Alkaline Hydrolysis Treatability Study for Nitroaromatic Compounds Contaminated Soil

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Agenda

• Introduction
• Technology Description
• Study Setup and Method
• Results
• Summary and Recommendations
Introduction

• The former Plum Brook Ordnance Works (PBow) was used to manufacture TNT from 1941 to 1945
• PBOW is located near Sandusky, OH
• Facility included 3 TNT manufacturing areas
• TNT production resulted in soil and groundwater contamination
• Complete decontamination was not achieved, so portions are still contaminated with nitroaromatic and other contaminants
Introduction

• The primary chemicals of concern in soil are trinitrotoluene (TNT), dinitrotoluene (DNT) isomers, amino-DNT isomers, poly aromatic hydrocarbon (PAH), poly chlorinated benzene (PCB), and lead

• TNT and DNTs exhibit the most elevated levels as high as 0.5 and 1 percent of soil mass

• Alkaline hydrolysis was selected as a preferred alternative for treating soil with high concentrations of nitroaromatics
Introduction

• As a precursor to full-scale remediation, an alkaline hydrolysis bench-scale treatability study was conducted to:
  – Determine the most effective reagent
  – Establish treatment duration
  – Determine the most effective neutralizing chemical
  – Examine effects on contaminants other than nitroaromatics

• Treatability study was conducted at Shaw’s Technology Development Laboratory (TDL) in Knoxville, TN
Plum Brook Ordnance Works
Technology Description

- Hydroxide ion (OH-) is a strong nucleophile
- It has been shown to react with TNT, DNT isomers, and their reduction products (e.g., amino-DNTs) under basic conditions
- This provides an energy source for indigenous microorganisms
- Nucleophilic substitutions of the nitro and methyl groups of TNT by hydroxide ion are the initial steps in the degradation process that result in a variety of potential reaction products
- Reaction products from alkaline hydrolysis of nitroaromatic compounds include nitrite, nitrate, ammonia, carbonate, acetate, and formate
- Following soil neutralization, the reaction products will be decomposed via multiple pathways including biodegradation
Initial Alkaline Hydrolysis Products
Study Setup and Method

• The most effective alkaline hydrolysis reagent is dependent on site-specific soil conditions
• Soil samples were collected from areas of known contamination at TNT Area C of PBOW
• Another important factor in reagent selection is cost
• Alkaline reagents used in the study included:
  – Caustic soda
  – Calcium oxide
  – Sodium carbonate
  – Portland cement
  – Lime kiln dust
  – Bed ash
Alkaline Hydrolysis Method

• Each reagent was tested individually
• Reagent effectiveness was quantified based on the differences between the initial and post-treatment nitroaromatic concentrations
• For each treatment, one kilogram of soil was mixed with the required quantity of alkaline reagent
• Required quantity of each reagent was determined by alkaline test
• Soil was mixed daily
• Each test sample was kept saturated throughout the treatment
• Samples from each test batch were collected weekly and analyzed for nitroaromatics
• Total treatment time was 43 days
Alkaline Test

pH vs Base Addition (NaOH)

Base Addition (meq/L per kg)

pH
# Alkaline Reagent Demand

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Equivalency Weight, g/eq.</th>
<th>Mass for 1 kg soil, g</th>
<th>Application Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caustic Soda (NaOH)</td>
<td>40</td>
<td>19.97</td>
<td>2.00%</td>
</tr>
<tr>
<td>Sodium Carbonate (Na$_2$CO$_3$)</td>
<td>106</td>
<td>52.92</td>
<td>5.29%</td>
</tr>
<tr>
<td>Quick Lime (CaO)</td>
<td>28</td>
<td>13.98</td>
<td>1.40%</td>
</tr>
<tr>
<td>Kiln Dust</td>
<td>50</td>
<td>24.96</td>
<td>2.50%</td>
</tr>
<tr>
<td>Bed Ash</td>
<td>60</td>
<td>29.96</td>
<td>3.00%</td>
</tr>
<tr>
<td>Portland Cement</td>
<td>60</td>
<td>29.96</td>
<td>3.00%</td>
</tr>
</tbody>
</table>
Neutralization Method

• After alkaline hydrolysis treatment, the following chemicals were tested for effectiveness of neutralization
  – anhydrous citric acid
  – ferrous sulfate
  – aluminum sulfate
  – elemental sulfur

• The demand for each reagent to reduce pH below 9 was determined by titration test

• NaOH treated soil was divided into four even portions and each portion was mixed with required naturalization reagent

• Once the neutralization step was completed, the soils were analyzed for pH, nitroaromatic explosives, PAHs, lead, and PCBs

• The analysis of PAHs, PCBs, and lead evaluated the effect of hydrolysis and neutralization on COCs other than nitroaromatic compounds
Results

- Alkaline reagents can effectively remove TNT; however, DNTs reacted differently.
- Only sodium hydroxide (NaOH) was shown to effectively degrade 2,4-DNT, however it was much less effective for 2,6-DNT.
- 6-amino-DNT was also degraded by NaOH; however, 4-amino-DNT was less reactive.
- TNT with the presence of three nitro groups which act as strong electron withdrawing groups leads to strongly reduced electron density of the aromatic ring.
- This favors the attack of bases such as OH-, resulting in rapid and complete hydrolysis of TNT.
- Significant reduction was achieved for other nitroaromatic compounds at a pH above 12.5 but with slower reduction rates.
- Among the six reagents tested, only NaOH was shown to effectively raise the pH above 12.5.
# Results

<table>
<thead>
<tr>
<th>Percent Reduction</th>
<th>NaCO₃</th>
<th>Portland Cement</th>
<th>NaOH</th>
<th>CaO</th>
<th>Bed Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNT</td>
<td>79%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>2,6-DNT</td>
<td>15%</td>
<td>28%</td>
<td>18%</td>
<td>18%</td>
<td>11%</td>
</tr>
<tr>
<td>2,4-DNT</td>
<td>20%</td>
<td>44%</td>
<td>100%</td>
<td>38%</td>
<td>39%</td>
</tr>
<tr>
<td>4-amino-2,6-DNT</td>
<td>50%</td>
<td>27%</td>
<td>64%</td>
<td>9%</td>
<td>18%</td>
</tr>
<tr>
<td>6-amino-2,4-DNT</td>
<td>-13%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
</tbody>
</table>
Alkaline Hydrolysis of TNT

- control (pH 7.8)
- NaCO3 (pH 10.6)
- Portland Cement (pH 10.5)
- NaOH (pH 12.64)
- CaO (pH 12.02)
- Bed Ash (pH 12.00)

Treatment Time vs. TNT (mg/kg)
Alkaline Hydrolysis of 2,4-DNT

The graph shows the decrease in 2,4-DNT (mg/kg) over treatment time for different pH conditions. The treatments include:

- Control (pH 7.8)
- NaCO3 (pH 10.6)
- Portland Cement (pH 10.5)
- NaOH (pH 12.64)
- CaO (pH 12.02)
- Bed Ash (pH 12.00)
Alkaline Hydrolysis of 2,6-DNT

![Graph showing the hydrolysis of 2,6-DNT under different pH conditions.](image)

- **Control (pH 7.8)**
- **NaCO3 (pH 10.6)**
- **Portland Cement (pH 10.5)**
- **NaOH (pH 12.64)**
- **CaO (pH 12.02)**
- **Bed Ash (pH 12.00)**
NaOH Alkaline Hydrolysis Treatment

TNT, DNTs, and amino-DNTs

Concentration mg/kg

- TNT
- 2,6-DNT
- 2,4-DNT
- 4-amino-2,6-DNT
- 6-amino-2,4-DNT

Day 0, 7, 14, 28, 40
# First Order Reaction Rate

<table>
<thead>
<tr>
<th>NaOH Treatment Hydrolytic Rate</th>
<th>Attenuation Rate Constant (day⁻¹)</th>
<th>Attenuation Half-life (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>0.003</td>
<td>NA</td>
</tr>
<tr>
<td>TNT</td>
<td>0.243</td>
<td>3</td>
</tr>
<tr>
<td>2,6-DNT</td>
<td>0.003</td>
<td>224</td>
</tr>
<tr>
<td>2,4-DNT</td>
<td>0.135</td>
<td>5</td>
</tr>
<tr>
<td>4Amino-2,6-DNT</td>
<td>0.024</td>
<td>28</td>
</tr>
<tr>
<td>2Amino-2,4-DNT</td>
<td>0.111</td>
<td>6</td>
</tr>
</tbody>
</table>
# Neutralization

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Day 0 Addition, g</th>
<th>Day 0 pH</th>
<th>Day 1 pH</th>
<th>Day 2 Addition, g</th>
<th>Day 2 pH</th>
<th>Day 3 Addition, g</th>
<th>Day 3 pH</th>
<th>Day 4 pH</th>
<th>Total chemical added, g</th>
<th>Dosing rate, g/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citric acid</td>
<td>2.88</td>
<td>9.62</td>
<td>9.84</td>
<td>1.44</td>
<td>8.67</td>
<td>1.00</td>
<td>8.52</td>
<td>5.32</td>
<td></td>
<td>23.65</td>
</tr>
<tr>
<td>Ferrous sulfate</td>
<td>6.26</td>
<td>9.07</td>
<td>9.17</td>
<td>1.00</td>
<td>8.5</td>
<td>0.80</td>
<td>8.3</td>
<td>8.06</td>
<td></td>
<td>35.80</td>
</tr>
<tr>
<td>Aluminum sulfate</td>
<td>5.00</td>
<td>8.76</td>
<td>8.84</td>
<td>0.50</td>
<td>8.22</td>
<td>0.50</td>
<td>8.2</td>
<td>6.00</td>
<td></td>
<td>26.66</td>
</tr>
<tr>
<td>Elemental sulfur</td>
<td>0.72</td>
<td>11.3</td>
<td>11.42</td>
<td>0</td>
<td>10.73</td>
<td>0</td>
<td>10.99</td>
<td>0.72</td>
<td></td>
<td>3.21</td>
</tr>
</tbody>
</table>
Summary and Recommendations

- Alkaline hydrolysis using sodium hydroxide (NaOH) was shown to effectively degrade TNT and 2,4-DNT; however, it was less effective for 2,6-DNT
- The hydrolysis reaction rate was significantly higher at pH above 12.5
- The NaOH dosing rate of 2% (weight based, or 500 meq/kg) used in this study maintained the soil pH above 12 for a week
- Recommend a higher initial dosing rate of 600 meq/kg NaOH be applied to avoid the cost of re-dosing in the field
- Higher temperatures are shown to enhance hydrolysis of DNTs
- Field execution during warmer summer months may enhance effectiveness of treatment
Summary and Recommendations

• In field application, acidity from natural recharge (precipitation) may eliminate or reduce the need for neutralization

• If chemical addition is necessary to lower pH, ferrous sulfate (FeSO4.7H2O) is recommended as the most effective and economic reagent at a dosing rate of 36 g/kg

• Alkaline hydrolysis and neutralization were not observed to have any measurable effect on PCB and lead

• Windrow composting has been previously implemented at PBOW to treat soil contaminated with nitroaromatics

• Although windrow composting effectively reduces TNT, and DNTs, 2-ADNT is produced as a breakdown product
Summary and Recommendations

- Presence of 2-ADNT prohibits on-site placement of treated soil.
- Use of alkaline hydrolysis for soil contaminated with TNT eliminates problems associated with residual 2-ADNT.
- Following alkaline hydrolysis treatment, windrow composting could be used as a polishing step to reduce concentrations of DNT that were not adequately reduced by the alkaline hydrolysis.