Treatability Testing--Fate of Chromium During Oxidation of Chlorinated Solvents

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ABSTRACT

Laboratory testing demonstrated that potassium permanganate ($KMnO_4$) could degrade chlorinated solvents in site groundwater. The amount of $KMnO_4$ needed was controlled by the soil, which also consumed $KMnO_4$. Soil chromium was oxidized to hexavalent chromium (Cr(VI)), but naturally attenuated during bench tests. A pilot test was conducted based on the results of this study.

INTRODUCTION

Site Background

- Former semiconductor manufacturing facility in Sunnyvale, California
- Groundwater contains up to 8 mg/L of cis-dichloroethylene (DCE) and trichloroethylene (TCE)
- Soil composed of sands, silts and clays
- Plume located under building

Permanganate Basics--I

- Relatively strong oxidant
- Used extensively in water and wastewater treatment for taste and odor control and oxidation of iron, manganese, and arsenic
- In recent years, used to treat PCE and TCE DNAPLs.

Permanganate Basics--II

- Reaction believed to occur as follows:

$$3C_2H_2Cl_2 + 8KMnO_4 \rightarrow 6CO_2 + 6KCl + 6KOH + 8MnO_2 + 2H_2O$$

$$C_2HCl_3 + 2KMnO_4 \rightarrow 2CO_2 + 2KCl + 2MnO_2 + HCl$$

- Dose requirements are: 4.3 g $KMnO_4$ / g DCE and 2.4 g $KMnO_4$ / g TCE

Factors to Consider When Evaluating Permanganate

- Contaminants destroyed, not moved from one compartment to another
- $KMnO_4$ is non-selective
- MnO_2 is a solid--may restrict aquifer flow
- $KMnO_4$ and MnO_2 may oxidize soil chromium to Cr(VI)
- $KMnO_4$ contains chromium impurities

Study Objectives

- Determine amount of $KMnO_4$ needed to degrade DCE and TCE in groundwater
- Estimate the soil $KMnO_4$ demand
- Measure effect of $KMnO_4$ on soil permeability
- Determine whether Cr(VI) is formed and if so, evaluate methods of management

EXPERIMENTAL PROCEDURES

- **$KMnO_4$ Dose Requirements for DCE, TCE Removal in Groundwater**--batch tests conducted on site groundwater using 0, 2X, and 5X stoichiometric amount of $KMnO_4$.
- **KMnO4 Dose Requirements for Soil**--$KMnO_4$ solution added to soil and $KMnO_4$ concentration monitored periodically.

- **Formation of Cr(VI)**
  - Soil column flushed with $KMnO_4$. Effluent analyzed for Total Cr and/or Cr(VI)
  - soil mixed with $KMnO_4$ soln. When $KMnO_4$ gone, aqueous phase analyzed for Cr(VI).
- **Fate of Cr(VI): Natural Attenuation**
  - soil mixed with $KMnO_4$ solution until $KMnO_4$ gone. Aqueous phase monitored for Cr(VI) over time.
  - Cr(VI)-containing water added to soil. After standing undisturbed about 7 days, pore water removed and analyzed for Cr(VI).

- **Fate of Cr(VI): Addition of Reducing Agents**--soil mixed with $KMnO_4$ solution until $KMnO_4$ gone. Aqueous phase decanted and replaced with solution of ferrous sulfate, ascorbic acid or molasses. Decanted again and replaced with clean site water. All aqueous phases analyzed for Cr(VI).

RESULTS AND DISCUSSION

$KMnO_4$ Dose Requirements--Groundwater

As shown in Table 1, five times the stoichiometric dose of $KMnO_4$ (40 mg/L) was required to completely destroy DCE and TCE in site groundwater. The excess $KMnO_4$ was presumably needed to react with dissolved organic matter and other oxidizable species in the water.

TABLE 1. DCE, TCE in Groundwater Treated with $KMnO_4$

Test	DCE, mg/L	TCE, mg/L
0X-Stoichiometric Dose (0mg/L $KMnO_4$)	1.9	0.18
2X-Stoichiometric Dose (16.1mg/L $KMnO_4$)	0.026	0.013
5X-Stoichiometric Dose (40.3mg/L $KMnO_4$)	< 0.001	< 0.001

$KMnO_4$ Dose Requirements--Soil

As shown in Figure 1 and Table 2, site soils consumed a significant amount of $KMnO_4$. The rate of consumption was initially fast, presumably due to rapid reaction of easily oxidizable species such as natural organic matter. This is consistent with the faster rate seen in the silt and clay, which had a higher organic carbon content than the sand (Table 3).

FIGURE 1. Consumption of $KMnO_4$ by Soil

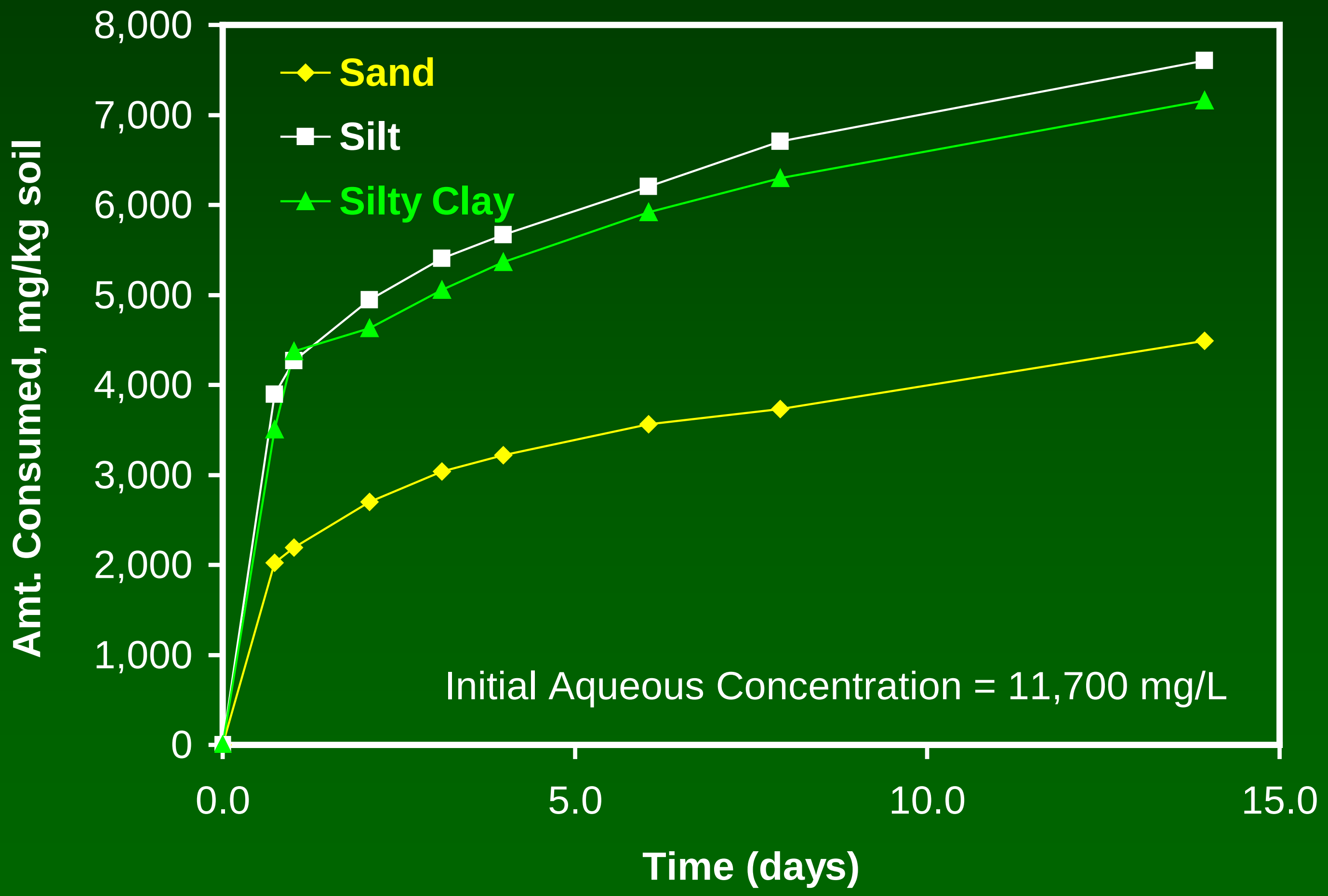


TABLE 2. Rate of $KMnO_4$ Consumption

Soil	Initial Rate (0-1 days), mg/kg/day	Later Rate (1-14 days), mg/kg/day
Sand	2288 ($r^2 = 0.962$)	162 ($r^2 = 0.924$)
Silt	4447 ($r^2 = 0.966$)	244 ($r^2 = 0.932$)
Clay	4419 ($r^2 = 0.994$)	218 ($r^2 = 0.956$)

TABLE 3. Selected Parameters of Site Soils

Material	TOC, mg/kg*	Cr(VI) Reducing Capacity, mg/kg	Total Cr, mg/kg
Sand	239	1,380	93
Silt	690	3,450	92
Clay	587	3,380	86
$KMnO_4$**	n/a	n/a	63

* TOC=Total Organic Carbon; ** EM Science, Guaranteed Reagent

Formation of Cr(VI)

As shown in Table 4, Cr(VI) was formed in batch tests in which site soils were exposed to $KMnO_4$. The amount of Cr(VI) measured was greater than the amount present in the $KMnO_4$, implying that some soil chromium was oxidized.

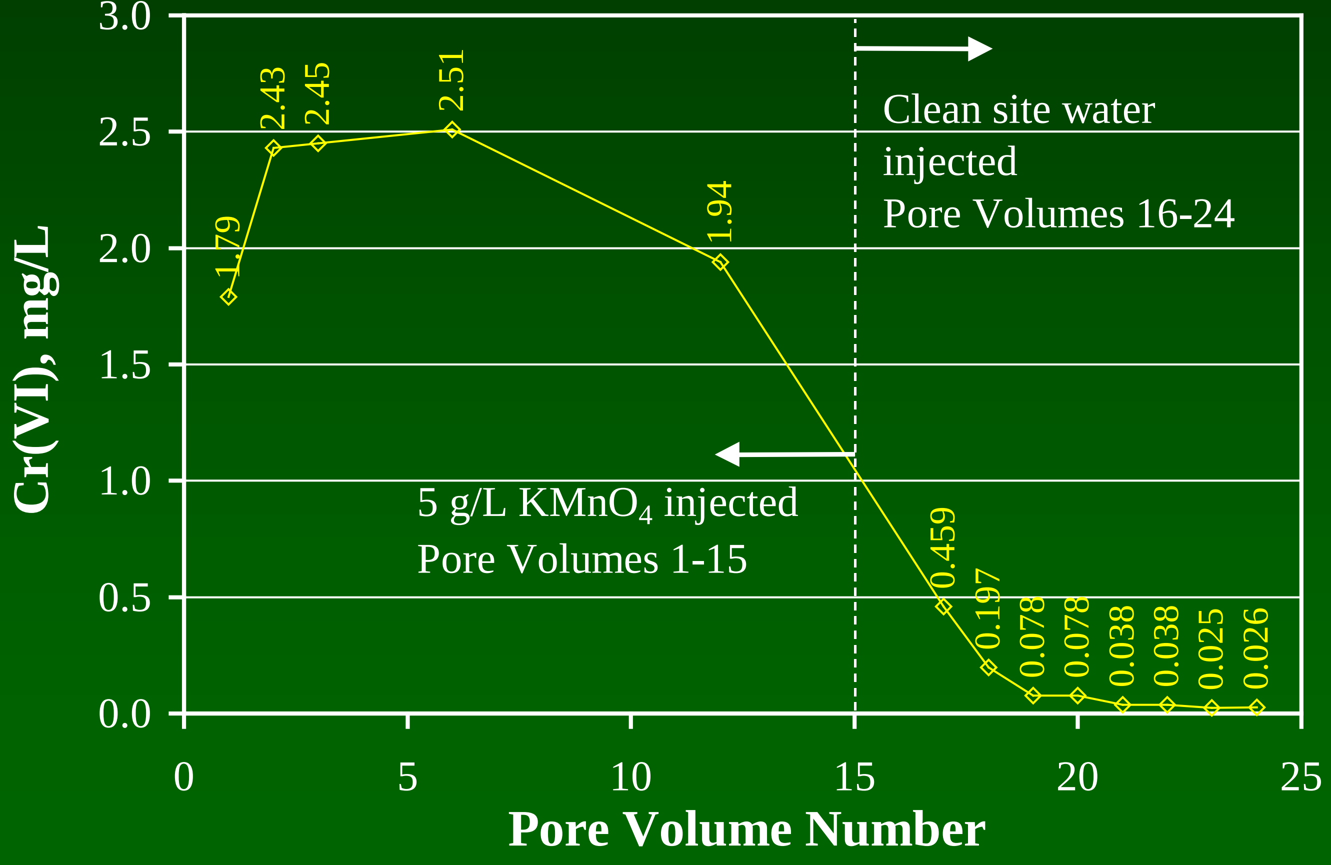
Figure 2 confirms the results of the batch test. Note that Cr(VI) concentration decreased sharply once $KMnO_4$ application ceased.

TABLE 4. Aqueous Cr(VI) in Batch Tests with Soil Exposed to $KMnO_4$.

Soil (g/L $KMnO_4$ added)	Cr(VI), mg/L (colorimetric)	Cr(VI), mg/L (ion chromatrography)
Sand (0.5)	0.81	0.69
Silt (0) Silt (1)	< 0.05 0.84	n.a. n.a.
Clay (0) Clay (1)	< 0.05 0.81	n.a. n.a.

n.a. = not analyzed

FIGURE 2. Cr(VI) in Column Effluent



Fate of Cr(VI)--Addition of Reducing Agents

In a batch test designed to simulate injection of $KMnO_4$ into the subsurface followed by injection of a reducing agent, $KMnO_4$-treated soil was washed with a reducing agent, then clean site water. Soil treated with $FeSO_4$ or ascorbic acid had less Cr(VI) in the aqueous phase than soil treated with clean site water or molasses (Table 6). This indicates that application of a reducing agent after treatment with $KMnO_4$ can hasten the removal of Cr(VI).

TABLE 5. Effect of Reducing Agents on [Cr(VI)]

Cummulative Time (days)	3	4	5	12	13	20
Replicate	Cr(VI), µg/L					
	After KMnO4	After Reductant	After Clean Water			
1-Fe(II)	234	< 10	< 10	< 10	n.a.**	< 10
2-Ascorbic Acid	225	28	< 10	< 10	n.a.	< 10
3-Molasses	242	40	12	< 10	n.a.	< 10
4-Clean Site Water	221	42	13	20	n.a.	< 10
5-None*	240	230	214	81	n.a.	< 10
6-None*	248	n.a.	n.a.	n.a.	155	< 10
7-None*	237	n.a.	n.a.	n.a.	153	< 10
8-None*	240	n.a.	n.a.	n.a.	163	13

* $KMnO_4$ solution not added
** n.a. = not analyzed

Fate of Cr(VI)--Natural Attenuation

In the batch test to assess the effect of reducing agents, some replicates were exposed to $KMnO_4$, but were otherwise untreated. After 13 days, the aqueous Cr(VI) had decreased, suggesting natural attenuation was occurring (Table 5, “None”).

To confirm this, soil was saturated with site water was spiked with Cr(VI). After 7 days, Cr(VI) in the porewater was measured. As shown in Table 6, the concentration decreased by 43%.

TABLE 6. Natural Attenuation

	Cr(VI) in pore water, mg/L
Initial* (Day 0)	**1.2**
Final (Day 7)	**0.68**
% Removed	***43%***

*Clean site water spiked with Cr(VI); used to saturate soil.

CONCLUSIONS

- $KMnO_4$ effectively removed contaminants from site groundwater
- $KMnO_4$ dose is controlled by soil $KMnO_4$ demand
- Soil chromium was oxidized to Cr(VI) upon exposure to $KMnO_4$
- Cr(VI) naturally attenuated in laboratory tests
- Formation and attenuation of Cr(VI) must be considered when evaluating $KMnO_4$ injection