

# Caustic Cleaning for Waste Heel Removal

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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# Caustic Cleaning for Waste Heel Removal

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# **Caustic Cleaning for Waste Heel Removal**

**WB Barton**

**Office of Waste Processing  
Technical Exchange  
May 19, 2009**



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I would like to acknowledge the work of Dan Herting, Heinz Huber, and the staff at the 222-S Laboratory. Without their work, this process would just be a glimmer of an idea.



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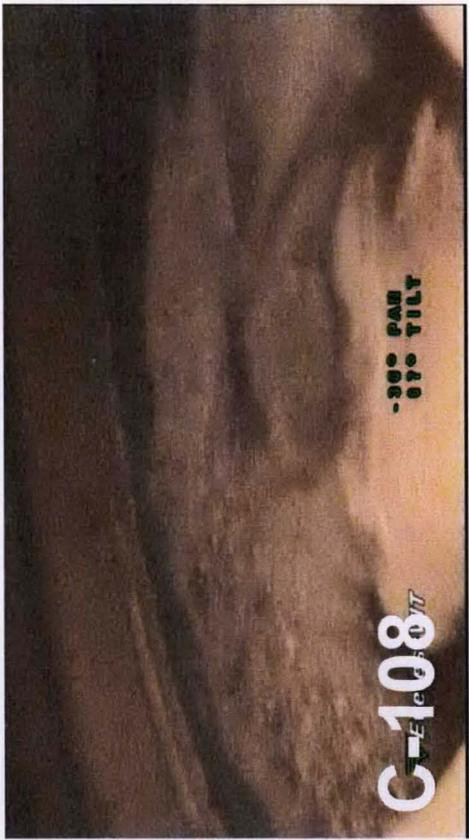
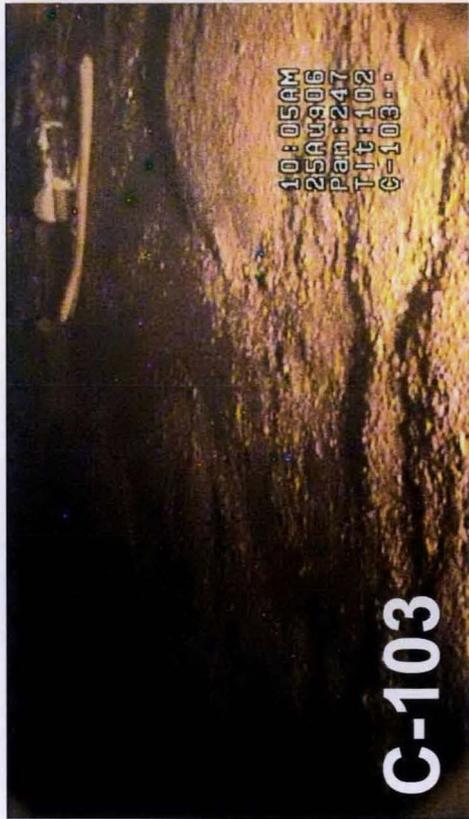


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# Background

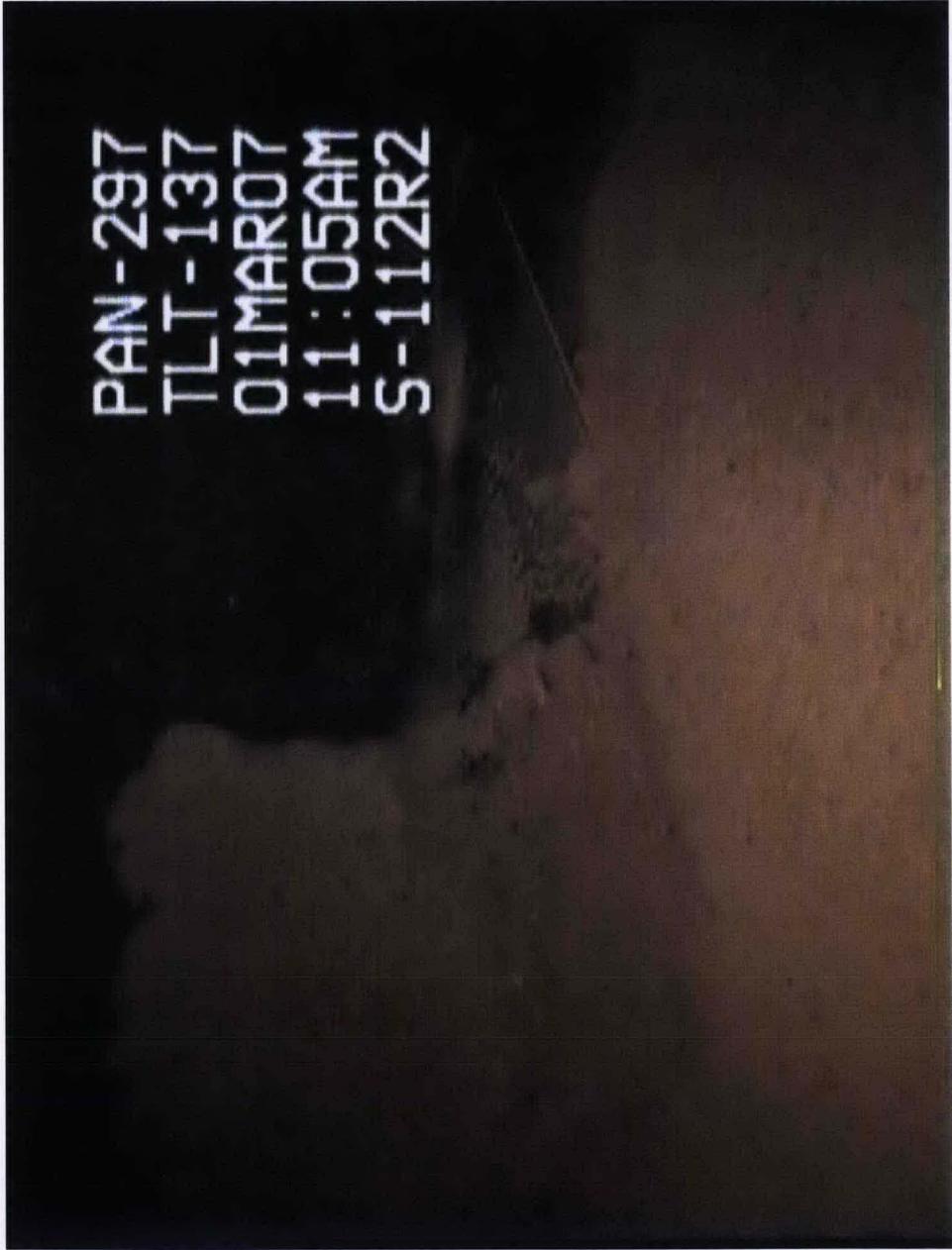
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- Only 1 of 5 C farm tanks has met the TPA goal for waste retrieval when they reached the “limit of the technology.”
  - On average about 10 % of the starting volume is not retrievable with current sluicing technology.
  - Waste heels have similar appearance, light tan sand and cobble.
  - C-103 heel sample was ~80 % Aluminum.
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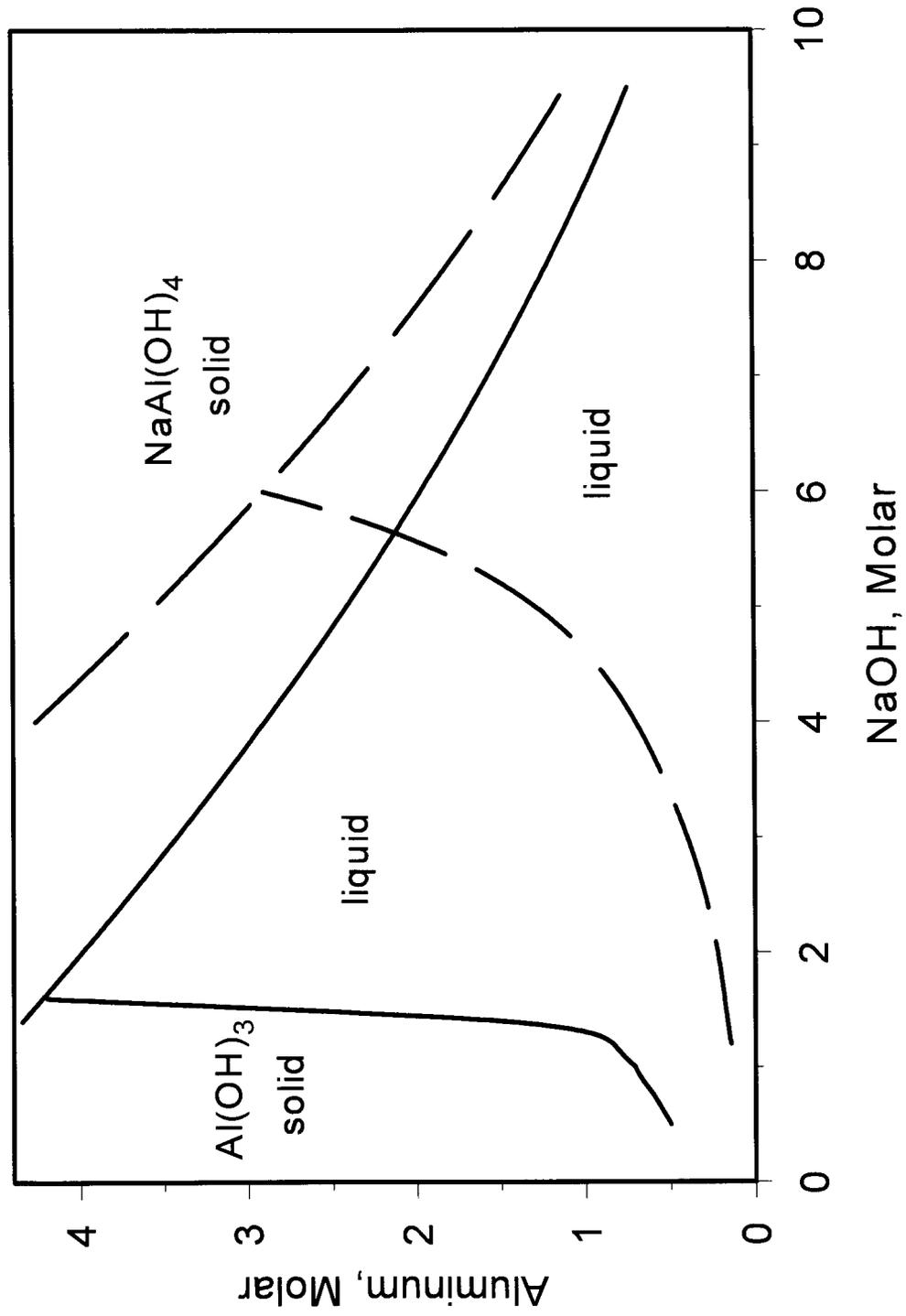
# Background



- Aluminum is a major component of the Tank Waste.
- Generally found in the waste in a mineral form  $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  (mostly gibbsite,  $\text{Al}(\text{OH})_3$ , some Boehmite,  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , & Dawsonite,  $\text{NaAl}(\text{CO}_3)(\text{OH})_2$ ).

- Aluminum hydroxide can be changed to sodium aluminate in strong caustic solutions.
    - Sodium aluminate is much more soluble than aluminum oxide
  - $\text{Al}_2\text{O}_3 + \text{NaOH} \leftrightarrow 2\text{NaAl}(\text{OH})_4$
  - Reaction kinetics are very slow. Most studies have shown that it takes months to reach equilibrium at room temperature and caustic concentrations below 8 M.
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# Barney Diagram



# History

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- June - August 2006 blind leaching of residuals in S-112 was attempted. 8 M caustic was used. Results were indeterminant. Subsequent sluicing retrieved ~1000 gallons of waste.
  - Feb. 2007 used S-112 to pass through 19 M caustic to SY-102. Remained in S-112 three days. Significant evidence of reaction was observed.
    - Intended to use the high density/viscosity to enhance solid suspension.
    - Large chunks of “cobble” in S-112 became piles of sand.
    - Foam seen throughout the tank.
    - ~1500 gallons of waste retrieved in pumpout, no sluicing.
-

- June-Sept. 2007 Sampled S-112 residues and requested supplemental analysis.
  - Residue was almost pure Gibbsite ( $\text{Al}(\text{OH})_3$ )
  - Leached in 8 and 19 M NaOH.
- August 2008 initiated development testing.

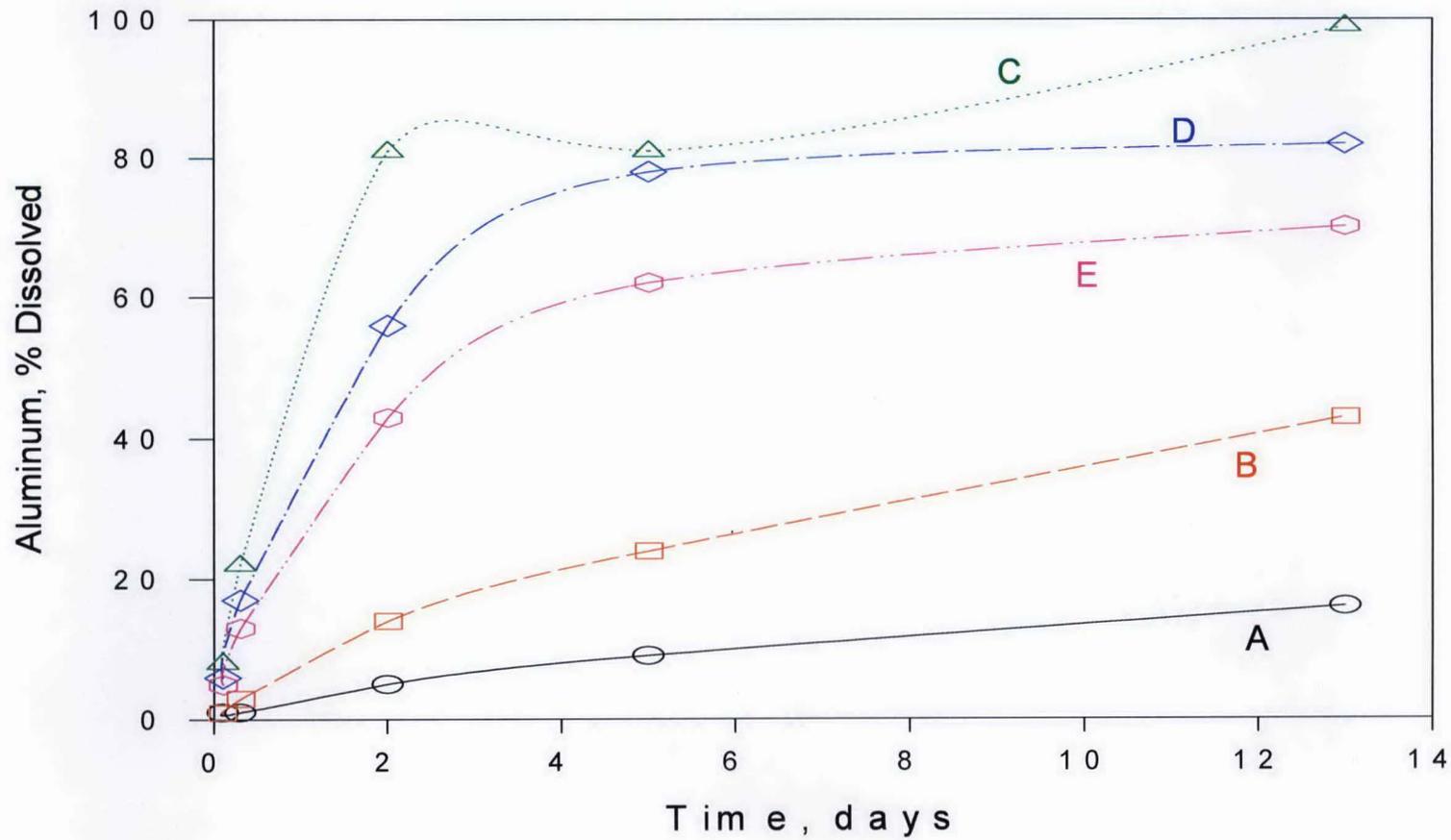


# Observations

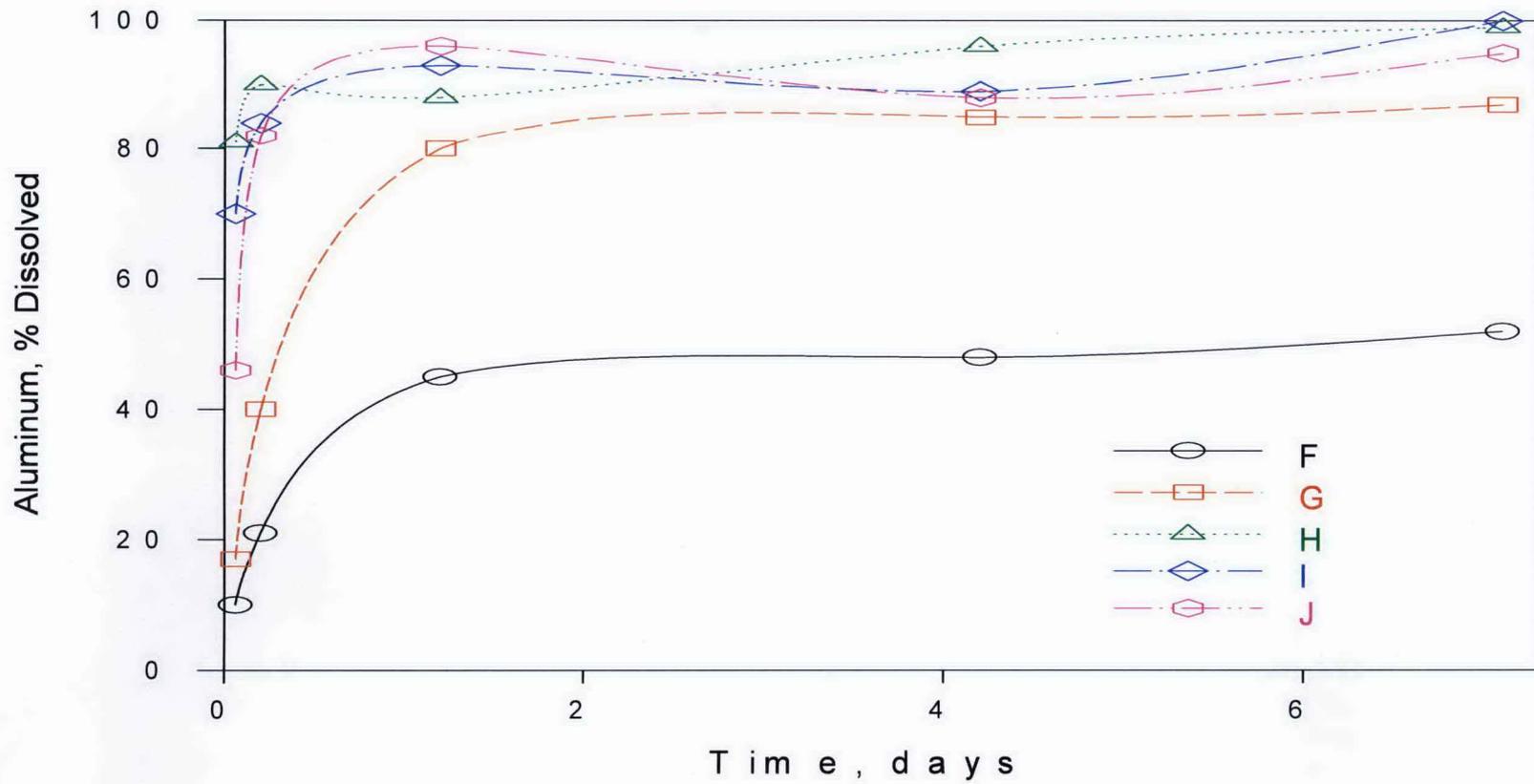
- S-112 19 M caustic showed unexpected chemical reaction. Composition of residues was unknown.
- Lab tests showed essentially no reaction at 8 M and complete reaction at 19 M in less than two weeks at hood temperature with S-112 sample.
- $\text{Al}(\text{OH})_3$  solids are converted to  $\text{NaAl}(\text{OH})_4$  solids

- $\text{NaAl}(\text{OH})_4$  dissolves easily in water and “weak” caustic solutions.
- Reaction rates are ~10 times previously reported values when NaOH concentration is above 6-9 M.

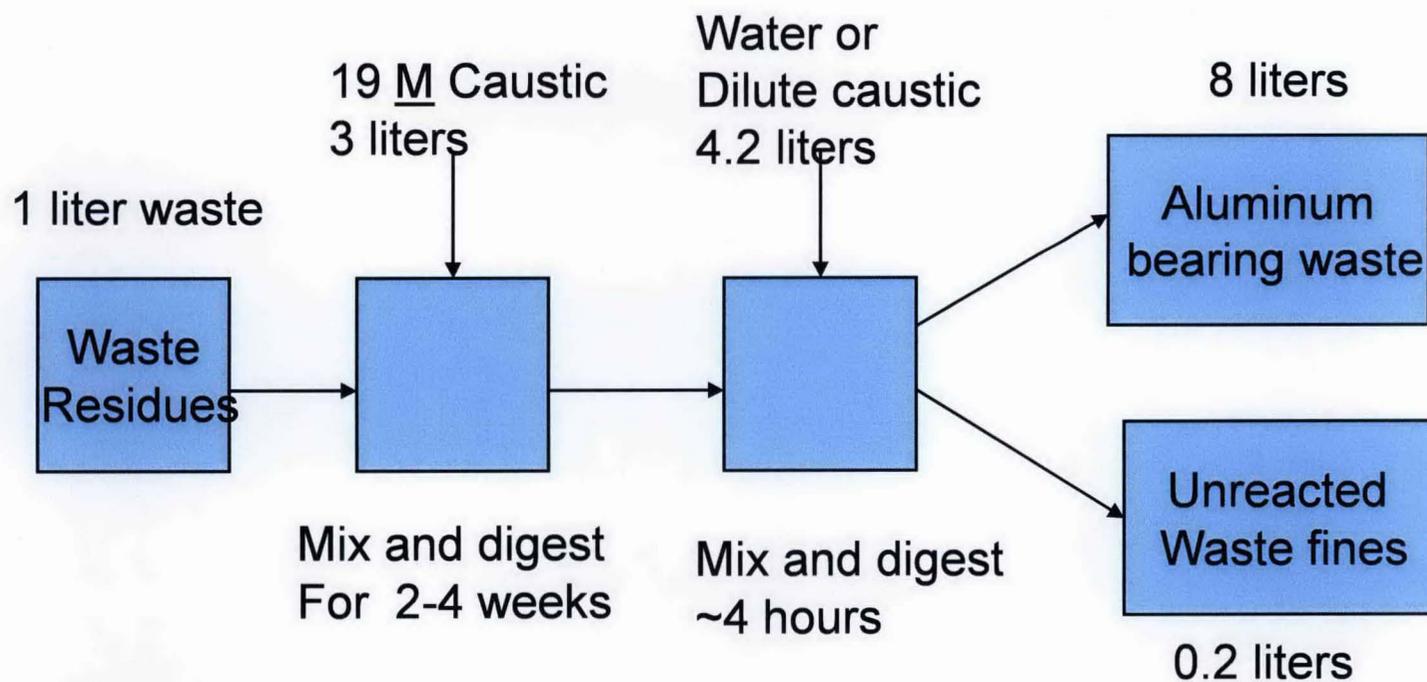
Gibbsite Test 1: 25 °C



## Gibbsite Test 2: 50 °C



# Process Flow Diagram



- Need to wash the waste residue with water prior to adding caustic to remove dissolved phosphate and oxalate which would otherwise precipitate.
  - May be implemented without modifications to C farm modified sluicing retrieval systems. Hardware needs to be evaluated. C-108/109 pumps are marginal.
  - Need residue samples to evaluate applicability to C-108/109/110.
  - Added caustic will impact available DST space.
  - Additional water to evaporate, ~ 4-6 l/l waste.
-

- Because of the size of the tanks the practical minimum batch size is probably 10,000 gallons of 50% caustic.
- Three truck loads of 50% caustic (~12,000 gallons) will react with about 4200 gallons of gibbsite sand/gravel.



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## ***Next Steps***

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- Sample heels in tanks C-108 (now), C-109, and C-110 (next year) and determine applicability of process.
- Complete scale up test with simulant. (end of May)
- Complete Process Test Plan. (early June)
- Conduct Process Test in selected tank. (Next year)



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***Is it a good use of resources to  
remove an inert mineral from  
the tank to meet a non-risk  
based volume goal?***



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# **Contact Information**

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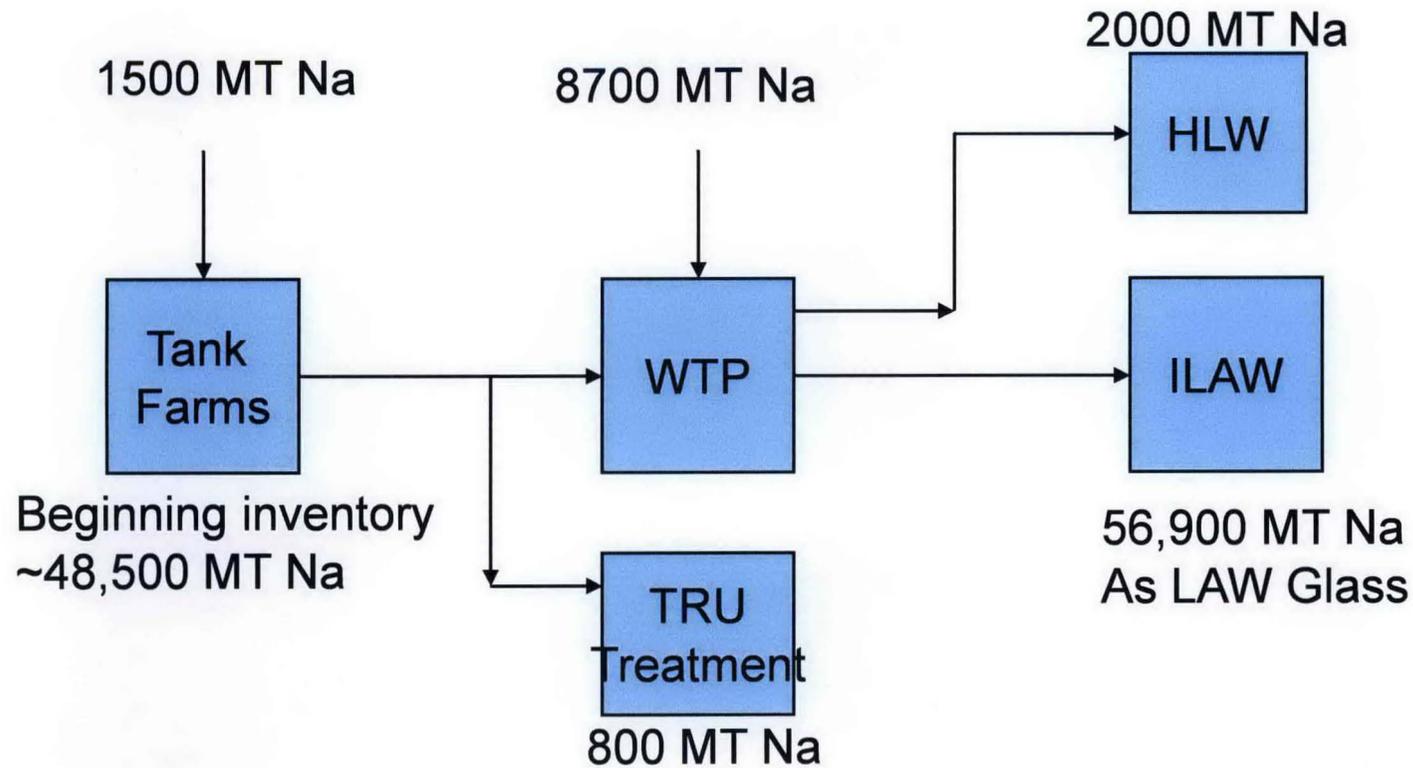


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# **Backup material**

- If we treated 120 of the SST using 12,000 gallons per tank, this would result in about 2400 MT Na being added to the tanks. This is ~ 5% of the existing Na inventory in the tanks.
- Caustic additions for heel treatment should offset additions planned for either DST corrosion control or WTP Al dissolution.

# Site Sodium Balance System Plan 3A



# Site Sodium Balance Draft System Plan 4

