Pilot-Scale Treatment of RDX-Contaminated Soil with Zerovalent Iron

S. D. Comfort, P. J. Shea,* T. A. Machacek, and T. Satapanajaru

ABSTRACT

Soils in Technical Area 16 at Los Alamos National Laboratory (LANL) are severely contaminated from past explosives testing and research. Our objective was to conduct laboratory and pilot-scale experiments to determine if zerovalent iron (Fe⁰) could effectively transform RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) in two LANL soils that differed in physicochemical properties (Soils A and B). Laboratory tests indicated that Soil A was highly alkaline and needed to be acidified (with H₂SO₄, Al₂(SO₄)₃, or CH₃COOH) before Fe⁰ could transform RDX. Pilot-scale experiments were performed by mixing Fe⁰ and contaminated soil (70 kg), and acidifying amendments with a high-speed mixer that was a one-sixth replica of a field scale unit. Soils were kept unsaturated (soil water content = 0.20-0.34 kg kg⁻¹) and sampled with time (0-120 d). While adding CH₃COOH improved the effectiveness of Fe⁰ to remove RDX in Soil A (98% destruction), CH₃COOH had a negative effect in Soil B. We believe that this difference is a result of high concentrations of organic matter and Ba. Adding CH₃COOH to Soil B lowered pH and facilitated Ba release from BaSO₄ or BaCO₃, which decreased Fe⁰ performance by promoting flocculation of humic material on the iron. Despite problems encountered with CH₃COOH, pilot-scale treatment of Soil B (12,100 mg RDX kg⁻¹) with Fe⁰ or Fe⁰ + Al₂(SO₄)₃ showed high RDX destruction (98-99%). This indicates that RDX-contaminated soil can be remediated at the field scale with Fe⁰ and soil-specific problems (i.e., alkalinity, high organic matter or Ba) can be overcome by adjustments to the Fe⁰ treatment.

Soil and water contamination from munitions stockpiles and decommissioned production plants continues to be a serious environmental problem at many locations throughout the USA. Much of this pollution occurred from past discharges of explosive-tainted wastewater to settling ponds or impoundments, resulting in severe ground water contamination. This type of contamination is present at the Los Alamos National Laboratory (LANL, Los Alamos, NM) where ground water sampling has identified several high explosives. Ground water samples taken between 228 to 592 m verified contamination can be linked to manufacturing activities that began in the 1940's at the southwestern edge of the laboratory known as Technical Area 16 (TA-16) (Environmental Restoration Project, 2001). Operations at TA-16 included high explosives research, development, testing, and manufacturing.

Soils located in TA-16 are grossly contaminated, with some soils containing high explosive concentrations of >20% (w/w). This magnitude of contamination is excessive and indicates that precipitated or solid-phase high explosives are present in the soil matrix. When soils contain solid-phase contaminants, soil solutions become saturated and natural attenuation processes are severely inhibited. Using ¹⁴C-RDX, Singh et al. (1998a) demonstrated that the presence of solid-phase RDX in the soil matrix prevented the formation of bound (unextractable) residue. Consequently, remediating highly contaminated soils requires aggressive soil treatments that are sustainable and can continue to remove contaminants from the soil solution as the solid-phase residues dissolve.

Zerovalent iron (Fe⁰) has an excellent potential to abiotically remediate RDX-contaminated water and soil (Hundal et al., 1997; Singh et al., 1998b, 1999). Hundal et al. (1997) found Fe⁰ effectively destroyed RDX in aqueous solution and soil slurries. Aqueous batch experiments indicated that as little as 1% Fe⁰ (w/v) effectively transformed 32 mg RDX L⁻¹. Moreover, transformation products (measured as ¹⁴C activity) were water-soluble and not strongly sorbed to the iron surface. Producing non-adsorbing transformation products can be advantageous if these products are biodegradable. Singh et al. (1998b) tested this hypothesis by using ¹⁴C-RDX in static microcosms and measuring mineralization by trapping evolved ¹⁴CO₂. Results showed that a single Fe⁰ amendment increased RDX mineralization, with greater than 60% of the ¹⁴C-RDX recovered as ¹⁴CO₂. Considering carbon use efficiencies for most organic compounds, these data indicate that the Fe⁰-induced transformation products of RDX are highly biodegradable. Subsequent studies (Wildman and Alvarez, 2001; Oh et al., 2001; Oh and Alvarez, 2002) further support synergistic effects between Fe⁰ treatment and enhanced biological degradation of RDX.

Although Hundal et al. (1997) observed that Fe⁰ effectively transformed RDX in soil slurries, working with soil slurries is problematic for several reasons. The equipment required for continuous agitation is expensive and limits the volume of soil that can be treated at any given time. Dewatering of treated soil is also required. A desirable alternative to slurry treatment would be on-site treatment in soil windrows. Using soil windrows allows much greater volumes of soil to be treated and is constrained by only the size of the windrows and acreage available.

Initial work with RDX-contaminated soil from the

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Published in J. Environ. Qual. 32:1717–1725 (2003). © ASA, CSSA, SSSA
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Abbreviations: Fe⁰, zerovalent iron; LANL, Los Alamos National Laboratory.
soil microcosms (Singh et al., 1998b). The effectiveness of Fe²⁺ treatment of RDX in static soil microcosms (Singh et al., 1998b) indicated that Fe²⁺ could be effective in static unsaturated soil microcosms (Singh et al., 1998b). The effectiveness of Fe²⁺ in transforming RDX in unsaturated soils opened the door for field-scale applications. Using zerovalent iron at the field scale requires machinery that can thoroughly mix the iron and other amendments into the soil matrix. The Microenfractionator (H & H Eco Systems, North Bonneville, WA) is the trade name of a soil mixing implement that can treat large volumes of soil (400–1000 m³). This machinery can also simultaneously spray liquids into the soil windrows during mixing to achieve any desired water content.

Our objective was to combine Fe²⁺ treatment of RDX-contaminated soil with the machinery required for field-scale use. This was accomplished by conducting batch experiments in the laboratory to optimize Fe²⁺ applications and then testing these treatments at the pilot scale with a table-top version of the field-scale mixer (Fig. 1). Two high explosives-contaminated soils, indicative of the contamination found at LANL TA-16, were used for pilot-scale testing.

**Laboratory Experiments**

Analysis of Soil A revealed an unexpected high pH (>9.9). Efforts were made to lower the pH of the soil slurry with acetic acid and determine the effectiveness of Fe²⁺. Five grams of the oven-dry soil was mixed with various amounts of 5% (w/v) acetic acid (total volume of acetic acid + H₂O = 11.75 mL) and allowed to equilibrate for 20 h. Solution pH was then determined with a meter and probe calibrated before each use with standard buffer solutions (Accumet, Fisher Scientific).

A separate experiment compared the effects of acids (HCl vs. CH₃COOH) on Fe²⁺-mediated destruction of RDX in aqueous solutions and soil washings under pH-stat conditions. The pH-stat experiments were conducted with a Metrohm Titrino (Model 718S; Brinkmann Instruments, Westbury, NY). Both the aqueous solutions of RDX (initial concentration = 20 mg L⁻¹) and aqueous soil washing of Soil A (concentration = 40 mg RDX L⁻¹) were treated with 1% (w/v) Fisher Scientific Fe²⁺. The pH was held at 4.5 with HCl or CH₃COOH and changes in solution RDX concentrations were determined at 2, 4, 8, and 24 h.

The effect of acidifying amendments on RDX destruction by Fe²⁺ in static soil microcosms was also investigated. In this experiment, triplicate samples from Soil A were incubated in Teflon centrifuge tubes at 30°C for 17 d at a gravimetric soil water content of 0.33 kg kg⁻¹. Treatments included: (i) Fe²⁺ + H₂O₂; (ii) Fe²⁺ + H₂SO₄; (iii) Fe²⁺ + Al₂(SO₄)₃; and (iv) Fe²⁺ + CH₃COOH. Controls (no Fe²⁺) were also included for each amendment [i.e., H₂O, H₂SO₄, Al₂(SO₄)₃, and CH₃COOH]. To increase soil water content to 0.33 kg kg⁻¹, 3 g of Soil A was

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**Fig. 1. Photographs of Microenfractionators. (A) Pilot-scale table-top unit (one-sixth scale of the field unit). (B) Field-scale Microenfractionator going through soil windrows; dimensions of the windrow are: base = 5.2 m, height = 1.98 m.**

**MATERIALS AND METHODS**

**Chemical Reagents and Soils**

Technical-grade RDX was obtained from the U.S. Biomedical Research and Development Laboratory (Frederick, MD). Analytical standards of RDX were obtained from the Indian Head Division, Naval Warfare Center (Indian Head, MD) and AccuStandard (New Haven, CT). Two forms of Fe²⁺ were used. Depregated Fe²⁺ (40-mesh) was obtained from Fisher Scientific (Pittsburgh, PA). Analysis of similar iron (Fisher Scientific) by an outside laboratory determined a surface area of 1.87 m² g⁻¹ using the Brunauer–Emmett–Teller (BET) method. The second Fe²⁺ source was unannealed iron from Peerless Metal Powders (Detroit, MI). This iron had a specific surface area of 2.55 m² g⁻¹ (Micromeritics, Norcross, GA). Commercial-grade Al₂(SO₄)₃ and glacial acetic acid were used as received.

Two LANL soils were used for experimentation (herein-after referred to as Soils A and B). Soil A was used in the first batch and pilot-scale experiment was obtained from the center of a discharge pond approximately 100 m east of Building TA-16-260 at LANL TA-16. Soil B was from the same outwash pond but was mixed with material from the sides of the pond and discharge areas.

Soil A was sent to the University of Nebraska in a 208-L metal drum. Physical handling involved spreading the soil onto the stainless steel table of the pilot-scale mixer (Fig. 1A) and removing large stones (approximately >5 cm in diameter). A table-top fan was used to gently pass air across the soil surface to facilitate air-drying overnight. We then ran the Microenfractionator through the soil four times. The pilot-scale Microenfractionator is a one-sixth replica of the field-scale unit (Fig. 1B) and can mix 70 to 100 kg of windrowed soil in one pass. Much of the larger consolidated soil not removed by hand was broken apart and pulverized by the Microenfractionator, producing a homogeneous soil that was easy to handle. Once the soil had been mixed, it was divided into two piles and placed in plastic bins with covers. Five soil samples from each plastic bin were taken and analyzed for RDX. An additional subsample was sieved (<2 mm) before RDX analysis. Representative subsamples from each soil were also sent to Midwest Laboratories (Omaha, NE) for characterization (Table 1). Soil B was handled similarly using the same pilot-scale mixer but experiments were performed on-site at LANL.
Soil property & Soil A & Soil B 
--- & --- & --- 
RDX, mg kg\(^{-1}\) & 2700 (1400\(^{t}\)) & 12100 (816) 
Peroxide, % & 0.6 (0.1) & 3.0 (0.2) 
Peroxide, % & 9.9 (0.1) & 7.0 (0.0) 
Acid soluble carbon content, cmol kg\(^{-1}\) & 28.0 (4.0) & 6.7 (0.3) 
Nitrates, mg kg\(^{-1}\) & 239.0 (36.3) & 17.0 (1.1) 
Potassium, mg kg\(^{-1}\) & 15.3 (0.4) & ND\(^{t}\) 
Magnesium, mg kg\(^{-1}\) & 522.0 (15.6) & 171.0 (14.7) 
Calcium, mg kg\(^{-1}\) & 26.0 (2.8) & 100.0 (15.0) 
Sodium, mg kg\(^{-1}\) & 3223.0 (895.9) & 1070.0 (33.5) 
Sulfur, mg kg\(^{-1}\) & 580.0 (15.6) & 20.0 (1.0) 
Sodium/ potassium ratio & 28.0 (2.8) & 14.0 (1.0) 
Iron (DTPA), mg kg\(^{-1}\) & 170.0 (7.5) & 14.0 (1.0) 
Manganese (DTPA), mg kg\(^{-1}\) & 6.0 (0.1) & 2.0 (0.1) 
Copper (DTPA), mg kg\(^{-1}\) & 5.1 (0.9) & 0.5 (0.1) 
Barium, mg kg\(^{-1}\) & 1.48 & 3720 
Sand, % & 64.0 (2.8) & 60.0 (4.0) 
Silt, % & 27.0 (1.4) & 30.0 (4.0) 
Clay, % & 9.0 (1.0) & 10.0 (0.0) 

\(^{t}\) Mean and sample standard deviation. 
\(^{\dagger}\) Determined. 
\(\ddagger\) Diethylenetriaminepentaacetic acid (DTPA)-extractable. 
\(\ddagger\) Acetate in water (5%) -extractable (single measurement). 

Pilot-Scale Experiments

Study I (Soil A)

Pilot-scale experiments were conducted with 70 kg (oven-dry) soil. The initial study was conducted with Soil A using two treatments: Fe\(^{0}\) + CH\(_3\)COOH and a control (H\(_2\)O only). The soil was placed on the stainless steel table of the mixer (Fig. 1) and Fe\(^{0}\) added to a V-shaped indentation along the top ridge of the soil windrow. Iron (3.5 kg) was added to the 70 kg of soil to yield a concentration of 5% (w/w). The soil and iron were then mixed by the Microenfractionator three times. The Fe\(^{0}\)-amended soil was evenly divided into five 16.25-kg volumes and placed in layers in a large plastic bin where 2.65 L of water-CH\(_3\)COOH was sprinkled onto the soil.

Batch Experiments Using Witherite and Acetic Acid

When acetic acid was added as an amendment, differences in RDX destruction were observed between Soil A and B (see Results). Acetic acid extracts of Soil A and B revealed large differences in Ba concentrations. Subsequent batch experiments were conducted to determine the effects of Ba and acetic acid on Fe\(^{0}\) performance. These included: (i) control (H\(_2\)O only); (ii) Fe\(^{0}\); (iii) Fe\(^{0}\) + CH\(_3\)COOH; and (iv) Fe\(^{0}\) + CH\(_3\)COOH + Al\(_2\)(SO\(_4\))\(_3\). In this experiment, Fe\(^{0}\) (5%, w/w) and acetic acid (1.05 L per 70 kg) were added at the same rate used in Study I and Al\(_2\)(SO\(_4\))\(_3\) was added at 2.0% (w/w). Soil samples were taken at 0.5 h and then 10, 20, 40, 60, 80, 100, and 120 d after treatment. The soil water content was increased to 0.34 kg kg\(^{-1}\) in Soil B and the soil bins were incubated in the dark at approximately 28°C.

Chemical and Physical Analyses

RDX was extracted from soil (3 g) with 15 mL CH\(_3\)CN by sonicating for 18 h at 30°C, centrifuging at 5000 × g, removing the supernatant, and centrifuging (12 000 × g) before analy-
ing with high performance liquid chromatography (HPLC). Acetonitrile extracts (10–25 μL) were injected onto a Keystone Betasil NE(R) or NA column (Keystone Scientific, Bellefonte, PA) with an isocratic (50:50 or 30:70) mixture of methanol and H2O at a flow rate of 1.0 mL min⁻¹ and quantified spectrophotometrically at 220 or 254 nm. In the second pilot-scale experiment (Study II, Soil B), TNT was also quantified using the same HPLC procedure.

Acetic acid extracts of Soil A and B were prepared by shaking 25 g soil with 50 mL of CH₃COOH (5%, v/v) for 24 h and centrifuging at 5000 × g for 30 min. The supernatant was analyzed for Ba by inductively coupled plasma (ICP) (Midwest Laboratories).

RESULTS

Soil Analysis

Analysis of Soil A revealed an average RDX concentration of 2700 ± 140 mg kg⁻¹ (n = 10) following mixing (Table 1). After passing the mixed soil through a 2-mm sieve, the sieved soil had a RDX concentration of 3150 ± 84.4 mg kg⁻¹ (n = 4) indicating that contamination is mainly associated with the finer soil fraction. Additional chemical analyses revealed that Soil A was very high in Na, Ca, and K. A discrepancy was noted in soil pH between the commercial laboratory (pH 9.9) and our laboratory (pH 11.1, n = 5). These very high pH values are probably a result of the high Na concentration. Based on the sodium adsorption ratio (SAR = 15.3), Soil A would be classified as either sodic or sodic-saline (the electrical conductivity of a paste extract was not measured).

The unexpected high pH of Soil A was in part the impetus for a second study using Soil B. Analysis of Soil B revealed a near-neutral pH with lower K, Ca, and Na concentrations but considerably greater RDX contamination (12100 ± 814 mg kg⁻¹). Soil B also contained more organic matter (Table 1).

Laboratory Experiments

Initial efforts to remove RDX from Soil A with Fe⁶ failed and it was believed that the high soil pH was rapidly passivating the Fe⁶ and reducing electron transfer from the iron surface. We hypothesized that the soil pH needed to be lowered before Fe⁶ would be effective. To accomplish this, various concentrations of acetic acid were added to a soil slurry. Following 20 h of equilibration, the initial pH of the slurry declined from 11.1 (no CH₃COOH added) to 4.7 (2.13% CH₃COOH, v/v). To determine how lowering pH would affect RDX destruction by Fe⁶, we used a pH-stat to maintain constant pH (4.5) and determined destruction kinetics. We observed that for both pure aqueous solutions and aqueous extracts of Soil A (soil washings), RDX destruction was faster when CH₃COOH was used to control pH rather than the mineral acid HCl (Fig. 2).

Additional acidifying amendments were then evaluated to determine RDX destruction in static soil microcosms incubated for 17 d. This experiment demonstrated that the acidifying amendments improved the effectiveness of Fe⁶ to remove RDX from Soil A (Table 2). The

![Image](https://example.com/image)

**Fig. 2.** Comparison of RDX destruction rates at constant pH 4.5 using HCl and CH₃COOH. Fisher Scientific Fe⁶ was used at a rate of 1% (w/v). Aqueous soil washing was prepared from Soil A by creating a 20% (w/v) soil slurry, removing the soil, and treating the supernatant. Soil extract Cₐ = approximately 40 mg RDX L⁻¹; pure solution Cₐ = approximately 20 mg RDX L⁻¹.

RDX destruction with CH₃COOH and Al₃(SO₄)₃ was 99%. Controls verified that these acidifying solutions had little to no effect on RDX concentrations in the absence of Fe⁶.

Pilot-Scale Experiments

Study I (Soil A)

Temporal changes in soil RDX concentrations revealed RDX destruction in both treatments (control and Fe⁶-CH₃COOH, Table 3). At each sampling, less RDX was present in the Fe⁶-CH₃COOH treatment than the control. At 110 d, 50 mg RDX kg⁻¹ remained in the Fe⁶-treated soil (98% destruction) versus 313 mg kg⁻¹ in the control. Monitoring pH revealed that the CH₃COOH was somewhat effective in lowering the pH to <9 while the control soil pH remained ≥ 10.5 (Table 3).

Loss of RDX in the control treatment was unexpected and probably resulted from the unusually high soil pH observed throughout most of the experiment (pH 10.4–11.1; Table 3). RDX is known to undergo alkaline hydrolysis through biomolecular elimination of HNO₂, leading to a cyclohexenyl derivative intermediate (Hoff-sommer et al., 1977; Crote and Okamoto, 1979). Further decomposition can lead to HCN, HNO₂, NO₃, HCHO, and N₂O (Hayari, 2000). Heilmann et al. (1996) also demonstrated rapid RDX hydrolysis (within 300 min) in solution at pH 11 and 50°C.

Monitoring soil water status during the experiment revealed that gravimetric water content was maintained between 0.25 and 0.30 kg kg⁻¹ (data not shown). It is noteworthy that treatments were initiated by mixing the soil with the high-speed mixer but no mixing was performed when additional H₂O and/or CH₃COOH was added. Rather, the solutions were added to the top of the soil and allowed to infiltrate. In the field, this
Table 2. Batch experiments demonstrating changes in RDX concentrations in Soil A following treatment with Fe° and acidifying amendments. Static microcosms were incubated 17 d at 0.30 kg kg\(^{-1}\) and 30°C.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>RDX concentration mg kg(^{-1})</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial concentration (C(_0))</td>
<td>2800 (101)‡</td>
<td></td>
</tr>
<tr>
<td>Iron treatments</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe° + H(_2)O</td>
<td>2240 (621)</td>
<td>22</td>
</tr>
<tr>
<td>Fe° + H(_2)SO(_4)</td>
<td>520 (190)</td>
<td>82</td>
</tr>
<tr>
<td>Fe° + Al(_2)(SO(_4))</td>
<td>21 (1.5)</td>
<td>99</td>
</tr>
<tr>
<td>Fe° + CH(_3)COOH</td>
<td>37 (24)</td>
<td>99</td>
</tr>
<tr>
<td>Controls</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(_2)O (pH = 5.33)</td>
<td>2520 (147)</td>
<td>12</td>
</tr>
<tr>
<td>H(_2)SO(_4) (pH = 2.62)</td>
<td>2870 (192)</td>
<td>0</td>
</tr>
<tr>
<td>Al(_2)(SO(_4)) (pH = 3.46)</td>
<td>2560 (175)</td>
<td>0</td>
</tr>
<tr>
<td>CH(_3)COOH (pH = 2.29)</td>
<td>2740 (136)</td>
<td>4</td>
</tr>
</tbody>
</table>

† Percent reduction = \([1 - (\text{RDX concentration/initial RDX concentration})] \times 100\).
‡ Values in parentheses represent sample standard deviations (n = 4).
§ pH values of solutions added to Soil A samples.

procedure would be recommended to minimize aeration of the soil windrow and accelerated aging (passivation) of the Fe°.

One qualitative difference between the treatments was the abundant growth of fungal hyphae on the Fe°-CH\(_3\)COOH-treated soil. This occurred within a few days after treatment and continued throughout the course of the experiment. No fungal growth was observed on the control soil.

We also noticed that the Fe°-CH\(_3\)COOH-treated soil became more dense and difficult to probe for sampling. Because of the added acidity, some of the carbonates dissolved and effervesced following CH\(_3\)COOH addition. Consolidation and cementation of the precipitates probably resulted in a denser soil matrix. Additional mixing with the Microfractionator following treatment would probably eliminate this problem.

Study II (Soil B)

High explosive concentrations in the control treatments (control and control + H\(_2\)O) indicated fairly constant RDX concentrations throughout the experiment with an average RDX concentration of 12.300 ± 634 mg kg\(^{-1}\) (Table 4). TNT concentrations, however, slowly declined with time indicating TNT degradation in the control. The variability and fluctuation in RDX concentrations is a function of the heterogeneity of contamination, which included solid-phase RDX intermixed throughout the soil matrix. Comparing results between the controls and the Fe°-based treatments revealed that TNT and some RDX were transformed shortly after mixing (t = 0.5 h; Table 4). This demonstrates that abiotic transformations induced by Fe° can occur fairly quickly even in static, unsaturated soils. Moreover, relative declines in TNT concentration versus RDX immediately after Fe° treatment support that TNT is a preferential electron acceptor and more prone to reductive transformation by Fe°.

Acidifying amendments were more effective in lowering and maintaining the pH of Soil B. The pH of the control ranged from 6.6 to 7.0 while the addition of Fe° increased pH from 7.2 (t = 0.5 h) to 8.6 (t = 120 d). Adding Fe° + CH\(_3\)COOH decreased the pH, which remained low throughout the incubation [pH 4.5 (t = 0.5 h), 5.0 (t = 120 d)]. Similar results were observed with Fe° + Al\(_2\)(SO\(_4\)) (4.8 (t = 0.5 h) to 6.3 (t = 120 d)) and Fe° + CH\(_3\)COOH + Al\(_2\)(SO\(_4\)) (3.9 (t = 0.5 h), 4.8 (t = 120 d)). Previous research has shown that RDX solubility is essentially constant between pH 4.2 and 6.2 (Lynch et al, 2001). Results from the second pilot-scale experiment were not consistent with the first study (using Soil A) or laboratory batch studies. Using Soil B, we found that the largest destruction of RDX (and TNT) occurred with the Fe°-only and Fe° + Al\(_2\)(SO\(_4\)) treatments. Using Fe° alone, RDX concentrations decreased to 540 mg kg\(^{-1}\) (t = 120 d) resulting in a 96% reduction from the average initial concentration of the control (12.100 mg RDX kg\(^{-1}\)). The Fe° + Al\(_2\)(SO\(_4\)) treatment was also equally effective and produced the lowest average concentration after 120 d (210 mg kg\(^{-1}\), 98% decline; Table 4). Adding CH\(_3\)COOH, which had a positive effect on Fe°-induced RDX destruction in solution (Fig. 2) and static soil microcosms (Soil A, Table 2), negatively affected RDX and TNT loss compared with Fe° alone in the second pilot-scale experiment (Table 4). When CH\(_3\)COOH was added, decreases in RDX and TNT concentrations occurred only within the first 10 d. This is in contrast to the Fe° and Fe° + Al\(_2\)(SO\(_4\)) treatments where RDX loss continued to decline after 20 d. While a beneficial effect was observed by adding Al\(_2\)(SO\(_4\)), this effect was negated when CH\(_3\)COOH was also added.

To determine why acetic acid had an inhibitory effect on Fe° performance in Soil B, an acetic acid extract of both soils was analyzed by inductively coupled plasma. This analysis revealed large differences in Ba concentra-

Table 3. Changes in RDX and pH following pilot-scale treatment of Soil A.†

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Days after application</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Control (H(_2)O only)</td>
<td>2230 (222)‡</td>
</tr>
<tr>
<td>Fe° + CH(_3)COOH</td>
<td>2310 (222)</td>
</tr>
<tr>
<td>Control (H(_2)O only)</td>
<td>10.35</td>
</tr>
<tr>
<td>Fe° + CH(_3)COOH</td>
<td>9.90</td>
</tr>
</tbody>
</table>

† Initial treatments were added at Day 0. Soil was incubated at 30°C and soil water content was maintained between 0.25 and 0.30 kg kg\(^{-1}\).
‡ Values in parentheses indicate standard deviation of subsample mean.
Table 4. Changes in RDX and TNT concentrations following pilot-scale treatment of Soil B with zero-valent iron.

<table>
<thead>
<tr>
<th>Soil treatment</th>
<th>High explosive</th>
<th>Time after application</th>
<th>mg kg$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5 h</td>
<td>10 d</td>
<td>20 d</td>
</tr>
<tr>
<td>Control (dry soil)</td>
<td>RDX 10 940 (1 023)</td>
<td>12 700 (512)</td>
<td>12 580 (2 285)</td>
</tr>
<tr>
<td>Control (H$_2$O only)</td>
<td>TNT 844 (133)</td>
<td>810 (84)</td>
<td>762 (233)</td>
</tr>
<tr>
<td>Fe$^2+$</td>
<td>RDX 12 700 (352)</td>
<td>12 500 (633)</td>
<td>12 000 (320)</td>
</tr>
<tr>
<td></td>
<td>TNT 960 (26)</td>
<td>778 (72)</td>
<td>750 (54)</td>
</tr>
<tr>
<td>Fe$^6+$</td>
<td>RDX 9 840 (735)</td>
<td>3 194 (3 684)</td>
<td>1 408 (1 590)</td>
</tr>
<tr>
<td></td>
<td>TNT 150 (53)</td>
<td>40 (40)</td>
<td>28 (2)</td>
</tr>
<tr>
<td>Fe$^6+$ + CH$_3$COOH</td>
<td>RDX 7 920 (413)</td>
<td>3 180 (416)</td>
<td>3 950 (2 460)</td>
</tr>
<tr>
<td></td>
<td>TNT 81 (12)</td>
<td>20 (8)</td>
<td>41 (24)</td>
</tr>
<tr>
<td>Fe$^6+$ + Al$_2$(SO$_4$)</td>
<td>RDX 10 200 (598)</td>
<td>1 960 (259)</td>
<td>210 (210)</td>
</tr>
<tr>
<td></td>
<td>TNT 370 (22)</td>
<td>15 (2)</td>
<td>20 (4)</td>
</tr>
<tr>
<td>Fe$^6+$ + CH$_3$COOH +</td>
<td>RDX 9 820 (387)</td>
<td>5 430 (977)</td>
<td>3 439 (1 373)</td>
</tr>
<tr>
<td>Al$_2$(SO$_4$)</td>
<td>TNT 180 (18)</td>
<td>45 (18)</td>
<td>32 (14)</td>
</tr>
</tbody>
</table>

$^1$ Values in parentheses indicate standard deviation of subsample mean.
$^2$ Not determined.
Fig. 3. RDX destruction by Fe⁶ treatments in an aqueous matrix and humic acid (50 mg L⁻¹) matrix. Witherite and CH₃COOH were added to the matrices as indicated treatments in Cycles 1 and 2 but not in Cycle 3.

appears to be more than simple acidification of the RDX solution. Studies have shown that the reduction of compounds that have a weak interaction with the iron surface can be blocked by strong ligands (e.g., catechol, ascorbate, citrate) occupying surface sites (Cornell and Schwertmann, 1979; Johnson et al., 1998). The surface complexation model suggested by Scherer et al. (1999) indicates that if ligand competition is operative, destruction kinetics should rapidly decline toward zero as ligand concentration increases. However, this was not observed for CCl₄ dechlorination by Fe⁶ in the presence of acetate (Johnson et al., 1998) nor in our experiments (RDX destruction increased). Because our experimental units were open to the atmosphere, formation of Fe(III) oxides was inevitable. Considering that the acetate ligand will complex with Fe⁷⁺ (log K₁ = 3.2, log K₂ = 6.1, log K₃ = 8.3; Dean, 1992), this complex appears more resistant to oxidation. Visual evidence for this was observed in Fe⁶–RDX–CH₃COOH mixtures where less Fe(III) species (i.e., rusting) occurred. High concentrations of CH₃COOH were used in our treatments; high concentrations of organic acids are known to inhibit crystallization of Fe(III) oxides (Cornell and Schwertmann, 1979). Acetic acid will also inhibit precipitation of Fe(OH)₃ and may promote formation of electron-conducting magnetite (Fe₃[Fe⁷Fe⁷O₁₄]₄) on the iron surface through reaction of Fe⁷⁺ with amorphous Fe (hydro)oxides or γ-Fe₂O₃(OH) (Tamaura et al., 1981, 1984). Unlike citrate and phosphate, acetate does not appear to suppress the crystal growth of magnetite (Sidhu et al., 1978). Thus by slowing down ferric oxyhydroxide formation on the iron surface and promoting magnetite formation, acetate would indirectly facilitate electron transfer from the iron. In addition, the increased microbial activity of Soil A after acetic acid addition (evidenced by fungal growth) may have further promoted RDX degradation.

Although Soil B had a high concentration of Ba (BaSO₄ or BaCO₃), it is unlikely that Ba alone reduced the effectiveness of the Fe⁶ treatment because RDX destruction increased when witherite was added with
Fe\(^6\) in an aqueous solution. Adding BaCO\(_3\) may have promoted the carbonate form of green rust and slowed down Fe\(^2\) corrosion because Ba does not readily hydrolyze (log \(K = 0.5\); Dzombak and Morel, 1990, p. 105, 187) and adsorbs to the \(>\text{FeO}\)H surface as \(>\text{FeO}\)HBa\(^2+\) (log \(K = 5.46\); Dzombak and Morel, 1990, p. 105, 187). Adding acetic acid promoted dissolution of wiheterite and saturation of the iron surface with Ba. When acetic acid was no longer present in the matrix (Cycle 3), the wiheterite + \(\text{CH}_3\text{COOH}\) treatment removed the least RDX. This residual effect may be due to passivation of the iron surface.

Our solution experiments indicate that RDX destruction by Fe\(^6\) was greater in the humic acid matrix than in aqueous solution (Cycle 1). Weber (1996) similarly observed that a Suwannee humic acid isolate acted as an electron transfer mediator in Fe\(^6\) treatment of 4-aminoazobenzene. This mediating effect, however, may be compound specific because natural organic matter (NOM) had an inhibiting effect on Fe\(^2\)-mediated reduction of CCl\(_4\) (Tratnyek et al., 2001). In our experiments, Fe\(^6\) was less effective when BaCO\(_3\) was added to the humic acid matrix. Considering that Ba is commonly used to determine soil acidity by displacing hydrogen on organic functional groups and results in flocculation of organic matter, we believe an indirect effect of high Ba in Soil B was precipitation of humic material at or near the iron surface, resulting in physical blocking and hindrance of electron transfer. Competition for surface sites on the iron may also be occurring, as observed between trichloroethylene and NOM (Tratnyek et al., 2001).

Because of the equilibrium between the soil solution and solid or crystalline phase, remediating soils containing solid-phase RDX will not only require treatments that demonstrate rapid destruction kinetics in solution but also those that continue to remove RDX as the solid phase dissolves. Dissolution of solid-phase RDX will depend on temperature and surface area (Lynch et al., 2002), crystal size and concentration gradients (Stumm and Morgan, 1996), as well as soil water content and saturation-desaturation cycles. Consequently, days to months may be required for all of the solid-phase RDX to enter the soil solution. For Fe\(^6\) to be effective, it must continue to act as a reductant and engage in electron transfer reactions. Our experiments demonstrated that acetic acid greatly facilitated Fe\(^2\)-mediated RDX destruction but this destruction rate may not be sustainable in all soils. Based on differing results with Soils A and B, we found that soil physicochemical properties can profoundly affect Fe\(^2\) performance, necessitating site-specific soil characterization before treatment. Alkaline soils such as Soil A will probably require pH adjustment whereas precipitation of humic material must be minimized in soils containing high concentrations of humic matter and/or Ba (as in Soil B). Moreover, variability arising from the nonuniform deposition of explosives and soil heterogeneity must be considered when treating munitions-contaminated soils.

ACKNOWLEDGMENTS

We thank Dr. Jasbir Singh for conducting some of the initial experiments. This research was supported by Sandia National Laboratories, the University of Nebraska-Lincoln (UNL) School of Natural Resources Sciences, and the UNL Water Center. We appreciate the technical assistance of Ron Horn and Steve Funk (H & H Eto Systems). Paper no. 13983 is a contribution of Agric. Res. Div. Projects NER-40-002 and -019.

REFERENCES


Sidhu, P.S., R.J. Gilkes, and A.M. Posner. 1978. The synthesis and