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In Situ Chemical Oxidation: Permanganate Oxidant Volume Design Considerations

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Abstract

Contaminant rebound and low contaminant removal are reported more frequently with in situ chemical oxidation than other in situ technologies. Although there are multiple causes for these results, a critical analysis indicates that low oxidant volume delivery is a key issue. The volume of oxidant injected is critical and porosity of the aquifer matrix can be used to estimate the pore volume. The total porosity (q_T) is the volume of voids relative to the total volume of aquifer material. The mobile porosity (q_M) is the fraction of voids that readily contributes to fluid displacement, and is less than q_T leading to smaller estimates of oxidant volume. Injecting low-oxidant volume may result in inadequate oxidant distribution and postinjection dispersal within the radius of influence, insufficient oxidant contact and oxidant loading, and incomplete treatment; whereas, greater oxidant volume achieves a greater oxidant footprint and may involve risk that the injected oxidant may migrate into nontarget areas and displacement of contaminated groundwater. Design guidelines and recommendations are provided that could help achieve more effective technology deployment, reduce the role of heterogeneities in the subsurface, and result in greater probability the oxidant is delivered to the targeted treatment zone.

Introduction and Background Information

The U.S. Environmental Protection Agency (US EPA) Superfund remedial program continues to select in situ chemical oxidation (ISCO) as one of the most frequently selected in situ treatment technologies (US EPA 2014). These trends in technology selection indicate the need for the continued development of ISCO, a technology that has the ability to transform contaminants in the subsurface while minimizing the use of fossil fuel energy,

chemicals, and environmental impact (Siegrist et al. 2001, 2011; Huling and Pivetz 2006). A review of ISCO design and performance was performed involving 242 case studies including 83 sites where permanganate was used for the remediation of chloroethanes (Krembs et al. 2010, 2011). The median reduction in contaminant concentration in groundwater using permanganate was 51% with contaminant rebound observed at 78% of the sites. In another review of ISCO case studies, a median reduction in total chlorinated volatile organic compounds (CVOCs) concentrations of 72% was observed at 12 ISCO sites, but rebound was more prevalent relative to bioremediation, thermal, or solvent/cosolvent treatment (McGuire et al. 2006). In another remediation survey at dense nonaqueous phase liquids sites, the occurrence of rebound was reported to be more prevalent at ISCO sites compared to sites implementing other technologies (GeoSyntec Consultants 2004).

The consistency in the conclusions from these surveys regarding ISCO treatment performance possibly suggests a systematic cause and effect in technology design, deployment, and performance results. The cause of contaminant rebound and low contaminant removal reported in these cases is attributed to multiple causes and mechanisms. Here, we propose that low oxidant volume delivery is a key issue. The objectives of this manuscript are to contrast and critically analyze two methods used in estimating the volume of oxidant to inject in the targeted treatment zone (TTZ), clarify the impact of this important design parameter, and recommend injection design options that limit the role of heterogeneities and its negative impact on oxidant distribution. Several forms of oxidant can be used in ISCO but the focus of this study is potassium and sodium permanganate (KMnO_4 and NaMnO_4). A detailed description of the fundamentals of ISCO using permanganate is described elsewhere (Siegrist et al. 2001, 2011; Petri et al. 2011). ISCO is often used as a source reduction remedy in TTZs where efficient oxidation can be achieved, and is not generally applied over the entire footprint of the groundwater plume. Therefore, the TTZ defined here refers to the contaminated volume of porous media in the source area requiring oxidative treatment to achieve the treatment objective.

Importance of Oxidant Volume

The delivery of a sufficient volume of oxidant is required to achieve adequate coverage of the oxidant in the TTZ. The oxidant volume must contain sufficient oxidant mass to achieve the oxidant loading and treatment objectives. The combination of both oxidant volume and oxidant concentration (i.e., oxidant loading) is required to address both oxidant distribution in the TTZ, and to target contaminant and noncontaminant oxidant losses including the natural oxidant demand (NOD) (Mumford et al. 2005; Urynowicz et al. 2008; Xu and Thomson 2009; Cha et al. 2012). The focus of this critical analysis is on the immediate contact between injected oxidant and aquifer media. The postinjection oxidant transport in the downgradient direction could result in greater contact between oxidant and aquifer solids, and is dependent on hydrogeologic conditions and oxidant loading. For example, the aquifer volume contact efficiency (E_V) is an empirical measure of the oxidant impact on aquifer solids relative to the total volume of the treatment zone (Cha and Borden 2012). In an evaluation of aquifer characteristics and ISCO injection system design, numerical simulations of oxidant injection, transport, and reaction in porous media indicate that increases in E_V are functionally dependent on oxidant loading, persistence, and advective

transport. Simulation results indicated that the mass and volume of permanganate injected had the greatest impact on E_V and contaminant treatment efficiency (Cha and Borden 2012). These parameters were also identified by others as a key aspect for ISCO design (Bachiochi et al. 2014).

Estimating Pore Volume

Porosity is a design parameter used to estimate the pore volume (PV) within the radius of influence (ROI). The total porosity (q_T) of unconsolidated porous media is the volume of voids (V_V) relative to the total volume (V_T) of aquifer material ($q_T = V_V/V_T$). In unconsolidated porous media, the volume of oxidant injected into the subsurface required to fill the pore spaces within the ROI can be estimated as $q_T \times V_{ROI}$ (i.e., PV), ideally where V_{ROI} is the total volume within the ROI and the vertical interval.

A fraction of the water in porous media is attracted to the surfaces of the solids through forces of molecular attraction and is functionally dependent on the surface area of the sediment minerals (Marsily 1986). Unconnected, poorly connected, and dead-end pores are responsible for the fraction of water in porous media that do not contribute to fluid displacement. Thus the concept of porosity is expanded to include effective porosity which is linked to the displacement of pore fluid rather than to the percentage of the volume occupied by the pore spaces. Payne et al. (2008) reported that a fraction of the total porosity that contributes to advective flow and transport of groundwater in aquifers is the mobile porosity (q_M), and the portion of the void space that does not contribute to the advective flow of groundwater behaves as immobile or slowly moving groundwater is the immobile porosity (q_I). The total porosity is the sum of mobile and immobile porosity ($q_T = q_M + q_I$). Decisions between the selection of mobile porosity and total porosity in designing the volume of oxidant to be injected into the TTZ is an important distinction and can have major implications in ISCO.

Critical Analysis of Oxidant Volume Estimation Methods

Mobile Porosity Method

Payne et al. (2008) reported that standard aquifer testing protocols obtain the average hydraulic conductivity (K) which combines the high and low K , and consequently understates the actual flow velocities. This implies that the breakthrough of a solute in groundwater, whether it is a tracer, contaminant, or oxidant will occur faster than predicted if based on the average K . The “actual groundwater velocity,” determined by tracer studies and used to estimate the mobile velocity, is significantly greater than the average velocity (Payne et al. 2008). Tracer study design, implementation, and data interpretation can be complex and very few sites yield the “ideal” tracer distributions that allow easy analysis (Payne et al. 2008). Complexities include tracer selection, tracer injection rates, monitoring network, tracer detection and analysis, retardation, reactive transport, and tracer test interpretation including variability in tracer breakthrough due to localized aquifer heterogeneities, poor or skewed recovery, depth-integration, and other factors (Ptak et al. 2004; Payne et al. 2008; Suthersan et al. 2014).

A summary of tracer test results ($n = 15$) conducted in various aquifer materials yielded estimated values of mobile porosity ranging from 0.0008 to 0.18 (Table 1) (Payne et al. 2008). The mobile porosity of sand and gravel aquifers was estimated to be less than 0.1, and it was suggested that mobile porosity values ranging from 0.02 to 0.10 would be more appropriate than using the often recommended 0.20 value as the effective porosity (Payne et al. 2008). In another summary of q_M values estimated through tracer tests in alluvial aquifers ($n = 73$), the q_M was £0.09 at 50% of the sites, and £0.15 for about 80% of the sites (Suthersan et al. 2014). It was concluded that a small portion of the total pore space meaningfully participated in flow and advective solute transport.

Site-specific tracer tests which are used to quantify q_M involve measuring the volume of tracer injected (Vol_{inj50}) to reach 50% of the maximum observed breakthrough concentration ($C_{MAX}/2$) in the dose response (i.e., monitoring) wells (Equation 1; Figure 1) (h = vertical injection interval). Ideally, the $C_{MAX}/2$ should be nearly half the injected tracer concentration (C_O); however, low tracer injection volume, long distances between injection and dose response wells, and structural failure of the aquifer matrix (Payne et al. 2008) contributes to low tracer recovery (i.e., $C_{MAX}/2 < C_O/2$) and to uncertainty in tracer transport and projections in solute transport. The inability to define tracer transport is also attributed to a poorly defined conceptual site model and insufficient monitoring well density and placement (Suthersan et al. 2014). The mobile fraction velocity (V_q) (refer to inset in Figure 1) is greater than the average groundwater velocity (V_{AVG}) and when used in conjunction with q_T , these parameters can be used to estimate q_M (Equation 2; Figure 1) (Payne et al. 2008).

$$\theta_M = Vol_{inj50} / (\pi \times ROI^2 \times h) \quad (1)$$

$$\theta_M = V_{AVG} \times \theta_T / V_\theta \quad (2)$$

In these equations, it is evident that the concept of micro-scale variability in mobile-immobile porosity characteristics is intrinsically extended from one distinct layer of limited scale, across the vertical injection (i.e., screened) interval involving varying geologic and hydrogeologic characteristics exhibiting a range in permeability (Figure 1). Under this condition, it is proposed that estimates of mobile porosity correspond to cross-sections of the formation with the highest permeability and the immobile porosity with the lowest permeability. Consequently, extrapolation of mobile porosity concepts across lengthy vertical intervals introduces complexity in assessing the specific role of porosity in groundwater and solute transport as it invites the role of other parameters that impact groundwater transport, including differing depositional processes and materials.

It has been proposed that q_M can be used to determine the injection volume to achieve adequate reagent coverage at a given radial distance from an injection well (Suthersan et al. 2014). Assuming a simplified radial flow-cylindrical porous media conceptual model, the q_M , the vertical injection interval, and the ROI, the volume of oxidant ($V_{OXIDANT, q_M}$) can be estimated (Equation 3) (Payne et al. 2008).

$$V_{\text{OXIDANT}, \theta_M} = \Pi \text{ROI}^2 \theta_m h \quad (3)$$

Tracer Testing, Mobile Porosity, and Contaminant Distribution—The most permeable and highly conductive aquifer media characterized through tracer testing is predominantly responsible for estimates of q_M , but may not correspond with the majority of contamination. Rigorous site characterization is needed to validate and establish a correlation between contaminated intervals in the TTZ and the intervals involved in tracer transport. Slow, steady diffusion of contaminants into low permeable materials may have occurred over decades accounting for significant contaminant storage relative to more permeable portions of the aquifer (Chapman and Parker 2005; Stroo et al. 2012) represented by mobile porosity. Specifically, “immobile pores” involving either lower permeability lenses or layers at the macro-scale, or “immobile pores” in which groundwater transport is slow or impeded at the micro-scale may not contribute to tracer transport, but may be highly contaminated.

Total Porosity Method

Total porosity measurements of aquifer media using laboratory methods (Danielson and Sutherland 1986) are relatively simple and low cost, or field geophysical methods (resistivity, neutron, and gamma-gamma radiation) can be used (Marsily 1986). Total porosity can also be calculated from site-specific measurements or estimates of the bulk density (ρ_{BULK}) and particle density (ρ_{PD}) of aquifer material (Equation 4). Values of total porosity tabulated from many measurements over a wide range of aquifer media (Table 1), and that exhibit similar compositional characteristics to the TTZ can be used for oxidant volume design. Assuming the simplified radial flow-cylindrical porous media conceptual model, total porosity, the vertical injection interval, and the ROI, the volume of oxidant ($V_{\text{OXIDANT}, \theta_T}$) can be estimated (Equation 5). This method does not differentiate between mobile and immobile pores.

$$\theta_T = 1 - \rho_{\text{BULK}} / \rho_{\text{PD}} \quad (4)$$

$$V_{\text{OXIDANT}, \theta_R} = \Pi \text{ROI}^2 \theta_T h \quad (5)$$

In this method, it is assumed the injected oxidant is eventually dispersed throughout the ROI PV. Consequently, long-term oxidant persistence and dispersal into the spectrum of lesser connected pores is critical. Oxidant dispersal involving the groundwater velocity continuum between mobile and immobile pores is dependent on different reactions, advection and diffusive transport mechanisms, ISCO design, and site conditions. In application of these principles to ISCO, soluble chemicals exchange between zones of mobile and immobile porosity. Preferential flow in structured media has been described using a variety of models (Simunek et al. 2003). Dual-porosity and dual-permeability models both assume that the porous medium consists of two interacting regions where solute exchange in groundwater, for example, between mobile pores and immobile pores, occurs through a rate-limiting

diffusion process (Russo 2012). In some cases, oxidant persistence is insufficient, either due to reaction or transport, to effectively penetrate porous media through diffusion (Goldstein et al. 2004) suggesting that the eventual dispersal assumption may be invalid under some conditions.

Oxidant Delivery Strategies to Improve ISCO Effectiveness

Relative to long injection screened intervals, short injection screened intervals have a lower probability of being screened across lithologic layers exhibiting a wide range in hydraulic conductivity. Therefore, short injection intervals limit the risk in delivering a disproportionate volume of oxidant into higher permeability layers and greater probability of injecting the oxidant into discrete zones within the TTZ (Figure 2). Where feasible, the length of a well screen in an injection well should be no more than 10 to 15 ft (3.05 to 4.57 m), particularly in heterogeneous formations and where treating highly contaminated source zones (Simkins et al. 2011). Shorter injection well screens (<10 to 15 ft) (<3.05 to 4.57 m), and direct-push injection using short injection intervals (2 to 4 ft) (0.61 to 1.22 m) can further limit the role of preferential pathways. Overall, a combination of short-screened injection intervals, a greater number of injection locations, and smaller ROI's per injection location reduces the risk of delivering excessive oxidant volumes into preferential pathways (Figure 2) and results in greater probability that the oxidant is delivered to the TTZ. Areal coverage of the TTZ with multiple, overlapping oxidant ROIs is critical to improve contact between oxidant and contaminated media.

Oxidant breakout into higher permeability zones, mounding, surfacing, and transport beyond the TTZ in general, can result from excessive injection pressure. The rate that an aquifer can accept fluids and the lateral migration of these fluids before reaching structural failure is significantly influenced by the vertical acceptance rate. Maximum injection pressure can be estimated by the density of the dry soil and saturated soil, the thickness of the vadose zone, and the height of the saturated zone above the injection point (Los Angeles Regional Water Quality Control Board - In Situ Remediation Reagents Injection Working Group 2009). Adhering to these injection guidelines will improve oxidant delivery to the TTZ.

Assuming the contamination is mainly in the most permeable zones as defined by tracer tests, the mobile porosity oxidant volume design could be an effective approach. However, assuming contamination is present in both high and low permeability materials suggests that oxidant injection into high permeability layers limits oxidant delivery into low permeability TTZs, and/or misses the target altogether. Chemical oxidation of contaminants in, or near, low permeability materials requires that the oxidant be delivered into or near lower permeability zones and persist for timeframes consistent with steep concentration gradients and diffusive transport (Cavanagh et al. 2014). Periodic batch delivery of oxidant could be used to address the back diffusion of contaminants. Alternatively, slow but constant oxidant delivery methods have been developed for sites with low conductivity lithology involving gravity delivery and/or constant head injection designs (Pac et al. 2014; Luhrs et al. 2015).

Critical Analysis of Mobile and Total Porosity Oxidant Injection Volume Estimation Methods

Contrasting tabulated values of q_M and q_T (Table 1; Equations 3 and 5) indicate that a larger volume of oxidant is estimated using total porosity vs. mobile porosity. Consider the illustrative example of an oxidant volume ISCO design where assumed values for q_M (0.10) and q_T (0.35) are used to estimate oxidant volume and where ROI = 10 ft (3.05 m), and h = 5 ft (1.52 m). The volume of oxidant required to achieve the ROI across the screened interval using q_M and q_T is 1170 gal (4428 L) and 4110 gal (15,556 L), respectively. Delivering a larger volume of oxidant associated with q_T translates into greater oxidant handling, preparation, and labor resulting in higher remedial cost.

The potential for groundwater displacement and oxidant transport beyond the design ROI and TTZ into nontargeted zones are risks that should be evaluated. Since ISCO is usually deployed in a source area, oxidant transport beyond the ROI into lesser-contaminated aquifer conditions, and/or downgradient transport during the postinjection drift phase could also occur. In these cases, chemical oxidation of contaminants would continue to occur, potentially in nontargeted zones with less contamination. Despite the seemingly benign consequence of oxidant transport beyond the immediate ROI in this case, adjustments to the ISCO design would need to consider the loss of oxidant from the ROI. Nearby receptors beyond the TTZ and potential discharge areas (i.e., seeps, creeks, water bodies, utility corridors, etc.) should be identified to determine whether migration of oxidant beyond the contaminated TTZ could occur and what steps, if any, to implement given potential contingencies.

Contaminants are distributed between aqueous, solid, and nonaqueous phases in the subsurface and can be estimated using equilibrium partitioning calculations (Feenstra et al. 1991; Newell and Ross 1992; Cohen and Mercer 1993). Under non-aqueous phase liquid (NAPL)- or heavily contaminated source area conditions, the contaminant mass may be present in all three phases but the majority of contaminant mass is generally found in the NAPL and solid phases relative to the dissolved aqueous phase contaminant mass. Under NAPL-free conditions, based on the hydrophobicity of CVOCs and the presence of natural organic matter in aquifer material, the majority of contaminant mass is adsorbed on the solid phase material. Assuming the majority of the CVOCs mass in the ROI is immobilized either as residual NAPL or through adsorption onto aquifer solids, the displacement of the dissolved CVOC contaminant mass in the groundwater is projected to be limited relative to the total contaminant mass.

Critical Analysis of Permanganate ISCO Design Parameters

Krembs et al. (2010, 2011) compiled permanganate ISCO design parameters including the design and observed ROI (ft), oxidant dosage (g/kg), number of PVs delivered, number of delivery events, and duration of delivery events (days) (Table 2). A critical analysis of these design parameters reported is preceded by the caveat that the number of case studies for the median value of each design parameter varied, and therefore only general observations are possible.

Radius of Influence

The ROI can be estimated by measuring appreciable concentrations of the oxidant in monitoring wells located in different directions from the injection location. When the observed ROI (25 ft) ($n = 11$) (7.62 m) is considerably greater than the design ROI (14 ft) ($n = 29$) (4.27 m) (Table 2), this suggests that oxidant distribution was more extensive than designed. However, given these ROIs, the volume of oxidant required to achieve a 25-ft ROI (7.62 m), relative to a 14-ft ROI (4.27 m), would involve injecting greater than three times more oxidant volume. A firm explanation cannot be provided regarding this anomalous difference but some speculation is warranted. For example, groundwater quality parameters (i.e., ORP, DO, temperature, conductivity) are sometimes used as indirect indicators of oxidant ROI. Spikes in these parameter values can occur in groundwater after the oxidant has fully reacted, yet the effects, or the residuals of the oxidant, can still be measured yielding false-positive results for the ROI.

In some cases, the hydraulic conductivity (K) profile measured across screened intervals in groundwater wells exhibits an order of magnitude change over short vertical sections of the screened interval (Zlotnik and Zurbuchen 2003). Under this condition, a disproportionate volume of oxidant could be delivered into high K layers (Figure 1), and could also yield an ROI artifact. Injection and monitoring well screens representative of discrete vertical intervals would be useful to diagnose this condition and to obtain a more accurate assessment of oxidant transport and ROI.

Due to heterogeneities in aquifer hydraulic properties, ROIs on the order of 25 ft (7.62 m) require the injection of a large volume of oxidant which invites vulnerability to disproportionate transport of the oxidant in preferential pathways. Decreased ROIs translate into smaller injection well spacing and would include installation of additional injection wells or more direct-push injection locations. Smaller ROIs have several advantages including lower probability that preferential pathways will play a role in oxidant transport, greater potential for hydraulic control, greater accuracy in the spatial emplacement of the oxidant, and greater confidence that the oxidant can be delivered to the designed ROI.

Natural Oxidant Demand

ISCO oxidant loading, defined here as mass of oxidant per mass of soil (i.e., g oxidant/kg aquifer material) is sometimes designed based on NOD values measured in bench-scale studies. The NOD for permanganate often involves a 48-h test procedure (ASTM 2007). This batch test does not differentiate between mobile or immobile pores. Judicious interpretation of test results is warranted given that the reaction between MnO_4^- and reactants varies with time, there are multiple reactive components that exhibit varying reactivity, the NOD may increase substantially with longer testing periods, and MnO_4^- reaction is concentration dependent (Mumford et al. 2005; Hønning et al. 2007; Urynowicz 2008; Urynowicz et al. 2008; Xu and Thomson 2008, 2009; Cha et al. 2012). Most of the NOD in soil and aquifer samples is slow reacting, and 48-h NOD measurements are poor predictors of total NOD and cannot accurately estimate long-term MnO_4^- consumption (Cha et al. 2012). However, an alternative, quick and economical permanganate chemical

oxidant demand test has been developed to estimate the maximum permanganate NOD for aquifer materials (Xu and Thomson 2008). Further, results from a broad range in aquifer materials indicated excellent linear relationship between the maximum NOD and the 7-day NOD test indicating that results could be used to support permanganate ISCO site screening and design (Xu and Thomson 2009). Once the fast NOD fraction is rapidly consumed, the remaining MnO_4^- may persist for weeks to months, and diffuse into lower permeability zones where contaminants may reside. Samples of aquifer solids from 12 sites ($n = 50$) in the U.S. were analyzed for NOD over a long period (up to 41 days). In 80% of the samples, a broad range in NOD (0.24 to 18.8 g MnO_4^- /kg soil; median value = 3.33 g/kg) was measured and the overall range was 0.2 to 150 g/kg (Cha et al. 2012). This was similar to previously reported NOD ranges (Mumford et al. 2005; Huling and Pivetz 2006; Hønning et al. 2007; Urynowicz 2008; Xu and Thomson 2009). The median value of MnO_4^- dosage reported by Krembs et al. (2010, 2011) is low (0.4 g/kg; $n = 24$) (Table 2) relative to long-term NOD values. Assuming that long-term persistence of MnO_4^- was needed to address contaminant mass transport and mass transfer limiting processes, this low MnO_4^- dosage applied suggests that the median range value used at many ISCO sites represents an under-design either in terms of oxidant volume or concentration. Overall, this low median value of oxidant dosage would unlikely persist long enough to broadly disperse within the ROI and TTZ while satisfying both the fast- and slow-acting NOD.

Pore Volume

A PV represents the volume of voids contained within the ROI spatially defined by the ROI, vertical interval, and porosity. The median number of permanganate PVs delivered (PV = 0.16; $n = 32$ sites) (Table 2) (Krembs et al. 2010, 2011) is significantly less than a single PV (PV = 1.0) and suggests an under-design of oxidant volume. In this case, significant postinjection oxidant persistence and dispersal would be required to achieve both (1) coverage in the remaining 0.84 PV of the ROI where oxidant was not initially delivered and (2) to address long-term NOD requirements. Postinjection oxidant dispersal of this magnitude is unlikely.

Summary

The median values reported for oxidant dosage (0.4 g/kg) and PV delivery (PV = 0.16) (Table 2) (Krembs et al. 2010, 2011) suggests a less aggressive, low oxidant volume ISCO design which may be consistent with a mobile porosity ISCO design. This design appears likely to result in incomplete oxidant delivery, insufficient oxidant dosage within the ROI, and short duration oxidant persistence. A more aggressive ISCO design based on total porosity would involve a greater oxidant dosage (33 g/kg) (i.e., Cha et al. 2012) and PV delivery (PV = 1) permitting greater distribution and longer duration oxidant persistence. It is noted that low oxidant concentration could have contributed to the low oxidant dosage, but oxidant concentration data were not reported by Krembs et al. (2010, 2011), and could not be evaluated.

Other Causes of Rebound and Low Contaminant Removal

Current ISCO deployment is increasingly reflective of an iterative design involving repeated oxidant injections with intermittent monitoring diagnostics used to guide subsequent oxidant injections that target persistent, high concentration source areas. Further, depletion of the “more accessible” contamination may be followed by an ISCO approach characterized by smaller oxidant batch injections, or long-term, slow oxidant delivery targeting the back diffusion of contamination (Pac et al. 2014; Luhrs et al. 2015). In the early years of ISCO design, short duration and/or single injection deployment (i.e., Table 2, number of delivery events = 2; $n = 65$) may not have fully recognized the technical challenges associated with hydrogeologic heterogeneities, oxidant distribution limitations, high contamination zones, contamination in low permeable or fractured systems, high oxidant demand zones, limited oxidant persistence, etc. Consequently, rebound and low contaminant removal through postoxidant injection groundwater monitoring would be a probable outcome. Projects involving these designs may be reflected in ISCO treatment performance conclusions in the ISCO surveys (GeoSyntec Consultants 2004; McGuire et al. 2006; Krembs et al. 2010, 2011).

Groundwater samples collected specifically to be analyzed may contain the injected oxidant and organic contaminants in a “binary mixture” (Huling et al. 2011; Johnson et al. 2012; Ko et al. 2012). Oxidative transformation of contaminants in the sample after it is collected, causes false-negative results. Upon complete reaction of the injected oxidant in the subsurface, the potential for false-negative results is eliminated and the contaminants present in groundwater samples are subsequently detected and quantified. Essentially this condition contributes to a determination of “rebound” although the contaminants may have been present all along. Given the relatively recent development in groundwater sample preservation guidelines (Ko et al. 2012), the interpretation of groundwater quality under this condition is likely reflected in the case study survey results and statistics that report rebounding contaminant concentrations at ISCO sites.

Summary

Critical reviews of in situ remediation technology treatment performance indicate that ISCO, compared to other in situ technologies, exhibits a higher degree of chemical rebound and a lower reduction in contaminant concentrations (GeoSyntec Consultants 2004; McGuire et al. 2006; Krembs et al. 2010, 2011). Although several mechanisms may provide a reasonable explanation for these observations, low oxidant volume delivery at ISCO sites is likely to be a key factor for rebound and the low reduction in contaminant concentrations.

In conjunction with porosity, a simplified radial flow, cylindrical, porous media conceptual model is often used to estimate the volume of oxidant required to achieve a ROI over a specific vertical interval. Mobile and total porosity values used in these calculations yield a wide range in estimates of oxidant volume. The mobile porosity method specifically recognizes that groundwater readily moves in “mobile pores” and can be measured using tracer tests. However, tracer tests are vulnerable to lithology-dependent variability in hydraulic conductivity where tracer transport in the most permeable sections of the media

will skew estimates of mobile porosity downward. Consequently, a smaller volume of oxidant is estimated resulting in a smaller oxidant footprint potentially leaving some TTZs oxidant-free within the ROI. Total porosity, often calculated or measured in the lab does not differentiate between mobile and immobile pores. This method involves a larger oxidant volume to inject, a larger oxidant footprint, and would likely impact ISCO field activities due to greater oxidant handling, preparation, and labor. Displacement of contaminated groundwater and oxidant migration beyond the ROI and TTZ are risks that must be evaluated. In source areas, phase distribution analysis suggests that the majority of contaminants are immobilized in soil and NAPL which limits the relative displacement of contaminants. Several oxidant injection methods and designs can be used to reduce the impact and risk of preferential pathways on oxidant delivery and provide greater probability that the oxidant is delivered to the ROI.

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References

- ASTM. 2007 ASTM D 7262-07. Standard Test Method for Estimating the Permanganate Natural Oxidant Demand of Soil and Aquifer Solids. West Conshohocken, Pennsylvania: ASTM International, 04.09.
- Bachiochi R, D'Aprile L, Innocenti I, Massetti F, and Verginelli I 2014 Development of technical guidelines for the application of in-situ chemical oxidation to groundwater remediation. *Journal of Cleaner Production* 77, no. 15: 47–55.
- Bear J 1988 *Dynamics of Fluids in Porous Media*. New York: Dover Publications.
- Cavanagh BA, Johnson PC, and Daniels EJ 2014 Reduction of diffusive contaminant emissions from a dissolved source in a lower permeability layer by sodium persulfate treatment. *Environmental Science and Technology* 48: 14582–14589. [PubMed: 25386986]
- Cha KY, Crimi ML, Urynowicz MA, and Borden RC 2012 Kinetics of permanganate consumption by natural oxidant demand – Modeling approaches and statistical analysis. *Environmental Engineering Science* 29, no. 7: 646–653.
- Cha KY, and Borden RC 2012 Impact of injection system design on ISCO performance with permanganate — mathematical modeling results. *Journal of Contaminant Hydrology* 128: 33–46. [PubMed: 22192343]
- Chapman SW, and Parker BL 2005 Plume persistence due to aquitard back diffusion following dense nonaqueous phase liquid source removal or isolation. *Water Resources Research* 41: W12411.
- Cohen R, and Mercer J 1993 DNAPL site evaluation. EPA 600/R-93/022. Washington, DC: U.S. Environmental Protection Agency.
- Danielson RE, and Sutherland PL 1986 Porosity. In *Methods of Soil Analysis Part 1: Physical and Mineralogical Methods*, 2nd. Monograph 9 ed., ed. Klute A Madison, Wisconsin: American Society of Agronomy/Soil Science Society of America.
- Feenstra S, Mackay DM, and Cherry JA 1991 A method for assessing residual NAPL based on organic chemical concentrations in soil samples. *Groundwater Monitoring Review* 11, no. 2: 128–136.
- GeoSyntec Consultants. 2004 *Assessing the Feasibility of DNAPL Source Zone Remediation: Review of Case Studies*. Port Hueneme, California: Naval Facilities Engineering Services Center.
- Goldstein KJ, Vitols A, Navon D, Parker BL, Chapman S, and Anderson GA 2004 Characterization and pilot-scale studies for chemical oxidation remediation of fractured shale. *Remediation Journal* 14, no. 4: 19–38.

- Holtz RD, and Kovacs WD 1981 An Introduction to Geotechnical Engineering. Englewood Cliffs, New Jersey: Prentice Hall.
- Hønning J, Broholm MM, and Bjerg PL 2007 Quantification of potassium permanganate consumption and PCE oxidation in subsurface materials. *Journal of Contamination Hydrology* 90: 221.
- Huling SG and Pivetz B 2006 In-situ chemical oxidation – Engineering issue. EPA/600/R-06/072. Ada, Oklahoma: US Environmental Protection Agency, National Risk Management Research Laboratory, R.S. Kerr Environmental Research Center.
- Huling SG, Ko S, and Pivetz B 2011 Ground water sampling at ISCO sites – Binary mixtures of volatile organic compounds and persulfate. *Groundwater Monitoring and Remediation* 31, no. 2 Spring: 72–79.
- Johnson KT, Wickham-St. M, Germain, Ko S, and Huling SG 2012 Binary mixtures of permanganate and chlorinated volatile organic compounds in groundwater samples: Sample preservation and analysis. *Groundwater Monitoring and Remediation* 32, no. 3 Summer: 84–92.
- Ko S, Huling SG, and Pivetz B 2012 Ground water sample preservation at in-situ chemical oxidation sites – Recommended guidelines, EPA Ground Water Issue Paper. EPA/600/R-12/049. Ada, OK: US Environmental Protection Agency, National Risk Management Research Laboratory, R.S. Kerr Environmental Research Center.
- Krembs FJ, Siegrist RL, Crimi ML, Furrer RF, and Petri BG 2010 ISCO for ground water remediation: Analysis of field applications and performance. *Groundwater Monitoring and Remediation* 30, no. 4: 42–53.
- Krembs FJ, Clayton WS, and Marley MC 2011 Chapter 8 Evaluation of ISCO field applications and performance In *In Situ Chemical Oxidation for Remediation of Contaminated Groundwater*. SERDP/ESTCP Remediation Technology Monograph Series, Ward CH (Series ed), ed. Siegrist RL, Crimi ML, and Simpkin TJ, 319–354. New York: Springer Science and Business Media, LLC.
- Los Angeles Regional Water Quality Control Board - In Situ Remediation Reagents Injection Working Group. 2009 Technical report: Subsurface injection of in situ remedial reagents within the Los Angeles Regional Water Quality Control Board Jurisdiction. http://www.swrcb.ca.gov/rwqcb4/water_issues/programs/ust/guidelines/ (accessed September 16, 2009).
- Luhrs R, Andrews S, and Dugan PJ 2015 Use of ISCO as a cost effective long term remedy. <http://www.caruscorporation.com/page/remediation/carus-remediation-newsletters> (accessed October 26, 2015).
- Marsily G 1986 Quantitative Hydrogeology. San Diego, CA: Academic Press, Harcourt Brace Jovanovich.
- McGuire TM, McDade JM, and Newell CJ 2006 Performance of DNAPL source depletion technologies at 59 chlorinated solvent-impacted sites. *Groundwater Monitoring and Remediation* 26, no. 1: 73–84.
- Mumford KG, Thomson NR, and Allen-King RM 2005 Bench-scale investigation of permanganate natural oxidant demand kinetics. *Environmental Science and Technology* 39: 2835. [PubMed: 15884383]
- Newell C and Ross RR 1992 Estimating potential for occurrence of DNAPL at superfund sites, OSWER Publication 9355.4-07FS Washington, DC.
- Pac TJ, Lewis RW, and Gyles EC 2014 Constant head injection for enhanced in-situ chemical oxidation. *Remediation Journal* 25: 71–83.
- Payne FC, Quinnan JA, and Potter ST 2008 Remediation Hydraulics. Boca Raton, Florida: CRC Press; Taylor & Francis Group LLC, 408 p.
- Perloff WH, and Baron W 1976 Soil Mechanics: Principles and Applications. New York: John Wiley & Sons.
- Petri B, Thomson NR, and Urynowicz MA 2011 Chapter 3 – Fundamentals of ISCO using permanganate In *In Situ Chemical Oxidation for Remediation of Contaminated Groundwater*. A volume in SERDP/ESTCP Remediation Technology Monograph Series, Ward CH (Series ed), ed. Siegrist RL, Crimi ML, and Simpkin TJ, 89–146. New York: Springer Science and Business Media.

- Ptak T, Piepenbrink M, and Martac E 2004 Tracer tests for the investigation of heterogeneous porous media and stochastic modelling of flow and transport—A review of some recent developments. *Journal of Hydrology* 294: 122–163.
- Russo D 2012 Numerical analysis of solute transport in variably saturated bimodal heterogeneous formations with mobile–immobile-porosity. *Advances in Water Research* 47: 31–42.
- Simunek J, Jarvis NJ, van Genuchten M, and Gardenas A 2003 Review and comparison of models for describing non-equilibrium and preferential flow and transport in the vadose zone. *Journal of Hydrology* 272: 14–35.
- Siegrist RL, Urynowicz MA, West OR, Crimi ML, and Lowe SL 2001 Principles and Practices of In Situ Chemical Oxidation Using Permanganate. Columbus, Ohio: Battelle Press, 336 pp.
- Siegrist RL, Crimi M, and Brown RA 2011 Chapter 1: In Situ Chemical Oxidation: Technology description and status In *In Situ Chemical Oxidation for Remediation of Contaminated Groundwater*. A volume in SERDP/ESTCP Remediation Technology Monograph Series, Ward CH (Series ed), ed. Siegrist RL, Crimi ML, and Simpkin TJ, 1–32. New York: Springer Science and Business Media.
- Simkins TJ, Palaia T, Petri BG, and Smith BA 2011 Chapter 11 Oxidant delivery approaches and contingency planning In *In Situ Chemical Oxidation for Remediation of Contaminated Groundwater*. A volume in SERDP/ESTCP Remediation Technology Monograph Series, Ward CH (Series ed), ed. Siegrist RL, Crimi ML, and Simpkin TJ, 449–480. New York: Springer Science and Business Media.
- Stroo HF, et al. 2012 Chlorinated ethene source remediation: Lessons learned. *Environmental Science and Technology* 46, no. 12: 6438–6447. [PubMed: 22558915]
- Suthersan S, Divine C, Cohen E, and Heinze K 2014 Tracer testing: Recommended best practice for design and optimization of in situ remediation systems. *Groundwater Monitoring and Remediation* 34, no. 3: 33–40.
- Urynowicz MA 2008 In situ chemical oxidation with permanganate: Assessing the competitive interactions between target and nontarget compounds. *Soil and Sediment Contamination* 17: 53.
- Urynowicz MA, Balu B, and Udayasankar U 2008 Kinetics of natural oxidant demand by permanganate in aquifer solids. *Journal of Contaminant Hydrology* 96, no. 1–4: 187–194. [PubMed: 18166244]
- US EPA. 2014 Superfund Remedy Report, 14th Ed. EPA 542-R-13-016. November 2013, Washington, DC: Solid Waste and Emergency Response.
- Xu X, and Thomson NR 2008 Estimation of the maximum consumption of permanganate by aquifer solids using a modified chemical oxygen demand test. *Journal of Environmental Engineering* 134, no. 5: 353–361.
- Xu X, and Thomson NR 2009 A long-term bench-scale investigation of permanganate consumption by aquifer materials. *Journal of Contaminant Hydrology* 110: 73–86. [PubMed: 19818529]
- Zheng C, and Bennet GD 1995 *Applied Contaminant Transport Modeling*. New York: Van Nostrand Reinhold.
- Zlotnik VA, and Zurbuchen BR 2003 Estimation of hydraulic conductivity from borehole flowmeter tests considering head losses. *Journal of Hydrology* 281: 115–128.

Article impact statement

Two approaches in designing the volume of oxidant to inject for ISCO are critically analyzed and help to clarify the advantages and limitations.

Figure 1. Schematic of tracer breakthrough in a heterogeneous porous media aquifer and mobile porosity (q_M) calculations. The tracer volume (Vol_{inj50}) is measured where 50% breakthrough of the maximum tracer concentration ($C_{MAX/2}$) occurs (refer to Equations 1 and 2).

Figure 2.

Schematic of idealized conceptual model illustrating the role of heterogeneities, and the impact of screen length, radius of influence, and injection spacing on the distribution of the permanganate oxidant. (A) The long well screen in heterogeneous lithology accounts for disproportionate oxidant distribution; (B to D) alternatively, advancing short, direct-push injection well screens, using small radii of influence and close injection locations, achieves more effective oxidant distribution (oxidant density effects excluded).

Table 1.

Mobile Porosity Values Determined by Tracer Tests, and Total Porosity and Density of Aquifer Materials

Materials	Mobile Porosity (L^3/L^3) (q M) 1, 2, 1, 2	Location/Aquifer
Poorly sorted sand/gravel	0.085	Quebec, Canada
Poorly sorted sand/gravel	0.04 to 0.07	Central Valley, CA
Poorly sorted sand/gravel	0.09	North TX, Ogallala
Fractured sandstone	0.001 to 0.007	NJ, Passaic formation
Alluvial formation	0.0102	Los Angeles, CA/Gaspur
Glacial outwash	0.145	Northern NJ
Weathered mudstone regolith	0.07 to 0.10	Northern MO
Alluvial formation	0.07	Sao Paulo, Brazil
Alluvial formation	0.07	Phoenix, AZ
Silty sand	0.05	Savannah R., SC
Fractured limestone	0.0008 to 0.001	Trifels formation
Alluvium sand/gravel	0.017	West TX
Alluvial poorly sorted sand/gravel	0.003 to 0.007	North TX/Ogallala
Alluvial sand/gravel	0.11–0.18	Central CO/Cherry Creek
Siltstone, sandstone, mudstone	0.01–0.05	Central CO/Denver Formation
Materials	Total Porosity (M^3/M^3) (q T)	Soil Density (r_{BULK}) (kg/m^3)
Gravel	0.24 to 0.38 ³	2,000 to 2,350 ⁴
Coarse sand	0.31 to 0.46 ³	1,400 to 1,900 ⁴
Fine sand	0.26 to 0.53 ³	1,400 to 1,900 ³
Silt	0.34 to 0.61 ³	1,300 to 1,920 ⁴
Clay	0.34 to 0.60 ³	600 to 1,800 ⁴
Glacial tills	0.20 ⁴	1,700 to 2,300 ⁴
Silts and clays (inorganic)	0.29 to 0.52 ⁵	600 to 1,800 ⁴
Silts and clays (organic)	0.66 to 0.75 ³	500 to 1,500 ⁴
Peat	0.60 to 0.80 ⁶	100 to 300 ⁴

Notes: Total porosities reflect the typical range for each material considering compaction and sorting. Soil bulk density (r_{BULK}) refers to the common ranges of density for unsaturated conditions and various degrees of compaction.

¹Percentage (%) values reported by Payne et al. (2008) were changed to units of length (L^3/L^3) for contrast to total porosity values.

²Payne et al. (2008).

³Zheng and Bennet (1995).

⁴Perloff and Baron (1976).

⁵Holtz and Kovacs (1981).

⁶Bear (1988).

Table 2.

A Compilation of the Median Value for ISCO Design Parameters from Field Application Case Studies (Krembs et al. 2010, 2011)

Design Parameter	Median Value Reported Krembs et al. (2010, 2011) ¹
Design ROI (ft)	14 (<i>n</i> = 29)
Observed ROI (ft)	25 (<i>n</i> = 11)
Oxidant dosage (g/kg)	0.4 (<i>n</i> = 24)
Number of pore volumes delivered	0.16 (<i>n</i> = 32)
Number of delivery events	2 (<i>n</i> = 65)
Duration of delivery events (days)	4 (<i>n</i> = 45)
Vertical injection interval (ft)	NA ²

¹The median design value and number of case study sites is reported.

²The vertical injection interval was not reported Krembs et al. (2010, 2011).