Destruction of TCE DNAPL using KMnO4: Delivery with Direct-push technology and distribution under density driven advection and diffusion *

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A direct push technology for injection of a near-saturated solution of potassium permanganate ($KMnO_4$) to a DNAPL zone at the base of a sandy aquifer was used for a pilot-scale field trial at an industrial site in Connecticut. The $KMnO_4$ solution was delivered to the DNAPL zone inside a sheet pile enclosure using moderate pressures and flow rates. After the injection episode, which had a duration of two days, the $KMnO_4$ solution was allowed to redistribute passively across the DNAPL zone under density-driven advection and diffusion. The movement of the $KMnO_4$ solution was monitored with time, and shown to spread to between 12 and 15 feet from the injection point. The resulting spread was slightly non-radial due to small differences in slope of the aquitard surface. Large chloride concentration increase and large TCE concentration decrease in this near-radial zone were evidence of the effectiveness of the injection episode.

Introduction

Accumulations of dense non-aqueous phase liquids (DNAPLs) on low permeability silt or clay layers at the base of sandy aquifers causes persistent aqueous plumes beneath many industrial sites. Permanent aquifer restoration can only be achieved through removal or in situ destruction of the DNAPL. The use of potassium permanganate ($KMnO_4$) for destruction of chlorinated ethene DNAPLs, such as tetrachloroethylene (PCE) or trichloroethylene (TCE) by oxidation was demonstrated by Schnarr et al. (1998) in batch, column, and field experiments. The key to successful implementation of *in situ* oxidation is the efficient delivery of the chemical solution to the DNAPL zone. Nelson et al. (2000) describe a semi-passive approach for delivery of the $KMnO_4$ solution, which they demonstrated in the shallow sand aquifer at Canadian Forces Base Borden, Ontario. This approach has subsequently been applied in a field trial at an industrial site in Connecticut, where a 30 foot thick medium to fine sand surficial aquifer is underlain by a 70 foot thick silt and clay aquitard. The DNAPL zone is comprised of thin DNAPL layers, from one to a few inches thick within the bottom 3 feet of the aquifer, with nearly all of the DNAPL in the bottom foot. Free-product pumping failed to removed much of the DNAPL, which lead to the $KMnO_4$ trial.

Field Methods

Figure 1a shows the injection set-up and Figures 1b and 1c illustrate conceptually the subsurface $KMnO_4$ distribution with time due to density-drive advection and diffusion. For the pilot-scale test the $KMnO_4$ solution was prepared in a mixing tank located on scaffolding, and then gravity fed to one of two vessels pressurized using nitrogen tanks. A line carried the $KMnO_4$ solution from the pressure vessel to the injection point, which was advanced into the aquifer to the desired injection depth using an EnviroCore direct-push rig. The injection point consisted of a stainless steel wire-wrapped well screen about 2.25 inches long, driven to the target depth of 27.5 feet below ground surface, approximately 2 feet above the aquitard interface. A total of

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4000 L of approximately 40 g/L $KMnO_4$ solution were injected into the aquifer over a two day period.

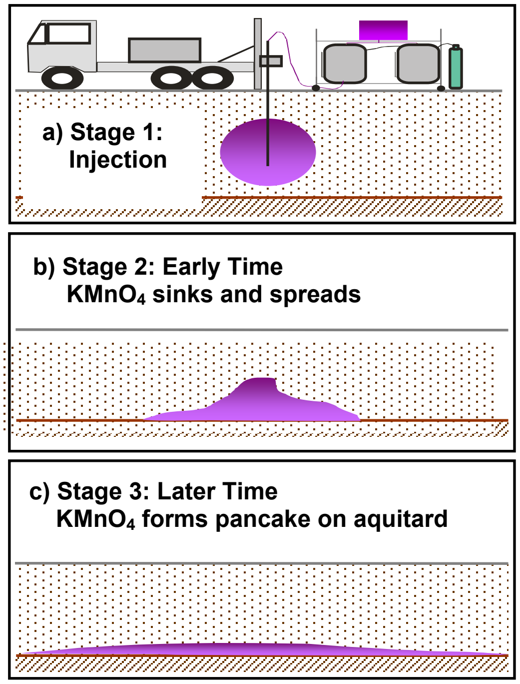

Figure 1: Schematic of KMnO4 injection set-up, and conceptual model of $KMnO_4$ distribution with time caused by density-driven advection.

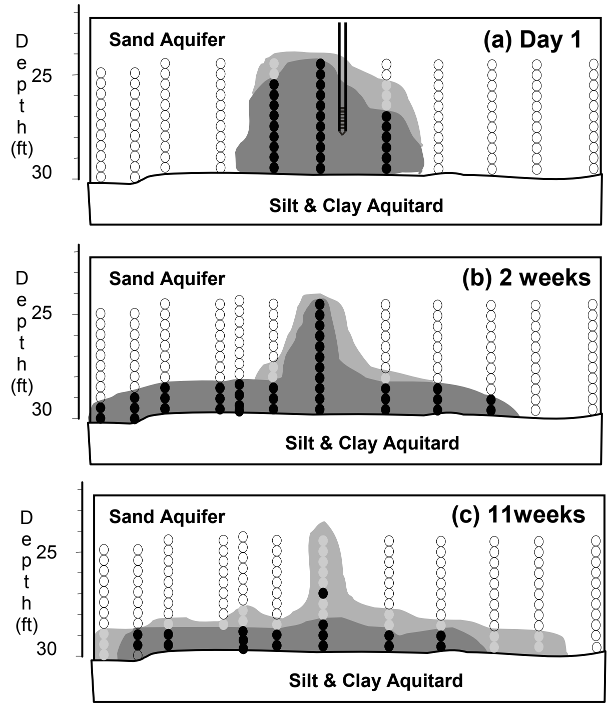

Figure 2: Observed $KMnO_4$ distribution with time. Light and dark shading indicates low and high concentrations of $KMnO_4$, respectively, based on colour with lab confirmation.

A series of multi-level bundle samplers of the type described by Cherry et al. (1983) were installed radially outward from the injection point. The distribution of $KMnO_4$ in the subsurface was monitored during and following injection by sampling these bundles and also by taking cores. The groundwater samples were analyzed for $KMnO_4$, chloride, TCE, and other VOC concentrations. In addition, the geochemical effects of the reaction and fate of manganese and trace metals in this unbuffered aquifer are being studied.

Results and Discussion

Figure 2 illustrates the distribution of $KMnO_4$ at three times during the field trial: the end of the first day of injection, 2 weeks after injection, and 11 weeks after injection. These observations show that the drive-point injection system effectively delivered the $KMnO_4$ solution to the bottom zone of the aquifer where it spread in an elliptical shape to a minimum distance of 12 ft from the injection point and a maximum distance of greater than 15 ft. The elliptical shape is due to slight differences of slope of the top of aquitard. Figures 3 and 4 present contours of chloride and TCE concentrations for pre-injection and 11 weeks post-injection, respectively. The widespread increase in chloride concentration and decrease in TCE concentration are evidence of the effective delivery of the $KMnO_4$ solution to the TCE zone.

Since the $KMnO_4$ injection solution is denser than the natural groundwater, it sank by density-induced advection and spread along the low permeability layers of DNAPL-invaded pores in the sand along the top of the aquitard. Hence, the dense $KMnO_4$ solution naturally seeks out the zones where DNAPL is likely present. The $KMnO_4$ will also diffuse due to it's concentration gradient; therefore, as it is consumed by reaction with TCE diffusion supplies additional $KMnO_4$ to the reaction zone.

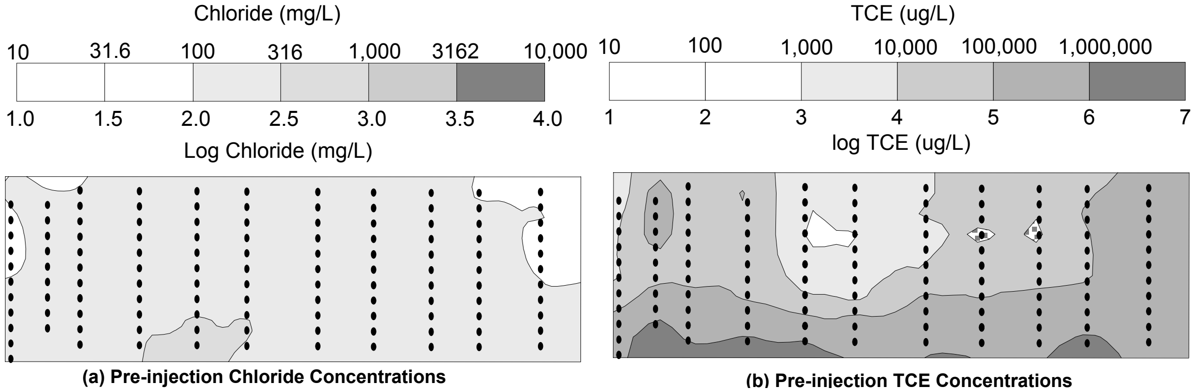

Figure 3: Pre-injection a) Chloride and b) TCE concentrations, showing chloride generally less than 300 mg/L, and TCE concentrations greater than solubility at aquitard interface where DNAPL presence was also confirmed in 50 % of the cores.

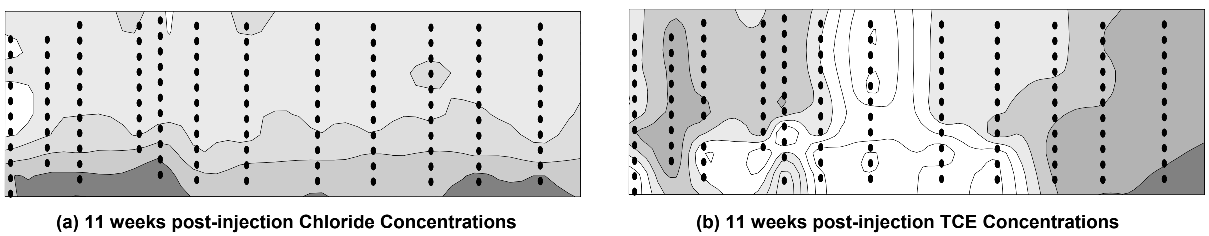

Figure 4: 11-weeks post-injection a) Chloride and b)TCE concentrations, showing increased chloride concentrations to greater than 5000 mg/L at the aquitard interface, and decreased TCE concentrations to less than laboratory detection limit.

Summary of Conclusions

Results of this field trial demonstrate the effectiveness of the inject-and-leave approach for distribution of $KMnO_4$ solution along the DNAPL pool. This approach relies on density-driven advection and diffusion. A single injection of 4,000 litres achieved a $KMnO_4$ spread of 12 to 15 feet after 2 weeks with minimal additional spreading. This was accomplished in a zone where TCE was consuming $KMnO_4$ as it spread across the top of the DNAPL layer. Manganese oxide observed in cores collected 7 weeks after injection and high chloride concentrations (>5,000 mg/L) confirm the large consumption of TCE. Complete TCE destruction was accomplished in local zones, while other thicker DNAPL accumulation zones would require additional loading of $KMnO_4$ solution to achieve complete destruction.

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