

ESTCP Cost and Performance Report

(ER-200626)



Development of a Design Tool for Planning Aqueous Amendment Injection Systems

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ACRONYMS AND ABBREVIATIONS

ρ_B	bulk density
φ	effective porosity
3-D	3-dimensional
AFCEE	Air Force Center for Environmental Excellence
BTV	base treatment zone
CE	contact efficiency
CE_{SS}	steady-state, volume average contact efficiency
CDISCO	Conceptual Design of In Situ Chemical Oxidation
C_I	substrate injection concentration
C_{min}	minimum concentration
DoD	Department of Defense
ESTCP	Environmental Security Technology Certification Program
E_v	aquifer volume contact efficiency
EVO	emulsified vegetable oil
GCG	Generalized Conjugate Gradient
GMS	Groundwater Modeling System
GW	groundwater
ISAB	in situ anaerobic bioremediation
ISCO	in situ chemical oxidation
ITRC	Interstate Technology & Regulatory Council
K	permeability
$KMnO_4$	potassium permanganate
MOC	Method of Characteristics
MODFLOW	Modular Flow Model
MnO_4^-	permanganate
MT3D	Modular 3-D Transport Model
NFESC	Naval Facilities Engineering Service Center
NOD	Natural Oxidant Demand
NOD_I	Instantaneous Natural Oxidant Demand
NOD_S	Slow Natural Oxidant Demand
NPV	net present value
OR_M	maximum oil retention
PV	pore volume

ACRONYMS AND ABBREVIATIONS (continued)

Q	injection rate per well
ROI	radius of influence
RT3D	Reactive Transport 3-D Model
SF _V	volume scaling factor
SF _M	mass scaling factor
SS	soluble substrate
S _R	row spacing
S _W	well spacing
T _H	half-life
T _R	time period between substrate reinjections
T _T	travel time
U	fraction of un-reacted MnO ₄ ⁻
USEPA	U.S. Environmental Protection Agency
Z	saturated thickness

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1.0 EXECUTIVE SUMMARY

In situ anaerobic bioremediation (ISAB) and chemical oxidation can be useful for treating a variety of groundwater (GW) contaminants. However, to be effective the treatment reagent must be brought into close contact with the target contaminant. To reduce costs and improve effectiveness, designers need tools to quickly identify efficient systems for distributing reagents.

1.1 PROJECT OBJECTIVES

The overall objective of this project was to develop a set of tools to assist remediation system designers in developing effective, reasonably efficient systems for distributing aqueous amendments for in situ treatment of K contaminants. This project focused on the development and application of tools for the design of ISAB systems using soluble substrates (SS) and emulsified vegetable oil (EVO), and in situ chemical oxidation (ISCO) systems using permanganate (MnO_4^-).

1.2 TECHNOLOGY DESCRIPTION

In the first phase of work, currently available numerical models were used to understand the effects of site conditions (e.g., permeability (K), site heterogeneity) and design variables (e.g., location of wells, injection rates, volumes, amount of reagent, etc.) on reagent contact efficiency (CE). Results from 3-dimensional (3-D) numerical simulations in heterogeneous aquifers were used to develop relationships between reagent distribution and amount of fluid/reagent injected. This information was then used to develop simple, spreadsheet-based design tools to assist in planning injection systems for in situ aquifer treatment with EVO, SS, and MnO_4^- . Using these tools, designers can evaluate the effect of different design variables (e.g., well spacing, amount of reagent, injection volume, etc.) on remediation system cost and expected performance.

1.3 DEMONSTRATION RESULTS

1.3.1 Anaerobic Bioremediation with Emulsified Vegetable Oil

Sensitivity analysis results showed that aquifer volume CE is primarily controlled by the volume of EVO injected and the volume of water injected to distribute the EVO. Simple curves were developed to estimate CE and then incorporated into spreadsheet-based tools to compare the cost and performance of different designs. Capital and life-cycle costs appear to be relatively insensitive to site conditions, for both barrier and area treatment. Obviously, total costs are often higher for large, wide, deep sites. Unit costs are often higher for smaller sites due to the proportionately higher fixed costs associated with planning, design, and monitoring. Errors in estimation of the maximum oil retention (OR_M) by the aquifer material can have a major impact on cost and performance for both barrier and area treatment. OR_M should be directly measured on field or lab samples whenever possible.

1.3.2 Anaerobic Bioremediation with Soluble Substrates

Anaerobic bioremediation with SS is most effective when the substrate concentration is greater than some minimum concentration (C_{\min}). However, CE will vary over time as substrate is depleted or washed out of the target treatment zone and as additional substrate is injected. To

account for these variations in time, the steady-state, volume average contact efficiency (CE_{SS}) was used as the primary measure of SS injection performance. Sensitivity analysis results showed that CE_{SS} greater than 50% can be achieved by periodic injection of 0.1 to 0.25 pore volumes (PV) of SS solution containing 20 to 100 times the C_{min} required for effective treatment. Operating costs can be reduced by injecting substrate less frequently, but can result in a dramatic drop in CE_{SS} . Results from these sensitivity analyses were incorporated into a spreadsheet based tool to allow designers to compare different designs, and used to evaluate costs and performance for a range of site conditions. In most cases, increasing CE_{SS} also results in increasing costs. The highest ratio of CE_{SS} to cost often occurs when CE_{SS} is between 70% and 80%.

1.3.3 Chemical Oxidation with Permanganate

MnO_4^- transport and distribution in the subsurface is controlled by reactions with the target contaminant and non-productive reactions with Instantaneous Natural Oxidant Demand (NOD_I) and Slow Natural Oxidant Demand (NOD_S). Model simulations indicate that the two parameters with the greatest impact on aquifer CE are: (1) the mass of MnO_4^- injected; and (2) the volume of water injected. When small amounts of MnO_4^- are injected, the reagent is rapidly consumed and pollutant removal efficiency does not increase with time after the first 30 days. However, when larger amounts of MnO_4^- are injected, the reagent can persist for several months resulting in a gradual increase in CE with time.

For constant MnO_4^- mass, increasing fluid volume injected initially results in improved treatment efficiency. However, further increases in the fluid volume injected result in little additional benefit. Conversely, when fluid volume is held constant and MnO_4^- mass is increased, treatment efficiency steadily increases, due to downgradient drift/dispersion of MnO_4^- . However, increasing the mass of MnO_4^- injected may also increase the amount of MnO_4^- that migrates out of the target treatment zone. The Conceptual Design of In Situ Chemical Oxidation (CDISCO) design tool was developed within an Microsoft Excel spreadsheet to allow users to design MnO_4^- injection systems based on a user specified minimum oxidant concentration and contact time, and evaluate the effect of different alternatives on costs.

1.4 IMPLEMENTATION ISSUES

The tools developed in this project are intended to help designers improve reagent distribution at a reasonable cost. However, designers should be aware of the numerous other factors that can lead to poor treatment including improper reagent selection, unfavorable environmental conditions, absence of required chemical catalysts or bacteria to facilitate the reaction, and chemical or biological inhibitors. Contaminant treatment efficiency will also be lower if the contaminants are primarily located in lower K zones that are not effectively contacted by the treatment reagent. Nonetheless, improving the fraction of aquifer contacted by the reagent should improve contaminant treatment efficiency at many sites.

Users should also be aware that these design tools are strictly focused on improving reagent distribution. In virtually all cases, the tools predict that CE can be increased by injecting more reagent with more water to distribute the reagent. While this should improve reagent distribution, it may also increase the potential for adverse secondary impacts, possibly including

displacement of the contaminant and changes in aquifer geochemistry. These potential impacts need to be carefully considered before implementing any in situ remediation approach.

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2.0 INTRODUCTION

This Cost & Performance Report summarizes results generated during the development of spreadsheet-based tools for the design of injection systems to treat contaminated aquifers by: 1) ISAB using EVO; 2) ISAB using SS; and 3) ISCO using MnO_4^- . The work was funded by ESTCP Project Number. ER-200626.

2.1 BACKGROUND

ISAB and ISCO can be effective approaches for treatment of a variety of K contaminants. However, to be effective the treatment reagent, EVO, SS, or MnO_4^- must be brought into close contact with the target contaminant. Although there are many common design features when injecting any reagent, each substrate has unique characteristics that impact the design process (notably longevity, mode of action, reactivity, and retention by aquifer materials), so that individual design tools are needed.

There are a variety of different approaches that can be used to distribute aqueous treatment amendments in the subsurface. Each approach has advantages and disadvantages with the “best” approach dependent on site-specific conditions. Cost and effectiveness are a function of the well layout and reagent injection procedures. Consequently, there will be an “optimum design” that will include a specific arrangement of injection wells, injection volumes and rates, and amount of reagent. Existing guidance documents provide general information on how the different remediation processes work and factors to consider when planning a remediation system. However, these documents do not provide specific information on how to actually design an injection system to provide good amendment distribution at a reasonable cost.

In recent years, a number of very powerful modeling packages have been developed that can be used to simulate the reagent transport in the subsurface under heterogeneous conditions and evaluate the effect of these reagents on treatment system performance. With these tools, users can evaluate alternative injection approaches and identify the “best” design based on site-specific conditions including aquifer K and heterogeneity, contaminant distribution, site access limitations, drilling, labor and material costs, etc.

Unfortunately, these models are rarely used to actually design in situ remediation systems. In the vast majority of cases, remediation systems are designed based on rules of thumb or prior experience. Sometimes this approach results in a good, efficient design. However, in some cases remediation systems are less effective and efficient than desired.

To reduce costs and improve effectiveness, remediation system designers need tools to quickly identify an efficient design for the specific conditions at their site without extensive site characterization or a high level of modeling expertise.

2.2 PROJECT OBJECTIVES

The overall objective of this project was to develop a set of tools to assist remediation system designers in developing effective, reasonably efficient systems for distributing aqueous amendments for in situ treatment of K contaminants. The work has focused on developing and

applying user-friendly tools to design ISAB systems using either SS or EVO, and ISCO systems using MnO_4^- . Specific objectives of this project are listed below.

1. Use currently available numerical models to understand the effects of site conditions (e.g., K, site heterogeneity, etc.) and design variables (e.g., location of wells, injection rates, volumes, amount of reagent, etc.) on reagent distribution and associated CE. Develop simple curves or procedures relating reagent distribution efficiency to amount of fluid/reagent injected. To the extent possible, present the results in a normalized or non-dimensional form (e.g., ratio of reagent injected to theoretical demand). The information learned from the modeling will provide guidance to design tool users in selection of important design parameters (e.g., PVs of injection fluid, amount of reagent, etc.).
2. Develop simple, spreadsheet-based design tools to assist designers in planning injection systems for in situ aquifer treatment with EVO, SS, and MnO_4^- . These tools will allow engineers to evaluate the effect of different design variables (e.g., well spacing [S_w], amount of reagent, injection volume, etc.) on remediation system cost and expected performance. Different tools will be developed for each of the major design alternatives (e.g., type of reagent). Experienced users who have already compiled the input data for their site (e.g., K, contaminant concentrations, etc.) should be able to develop a preliminary design for one alternative in about 1 hour.
3. Develop materials to train engineers with little or no modeling experience in the use of these design tools.

2.3 REGULATORY DRIVERS

The primary objective of this project was to develop design tools that are easy to learn, simple to use, and therefore will be widely applied. Educational materials were developed to allow new users to download the required materials, review background information, and then complete a preliminary injection system design in a few hours. The design tool is structured to allow easy use by designers with no K modeling experience. However, users are expected to be familiar with basic fundamentals of K flow, solute transport, and in situ remediation using chemical oxidation and anaerobic bioremediation.

3.0 TECHNOLOGY DESCRIPTION

3.1 TECHNOLOGY DEVELOPMENT AND APPLICATION

ISCO and ISAB are being implemented at numerous private and Department of Defense (DoD) sites. The general approach for both technologies is fairly similar. A chemical reagent (aqueous chemical oxidant or organic substrate) is distributed throughout the treatment zone using a system of temporary or permanent wells. With ISCO, an abiotic chemical reaction occurs between the chemical reagent and the contaminant to be treated. With ISAB, the organic substrate (e.g., lactate, molasses, EVO, etc.) stimulates growth of desired bacteria which catalyze a chemical reaction converting the contaminant (typically chlorinated solvents, perchlorate, or explosives) to a less toxic or less mobile form.

For both ISCO and ISAB to be effective, sufficient reagent must be brought into close contact with the contaminant to be treated. This CE becomes the critical issue—distributing reagents effectively over large areas can be very expensive. Significant costs are associated with the planning and design of the injection system, temporary or permanent wells, labor to perform the injection, and material costs for the chemical reagent or substrate.

3.2 PREVIOUS TESTING OF TECHNOLOGY

ISCO and ISAB have been applied at thousands of contaminated sites throughout the United States. While these technologies have been very effective at some sites, there are other sites where treatment results have been less than desired. The most common problem is believed to be poor delivery of the chemical reagent to the treatment zone. Poor delivery can result from: (1) not injecting sufficient reagent; (2) not injecting enough water to thoroughly distribute the reagent; and/or (3) not properly locating the injection wells.

Over the past two decades, considerable advances have been made in the ability to model transport of dissolved solutes (i.e., reagents) in the subsurface. This progress includes development of: (1) advanced numerical models for simulating the 3-D transport of reactive and non-reactive solutes in heterogeneous aquifers; (2) advanced stochastic techniques for describing subsurface heterogeneity with reasonably good databases on the statistical properties of a number of different aquifers; and (3) excellent visualization tools for examining the spatial and temporal distribution of contaminants in 3-D. With sufficient time and data, K modelers can simulate reagent movement in the subsurface. Unfortunately, at real sites, there is rarely enough time, data, or resources for modeling, so these advanced simulation and visualization models are rarely if ever used. However, these validated models can provide a credible basis for developing simpler, user-friendly design tools.

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4.0 TECHNICAL APPROACH AND METHODOLOGY

In the first phase of this project, a series of numerical model simulations were generated to evaluate the performance of different injection systems and develop guidelines on how to effectively distribute aqueous reagents in heterogeneous aquifers. Model simulations were performed using the numerical modeling packages Modular Flow Model (MODFLOW) (Harbaugh et al., 2000), Modular 3-D Transport Model (MT3D) (Zheng, 1990), and Reactive Transport 3-D Model (RT3D) (Clement, 1997) within Groundwater Modeling System (GMS) (Aquaveo, 2011) where transport of each reagent or compound was simulated by

$$R_A \frac{\partial A}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial A}{\partial x} \right) - \frac{\partial (vA)}{\partial x} + \frac{q_s}{\phi} A_s + r_A$$

- A = aqueous phase concentration of compound A
- R_A = retardation factor for compound A
- D = dispersion coefficient (m/d^2)
- v = velocity (m/d)
- ϕ = porosity (dimensionless)
- q_s = volumetric water flux of sources and sinks
- A_s = source/sink concentration for contaminant A
- r_A = reaction rate of compound A

Chemical reactions between the injected reagent (MnO_4^- , SS, or EVO), the aquifer matrix, and the contaminant(s) were simulated using the user defined modules in RT3D, implemented using Visual Fortran compiler in dynamic link libraries.

Numerical simulations were performed for the hypothetical injection grid shown in figure 1. The injection system consists of five rows of injection wells. Alternating rows are offset to improve reagent distribution. It is not practical to simulate this large area with a 3-D heterogeneous K distribution, so a subsection of the treatment area (dashed rectangle near the center of figure 1) was simulated.

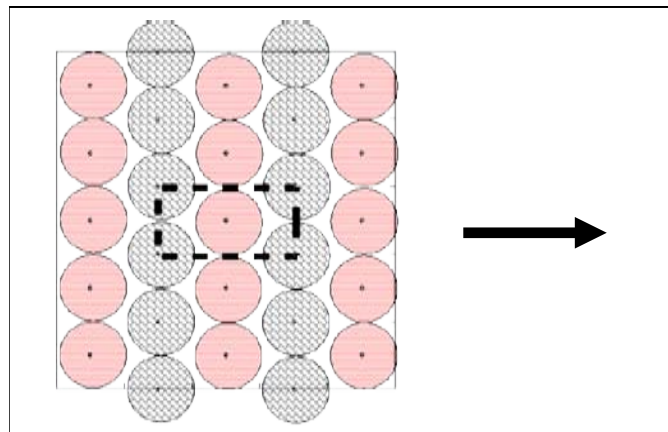


Figure 1. Hypothetical injection grid showing model domain subarea.

Figure 2 shows an enlarged view of the model domain subsection. CE was calculated for the rectangular zone between the first and third rows of wells (shaded red).

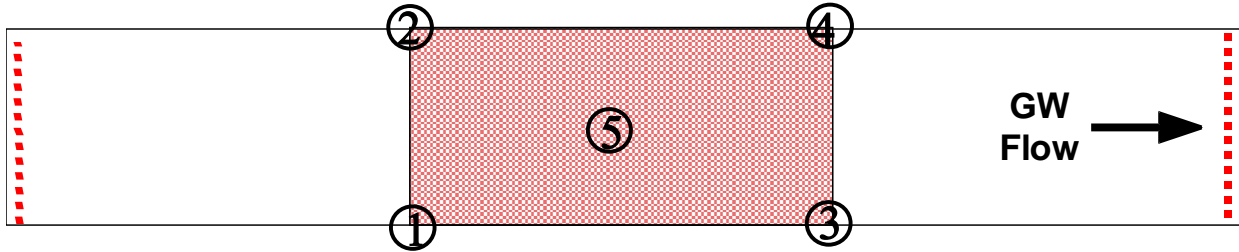


Figure 2. Model domain for base case condition-area treatment.

The effects of varying site conditions and design parameters on CE were evaluated for a standard “base case” condition (table 1). For the base case, S_w perpendicular to K flow was 3.25 m and row spacing (S_R) along the direction of K flow was 3.0 m. The model domain was 3.25 m by 18.25 m with an effective saturated thickness (Z) of 3 m. A bulk density (ρ_B) of 2 g/cm³ and an effective porosity (ϕ) of 0.2 were assumed. In addition to flow induced by the injection wells, constant head boundaries located at the upgradient and downgradient limits of the model result in a background hydraulic gradient through the treatment zone. No flow boundaries are placed to simulate a recurring pattern of injection wells perpendicular to K flow. Emulsion transport was simulated with the Method of Characteristics (MOC) solver within the MT3D and RT3D numerical models. Dispersion was simulated with the Generalized Conjugate Gradient (GCG) Package including the full dispersion tensor. Chemical reaction terms were solved using the fourth order Runge-Kutta solver. Grid discretization was $\Delta x = 0.23$ m, $\Delta y = 0.25$ m and $\Delta z = 0.05$ m resulting in a 13x72x60 grid containing 56,160 cells.

Table 1. Base case simulation conditions.

Parameter	Value	Units
Well spacing perpendicular to flow (S_x)	3	m
Well spacing parallel to flow (S_y)	6	m
Vertical thickness of treatment zone (Z)	3	m
Effective porosity (ϕ)	0.2	...
Bulk density (ρ_B)	2,000	kg/m ³
Longitudinal dispersivity (α_L)	0.01	m
Transverse dispersivity (α_T)	0.001	m
Vertical dispersivity (α_V)	0.0002	m
Molecular diffusion coefficient	1.7×10^{-5}	m ² /d
Horizontal correlation length ($\lambda_x = \lambda_y$)	2.0	m
Vertical correlation length (λ_z)	0.2	m
Injection rate per well (Q)	5.76	m ³ /d

The hydraulic conductivity field was represented as a spatially correlated random field with low, medium, and high levels of heterogeneity (i.e., the variance of $\ln K$ (σ^2) = 0.25, 1.0, and 4.0). Five realizations of the K distribution were simulated for each level of heterogeneity. The realizations were generated using the turning bands method (Tompson et al., 1989) with a horizontal correlation length of 2 m and a vertical correlation length of 0.2 m.

Figure 3 shows the hydraulic conductivity distribution in plan and longitudinal cross-section (profile) view. Higher K is indicated by the darker red and lower K is indicated by the lighter pink color. In plan view, the injected reagents appear to be concentrated close to the injection wells (data not shown). However in profile view, the effects of the heterogeneous K distribution are more apparent, causing reagents to be transported farther in high K layers and much less in lower K layers. Once injection ends, the ambient hydraulic gradient can carry a portion of the reagent downgradient, increasing CE. The extent of downgradient transport is controlled by the rate of K flow and the kinetics of reagent consumption/attachment to the solid aquifer material.

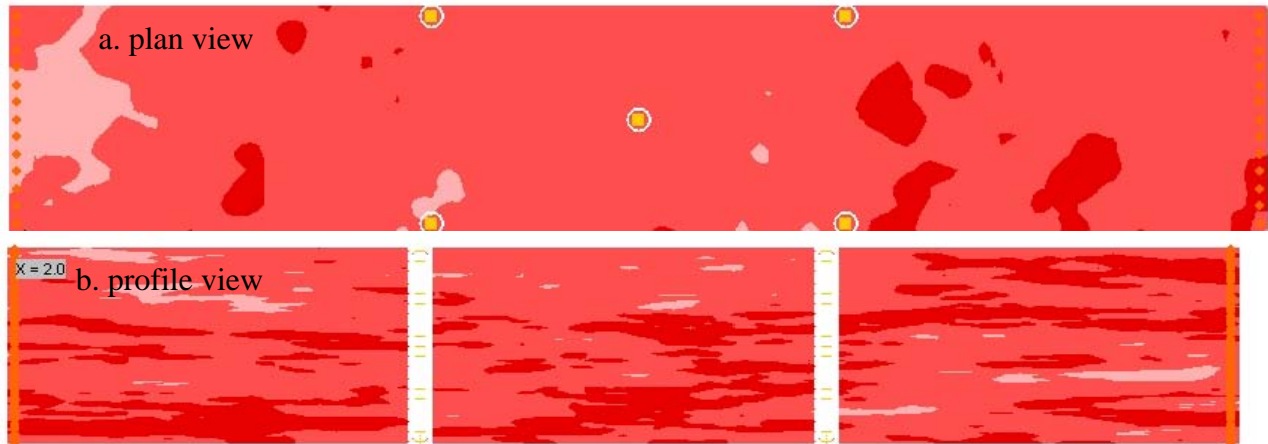


Figure 3. Hydraulic conductivity distribution used in model simulations: (a) plan view; and (b) profile view for moderately heterogeneous aquifer (realization #1).

4.1 CONTACT EFFICIENCY

For in situ treatment to be effective, two things must occur: (1) the treatment reagent (EVO, SS, or MnO_4^-) must be brought into close contact with the contaminants; and (2) environmental conditions must be appropriate for the desired chemical or biological reaction. Potentially important environmental conditions include presence of required chemical catalysts or bacteria to facilitate the reaction, appropriate pH, temperature, nutrients, and absence of chemical or biological inhibitors.

The focus of this project was on developing designs that result in improved distribution of treatment reagent throughout the target treatment zone. Good reagent distribution does not guarantee good treatment. However, it is virtually impossible to get good treatment with poor reagent distribution.

Users should be aware that contaminant treatment efficiency will often be less than the CE due to non-ideal environmental conditions (e.g., pH, temperature, etc.) and can be much lower if the contaminants are primarily located in lower K zones that are not effectively contacted by the treatment reagent. Nonetheless, improving reagent distribution can be reasonably expected to result in some improvement in contaminant treatment efficiency.

4.2 SPREADSHEET-BASED DESIGN TOOLS

For each of the technologies evaluated in this project (anaerobic bioremediation with EVO, anaerobic bioremediation with SS, and chemical oxidation with MnO_4^-), simple spreadsheet-based tools were developed to allow designers to evaluate the effect of different design variables (e.g., well spacing, amount of reagent, injection rate, etc.) on remediation system cost and expected performance. The design tools consist of a series of linked worksheets for data entry and evaluation of different design alternatives. In the first worksheets, users enter information on site characteristics (e.g., depth, aquifer material, K, porosity, etc.) and costs (e.g., labor, drilling, site access restriction, discount rate, etc.). This information feeds into separate spreadsheets for planning the remediation system and evaluating overall costs. However, the design tools are not intended to generate detailed cost estimates.

5.0 ANAEROBIC BIOREMEDIATION WITH EMULSIFIED VEGETABLE OIL

5.1 NUMERICAL MODELING OF EMULSIFIED VEGETABLE OIL DISTRIBUTION

Transport and retention of EVO in K was simulated using a rate limited sorption approach where the rate of mass transfer between the mobile and immobile phases is proportional to the concentration gradient between both phases. The rate of exchange with the solid phase can be simulated as:

$$\frac{\partial C_s}{\partial t} = K_m \frac{\phi}{\rho} (C_a - C^*)$$

where C_s is the solid phase concentration, C_a is the aqueous phase concentration, C^* is the sorbed concentration in equilibrium with the aqueous phase, and K_m is the aqueous-solid mass transfer rate. Retention of oil droplets by the aquifer solids was represented with a Langmuir isotherm:

$$C^* = C_s (K_1 K_2 - K_1 C_s)^{-1}$$

where K_1 is the binding constant and K_2 is the maximum sorption capacity.

5.2 AQUIFER VOLUME CONTACT EFFICIENCY

The performance of different injection systems for distributing EVO was evaluated based on the aquifer volume contact efficiency (E_v) or the fraction of the target treatment zone where the oil concentration after injection is greater than 5% of the maximum possible oil retention (K_2). Currently, there is no well-established procedure to determine what oil concentration is required for effective treatment. Even very small amounts of oil will initially support anaerobic biodegradation. However, if the amount of oil retained is too low, the oil will be rapidly depleted and long-term performance will be reduced.

5.3 EFFECT OF SCALING FACTORS ON CONTACT EFFICIENCY

Results from an extensive series of sensitivity analyses demonstrated that E_v is primarily controlled by the volume of EVO injected and the volume of water injected to distribute the reagent. To allow easy comparison between different simulations, the mass of oil injected and volume of fluid injected are presented as dimensionless scaling factors. The volume scaling factor (SF_v) is the ratio of fluid (emulsified oil plus water) injected per well to the PV within a base treatment zone (BTV) around each well or:

$$SF_v = \text{Volume fluid injected per well} / (\phi BTV)$$

where ϕ is the effective porosity. For area treatment, the $BTV = S_w S_R Z$.

The mass scaling factor (SF_M) is the ratio of oil injected per well to the oil required to fill all the attachment sites within the BTV or:

$$SF_M = \text{Mass oil injected per well} / (\text{OR}_M \rho_B \text{ BTV})$$

where OR_M is the maximum oil retention per unit weight aquifer material. OR_M is identical to K_2 used in the emulsion transport model.

Figure 4 shows the effect of varying water injection volume (represented by SF_V) and mass of EVO (represented by SF_M) on E_V . The highest E_V are obtained for large values of SF_M and SF_V .

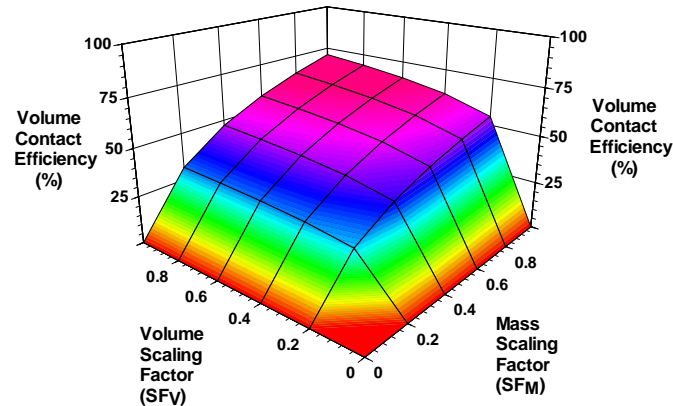


Figure 4. Effect of SF_V and SF_M on volume contact efficiency for a moderately heterogeneous aquifer with well spacing approximately equal to row spacing.

Overall, the model simulation results indicate that it is relatively easy to achieve a volume CE of 50-60% for a moderately heterogeneous aquifer. However, it becomes progressively more difficult to achieve higher contact efficiencies and it may not be practical to achieve contact efficiencies above 70% in heterogeneous aquifers.

Readers are reminded that CE is not the same as treatment efficiency. When emulsified oil is injected into the subsurface, it primarily migrates through and contacts the higher K zones. Contaminants present in these higher K zones will come in direct contact with the oil and should biodegrade relatively rapidly. Once contaminants in the higher K zones are degraded, contaminants will begin to slowly diffuse out of the lower K zones and will be treated. However, diffusion out of these lower K zones is a slow process, requiring years or even decades to occur. One of the major advantages of the emulsified oil process is that the oil biodegrades slowly, supporting biodegradation for years. As long as significant oil remains in the higher K zones, contaminant concentrations in monitor wells will remain low and the flux of contaminants transported downgradient will remain low. In addition, diffusion of contaminants out of the lower K zones will be enhanced and the rate of source area treatment will be increased. Under these conditions, E_V of 40-50% may provide good treatment, and increasing E_V to 60% may provide little additional benefit. Unfortunately, the project team does not currently have any way to quantitatively relate volume CE to cleanup rate.

5.4 EMULSIFIED VEGETABLE OIL DESIGN TOOL DEVELOPMENT AND EVALUATION

A design tool was developed to assist engineers with the design of systems for distributing EVO for ISAB of K contaminants in barrier and area treatments. The design tool consists of several worksheets broken into four sections entitled: Site Data, Installation and Injection, Barrier Treatment, and Area Treatment. Details of the model development and all calculations are presented in Borden et al. (2008a, 2008b). Additional information on design of anaerobic bioremediation systems is available in Air Force Center for Environmental Excellence (AFCEE) et al. (2004) and in Solutions-IES (2006).

A series of sensitivity analyses were performed to identify factors that had a major influence on cost and performance. In all analyses, results are presented for the well spacing with the lowest 30-year net present value (NPV). Results are compared to a base case intended to represent a typical site.

- For optimum contaminant removal, emulsified oil barriers and area treatments should be designed to achieve the highest CE that can be cost-effectively achieved. However, increasing CE also increases costs.
- Sensitivity analysis results indicate that both capital and life-cycle costs are relatively insensitive to site conditions, for both barrier and area treatment. Obviously, total costs are often higher for large, wide, deep sites. Unit costs are often higher for smaller sites due to the proportionately higher fixed costs associated with planning, design, and monitoring.
- The target CE for barriers does not typically have a major impact on cost for values less than 85%. However, increasing in the target CE for a barrier above 85% often results in a substantial cost increase. For area treatment, estimated costs increase approximately linearly with target CE.
- Errors in estimation of the OR_M by the aquifer material can have a major impact on cost and performance for both barrier and area treatment. Given the importance of this parameter, OR_M should be directly measured on field or lab samples whenever possible.

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6.0 ANAEROBIC BIOREMEDIATION WITH SOLUBLE SUBSTRATE

6.1 NUMERICAL MODELING OF SOLUBLE SUBSTRATE DISTRIBUTION

A series of numerical model simulations were conducted to evaluate the effect of important design parameters on SS distribution assuming SS can be represented using first order irreversible kinetic reaction. Contaminant biodegradation was not explicitly simulated. Instead, contaminant biodegradation was assumed to be enhanced when the concentration of the organic substrate is greater than a user defined C_{min} .

6.2 STEADY STATE CONTACT EFFICIENCY

In this work, effective treatment was assumed to occur when the substrate concentration is greater than a user defined C_{min} . However, CE varies over time as the SS is depleted or washed out of the target treatment zone and as additional substrate is injected (figure 5). Immediately after the start of injections, CE increases steadily with time as more and more of the treatment zone becomes contacted. However, CE eventually reaches a quasi-steady-state value when the amount of substrate injected is balanced by the loss of substrate due to decay and downgradient transport. This steady-state value is defined as the CE_{SS} and was used as the primary measure of SS treatment performance.

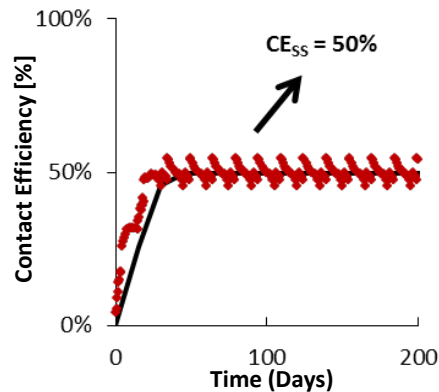


Figure 5. Variation of SS treatment zone contact efficiency with time.

6.3 EFFECT OF DESIGN PARAMETERS ON STEADY-STATE, VOLUME AVERAGE CONTACT EFFICIENCY

An extensive series of sensitivity analyses were conducted to examine the impact of substrate injection concentration (C_I), C_{min} , K travel time (T_T) between rows of injection wells, substrate half-life (T_H), time period between substrate reinjections (T_R), PVs of substrate solution injected, and CE_{SS} . Analysis of these results revealed that CE_{SS} can be accurately predicted based on four dimensionless variables: 1) C_I/C_{min} ; 2) PV; 3) T_T/T_H ; and 4) T_R/T_T .

Figure 6 shows the effect of the dimensionless variables C_I/C_{min} , PV, T_T/T_H , and T_R/T_T on CE_{SS} . The highest contact efficiencies are indicated by the dark red or maroon color while the

lowest CEs are indicated by the blue color. As expected, CE_{SS} can be increased by injecting larger volumes of water (increasing PV) containing higher concentrations of organic substrate (higher C_I/C_{min}). CE_{SS} can also be increased when T_R is less than the T_T between wells ($T_R/T_T < 1$) and when the substrate T_H is greater than T_T between rows of injection wells ($T_T/T_H < 1$).

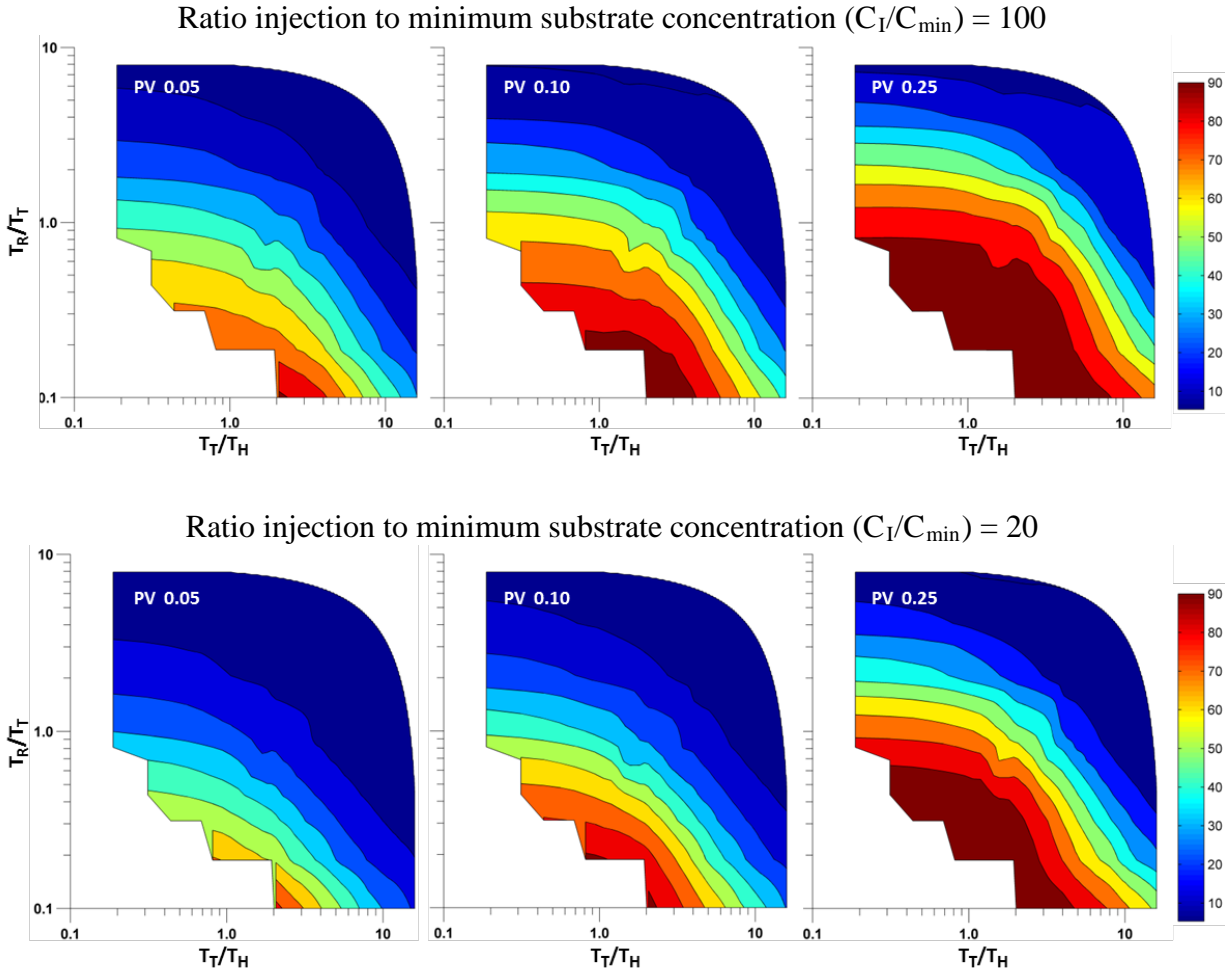


Figure 6. Effect of dimensionless variables C_I/C_{min} , PV, T_T/T_H , and T_R/T_T on CE_{SS} .

The effect of these parameters on remediation system design can be evaluated by considering a typical site where the K velocity is 120 ft/year and rows of injection wells are spaced 10 ft apart ($T_T = 1$ month). Assuming the SS solution is injected once per month ($T_R = 1$ month), then $T_R/T_T = 1$. If the SS has a T_H of 1 month, then $T_T/T_H = 1$. Assuming the minimum SS concentration for effective treatment (C_{min}) is 50 mg/L, injecting 0.25 PV of a solution containing 1,000 mg/L SS ($C_I/C_{min} = 20$) would result in a CE_{SS} close to 70%. A similar CE_{SS} could be achieved by injecting 0.1 PV of solution containing 5,000 mg/L SS ($C_I/C_{min} = 100$). However, this high injection concentration could lead to an excessive drop in pH or biofouling of the injection wells. These other, potentially critical factors, were not considering in this modeling analysis. Costs could be reduced by increasing the time between injections to 2 months ($T_R/T_T = 2$), but would reduce CE_{SS} to below 30%.

6.4 SOLUBLE SUBSTRATE DESIGN TOOL DEVELOPMENT AND EVALUATION

A design tool was developed to assist engineers with the design of systems for distributing SS for ISAB of K contaminants in area treatments. The design tool consists of several worksheets broken into four sections entitled: Site Data, Installation and Injection Cost, Substrate, and Remediation Design. Within each section, there are several subsections for data entry and design calculations. Details of how the model was developed and all calculations are presented in Borden et al. (2012). Additional information on design of anaerobic bioremediation systems is available in AFCEE et al. (2004).

A series of sensitivity analyses were conducted with the design tool to identify factors that had a major influence on costs and performance. In all analyses, results are presented as NPV assuming a 5-year operating period. Results are compared to a base case condition intended to represent a typical site. Major results of this analysis include the following:

- Total costs to treat a site for 5 years using SS is relatively insensitive to site conditions. Obviously, total costs are often higher for large, wide, and deep sites. Unit costs are often higher for smaller sites due to the proportionately higher fixed costs associated with planning, design, and permitting.
- Estimated CE_{SS} can be increased by varying different design parameters including C_I , C_{min} , K , T_T between rows of injection wells, SS , T_H , T_R , and PVs of substrate solution injected. In most cases, increasing CE_{SS} results in increasing costs. For many parameters, there is some middle range where the ratio of CE_{SS} to 5-year costs is highest.
- Optimized designs can be developed by simultaneously varying several different design parameters to generate alternatives that result in the lowest cost for a specified value of CE_{SS} . In many cases, the highest ratio of CE_{SS} to cost occurs for CE_{SS} in the range of 70-80%. If higher CE_{SS} results in more rapid cleanup, it may be desirable to aim for higher contact efficiencies to reduce total life cycle costs.

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7.0 CHEMICAL OXIDATION WITH PERMANGANATE

7.1 NUMERICAL MODELING OF PERMANGANATE DISTRIBUTION

A series of numerical model simulations were conducted to evaluate the effect of important design parameters on MnO_4^- distribution. MnO_4^- consumption was simulated as an instantaneous reaction with the contaminant and NOD_I , and a second order reaction with NOD_S .

Model simulation results indicate that the two parameters with the greatest impact on E_V and pollutant treatment efficiency are: (1) the mass of MnO_4^- injected; and (2) the volume of water injected. When small amounts of MnO_4^- are injected, the reagent is rapidly consumed and CE does not increase with time after the first 30 days. However, when larger amounts of MnO_4^- are injected, the reagent can persist for several months resulting in a gradual increase in CE with time. For constant MnO_4^- mass, increasing fluid volume injected initially results in an improvement in CE. However, further increases in fluid volume injected result in little additional benefit. Conversely, when fluid volume is held constant and MnO_4^- mass is increased, CE steadily increases, due to downgradient drift/dispersion of MnO_4^- . However, increasing mass of MnO_4^- injected also increases the amount of MnO_4^- that migrates out of the target treatment zone.

Common approaches for improving remediation system performance include: (1) reducing the injection well spacing; and (2) performing multiple MnO_4^- injections in the same well. Numerical model simulation results indicate that both well spacing within a row and S_R have only a modest impact on either E_V or fraction of un-reacted MnO_4^- (U), when relatively small amounts of MnO_4^- and fluid are injected (SF_V and $SF_M < 0.25$). However, for larger amounts of reagent and fluid injected, increased S_R has a substantial negative impact, reducing volume CE and increasing the amount of U released downgradient.

Numerical model simulation results indicate that if the total volume of fluid injected and mass of reagent is held constant, multiple injection events will not increase CE compared to a single large injection event, and can increase the amount of U released downgradient. This result occurs because several small injections through the same wells repeatedly treat the same area around the wells, resulting in more complete removal of NOD_S near the injection well. In contrast, a single large injection can more rapidly transport MnO_4^- away from the injection well, increasing the fraction of aquifer contacted. However, at many sites it may not be practical to inject a large amount of water in a single injection due to pressure buildup in the aquifer and multiple injections are therefore required. In these cases, multiple small injections can significantly improve performance compared to a single small injection.

Aquifer heterogeneity appears to have a complex relationship with remediation system performance. The presence of higher K channels in the moderate and high heterogeneity simulations may allow more rapid transport of MnO_4^- away from the injection well when only a small amount of fluid is injected, improving contaminant treatment. However, MnO_4^- cannot penetrate the lower K zones in highly heterogeneous formations, reducing the maximum level of treatment that can be achieved.

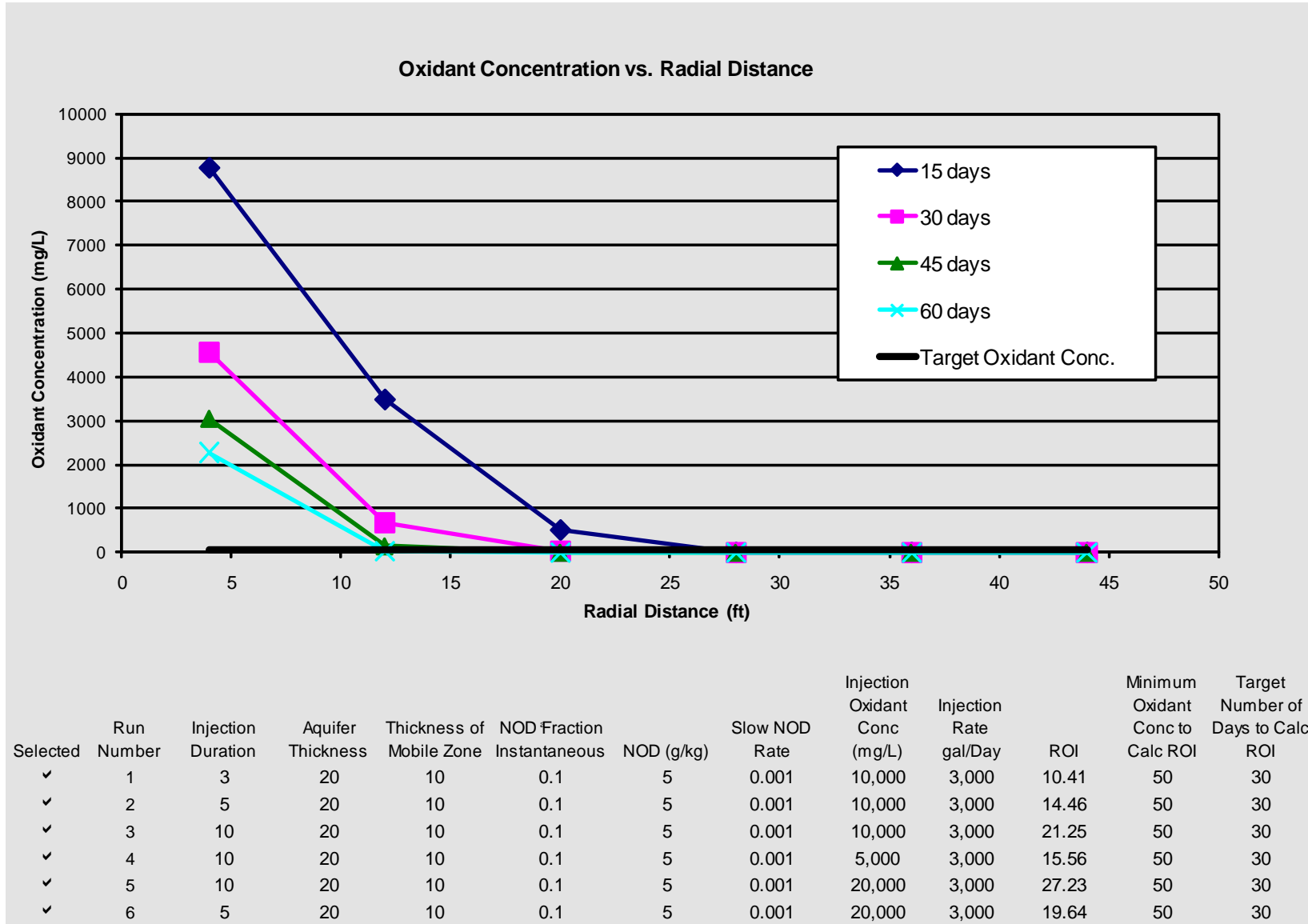
7.2 CONCEPTUAL DESIGN OF IN SITU CHEMICAL OXIDATION DEVELOPMENT AND EVALUATION

The CDISCO design tool was developed in cooperation with ESTCP project ER-200623 to assist in planning MnO_4^- injection systems. CDISCO is used to estimate the effective radius of influence (ROI) based on user-specified values for contact time and the critical MnO_4^- concentration. This ROI is then used to determine required well spacing and injection parameters, and to generate preliminary cost estimates. Injection parameters can be quickly changed, allowing designers to easily evaluate multiple alternatives and identify lower cost, more effective designs. Details of how CDISCO was developed and all calculations are presented in Borden et al. (2010). Additional information on design of ISCO systems is available in United States Environmental Protection Agency (USEPA) (1998), Interstate Technology & Regulatory Council (ITRC) (2005), Huling and Pivetz (2006), and Siegrist et al. (2009).

CDISCO is implemented within a Microsoft Excel spreadsheet. On the first worksheet, users enter information on aquifer characteristics (e.g., porosity, hydraulic conductivity, injection interval, NOD, contaminant concentrations, etc.), injection conditions (MnO_4^- injection concentration, flow rate, and duration), and target conditions (minimum oxidant concentration and duration to calculate ROI). The MnO_4^- transport model then computes the spatial distribution of MnO_4^- , NOD_I , and NOD_S as a function of radial distance at various times. Figure 7 shows typical output from the MnO_4^- transport model simulations. The graph shows the variation in MnO_4^- concentration versus distance at several different times (15, 30, 45, and 60 days for this simulation). The table at the bottom shows input parameters for a series of prior simulations. The effective ROI is computed for a user specified time and minimum oxidant concentration.

CDISCO also includes a simplified procedure to generate preliminary cost estimates based on the user-specified treatment area dimensions, injection ROI overlap (%), number of injection events planned; fixed cost; and unit costs for injection point installation, chemical reagents, and labor for injection. Two injection approaches are considered— injection through direct push rods or through wells. Cost factors are included for mobilization, labor, materials, equipment rental, travel, and subcontractor costs.

Figure 8 shows typical output from the cost estimating procedure comparing preliminary estimates for several different design alternatives. Aquifer parameters, treatment area dimensions (100 ft x 100 ft), ROI overlap (25%), time to calculate ROI (30 days), minimum oxidant concentration (50 mg/L), and number of injection events (5) are constant for all alternatives. Alternative 1 has a relatively high cost because the short injection duration (3 days) required a large number of injection points. Alternative 5 has a lower cost because the longer injection duration (10 days) and higher oxidant concentration (20,000 mg/L potassium permanganate [KMnO_4]) reduced number of injection points required.



^aNatural Oxidant Demand

Figure 7. Typical output from permanganate transport model.

Run	1	2	3	4	5	6
Total Fixed Costs (injection)	\$94,800	\$94,800	\$94,800	\$94,800	\$94,800	\$94,800
Total Well Installation Costs	\$85,667	\$47,700	\$25,367	\$41,000	\$18,667	\$29,833
Total Injection Costs	\$478,800	\$410,400	\$364,800	\$684,000	\$228,000	\$228,000
Total Oxidant Cost	\$378,547	\$324,469	\$288,417	\$270,391	\$360,521	\$360,521
Total Installation and Injection Costs	\$1,037,814	\$877,369	\$773,384	\$1,090,191	\$701,988	\$713,155
Number of probes or wells required	35	18	8	15	5	10
NOD (g/kg)	5	5	5	5	5	5
Injection Oxidant Concentration	10000	10000	10000	5000	20000	20000
Injection Oxidant Mass (lbs)	26288	22533	20029	18777	25036	25036
Injection Duration (days)	3	5	10	10	10	5
Volume Injected per Day (gal/d)	3000	3000	3000	3000	3000	3000
Thickness of Mobile/Target Thickness	0.5	0.5	0.5	0.5	0.5	0.5

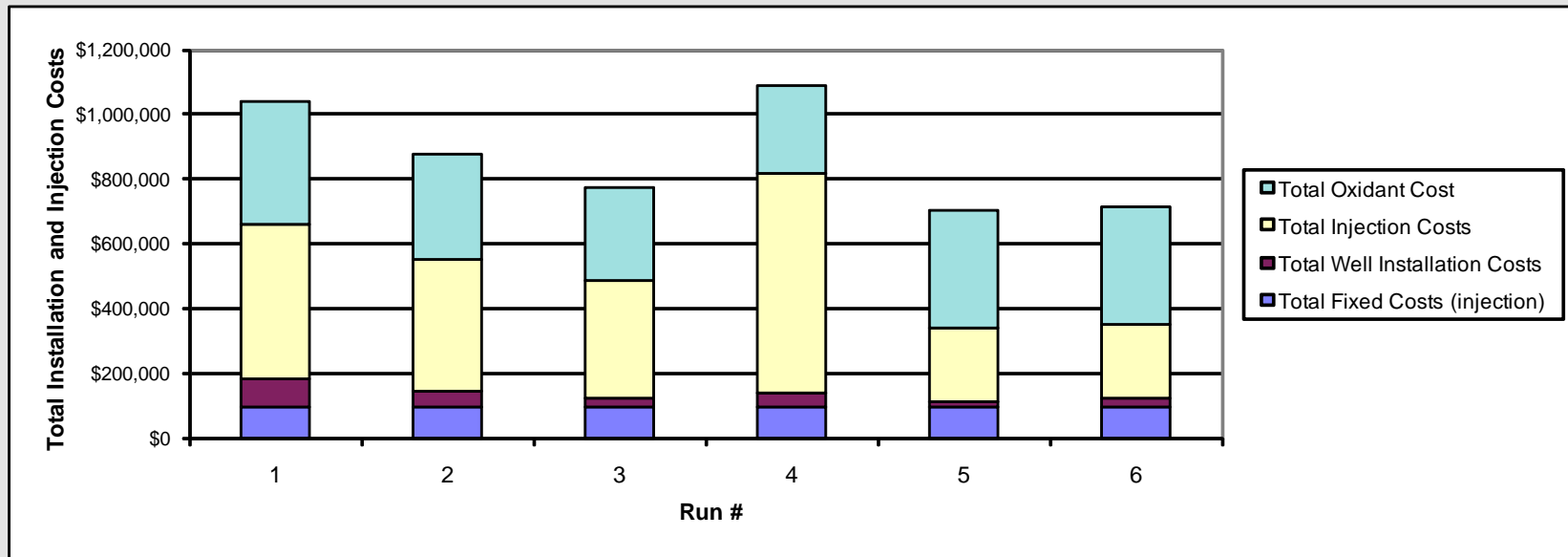


Figure 8. Typical output from injection scenario cost comparison.

8.0 IMPLEMENTATION ISSUES

In this project, a series of spreadsheet-based tools were developed to assist in the design of injection systems to treat contaminated aquifers by: 1) ISAB using EVO; 2) ISAB using SS; and 3) ISCO using MnO_4^- . The tools are relatively simple to use, allowing designers to evaluate the effect of different design variables (e.g., S_w , amount of reagent, injection volume, etc.) on remediation system cost and expected performance. After a few hours of study, designers can evaluate a proposed injection system in about an hour.

Design tool users do not need any formal training or background in K modeling. However, they should have a good understanding of the remediation technology being considered (anaerobic bioremediation or chemical oxidation) and common injection technologies. Prior to beginning use of these tools, users should already have completed a site characterization to define general site characteristics (lithology, K, flow velocity), contaminant distribution and conducted a preliminary screening to determine if the remediation approach is appropriate for the conditions at their site.

8.1 DESIGN TOOL LIMITATIONS

For effective treatment, the injected reagents must come into contact with the contaminant. The tools developed in this project are intended to help designers improve reagent distribution at a reasonable cost. In many cases, this should improve contaminant treatment efficiency. However, designers should be aware of the numerous other factors that can lead to poor treatment including improper reagent selection, unfavorable environmental conditions (e.g., pH, temperature, nutrients, etc.), absence of required chemical catalysts or bacteria to facilitate the reaction, and chemical or biological inhibitors. Contaminant treatment efficiency will also be lower if the contaminants are primarily located in lower K zones that are not effectively contacted by the treatment reagent. Nonetheless, improving the fraction of aquifer contacted by the reagent should improve contaminant treatment efficiency at many sites.

Users should also be aware that these design tools are strictly focused on improving reagent distribution. In virtually all cases, the tools predict that CE can be increased by injecting more reagent and by injecting more water to distribute the reagent. While this approach should improve reagent distribution, it may also increase the potential for adverse secondary impacts, possibly including displacement of the contaminant and changes in aquifer geochemistry (e.g., increases in dissolved manganese, iron, sulfide, total organic carbon, methane, odor, color, etc.). These potential impacts need to be carefully considered before implementing any in situ remediation approach.

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9.0 COST ANALYSIS

The tools developed in this project for design of remediation systems with EVO, SS, and MnO_4^- are based on the Microsoft Excel spreadsheet, so the actual training required to use the tools is minimal. Experienced remediation professionals can easily learn to use these tools after a 45 min overview presentation. Once trained, remediation system design with these tools is quicker and less expensive than current hand calculation approaches. Based on experience of the project team, it is relatively easy to reduce the cost of a \$500,000 remediation project by 10-20% saving \$50,000-\$100,000 with 1-2 hours of work.

In addition to cost savings, the most important benefit of using these tools is the improved performance and reliability of the remediation systems. Prior to this project, remediation professionals did not have any way to quantify the potential benefits of a more effective design, but did have excellent tools for evaluating the impact on cost. Given the uncertain benefits associated with more robust designs (i.e., injecting more material or using more closely spaced wells) and the specific quantitative information on costs, most people will bias towards cheaper, less effective designs. While it is difficult to quantify the economic benefit of improved performance, remediation efforts are expensive. Reducing the likelihood of remediation system failure should have a strong economic benefit.

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APPENDIX A
POINTS OF CONTACT

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