

A Review on In-Situ Chemical Oxidation and Heterogeneity

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ABSTRACT

Chemical oxidants are increasingly being used for in-situ destruction of organic contaminants in ground-water. The most common implementation involves using an injection/withdrawal system to circulate oxidants (e.g., potassium permanganate, hydrogen peroxide, and Fenton's Reagent) through a DNAPL-source zone. Since the efficiency of chemical oxidation is highly dependent on geological heterogeneities, effective delivery schemes are essential for successful remediation. This paper reviews the impact of heterogeneities on the success of in-situ chemical oxidation. Physical heterogeneities are primarily concerned with the permeable pathways along which oxidants are transported to the zone of contamination. Chemical heterogeneities refer generally to variability in geochemical-related properties that also bear on the efficiency of oxidant flooding. Both types of heterogeneities work against bringing the oxidant to zones of high contaminant saturations. The highly heterogeneous distribution of contaminants and difficulties in characterization make it difficult to target specific zones for treatment. As a result, large volumes of sediments will be often treated whether contaminated or not. Heterogeneities in hydraulic conductivity at most sites provide intensive dose of chemical reagents into permeable pathways and little treatment of low conductivity zones. Large quantities of oxidizable materials in the geologic units are capable of consuming the oxidant during delivery. Reaction products (e.g., CO₂, MnO₂, Fe(OH)₃) tend to plug the porous medium, especially in zones with large contaminant saturations. The oxidant flood is diverted away from these zones making the flooding inefficient. The efficiency of oxidant injection can be deteriorated and subsequent developments to overcome these problems are required.

1. INTRODUCTION

There has been considerable interest in the use of chemical oxidants for the in-situ destruction of organic contaminants in ground-water. The most common implementation involves using an injection/withdrawal system to circulate oxidants through a source zone of

dense nonaqueous phase liquid (DNAPL) to affect the destruction. The variety of different oxidants suitable for this purpose includes permanganates, hydrogen peroxide, and Fenton's Reagent.

There is considerable research demonstrating the effectiveness of these oxidants in destroying particular types of organic compounds (e.g. Glaze and Kang, 1988; Vella and Veronda, 1992; Yan Schwartz, 1999). Our review here discusses these reactions in detail in terms of heterogeneity and technology efficiency. There is much less information available on the efficiency of oxidant flooding in porous media. Numerical studies (Ibaraki and Schwartz, in revision), small and large tank experiments (Reitsma and Marshall, 2000; Li and Schwartz, 2000) and column experiments point to difficulties in bringing the treatment fluid into contact with the nonaqueous phase contaminants. Interestingly, these difficulties have not been reported with field experiments or site clean ups. However, it is likely that in most of these cases monitoring has not been appropriate to examine this issue in detail.

The performance of oxidant injections in the destruction of DNAPLs is influenced by physical and chemical heterogeneities developed at a variety of scales. Physical heterogeneities are primarily concerned with the permeable pathways along which oxidant are transported to the zone of contamination. In this respect, the primary control is provided by hydraulic conductivity and its pattern of variability in the subsurface. Chemical heterogeneities refer generally to variability in geochemical-related properties that also bear on the efficiency of flooding. A major objective of this review paper is to elucidate the role of these heterogeneities in determining how well in-situ oxidation schemes work.

2. OVERVIEW OF IN-SITU CHEMICAL OXIDATION TECHNOLOGIES

Chemical oxidation decomposes chlorinated organic contaminants by converting them to carbon dioxide, chloride and water. In the saturated zone, the commonly used oxidants are hydrogen peroxide, Fenton's reagent, and potassium permanganate. In the vadose zone, hydrogen peroxide and ozone in gaseous form are often used. In-situ oxidation works for a variety of organic contaminants including VOCs, BTEX, PAHs, and PCBs. It works as an economical, stand-alone treatment or can be used in conjunction with other technologies like bioremediation, surfactant flushing, or pump-and-treat. The following section reviews the basic chemistry of these in-situ oxidation processes.

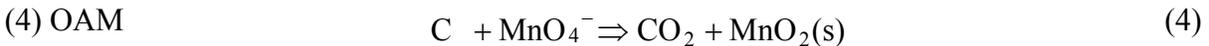
2.1. Permanganate Oxidation

The oxidation of organic compounds by potassium permanganate (KMnO_4) to non-selectively oxidize organic contaminants has been used for many years in the treatment of drinking water and waste water (Vella et al, 1990; Vella and Veronda, 1992). Recent research also points to the potential of chemical oxidation as a technique for ground-water remediation (Gates et al., 1995; Schnarr et al., 1998; Yan and Schwartz, 1999; Zhang and Schwartz, 2000; Seol and Schwartz, 2000). Although the reactions between various contaminants and KMnO_4 are all quite similar, the geological media, which host the ground-water, complicates the reaction mechanism. Oxidizable inorganic and organic solids in the geological media react with KMnO_4 and compete with degradation reactions involving the organic contaminants.

Let us examine the oxidation reactions in greater detail. When dissolved in water, the common contaminants, PCE (C_2Cl_4), TCE (C_2HCl_3), and DCE ($\text{C}_2\text{H}_2\text{Cl}_2$) react with MnO_4^- as follows;



Reactions between MnO_4^- and natural organic matter or other oxidizable aquifer materials (OAM) are generally written as



Permanganate readily oxidizes dissolved chlorinated alkenes and organic compounds containing carbon-carbon double bonds, aldehyde groups or hydroxyl groups. With pHs in the range of 4 to 8 and typical ground-water temperatures, the primary oxidation reaction with alkenes occurs spontaneously via cleavage of the carbon-carbon bond. Yan and Schwartz (2000) discusses details of the reaction pathways and describe the short-lived intermediates, formed from the oxidation of chlorinated alkenes. A key result, however, is that the breakdown yields glyoxylic acid or oxalic acid at high pH and formic acid at low pH. These organic acids are mineralized to carbon dioxide by further oxidation with MnO_4^- . In addition, a solid, manganese dioxide (MnO_2) forms, which can cause problems with plugging. Also, various experiments have shown that MnO_2 in colloidal form acts as a catalyst, enhancing the rate of oxidation (Yan, 1998; Pérez-Benito, 1987; Garrido et al., 1987; Šumichrast et al., 1994).

Although KMnO_4 has been used for decades, due to its higher aqueous solubility, sodium permanganate (NaMnO_4) is the permanganate salt of choice at sites where a reagent with high concentration is required. Despite its high price, the ease of delivery and the relatively high solubility keep the total cost of operation and remediation times relatively low.

Many field investigations have been conducted to evaluate the efficiency of in-situ permanganate flooding using small pilot scale tests (Huang et al., 2000; Schnarr et al., 1998; West et al., 1998). Selected field applications of in-situ permanganate oxidation with different oxidant delivery schemes are summarized in Table 1. A concentrated solution of KMnO_4 at 10-25 g/L was injected through parallel horizontal wells (West et al., 1998) or multilevel vertical wells (Schnarr et al., 1998) into aquifers contaminated with chlorinated solvents. Results indicated that in-situ flooding was effective in removing contaminants. In the Borden test (Schnarr et al., 1998) nearly complete removal of DNAPLs was achieved in a time frame judged faster than conventional pump-and-treat schemes. Removal efficiencies of the contaminants range from 60 % to near 100% as the occurrence of the contaminants and geologic heterogeneity varies at various scales. Slowly leaking contaminants into the flow field will distribute according to geologic heterogeneity and as a result the gravity driven distribution of contaminants will be more complicated than that of the residually emplaced contaminant source (Schnarr et al., 1998). The results from these and other tests suggest that careful site characterization is required for successful oxidant flooding, particularly with respect to the heterogeneity in hydraulic conductivity, the potential for the competitive utilization of the oxidant (e.g. OAM), and distribution of DNAPLs (Schnarr et al., 1998)

Injecting an oxidant solution at or near solubility limit directly to the contaminant source zone overcomes some of the oxidant delivery problems including hindrance of geological heterogeneity. Direct-push oxidant injection has been evaluated in a variety of conditions such as non-uniform clay/silt sediments with residually saturated DNAPLs (Moes et al., 2000), TCE contaminated low-permeability layers in vadose zone (McKay and Hewitt, 1998), sand or fine grained layers with high saturations of TCE (Mott-Smith et al., 2000), and a sandy aquifer with

layered distribution of DNAPL (Nelson et al., 2000). This technique is proven effective or locally effective when it was used in combination with detail characterization of source zones (Table 1).

Emplacement of oxidants by soil mixing as either liquid or solid phases (Cline et al., 1997) or by fracture filling with particle mixtures (Siegrist et al., 1999) may be beneficial at some sites with low permeability units that are not suitable for flooding. The main challenge on this technique is to provide a sufficient mass of oxidants to span a practical operational time frame. Additional design and performance studies are also needed. Siegrist et al. (1999) completed a pilot-scale field experiment to evaluate reactive-solid filled fractures for remediating contaminants in low permeable media (Table 1). By injecting an oxidative particle mixture (granular KMnO_4 suspended in a mineral-based gel), permanganate-filled fractures were created in a fine-grained silt-sand matrix at four different depths. The diffusive reaction zone around the fractures showed a greater than 99% removal efficiency in 10 months following the installation (Siegrist et al., 1999). These new techniques offer better efficiency in delivering the reagents into the contamination zone and overcoming the geological heterogeneity even though careful reviews on contaminant removal efficiency, operational costs and long-term potential hazards are still in need.

2.2. Fenton's Reagent Oxidation

Although hydrogen peroxide alone can be used for the oxidation of organic compounds, Fenton's reagent provides much more powerful oxidation potential (electrode potential of hydrogen peroxide is 1.77 v and that of hydroxyl radical is 2.76 v). Fenton's reagent is a mixture of hydrogen peroxide, a catalyst (ferrous sulfate) and an optimum pH (3-5) adjuster (sulfuric

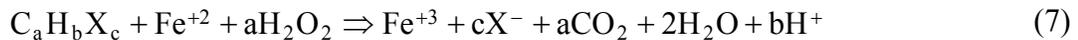
acid). Hydroxyl radical (OH*) is produced by the reaction of hydrogen peroxide (H₂O₂) and ferrous iron (Fe⁺²).



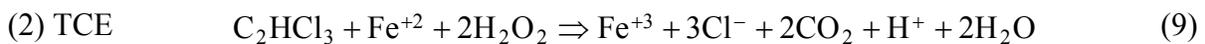
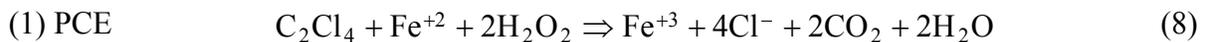
Reaction rates with Fenton's reagent are generally limited by the rate of the hydroxyl radical generation. Under the favorable conditions, the ferric iron (Fe³⁺) may be reduced to ferrous iron (Fe⁺²) as;



where HO₂* is perhydroxyl radical. The general form of oxidation reactions involving Fenton's reagent is



where C_aH_bX_c is an organic compound with a halide element, X (e.g. chloride). For example, the reaction between the PCE, TCE, DCE and the Fenton's reagent can be written as;



The hydroxyl radical reacts non-selectively with most organic contaminants. In the treatment process, ground-water pH level should be maintained between 4 to 6 to keep iron in solution as Fe⁺². At higher pHs (>8), the iron occurs as a colloidal solid, which lowers the reaction efficiency. Fe(OH)₃ catalytically decomposes hydrogen peroxide into oxygen and water. The products of the reaction are carbon dioxide, water, and chloride ion.

Reactions involving Fenton's reagent are highly exothermic, requiring caution in properly handling the reagent. Fenton's reagent degrades rapidly in contact with soil components. Consumption of hydroxyl radicals by carbonate, bicarbonate and organic matter

hinders the success of the treatment. In addition to scavenging of free radicals, reactions with Fenton's reagent are inhibited by iron chelates formed with phosphate, EDTA, or citric/oxalic acids. Fenton's reagent is not suitable for use with bioremediation schemes because hydroxyl radical, which is the main oxidant in the Fenton's oxidation, will react with a multitude of biological constituents and show little discrimination and also, heat and pressure generated from the reaction as well as the low pH condition would adversely affect for biological activity.

Fenton's reagent can be implemented by liquid injection (Jerome et al., 1998; Greenburg et al, 1998). However, it is often necessary to adjust pH in the subsurface condition to 3-5 by injecting an acid solution. Treatment begins with the slow addition of the iron catalyst (ferrous sulfate heptahydrate) and the hydrogen peroxide. Because the reaction involves extreme heat and pressure, proper injection tools have to be employed to ensure the safe injection of the reactants, utilizing steel injectors with special screens (Jerome et al., 1998; Levin et al., 2000). However, it is likely that the in-situ flushing will be only effective in highly permeable deposits. Fenton's reagent can lead to permeability reductions due to the precipitation of $\text{Fe}(\text{OH})_3$ or the production of CO_2 .

Recent studies (Ravikumar and Gurol, 1994; Lin and Gurol, 1996) showed that natural iron minerals such as iron oxide (goethite, $\alpha\text{-FeOOH}$) particles in soils can be utilized as an intrinsic catalyst for Fenton's reaction to oxidize organic pollutants instead of providing additional iron catalyst into the system. Organic contaminants are oxidized effectively by hydroxyl radical generated from the interaction of hydrogen peroxide and FeOOH particles and the effectiveness is controlled by availability of hydrogen peroxide and the iron oxide mineral rather than the soil pH and alkalinity (Lin and Gurol, 1996). However, application of hydrogen peroxide at high concentration (> 50%) generates large quantities of gas in a short period of time

when ferrous iron is not available, and the soil induced decomposition of hydrogen peroxide results in gas-sparging effect to strip the dissolved organic contaminants from aqueous phase (Chen et al, 2001). Therefore, the geological medium conditions including pH and iron content, as well as hydrogen peroxide dosage would significantly limit the effectiveness of the oxidation technology.

2.3. Ozone Oxidation

Ozone (O₃) has strong oxidation capabilities (electrode potential = 2.07 v). There is also a tendency to generate hydroxyl radicals through catalytic reactions utilizing hydrogen peroxide and ultraviolet ray. Ozone is generated artificially by a high voltage discharge in air or oxygen, although the ozone generation system is expensive;



Ozone reacts with organic and inorganic molecules to produce oxygen, hydroxide molecules, and water. There have been a variety of studies exploring the use of ozone in oxidative treatments. Masten and Davies (1997) conducted laboratory experiments to investigate the effectiveness of ozone treatment of polycyclic aromatic hydrocarbons (PAHs). Marvin et al. (1998) used laboratory and field experiments to study the treatment of pentachlorophenol (PCP) and PAHs in both the vadose and saturated zones. However, the short half-life of ozone limits the distances over which it can be delivered. Ozonation works well with aerobic bioremediation because oxygen is produced from the ozone reaction.

Ozone is somewhat more problematical to use with injection/extraction system. The half-life of the ozone is short and it dissipates quickly after generation. Thus, ozone needs to be generated as closely as possible to the target treatment area, and delivered quickly. Because

ozone is used as a gas, the pattern of flooding is vertical rather than horizontal. Careful design of injection scheme utilizing multilevel injection tools helped to achieve greater than 90 % of ozone utilization with PCP or PAH destruction (Marvin et al., 1998). Recently, there have been efforts to enhance the treatability by combining the ozone/air injection with air stripping via vertical recirculation wells. The idea is to enhance the mass transfer of dissolved contaminants into bubbles where ozone is available to decompose them (Dreiling et al., 1998; Kerfoot et al., 1998; Kerfoot, 2000;).

Ozone/hydrogen peroxide injection is a very effective tool for the removal of chlorinated hydrocarbon which do not directly react with ozone (Clancy et al., 1996; Sunder and Hempel, 1997). Glaze and Kang (1988) studied treatability of TCE and PCE using an ozone/hydrogen peroxide process, showing the addition of hydrogen peroxide to ozone increased the oxidation of the chlorinated solvents significantly. The combination results in the formation of hydroxyl radicals, which is more reactive and less selective than ozone.

3. PHYSICAL HETEROGENEITY

Heterogeneity has a major impact on the efficiency and overall success of in-situ oxidation schemes. Experience in the petroleum industry, related for example to alcohol and surfactant flooding for enhanced oil recovery, has shown that it can be difficult to deliver appropriate volumes of treatment chemicals to the right place. In practice, details of the hydraulic conductivity and hydrocarbon distribution cannot usually be characterized in sufficient detail to avoid uncertainties in the performance of the chemical flood. When difficulties, like high permeability pathways, are present and recognized, it also can be difficult to engineer

around these problems. These same problems apply to contaminant treatment systems and likely are more acute. For example, at many sites, ground-water hydrologists are attempting to affect a nearly perfect clean up (90% plus mass recovery) of relatively small volumes of widely distributed DNAPLs.

There are two types of physical heterogeneity that potentially could influence the efficiency of schemes for the in-situ oxidation of contaminants. First, there is usually heterogeneity in the original distribution of DNAPL in the subsurface. Human influences are an important contributing factor in this respect, with DNAPLs spread out at many locations as disposal locations shifted with time. Once in the ground, the geologic setting can profoundly influence the pattern of DNAPL distribution.

In granular sediments, subtle variability in the local pattern of layering and grain-size distribution can have a significant impact on the pattern of DNAPL spreading and saturation. This behavior was illustrated by an experiment conducted by Poulsen and Kueper (1992) at the Canadian Forces Base at Borden. They released PCE into unsaturated sand and observed patterns of residual saturation. Flow of the DNAPL was extremely sensitive to variations in permeability and capillary characteristics. These same kinds of complexities are evident in saturated porous media as well. Figure 1 from Oostrom et al. (1999) illustrates how heterogeneity affected TCE flow in a sand tank experiment. TCE migrated in the coarse-grained sand (#12) and tended to pool rather than enter the finer grained sands (F65 and F75) having high entry pressures. Small quantities of TCE were able to enter the medium sand lenses (#15). Eventually, most of the TCE accumulated at high saturations (i.e., DNAPL pool) on the F65 sand (Figure 1). Such high DNAPL saturations are often problematical for in-situ remediation schemes because locally the permeability to water is considerably reduced.

The occurrence of DNAPLs in porous media also depends on the wettability of mineral surfaces (Dekker and Ritsema, 1994; Bradford et al., 1998). Heterogeneity in the wettability of the aquifer formation can originate from variations in mineralogy and organic matter distributions. Organic matter coated sediment surface is preferably wetted with organic liquids, leading to localization of NAPLs. The presence of non-wetting fluid results in reduction in interstitial pore space accessible for aqueous oxidant flow and localized intense loading of the contaminants.

A second type of physical heterogeneity that is important in a remediation context is caused by variability in hydraulic conductivity. For a source-zone flooding scheme to be successful, many pore volumes of the oxidizing fluid need to be delivered. The stoichiometry of the breakdown reactions dictates exactly how many moles of reactants are required to transform a mole of the contaminant. Thus, if zones only receive a small quantity of the oxidant due to competitive consumption of oxidant by oxidizable substances in subsurface or limited hydraulic conductivity with low permeable layer, only a small quantity of contaminant can be transformed.

In the subsurface, a high permeability pathway can create a hydraulic short circuit, causing the injected oxidants to bypass the zone of interest. This type of problem has been known for a long time in the petroleum industry. Promising approaches for enhanced oil recovery that worked so well in the laboratory were disappointing in the field. The term “sweep efficiency” has been used in the petroleum industry to describe the fraction of the reservoir influenced by the flushing process. In essence, it quantifies the extent to which a unit is either treated or not treated. Ibaraki and Schwartz (in revision) argue that this concept is less useful in a contaminant context because most of the treatment zone will be flushed to some extent.

High sweep efficiency is a necessary but not sufficient condition to success in a remedial scheme. Ibaraki and Schwartz (in revision) developed the concept of “theoretical treatment flux ratio”. It is the cumulative magnitude of advective flux of the treatment chemical that reaches points of interest in the zone of contamination as compared to fluxes in the injection wells. Because the treatment flux is defined at various points, contoured cross-sections are useful in illustrating how well treatment fluids are delivered. Their analysis does not account for the consumption of these chemicals.

Figure 2 illustrates simulation results for two-dimensional cases where a hypothetical zone of DNAPL contamination is treated via chemical flooding. The injection and withdrawal wells are located 5 meters apart. Two different types of heterogeneous systems are considered. Medium B (Figure 2a) contains two layers with permeability 57x higher than the background value of $5 \times 10^{-11} \text{ m}^2$. Ibaraki and Schwartz (in revision) provide other pertinent details. Medium C (Figure 3a) is constructed as a correlated random permeability field with a ln-transformed mean of -23.72 , a variance of 0.9 a horizontal correlation length of 1.8 m and a vertical correlation length of 0.15 m . The realization of the field provides for locally high-permeability pathways through the source zone.

Figure 2b shows the calculated treatment flux ratio for Medium B. Not surprisingly the two high permeability zones have flux ratios >1 and receive approximately 10 times more treatment chemicals than the lower permeability zones, which are receiving minimal fluxes. The tendency for the flood to under-ride the treatment zone between the wells is due to a slight contrast in density between the treatment fluid and the ambient ground-water.

With Medium C (Figure 3b), two zones short circuit the injection and withdrawal wells. At early time, the flux ratio is > 1 along these zones. Elsewhere the flux ratios are low, 0.01 to

0.05. If the remediation strategy requires that large volumes of the treatment chemicals be delivered, then most of the clean up will be affected within the high permeability zones.

With low permeability units, flooding is only feasible if there is a fracture system to facilitate the flow of fluids. Although work is relatively limited, one could expect extremely heterogeneous permeability distributions, which are dependent on the geometry and hydraulic characteristics of the fracture network. There is some likelihood of treating DNAPLs occurring in fractures, although one should expect low treatment efficiencies. If the DNAPLs enter the unfractured blocks of the medium (Slough et al., 1999), reactions will occur as KMnO_4 diffuses from the fractures into the matrix. Obviously this process will be inefficient because circulation through the fractures would need to be maintained while this slow matrix diffusion is occurring. Our present position is that treating this kind of problem is not practical because there is little opportunity for stoichiometrically appropriate mass transfers.

A few case studies have documented the difficulties in flooding low permeability sediments in the field. Previously, we mentioned the pilot study of Moes et al. (2000) that involved KMnO_4 injection to a clay rich sediment near San Francisco Bay that was contaminated by TCE. A lance-injection scheme was used at close spacing (1.2 m) over the treatment area. Locally, the treatment fluid could not be injected into low permeability zones. Thus, it was difficult to provide even distribution of the oxidant. In zones, where the KMnO_4 could be injected the treatment was effective. However, with these delivery problems, the proposed treatment approach could not meet overall remedial objectives (Moes et al., 2000).

The best chance for providing sufficient KMnO_4 to react with contaminants in a low permeability material is through solid mixing. Soil mixing augers appear to hold promise in terms of a mixing and delivery system. Additional studies are required to establish the best ways

in which to maintain the oxidants in the treatment zone, and to quantify the competitive utilization of oxidants in these sediments.

4. CHEMICAL HETEROGENEITY

The term chemical heterogeneity refers to geochemical processes that are variable in space and time. The impact of chemical heterogeneity on the treatability of chemical oxidants has been the subject of extensive research. At least three chemical processes influence oxidation-based remediation schemes in the subsurface. First, other reduced minerals, organic matter, and dissolved organic matter in ground-water reacts with KMnO_4 , peroxide or Fenton's reagent, as it is transported through the subsurface. These competing reactions require that additional oxidants must be provided to deal with all oxidizable materials, including the contaminants. Heterogeneous distribution of soil organic matter and oxidizable inorganic components is mainly represented as chemical heterogeneity in subsurface condition. The heterogeneity results in variability in the distribution of DNAPLs, in the effectiveness of the oxidation process, and in the distribution of reaction products.

The interaction between these various oxidants and mineral phases can release environmentally significant quantities of chromium, selenium and rubidium (Li and Schwartz, 2000). In particular, chromium (Cr^{+3}) occurring as perhaps a Cr_2O_3 solid can be oxidized to produce the soluble form (Cr^{+6}), which can be hazardous.

Another chemical problem related to hydrogen peroxide is the consumption of hydroxyl radicals by carbonate and bicarbonate (Hoigné and Bader, 1983). Because the treatability of

hydrogen peroxide depends on maintaining an optimum pH in the subsurface condition, the extent acid/base reactions is critical factor to evaluating the likely success of the approach.

Natural organic matter in geological media can affect the oxidant delivery, through competitive utilization of the oxidant and the distribution of DNAPL, by changing the wettability of surfaces. The variability in the organic matter content directly influences the oxidant demands of different soil types (Chambers et al., 2000; Oberle and Schroder, 2000). Typically, sandy soil has < 0.5 % organic carbon. Organic matter is often more abundant in silty or clayey soil (\approx 2.5 % organic carbon). Drescher and others (1998) reported the significant consumption of MnO_4^- by humic acid in a sand column spiked with TCE. Besides the utilization of oxidant, these incidental reactions with minerals and organic matter produce oxidation products such as solid manganese dioxide and carbon dioxide gas. With time, these reactions can plug the conduit and reduce the efficiency of delivery.

The problem of plugging, however, is most serious within the zone of contamination, where DNAPL saturations can be relatively large. Figure 4 is a visualization data from an experiment from Conrad et al. (1999), which illustrates this problem of chemical heterogeneity. In a two-dimensional flow tank constructed with a heterogeneous medium, they created zones of locally high TCE saturation (red areas, Figure 4). After minimal flooding with 1gm/L KMnO_4 , low permeability rinds of MnO_2 (brown color in Figure 4) formed and sequestered the TCE from further contact with the oxidant. There is also no remedial advantage to this encapsulation. Conrad et al. (1999) found that once MnO_4^- flooding was halted, TCE slowly leaked out of these zones.

Li and Schwartz (2000) obtained similar results using a small 2-D glass flow tank (30.5 cm long, 5 cm high, 0.3 cm thick) packed with clear 1mm borosilicate glass beads. 1 mL of TCE

was added, which provided a zone of residual saturation above a small DNAPL pool. Flushing with MnO_4^- continued for 313 hr until the tank was plugged with precipitates. Small gas bubbles also had formed, which contributed to a reduction in permeability. Precipitates began to form once MnO_4^- came in contact with the residual TCE. As precipitates continued to form there was a tendency for MnO_4^- flooding to bypass the zone with the greatest TCE saturations. A permeable pathway formed close to the top of the tank, which conducted most of the flow. A low permeability rind formed above the TCE pool at the bottom of the tank, effectively sequestering this mass for the entire experiment (Li and Schwartz, 2000).

During this entire experiment, only 34.9% of the initial TCE added was removed – both as dissolved TCE and as TCE oxidized by MnO_4^- . Half of this mass was removed during the first quarter of the experiment. Figure 5 shows the observed TCE concentration at the downstream end of the tank (closed circles), the estimated TCE destroyed (open circles) as determined from Cl^- concentrations and reaction stoichiometry. Most of the remaining TCE in the column remained in the small TCE pool. Once flushing by MnO_4^- was halted, a rebound in concentration was evident (Figure 5).

The production of CO_2 gas, as MnO_4^- reacts with organic contaminants, also causes problems with the flooding. If the gas remains localized in the vicinity of the spill, it can reduce the permeability to the medium for fluid flow and interfere with subsequent flooding. The deleterious impact of gas and MnO_2 problems has been noted particularly in flow-tank experiments. Reitsma (2000) showed that under some conditions, gas pressures can become so high that they lead to remobilization of DNAPLs through a gas-drive scheme and transport of contaminants within the CO_2 vapor (Reitsma, 2000). These results suggest that relatively high

concentrations of MnO_4^- (greater than 5g/L) should be avoided because of the potential problems related to gas production.

5. SUMMARY AND CONCLUSION

This review has examined the use of chemical oxidants for the in-situ destruction of organic contaminants in ground-water. In general, there is undisputed evidence from various laboratory and field demonstrations that oxidants such as hydrogen peroxide, Fenton's reagent, and potassium permanganate are capable of oxidizing a variety of common organic contaminants. In addition, workable engineering schemes have been developed to deliver oxidants to DNAPL source zones.

In spite of the promise of these approaches, there are problems of efficiency that will likely plague most deployments. These problems are now being observed in laboratory demonstrations and computer-based experiments, where it is possible to observe processes in detail. In general, most field demonstrations or site cleanups are not adequately instrumented to elucidate problems with oxidation schemes.

Physical and chemical heterogeneities in the subsurface work against bringing the oxidant to zones of high concentrations. The highly heterogeneous distribution of contaminants and difficulties in characterization make it difficult to target specific zones for treatment. Thus, often, large volumes of sediments will be treated whether contaminated or not. Heterogeneities in hydraulic conductivity at most sites provide intensive flooding of permeable pathways and little treatment of low conductivity zones. Large quantities of oxidizable materials in the

geologic units are capable of consuming the oxidant during delivery. Reaction products (e.g., CO₂ gas, minerals) tend to plug the porous medium, especially in zones with large saturations of pure-phase contaminants. With time, the oxidant flood is diverted away from these zones of large contaminant saturations.

In most studies, potential problems are de-emphasized to shed the “best light” on the remediation approach. Thus, there is not an extensive literature that provides examples of the problems that accompany in-situ oxidation schemes. However, we would urge practitioners to be cautious in their assessments of the likely success of any in-situ remediation scheme of this type. There are likely more situations when the approach will fail rather than succeed. Most of the factors contributing to failure should be known and evaluated even before a field pilot is run. Much more work is required before these problems are likely overcome.

ACKNOWLEDGEMENTS

This work was supported by the Environmental Management Science Program at the Ohio State University, under Contract No. DE-FG07-00ER15115, through Lawrence Berkeley National Laboratory under Contract DE-AC03-76SF00098. We thank Dr. Stephen Conrad for kindly providing the visualization of DNAPL surrounded by rinds of MnO₂ and our thanks extend to anonymous reviewers for their careful reviews and constructive comments.

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Table 1. Summary of field applications of in-situ permanganate oxidation utilizing different oxidant delivery schemes.

References	Site	Site Description	Contaminant	Reagent	Delivery Scheme	Efficiency
West et al., 1998	X701 B at DOE Postsmout Gaseous Diffusion Plant	Sand and gravel zone 5-6 ft thick, 30 ft deep 200×90 ft (L×W)	TCE (54-302 mg/kg soil)	KMnO ₄ (15-25 g/L)	Recirculation, Parellel horizontal well (90 ft apart, 200ft)	Effective, but inconclusive
Schnarr et al., 1998	CFB Borden Research Site	Fine-medium sand $K_h=7.2 \times 10^{-3}$ cm/s, $\phi = 0.33$ O.D. = 7 kg KMnO ₄ /m ³ sand 3×1×2.5 m (L×W×D)	PCE (8% residual sat.), PCE/TCE mixture	KMnO ₄ (10 g/L)	Source zone flushing, Multilevel vertical wells, Flow rate = 50-100 L/day	>90% PCE in 120 days
Huang et al., 2000	A contaminated site in Connecticut	Uniform sand on clay aquitard, 1.2×3.8×9.3 m	TCE	NaMnO ₄ (10 g/L)	Source zone flushing, Flow rate = 0.6 L/min	Effective
McKay et al., 1998	Cold Region Research & Engineering Lab.	Fine sand w/ some silt interbeded w/ thin sand or thinker layer. Unsaturated	TCE (80-150 mg/kg soil, 15-60g/kg soil)	KMnO ₄ (15 g/L)	Direct-push wells Injection pressure = 6-12 psi, 200 gal/53 day and 358 gal/21 day	Inconclusive or undetermined.
Nelson et al., 2000	CFB Borden Research Site	Borden sand, clay aquitard at 3.5 ft depth. 9×9 m ($K_h=4 \times 10^{-3}$ - 4×10^{-7})	PCE (70-160 L in the cell)	KMnO ₄ (64 g/L)	Drive point delivery system (inject-and-leave), 860 L, 400-600 kPa	Effective
Moes et al., 2000	Former industrial site in California	Saturated clay and silt, high salinity groundwater	TCE (38mg/L)	KMnO ₄ (50-60 g/L)	Lance permeation (550 kg), Average loading = 0.9 mg/g	Locally effective, unsatisfactory.
Mott-Smith et al., 2000	IDC Cape Canaveral Demonstration Site	Sandy clay to shell hash, targeted on sandy units	TCE (842-4228 kg)	KMnO ₄ (15-20 mg/L)	Direct push pressure injection (159kg/hr), 35340 kg injected.	>90%
Siegrist at al., 1999	X231-A at DOE Portsmouth Gaseous Diffusion Plant	Unconsolidated Quaternary deposit (pebbles and gravel in fine silty-sand matrix) underlined by clays and silts	TCE (300 mg/kg soil)	KMnO ₄ (400-600 kg per each fracture)	Oxidative Particle Mixture (mineral based gel) emplaced by hydraulic fracture	>99% after 2 hr, <70% at highly contaminated site
Korte et al., 1996 Cline et al., 1997	DOE Kansas City Plant	Silty-clay zone, 45 ft deep	TCE (1,500 mg/kg soil)	KMnO ₄ (5-7 g KMnO ₄ /kg soil)	Mixed region chemical oxidation, Injection rate = 115-230 L/0.33 m	Average 67%, 81% in a cell mixed to 8 m.
Oberle and Schroder, 2000	1. Northern Ohio 2. Michigan	1. Saturated sandy above clay, O.D. < 200 mg/kg soil 2. Unsaturated sandy clay O.D. = 15-20g/kg	1. 1,2-DCE (81 µg/L) 2. PCE (60 mg/kg), TCE (40 mg/kg)	Dry KMnO ₄	Backhoe mixing of Dry KMnO ₄	1. Complete destruction 2. 99.9%

O.D.; Oxidant demand by natural material

FIGURES

- Figure 1. Trichloroethylene (TCE) saturation resulting after 3.5 days of flow in the heterogeneous medium shown in the insert. TCE tended to pond above the low-permeability units, which are the small lenses and the lowest unit indicated as F65 (modified from Oostrom et al. 1999)
- Figure 2. Flooding of a homogeneous medium with two high-permeability zones (panel a) would yield the distribution in the treatment flux ratio (TFR) shown in panel b (modified from Ibaraki and Schwartz, 2001)
- Figure 3. Flooding of a heterogeneous medium with at least two permeable pathways would yield the distribution in the treatment flux ratio (TFR) shown in panel b (modified from Ibaraki and Schwartz, 2001). Note that the scale for panel a refers to $\ln k$.
- Figure 4. This photograph shows rinds of MnO_2 (brown) that form around zones having high saturations of trichloroethylene (TCE) (red) after flooding with $KMnO_4$. The low-permeability rinds isolate the TCE from the oxidant. The tank is 60 cm long (from Conrad et al., 2002)
- Figure 5. Concentration of trichloroethylene (TCE) in the effluent from a small, two-dimensional flow tank. The figure also shows the estimated quantity of TCE destroyed in the tank and the total quantity of TCE removed (from Li and Schwartz, 2000).

Figure 1.

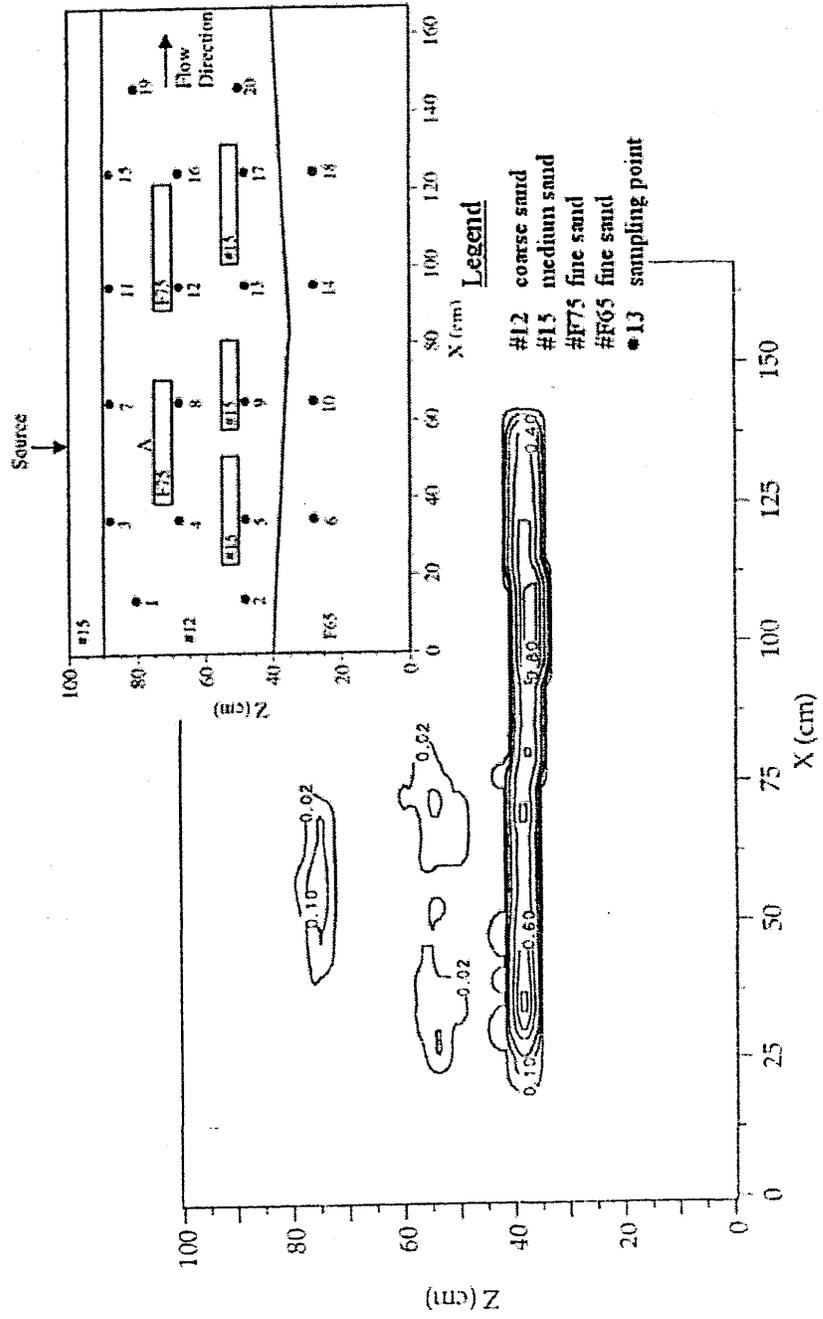


Figure 2.

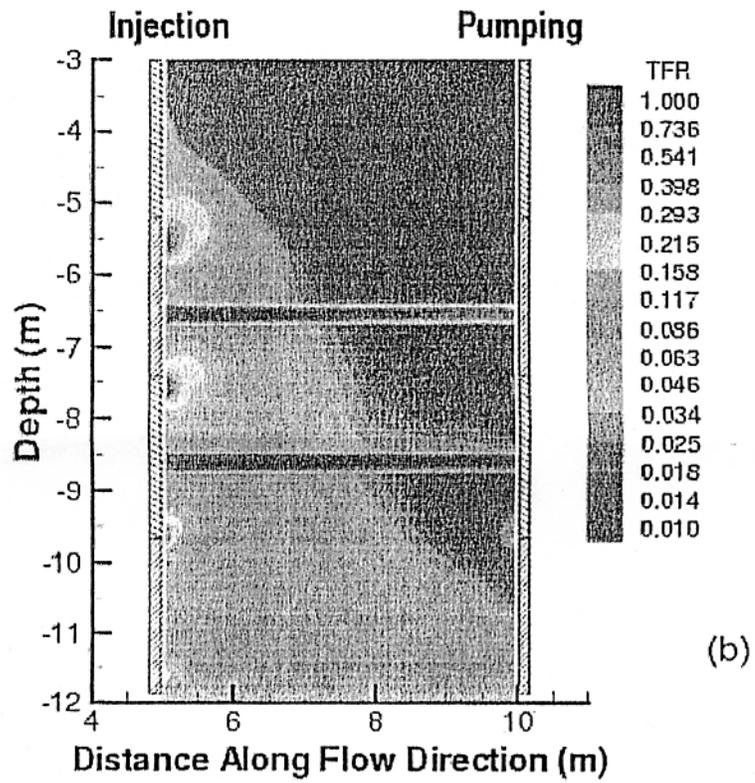
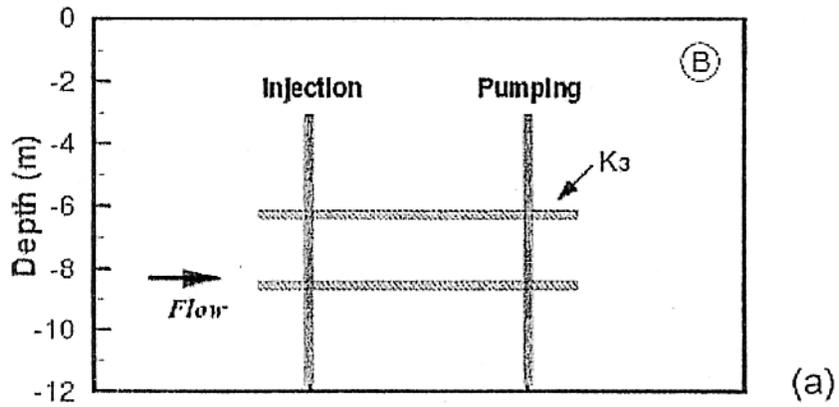


Figure 3.

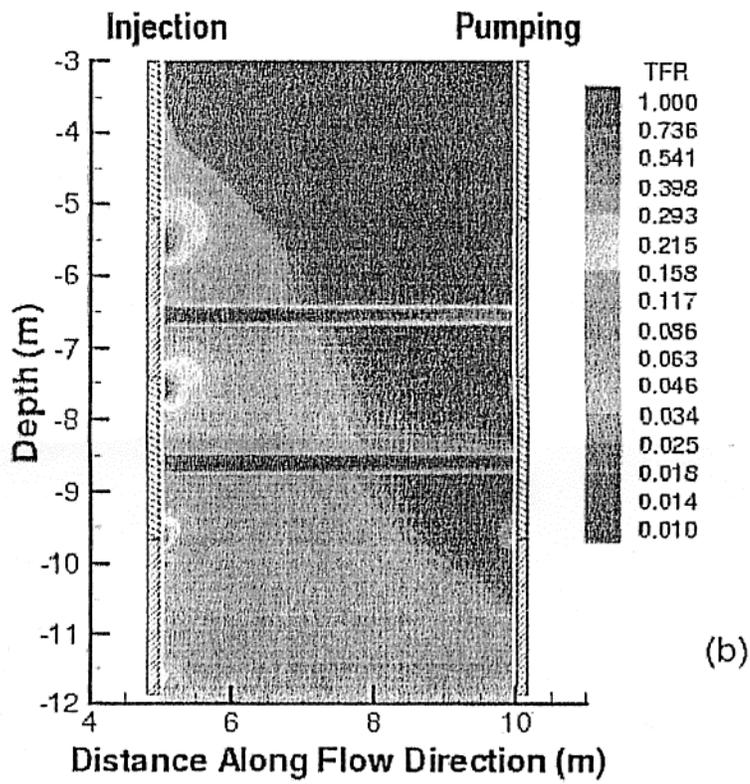
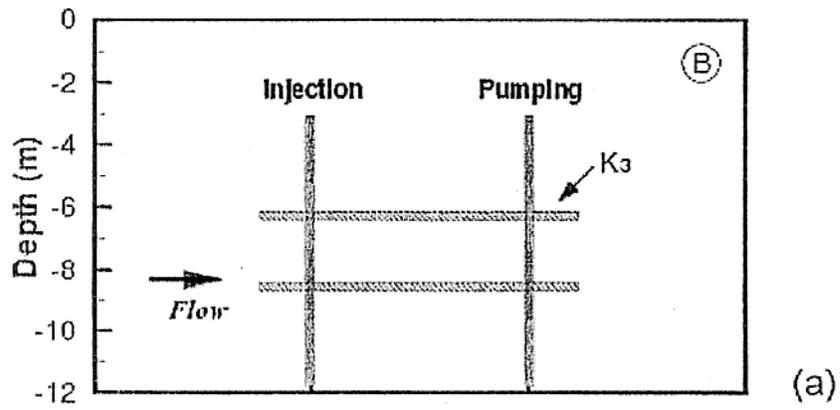
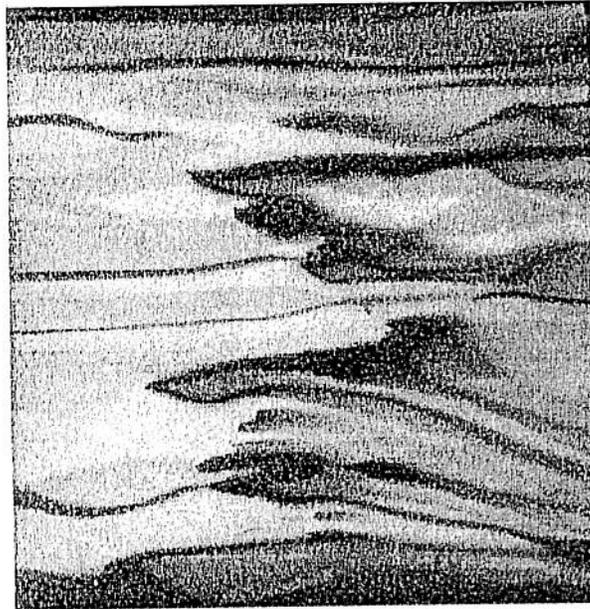


Figure 4.



- Sand
- Red-stained TCE in lense
- MnO₂ rind

Figure 5.

