WRPS-41325-VA
Revision 0

Waste Tank Heels and Heel Simulants

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Contractor for the U.S. Department of Energy
Office of River Protection under Contract DE-AC27-08RV14800

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Washington River Protection Solutions

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- Don Geniesse did extensive chemical modeling to determine mineral forms expected.
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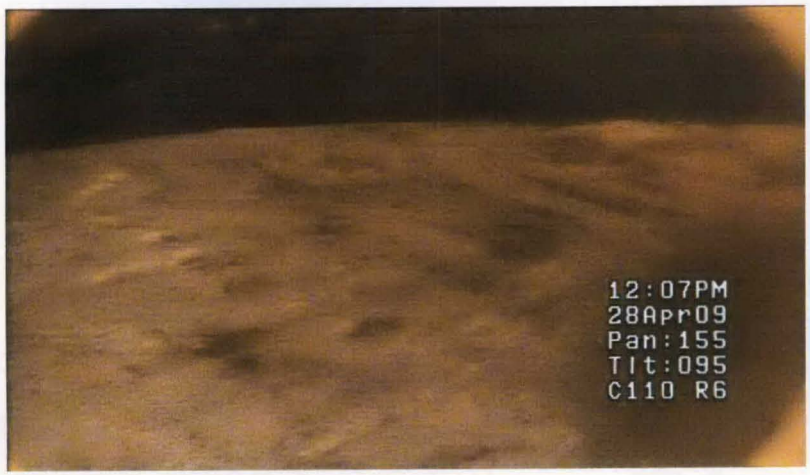
Background

- 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

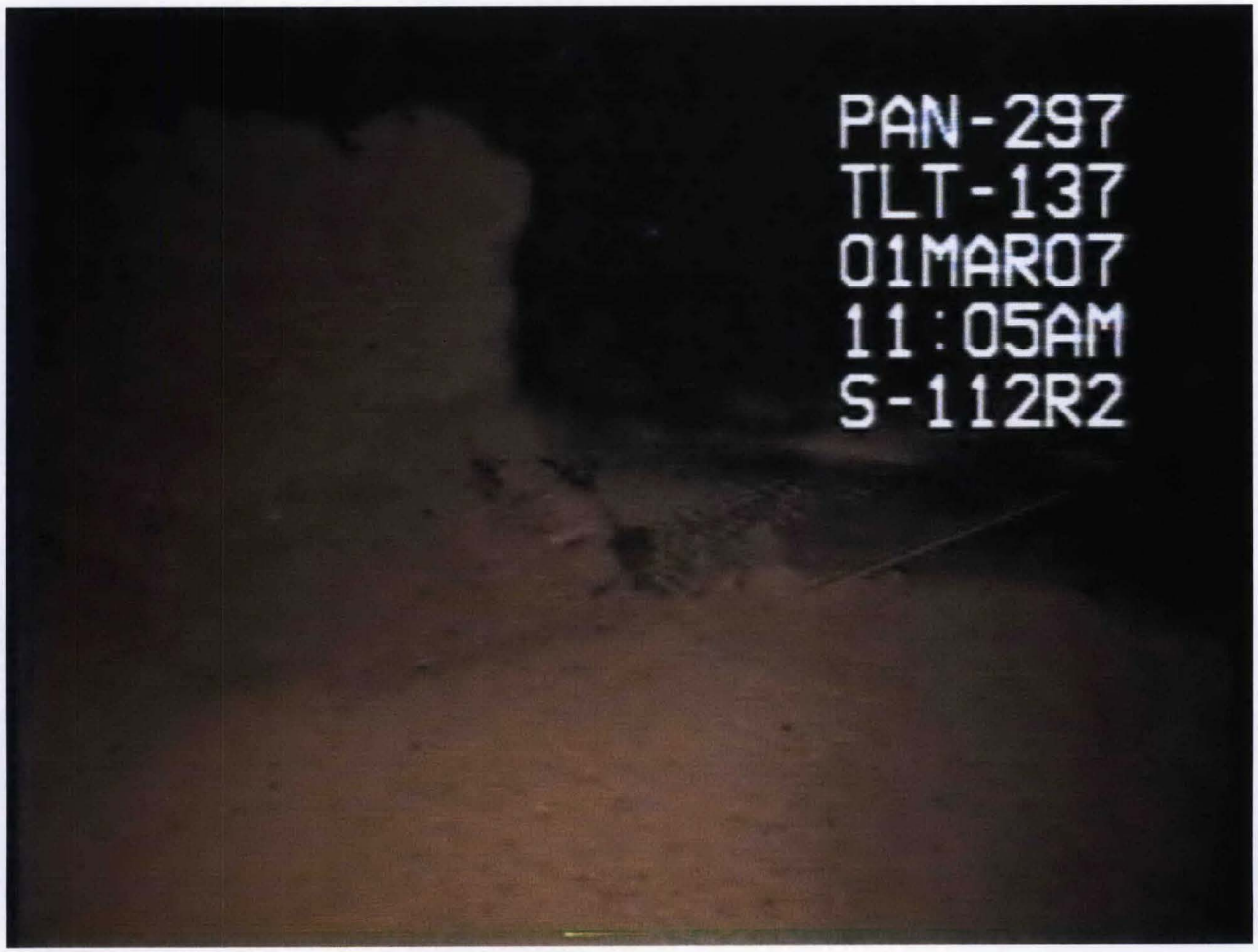
C-109



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?

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Method of Attack

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

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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%
Ni	0.5%	1.5%	1.9%	0.0%	2.6%	2.0%	1.0%

Best Basis Inventory, mole fraction

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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

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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

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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

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- 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

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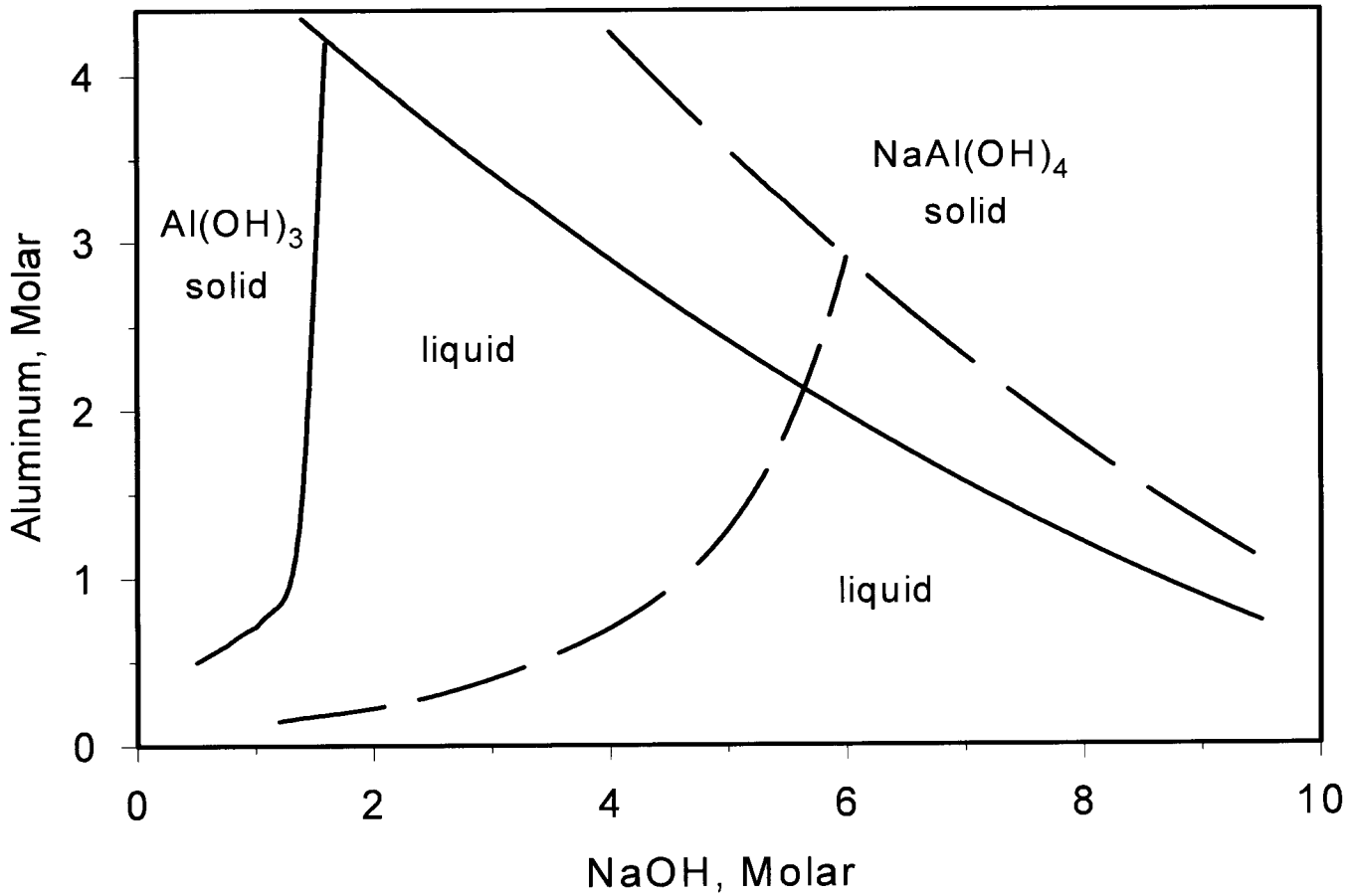
"Barney Diagram"



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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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