

# Pd-Catalyzed TCE Dechlorination in Groundwater: Solute Effects, Biological Control, and Oxidative Catalyst Regeneration

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The performance of a Pd-on- $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst for dechlorination of trichloroethylene (TCE) was evaluated in synthetic and real groundwater. Low initial TCE conversions were used to provide maximum sensitivity to changes in catalyst activity. TCE conversions of >24% were maintained in DI water for 60 days using 0.5 g of 1% (w/w) Pd-on- $\gamma$ - $\text{Al}_2\text{O}_3$  and a retention time of 4.3 min. Slow catalyst deactivation was reversed by treatment with a dilute sodium hypochlorite solution. The presence of high concentrations of  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ , and  $\text{Cl}^-$  did not adversely affect catalyst activity. TCE conversion increased 30% upon increasing the solution pH from 4.3 to 11. The presence of 87 mg/L  $\text{SO}_3^{2-}$  or 0.4 mg/L  $\text{HS}^-$  caused rapid catalyst deactivation, presumably due to chemisorption to active sites. Dilute sodium hypochlorite solutions regenerated catalysts deactivated by  $\text{HS}^-$  and  $\text{SO}_3^{2-}$ . Sulfate-reducing bacteria that developed in natural groundwater amended with  $\text{H}_2$  deactivated the catalyst, but activity was restored after flushing with a dilute sodium hypochlorite solution. TCE conversion remained stable between 20 and 28% during a 63-day experiment using natural groundwater and periodic (4–7-day intervals) 90-min pulses of a dilute sodium hypochlorite solution.

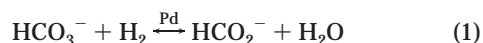
## Introduction

Chlorinated hydrocarbons such as trichloroethylene (TCE) and tetrachloroethylene (PCE) and their anaerobic degradation products, dichloroethylene (DCE) isomers and vinyl chloride (VC), are prevalent groundwater contaminants. The inefficiency of traditional groundwater remediation technologies such as air sparging and granular activated carbon (GAC) contacting has spurred an effort to create novel treatment technologies that transform these contaminants to innocuous compounds in situ. The potential of palladium-(Pd) based catalysts and  $\text{H}_2$  gas for aqueous-phase destruction of halogenated organic compounds in groundwater at ambient pressure and temperature has been studied (1–9). These studies cite three key advantages of Pd technology in that it (i) is effective for a range of contaminants, (ii) results in few or no toxic reaction byproducts, and (iii) provides rapid in situ contaminant destruction yielding no secondary waste streams. Since Pd catalysts rapidly dechlorinate many compounds (1), it is possible to construct in situ fixed-bed treatment reactors capable of placement within a well bore

hole (7, 8), thereby reducing pumping costs and lowering operation and maintenance costs. The footprint of the treatment facility is limited as the reactor can be installed beneath the ground surface. Other significant advantages over traditional pump-and-treat technologies are discussed in ref 8.

Previous studies, with the exception of McNab et al. (7, 8), did not address the complexities of treating groundwater and neglected the potentially adverse effects of biological activity expected under  $\text{H}_2$ -rich anaerobic conditions. In this paper, the effects of natural groundwater solutes (carbonate species, sulfur species, and chloride) and biological activity on catalyst performance are investigated, and regeneration methods to sustain catalyst activity are tested.

Bicarbonate present in groundwater has been suggested as a potential catalyst deactivator in a pilot-scale Pd-based groundwater treatment reactor (7). Also, previous work on the aqueous phase conversion of bicarbonate ( $\text{HCO}_3^-$ ) to formate ( $\text{HCO}_2^-$ ) using Pd catalysts and  $\text{H}_2$  gas indicate a potential for  $\text{HCO}_3^-$  to compete with TCE for active catalyst sites or to promote catalyst deactivation (10–13). The reaction of interest is



A Pd catalyst and  $\text{H}_2$  gas (1 atm, 20 °C) facilitate the forward reaction, and the reverse reaction generates  $\text{H}_2$  at ambient pressure and temperatures ranging from 20 to 70 °C. The formation of carbon monoxide (CO) from the Pd-catalyzed decomposition of formate has been suggested as a cause of catalyst deactivation in these systems because CO sorbs strongly to Pd (10, 13).

Chloride ion and HCl derived from the dechlorination reaction has also been shown to inhibit the activity of Pd and Rh catalysts in the gas-phase dechlorination of TCE, dichloroethane, and chlorobenzene (14–16). Similarly, catalyst deactivation by  $\text{H}_2\text{S(g)}$  and  $\text{SO}_2(\text{g})$  at parts per million concentrations are reported in the catalysis literature, but these studies are at elevated temperatures and pressures and involve gas-phase processes (17, 18). Catalyst poisoning by sulfur species ( $\text{HS}^-$  or  $\text{SO}_3^{2-}$ ) in aqueous-phase batch studies has been reported. The presence of 66 mg/L  $\text{HS}^-$  resulted in complete catalyst deactivation in ref 19, and the presence of 30 mg/L  $\text{SO}_3^{2-}$  deactivated the catalyst after 5 min in the reactor (9). No attempts to regenerate the catalyst were reported. Details of the deactivation mechanism are unclear but may involve processes similar to those in the gas phase, such as the diffusion of S atoms into the bulk of the Pd metal sites or the formation of adlayers of sulfur compounds that block or modify charge mobility at active catalyst sites. These changes inhibit adsorption of reactants or formation of essential intermediates resulting in a less active or inactive catalyst (17, 18, 20–22).

Small (10.5 mL) column reactors are used to evaluate the effects of major groundwater solutes, pH, reduced sulfur species, biological activity, and groundwater from a contaminated site on the catalyst's ability to transform TCE to ethane. TCE conversion is used to monitor catalyst performance on time scales of weeks to months. Major solutes include  $\text{CO}_2$ , sodium bicarbonate, sodium carbonate, sodium chloride, and sodium sulfate. Catalyst performance is evaluated over a pH range from 4.3 to 11. Sodium sulfite and sodium sulfide demonstrate the inhibitory effects of reduced sulfur species. In real groundwater, biological activity leads to the production of bisulfide, which strongly inhibits catalyst performance. Sodium hypochlorite treatment is effective for

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TABLE 1. Catalyst Physical Properties

property (units)	value
particle diameter (mm)	1.6
Pd content (% w/w)	1
BET surface area (m <sup>2</sup> /g)	300
pore vol. (cm <sup>3</sup> /g)	0.33
pore size distribution (nm)	<8 (78%), >8 (22%)
Pd distribution	shell (~70 $\mu$ m)
Pd surface area (m <sup>2</sup> /g)	200
metal dispersion (%)	45

TABLE 2. Moffett Groundwater Quality Data

cations	concn (mg/L)	anions	concn (mg/L)
Ca <sup>2+</sup>	118	HCO <sub>3</sub> <sup>-</sup>	333
Mg <sup>2+</sup>	40.9	SO <sub>4</sub> <sup>2-</sup>	177
Na <sup>+</sup>	39.2	Cl <sup>-</sup>	38.8
K <sup>+</sup>	1.95	NO <sub>3</sub> <sup>-</sup>	4.81
alkalinity	273 <sup>a</sup>	TDS	636
hardness	468 <sup>b</sup>	pH	7.9 <sup>c</sup>

<sup>a</sup> Alkalinity is bicarbonate alkalinity as CaCO<sub>3</sub>. <sup>b</sup> Hardness as CaCO<sub>3</sub>. <sup>c</sup> pH units.

catalyst regeneration, suppressing biological activity and extending catalyst lifetime.

## Experimental Section

**Chemicals.** All chemicals were reagent grade and 99+% pure unless noted. TCE was supplied by Fisher Scientific. Sodium sulfite (anhydrous), sodium sulfate (anhydrous), sodium bicarbonate, and sodium carbonate (anhydrous) were supplied by JT Baker. Formic acid (96%) and sodium sulfide nonahydrate were supplied by Aldrich. Pure hydrogen gas (zero grade) and the hydrogen/carbon dioxide (70%/30%) gas mixture were supplied by Praxair. Sodium hypochlorite solutions used for catalyst regeneration were made from dilutions of standard Clorox bleach (The Clorox Company, Oakland, CA).

**Catalysts.** Pre-reduced 1% Pd-on- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was supplied by PMC (Precious Metals Corporation, Sevierville, TN). No special precautions were taken to avoid catalyst exposure to air prior to column experiments. Catalyst physical properties are given in Table 1. BET surface area, pore volume, and pore size distribution were measured using a Coulter SA 3100 surface area and pore size analyzer. Metal surface area and dispersion (% of metal available for catalysis) were also determined (Coulter Corporation, Hialeah, FL). The 1 wt % palladium content specified by the manufacturer was assumed to be accurate.

**Groundwater Matrix.** Groundwater samples were obtained from a site at Moffett Field in Mountain View, CA. Groundwater samples were stored at 4 °C prior to use to suppress biological activity. Moffett groundwater is very hard (468 mg/L as CaCO<sub>3</sub>) and high in TDS (636 mg/L). The sulfate concentration (177 mg/L) is typical for groundwater in estuarine environments. Water quality analysis (Table 2) was performed by Sequoia Analytical (Morgan Hill, CA).

**Column Reactors.** The reactor design is shown in Figure 1. All tubing, valves, and fittings are stainless steel. The feed tank is either an 11-L or a 19-L stainless steel pressure vessel used for storing DI water/solutes or groundwater amended with TCE under hydrogen pressure (1.24–1.27 atm). A positive displacement pump (Beckman, Scilog/Fluid Metering Inc., Rainin) drives flow through the column in an upflow configuration at 1 mL/min. A 0.68 atm check valve is placed in the column effluent line to eliminate the formation of air bubbles in the column due to degassing of H<sub>2</sub>. Column

influent and effluent sampling points were equipped with a 10-32 female to 1/4-28 female adapter.

The column reactors are 1.27 cm in diameter and 9.8 cm in length with an empty bed volume of 10.5 mL. A catalyst loading of 0.5 g was used to give approximately 40–50% initial TCE conversion. The low initial conversions provide maximum sensitivity to small changes in catalyst performance. Columns were packed wet with 6 g of inert 1.6 mm diameter borosilicate glass beads below the 0.5 g catalyst bed and 8.5 g of the inert glass beads above the catalyst bed. This packing minimizes end and wall effects because the column i.d. is 7.4 times the particle diameter, and the column length is 8.4 times the column i.d. Ideal plug flow is assumed. Column porosity was  $0.42 \pm 0.02$ , giving a fluid residence time of  $4.4 \pm 0.2$  min in the column.

Column reactor experiments were conducted as follows: the feed tank was filled with deionized (DI) water or groundwater and sparged for 30 min with pure H<sub>2</sub> gas to remove dissolved oxygen (DO < 0.15 mg/L after sparging) and saturate the water with H<sub>2</sub>. This provided dissolved H<sub>2</sub> concentrations of approximately 2 mg/L (1 mM), well in excess of the stoichiometric requirements for complete TCE conversion, i.e., 0.2 mg/L (0.1 mM) in the absence of other reducible species competing for hydrogen. Concentrated solutions of solutes and TCE were added to the tank after sparging to give the desired solute concentration and a TCE concentration of approximately 3.5 mg/L (27  $\mu$ M). Flow through the column was started, and column influent and effluent samples were typically taken at 1–2-day intervals for the duration of the experiment.

All catalyst regenerations were performed with dilute sodium hypochlorite solutions. Typically, 2 mL of Clorox (~5.25% sodium hypochlorite) was added to 700 mL of DI water, resulting in a solution with  $75 \pm 12$  mg/L free chlorine (as Cl<sub>2</sub>). A 1:25 dilution of the regeneration solution was used for analysis to keep within the 1–5 mg/L comparator range. A higher hypochlorite concentration was sometimes used ( $750 \pm 120$  mg/L free chlorine) and is noted in the text.

**Analytical Methods.** Reactor influent and effluent samples (0.5 mL) were taken using a 1/4-28 threaded nose 2.5-mL gas-tight syringe (Unimetrics) and extracted into 1 mL of hexane containing 1.3 mg/kg PCE as an internal standard. Extract samples of 1  $\mu$ L were analyzed for TCE using a HP 5890 series II GC equipped with an ECD as described in ref 1. Nonhalogenated reaction products were not measured using this method.

Reactor influent and effluent samples were also periodically analyzed for halogenated reaction intermediates (*cis*-DCE, *trans*-DCE, 1,1-DCE, and vinyl chloride) and nonhalogenated reaction products (ethane and ethylene) to evaluate a carbon mass balance for the TCE transformation and to screen for the formation of undesired reaction intermediates. Aqueous 2.5-mL column influent and effluent samples were collected in a 5.0-mL gas-tight 1/4-28 threaded nose syringe (Unimetrics). A 2.5-mL headspace was created in the syringe and then capped and shaken to equilibrate the aqueous and gas phases. A 200- $\mu$ L headspace sample was withdrawn from the syringe and analyzed with a HP 5890 series II GC equipped with an FID detector as described in ref 1.

Influent and effluent pH measurements were made using a Ross semi-micro combination pH electrode and EA940 ion analyzer (Orion Research, MA). The instrument was calibrated prior to each set of measurements using pH buffers of 4.01, 7.00, and 10.01. Column influent and effluent samples were collected in 4-mL glass vials, capped, and stored no longer than 15 days prior to analysis.

Formate analysis was performed with a Dionex series 4000I ion chromatograph (Dionex, CA) equipped with a Dionex IonPac AS4A column (4  $\times$  250 mm), an AG4A guard column

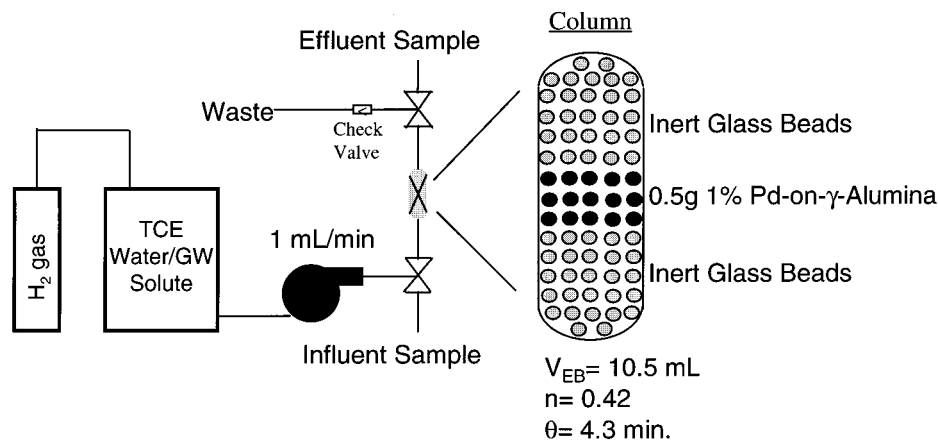


FIGURE 1. Column experimental apparatus.  $V_{EB}$ ,  $n$ , and  $\theta$  are the column empty bed volume, column porosity, and fluid retention time, respectively.

(4 × 50 mm), and a conductivity detector. Sodium tetraborate (5 mM, pH 9.3) was used as an eluent. The instrument was calibrated prior to analysis using volumetric dilutions of a sodium formate stock solution.

Dissolved oxygen measurements were made with a Hansatech DW1 oxygen electrode. A 2-mL column influent/effluent sample was collected in a 2.5-mL gas-tight syringe and carefully injected into the electrode cell for analysis. The electrode was calibrated using a two-point calibration, with  $N_2$ -sparged water as DO = 0 mg/L and air saturated water as 8.8 mg/L. It was assumed that the electrode response was linear.

Free chlorine and total soluble sulfide measurements were made using Chemets colorimetric test kits supplied by Cole-Parmer. Comparator standards for free chlorine ranged from 1 to 5 mg/L with an accuracy of approximately ±0.5 mg/L. Comparator standards for total soluble sulfide ranged from 0 to 1 mg/L with an accuracy of approximately ±0.05 mg/L.

**Evaluation of Reaction and Deactivation Kinetics.** TCE conversion through the column was calculated using eq 2:

$$\% \text{ TCE conversion} = \frac{(C_{in} - C_{eff})}{C_{in}} \times 100 \quad (2)$$

where  $C_{in}$  and  $C_{eff}$  are the measured influent and effluent TCE concentrations, respectively. TCE transformation rate constants were calculated assuming pseudo-first-order reaction kinetics and ideal plug flow (1, 3). Pseudo-first-order TCE transformation kinetics were verified in the column reactors by noting that % TCE conversion remained unchanged when varying influent TCE concentrations from 0.5 to 20 mg/L (4–152  $\mu\text{M}$ , data not shown). Pseudo-first-order rate constants were calculated using eq 3:

$$k_{obs} = \frac{-\ln\left(\frac{C_{eff}}{C_{in}}\right)}{\theta} \quad (3)$$

where  $k_{obs}$  is the observed pseudo-first-order TCE reaction rate constant and  $\theta$  is the fluid residence time in the column. To correct for slight variances in catalyst concentration between experiments, the observed reaction rate constants are normalized by the catalyst concentration ( $g_{cat} n^{-1} V_{EB}^{-1}$ ) such that the reported reaction rate constants,  $k_{rxn}$ , have units of  $\text{mL } g_{cat}^{-1} \text{ min}^{-1}$ . The fluid residence time in the column,  $\theta$ , is calculated using eq 4:

$$\theta = \frac{nV_{EB}}{Q} \quad (4)$$

where  $n$  is the column porosity,  $V_{EB}$  is the column empty-bed volume, and  $Q$  is the fluid flow rate through the column. The column porosity was calculated from gravimetric measurements using eq 5:

$$n = \frac{(W_{c,packed} - W_{c,dry} - W_{glass} - W_{cat})}{(W_{c,water} - W_{c,dry})} \quad (5)$$

where  $W_{c,packed}$ ,  $W_{c,dry}$ ,  $W_{c,water}$ ,  $W_{glass}$ , and  $W_{cat}$  are the weight of the fully packed and water-filled column, empty column, water-filled column, glass beads, and catalyst, respectively.

Catalyst deactivation rate constants,  $k_d$ , were calculated using the methods of Levenspiel for batch solids and a constant plug flow (23). This method assumes pseudo-steady-state conditions within the column. Since the characteristic time for catalyst deactivation (days to weeks) is significantly longer than the characteristic time for TCE transformation (min), the pseudo-steady-state assumption is reasonable. Using the pseudo-first-order TCE transformation rate equation in the plug flow reactor performance equation and assuming first-order deactivation kinetics yields (eq 6) upon integration:

$$\frac{g_{cat}}{Q} = \frac{1}{k_{obs} e^{-k_d t}} \ln \frac{C_{in}}{C_{eff}} \quad (6)$$

Rearrangement of eq 6 yields eq 7, which can be used to evaluate  $k_d$  from linear regression of TCE conversion data vs time on stream (23):

$$\ln \ln \left( \frac{C_{in}}{C_{eff}} \right) = \ln \left( \frac{k_{obs} g_{cat}}{Q} \right) - k_d t \quad (7)$$

## Results and Discussion

**Baseline Catalyst Activity in DI Water.** Baseline catalyst activity was determined in a column experiment using DI water, TCE, and hydrogen (Figure 2). A rapid decline in catalyst activity is evident during the first 2–3 days on stream with TCE conversion dropping from 45% to 33%. This short-lived superactive behavior occurred in most of the experiments conducted in this study and is commonly seen in heterogeneous catalytic systems (17, 18, 20). This behavior may be due to microscale changes in catalyst active sites such as a loss of hyperactive corner and edge sites, a rapid initial carbon deposition on active sites, loss of loosely bound Pd particles, or apparent TCE loss via adsorption to the alumina surface. Reasons for this transient behavior are not relevant for long-term operations and are not further investigated. Calculations of TCE reaction and catalyst



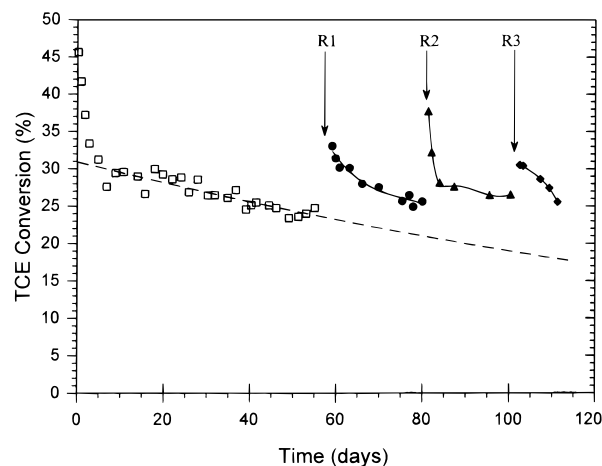


FIGURE 2. Baseline catalyst performance in DI water. R1–R3 indicate catalyst regeneration. Dashed line represents deactivation model fit using eq 7.

deactivation rate constants are made from steady-state TCE conversion in all cases, ignoring the initial rapid decline in catalyst activity.

A steady-state TCE conversion of greater than 24% was maintained for 60 days using 0.5 g of catalyst and a retention time of 4.3 min, indicating that catalyst activity is sustainable for months or longer. Ethane and trace amounts of ethylene (<1%) were the only reaction products observed, and a carbon mass balance of greater than 85% was achieved in the system. Steady-state TCE conversion did decrease from 31% to 24% over the 60-day test period, indicating that slow catalyst deactivation occurs. Regression of steady-state TCE conversion data (eq 7) prior to regeneration result in a deactivation rate constant,  $k_d$ , of  $5.6 \times 10^{-3} \text{ day}^{-1}$ . This value is used for comparison to evaluate the deactivating effects of other solutes.

Figure 2 also shows that catalyst activity is restored after a 90 min (~21 pore volumes) column flushing with the hypochlorite solution. A 1–2-day transient period of hyperactivity occurred after each hypochlorite treatment, followed by steady-state TCE conversions at values similar to the initial steady-state TCE conversions (~30%). Three regenerations were performed, indicating that repetitive hypochlorite exposure is not detrimental to the catalyst and that it may be possible to extend catalyst lifetime in groundwater treatment applications with periodic hypochlorite treatment.

#### Effects of Carbonate Species and pH on Catalyst Activity.

The effects of dissolved  $\text{CO}_2$  ( $\text{H}_2\text{CO}_3$ ),  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$  on catalyst activity are shown in Figure 3. Comparison of these systems with the baseline DI test reveals that none of the carbonate species significantly interfere with the TCE reduction reaction or promote catalyst deactivation, even though they are present at concentrations more than an order of magnitude higher than TCE. The presence of  $\text{CO}_3^{2-}$  and  $\text{H}_2\text{CO}_3$  appears to inhibit catalyst deactivation as the  $k_d$  values for these systems are less than the DI baseline test by a factor of 2 (Table 3), but this may be also be a result of the change in solution pH.

Figure 3 also shows that solution pH has a relatively minor effect on TCE conversion in the reactor, but the average TCE reaction rate constant did increase with increasing pH. The average  $k_{\text{rxn}}$  value in the  $\text{CO}_3^{2-}$  column (pH 10.9) is approximately 30% larger than in the  $\text{H}_2\text{CO}_3$  column (pH 4.4). The average  $k_{\text{rxn}}$  value in the  $\text{HCO}_3^-$  column (pH 8.6) lies between these two extremes. These results are consistent with catalysis literature, where bases are often used to

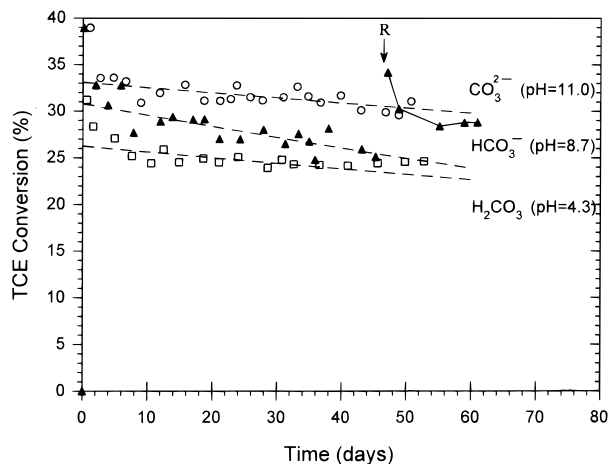


FIGURE 3. Effect of carbonate species and pH on catalyst performance. Solute concentrations were as follows:  $[\text{H}_2\text{CO}_3] = 580 \text{ mg/L}$ ,  $[\text{HCO}_3^-] = 660 \text{ mg/L}$ ,  $[\text{CO}_3^{2-}] = 659 \text{ mg/L}$ . Dashed lines represent deactivation model fits using eq 7. R indicates catalyst regeneration on the  $\text{HCO}_3^-$  column.

TABLE 3. Operating Conditions and Rate Constants for Model Solute Experiments

solute	concentrate (mg/L)	pH <sup>a</sup> (±0.2)	$k_{\text{rxn}}^b$ (mL (g of catalyst) <sup>-1</sup> min <sup>-1</sup> )	$k_d$ (day <sup>-1</sup> × 10 <sup>3</sup> )
none (DI)		6.4–4.9	0.77–0.56	5.6
$\text{H}_2\text{CO}_3$	580 <sup>c</sup>	4.4	0.64–0.51	2.8
$\text{HCO}_3^-$	660	8.6	0.81–0.59	5.0
$\text{CO}_3^{2-}$	659	10.9	0.80–0.69	2.1
$\text{SO}_4^{2-}$	690	6.1–5.0	0.78–0.59	7.6
$\text{SO}_3^{2-}$	87	6.2–4.6	0.55–0.12	>500 <sup>e</sup>
	44 <sup>d</sup>		0.76–0.02	>900 <sup>e</sup>
$\text{HS}^-$	0.4	8.1	0.85–0.04	424
	0.8 <sup>d</sup>		0.55–0.04	>2000 <sup>e</sup>
$\text{Cl}^-$	1003	9.6 <sup>f</sup>	0.84–0.72	3.7

<sup>a</sup> pH ranges for unbuffered systems (influent–effluent). <sup>b</sup>  $k_{\text{rxn}}$  ranges are for slow deactivating systems (initial s.s.–final s.s. TCE conversions rate constants). <sup>c</sup> Concentration based on Henry's constant for  $\text{CO}_2$ .

<sup>d</sup> Two  $\text{SO}_3^{2-}$  and  $\text{HS}^-$  concentrations were used. <sup>e</sup> Too few data points to accurately determine deactivation rate constant. <sup>f</sup> Reason for high pH unknown.

enhance activity in catalytic dehalogenation reactions by neutralizing the mineral acids produced (24). Kovenklioglu (5) reported that base was required to achieve significant dechlorination of dichloromethane, and Hoke et al. (25) reported that ammonium hydroxide was necessary for dechlorination of chlorophenol using a Pd-on-carbon catalyst. Although the TCE transformation reaction is sensitive to changes in pH, the effect is minimal in this case considering the 7 unit pH range covered.

Column effluent was monitored for formate to check whether  $\text{HCO}_3^-$  reacts to formate. Formate was detected in the effluent in all three column experiments, with  $0.7 \pm 0.1$ ,  $5.9 \pm 0.5$ , and  $0.6 \pm 0.01 \text{ mg/L}$  measured in the  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$  columns, respectively. This represents a  $1.2 \pm 0.1\%$  conversion of  $\text{HCO}_3^-$  and  $0.1 \pm 0.02\%$  conversion of  $\text{H}_2\text{CO}_3$  and  $\text{CO}_3^{2-}$  to formate. Formate production in this study is considerably lower than those found in ref 13, but the  $\text{HCO}_3^-$  concentration and  $\text{H}_2$  pressure are lower. The higher concentration of formate produced in the  $\text{HCO}_3^-$  column may contribute to the increased catalyst deactivation observed in this column relative to the  $\text{H}_2\text{CO}_3$  and  $\text{CO}_3^{2-}$  columns (Figure 3), but the deactivation rate constant ( $k_d = 5.0 \times 10^{-3} \text{ day}^{-1}$ ) is nearly identical to that of the DI column. The production of formate does not appear to have a significant influence on catalyst activity under these condi-

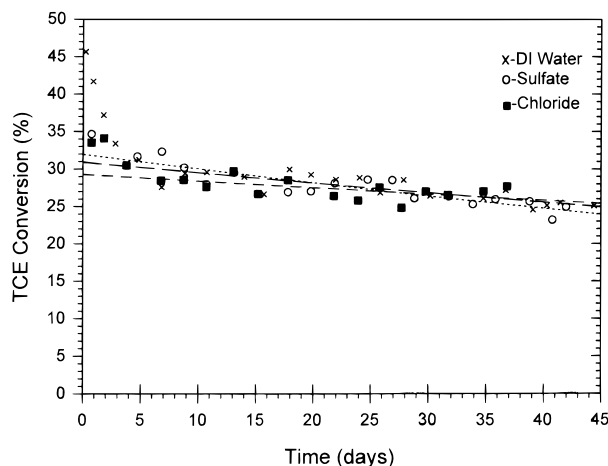


FIGURE 4. Effect of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  on catalyst performance. Dashed lines represent deactivation model fits using eq 7.

tions. It may potentially serve as a carbon source and stimulate biological growth when using Pd-based reactors to treat contaminated groundwater, where biofouling may become an issue.

Catalyst regeneration using a 90-min flushing with the hypochlorite solution was performed in the  $\text{HCO}_3^-$  column to test whether this procedure was as effective at restoring catalyst activity as it was in the DI column. Figure 3 shows that steady-state TCE conversion is restored to levels observed at the beginning of the experiment ( $\sim 29\%$ ).

**Effects of Sulfur Species and Chloride.** Because reduction of  $\text{SO}_4^{2-}$  to various species (i.e.  $\text{SO}_3^{2-}$ ,  $\text{SO}_2^-$ ,  $\text{HS}^-$ ,  $\text{S}^{2-}$ ,  $\text{S(s)}$ ) is thermodynamically feasible under the reactor conditions and  $\text{Cl}^-$  derived from the hydrodechlorination reaction will presumably be in close contact with the catalyst surface, the effects of these ions on catalyst activity were investigated. Catalyst activity in the presence of high concentrations of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  are shown in Figure 4. Neither  $\text{SO}_4^{2-}$  nor  $\text{Cl}^-$  show any negative effects on catalyst activity relative to the baseline DI column test. Deactivation rate constants,  $k_d$ , in the  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  columns are  $7.6 \times 10^{-3}$  and  $3.7 \times 10^{-3}$   $\text{day}^{-1}$ , respectively, and similar to  $k_d$  observed in the DI column test ( $5.6 \times 10^{-3}$ ). The negligible effect of  $\text{SO}_4^{2-}$  on catalyst activity and absence of detectable  $\text{HS}^-$  indicate that  $\text{SO}_4^{2-}$  is not converted to  $\text{SO}_3^{2-}$  or  $\text{HS}^-$  (known catalyst poisons) under the conditions tested. Additionally, the deactivating effects of chloride ion and HCl seen in gas-phase studies are apparently mitigated by solvation in aqueous solution.

The effect of  $\text{SO}_3^{2-}$  on catalyst activity in column studies is shown in Figure 5a. The presence of 87 mg/L  $\text{SO}_3^{2-}$  resulted in rapid catalyst deactivation. As seen in the first portion of Figure 5a (time < 8 days), TCE conversion was reduced to 23.9% after only 6 h on stream and 8.5% after 26 h on stream. No  $\text{HS}^-$  was detected in the reactor effluent, so catalyst deactivation is not a result of  $\text{SO}_3^{2-}$  reacting to produce reduced sulfur species, unless the  $\text{HS}^-$  produced is strongly adsorbed to the catalyst surface making it undetectable in the reactor effluent. TCE conversions stabilized at 3–5% after 4 days on stream, indicating that some residual catalyst activity remains in the presence of a seemingly strong catalyst poison. These low TCE conversions were verified by the presence of ethane in the reactor effluent and a carbon mass balance of  $89 \pm 26\%$ . The presence of residual activity suggests that  $\text{SO}_3^{2-}$  may compete for active sites and/or  $\text{H}_2$  resulting in the lower steady-state TCE conversion observed or that some catalytic sites may be resistant to deactivation, possibly due to mass transfer limitations, steric hindrances, or ion exclusion as suggested in ref 9.

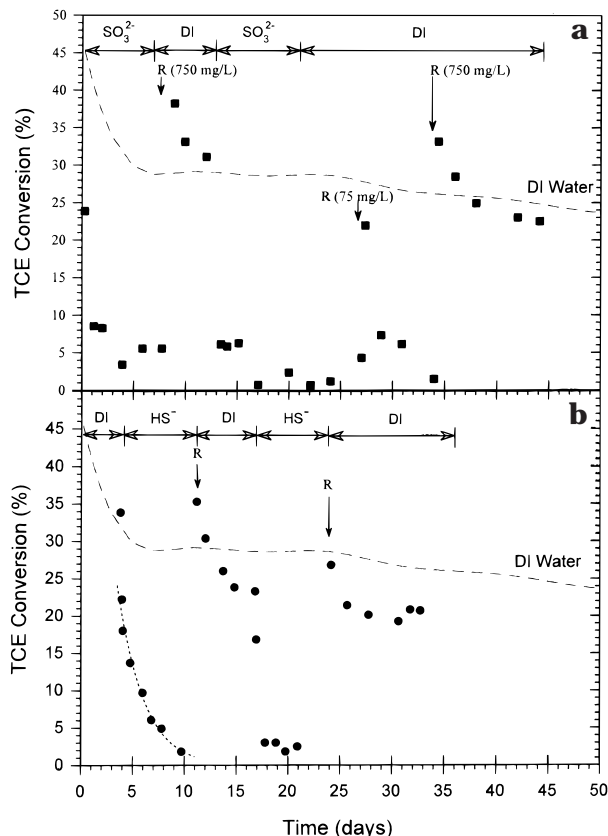


FIGURE 5. (a) Effect of  $\text{SO}_3^{2-}$  and hypochlorite regeneration on catalyst performance. (b) Effect of  $\text{HS}^-$  and hypochlorite regeneration on catalyst performance. Grid dash line in panel b represents deactivation model fit using eq 7. R indicates catalyst regeneration. Horizontal arrows indicate regions where the solute was present in the column influent and where only DI water was used.

Catalyst regeneration was attempted using a high dose of sodium hypochlorite (750 mg/L), and Figure 5a (time 8–13 days) shows that catalyst deactivation by  $\text{SO}_3^{2-}$  is completely reversible. A 90-min pulse of the hypochlorite solution restored steady-state TCE conversions to values similar to the DI column (31%).

$\text{SO}_3^{2-}$  (44 mg/L) was again added to the column influent after regeneration, and TCE conversion dropped to 5–6% after 10 h on stream and dropped to 2% after 7 days. At 20 days, the column was flushed with DI water (with  $\text{H}_2$  and TCE) for 7 days. No catalyst activity was recovered during the DI flushing, indicating that lower TCE conversions were not a result of  $\text{SO}_3^{2-}$  out competing TCE for active sites or depleting the reactor of  $\text{H}_2$ . This suggests that  $\text{SO}_3^{2-}$  or other reduced sulfur species may be chemisorbed to active catalyst sites making them inaccessible to TCE and/or  $\text{H}_2$ .

A standard dose hypochlorite regeneration (75 mg/L) was performed at 27 days resulting only in a short-lived recovery of catalyst activity. At 34 days, a high dose regeneration was again performed (750 mg/L), and TCE conversion was restored to values similar to those observed in the DI system after an equivalent number of days on stream (22%). The extent and duration of catalyst reactivation is therefore dependent on the hypochlorite dose, suggesting that the reactivation process is rate limited.

The disparate deactivating effects of  $\text{SO}_4^{2-}$  and  $\text{SO}_3^{2-}$  may be due to their relative sorption affinities to the  $\text{Al}_2\text{O}_3$  catalyst support. Studies involving sorption of  $\text{SO}_4^{2-}$  onto metal oxides suggest that  $\text{SO}_4^{2-}$  adsorbs via weak outer sphere complexes at  $\text{pH} > 6$  so that the negligible effect of  $\text{SO}_4^{2-}$  may be a result of its weak interaction with the catalyst surface (26, 27). It

has been demonstrated that selenite ( $\text{SeO}_3^{2-}$ ) adsorbs significantly stronger than selenate ( $\text{SeO}_4^{2-}$ ) to  $\gamma\text{-Al}_2\text{O}_3$  in aqueous solution (28, 29). The  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$  structures are analogous to  $\text{SeO}_3^{2-}$  and  $\text{SeO}_4^{2-}$  and can be expected to follow similar trends in sorption affinity. Therefore, it is likely that  $\text{SO}_3^{2-}$  deactivates the catalyst while  $\text{SO}_4^{2-}$  does not because of the stronger sorption affinity of  $\text{SO}_3^{2-}$  to the catalyst. Significant amounts of  $\text{SO}_3^{2-}$  strongly adsorbed to the catalyst surface may also explain the higher dose of hypochlorite required to recover catalyst activity after deactivation with  $\text{SO}_3^{2-}$ .

The effects of  $\text{HS}^-$  on catalyst activity in column studies are shown in Figure 5b. Addition of 0.4 mg/L  $\text{HS}^-$  (pH 8.1, buffered with 50 mg/L sodium bicarbonate) resulted in rapid catalyst deactivation with TCE conversion dropping from 34% to 22% after 80 min on stream and dropping to 1.8% after 5 days on stream. The deactivation rate constant,  $k_d$ , of  $424 \times 10^{-3} \text{ day}^{-1}$  is 2 orders of magnitude higher than those seen in the DI system. Although  $\text{HS}^-$  is a strong Pd catalyst poison, Figure 5b shows that catalyst activity is readily recovered by a 90-min flushing with a standard dose hypochlorite solution. Steady-state TCE conversions of 23% were sustainable in DI water after regeneration, indicating that poisoning by  $\text{HS}^-$  is a reversible process at ambient temperatures and pressures. At 17 days,  $\text{HS}^-$  (0.8 mg/L) was again added to the reactor influent and TCE conversion dropped from 23% to 3% in 24 h. A standard 90-min hypochlorite regeneration was performed at 24 days, and catalyst activity was restored with steady-state TCE conversions of  $\sim 20\%$  sustainable in DI water. TCE conversion after regeneration was slightly lower than observed in the DI system after a similar time on stream indicating that catalyst activity may not be 100% recoverable. A higher hypochlorite dose or increased regeneration time may be necessary for complete recovery or perhaps a fraction of catalyst sites are irreversibly poisoned.

**Reactor Performance in Groundwater.** Two experiments using groundwater samples from Moffett Field (Figure 6) were conducted to assess catalyst performance and lifetime under realistic groundwater treatment conditions. Catalyst performance in the first experiment (Figure 6a) was similar to the DI system, but the steady-state TCE conversions of 16–18% were approximately 50% lower than those in the DI system. The cause of the inhibitory effects of natural groundwater on catalyst activity is still not clear but may be due to competitive sorption of natural organic matter or some unknown inorganic species as sorption of such compounds to metal oxides is well documented (30). At 20 days,  $0.1 \pm 0.05 \text{ mg/L HS}^-$  was detected in the reactor effluent, and TCE conversion dropped from 18% to 5% over an 8-day period, where it remained stable for another 6 days. This again suggests that some catalyst sites remain active even in the presence of low concentrations of a strong catalyst poison.  $\text{HS}^-$  concentrations were monitored periodically and remained constant at  $0.1 \pm 0.05 \text{ mg/L}$  until a catalyst regeneration was attempted.  $\text{HS}^-$  production ceased after the first regeneration with hypochlorite (75 mg/L) but was again detected at  $0.1 \pm 0.05 \text{ mg/L}$  6 days later. The  $\text{HS}^-$  is most likely generated by sulfate reducing bacteria as these bacteria are ubiquitous in the environment and have been shown to grow in  $\text{H}_2$ -amended microcosms using soil and groundwater samples from a nearby well field at Moffett Field (unpublished results). The high concentrations of sulfate in Moffett groundwater (177 mg/L, Table 2) coupled with  $\text{H}_2$ -rich anaerobic conditions in the reactor are ideal conditions for the growth of sulfate-reducing bacteria (31).

Catalyst regeneration with the standard hypochlorite dose was attempted at 34 days, but no sustainable increase in steady-state TCE conversion was observed. Catalyst regeneration with a high hypochlorite dose (750 mg/L) was then

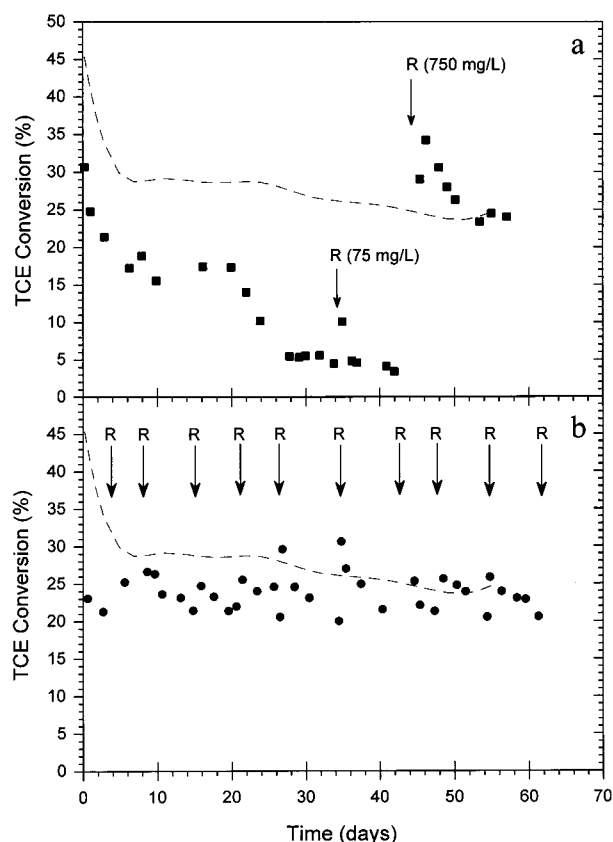


FIGURE 6. Catalyst performance in groundwater from Moffett Field. R indicates catalyst regeneration. Dashed line shows catalyst performance in DI water.

performed and resulted in complete catalyst reactivation, with sustained steady-state TCE conversions of approximately 25%. This again demonstrates a dose–response behavior for catalyst regeneration.

A second experiment with Moffett groundwater (Figure 6b) was conducted using periodic 90-min standard dose hypochlorite treatments at 4–7-day intervals to sustain catalyst activity and inhibit growth of sulfate-reducing bacteria. TCE conversions of 20–28% were maintained for 64 days operating the column in this manner. The saw tooth appearance of the data is a result of the small decline in catalyst performance between regenerations, but the overall activity of the catalyst remained high. Periodic hypochlorite pulsing increased TCE conversion relative to the first groundwater experiment and eliminated the production of  $\text{HS}^-$  from sulfate-reducing bacteria. This implies that catalyst activity, and hence reactor performance, may be sustainable for periods of months to years in field-scale groundwater treatment applications with periodic hypochlorite pulsing.

**Catalyst Regeneration.** Catalyst regeneration through oxidative treatment with a hypochlorite solution was effective in all cases tested in this study and helped maintain catalyst activity during treatment of TCE in natural groundwater systems, but the mechanisms involved are not understood. Oxidative regeneration was employed in ref 8 by exposing the catalyst to air for 15 h after 9 h of operation each day, and Kramer et al. (13) used oxygen gas to regenerate deactivated Pd catalysts used in the transformation of  $\text{HCO}_3^-$  to  $\text{HCO}_2^-$ . The reactivation process may involve (i) the oxidation and subsequent desorption of reduced sulfur or organic molecules strongly sorbed to the catalyst active sites; (ii) the oxidation and removal of carbon deposited on the catalyst surface, as carbon buildup (coking) is observed on most metal based catalysts (32); (iii) redispersion of sintered

Pd particles (33); (iv) oxidation of less active palladium hydride ( $\text{PdH}_x$ ) to more active  $\text{Pd}_{(0)}$  or perhaps palladium oxide ( $\text{PdO}$ ); or (v) elimination of a biofilm formed on the catalyst surface.

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