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Using slow-release permanganate candles to remove TCE from a low permeable aquifer at a former landfill

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HIGHLIGHTS

- ▶ We developed slow-release permanganate-paraffin candles for field scale use.
- ▶ We compared two methods of inserting the candles into a low permeable aquifer.
- ▶ Laboratory experiments documented candle longevity and radius of influence.
- ▶ A pneumatic circulator was developed to facilitate permanganate distribution.
- ▶ TCE concentrations in field decreased 67–85% in candle treatment zone.

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ABSTRACT

Past disposal of industrial solvents into unregulated landfills is a significant source of groundwater contamination. In 2009, we began investigating a former unregulated landfill with known trichloroethene (TCE) contamination. Our objective was to pinpoint the location of the plume and treat the TCE using in situ chemical oxidation (ISCO). We accomplished this by using electrical resistivity imaging (ERI) to survey the landfill and map the subsurface lithology. We then used the ERI survey maps to guide direct push groundwater sampling. A TCE plume (100–600 $\mu g\ L^{-1}$) was identified in a low permeable silty-clay aquifer ($K_h = 0.5\ m\ d^{-1}$) that was within 6 m of ground surface. To treat the TCE, we manufactured slow-release potassium permanganate candles (SRPCs) that were 91.4 cm long and either 5.1 cm or 7.6 cm in dia. For comparison, we inserted equal masses of SRPCs (7.6-cm versus 5.1-cm dia) into the low permeable aquifer in staggered rows that intersected the TCE plume. The 5.1-cm dia candles were inserted using direct push rods while the 7.6-cm SRPCs were placed in 10 permanent wells. Pneumatic circulators that emitted small air bubbles were placed below the 7.6-cm SRPCs in the second year. Results 15 months after installation showed significant TCE reductions in the 7.6-cm candle treatment zone (67–85%) and between 10% and 66% decrease in wells impacted by the direct push candles. These results support using slow-release permanganate candles as a means of treating chlorinated solvents in low permeable aquifers.

1. Introduction

The disposal of solid waste into unregulated landfills has resulted in numerous examples of groundwater contamination throughout the United States. Although federal regulations have been enacted to promote safe disposal of nonhazardous waste (e.g., Federal Resource Conservation and Recovery Act, Subtitle D), not all landfills have been in compliance. For example, from 1972 through 1991, small communities in the state of Nebraska with populations of 5000 or less were exempt from solid waste rules and regulations (NDEQ, 1990). These small landfills were not required to have liners, conduct groundwater monitoring, or take appropriate steps to prevent the disposal of industrial solvents. Although this original exemption was intended to limit the financial burden on small communities, the consequences of not requiring preventative actions have resulted in widespread groundwater contamination. In 1990, Nebraska had 294 unregulated landfills, of which, 135 were identified as having groundwater concerns (Woldt et al., 1998). While many of these solid waste disposal facilities have since closed, several local communities are now strapped with the financial costs of removing industrial solvents such as tetrachloroethene, trichloroethene, and 1,1,1-trichloroethane from their groundwater.

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During the past decade, significant efforts have been devoted to developing innovative remedial technologies to treat contaminants at the source. One technology that is relatively mature is the injection of liquid oxidants into contaminated aquifers or in situ chemical oxidation (ISCO) (Watts and Teel 2006). Permanganate is widely accepted as an efficient oxidant for ISCO applications and is extremely efficient in oxidizing chlorinated ethenes to CO_2 (Yan and Schwartz, 1999; Yan and Schwartz, 2000). While the chemistry is sound, the application and delivery of permanganate to the contaminants is still a challenge at many sites. Most ISCO treatments to date have involved injecting oxidants into aquifers as liquids. A common problem with any chemical injection however, is that certain sites have finer textured soils that do not readily accept liquid injections. When this occurs, the chemical oxidant can be observed coming back out of the injection borehole because it offers the path of least resistance. Difficulty in addressing contamination in low permeable soils may be alleviated to some degree by taking a passive approach where a controlled-release oxidant is inserted into the formation and allowed to dissolve and intercept the contaminant over many years.

The idea of encapsulating permanganate for sustained release was first proposed several years ago (Kang et al., 2004; Ross et al., 2005; Schwartz, 2005; Swearingen and Swearingen, 2008) and since then, a number of publications have documented the efficacy of slow-release oxidant dispersal systems to remove chlorinated solvents at the laboratory-scale and in larger flow-tank systems (Lee and Schwartz, 2007a,b; Lee et al., 2008a,b; Lee et al., 2009). Although excellent results have been reported, examples of field-scale applications by practitioners have been limited, in part because commercial sources of slow-release oxidants have not been readily available.

In 2009, we began investigating a former unregulated landfill with known TCE contamination. Our objective was to pinpoint the location of the plume and implement an ISCO remedial strategy. This was accomplished by using a geophysical approach, which characterized the lithology of the landfill and guided groundwater sampling. Because TCE was found to be located in a low permeable aquifer, we hypothesized that using slow-release permanganate candles would be effective at reducing TCE concentrations in the contaminated aquifer. This paper reports the manufacturing and deployment of slow-release permanganate candles (SRPCs) and provides results from both laboratory and field testing aimed at demonstrating the release rates and radius of influence of the SRPCs as well as their efficacy in reducing TCE concentrations.

2. Materials and methods

2.1. Site history and characterization

The former Cozad Solid Waste Disposal Facility is a small community landfill in western Nebraska (Cozad, NE) that operated for 20 yr. During this time, unknown quantities of TCE were deposited into the landfill from residential, commercial, and industrial sources. The facility was closed in 1989 after TCE was detected in monitoring wells located down-gradient from the refuse cells at concentrations above the USEPA's Maximum Contaminant Level (MCL). Remedial attempts to date have included a dual phase extraction facility, poplar tree plantings to induce phytoremediation, and volatilization ponds. Despite these efforts, TCE contamination remains and the migrating plume has not been contained.

To characterize the landfill and identify the location of the plume, several spatial measurements were made. These included: electrical resistivity imaging (ERI, Fig. 1), direct push electrical conductivity logging, hydraulic conductivity measurements and the measurement of soil texture, soil oxidant demand and groundwater chemistry. Details of these measurements along with chemical standards, and analytical instruments used are provided in supplementary material (in Supplementary Material (SM) SM Section 1.1–1.6, Fig. SM-1).

2.2. Slow-release permanganate candle production

A drying oven (Fisher Scientific-Isotemp Oven 630F), hot plate (Fisher Scientific-Isotemp Hot Plate 11-100-49SH), 6-quart electric skillet and a 2-quart ceramic cooker were preheated to 93 ± 5 °C. Straight solid paraffin wax (Peak Candle Supply-IGI 1343A) was placed into an electric skillet until melted and subsequently transferred to the ceramic cooker to be kept melted and ready for use. Approximately 600 g of $KMnO_4$ (Carus Corp-RemOxS) were put into glass mason jars and placed into a drying oven to preheat (93 °C) for at least 15–20 min. 250 mL of melted wax was added to an aluminum wax pouring pot and placed on the hot plate. A stand-alone mixer with propeller blade was inserted into the wax, and 600 g of preheated $KMnO_4$ were quickly added to the melted wax. The mixture was stirred at approximately 2000 rpm until all $KMnO_4$ particles were blended with the wax. Additional melted wax and/or $KMnO_4$ was added to the mixture to achieve a mixture with a milkshake like consistency that was just barely pourable. The final ratio by mass of $KMnO_4$ to paraffin was on average 4.6:1 (w/w). Additional text discussing how the 4.6:1 ratio was chosen is provided in supplementary material (in SM Section 1.7). If the mixture cooled too quickly it was briefly placed back into the drying oven to reheat to 93 ± 5 °C. The mixture was then poured into a 7.6 cm (3 in.) or 5.1 cm (2 in.) by 91.4 cm (36 in.) stock cardboard tube (Yazoo Mills) with a poly tube plug inserted at the bottom. The cardboard tube was gently tamped to remove trapped air bubbles. Once filled, the candle was set aside to cool vertically at room temperature for at least 12 h. Material costs (US$) per candle (91.4 cm long) were approximately $18 (5.1-cm dia) and $40 (7.6-cm dia).

2.3. Laboratory testing of SRPCs

To quantify permanganate release rates and radius of influence, laboratory experiments were conducted with 1.27 cm lengths of the 5.1 and 7.6-cm dia (disc-SRPCs) as well as with miniature candles (mini-SRPCs). The 5.1 and 7.6-cm disc-SRPCs were sealed on the flat top and bottom with a layer of pure wax to ensure diffusion was in the radial direction only, so results could be scaled to any candle length. The miniature candles were prepared in a similar manner to ones used in the field trial but were cast in 0.71-cm dia molds, 2.38 cm in length.

For the mini-SRPCs, we placed individual mini-candles into clear glass jars with 200 mL of deionized water. Sample temperature was maintained at 15 °C and room temperature in two separate experiments. Immediately prior to sampling, the solutions were gently swirled to mix. The solution was sub-sampled via pipette every 10 min for the first hour, hourly for the first 4 h, and approximately daily for the remainder of the experiment. Similarly, the disc-SRPCs were placed in 12.5 L of room temperature deionized water and sub-sampled in the same manner as above with the exception that samples were stirred to mix prior to sampling and collected weekly after the first 10 weeks. Samples were diluted when necessary, and analyzed on a Hach DR 2800 Visual Spectrum Spectrophotometer at 525 nm.

To characterize SRPC performance, we determined temporal $KMnO_4$ release rates (Flux, J) and concentration ratio (C_r). Flux was calculated using the following equation.

$$J = \frac{1}{A_{SRPC}} \frac{(C_{n+1}V - C_nV)}{(t_{n+1} - t_n)} \qquad (1)$$