CHLORINATED ETHENE REDUCTION BY CAST IRON: SORPTION AND MASS TRANSFER

By David R. Burris, Richelle M. Allen-King, Valipram S. Manoranjan, Timothy J. Campbell, Gregory A. Loraine, and Baolin Deng

ABSTRACT: Tetrachloroethylene (PCE) and trichloroethylene (TCE) exhibited significant nonlinear sorption to nonreactive sites when exposed to four cast irons. Cast iron is a reactive material that promotes reductive dechlorination and has recently been used for in-situ remediation of chlorinated solvent contaminated ground water. Comparisons between PCE sorption to cast iron, graphite, and iron-containing minerals indicate that nonreactive sorption is due to exposed graphite inclusions in the cast iron. Sorption of the homologous series of chloroethenes to a cast iron adheres to Traube's rule; thus, the extent of sorption is related primarily to compound hydrophobicity. An analytical model incorporating rate-limited sorption/desorption to nonreactive sites was used to assess sorption nonequilibrium. Effective sorption and desorption rate coefficients determined how significant mass transfer limitations to nonreactive sorption sites exist for PCE and not for TCE. The nonreactive sorption observed indicates that flow-through cast iron treatment systems will exhibit significant delayed attainment of steady-state conditions for chlorinated ethenes, particularly PCE and TCE.

INTRODUCTION

An in-situ permeable reactive barrier of metallic iron is an innovative ground-water remediation technology for chlorinated solvents (Gillham and O’Hannesin 1994; NRC 1994, 1997) that is being implemented at several field sites (U.S. EPA 1995, 1997). Through this technology, chlorinated ethenes such as perchloroethylene and trichloroethylene (PCE and TCE) are reduced primarily to nontoxic hydrocarbons (Senzaki and Kumagai 1989; Gillham and O’Hannesin 1994; Orth and Gillham 1996) via either hydrolysis or reductive β-elimination (Roberts et al. 1996; Campbell et al. 1997). The reduction reactions take place on the iron surface and are linked to the anaerobic corrosion of iron (Matheson and Tratnyek 1994; Weber 1996). Cast iron is a relatively low cost form of Fe, making it the iron of choice in field applications to date. In addition to the reduction reactions, substantial nonlinear sorption to nonreactive sites has been observed for PCE and TCE with a cast iron (Burris et al. 1995). In the same study, the batch system data suggested that mass transfer resistance to nonreactive sorption sites exists for PCE but not for TCE. Sorption to nonreactive sites will lead to delayed attainment of steady-state conditions in flow-through treatment systems (e.g., packed bed or permeable reactive barrier) (Hatfield et al. 1996). Delayed attainment of steady-state conditions becomes problematic when designing treatment systems or evaluating treatment system performance (i.e., performance may appear to be decreasing when steady-state conditions are simply being approached).

Zero-valent iron can occur in a wide array of forms with differing purities and macroscopic structures. Cast irons are iron/carbon/silicon alloys (2–4% C; 1–3% Si) in which more carbon is present than can be retained in solid solution (Metals 1978). As a consequence, carbon precipitates as flakes or nodules of graphite that become embedded within the metal. Deng et al. (1997) confirmed the presence of graphite in Fisher 40 mesh cast iron [used by Burris et al. (1995)] by dissolving the iron in strong acid and analyzing the residual by X-ray diffraction.

In this study, the sorption of chlorinated ethenes to cast iron surfaces was further examined to assess the generality of nonreactive sorption behavior for cast irons; determine the predominant nonreactive sorbent on the cast iron surface; (3) determine whether sorption to cast iron adheres to Traube’s rule (sorption proportional to hydrophobicity); and (4) evaluate rate-limited sorption/desorption for the nonreactive sites. Understanding the nature of nonreactive sorption of chloroethenes to cast iron will improve the ability to design, and evaluate performance of, in-situ permeable reactive barriers based upon cast iron.

MODEL DEVELOPMENT

Reduction kinetics without and with accounting for nonreactive sorption onto the irons, respectively, in batch systems have been described by Burris et al. (1995) as

\[
\frac{dC_r}{dt} = -\lambda_C C_r^N
\]

(1)

where \( C_r \) and \( C_r' \) = total system and aqueous-phase concentrations, respectively; \( \lambda_C \) = reaction rate constants; and \( N_r \) = reaction orders. Eq. (2) assumes that transformation is dependent upon aqueous-phase concentrations and that the observed sorption is primarily to nonreactive sorption sites.

A conceptual model incorporating reaction and rate-limited sorption/desorption to nonreactive sites is proposed for the chloroethenes in a water/cast iron system (Fig. 1). In the proposed model, the reaction reactions occur at the Fe surface rather than in the aqueous phase. The contaminant molecules in the aqueous phase have access to the cast iron surface where they can either adsorb to nonreactive sorbent sites or reach reactive sites where the reduction reactions can take place. Adsorption to the nonreactive sorption sites is nonlinear (Bur-
ris et al. 1995; Allen-King et al. 1997), and competition occurs between solute molecules for the limited number of available sorption sites (Burris et al. 1995). Rate-limited sorption and desorption may occur with the nonreactive sorbent sites [as suggested by Burris et al. (1995)]; αi and α−i are the sorption and desorption rate coefficients, respectively. The reactive sites have an associated intrinsic chemical reaction rate k. There may also be reactant (contaminant) and product mass transfer resistances with respect to the reactive sites; αi and α−i are the associated mass transfer rate coefficients. Solute competition for reactive sites was not observed (Burris et al. 1995). Note that λαi incorporates k and the reactive site mass transfer terms.

Assuming transformation is dependent upon aqueous-phase concentration (i.e., observed sorption is to nonreactive sites), the rate of change in aqueous-phase concentration with respect to time can be described as a combination of (1) the loss due to transformation (in this case, the mathematics are the same for either an aqueous-phase homogeneous reaction or a surface-mediated heterogeneous reaction that is dependent upon aqueous-phase concentration); (2) the loss due to sorption; and (3) the gain due to desorption

\[ \frac{dC}{dt} = \left[ -\lambda_1 C_{aq} \right] + \left[ -\alpha_1 C_s \right] + \left[ \alpha_{-1} C_i \right] \]  

The rate of change in sorbed concentration C_s can be described as

\[ \frac{dC_s}{dt} = \alpha_1 C_s - \alpha_{-1} C_i \]  

Combining (3) and (4), we get

\[ \frac{dC_s}{dt} = -\lambda_1 C_{aq} - \frac{dC_i}{dt} \]  

Nα was essentially 1.0 for both PCE and TCE using Fisher cast iron, implying that the observed reaction is first order with respect to aqueous concentrations. Substituting 1.0 for Nα in (3) gives

\[ \frac{dC_i}{dt} = -\lambda_1 C_{aq} - \left( \alpha_1 C_s - \alpha_{-1} C_i \right) \]  

Using these assumptions and relationships, exact solutions for C_i and C_s that incorporate rate-limited sorption and desorption to the nonreactive sites can be derived (see Appendix I). The exact solution for the aqueous-phase concentration is

\[ C_s = \frac{C_0}{2 \left[ \sqrt{\left( \lambda_1 + \alpha_1 + \alpha_{-1} \right)^2 - 4 \lambda_1 \alpha_{-1}} \right]} \left[ \exp \left( \frac{\left( \lambda_1 + \alpha_1 + \alpha_{-1} \right)^2 - 4 \lambda_1 \alpha_{-1}}{2 \left( \lambda_1 + \alpha_1 + \alpha_{-1} \right)^2} \right) \right] \]

+ \frac{C_0}{2 \left[ \sqrt{\left( \lambda_1 + \alpha_1 + \alpha_{-1} \right)^2 - 4 \lambda_1 \alpha_{-1}} \right]} \left[ \exp \left( \frac{-\left( \lambda_1 + \alpha_1 + \alpha_{-1} \right)^2 - 4 \lambda_1 \alpha_{-1}}{2 \left( \lambda_1 + \alpha_1 + \alpha_{-1} \right)^2} \right) \right] \]

where C_0 is initial aqueous concentration.

**MATERIALS AND METHODS**

**Chemicals**

Deionized Milli-Q water (18 MΩ-cm resistivity, Millipore Corp., Milford, Mass.) was used in all experiments. PCE (UV-Spec Grade) was obtained from Baker,Phillipsburg, N.J. TCE (ACS Reagent Grade) and graphite powder (99%) were obtained from Fisher Scientific, Fair Lawn, N.J. 1,4-Dichlorobenzene was obtained from Aldrich, Milwaukee, Wis. Pyrite, used for pH control, was obtained from Ward’s Natural Scientific Est., Inc., Rochester, N.Y. The pyrite was ground to a fine powder with mortar and pestle prior to use. Activated carbon powder was supplied by Mallinckrodt, Chesterfield, Mo. The iron oxides examined were hematite (red ochre, pulverized in a shatterbox, Ward’s Natural Scientific Est., Inc., Rochester, N.Y.), goethite (synthesized by B. R. Coughlin and A. T. Stone, Johns Hopkins University, Baltimore, Md.), and magnetite (provided by Dr. Tim Sivavec, GE Corporate Research and Development, Schenectady, N.Y.). The metallic iron examined in this study included Fisher iron filings (cast

<p>| <strong>TABLE 1. Carbon Content and Surface Areas of Study Materials</strong> |
|----------------|----------------|----------------|</p>
<table>
<thead>
<tr>
<th>Material</th>
<th>Surface area (m²/g)</th>
<th>Carbon content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fisher cast iron</td>
<td>1.0</td>
<td>3.1</td>
</tr>
<tr>
<td>Master Builder’s GX-27 cast iron</td>
<td>1.74</td>
<td>2.8</td>
</tr>
<tr>
<td>Connelly-GPM cast iron</td>
<td>1.58</td>
<td>3.2</td>
</tr>
<tr>
<td>Peerless cast iron</td>
<td>0.87</td>
<td>3.1</td>
</tr>
<tr>
<td>Electrolytic iron</td>
<td>0.30</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Carbylol iron</td>
<td>0.47</td>
<td>0.82</td>
</tr>
<tr>
<td>Activated carbon powder</td>
<td>2,480</td>
<td>~100%</td>
</tr>
<tr>
<td>Graphite powder</td>
<td>7.5</td>
<td>~100%</td>
</tr>
<tr>
<td>Goethite</td>
<td>7.1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Hematite</td>
<td>49.1</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

*Assumed to be near 100% by definition.

Not determined.
iron, 40 mesh, Fisher Scientific, Fair Lawn, N.J.), Master Builder's (MB's) GX-27 iron (cast iron, Master Builder's Inc., Cleveland, Ohio), Peerless iron (cast iron, aggregate size 8/50, Peerless Metal Powders and Abrasive, Detroit, Mich.), Connelly-GPM (cast iron, Connelly-GPM, Chicago, Ill.), carbonyl iron (97+-% zero-valent iron produced by the reduction of Fe(CO)₅ by hydrogen, Sigma Chemical, St. Louis, Mo.), and electrolytic iron (powder, Fisher Scientific, Fair Lawn, N.J.). The cast irons and electrolytic iron were pretreated by washing in Ar-sparged 1N HCl with periodic shaking for 30 min, rinsed thoroughly with Ar-sparged deionized water, and dried at 100°C under N₂. This treatment yielded gray, metallic solids with no visible ferric oxyhydroxides on the surface. Carbon contents of the iron samples were determined using UIC and Leco WR-112 carbon analyzers. Surface areas were determined by the BET (N₂) method. The surface areas and carbon contents of the materials examined in this study are given in Table 1.

**Metallic Iron Batch Systems**

The experimental procedures used for the cast irons examined in this study are the same as those used in Burris et al. (1995). The present study uses the Fisher 40 mesh cast iron results from Burris et al. (1995). Portions of the cast iron system experimental methodology are repeated here due to similarities with experiments using the other irons examined as well as for clarity.

All cast iron experiments were carried out in 15-mL clear borosilicate crimp-top serum vials. In these systems, reduction of PCE and TCE is occurring at the same time as sorption so that concentrations must be determined in both aqueous and solid phases as a function of time. Four vials were used per time point: two controls and two Fe vials. In the case of cast iron, 5.00 ± 0.05 g of iron filings and 0.100 ± 0.005 g pyrite powder were weighed into each Fe vial. The pyrite was added for pH control (pH remained near neutral). No sorption or reaction due to the pyrite alone was detected, with or without H₂ headspace. Aqueous solutions of PCE and TCE were prepared by spiking Ar-sparged, deionized, Milli-Q water with stock solutions in methanol (500-mg PCE or TCE/mL) to achieve the desired concentrations. Resultant methanol concentrations were always below 10⁻⁴ mol fraction, below which aqueous infinite dilution activity coefficients for halogenated hydrocarbons are unaffected (Munz and Roberts 1986). In an anaerobic glovebox (10% H₂, 90% N₂), control and Fe + pyrite vials were filled completely with aqueous PCE or TCE solution from a separatory funnel, then crimp-sealed without headspace using Teflon-lined rubber septa. Water volumes were determined gravimetrically. Vials were then placed on a roller drum and rotated (5–8 rpm) vertically as the vial axis remained horizontal, creating a well-mixed system. The reaction was carried out at ambient temperature (21 ± 1°C). Vials were removed for analysis at specified times.

The experiments with electrolytic and carbonyl iron powders were essentially the same as those for cast iron, except pyrite was omitted. In the case of electrolytic iron, 10.0 ± 0.1 g iron powder was used. Chlorinated solvent concentration on the metallic iron solid phase was calculated using the difference between the measured total extract and aqueous-phase chlorinated solvent masses and the mass of iron in the system (analytical methods described later). In the case of the reactive metallic irons, the sorption isotherms cannot be viewed as true equilibrium isotherms as the reaction is also occurring. Sorption quasi-equilibrium onto cast iron was established by 2 h for TCE and 24 h for PCE (Burris et al. 1995).

### Carbon and Iron Oxide Batch Systems

Sorption experiments with activated carbon and graphite were conducted in 25-mL serum vials with zero headspace. Initial aqueous PCE concentration was 60 μM, and final aqueous concentrations were varied by using a range of sorbent masses (0–36 mg for activated carbon and 0–3 g for graphite). Initial aqueous TCE concentrations and sorbent mass ranges for activated carbon were 700 μM and 0–55 mg, respectively, and for graphite were 450 μM and 0–6 g, respectively. Vials were prepared aerobically, with duplicates for each sorbent loading and corresponding controls without sorbent. The vials were filled, leaving no headspace, and crimped with Teflon-lined septa. Water volumes were determined gravimetrically. Vials were equilibrated while mixing on the roller drum at 20 ± 1°C for 1 day. Aqueous samples were obtained from each vial (after being centrifuged for phase separation) and analyzed as subsequently discussed. The amount sorbed was determined by the aqueous phase mass difference between the sample and control vials.

The magnetite, goethite, and hematite sorption experiments were similar to those with carbon except 15-mL vials and 1-g sorbent were used. PCE concentrations were varied by using different initial concentrations (4–45 μM).

### Analysis

For the iron experiments, each control and Fe vial was analyzed for PCE or TCE by two different methods to determine aqueous and total system (mass per vial) concentrations. Duplicate 20-μL aliquots of the aqueous phase were sampled from the vial after injecting 40 μL of deionized water into the vial to ensure positive pressure inside the vial during sampling. Each 20-μL aliquot was injected into 1.0-mL acetonitrile containing 10-mg/L 1,4-dichlorobenzene as an internal standard, mixed and analyzed by gas chromatography (GC). Aqueous-phase samples for the carbon and iron oxide sorption experiments were also obtained and analyzed by this method. Total system concentration was determined next by acetonitrile extraction. The entire aqueous content of the vial was transferred by air displacement through a cannula to a 40-mL vial containing 10-mL acetonitrile. A 2.5-mL aliquot of acetonitrile containing 1.20-g/L 1,4-dichlorobenzene as internal standard was then added to the original sample vial by syringe through the septum. The vial was vortex-mixed for 1 min, and the extract was transferred by syringe to the 40-mL vial. A 2.5-mL aliquot of acetonitrile without internal standard was then added to the original sample vial, mixed and transferred to the 40-mL vial. The extract solution was diluted 1:10 in acetonitrile and analyzed by GC.

PCE and TCE concentrations were determined by GC on a 15 m × 0.53 mm DB-1 column with a stationary-phase film thickness of 3 μm using a temperature-programmed run. De-

| TABLE 2. Kinetic Parameters Determined for PCE and TCE in Water/Cast Iron System for Fisher Iron (Burris et al. 1995) and Other Irons Examined in This Study |
|-----------------|-------|-----------------|-----------------|-----------------|-----------------|
| Iron (1)        | N (2) | In λ (μg/L)/(μg/g) (3) | N₄ (4) | In λ₄ (μg/L)/(μg/g) (5) |
| Tetrachlormethane Master Builder's | 4.3 (±1.3) | -24 (±7) | 1.1 (±0.6) | -3.3 (±2.0) |
| Peerless        | 2.7 (±0.8) | -15 (±4) | 1.0 (±0.4) | -3.9 (±2.7) |
| Connelly        | 2.2 (±0.8) | -11 (±4) | 1.1 (±0.5) | -4.3 (±2.1) |
| Fisher          | 2.7 (±0.9) | -15 (±5) | 0.94 (±0.3) | -2.9 (±1.0) |
| Trichloroethylene Master Builder's | 1.5 (±1.4) | -3.4 (±3.3) | 0.63 (±0.60) | -0.15 (±2.04) |
| Peerless        | 1.1 (±0.3) | -4.9 (±1.7) | 0.87 (±0.20) | -3.2 (±2.1) |
| Connelly        | 1.2 (±0.3) | -5.1 (±1.8) | 0.93 (±0.27) | -3.4 (±2.4) |
| Fisher          | 1.3 (±0.1) | -5.9 (±0.6) | 0.94 (±0.10) | -3.1 (±2.04) |

Note: Numbers in parentheses indicate 95% confidence intervals.
tection was by Ni{sup 61} ECD. Quantification was by the internal standard method.

Sorption and desorption rate constants for the nonreactive sorbent sites (\( \alpha_1 \) and \( \alpha_{-1} \)) for PCE with Fisher iron were estimated by nonlinear least-squares fit (Statistica) of the exact solution for \( C_T \) ([8]) to experimental \( C_T \) values. The experimentally derived \( K_T \) value for PCE with Fisher iron (see Table 2) was used. The \( \alpha_1 \) and \( \alpha_{-1} \) values obtained were used in the exact solution for \( C_a \) ([7]) to predict the aqueous-phase concentrations.

RESULTS AND ANALYSIS

Sorption and Reaction with Different Cast Irons

PCE concentrations (as micrograms/vial and micrograms in water/vial) in the MB’s cast iron system as a function of time are shown in Fig. 2. The difference between the total and solution masses is the amount sorbed onto the iron. The rate of total system mass loss is greater when there is more PCE in the aqueous phase, indicating that sorption is to nonreactive sites, in agreement with the comparable results for Fisher cast iron (Burriss et al. 1995). Although PCE exhibited the greatest sorption on MB, the trends shown in Fig. 2 are similar to those observed for PCE and TCE on all the cast irons (data not shown).

The reduction kinetic parameters [see (1) and (2)] determined for PCE reflect the large magnitude of nonreactive sorption onto all of the cast irons and generally agree with those obtained by Burriss et al. (1995) for Fisher iron (Table 2). PCE \( N \) values were significantly greater than 1.0, whereas PCE \( N_e \) values are essentially 1.0 indicating that the reaction is nearly first order when nonreactive sorption is accounted for. TCE \( N \) and \( N_e \) values were both relatively close to 1.0, reflecting the lower extent of TCE sorption onto the cast irons.

Significant nonlinear sorption was observed for both PCE and TCE with all four irons (Fig. 3; Table 3), suggesting that nonlinear sorption of this type is common for cast irons. The sorption isotherms were relatively similar to another for a particular compound. Sorption of PCE was greater than TCE for all the irons. MB iron exhibited the greatest degree of sorption and Connelly and Peerless irons showed the least for both compounds.

The cast iron sorption isotherms indicate that substantial retardation of PCE and TCE transport in flow-through cast iron treatment systems would be expected. This retardation will delay the attainment of steady-state conditions within the flow-through system (Hattfield et al. 1996). The practical implication of the observed nonreactive sorption is that numerous pore volumes (tens or possibly hundreds in the case of low PCE concentrations) may be required to attain an accurate assessment of treatment system performance (i.e., kinetics at steady-state conditions).

Potential Sorbent(s) in Cast Iron/Water System

Possible sorbents for the sorption of chlorinated solvents in cast iron/water systems considered in this study include (1) outer passive iron oxide layer; (2) zero-valent iron surface itself; (3) carbon present as iron carbide; and (4) embedded graphite. Sorption onto various pure materials was determined to assess the roles of the outer passive oxide layer, the zero-valent iron surface, and graphite nodules or flakes. Sorption onto carbonyl iron (carbon as iron carbide only) was used to assess the contribution of carbide carbon.

Sorption of PCE onto the iron oxides (hematite, goethite, and maghemite) was not detected above analytical background (results not shown). TCE is less hydrophobic than PCE and sorbed less than PCE for the cast irons; it was not tested for sorption on these materials. The cast iron used was pretreated with acid prior to use to minimize the presence of an iron oxide coating; thus, not much was likely to be present to act
as a sorbent. It can therefore be concluded that the outer passive oxide layer is not a significant sorbent phase for chlorinated solvents in the cast iron.

Sorption of PCE onto electrolytic iron was very low (Fig. 4), close to analytical background. Since sorption onto relatively pure iron surfaces is negligible, sorption of the chloroethenes onto the zero-valent metal surface of cast iron can be assumed to be minor.

PCE sorption onto carbonyl iron (0.82% C, as carbide) was also very low (Fig. 4). This observation suggests that carbon present in cast iron in carbide form contributes very little to the observed sorption of the chloroethenes.

The sorption trends for PCE and TCE onto graphite were similar to their sorption behavior with cast iron (Fig. 4; Fisher iron results shown for comparison) and greater in magnitude. Sorption is nonlinear in all four cases. These observations strongly suggest that the embedded graphite nodules and/or flakes are the most likely nonreactive sorption sites on cast iron. The graphite embedded within the cast iron may be a more effective sorbent than the graphite powder examined in this study. Sorption onto activated carbon was also examined for comparison since it is widely used as a sorbent in hazardous waste engineering applications. It is interesting to note that when sorption onto activated carbon is examined on a "per surface area" basis it also has quite similar sorption behavior when compared with graphite and cast iron, illustrating that cast iron is a strong sorbent for the chlorinated solvents on a surface area basis.

Although graphite appears to be the predominant sorbent, the magnitude of sorption was not directly proportional to the C concentration of the cast iron. For example, MB iron exhibited the greatest sorption, but has the lowest C content of the four iron tested. The degree of sorption isotherm nonlinearity, as captured in the Freundlich exponent, also varies between some of the cast iron tested. Another consideration is that some irons may have more graphite exposed on a surface area basis. These results suggest that the quality, as well as the quantity, of the graphite present in the cast iron affects nonreactive sorption.

Cast iron's observed nonlinear and competitive sorption behavior (Burris et al. 1995) implies a limited number of sorption sites. The sorption isotherm plateaus for PCE and TCE were ~500 mmol/g for Fisher cast iron. Fisher cast iron has a surface area of 1.0 m²/g. Assuming monolayer coverage with the PCE molecule laying flat on the surface and a planar cross-sectional area of PCE of ~30 Å²/molecule (HyperChem), the PCE surface coverage corresponding to the sorption plateau is ~8%. If the PCE molecules were packed on the surface more efficiently using an end-on attachment, the surface coverage would be ~5%. Surface coverage should be similar for TCE. The Fisher 40 mesh cast iron has a carbon content of 3.1%. Assuming that the majority of the carbon present in the cast iron is graphite and the density of graphite as 3.5 times less than zero-valent iron, the amount of exposed surface area of the cast iron being graphite could conceivably be in the 10% range, which is quite close to the estimated 5~8% PCE surface area coverage at the plateau. This analysis further supports the conclusion that graphite, as nodules and/or flakes embedded in cast iron, is the active sorbent component within cast iron for chloroethenes.

Sorption to carbon by hydrophobic organic solutes within a homologous series tends to conform to Traube's rule, which states that sorption increases strongly and regularly as one move up the series (Mattson and Mark 1971). Conformance to Traube's rule can be determined by plotting sorption isotherms as the concentration on the solid phase versus the reduced aqueous concentration (Cₐ divided by the component's aqueous solubility). Traube's rule is adhered to if there is a superimposition of the reduced isotherms. Sorption isotherms on Fisher cast iron for PCE and TCE (Burris et al. 1995), cis-1,2-dichloroethylene (cis-DCE) and trans-DCE (Allen-King et al. 1997), and vinyl chloride (VC) (Deng et al., unpublished paper, n.d.) were examined to determine if sorption of the chloroethenes onto cast iron conforms to Traube's rule (Fig. 5).

FIG. 4. PCE and TCE Sorption Isotherms for Activated Carbon, Graphite, Cast Iron (Fisher), Electrolytic Iron (PCE only), and Carbonyl Iron (PCE only)

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FIG. 5. Normal and Aqueous Solubility Reduced Sorption Isotherms of Chloroethenes (PCE, TCE, cis-DCE, trans-DCE, and VC) on Fisher Cast Iron Plotted as log-log
and Henry's law constant values at 20°C [354,578 Pa, as cited in Mackay et al. (1993) and 2.18 L atm/mol calculated using the temperature regressions of Gossett (1987)], consistent with the method of Pankow and Cherry (1996). This VC solubility value is similar (within 15%) to the value determined in a solubility bomb [as cited in Mackay et al. (1993)]. The near superimposition of the reduced isotherms indicates conformance to Traube's rule. Furthermore, the ratio of the PCE: TCE Freundlich isotherm \( K_F \) for all of the cast irons tested is nearly uniform, in the range of 5–10. This analysis provides additional information suggesting that the nonreactive sorbent in cast iron is graphite.

**Mass Transfer Limitations**

Significant mass transfer resistance was observed for PCE with Fisher cast iron (Fig. 6). The sorption/desorption rate constant (\( \alpha_1 \) and \( \alpha_{-1} \)) were estimated by fitting the \( C_T \) data with (8) (see Materials and Methods section). The prediction of \( C_a \) [(7)] using \( \alpha_1 \) and \( \alpha_{-1} \) estimates based upon fitting the \( C_T \) data was extremely accurate. To compare the results with a situation in which no mass transfer limitations to the nonreactive sorption sites occurred, the model predictions were also shown using \( \alpha_1 \) and \( \alpha_{-1} \) values equal to infinity (10 h\(^{-1} \)) was used, above which no changes were observed). The results indicate rate-limited sorption and even greater rate-limited desorption.

In contrast, TCE (Fig. 6) did not exhibit significant mass transfer limitations. The sorption equilibrium model (i.e., \( \alpha_1 \) and \( \alpha_{-1} = \infty \)) fits the data quite well. The modest departure from the sorption equilibrium model at low concentrations may indicate some rate-limited desorption in that region.

Comparable results with respect to PCE and TCE mass transfer behavior were obtained for the MB, Peerless, and Connelly irons, with a few exceptions. The comparable generalized trends include (1) mass transfer limitations observed for PCE; (2) sorption rate constant is larger than desorption rate constant for PCE; and (3) no mass transfer limitations observed for TCE. The data sets used to obtain the kinetic parameters for MB, Peerless, and Connelly irons (see Table 2) were more limited than the more extensive data sets used for Fisher iron, which led to a greater imprecision in the reaction kinetic parameter (particularly \( \lambda \)) estimates for those three irons. More accurate data fits were obtained when the \( \lambda \) values were altered within the confidence intervals indicated. Another exception was that PCE with Peerless iron could be simulated reasonably well assuming no mass transfer limitations.

Differences in apparent diffusion coefficients with respect to intraparticle diffusion into the sorbent phase may explain why PCE exhibits sorption mass transfer limitations while TCE does not. Graphite tends to be very platey so that the graphite exposed on the surface of the iron could be expected to have internal porosity as opposed to simply being a smooth, solid surface. In this situation the retardation of the solute due to sorption as it diffuses toward the interior of the particle may have a significant effect on observed sorption rates. Apparent diffusion coefficients for intraparticle diffusion has been described in detail by Ball and Roberts (1991)

\[
D_r = \frac{D_a}{R_m}
\]

\( D_a, D_p, \) and \( R_m \) = apparent diffusion coefficient, effective pore diffusion coefficient, and internal retardation factor for intraparticle diffusion, respectively. \( D_r \) is similar for both solutes since their aqueous diffusion coefficients are nearly identical (Reid and Sherwood 1966). Because sorption of PCE on the cast iron is much greater than for TCE, the \( R_m \) for PCE is significantly greater than that for TCE (possibly in the order of magnitude range). The resulting PCE \( D_r \) will be considerably smaller than the TCE \( D_r \). Thus, retarded intraparticle diffusion may offer a suitable explanation for why rate limited sorption was not observed for TCE and was observed for PCE.

The estimated rate coefficients should be viewed as being either apparent or effective (i.e., system dependent) sorption and desorption rate coefficients. In a dynamic reactive system with sorption mass transfer limitations to nonreactive sites, as is the case with PCE with cast iron, a situation can exist where the solute is attempting to diffuse through the intraparticle pores to reach equilibrium with respect to sorption, while the concentration in the bulk aqueous phase is decreasing due to the reduction reactions taking place. In this situation, there will be apparent slow desorption since, for a period of time, the solute molecules within the intraparticle pores will have movement both into and out of the sorbent (i.e., concentration gradients will exist in both directions). This is the likely explanation for the PCE sorption rate coefficients being significantly greater than the desorption rate coefficients.

**CONCLUSIONS**

This study shows that cast irons, as a class of irons, exhibit significant nonlinear sorption to nonreactive sites on the iron surface. The source of this nonreactive sorption appears to be exposed graphitic nodules or flakes embedded in the cast irons. Traube's rule holds for sorption of the homologous series of chloroethenes onto the iron, illustrating the role of solute hydrophobicity on the extent of sorption. Rate-limited sorption/desorption of PCE was observed with cast iron, whereas TCE did not exhibit mass transfer limitations with respect to the nonreactive sorption sites. The nonreactive sorption observed indicates that packed bed cast iron treatment systems for chlorinated ethenes, particularly PCE and TCE, should exhibit significant delayed attainment of steady-state conditions. Determination of flow-through system kinetics prior to attainment
of steady-state conditions will yield overly optimistic estimates of treatment system performance.

**APPENDIX I. ANALYTICAL SOLUTION**

Differentiate (6) with respect to \(t\)

\[
\frac{d^2C_T}{dt^2} = - (\lambda_T + \alpha_T) \frac{dC_T}{dt} + \alpha_T \frac{dC_T}{dt} \tag{10}
\]

A second-order differential equation for aqueous-phase concentration is obtained by replacing \(dC_T/dt\) in (10) using (5), where \(N_a = 1.0\)

\[
\frac{d^2C_{aq}}{dt^2} + (\lambda_a + \alpha_a + \alpha_{a\rightarrow}) \frac{dC_{aq}}{dt} + (\lambda_a \alpha_{a\rightarrow})C_{aq} = 0 \tag{11}
\]

Eq. (11) is a linear, homogeneous differential equation and its solution can be written as

\[
C_{aq}(t) = A_1 \exp \left[ \frac{-(\lambda_a + \alpha_a + \alpha_{a\rightarrow}) + \sqrt{(\lambda_a + \alpha_a + \alpha_{a\rightarrow})^2 - 4\lambda_a \alpha_{a\rightarrow}}}{2} \right] + A_2 \exp \left[ \frac{-(\lambda_a + \alpha_a + \alpha_{a\rightarrow}) - \sqrt{(\lambda_a + \alpha_a + \alpha_{a\rightarrow})^2 - 4\lambda_a \alpha_{a\rightarrow}}}{2} \right] \tag{12}
\]

where \(A_1\) and \(A_2\) are constants. The initial conditions

\[
C_{aq}(0) = C_0 \tag{13}
\]

and

\[
C_{aq}(0) = 0 \tag{14}
\]

are used to determine \(A_1\) and \(A_2\). Employing condition (13) on (12), we obtain

\[
A_1 + A_2 = C_0 \tag{15}
\]

To use condition (14), we need the exact solution for \(C_{aq}(t)\).

This can be found using (16)

\[
\frac{dC_{aq}}{dt} = \frac{1}{\alpha_{a\rightarrow}} \left[ -\lambda_aC_{aq} + \alpha_aC_T \right] \tag{16}
\]

where \(dC_{aq}/dt\) can be obtained by differentiating (12) with respect to \(t\). Now, using condition (14) on (16) will give

\[
\frac{1}{\alpha_{a\rightarrow}} \left[ A_1 \frac{-(\lambda_a + \alpha_a + \alpha_{a\rightarrow}) + \sqrt{(\lambda_a + \alpha_a + \alpha_{a\rightarrow})^2 - 4\lambda_a \alpha_{a\rightarrow}}}{2} + A_2 \frac{-(\lambda_a + \alpha_a + \alpha_{a\rightarrow}) - \sqrt{(\lambda_a + \alpha_a + \alpha_{a\rightarrow})^2 - 4\lambda_a \alpha_{a\rightarrow}}}{2} + \lambda_a C_T + \alpha_a C_T \right] = 0 \tag{17}
\]

Now, we have two equations [(15) and (17)] and two unknowns \((A_1\) and \(A_2\)). Thus, we can determine \(A_1\) and \(A_2\) as

\[
A_1 = \frac{C_0 \sqrt{(\lambda_a + \alpha_a + \alpha_{a\rightarrow})^2 - 4\lambda_a \alpha_{a\rightarrow}} - (\lambda_a + \alpha_a + \alpha_{a\rightarrow})}{2\sqrt{(\lambda_a + \alpha_a + \alpha_{a\rightarrow})^2 - 4\lambda_a \alpha_{a\rightarrow}}} \tag{18}
\]

and

\[
A_2 = \frac{C_0 \sqrt{(\lambda_a + \alpha_a + \alpha_{a\rightarrow})^2 - 4\lambda_a \alpha_{a\rightarrow}} + (\lambda_a + \alpha_a + \alpha_{a\rightarrow})}{2\sqrt{(\lambda_a + \alpha_a + \alpha_{a\rightarrow})^2 - 4\lambda_a \alpha_{a\rightarrow}}} \tag{19}
\]

Hence, the exact solution for \(C_{aq}\) is (7). And by using the mass balance equation, \(C_a + C_T = C_r\), the exact solution of \(C_r\) is (8).

**ACKNOWLEDGMENTS**

Support for this work was provided, in part, by the Air Force Office of Scientific Research (AFOSR) NRC Postdoctoral Research Program, AFOSR Summer Faculty Research Extension Program, and the Strategic Environmental Research and Development Program (SERDP). This support is gratefully acknowledged.

**APPENDIX II. REFERENCES**


**APPENDIX III. NOTATION**

The following symbols are used in this paper:

\(A_1\) = constant, (Eq. 12);

\(A_2\) = constant, (Eq. 12);

\(C_T\) = total system substrate concentration (mass in system);

\(C_{aq}\) = aqueous phase concentration (mass in aqueous phase of system);

\(C_s\) = sorbed phase concentration (mass in solid phase of system);

\(C_0\) = initial aqueous phase concentration;
\( D_p \) = apparent diffusion coefficient;  
\( D_e \) = effective pore diffusion coefficient;  
\( N \) = reaction order;  
\( N_r \) = reaction order relative to aqueous phase concentration;  
\( R_{int} \) = internal retardation factor;  
\( k_1 \) = intrinsic chemical reaction rate;  
\( t \) = time;  
\( \alpha_i \) = nonreactive site sorption rate coefficient;  
\( \alpha_{-1} \) = nonreactive site desorption rate coefficient;  
\( \alpha_i \) = reactive site mass transfer rate coefficient;  
\( \alpha_{-1} \) = reactive site mass transfer rate coefficient;  
\( \lambda \) = degradation rate coefficient; and  
\( \lambda_r \) = degradation rate coefficient relative to aqueous phase concentration.