FINAL REPORT

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Semi-passive, Chemical Oxidation Schemes for the
Long-term Treatment of Contaminants

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TABLE OF CONCENTS

EXECUTIVE SUMMARY AND RESEARCH OBJECTIVES -----	3
METHODS AND RESULTS -----	4
1. Development of controlled release KMnO_4 scheme for remediation of groundwater contaminated by chlorinated ethylenes-----	4
<u>Manufacturing controlled release KMnO_4</u> -----	5
<u>Column and flow-tank experiments</u> -----	5
<u>Release rate measurement</u> -----	8
<u>Mathematical model and simulations</u> -----	9
<u>Efficacy of the controlled release KMnO_4 scheme</u> -----	12
2. Numerical optimization of controlled release system: A custom-made approach for subsurface remediation-----	15
<u>Construction and simulations of the matrix-type controlled release system</u> -----	17
<u>Numerical optimization</u> -----	22
<u>Potential applications and future work</u> -----	24
RELEVANCE, IMPACT AND TECHNOLOGY TRANSFER-----	26
PROJECT PRODUCTIVITY-----	26
PERSONNEL SUPPORTED-----	26
PUBLICATIONS-----	27
INTERACTIONS-----	27
LITERATURE CITED-----	28
APPENDIX-----	29

EXECUTIVE SUMMARY AND RESEARCH OBJECTIVES

This research involves a combined experimental and modeling study that builds on our previous DOE-sponsored work in investigating how KMnO_4 can be better used with *in situ* remediation of groundwater contaminated by chlorinated ethylenes (e.g., PCE, TCE, DCE). This study aims to provide scientific basis for developing a new long-term, semi-passive ISCO scheme that uses controlled release KMnO_4 as a reactive barrier component. Specific objectives of the study are (1) to construct controlled release KMnO_4 as a new reactive barrier component that could deliver permanganate at a controlled rate over long time periods of years, (2) to quantitatively describe release mechanisms associated with the controlled release KMnO_4 , (3) to demonstrate efficacy of the new remediation scheme using proof-of-concept experiments, and (4) to design advanced forms of controlled release systems through numerical optimization.

The new scheme operates in a long-term, semi-passive manner to control spreading of a dissolved contaminant plume with periodic replacement of the controlled release KMnO_4 installed in the subsurface. As a first step in developing this remedial concept, we manufactured various prototype controlled release KMnO_4 forms. Then we demonstrated using column experiments that the controlled release KMnO_4 could deliver small amount of permanganate into flowing water at controlled rates over long time periods of years. An analytical model was also used to estimate the diffusivities and durations of the controlled release KMnO_4 . Finally, proof-of-concept flow-tank experiments were performed to demonstrate the efficacy of the controlled release KMnO_4 scheme in controlling dissolved TCE plume in a long-term, semi-passive manner.

Another important thrust of our research effort involved numerical optimization of controlled release systems. This study used a numerical model that is capable of describing release patterns of active agent from controlled release systems of varied forms and applications. We manufactured prototype single- and double-layered matrix-type controlled release systems and tested their release patterns using numerical simulations and column experiments. In a series of simulations, we demonstrated that an encapsulated, dispersed-agent polymeric matrix-type controlled release system could deliver active agent at a predetermined constant rate for long time periods of years and decades. Such long-term, constant release system is useful in the construction of fertilizers, herbicides, or implantable drug delivery devices as well as in subsurface treatment. Construction of more advanced forms of controlled release systems is currently under way.

METHODS AND RESULTS

1. Development of Controlled Release KMnO_4 Scheme for Remediation of Groundwater Contaminated by Chlorinated Ethylenes

Over the past decade, advanced oxidation schemes are being used increasingly to address problems of ground-water contamination by chlorinated solvents. Of the potential oxidants, potassium permanganate (KMnO_4) is often used because of its ease of handling and relatively low cost (Siegrist et al., 2001). Studies have shown KMnO_4 rapidly transforms most chlorinated ethylenes to short-lived intermediates, and eventually innocuous by-products (Yan and Schwartz, 1999, 2000).

In most applications, KMnO_4 is applied in a concentrated aqueous solution as a flood of some source zone. This scheme treats the problem of contamination through mass removal. When this method works, it is usually because units are permeable and solvents are present at low saturations. When it fails, the main problem is commonly inability to deliver the oxidant due to physical heterogeneity in hydraulic conductivity and/or chemical heterogeneity related to pore plugging by solid reaction products like MnO_2 (Seol et al., 2003). Column and flow-tank experiments (Lee et al., 2003; Li and Schwartz, 2004) showed how plugging caused the KMnO_4 flood to bypass zones of relatively high DNAPL saturation. In field settings, leaving volumes of untreated DNAPL in place contributes to a rebound in aqueous concentrations once flushing is discontinued.

This study examines aspects of using KMnO_4 as the active component of a permeable reactive barrier. KMnO_4 used in this way would provide plume control rather than mass removal. With the typically low dissolved concentrations of contaminants in most plumes, there will be much less tendency for the porous medium to plug up. In this application, KMnO_4 is emplaced as a controlled release solid to create the chemically active zone. The solids are wax- KMnO_4 composites, cylindrical in form. They could be emplaced in lines across a plume in closely spaced wells. Ideally, these forms would dissolve and release low concentrations of KMnO_4 at a controlled rate to mix with the plume. Such a barrier could function over a period of several years. When the KMnO_4 is exhausted, it would be replaced.

One of the necessary steps in developing this remedial concept is manufacturing and testing the prototype controlled release KMnO_4 that can deliver permanganate ion in a reasonably controlled fashion over a period of months to years. In this study we describe a wax- KMnO_4 solid that has some of the necessary release

characteristics and column experiments designed to provide release data. It also provides a theoretical approach capable of modeling this process. Finally our study concludes with a proof-of-concept experiment with a flow tank, demonstrating how controlled release KMnO_4 could be used to remediate a dissolved TCE plume in porous media.

Manufacturing controlled release KMnO_4

Our implementation of controlled release technology takes advantage of a low-permeability matrix to provide for diffusion-controlled dissolution and release of solid active ingredients in the porous medium. A prototype controlled release KMnO_4 was manufactured by dispersing KMnO_4 granules in an organic crystalline matrix. Paraffin wax was chosen as this matrix because it is thermoplastic (melting temperatures: 45 to 71°C), cheap, non-toxic, and inert to oxidants as well as most organic chemicals, including chlorinated solvents. The mixture of KMnO_4 granules and molten wax was cooled in a specially designed cylindrical mould at room temperature, providing candle-shaped solids. The outside diameter of the controlled release KMnO_4 (2.5cm) was selected in order to fit the inside diameter of the delivery wells (2.6 cm) used for the later flow-tank experiments. Controlled release KMnO_4 used for the column tests were 5cm-long, had a diameter of 2.5 cm, and contained 35g of KMnO_4 . Controlled release KMnO_4 manufactured for the flow-tank experiments were 10cm long with a diameter of 2.5 cm, and contained 70g of KMnO_4 .

Column and Flow-tank Experiments

Column tests were performed using CHROMAFLEX (Kontes) glass column (ID = 4.8cm, length = 15cm, volume = 270 mL) to determine release rates of KMnO_4 into flowing water. Ambient flow rates of 19 to 21 mL/min were maintained using Ismatec peristaltic pumps (Cole Palmer Instrument Company, Chicago, Illinois) providing a flow velocity of approximately 16.7 m/day.

A glass tank was constructed (L x W x D = 100 cm x 20 cm x 50 cm) for flow-tank experiment (Figures 1-3). The tank was filled with ~170 kg of silica sand (U.S. Silica, Ottawa, Illinois), which was packed to an approximate bulk density of 1.65 and porosity of 0.35. Input and output chambers on the upstream and downstream ends of the tank helped to control inflow and outflow rates. These chambers were separated from the sand by rigid metal screens that were covered with non-reactive porous material to prevent sand from entering the chambers.

Figure 1 Schematic diagram of the glass flow-tank set up (L x W x D = 100 x 20 x 50 cm). Scales are exaggerated to show the compartments. Controlled release KMnO_4 source zone is located at the upstream part of the flow tank. Only the boundaries of the sandy media are drawn to show well locations in the flow tank.

Figure 2 Flow-tank set up. Photo showing the side-view of the flow tank placed in the full-size fume hood was taken immediately after application of controlled-release KMnO_4 . The KMnO_4 source zone is located at the upstream end of the flow tank where purple color is evident. Flow rate control and sample collection were performed using three peristaltic pumps shown in front of the flow tank. Water samples were taken daily from the four multi-level sampling wells.

Figure 3 Three controlled-release KMnO_4 (ID x L = 2.5 x 10 cm), each containing 70g of KMnO_4 granules were thrown into each of the two PVC pipes emplaced against the groundwater flow of ~ 69 cm/day. The PVC pipes were then removed from the sandy media leaving the two vertical lines of controlled-release KMnO_4 sources in the subsurface. Photos show the top views of the KMnO_4 source zone before and after the delivery of controlled-release KMnO_4 . Purple color at the KMnO_4 source zone formed by the initial surface dissolution disappeared in ~ 4 days as permanganate release rate decreased with time.

Water was pumped into inflow chamber using Ismatec peristaltic pumps (Cole Palmer Instrument Company, Chicago, Illinois) to create a uniform flow into the upstream end of the tank. The outflow rate was controlled in the same manner. An inflow rate of 19.2 L/day to the tank every day provided an ambient flow velocity of ~ 69 cm/day in the sandy porous medium. At this velocity, it required 28 hours (~ 1.2 days) for the water to flow through the tank. Effluent from the tank was collected in a waste container and treated to remove TCE and MnO_4^- before disposal. The excess MnO_4^- was removed from the effluent through reduction by sodium thio-sulphate ($\text{Na}_2\text{S}_2\text{O}_3$).

Four, small multi-level wells were emplaced along the centerline of the tank to facilitate sample collection (Figures 1-3). They were constructed with diffusion stones attached to the end of 1.52 mm ID Teflon tubing. Sampling points were set at approximate depths of 13, 26, and 39cm below the top of the sand medium. Approximately 6 milliliters of water sample was pumped out from each sampling point using a peristaltic pump and prepared for TCE and permanganate analyses. Permanganate concentration was analyzed using a Varian Cary 1 UV-visible spectrophotometer at wavelengths ranging from 400 to 700 nm. Water samples (3 mL) were prepared and analyzed for MnO_4^- using a UV-VIS immediately after sample collection. Hydrazine hydrate solution (0.2 mL) was added to the remaining samples to quench further reaction between permanganate and TCE. A small volume of the quenched sample (2 mL) was transferred to a vial and mixed with 4 mL of pentane. The

vial was shaken for 30 minutes and stored for 30 minutes to allow the sample to reach equilibrium. The upper layer, a TCE-pentane phase, of the mixture was extracted and analyzed for TCE. Samples were taken every day for the first three weeks and every other day for the next three weeks. TCE concentrations in water samples were analyzed using a GC-ECD (Shimadzu GC 17A).

After the experiment, the KMnO_4 solids were removed and the tank was allowed to drain for one week. The sand medium was excavated and collected in a large stainless steel container and thoroughly mixed. Sand samples ($n=17$) were collected randomly throughout the mixed sandy media for chemical analyses of MnO_2 content. The MnO_2 analyses were conducted using an ICP-MS (PerkinElmer Elan 6000). The MnO_2 distribution in sands was used as an indicator for estimating the extent of TCE destruction because MnO_2 is relatively immobile and unlike the dissolved TCE, survived the controlled tank excavation process. To quantify the efficiency of TCE destruction, mass balance calculations were performed using the reaction stoichiometry between TCE and MnO_2 .

Release Rate Measurement

Figure 4 shows the temporal changes in permanganate concentrations in the column discharge over the 28 days of testing. Inset in the figure is a photo that visually shows the release of KMnO_4^- into the flowing stream of water from the controlled release solid. Permanganate concentrations were initially high at 238 mg/L after 12 hours, but rapidly decreased to ~24 mg/L over the next 12 hours. Permanganate concentrations then gradually decreased from 11 mg/L on day 3 to 3 mg/L on day 10 over a seven-day period, and remained within a range of 1 to 3 mg/L throughout the remaining 16 days of testing. The initial, large concentration spike was likely caused by the rapid dissolution of KMnO_4 granules attached to the surface of the KMnO_4 solid. Mass balance calculations indicate that approximately 6.8 g (~0.057 mole) of permanganate were released during the first-day spike. This calculation indicates that ~0.164 mole (~26.0g) of KMnO_4 was subject to diffusion-controlled release. The gradual decrease in permanganate concentration after the initial flushing can be attributed to diffusion-controlled release through the secondary permeability formed in the matrix (Higuchi, 1963). Despite the short-term measurements, these experimental data clearly demonstrated that the controlled release KMnO_4 could deliver permanganate into flowing water in a controlled fashion over an extended period of time.

Figure 4 Temporal variations in the permanganate concentrations in the column outflow. Outflow samples were taken every 12 hours. Photo data shows how permanganate is released from the controlled release KMnO_4 in flowing water. The photo was taken 9 days (216 hours) after the column test began when permanganate concentration in the outflow water was measured as ~ 3 mg/L.

Mathematical Model and Simulations

In the controlled release solid, KMnO_4 granules are dispersed throughout the rigid paraffin-wax matrix, which essentially lets the shape and dimension be maintained as permanganate is released. In this case, release occurs via dissolution-diffusion. Release of active agent from a finite-height controlled release cylinder can be described with an analytical model developed by Roseman and Higuchi (1970). The analytical model was derived for non-porous, dispersed agent (solid) matrix system, which assumes pseudo-steady-state, $A \gg C_s$; constant diffusivity; a perfect sink condition, homogeneous initial agent distribution, no matrix degradation or swelling; and diffusion as the rate-controlling step. To provide context for our model analysis, we have included the salient points of the Roseman and Higuchi model (1970).

The quantity (Q') of permanganate released per unit time is:

$$\frac{dQ'}{dt} = -2\pi h D_e r \frac{dC}{dr} \quad (1)$$

satisfying the boundary condition

$$C = 0 \quad t > 0 \quad r = r_0 \quad h = h_0 \quad (2)$$

and the initial condition

$$C = C_s \quad t = 0 \quad r = 0 \quad h = 0 \quad (3)$$

where D_e is the effective diffusion coefficient, C_s is the solubility, t is time; h and r are the height and the radius of the area under consideration, and r_0 and h_0 are radius and height of the cylinder, respectively. In a cross-sectional view of the cylinder,

$$C = C_s \text{ at } r = r \quad (4)$$

and

$$C = C_s' \text{ at } r = r_0 \quad (5)$$

where diffusion distance (zone of depletion) $= r_0 - r$. Integration of Equation (1) yields

$$\frac{dQ'}{dt} = \frac{-2\pi h D_e (C_s' - C_s)}{\ln \frac{r_0}{r}} \quad (6)$$

where C_s is solubility and C_s' is concentration in the matrix at $x=0$.

Assuming no boundary layer effect, the rate of diffusion from the surface is given by

$$\frac{dQ'}{dt} = \frac{2\pi h r_0 D_a}{h_a} C_a' \quad (7)$$

The partition coefficient, K is defined as:

$$K = \frac{C_a}{C_s} = \frac{C_a'}{C_s'} \quad (8)$$

where C_a is solubility in the aqueous phase. After equating Equations (6) and (7), substituting Equation (8), solving for C_s' , and rearranging, the rate becomes:

$$\frac{dQ'}{dt} = \frac{2\pi h r_0 K D_a}{h_a} \left(\frac{D_e C_s h_a}{-K D_a r_0 \ln \frac{r_0}{r} + D_e h_a} \right) \quad (9)$$

where D_a is diffusion coefficient in aqueous phase.

For $A \gg C_s$

$$\frac{dQ'}{dt} = -2\pi h A r' \frac{dr}{dt} \quad (10)$$

Equating Equations (9) and (10);

$$\int_{r_0}^r \left(K D_a r_0 \ln \frac{r_0}{r} - D_e h_a \right) r dr = \frac{K D_e C_s D_a r_0}{A} \int_0^t dt \quad (11)$$

Integration and substitution yield:

$$\frac{r^2}{2} \ln \frac{r}{r_0} + \frac{1}{4} (r_0^2 - r^2) + \frac{D_e h_a}{2KD_a r_0} (r_0^2 - r^2) = \frac{C_s D_e t}{A} \quad (12)$$

For the matrix-controlled system, this reduces to

$$\frac{r^2}{2} \ln \frac{r}{r_0} + \frac{1}{4} (r_0^2 - r^2) = \frac{C_s D_e t}{A} \quad (13)$$

Because

$$Q' = \pi h A (r_0^2 - r^2) \quad (14)$$

Equations (12), (13), and (14) define the Q' versus t plots. This model was verified against experimental data by (16).

Equations were solved numerically using the bisection method (Nakamura, 2002). Parameters used for simulation were: r (radius) = 12.5 mm; h (height) = 50 mm, C_s (solubility) = 64 $\mu\text{g}/\text{mm}^3$; A (amount of available permanganate per unit volume) = 875 $\mu\text{g}/\text{mm}^3$, and D_e (effective diffusion coefficient) = $3.125 \times 10^{-8} \text{ cm}^2/\text{s}$. The A value was estimated from the measured amount of permanganate left in the controlled release KMnO_4 after the initial flushing period (0.181 mole or 21.5 g). The total quantity of permanganate released over the 25 days of testing period was measured as 3.3 g. The D_e value was obtained from the best-fit curve for the total amount released (3.3 g permanganate in 25 days). The simulation model specifically applies to the diffusion-controlled release of KMnO_4 after the initial dissolution-controlled period (0 - 12 hours). It does not describe the early time concentration spike due to fast dissolution of KMnO_4 on the surface.

Simulated data generally matched with the experimental data (Figure 5), but slight discrepancy was identified between the measured and simulated values. This difference was attributed to incomplete mixing of KMnO_4 granules with paraffin wax in the prototype controlled release KMnO_4 . The analytical model (16) assumes homogeneously dispersed agent in the matrix. Such dispersed-agent matrix system can be manufactured, for example, by compression, co-injection molding, or photo-polymerization techniques (Lu and Anseth, 1999). Construction of advanced forms of KMnO_4 -dispersed matrix system is warranted. Simulation results indicated that the duration of the controlled release KMnO_4 would be approximately 5.4 years (Figure 6).

Figure 5 Column and simulation data showing the cumulative amount of permanganate (MnO_4^-) released from the controlled release KMnO_4 over 25 day period.

Efficacy of the controlled release KMnO_4 scheme

An experiment was performed using a glass flow tank (Figures 1-3) to demonstrate the release and spreading pattern of the controlled release KMnO_4 by itself in medium with an ambient flow of water. Three pre-washed controlled release KMnO_4 forms (ID x L = 2.5cm x 10 cm), each containing 70g KMnO_4 granules were set in each of two PVC pipes (ID x L = 2.6cm x 40 cm) placed in the upstream end of the flow tank. The PVC pipes were then removed from the porous medium leaving the two vertical lines of controlled release KMnO_4 . Permanganate concentrations were monitored daily over 93 days. Permanganate contours across the flow tank ranged from $\sim 900\mu\text{g/L}$ in the upstream KMnO_4 delivery zone to $\sim 100\mu\text{g/L}$ in the downstream end of the tank and showed little variation throughout the testing period of 93 days (Figure 7). This experiment demonstrated that the controlled release KMnO_4 scheme delivered permanganate in a controlled fashion over an extended period of time. Predetermined concentrations of MnO_4^- could be maintained in the porous medium to provide for the efficient destruction of dissolved TCE.

Figure 6 Simulation data showing the duration of the controlled release KMnO_4 .

Figure 7 Permanganate contours in the flow-tank after 63 days (unit: g/L). Permanganate concentration ranged from $\sim 100 \mu\text{g/L}$ at the downstream end to $\sim 900 \mu\text{g/L}$ near the KMnO_4 source in the upstream end of the flow tank. Permanganate contours remained constant at this range throughout the entire testing period of 93 days.

A second experiment was performed to demonstrate the efficacy of the controlled release KMnO_4 in treating dissolved TCE. The flow tank was again set up with two

delivery wells (ID x L = 2.6 cm x 40 cm) containing total of six controlled release KMnO_4 forms (ID x L = 2.5 cm x 10 cm; 100 g KMnO_4). The mass of KMnO_4 in the controlled release KMnO_4 was adjusted to release a concentration of MnO_4^- appropriate for destroying TCE at concentrations as high as ~2,000 g/L. Permanganate concentrations in the flow tank were initially high, ranging from 10 to 70 mg/L during the first five days, and decreased and stabilized in the range of 10 to 30 mg/L. When the permanganate contours became stabilized on day 6, the inflow water was replaced by a solution containing variable TCE concentrations (42 to 1,639 $\mu\text{g/L}$). Temporal and spatial variations in TCE concentrations across the flow tank are summarized in Table 1. The TCE concentrations initially high in the inflow water were much lower across the flow tank downstream of the active treatment zone. Clearly, there was active destruction of dissolved TCE by the controlled release of MnO_4^- from the solid forms. The TCE concentrations, however, remained in many cases above the EPA drinking water standard of 5 $\mu\text{g/L}$ (Table 1). In addition, the TCE concentrations in the outflow

Table 1 Variations in the TCE concentrations in the flow tank (unit: $\mu\text{g/L}$, input: input water, Sampling wells were numbered from 1 to 4 starting from the upstream end. B, m, t indicate sampling points at the bottom, middle, and top of the multi-level sample wells.)

sample ID	Day 3	Day 10	Day 16	Day 40
input	595	1639	42	245
output	345	483	18	95
1b	23	12	2	10
1m	74	14	12	6
1t	104	15	10	89
2b	104	14	1	7
2m	80	8	5	45
2t	69	8	8	47
3b	74	7	1	1
3m	45	27	1	1
3t	30	10	5	4
4b	22	4	5	39
4m	28	13	3	40
4t	9	52	2	1

water were higher than in the water samples collected from the monitoring wells that

were emplaced along the centerline of the flow tank (See Figure 1 for well locations.). These data indicated that the TCE plume (<2 mg/L TCE) was not completely destroyed by permanganate oxidation in the flow tank.

Based on the reaction stoichiometry between TCE and permanganate (1), ~ 3.6 mg/L (~ 30 μ M) of permanganate is required to completely destroy up to ~ 2 mg/L (~ 15 μ M) TCE solution. In their detailed studies on the reaction kinetics associated with permanganate oxidation of TCE, Yan and Schwartz (5,6) reported that TCE oxidation by permanganate is independent of pH and TCE has estimated half-life ($T_{1/2}$) of ~ 17.8 minutes. In their batch experiment, 0.06 mM of TCE was almost completely destroyed by permanganate (1 mM) solution in less than 100 minutes. The estimated residence time for permanganate and TCE plume in the flow tank was ~ 28 hours, which is long enough for complete destruction of TCE by permanganate oxidation. These observations suggested that the incomplete destruction of dissolved TCE in the flow tank was probably due to the lack of lateral spreading of MnO_4^- and the resulting incomplete with dissolved TCE.

The average MnO_2 content for sandy materials collected in the container was measured as 22.1 mg-Mn/kg-sands ($n=17$, standard deviation=1.8). This value indicated that ~ 5.9 g (~ 0.07 mole) of MnO_2 precipitates were produced in the flow tank, suggesting destruction of ~ 4.5 g (~ 0.03 mole) of TCE by ~ 5.4 g (~ 0.07 mole) of KMnO_4 over 37 days. The total amount of KMnO_4 released from the six controlled release KMnO_4 comprising the two vertical lines of permanganate source was 15.5 g (~ 0.098 mole). Mass balance calculations indicated that only $\sim 1/3$ of the permanganate released from the controlled release KMnO_4 was used for TCE oxidation, indicating uneven mixing of MnO_4^- solution due to lack of lateral spreading away from the solid forms. These data demonstrated that the controlled release KMnO_4 scheme is capable of destroying dissolved TCE plume in a long-term, controlled manner. Incomplete destruction of the TCE, however, suggested that development of a delivery system that can facilitate lateral spreading and mixing of permanganate with the dissolved contaminant plume is required.

2. Numerical Optimization of Controlled Release System: A Custom-made Approach for Subsurface Remediation

Controlled release of active materials (agents) like drugs, nutrition, fertilizers, or other bioactive chemicals is becoming increasingly important for wide variety of applications and technologies in pharmacy, biomedicine, food science, agriculture, and

environmental sciences (Langer, 1990). The ability to release a compound at a controlled rate is important in variety of different applications. The controlled release system transfers active agent from a reservoir to a target host, in order to maintain a predetermined concentration or emission level of the agent for a specified period of time or desired fraction. Controlled release systems provide advantages over conventional delivery systems. For example, risks for toxicity (overdose) and ineffectiveness (under-dose) can be eliminated by maintaining the agent concentrations within the desired range. Other advantages include localized delivery of agents to a particular compartment, thereby lowering the overall agent level; preservation of agents that can be rapidly destroyed by environmental conditions; reduced need for maintenance; and low cost. In our particular application, the oxidant, KMnO_4 , can be released in a controlled manner over years and perhaps decades without active control. Through sophisticated control of the release rates of active chemicals, custom-made type remedial approach can be made in contaminated sites where detailed site investigation data are available. As a first step of developing the new custom-made type remedial approach, we thoroughly reviewed major pharmaceutical controlled release technologies developed over the past four decades.

There are two types of controlled release systems: reservoirs and matrices. In both cases, diffusion controls the release process. Diffusion occurs through a reservoir, in which an agent core is surrounded by encapsulation or coating, or in a matrix, where the agent is uniformly dispersed through the polymeric system (e.g., Langer, 1990). Increasingly sophisticated encapsulation techniques are being developed to create controlled release systems that can meet the demanding requirements in the biomedical applications. These approaches use emulsion, electrospray, selective withdrawal, flow focusing, electrohydrodynamic force technique, or self-assembly process to generate co-axial jets of immiscible liquids with diameters in the micrometer/ nanometer range. Despite the enormous progress in encapsulation technologies, however, these methods are often limited in their applicability, in the range of materials that can be used, in the uniformity of pore sizes, in the accessible permeabilities and elasticities, durations, or in the ease of synthesis, filling efficiency, and yield estimation.

In matrix-type release systems, dissolution of granules of agents dispersed in the matrix creates inward development of secondary porosity and permeability, through which dissolved agent is released by diffusion. Compared with reservoir-encapsulation systems, matrix systems have advantages of low cost, easy fabrication, and less risk of dose dumping which is mainly resulted from the damage of the encapsulation. Controlled release tablets can be manufactured by compressing the homogeneous

powder mixtures of drugs and fillers, i.e., starches or other innocuous binders such as amylase (Langer, 1990). More complex bi- and multi-layered matrix systems can also be relatively easily fabricated using co-injection molding or photo-polymerization techniques (Lu and Anseth, 1999). Durations and release rate of matrix-type controlled release systems can be controlled by adjusting diffusion length, diffusivity, and geometry of the matrices. However, the kinetics of agent release in matrix systems is more complicated to describe, especially when a complex geometry, non-uniform initial loading, and composite structures are applied in the design of the devices.

In this study we used numerical modeling approach to aid the design of matrix devices for long-term controlled release system. More specifically, this study is focused on the analyses of diffusion-controlled agent release from matrices of composite structures, for which the release kinetics is improbably predicted by analytical solutions. The matrices considered in this study are idealized as rigid materials during the diffusion process, which simulate the matrices with negligible dimension change such as silicone rubber, polyurethane, bone cements/ceramics, pre-swollen hydrogels, or waxes.

Construction and Simulations of the Matrix-type Controlled Release System

We used a numerical model to optimize release processes associated with different types of controlled release systems under varied environmental conditions. Agent transport through polymeric matrix can be described by Fick's law of diffusion. A non-steady-state diffusion in non-homogeneous media is described by (modified from Crank, 1975):

$$J = -\frac{T}{S} \frac{\partial C(x,t)}{\partial x} \quad (1)$$

where J is the particle flux, C is the concentration of the solute, T is the transmittivity, S is the media storage coefficient, x is the distance, and t is the diffusion time. The negative sign indicates that the diffusing mass flows in the direction of decreasing concentration. From the conservation of mass, we also know that:

$$\frac{\partial C}{\partial t} = -\frac{\partial J}{\partial x} \quad (2)$$

If we combine equation (2) with equation (1), and expand it to 2-dimension, we obtain modified version of the 2nd Law of Diffusion (otherwise known as Fick's Law), which states:

$$\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} = \frac{S}{T} \frac{\partial C}{\partial t} \quad (3)$$

There is no analytical solution to the 2-dimensional partial differential equation (3). Therefore, a numerical solution was obtained through a finite difference approach:

$$\frac{T(C_{i-1,j} - C_{i,j})}{\Delta x^2} + \frac{T(C_{i+1,j} - C_{i,j})}{\Delta x^2} + \frac{T(C_{i,j+1} - C_{i,j})}{\Delta y^2} + \frac{T(C_{i,j-1} - C_{i,j})}{\Delta y^2} = \frac{S(C_{i,j} - CP_{i,j})}{\Delta t} \quad (4)$$

where $CP_{i,j}$ is the calculated concentration at node i,j at the end of the previous time increment and Δt is the time increment elapsed since last calculation of concentrations. The numerical model was verified against the 1-D analytical model developed by Crank (1975).

We constructed controlled release cuboidal matrix (25mm x 25mm x 50mm) system containing 25 g of agent (water solubility = 64g/L) for simulation (Figure 8). Our system allows no degradation, swelling, or structural relaxation of the polymeric matrices and assumed that boundary effects were negligible. Agent granules are assumed to be homogeneously dispersed in the non-porous, inert matrix. Top and bottom of the cuboid were assumed to be sealed with impermeable film to satisfy the 2-D representation. Diffusion coefficient of the matrix was assumed to be $1.4 \times 10^{-7} \text{ cm}^2/\text{s}$ ($\sim 1.2 \text{ mm}^2/\text{day}$). This value was within the typical range of drug diffusion coefficients (10^{-6} to $10^{-7} \text{ cm}^2/\text{s}$) in rubbery polymer (Narasimhan, 2000).

Temporal changes in concentration distributions are presented in figure 9. In 100 days, the dissolution front receded approximately 2 mm from the surface, creating a $\leq 2\text{mm}$ -long diffusion path in the secondary permeabilities (depleted cells). In 300 days, the dissolution front further receded creating approximately $\leq 7\text{mm}$ -long diffusion path in the depleted cells. In 600 days, all monolithic cells were depleted, showing agent concentrations $\leq \sim 9 \text{ } \mu\text{g}/\text{mm}^3$ with maximum concentrations in the core nodes. In 800 days, the matrix was almost exhausted, showing agent concentrations $\leq 0.1 \text{ } \mu\text{g}/\text{mm}^3$ throughout the matrix. Using the simulated concentration data, horizontal diffusive fluxes were calculated for the 2-D plane (25mm x 25mm) with time increment of 1 day. Release rates (in mg/day) were then calculated for the rectangular parallelepiped (25mm

Figure 8 Top and bottom photos are controlled release cuboids (24cm x 24cm x 50cm) containing 25 g of KMnO_4 (water solubility = 64g/L) before and after the column leaching tests. Column test created tiny numerous holes on the surface of the cuboid.

x 25mm x 50mm), of which top and bottom planes are sealed.

Figure 10 shows the release (amount agent released) vs. time profiles for single- and double-layered, dispersed agent, nonporous matrix systems. Release rates in the single-layered system were initially high (burst effect), then rapidly decreased before stabilized while continued to decrease until stopped. Such first-order release pattern can be attributed to the recession of boundary in the matrix at which agent dissolution occurs and from which the agent is released as the matrix is depleted and the secondary permeability develops from the surface. As a result, the diffusion path length increases, thus the release rates decrease with time. This observation is in keeping with the simulation and experimental data demonstrated by Higuchi (1963) and others (Narasimhan, 2000 and references therein) for the dispersed drug, non-porous matrix system. Our study constructed a single-layered, matrix-type controlled release system in cylindrical form by mixing KMnO_4 granules with paraffin wax and demonstrated its efficacy as a long-term, semi-passive treatment scheme for groundwater contaminated by chlorinated ethylenes. Likewise, they reported the first-order decay in release rates with the initial burst followed by rapid attenuation using column experiment. They also generated comparable first-order release data through simulations using an analytical solution. In the double-layered system, the initial concentration burst effect was reduced and the subsequent rapid decrease in the release rates was attenuated considerably, yielding much less variable release rates over longer period of time compared to the single-layered system. Durations of single-layered and double-layered systems were

estimated as 470 days and 590 days, respectively. This observation clearly demonstrates that utilizing composite structure, or non-homogeneous initial agent loading, would be useful in creating more constant release systems.

Figure 9 Concentrations (mg/mm^3) of active agent (solubility in water: $64\text{g}/\text{L}$) in 2-D the matrix-type controlled release system ($25 \times 25 \text{ mm}^2$). Simulations were made for A. 100 days, B. 300 days, C. 600 days, and D. 800 days, respectively.

Figure 10 First-order release of agent from the single-layered, dispersed agent, nonporous matrix system ($24 \times 24 \times 50 \text{ mm}^3$) containing 25g of agent (solubility = 64g/L). In the double-layered system, 10g of agent is dispersed in the middle ($12 \times 12 \times 50 \text{ mm}^3$) and 15g of agent is dispersed in the rest of the barrier area of the nonporous layered system ($24 \times 24 \times 50 \text{ mm}^3$).

Numerical Optimization

The initial burst and the subsequent rapid first-order decrease of the release rates are in many cases not desirable for applications that require precise control of agent concentration in the target host. To achieve constant release rates, various approaches have been developed by pharmaceutical scientists and engineers utilizing variable geometry, swelling or surface eroding polymeric matrices, or non-uniform initial drug loadings (Lu and Anseth, 1999). The approaches using variable geometries or swelling or surface eroding polymers were successful in achieving the zero-order release, but they failed to eliminate the initial burst effect. In addition, these systems are short-term in nature because they are essentially dissolution-controlled system. On the other hand, the approaches using non-uniform initial agent loadings eliminated the burst effect, while moderating the time variations of the underlying release rate.

We performed release rate simulations for controlled release systems of various non-uniform initial agent loadings. In a series of simulations, we found that an encapsulated, single-layered matrix system would yield long-term, constant release

while eliminating the initial burst effect. For demonstration, we constructed a conceptual model of an encapsulated matrix system, in which non-porous polymeric matrix (9mm x 9mm x 9mm) containing ~3.9 g of dispersed granules of active agent (solubility = 64g/L) is covered by 1mm-thick encapsulation. Diffusion coefficients (D_e) were assumed to be $2.31 \times 10^{-6} \text{ cm}^2/\text{s}$ in the core matrix and $1.16 \times 10^{-9} \text{ cm}^2/\text{s}$ in the encapsulation of the side planes. Here, the diffusivity in the core matrix is constrained by the agent/matrix ratio. These values were within the typical ranges for drug diffusion in rubbery polymers (10^{-7} to $10^{-6} \text{ cm}^2/\text{s}$) and in glassy polymers (10^{-12} to $10^{-7} \text{ cm}^2/\text{s}$), respectively (Narasimham, 2000). The encapsulations of the top and bottom planes of the matrix were assume to be impermeable. Simulation results are presented in figure 12. Initial release rates were 1358 $\mu\text{g}/\text{day}$ on day 1, increased to 1422 $\mu\text{g}/\text{day}$ on day 2, and gradually increased to 1465 $\mu\text{g}/\text{day}$ on day 136. Afterwards, the release rates infinitesimally decreased to 1458 $\mu\text{g}/\text{day}$ on day 2397 over 2260 days, yielding a long-

Figure 12 Long-term, constant release in the encapsulated single-layered matrix system.

term zero-order release without the initial flushing. Approximately 90.1% of agent was released during the first 2397 days of almost constant release period, with release rates

ranging from 1458 to 1465 $\mu\text{g/day}$. After the zero-order release period, release rate rapidly decreased to become approximately 400 $\mu\text{g/day}$ over the next 700 days, and gradually approached zero.

Potential Applications and Future Work

Our numerical modeling approach can be refined almost indefinitely to describe release processes associated with various types of controlled release systems like the dispersed agent matrices, dissolved agent matrices, multi-layered matrices, encapsulated reservoirs, or encapsulated matrices of variable forms, geometries, and dimensions. The modeling approach could also describe moving boundary conditions, variable boundary effects, or transformation of matrices. Considering the time-consuming, costly experiments required for manufacturing and physically testing the controlled release systems, utilization of the versatile computer model for system optimization would provide efficiency in the construction of controlled release systems. Our current finite model is in its primitive form, and requires numerous stages of refinements. For example, our model currently uses millimeter-scale grids and describing micro- and nano-scale molecular-level diffusion problems is a challenge. In addition, modification of algorithm is required to describe controlled release systems of variable geometries. Our current model also lacks user-friendly interface and hands-on User's Manual.

The long-term, constant release schemes could provide wide spectrum of applications in environmental sciences. For example, the release system could provide for innovation in new concept in long-term, passive treatment of contaminants and strategy for controlling the releases in the subsurface. Advanced natural attenuation or bioremediation techniques have been used to remediate soils, sludge, and ground water contaminated with petroleum hydrocarbons, chlorinated solvents, pesticides, wood preservatives, sewage effluent, and other organic chemicals. Successful use of these schemes often requires continuous supply of nutrients to the target area. Here, overdose or under-dose could cause secondary water pollution or ineffectiveness. Advanced chemical oxidation, chemical reduction, or *in situ* redox manipulation schemes also require introduction of chemical agents to the target subsurface zones. The dilemma in developing strategies for better utilizing these methods has been how to control the tendency for rapid dissolution of agents in water. Rapid dissolution can not only create undesirably high concentrations of chemical agents but also make the treatment schemes short-term in nature, thus requiring major operational cost. Treatment chemicals such as aluminum sulfate or 'alum' ($\text{Al}_2(\text{SO}_4)_3$; solubility = 31.3 g/100 ml at 0 °C) and herbicides have been used to control excess algae, i.e., eutrophication, or

turbidity and plant infestations in lakes and public water supply reservoirs. In these applications, maintaining low dose concentration for prolonged period of time is the key for successful and efficient treatment. The long-term constant release system can deliver nutrients and other treatment chemicals to maintain constant levels of agents in the target media for years, thus providing an efficient long-term management and treatment scheme for soils and water resources. In our study on the potential applications of the controlled release system to groundwater remediation with advanced oxidation schemes using KMnO_4 , we suggested that utilization of such system in subsurface remediation would help addressing inefficiency problems associated with over- and under-dose, contaminant rebound and high operation cost.

The technique is also applicable to other areas. For example, in agriculture, controlled release system has been used to provide the plants with a controlled and consistent flow of nutrients, eliminating the peaks and troughs that can occur when using conventional methods. There are numerous slow-release fertilizer products available in the market. These products generally use encapsulations, to sustain or chemically control the release rates of the agents. Encapsulations are generally short term in nature, however, and limited in the precise control and estimation of release rates and durations. Application of the constant release system and associated numerical modeling approach could provide an efficient concept in long-term, custom-made approach for controlling levels of nutrition and herbicides/pesticides in the farmlands or rice paddies over an extended period of time.

The most promising application of the long-term constant release system and associated numerical modeling approach in biomedicine would be in the polymeric implantable drug delivery systems. Polymeric medical microchips or implants may contain small grooves or reservoirs that comprise drugs dispersed in biodegradable matrices. Implants are then encapsulated with different types of polymer that biodegrade at different rates under different environmental conditions, allowing multiple drug loads, constant release, and direct delivery of small doses to the target organs. This type of delivery system is known to be useful for reduction of refractory pain, periodontal treatment, or treatment of diseases like prostratitis, diabetes, or AIDS that require long-term prescriptions of a cocktail of different drugs (e.g., Smith et al., 2005). Drug release processes in these multi-laminated, encapsulated matrix systems are essentially constrained by reaction-diffusion and degradation of encapsulations and matrices.

RELEVANCE, IMPACT, AND TECHNOLOGY TRANSFER

Over the last seven years, our hydrogeology research group at the Ohio State University has performed extensive research on the use of ISCO schemes for the clean up of organic contaminants in the subsurface. With these efforts, we have contributed to the basic understanding of physical and chemical processes associated with KMnO_4 as an oxidant. These studies support proof-of-concept research showing that KMnO_4 scheme is capable of destroying chlorinated ethylenes in the subsurface rapidly and efficiently.

Our most recent work has focused on investigating potential applications of pharmaceutical controlled release technologies to problems of subsurface remediation using KMnO_4 . Fundamentally, this new approach has merit in wide spectrum of treatment schemes that involve release of treatment chemicals. This technique is being deployed in proof-of-concept applications in the hopes of achieving custom-made remedial approach by maintaining optimal level of agent concentration in the target host for an extended period of time. Construction of mathematical and numerical models for describing release processes of various types of controlled release systems would benefit varied delivery schemes in agriculture, engineering, and biomedicine.

PROJECT PRODUCTIVITY

From this two year-long study we have gained significant understanding on fundamental scientific issues associated with controlled release systems and their potential applications to subsurface remediation. We have also made important progresses in helping put this technology into field and industrial practice. While developing the remediation techniques, we keep our research results updated with colleagues around the world. We are in the process of publishing two articles on top academic journal. More than five conference presentations have been made at prominent national and international occasions. We have communicated with field engineers working at the remediation sites, and their responses are very helpful. We have collaborated with scientists in Japan (Kurita Water Industries Ltd.) and Korea (Korea Agricultural and Rural Infrastructure Corporation), which have greatly helped promoting and marketing this technology.

PERSONNEL SUPPORTED

Faculty:

Dr. Franklin W. Schwartz, Professor and Ohio Eminent Scholar in Hydrogeology, The Ohio State University

Dr. Motomu Ibaraki, Associate Professor in Hydrogeology, The Ohio State University

Research Scientist:

Dr. Eung Seok Lee, Research Associate 2-Phy in Hydrogeology, The Ohio State University.

PUBLICATIONS

Lee, Eung Seok, Schwartz, F.W., Remediation of groundwater contaminated by chlorinated hydrocarbon using controlled release KMnO_4 , in review, *Environmental Science and Technology*.

Lee, Eung Seok, Schwartz, F.W., Numerical optimization of controlled release system: A new custom-made remedial approach, in review, *Environmental Science and Technology*.

INTERACTIONS

Participation/Presentation at meetings, workshops, and conferences

Lee, E.S. and Schwartz, F.W., Groundwater remediation using slow-release KMnO_4 , Korea Agricultural and Rural Infrastructure Corporation, Korea, May 2004.

Lee, E.S. and Schwartz, F.W., Semi-passive treatment of DNAPL using controlled release KMnO_4 , Korea Agricultural and Rural Infrastructure Corporation, Korea, May 2005.

Schwartz, F.W. and Lee, E.S., Semi-passive treatment of DNAPL using controlled release KMnO_4 , Korea Institute of Geology, Mining, and Materials, Korea, May 2005.

Schwartz, F.W., Lee, E.S., Semi-passive treatment of DNAPL using controlled release KMnO_4 , Korea Water Resources Corporation, Korea, May 2005.

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APPENDIX : Analytical Model -Controlled Release Cylinder

```
C      EUNG SEOK LEE AND FRANKLIN W. SCHWARTZ
C      OHIO STATE UNIVERSITY HYDROLAB
C      CONTROLLED RELEASE KMnO4 CYLINDER
C
C      NSTEPS-----NO. OF TIME INCREMENTS
C      DELTA-----TIME INCREMENTS (DAYS)
C
C
C      DEFINE INPUT AND OUTPUT DEVICE NUMBERS
C
      CHARACTER*20 INFILE
      CHARACTER*20 OUTFILE
      INTEGER*4 NSTEPS,I
      REAL*8 TOLERANCE
      REAL*8 TIME,DELTA,R0,R,DR,ROOT_R,TMAX
      REAL*8 Q
      REAL*8 H,A,CS,DE
C      SET CONSTANTS
      DR=0.001D0
      TOLERANCE=0.001D0
      H=50.0D0
      CS=64.0D0
      DE=0.27D0
      A=875.0D0
C      WRITE(*,900)
C 900 FORMAT (' INPUT FILE NAME- ')
C      READ(*,910) INFILE
C 910 FORMAT (A)
C      WRITE(*,920)
C 920 FORMAT(' OUTPUT FILE NAME-')
C      READ(*,910) OUTFILE
      INFILE='model06.txt'
      OUTFILE='output.dat'
      OPEN(5,FILE=INFILE)
```

```

OPEN(6,FILE=OUTFILE,STATUS='NEW')
C
C   READ DEFAULT VALUE
C
      READ(5,10)NSTEPS,DELTA,R0
10   FORMAT(I6,2F6.0)

C  DETERMINE MAXIMUM ITERATION STEP BASED ON THE PARAMETERS
      NSTEPS=INT(((0.0001*0.0001*0.5*DLOG(0.0001/R0)+
      .      0.25*(R0*R0-0.0001*0.0001))/CS/DE*A)-1

      WRITE(6,77743)NSTEPS,DELTA,R0
77743 FORMAT(I10,' : NSTEPS'/F10.2,' : DELTA'/1F10.2,' :  R0'//)

      TIME=0.0
      DO I=1,NSTEPS
          PRINT*, 'TIME STEP : ',I
          CALL
BISECT_METHOD(DR,DR,R0,TOLERANCE,R0,CS,DE,A,TIME,ROOT_R)
          Q=3.141592*H*A*ROOT_R*ROOT_R
          QQ=3.141592*H*A*(R0*R0-ROOT_R*ROOT_R)

      WRITE(6,390) QQ
390   FORMAT(F15.3)
          TIME=TIME+DELTA
      END DO

      CLOSE(5)
      CLOSE(6)

      STOP
      END PROGRAM

C   EVALUATION OF FUNCTION
      SUBROUTINE F(R0,R,CS,DE,A,T,OUT)

```

```

REAL*8 R0,R,CS,DE,A,T,OUT
OUT=0.5d0*R*R*DLOG(R/R0)+0.25d0*(R0*R0-R*R)-CS*DE*T/A

```

```

END SUBROUTINE

```

C FIND ROOT USING BISECTION METHOD

```

SUBROUTINE BISECT_METHOD(X0,DX,MAXX,TOLERANCE,R0,CS,DE,A,T,OUT)

```

```

REAL*8 X0,DX,MAXX,TOLERANCE,R0,CS,DE,A,T,OUT

```

```

REAL*8 LVAL,RVAL,VAL,XL,XR,XMID

```

```

XL=X0

```

```

XR=XL+DX

```

```

DO WHILE (XR.LE.MAXX)

```

```

    CALL F(R0,XL,CS,DE,A,T,LVAL)

```

```

    CALL F(R0,XR,CS,DE,A,T,RVAL)

```

```

    IF ((LVAL*RVAL).LT.0.0) THEN

```

```

        EXIT

```

```

    ELSE IF (LVAL.EQ.0.0) THEN

```

```

        OUT=XL

```

```

        RETURN

```

```

    ELSE IF (RVAL.EQ.0.0) THEN

```

```

        OUT=XR

```

```

        RETURN

```

```

    END IF

```

```

    XL=XR

```

```

    XR=XL+DX

```

```

END DO

```

```

XMID=(XL+XR)/2.0

```

```

DO WHILE (.TRUE.)

```

```

    CALL F(R0,XMID,CS,DE,A,T,VAL)

```

```

    IF (DABS(VAL).LT.TOLERANCE) THEN

```

```

        OUT=XMID

```

```

        RETURN

```

```
ELSE
    IF (LVAL*VAL.LT.0) THEN
        XR=XMID
    ELSE IF (RVAL*VAL.LT.0) THEN
        XL=XMID
    END IF
    XMID=(XL+XR)/2.0
END IF
END DO
END SUBROUTINE
```