PGDP Nano-Particle Remediation Project

\[
\begin{align*}
\text{Cl} & \rightarrow \text{Fe}^{2+} & \text{e}^- & \rightarrow \text{Fe}^0 & \rightarrow \text{Pd}^0 & \rightarrow \text{H}_2 & \rightarrow \text{RH + Cl}^- \\
\text{Cl} & \rightarrow \text{H}_2 & \rightarrow \text{H}^* & \rightarrow \text{RCl} & \rightarrow \text{H}_3C-\text{CH}_3
\end{align*}
\]
# OUTLINE

<table>
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### PGDP Nano-Particle Remediation Project
#### University Project Participants

<table>
<thead>
<tr>
<th>Name</th>
<th>Institution and Role</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dr. Rodney Andrews</td>
<td>UK/CAER (Director)</td>
</tr>
<tr>
<td>Dr. Lindell Ormsbee</td>
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<td>UK CAER/KRCEE (PM)</td>
</tr>
</tbody>
</table>
PGDP Nano-Particle Remediation Project
University Project Participants

Supplemental Funding from
NIEH Superfund Basic Research Program (SBRP)
UC Berkeley – Sedlak
UK Ky. Water Resources – Ormsbee
UK Chemical & Materials Engineering – Bhattacharyya
UK/KRCEE & UK/ChemE
Technical Background
Objectives

- Development of effective methods for the dechlorination of toxic organics
- Determine role of dopant metal in bimetallic nanoparticle reactivity
- Study potential for on-site generation of chemicals needed for chelate-modified Fenton reaction
- Determine effectiveness of both reductive and oxidative dechlorination in column studies to simulate groundwater flow
UK/ChemE Technical Background

Removal of TCE at Ambient Temperature

Nanosized Metals

Hydroxy-Radical & Chelates

Reductive Dechlorination of TCE

(nano)Fe\(^0\) + TCE → Fe\(^{2+}\) + Ethane + 3Cl\(^-\)

(Bulk)Fe\(^0\) + TCE → Fe\(^{2+}\) + intermediates + nCl\(^-\)

Systems Used:
Zerovalent metals (Fe), Bimetallic systems (Fe/Pd, Fe/Ni), Supported Platforms

Oxidative Destruction of TCE

TCE + OH\(^-\) → CO\(_2\), Organic Acids

Systems Used:
Standard Fenton Reaction,
Modified Fenton Reaction using nontoxic chelate (citrate, gluconic acid) (L) as a chelating agent (FeL).
UK/ChemE Technical Background

Reductive Methods – Nanoparticle Background

• Nanoscale Metals Characteristic length < 100 nm
• Chloro-organic degradation rate increases 1-2 orders of magnitude over larger Fe particles
  • Increase in reactive surface area per reactant volume
• Minimal intermediate formation
• The use of a bimetallic system (Fe + Pd or Ni, etc.) increases the reactivity of the particle surface by incorporating a second metal
  • Second metal typically acts as hydrogenation promoter
• H also reacts to destruct chloro organic compounds
• 2nd Metal also
  • Reduces particle-soil interactions of Fe and
  • Increases in-situ particle mobility
• Evaluated aerobic and anaerobic groundwater & range of pH values
• Used RGA Groundwater
• Used RGA Matrix
Mechanism of Reductive Dechlorination

**Single Fe⁰ system**

\[ \text{Fe}^0 \rightarrow \text{Fe}^{2+} + 2e^- \]
\[ \text{RCI} + 2e^- + \text{H}^+ \rightarrow \text{RH} + \text{Cl}^- \]
\[ \text{RCI} + \text{Fe}^0 + \text{H}^+ \rightarrow \text{Fe}^{2+} + \text{RH} + \text{Cl}^- \]

(Xu & Bhattacharyya, Environ. Prog., 24, 358, 2005)

**Bimetallic system**

\[ \text{Fe}^0 + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2 \]
\[ \text{H}_2 + \text{Pd} \rightarrow \text{Pd-H} + \text{H}^* \]
\[ \text{RCI} + \text{H}^* \rightarrow \text{RH} + \text{Cl}^- \]

UK/ChemE Technical Background

Reductive Dechlorination of TCE

Metal Nanoparticles

Synthesis

Solution Phase
- NaBH₄
- Fe⁰
- Fe⁰/Ni, Fe⁰/Pd

(Bimetallic via Postcoating)

Polymer Domain
- Phase Inversion
- Ion-Exchange
  - NaBH₄
  - Supported Fe⁰, Fe⁰/Ni, or Fe⁰/Pd

TCE Solution

Ethane
UK/ChemE Technical Background

Figure 3. Evaluation of Pd/Fe nanoaggregates (0.8-wt% Pd) for the ideal dechlorination of 16.6 mg.L\(^{-1}\) TCE at pH 6 using 1.0 g.L\(^{-1}\) metal loading.
Figure 4. Examination of the effects of metal loading and Pd-deposition on the dechlorination of 20.5 mg.L⁻¹ TCE in de-oxygenated DIUF water at pH 5.
Figure 5. Reduction of a 21.1-mg.L\(^{-1}\) TCE solution in Paducah sample water under aerobic conditions in the presence of aquifer gravel using 0.9 g.L\(^{-1}\) of Fe nanoaggregates post-coated with 0.5-wt% Pd.
Figure 9. Results for circulating column dechlorination of TCE ($C_0 \approx 16$ mg/L TCE) at pH 6.4-7 using 0.5 g.L$^{-1}$ of Fe/Pd nanoaggregates (0.4-wt% Pd) showing the negligible effects of groundwater velocity over the range of 12.9-82 ft per day.
UK/ChemE Technical Background

Reductive Methods – Bimetallic Nanoparticles

• Increasing 2\textsuperscript{nd} metal surface loading will eventually result in a decline in the hydrogen generation rate
  • Lack of available exposed Fe surface area for corrosion.
• The influence of pH on hydrogen generation is insignificant over a broad range (5-8),
  • Indicates capability for dechlorination over this range.
• Dechlorination rates involving bimetallic systems are more accurately represented as a strong function of the rate of Fe corrosion with water because
  • The corrosion-generated hydrogen interacts with the 2\textsuperscript{nd} metal (Pd, Ni, etc.) to form highly active H where it undergoes reaction with chloro-organics.
• This is a significant finding that will allow for more accurate modeling of ground water remediation involving bimetallic systems.
• TCE Destruction rates from 60 to 100\% over a range of pH, TCE concentrations, times, dopant variations, Oxygen conditions, source water
Groundwater Remediation Using Combined Strategies For Reduction and Oxidation

**Reduction**
- Fe, Fe/Pd, Fe/ Ni

**Oxidation**
- Fe$^{2+}$ + nontoxic chelate
- H$_2$O$_2$

---

**Ground level**
- Ethane
- Non-dissolved CO$_2$

**Groundwater**
- TCE, PCB, etc
- Dechlorination Products and/or Intermediates
- Organic Acids and/or CO$_2$

Enhanced downstream bio-attenuation of products because of biodegradable chelate (gluconic acid, citrate)
PGDP Nano-Particle Remediation Project

Fe$^{0}$ + H$_2$O $\rightarrow$ Fe$^{2+}$ + e$^-$

Pd$^{0}$ + Cl$^-$ $\rightarrow$ H$_2$ + RCl

RH + Cl$^-$ $\rightarrow$ H$_3$C$\equiv$CH$_3$

Center for Applied Energy Research

UK

Center for Applied Energy Research

KRCEE

Kentucky Water Research Institute
# PGDP Nano-Particle Remediation Project

## Project Team

<table>
<thead>
<tr>
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<td>Ky. EEC</td>
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<td></td>
<td>Paducah Remediation Services</td>
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<td>DOE PPPO &amp; PRC</td>
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## Preliminary Project Schedule

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<tr>
<th>Activity</th>
<th>Start</th>
<th>Completed</th>
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<tr>
<td>UK Project Planning</td>
<td>5/1/2009</td>
<td>9/30/2009</td>
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<td>PROJECT TEAM KICKOFF</td>
<td>10/28/2009</td>
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<td>D1 Draft TS Workplan Start</td>
<td>11/13/2009</td>
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<td>D1 TS Workplan Revisions</td>
<td>12/18/2009</td>
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<tr>
<td>D1 Submitted to DOE</td>
<td>1/30/2009</td>
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PGDP Nano-Particle Remediation Project

Objective:

“Develop A Treatability Study Workplan for Nano Particle GW Pilot Demonstration at the PGDP”

• Complete within timeframe to support DPP activities
• Address implementation, applicability, effectiveness, environmental stability of particles, aquifer geochemical impacts, & health and safety for proposed TS work
Treatability Study

- Treatability studies are laboratory or field tests designed to provide critical data needed to evaluate and, ultimately, to implement one or more treatment technologies. Factors that influence the type or level of testing include:
  - Phase of the project (i.e. RI/FS or RD/RA)
  - Technology-specific factors
  - Site-specific factors
PGDP Site Regulatory Project Considerations
The Superfund Process

- PA/Sl
- NPL Listing Process
- RI/FS
- ROD
- RD/RA
- Construction Completion
- Post-Construction Completion
- NPL Deletion
- Reuse
Groundwater Operable Unit Schedule

SMP Milestones

1. SW Plume FFS - 7/28/09
2. SW Plume Proposed Plan — 3/25/10
3. SW Plume ROD — 9/17/10
4. SW Plume Remedial Action Completion Report — 6/28/15
6. Dissolved-Phase Plume RI/FS Work Plan — 3/10/11 (planning date)

- FY-07 SMP Approved Enforceable Milestone included in FY-08 SMP
- FY-08 SMP Proposed New Milestone
- Out-year milestone proposed for evaluation/modification in FY09 SMP
Dissolved Phase Plume Schedule Overview and Status

Near-Term 2006 - 2009
- Support TCE Fate & Transport analysis by performing necessary fieldwork and analysis as identified by Fate & Transport Working Group
- Update groundwater model
- Develop and submit to regulators RI/FS Scoping Document

Out-Year 2010-2019
- Development and regulatory approval of RI/FS Work Plan
- Implement RI fieldwork
- Development and regulatory approval of RI Report
- FS development and regulatory approval
- Development and regulatory approval of Proposed Plan
- Development and regulatory approval of ROD and LUCIP
- Development and regulatory approval of Remedial Design Work Plan
- Development and regulatory approval of Remedial Design Report and Remedial Action Work Plan
- Implement remedial action
- Development and regulatory approval of Remedial Action Completion Report

Date is now 10/10/11 (2009 SMP)
PGDP Site Regulatory Project Considerations

Identification of all Federal and State ARAR’s that address the injection of substances into ground/groundwater for purposes of remediation
TS Workplan Template
(from Iron Filings TS)
Example Work Plan

• EXECUTIVE SUMMARY

• 1.0 INTRODUCTION
  – 1.1 BACKGROUND INFORMATION
    • 1.1.1 Project Description
    • 1.1.2 Background Information
      – Location
      – Demography and Land Use
      – Climate
      – General History
  – 1.2 REGULATORY COMPLIANCE
    • 1.2.1 Location Specific ARARs
    • 1.2.2 Chemical Specific ARARs
    • 1.2.3 Action-specific ARARs

• 2.0 TREATABILITY STUDY GOAL AND OBJECTIVES
  – 2.1 TREATABILITY STUDY GOAL
  – 2.2 TREATABILITY STUDY OBJECTIVES
  – 2.3 DATA QUALITY OBJECTIVES
    • 2.3.1 Intended uses of Acquired Data
    • 2.3.2 Intended Users of Data
    • 2.3.3 Analytical Quality Levels and Quality Control Levels
Example Work Plan

• 3.0 DESCRIPTION OF TREATMENT TECHNOLOGY
  – 3.1 BACKGROUND
  – 3.2 DESCRIPTION OF TECHNOLOGY
  – 3.3 REVIEW OF LITERATURE
    • 3.3.1 Degradation of Trichloroethylene
      – Overview of research
      – Summary of findings
    • 3.3.2 Precipitation of Technetium-99

• 4.0 EXPERIMENTAL APPROACH/DESIGN
  – 4.1 EXPERIMENTAL APPROACH
    • 4.1.1 Tier I: Evaluate Iron Sources
    • 4.1.2 Tier II: Optimize Process Variables
    • 4.1.3 Tier III: Assess Long-term Performance
  – 4.2 VARIABLES AFFECTING PERFORMANCE
Example Work Plan

• **5.0 EQUIPMENT DESIGN AND EXPERIMENTAL PROCEDURES**
  – **5.1 DESIGN CRITERIA**
  – **5.2 PROCEDURE DESCRIPTION**
  – **5.3 EQUIPMENT DESCRIPTION**
    • 5.3.1 Bag Filter (G-004)
    • 5.3.2 Flow Control Valves
    • 5.3.3 Static Mixers (L-011 and L-002)
    • 5.3.4 Iron Filings Reactor Vessel and Reactive Media
    • 5.3.5 Acid Feed System
    • 5.3.6 Reducing Agent Feed System
    • 5.3.7 Instruments and Controls
    • 5.3.8 Piping, Valves, and Fittings
    • 5.3.9 Equipment Support Skid
  – **5.4 OPERATION AND MAINTENANCE REQUIREMENTS**
    • 5.4.1 Process Operation and Control
    • 5.4.2 System Maintenance
Example Work Plan

• 5.5 EXPERIMENTAL PROCEDURES
  – 5.5.1 Pretest Setup and Testing
  – 5.5.2 Tier 1 Testing
  – 5.5.3 Tier II Testing
  – 5.5.4 Tier III Testing

• 5.6 SAMPLING AND ANALYSIS

• 5.7 DATA MANAGEMENT

• 5.8 DATA REPORTING

• 5.9 WASTE MANAGEMENT PLAN
  – 5.9.1 References
  – 5.9.2 Definitions
  – 5.9.3 General Waste Classification and Management Procedures
  – 5.9.4 Waste Streams
  – 5.9.5 Spill Containment
  – 5.9.6 Waste Handling and Segregation
  – 5.9.7 Packaging and Marking
  – 5.9.8 Storage, Transportation, and Transfer
  – 5.9.9 Waste Classification Requirements
Example Work Plan

• REFERENCES

• APPENDIX A: TREATABILITY STUDY SAMPLING AND ANALYSIS PLAN FOR THE Fe/Pd NANO PARTICLE TREATMENT STUDY, NORTHWEST PLUME INTERIM REMEDIAL ACTION, PADUCAH GASEOUS DIFFUSION PLANT, PADUCAH, KENTUCKY

• APPENDIX B: MAINTENANCE SHEETS
• APPENDIX C: EXAMPLE LOG SHEETS FOR TREATABILITY STUDY TESTS
• APPENDIX D: HEALTH AND SAFETY PLAN ADDENDUM
• APPENDIX E: WASTE DISPOSAL FORMS AND LOGS
Technical Issues
to be addressed by Treatability Study

1. Delivery capabilities for nanoparticle introduction (in-situ)
   a. Method
   b. Optimization of delivery
2. Performance at site RGA temps – (60° F avg. vs. 70° F)
3. Performance at site groundwater velocities (1 – 3 ft/day vs 12 – 83 ft/day)
4. Reactivity of nanoparticles in-situ
   a. TCE
   b. Tc-99
5. Spatial reactivity limits relative to
   a. TCE concentration
   b. Matrix interaction
   c. Geochemical effects
Technical Issues
to be addressed by Treatability Study

6. Fate of nano particles
   a. Chemical form of Fe
   b. Chemical form of dopant
   c. Geochemical stability of Fe
   d. Geochemical stability of dopant
   e. Concentration changes relative to CWA constituents

7. Bimetallic nanoparticles & Tc-99
   a. Fate
      i. precipitate
      ii. matrix
   b. Chemical form
   c. Stability

8. General Implementability

9. Data Quality

10. Costs
Technical Issues
to be addressed by Treatability Study

How will TS Workplan Address these issues?
Laboratory/Bench Experiments

Treatment

Stabilization

$H_2O_2$ Injection

0.5'

1'

1.5'

3-in ID Tube

2.0'

2.5'

3.0'

3.5'

0.25'' Sample Port (PTFE)

0.25'' Outlet (PTFE)

RGA Gravel

Sample Water, Gravel, pH=8.8

DIUF H2O, pH=6.2

$TCE (C/C_0)$

$t (h)$

0.0 0.1 0.2 0.3 0.4 0.5 0.6

0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0

- DIUF H2O, pH=6.2
- Sample Water, Gravel, pH=8.8
Perform Ex-situ Experiments at P&T site
Perform In-Situ Experiments
Characterize Aquifer Flow Path
Characterize Aquifer Geology
Characterize Seeps
Perform Tracer Study to Confirm Flow Path(s)
Characterize Aquifer Chemistry

**Table C.18: Surveillance Geochemical Weekly**

|-------|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|

**Table C.19: Surveillance Geochemical Annual**

| Cl-   | Sulfate | Nitrate | Barium | Beryllium | Calcium | Cadmium | Calcium | Chromium | Cobalt | Copper | Iron | Lead | Magnesium | Manganese | Molybdenum | Nickel | Potassium | Silver | Sodium | Zinc | Arsenic | Mercury | Selenium | Uranium | PCBs | PCB Total | PCB-1015 | PCB-1221 | PCB-1232 | PCB-1242 | PCB-1248 | PCB-1254 | PCB-1259 | PCB-1261 |
|-------|---------|---------|--------|----------|---------|---------|---------|---------|---------|--------|--------|------|------|-----------|-----------|------------|--------|-----------|--------|--------|------|---------|---------|----------|---------|------|---------|---------|---------|---------|---------|---------|---------|

Field Parameters
- Barometric Pressure
- Specific Conductance
- Depth to water
- Dissolved Oxygen
- Eh
- pH
- Temperature
- Turbidity
- Alkalinity
- Ferric Iron
- Volatiles
- Ethene
- Ethane
- Methane

PCBs

- PCB Total
- PCB-1015
- PCB-1221
- PCB-1232
- PCB-1242
- PCB-1248
- PCB-1254
- PCB-1259
- PCB-1261