

# Degradation kinetics of TNT in the presence of six mineral surfaces and ferrous iron

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Received 12 February 2003; received in revised form 15 January 2004; accepted 6 July 2004

Available online 14 June 2005

## Abstract

Trinitrotoluene (TNT), a nitroaromatic explosive, is a commonly encountered groundwater contaminant in the United States that can pose a human health risk, even at very low aqueous concentrations. This study describes the process characteristics of abiotic degradation of dissolved TNT in the presence of ferrous iron ( $\text{Fe}^{2+}$ ) and six different minerals—processes relevant to a more complete understanding of reduced iron technologies in TNT cleanup.

Kinetic degradation batch reactions involving combinations of TNT, ferrous iron, six minerals with varying cation exchange capacity, and two pH buffers were performed. The rate of TNT degradation was quantified using high performance liquid chromatography (HPLC). Unbuffered reactions between TNT,  $\text{Fe}^{2+}$ , and magnetite, pyrite, quartz, and goethite/quartz were insignificant. However, unbuffered reactions between TNT,  $\text{Fe}^{2+}$ , and calcite and siderite proceeded rapidly to completion. The difference in reaction rates was attributable to the elevated pH in the presence of the latter minerals. For reactions performed in buffered systems with pH 7.4, degradation followed a second-order kinetics rate law. For reactions in buffered systems with pH 9.0, the reactions proceeded to completion almost instantaneously. The presence of the mineral solid surface was necessary for TNT reduction to proceed, with the most rapid reaction rates occurring in the presence of a suspected hydroxy solid phase that formed at high pH.

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**Keywords:** Cation exchange capacity; Ferrous iron; Oxidation–reduction reaction; Reactive barriers; Trinitrotoluene

## 1. Introduction

2,4,6-Trinitrotoluene (TNT), a nitroaromatic explosive, is a frequently encountered groundwater contaminant at explosives manufacturing plants, packing and storage facilities, and military training sites in the United States. TNT is toxic, mutagenic, and a suspected carcinogen [1], with an EPA lifetime health advisory of  $2 \mu\text{g}/\text{L}$  [2]. Consequently, the fate and remediation of TNT in the natural environment is of significant concern.

Current research on the remediation of TNT includes the assessment of zero-valent iron or ferrous iron ( $\text{Fe}^{2+}$ ) to transform TNT and other nitroaromatic and nitramine compounds to less hazardous or more biodegradable products [3–8]. When TNT undergoes chemical reduction under anaerobic conditions, the nitro groups in the original structure can be transformed sequentially to amino groups [6], ultimately yielding triaminotoluene (TAT) [3] (Fig. 1). Because TAT and the other intermediates are also of environmental concern, field applications relying on the reduction of TNT using iron species must also consider subsequent reactions such as biodegradation or covalent binding of the intermediate products to natural organic matter, which are effectively irreversible [3,9].

In the oxidation–reduction reaction involving TNT and ferrous iron, oxidation takes place when the aqueous ferrous

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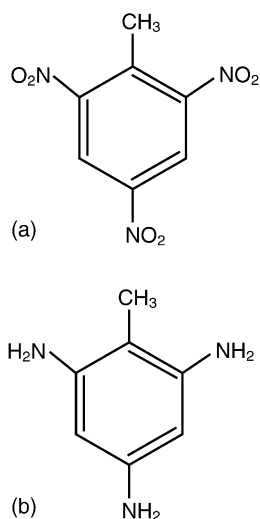


Fig. 1. Chemical structure: (a) 2,4,6-trinitrotoluene and (b) 2,4,6-triaminotoluene.

iron ion [ $\text{Fe}^{2+}$ ] loses one electron to become aqueous ferric iron [ $\text{Fe}^{3+}$ ]. Each nitro [ $-\text{N}(\text{V})\text{O}_2$ ] to amino [ $-\text{N}(\text{I})\text{H}_2$ ] reduction requires six electrons. Consequently, the complete reduction of 1 mol of TNT to TAT requires eighteen moles of ferrous iron (molar ratio  $\text{Fe}^{2+}/\text{TNT} = 18$ ). It is important to note that the reduction of TNT is a surface-activated reaction, such as when  $\text{Fe}^{2+}$  is adsorbed to mineral surfaces, and acts as the reductant for nitroaromatic compounds [7]. The direct reduction of TNT by aqueous  $\text{Fe}^{2+}$  is a very slow reaction [7,10]; however, in the presence of an iron hydroxide mineral surface or surface coating, it was observed that 10 monosubstituted nitrobenzenes were readily reduced to their corresponding anilines in a strongly pH dependent reaction [7]. Brannon et al. [4] observed that aluminosilicate surfaces also catalyze the nitro-to-amino reduction of TNT in the presence of ferrous iron at a molar ratio of approximately 10 (0.00134 mol/L  $\text{Fe}^{2+}$  and 0.00011 mol/L TNT).

The objective of this study was to evaluate the reactivity of TNT in the presence of excess ferrous iron ( $\text{Fe}^{2+}$ ) and six common minerals as catalysts, representing a range of cation exchange capacities. Several initial hypotheses were developed, including: (1) minerals containing structural ferrous iron would be more reactive, (2) a positive correlation between reaction rates and the number of activation sites would be observed if, as has been suggested, the reduction of TNT by  $\text{Fe}^{2+}$  is surface-catalyzed. Cation exchange capacity (CEC) for  $\text{Na}^+$  was taken as an indicator of the adsorption capacity for ferrous iron, with the expectation that  $\text{Fe}^{2+}$  sorption would increase as the CEC increased. The subject minerals—calcite, siderite, magnetite, pyrite, quartz, and goethite/quartz—also were selected because they are likely to precipitate in zero-valent iron (ZVI) systems and/or are common aquifer materials or other components that could be mixed with granular iron to reduce the associated material costs of permeable reactive barrier (PRB) construction. Evaluation of TNT reactivity with these minerals in the presence

of dissolved ferrous iron provides a basis for the more thoroughly understood TNT-degrading reactions in ZVI systems. The quantitative understanding of the reactions, other than those directly involving metallic iron, provide data useful in the design of zero-valent iron permeable reactive barriers, particularly with respect to issues of longevity, once the iron surfaces have undergone some degree of corrosion.

## 2. Experimental methods

### 2.1. Materials

Six mineral phases were purchased from Ward's Natural Science Establishment: calcite, siderite, magnetite, pyrite, quartz, and goethite (which contained considerable amounts of quartz). The minerals were received as large blocky samples. In order to prepare the minerals for experimentation, they were crushed (dry ground) into finer particles using a Baldwin Tate Emery Load Frame. After crushing, a sieve analysis was performed on the minerals according to ASTM D422; the same size fraction was used in all experimentation. The  $\text{N}_2$ -BET surface areas of the crushed minerals were measured by the BET single point surface area analysis method using a surface area analyzer (Gemini 2360, Micromeritics). The cation exchange capacities of the minerals used in the experiments were measured by Hazen Research (Golden, CO), according to the following method [11]. In order to measure the CEC, the minerals were loaded with sodium through several contacts with a 1.0N sodium acetate solution, followed by multiple washes with 95% ethanol. The adsorbed sodium was then displaced through contact with a 1.0N ammonium acetate solution, and the resulting solution was assayed for sodium content using atomic absorption spectrophotometry.

### 2.2. X-ray diffraction

Mineral purity assessed by X-ray diffraction (XRD) analysis is summarized in Table 1. Semi-quantitative XRD analyses were conducted on a Philips PW1800 diffractometer, using monochromatic  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54050$ ), at a power setting of 40 kV and 45 mA. A 5 g sample of each material was obtained using ASTM C 702 guidance (standard practice for reducing samples of aggregate to testing size). The samples were ground dry by a mortar and pestle to a fine powder passing a 45  $\mu\text{m}$  sieve. The powders were packed into a back-filled mount with a circular cavity that was 15 mm in diameter. This packing procedure reduces preferred orientation of crystallites and accommodates sample rotation during analysis. The samples were scanned using a step size of  $0.05^\circ$  and a dwell time of 3 s ( $1^\circ/\text{min}$ ) over the range  $2$ – $65^\circ$ . XRD patterns were evaluated using a popular PC-based analysis program (Jade 6.0 XRD Pattern Processing for the PC [12]). Common mineral phases, such as those analyzed here (e.g., quartz, calcite, ankerite, magnetite) are readily identifiable

Table 1  
Characterization of minerals used in the kinetic degradation experiments

Mineral	Chemical composition	Mineral purity (%)	$D_{50}^a$ (mm)	$D_{10}^b$ (mm)	BET surface area (m <sup>2</sup> /g)	Cation exchange capacity (meq/100 g)
Calcite	CaCO <sub>3</sub>	100	0.24	0.058	0.008	0.10
Magnetite	Fe <sup>c</sup> Fe <sub>2</sub> <sup>d</sup> O <sub>4</sub>	65 (10% muscovite, 20% plagioclase feldspar, minor kaolinite, vermiculite)	0.58	0.10	0.01	0.26
Pyrite	FeS <sub>2</sub> <sup>c</sup>	95 (5% calcite)	0.71	0.11	0.009	0.02
Quartz	SiO <sub>2</sub>	100	0.56	0.11	0.008	<0.02
Quartz/goethite	SiO <sub>2</sub> , FeO(OH) <sup>d</sup>	50 Quartz, 40 goethite (minor calcite, kaolinite, pyrite)	1.1	0.34	0.4	2.4
Siderite/ankerite	FeCO <sub>3</sub> <sup>c</sup> , Ca(Fe <sup>c</sup> , Mg, Mn)(CO <sub>3</sub> ) <sub>2</sub>	60 (30% ankerite, 5% quartz, 5% calcite)	0.33	0.048	0.1	0.35

<sup>a</sup>  $D_{50}$  = mineral grain size at which 50% is finer by weight.

<sup>b</sup>  $D_{10}$  = mineral grain size at which 10% is finer by weight.

<sup>c</sup> Fe[III].

<sup>d</sup> Fe[III].

by their reference intensity ratio (RIR), tabulated in the joint committee on powder diffraction standards (JCPDS) database. These minerals serve as reliable internal references for peak positions. Use of RIRs yields the proportions of minerals present within an accuracy of 10%. However, if no RIR minerals are present, alternative methods are required for quantitative analysis, such as the use of external standards. The proportions quantified here are normalized for crystalline phases; amorphous phases are not quantifiable by XRD.

The chemicals used in this investigation included: powdered 2,4,6-trinitrotoluene (TNT) (C<sub>6</sub>H<sub>2</sub>CH<sub>3</sub>(NO<sub>2</sub>)<sub>3</sub>) submerged in water (Chem Service); 2-amino-4,6-dinitrotoluene in acetonitrile (Supelco); 4-amino-2,6-dinitrotoluene in acetonitrile (Supelco); 2,6-diamino-4-nitrotoluene in acetonitrile (Accu Standard); 2,4-diamino-6-nitrotoluene in acetonitrile (Accu Standard); 2,4,6-triaminotoluene trihydrochloride salt powder (Accu Standard); 2,2',6,6'-tetranitro-4,4'-azoxytoluene in acetonitrile (Accu Standard); 4,4',6,6'-tetranitro-2,2'-azoxytoluene in equal ratio acetonitrile and methanol (Accu Standard); 1,3,5-trinitrobenzene in equal ratio acetonitrile and methanol (Accu Standard); 1,3-dinitrobenzene in equal ratio acetonitrile and methanol (Accu Standard); 2,4-dinitrotoluene in equal ratio acetonitrile and methanol (Accu Standard); 2,6-dinitrotoluene in equal ratio acetonitrile and methanol (Accu Standard); ferrous chloride tetrahydrate powder (FeCl<sub>2</sub>·4H<sub>2</sub>O) (Fluka Chemika); hydrochloric acid (HCl) (Fisher Scientific); 1,10-phenanthroline monohydrate powder (C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>·H<sub>2</sub>O) (Fisher Scientific); HPLC grade methanol (CH<sub>3</sub>OH) (Fisher Scientific); HPLC grade acetonitrile solution (CH<sub>3</sub>CN) (Allied Signal); HPLC grade isopropanol (CH<sub>3</sub>CHOHCH<sub>3</sub>) solution (Fisher Scientific); ammonium acetate crystals (NH<sub>4</sub>C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>) (J.T. Baker); potassium phosphate monobasic–sodium hydroxide pH buffer (pH 7.4) (Fisher Scientific); boric acid–potassium chloride–sodium hydroxide pH buffer (pH 9.0) (Fisher Scientific); and acetic acid (CH<sub>3</sub>COOH) (Fisher Scientific). All chemicals were used

as received. The water used in all experimentation was deionized (Barnstead Nanopure) prior to use.

### 2.3. Stock and buffer solutions

Deionized water was used in the preparation of all stock and standard solutions, and all reagents had non-detectable levels of iron. Solutions were stored in volumetric flasks with ground glass stoppers. An ammonium acetate buffer solution was prepared by dissolving ammonium acetate crystals in deionized water, followed by the addition of concentrated acetic acid. A phenanthroline solution was prepared by dissolving 1,10-phenanthroline monohydrate in a solution of hydrochloric acid and deionized water. The iron stock solutions were prepared by dissolving ferrous chloride tetrahydrate powder in deionized water. Standard iron solutions were prepared by diluting the stock solution with deionized water. TNT stock solutions were prepared by first drying the wet, powdered TNT in a glove box filled with nitrogen gas, then dissolving the dried TNT in deaired, deionized water. In order to remove oxygen from the water, nitrogen gas was sparged through the de-ionized water for approximately 0.5 h. A stock solution was then prepared at a concentration of 16 mg/L, and was stored in a volumetric flask sealed with a ground glass stopper. Stock solutions of anticipated TNT reduction by-products—including 2-amino-4,6-dinitrotoluene (2A-46DNT), 4-amino-2,6-dinitrotoluene (4A-2,6-DNT), 2,6-diamino-4-nitrotoluene (2,6-DA-6NT), 2,4-diamino-6-nitrotoluene (2,4-DA-6-NT), 2,2',6,6'-tetranitro-4,4'-azoxytoluene, 4,4',6,6'-tetranitro-2,2'-azoxytoluene, 1,3,5-trinitrobenzene (TMB), 1,3-dinitrobenzene (1,3-TNB), 2,4-dinitrotoluene (2,4-DNT), and 2,6-dinitrotoluene (2,6-DNT) were prepared in a similar manner, except the chemicals were dissolved in methanol.

### 2.4. Analytical procedures

The concentrations of TNT and its transformation products in the aqueous samples were measured according to US

EPA Standard Method 8330 for the trace analysis of explosive residues by high performance liquid chromatography (HPLC) using a UV detector. The HPLC included a data module (model 746, Waters), pump (Acuflow Series IV, ECOM-spol.s.r.o), and a tunable absorbance detector (model 486, Waters) set at a fixed wavelength of 254 nm. A Nova-Pak C<sub>8</sub> reversed phase column was used as the stationary phase (4 μm particle size, 3.9 mm × 150 mm, WAT035876, Waters). In exception to the method, the mobile phase was 82% deionized water and 18% HPLC grade isopropanol with a flow rate of 1.0 mL/min. All samples were introduced into the HPLC using direct injection. Transformation products were identified by retention time in the system. Detection limit for the method was approximately 3 μg/L.

Calibration of the HPLC was performed using external standards with concentrations ranging from 0 to 10,000 μg/L. Calibration standard solutions were prepared in both acetonitrile and deionized water using serial dilution of the stock solutions. From the HPLC analysis, it was observed that the retention time of TNT and suspected by products of TNT reduction in aqueous solution were slightly longer when compared to acetonitrile solution. However, magnitude of the concentrations was not affected. Intermediate stock solutions, for all chemicals prepared, were refrigerated and stored for a maximum of 30 days. Photodegradation of TNT was minimized by wrapping all glassware with aluminum foil. Five concentration standards were prepared in all cases for HPLC calibration. For all experiments, the HPLC was allowed to warm up for at least 30 min, and at least 15 void volumes of the mobile phase were passed through the column. The mobile phase, pumped at a flow rate of 1 mL/min, was passed through the column until the base line was level at the UV detector's greatest sensitivity. Injections of each calibration standard over the concentration range of interest were made sequentially into the HPLC in random order. Peak areas were obtained for each injection and calibration curves for concentrations of TNT and its transformation products were developed.

Quantification of ferrous iron (Fe<sup>2+</sup>) concentrations was performed photometrically using complexation reactions with phenanthroline and ammonium acetate buffer solutions, according to Method 315B—phenanthroline method for the detection of dissolved iron [13]. The spectrophotometer (model SP-830, Turner) was set to a wavelength of 510 nm, with a light path 1 cm long. A 100 mL portion of the ferrous iron standard was acidified with 2 mL of 1.0N hydrochloric acid. A 50 mL portion of this acidified sample was withdrawn, mixed with 20 mL of the phenanthroline solution and 10 mL of the ammonium acetate buffer solution, and stirred vigorously. The solution was then diluted to 100 mL with deionized water. Color intensity, which developed because three molecules of phenanthroline chelate each atom of ferrous iron to form an orange–red complex, was measured using the spectrophotometer. A calibration curve was prepared by measuring the absorbance of the Fe<sup>2+</sup> solutions prepared at three known concentrations, within the range of 0–50 mg/L.

## 2.5. Sorption of TNT to mineral surfaces

Adsorption of TNT to quartz, the least reactive mineral used in the experiments, was carried out by a conventional batch equilibration technique. No degradation products were detected in the reaction of TNT with buffered or unbuffered (pH) quartz in the absence of supplemental ferrous iron; consequently, the only likely mechanism for removal of TNT from these solutions was sorption.

Four batch reactors were used for the sorption tests, each containing different masses of quartz (ranging from 1 to 10 g) and equal volumes of 10,000 μg/L TNT. All reactors were wrapped in aluminum foil to prevent photodegradation. The sorbent and solute were placed in 15 mL centrifuge tubes with Teflon-lined caps. The reactors were evacuated with nitrogen for approximately 1.5 h before TNT was added to the tubes, and the batch reactors were then placed horizontally on an enclosed shaker. The reactors were rotated at a rate of 6 rpm at room temperature (22–23 °C) until sorption equilibrium was achieved. Preliminary experimentation indicated that 24 h was sufficient time to reach equilibrium (concentration did not change after 24 h); consequently, after 24 h the reactors were placed in a glove box that was evacuated with nitrogen gas and the supernatant was withdrawn using a syringe equipped 0.45 μm filter, and placed into a vial that had been evacuated with nitrogen. These solutions were then analyzed on the HPLC, and the concentrations of dissolved TNT were estimated. Sorbed concentrations were estimated as the difference between the original concentration and the final aqueous concentration. Blank and spiked reactors were also analyzed to quantify losses and background interferences; losses from the spiked reactors ranged between 2 and 5%, and no TNT was detected in the blank reactor.

Data obtained from the TNT-quartz sorption experiment were modeled with linear, Langmuir, and Freundlich isotherms. Best fits of the experimental data to the various isotherm models were compared by linear and non-linear regression analysis. It was not possible to measure sorption parameters for the minerals calcite, magnetite, pyrite, quartz/goethite, and siderite because these minerals spontaneously degraded TNT.

## 2.6. TNT degradation in the presence of ferrous iron

Kinetic reaction tests were performed to facilitate comparison of the effects of iron concentration, mineral type, pH, and temperature as experimental variables. The first series of tests was carried out in order to quantify how well the different mineral surfaces catalyzed the reduction of TNT in the presence of excess Fe<sup>2+</sup> (molar ratio Fe<sup>2+</sup>/TNT = 180; 10 times the stoichiometric requirement for the reduction of TNT to TAT). The other two series of tests were designed to assess the pH and temperature dependence of the degradation processes. In assessing the pH dependence, experiments were performed in buffered systems with a potassium phosphate monobasic–sodium hydroxide buffer at pH 7.4, and a boric

acid–potassium chloride–sodium hydroxide buffer at pH 9.0. Both sets of experiments in buffered systems were performed with the excess  $\text{Fe}^{2+}$ . In the buffered system at pH 7.4, a molar ratio  $\text{Fe}^{2+}/\text{TNT} = 234$  (13 times the ratio required for 100% theoretical reduction) was used, while a molar ratio  $\text{Fe}^{2+}/\text{TNT} = 180$  was used in the buffered system at pH 9.0. In order to evaluate the temperature dependence, temperature controlled experiments were conducted at temperatures of 10 and 20 °C with excess ferrous iron (molar ratio  $\text{Fe}^{2+}/\text{TNT} = 234$ ) and pH buffer solution (pH 7.4). A molar ratio of ferrous iron to TNT of 18 is needed to completely reduce TNT to TAT; however, preliminary experimentation demonstrated that TNT reduction was most readily achieved when the molar ratio of ferrous iron to TNT was 10–13 times the required ratio for 100% theoretical reduction. A summary of the experimental conditions is given in Table 2.

The kinetic experiments were conducted in triplicate in 15 mL glass centrifuge tubes with Teflon-lined caps. In all experiments, 0.5 g of mineral was first washed with dilute hydrochloric acid. For the non-carbonate minerals, approximately 10% hydrochloric acid in deionized water by volume was used and for the carbonate minerals, between 1 and 3% hydrochloric acid in deionized water by volume was used. After washing with the appropriate HCl solutions, the minerals were additionally rinsed with deionized water. In the buffered reactions, the minerals were placed in the centrifuge tubes, and 5 mL of the appropriate buffer solution (pH 7.4 or 9.0) was added. A 5 mL volume of aqueous hydrous ferrous chloride ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) solution at a concentration of 3160 mg/L was then added to the centrifuge tube. For the experiments performed in unbuffered systems, the washed

minerals were placed in the batch reactors and 5 mL of 3160 mg/L ferrous iron solution was added to the reactors. The pH of the resulting solution was measured before TNT was added to the reactor, and at the completion of each reaction. Nitrogen gas was sparged through all batch reactors containing minerals, aqueous ferrous iron, and pH buffer solution for approximately 0.5 h in order to minimize re-aeration before the TNT was added.

The batch reactors were placed in a glove box that had been evacuated with nitrogen gas. For the reactions in the buffered system at pH 7.4, 5 mL of TNT stock solution (16 mg/L) were added to the centrifuge tubes. For reactions in both the unbuffered systems and the buffered systems at pH 9.0, 6 mL of TNT stock solution (16 mg/L) were added to centrifuge tubes containing reaction mixtures. The reactors were then placed in a temperature-controlled vertically rotating shaker, set at a specified temperature (10 or 20 °C). At progressing times of approximately 30 min, 1, 4, 6, 24, and 48 h the batch reactors were removed from the shaker and placed into a nitrogen-evacuated glove box, and approximately 1 mL of the supernatant was withdrawn from each tube using a syringe. The supernatant was then filtered through a 0.45  $\mu\text{m}$  syringe driven filter to remove solid particles, and the samples were analyzed immediately using the HPLC. HPLC analyses were performed in triplicate and were reproducible within 5–12%.

Two types of control tests were performed, with all control tubes processed in the same manner as the experimental batch reactors. In order to assess potential TNT losses during the experiments, one control was a spike that had only TNT dissolved in water. The other control test was a blank, which included only water and mineral with no TNT. The losses

Table 2  
Experimental conditions for measuring the kinetic degradation of TNT

Mineral	Molar ratio $\text{Fe}^{2+}/\text{TNT}$	Temperature (°C)	pH conditions
Calcite	180	20	Unbuffered, initial pH = 6.33, final pH = 6.54
Magnetite	180	20	Unbuffered, initial pH = 4.27, final pH = 4.50
Pyrite	180	20	Unbuffered, initial pH = 3.73, final pH = 3.41
Quartz	180	20	Unbuffered, initial pH = 3.79, final pH = 4.21
Goethite/quartz	180	20	Unbuffered, initial pH = 2.75, final pH = 2.33
Siderite	180	20	Unbuffered, initial pH = 5.51, final pH = 6.20
Calcite	234	20	pH buffer = 7.4
Magnetite	234	20	pH buffer = 7.4
Pyrite	234	20	pH buffer = 7.4
Quartz	234	20	pH buffer = 7.4
Quartz/goethite	234	20	pH buffer = 7.4
Siderite	234	20	pH buffer = 7.4
Calcite	234	10	pH buffer = 7.4
Magnetite	234	10	pH buffer = 7.4
Pyrite	234	10	pH buffer = 7.4
Quartz	234	10	pH buffer = 7.4
Quartz/goethite	234	10	pH buffer = 7.4
Siderite	234	10	pH buffer = 7.4
Calcite	180	20	pH buffer = 9.0
Magnetite	180	20	pH buffer = 9.0
Pyrite	180	20	pH buffer = 9.0
Quartz	180	20	pH buffer = 9.0
Quartz/goethite	180	20	pH buffer = 9.0
Siderite	180	20	pH buffer = 9.0

measured from the spiked tests were between 2 and 5%, and no measurable concentrations of TNT were detected in the blanks. In addition, reactors containing TNT in the presence of the pH buffer solutions and excess  $\text{Fe}^{2+}$  concentrations (no minerals), and TNT in the presence of excess  $\text{Fe}^{2+}$  alone (no minerals, no buffer) were tested.

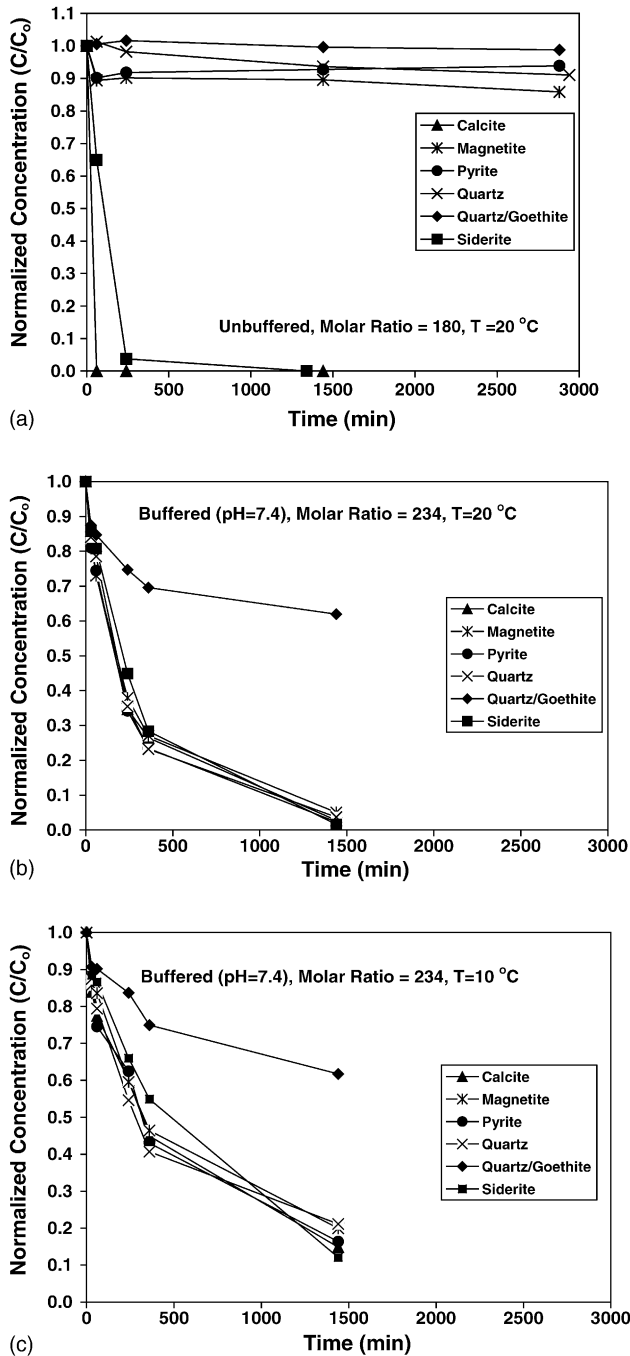


Fig. 2. TNT degradation as a function of experimental conditions: (a) unbuffered, excess iron (molar ratio  $\text{Fe}^{2+}/\text{TNT} = 180$ ), 20 °C; (b) buffered (pH 7.4), excess iron (molar ratio  $\text{Fe}^{2+}/\text{TNT} = 234$ ), 20 °C; (c) buffered (pH 7.4), excess iron (molar ratio  $\text{Fe}^{2+}/\text{TNT} = 234$ ), 10 °C; (d) buffered (pH 9.0), excess iron (molar ratio  $\text{Fe}^{2+}/\text{TNT} = 180$ ), 20 °C; (e) control experiments performed in the absence of mineral surfaces.

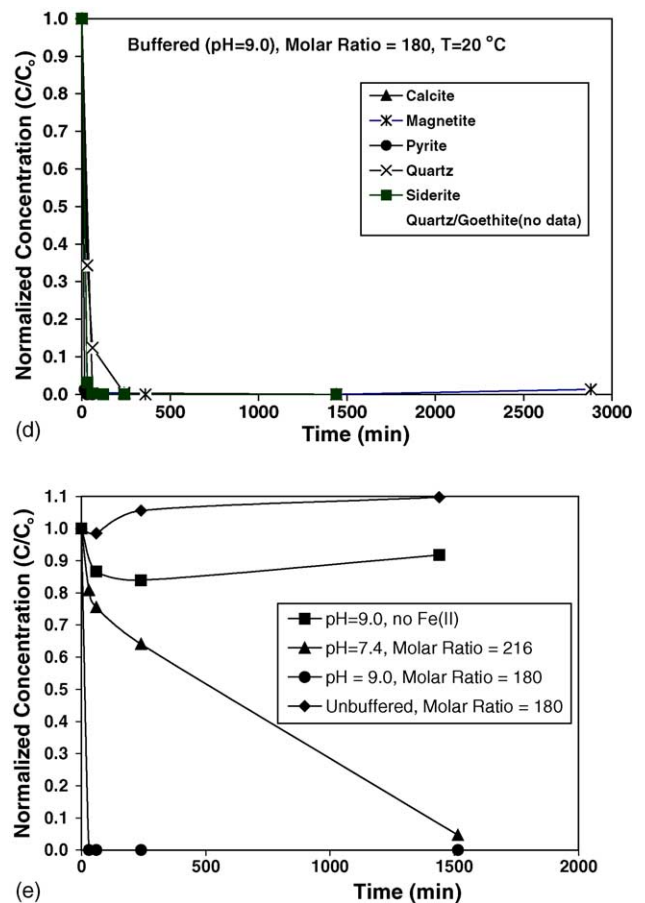


Fig. 2. (Continued).

### 3. Results and discussion

The batch sorption experiments performed with quartz demonstrated that sorption of TNT to quartz was negligible, with the measured TNT sorption equal to the losses of TNT measured in the spiked reactor (data not shown). Consequently, sorption of TNT to quartz was not a major mechanism for removal from solution.

The unbuffered degradation experiments, performed with 0.5 g of mineral and TNT in the presence of excess  $\text{Fe}^{2+}$  (molar ratio  $\text{Fe}^{2+}/\text{TNT} = 180$ ), demonstrated that only calcite and siderite catalyzed the reduction of TNT (Fig. 2a). Both minerals completely reduced the TNT concentrations of 8.4 and 8 mg/L to less than detectable limits within 24 h. TNT was reduced in less than 100 min in the presence of calcite (the reaction was too fast to determine a rate constant), and followed a first-order kinetic rate law during the first 240 min of the reaction in the presence of siderite ( $k = 0.0133 \text{ min}^{-1}$ ). None of the other minerals (magnetite, pyrite, quartz, and goethite/quartz) demonstrated significant reactivity in unbuffered systems within 48 h. One of the more interesting differences in the unbuffered experimental conditions was the elevated terminal pH in the systems containing calcite and siderite (average of 6.44 and 5.86, respectively)

relative to the pH observed in systems containing the other minerals (average of 4.39 for magnetite, 3.57 for pyrite, 4.00 for quartz, and 2.54 for goethite/quartz. (Note: the pH of the deionized water was 5.28 and the pH of Fe<sup>2+</sup> solution was 3.69.) The increase in pH was observed due to the release of carbonate during mineral dissolution.

For TNT reactions in the presence of minerals, excess ferrous iron, and pH buffer (7.4), second order with respect to TNT concentration kinetic reduction of TNT was observed (Table 3), based on goodness-of-fit. The reaction proceeded more quickly at 20 °C than at 10 °C, as anticipated (Fig. 2b and c). Reactions in the presence of all minerals except for goethite/quartz showed relatively high reactivity and similar reaction rates:  $k = 0.0012\text{--}0.0017 \text{ L mg}^{-1} \text{ min}^{-1}$  at 20 °C and  $k = 0.0002\text{--}0.0007 \text{ L mg}^{-1} \text{ min}^{-1}$  at 10 °C. These systems all led to similar amounts of TNT being removed from solution after 24 h: 95–98% at 20 °C and 80–88% at 10 °C, based on duplicate to triplicate analyses. The total concentration of TNT transformed ranged from 5.0–5.2 mg/L, depending on experimental condition. Reactions in the presence of goethite/quartz resulted in less than 40% of TNT removal from solution ( $38.1 \pm 5.5\%$  at 20 °C and  $38.3 \pm 1.5\%$  at 10 °C), and fairly slow reaction rates ( $k = 0.0003 \text{ L mg}^{-1} \text{ min}^{-1}$  at 20 °C and  $k = 0.0002 \text{ L mg}^{-1} \text{ min}^{-1}$  at 10 °C) compared to reaction rates obtained in the presence of other minerals (Table 3). The reaction rate constants determined for experiments at 20 °C were two to three times larger than the experiments performed at 10 °C (Table 3).

TNT was removed from solution almost instantaneously for all experiments performed with excess Fe<sup>2+</sup> (molar ratio Fe<sup>2+</sup>/TNT = 180) and the pH buffered at 9.0 (Fig. 2d; no data obtained for quartz/goethite). Even in the presence of a Fe<sup>2+</sup>/TNT molar ratio that was less than in the pH 7.4 experiments (molar ratio of 180 versus 234), buffered systems at pH 9.0 led to greater removal of TNT and much faster reaction

rates. This result suggests that an elevated pH either accelerated the surface catalyzed reduction of TNT or that additional TNT transformation reactions are occurring. Unfortunately, the reaction in the presence of the pH 9.0 buffer occurred so rapidly as to preclude the measure of enough data points to calculate a statistically accurate rate constant.

Control tests in the absence of mineral surfaces were performed with the following combinations: (1) pH 7.4 buffer, ferrous iron, and TNT; (2) pH 9.0 buffer, ferrous iron, and TNT; (3) pH 9.0 buffer and TNT (no iron); (4) ferrous iron and TNT (no buffer).

Reactors containing only excess ferrous iron and TNT or pH buffer and TNT did not reduce significantly the concentration of TNT over a time period of 48 h. In reactors with pH 7.4 buffer, ferrous iron, and TNT (Fig. 2e), the TNT removal was slower by a factor of at least 2, relative to systems containing mineral surfaces at significantly lower pHs (Fig. 2b; Table 2), though similar conditions were observed after 1500 min. TNT was removed very quickly in the systems containing pH 9.0 buffer, ferrous iron, and TNT. Clearly, the absence of mineral surfaces does not impede TNT removal at elevated pH under reducing conditions (high [Fe<sup>2+</sup>]), though the reaction mechanism may be different at elevated pH. These control experiments indicated that the presence of a solid surface or high pH, in combination with excess ferrous iron, was necessary for the removal of TNT.

Comparison of the unbuffered to the buffered experiments showed that the rate of TNT degradation was much more rapid in the buffered systems. It is believed that the drastic effect on TNT transformation in the presence of the pH buffer was due to the formation of an iron (III) hydroxide suspension in the reaction that catalyzed the reduction of TNT, although the second solid phase was not identified by X-ray diffraction analysis. The effect was most pronounced at pH 9.0. Only minor decreases in the pH of the buffered systems were observed during experimentation.

Table 3  
Rate constants determined for the reaction of ferrous iron and TNT in the presence of six mineral surfaces in buffered and unbuffered systems

Mineral	Molar ratio Fe <sup>2+</sup> /TNT <sup>a</sup>	Buffered pH	Temperature (°C)	Best fit model	Rate constant, $k^b$	$r^2$
Calcite	180	NA	20	–	Not determined	–
Siderite	180	NA	20	First order	0.0133	0.978
Non-carbonates	180	NA	20	–	Negligible	–
Calcite	234	7.4	20	Second order	0.0015	0.998
Siderite	234	7.4	20	Second order	0.0012	0.963
Magnetite	234	7.4	20	Second order	0.0014	0.996
Pyrite	234	7.4	20	Second order	0.0017	0.990
Quartz	234	7.4	20	Second order	0.0016	0.979
Goethite/quartz	234	7.4	20	Second order	0.0003	0.804
Calcite	234	7.4	10	Second order	0.0006	0.963
Siderite	234	7.4	10	Second order	0.0004	0.989
Magnetite	234	7.4	10	Second order	0.0006	0.988
Pyrite	234	7.4	10	Second order	0.0006	0.931
Quartz	234	7.4	10	Second order	0.0007	0.991
Goethite/quartz	234	7.4	10	Second order	0.0002	0.852

<sup>a</sup> Molar ratio of 18 required to completely reduce TNT to TAT.

<sup>b</sup> Units of rate constant,  $k$ : first order ( $\text{min}^{-1}$ ), second order ( $\text{L mg}^{-1} \text{ min}^{-1}$ ).

Examination of the results by mineral type demonstrated that all minerals, except for calcite and siderite, exhibited the same relative behavior in the degradation of TNT, with degradation rate increasing in the following order: (a) unbuffered with excess ferrous iron (molar ratio = 180), (b) buffered (pH 7.4) with excess ferrous iron (molar ratio = 234) at 10 °C, (c) buffered (pH 7.4) with excess ferrous iron (molar ratio = 234) at 20 °C, and (d) buffered (pH 9.0) with excess ferrous iron (molar ratio = 180). TNT degraded at equally rapid rates for calcite in both unbuffered and buffered (pH 9.0) systems. For calcite reactions, the least TNT degradation was observed in buffered systems (pH 7.4) at 10 °C. Unbuffered systems in presence of siderite showed greater TNT degradation than the buffered systems at pH 7.4, but reactions in buffered systems at pH 9.0 still produced the greatest TNT degradation. No strong correlation between TNT reaction rate and mineral cation exchange capacity was evident for the range of conditions evaluated here.

The TNT transformation products detected included 2-amino-4,6-dinitrotoluene (2A-DNT), 4-amino-2,6-dinitrotoluene (4A-DNT), 2,6-diamino-4-nitrotoluene (2,6-DA-NT), 2,6-dinitrotoluene (2,6-DNT), and several unidentified products (all eluted at retention times longer than TNT). Only trace amounts of 1,3,5-TNB were detected (0.01–0.02 mg/L) in a few reactions, indicating that photodegradation was minimized. For the unbuffered reactions in the presence of calcite, TNT first transformed to 2,6-DNT and an unidentified compound. Those compounds transformed to 2-amino-4,6-dinitrotoluene and another unidentified compound. It is most likely that 2-A-DNT appeared later on as a result of transformation from TNT and not 2,6-DNT. The final transformation products detected were 2,6-DA-NT and one more unidentified product. The reaction pathway taking place was TNT transforming to 2,6-dinitrotoluene followed by 2-amino-4,6-dinitrotoluene then 2,6-diamino-4-nitrotoluene, which transforms to the final triaminotoluene (TAT), although TAT was not resolvable in these experiments. It is possible that there are two pathways of transformation. In this reaction, 2,6-DNT was a product identified to form at earlier reaction times, followed by identification of 2-A-4,6-DNT at intermediate reaction times and finally 2,6-DA-NT at ultimate reaction times. In addition, there were several unidentified products formed during the reaction. Therefore, it is possible that TNT transforms to 2,6-DNT in one pathway and transforms to 2A-4,6-DNT followed by 2,6-DA-NT through a different pathway.

In the buffered reactions with all minerals, it was observed that intermediate products such as 2,6-DNT, 2A-DNT, 4A-DNT and one unidentified product were detected within the first 4–6 h of reaction times. The intermediate product, 4A-DNT was produced at the later reaction times, depending on the rate of the reaction carried out. These intermediate products were observed to decrease in concentration as the reaction progressed, sometimes to less than detection. For reactions where TNT was degraded at faster rates,

such as reactions in presence of calcite and excess  $\text{Fe}^{2+}$  (molar ratio = 68) and reactions in presence of siderite and excess ferrous iron (molar ratio = 180), other intermediate products such as 2,6-DA-NT and two unidentified products were detected. Retention times of the unidentified products detected in the reactions ranged from 1.69 to 1.79 and 1.92 to 2.01 min, compared to a retention time of 6.24–6.35 for TNT. For these reactions, these were the only products detected at the end of the reaction times. In reactions where TNT was degraded at accelerated rates, such as in buffered systems at pH 9.0 and in unbuffered systems with calcite and excess ferrous iron (molar ratio = 180), smaller concentrations of the various intermediate products mentioned above (2,6-DA-NT produced at the highest concentration) were detected within the first 4 h of reaction times. While the reaction pathway was not studied in detail in this work, the intermediate compounds detected in this study, including 2A-DNT and 4A-DNT, were also encountered in various types of TNT reduction reactions by other researchers [4,5,14,15]. Products including 2,4-diamino-6-nitrotoluene (2,4-DA-NT), hydroxylaminodinitrotoluenes, 4,4',6,6'-tetranitro-2,2'-azoxytoluene (4,4-AZOX) and 2,2',6,6'-tetranitro-4,4'-azoxytoluene (2,2-AZOX) have been identified to form as intermediates of TNT reduction under certain reaction pathways [4,14]; while these products were not identified in the present study, it is possible they were among the unknown compounds detected. 2,2',6,6'-tetranitro-4,4'-azoxy toluene, 4,4',6,6'-tetranitro-2,2'-azoxy toluene and 2,4,6-triaminotoluene were not resolvable in this investigation. The average mass balance of TNT and measured transformation products in all experiments was 48%, with a range from 34 to 67%.

The rates of TNT degradation under the various experimental conditions for all minerals followed the same pattern. In reactions with all minerals, buffered systems (pH 9.0) produced the fastest degradation rates; however, unbuffered reactions with calcite present also produced equally rapid degradation rates of TNT (Table 3). The experiments that were performed in buffered systems (pH 7.4) followed a second-order kinetics rate law, indicating that the rate of the reaction was a function of the square of the concentration of TNT. Nearly equal magnitudes of the rate constants were obtained for all minerals, except goethite/quartz, which reacted more slowly than the other minerals in reactions of buffered systems (pH 7.4) at the various temperatures. As was anticipated, the rate constants measured at 10 °C were smaller than the rate constants measured at 20 °C.

The results determined here differed from other studies that found a best fit for a first-order rate law in similar reactions with nitroaromatic contaminants [4,5,7]. Only for siderite in an unbuffered system did a first order rate constant best fit the experimental data obtained in this study. However, the values obtained in this study compared well with the rate constants obtained for TNT removal in the presence of montmorillonite and  $\text{Fe}^{2+}$  obtained by Brannon et al. [4] under various experimental conditions. In all cases in this study, it was determined that the reaction rates were



strongly dependent on pH, and that unbuffered reactions in the presence of magnetite, pyrite, quartz and quartz/goethite, which led to pH values <5.0, were non-reactive with TNT. The reverse was true for those reactions that lead to higher pH values >5.5. These results compared well with studies by Klausen et al. [7] where it was determined that nitroaromatic compounds were able to undergo surface catalyzed reductions at pH values above 6.5. Also, Brannon et al. [4] have determined that the abiotic reduction of TNT in the presence of Fe<sup>2+</sup> and montmorillonite was pH sensitive, in that the reduction of TNT was more rapid and complete at pH 9.0.

#### 4. Conclusions

It was demonstrated that mineral surfaces such as calcite and siderite catalyzed the reduction of TNT when reacted with dissolved ferrous iron in an unbuffered reaction. In contrast, minerals such as magnetite, pyrite, quartz, and goethite/quartz did not play an active role in the reduction process of unbuffered TNT with dissolved ferrous iron. Experiments demonstrated that TNT remained stable in unbuffered reactions in the presence of these minerals and ferrous iron at various initial concentrations. The measured pH values for TNT reactions with calcite and siderite in unbuffered systems were greater than the pH values measured in reactions with the four other minerals; it is believed that this difference in pH was responsible for the reduction of TNT in the presence of calcite and siderite.

The presence of structural ferrous iron in the minerals (pyrite, magnetite, siderite) versus its absence (quartz, goethite, calcite) did not appear to be the major influence on TNT reaction rates. Thus, the working hypothesis that structural ferrous iron would enhance the TNT transformation rates was not supported. Exchangeable ferrous iron and system pH appeared to overwhelm any influence of structural ferrous iron.

System pHs were generally above the zero points of charge (ZPC) for the substrate minerals, with the intriguing exception of the carbonate minerals (data not shown). Thus, it may be that anion exchanger resins, rather than mineral surfaces, are the preferred substrate to catalyze the reduction of TNT, i.e., that TNT adsorption at activation sites is more important than Fe<sup>2+</sup> adsorption. Thus, the second working hypothesis proposing a positive correlation between reaction rates and activation sites, as characterized by CEC, was not supported. However, if the activation sites are characterized as anion exchange sites instead of cation sites, the hypothesis would not be rejected. Future investigations will probe this question further through the use of anion exchange resins.

As anticipated, experimental variables such as pH and temperature affected the degradation rate of TNT. It was evident that TNT degradation rates were faster at 20 °C than at 10 °C. Reactions that were performed in pH buffers at an elevated pH (9.0) led to essentially instantaneous complete degradation of TNT, while those performed in pH buffers at

pH 7.4 degraded at slower rates. It was noted that reactions performed in buffered systems produced similar degradation rates of TNT, regardless of the mineral present, except in the case of goethite/quartz. It is believed that an iron hydroxide solid suspension that formed in reaction mixtures with the addition of buffer solutions was the surface-catalyzing agent for the reduction of TNT.

Clearly, pH played an important role in the surface catalyzed reactions performed here. It is believed that the high pH in the unbuffered reaction mixtures containing calcite and siderite was partly responsible for the reactivity achieved in reactions with these minerals. Several TNT transformation products were identified, but there were a few products that could not be identified.

The results of this study suggest that the presence of mineral phases (or precipitates) in ZVI permeable reactive barriers (PRBs) will not necessarily incapacitate the transformation of TNT, as long as the ZVI corrosion can supply sufficient Fe<sup>2+</sup>. The elevated pH common in ZVI PRBs actually may enhance the degradation of TNT. Explosives are known to contaminate carbonate aquifers. The present results suggest that the slow release of ferrous iron (e.g., as a hydroxide), into an explosive plume may be worthy of consideration in carbonate terrain. Such techniques could prove to be highly cost effective because the only cost would be in injecting ferrous iron solutions into the subsurface site, especially when combined with functioning reactive barriers. In all cases, anaerobic reduction of TNT to intermediate products would have to be coupled with an additional remedial method to treat any soluble products.

#### Acknowledgments

The authors thank Mr. James E. Danberg for his assistance with equipment preparation and Dr. Roseanne Ford (UVA Chemical Engineering) for the use of her HPLC. Mr. Sam Wong conducted the XRD analyses at the US Army Engineer Research and Development Center -Geotechnical and Structures Laboratory. The authors gratefully acknowledge the support of the US Army, Environmental Quality Technology program (Dr. John Cullinane, Technical Director) and the National Science Foundation and Civil and Mechanical Systems Program Director, Dr. Cliff Astill, Grant No. 9984206 through which this project was partially funded.

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