Organic Compounds in the Environment

Remediating Munitions-Contaminated Soil with Zerovalent Iron and Cationic Surfactants

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

ABSTRACT
Sols contaminated from military operations often contain mixtures of HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), and TNT (2,4,6-trinitrotoluene) rather than a single explosive. Differences among explosives in solubility and reactivity make developing a single remediation treatment difficult. When Fe⁰ was used to treat a munitions-contaminated soil, we observed high rates of destruction for RDX and TNT (98%) but not HMX. Our objective was to determine if HMX destruction by Fe⁰ could be enhanced by increasing HMX solubility by physical (temperature) or chemical (surfactants) means. To determine electron acceptor preference, we treated RDX and HMX with Fe⁰ in homogeneous solutions and binary mixtures. Increasing aqueous temperature (20 to 55°C) increased HMX solubility (2 to 22 mg L⁻¹) but did not increase destruction by Fe⁰ in a contaminated soil slurry that also contained RDX and TNT. Batch experiments using equal molar concentrations of RDX and HMX demonstrated that RDX was preferentially reduced over HMX by Fe⁰. By testing various surfactants, we found that the cationic surfactants (HDTMA [hexadecyltrimethylammonium bromide], didecyl, and didodecyl) were most effective in increasing HMX concentration in solution. Didecyl and HDTMA were also found to be highly effective in facilitating the transformation of HMX by Fe⁰. Using HDTMA or didecyl solutions (3%, w/v) containing solid-phase HMX, we observed that 100% of the added HMX was transformed by Fe⁰ in the didecyl matrix and 60% in the HDTMA matrix. These results indicate that cationic surfactants can increase HMX solubility and facilitate Fe⁰-mediated transformation kinetics but HMX destruction rates will be slowed when RDX is present.

Past site assessments of munition production facilities have determined that soils contaminated from military operations often contain mixtures of RDX, HMX, and TNT rather than a single explosive. Two reasons for this heterogeneity include the manufacturing practice of blending two or more explosives for specific compositions (e.g., octol contains approximately 75% TNT and 25% RDX; Akhavan, 1998) and synthesis impurities. The two grades of HMX used for military purposes contain between 2 and 7% (w/w) RDX. Likewise, the Bachmann synthesis of RDX (Bachmann and Sheehan, 1949) commonly results in HMX impurities of 8 to 12% (Fedoroff and Sheffield, 1966). Consequently, a remediation treatment designed and optimized for a single high explosive may have little practical value unless it is robust enough to remediate multiple energetics.

Abbreviations: CMC, critical micelle concentration; HDTMA, hexadecyltrimethylammonium bromide; HE, high explosives; HMX, hexahydro-1,3,5-trinitro-1,3,5,7-tetrazocine; HPLC, high performance liquid chromatography; LANL, Los Alamos National Laboratory; LUMO, lowest unoccupied molecular orbital; RDX, hexahydro-1,3,5-trinitro-1,3,5-triazine; TNT, 2,4,6-trinitrotoluene.

Although HMX and RDX are similar in that both consist of multiples of the CH₂ = N-NO₂ monomer unit, these polynitramines differ with HMX being less water soluble (approximately 5 mg L⁻¹) than RDX (40 mg L⁻¹) and chemically more stable and resistant to attack by strong base (Akhavan, 1998). Recent bio-degradation studies have also confirmed that HMX is more resistant to microbial attack than RDX (Shen et al., 2000).

Past research has demonstrated that zerovalent iron (Fe⁰) can abiotically degrade RDX and TNT in soil and water under laboratory conditions (Hundal et al., 1997; Singh et al., 1998, 1999). In an attempt to scale-up this treatment technology, we conducted pilot-scale experiments (70 kg soil) with Fe⁰ and treated contaminated soil from an outwash pond that had previously been used for munitions wastewater disposal (Los Alamos National Laboratory, NM). Zerovalent iron effectively removed 98% of the RDX and TNT within 120 d (Comfort et al., 2003). Because HMX is considered less toxic than RDX (McLellian et al., 1988a, 1988b), it was not initially considered a contaminant of concern. Further soil analysis, however, revealed that HMX was present at very high concentrations (>40 000 mg kg⁻¹) and that this energetic compound was not effectively destroyed by the Fe⁰ treatment.

Our objective was to determine if HMX destruction by Fe⁰ could be enhanced by increasing HMX solubility by physical (temperature) or chemical (surfactants) means. We accomplished this by increasing temperature or adding surfactants to increase HMX solubility. To determine how mixtures of explosives would affect destruction rates, we compared Fe⁰-mediated destruction kinetics of RDX and HMX in homogeneous solutions versus binary mixtures.

MATERIALS AND METHODS
Chemical Reagents and Soils

Technical-grade RDX and TNT were obtained from the U.S. Biomedical Research and Development Laboratory (Frederick, MD); HMX was obtained from Sandia National Laboratories (Albuquerque, NM). Analytical standards of all explosives were obtained from the Indian Head Division, Naval Warfare Center (Indian Head, MD); additional analytical...
RDX was obtained from AccuStandard (New Haven, CT). Surfactants (Table 1) were obtained from Aldrich (Milwaukee, WI). Two forms of Fe⁰ (Peerless Metal Powders, Detroit, MI) were used in batch experiments: annealed (heat treated under N₂ and H₂ atmosphere) and unannealed iron. Specific surface areas were 0.134 m² g⁻¹ (annealed Fe⁰) and 2.55 m² g⁻¹ (unannealed Fe⁰) (Micromeritics, Norcross, GA).

Soil used for experimentation was collected from the southwestern sector of the Los Alamos National Laboratory (LANL) (Los Alamos, NM) known as Technical Area 16 (TA-16). Operations conducted at TA-16 included high explosives research, development, testing, and manufacturing. Soil samples were collected from the middle and sides of a discharge pond that had been previously used for munitions wastewater disposal. Representative subsamples (n = 3) of the LANL soil were characterized by Midwest Laboratories (Omaha, NE) for particle size analysis (25% sand, 29% silt, and 15% clay), organic matter (2.8%), Walkley-Black, pH (7.1:1:1 soil:H₂O), and cation exchange capacity (6.7 cmol, kg⁻¹; Rhoades, 1982).

### Temperature Effects on High Explosive Solubility and Destruction by Zerovalent Iron

TNT, RDX, and HMX aqueous solubilities were determined at varying temperatures. This was accomplished by shaking replicates (n = 3 or 4) of a saturated high explosives (HE)-H₂O solution (distilled, deionized water containing solid-phase HE) at temperatures ranging from 20 to 55°C. To describe temperature effects on HE solubility, polynomial or power function equations were fit to temperature versus TNT and RDX concentration data.

The effect of temperature on Fe⁰-mediated destruction of HMX, RDX, and TNT was determined by conducting batch experiments with LANL soil in 50-mL Teflon tubes. Experimental units consisted of 3 g of LANL soil, 0.15 g unannealed iron, and 10 mL H₂O. The soil slurries were placed on a reciprocating shaker and agitated at 25 or 55°C. Controls (no Fe⁰) were run at each temperature and all treatments were replicated (n = 4). Temperature treatments of 25 and 55°C were imposed by placing experimental units inside an insulated case containing coils of circulating water connected to an insulated case containing coils of circulating water connected to a water bath. This insulated case was placed on a reciprocating shaker. Solutions were sampled (1.5 mL) at 0, 1, 2, 3, 4, 6, 8, and 24 h, centrifuged at 13 000 × g for 10 min, and analyzed by HPLC.

Temporal changes in HMX and RDX concentrations followed zero- or first-order kinetics and the appropriate equations were fit to the data by linear (zero-order) and nonlinear (first-order) regression using SigmaPlot 2000 computer software (SPSS, 2000). In an attempt to explain differences in chemical reactivities toward Fe⁰, lowest unoccupied molecular orbital (LUMO) energies of RDX and HMX were calculated with a Hartree Fock approximation using the 6-31G* basis set. The geometry of each compound was optimized and calculations were performed with the Windows-based SPARTAN (Version 02) computer program (Wavefunction, 2002). It should be noted that attempts to obtain LUMO energies with semi-empirical models (i.e., AM1) did not yield similar relative differences between HMX and RDX.

### Surfactant Effects on High Explosive Solubility and Destruction by Zerovalent Iron

Increasing HMX solubility was determined by adding solid-phase HMX in excess of its aqueous solubility (i.e., 0.1 g HMX added to 100 mL distilled, deionized H₂O) and spiking in the surfactants (HDTMA, Tween 80, and Triton X-100; Table 1) and the solvent DMSO (dimethyl sulfoxide) as individual treatments. Concentrations of surfactants and DMSO ranged between 1 and 5% (v/v or w/v). HDTMA was later compared with didecyl and didodecyl in a separate experiment. The effect of individual surfactant concentrations was determined by first adding 1% of surfactant to the reaction flasks (n = 3). Flasks were then agitated at 25°C for 24 h and a 1.5-mL sample removed, centrifuged (12 000 × g), and analyzed for HE by HPLC. Higher surfactant concentrations were obtained by spiking in an additional 1% surfactant each day for the next 4 d and repeating the analysis steps.

To determine the effects of the surfactants on TNT, RDX, and HMX concentrations in a contaminated soil, soil slurries were prepared by mixing 3 g of LANL soil with 25 mL H₂O and spiking in 5% HDTMA, Tween 80, or Triton X-100. Replicates (n = 3) from each treatment were agitated at 25°C for 24 h before determining HE concentrations.

Because HDTMA and didecyl were the most successful at increasing HMX concentration, we repeated the equal molar concentration experiment using 3% didecyl or HDTMA and treated HMX and RDX as homogeneous and binary mixtures with 5% unannealed Fe⁰. To determine if Fe⁰ could continuously transform HMX as the solid phase dissolved in a cationic surfactant matrix, we added 75 mg HMX to 25 mL of H₂O and spiked in HDTMA (5%). This experiment was later repeated using 3% (v/v) didecyl. Reaction flasks were agitated at 25°C

<table>
<thead>
<tr>
<th>Surfactant or trade name</th>
<th>Type</th>
<th>Molecular weight</th>
<th>Chemical name</th>
<th>Formula</th>
<th>CMC (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDTMA</td>
<td>cationic</td>
<td>406.8</td>
<td>dodecyltrimethyl ammonium bromide</td>
<td>C₁₂H₂₅N(CH₃)₂Br⁻</td>
<td>9.2 × 10⁻⁴</td>
</tr>
<tr>
<td>Didodecyl</td>
<td>cationic</td>
<td>524.8</td>
<td>didecyltrimethyl ammonium bromide</td>
<td>C₁₄H₂₇N(CH₃)₂Br⁻</td>
<td>1.85 × 10⁻⁴</td>
</tr>
<tr>
<td>Triton X-100</td>
<td>nonionic</td>
<td>624.8</td>
<td>isooctyl phenyl polyoxyethylene sulfonate</td>
<td>C₆H₅(CH₂CH₂O)₆H</td>
<td>1.65 × 10⁻⁴</td>
</tr>
<tr>
<td>Tween 80</td>
<td>nonionic</td>
<td>1309.7</td>
<td>polyoxyethylene sorbitan monooleate</td>
<td>C₁₈H₃₇O₆P</td>
<td>9.9 × 10⁻⁴</td>
</tr>
</tbody>
</table>

† Data for HDTMA, didecyl, and didodecyl (25°C) from Rosen (1989); Triton X-100 from Guha and Jaffé (1996); and Tween 80 from Yeh et al. (1998).
for 48 h to allow partial dissolution of the solid-phase HMX and equilibrium HMX concentrations were determined. Five grams of Fe\textsuperscript{0} was then added to half of the experimental units to produce the following paired treatments: control (H\textsubscript{2}O only), H\textsubscript{2}O + Fe\textsuperscript{0}, HDTMA (5%), HDTMA + Fe\textsuperscript{0}, and didecyl (3%), didecyl + Fe\textsuperscript{0}. After 6 d of additional shaking at 25°C (following Fe\textsuperscript{0} additions), all flasks were extracted with 100 mL CH\textsubscript{3}CN to determine the total mass of HMX remaining.

Long-term changes in the surface morphology of unannealed iron following treatment of HMX, with and without didecyl, were determined by mixing 1 g unannealed Fe\textsuperscript{0} with 25 mL H\textsubscript{2}O (with and without 2% didecyl) and solid-phase HMX (1.125 g). Batch flasks were agitated on a reciprocating shaker for 7 mo and then filtered, and iron samples were dried in a desiccator. Photographs were taken by mounting samples of the iron treatments with carbon tabs, sputter-coating with gold-palladium, and observing with a Hitachi (Tokyo, Japan) S-3000N scanning electron microscope (SEM) operated at 15 kV.

Chemical Analyses

HMX, RDX, and TNT were extracted from soil (3 g) with 15 mL CH\textsubscript{3}CN by sonicing for 18 h at 30°C, centrifuging at 5000 \(\times\) g, removing the supernatant, and microcentrifuging (12,000 \(\times\) g) before analyzing by HPLC.

Aqueous samples and acetonitrile extracts (10-25 \(\mu\)L) were injected into a Keystone NA column (Keystone Scientific, Bellefonte, PA) with an isocratic (30:70) mixture of methanol and H\textsubscript{2}O at a flow rate of 1.0 mL min\(^{-1}\) and quantified spectrophotometrically at 220 nm. Linear response ranges were established to bracket concentrations observed during experiments (0.25-10 mg L\(^{-1}\) without surfactants; 1-500 mg L\(^{-1}\) with surfactants). Limits of quantitative detection for RDX and HMX were 0.1 mg L\(^{-1}\).

RESULTS AND DISCUSSION

Effect of Temperature on High Explosive Solubility

We conducted a temperature versus HMX aqueous solubility experiment and compared results to our previous findings with RDX and TNT (Bier et al., 1999; Li et al., 1997). HMX solubility increased linearly from approximately 2 mg L\(^{-1}\) at 20°C to 8 mg L\(^{-1}\) at 45°C and then rose abruptly to 22 mg L\(^{-1}\) at 55°C (Fig. 1). These results differed significantly from those observed with RDX and TNT and clearly indicate that HMX is the least soluble of the three major HE across a range of temperatures. Lynch et al. (2001) reported similar differences in HE solubilities in response to increasing temperature.

Based on the HMX concentration in the LANL soil (>40 000 mg kg\(^{-1}\)), it is clear that solid-phase HMX will be present at ambient temperatures. Therefore, for a remediation treatment to be effective (abiotic or biotic), it must continuously remove what is in the soil solution as the solid phase dissolves with time. Although Lynch et al. (2002) reported a faster dissolution rate for HMX than RDX, the lower solubility of HMX will make this compound more difficult to remove. To increase HMX destruction rates, a successful remediation technology will likely need to focus on increasing the HMX concentration in the soil solution.

![Fig. 1. Effect of temperature on the aqueous concentration of HMX, RDX, and TNT.](image-url)

Because modest increases in HMX concentration were observed with increased temperature, we conducted an experiment in which the LANL soil was treated with Fe\textsuperscript{0} at two temperatures (25 and 55°C). HMX destruction by Fe\textsuperscript{0} did not occur at either temperature after agitating for 24 h (Table 2). By contrast, Fe\textsuperscript{0} effectively reduced RDX and TNT and was more effective at the higher temperature (Table 2). While the relative increase in destruction at the higher temperature was the same for RDX and TNT (both increased by 1%), this increase was only significant (\(\alpha = 0.05\)) for TNT. Because TNT was the most soluble at the higher temperatures (Fig. 1), total destruction by Fe\textsuperscript{0} was greatest for TNT (98%).

RDX and HMX Destruction by Zerovalent Iron: Homogenous versus Binary Mixtures

Because RDX will almost always be present with HMX, we compared Fe\textsuperscript{0}-mediated destruction rates of HMX and RDX in homogeneous solutions versus binary mixtures. Destruction kinetics differed with Fe\textsuperscript{0} type (annealed vs. unannealed; Fig. 2). This was espe-
Table 2. Effect of temperature on high explosive (HE) destruction by zerovalent iron in a soil slurry. Soil was obtained from the Los Alamos National Laboratory, New Mexico.

<table>
<thead>
<tr>
<th>High explosive</th>
<th>Treatment</th>
<th>Extractable HE at 25°C</th>
<th>Reduction†</th>
<th>Extractable HE at 55°C</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>mg kg⁻¹</td>
<td>%</td>
<td>mg kg⁻¹</td>
<td>%</td>
</tr>
<tr>
<td>HMX</td>
<td>control (no Fe⁰⁻)</td>
<td>36 794 (14663)</td>
<td>0.1</td>
<td>37 774 (2325)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Fe⁰⁻</td>
<td>36 759 (2834)</td>
<td></td>
<td>38 577 (7177)</td>
<td></td>
</tr>
<tr>
<td>RDX</td>
<td>control (no Fe⁰⁻)</td>
<td>10 992 (4599)</td>
<td>41</td>
<td>11 351 (1313)</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>Fe⁰⁻</td>
<td>6 468 (949)</td>
<td></td>
<td>5 931 (361)</td>
<td></td>
</tr>
<tr>
<td>TNT</td>
<td>control (no Fe⁰⁻)</td>
<td>726 (72)</td>
<td>91</td>
<td>686 (63)</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>Fe⁰⁻</td>
<td>69 (13)</td>
<td></td>
<td>13 (3)</td>
<td></td>
</tr>
</tbody>
</table>

† Percent reduction = \( \left| 1 - \frac{([\text{extractable HE concentration from Fe⁰⁻ treatment}])}{([\text{extractable HE concentration of control}])} \right| \times 100 \) at the same temperature.

Values in parentheses are sample standard deviations of means (n = 4).

1. From reactive to nonreactive sites. In the reduction of azo dyes by Fe⁰⁻, Nam and Traitneyk (2000) observed a transition from zero-order to first-order kinetics with decreasing initial concentrations of the dyes and attributed this to the saturation of reactive sites.

Regardless of the iron source, RDX destruction rates were faster than HMX in homogenous solutions (Fig. 2). When HMX and RDX were present together at nearly equal molar concentrations, RDX destruction rates decreased by approximately 35% for annealed iron (0.992 vs. 0.644 h⁻¹; Fig. 2) and 23% with unannealed iron (1.167 vs. 0.893 h⁻¹; Fig. 2). By comparison, HMX destruction decreased by 74% when RDX was present in the matrix (0.373 vs. 0.097 mg L⁻¹ h⁻¹; Fig. 2) and was completely halted in the unannealed treatment for 12 h until all of the RDX had been removed from solution and an additional lag period of 6 h had occurred (Fig. 2). Other researchers have also observed a delayed response to contaminant destruction by Fe⁰⁻ and have attributed this lag time to the formation of secondary reductants such as coordinated Fe(ITI)- or Fe(III)-containing oxides (Alowitz and Scherer, 2002; Satapanajaru et al., 2003). The reduction sequence observed in the binary

![Fig. 2. Destruction of HMX and RDX by zerovalent iron (annealed and unannealed) when present alone or in combination. Error bars on symbols represent sample standard deviations of means (n = 4); where absent, bars fall within symbols.](image-url)
mixtures clearly shows that when present at equal concentrations, RDX is preferentially reduced over HMX during Fe⁰ treatment (Fig. 2).

Differences in chemical reactivity toward Fe⁰ are linked, at least in principle, to differences in the susceptibility of a molecule to accept electrons. The ease with which oxidized compounds can be reduced varies considerably and attempts have been made to correlate this process with a number of chemical descriptors such as bond dissociation energies, electronegativities of the leaving groups, stabilities of the carbon radicals, one-electron reduction potentials (Jafvert and Wolfe, 1987; Schwarzenbach and Gschwend, 1990; Larson and Weber, 1994), and LUMO energies. While many researchers have developed successful linear free energy relationships (LFER) using one-electron reduction potentials, Scherer et al. (1998) developed a LFER between the LUMO energies of various chlorinated aliphatics and destruction rate constants observed with Fe⁰ treatment. Of the quantum-chemical descriptors, LUMO energies are perhaps the most justified because they represent the frontier molecular orbital into which electron transfer takes place. Compounds with lower LUMO energies would be favored over compounds with higher LUMO energies in electron transfer reactions. Scherer et al. (1998) showed that for a series of chlorinated aliphatics, the lower the LUMO energy the greater the destruction kinetics observed with zerovalent iron. Nam and Tratnyek (2000) similarly reported a correlation between LUMO energies of a series of azo dyes and reaction rates for reduction by Fe⁰. Our calculated LUMO energies for RDX (2.49 eV) and HMX (2.76 eV) indicate that RDX would be favored over HMX in reduction by Fe⁰ but without a larger data set (series of nitrarnines and rate constants) to develop a correlation LFER, it is unclear if this relative difference is enough to explain our observed results. Moreover, differences in HMX destruction kinetics (both rate and order) between iron sources complicate LFER development for predictive purposes.

Although our abiotic approach to treating HMX and RDX demonstrates that HMX is more difficult to destroy, several researchers have come to this same conclusion using microbial treatments (McCormick et al., 1981; Kitts et al., 1994; Shen et al., 2000). One reason given for HMX recalcitrance is that HMX has more steric constraints caused by the crowding of atoms in the –CH₂–N=NO₂ reacting group (Croce and Okamoto, 1979; Hawai, 2000). Consequently, differences between RDX and HMX reactivity toward Fe⁰ may perhaps also be a function of accessibility or differences in orientation of the molecules on the iron oxide surface.

Based on results from the equal molar and temperature experiments, it became apparent that for Fe⁰ to effectively destroy HMX, higher concentrations than what was achieved by increased temperatures may be needed. To accomplish this, we surveyed a variety of surfactants to determine their effects on HMX solubility.

**Effect of Surfactants on High Explosive Solubility**

A factorial test of three surfactants (HDTMA, Tween 80, and Triton X-100) and DMSO at five concentrations demonstrated that HDTMA was far superior in increasing HMX solubility (Fig. 3A). Using concentrations well above the critical micelle concentration (CMC) for these surfactants (Table 1), HMX concentrations were not significantly increased until surfactants were added in percentage concentrations. At the 5% concentration, HDTMA increased HMX solution concentration to >250 mg L⁻¹ in a pure HMX-H₂O suspension. When we tested the surfactants (5% HDTMA, Tween 80, or Triton X-100) on the LANL soil, we found that HDTMA increased HMX concentration to 230 mg L⁻¹ in a contaminated soil slurry. In addition to increasing HMX concentration, RDX concentration also increased by the nonionic surfactants (Fig. 3B). The nonionic surfactants (Twee 80 and Triton X-100) were not as effective in increasing HMX concentration but did increase RDX concentrations in the soil slurry. TNT was also slightly increased by the nonionic surfactants (Fig. 3B) but considering that TNT never reached its solubility limit in the control (H₂O only), it is likely that solid-phase TNT was not present in the LANL soil and therefore our observations do not reflect the potential of the nonionic surfactants to increase TNT concentrations.

We subsequently investigated two other cationic surfactants (didecyl and didodecyl) and compared results
with HDTMA. Both of these surfactants increased the solubility of HMX above that obtained with HDTMA; however, the high viscosity of the didodecyl solutions limits its practicality (Table 3). Didodecyl solutions were also quite viscous at concentrations of >3% so experiments were conducted at concentrations of ≤3%.

**Destruction of RDX and HMX by Zerovalent Iron in the Presence of Surfactants**

The rationale for using a surfactant was to get more HMX into solution so that it could interact with the iron surface. The utility of this approach was contingent on determining whether the Fe⁰ was effective in transforming HMX in a surfactant matrix. Results showed that HMX (approximately 200 mg L⁻¹) destruction by unannealed iron was rapid in both HDTMA and didodecyl matrices and far greater than observed in H₂O alone (Fig. 2 and 4). High RDX concentrations (176–192 mg L⁻¹) in a HDTMA or didodecyl matrix were also quickly decreased by unannealed Fe. As observed in the earlier equal molar experiment (H₂O matrix, unannealed Fe⁰; Fig. 2), RDX was transformed faster than HMX in the presence of cationic surfactants (Fig. 4), but the relative differences in destruction kinetics between HMX and RDX were less, especially in the didodecyl matrix (Fig. 4C). Interestingly, we observed a somewhat similar lag time in HMX destruction after the RDX had been transformed in the HDTMA matrix (Fig. 4F) as in H₂O (Fig. 2).

A scenario that may be encountered in some munitions-contaminated soils is one where HMX is present at greater concentrations than RDX. When we conducted a similar batch experiment but increased the HMX to RDX ratio from 1 to 10 in a 3% didodecyl matrix, initial loss of HMX was observed but RDX was still preferentially removed from solution before HMX (data not shown). These results indicate that there is probably a HMX to RDX ratio at which HMX can compete with RDX as an electron acceptor.

What makes remediating the LANL soil such a formidable task is the sheer magnitude of HMX present. As the Fe⁰ transforms the HMX dissolved in the soil solution, solid-phase HMX will continue to replenish the soil solution with HMX. Given that both HDTMA and didodecyl effectively increased HMX concentration and Fe⁰ effectively transformed HMX in the presence of the surfactants, we combined Fe⁰ with HDTMA or didodecyl to treat an aqueous solution containing solid-phase HMX. Results from this experiment showed that only about 3% of the added HMX was destroyed by Fe⁰ when used alone whereas approximately 60% of the HMX was transformed within 6 d when HDTMA was added with the Fe⁰ (Table 4). The Fe⁰ + didodecyl treatment, however, removed all of the solid-phase HMX present in the batch reactor (Table 4).

Because the polar regions of HDTMA and didodecyl...
Table 4. Effect of Fe²⁺ with and without HDTMA (5%, w/v) or didecyl (3%, w/v), on HMX destruction in an aqueous solution containing solid-phase HMX.

<table>
<thead>
<tr>
<th>Treatment matrix</th>
<th>Equilibrium concentration before Fe²⁺ treatment (mg L⁻¹)</th>
<th>Equilibrium concentration after Fe²⁺ treatment (6 d) (mg L⁻¹)</th>
<th>Mass of HMX extracted (mg)</th>
<th>Reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>2.70 (0.62)</td>
<td>2.91 (0.30)</td>
<td>78.5 (0.66)</td>
<td>2.7</td>
</tr>
<tr>
<td>H₂O + Fe²⁺</td>
<td>2.31 (1.31)</td>
<td>1.74 (0.17)</td>
<td>70.3 (0.94)</td>
<td>2.7</td>
</tr>
<tr>
<td>HDTMA</td>
<td>343 (15)</td>
<td>265 (29)</td>
<td>76.0 (1.05)</td>
<td>2.7</td>
</tr>
<tr>
<td>HDTMA + Fe²⁺</td>
<td>326 (40)</td>
<td>294 (62)</td>
<td>30.4 (2.63)</td>
<td>60</td>
</tr>
<tr>
<td>Didecyl</td>
<td>316 (13)</td>
<td>328 (14)</td>
<td>77.0 (2.80)</td>
<td>2.7</td>
</tr>
<tr>
<td>Didecyl + Fe²⁺</td>
<td>293 (7)</td>
<td>0 (0)</td>
<td>100</td>
<td>2.7</td>
</tr>
</tbody>
</table>

* Percent reduction = [(mass of HMX extracted from surfactant + Fe²⁺ treatment) / (mass of HMX extracted from surfactant only treatment)] x 100.

Values in parentheses are sample standard deviations (n = 3).

These results indicate that Fe²⁺ can enhance HMX destruction, but the mechanism of this enhancement is complex and may involve both direct and indirect effects. The presence of surfactants such as HDTMA and didecyl can influence the efficacy of Fe²⁺ treatment by altering the physicochemical properties of the system. Further research is needed to better understand the interplay between Fe²⁺, surfactants, and HMX in the context of remediation efforts.
Fig. 5. (A) Scanning electron microscope (SEM) photo of unannealed iron. (B) Surface of unannealed iron after treating an aqueous solution containing solid-phase HMX. (C) Surface of unannealed iron following treatment of an aqueous-solid-phase HMX mixture with 2% (v/v) didecyl.

iron without didecyl, which was much more irregular and rough with some noticeable cracks in the oxide observed (Fig. 5). These photos illustrate that cationic surfactants influence the physical characteristics of the oxides formed during contaminant treatment and may help explain the increased effectiveness of the Fe⁶⁺ cation surfactant treatment in removing solid-phase HMX from an aqueous solution.

CONCLUSIONS

The water solubilities of HMX, RDX, and TNT increase with increasing temperature, but HMX is the least soluble of the three HEs at any temperature. HMX can be chemically reduced by Fe⁶⁺ but kinetics will be slowed when RDX is present. This indicates that when multiple energetics are present in a contaminated soil, most of the RDX may need to be transformed before effective HMX reduction by Fe⁶⁺ is observed. Because cationic surfactants increase solution concentrations of both RDX and HMX, it is likely that removal of the RDX is critical to removing HMX from the contaminated soil when Fe⁶⁺ and surfactants are used. Our results indicate that the cationic surfactants HDTMA and didecyl can be used to greatly increase HMX and RDX concentrations and destruction kinetics by Fe⁶⁺.

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