Catalytic Treatment of NDMA- and TCE-Contaminated Groundwater

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Presentation Outline

• Background
  – precious metal catalysts for treating water at ambient T & P

• Evaluation of Ni Catalysts
  – mixtures, kinetics, end products

• Bench-Scale Ni Catalyst Reactor

• Treatment of NDMA and TCE at former Air Force Plant PJKS

• Cost Comparisons

• Conclusions
Background

Treatment of dissolved contaminants using metal catalysts at ambient temperature & pressure has been studied....

• Pd or Ni catalysts for treatment of chlorinated solvents
  Lowry and Reinhard, 1999; Schrick et al., 2002; Fritsch et al., 2003

• Bimetallic Pd-ZVI or Ni-ZVI particles for treatment of chlorinated solvents
  Elliot and Zhang, 2001; Feng and Lim, 2005

• Bimetallic Ni-ZVI for treatment of NDMA
  Gui et al., 2000

• Pd catalysts for nitroso and nitro-aromatic compounds
  Figueras and Coq, 2001; Vincent and Guibal, 2004; Selvam et al., 2004

...but treatment kinetics, end products, and longevity for energetic compounds such as TNT, RDX, and NDMA is still generally unknown
Treatment Mechanism

Assume surface reaction is the limiting step

Adsorption of H$_2$:

\[ S_1 + H_2 \rightleftharpoons 2H\cdot S_1 \]

Surface reaction:

\[ 2H\cdot S_1 + TCE\cdot S_2 \rightleftharpoons DCE\cdot S_2 + H^+ + Cl^- + S_1 \]

\[ 2H\cdot S_1 + TNT\cdot S_2 \rightleftharpoons 2ADNT\cdot S_2 + O_2 + S_1 \]

Reactions occur at ambient T&P
Selection of Nickel Catalysts

- Increased longevity and reactivity compared to ZVI
- Lower costs than other precious metal catalysts
- Preliminary studies have shown that Ni catalysts are not susceptible to deactivation from sulfide
- Ni catalysts facilitate the breaking of C-C bonds
## Catalyst Properties

<table>
<thead>
<tr>
<th>Metal</th>
<th>Vendor</th>
<th>Avg. Particle Size (μm)</th>
<th>Surface Area (m²/g)</th>
<th>Misc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel Catalyst</td>
<td>Sigma-Aldrich</td>
<td>15</td>
<td>190</td>
<td>65% by weight Ni on silica-alumina</td>
</tr>
</tbody>
</table>
Compounds Treated by Ni Catalysts

- Chlorinated solvents (PCE, TCE, TCA, TCP)
- Explosives (e.g., TNT, RDX, HMX)
- NDMA
- Nitrate
- NOT: perchlorate, 1,4-dioxane, MTBE, sulfate
Batch Studies

Degradation of TNT in DI Water using Ni Catalyst

- Ring cleavage
- No accumulation of TAT
- RDX and HMX degraded more quickly
Batch Studies

Degradation of NDMA in DI Water using Ni Catalyst

• PCE and NO₃ also degraded
• NDMA generates ammonia and methane:

\[ \text{H}_3\text{C} > \text{N} - \text{N} = \text{O} \]

\[ \text{NH}_3 + \text{CH}_4 \]
Bench Scale Reactor Studies

- 3-L reactor
- Operated at ambient T&P
- Hydrogen added via diffusion through silicone tubing
- Membrane filter used to retain catalyst particles within vessel

Patent pending
Degradation of NDMA and TCE in Artificial Ground Water using Ni Catalyst

- 3-hr residence time
- No Ni detected in reactor effluent
- NDMA below detection (<60 ppb)

Reactor Data
Reactor Data

Degradation of TCE in Artificial Ground Water using Ni Catalyst

14g of TCE treated by 3g of Ni catalyst
NDMA Groundwater Plumes

Fountain Formation (Bedrock) Aquifer: Bench Scale

Alluvial Aquifer: Field Trial

Groundwater Flow Path

PJKS Boundary
### Natural Groundwater - Former AFP PJKS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDMA</td>
<td>30 μg/L</td>
</tr>
<tr>
<td>TCE</td>
<td>300 μg/L</td>
</tr>
<tr>
<td>pH</td>
<td>7.3 S.U.</td>
</tr>
<tr>
<td>Nitrate (as N)</td>
<td>9.9 mg/L</td>
</tr>
<tr>
<td>Nitrite (as N)</td>
<td>&lt;0.1 mg/L</td>
</tr>
<tr>
<td>Total iron</td>
<td>&lt;27 μg/L</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>209 mg/L</td>
</tr>
<tr>
<td>Hardness</td>
<td>450 mg/L</td>
</tr>
<tr>
<td>Total Dissolved Solids</td>
<td>1310 mg/L</td>
</tr>
</tbody>
</table>
## Treatment Effectiveness

**NDMA – Influent concentration ~ 26,000 ppt**

<table>
<thead>
<tr>
<th>Elapsed Time (days)</th>
<th>Effluent Concentration (ppt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.2</td>
</tr>
<tr>
<td>8</td>
<td>1,500</td>
</tr>
<tr>
<td>13</td>
<td>&lt;31</td>
</tr>
<tr>
<td>14</td>
<td>13</td>
</tr>
<tr>
<td>28</td>
<td>&lt;56</td>
</tr>
</tbody>
</table>

TCE: >90% removal (no DCE or VC generation)
Nitrate: > 99% removal (no nitrite generation)

Water softening prior to catalyst treatment
Evaluation of NDMA Treatment Kinetics

<table>
<thead>
<tr>
<th>Metal</th>
<th>Matrix</th>
<th>$\rho_m$ (L/h/g)</th>
<th>$\rho_a$ (L/h/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>PJKS gw</td>
<td>0.77</td>
<td>0.0041</td>
</tr>
<tr>
<td>Ni</td>
<td>DI H₂O</td>
<td>1.9</td>
<td>0.010</td>
</tr>
<tr>
<td>ZVI*</td>
<td>DI H₂O</td>
<td>7.6 x 10⁻⁶</td>
<td>4.2 x 10⁻⁶</td>
</tr>
<tr>
<td>ZVI/Ni*</td>
<td>DI H₂O</td>
<td>2.8 x 10⁻³</td>
<td>9.0 x 10⁻⁴</td>
</tr>
<tr>
<td>nZVI/Pd</td>
<td>DI H₂O</td>
<td>3.8 x 10⁻⁴</td>
<td>3.2 x 10⁻⁵</td>
</tr>
</tbody>
</table>

* Calculated based on data published by Gui et al., 2000

Preliminary studies show Ni and Pd catalysts degrade NDMA at similar rates
## Evaluation of TCE Treatment Kinetics

<table>
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<tr>
<th>Metal</th>
<th>Matrix</th>
<th>$\rho_m$ (L/h/g)</th>
<th>$\rho_a$ (L/h/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>PJKS gw</td>
<td>0.11</td>
<td>0.00058</td>
</tr>
<tr>
<td>Ni</td>
<td>DI H₂O</td>
<td>0.9</td>
<td>0.005</td>
</tr>
<tr>
<td>nNi*</td>
<td>DI H₂O</td>
<td>0.3</td>
<td>0.008</td>
</tr>
<tr>
<td>nZVI/Ni*</td>
<td>DI H₂O</td>
<td>5.8</td>
<td>0.098</td>
</tr>
<tr>
<td>ZVI**</td>
<td>DI H₂O</td>
<td>NA</td>
<td>0.0022</td>
</tr>
<tr>
<td>Pd (1%)***</td>
<td>DI H₂O</td>
<td>20</td>
<td>0.13</td>
</tr>
</tbody>
</table>

* Schrick et al., 2002  
** Miehr et al., 2004  
*** Lowry et al., 1999  
NA - Not Available
Pilot Scale Design

- 0.1 gpm system
- Will operate for at least 3 months
- Evaluate:
  - Catalyst longevity
  - Filterability
  - Effluent quality
Pilot Testing

Patent pending
Cost Evaluations

Basis: 40 gpm PJ KS groundwater

Treat **NDMA** from 1000 ppt to 1 ppt
Treat TCE from 500 ppb to 5 ppb

<table>
<thead>
<tr>
<th>Technology</th>
<th>Capital Costs</th>
<th>Operating Costs/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAC</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>UV</td>
<td>$515,000</td>
<td>$250,000</td>
</tr>
<tr>
<td>Ni Reactor (with membrane)</td>
<td>$540,000</td>
<td>$130,000</td>
</tr>
</tbody>
</table>
Cost Evaluations

Basis: 10 gpm; treat **RDX&HMX** from 1000 ppb to 10 ppb
(wash-out or pink water)

<table>
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<tr>
<th>Technology</th>
<th>Capital Costs</th>
<th>Operating Costs/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAC</td>
<td>$25,000</td>
<td>$590,000</td>
</tr>
<tr>
<td>UV</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Ni Reactor (with membrane)</td>
<td>$330,000</td>
<td>$80,000</td>
</tr>
</tbody>
</table>
Conclusions

• Nickel catalysts are able to degrade a wide range of contaminants

• Relatively fast degradation kinetics for NDMA

• Ni catalyst was able to treat NDMA-contaminated groundwater to low ppt levels

• Potential to serve as a cost-effective groundwater treatment (dependent on contaminant mixture, concentrations, and groundwater matrix)