

# In-Situ Chemical Treatment of Chlorobenzene & Chlorofluorocarbon DNAPL in Aquifer Materials Under a Major River Dan Bryant (jbryant@woodardcurran.com, East Windsor, NJ), Brant Smith (brant.smith@peroxychem.com, Philadelphia, PA), Brianna Desjardins (brianna.desjardins@peroxychem.com, Tonawanda, NY)

# **Background / Objectives**

In-situ chemical treatment is usually considered either oxidative or reductive. This dichotomy reduces applicability at sites impacted with mixtures of contaminants susceptible only to oxidation and others to reduction. A residual DNAPL comprised predominantly of chlorobenzenes (70%), BTEX (13%), chlorinated VOCs (5%), and chlorofluorocarbons (CFCs) (12%), found 8-11 ft below the sediment-water interface in aquifer deposits under a major river offshore of an industrial facility, poses this problem. CFCs must be reduced while the other VOCs must be oxidized. A conceptual remedy is to inject slightly soluble, solid potassium persulfate (Klozur KP) blended with a metal base as a solid slurry into the impacted aquifer interval, via a barge-mounted direct-push system. The solids slowly dissolve over a long period of time, potentially decades, to release persulfate that is activated by the high pH base to generate hydroxyl radicals (strong oxidants to destroy chlorobenzenes) and superoxide radicals (reductant/nucleophile to destroy CFCs). Bench tests were designed to evaluate feasibility as a reactive treatment zone with single-pass columns, and as a gridded injection design for source area treatment with **recirculating** columns.



# **Conceptual Site Model**



# **Activated Persulfate Chemistry**

Alkaline-activated Klozur KP persulfate produces both strong oxidants (sulfate radical and hydroxyl radical) and a nucleophile/chemical reductant (superoxide radical):

 $K_2S_2O_8 \rightarrow 2K^+ + S_2O_8^{2-1}$  $S_2 O_8^{2-} + H_2 O \rightarrow SO_5^{2-} + SO_4^{2-} + 2H^+$  $SO_{5}^{2} + H_{2}O \rightarrow HO_{2} + SO_{4}^{2} + H^{+}$  $HO_{2}^{-} + S_{2}O_{8}^{2-} \rightarrow SO_{4}^{--} + SO_{4}^{2-} + H^{+} + O_{2}^{--}$  $SO_{A}^{-} + OH^{-} \rightarrow SO_{A}^{2-} + OH^{-}$ 

Superoxide Radical Strong Nucleophile – Destroys CFCs Superoxide production enhanced at pH >12

Sulfate Radical & Hydroxyl Radical Strong Oxidants – Destroy Everything Else \*Predominant species formed

# Column Setup – 5 Columns

RECIRCULATING COLUMNS – Simulate grid-pattern injection for source area

- 1. Clean control Sand & oxidant, no site soil or groundwater
- 2. Contaminated control Site soil & groundwater, no oxidant
- 3. Test column Site soil & groundwater, with oxidant

SINGLE-PASS COLUMNS – Simulate permeable reactive treatment zone

- **4.** Contaminated control Site soil & groundwater, no oxidant
- **5**. Test column with oxidant Site soil & groundwater, with oxidant





## Results



### **VOC RESULTS**

>99% for chlorobenzenes, BTEX, PCE; CFC results variable, -34% in recirculation column



### **CHLORINE AND FLUORINE MASS BALANCE**

Confirms relatively little VOC loss during experiments



# Conclusions

In the single-pass column effluent total chlorobenzenes, BTEX, and PCE concentrations were reduced >99% relative to control with 98% CI mass balance. CFC degradation was negligible with 122% F mass balance, indicating soil heterogeneity and/or sorption from the dissolved phase. Persulfate concentration was 23.5 g/L and pH was 12.3 after 23 pore volumes. CFC reduction and reagent persistence were improved in the recirculating column. Effluent total chlorobenzenes, BTEX, and PCE were reduced >99% and CFCs by 34% relative to control. Mass balance was 98% for CI and 96% for F. Persulfate remained 42-48 g/L and pH 12.5-12.9 after about 90 pore volumes, higher than the singlepass columns.



### **Key Lessons Learned**

**Chlorobenzenes, BTEX, and PCE (degraded** oxidatively) and CFCs (degraded reductively) are destroyed effectively in recirculating column simulating gridded injection for source area treatment.

The gridded pattern (source area) approach likely to yield decades of treatment with one injection.

**Chlorobenzenes, BTEX, PCE (but not CFCs)** degraded in single-pass column; likely contact time issue.