Persulfate Oxidation of PCE in Solids Containing Reactors

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Experimental Objectives

Determine rate of PCE oxidation using heat activated sodium persulfate

1. Evaluate the affect of subsurface solids PCE oxidation rate and extent
2. Measure PCE disappearance and chloride appearance to demonstrate complete dechlorination
3. Measure sulfate to evaluate persulfate utilization

Experimental System

Identically prepared batch of 12 vials, where each vial contained:

- 6 grams solids
- 3.5 to 5.5 mL of PCE stock solution (0.06 to 0.1mM)

Incubated at 50°C for 10 minute to preheat

Six Active Vials

Add 0.5 mL of 32 mM sodium persulfate (Sigma) solution phosphate buffered to pH 7

Six Control Vials

Add 0.5 mL of pH 7 phosphate buffer

Return vials to 50°C water bath and remove at selected times

Quench in Ice Bath for at least 10 min and collect Aq. samples

- 1 mL for Headspace GC/FID (i.e., PCE)
- 0.1 mL for Ion Chromatography (i.e., chloride, sulfate)

Solids

Glass Beads

- Borosilicate — 3±0.5mm dia.
- Soda Lime — 0.3 to 0.45 mm (40-50 mesh)

Reference Sands (U.S. Silica Sands)

- 20-30 mesh Ottawa — 0.85 to 0.6 mm (20 and 30 mesh)
- F70 — 0.35 to 0.075 mm (50 to 200 mesh)

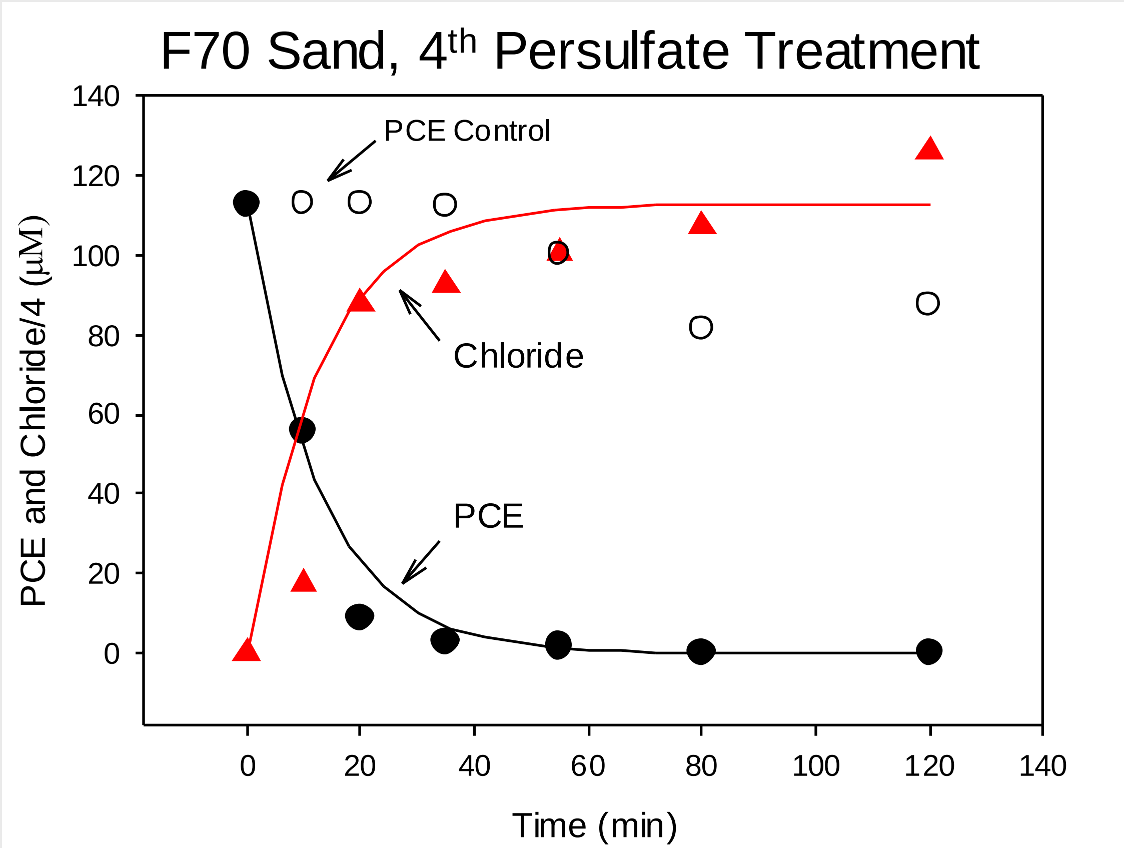
Reference Clays (Clays Mineral Society)

- Montmorillonite (SAz), Kaolinite (KGa), Illite-Smectite (ISCz)

Field Soils

- Great Lakes — Silty clay loam; Great Lakes, IL
- Fort Lewis — Gravel in a matrix of sand, silt, and clay; Fort Lewis, WA
- Appling — Loamy coarse sand; Eastville, GA

Experimental Results

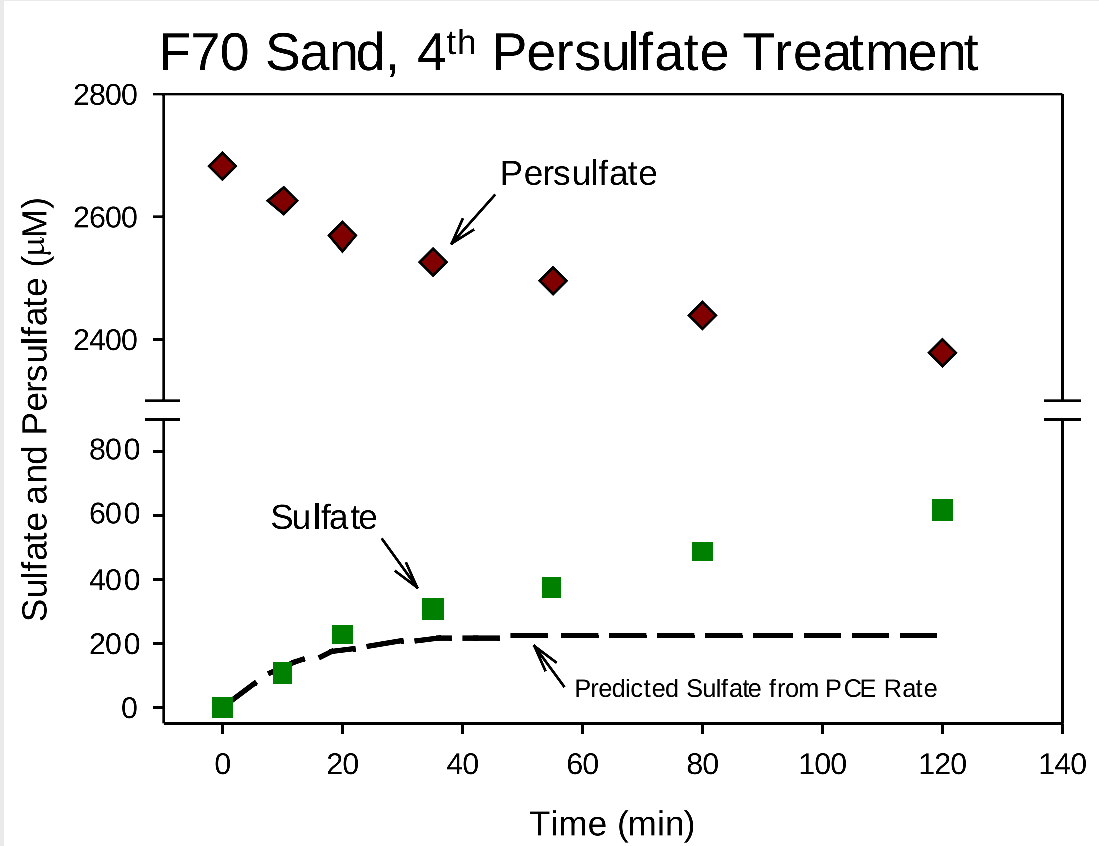


Typical result for clean F70 sand

PCE and chloride follow first-order rate, 3-log PCE removal (99.9%)

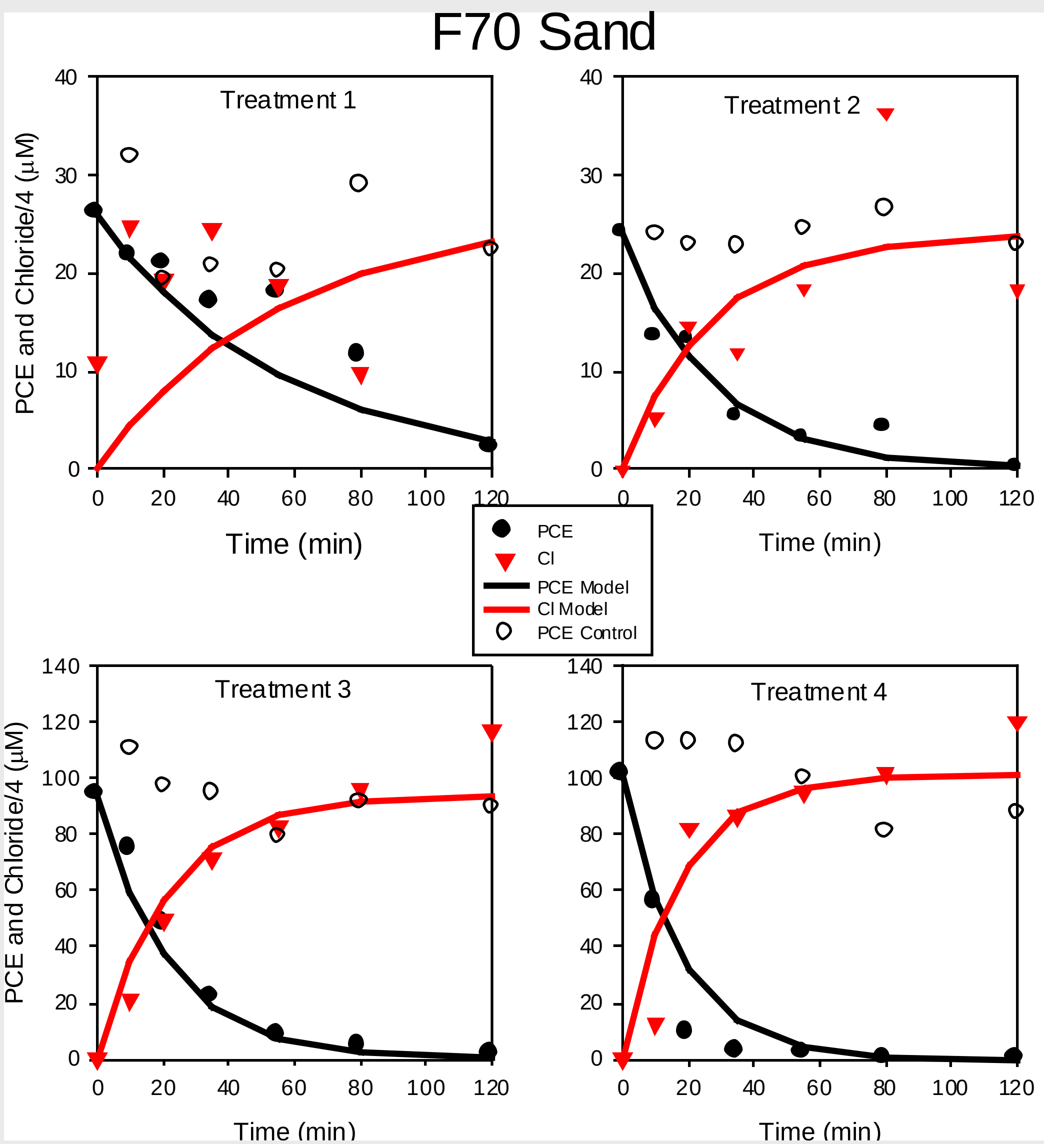
At 120 min, amount of chloride was within 10% of initial PCE present (i.e., 90% mass balance)

Sulfate Results



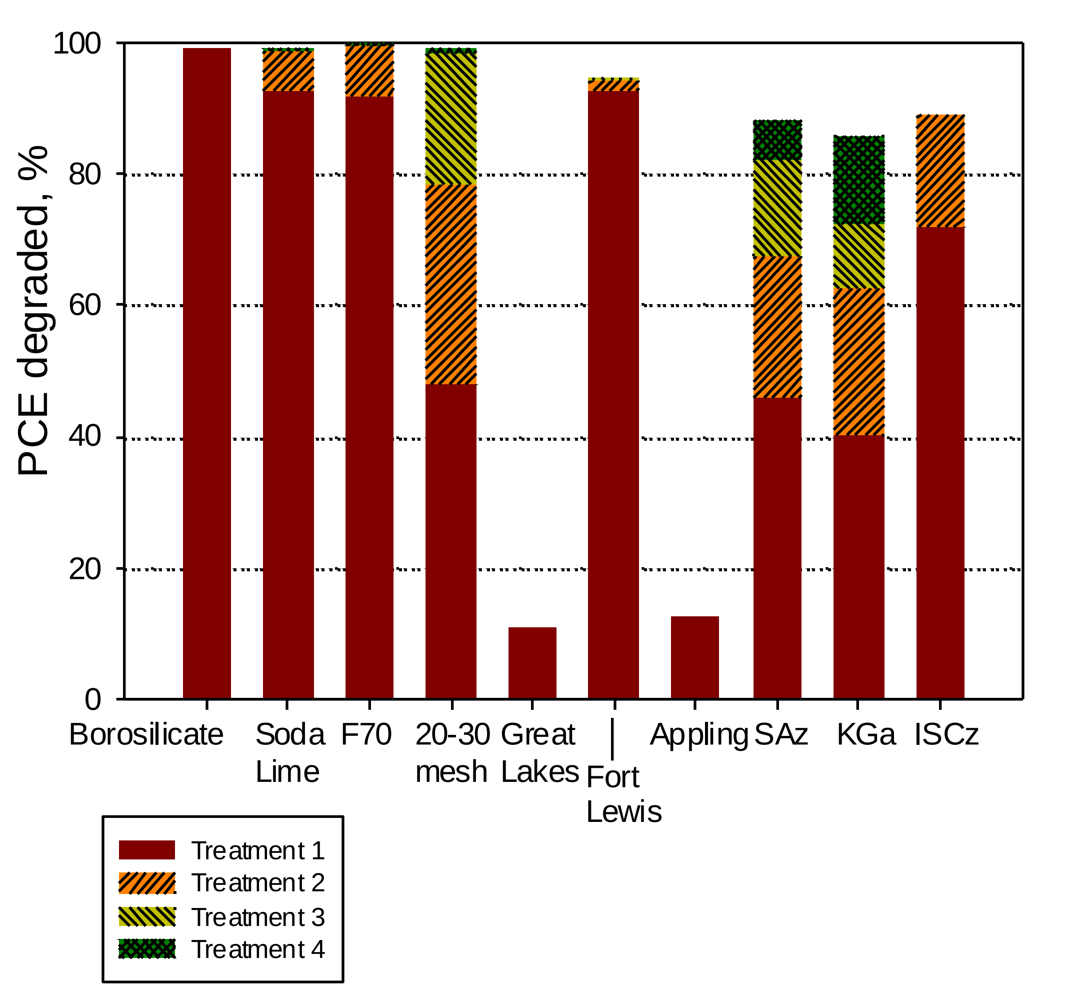
- Sulfate levels increased with reaction time, amount of persulfate at least 10:1 excess of PCE
- Sulfate increase was first-order within 30 min, 2nd order thereafter
- Amount of sulfate in excess of the expected 2:1 sulfate to PCE mole ratio after 30 min indicating auto-oxidation of persulfate

Repeated Treatment Improves Rate



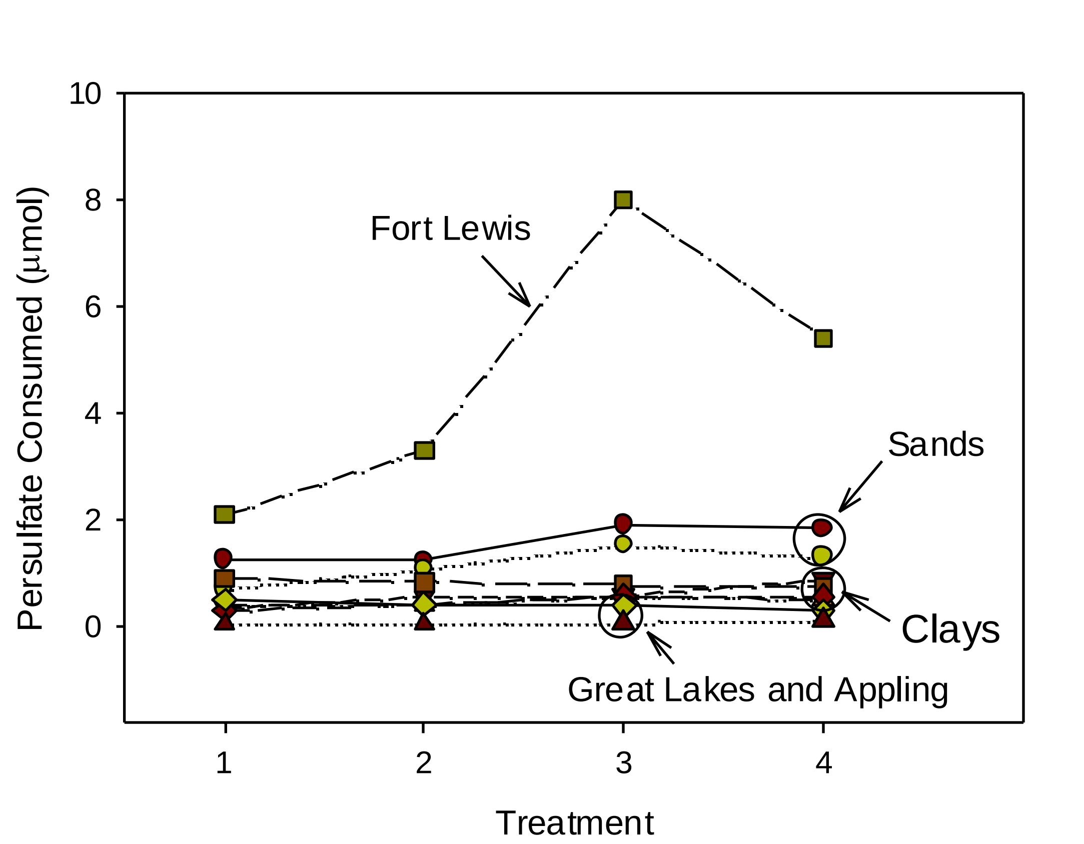
- After collecting samples, refill vials with PCE stock and repeat treatment
- Performed to satisfy "intrinsic oxidant demand" and restore rate to glass-bead conditions
- Rate of PCE oxidation increases with each subsequent treatment

Summary of Repeated Treatments



- Repeated treatments improves extend and rate of PCE degradation with
  - Glass Beads
  - Reference Sands and Clays
  - Fort Lewis
- *No improvement with*
  - Great Lakes
  - Appling

Intrinsic Oxidant Demand



- Amount of persulfate consumed calculated from amount of sulfate measured after 120 min.

Expected greatest demand for Great Lakes and Appling assuming intrinsic "Oxidant Demand" model

Intrinsic oxidant demand can be overcome by using an oxidant solution containing excess oxidant to satisfy the intrinsic soil oxidant demand and degrade the target organic compound (Haselow et al., 2003).

Deconstruct Soils

Alternative explanation is that radical quenching compounds were present and interrupted the activation of persulfate

Soils were treated to selectively remove potential quenching compounds

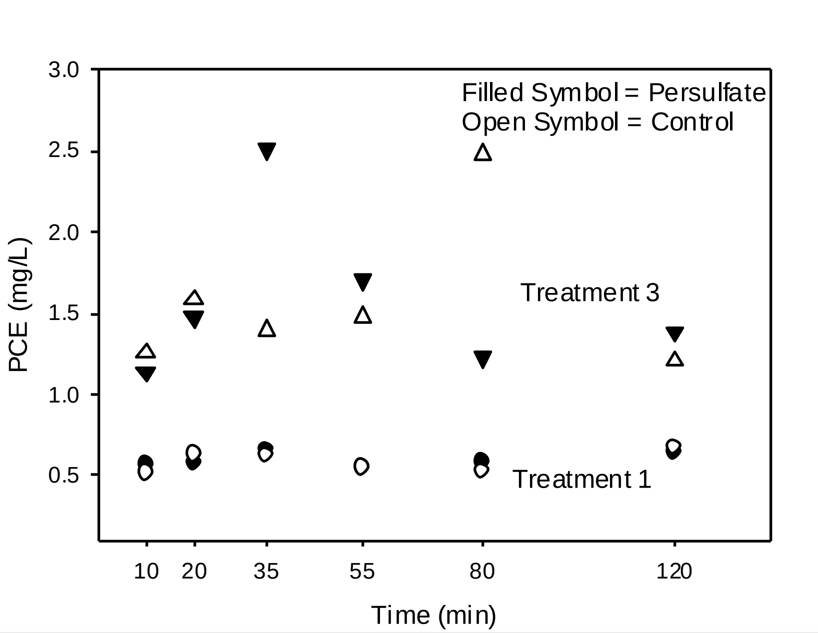
1. Acetic acid treatment to remove carbonates
2. 30% H_2O_2 treatment to remove soil organic matter

Soils were air died after treatment and then used in subsequent persulfate experiments

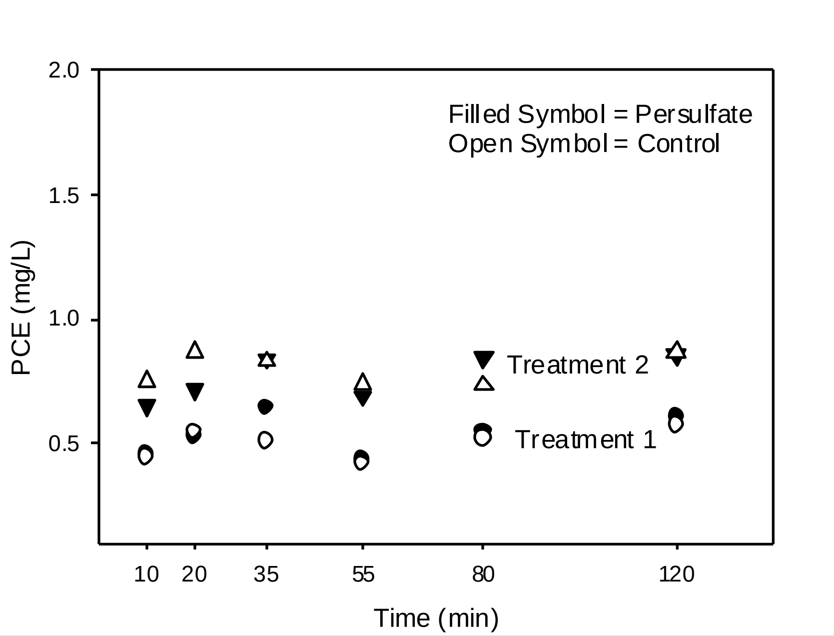
Results for Treated Great Lakes Soil

No improvement in persulfate degradation of PCE after either acetic acid treatment or 30% H_2O_2 treatment

30% H_2O_2 treatment performed over a one week period involving 4 applications of peroxide while heating soil to 70°C



Acetic Acid Treated Great Lakes

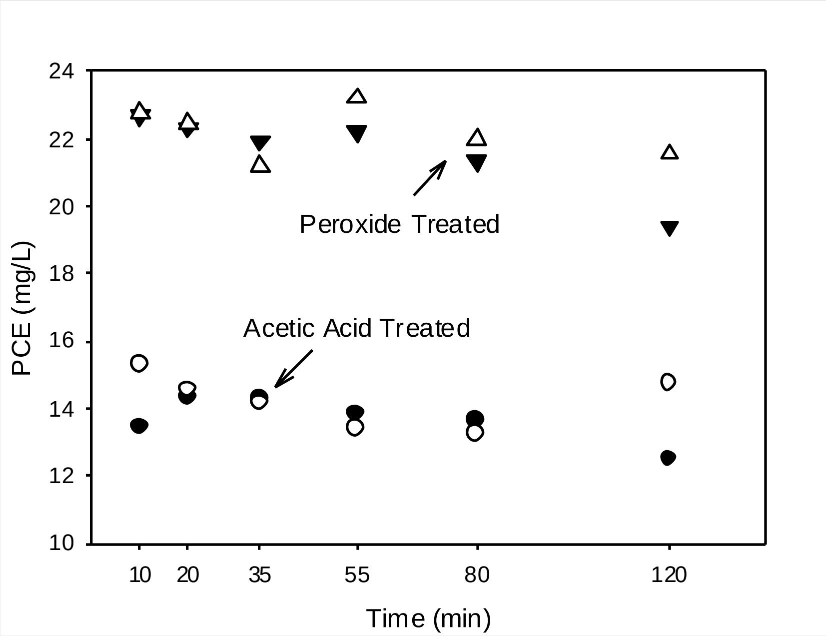


Peroxide Treated Great Lakes

Results for Treated Appling Soil

No improvement in persulfate degradation of PCE after either acetic acid treatment or 30% H_2O_2 treatment

Peroxide treated Appling soil adsorbed significantly less PCE after addition of stock solution



Acetic Acid and Peroxide Treated Appling

Sorption Losses

39% loss with Peroxide treated vs. 61% loss for Acetic Acid treated soil (not accounting for PCE volatile losses)

Summary and Conclusions

Glass beads, clean sands, and reference clays do not impede rate and or extent of persulfate oxidation of PCE

Field soils either don't inhibit (Fort Lews) or completely inhibit (Great Lakes and Appling) persulfate oxidation of PCE

Inhibitory mechanism related to quenching of radical chain degradation process rather than "intrinsic oxidant demand"

Radical quenching compounds associated with mineral fraction of soils, however, more work required to positively identify the fraction

Acknowledgements

Strategic Environmental Research and Development Program (SERDP), contract W912HQ-05-C-008, Project ER-1419: “Investigation of Chemical Reactivity, Mass Recovery and Biological Activity During Thermal Treatment of DNAPL”.