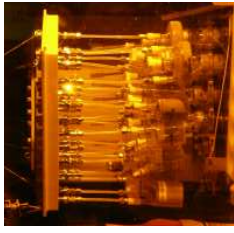
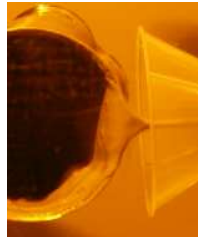


Flammable Gas Generation During Immobilization of Tetraphenylborate in a Cementitious Waste Form



We Put Science To Work

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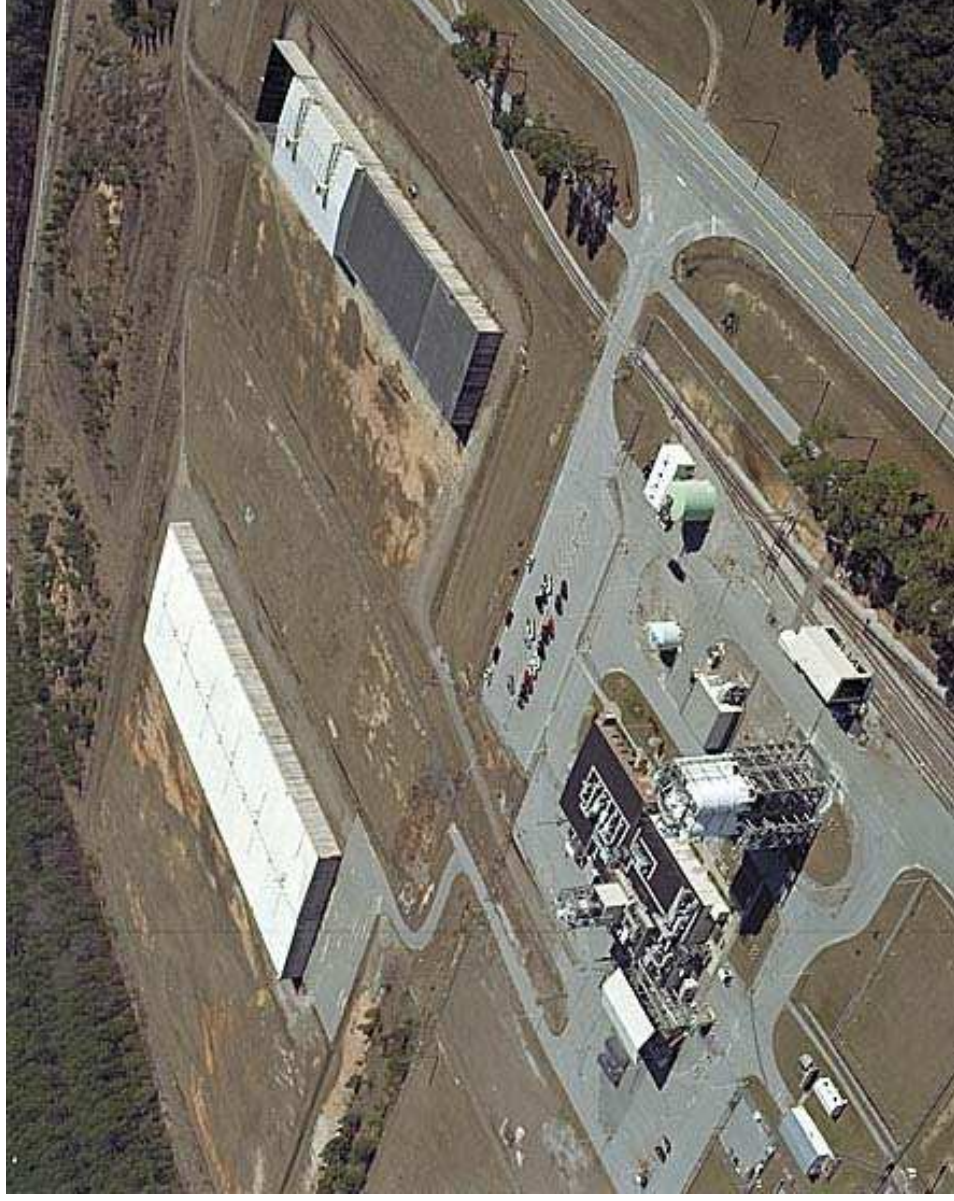
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Background

- Savannah River Site has 240k gallons of tetraphenylborate (TPB) containing radioactive waste for disposal
 - From testing of ^{137}Cs removal by tetraphenylborate
 - Contains significant ^{137}Cs
 - High salt (nitrite, nitrate) content, high pH (~14)
- Proposed to aggregate this waste with other tank waste
- Immobilize in “Saltstone” – a cementitious waste form currently used to immobilize low-level decontaminated salt waste

Saltstone Facility



- Salt solution: 40 wt% of saltstone
- Premix: 60 wt% of saltstone
 - Ground granulated blast furnace slag (45 wt%)
 - Class F power plant fly ash (45 wt%)
 - Portland cement (10 wt%)
 - Additional trace additives – antifoam, set retarder

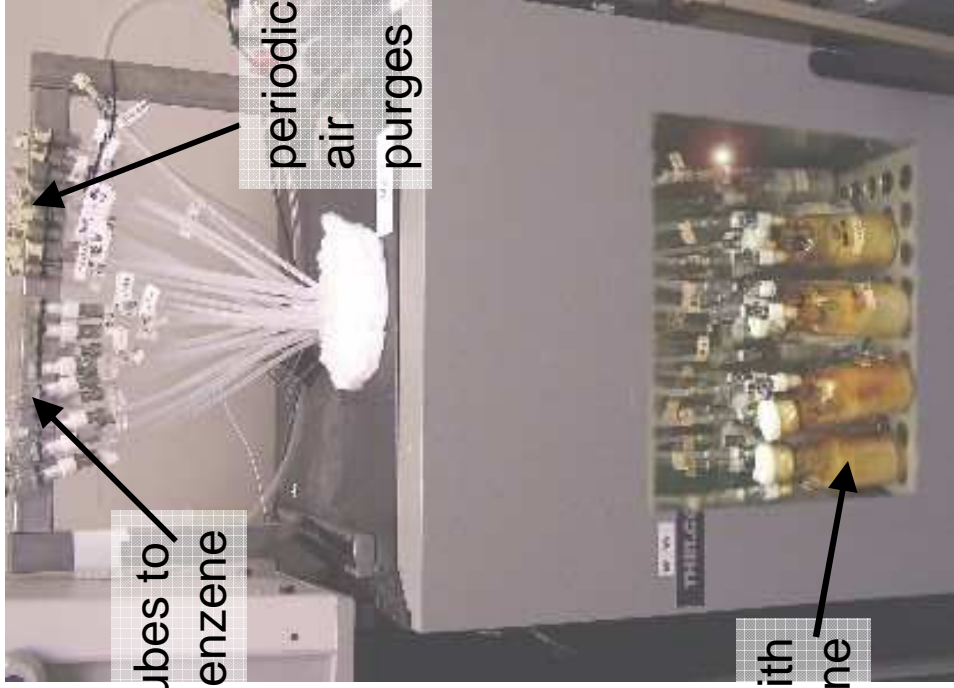
Concerns & Issues

- **Saltstone will be significantly higher in radioactivity**
 - About 0.2 Ci/gal (1955 MBq/L) in feed
 - Required modifications of Saltstone Facility and operating strategy
- **Tetraphenylborate may decompose to form benzene**
 - Flammability concern in headspace of vaults
 - Vaults not purged or inerted
 - Hazardous waste concern (limit of 10 mg/kg benzene)
 - Desirable to operate at accelerated production rates, resulting in higher temperatures in vaults due to cement hydration reactions

Tests & Methods

- **Tested with simulants and actual radioactive waste**
 - 25, 55, 75, 84, 95 °C
 - 30, 1000, 3000 mg/L TPB + biphenyl in salt feed
 - Simulant tests – cylindrical monoliths, 11X surface area monoliths, randomly crushed, crushed & sized (55 °C only)
 - Radioactive tests – monoliths only
- **Carbon tubes to adsorb benzene**
 - Type used for personnel monitoring (SKC)
- **Collect benzene over specific time periods**
- **Analysis**
 - Desorb carbon tubes with carbon disulfide
 - Analyze by GC/FID or GC/MS

Test Equipment



Simulant

carbon tubes to
adsorb benzene

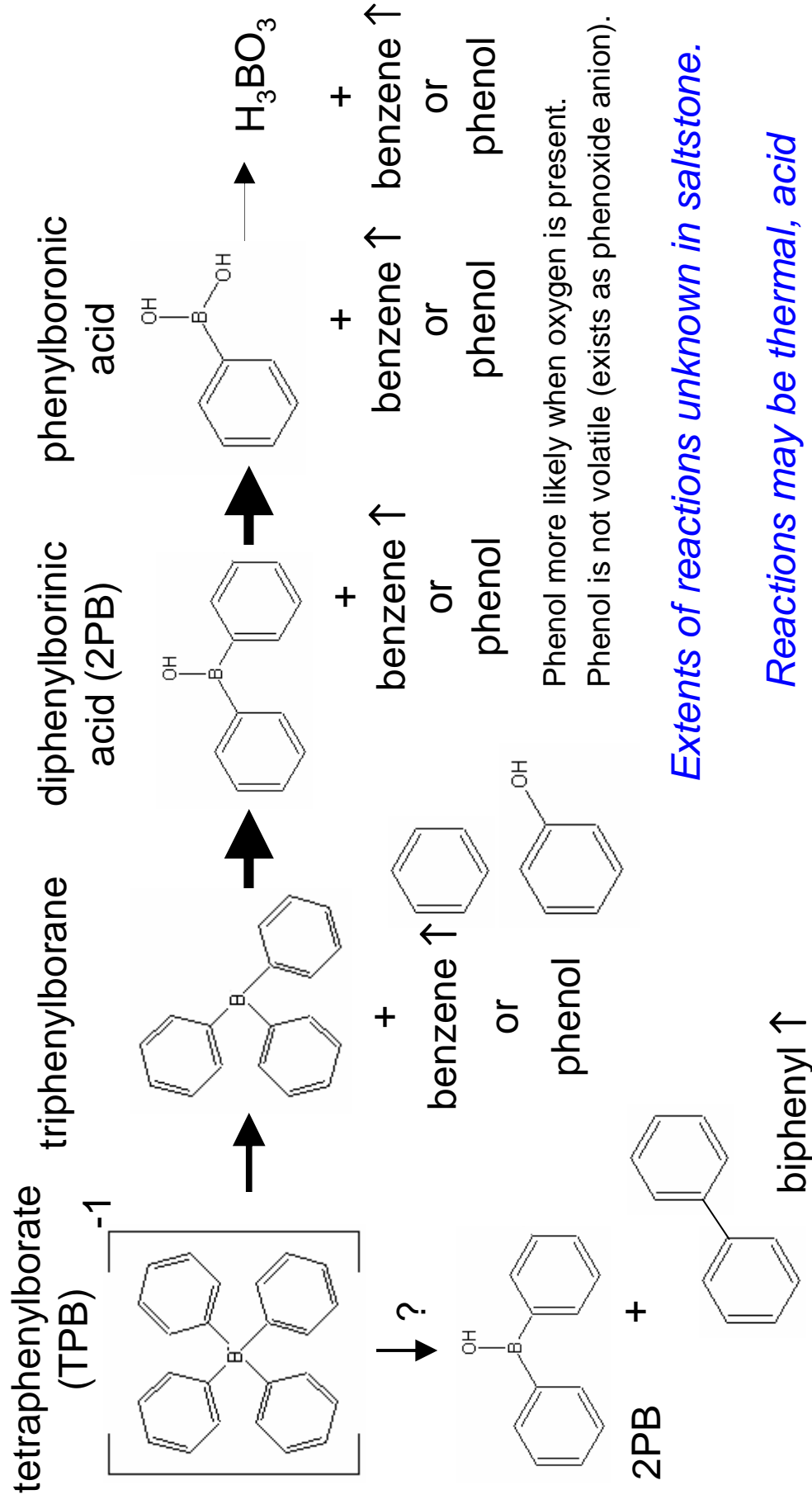
periodic
air
purges

vessels with
saltstone

Radioactive



TPB Decomposition

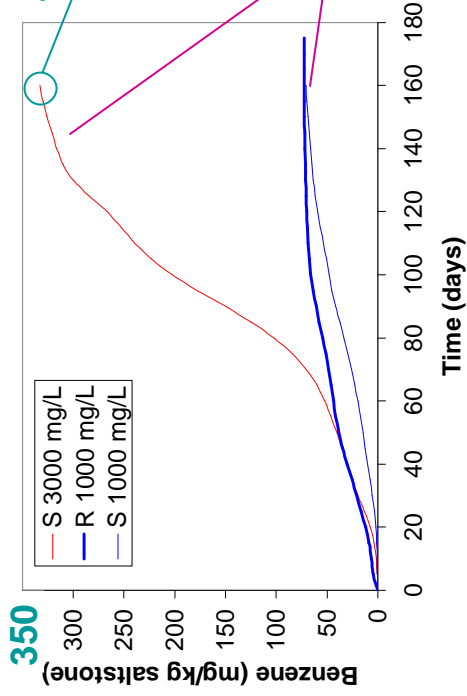


Products Quantified or Identified

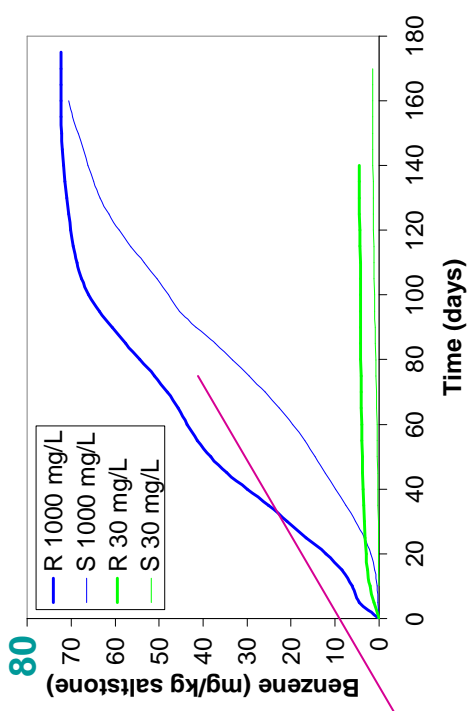
- Benzene
- Biphenyl (for some tests)
- Phenol
- Toluene & Xylenes
 - Found to be present in fly ash
 - Quickly depleted
- Ammonia (qualitative)
 - Released from fly ash, slag, & cement
- Trimethylamine (qualitative)
 - Byproduct of unknown reaction with aged set retarder

Benzene Generation Rates

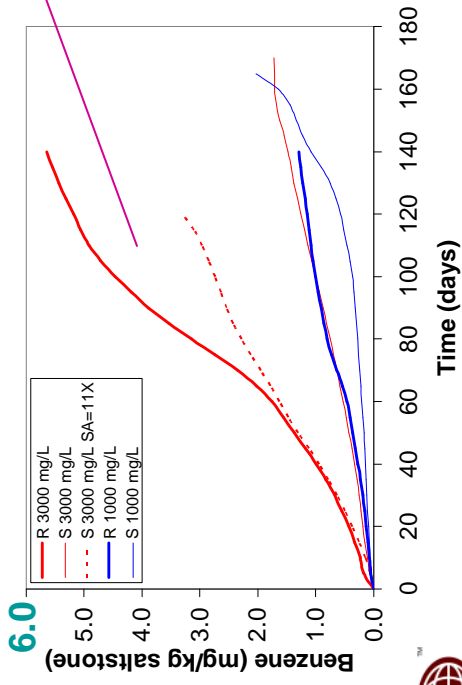
95 °C, 3000 & 1000 mg/L TPB



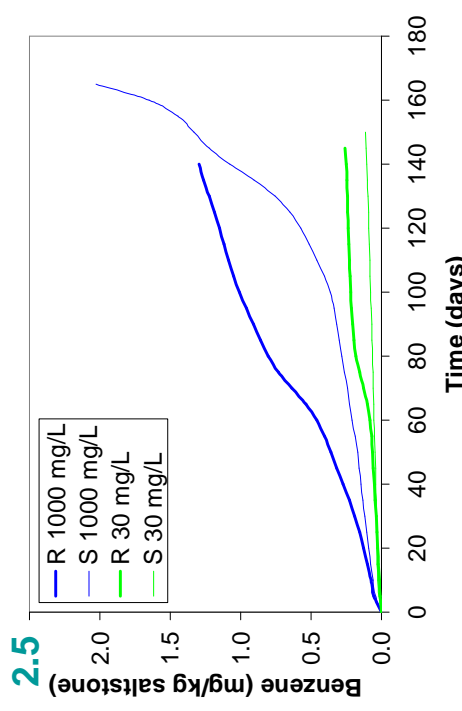
95 °C, 1000 & 30 mg/L TPB



75 °C, 3000 & 1000 mg/L TPB

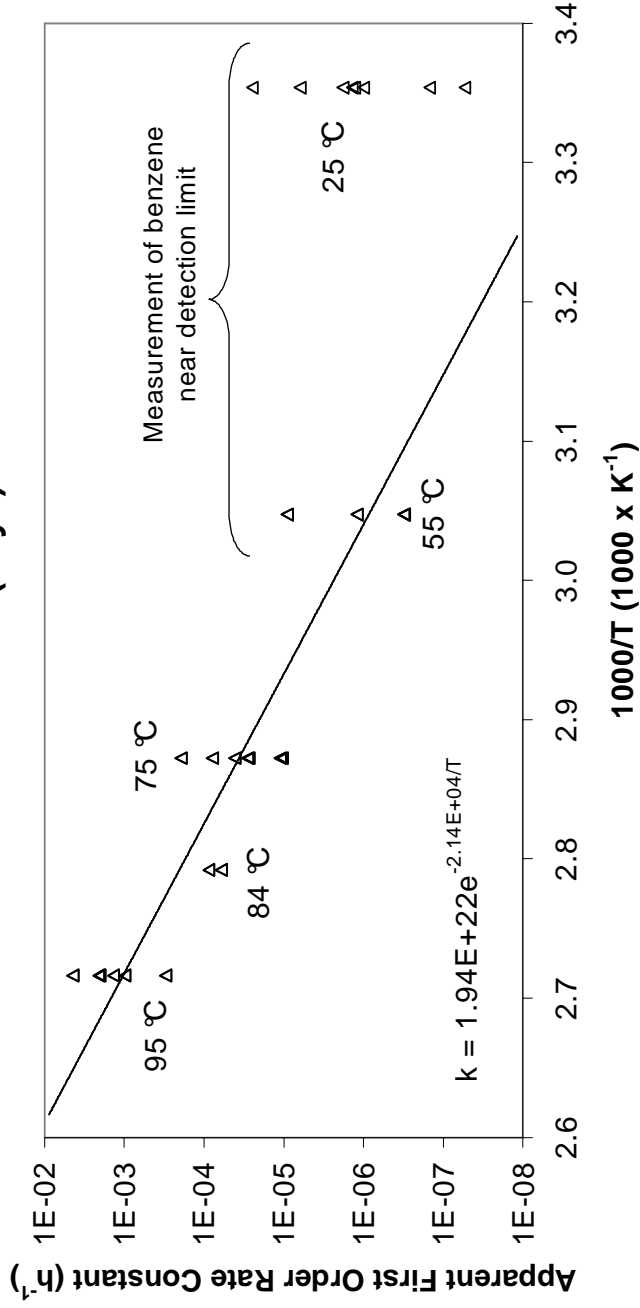
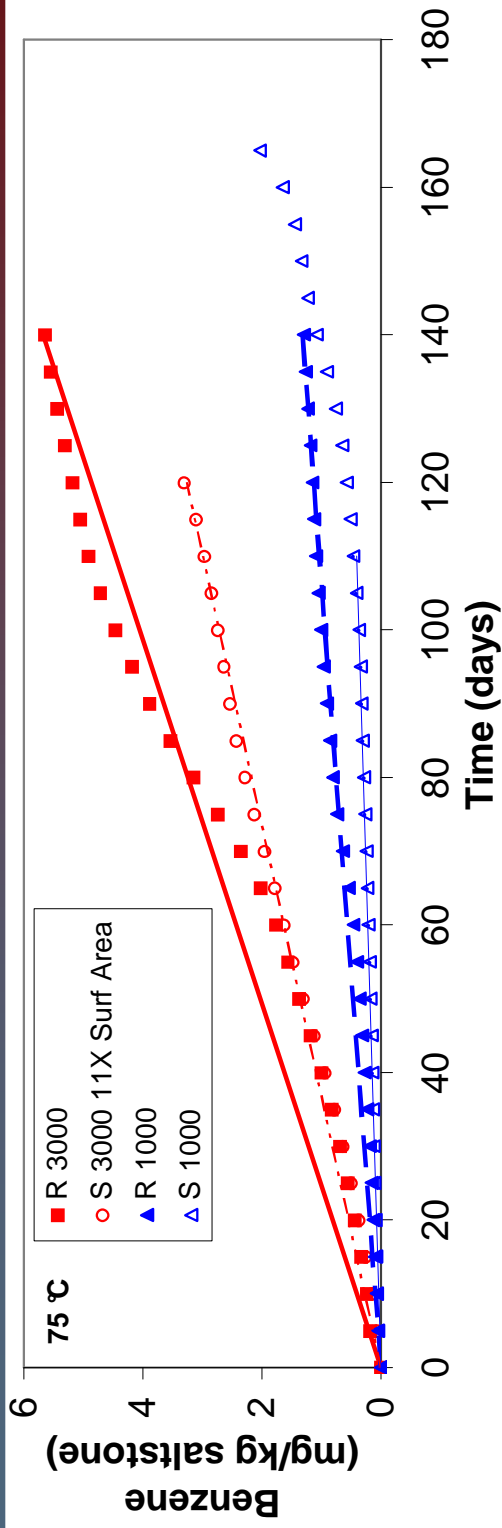


75 °C, 1000 & 30 mg/L TPB

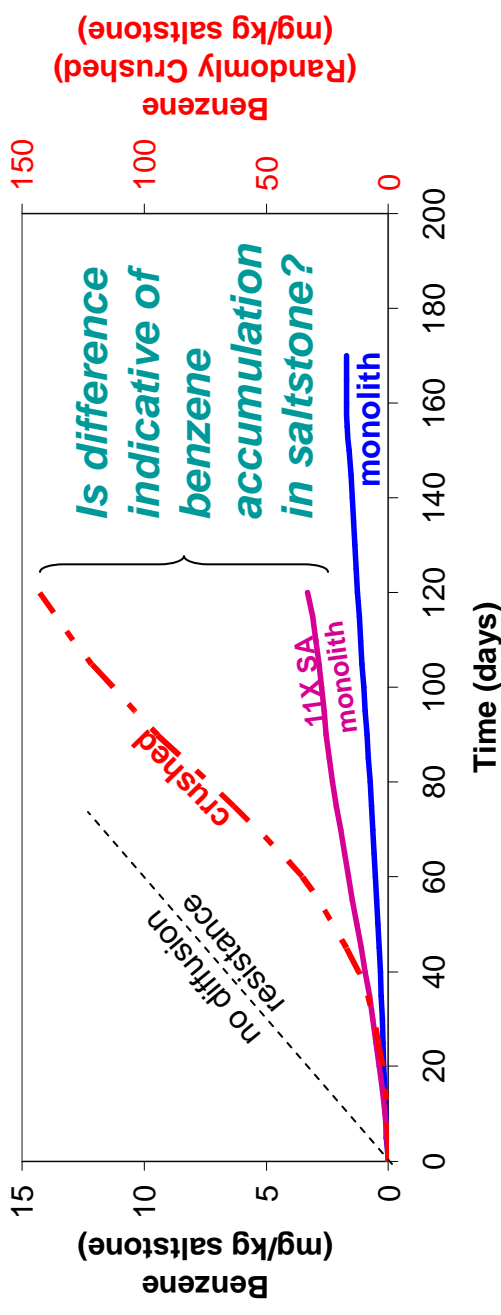
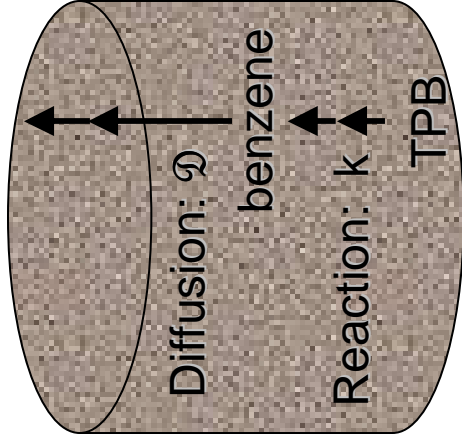


R: radioactive
S: simulant

Apparent 1st Order Rate

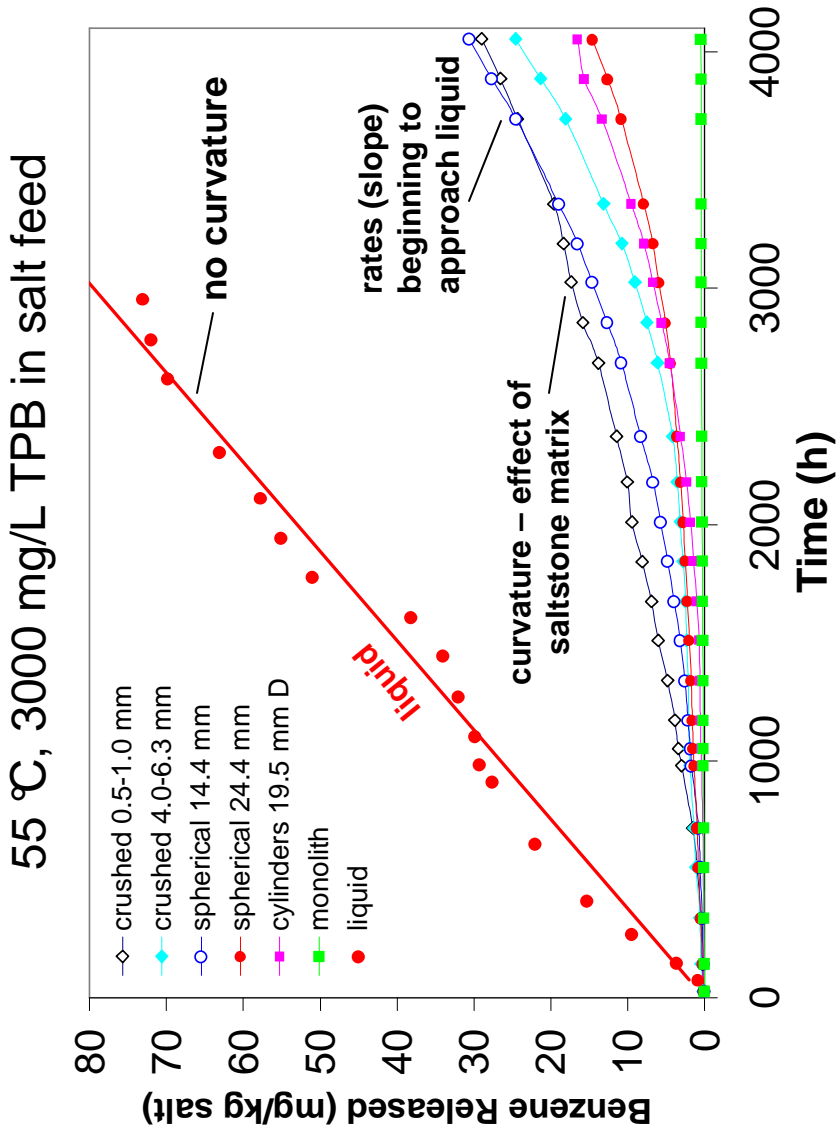
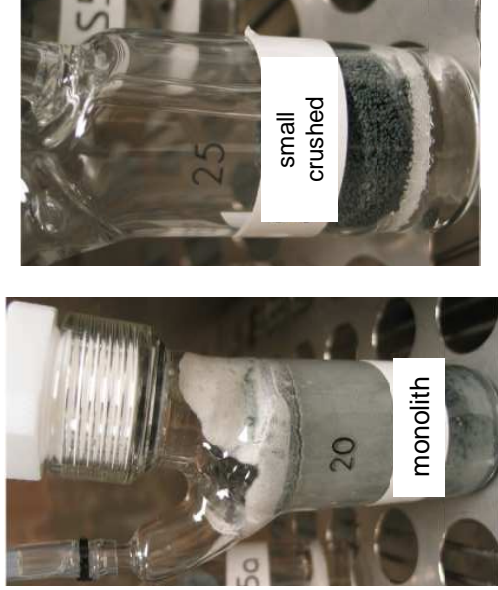


Benzene Accumulation in Saltstone



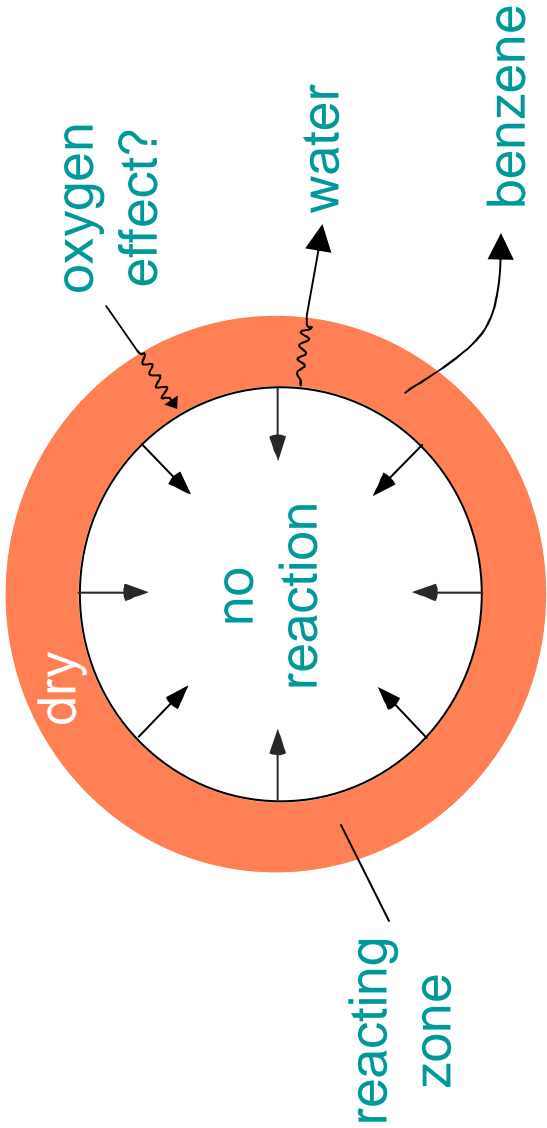
- Model predicts accumulation if reaction rate > diffusion rate
- Could exceed 10 mg/kg benzene limit
- However, analysis of remaining saltstone shows negligible benzene accumulation

Effect of Surface Area / Volume



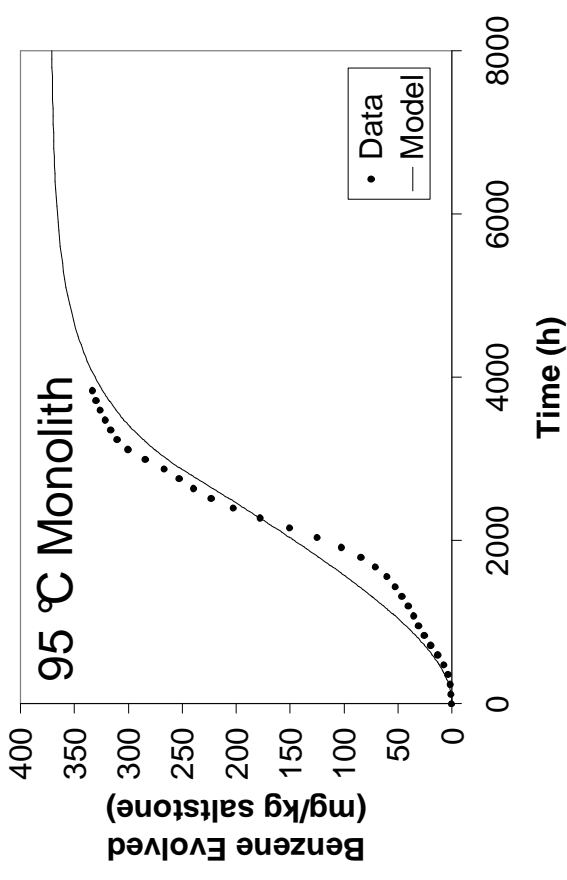
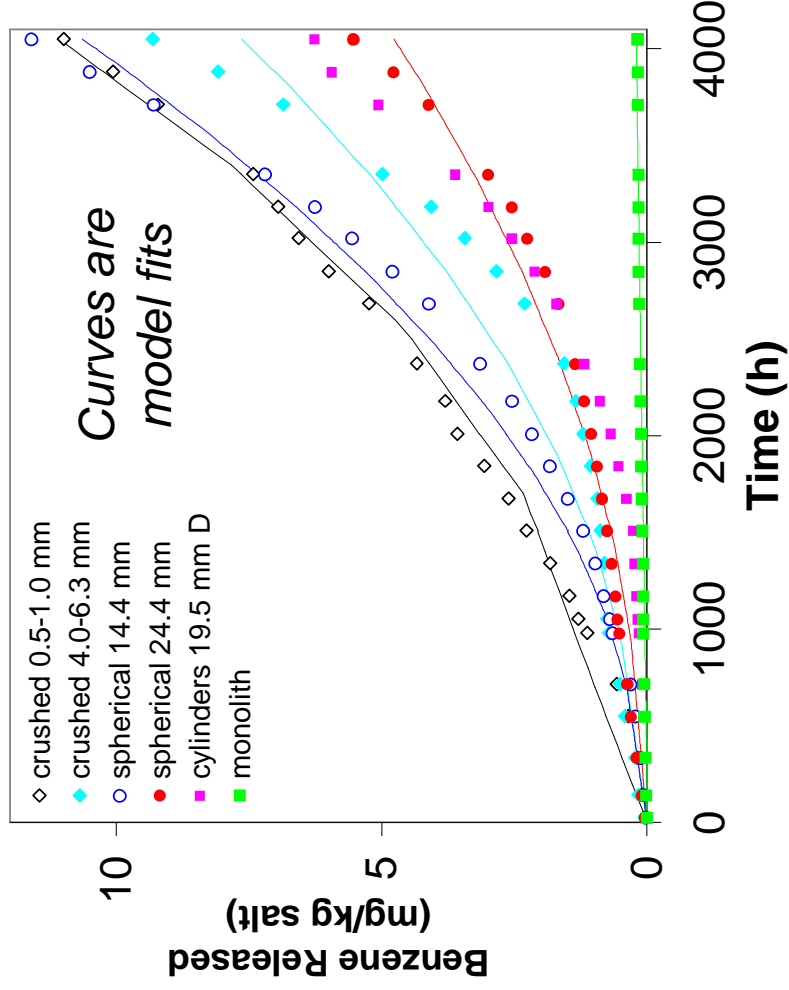
crushed & spheres rates (slopes) exceed flammable limit, but monolith does not

Contracting Shell Model

- S-shaped curvature
 - Negligible accumulation of benzene
- 
- The diagram illustrates the Contracting Shell Model. It features a central white circle labeled "no reaction" with arrows pointing inward from its perimeter. This is surrounded by an orange ring labeled "reacting zone". From the outer edge of this ring, arrows point outward, labeled "water" and "benzene". A wavy arrow labeled "oxygen effect?" points inward from the outer edge of the orange ring. The word "dry" is written on the left side of the orange ring.
- No reaction until free water evaporated
 - Oxygen may be involved in reaction
 - Reacting zone expands inward

Contracting Shell Model

55 °C, 3000 mg/L TPB in salt feed



- Best model that fits curvature
- Predicts little accumulation of benzene in saltstone

Conclusions

- Premix materials can also generate benzene, toluene, and xylenes
- Benzene is formed from decomposition of TPB
- Rates exceed flammable limits at 75 & 95 °C and for crushed & small spheres at ≥ 55 °C
- Benzene does not accumulate in saltstone, so will not generate hazardous waste
- Contracting shell is best model
 - Accounts for curvature of generation curves
 - Predicts low benzene retention

Acknowledgements

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