In Situ Remediation of Explosives Contaminated Ground-Water with Sequential Reactive Treatment Zones

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1. ABSTRACT

Most explosives that occur as groundwater pollutants at DoD sites are nitro aromatic compounds (TNT, trinitrobenzene, and various di- and mono-nitrotoluenes) or nitramines (RDX, HMX, and Tetryl). Under favorable conditions, nitro aromatic compounds (NACs) react rapidly with zero-valent iron (Fe^0), which suggests that permeable reactive barriers containing zero-valent iron (FePRBs) might be useful in the remediation of groundwater contaminated with explosives. Unfortunately, reduction of NACs by iron metal produces aromatic amines as the primary products, and these products are still substances of regulatory concern. As a result, full-scale implementation of FePRBs to treat explosives contaminated groundwater has been delayed until an effective treatment for the amines has been developed and tested. The goal of this project was to develop an oxidative treatment step to treat the products of nitro reduction, so that the combination would form a sequential reactive treatment zone (SRTZ) that could be used to reach treatment goals for TNT-contaminated groundwater under field conditions.

To generate simulated effluent from an FePRB we prepared bench scale columns, packed initially with 100% construction-grade, granular iron metal. We found that 100% iron columns, even at flow rates as high as 125 ft/day, produced no TNT or degradation products. Some of the columns were operated for ~1600 pore volumes with no TNT or any reaction products detected (by HPLC) in the effluent. The capacity of these columns to reduce TNT and sequester all of the reduction products suggested that simple FePRBs (with out the additional treatment zones associated with an SRTZ), might be sufficient for full-scale remediation of TNT-contaminated groundwater. A variety of follow-up experiments were performed (varying flow rate and input concentrations, extracting and analyzing products, etc.), and these suggest that the performance of an 100% Fe^0 PRB should be a robust technology for remediation of NACs, and this prospect merits further investigation.

To achieve the original goals of the project, we redesigned the generator columns with less Fe^0, and these columns were used to produce mixtures of TNT reduction products for treatment by oxidation. Several oxidation methods were tested in batch systems, with most work focusing on hydrogen peroxide (H_2O_2). Addition of H_2O_2 to the column effluent did decrease the concentration of some TNT reduction products, presumably due to a mixture of direct chemical oxidation and Fenton reaction. However, we were not able to find conditions where this treatment was sufficiently effective or reproducible to justify pursing application at the field scale. Thus, although we believe that variations on the SRTZ concept will eventually prove to be effective for some contaminants under some field conditions, a conventional FePRB is a more promising treatment technology for TNT and other NACs.

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4. INTRODUCTION

Most explosives that occur as groundwater pollutants at DoD sites are nitro aromatic compounds (TNT, trinitrobenzene, and various di- and mono-nitrotoluenes) or nitramines (RDX, HMX, and Tetryl). Under favorable conditions, nitro aromatic compounds (NACs) react rapidly with zero-valent iron, which suggests that permeable reactive barriers containing zero-valent iron (FePRBs) might be useful in the remediation of groundwater contaminated with explosives. Unfortunately, reduction of NACs by iron metal produces aromatic amines as the primary products, and these products are still substances of regulatory concern. As a result, full-scale implementation of FePRBs to treat explosives contaminated groundwater has been delayed until an effective treatment for the amines has been developed and tested.

There are at least four processes by which NAC reduction products might be removed from the effluent of an FePRB: (*i*) adsorption, (*ii*) oxidative polymerization, (*iii*) degradation with chemical oxidants, and (*iv*) biodegradation. Simple procedures such as sparging the FePRB effluent with air could stimulate several of the above removal processes, thereby providing a sequence of redox treatment zones (SRTZ) that would be an effective remediation technology for groundwater contaminated with explosives. Despite the potential of such an approach, very little work appears to have been done on developing oxidative treatment zones that can be used in sequence after an FePRB [the only major exception being ref. 1].

This project was to evaluate methods of treating the effluent from an FePRB by in situ chemical and/or enzymatic oxidation. Some oxidative degradation was expected, but complete mineralization would be difficult to achieve. Therefore, emphasis was to be placed on optimizing the (permanent) sequestration of NACs by oxidative polymerization and coprecipitation with iron oxides in an open cell or coarsely packed permeable treatment zone. A variety of oxidants (air, O_2, H_2O_2), delivery systems (sparging, direct injection, passive infiltration), and process variables (flow rate, pH, carbonate, iron) were to be tested at the column scale. Design criteria for pilot and full scale SRTZs were to be developed using column test results and computer modeling.

5. TECHNICAL BACKGROUND

5.1. Nitro Reduction with Iron Metal

Although research on the reduction of NACs to amines by iron metal goes at least as far back as 1927 [2], recognition that this reaction might have relevance to remediation of environmental contaminants did not take place until about 1994, several years after Gillham's invention of the FePRB had become widely known to contaminant hydrologists. All of the early work on remediation of NACs by iron metal [3-7] focused on nitrobenzene as a model compound. Those studies showed that reduction of NACs is faster than dehalogenation of chlorinated solvents; so fast, in fact, that the kinetics of nitro reduction are likely to be influenced by mass transport over a range of relevant conditions [8]. Nitrobenzene also proved to be a good

model compound for studying the products formed by reduction with iron metal. The primary product appears to be aniline, with small amounts of the nitroso (and possibly hydroxylamino) intermediates. It is important to keep in mind, however, that product distributions are highly sensitive to experimental conditions (Figure 1).

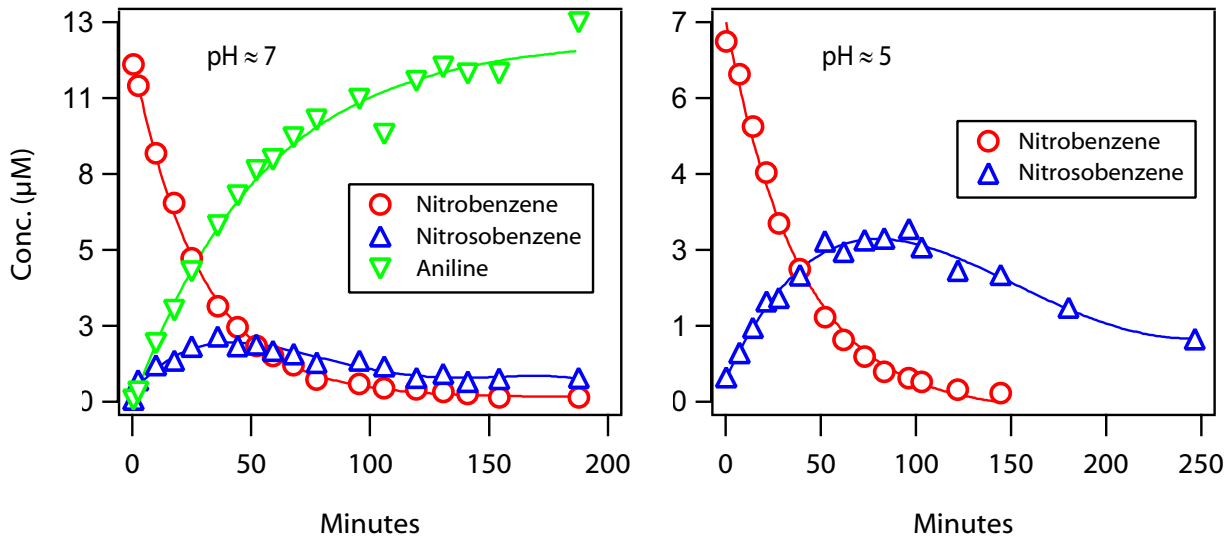

Figure 1. Illustration of the affect of pH on the appearance of nitrobenzene reduction products during exposure to 33.3 g/L of Fluka iron in carbonate buffered batch experiments (Agrawal and Tratnyek, unpublished data). Reduction of the parent compound is rapid in both cases, but aniline only accumulates in solution at near-neutral pH. Method details are similar to those used in ref. [6].

Recently, a second wave of research on nitro reduction by iron metal has begun to appear in the literature, this time with emphasis on specific environmental contaminants such as TNT and RDX [9-11]. As expected, TNT and RDX are rapidly reduced by iron metal in batch tests, yielding a complex mixture of products. Some of these products appear as early-eluting peaks when solution samples are analyzed by HPLC (personal communication with Christian McGrath, WES), but most of this material eventually is sequestered on to iron and mineral surfaces, as evidenced by the mass balances obtained from sequential extractions for ^{14}C from labeled substrates [10, 11]. Although the accumulation of nitro reduction products can make the surface of iron metal less reactive [12], most NACs react rapidly with the Fe(II) oxides that form as an FePRB ages [13, 14].

5.2. Oxidation of Aromatic Amines.

Aromatic amines are the major products of concern with respect to reduction of TNT (and other nitro aromatic contaminants), and the formation of these products is well documented in environmental media [e.g., 15]. Fortunately, aromatic amines are highly susceptible to oxidation and then oxidative polymerization of the resulting aryl amino free radical, as shown below for the simplified case of nitrobenzene.

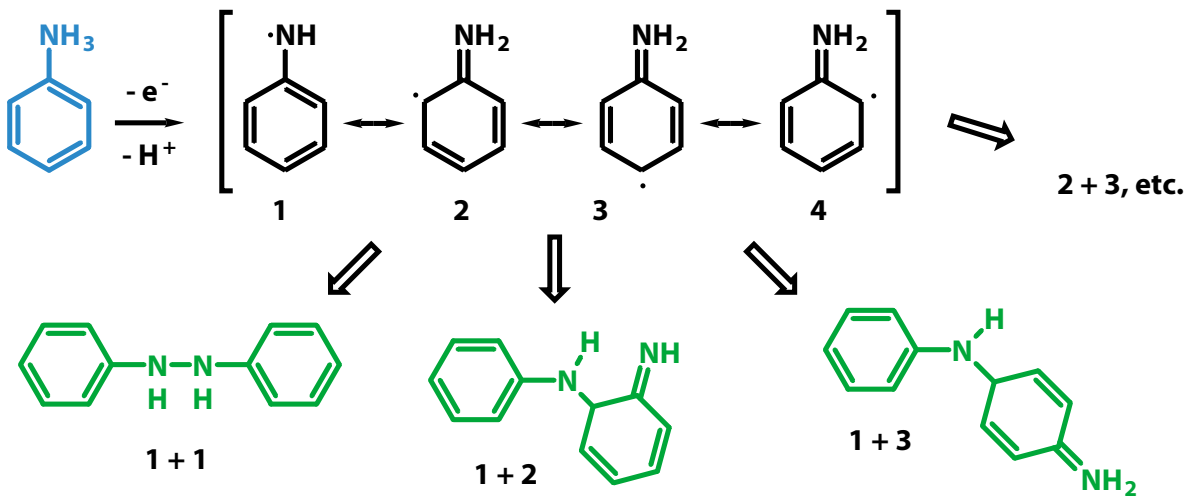

Figure 2. Schematic of the oxidation of an aromatic amine to the corresponding aryl amino radical (resonance structures shown in brackets) followed by coupling to form various dimers.

Covalent binding also occurs between amines and phenolic compounds (by essentially the same mechanism as shown above), which results in the incorporating of the amines into soil organic matter. This processes has been thoroughly investigated by soil scientists, because it is largely responsible for the formation of "bound residues" involving agricultural chemicals that contain aromatic amino (or nitro) groups [16, 17 and numerous addition refs. cited in 18, 19]. Recently, this sort of "humification" has been demonstrated for TNT and some of its metabolites [20, 21]. Since sequestration by this mechanism is essentially irreversible, it is generally considered to be a sufficient end point for remediation of contaminants that are characterized by aromatic nitro or amino functional groups. In fact, this chemistry is likely to be a major contributor to the remediation of explosives contaminated soils by land farming at DoD sites such as the Umatilla Army Depot [22].

The major scientific goal of this project was to develop a method for optimal removal of aromatic amines from FePRB effluent by oxidative polymerization. The two most promising approaches for this appear to be (*i*) addition of chemical oxidants such as air, O_2, or H_2O_2, and (*ii*) provision of oxidizing enzymes such as laccases and peroxidases. The effectiveness of chemical oxidants at initiating polymerization is well documented for phenols [23], and this information helped guide our preliminary experiments with the reduction products of explosives (Task 1). Although the addition of these chemical oxidants also precipitates ferric oxides from the FePRB effluent, this may be a benefit because ferric iron can initiate oxidative polymerization of phenols [23], and some contaminants may be coprecipitated with the flocculation of iron oxides. Clearly, the use of H_2O_2 as the oxidant in an iron-rich system also results in some (non-selective) oxidation of organic substances by Fenton-like chemistry. This, too, may be beneficial, if it results in ring hydroxylation (which will favor more polymerization) or ring cleavage (which could lead to mineralization).

The use of enzymes to catalyze oxidative polymerization of phenols and aromatic amines is well documented, and, in this case, the process has been studied extensively for its possible role in the remediation of contaminated soils [24, 25, and refs. cited therein]. Clearly, this process could be very effective at removing aromatic amines from FePRB effluent if it can be engineered into a treatment zone at a reasonable cost. More likely, it will only be possible to stimulate enzyme activity that is intrinsic to the microbiology of our treatment zone, so this will end up playing a secondary role in overall design.

5.3. Sequential Reactive Treatment Zones.

The major engineering goal of this project was to develop a sequence of reactive treatment zones (SRTZ) consisting of an PRB to reduce nitro groups to amines, followed by a PRB or open trench to oxidize the amines to immobilized products (Figure 3). Like most other SRTZs that have been proposed [e.g., 26], our first treatment zone is a conventional "iron wall", for which design considerations are now fairly well established. Our second treatment zone, however, appears to be a novel concept, so its design and integration with the FePRB, was to be the focus of this project.

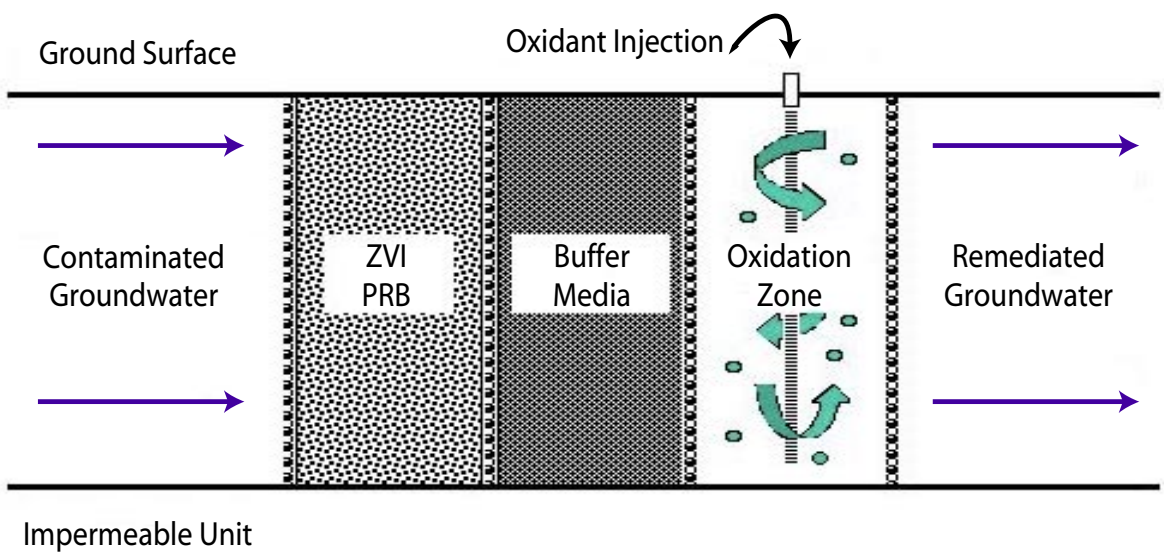

Figure 3. Schematic of an SRTZ consisting of a permeable reactive barrier containing iron metal followed by permeable treatment zone or open trench for oxidation.

The novel portion of the SRTZ that we proposed to develop has three key elements: the buffer zone, the trench or fill of the oxidizing zone, and the method of oxidant delivery. The buffer zone is optional, but probably will be necessary to prevent excessive precipitation of iron oxides at the down-gradient end of the FePRB. This zone may be quartz sand, or may include other minerals for conditioning of the groundwater chemistry [e.g., as proposed in ref. 27]. The oxidizing zone may be open, as in a sparge trench, or packed with gravel. The porosity of this zone will influence the lifetime of a treatment zone where iron oxides and organic material may

be precipitating. However, preliminary calculations indicate that porosity losses will not become significant until ~18 years.[1]

For delivery of oxidant, there are many options. Air or O_2 could be introduced by sparging. In principle, H_2O_2 can be introduced in a variety of ways that are passive or semi-passive. Injection of liquid H_2O_2 (usually 30%) is the conventional approach and has proven to be effective in a variety of applications [28-31]. Another more innovative means of introducing H_2O_2 is through the use of diffusion bags [32]. Diffusion bags can be filled (and refilled) and placed in the permeable barrier where they slowly release H_2O_2. Alternatively, loops of Teflon tubing could be placed within the oxidative treatment cell and the H_2O_2 could be pumped slowly through the tubing to give a steady input of H_2O_2 by diffusion through the tubing.

6. TECHNICAL OBJECTIVES

Identify an oxidative polymerization process suitable from sequestering the reduction products resulting from treatment of nitro aromatic explosives with zero-valent iron.

- Screen potential oxidants and catalysts for removal of model amines (*Task 1*).
- Test promising oxidative treatments with mixtures of reduction products (*Task 2*).

Characterize the major process variables controlling the effectiveness of sequential treatment zones involving nitro reduction followed by oxidative polymerization.

- Design a bench-scale model system for sequential reduction and oxidation zones (*Task 3*).
- Test input and treatment variables to identify optimal treatment conditions (*Task 4*).

Evaluate options for design and implementation of sequential treatment zones that can be used for in situ remediation of groundwater contaminated with explosives.

- Design and test configurations of sequential treatment zones at the bench scale (*Task 5*).

7. RESULTS

7.1. Analytical Method and Product Identification

The major intermediates for sequential nitro reduction of TNT are shown in Figure 4. These are the main products that we expected to find after treatment of TNT with Fe^0. However, each nitro reduction step presumably occurs via a series of three 2-electron transfers with the nitroso and hydroxylamine compounds as intermediates. These two possibilities are not shown in the figure, but are implied by representing the arrows as sets of three.

[1] Calculation based on groundwater velocity = 30 cm/day, porosity = 0.33, total amine concentration = 10 mg/L, density of precipitate = 1 g/mL, penetration in the oxidizing zone = 10 cm, fraction of pore volume necessary to significantly decrease permeability = 0.2.

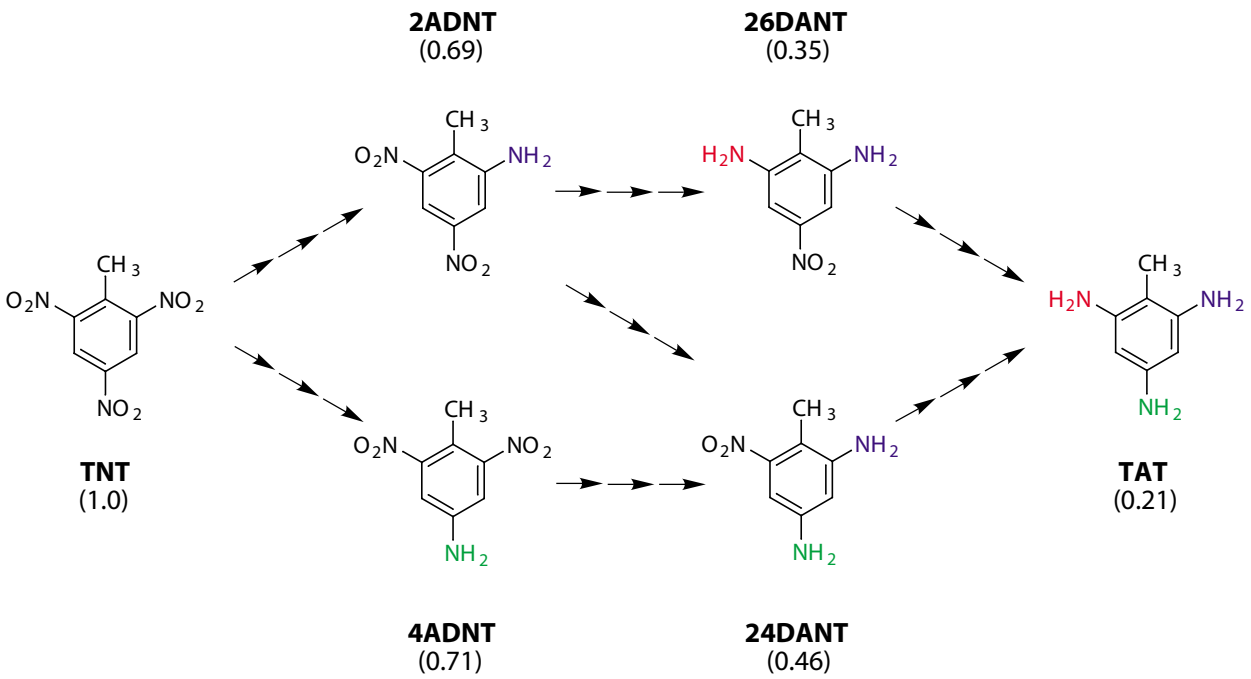

Figure 4. Pathway for nitro reduction of TNT, via two amino dinitro isomers and two diamino nitro isomers, to triaminotoluene. Abbreviations are defined in Table 1. Parenthetical values are retention times normalized to TNT, as defined below. Figure is adapted from [33].

Standards were obtained from commercial sources for all five of the products shown in Figure 4. These were used to develop an HPLC method that could be used to routinely monitor disappearance of TNT, and appearance of most of the five expected products. Details regarding the HPLC method used are given in Appendix A. The performance of our method proved to be somewhat problematic because absolute retention times were too variable to routinely distinguish the isomers of ADNT and DANT, or to distinguish these peaks from the occasional peaks that could not be identified. To help overcome this, we started normalizing all retention times to the retention time of TNT, and the results are shown in Table 1 and Figure 5.

Table 1. Summary of standards and unknowns monitored by HPLC.

Name	Abbr.	Source	Retention Time (min)	Retention Time (relative to TNT)
triaminotoluene	TAT	Standard	2.1	0.12
Unknown	Unk1	Product	5.2	0.30
2,6-diamino-4-nitrotoluene	26DANT	Standard	6.1	0.35
2,4-diamino-6-nitrotoluene	24DANT	Standard	7.9	0.46
Unknown	Unk2, Unk3	Product	8.5	0.49
2-amino-4,6-dinitrotoluene	2ADNT	Standard	11.9	0.69
4-amino-2,6-dinitrotoluene	4ADNT	Standard	12.2	0.71
2,4,6-trinitrotoluene	TNT	Standard	17.2	1

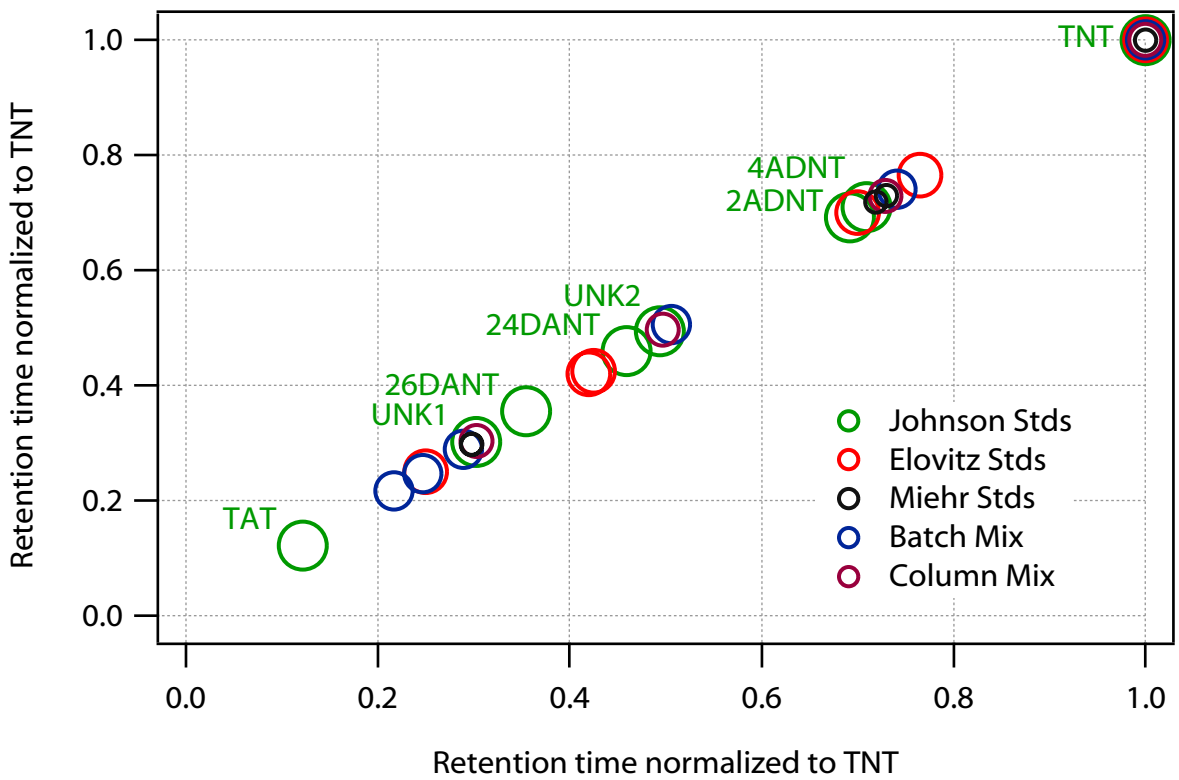

Figure 5. Comparison of retention times normalized to the retention time of TNT. The first four data sets represented are from calibrations done during the course of this study. The last is based on retention times reported previously [33]. All were obtained by HPLC under conditions similar to those detailed in Appendix A.

From Figure 5, it is clear that some peaks could be identified routinely without ambiguity (mainly TNT and generic ADNT), but this would require considerable effort for most peaks (e.g., both DANTs and the various unknowns). Rather than devote what would be a considerable portion of this one-year project to optimizing and validating our HPLC method, we decided that identifying peaks by their retention time normalized to TNT would be sufficient for most purposes of this project. In the following, we have only assigned structures to the product peaks where unambiguous assignments were possible.

7.2. Batch Experiments with Iron

Qualitative results—Products. In part to validate our analytical method (Figure 5), but primarily to determine which source of Fe^0 to use in the bulk of our work, we did a series of batch studies starting with TNT and eight types of granular iron metal. Details on the method used are given in Appendix A, and the results are summarized below (Figure 6).

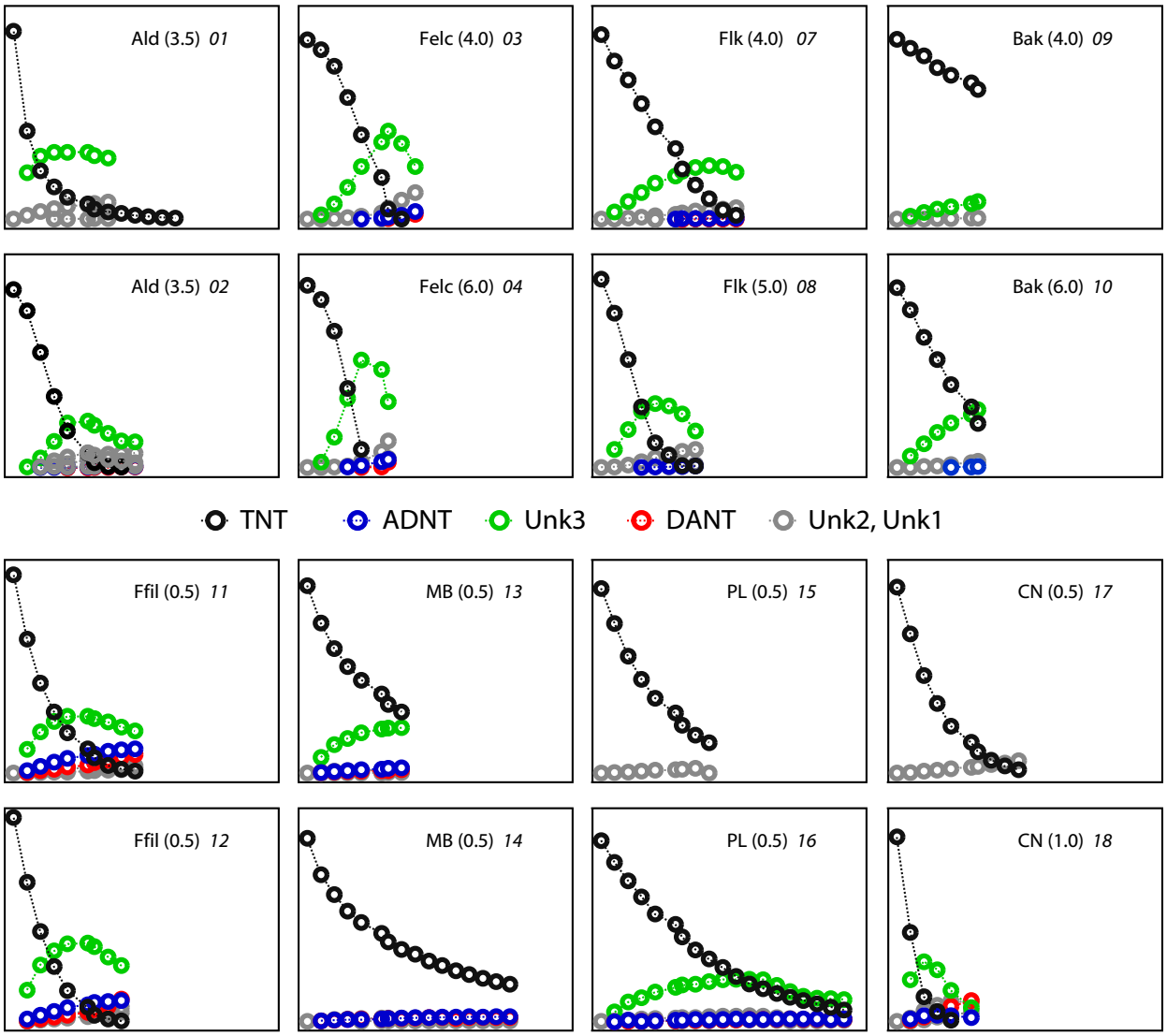

Figure 6. Results from batch experiments for removal of TNT (black) by eight types of zero-valent iron (Ald: Aldrich, Felc: Fisher electrolytic, Flk: Fluka, Bak: Baker, Ffil: Fisher filings, MB: Master builders, PL: Peerless, CN: Connelly). Products identified include ADNT (both isomers, blue) and DANT (both isomers, red), the early eluting product (green), and other later eluting unidentified products (gray). Plots are linear peak areas vs. time. Parentheses indicate grams of iron used. Italicized numbers refer to experiment numbers in Table 2. These data to be published in ref. [34].

In all cases the batch data in Figure 6 show rapid disappearance of TNT and transient appearance of various degradation products. In general, the largest intermediate was an unidentified peak (which was most likely to be one of the nitroso or hydroxylamine intermediates for which we were not able to obtain standards). Lesser amounts of the ADNTs, DANTs, and other unknowns, were also observed. The amount of product appearance was generally least with the construction grade iron samples (MB, PL, and CN). Long-term batch

experiments (not shown) showed that many of the products shown in Figure 6 were eventually sequestered.

Quantitative results—Kinetics. The kinetics of TNT disappearance in the batch experiments represented by Figure 6 turned out to more complex than has generally been observed with other contaminants. Rather than fitting the disappearance data to a pseudo first order model, as is usually done [35], we discovered that the kinetics were best described as transitional from zero-order to first-order, so they were modeled accordingly. Details of the justification and computations for this analysis will be presented elsewhere [34, 36]. For present purposes, the results have been reduced to surface area normalized rate constants, k_{SA}, and are summarized in Figure 7 (and Table 2). Note that normalization for surface area gives relatively small values of k_{SA} for the iron samples that contain a large amount of iron oxide (denoted in green) because the iron oxide gives these samples a large specific surface area.

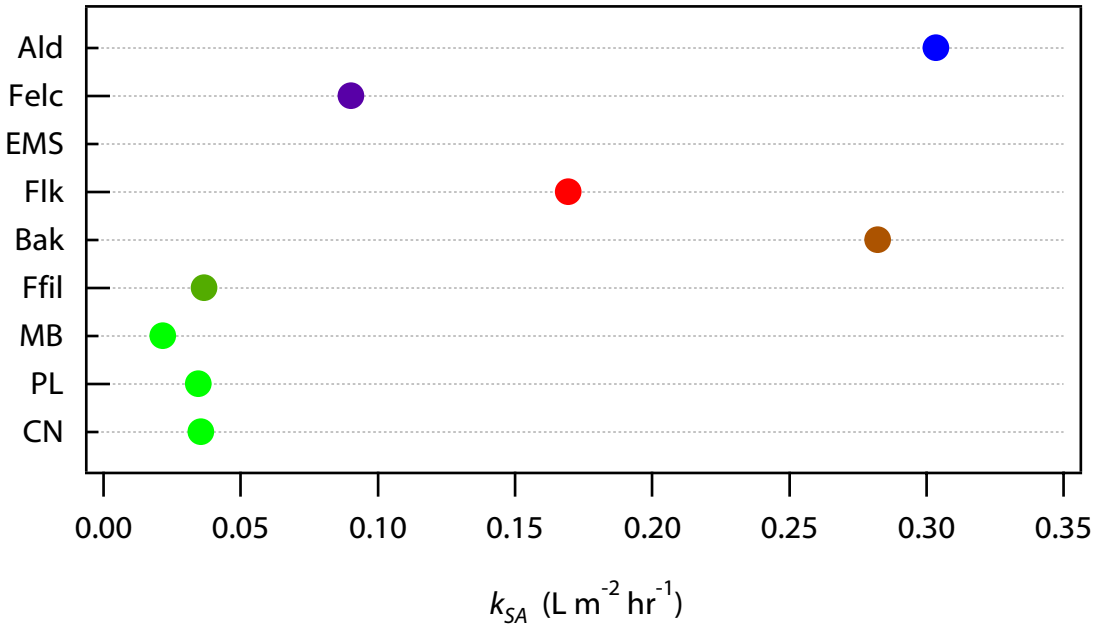

Figure 7. Comparison of k_{SA} from batch studies with TNT and eight types of Fe^0. A ninth row is included in this plot for EMS iron, which is empty because EMS did not react significantly with TNT. This unusual result was reproduced and will be discussed in future publications [34, 37]. The data for this figure are summarized in Table 2. Note that the last four types of iron (denoted in green) contain the most iron oxide, whereas the blue and orange symbols represent iron samples that are largely free of oxides.

Even though the construction grade samples of iron give low rates of TNT removal relative to high purity iron, all of these rates are quite high when compared to most other contaminants. This can be seen in Figure 8, which shows the eight values of k_{SA} from this study plotted versus various literature values of k_{SA} for a wide range of contaminants.

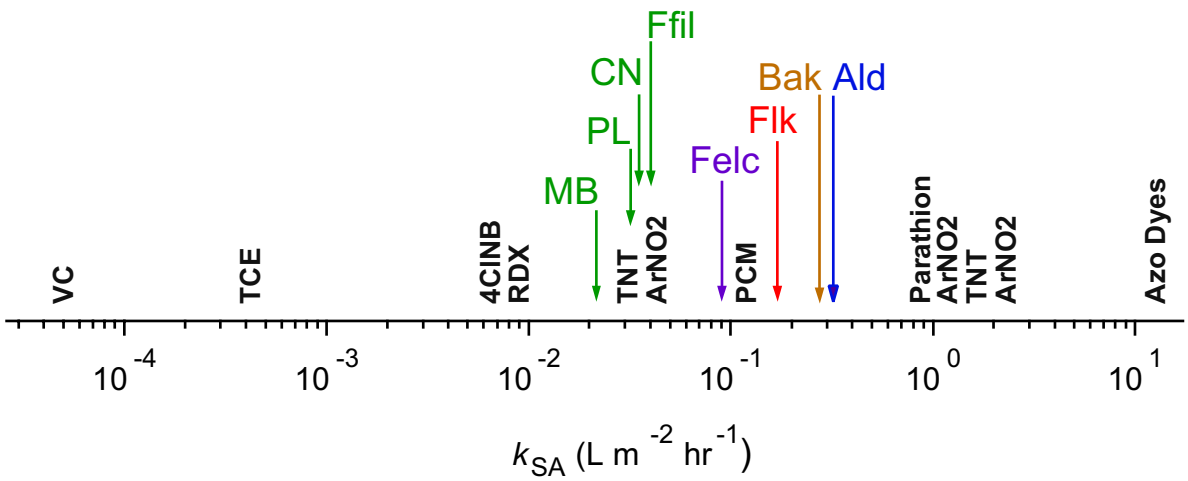

Figure 8. Comparison of k_{SA} from batch studies with TNT and eight types of Fe^0 vs. rate constants for other contaminants obtained from the literature. This figure adapted from [38], where the sources of all the literature data (in black) are identified.

The comparison presented in Figure 8 shows the k_{SA} measured in this study fall within the range of previously reported values for nitro aromatics (TNT, ArNO2, 4ClNB, and parathion). It can also be seen that these compounds react considerably more rapidly than most chlorinated hydrocarbons, including trichloroethylene (TCE) and vinyl chloride (VC). In general, these highly reactive contaminants are more prone to give mass transport limited kinetics. In fact, we have recently shown that nitrobenzene (ArNO2) exhibits kinetics that reflect a mixture of reaction and mass transport effects, and that this has a variety of important implications for design of PRBs to treat very reactive contaminants [38]. It appears that TNT is comparable to ArNO2 in reactivity, so we expect that some of the kinetic data reported here (and previously by others) reflect mass transport effects.

Quantitative results—Treatment Effects. Additional batch experiments were done to investigate the effects of critical variables, with the ultimate goal of clarifying what kinetic parameters are most appropriate for modeling column and field performance. Most of these results are summarized in Figure 9 and Table 2.

The most important design variable that can used to influence k_{obs} is the amount of iron exposed to the contaminant, or more precisely, the amount of iron surface area per unit volume of aqueous solution [35, 39]. This parameter (usually designated ρ_a) is readily calculated from the mass, specific gravity, and specific surface area of the iron used and the total volume of the reaction vessel. As has been shown for many other contaminants, increasing ρ_a causes a linear increase in k_{obs} for TNT (Figure 9). Fitting such data is the more statistically robust way to estimate the surface area normalized rate constant, k_{SA}, if all other experimental variables are held constant. This was the case for the data represented in blue in Figure 9 and regression of

Table 2. Conditions and results of batch experiments with TNT and Fe^0.

	Iron source	Iron a_s ($m^2\ g^{-1}$)	Iron mass (grams)	Solution volume (mL)	TNT C_0 (mg/L)	Equilib. time (hours)	Kinetic model fitted	k_{obs} (min^{-1})	k_{SA} ($L\ m^{-2}\ hr^{-1}$)
1.	Ald	0.0941	3.50	43.92	40	0	Mixed[2]	1.84e-2	1.48e-1
2.	Ald	0.0941	3.50	43.92	40	0	Mixed	5.74e-2	4.59e-1
3.	Felc	1.27	4.00	43.88	40	0	Mixed[3]	1.74e-1	9.00e-2
4.	Felc	1.27	6.00	43.67	40	0	Mixed[3]	5.80e+2	1.99e+2
5.	EMS	0.075	5.00	43.74	40	0	Mixed	3.84e-6	2.76e-5
6.	EMS	0.075	8.00	43.41	40	0	Mixed	2.16e-5	9.38e-5
7.	Flk	0.229	4.00	43.83	40	0	Mixed	5.77e-2	1.66e-1
8.	Flk	0.229	5.00	43.72	40	0	Mixed[3]	7.56e-2	1.73e-1
9.	Bak	0.0401	4.00	43.88	40	0	Mixed	2.77e-3	4.55e-2
10.	Bak	0.0401	6.00	43.67	40	0	Mixed	4.76e-2	5.19e-1
11.	Ffil	4.0915	0.50	44.24	40	0	Mixed	2.34e-2	3.04e-2
12.	Ffil	4.0915	0.50	44.24	40	0	Mixed	3.29e-2	4.27e-2
13.	MB	1.45	0.50	44.23	40	0	Mixed[2]	7.25e-3	2.65e-2
14.	MB	1.45	0.50	44.23	40	0	Mixed[2]	4.50e-3	1.65e-2
15.	PL	1.54	0.50	44.23	40	0	Mixed	8.77e-3	3.02e-2
16.	PL	1.54	0.50	44.23	40	0	Mixed	1.12e-2	3.88e-2
17.	CN	4.9377	0.50	44.23	40	0	Mixed	2.31e-2	2.48e-2
18.	CN	4.9377	1.00	44.17	40	0	Mixed	8.57e-2	4.60e-2
19.	PL[1]	1.54	0.75	59.90	40	164	First	1.11e-3	3.45e-3
20.	PL[1]	1.54	0.75	59.90	40	211	First	1.89e-4	5.89e-4
21.	PL[1]	1.54	0.75	59.90	40	24	First	5.03e-4	1.56e-3
22.	PL[1]	1.54	2.00	59.73	40	24	First	1.69e-2	1.96e-2
23.	PL[1]	1.54	2.90	59.61	20	24	First	1.54e-1	1.24e-1
24.	PL[1]	1.54	2.90	59.61	40	24	First	5.70e-2	4.57e-2
25.	PL[1]	1.54	2.90	59.61	70	24	First	7.64e-3	6.12e-3
26.	PL[1]	1.54	3.75	59.49	40	24	First	7.03e-2	4.34e-2
27.	PL[1]	1.54	5.00	59.32	40	24	First	8.65e-2	4.00e-2
28.	PL[1]	1.54	7.50	58.99	40	24	--[4]	--[4]	--[4]
29.	PL[1]	1.54	15.0	57.97	40	24	--[4]	--[4]	--[4]

[1] Special lot of "improved" iron aggregate that was provided by Peerless. For this material, we assumed the specific surface area and specific gravity was the same as previously characterized iron from Peerless, [2]Excluded initial data that were dominated by adsorption, [3]Excluded initial data that exhibited a lag phase. [4]Disappearance of TNT was too fast to measure.

these data gave a slope from which we estimate k_{SA} = 0.050±0.007 L m^{-2} hr^{-1} for the Peerless iron metal used in these experiments. This sample of iron was from a custom batch prepared by Peerless to give more rapid degradation of chlorinated solvents. Superimposing the k_{SA} we obtained for this iron on Figure 7 or Figure 8 shows that the collective results are quite reasonable: "improved" Peerless iron removed TNT slightly more rapidly than other construction grade iron materials, but still more slowly than the high-purity reagent grade irons.

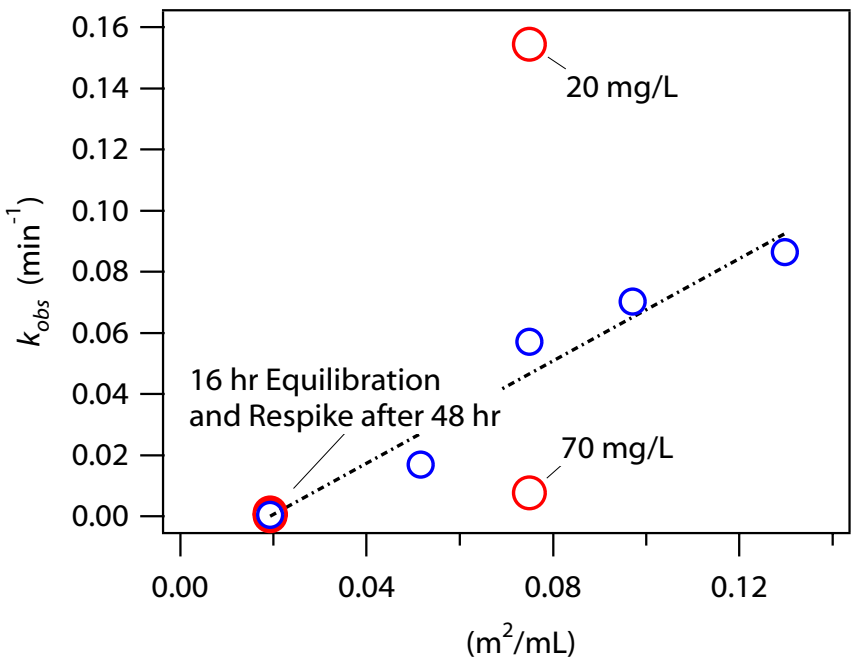

Figure 9. Results of batch experiments done with "improved" Peerless iron. Data represented in blue show the effect of varying the amount (and therefore surface area) of iron, with 24 hr of preequilibration before adding TNT at 40 mg/L. The regression line from these data has slope = 0.8±0.1, intercept = -0.02±0.01, and r^2 = 0.95. Data in red illustrate effects of other variables, including initial concentration of TNT, equilibration time before adding TNT, and respiking with TNT. Data in Table 2.

Several other factors that appear to influence the kinetics of TNT disappearance by iron were investigated, and some of the data are shown as red points in Figure 9. Varying the initial concentration of TNT (at constant ρ_a) gave a notable result: both rates (not shown) and rate constants decrease with increasing initial concentration of TNT. These results are not consistent with the site saturation effects that have been observed for many chlorinated solvents [36, 40-43], but they are consistent with inhibition by accumulation of adsorbed products of nitro reduction [12]. This effect may also be responsible for the slower disappearance rate of TNT in one experiment where we respiked with TNT (overlapping red points in Figure 9).

7.3. Column Experiments with 100% Iron

To begin our study on SRTZs, we set up small columns of granular Fe^0 to generate effluent with a mixture of TNT degradation products that could be used to test methods of oxidizing these products. However, we found that 100% iron columns produced no detectable TNT or degradation products in the column effluent. This result presented a minor problem with respect to our original plan to use these columns to generate effluent for follow-up treatment by oxidation. On the other hand, the result was our first indication that column model systems would give profoundly different (and more promising) results than batch systems.

To verify our preliminary results and discover the limits of TNT removal by columns of Fe^0, several columns were run at a variety of extreme conditions. Figure 10 shows the cumulative loading of a column packed with 100% Connelly Fe^0 and exposed to high concentrations of TNT (20 mg/L) at an average linear velocity of 125 ft/day. No TNT or detectable products were eluted from the column over the coarse of this experiment. These results demonstrate a remarkable capacity for Fe^0 to remove TNT and to retain the degradation products that appeared to be a problem based on batch studies. Similar results were obtained with columns using Peerless iron subjected to high concentrations of TNT and flow rates varying from 10 to 500 ft/day (data not shown). Some columns received nearly 5000 pore volumes of water of the course of several weeks. These results suggests that the removal performance is not related to a specific type of iron or limited to short time periods of exposure.

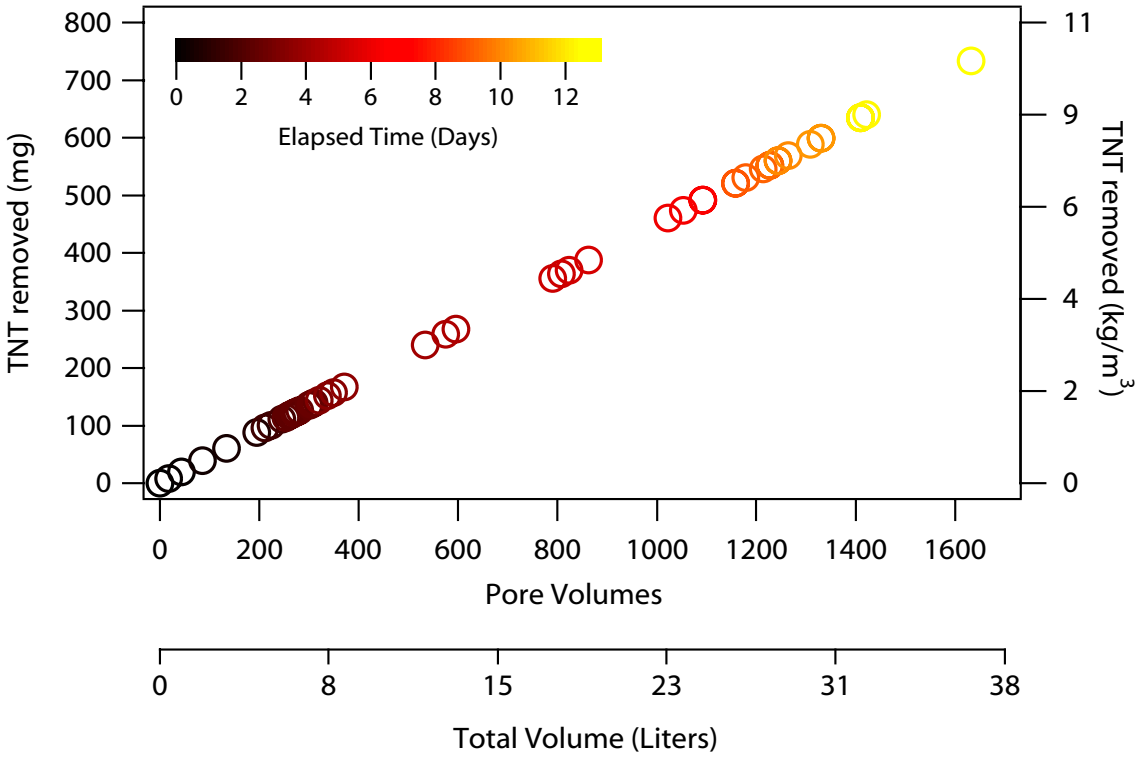

Figure 10. Graphical summary of cumulative TNT loading onto a 100% Fe^0 column run at a high flow rate showing that loading rates of at least 10 kg/m^3 of Fe^0 are possible. Points represent effluent sampling, none of which was found to contain TNT or products that could be detected by HPLC. Data to be published in ref. [44].

To illustrate the implications of the results in Figure 10, we added the right axis showing the cumulative mass of TNT removed per cubic meter of FePRB volume. This does not represent the full "capacity" of the FePRB, but rather the loading of TNT that may be achieved without any significant breakthrough of TNT through the FePRB. In that context, the maximum cumulative mass observed here can be thought of as the minimum of TNT that can be taken up by the FePRB. However, because the TNT is being degraded on the iron surface, and because

there will likely be the precipitation of iron to form new reactive surfaces, it is likely that the capacity of the FePRB may not be limited by the mass of TNT. In either case, given typical groundwater concentrations and velocities, the data in Figure 10 represents the ability to treat an extremely large volume of contaminated groundwater.

7.4. Column Experiments with Iron and Sand

After discovering that the effluent from 100% Fe columns did not contain residues for treatment by oxidation, we began testing columns with increasing proportions of sand in order to obtain less efficient contaminant removal. We also expected that the results from these tests would provide insights that would help explain the difference between the results from batch and 100% iron columns. Representative results are shown in Figure 11, including the breakthrough curve for TNT in a 100% sand column (*A*) and a partial breakthrough curve for TNT in a column filed with 10% sand (*B*).

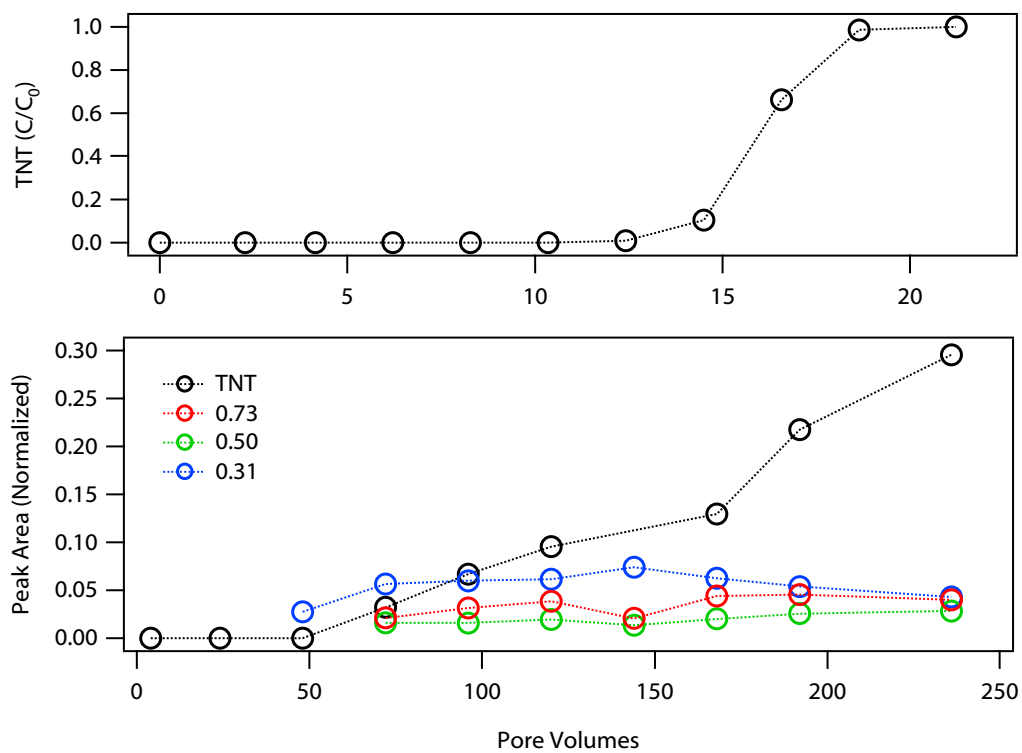

Figure 11. Breakthrough curves for TNT and degradation products in two columns (A) packed with 100% sand and run at 75 ft/d. (B) 10% Connelly Fe^0 (by weight) and 90% sand, and run at 125 ft/d. Initial TNT concentration was 20 mg/L for both. Legend refers to retention times normalized to TNT, as described in Section 7.1.

Figure 11A shows the breakthrough curve for TNT from a 15 cm long column packed with 100% silica sand. The column data were fit to a one-dimensional numerical model (MODFLOW/MT3D) where sorption was fit with a linear Freundlich isotherm. A retardation factor (R_{sand}) of ~16.5 and a longitudinal dispersivity of 0.2 cm provided the best fit to the data.

If a porosity (n) of 0.35 and a bulk density of the sand (ρ_{sand}) of 1.65 are assumed, a partition coefficient for the sand ($K_{D\text{-}Sand}$) of 3.29 mL/g can be calculated.

The breakthrough curve in Figure 11B is for a column containing 10% by weight (~3% by volume) Fe^0. In this case, the observed retardation factor is significantly greater. Simulation of this case with a one-dimensional model that includes a first-order degradation term for TNT could not provide a good fit to the data unless a very large dispersivity term was used (i.e., on the order of 20 cm or 100 times larger than the values used in the 100% sand column). A dispersivity value of that magnitude is not reasonable and the conclusion is that the sorption and/or degradation terms must be more complicated than the "simple" approaches used in the model, perhaps due to the very high flow rate in the column (~1 pore volume / 6 min). In any event, to fit the column data an overall retardation factor of at least 50 was necessary. If the silica sand is assumed to provide a retardation factor (R_{Sand}) of 15 and an overall retardation factor (R_{Tot}) of 50 is assumed, then the K_D value for Fe^0 needed for a R_{Tot} of 50 can be estimated using the equation:

$$R_{Tot} = \frac{n + \rho_{sand} K_{D-sand} + \rho_{"10\%"Fe} K_{D-Fe}}{n}$$

$$50 = \frac{.35 + 1.6 * 3.29 + .16 * K_{D-Fe}}{.35}$$

where the bulk densities of the sand and the Fe^0 in the "10% iron column" are assumed to be 1.6 and 0.16 g/mL, respectively. Solving the equation for $K_{D\text{-}Fe}$ gives a value of approximately 74. For a 100% iron column, this $K_{D\text{-}Fe}$ value would translate into a retardation factor of

$$\begin{aligned} R_{100\%Fe} &= 1 + \frac{\rho_{100\%Fe} K_{D-Fe}}{n} \\ &= 1 + \frac{5 * 74}{0.35} \\ &= 1060 \end{aligned}$$

7.5. Batch Oxidation Experiments

Using the effluent from columns such as the one that produced Figure 11B, we tested a variety of oxidants under a variety of conditions in order to treat the products of TNT reduction. In most cases, the oxidant used was H_2O_2, but a few experiments were performed by sparging with O_2 and air. Where H_2O_2 was the oxidant, we expected both oxidative coupling (Section 5.2) and oxidative degradation (directly by H_2O_2 or by H_2O_2/Fe(II), i.e., the Fenton reaction). In an effort to optimize the conditions for coupling and/or Fenton reaction, we varied the concentration of added H_2O_2, pH, and the amount and form of added Fe(II).

The initial concentration of H_2O_2 was varied from 1 to 50 mg/L. Although higher concentrations of H_2O_2 did cause larger decreases in the peak areas of products from the TNT/Fe^0 reaction, the improvements were modest, which suggested that some other factor was limiting. Since it is well known that Fenton reaction is most efficient at low pH and oxidative couple is favored at high pH, we tried adding H_2O_2 after adjusting the pH to 3, 4.5, and 8. Removal of the product peaks was best at low pH, but again, the differences between the treatments were modest, suggesting that pH was not the primary factor responsible for poor removal efficiencies that we observed. A representative example of these results is shown in Figure 12.

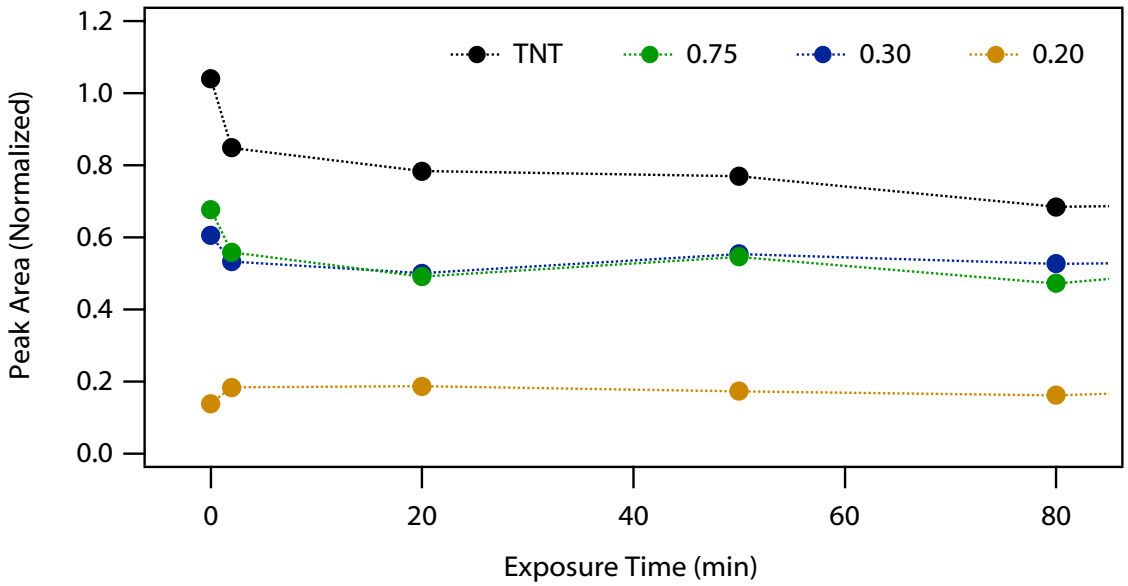

Figure 12. Concentration vs. time plot for TNT and the three most significant products of TNT treatment with Fe^0 after addition of 50 mg/L H_2O_2 and pH 3.

The fast initial decrease in product peak areas shown in Figure 12, suggest that the rapid reaction that we hoped to achieve may be occurring, but a necessary reactant is being used up or that reaction is altering conditions in a way that is autoinhibitory. Although we did not measure the amount of H_2O_2 remaining at the end of these experiments, it is unlikely that this reactant is limiting because the initial concentrations used were quite high. At first, we assumed that exposure to Fe^0 would result in enough soluble iron for sustained Fenton reaction, but the availability of this iron might vary in ways that are hard to quantify. Instead, we investigated the possibility that iron might be limiting by adding ferrous nitrate at concentrations ranging from 1 to 20 mg/L. However, the results (not shown) were not substantially different than those shown in Figure 12.

From the results described in this section, we concluded that there is potential for using Fenton oxidation to treat the aromatic amines formed by treatment of TNT with Fe^0. However, the effectiveness of this procedure was highly variable, and this variability prevented us from

optimizing the process even using batch systems in the laboratory. Even assuming that the process can be optimized to give better performance, our difficulty in doing this in the laboratory suggests that it is unlikely to be practical in the field. There are, of course, other ways of stimulating oxidation polymerization of aromatic amines (such as with extracellular enzymes as described in Section 5.2) that we did not have time to investigate as part of this project. These options may still warrant investigation, but the possibility that treatment zones containing 100% Fe^0 may be sufficient to remediate TNT without any follow up treatment (Section 7.3) is more likely to lead to a full-scale remediation technology in the foreseeable future.

7.6. Modeling

The one-dimensional model used above can provide insight into the expected performance of a 100% Fe^0 column or PRB. Although the 10% Fe^0 column data (Figure 11B) showed the behavior to be complex, we can use conservative parameters and the simple model to make a preliminary estimate of what the breakthrough concentrations would be for a 100% Fe^0 column at a flow rate of 125 feet per day.

Using the surface area normalized rate constant (k_{SA}) and specific surface area (a_s) from experiments 22 to 30 in Table 2 (since they represent the largest number of replicates in our batch data), we can estimate a rate constant for the 100% Fe^0 case. Because the iron to water ratio is approximately 1300 times greater in the column than in the batch test, the resulting first order rate constant is very large (corresponding to a half life for TNT of ~2 seconds):

$$
\begin{aligned}
k_{obs} &= k_{SA}\,\rho_a \\
&= 0.05\ \text{L m}^{-2}\ \text{hr}^{-1}\ \text{x}\ 1.54\ \text{m}^2\ \text{g}^{-1}\ \text{x}\ 5000\ \text{g Fe}^0\ /\ 0.3\ \text{L Solution} \\
&= 1283\ \text{hr}^{-1} = 21.4\ \text{min}^{-1} \\
t_{1/2} &= 0.69 / 21.4\ \text{min}^{-1} = 0.03\ \text{min} \approx 2\ \text{sec}
\end{aligned}
$$

As discussed above, based on the 10% Fe^0 column, it appears that partitioning of TNT onto Fe^0 is more complex than can be represented by a linear isotherm. Nevertheless, based on the available data, it would appear that a minimum value of K_D for TNT in an Fe^0 column is ~1060. Based on that K_D and the rate constant described above, the calculated breakthrough concentration of TNT from a 100% iron column is extremely low (i.e., based on the two-second half life calculated above and a residence time in the column of six minutes [180 half lives], even without the effects of sorption, the C/C_0 concentration would be expected to drop to about 1 x 10^{-34}). Thus, the expected concentration out of such a column is very small and far below the detection limit by current analytical methods. As a result, it would be expected that, unless conditions in the column change with time, there would never be any "observed" breakthrough of TNT from the column. For the case of an FePRB, groundwater velocities are likely to be significantly slower than used in the column and the barrier is likely to be significantly thicker. Thus, it is anticipated that no breakthrough of TNT from an FePRB would be observed either.

8. DISCUSSION OF RESULTS

8.1. "Higher Order" Scaling Effects

The stark difference in products found with the batch versus column model systems suggests significant differences in the processes controlling the fate of the reduction products of TNT. This could be due to a variety of effects. For example, (*i*) more corrosion in the columns produces a high solution pH which may stimulate the polymerization, adsorption, and/or degradation of the aromatic amines that form from TNT reduction; or (*ii*) the abundance of oxide surfaces in the columns may catalyze sequestration of TNT reduction products by coprecipitation and/or adsorption. Due to the complexity of these processes and the products they form, we were not able to determine which of these processes are most responsible for highly effective removal of TNT that we observed with 100% Fe^0.

Our tentative explanation of the difference between batch and column results suggest that the difference between the systems is a "higher order" effect in that it gives results that are *qualitatively* different rather than being a scaling effect that might be expected based on extrapolation of simple quantitative model. Some of the latter are already well established for the iron metal system, such as the relation between rate of reduction and the surface area of iron, initial concentration of contaminant, or efficiency of mixing. In contrast, "higher order" effects involve changes in process caused by changes in properties, and the relationship between processes and properties are usually described by mechanistic models that are only qualitative.

As the state of our understanding of the processes that control contaminant remediation by Fe^0 improves, we think that these "higher order" will be detected more frequently. In fact, we recently noted two other examples from previously published data, and have begun to develop this idea as a general theme (See the abstract provided in Section 11).

8.2. Prospects for FePRBs to Treat Energetics

Before taking this technology to the field it is appropriate to determine if the results from the batch and small column data can be scaled up to the field. This will involve answering the following questions:

- Can the level of performance observed in the column and batch tests be achieved in a full-sized barrier?
- How long will barriers in the field maintain the high level of performance (including retention of daughter products) observed in the laboratory?
- How will ground water chemistry and related characteristics unique to individual field sites affect long-term performance?

Based on the performance of FePRB to treat chlorinated solvent groundwater plumes, it is anticipated that excellent long-term performance can be achieved. The next steps in evaluation of the FePRB technology for TNT and other energetics are continued laboratory investigations

coupled with aboveground Fe^0 canisters at one or more sites where groundwater pump-and-treat systems are already in place. The canister approach provides an opportunity to test the questions listed above in an accelerated timeframe under realistic geochemical conditions. Since the technology for installing FePRBs is already well known, following successful demonstration of the aboveground canisters, it should be possible to go directly to the field with an FePRB for TNT.

9. SUMMARY OF CONCLUSIONS

- Batch experiments with TNT and a variety of types of Fe^0 gave results consistent with those reported previously: rapid disappearance of TNT and gradual accumulation of a complex mixture of transformation products, a small portion of which were the aromatic amines ADNT and DANT.
- Columns packed with iron at loading similar to those typically used in full-scale FePRBs removed very large quantities of TNT and allowed no products that were detectable by HPLC to pass into the effluent, even with average linear velocities as high as 125 ft/day.
- The stark difference between batch and column results probably reflects differences in "geochemical" conditions (low Eh, high pH, and abundance of amorphous authigenic iron oxides) that favor enhanced sequestration of TNT reduction products.
- If the 100% Fe^0 column results apply to the field scale, then FePRBs may be sufficient (without sequential reactive treatment zones or other enhancements) to remediate groundwater that is contaminate with TNT and other explosives.
- Columns packed with mixtures of iron and sand could be made to produce effluent that contained mixtures of TNT reduction products comparable to those found in batch experiments.
- Batch experiments using the effluent from iron/sand columns showed the addition of hydrogen peroxide did remove some of the TNT reduction products, but good efficiencies were not obtained consistently using this method.
- Although sequential reactive treatment zones may prove to be of considerable value at some sites for certain contaminants, it appears that simple FePRBs may be sufficient for remediation of TNT and possibly other organic contaminants containing nitro groups.

10. APPENDIX A: EXPERIMENTAL DETAILS

10.1. Reactants

Trinitrotoluene was obtained in high purity from ChemService, West Chester, PA and used as received. 2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene were purchased from Sigma/Supelco, Bellefonte, PA. 2,4-diamino-6-nitrotoluene, 2,6-diamino-4-nitrotoluene, and 2,4,6-triaminotoluene trichloride were purchased from AccuStandard, New Haven, CT and used as received. The ten types of granular Fe(0) used in this study were Aldrich powder (Ald), Fisher electrolytic powder (Felc), EM Science degreased filings (EMS), Fluka filings (Flk), Baker chips (Bak), Fisher filings (Ffil), Master Builders (MB), Peerless Powders and Abrasives (PL), "improved" Peerless cast iron and Connelly (CN). To remove fines but minimize other changes, all metal samples were rinsed with DI water, and dried with acetone before use.

10.2. Batch Experimental Protocols

Batch experiments were prepared in an anaerobic chamber with a 95% N_2/5% H_2 atmosphere to maintain anoxic conditions. The degradation experiments were either conducted in 40 mL VOA vials or 60 ml serum bottles, containing varying concentrations of iron and filled with DI water leaving no headspace. The bottles were spiked with 0.1 mL and 0.15 mL TNT stock solution, respectively, to get an initial concentration of 40 mg/L and subsequently mixed end-over end on a rotary mixer at a moderate speed (20 rpm). Approximately 200 µL samples were collected from the vial, filtered through a 0.45 µm Nalgene 4 mm nylon filter (Fisher, Pittsburgh, PA), and analyzed by HPLC.

10.3. Column Description and Operation

Eight metal columns (2.54 x 15 cm) were packed with commercial grade iron, four with Peerless brand and four with Connelly. For each type of iron there was a column with 100% iron, 50% iron, 30% iron, and 10% iron (all percent by mass and as homogenized as possible). The columns were attached to an HPLC pump, which drew from a reservoir of DI water containing 30 mg/L. The effluent flow from each column was periodically collected and analyzed by HPLC.

10.4. Analytical Methods

Samples were manually injected immediately after collection and filtration on a Rainin HPLC with an Econosil C-18 column (length 250 mm, ID 4.6 mm column; Alltech, Deerfield, IL). Two mobile phases were used during different portions of the experiments, one method used 45:55 acetonitrile/water and a flow rate of 1.0 mL/min. The other used 50:50 methanol/water mixture at a flow rate of 1.1 mL/min. It was determined that the methanol method provided better separation of the degradation products. TNT and the products were monitored at 254 nm. Identification of nitroaromatic products was achieved by matching retention times of unknowns to those of standards. Redox potential and pH were measured with an Orion 720 meter and the appropriate electrode. Iron was determined using a Hach field spectrometer and iron reagent kit.

11. APPENDIX B: DELIVERABLES

Presentations:

1. Tratnyek, P. G. "A geochemical perspective on the design, performance, and enhancement of iron walls". *Theis Conference on Iron in Groundwater*, 15-18 September 2000, Jackson Hole, WY (invited, plenary).
2. Johnson, T. L.; Tratnyek, P. G.; Johnson, R. L. "Removal of aqueous trinitrotoluene (TNT) from packed columns of zero-valent iron". *Focus Conference on Pacific Northwest Groundwater Issues*, 22-23 February 2001, Portland, OR.
3. Tratnyek, P. G. "A chemical perspective on the design, performance, and enhancement of iron walls". *Groundwater Quality 2001: Third International Conference on Groundwater Quality*, 18-21 June 2001, Sheffield, UK. (invited).

Publications:

1. Tratnyek, P. G. (2000) A geochemical perspective on the design, performance, and enhancement of iron wall. *Theis Conference on Iron in Groundwater*, American Ground Water Association, Westerville, OH, extended abstract (attached below).
2. Miehr, R.; Tratnyek, P. G.; Bandstra, J. Z.; Scherer, M. M.; Alowitz, M.; Bylaska, E. J. (2001) The diversity of contaminant reduction reactions by zero-valent iron: role of the reductate. *Environ. Sci. Technol.*, in prep.
3. Tratnyek, P. G.; Johnson, T. L.; Johnson, R. L.; Miehr, R. (2001) Spatial and temporal dynamics in the remediation of TNT by zero-valent iron; *Groundwater Quality 2001: Third International Conference on Groundwater Quality,* Sheffield, UK, IAHS Press, in prep.

Proposals:

1. Tratnyek, P. G.; Johnson, R. L. "Remediation of Explosives Contaminated Ground-Water with Zero-Valent Iron", SERDP CUSON-01-08, $598,043 (2 years), pending.
2. Johnson, R. L. et al. ESTCP, in preparation.

A Geochemical Perspective on the Design, Performance, and Enhancement of Iron Walls*

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Permeable reactive barriers (PRBs) of zero-valent iron (ZVI) create an in situ environment with geochemistry that is complex and variable in both spatial and temporal dimensions. Some of the processes that create this environment are specific to the chemistry of iron metal, but many are representative of the (bio)geochemistry of ferrous/ferric iron in the environment as a whole. In fact, some evidence suggests that the main effect of ZVI in PRBs is to create and sustain an environment that is rich in highly-reducing, high-surface area iron oxides, and it may be the high reactivity of these authigenic solids that is primarily responsible for contaminant removal.

The question of the role of Fe^{II} relative to that of Fe^0 in ZVI PRBs has become more difficult, and more interesting, as our understanding of these systems has become more sophisticated. Back in 1994 [1], we tried to capture the essential features of this problem in a conceptual model that distinguished between contaminant reduction by Fe^0, Fe^{II}, and H_2 (Fig. 1A). The major weakness of this model was that it did not make explicit the role of iron oxides or other precipitates on the iron metal. Recently [2], we proposed another conceptual model, which attempts to classify the possible roles of iron oxides vis-a-vis the reduction of contaminants by ZVI (Fig. 1B). These oxides can block the surface, allowing reaction only at pits and other defects; they can transmit electrons by acting as conductors or semiconductors; and they can complex iron, thereby creating reactive sites of adsorbed or structural Fe^{II}.

As with Fig. 1A, the conceptual model represented by Fig. 1B does more to highlight (and hopefully clarify) unresolved issues than it does to answer established questions. Addressing the fundamental issues raised by the new model has been the main focus of our recent research on ZVI PRBs. For example, what are the "reactive sites" that are responsible for the site saturation kinetics that have been reported for various contaminants? Simple answers to these questions have been hard to come by, even for highly-controlled model systems. In addition, it is becoming increasingly apparent that the controlling processes vary with several key system variables, including chemical properties of the contaminants, and temporal and spatial changes in "geochemical" conditions. In other words, the balance between the processes distinguished in Figs. 1A and 1B probably changes along the flow path of a ZVI PRB, evolves as the PRB ages, and shifts with the chemical composition of the influent contaminants.

These dynamics represent "higher order" research questions that have only been addressed qualitatively to date. As we learn more, however, the results are likely to have important practical implications. For example, as a treatment zone ages, the accumulation of iron oxides may provide adsorptive surface area that effectively sequesters the products of contaminant reduction even where these products might otherwise be problematic in the effluent of a ZVI

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* Extended Abstract from the 2000 Theis Conference on Iron in Groundwater.

PRB. This appears to be the case with nitro aromatics such as TNT, which produce almost stoichiometric amounts of undesirable aromatic amines in batch studies [3], but hardly any detectable products in column studies [4]. The conditions that make the column systems so much more useful for treating TNT respond dynamically to changes in flow rate and concentrations of influent oxidants. A specific goal of our current research is to develop a model than can describe these changes as a function of space and time.

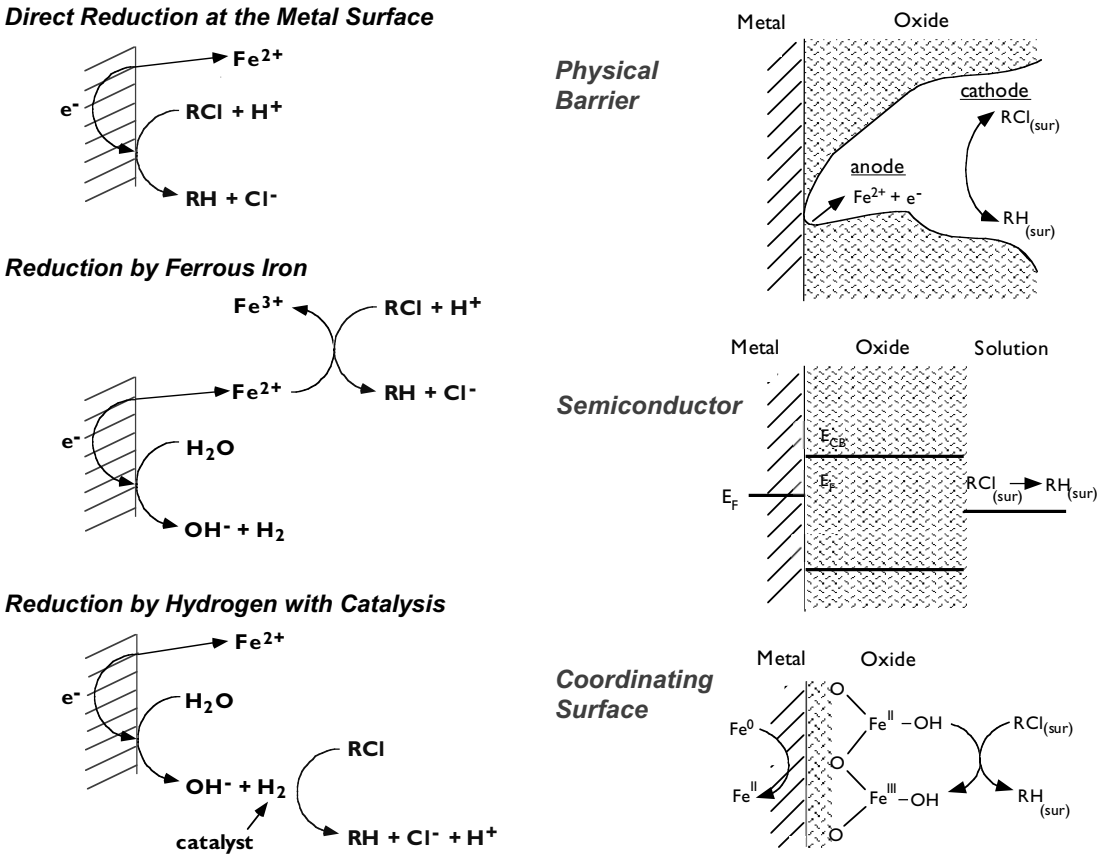

Figure 1. (A) 3 possible pathways for reduction of halogenated aliphatics, RCl, by ZVI. (B) 3 possible roles of the oxide film in reduction of RCl. Adapted from http://cgr.ese.ogi.edu/iron/.

References:

1. Matheson, L. J.; Tratnyek, P. G. Reductive dehalogenation of chlorinated methanes by iron metal. *Environ. Sci. Technol.* 1994, *28*, 2045-2053.
2. (Scherer, M. M.; Balko, B. A.; Tratnyek, P. G. The role of oxides in reduction reactions at the metal-water interface. In *Mineral-Water Interfacial Reactions: Kinetics and Mechanisms*; Sparks, D. L.; Grundl, T. J., Eds.; American Chemical Society: Washington, DC, 1998; ACS Symp. Ser. 715; pp. 301-322.
3. Agrawal, A.; Tratnyek, P. G. Reduction of nitro aromatic compounds by zero-valent iron metal. *Environ. Sci. Technol.* 1996, *30*, 153-160.
4. Johnson, T. L.; Johnson, R. L.; Tratnyek, P. G. Spatial and temporal dynamics in the remediation of TNT by zero-valent iron. in prep.

12. APPENDIX C: REFERENCES CITED

(1) *Sequenced Reactive Barriers for Groundwater Remediation* (2000); Fiorenza, S.; Oubre, C. L.; Ward, C. H., Eds.; Lewis: Boca Raton, FL.

(2) Lyons, R. E.; Smith, L. T. (1927) Die Reduktion von nitroverbindungen mit eisen und löslichen chloriden. *Chem. Ber.*, *60*, 173-182.

(3) Agrawal, A.; Tratnyek, P. G. (1994) Abiotic remediation of nitro-aromatic groundwater contaminants by zero-valent iron; *207th National Meeting,* San Diego, CA, American Chemical Society, Vol. 34, No. 1, pp. 492-494.

(4) Agrawal, A.; Tratnyek, P. G.; Stoffyn-Egli, P.; Liang, L. (1995) Processes affecting nitro reduction by iron metal: mineralogical consequences of precipitation in aqueous carbonate environments; *209th National Meeting,* Anaheim, CA, American Chemical Society, Vol. 35, No. 1, pp. 720-723.

(5) Agrawal, A. (1995) Reduction of Nitro Aromatic Compounds in Fe^0-CO_2-H_2O Systems: Implications for Groundwater Remediation with Iron Metal. M.S. Thesis, Oregon Graduate Institute.

(6) Agrawal, A.; Tratnyek, P. G. (1996) Reduction of nitro aromatic compounds by zero-valent iron metal. *Environ. Sci. Technol.*, *30(*1*)*, 153-160.

(7) Burris, D. R.; Hatfield, K.; Wolfe, N. L. (1996) Laboratory experiments with heterogeneous reactions in mixed porous media. *J. Environ. Eng.*, *122(*8*)*, 685-691.

(8) Scherer, M. M.; Westall, J. C.; Tratnyek, P. G. (1999) The kinetics of nitro reduction by iron metal: A case of mixed control; *217th National Meeting,* Anaheim, CA, American Chemical Society, Vol. 39, No. 1, pp. 346-348.

(9) Singh, J.; Comfort, S. D.; Shea, P. J. (1999) Iron-mediated remediation of RDX-contaminated water and soil under controlled Eh/pH. *Environ. Sci. Technol.*, *33(*9*)*, 1488-1494.

(10) Singh, J.; Comfort, S. D.; Shea, P. J. (1998) Remediating RDX-contaminated water and soil using zero-valent iron. *J. Environ. Qual.*, *27(*5*)*, 1240-1245.

(11) Hundal, L. S.; Singh, J.; Bier, E. L.; Shea, P. J.; Comfort, S. D.; Power, W. L. (1997) Removal of TNT and RDX from water and soil using iron metal. *Environ. Poll.*, *97(*1/2*)*, 55-64.

(12) Devlin, J. F.; Klausen, J.; Schwarzenbach, R. P. (1998) Kinetics of nitroaromatic reduction on granular iron in recirculating batch experiments. *Environ. Sci. Technol.*, *32(*13*)*, 1941-1947.

(13) Haderlein, S. B.; Schwarzenbach, R. P. (1995) Environmental processes influencing the rate of abiotic reduction of nitroaromatic compounds in the subsurface. In: *Biodegradation of Nitroaromatic Compounds*; Spain, J. C., Ed.; Plenum: New York, NY; pp. 199-225.

(14) Klausen, J.; Trüber, S. P.; Haderlein, S. B.; Schwarzenbach, R. P. (1995) Reduction of substituted nitrobenzenes by Fe(II) in aqueous mineral suspensions. *Environ. Sci. Technol.*, *29(9)*, 2396-2404.

(15) Hofstetter, T. B.; Heijman, C. G.; Haderlein, S. B.; Holliger, C.; Schwarzenbach, R. P. (1999) Complete reduction of TNT and other (poly)nitroaromatic compounds under iron-reducing subsurface conditions. *Environ. Sci. Technol.*, *33(9)*, 1479-1487.

(16) Saxena, A.; Bartha, R. (1983) Binding of 3,4-dichloroaniline by humic acid and soil mechanism and exchangeability. *Soil Sci.*, *136(2)*, 111.

(17) Parris, G. E. (1980) Covalent binding of aromatic amines to humates. I. Reactions with carbonyls and quinones. *Environ. Sci. Technol.*, *14(9)*, 1099-1106.

(18) Parris, G. E. (1980) Environmental and metabolic transformations of primary aromatic amines and related compounds. *Res. Rev.*, *76*, 1-30.

(19) Marco, G. J.; Novak, R. A. (1991) Natural product interactions during aniline metabolism including their incorporation in biopolymers. *J. Agric. Food Chem.*, *39(12)*, 2101-2111.

(20) Knicker, H.; Bruns-Nagel, D.; Drzyzga, O.; Von Low, E.; Steinbach, K. (1999) Characterization of ^{15}N-TNT residues after an anaerobic/aerobic treatment of soil/molasses mixtures by solid-state ^{15}N NMR spectroscopy. 1. Determination and optimization of relevant NMR spectroscopic parameters. *Environ. Sci. Technol.*, *33(2)*, 343-349.

(21) Dawel, G.; Kästner, M.; Michels, J.; Poppitz, W.; Günther, W.; Fritsche, W. (1997) Structure of a laccase-mediated product of coupling of 2,4-diamino-6-nitrotoluene to guaiacol, a model for coupling of 2,4,6-trinitrotoluene metabolites to a humic organic soil matrix. *Appl. Environ. Microbiol.*, *63(7)*, 2560-2565.

(22) Defense Environmental Network and Information Exchange (1999) Windrow Composting of Explosives Contaminated Soil at Umatilla Army Depot Activity, Hermiston, Oregon. http://denix.cecer.army.mil/denix/Public/Library/Remedy/Umatilla/umati01.html.

(23) Musso, H. (1967) Phenol coupling. In: *Oxidative Coupling of Phenols*; Taylor, W. I.; Battersby, A. R., Eds.; Marcel Dekker: New York; pp. 1-94.

(24) Bollag, J.-M. (1992) Decontaminating soil with enzymes. *Environ. Sci. Technol.*, *26(10)*, 1876-1881.

(25) Sjoblad, R. D.; Bollag, J.-M. (1981) Oxidative coupling of aromatic compounds by enzymes from soil microorganisms. In: *Soil Biochemistry*; Paul, E. A.; Ladd, J. N., Eds.; Dekker: New York; Vol. 5; pp. 113-152.

(26) Morkin, M.; Barker, J.; Devlin, R.; McMaster, M. (1998) In situ sequential treatment of a mixed organic plume using granular iron, O_2, and CO_2 sparging. In: *Designing and Applying Treatment Technologies: Proceedings of the First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, 18-21 May 1998, Monterey, CA*; Wickramanayake, G. B.; Hinchee, R. E., Eds.; Battelle Press: Columbus, OH; Vol. 1(6); pp. 289-294.

(27) Powell, R. M.; Puls, R. W. (1997) Proton generation by dissolution of intrinsic or augmented aluminosilicate minerals for in situ contaminant remediation by zero-valence-state iron. *Environ. Sci. Technol.*, *31(*8*)*, 2244-2251.

(28) Ravikumar, J. X.; Gurol, M. D. (1994) Chemical oxidation of chlorinated organics by hydrogen peroxide in the presence of sand. *Environ. Sci. Technol.*, *28(*3*)*, 394-400.

(29) Hurst, D. H.; Robinson, K. G.; Siegrist, R. L. (1993) Hydrogen peroxide treatment of TCE contaminated soils; *3nd International Symposium, Chemical Oxidation: Technology for the Nineties,* Nashville, TN, Technomic, Vol. 3, pp. 156-164.

(30) Gates, D. D.; Siegrist, R. L. (1995) In-situ chemical oxidation of trichloroethylene using hydrogen peroxide. *J. Environ. Eng.*, *121(*9*)*, 639-644.

(31) Tyre, B. W.; Watts, R. J.; Miller, G. C. (1991) Treatment of four biorefractory contaminants in soils using cataylzed hydrogen peroxide. *J. Environ. Qual.*, *20*, 832-838.

(32) Wilson, R. D.; Mackay, D. M. (1995) Method for passive release of solutes from an unpumped well. *Ground Water*, *33(*6*)*, 936-945.

(33) Elovitz, M. S.; Weber, E. J. (1999) Sediment-mediated reduction of 2,4,6-trinitrotoluene and fate of the resulting aromatic (poly)amines. *Environ. Sci. Technol.*, *33(*15*)*, 2617.

(34) Miehr, R.; Tratnyek, P. G.; Bandstra, J. Z.; Scherer, M. M.; Alowitz, M.; Bylaska, E. J. (2001) The diversity of contaminant reduction reactions by zero-valent iron: role of the reductate. *Environ. Sci. Technol.*, in prep.

(35) Johnson, T. L.; Scherer, M. M.; Tratnyek, P. G. (1996) Kinetics of halogenated organic compound degradation by iron metal. *Environ. Sci. Technol.*, *30(*8*)*, 2634-2640.

(36) Tratnyek, P. G.; Bandstra, J. Z.; Agrawal, A.; Ferguson, W. J.; Christ, J. (2001) Effects of carbonate on contaminant reduction by zero-valent iron. *Environ. Sci. Technol.*, in review.

(37) Miehr, R.; Tratnyek, P. G.; Johnson, T. J.; McCubbery, D.; Westall, J., C. (2001) The diversity of contaminant reduction reactions by zero-valent iron: role of the reductant. *Environ. Sci. Technol.*, in prep.

(38) Scherer, M. M.; Johnson, K.; Westall, J. C.; Tratnyek, P. G. (2001) Mass transport effects on the kinetics of nitrobenzene reduction by iron metal. *Environ. Sci. Technol.*, in review.

(39) Tratnyek, P. G.; Johnson, T. L.; Scherer, M. M.; Eykholt, G. R. (1997) Remediating groundwater with zero-valent metals: Kinetic considerations in barrier design. *Ground Water Monit. Rem.*, *17(*4*)*, 108-114.

(40) Johnson, T. L.; Fish, W.; Gorby, Y. A.; Tratnyek, P. G. (1998) Degradation of carbon tetrachloride by iron metal: Complexation effects on the oxide surface. *J. Contam. Hydrol.*, *29(*4*)*, 377-396.

(41) Wüst, W.; Schlicker, O.; Dahmke, A. (1998) Degradation of TCE at zero-valent iron: chemical processes effecting the design and performance of permeable, reactive Fe(0) walls; *NATO/CCMS Pilot Study on Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Groundwater (Phase III). Special Session on Treatment Walls and Permeable Reactive Barriers, No. 229,* Vienna, Austria, U.S. Environmental Protection Agency, Vol. EPA 542-R-98-003, pp. 30-35.

(42) Arnold, W. A.; Roberts, A. L. (1999) Pathways and kinetics of chlorinated ethylene and chlorinated acetylene reactions with Fe(0); *218th National Meeting,* New Orleans, LA, American Chemical Society, Vol. 39, No. 2, pp. 158-160.

(43) Devlin, J. F.; Morkin, M.; Repta, C. (2000) Incorporating surface saturation effects into iron wall design calculations. In: *Chemical Oxidation and Reactive Barriers: Proceedings of the Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds, 20-25 May 2000, Monterey, CA*; Wickramanayake, G. B.; Gavaskar, A. R.; Chen, A. S. C., Eds.; Battelle Press: Columbus, OH; Vol. C2-6; pp. 393-400.

(44) Tratnyek, P. G.; Johnson, T. L.; Johnson, R. L.; Miehr, R. (2001) Spatial and temporal dynamics in the remediation of TNT by zero-valent iron; *Groundwater Quality 2001: Third International Conference on Groundwater Quality,* Sheffield, UK, IAHS Press, pp. in prep.