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Kinetics of Nitroaromatic Reduction on Granular Iron in Recirculating Batch Experiments

JOHN F. DEVLIN,^{*,†}
JÖRG KLAUSEN,^{‡,§} AND
RENÉ P. SCHWARZENBACH[‡]

Department of Earth Sciences, University of Waterloo,
Waterloo, Ontario, Canada, N2L 3G1, and Swiss Federal
Institute for Environmental Science and Technology (EAWAG)
and Swiss Federal Institute of Technology (ETH),
CH-8600 Dübendorf, Switzerland

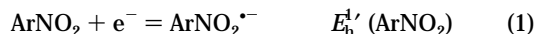
Granular iron has been determined to be a potentially useful reductant for the removal of common organic contaminants from groundwater. This research is aimed at improving our understanding of the processes that control the reactivity and longevity of the iron particles when they are used for groundwater treatment. A suite of nitroaromatic compounds (NACs) including 4-chloronitrobenzene (4ClNB), 4-acetylnitrobenzene (4AcNB), nitrobenzene, 2-methylnitrobenzene (2MeNB), and 2,4,6-trinitrotoluene (TNT) was used to investigate granular iron reactivity in anoxic pH 10, 0.008 M KNO₃ solution. Master Builder's brand of granular iron with a surface area of about 1 m²/g was used in all experiments. The NACs were reduced rapidly to anilines that were found to sorb reasonably strongly to the solid particles and to interfere with the reduction of NACs. The granular iron was found to lose reactivity quite rapidly over the first few days of exposure and then more slowly over the next several months. Reactivity loss due to reversibly sorbed products was minimized by flushing the system with background electrolyte between experiments. Competition experiments with binary mixtures of 4ClNB and each one of the other NACs were performed to investigate relative affinities of these compounds for the solid surface. Despite the overall loss in reactivity observed for the granular iron, the relative rate constants in the competition experiments appeared to remain constant in time.

Introduction

Zero-valent iron (Fe⁰) is capable of reducing a variety of important organic pollutants (1–7), and as a result, its application in in situ reactive barriers as well as in above-ground treatment systems has recently drawn considerable interest, particularly with respect to the reductive treatment of polyhalogenated compounds (8). For example, chlorinated solvents, including trichloroethene (TCE), tetrachloroethene (PCE), and carbon tetrachloride (CT), comprise a class of chemicals that are common groundwater contaminants,

often quite recalcitrant and considered toxic to humans. Preliminary field and laboratory studies of the performance of zero-valent iron in removing such compounds from groundwater were extremely encouraging (8). These studies have triggered research into the fundamental understanding of the reactions occurring at the iron/water interface. However, to date, the mechanisms of these reduction reactions have not yet been completely elucidated although progress is rapidly being made. There is compelling evidence to suggest that contact between the organic solute and the solid surface is required (9) and that sorption of chlorinated solvents (TCE and PCE) to iron does in fact occur (10). The reductions themselves may occur, at least partly, by two electron transfers (11, 12) resulting in the oxidative dissolution (corrosion) of the iron (13). Reaction rates have been found to be dependent on both iron surface area and solute concentration (7, 14), although pseudo-first-order kinetics are usually observed. It has been suggested that the reaction kinetics are diffusion controlled (13, 15) on the basis of batch tests involving acid-washed granular iron. However, recent electrochemical evidence suggests that, in the case of carbon tetrachloride, transport times through the diffusion layer surrounding an oxide-free metal surface are minimal (16). It has also been observed that hydrogen is evolved shortly after water (at neutral or slightly acid pH) contacts the Fe⁰ (17). Hydrogenolysis of PCE on palladium has been demonstrated in the laboratory and shown to be faster than PCE reductive dechlorination in the presence of iron (18). Thus, with hydrogen present, the possibility that organic reductions occur by hydrogenolysis cannot be ruled out.

As has been demonstrated in earlier work (19–22), nitroaromatic compounds (NACs) are very useful probe compounds for evaluating redox reactions in homogeneous and heterogeneous aqueous systems. Generally, NACs are reduced to well-defined, easily detectable products, thus allowing one to establish mass and electron balances. Furthermore, the transfer of the first electron to a given NAC is reversible. Therefore, the corresponding one-electron reduction potential, E_h^1 (ArNO₂) (eq 1), can be determined relatively easily and is available for a variety of environmentally relevant NACs (23).



Using 10 monosubstituted nitrobenzenes (NBs) as model compounds, Klausen et al. (20) and Heijman et al. (21) have shown that, for both batch and column systems and using single compounds as well as binary mixtures, plots of the logarithms of reduction rate data versus E_h^1 values yielded important information on the factors that determine the reduction kinetics of NACs by surface-bound Fe(II) species.

As shown by Agrawal and Tratnyek (15), NACs were readily reduced by zero-valent iron in carbonate-buffered batch systems. In that work, attempts were made to elucidate the factors controlling the reduction kinetics by comparing pseudo-first-order rate constants for several substituted NACs, including TNT and parathion, as a function of one-electron reduction potentials. No correlations were observed, leading the authors to suggest that mass transport was rate limiting. They cited as additional evidence for this an observed dependence of the reaction kinetics on the stirring rate of the solution (and iron particles) in their batch systems. However, increasing surface reactivity with increasing stirring rate could also be due to increasing abrasion of the agitated particles (24). Therefore, one objective of this work was to reexamine nitroaromatic reductions on granular iron, this

* Corresponding author e-mail: jfdevlin@sciborg.uwaterloo.ca.

† University of Waterloo.

‡ EAWAG/ETH.

§ Present address: Department of Geography and Environmental Engineering, The Johns Hopkins University, Baltimore, MD, 21218-2686.

TABLE 1. Diffusion Coefficients in Water, Log Octanol–Water Partition Coefficients, and One-Electron Reduction Potentials of the Compounds Studied

compound	abbreviation	molecular formula	D^a (cm ² s ⁻¹)	log (K_{ow})	$E_h^{1'}$ (ArNO ₂) ^b (V)
2,4,6-trinitrotoluene	TNT	C ₇ H ₅ N ₃ O ₆	6.1×10^{-6}	1.86 ^c	-0.30 ^e
4-acetylnitrobenzene	4AcNB	C ₈ H ₇ NO ₃	6.8×10^{-6}	1.49 ^d	-0.36
4-chloronitrobenzene	4ClNB	C ₆ H ₄ NO ₂ Cl	7.4×10^{-6}	2.40 ^d	-0.45
nitrobenzene	HNB	C ₆ H ₇ NO ₂	8.2×10^{-6}	1.84 ^c	-0.49
2-methylnitrobenzene	2MeNB	C ₇ H ₇ NO ₂	7.4×10^{-6}	2.30 ^c	-0.59

^a Diffusion coefficients in water at 22 °C calculated according to the method of Hayduk and Laudie as described in ref 37. ^b From ref 19. ^c From ref 38. ^d From ref 39. ^e From ref 23.

time with batch experiments in which the solid particles were held stationary. A recirculating batch design was adopted with the advantages of an immobilized solid phase with a travel path length short enough to prevent the formation of zones of different reactivities within the solid matrix. Another important objective was to contribute to the investigation of the long-term behavior of commercial zero-valent iron and to assess whether changes would occur that might lead to preferential reactivity toward variously substituted compounds. To this end, the relative rates of reduction of substituted NACs, present as single compounds and as binary mixtures, were studied as a function of age of the iron particles.

Materials and Methods

Chemicals. All chemicals including nitrobenzene (NB), 2-methylnitrobenzene (2MeNB), 4-acetylnitrobenzene (4-AcNB), and 4-chloronitrobenzene (4ClNB), 2,4,6-trinitrotoluene (TNT), and the corresponding anilines (except 2,4,6-triaminotoluene, purchased from Promochem, GmbH, Wesel, Germany) were obtained in the highest purity available from Fluka (Buchs, Switzerland) and were used as received without additional purification (cf. Table 1). The NACs were selected for two reasons: first, they span a wide range of one-electron reduction potentials; second, these same compounds had been used previously in experiments investigating electron transfer in heterogeneous systems (20, 23).

Granular Iron. Master Builder's brand granular iron was used in all experiments without pretreatment. The material was dry sieved prior to use to remove the size fraction below 0.3 mm diameter, minimizing the possibility of fine solids circulating through the experimental apparatus during the tests. X-ray photoelectron spectroscopy (XPS) analysis of the material showed that the surface iron was entirely Fe(III) and resulted in a spectrum nearly identical to the one obtained with the commercially available magnetite from Macherey-Nagel (Düren, Germany, No. 14439, 97%). BET analysis of a sample of the granular iron indicated a surface area of 0.964 m² g⁻¹. The elemental analysis of Master Builder's granular iron is given elsewhere (17, 25).

Recirculating Batch Experiments. The iron filings were packed in a 5 cm diameter glass column with fritted glass/PTFE end-plates. The column was packed with 52.0 g of iron to a length of 0.9 cm. The relatively short travel path was desirable to prevent the development of zones of geochemically altered iron along the flow path. For the purposes of this work, it was preferred that the iron throughout the column react as uniformly as possible.

The column was connected on the outlet side to a 300 mL round-bottom flask and on the inlet side to a single-piston HPLC pump (Figure 1). The pump and the flask were also connected to complete a closed loop. The flask was equipped with two openings: the first was fitted with a rubber stopper through which tubing to and from the column and to a sampling syringe was passed. The second was used as a port for a combined glass pH electrode with Ag/AgCl reference

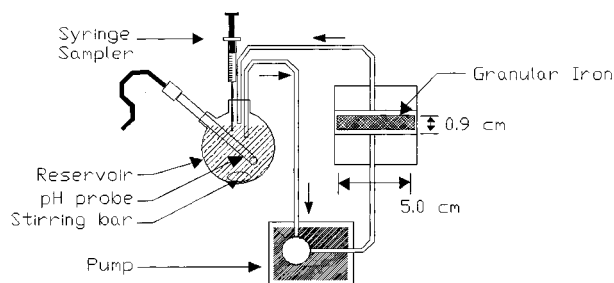


FIGURE 1. Recirculating batch test apparatus. The reservoir volume was 300 mL, the column diameter was 5 cm, and the path length through the granular iron was 0.9 cm.

and double junction. PEEK tubing with 0.1–0.5 mm i.d. was used throughout the assembly. All aqueous solutions were carefully deaerated by bubbling N₂ or Ar gas prior to use. However, during the experiments, the gas stream was suspended in order to avoid evaporative losses of the organic compounds.

The column was initially saturated by circulating 282 mL of 0.008 M KNO₃ at near-neutral pH through the system. Nitrate was chosen as the electrolyte in order to maintain a constant ionic strength and because it is a common groundwater constituent. Recent results indicate that nitrate may also be reduced by zero-valent iron (26, 27), although the reported rates strongly decreased with increasing pH. Within 30 min of circulation, the pH had risen to 9.3, and after several hours it reached 9.9, where it eventually stabilized. On the basis of this pseudo-steady-state pH, all subsequent experiments were conducted with an initial pH of 10, which is also expected to develop in typical groundwater passing through a permeable reactive barrier (7). Adjustments of pH were made with the addition of either KOH or HNO₃.

Kinetic experiments were conducted by weighing about 250 mL of 0.008 M KNO₃ solution into the round-bottom flask, adjusting the pH to 10, deaerating the solution by bubbling Ar gas through it while stirring for at least 1 h, and finally spiking it with the nitrobenzene(s) of interest to bring the initial concentration of the organic compound to about 100 μM. Initial samples of 200–250 μL were then collected with a 1 mL polypropylene syringe and immediately dispensed into an HPLC sample vial that was subsequently capped and stored in a refrigerator at 4 °C. The pump was then turned on at a flow rate of between 3 and 4 mL min⁻¹, and additional samples were collected at increasing time intervals for about 10 h. All samples were collected and stored as described above. Between each kinetic experiment, the granular iron was washed by flushing the column (to waste) with about 1.5 L (corresponding to about 85 pore volumes) of deaerated 0.008 M KNO₃ solution at pH 10 over a period of about 12 h.

The design of the kinetic experiments, i.e., a reactive porous medium and a well-mixed reservoir connected by advective links (see Figure 1), necessitated the use of a

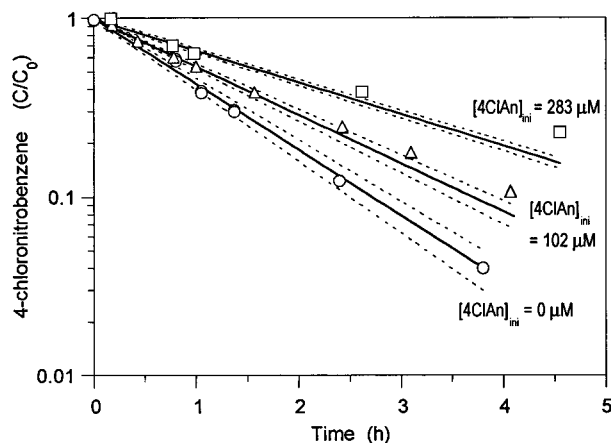


FIGURE 2. Effect of background 4-chloroaniline on the kinetics of 4-chloronitrobenzene reduction.

transport model to calculate a pseudo-first-order rate constant for the reaction of the nitroaromatic compounds in the column using concentration data obtained from the reservoir. Using the modeling tool AQUASIM (28, 29), the system was described by the one-dimensional advection–dispersion equation with a pseudo-first-order reaction term, where the calculated concentration at the end of the column served as the input for a mixed reservoir and vice versa. Parameters obtained by nonlinear least-squares fitting of the model to the experimental data included the pseudo-first-order rate constant for the reduction of the NAC in the column and the initial NAC concentration in the reservoir (see Figure 2 for a representative example) (28). The upper limit of rate constants that can be determined in this system is a function of the volumetric flow. It is asymptotically approached when the concentration of the NAC leaving the column compartment approaches zero (full conversion). The flow rate was similar in all experiments and was chosen so that the NAC was never fully converted in the column compartment. Possible mass-transport limitations, at the grain scale, were not accounted for in this treatment. Only data of the first 2–4 h of a kinetic experiment were included in the fit since pronounced deviations from pseudo-first-order kinetics (possibly due to product accumulation) became apparent at later times.

To facilitate comparison between experiments conducted with different single compounds, pseudo-first-order rate constants were re-expressed as relative rate constants, $k_{X-NB} \text{ (relative)}$ according to

$$k_{X-NB} \text{ (relative)} = \frac{k_{X-NB}}{k_{4ClNB}} \quad (2)$$

where k_{X-NB} refers to the rate constant for an X-substituted NB and k_{4ClNB} is the rate constant for 4ClNB, both determined from single-compound experiments performed close together in time. Competition experiments were conducted with 4ClNB as one of the competing compounds, so relative rate constants, Q_{X-NB} , in these cases were calculated from

$$Q_{X-NB} = \frac{k_{X-NB} \text{ (binary)}}{k_{4ClNB} \text{ (binary)}} \quad (3)$$

where the $k_{X-NB} \text{ (binary)}$ and $k_{4ClNB} \text{ (binary)}$ refer to the rate constants measured for the two compounds reacting together in competition.

Adsorption Isotherms. Batch experiments were performed to evaluate the sorptive properties of the aniline compounds. A typical batch sample was prepared as follows: about 8 g of granular iron and 45 g of deaerated

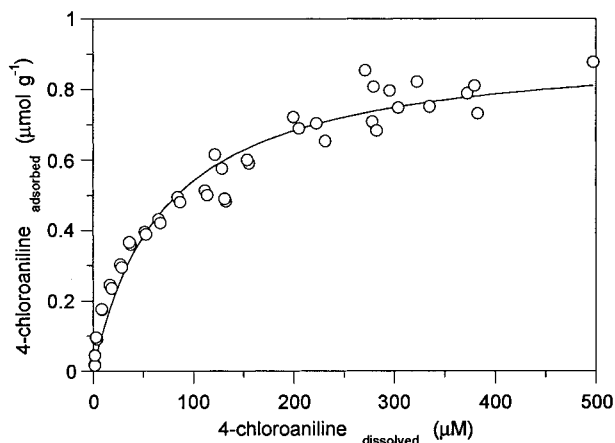


FIGURE 3. Isotherm of 4ClAn sorption from solution to Master Builder's granular iron. Data were collected at about 22 °C in 3-day batch tests with minimal particle abrasion.

0.008 M KNO_3 solution were weighed into a 60 mL glass vial and immediately spiked with a stock solution of 4-chloroaniline (4ClAn) to bring the final dissolved concentration to between 0 and 600 μM . The vials were prepared in duplicate, sealed with Viton stoppers, and stored at room temperature in the dark for a minimum of 3 days prior to reopening them for analysis. The vials were gently rotated once per day over the 3 day test to minimize transport limitations without causing excessive abrasion of the particles. Stock solutions were prepared in methanol, and final methanol concentrations in the vials never exceeded 1 vol %. Good agreement between the duplicates within any particular experiment and experiments performed on different days (with different concentration ranges) indicated that the protocol was an acceptable one. For example, combined data from three experiments are presented in Figure 3 for the sorption of 4ClAn.

Analytical Methods. Substituted NBs and the corresponding anilines were determined by HPLC analysis on an RP-18 or RP-8 reversed-phase column (125 \times 4 mm) equipped with a precolumn (4 \times 4 mm; both LiChroCart stainless steel cartridge, 5 μm spheres; Merck AG, Darmstadt, Germany) connected to a pumping system (Jasco 980-PU; Jasco Spectroscopic Co., Ltd., Tokyo, Japan; flow rate ca. 1 mL min^{-1}) supplemented with an autosampler (Gina 50; Gynkoteck, Germering b.M., Germany; injected volume 20 μL) and a variable-wavelength UV/vis detector (Jasco 875-UV) set to 228–246 nm. The mobile phase was typically CH_3OH/H_2O (60/40 v/v). 2,4,6-Triaminotoluene (TAT) was determined using 5 mM phosphate, pH 7, buffer/acetonitrile (99/1 v/v) with the detector set to 220 nm. The analysis of TNT and its reaction products (except for TAT) was performed on a Supelcosil LC-18 column (250 \times 4.6 mm; Supelco, Buchs, Switzerland) with LC-18 precolumn (20 \times 4.6 mm) using 2-propanol/acetonitrile/ H_2O (20/10/70 v/v/v) with the detector set to 220 nm.

Results and Discussion

Reaction Kinetics and Product Inhibition. The disappearance of any single NB did not strictly follow pseudo-first-order kinetics. Rates of reaction often declined as the reaction progressed. A series of experiments was performed with 4-chloronitrobenzene (4ClNB) to examine the effect of 4-chloroaniline (4ClAn) accumulation on the reaction rate (cf. Figure 2). To this end, the reservoir was spiked with about 100 μM 4ClNB, and the disappearance was monitored until 4ClNB was no longer detectable. The reservoir was subsequently respiked three more times, each time with about 100 μM 4ClNB and, before the last experiment only, an

TABLE 2. Langmuir Isotherm Parameters Determined from Individual and Competition Sorption Experiments

compound	abbreviation	<i>n</i>	<i>C</i> _{max} (μmol g ⁻¹) ^a	<i>K</i> _L (μM ⁻¹) ^a
Individual Sorption Experiments				
4-chloroaniline	4ClAn	44	0.926 ± 0.028	0.014 ± 0.002
4-acetylaniline	4AcAn	18	1.260 ± 0.063	0.005 ± 0.001
2-methylaniline	2MeAn	17	0.779 ± 0.031	0.009 ± 0.001
Competition Sorption Experiments				
4-chloroaniline	4ClAn	17	0.482 ± 0.024	0.014 ± 0.003
4-acetylaniline	4AcAn	17	0.881 ± 0.026	0.011 ± 0.002
4-chloroaniline	4ClAn	18	0.940 ± 0.038	0.011 ± 0.002
2-methylaniline	2MeAn	18	0.668 ± 0.033	0.006 ± 0.001

^a Errors shown are 95% confidence intervals.

additional 100 μM 4ClAn. This resulted in increasing initial 4ClAn concentrations but constant initial 4ClNB concentrations in the first four experiments. The reduction rates for 4ClNB decreased significantly with increasing initial 4ClAn concentration (cf. Figure 2; the first, third, and fourth experiments are shown), indicating blocking of reactive surface sites by the aniline. This may also explain the deviation from pseudo-first-order behavior at longer reaction times during an experiment, because the number of available reactive sites may have decreased during the experiment under these conditions. Notice that, even though 4ClNB appeared to be converted completely, stoichiometric amounts of 4ClAn were not observed in solution, indicating either sorption of 4ClAn to the iron particles or further reaction.

Three-day static batch experiments confirmed that various anilines (including 4ClAn, 4AcAn, and 2MeAn) sorbed significantly to the granular iron at pH 10 (Figure 3). The isotherms produced were nonlinear over the range tested (0–600 μM in the water) and could be well described by a Langmuir model with a constant of $K_L = 1.4 \times 10^{-8} \text{ M}^{-1}$ and a saturation concentration of $C_{\text{max}} = 0.9 \text{ μmol g}^{-1} \text{ Fe}$. However, C_{max} was found to depend on the range over which the isotherm was generated, increasing steadily as the range was expanded. Thus, the sorption interaction does not appear to be truly Langmuirian in nature. Extractions of the drained iron particles with acetonitrile, following one experiment, were performed on a set of 12 bottles containing 4ClAn at concentrations in the range of 100–500 μM. This procedure yielded mass recoveries exceeding 90% in all bottles, indicating that the 4ClAn was reversibly sorbed to the granular iron and not further transformed. Experiments were also performed to test the dependence of the sorption interaction on the type of anion and cation prevailing in the solution at constant ionic strength ($I = 0.008$). Substitution of calcium for potassium and sulfate for nitrate had no effect on the isotherms. However, when pairs of anilines were tested together in the batch sorption experiments, competition for sorption sites between the various compounds was observed with 4AcAn > 4ClAn > 2MeAn being the order of affinity (cf. Table 2).

As described above, the column was flushed between experiments in order to desorb the anilines from the iron surface. In some experiments, aniline desorption curves were recorded which confirmed that the anilines had deposited on the solid surfaces as expected from the static batch adsorption experiments. After the first flush, only partial recovery of the iron reactivity was observed (Figure 4). This may indicate irreversible blocking or loss of a fraction of the reactive sites as a consequence of either the initial hydration of the iron particles or the reduction of the nitroaromatic compound. Although a complete recovery of the initial reactivity was not achieved, subsequent experiments performed in succession, separated only by a flushing step, exhibited similar reaction rates, indicating that the reactivity

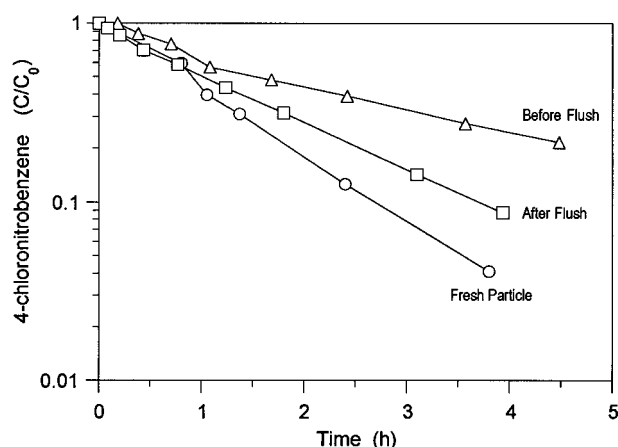


FIGURE 4. Effect of removal of 4ClAn from the granular iron on the kinetics of 4ClNB reduction. Before flush: last of a series of experiments conducted in the course of ca. 4 weeks. After flush: experiment conducted immediately after removal of 4-chloroaniline from the column.

of the iron was reproducible between experiments over short time intervals (several days to 2 weeks) and was only slowly decreasing.

Aging and Substituent Effects. The reactivity of the column was investigated for a total of 8 months. Over this extended time period, pseudo-first-order rate constants for individual compounds were found to decline with time, indicating a continuous loss of reactivity of the solids despite the flushing procedure (Figure 5). As a result, relative rate constants from these experiments were only calculated for X-NB and 4ClNB experiments conducted close together in time. Note that over this same time, relative rate constants ($Q_{2\text{MeNB}}$) for 2MeNB obtained from competition experiments in binary mixtures with 4ClNB remained essentially constant (Figure 5), indicating that both compounds were similarly affected by the apparent loss in reactivity of the iron material (see below).

Kinetic experiments involving single compounds revealed only small differences between the rate constants of 4ClNB, 2MeNB, and 4AcNB, even though these compounds exhibit very different one-electron reduction potentials. Little or no correlation was observed between $\log(k_{\text{X-NB}} \text{ (relative)})$ and the corresponding one-electron reduction potentials (Figure 6A). This result is consistent with previously reported data for various NACs reacting on a different iron that had been pretreated with hydrochloric acid (15). This finding indicates that the (hydr)oxide layer present on the surface of Master Builder's iron has little effect on the relative reaction rates of variously substituted NACs and suggests that the actual electron transfer is not the rate-determining process in these reactions. Thus, other rate-controlling steps have to be considered, including the formation of the precursor complex

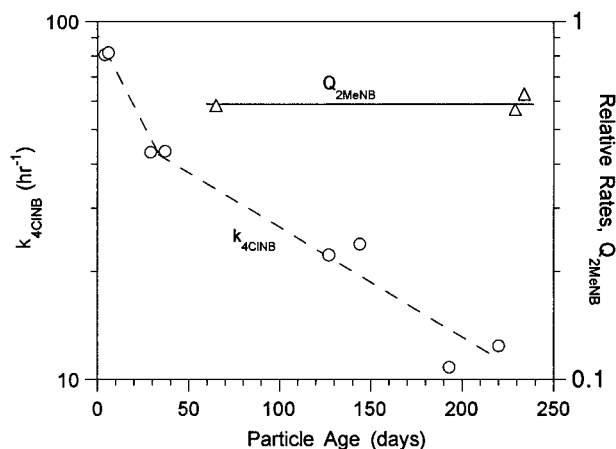


FIGURE 5. Reactivity changes with time for 4CINB in single-compound kinetic experiments (circles) and in competition experiments with 2MeNB (triangles). While absolute reactivity was lost, relative reactivity in competition experiments remained constant over time.

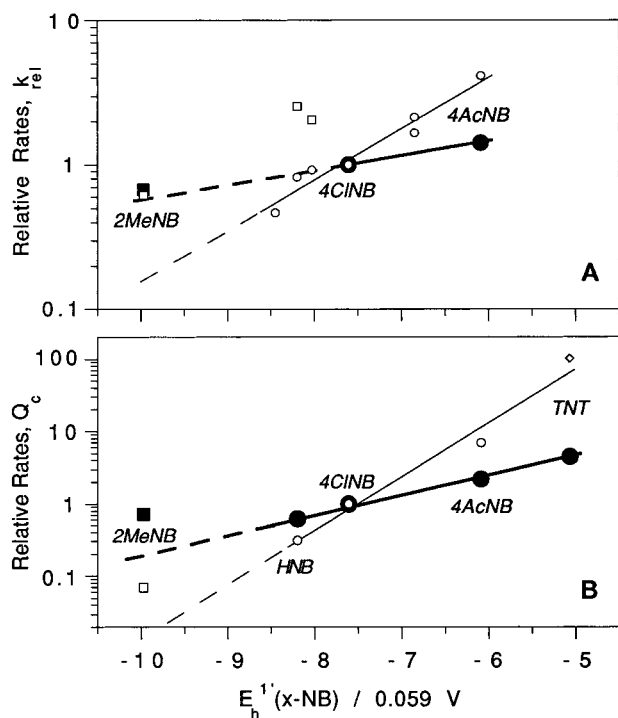


FIGURE 6. (A) Relative rate constants as a function of one electron reduction potentials for single-compound kinetic experiments. (B) Relative rate constants as a function of one-electron reduction potentials for competition experiments. Circles represent meta- and para-substituted compounds, and squares represent ortho-substituted compounds. Filled symbols represent data generated in this work while open symbols are from ref 20. The open diamond is from ref 23. 4CINB was used as the reference compound in generating this plot (eqs 2 and 3).

between the organic compound and the solid surface, the release of the aniline product from the successor complex, physical transport limitations in delivering the nitrobenzenes to the solid surface, and electron transport from the zero-valent iron core through the surface coating(s) of the iron particles to the NAC in question (directly or possibly via species such as hydrogen gas, in a hydrogenation reaction, or ferrous ion).

In contrast to the results obtained here, Klausen et al. (20) reported a somewhat stronger correlation for $\log(k_{X-NB}(\text{relative}))$ vs $E_h^1/0.059$ V for nitroaromatic reductions in mag-

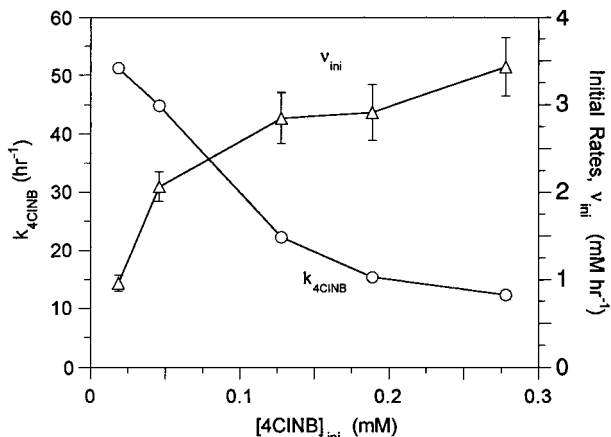


FIGURE 7. Initial rates, $v_{ini} = k_{4CINB} \times [4CINB]_{ini}$, and rate constants for 4CINB reduction as a function of initial 4CINB concentration. Rates began to slow when the initial concentrations exceeded 0.125 mM.

netite-ferrous iron systems (Figure 6A). Given that the solids used in this study comprise a zero-valent iron core surrounded by a magnetite and/or maghemite (30–32) coating that may be several micrometers thick (33) and given that the corrosion reaction is thought to release ferrous iron in the first step, a pattern very similar to that reported by Klausen et al. (20) might have been expected in the granular iron columns. However, the comparability of the two systems is limited since the zero-valent iron core may exert a considerable and sustained influence, through the semiconductive (hydr)oxide coating on the redox potential at the particle-water interface (32, 34, 35). Thus, even though the surface coatings of the iron particles may be similar to the magnetite used by Klausen et al., this distinction could result in (a) a much more negative redox potential of the iron particles, giving rise to different electron-transfer characteristics, and/or (b) different tendencies to sorb either ferrous iron or nitroaromatics.

Competition Experiments. Unlike single-compound experiments, experiments with binary mixtures of compounds offer the opportunity to study the relative affinities of the reacting species for the solid surface and gain further insight into the nature of the interactions between the nitroaromatics and the granular iron. Prior to initiating these tests, a series of experiments was performed to evaluate the concentration above which saturation kinetics would apply. Initial concentrations (C_0) of 4CINB were varied from 8 to 387 μM , and depletion curves were compared. As shown in Figure 7, pseudo-first-order reaction rate constants decreased significantly with increasing initial 4CINB concentration while initial reaction rates began to plateau at higher concentrations, indicating increasing saturation of reactive sites. On this basis, it was decided that meaningful competition experiments could be conducted with total nitrobenzene concentrations of 200 μM or more. While the single-compound experiments did not reveal any pronounced differences in the reaction rates of the various NACs tested, these differences were clearly evident in the competition experiments (Figure 6B), even though the effect was not as pronounced as in similar experiments conducted previously (20). In that study, the relative rates (Q_{X-NB}) of meta- and para-substituted NBs in the magnetite-ferrous iron system correlated strongly with the one-electron reduction potentials in a fashion very similar to that observed in other ferrous iron-containing systems (19, 21). It was suggested that such a correlation could serve as a probe for the reactive species (namely, the ferrous-ferric redox couple) involved in these nitro reductions. Thus, a similarly strong correlation in this work would be suggestive of Fe(II) involvement in the rate-

determining step of nitroaromatic reduction by zero-valent iron. In fact, competition between the various nitrobenzene compounds was observed but was considerably weaker than what has been reported for the other systems mentioned above (Figure 6B). This finding indicates that the granular "zero-valent" iron particles interact in a quantitatively different fashion with NACs than the iron(II)/iron(III) (hydr)-oxide systems previously studied, probably due to the underlying zero-valent metal core. Remarkably, the order of affinity of the compounds tested was the same in all studies: TNT > 4AcNB > 4ClNB > nitrobenzene, 2MeNB. It is also of interest to note that the orders of affinity of the nitrobenzenes to Master Builder's granular iron, as inferred from their relative reaction rates (Q_{X-NB}), and those of the corresponding anilines, as determined in the static batch adsorption tests, are identical. This raises questions about possible similarities in the ways the two classes of compounds interact with the solid surface. Furthermore, these rankings do not match the order expected on the basis of either hydrophobicity or diffusion alone, but do match the order of the NAC reduction potentials (Table 1). This argues against either hydrophobic sorption or diffusional transport limitations governing the reaction kinetics. Further investigation of the mechanisms of interaction of these types of compounds with (hydr)oxide-coated zero-valent iron surfaces is currently in progress.

The behavior of 100 μ M TNT in this system was somewhat different from the other compounds in that the mass balance (i.e., the sum of TNT, 2,4-dinitro-6-toluidine, 2,6-dinitro-4-toluidine, 2,4-diamino-6-nitrotoluene, 2,6-diamino-4-nitrotoluene, and 2,4,6-triaminotoluene) decreased almost at the same rate as the parent compound, indicating strong sorption of TNT or of its reduction products on the granular iron (data not shown). Remarkably, even though the concentrations of the intermediates reached a maximum, totalling 12 μ M after about 4 half-lives of the TNT, the final reduction product (2,4,6-triaminotoluene) was only found in traces (≤ 1 μ M) throughout the whole experiment. This indicates that TAT may be almost irreversibly bound to the granular iron surface. Thus, treatment of TNT with granular iron may lead to very small residual dissolved concentrations over prolonged periods of time. Under certain conditions, this might be a viable remediation strategy.

Implications. The experiments performed here were designed to model the conditions that might exist in the center of a granular iron treatment wall or treatment canister. The pH was maintained at an elevated level (pH = 10) with a solution ionic strength (0.008) representative of groundwater from a sandy aquifer. Solutions were recirculated through the solid in a fashion that minimized its partitioning into geochemically distinct zones. It was found that, over a period of months, the reactivity of the iron toward NACs noticeably declined, most rapidly at first and more slowly later. This decline in reactivity may occur quickly due to the accumulation of anilines and other competing cosolutes on the solid surface, or it may occur more slowly due to other less well-defined processes, e.g., buildup of a less conducting (hydr)oxide coating. It remains uncertain if this long-term "aging" also applies to systems containing chlorinated solvents. O'Hannesin and Gillham (36) have reported continuously high rates of removal of TCE by an *in situ* granular iron wall in the Borden aquifer over a 5-year period. However, the granular iron used in that study was different from the type used in this work and all subsequent pilot tests. As the results of these latter tests become available, more meaningful assessments of the effects of aging in the laboratory and in the field will be possible. Further long-term studies are needed to investigate the nature of the passivation process and whether it continues until the reaction is no longer useful or whether it reaches a steady

state while the reaction is still relatively rapid. Additional studies are also needed to assess the effects of various background geochemistries on these passivation rates.

Acknowledgments

This research was supported by the Solvents in Groundwater Consortium of the University of Waterloo and the Swiss Federal Institute for Environmental Science and Technology (EAWAG). The authors are grateful to Thomas Hofstetter for assistance with the HPLC analysis; to Klaus Pecher, Stefan Haderlein, Werner Angst, John C. Westall, and Thomas Suter for valuable discussions; and to John Cherry and Bob Gillham, who initiated the EAWAG–Waterloo collaboration.

Literature Cited

- (1) Sweeney, K. H.; Fischer, J. R. U.S. Patent No. 3,640,821; Feb 8, 1972.
- (2) Sweeney, K. H. *American Institute of Chemical Engineers Symposium Series, Water-1980*; Vol. 77; AIChE: New York, 1981; pp 67–71.
- (3) Sweeney, K. H. *American Institute of Chemical Engineers Symposium Series, Water-1980*; Vol. 77; AIChE: New York, 1981; pp 72–78.
- (4) Senzaki, T.; Kumagai, Y. *Kogyo Yosui* **1988**, 357, 2–7 (in Japanese).
- (5) Senzaki, T. *Kogyo Yosui* **1991**, 391, 29–35 (in Japanese).
- (6) Reynolds, G. W.; Hoff, J. T.; Gillham, R. W. *Environ. Sci. Technol.* **1990**, 24, 135–142.
- (7) Gillham, R. W.; O'Hannesin, S. F. *Ground Water* **1994**, 32, 958–967.
- (8) Gillham, R. W.; O'Hannesin, S. F. *Proceedings of the IAH Conference*, May 10–13, Hamilton, Ontario, 1992; pp 94–103.
- (9) Weber, E. J. *Environ. Sci. Technol.* **1996**, 30, 716–719.
- (10) Burris, D. R.; Campbell, T. J.; Manoranjan, V. S. *Environ. Sci. Technol.* **1995**, 29, 2850–2855.
- (11) Roberts, A. L.; Totten, L. A.; Arnold, W. A.; Burris, D. R.; Campbell, T. J. *Environ. Sci. Technol.* **1996**, 30, 2654–2659.
- (12) Totten, L. A.; Roberts, L. A. *209th ACS National Meeting: Division of Environmental Chemistry Preprints of Extended Abstracts*, Vol. 35/1, Anaheim, CA; American Chemical Society: Washington, DC, 1995; pp 706–709.
- (13) Matheson, L. J.; Tratnyek, P. G. *Environ. Sci. Technol.* **1994**, 28, 2045–2053.
- (14) Johnson, T. L.; Scherer, M. M.; Tratnyek, P. G. *Environ. Sci. Technol.* **1996**, 30, 2634–2640.
- (15) Agrawal, A.; Tratnyek, P. G. *Environ. Sci. Technol.* **1996**, 30, 153–160.
- (16) Scherer, M. M.; Westall, J. C.; Ziomek-Moroz, M.; Tratnyek, P. G. *Environ. Sci. Technol.* **1997**, 31, 2385–2391.
- (17) Reardon, E. J. *Environ. Sci. Technol.* **1995**, 29, 2936–2945.
- (18) Schreier, C. G.; Reinhard, M. *209th ACS National Meeting: Division of Environmental Chemistry Preprints of Extended Abstracts*, Vol. 35/1, Anaheim, CA; American Chemical Society: Washington, DC, 1995; pp 749–751.
- (19) Schwarzenbach, R. P.; Stierli, R.; Lanz, K.; Zeyer, J. *Environ. Sci. Technol.* **1990**, 24, 1566–1574.
- (20) Klausen, J.; Tröber, S.; Haderlein, S. B.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1995**, 29, 2396–2404.
- (21) Heijman, C. G.; Grieder, E.; Holliger, C.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1995**, 29, 751–761.
- (22) Dunnivant, F. M.; Schwarzenbach, R. P.; Macalady, D. L. *Environ. Sci. Technol.* **1992**, 26, 2133–2141.
- (23) Hofstetter, T. B.; Heijman, C. G.; Haderlein, S. B.; Schwarzenbach, R. P. In *213th ACS National Meeting: Division of Environmental Chemistry Preprints of Extended Abstracts*, Vol. 37/1, San Francisco, CA; American Chemical Society: Washington, DC, 1997; pp 85–86.
- (24) Keddam, M.; Oltra, R.; Colson, J. C.; Desestret, A. *Corros. Sci.* **1983**, 23, 441–451.
- (25) Hardy, L. O.; Gillham, R. W. *Environ. Sci. Technol.* **1996**, 30, 57–65.
- (26) Cheng, I. F.; Muftikian, R.; Fernando, Q. In *213th ACS National Meeting: Division of Environmental Chemistry Preprints of Extended Abstracts*, Vol. 37/1, San Francisco, CA; American Chemical Society: Washington, DC, 1997; pp 165–166.
- (27) Rahman, A.; Agrawal, A. In *213th ACS National Meeting: Division of Environmental Chemistry Preprints of Extended Abstracts*, Vol. 37/1, San Francisco, CA; American Chemical Society: Washington, DC, 1997; pp 157–159.
- (28) Reichert, P. *Concepts underlying a Computer Program for the Identification and Simulation of Aquatic Systems*. Swiss Federal

- Institute for Environmental Science and Technology (EAWAG): Dübendorf, Switzerland, 1994.
- (29) Reichert, P. *Water Sci. Technol.* **1994**, 30, 21–30.
 - (30) West, J. M. *Basic Corrosion and Oxidation*, 2nd ed.; Ellis Horwood Limited: Chichester, England, 1986; p 265.
 - (31) Odziemkowski, M. S.; Gillham, R. W. *213th ACS National Meeting: Division of Environmental Chemistry Preprints of Extended Abstracts*, Vol. 37/1, San Francisco, CA; American Chemical Society: Washington, DC, 1997; pp 177–180.
 - (32) Cornell, R. M.; Schwertmann, U. *The Iron Oxides. Structure, Properties, Reactions, Occurrence and Uses*; VCH: Weinheim, Germany, 1996; p 573.
 - (33) Sivavec, T. M.; Horney, D. P.; Mackenzie, P. D.; Salvo, J. J. *Zero-valent iron treatability study for groundwater contaminated with chlorinated organic solvents at the Paducah Gaseous Diffusion Plant (PGDP) site—Final report*; GE Corporate Research & Development: Schenectady, NY, 1995; p 181.
 - (34) Schmickler, W. *Interfacial Electrochemistry*; Oxford University Press: New York, 1996; p 288.
 - (35) Vijn, A. K. *Electrochemistry of Metals and Semiconductors. The Application of Solid State Science to Electrochemical Phenomena*; Marcel Dekker: New York, 1973; p 297.
 - (36) O'Hannesin, S. F.; Gillham, R. W. *Ground Water* **1998**, 36, 164–170.
 - (37) Lyman, W. J.; Rhee, W. F.; Rosenblatt, D. H. *Handbook of Chemical Property Estimation Methods*; McGraw-Hill Inc.: New York, 1982.
 - (38) Haderlein, S. B.; Weissmahr, K. W.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1996**, 30, 612–622.
 - (39) Haderlein, S. B.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1993**, 27, 316–326.

Received for review October 13, 1997. Revised manuscript received March 25, 1998. Accepted April 7, 1998.

ES970896G