washington river protection solutions

Waste Tank Heels and Heel Simulants

WB Barton

Office of Waste Processing
Technical Exchange
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Acknowledgements

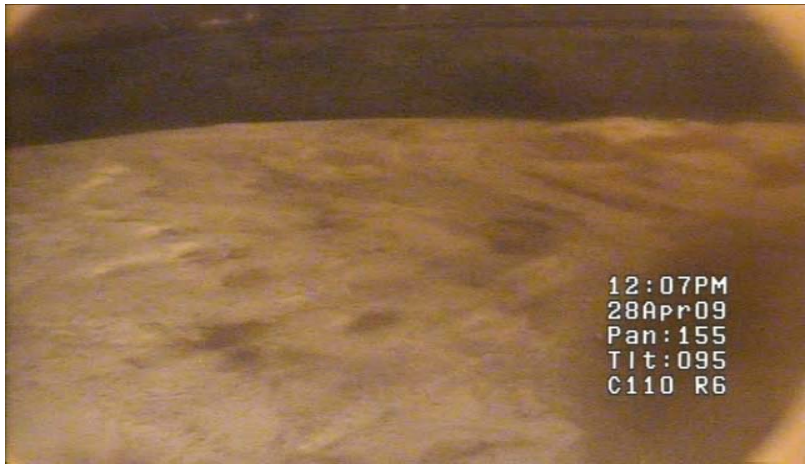
- Dan Herting and Heinz Huber did most of the chemistry work.
- Don Geniesse did extensive chemical modeling to determine mineral forms expected.
- Leela Sasaki, Duc Nguyen, and Doug Adkisson provided valuable insights.

Background

- WRPS proposed to investigate the ECC process for deployment in Hanford tanks as a heel treatment process.
- Needed a chemical simulant of the heel for testing of the ECC process.
- Retrieval is focused on C Farm tanks for the next 5 years.

C-108

C-109



C-110

C-103

Background

Objectives

- What is the composition of the waste heel remaining after sluicing?
- How do we make a simulant of the heel?

Method of Attack

- Bulk tank chemistry.
- Heel analysis results.
- Mineralogy.
- Method of retrieval.

Pre-Retrieval Waste Composition

Analyte	C-101	C-102	C-103	C-104	C-105	C-106
Na	29.6%	21.3%	0.5%	41.6%	15.8%	47.5%
Al	40.9%	53.5%	47.6%	20.2%	61.5%	10.6%
NO3	13.2%	4.9%	0.4%	1.7%	1.2%	0.1%
TIC as CO3	1.6%	5.8%	0.1%	4.3%	2.1%	22.7%
PO4	4.0%	0.8%	3.0%	0.2%	0.6%	1.0%
NO2	2.0%	1.9%	0.3%	4.3%	1.4%	2.8%
Fe	2.2%	1.5%	0.0%	2.7%	0.7%	7.0%
F	0.4%	1.0%	20.8%	9.8%	0.4%	0.1%
TOC	1.7%	0.7%	11.1%	6.3%	3.4%	3.2%
Si	1.7%	5.8%	0.9%	2.0%	10.5%	0.3%
Ca	0.6%	0.8%	1.2%	0.4%	0.5%	0.3%
Ni	0.0%	0.5%	2.8%	0.2%	0.3%	0.2%

Best Basis Inventory, mole fraction

Pre-Retrieval Waste Composition

Analyte	C-107	C-108	C-109	C-110	C-111	C-112	Average
Na	35.4%	41.9%	37.5%	44.5%	17.2%	39.1%	31.0%
Al	20.9%	22.3%	24.1%	7.4%	37.4%	8.7%	29.6%
NO3	6.6%	7.2%	7.2%	21.4%	9.5%	12.0%	7.1%
TIC as CO3	1.6%	1.8%	3.8%	2.1%	3.5%	3.8%	4.4%
PO4	5.3%	8.9%	6.5%	8.1%	5.8%	7.3%	4.3%
NO2	6.6%	5.4%	6.6%	1.9%	6.6%	9.5%	4.1%
Fe	15.7%	1.3%	2.9%	2.4%	7.5%	4.0%	4.0%
F	2.9%	2.3%	0.8%	4.8%	1.4%	1.1%	3.8%
TOC	0.5%	0.8%	1.6%	0.5%	0.6%	3.1%	2.8%
Si	0.6%	1.6%	1.8%	3.1%	2.5%	1.2%	2.7%
Ca	0.3%	3.2%	3.5%	0.4%	3.2%	4.5%	1.6%
N	0.5%	1.5%	1.9%	0.0%	2.6%	2.0%	1.0%

Best Basis Inventory, mole fraction

Bulk Tank Chemistry

- On average the sodium and the major anions are in equilibrium. Probably in dissolved form with the liquid.
- Major remaining insoluble constituents are aluminum and in some tanks iron.

Heel Analysis Results

Analyte	C-103	S-112
Na	2.5%	18.7%
Al	91.6%	78.7%
NO3	0.0%	0.0%
TIC as CO3	0.2%	1.2%
PO4	0.2%	0.0%
NO2	0.0%	0.0%
Fe	1.3%	0.2%
F	0.0%	0.0%
TOC	0.6%	0.7%
Si	2.7%	0.0%
Ca	0.3%	0.1%
Ni	0.0%	0.0%

Best Basis Inventory, mole fraction

Heel Analysis Results

- Only two tanks have post retrieval samples.
- The single overwhelming constituent in both heels is aluminum.
- S-112 waste heel was mostly 200 micron gibbsite.
- C-103 waste heel was mostly 70 micron gibbsite.

Potential Mineral Forms

- Gibbsite $Al(OH)_3$
- Cancrinite $Na_8Al_6Si_6O_{24}CO_3.2H_2O$
- Iron Hydroxide Fe_2O_3
- Dawsonite $NaAlCO_3(OH)_2$
- Sodium Oxalate $Na_2C_2O_4$
- All the mineral forms tend to precipitate as very small particles(< 10 microns).

Potential Mineral Forms

- Over time re-crystallization will result in crystal growth.
  - Oswald Ripening or thermal gradient.
- We postulate this growth rate is proportional to the solubility of the mineral.

Chemical	Mineral Form	Solubility @ pH 12 (M)
Aluminum		
	Gibbsite	0.00005
	Dawsonite	0.00008
	Beohmite	0.0001
Iron		
	Fe(OH)3	0.00001
	Fe2O3	1.00E-10
Ni		
	NiO	5.00E-07
	Ni(OH)2	6.00E-08
Ca		
	Ca5OH(PO4)3	8.00E-07
	CaF(PO4)	7.00E-08

Method of Retrieval

- Sluicing is the primary method of retrieve for the 100 series tanks.
- Tends to separate the particles by size and density.
  - Settling rate controls the ability to get waste into the pump.
  - Pump suction velocity will not reliably suspend particles greater than about 50 microns.

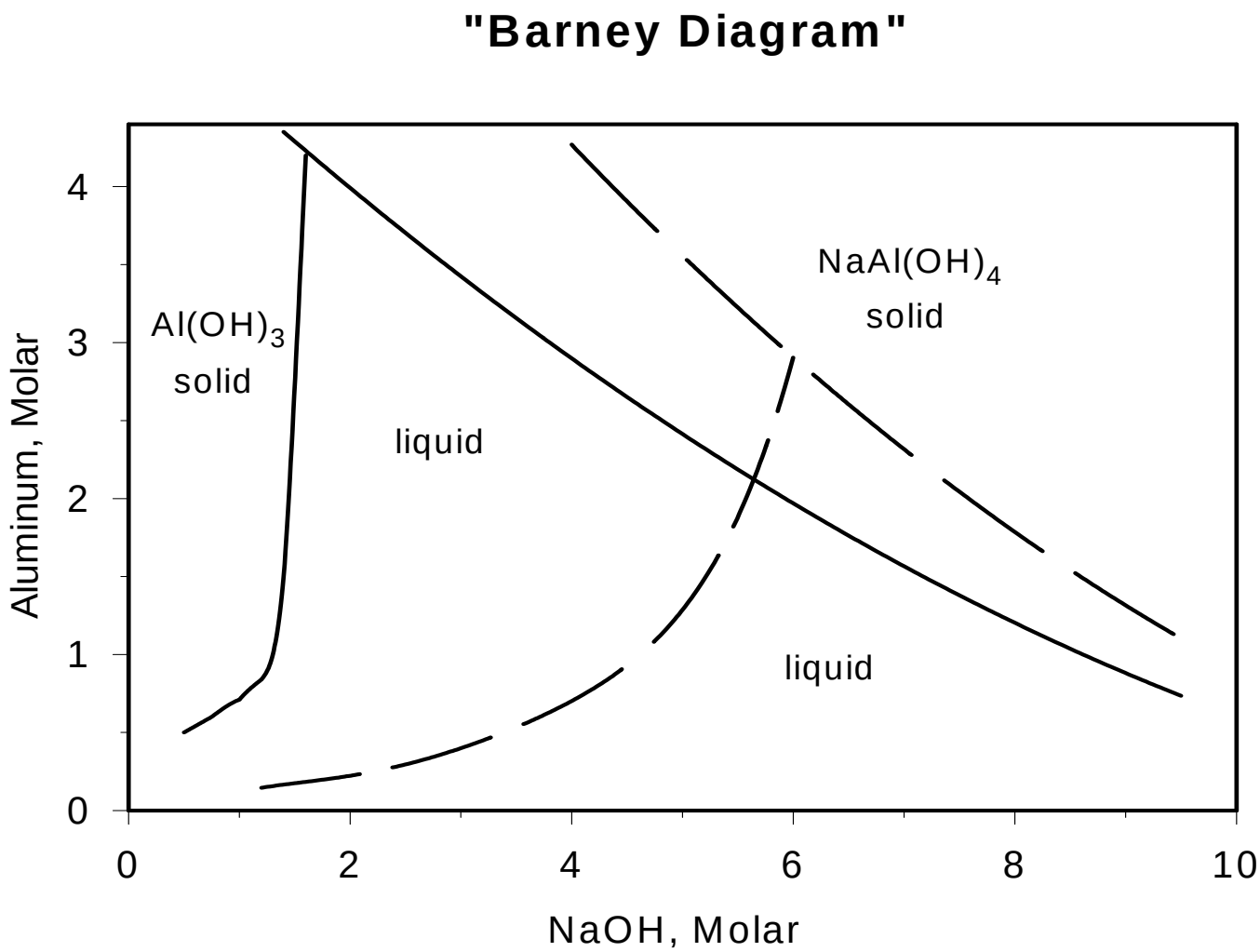
Hypothesis

- The major constituent of waste heels will be gibbsite if the tank starts out with significant aluminum.
  - Sampling of C-108, C-109, and C-110 will test the hypothesis.

Simulant

- Gibbsite crystal growth kinetics are very slow.
  - It took 20-30 years to grow the particle size we see in the tanks.
- Acceleration by heating is limited by the stability of the mineral form.
  - Forms Boehmite above 100 C.

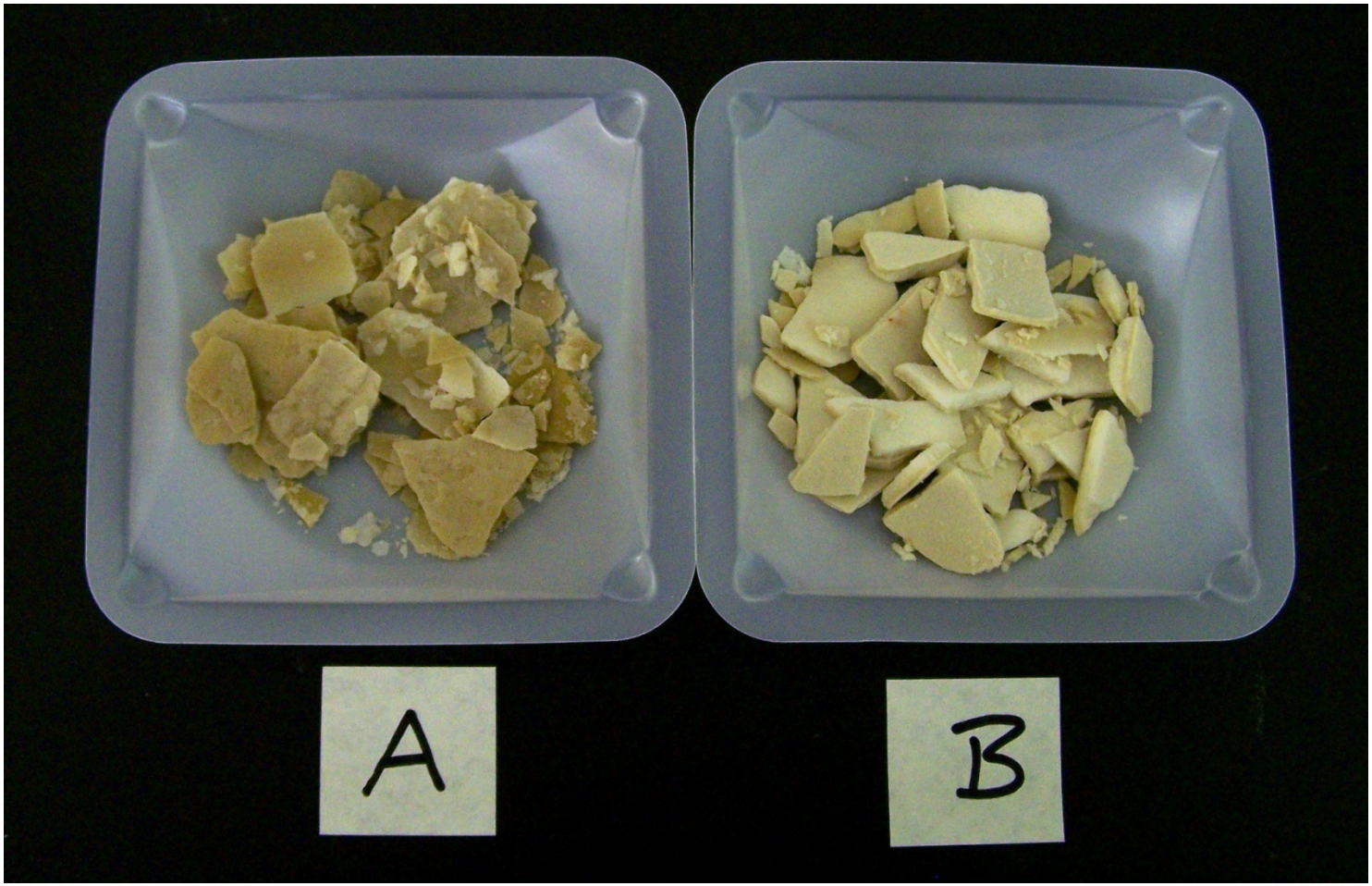
Simulant


"Barney Diagram"
Aluminum, Molar
NaOH, Molar
0
1
2
3
4
0
2
4
6
8
10
Al(OH)3
solid
liquid
NaAl(OH)4
solid
liquid

Simulant

- Sodium aluminate dissolves readily in water.
- Disproportionates to $Al(OH)_3$ and NaOH.
- At high supersaturation and 80°C, gibbsite precipitates and forms a hard mass.
- Demonstrated in the lab.
- Contract to product 100 pounds of simulant.

Simulant



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