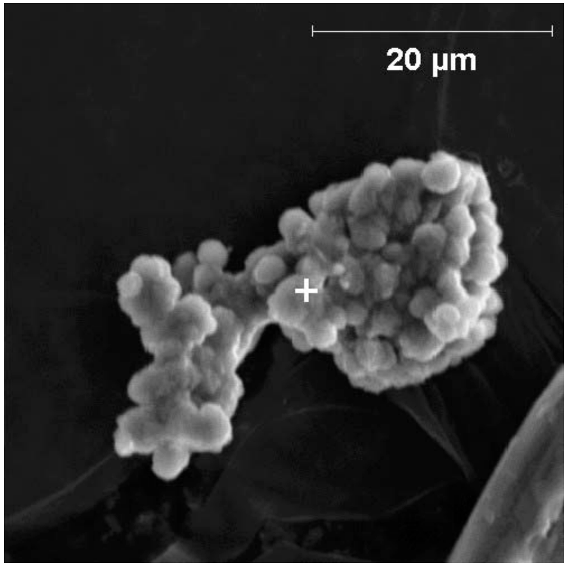


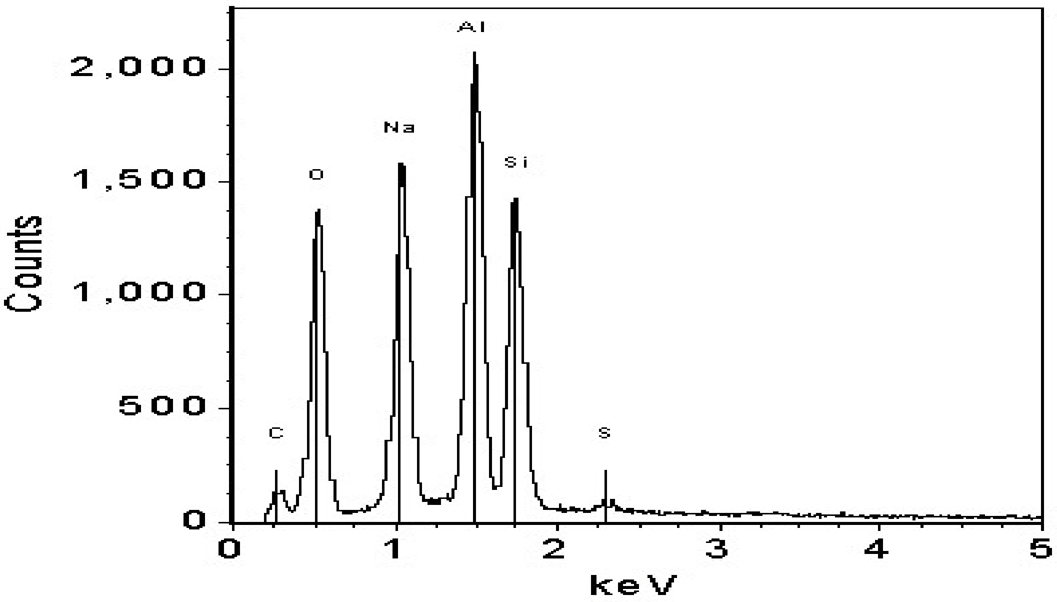
S-112

Cancrinite

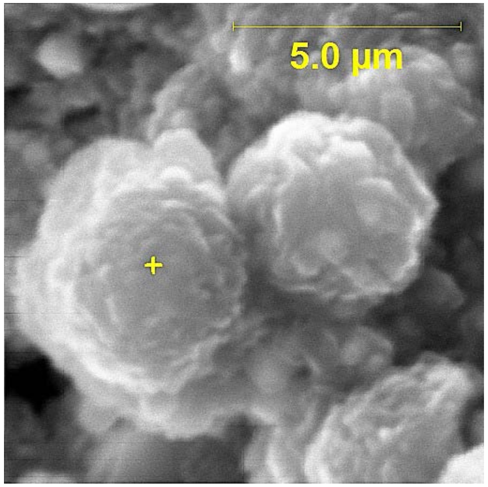
- Most common member of a family of minerals containing Na-Al-Si-O
  - Also sodalites, zeolites
- Often generically called “aluminosilicates”
- Often incorporate other metals (Ca, Fe, Cr)
- Relatively insoluble in NaOH; won’t leach

Cancrinites





BY-109



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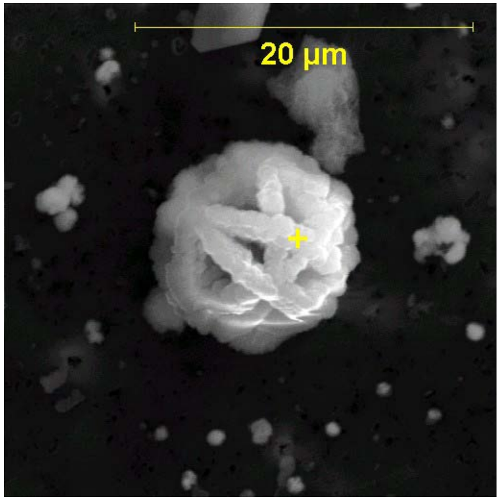


C-103

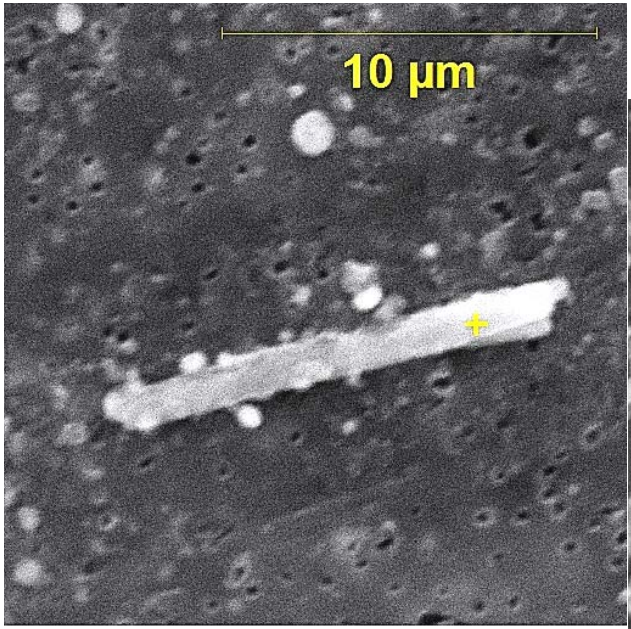
Dawsonite, $NaAlCO_3(OH)_2$

- Likely formed by absorption of atmospheric CO_2

$$NaAl(OH)_4 + CO_2 \rightarrow NaAlCO_3(OH)_2 + H_2O$$

- Inferred from caustic demand test results
- Predicted by ESP calculations
- Now identified in several tanks by SEM & XRD
- Relatively soluble in NaOH

Dawsonite



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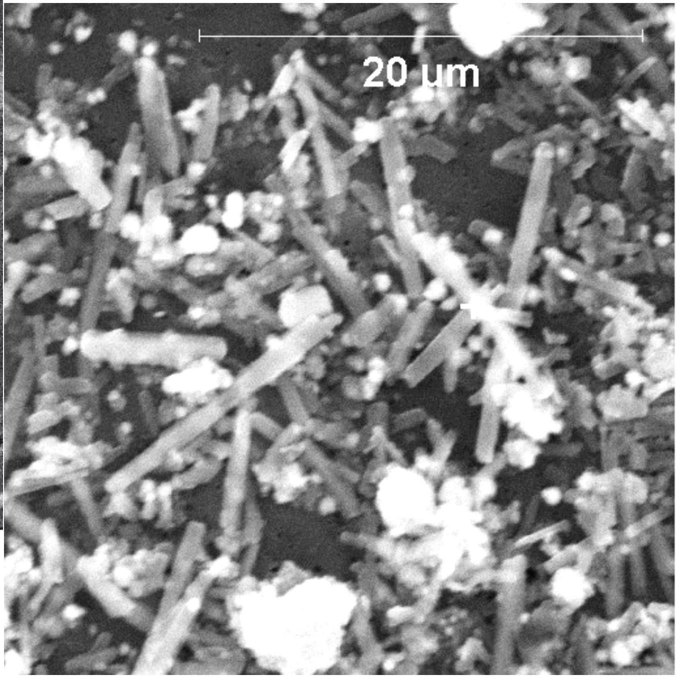

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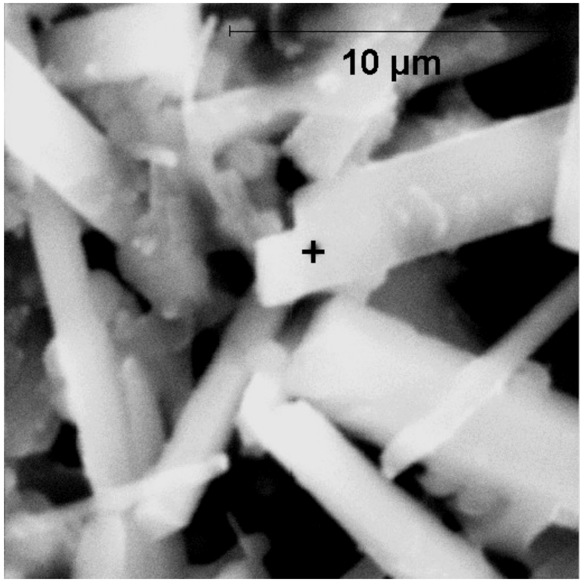


AN-107

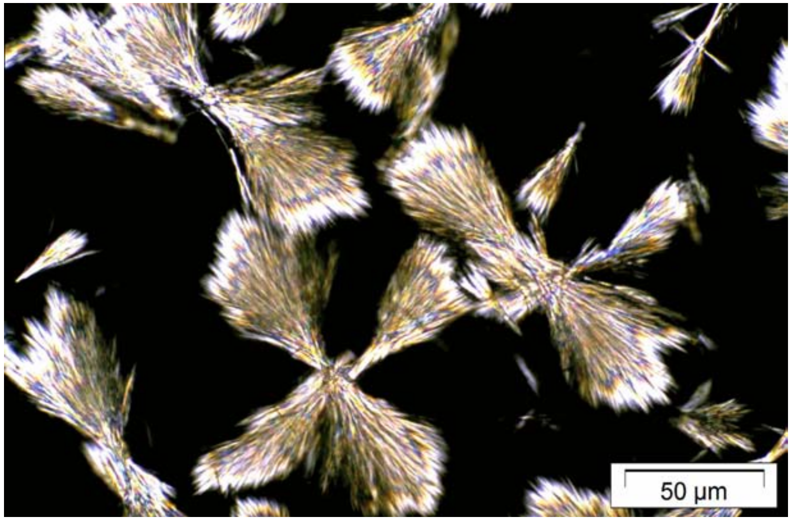
Sodium Aluminate, $NaAl(OH)_4$

- Formula also written $NaAlO_2$

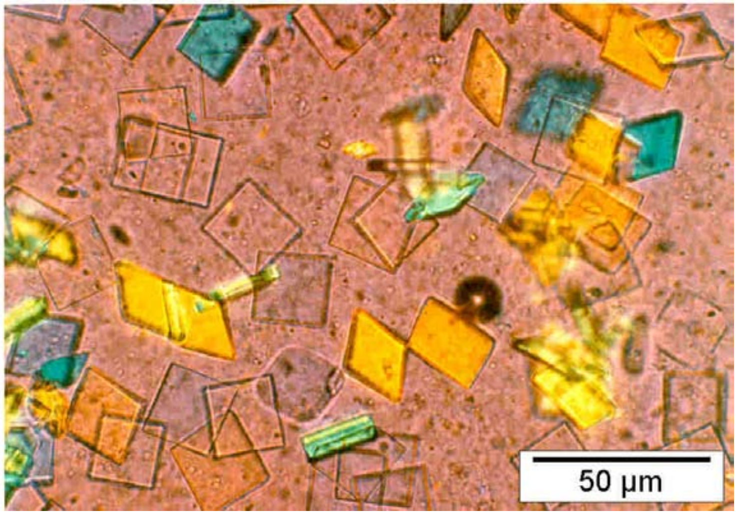
  $$[NaAlO_2 + 2\ H_2O \cong NaAl(OH)_4]$$

- Soluble at high pH
- The one species in Hanford waste that can be precipitated by adding water!
- Defines the difference between double shell slurry feed (DSSF) and double shell slurry (DSS)

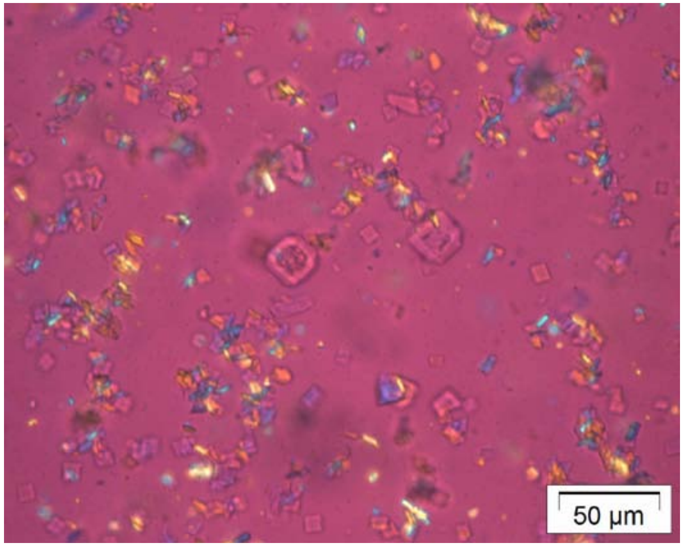
Sodium Aluminate



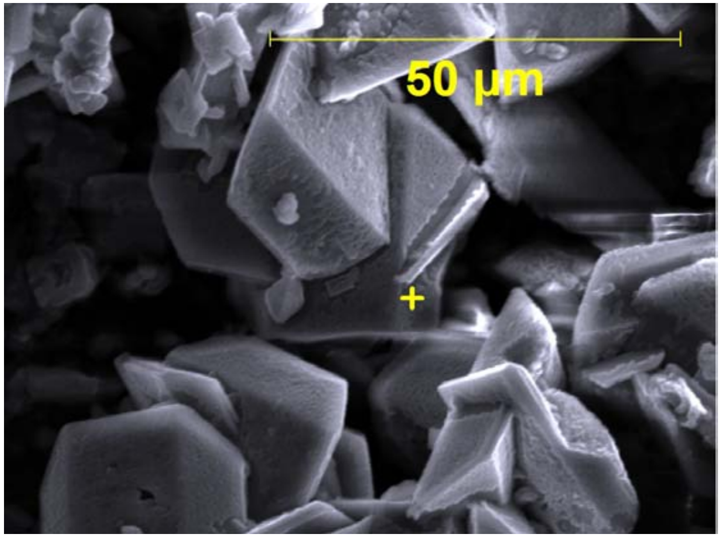
Needle form: Simulant



“Cracker” form: Simulant

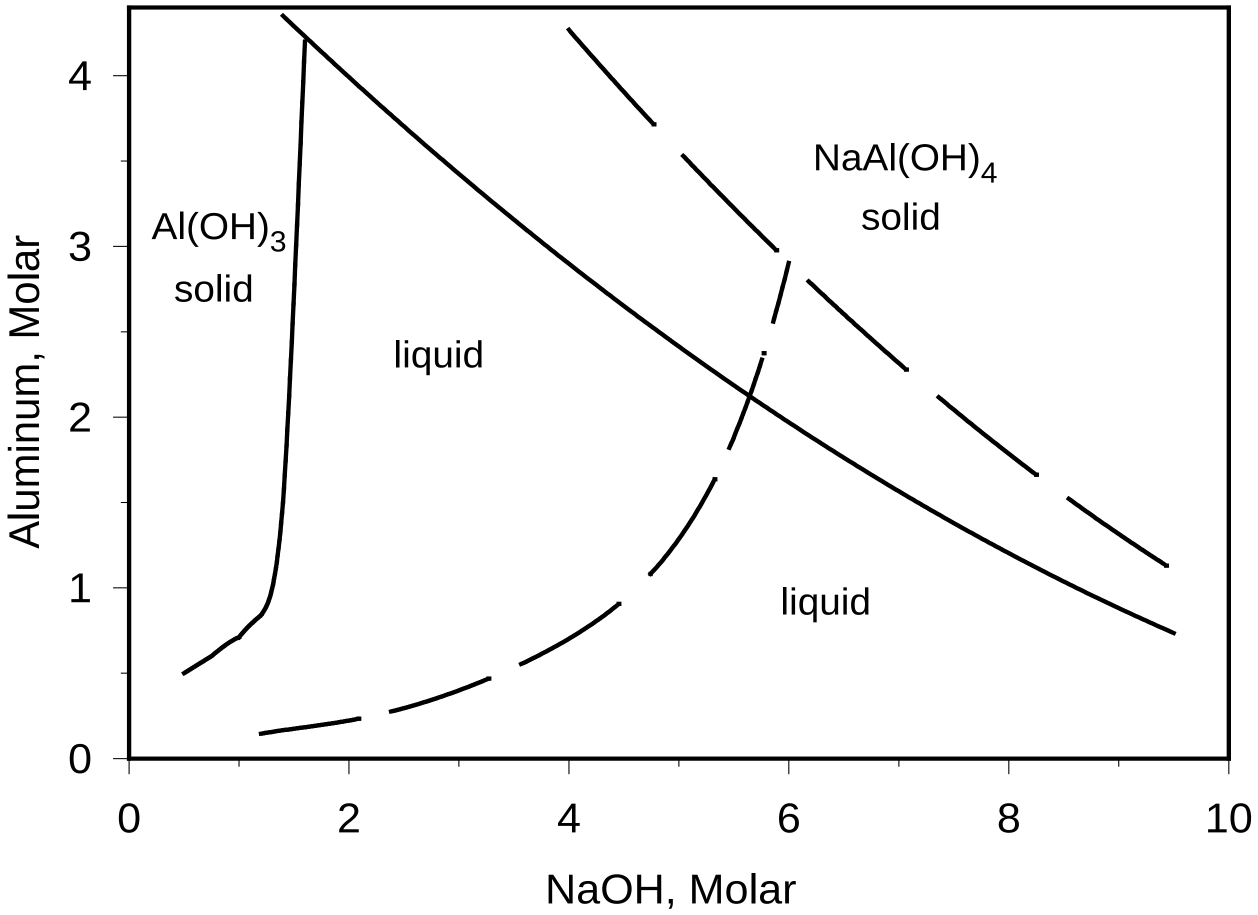


Tank S-112



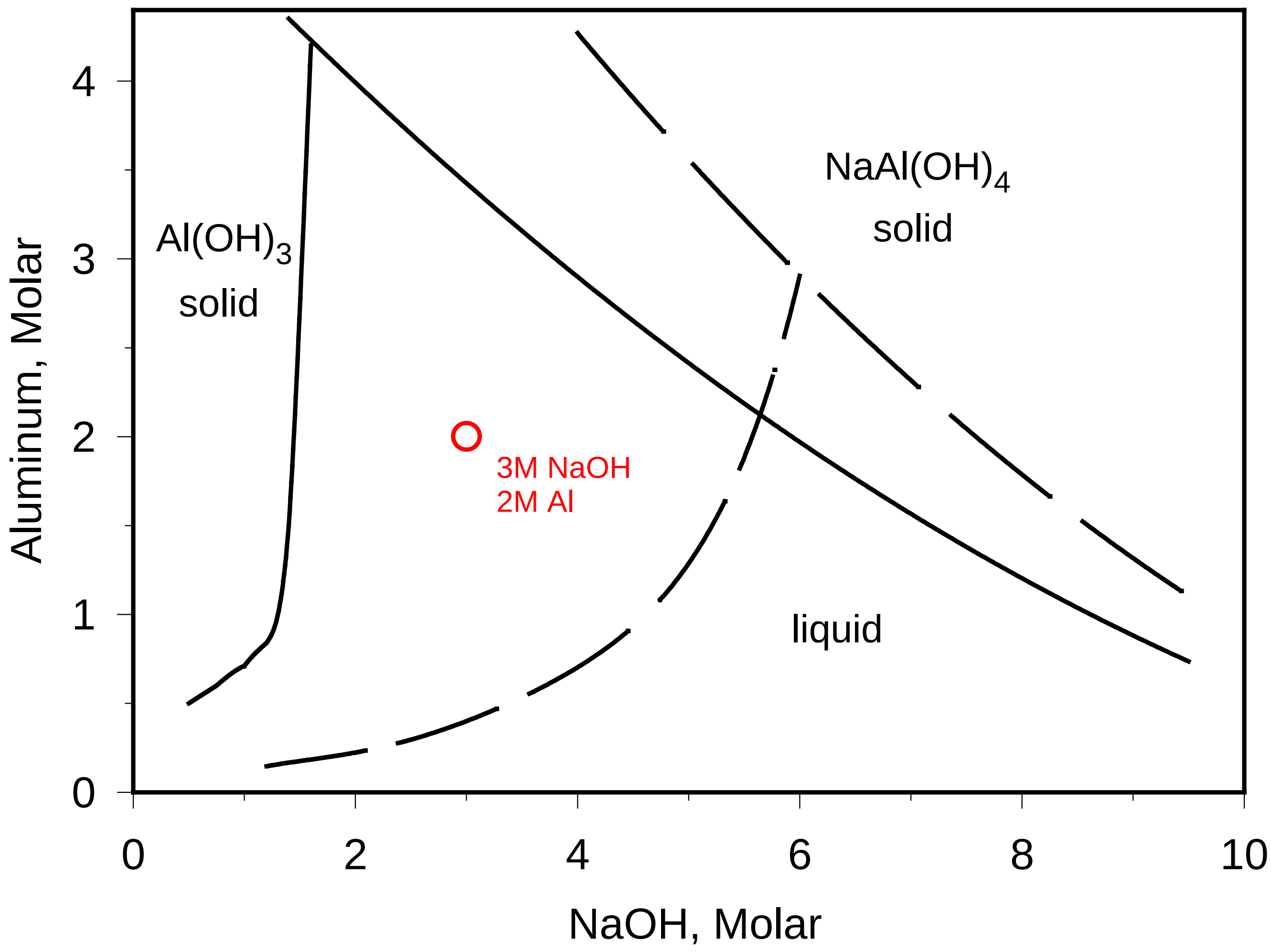
Tank S-112

"Barney Diagram"

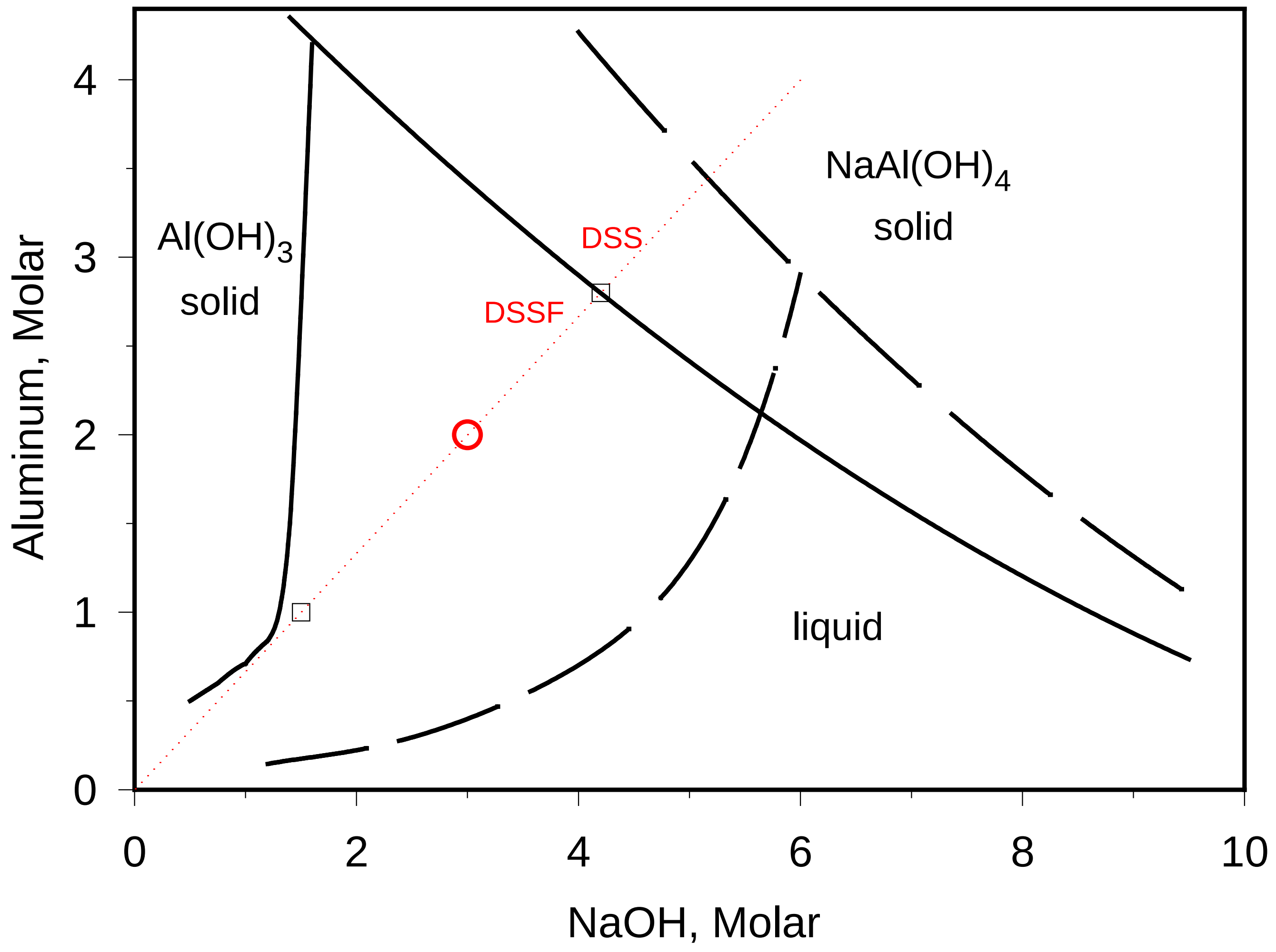


Solid lines: Al solubility in Tank Farms (high ionic strength)
Dashed lines: Al “pure-component” solubility (low ionic strength)

"Barney Diagram"



"Barney Diagram"



What Don't We Know?

- Relative amounts of gibbsite, boehmite, etc.
- Al solubility under WTP operating conditions
  - Major use of Na in WTP is to keep Al in solution
  - Current flowsheet assumes pure-component solubility
  - Need basis to support less-conservative algorithm
- Why Al is so soluble in tank waste
  - Supersaturation due to kinetic effects?
  - Unaccounted-for speciation?
- Whether proposed alternative processes are viable

How Do We Fill In the Gaps?

- Al solubility work under WTP operating conditions ongoing at Mississippi State University / Institute for Clean Energy Technology and at 222-S Laboratory to improve solubility correlations
- Continuing sludge characterization work aimed at Al speciation, especially during retrieval operations (WRPS)
- Lithium hydrotalcite process development work ongoing at AREVA and WRPS
- Tank farm continuous leaching process development work ongoing at PNNL
- Caustic recycle development work ongoing at Ceramtec
- Improved glass loading research ongoing at Catholic University / Vitreous State Laboratory and at Energy Solutions
- All work sponsored by DOE-EM program