Gibbsite Precipitation Inhibitors

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EM Waste Processing Technical Exchange

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Mission Drivers

- There are high concentrations of aluminum as gibbsite or boehmite in Hanford High Level Waste
- This aluminum will be dissolved in the WTP, with leaching to be performed at 80-90°C, followed by ion exchange at up to 45°C
- Current plans are to add sufficient NaOH to prevent gibbsite precipitation as the temperature is lowered
  - Increases LAW volume and overall mission schedule and cost
- An alternative approach would be to introduce an additive that would prevent or slow gibbsite precipitation, thereby reducing the amount of caustic needed
- This could increase the plant throughput dramatically

Background

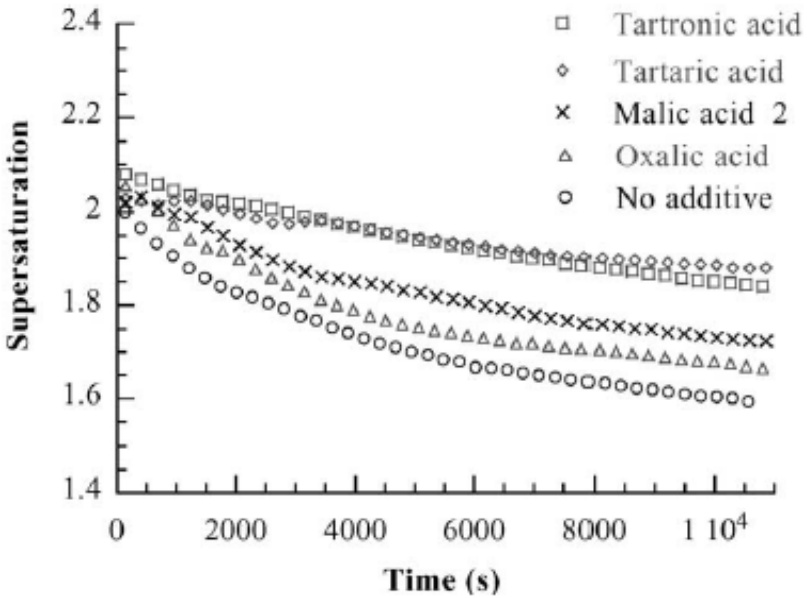
- It is well known* that certain organic molecules can inhibit gibbsite crystallization from alkaline aluminate solutions
- Bayer process is the principal industrial means of refining bauxite to produce alumina
  - gibbsite is crystallized from seeded sodium aluminate liquors
- The precipitation of gibbsite is the rate limiting step
  - Made slower by organic impurities in the liquor
- For the WTP, we want to prevent gibbsite precipitation
- Their **problem** is our **solution**

*Smith et al. (1996); Watling (2000); Paulaime et al. (2003).

Previous Testing with Polycarboxylic Acids

- Overhead mixing was used
- Supersaturated solutions with gibbsite seeding
- Effect of polycarboxylic acids (20 mM) on precipitation
- 7 day test

Acid	Formula
Tartaric	COOH-$(CHOH)_2$-COOH
Tartronic	COOH-(CHOH)-COOH
Malic	COOH-(CHOH)-CH_2-COOH
Oxalic	COOH-COOH

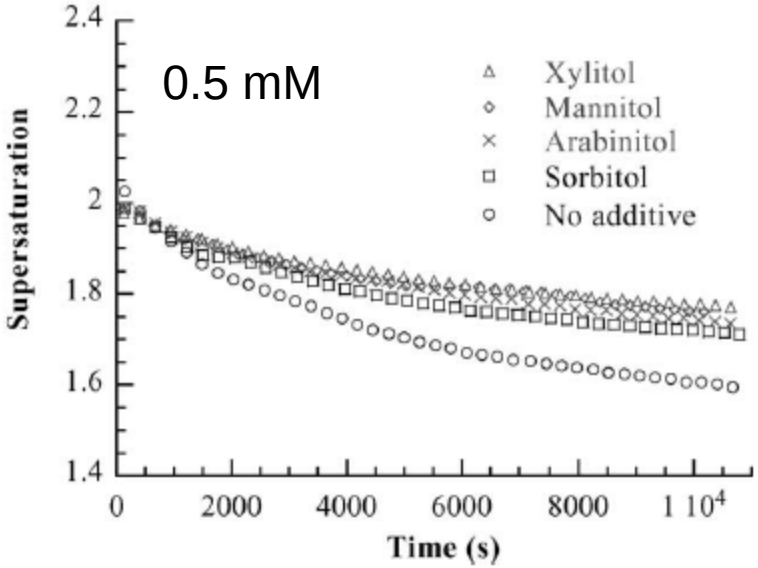


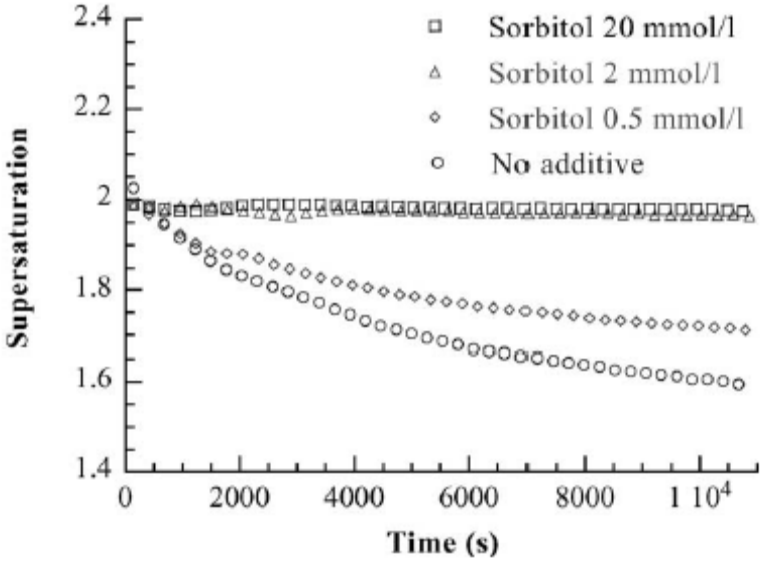
- Precipitation is inhibited
- Ability of acid to inhibit increases with number of OH groups
- When two acids have the same number of OH groups, the one with the shortest carbon chain is the best inhibitor (tartronic and malic acid)

A.-M. Paulaime et al. Powder Technology 130 (2003) 345-351.

Previous Testing with Alditols

- Alditols at 0.5 mM inhibit precipitation to a small degree
- Sorbitol at 2 mM is much better at inhibiting than at 0.5 mM
- 20 mM is the same as 2 mM
- Polycarboxylic acids inhibit precipitation, while alditols can completely stop precipitation

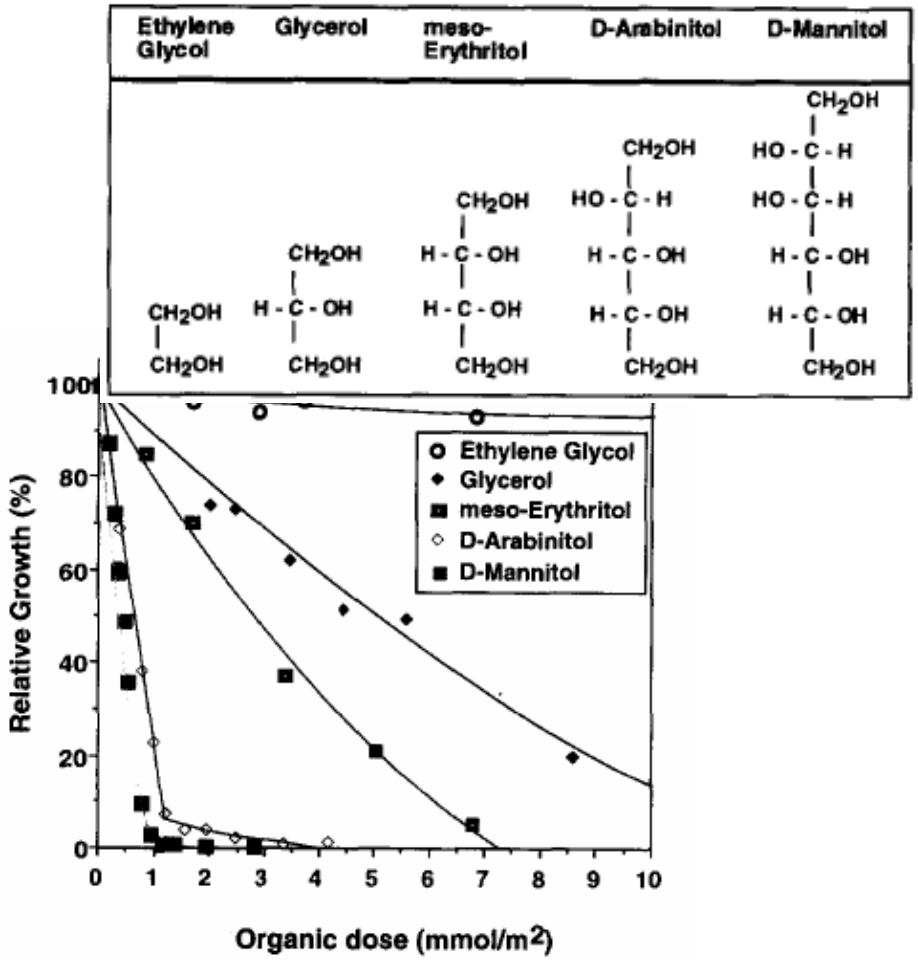


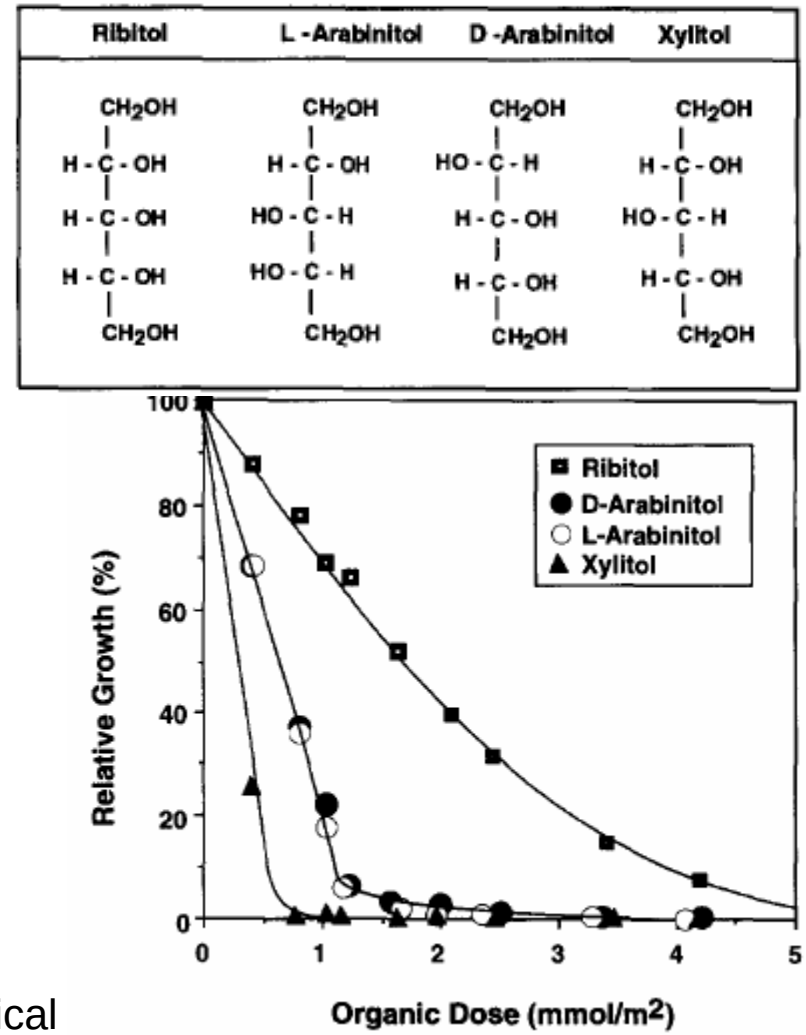


A.-M. Paulaime et al. Powder Technology 130 (2003) 345-351.

Previous Testing with Alditols

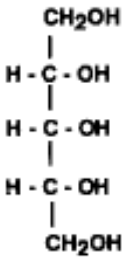
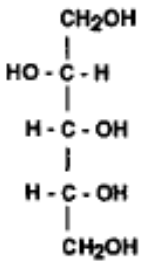
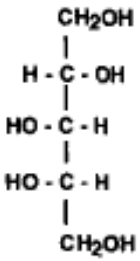
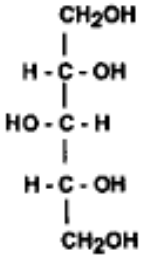
- A temperature-controlled water bath with bottle roller was used
- Supersaturated solutions with gibbsite seeding, 105 min test



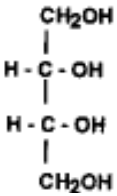
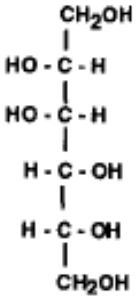
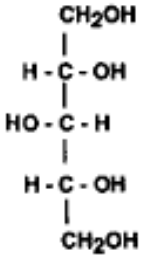
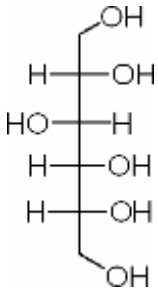


P.G. Smith et al. Colloids and Surfaces A: Physicochemical and Engineering Aspects 111 (1996) 119-130.

Previous Testing with Alditols, Discussion of Results at 0.5 mmol/m^2

Compound	Ribitol	D-Arabinitol	L-Arabinitol	Xylitol
Structure				
Precip Inhib (%)	15	42	42	89

- Differences in inhibition caused by stereochemistry differences are substantial

Compound	Erythritol	Mannitol	Xylitol	Sorbitol
Structure				
Precip Inhib (%)	8	56	89	94

- Increasing carbon length leads to better precipitation inhibition
- In the case of Xylitol, stereochemistry is a larger influence than number of carbons

P.G. Smith et al. Colloids and Surfaces A: Physicochemical and Engineering Aspects 111 (1996) 119-130.

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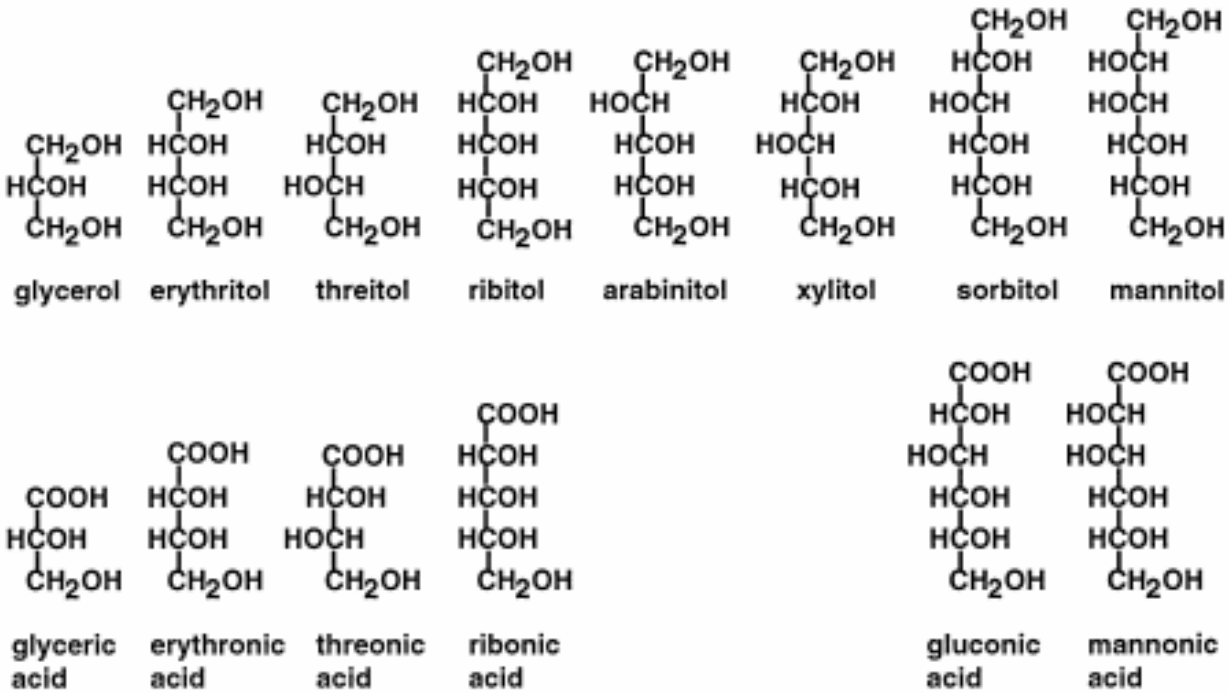
Previous Testing with Alditols and Polycarboxylic Acids

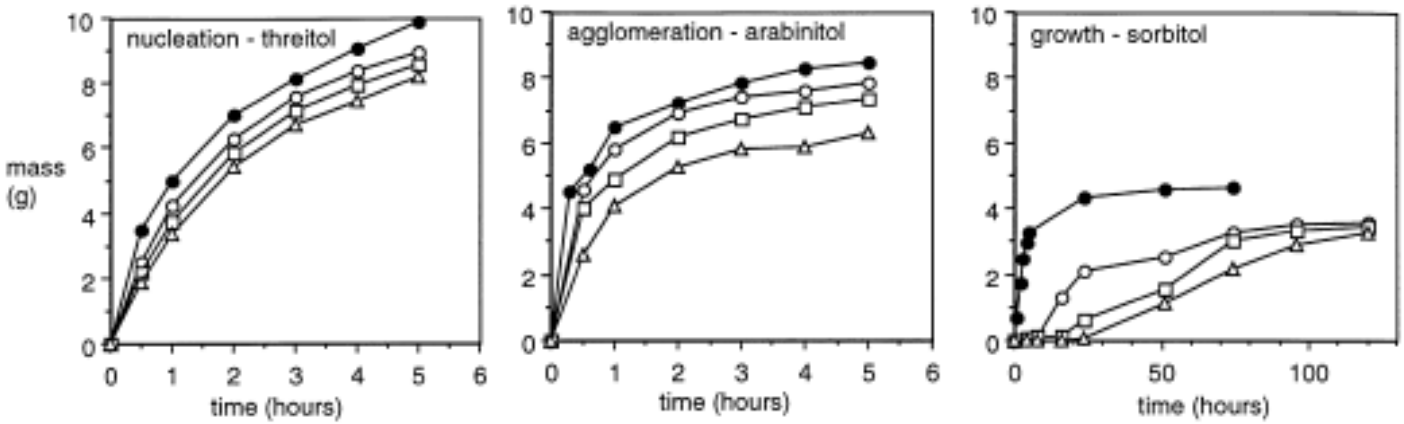
- A temperature-controlled water bath with bottle roller was used
- Supersaturated solutions with gibbsite seeding
- Effect of alditols and polycarboxylic acids on precipitation
- 3 concentrations of each additive were tested



H. Watling Hydrometallurgy 55 (2000) 289-309.

Previous Testing with Alditols and Polycarboxylic Acids

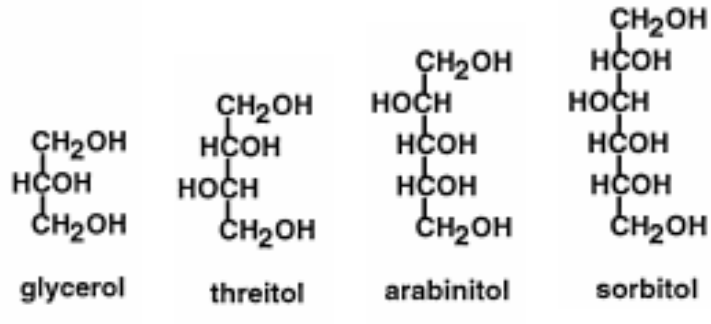
- Results for threitol (a weak inhibitor) on nucleation; arabinitol (intermediate strength) on agglomeration, and sorbitol (a strong inhibitor) on crystal growth
- Results are typical of all the tested compounds
- In each case, increased concentrations of the additive decreased precipitation



Threitol (3, 6, 9 mM); Arabinitol (2, 4, 6 mM); Sorbitol (2, 4, 6 mM)

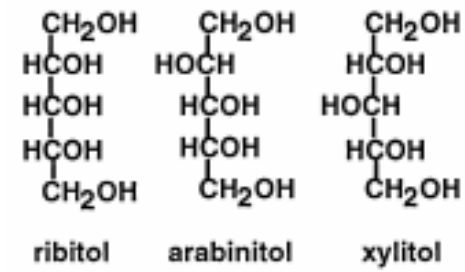
H. Watling Hydrometallurgy 55 (2000) 289-309.

Gibbsite Precipitation (as a % of that in control) from 6 mM Solutions



increased number of hydroxyl groups play a role in inhibition of gibbsite precipitation

Compound	Nucleation at 2 hr Yield (%)	Agglomeration Yield (%)	Growth at 24 hr Yield (%)
Glycerol	100	93	100
Threitol	83	90	83
Arabinitol	72	73	42
Sorbitol	3	2	<1
Ribitol	89	97	86
Arabinitol	72	73	42
Xylitol	3	5	2



stereochemistry also plays a role

H. Watling Hydrometallurgy 55 (2000) 289-309.

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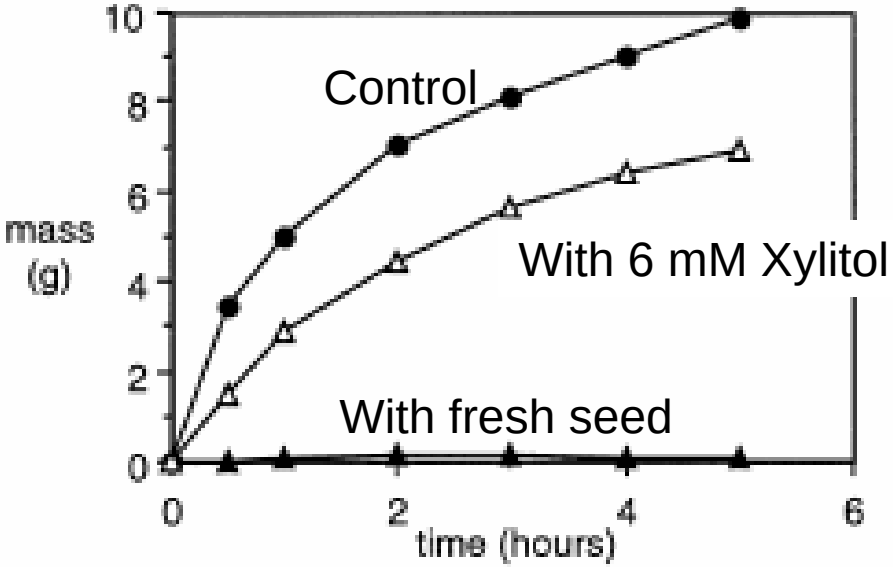
Why is Gibbsite Precipitation Inhibited?

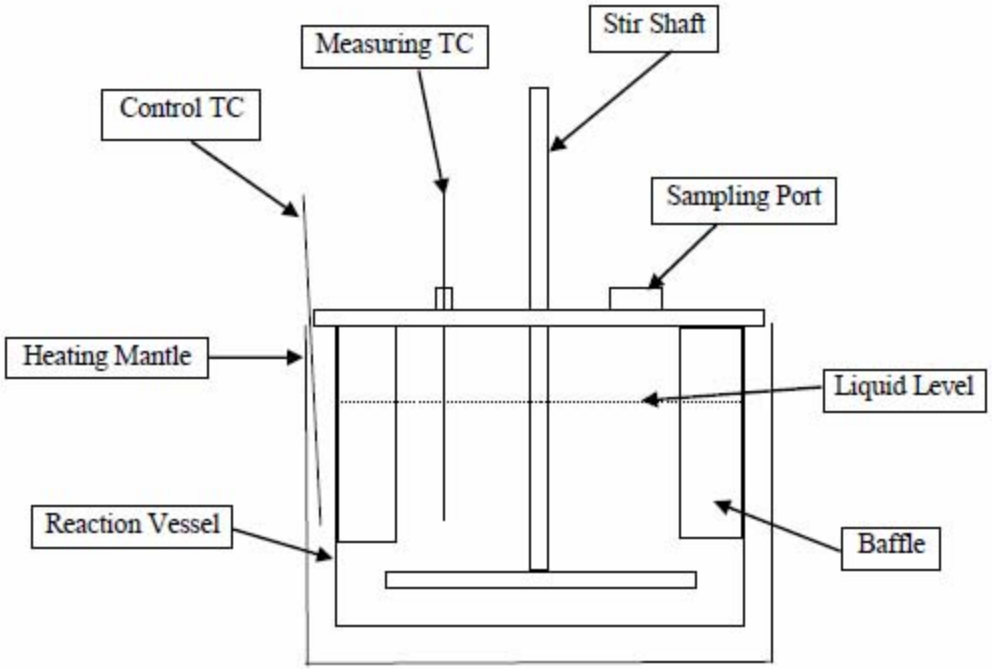
- Adsorption of the organic compound on the basal face at a specific site is a key step in inhibition
- Demonstrated with xylitol (6 mM)
- Seeded suspensions were filtered after a 30 min equilibration at 60°C
  - No gibbsite precipitation occurred during this time
  - Supersaturation remained high
- The hot, filtered solutions were seeded with more gibbsite and precipitation monitored
- Results show that initial seed adsorbed the xylitol, making it possible for gibbsite to deposit on the fresh seed surface



H. Watling Hydrometallurgy 55 (2000) 289-309.

Experimental: Scoping Tests

- Scoping tests with 8 additives
- 60°C
- 600 mL solution
- 2x solubility limit
- Overhead mixing
- 4 hours
- Samples taken at 0, 1, 2, and 4 hrs
- Samples filtered and diluted in HNO_3 for ICP analysis of Al



Note: All results are preliminary, still under review

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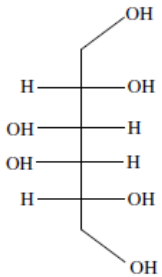
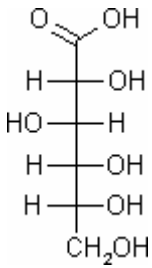
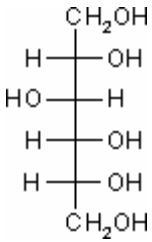
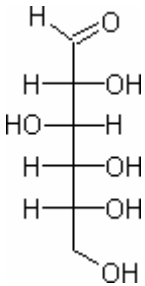
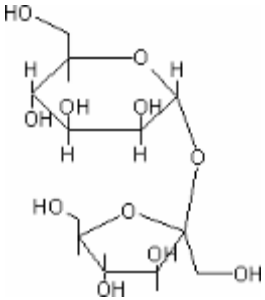
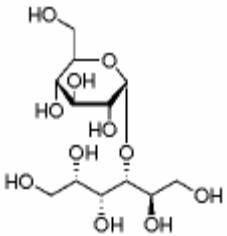
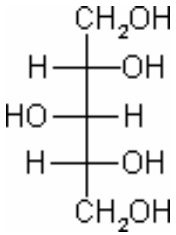
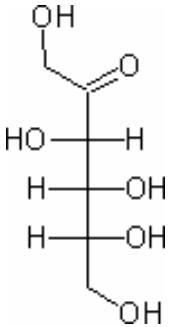
Scoping Tests: Compounds

Compound	dulcitol	gluconic acid	sorbitol
Structure			
% Precip	3.5	7.2	8.3

Compound	Dextrose (D-glucose)	Sugar (sucrose)	Maltitol	xylitol	fructose
Structure					
% Precip	20	25	48	48	74

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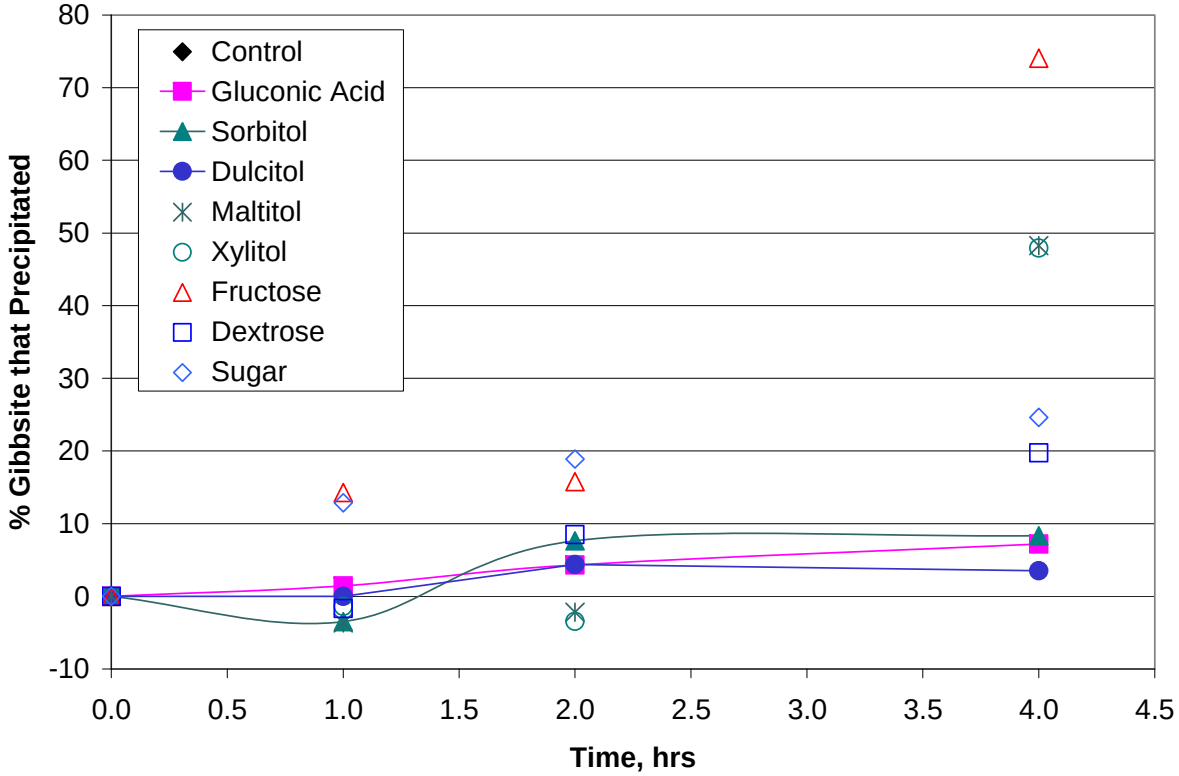
Scoping Tests

- 8 additives were tested, all at 6 mM
- Gluconic acid, sorbitol, and dulcitol performed the best
  - Less than 10% of the Gibbsite precipitated after 4 hours
- For all other additives, 20-75% of the gibbsite precipitated after 4 hours



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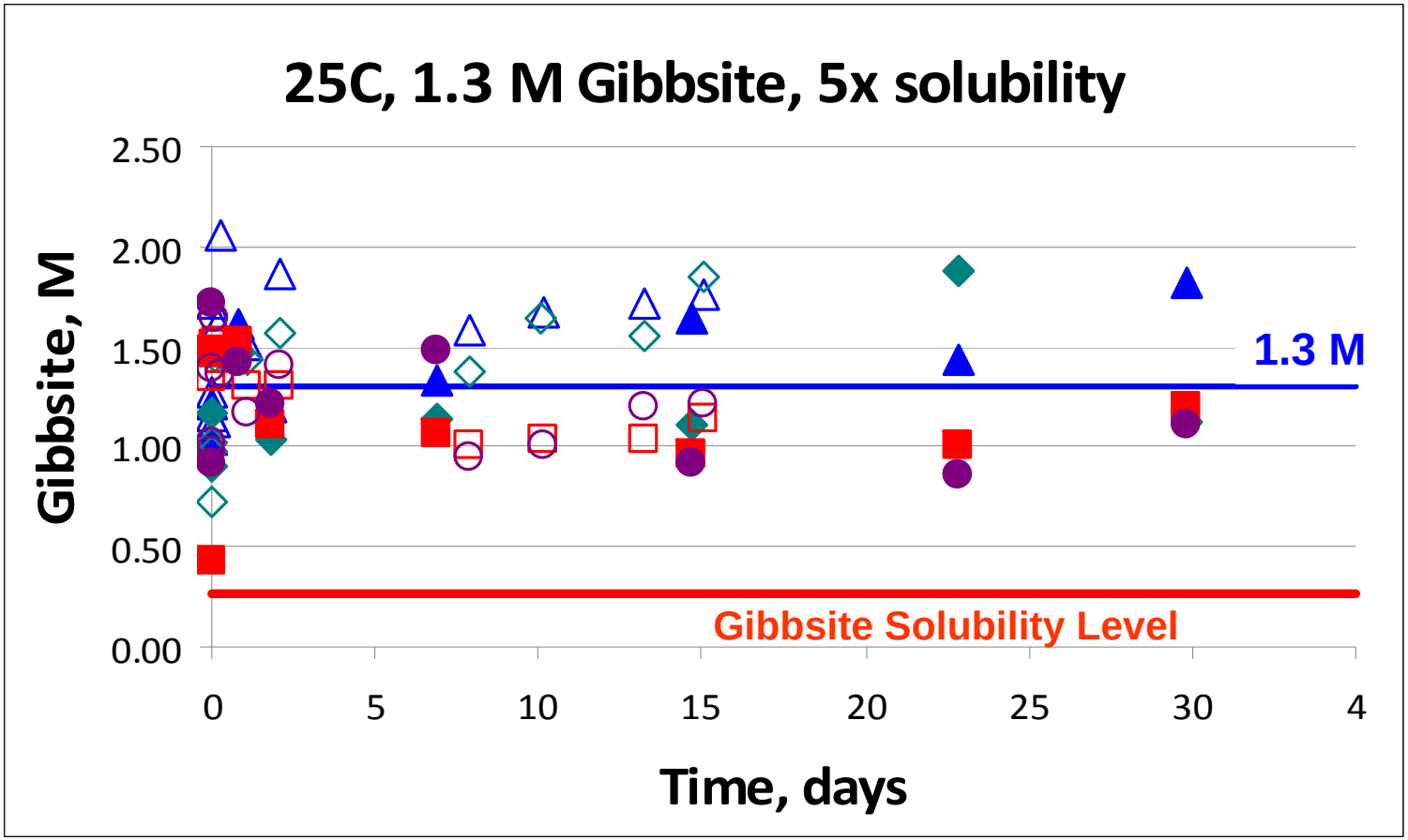
Experimental

- Additives for further study: gluconic acid, sorbitol, dulcitol, and sodium carbonate
- Testing was performed at 25 and 45°C, 100 mL solution, on a shaker table
- For 45°C testing, conditions were:
  - 30 day: 3.33 M NaOH, 1.2 M Gibbsite, 2x solubility limit
  - 15 day: 2.87 M NaOH, 1.95 M Gibbsite, 4x solubility limit
  - With 32 g solid gibbsite added as “seed” in both cases
- For 25°C testing, conditions were:
  - 30 day: 2.69 M NaOH, 1.3 M Gibbsite, 5x solubility limit
  - 15 day: 2.57 M NaOH, 1.3 M Gibbsite, 5x solubility limit
  - With 20 g solid gibbsite added as “seed” in both cases

Comparison of Additives at 25°C



- ▲ Gluconic Acid (5.79 mM)
- ◆ Sorbitol (5.26 mM)
- ■ Dulcitol (4.14 mM)
- ● Na2CO3 (0.186 M)
- △ Gluconic Acid (5.98 mM)
- ◇ Sorbitol (5.66 mM)
- □ Dulcitol (4.26 mM)
- ○ Na2CO3 (0.192 M)

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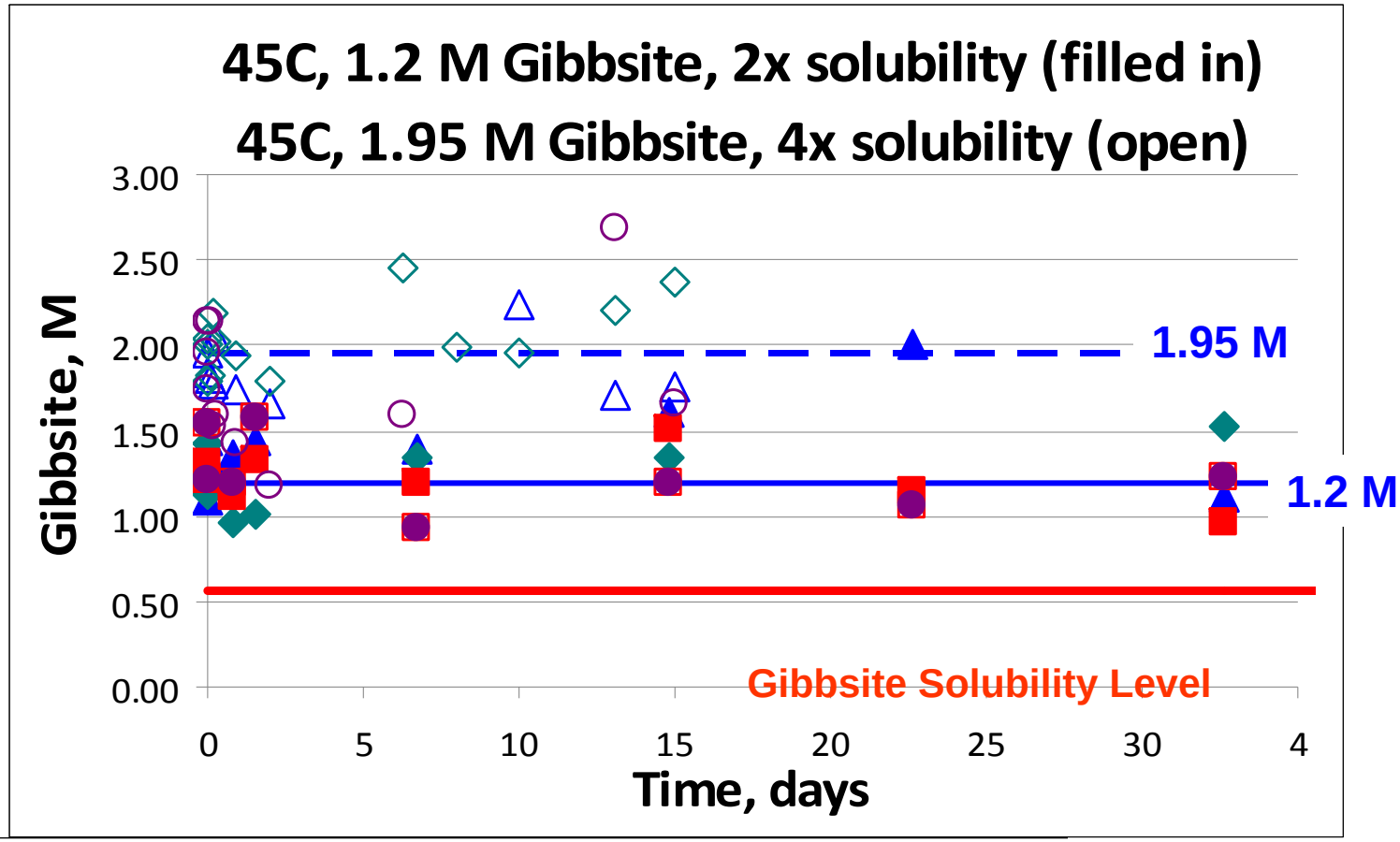
Comparison of Additives at 45°C



▲ Gluconic Acid (5.75 mM) △ Gluconic Acid (5.58 mM)

◆ Sorbitol (9.00 mM) ◇ Sorbitol (8.72 mM)

■ Dulcitol (3.79 mM) □ Dulcitol (3.79 mM)

● Na2CO3 (0.1 M) ○ Na2CO3 (0.09 M)

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Discussion of Results

- Scoping tests with gluconic acid, dulcitol, and sorbitol showed a strong ability to prevent gibbsite precipitation
- For all additional tests, gibbsite stayed in solution at well above the solubility limit over 15 and 30 days of testing
- In the 25°C tests:
  - Gluconic acid and sorbitol tests ended up with increased concentrations of gibbsite in solution at the end of testing
  - There was some precipitation of gibbsite from the dulcitol and sodium carbonate tests
- In the 45°C tests:
  - For all additives at both solubility limits, gibbsite concentration did not change within experimental error

FY-11 Work

- Re-test a select subset of conditions
  - Use overhead mixing rather than shaking
  - 30 day tests
  - Determine the best two additives
  - With the best two additives at the most effective concentration, determine what conditions are needed to keep gibbsite in solution as the temperature is lowered:
    - test a supersaturated solution at 85°C, then lower to 45°C
    - test a supersaturated solution at 85°C, then lower to 25°C
- Test the best 2 additives in simulant
  - 30 day tests
- Test in actual waste samples with 1 or 2 additives

Acknowledgements

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Q&A

Questions???

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