

Degradation of 1,2,3-Trichloropropane by Zero-Valent Zinc: Laboratory Assessment for Field Application

Alexandra J. Salter (saltera@ebs.ogi.edu), Paul G. Tratnyek, and Richard L. Johnson
(Oregon Health & Science University, Portland, OR, USA)

ABSTRACT: Bench-scale batch reactor and column tests were performed to identify types of granular zero-valent zinc (ZVZ) that might be suitable for remediation of 1,2,3-trichloropropane (TCP) contaminated groundwater. Two industrial grade materials, Zn64 and Zn1210, were selected for further analysis in a scaled-up, ex-situ field test. Groundwater was found to inhibit the reduction of TCP by zinc, but this affect was overcome in some instances by lowering pH. Also illustrated are several of the general issues involved in scaling between batch and column data for treatments with zero-valent metals.

INTRODUCTION

Zero-valent zinc (ZVZ) is known to reduce most chlorinated solvents (Boronina et al. 1995; Roberts et al. 1996; Arnold et al. 1998; Feng et al. 2005), and but the advantages of ZVZ over zero-valent iron (ZVI) have not been sufficient to generate significant interest in using ZVZ for remediation of contaminated groundwater. Recently, it has been shown that the emerging contaminant 1,2,3-trichloropropane (TCP) is degraded much more rapidly by ZVZ than ZVI in batch experiments (Sarathy et al. 2010). Since there are currently few options for remediation of TCP-contaminated groundwater, these results have sparked interest in the application of ZVZ to remediate several TCP contaminated sites.

TCP contamination can occur at industrial and agricultural sites due to its use as a solvent for degreasing, feedstock for polymer production, and as a precursor to (and impurity in) some soil fumigants. At Camp Pendleton Marine Corps base in southern California, solvent/degreasing activities are presumed to be responsible for TCP contamination exceeding the State of California notification level¹ (0.005 µg/L (California Environmental Protection Agency 2009)). This contamination has necessitated closure of several drinking water production wells at the site, and prompted a search for effective treatment options so these wells can be put back into production.

¹ Currently, there are no State of California or federal MCLs for TCP (California Environmental Protection Agency 2009); this is consistent with the status of TCP as an emerging contaminant.

Currently, a pilot project utilizing ex-situ treatment columns is being prepared to test the use of ZVZ to treat the TCP-contaminated groundwater at Camp Pendleton. As field-scale tests are consuming of time and resources, initial material analysis and treatability assessments are being performed with bench-scale batch and column tests. In this case, the usual challenges of scaling from laboratory bench to field are compounded by the complete absence of any prior use of granular ZVZ in column or field applications. With this in mind, this paper focuses on the results of the bench-scale portion of this project and then explores the scalability of these results for design of the next, field stage of this project.

METHODS

Reagents. ZVZ used in this study included three industrial-grade materials, Zinc Dust 64 and Zinc Powders 1210 and 1239 (Horsehead Corporation, Monaca, PA). Properties of these materials are given in Table 1. All ZVZ materials and the sand used for batch and column fill (#17, U.S. Silica, Berkeley Springs, WV) were used as received. Saturated stock solutions of 1,2,3-trichloropropane (>98%, Fluka) were prepared in deionized (MilliQ) water. In most batch and column experiments, deionized water was used without further treatment. Deoxygenated, deionized (DO/DI) water was prepared by sparging with either nitrogen or argon. Groundwater was obtained from a well at Camp Pendleton unless otherwise noted.

Batch Experiments. Batch reactor experiments were performed in 160-mL serum vials sealed with Hycar septa (Thermo Scientific) and aluminum crimp caps. Batches contained 20 g ZVZ (with the exception of the Zn64/Zn1210 combination batch, Batch 8, which contained 100 g total ZVZ) and 80 mL of either DI water, DO/DI water, or groundwater. In some cases, batches also contained silica sand in addition to the 20 g ZVZ. Before reaction initiation, the batches pre-equilibrated for 20-28 hours while rotating. If the pH of the batch reactor was adjusted, HCl or NaOH were added after 1 hour of pre-equilibration. Experiments were initiated through the injection of 200 μ L saturated TCP stock solution and rotated end-over-end at \sim 32 rpm for the duration. Initial batch pH measurements were made after pre-equilibration and prior to TCP injection. All batch experiments were performed at room temperature.

Column Experiments. Column experiments were performed in 15-cm long, 2.5-cm I.D. columns (Kontes) filled completely with packing material that corresponded to specific batch experiments. The column packing material consisted either entirely of ZVZ or a ZVZ/sand combination; all reported percentages of materials (e.g., 25% Zn64 in sand) are mass percentages. Columns were prepared by adding a small amount of column influent and, subsequently, column packing material. Pore volume was determined by the mass difference between the dry and wet column. Columns were run in an up-flow manner, with the influent entering the bottom of the column and effluent exiting the top. The column influent was prepared by spiking the chosen solution (i.e., DI water or groundwater) with TCP. This influent was pumped from a reservoir into the column with an HPLC pump (Rainin). Any pH perturbations to the system were made in the reservoir from which the column influent was pumped. Fractions of the column effluent were

collected at intervals and analyzed for pH and TCP concentration. All column experiments were performed at room temperature.

Analysis. Aliquots (1 mL) were removed from the batch reactor or column effluent fraction and analyzed by gas chromatography (GC) with a DB-624 column (J&W/Agilent) and electron capture detection. GC analysis was either performed by headspace analysis of the 1 mL aliquot in a 20 mL headspace vial or by direct injection of a 1:1 hexane extraction of the aliquot. In both cases, TCP concentrations were determined by comparison to identically analyzed calibration curves prepared by analyzing no-zinc batch reactors containing varying concentrations of TCP in DI water.

TABLE 1. ZVZ Properties

Material	Designation	Mesh ¹	Specific Surface Area (m ² /g) ²	Bulk Density (g/cm ³)
Zinc Dust 64	Zn64	through 325	0.620	2.60
Zinc Powder 1210	Zn1210	20-60	0.016	2.34
Zinc Powder 1239	Zn1239	200-325	0.160	3.27

¹ Provided by manufacturer. ² Measured by BET gas adsorption.

RESULTS

Batch Experiments. As a first step in selecting candidate materials for future field-scale tests, several types of ZVZ were screened in batch reactor experiments to determine their reactivity towards TCP. The kinetics of TCP degradation in these batch experiments was described by fitting concentration versus time data to a pseudo first-order model to obtain observed rate constants, k_{obs} .

$$[\text{TCP}] = [\text{TCP}_0]e^{-k_{\text{obs}}t} \quad (1)$$

Unlike groundwater in permeable reactive barriers (PRBs), the water to be run through the ex-situ treatment columns planned for Camp Pendleton will be at or near equilibrium with the atmosphere. Because of this, batch experiments were carried out in deoxygenated, deionized (DO/DI) and unsparged deionized (DI) water to isolate any effects of oxygen on the material reactivity. As seen in Figure 1a and 1b, Zn64 degraded TCP at the fastest rate, and the rate did not appear to be effected by the presence or absence of oxygen. Degradation of TCP by Zn1210 was slower (by about one order of magnitude), but again did not appear to be effected by the presence of oxygen. Zn1239 gave TCP degradation kinetics similar to Zn1210 in DO/DI water (despite its higher surface area), but much slower rates in the presence of oxygen (Figure 1b).

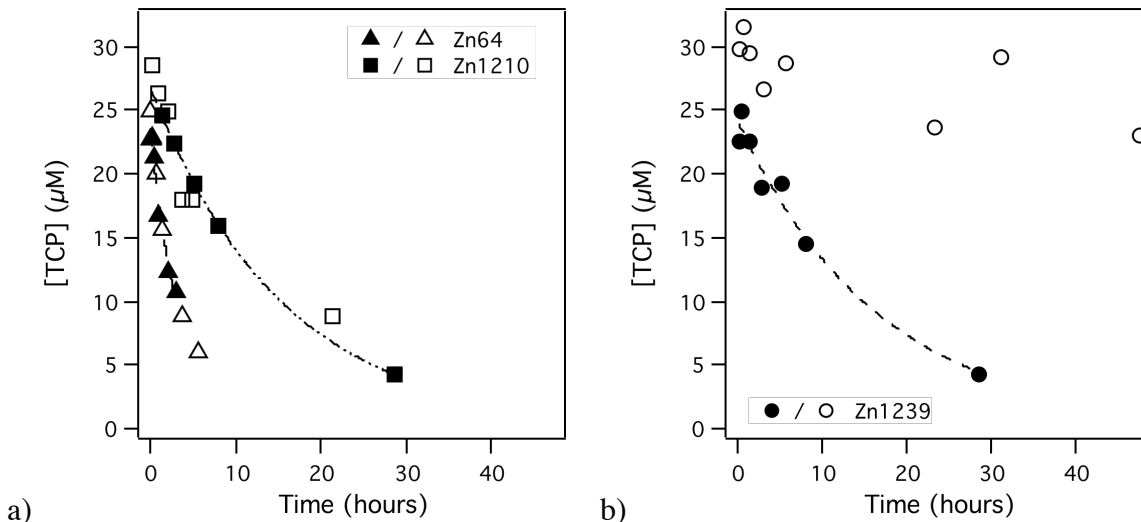


FIGURE 1. (A) Degradation of TCP by Zn64 and Zn1210 in DO/DI and DI water. (B) Degradation of TCP by Zn1239 in DO/DI and DI water. In both figures, solid symbols represent DO/DI data, with fit curves shown (see Equation 1). Hollow symbols represent data from unsparged DI water batches. All batches contained an equal mass dose of ZVZ (250 g/L).

After establishing the reactivity of the ZVZ materials in DI water, the rates of TCP reduction by Zn64 and Zn1210 were measured in site groundwater obtained from Camp Pendleton. The degradation of TCP in batch experiments containing site water was significantly slower than TCP degradation in the analogous batch experiments with DI water (mass normalized rate constants, k_M , given in Table 2). A similar reduction in reactivity was seen when Zn64 was mixed with sand (a practice often employed in treatment columns made from fine reactive materials in order to minimize back pressure and clogging). However, it was observed that the inhibitory effects of both site water and sand could be overcome, to some degree, by titrating the pH of the batch reactor to below ~ 7 . This is consistent with known effects of pH on zinc oxyhydroxide solubilities (Pourbaix 1974; Vega et al. 1995) and corrosion rates (Roetheli et al. 1932).

Based on the above batch data, Zn64 was selected for further investigation in small-scale column experiments because of its high overall reactivity. Zn1210 was also selected because of its large particle size, which may negate the need to mix the material with sand, allowing for 100% of the column to be packed with reactive material and avoiding the inhibitory effect caused by the presence of the sand. Zn1239 was not selected for column testing because of its reduced reactivity in the presence of oxygen and because it did not offer any benefits, either in reactivity or size, that were not represented by the other two materials.

TABLE 2. Batch and Column Data and Comparison

		Batch Data		Column Data					Batch/Column Comparison	
Batch or Column Solids	Solution	Initial Batch pH ¹	$k_{M,B}$ (L hr ⁻¹ g ⁻¹)	Column Influent pH ²	Column Effluent pH	$\rho_{M,C}$ ³ (g L ⁻¹)	$k_{obs,C}$ (hr ⁻¹)	θ ⁴	$k_{obs,C}^*$ (hr ⁻¹)	$k_{obs,C} / k_{obs,C}^*$
1 Silica Sand Only	DI Water	7.77	2.67×10^{-5}	8.17	8.88-8.93	0	~ 0.024 ⁷	0.45	0	N/A
2 33% Zn64/sand	DI Water	6.90	3.08×10^{-4}	3.57	7.43-7.50	1579	2.094	0.43	0.486	4.31
3 33% Zn64/sand	Site Water ⁵	6.89	3.76×10^{-4}	2.26	6.77-6.99	2264	0.436	0.36	0.852	0.512
4 25% Zn64/sand	Site Water ⁶	9.40	3.05×10^{-5}	8.57	8.0-8.8	2000	0.185	0.29	0.061	3.02
5 25% Zn64/sand	Site Water ⁶	6.82	1.33×10^{-3}	2.56	6.82-6.96	2009	0.447	0.29	2.671	0.167
6 100% Zn1210	Site Water ⁶	10.30	2.17×10^{-5}	8.08	7.5-8.5	4186	0.066	0.58	0.091	0.730
7 100% Zn1210	Site Water ⁶	6.62	2.88×10^{-4}	2.45	6.5-6.9	4884	0.379	0.58	1.408	0.269
8 20% Zn64/Zn1210	Site Water ⁶	7.05	7.10×10^{-4}	2.36	7.00-7.24	7895	0.458	0.39	5.608	0.082

¹ Bold values indicate pH values that resulted from titration of the batch reactor with HCl.

² Bold value indicate pH values that resulted from titration of the influent with HCl.

³ Mass concentration: ZVZ mass measured prior to column assembly, solution volume determined from the mass difference between the dry and wet column.

⁴ Porosity: determined from the mass difference between the dry and wet column.

⁵ Data for Batch 3 were collected in water from another TCP-contaminated site with composition similar to that of Camp Pendleton; the column was run with Camp Pendleton site water.

⁶ Obtained from Camp Pendleton.

⁷ The TCP concentration of the influent was not measured for this control, so $k_{obs,C}$ is based on a calculated influent concentration.

Column Experiments. After selecting Zn64 and Zn1210 from batch experimental results, short-term, small-scale columns were run to assess performance in flow-through systems and to identify an effective mixing ratio of Zn64 with sand. The columns were allowed to run until they reached a steady-state concentration (~24-48 hrs) after which an experimental observed rate constant for the column ($k_{obs,C}$) was determined. The rate constant was extracted from the data by assuming pseudo first-order behavior (see Equation 1) and treating the influent TCP concentration as $[TCP_0]$ and the average of the measured concentrations at steady-state as the TCP concentration at the residence time (t). Rearranging Equation 1 yields:

$$k_{obs} = -\frac{\ln([TCP]/[TCP_0])}{t} \quad (2)$$

which can be rewritten in terms of measured values:

$$k_{obs,C} = -\frac{\ln([TCP]_{eff}/[TCP]_{inf})}{\text{residence time}} \quad (3)$$

where $[TCP]_{eff}$ is the average concentration of TCP after the column has reached steady state and $[TCP]_{inf}$ is the concentration of the influent. The resulting rates constants for the column experiments are summarized in Table 2.

The main factors in controlling $k_{obs,C}$ appear to be pH and ZVZ type. Columns run at a low pH consistently showed faster $k_{obs,C}$ than columns run without pH adjustment (for both Zn64 and Zn1210). In columns run at a similar pH, all ratios of Zn64/sand produced a higher $k_{obs,C}$ than 100% Zn1210. In addition, differences in the Zn64/sand mixing ratio (Column 3 and 5) did not have a large effect on $k_{obs,C}$ despite variations in total Zn64 mass (#3 contained 60 g Zn64, #5 contained 43 g). Substituting Zn1210 for sand as a mixing material for Zn64 also had little effect on $k_{obs,C}$, as Columns 5 and 8 (25% Zn64/sand vs. 20% Zn64 in Zn1210, but with equal mass of Zn64) showed a similar $k_{obs,C}$.

In order to test whether or not the fast kinetics observed in pH adjusted, 15-cm columns would be maintained throughout the length of a larger column, a 1-m column with the same packing material and influent as Column 5 was run at a flow rate predicted to give about 80% TCP reduction (see scaling calculations below). The $k_{obs,C}$ was determined to be 0.17 hr^{-1} , which is slower than anticipated and closer to the value from Column 4, the analogous column without pH adjustment, than Column 5. It is likely that fast kinetics like those observed in Column 5 only persisted in the first section of the 1-m column (where pH remained low) and did not apply to the overall $k_{obs,C}$.

Since manipulation of influent pH to the large column did not produce the higher rates of TCP degradation that were observed in batch and small column experiments, the evaluation of materials for the ex-situ field tests at Camp Pendleton is based on results from columns run without pH adjustment. Of these columns, #4, containing 25% Zn64/sand, displayed a $k_{obs,C}$ three times faster than #7, which contained 100% Zn1210. With respect to the rate of TCP degradation, the 25% Zn64/sand mixture is a favorable choice for further analysis. Other factors must be considered, however, such as the quantity of hydrogen production. In the short-term column experiments, Zn64 appeared

to produce a larger volume of hydrogen gas than Zn1210 columns (although this result has yet to be quantified). It is unclear what consequences this will have in the long term. It is also unclear how other factors such as clogging, aging, and inhibition by sand will affect columns made from Zn64/sand and Zn1210 in the long term. Given these uncertainties, it will be desirable to compare both the 25% Zn64/sand mixture and Zn1210 during the ex-situ field test at Camp Pendleton.

Batch/Column Comparison. To help with design of the columns to be tested at Camp Pendleton, scaling calculations can be performed using the batch and small-column data described above. To do this, rate constants for column conditions were calculated from batch results, ($k_{\text{obs,C}}^*$), and compared to the measured values of $k_{\text{obs,C}}$. $k_{\text{obs,C}}^*$ was determined by assuming first-order behavior and a linear dependence of k_{obs} on mass load. As such, $k_{\text{obs,C}}^*$ was determined by multiplying the mass-normalized batch-determined rate constant ($k_{\text{M,B}}$), expressed in $\text{L g}^{-1} \text{hr}^{-1}$, by the mass concentration of ZVZ in the theoretical column ($\rho_{\text{M,C}}$), expressed in g L^{-1} . The equation for this calculation is given below.

$$k_{\text{obs,C}}^* = k_{\text{M,B}} \times \rho_{\text{M,C}} \quad (4)$$

To facilitate direct comparison between the theoretical and experimental columns, the measured mass concentrations of ZVZ from the experimental columns ($\rho_{\text{M,C}}$, given in Table 2) were used in the calculations for the theoretical columns. The results of these calculations are given in Table 2.

Table 2 shows varying degrees of agreement between $k_{\text{obs,C}}$ and $k_{\text{obs,C}}^*$. For batches/columns that were not pH adjusted (4 and 6), $k_{\text{obs,C}}$ was similar or faster than $k_{\text{obs,C}}^*$. For pH adjusted columns, the DI water column showed a faster $k_{\text{obs,C}}$ than $k_{\text{obs,C}}^*$ but the site water columns showed slower $k_{\text{obs,C}}$ than $k_{\text{obs,C}}^*$, most likely because of differences in pH down the length of the column. The poorest agreement was observed in Column 8, presumably because the residence time was not long enough for Zn1210 to have much effect, and the kinetics were dominated by the mass of Zn64.

Implications for Scale-Up. If first-order behavior and a linear dependence on mass concentration are assumed, scaling calculations can be used to estimate the column parameters (i.e., flow rate, column size) required to treat the well water at Camp Pendleton. This can be done by rearranging Equation 3 to solve for residence time (t_{R}),

$$t_{\text{R}} = -\ln\left(\frac{[\text{TCP}]_{\text{eff}}/[\text{TCP}]_{\text{inf}}}{k_{\text{obs,C}}}\right) \quad (5)$$

and inserting the TCP concentration of the well water for $[\text{TCP}]_{\text{inf}}$ and the desired concentration of the treated water for $[\text{TCP}]_{\text{eff}}$. Since residence time is determined by the pore volume and the flow rate, these parameters can be substituted into Equation 5, which can then be rearranged to yield Equation 6.

$$\text{pore volume} = -\ln\left(\frac{[\text{TCP}]_{\text{eff}}/[\text{TCP}]_{\text{inf}}}{k_{\text{obs,C}}}\right) \times \text{flow rate} \quad (6)$$

If pore volume is expressed in terms of the material porosity (θ) (empirically determined, see Table 2) multiplied by the column volume, the equation becomes,

$$\theta \times \text{column volume} = -\ln\left(\frac{[\text{TCP}]_{\text{eff}}/[\text{TCP}]_{\text{inf}}}{k_{\text{obs,C}}}\right) \times \text{flow rate} \quad (7)$$

which can be solved for either column volume or flow rate after entering in experimentally determined values from this study. Whether or not the equation is solved for column volume or flow rate will be determined by which of these parameters has been predetermined for the treatment scenario in question. In the upcoming pilot tests, the column size is relatively restricted so the flow rate will need to be varied to control the column effluent concentration. In potential large-scale drinking water treatment the flow rate will likely be dictated by supply demands and a column(s) will need to be sized to accommodate that parameter.

Assuming the columns employed in the pilot tests at Camp Pendleton will be 120 inches (3 m) long with a 6 inch (15.2 cm) I.D., the flow rate required to reduce the well water from 5 $\mu\text{g/L}$ (one of the highest values at the site) to 0.005 $\mu\text{g/L}$ (the California EPA notification level (California Environmental Protection Agency 2009)) can be estimated using Equation 7. A column packed with 100% Zn1210 will require a 310 mL/hr flow rate (104 hr residence time) and a column packed with 25% Zn64/sand will require a 430 mL/hr flow rate (37 hour residence time). This level of performance is less than desired, but is comparable or better than any other reduction-based (Sarathy et al. 2010) or chemical oxidation or enhanced bioremediation treatments (Tratnyek et al. 2008), although quantitative comparisons under the specific groundwater conditions have not been made. To fully utilize ZVZ as a reductant, methods of eliminating or reducing groundwater inhibition must be identified. Future research should focus on identifying methods of either maintaining low pH throughout the column (e.g., using a pH buffering mixing material), or removing the constituents responsible for groundwater inhibition (e.g., a pretreatment column).

CONCLUSIONS

Based on our bench-scale analyses, we recommend Zn64 and Zn1210 for further testing at Camp Pendleton. Zn64 clearly showed the fastest kinetics of the materials tested, but due to material size considerations and apparent hydrogen production rates, Zn1210 may be a more practical choice in long-term applications. It was seen that groundwater inhibition greatly reduces the ability of ZVZ to reduce TCP. While this inhibition can be overcome in batch experiments by lowering the pH to below ~ 7 and in small-scale column experiments by titrating the influent pH to ~ 2 , pH adjustments do not appear to overcome inhibition in larger (i.e., 1 m long) columns. Treatment of TCP with ZVZ will be more effective in a system that either maintains low pH or employs a method of removing inhibiting groundwater constituents.

ACKNOWLEDGMENTS

This work was supported by grants from the Navy Environmental Sustainability Development to Integration Program (NESDI) and the Strategic Environmental Research and Development Program (SERDP). It has not been reviewed by either agency and therefore does not necessarily reflect their views and no official endorsement should be inferred.

REFERENCES

- Arnold, W. A. and A. L. Roberts. 1998. "Pathways of chlorinated ethylene and chlorinated acetylene reaction with Zn(0)." *Environmental Science & Technology* 32(19): 3017-3025.
- Boronina, T., K. J. Klabunde and G. Sergeev. 1995. "Destruction of organohalides in water using metal particles: Carbon tetrachloride/water reactions with magnesium, tin, and zinc." *Environmental Science & Technology* 29(6): 1511-1517.
- California Environmental Protection Agency. 2009. Public Health Goal for 1,2,3-Trichloropropane in Drinking Water.
- Feng, J. and T.-T. Lim. 2005. "Pathways and kinetics of carbon tetrachloride and chloroform reductions by nano-scale Fe and Fe/Ni particles: comparison with commercial micro-scale Fe and Zn." *Chemosphere* 59(9): 1267-1277.
- Pourbaix, M. (1974). Corrosion. *Atlas of Electrochemical Equilibria in Aqueous Solutions*. Houston, TX, National Association of Corrosion Engineers: 70-83.
- Roberts, A. L., L. A. Totten, W. A. Arnold, D. R. Burris and T. J. Campbell. 1996. "Reductive elimination of chlorinated ethylenes by zero-valent metals." *Environmental Science & Technology* 30(8): 2654-2659.
- Roetheli, B. E., G. L. Cox and W. B. Littreal. 1932. "Effect of pH on the Corrosion Products and Corrosion Rate of Zinc in Oxygenated Aqueous Solutions." *Metals and Alloys* 3: 73-76.
- Sarathy, V., P. G. Tratnyek, A. J. Salter, J. T. Nurmi, R. L. Johnson and G. O'Brian Johnson. 2010. "Degradation of 1,2,3-trichloropropane (TCP): Hydrolysis, elimination, and reduction by iron and zinc." *Environmental Science and Technology*. 44(2): 787-793.
- Tratnyek, P. G., V. Sarathy and J. H. Fortuna (2008). *Fate and remediation of 1,2,3-trichloropropane*. International Conference on Remediation of Chlorinated and Recalcitrant Compounds, 6th, Monterey, CA.
- Vega, M., R. Pardo, M. M. Herguedas, E. Barrado and Y. Castrillejo. 1995. "Pseudopolarographic determination of stability constants of labile zinc complexes in fresh water." *Analytica Chimica Acta* 310(1): 131-8.