

The Use of Carbon Fiber Composite as Substrate for a Zero-Valent Metal Dechlorination System

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Outline

- Introduction
- Background
- Experimental & Results- TCE
- Experimental & Results- PCP
- Conclusions
- Future Goals



Basis for Work

- Carbon fiber systems offer distinct advantages for sorption and catalysis
 - gas or liquid phase
 - high surface area
 - many possible chemistries
- Carbon fiber composites offer:
 - convenient mechanical structure
 - uniform and reproducible properties



Water Treatment Applications

- Volatile organic compounds (VOC's) are widespread industrial contaminants
- 4.5% of 2600 community wells are contaminated at > 1 ppb.
 - L.W. Canter and K.M. Maness, “Ground Water Contaminants and their Sources- A Review of State Reports”, Intern. J. Environmental Quality, Vol. 47, pp. 1-17.



Scope of problem

- 1,1,1-trichloroethane and trichloroethylene (TCE) are among the most common VOC's in groundwater.
- non-aqueous phase liquid TCE common in industrially contaminated groundwaters



Scope of Problem

- Pentachlorophenol (PCP) is a common chlorinated hydrocarbon contaminant in aqueous systems.
- Used extensively as a wood preservative.
- Most previous work has focused on biological methods of remediation: slow rates of decontamination.



Why use zero valent metal?

- Metal dissolution provides energy for decomposition of Cl-C bond
- Low cost
- High reaction rates: 5 to 15 orders of magnitude faster than biological processes
 - O'Hannesin, Gillham and Vogan. "TCE Degradation in Groundwater Using Zero-Valent Iron", Special Symposium on Emerging Technologies in Hazardous Waste Management, Industrial and Engineering Chemistry Division, ACS, Sept. 17-20,1995.



Zero-Valent Metal Catalysis

- Zn, Sn, Mg, and Fe are most common
 - Palladium modified iron.
- Inert (anoxic) environment
- Test site: O'Hannesin et. al.- Borden, Ontario
 - Fe filings
 - 90% TCE removal
 - rate independent of TCE concentration



Rate controlling factors

- Dissolved oxygen
- pH and ionic strength of groundwater
- Presence of metal oxide or carbonate
 - 10x alkalinity reduced rate 3x
 - MacKenzie et. al. “Pilot-Scale Demonstration of Chlorinated Ethene Reduction by Iron Metal: Factors Affecting Iron Lifetime.” op. cit.
- Rate of metal dissolution



Effect of metal surface area

■ Surface area of metal is rate controlling

- Boronina, Klabunde and Segeev. “Destruction of Organohalides in Water using Metal Particles: Carbon Tetrachloride/Water Reactions with Magnesium, Tin and Zinc.” Environmental Science & Technology, Vol. 29, no. 6, pg. 1511, June, 1995.

■ Cryo-particle Zn ($>65 \text{ m}^2/\text{g}$)

- CCl_4 reduced 90% in 3 hours

■ Granular Zn ($<1 \text{ m}^2/\text{g}$)

- CCl_4 reduced 25% in 3 hours

■ CF composites may provide high rates and high surface areas



Carbon Fiber Composite

- Support Zn on carbon fiber substrate for convenient preparation and use
- Composite has higher surface area and lower ΔP than comparable particulate metal
- Composites should have high decomposition rates



Granular Zn/TCE Experiments

- 75 - 250 micron diameter Zn particles
- Washed with 0.01 M HCl
- Deoxygenated water
 - vacuum broken with nitrogen sparge
- 1000 ppm TCE in water
- Standard stirred tank reactor
- Chloride-selective electrode

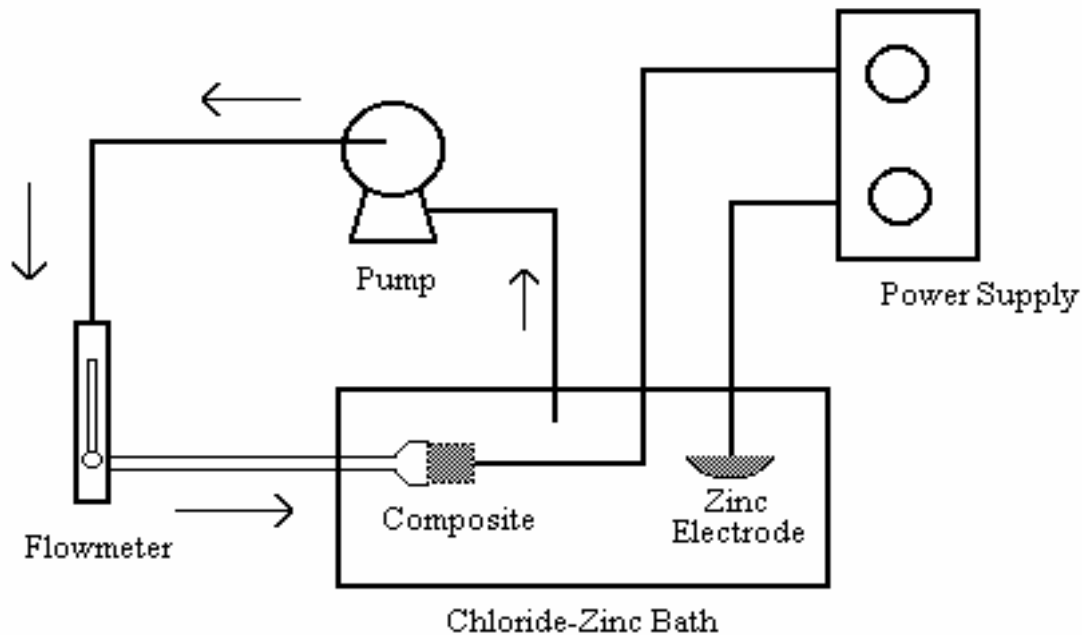


Carbon Supported Zinc

- Heat treated carbon fiber composite
- Zinc plating
 - low current density
- Flow cell to obtain uniform coating



Plating apparatus



Zn-CFC/TCE Experiments

- 1000 ppm TCE in deoxygenated water
 - vacuum broken with nitrogen sparge
- Composite used as paddle in reactor
- Flow lines pass through composite
- Chloride-selective electrode

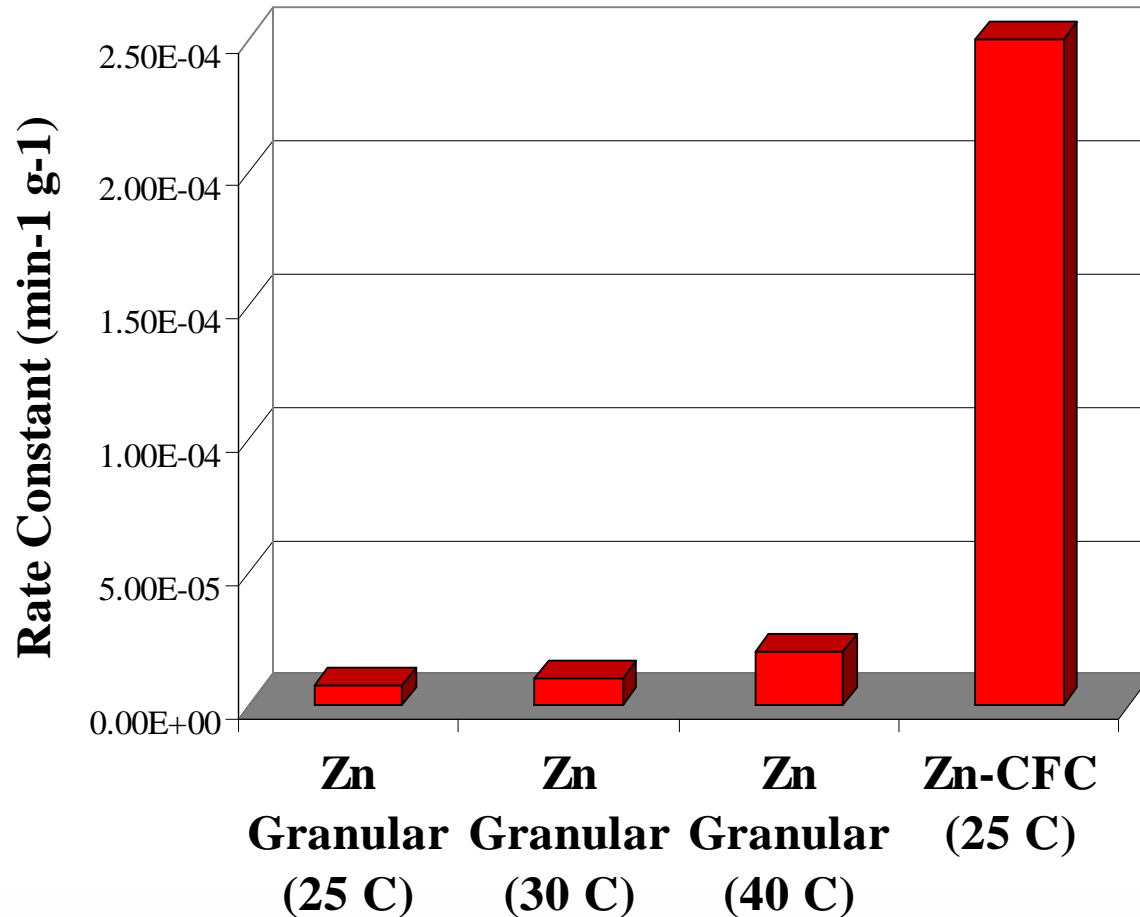


Reaction kinetics - TCE

- Chloride ions in solution measured
- first order kinetics assumed
- per gram of Zn basis
- several proposed degradation pathways
- assume:
 - TCE DCE + Cl⁻
 - no other reactions



Reaction rate constants - TCE



Summary -TCE

- Demonstrated adequate Zn loadings
 - Plated 0.64 g/cm^3 Zn on composite
 - void fraction of composite decreased from 0.84 to 0.75
- Demonstrated high rate for composite
 - rate increases with temperature
 - rate is 35 times faster for the Zn-CFC vs. granular Zn and literature values.



Further work - TCE

- Study complete degradation pathway
 - close Cl and C balances
- Complication is gas phase partitioning of DCE, VC and other products



Why use PCP?

- PCP is a widespread contaminant
- Dechlorination rate should be dependent on surface area of metal.
- Measure PCP using UV/VIS spectroscopy at 319.7 nm.



Granular Zn/PCP Experiments

■ Granular Zinc

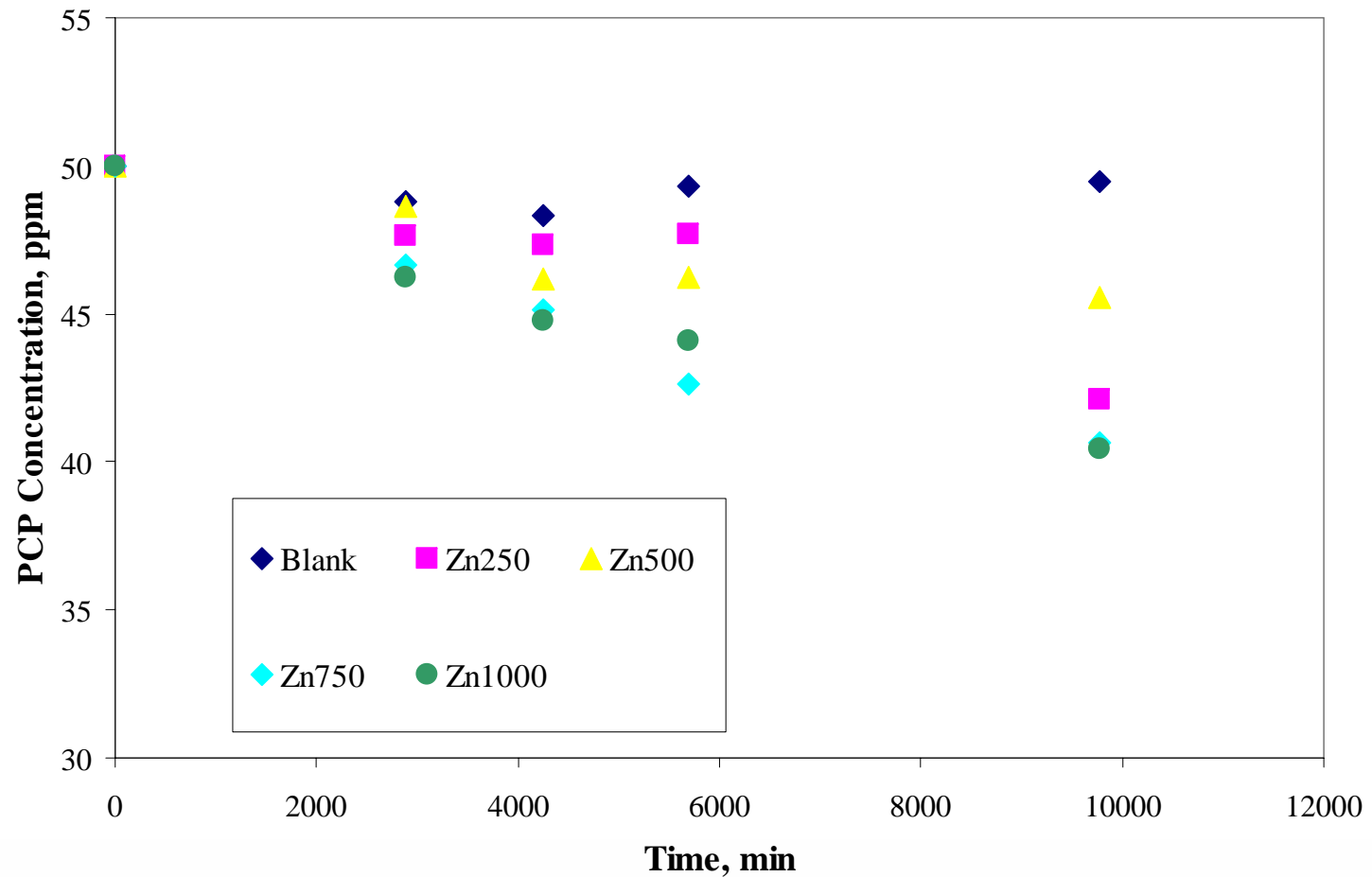
- surface area: $2.2 \cdot 10^{-3} \text{ m}^2/\text{g}$

■ Batch Reactions:

- 18° C
- 50 ppm PCP initially
- 100 ml water/PCP charged with:
 - » 250, 500, 750 and 1000 mg Zn
 - » $5.5 \cdot 10^{-4}$, $1.1 \cdot 10^{-3}$, $1.65 \cdot 10^{-3}$ and $2.2 \cdot 10^{-3} \text{ m}^2 \text{ Zn}$



Granular Zn/PCP Experiments



Batch Kinetics -PCP

- Reaction kinetics for degradation
 - apparent 1st order
 - rate constant is $0.012 \text{ min}^{-1} \text{ m}^{-2}$
 - 2% standard error between predicted and experimental values.
 - reaction is dependent on surface area of metal



Zn-CF/PCP Experiments

- Batch experiments with Zn-CF were designed to extend surface areas studied.
- Zn was plated onto **activated** carbon fibers
 - Osaka Gas OG-5a: $\sim 750 \text{ m}^2/\text{g}$ BET surface area
- Batch Experiment
 - Suspension of ACF with 0.018, 0.045 and 0.079 m^2 of Zn.
 - blank of unplated activated fibers (0.045 m^2).



Zn-CF/PCP Batch Experiments

- After 36 hours, **plated and unplated** fiber suspensions contained no PCP
- Cl^- in plated fiber systems was <6 ppm
 - corresponding to removal of 1 Cl from PCP
- Cl^- in unplated fiber systems was 6 ppm!
- Unplated fibers may have higher rate than Zn plated fibers

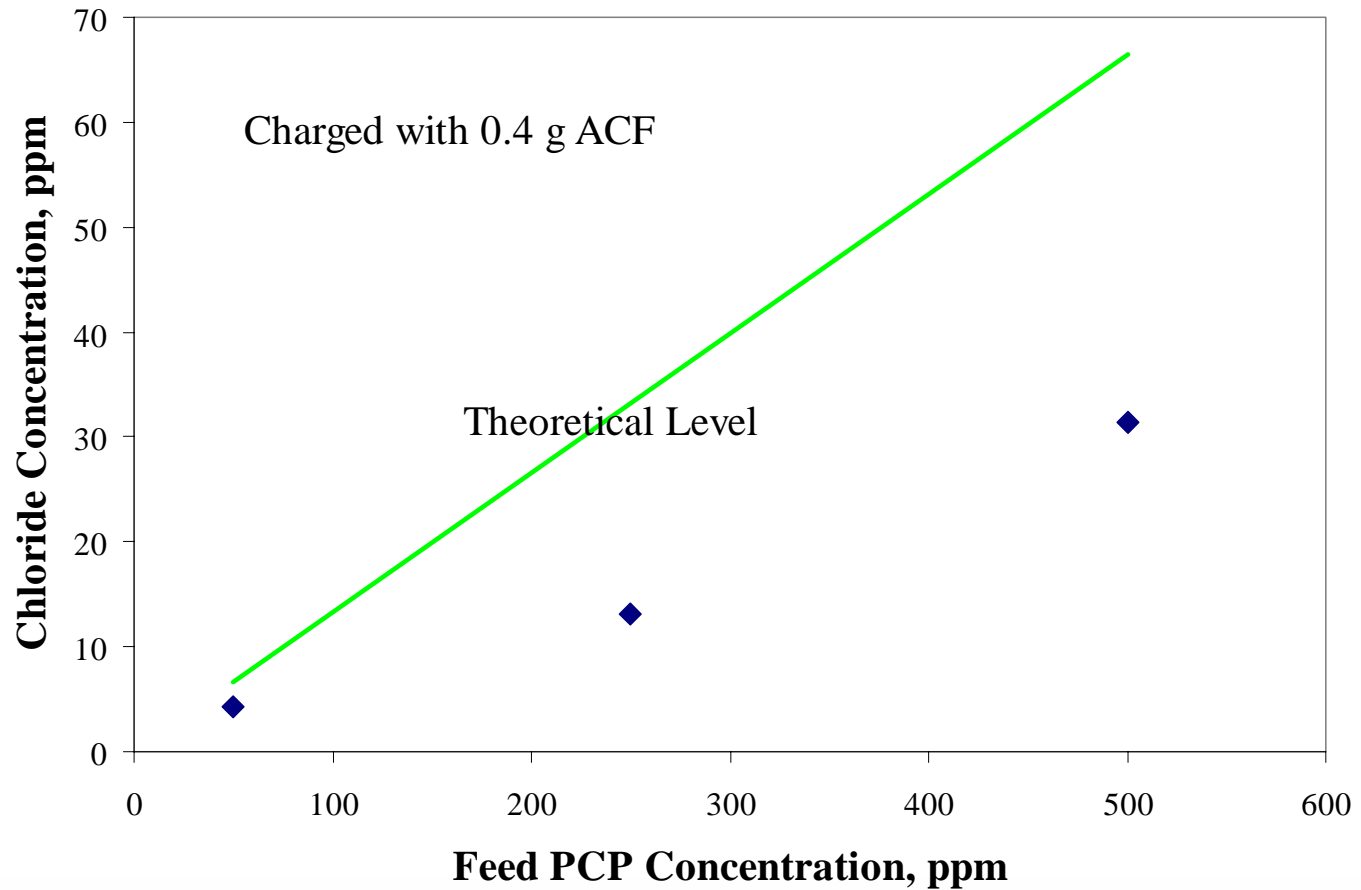


PCP/Carbon Experiment

- Batches of 50, 250, 500 ppm PCP were run with 0.4 grams of activated carbon fibers.
- PCP concentration measured after 36 hrs
 - all at 0 ppm
- Chloride ion concentration measured
 - present in amounts approaching single chlorine removal



PCP Degradation on ACF



Summary - PCP

- Zn may not be the most active catalyst for PCP
- Activated carbon fibers appear to act as an effective catalyst for dechlorinating PCP
- This result is similar to that observed in solvent recovery plants using GAC.
 - Hydrolysis of the C-Cl link occurs on the carbon surface (ex. Carbon tetrachloride)
 - J. Wildman “Practical Problems in Solvent Recovery using Activated Carbon”. Sutcliffe Speakman Carbons, Limited.



Summary - PCP

- Zn metal dechlorinates PCP
- Zn-PCP reaction is surface area dependent
- Zn surface area for reaction can be increased by plating on CF composite
- Unplated activated carbon fibers appear to have catalytic activity



Overall Conclusions

- Developed carbon fiber supported catalysts which actively attack chlorinated hydrocarbons
- CF supports (Zn plated) have higher activity and lower ΔP than similar particulates

Future Work

- Explore the mechanism of PCP degradation by ACF:
 - complete a mass balance on the PCP system
 - » GC for degradation products in bulk phase
 - » Cl⁻ balance: bulk phase
 - » determination of adsorbed species on carbon
 - Demonstrate activated carbon fiber composite in a continuous reactor



Acknowledgments

- Center of Applied Energy Research and Chemical & Materials Engineering, University of Kentucky for financial support
- Peter Löwenhielm for experimental help.
- Dr. Chris Lafferty for analysis.
- Craig Fowler and Rodney Johnson for composite manufacture.

