washington river protection solutions

Update on Caustic Cleaning for Waste Heel Removal

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Office of Waste Processing Technical Exchange
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Acknowledgments

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Agenda

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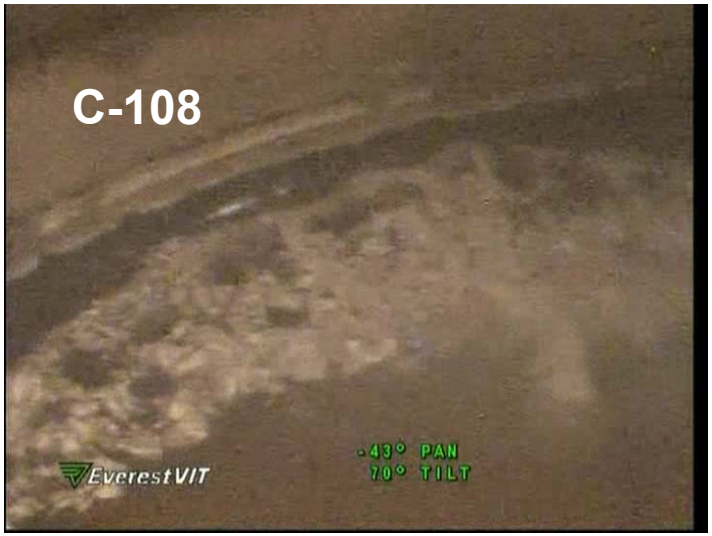
- Update on Laboratory Testing
  - Large-scale gibbsite dissolution
  - Testing and analysis of tank C-108 samples
- Near Term Plans
  - Testing and analysis of tank C-110 samples
  - Comparative dissolution testing
  - Boehmite dissolution testing
  - Caustic cleaning in tank C-108
- Q&A

Background

- Only one in five C-100 Series tanks (C-103) has met the Tri-Party Agreement volume goals when they reached the "limit of technology" for sluicing
  - C-106 retrieval completed with oxalic acid dissolution
  - C-108, C-109, C-110 require further retrieval
- Aluminum is a major component of tank waste
  - $Al(OH)_3$ (gibbsite)
  - AlO(OH) (boehmite)
  - $NaAl(CO_3)(OH)_2$ (dawsonite)
- Waste heels in tanks S-112 and C-103 were primarily gibbsite
- Tanks C-103, C-108, C-109, and C-110 are similar in appearance.

Background

C-103
10:04AM
25Aug06
Pan:007
Tlt:120
C-103


C-108
EverestVIT
-43° PAN
70° TILT

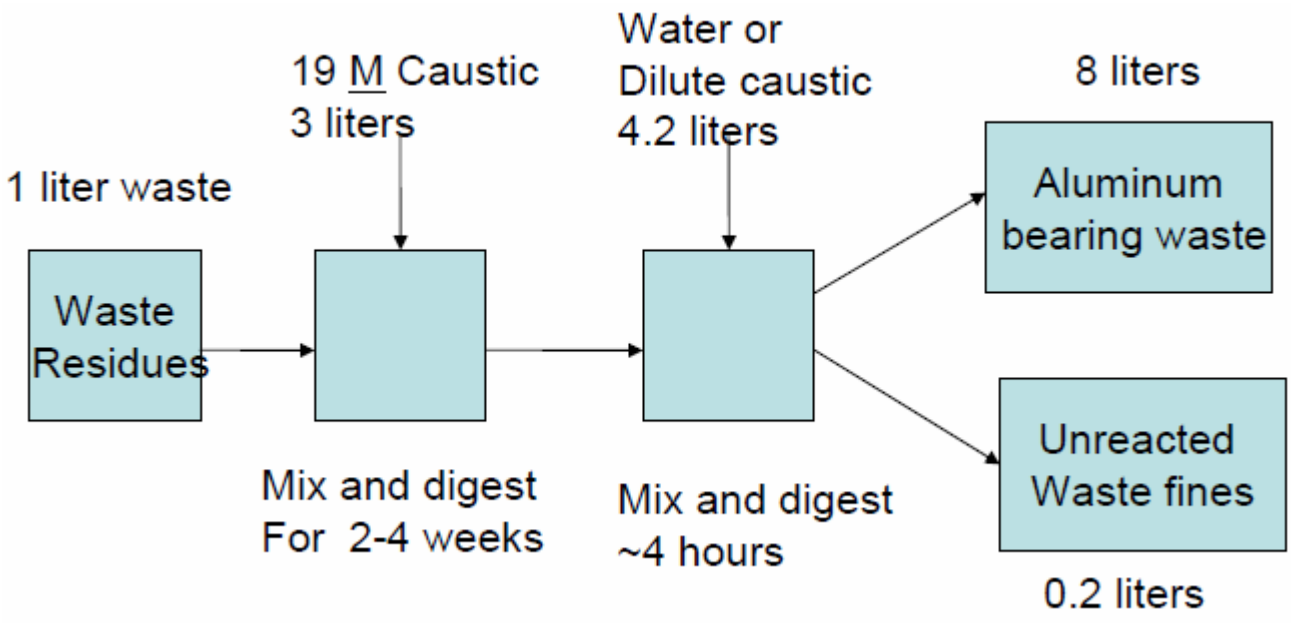
C-109

C-110
12:07PM
28Apr09
Pan:139
Tlt:097
C110 R6

Background

- **Laboratory testing has shown that insoluble gibbsite can be converted to soluble sodium aluminate in strong caustic solutions:**

$$Al(OH)_3 + NaOH \rightarrow NaAl(OH)_4$$



Update on Laboratory Testing: Large-Scale Gibbsite Dissolution

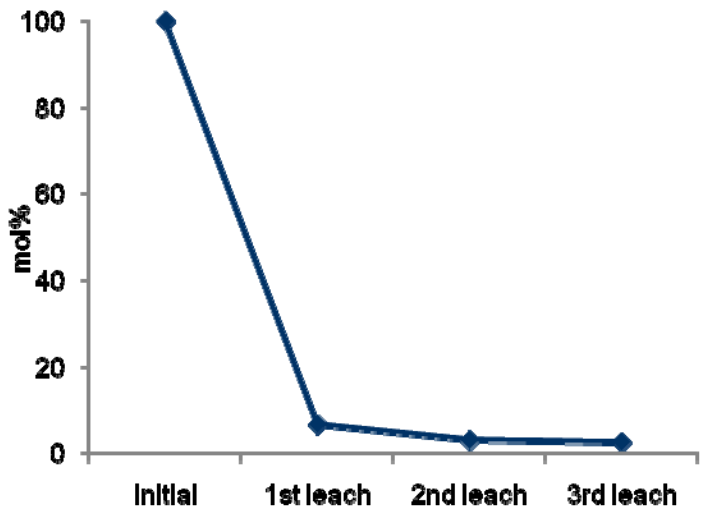
- **Kilogram-scale testing performed to compare with previous gram-scale tests (3.4 kg gibbsite and 0.38 kg sodium oxalate in 5.1 L 19.4 *M* NaOH solution)**
- **Two tests performed:**
  - **Caustic added in a single batch**
  - **Caustic addition split in two with wash step in between**

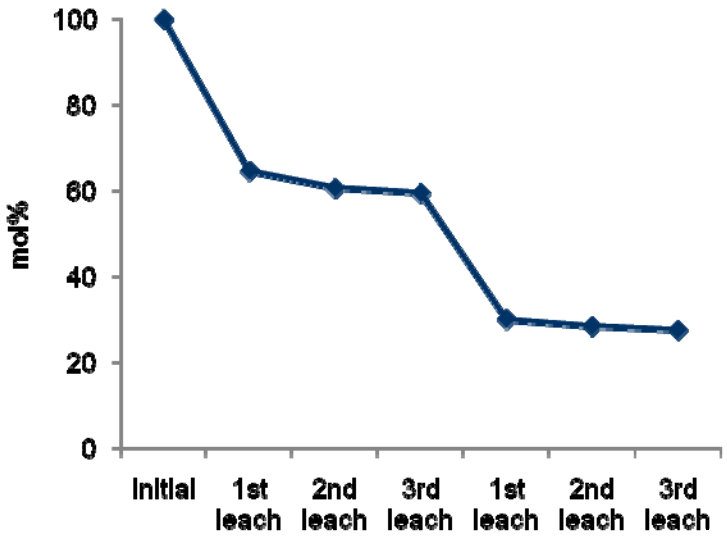
	Large Scale Tests	Small Scale Test
Mixing	Twice a day	Continuous
OH:Al molar ratio	3.5	3.5
Extent of gibbsite metathesis	>70% for 2 half batches >90% for full batch	60%

Update on Laboratory Testing: Large-Scale Gibbsite Dissolution

- **Stirring may have been a more effective means of mixing than the continuous "rotisserie" mixer used in the small-scale tests**

Amount of Aluminum Remaining After Caustic Dissolution and Water Leaches





Update on Laboratory Testing: Tank C-108 Samples

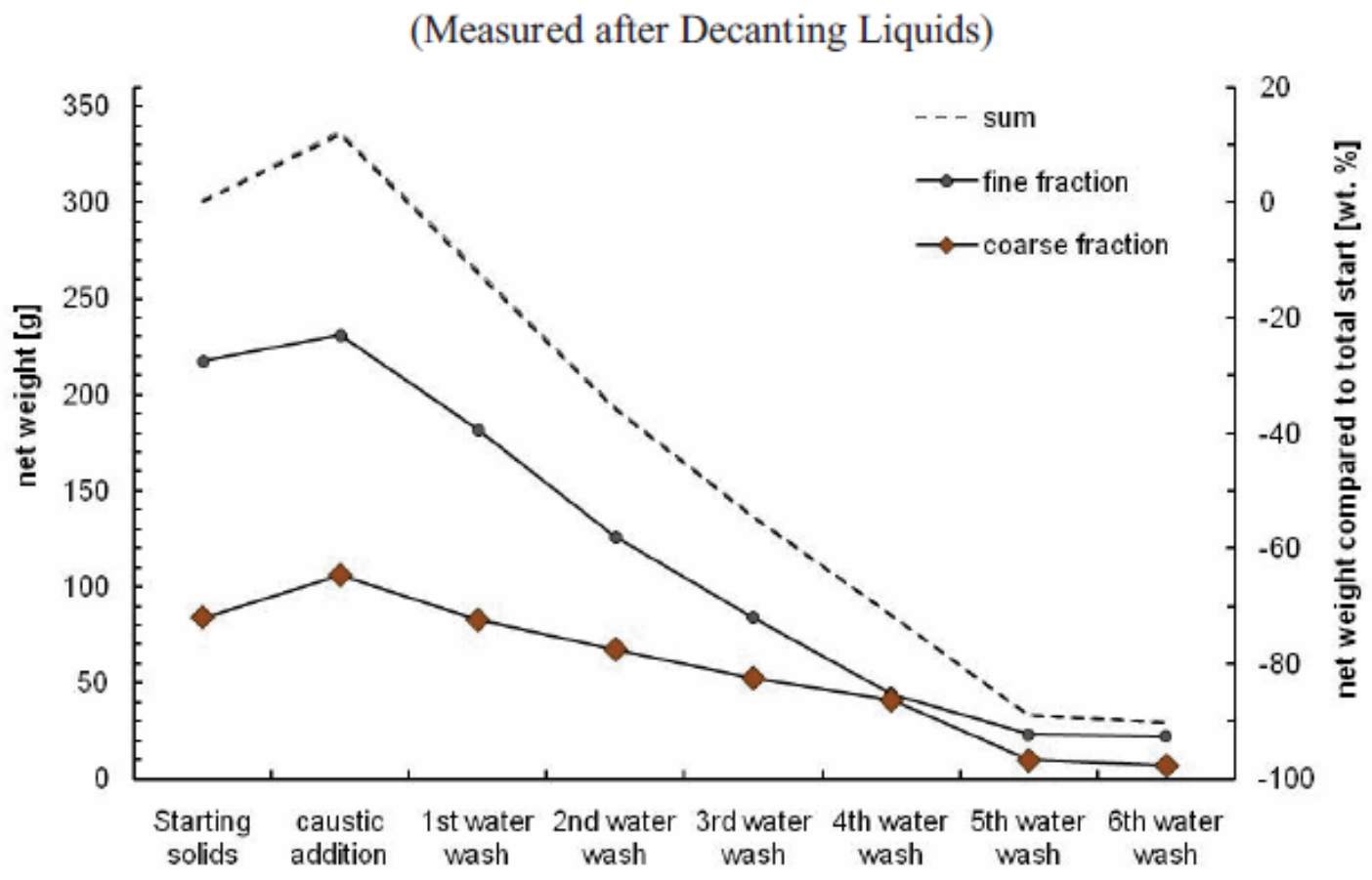
- **Tank C-108 was sampled in July 2009**
- **Sodium fluoride phosphate (natrophosphate) was the primary solid phase; then gibbsite**
  - **65 wt % $Na_7F(PO_4)_2 \cdot 19H_2O$**
  - **30 wt% $Al(OH)_3$**
  - **Smaller amounts of a Ni-Al-(U)-phosphate, flakes of steel scale (FeO_x)**
  - **Trace amounts of an Fe-Al-Pb-phosphate and $NaSrPO_4 \cdot 9H_2O$**
- **Sodium fluoride phosphate may have been present in tanks C-103 and S-112; waste in both tanks was rinsed with water before they were sampled.**

Update on Laboratory Testing: Tank C-108 Samples

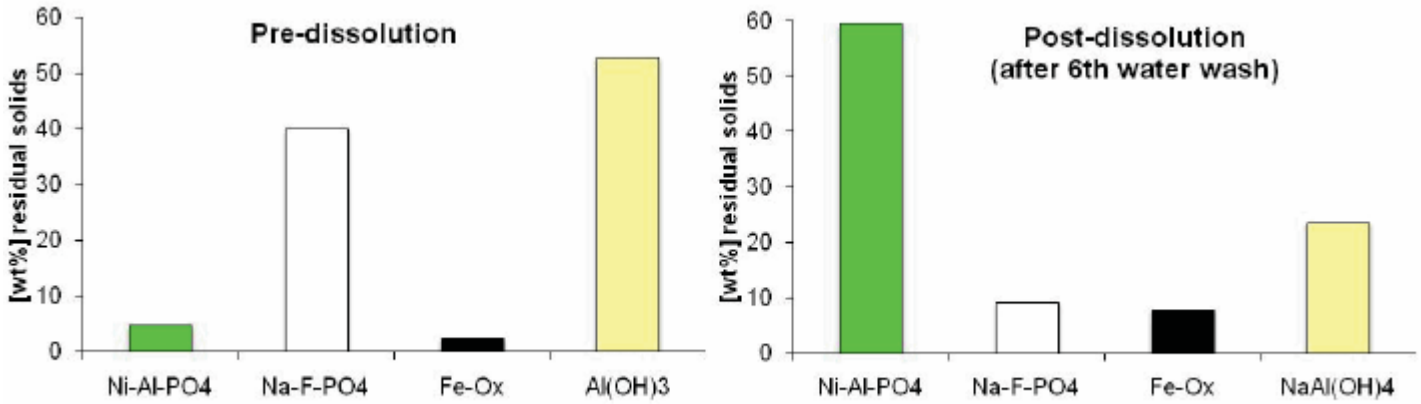
Update on Laboratory Testing: Tank C-108 Samples

- A sample composite was made and separated by sieving into coarse (>¼ in.) and fine composites
- Each phase treated with 19.4 *M* NaOH at OH:Al = 3:1
- Multiple water washes used to dissolve solids
- Chemical analysis and solid phase characterization (PLM, XRD, SEM) performed on composite and residues; liquid phases also analyzed
- ~90 vol% solids reduction observed

Mass During Caustic Dissolution and Water Leaching



Mass Distribution of the Residual Coarse-Grained Phases



These graphs are based on the mass of the separated coarse phases and their residual mass.

- **Predominant solids in the ~10% remaining is a Ni-Al-PO_4 solid.**

Test Summary and Projection for Tank C-108

	Initial amount	NaOH added	Water needed	Avg. water /wash	Residual amount
Fine	125 mL	175 mL	1,639 mL	273 mL	12.5 mL
Coarse	48 mL	135 mL*	1,484 mL	247 mL	4.5 mL
Tank C-108	6,800 gal	9,520 gal	89,200 gal	14,800gal	680 gal

*OH:Al > 3:1; additional NaOH needed to cover solids

Near Term Plans: Testing of Tank C-110 Samples

- **Tank C-110 was sampled in September 2010**
  - **3 of 9 samples look similar to tank C-103 and C-108 samples and appear to represent the majority of the waste in the tank**
  - **6 samples are more red/brown in color**
- **Test Plan**
  - **Composite and analyze samples (two composites)**
  - **Remove water-soluble components with water wash**
  - **If primarily aluminum solids (expected):**
    - **Perform dissolution testing with 19.4 *M* NaOH at OH:Al ratio of 3:1**
    - **Analyze residual solids and leach solutions**
  - **If primarily iron solids, perform dissolution testing with 1 *M* oxalic acid**
    - **Optimize ratio of oxalic acid to heel solids**
    - **Determine treatment time duration**
    - **Analyze residual solids and leach solutions**

Near Term Plans:
Testing of Tank C-110 Samples

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Near Term Plans: Comparative Dissolution Testing

- **Tank C-106 waste was dissolved with oxalic acid and tank C-108 will be treated with NaOH solution**
- **Testing will provide a side-by-side comparison of acid and caustic dissolution for various tank samples:**
  - **Tank C-103**
  - **Tank C-106**
  - **Tank C-108**
  - **Tank C-110**

Near Term Plans: Comparative Dissolution Testing

- **Caustic dissolution:**
  - **19.4 M NaOH at OH:Al = 3:1**
- **Acid dissolution:**
  - **Reactions of the type:**

    $2\ Al^{3+} + 3\ C_2O_4^{2-} \rightarrow Al_2(C_2O_4)_3$

    $Fe^{3+} + 2\ C_2O_4^{2-} \rightarrow [Fe(C_2O_4)_2\ ]^-$
  - **0.9 M oxalic acid at (Al+Fe):oxalic acid = 1:1 to 1:4**

Near Term Plans: Boehmite Dissolution Testing

- **Testing to measure the rate of boehmite conversion to sodium aluminate:**

$$AlO(OH) + NaOH + H_2O \rightarrow NaAl(OH)_4$$

- **The boehmite reaction was significantly slower than the gibbsite reaction in tests with tank samples in 3 to 6 *M* NaOH solution**
- **A commercially available boehmite sample reacted much faster than anticipated in tests with 19 *M* NaOH solution**

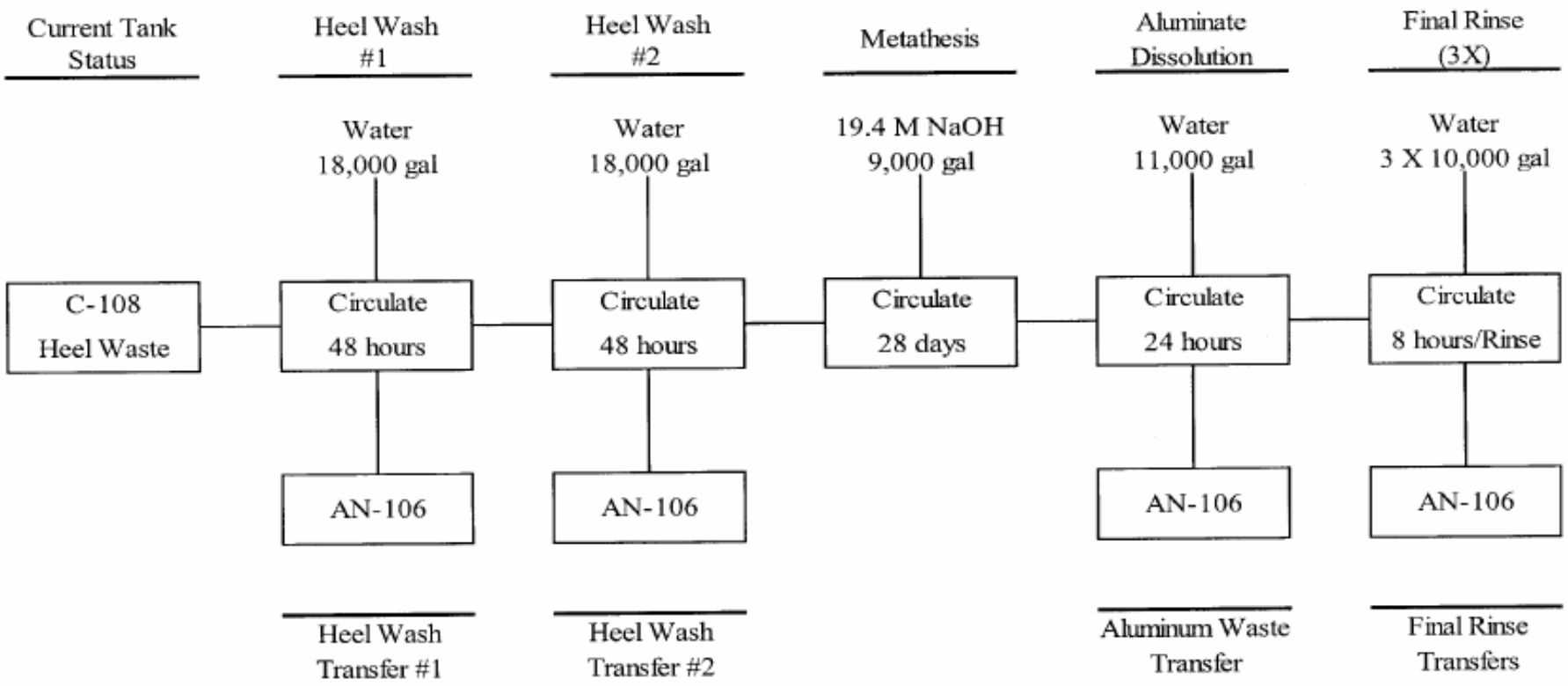
Near Term Plans: Boehmite Dissolution Testing

- **Tests to be performed with 19 *M* NaOH solution and the following samples:**
  - **Commercially available boehmite (CATALPA-A)**
  - **Boehmite prepared in the lab from high-temperature conversion of gibbsite**
  - **Samples from tanks S-101 and S-107 containing boehmite from different waste sources**

Near Term Plans: Caustic Cleaning in Tank C-108

- The ~6,800 gal of waste in tank C-108 is primarily sodium fluoride phosphate and gibbsite
- Caustic cleaning scheduled for Spring 2011
- A change from the laboratory work will be to dissolve and remove sodium fluoride phosphate before adding NaOH
- Liquid-phase sampling will be performed to monitor progress and provide information for future tanks
- Mixing to be provided by slurry pump and sluicers

Near Term Plans: Caustic Cleaning in Tank C-108



Q&A/Contact

- **Q&A**

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