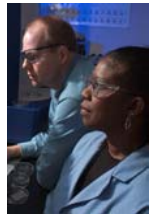
Copper Catalyzed Peroxide Oxidation Testing for Tetraphenylborate Decomposition

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Background

- High Level Waste Tank containing legacy organic waste from a prior process for cesium removal
  - 5.3 million liter (1.4 million gallon) carbon steel tank
  - Contains 910,000 liters (240,000 gallons)
  - 460,000 Ci Cs-137
  - 19,100 kg tetraphenylborate (TPB)
- Organic species are not compatible with downstream facilities
- Site pursuing Aggregation to grout as disposal path
- This study investigated an alternative approach in the event that regulatory approval is not obtained for the baseline strategy

Tetraphenylborate in High Level Nuclear Waste

- *Precipitation Reactions*
- $Cs^+ + (C_6H_5)_4B^- \Rightarrow CsB(C_6H_5)_4$ Highly Insoluble
- $K^+ + (C_6H_5)_4B^- \Rightarrow KB(C_6H_5)_4$ Very Insoluble
- $Na^+ + (C_6H_5)_4B^- \Rightarrow NaB(C_6H_5)_4$ Slightly Soluble

Instantaneous Precipitation

Decomposition Product

$(C_6H_5)_4B^- + 4H_2O \rightarrow B(OH)_4^- + 4C_6H_6$ Flammable

Catalyst + High Temp + Low pH

Objectives

- Develop tetraphenylborate decomposition process
  - pH > 10 to minimize corrosion of Tank and Internals
  - Minimize production of benzene
  - Reaction rate moderate and controllable
  - Reaction temperature <75 °C

Testing Objectives

- Determine tetraphenylborate decomposition at pH 11 and 14 (i.e., acceptable conditions for existing tanks)
  - Builds upon prior studies conducted by ORNL (Paul Taylor), AEA Technology (Jeff Wilkes), and SRNL
- Determine impact of temperature (ambient to 75 °C), copper concentration (up to 560 mg/L), and selected peroxide addition rate (0.124 g H_2O_2/hr)
- Measure offgas composition utilizing Gas Chromatography
  - Purge Rate and Oxygen Concentration Limits to Match SRS Tank
  - Offgas passes through condenser
  - Measure benzene (TPB decomposition product) and oxygen (hydrogen peroxide decomposition product)

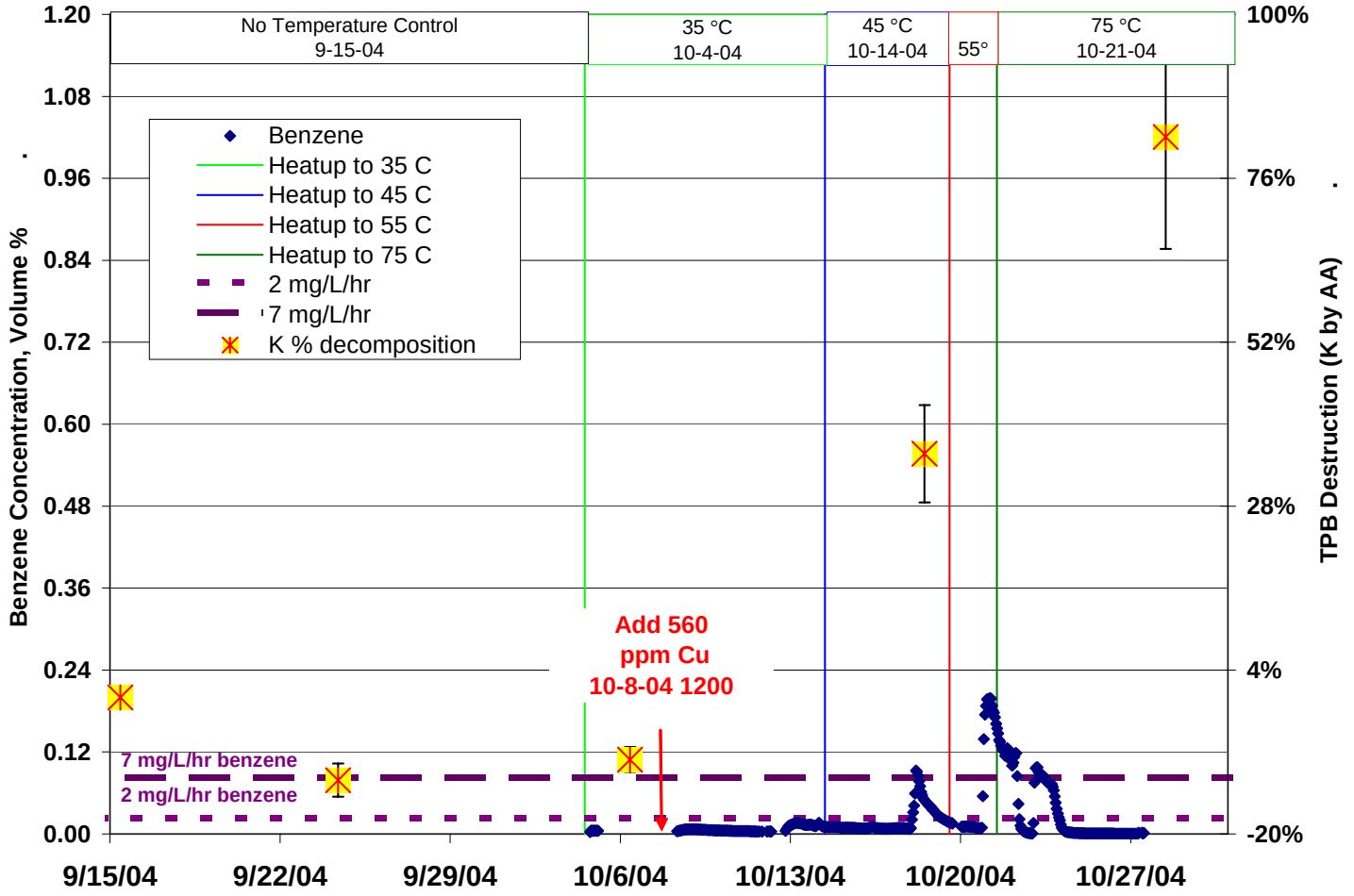
Expected Reactions for Proposed Treatment

- Peroxide Oxidation (desired reaction)
  - $BC_{24}H_{20} + 61H_2O_2 \rightarrow BO_3 + 71H_2O + 24CO_2$
  - Requires ~60 moles H_2O_2:mol TPB or ~2.4 moles H_2O_2:mol C
  - 5.593 g TPB^- → 36.35 g H_2O_2
- Hydrolysis (attempt to minimize this reaction by temperature and pH control)
  - $NaBC_{24}H_{20} + 2H_2O \rightarrow NaBO_3 + 4C_6H_6$
  - 5.593 g TPB^- → 5.475 g C_6H_6
- Peroxide Self Destruction (minimize reagent loss by this path by controlling addition sequence and rate)
  - $H_2O_2 \rightarrow H_2O + ½O_2$

Photograph of Experimental Setup

Benzene Concentration/Temperature Profile

- Decomposition
  - Began ~10-8
  - Complete ~ 10-28
- 35 °C adequate for decomposition
- Low Benzene Production



Photograph of Product

Mixed Original Sample

Settled Final Sample

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Mass Balance

- Volume increase of 50% due to dilution
- Tank freeboard decrease from 1.2E6 to 1.1E6 gal
- Benzene
  - 0.0073 g benzene quantified in gas
  - 0.13% yield to benzene (as measured by GC)
- Hydrogen Peroxide (20 day period)
  - Added 187% H_2O_2 required for complete oxidation of TPB
  - Average 54% efficiency (61 moles required, 112 moles fed)

Carbon Balance

- >99.8% decomposition
- No measured decomposition products remaining
- No phenol or biphenyl

- Ended with 3.261 g/L oxalate
- Began with 1.146 g/L oxalate
- Produced 2.115 g/L oxalate * 0.5 L = 1.057 g oxalate

- Began with 5.05 g C from TPB^-
- Produced 0.29 g C from oxalate
- 5.7% C from TPB^- produced oxalate

Decomposition of Solid Tetraphenylborate Filtrate Analyses

- Minimal decomposition before addition of Cu catalyst
- Measurable decomposition after addition of Cu 10/8/05

Added 560 ppm Cu 10/8/04 →

	% Decomposition	
Date	**K AA**	**ICP-ES B**
9/15/04	**<5%**	**<5%**
9/24/04	**<5%**	**<5%**
10/6/04	**<5%**	NA
10/18/04	42%±8.4%	50%±10%
10/28/04	97%±20%	91%±18%

Predictions based on Mass balance

Soluble Cations of Interest (potassium and boron)

- Tracked soluble and total potassium and boron
  - Insoluble K and B convert to soluble species as KTPB reacts

ICP-ES	% Soluble
Al	3%±0.6%
B	95%±19%
K	111%±22%
AA K	117%±23%

- Increase in soluble K and B confirms decomposition

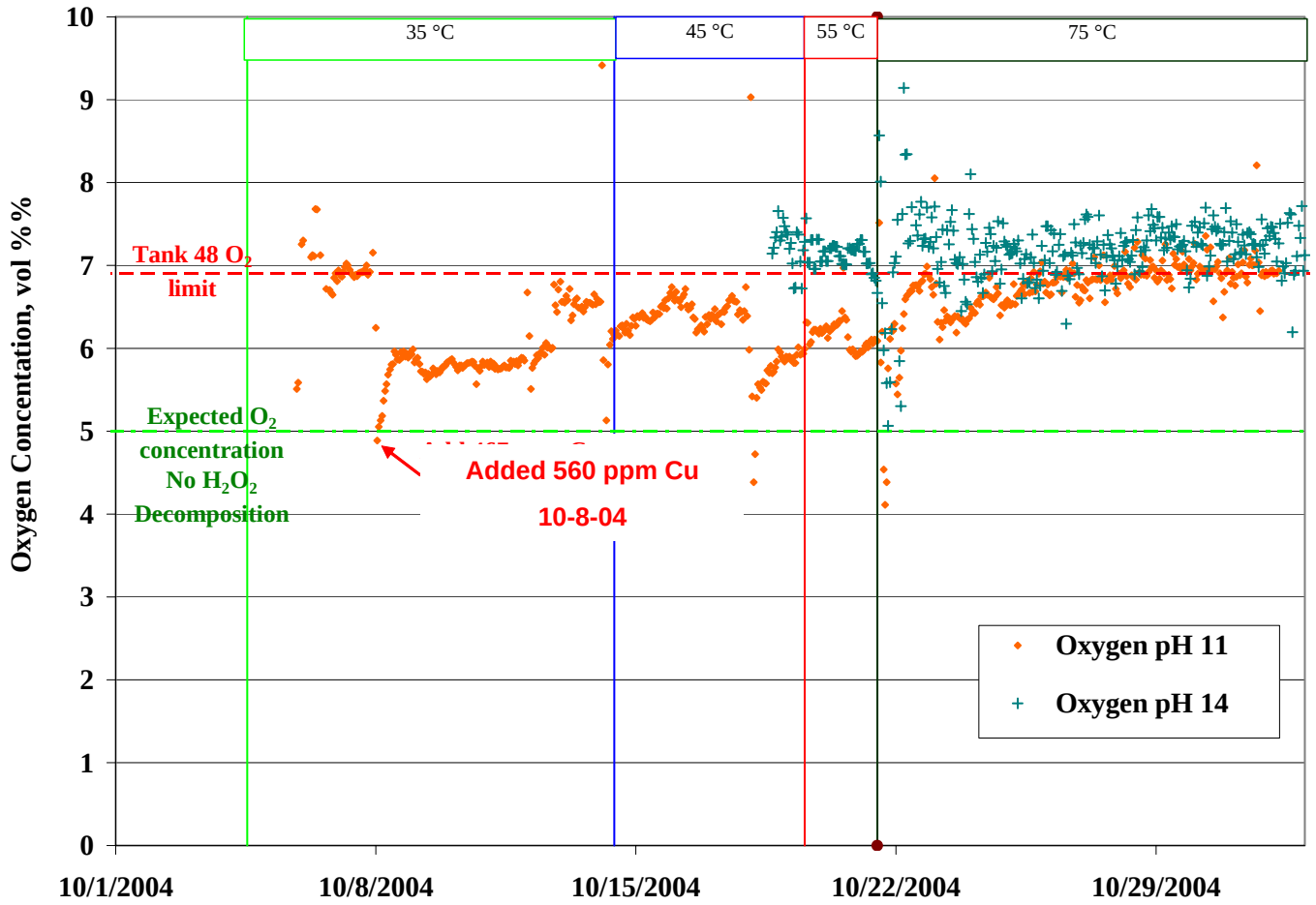
Soluble Anions of Interest (nitrite, oxalate)

- Tracked anions to monitor corrosion inhibitor (nitrite)
  - Nitrite decreased to half of original mass
  - Nitrite concentration can be controlled with addition of nitrite
- Tracked oxalate to determine decomposition products
  - Oxalate increased by 200%

Analyte	Actual	Predicted	Units
Nitrite	0.236±0.024	0.465±0.093	M
Oxalate	0.0370±0.0037	0.0130±0.0026	M

Oxygen Concentration

- 560 ppm Cu added 10/8/2004
  - –O_2 concentration dropped in pH 11 experiment
  - – Reaction initiated at 35 °C
  - –No change in pH 14 experiment



Conclusions

- TPB decomposition began at 35 °C
  - Lower temperature minimizes hydrolysis reactions
  - Low benzene generation rates up to 75 °C (below 7 mg/L/hr)
- TPB decomposition at pH 11 complete in ~3 weeks
- Oxidized all benzene producing intermediates
  - no benzene potential left in solution
- Approximately 50% increase in volume (240,000 to 360,000 gal)
- Corrosion risk to carbon steel – more testing needed
- Copper catalyzed peroxide decomposition process potentially viable for HLW Tank

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