Published in final edited form as:

J Contam Hydrol. 2010 September 20; 117(1-4): 82–93. doi:10.1016/j.jconhyd.2010.07.002.

IN SITU OXIDATION AND ASSOCIATED MASS-FLUX-REDUCTION/MASS-REMOVAL BEHAVIOR FOR SYSTEMS WITH ORGANIC LIQUID LOCATED IN LOWER-PERMEABILITY SEDIMENTS

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Abstract

The effectiveness of permanganate for *in situ* chemical oxidation of organic liquid (trichloroethene) trapped in lower-permeability (K) zones located within a higher-permeability matrix was examined in a series of flow-cell experiments. The permanganate solution was applied in both continuous and pulsed-injection modes. Manganese-oxide precipitation, as confirmed by use of SEM-EDS, occurred within, adjacent to, and downgradient of the lower-K zones, reflective of trichloroethene oxidation. During flow interruptions, precipitate formed within the surrounding higher-permeability matrix, indicating diffusive flux of aqueous-phase trichloroethene from the lower-K zones. The impact of permanganate treatment on mass flux behavior was examined by conducting water floods after permanganate injection. The results were compared to those of water-flood control experiments. The amount of water flushing required for complete contaminant mass removal was reduced for all permanganate treatments for which complete removal was characterized. However, the nature of the mass-flux-reduction/mass-removal relationship observed during water flooding varied as a function of the specific permanganate treatment.

Keywords

chlorinated solvent; heterogeneity; permanganate; ISCO; nonaqueous phase liquid

1. INTRODUCTION

The presence of organic immiscible liquid in the subsurface is generally considered the primary constraint for characterization, risk assessment, and remediation of organic-contaminated sites, and can greatly impact the costs and time required for site remediation (e.g., NRC, 1994; NRC, 2004). Thus, there is great interest in remediation methods that can be used to achieve enhanced mass removal or *in situ* mass reduction for organic-liquid source zones. In-situ chemical oxidation (ISCO) using permanganate is one such method

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that has received significant interest over the past several years. Recent reviews of ISCO application to subsurface remediation discuss some of the issues associated with this method (e.g., Seol et al., 2003; Soga et al., 2004; Oostrom et al., 2006).

Schroth et al. (2001) evaluated the impact of permanganate-TCE oxidation reaction products on aqueous-phase relative permeability for homogeneous porous-medium systems, and observed declines in permeability of up to 96%. Several researchers have observed by-pass flow effects attributed to oxidation reaction products (e.g., Urynowicz and Siegrist, 2000; Reitsma and Marshall, 2000; Schroth et al., 2001; Conrad et al., 2002; MacKinnon and Thomson, 2002; Li and Schwartz, 2004a; Li and Schwartz, 2004c; Heiderscheidt et al., 2008). For example, Conrad et al. (2002) conducted flow-cell experiments to examine permanganate treatment of organic-liquid contamination in a heterogeneous system in which the organic liquid occurred primarily in higher-permeability media. They observed manganese oxide formation that appeared to encapsulate the organic liquid, which limited the effectiveness of ISCO treatment but did not eliminate organic-liquid dissolution or resultant aqueous-phase contamination. Heiderscheidt et al. (2008) conducted a flow-cell experiment wherein units of higher-permeability media contaminated with differing amounts of organic liquid were emplaced within a lower-permeability matrix. A substantial reduction in contaminant mass transfer was observed for a zone with high organic liquid saturation (pool), which was attributed to increased by-pass flow due to a decrease in permeability caused by manganese-oxide formation at the perimeter. Conversely, increased mass transfer was observed for a mixed pool/residual source zone, which was attributed to precipitate-induced permeability reductions in the residual-saturation region and a concomitant increase in flow through the pool region.

The distribution of organic liquid in subsurface environments is typically very nonuniform, and is affected greatly by porous-media heterogeneity. Under certain conditions, organic liquid may become entrapped in lower-permeability (lower-K) zones. For example, trapping of organic liquid in lower-K zones can occur in variably saturated aquifers with changes in water table elevations (Illangasekare et al., 1995a, 1995b; Oostrom et al., 2003). A review of the literature indicates that there has been minimal examination of the efficacy of permanganate treatment for the specific scenario of organic liquids trapped within lower-K zones. This scenario is likely to pose the greatest challenge to hydraulic-based remediation efforts due to poor accessibility of the organic liquid (e.g., Brusseau et al., 2000; 2008; Soga et al., 2004; SERDP, 2006).

The contaminant mass flux or mass discharge emanating from a source zone, also referred to as the source strength or source function, is recognized as a primary determinant of the risk associated with a contaminated site. Thus, the reduction in mass flux achieved with a specific level of source-zone mass removal (or mass depletion) is a key metric for evaluating the effectiveness of a source-zone remediation effort employing methods such as ISCO. The mass reduction associated with permanganate treatment would be expected to lead to a reduction in mass flux. A critical question is to what extent. In addition, the alteration of permeability associated with reaction product formation during ISCO applications observed in several studies (e.g., Reitsma and Marshall, 2000; Schroth et al., 2001; Heiderscheidt et al., 2008) may affect the mass flux and mass removal behavior. For example, the results of a recent multi-year field trial of permanganate-based oxidation for a creosote-contaminated site showed an initial (1–2 years post injection) decrease in mass discharge, followed by longer-term (4 years post injection) rebound in mass discharge up to or above preinjection levels (Thomson et al., 2008). As noted (Soga et al., 2004), minimal effort to date has been devoted to specifically examining mass flux reduction and mass removal behavior associated with ISCO treatment of organic liquid in heterogeneous porous media.

The purpose of this research was to investigate the effectiveness of permanganate treatment and the resultant mass-flux reduction/mass-removal behavior for systems in which organic liquid is trapped within lower-K zones. Flow cells that contained trichloroethene-contaminated lower-K zones surrounded by a coarser matrix were treated with permanganate solutions to investigate the ability of permanganate to oxidize entrapped organic liquid. The flow cells were subsequently flushed with water to evaluate mass-flux behavior. The impact of permanganate treatment on mass-flux reduction/mass-removal was evaluated by comparison to the results obtained from water-flooding experiments.

2. MATERIALS AND METHODS

2.1. Materials

One set of experiments was conducted with a rectangular flow cell constructed of 1.78 cm thick Type 304 stainless steel, with inner dimensions of 39.5 cm long by 20.2 cm high by 5.6 cm wide. Series 1100 0.1 cm thick stainless steel porous plates (Mott Corporation) with 0.22 μm pore diameter were welded into both ends of the flow cell. Four evenly spaced connectors (Swagelock, SS-200-7-2) were welded at both ends to serve as inlet and outlet ports. A tempered glass plate (Romanoski Glass, Tucson, AZ) was attached to the flow cell with 7.62 cm C-clamps (Wilton 540A-3). A 0.64 cm wide by 0.24 cm thick expanded-PTFE joint sealant (John Crane, Morton Grove, IL) was placed between the glass plate and the flow cell flange to prevent leaks. All tubing was stainless steel (Alltech), either 1.02 mm or 2.16 mm inner diameter. A schematic of the rectangular flow cell is shown in Figure 1a.

Another set of experiments was conducted with a stainless steel cylindrical flow cell, 7.6 cm in diameter and 9.8 cm in length (MODcol, St. Louis, MO). Media were supported at both ends by stainless steel porous frits and bed support frits. Stainless steel tubing (Alltech) was used throughout and was either 1.02 mm or 2.16 mm inner diameter. A schematic of the cylindrical flow cell is shown in Figure 1b.

The porous media used in the experiments are commercially available, natural silica sands (Unimin Corporation, Le Sueur, MN) selected for their low oxidant demand typical for sedimentary aquifer systems (e.g., Marble, 2006; Xu and Thomson, 2008). Three media with different mean particle diameters were used, 724 μm (20–30 mesh), 360 μm (40–50 mesh), and 172 μm (70–100 mesh) with an organic carbon content of approximately 0.04% (Schroth et al., 1996; Yolcubal et al., 2002). Representative hydraulic conductivities, as well as other properties, for the three media are presented in Table 1. The 724 μm sand was used as the flow-cell matrix for all experiments, and the two finer media comprised the lower-K zones for the experiments employing physically heterogeneous systems.

Distilled-deionized (NANOpure Series 550, Barnstead Thermolyne Corp., Dubuque, Indiana) water was used for the aqueous dissolution (water flooding) and miscible-displacement experiments. Two concentrations: 15 mM (2370 mg/L) or 63.3 mM (10003 mg/L) of permanganate solutions were prepared with ACS reagent grade KMnO_4 (Aldrich Chemical Co., Inc., Milwaukee, WI) in NANOpure water. These concentrations were selected to represent a lower to higher range of oxidant applications to evaluate the associated impact on mass-flux-reduction/mass-removal behavior. A 1 M sodium thiosulfate pentahydrate solution was used (Aldrich Chemical Co., Inc., Milwaukee, WI) to quench the effluent samples (Hood et al., 2000). Trichloroethene (TCE) was ACS grade (Aldrich Chemical Co., Inc., Milwaukee, WI), and was dyed with certified Sudan IV (Aldrich Chemical Co., Inc., Milwaukee, WI) at a concentration of 100 mg/L. Dichloromethane used in extractions was ACS/HPLC certified solvent (Burdick and Jackson, Muskegon, MI).

2.2. Design

A summary for each of the experiments described herein is presented in Table 2. The rectangular flow cell experiments were conducted to visualize the impact of ISCO on the heterogeneous permeability field and examine the initial impact on mass-flux-reduction versus mass-removal behavior. The cylindrical flow cell experiments were conducted to examine mass-removal and mass-flux-reduction behavior for conditions of complete mass removal.

The flow-cell systems were designed to represent, in an idealized manner, source zones that have undergone an extensive degree of natural dissolution associated with groundwater flow (i.e. aged systems), such that the organic liquid remaining is primarily the fraction that is poorly accessible to groundwater flow. As mentioned previously, there are conditions under which organic liquid may become entrapped in lower-K zones (e.g., Illangasekare et al., 1995a; Oostrom et al., 2003; Brusseau et al., 2008). The systems were designed to represent such a scenario.

2.3. Rectangular Flow Cell Experiments

The rectangular flow cell was packed with dry sand to a consistent porosity (1% standard error) and connected to a single-piston HPLC pump (Gilson model 305) prior to saturating with water in the upward direction. Attainment of saturation was assumed upon achieving constant mass. Stainless-steel forms (2.5 cm wide and 16 cm long) were used to allow packing of different media into zones 1 and 2 for the experiments with permeability heterogeneity (Figure 1a, Table 2). The organic liquid was mixed with damp media prior to packing within the forms. Subsamples were collected during packing for solvent extraction analysis to determine initial TCE saturation (Table 2). TCE-saturated water was added to the stainless-steel forms to saturate the zones, the forms were removed, and the glass plate was reattached in a manner preventing air entrapment or creation of preferential flow along the glass plate. The absence of artifacts due to the packing was confirmed by results of dye tracer tests and examination of the media upon excavation. The water flood or permanganate treatment was then initiated. The mean pore-water velocity for the experiments was approximately 4 cm/h (Table 2). This velocity was selected to represent induced-gradient conditions associated with hydraulic-based remediation methods. The pore volume for this system was approximately 1630 mL.

An initial permanganate-injection experiment was conducted to specifically evaluate precipitate formation. The permanganate solution (15 mM) was injected continuously for this experiment. After the experiment, sediment samples were collected for scanning electron microscope (SEM) analysis to evaluate the occurrence and spatial distribution of manganese oxide reaction products. This was done using a Hitachi S-2460N with an energy dispersive X-ray spectroscopy (EDS) detector. The second permanganate-injection experiment consisted of a series of three 15 mM permanganate solution pulses totaling 4.5 pore volumes (1.1, 0.9, and 2.5 pore volumes). There was no flow for 12 days between pulse 1 and 2, 21 days between pulse 2 and 3, and 6 days between pulse 3 and the water flood. These flow interruptions were employed to potentially enhance permanganate utilization by promoting diffusion of permanganate into (and TCE out of) the low-K zones. The final permanganate solution injection was followed by a water flood of 37 pore volumes. Effluent discharge rates were measured, and effluent samples were collected for chemical analysis. A control experiment consisting of a continuous water flood was conducted to characterize TCE dissolution and mass flux without permanganate treatment. Sediment samples were collected after each experiment to determine remaining TCE mass (described below).

2.4. Cylindrical Flow Cell Experiments

Experiments for the cylindrical flow cell were conducted similarly to the rectangular flow cell system. The cylindrical flow cell was wet-packed (2% porosity standard error) with an initial 20% moisture content. A form was used while packing to create the low-K zone (Figure 1b), which was done using sand premixed as above with TCE. Subsamples were collected during packing and subjected to solvent extraction to determine initial saturations (Table 2). The mean pore-water velocity for these experiments was approximately 20 cm/h. This velocity was set to be five times the velocity of the previously described experiments to evaluate the impact of decreased residence time on diffusive mass transfer and TCE oxidation. The pore volume for this system was approximately 150 mL.

The first permanganate-injection experiment consisted of a single, one pore-volume injection of 63.3 mM solution, followed by a no-flow period of five days, and then a period of water flooding. The second experiment was conducted similarly, except that 4.2 pore volumes of 63.3 mM solution was injected in four approximately equal pulses with flow interruptions of three, three, five, and six days prior to the water flooding. In addition to the permanganate experiments, a continuous water-flood experiment was conducted as above to serve as a control.

Additionally, two water-flood column experiments were conducted with uniform distributions of organic liquid to evaluate the impact of initial TCE saturation on mass-flux-reduction/mass-removal behavior. The column experiments were conducted with stainless-steel columns (7 cm in length) packed with the 724 μm sand. Initial organic-liquid saturations of 3 and 12% were established as described above for the flow cells. These initial saturations were selected to approximate the initial conditions of the water-flood components of the flow-cell experiments with and without permanganate treatment, respectively.

2.5. Sample Analysis

Flow-cell effluent samples were collected with a 1 mL glass syringe and injected into a 20 mL autosampler glass vial with 4 mL of 1M sodium thiosulfate pentahydrate solution for permanganate injection experiments. The samples were analyzed using a gas chromatograph (Shimadzu GC 17A) with either an electron capture detector (ECD) or flame ionization detector (FID) and a Tekmar 7000 headspace autosampler. High concentration samples were also analyzed with a Shimadzu UV-VI Model 1501 spectrophotometer. Standards prepared in NANOpure water and sodium thiosulfate pentahydrate solutions depending on the experiment were used for linear standard curve quantification (0.998 or better r^2), estimated analytical error varied from 0.2 to 5%, and the TCE quantifiable method detection limit was approximately 1 mg L^{-1} , 0.05 mg L^{-1} , and $0.5 \mu\text{g L}^{-1}$ for UV, FID, and ECD, respectively.

During preparation and upon completion of each experiment, subsamples of the porous media were collected for solvent extraction using dichloromethane. Subsamples (ranging from 5 to 10 grams) of the porous media were collected with open-ended syringes and immediately placed into vials containing known masses of solvent, and porous media masses were determined gravimetrically after analysis. Typically, five samples were collected from each zone. The typical combined sampling and analysis standard error based on replicate variability ranged from 1 to 13%. Aliquots of the extractant were analyzed for TCE using GC-FID (with a quantifiable detection limit of 1.3 mg/L). Organic-liquid saturation (S_n) values were calculated from the solvent extraction data (Table 2), and were used along with effluent monitoring data for mass balance analysis.

2.6. Mass-transfer and mass-flux reduction analyses

The water flood and post-ISCO water flood results obtained for each of the flow cell experiments were evaluated based on mass-flux reduction/mass-removal analysis. Fractional mass removal (MR) was defined as the mass removed relative to the initial contaminant mass, and it is typically compared to fractional mass-flux reduction (MFR) as defined as:

$$MFR = 1 - \frac{J_f}{J_i} = 1 - \frac{Q_f C_f}{Q_i C_i} \quad (1)$$

where J is the mass flux, Q is the volumetric flow rate, C is aqueous concentration, and the subscripts i and f indicate initial and final times, respectively. The evaluation focused on comparisons of mass flux and mass removal during water flooding with or without prior ISCO treatment. The initial TCE mass values for the water flooding portion of the experiments were calculated using mass recoveries determined from effluent concentration data and post-experiment solvent extraction results.

3. RESULTS AND DISCUSSION

3.1. Permanganate Transport and Oxidation-Reaction Product Formation

The first experiment conducted with the rectangular flow cell comprised continuous injection of 4.5 pore volumes of a 15 mM permanganate solution. The permanganate solution exhibited plug flow until reaching the lower-K zones, at which point the solution bypassed the lower-K zones and continued to move downgradient toward the outlet of the flow cell. A time series of photographic images of one of the lower-K zones and surrounding higher-K matrix during permanganate solution injection is presented in Figure 2. Brown manganese oxide precipitates initially formed at the interface between the surrounding media and the lower-K zones, except at the downgradient end. Conrad et al. (2002) also observed the formation of manganese oxide precipitate adjacent to zones of high saturation of organic liquid. In addition, gas bubbles, presumed to be carbon dioxide, formed at the interfaces. “Shadow” zones within the higher-K matrix into which the permanganate solution did not enter were observed downgradient of both lower-K zones (Figure 3), and were attributed to by-pass flow effects. Precipitates formed at the top and bottom edges of the shadow zones, forming tails. The precipitate-affected zones increased in thickness during the experiment, indicating continued flux of aqueous TCE from the lower-K zones into the higher-K matrix. Similar behavior was also observed in experiments conducted by Reitsma and Marshall (2000).

Following completion of the permanganate treatment, subsamples were collected to determine remaining TCE mass and for SEM analysis. SEM photomicrographs of samples collected from the matrix and from the center of the lower-K zones indicate precipitates did not form at those locations during the treatment (Figure 4a). In addition, solid-phase manganese was not detected with the EDS analysis. Conversely, the samples collected from the interface between the matrix and lower-K zones had noticeable precipitates, which were observed to have a fibrous and semi-amorphous crystalline structure that formed as a coating on the surface of the sand grains (Figure 4b). Previous researchers have used X-Ray diffraction to determine that the precipitate typically formed is potassium-rich birnessite (Li and Schwartz, 2004b). The EDS analysis of the precipitates described herein revealed the presence of manganese, chlorine, and potassium in addition to the quartz sand components (silica and oxygen), indicating that chlorine and potassium by-products of TCE oxidation were being incorporated (e.g., coprecipitation) into the manganese oxide crystal structure.

The second experiment conducted with the rectangular flow cell consisted of a series of three pulses totaling ~4.5 pore volumes, with periods of no flow between the pulses. The transport behavior observed during the first pulse was similar to that of the constant-injection experiment wherein the permanganate solution exhibited plug flow until coming into contact with the lower-K zones, which were bypassed, causing shadow zones to form downgradient of both lower-K zones. During the no-flow periods, permanganate solution diffused into the shadow zones. In addition, pore water in the matrix changed from purple to clear, and precipitation occurred in the matrix surrounding both lower-K zones. This indicates that TCE was diffusing from the lower-K zones and reacting with permanganate during the flow interrupts. At the completion of the permanganate treatment, 54% of the area comprising lower-K zone 2 contained noticeable precipitates compared to 21% for lower-K zone 1. Differences in the extent of precipitate formation likely reflect the differences in advective penetration of the zones by the permanganate solution (Figure 5), consistent with the permeability differences between the two media comprising the zones.

The formation of brown manganese-oxide precipitates and gas bubbles was also observed during the cylindrical flow cell experiments. Two permanganate-injection experiments were conducted with the cylindrical system, both employing a 63.3 mM permanganate solution. One experiment comprised a continuous injection of 1 pore volume of permanganate solution, and the other comprised four equal-volume injections (total of 4.2 pore volumes of solution) alternated with flow interruptions. For the continuous-injection experiment, manganese-oxide precipitate was observed in the matrix but not in the lower-K zone. Precipitate formation was more extensive for the pulsed-injection experiment compared to the continuous-injection experiment, consistent with the greater volume of permanganate solution injected. In addition, a significant amount of precipitate was observed within the lower-K zone. This indicates that permanganate diffused into the lower-K zone during the flow-interruption periods. Diffusive mass transfer of permanganate into lower-K zones has been observed in a prior study (Struse et al., 2002).

3.2. Mass Removal and Mass Flux

Loss of TCE mass from the lower-K source zones during the experiments occurred first by permanganate-induced oxidation and then by dissolution and associated mass flux during the subsequent water flood. Concentration data from solvent extraction and effluent samples were used to determine mass removed due to dissolution and subsequent transport and elution. Mass loss due to transformation was calculated by mass balance (Table 2). For the pulsed permanganate-injection experiment conducted with the rectangular flow cell, 3.1(±0.4) grams of TCE were eluted during the permanganate injection and 26.3(±2.6) grams were eluted during the subsequent water flood, for a total of 29.4(±3) grams. The mass of TCE remaining at experiment completion was determined to be 6.7(±0.9) grams. A total of 5.7(±0.7) grams of TCE was calculated to have been oxidized by permanganate, which is approximately 14% of the initial TCE mass. Approximately 13.7(±1.8) grams of permanganate would be required for oxidation of this quantity of TCE, which is approximately 80% of the total amount injected. This value is somewhat uncertain given the uncertainties in determining mass remaining.

As noted above, the permanganate injection caused a reduction in TCE mass. A question of interest is what impact, if any, did this mass reduction have on post-treatment effluent concentrations and associated mass flux. After the multiple permanganate pulses, water was flushed through the flow cell for an additional 37 pore volumes to characterize mass flux following the permanganate treatment. TCE effluent concentration data exhibit an initial increase to 750 mg/L (Figure 6), which was attributed to the concentration rebound during the flow interruption period. The concentration gradually decreased to 290 mg/L by the end of the water flood. TCE effluent concentrations were 230 mg/L after 40 pore volumes for

the water-flood (aqueous dissolution) control experiment. The relatively small observed difference in concentrations for the two experiments may reflect experiment variability, or may be associated with the impact of permanganate treatment on subsequent water flow and organic-liquid dissolution, as observed by Heiderscheidt et al. (2008). The similarity of effluent TCE concentrations observed during the control and permanganate experiments suggests that manganese oxide precipitates did not significantly inhibit mass transfer from the lower-K zones.

The similarity in mass fluxes observed for the experiments discussed above indicates that the permanganate treatment did not significantly impact post-treatment mass flux. However, the fraction of mass reduction associated with permanganate treatment was relatively small. As noted above, the cylindrical flow cell experiments were conducted to examine mass-removal and mass-flux-reduction behavior for conditions of complete mass removal. The results are presented in Figure 7.

For the water-flood experiment, the effluent concentration dropped quickly and then remained steady for an extended period. A steady-state phase was also observed for the continuous permanganate-injection experiment. The steady-state concentration of approximately 90 mg/L observed for the experiments is much lower than aqueous solubility, and reflects the impact of dilution given that the TCE-contaminated zone encompassed only a portion of the flow-cell cross section. The steady-state period was shorter for the continuous permanganate-injection experiment as compared to the water-flood control experiment despite nearly identical initial saturations (Table 2), which reflects the impact of mass removal by *in situ* oxidation. In contrast to the prior two experiments, there was no extended period of relatively constant effluent concentrations for the pulsed permanganate-injection experiment, due presumably to permanganate oxidation of the majority of the organic liquid prior to water flooding.

Approximately 140 pore volumes of water flushing were required to decrease effluent concentrations to approximately 0.1 mg/L for the water-flood control experiment. Conversely, 60 pore volumes were required for the continuous permanganate-injection experiment and less than 50 pore volumes for the pulsed permanganate-injection experiment. These results indicate that the permanganate treatment had a significant impact on long-term mass flux, and concomitantly the amount of water flushing required to reach a relatively low aqueous concentration.

3.3. Relationship between Mass Flux Reduction and Mass Removal

Several factors influence the nature of the mass-flux-reduction/mass-removal relationship for a given system. These include the amount of contaminant and its distribution, mass-transfer processes, and flow-field dynamics. Implementation of a source-zone remediation effort may alter mass-flux-reduction/mass-removal behavior. For example, preferential removal of contamination from particular locations or the formation of oxidation reaction products may alter the flow field and modify contaminant accessibility. This was evaluated by conducting water floods after completion of the permanganate injections.

The mass-flux-reduction/mass-removal data for the rectangular flow-cell experiments conducted with and without permanganate treatment are compared in Figure 8a. The TCE saturation was approximately 15% at the start of the water flood conducted for the permanganate experiment, which is similar to the initial saturation of 18% for the water-flood control experiment. An approximately one-to-one relationship between mass flux reduction and mass removal was observed for the water-flood control experiment. This behavior is expected for a system in which a portion of the contamination is poorly accessible (e.g., Fure et al., 2006; Brusseau et al., 2008). In contrast, a minimal reduction in

mass flux was observed until approximately 30% mass removal for the water flood conducted after the permanganate injection. After this point, mass flux decreased at an increasing rate through the end of the experiment. These results suggest that mass-transfer and mass-removal efficiency were greater for the post-permanganate water flood compared to the water-flood control. As noted above, a significant degree of manganese-oxide precipitation occurred in the matrix surrounding the lower-K zones. This precipitate formation may have decreased the effective permeability of the matrix adjacent to the lower-K zones, thus reducing the permeability contrast and concomitantly by-pass flow, thereby leading to a greater degree of flushing (greater hydraulic accessibility) for the source zone.

The mass-flux-reduction/mass-removal data for the experiments conducted with the cylindrical flow cell are presented in Figure 8c. The fraction of mass removed during the permanganate treatments was significantly greater for the two cylindrical flow-cell experiments (65% and 92% for the continuous and pulsed experiments, respectively) compared to that of the rectangular flow-cell experiments. These mass reductions resulted in initial TCE saturations of approximately 3–4% for the post-permanganate water floods, which are significantly smaller than the initial saturation of 12% for the water-flood control experiment. The impact of initial organic-liquid saturation on mass-flux reduction/mass-removal behavior was evaluated with control experiments wherein TCE was uniformly distributed in homogeneously packed columns at initial saturations of 3% and 12%. The data exhibit relatively efficient mass-removal behavior as expected, with significant mass-flux reductions occurring only after the majority of mass has been removed (Figure 8b). Mass flux begins to decrease at a smaller mass-removal fraction for the lower-saturation experiment (~0.5 vs ~0.7), reflecting the impact of reduced initial contaminant mass.

Inspection of Figure 8c shows that the initial mass-flux reduction behavior was relatively similar for the water flood conducted after the continuous permanganate-injection and for the water-flood control experiment, whereas it differed for the water flood conducted after the pulsed-permanganate experiment (the latter experiment will be discussed in a following section). However, a smaller reduction in mass flux was observed for the post-permanganate water flood at larger mass-removal fractions. This latter result suggests that mass-transfer and mass-removal efficiency were greater for the post-permanganate water flood compared to the water-flood control. For the continuous- injection permanganate experiment, manganese-oxide precipitate was observed within the matrix but not within the lower-K zone. Similarly to the results of the rectangular flow-cell experiments discussed above, it is possible that the precipitate reduced the permeability contrast between the matrix and the lower-K source zone, thereby increasing the hydraulic accessibility of the source zone. As noted above, the initial TCE saturation at the start of the water flood was significantly smaller for the permanganate-injection experiment. Thus, the potential impact of lower initial mass on mass-flux-reduction/mass-removal behavior (as illustrated in Figure 8b) appears to have been offset by the greater mass-removal efficiency.

An apparent increase in mass-transfer and mass-removal efficiency has been observed for the post-permanganate water floods compared to the water-flood controls for both the cylindrical and rectangular flow-cell experiments. For both cases, manganese-oxide precipitate formed in the matrix surrounding the lower-K source zones, which is suspected to have influenced the flow field and thus hydraulic accessibility of the contaminant. For the continuous-injection cylindrical flow-cell experiment, one pore volume of permanganate solution was injected in continuous mode, and the concentration of permanganate was four times higher than that used for the rectangular flow-cell experiment. Conversely, 4.5 pore volumes of lower-concentration solution were injected in successive pulses for the rectangular flow-cell experiment. Thus, similar relative amounts of permanganate were introduced for the two experiments. The similarity of overall results suggests that the

injection mode did not have a significant impact on behavior for the conditions and configurations employed.

For the water flood conducted after the pulsed permanganate injection (cylindrical flow-cell experiment), mass flux decreased essentially immediately, in contrast to the water flood conducted after the continuous permanganate injection (Figure 8c). In addition, the reduction in mass flux was significantly greater for essentially the entire water flood. Thus, the mass-flux-reduction/mass-removal behaviors are significantly different for the two permanganate experiments, despite the fact that both experiments had similar initial TCE saturations at the start of their respective water floods. These results indicate that mass transfer and mass removal was more constrained for the water flood conducted after the pulsed-injection experiment compared to the single-injection experiment. The amount of permanganate injected was 4 times greater for the pulsed-injection experiment, and manganese-oxide precipitation was significantly greater (as noted above). In addition, precipitate was observed to have formed inside the lower-K source zone for the pulsed experiment (and not for the continuous experiment), which is hypothesized to have resulted in decreased permeability and hence reduced hydraulic accessibility, thereby constraining mass transfer and mass removal. This is consistent with the observation that the reduction in mass flux for the water flood conducted after the pulsed permanganate injection was greater than that observed for the water-flood control experiment for mass-removal fractions greater than approximately 0.7 (Figure 8c).

4. SUMMARY

A series of flow-cell experiments was conducted to determine the effectiveness of ISCO using permanganate, and the associated impacts on contaminant mass flux, for systems wherein organic-liquid contaminant was located in hydraulically poorly-accessible lower-K zones. Permanganate was able to degrade TCE in the lower-K zones as confirmed by the formation of dissolved gas and manganese-oxide precipitates. The impact of permanganate treatment on long-term mass flux behavior was examined by conducting water floods after permanganate injection. The results were compared to those of water-flood control experiments. The amount of water flushing required for complete contaminant mass removal was reduced for all permanganate treatments for which complete mass removal was evaluated. However, the nature of the mass-flux-reduction/mass-removal relationship observed during water flooding varied as a function of the specific permanganate treatment. The disparity in behavior was attributed to the varied impact of precipitate formation on the flow field and contaminant accessibility. The results presented herein illustrate the impact of ISCO on mass-flux reduction/mass-removal behavior.

Acknowledgments

This research was supported by The National Institute of Environmental Health Sciences Superfund Basic Research Program (ES04940) and by the Strategic Environmental Research and Development Program (SERDP) (Grant Number ER-1614). In addition, the authors wish to thank Asami Murao at the University of Arizona in the Contaminant Transport Group, Larry Acedo at the University of Arizona in the University Research Instrumentation Center, and Gary Chandler at the University of Arizona in the Department of Materials Science and Engineering.

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Figure 1. (b)

Figure 1.

Flow-cell schematics (a) rectangular flow cell with a coarser sand (20/30 mesh; $724 \mu\text{m}$) that comprised the matrix and two finer sands were used to create zones 1 (70/100 mesh; $172 \mu\text{m}$) and 2 (40/50 mesh; $360 \mu\text{m}$); (b) cylindrical flow cell with a coarser sand ($724 \mu\text{m}$) comprised the matrix and a finer sand ($360 \mu\text{m}$) was used to create the zone.

Figure 2. Photographic images cropped to focus on the lower-K zone 2 (40/50 mesh; 360 μm) and surrounding higher-K matrix sand during the constant permanganate injection: (a) 0.01 pore volume, (b) 0.03 pore volume, (c) 0.14 pore volume (d) 1.0 pore volume, and (e) 4.0 pore volumes.

Figure 3. Photographic image of the lower-K zone 2 and surrounding area after permanganate injection, exhibiting the shadow zone downgradient of the lower-K zone, downgradient manganese oxide tails, and manganese oxide formation around the lower-K zone. The white box represents the outline of the source zone.

Figure 4. (a)

Figure 4. (b)

Figure 4. SEM images sand grains: (a) (grain) located in the middle of a low-K zone; (b) grain located at the boundary of a low-K zone. Qualitative elemental analyses of the mineral-surface chemistry collected at locations indicated (circles) on the SEM photomicrographs were obtained using an energy dispersive x-ray spectroscopy detector.

Figure 5. Distances in centimeters measured along rectangular flow cell that manganese oxides formed inside and outside of the lower-K zones during flow interruptions of the pulsed permanganate injection experiment.

Figure 6.

Effluent TCE concentrations from rectangular flow-cell experiments with water flooding only (open symbols) and water flooding after pulsed injection of 4.5 pore volumes (PV) of 15 mM permanganate (ISCO) (closed symbols).

Figure 7. Effluent TCE concentrations for the cylindrical flow-cell experiments with water flooding only (open symbols) vs. water flooding after permanganate treatment (ISCO) (closed symbols) for 1 PV and 4 PV injections of the 63.3 mM solution.

Figure 8.
Fractional mass-flux reduction as a function of fractional mass removal: (a) rectangular flow-cell experiments; (b) column experiments; (c) cylindrical flow-cell experiments.

Table 1

Physical properties of porous media used in the flow cell experiments

Mesh size	20/30	40/50	70/100
d ₅₀ (μm)	724	360	172
Hydraulic conductivity (cm/hr)	464.4	72	7.2
Dry bulk density (g/ml)	1.76	1.74	1.65
Porosity (–)	0.34	0.36	0.38

Table 2

Summary of experimental conditions

Flow Cell	System Description	Matrix Mesh	Zone 1 Mesh (upper)	Zone 2 Mesh (lower)	System Length (cm)	Organic-Liquid Source Length (cm)	Average Pore Velocity (cm/hr)	Initial S_N (-)	Initial Experiment Mass (g)	Initial Water Flood Mass (g)	Fraction Oxidized by $KMnO_4$	Source Zone Treatment
Rectangular	2 lower K zones with organic liquid	20/30	70/100	40/50	40	16	3.5	0.15	32.2	-	0.20	Constant injection of 15mM $KMnO_4$ to 4.9 PV
Rectangular	2 lower K zones with organic liquid	20/30	70/100	40/50	40	16	4.5	0.19	41.8	33.0	0.14	Pulsed injections of 15mM $KMnO_4$ to 4.5 PV followed by water flood
Rectangular	2 lower K zones with organic liquid	20/30	70/100	40/50	40	16	4.0	0.18	38.8	38.8	-	Water flood control experiment
Cylindrical	1 lower K zone with organic liquid	20/30	40/50	-	10	2.5	20	0.11	1.1	0.4	0.65	Constant injection of 63.3 mM $KMnO_4$ to 1 PV followed by water flood
Cylindrical	1 lower K zone with organic liquid	20/30	40/50	-	10	2.5	21	0.17	1.1	0.1	0.92	Pulsed injection of 63.3 mM $KMnO_4$ to 4.2 PV followed by water flood
Cylindrical	1 lower K zone with organic liquid	20/30	40/50	-	10	2.5	20	0.12	1.1	1.1	-	Water flood control experiment
Cylindrical	Uniform organic liquid distribution	20/30	-	-	7	7	21	0.12	1.5	1.5	-	Homogeneous medium/source water flood
Cylindrical	Uniform organic liquid distribution	20/30	-	-	7	7	21	0.03	0.4	0.4	-	Homogeneous medium/source water flood