

## CHEMICAL AND ENGINEERING CHALLENGES TO IN SITU PERMANGANATE REMEDIATION

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**ABSTRACT:** In situ chemical oxidation using permanganate ( $\text{MnO}_4^-$ ) is an attractive option to aggressively remediate chlorinated alkenes and other chemicals in soil and groundwater. A compound's potential reactivity with  $\text{MnO}_4^-$  may be assessed by examining the structure. Site-specific conditions should then be assessed, including the type and distribution of chemicals of concern (COCs) and lithologic setting (heterogeneity and geochemistry). Bench-scale and field treatability studies should be completed in order to estimate the  $\text{MnO}_4^-$  soil oxidant demand over time, evaluate the dose requirements, and ascertain the effect of  $\text{MnO}_4^-$  treatment on site geochemistry (formation and fate of byproducts, including chromium and manganese oxides) and permeability. The  $\text{MnO}_4^-$  soil demand varies widely with soil type and subsurface  $\text{MnO}_4^-$  concentration. The full-scale remediation program should be designed using the data from site characterization, and bench-scale and pilot tests. The field monitoring program should evaluate the efficacy of treatment design, including the effect on soil permeability, soil demand, and by-product attenuation.

### INTRODUCTION

In situ chemical oxidation using permanganate ( $\text{MnO}_4^-$ ) can be an attractive option for aggressive remediation of various chemicals in soil and groundwater. This technology has the potential to restore groundwater quality more rapidly than typical pump-and-treat remedies. The authors have overseen and completed laboratory testing and pilot- and full-scale in situ remediation of a variety of chemicals using  $\text{MnO}_4^-$ . Based on our experience, it is critical that site-specific conditions be assessed carefully prior to implementing remediation. The site should be adequately characterized, and bench-scale treatability studies should be completed to provide a first estimate of field design parameters. A field pilot test should then be performed prior to full-scale deployment.

Several key factors are required to determine the appropriateness of  $\text{MnO}_4^-$  technology. These factors include 1) the type and distribution of chemicals of concern (COCs); 2) lithologic setting (soil type and subsurface heterogeneity); 3) soil oxidant demand (SOD); and 4) site geochemistry. A combination of bench and field testing may be used to further evaluate secondary effects on soil permeability, mobilization and attenuation of redox-sensitive metals (including chromium) and the potential for COC rebound after treatment.

Because of its more moderate oxidation potential,  $\text{MnO}_4^-$  has several advantages over other oxidants (such as hydrogen peroxide-based treatments and ozone injection) for in situ chemical oxidation. Reactions between  $\text{MnO}_4^-$  and the aquifer matrix are relatively slow compared with these other oxidants. As a result,  $\text{MnO}_4^-$  may persist in the

subsurface for longer periods of time and may be transported by advective-dispersive processes. In addition, the reaction of  $\text{MnO}_4^-$  with the aquifer matrix does not produce excessive heat or gases, so relatively simple delivery systems may be used. When COCs are not susceptible to oxidation by  $\text{MnO}_4^-$ , other oxidants become more favorable.

## REACTIVITY AND KINETICS

To date, most in situ applications of  $\text{MnO}_4^-$  have focused on sites impacted with chloroethenes (e.g., trichloroethene). However,  $\text{MnO}_4^-$  has also been shown to oxidize additional compounds including polycyclic aromatic hydrocarbons (PAHs), chlorinated pesticides (e.g., Aldrin and Dieldrin), and high explosives (Gates-Anderson et al, 2001; Harris et al, 2001). This oxidant may have little to no effect on chlorinated alkanes (e.g. dichloroethane) and aromatic hydrocarbons (e.g. benzene and chlorobenzene), yet reacts with some chlorophenols. Consideration of the chemical structure of the contaminants and the general mechanism by which oxidation occurs may help explain the degree of reactivity.

Several authors have published summaries of the relative reactivity of common COCs (Clayton, 2000). The evaluation of new classes of compounds for permanganate oxidation is best performed in the laboratory under controlled conditions. Prior to bench testing, a chemical structural evaluation may be performed to assist in the development of a laboratory testing program. If the structural evaluation is promising, a simple jar test may be performed to show “proof of concept,” followed by a detailed laboratory study to examine the extent of oxidation, possible intermediate accumulation, and to develop kinetic data.

**Structural Evaluation.** In general,  $\text{MnO}_4^-$  initiates oxidative attack at multiple bonds within organic molecules (Ege, 1989). The chemical structure of the COC appears to affect the rate of oxidation by  $\text{MnO}_4^-$ . For example, 1,1-dichloroethene is oxidized more

**TABLE 1. Half Lives of Chloroethenes in Water.**

$\text{KMnO}_4$ (mg/L)	TCE (min)	1,2 DCE (min)	VC (min)
1000	2.8	--	Instantaneous
750	3.6	--	↓
700	3	1.8	
500	4.9	2.8	
300	8.6	4.3	
250	11.5	--	
20	122	114	9.4
15	122	158	10.1
10	217	None	13.0
5	347	None	14.8

rapidly than 1,2-dichloroethene (see Table 1). Furthermore, the electron withdrawing properties of functional groups (inductive effects) may also affect the overall reactivity of a target organic molecule. For example, the

sequential addition of chlorine atoms (which have strong negative electrical potential) tends to reduce the reactivity of the chemical structure. (Yan and Schwartz, 1998). Other functional groups, such as a hydroxyl group (OH), may increase the reactivity of a

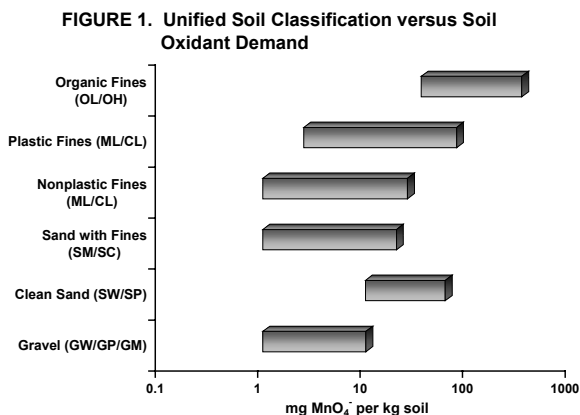
compound with respect to oxidation by  $\text{MnO}_4^-$ . Finally, the functional groups themselves (such as nitroso groups) may be susceptible to oxidation leading to step-wise oxidation of the functional groups with parent structure attack occurring after, or much slower rate than, functional group attack. In some instances the functional group is oxidized but the parent structure is not attacked (e.g., oxidation of methyl tert butyl ether to tert butyl alcohol).

**Implications Of Kinetics.** Several researchers have documented that the rate of reaction of a COC with  $\text{MnO}_4^-$  in the aqueous phase is dependent on the concentration of the COC and  $\text{MnO}_4^-$  (Yan and Schwartz, 1999). This second-order behavior has several practical implications for  $\text{MnO}_4^-$  remediation. First, increasing the concentration of  $\text{MnO}_4^-$  in the injection solution will not only increase the rate of COCs oxidation, but will also increase the consumption of  $\text{MnO}_4^-$ . Next, the effect of dilution needs to be considered when planning the injection and target formation concentrations of  $\text{MnO}_4^-$ . Finally, very slow reaction kinetics at low  $\text{MnO}_4^-$  concentrations may cause  $\text{MnO}_4^-$  and contaminant to coexist.

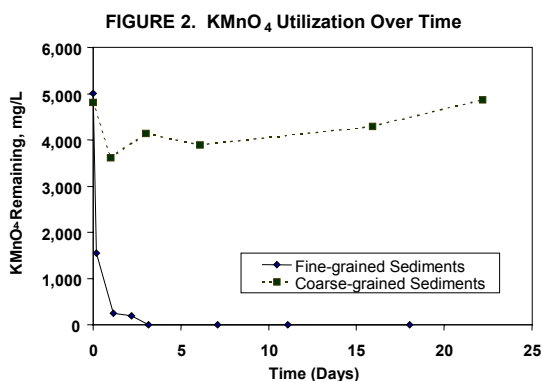
Overall, the kinetics of COC destruction is an important component of permanganate remediation. However, the kinetics of permanganate consumption have a larger effect on remediation costs and implementation time frame.

## SOIL OXIDANT DEMAND

Soil oxidant demand is the amount of oxidant consumed per unit mass of aquifer



solids over time. In most cases, the amount of  $\text{MnO}_4^-$  needed for in situ remediation of groundwater is controlled by the SOD rather than by the COC concentration. In fact, soils that exhibit a high SOD may require approximately 1,000 times more  $\text{MnO}_4^-$  than the amount needed to treat the COC based on reaction stoichiometry. For this reason, the site-specific SOD should be well understood as a first step to assessing the appropriateness of permanganate treatment.



In general, fine-grained soils with high organic content exhibit a higher SOD in comparison to coarse-grained soils. Figure 1 illustrates this effect. The SOD may vary over more than an order of magnitude within a particular soil classification.

Figure 2 illustrates the  $\text{MnO}_4^-$  SOD for two distinct soil types, one with very high SOD, and the other with very low SOD. As shown in this figure,

the rate of  $\text{MnO}_4^-$  consumption in high SOD soils is initially rapid, with more than 50 percent of the  $\text{MnO}_4^-$  consumed within the first 48 hours. Most soils tested consume more than 90 percent of the ultimate SOD within 2 weeks, but low-rate consumption may continue for several months.

Although difficult to precisely correlate to batch bench test results, field observations confirm that  $\text{MnO}_4^-$  is rapidly utilized in high SOD soils. Bench scale tests generally provide conservative SOD consumption values. Once the readily oxidized fraction of soil organic matter and other oxidizable species are removed,  $\text{MnO}_4^-$  may persist in the subsurface and be transported by advective flow. However, migration of  $\text{MnO}_4^-$  downgradient will continue to be retarded by continued consumption. Therefore, migration in low permeability, low SOD soils is a challenging engineering delivery issue. Additionally, high SOD soils will result in relatively greater manganese dioxide ( $\text{MnO}_2$ ) precipitation and deposition, potentially, decreasing the effective permeability of the aquifer. The application of low permanganate concentrations at higher flow rates will assist in reducing the production and deposition of  $\text{MnO}_2$  in these types of sediments.

To avoid utilizing a larger fraction of the  $\text{MnO}_4^-$  on non-COC reactions in high SOD soils, it is critical to have a good understanding of the source area chemical distribution as well as the subsurface heterogeneities. A good understanding of the site-specific flow regime will assist in engineering an appropriate delivery system. Permanent wells or recirculating systems in these types of soils may not prove to be technically appropriate or cost effective given the potential limited treatment area and the increased potential for  $\text{MnO}_2$  deposition. If temporary injection well points are used, batch injections may be distributed periodically over a larger area and volume and reasonable injections rates may be achieved.

On the other hand, studies also confirm that sandy, low organic-content soils may require less hydrogeologic analysis reducing engineering design requirements. Additionally, sandy soils with low SOD generally require much less  $\text{MnO}_4^-$  to achieve remediation. Although this reduces costs and maximizes the likelihood of uniform treatment, there is increased potential for  $\text{MnO}_4^-$  migration beyond the treatment zone; long-term persistence of  $\text{MnO}_4^-$  causing discoloration of groundwater; and mobilization of metals. Evaluation of SOD at several concentrations, coupled with a thorough evaluation of the depth and hydraulic properties of the formation, will enable proper design of an  $\text{MnO}_4^-$  delivery system. Operational schemes such as batch injections at intervals reduce the potential for long-term persistence of  $\text{MnO}_4^-$  at low concentrations if drilling costs do not preclude this approach.

The natural geochemical conditions of the aquifer may also play an important role in in situ permanganate remediation. Reduced aquifers tend to produce soils with high SOD while naturally oxidizing aquifers tend to have lower SOD soils. A baseline characterization of the redox potential of the system is an important first step in the planning of a permanganate remediation system. The redox state of the aquifer may also play a significant role in the mobilization and attenuation of redox-sensitive metals.

## **EFFECTS ON METAL CHEMISTRY**

As a moderately strong oxidant,  $\text{MnO}_4^-$  has the potential to alter the solubility and mobility of certain metals (Cr, As, Se, Hg). The authors have previously documented the formation of hexavalent chromium [ $\text{Cr(VI)}$ ] in groundwater after  $\text{MnO}_4^-$  treatment

(Chambers, et al., 2000; Clayton, et al., 2000). Recent literature has also reported peroxide-based oxidation of Cr(III) to Cr(VI) (Rock et al, 2001). The transport of other metals may also be increased after oxidation of organic ligands and changes in the ionic chemistry of the aquifer system.

The following discussion focuses on the formation, attenuation, toxicity, and solubility of Cr(VI). The U.S. Environmental Protection Agency's Maximum Contaminant Level (MCL) for total chromium is 100  $\mu\text{g/L}$ . In California, the MCL for total chromium is 50  $\mu\text{g/L}$ . Transient dissolved chromium concentrations more than ten times the MCLs have been measured in the laboratory and field.

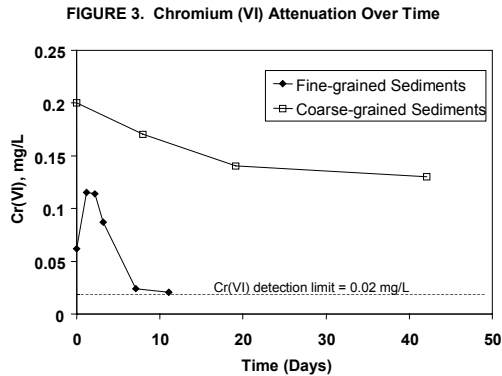
The occurrence of Cr(VI) in groundwater at permanganate remediation sites is related to several factors, including the native chromium content of aquifer sediments, the introduction of chromium as an impurity in permanganate, and the natural attenuation capacity of the soil and groundwater.

Chromium occurs naturally in soils throughout the United States, typically in the trivalent form Cr(III). The U.S. Geological Survey reported an arithmetic mean chromium concentration of 54 mg/kg across the United States, with concentrations of several hundred mg/kg in some areas (Shacklette and Boergen, 1984). Concentrations of chromium in coastal soils in California are frequently higher than the national mean, with background concentrations of approximately 100 mg/kg (Shacklette and Boergen, 1984). Permanganate, its byproduct  $\text{MnO}_2$ , and other oxidants can oxidize Cr(III) to Cr(VI). Hexavalent chromium is much more soluble in water than is Cr(III).

**Source of Mobilized Chromium.**  $\text{KMnO}_4$  and, to a lesser extent  $\text{NaMnO}_4$ , typically contain chromium as an impurity in the range of 8 to 60 mg/kg. Therefore it is important to determine the chromium concentration of the  $\text{MnO}_4^-$  and track the injection concentration, to estimate the amount of chromium that will be added to the aquifer. In general, the chromium contained within the permanganate product is not adequate to account for the total mass of Cr(VI) observed. In addition, the mass of Cr(VI) typically observed in field pilot studies is lower than the total chromium available from soils. Therefore, it can be concluded that only a fraction of the naturally occurring mass of chromium in the subsurface is oxidized to the hexavalent state. Therefore assessment of the chromium content of both the  $\text{MnO}_4^-$  product and site soils is essential to understanding the potential for mobilization.

**Chromium Attenuation Capacity.** The natural attenuation of Cr(VI) to Cr(III) in soil and groundwater has been well documented. The U.S. EPA has identified various physical and chemical factors including surface exchange, adsorption, and precipitation that together result in natural attenuation of metals (Palmer and Puls, 1994). Precipitation is likely controlled by solution composition while adsorption and surface exchange may be controlled by solid phase. Manganese dioxides sorb and surface exchange with cations such as Cr(VI) (Posselt et al, 1968). In addition, naturally occurring manganese oxides participate in metals attenuation processes (McLean and Bledsoe, 1992). Therefore, when combined with observed increases in cation exchange capacity of soils following  $\text{MnO}_4^-$  treatment it is likely that the byproduct  $\text{MnO}_2$  participates in the attenuation of chromium.

Based on the authors' experience, Cr(VI) concentrations often attenuate within



several weeks following  $\text{KMnO}_4$  treatment. However, this is not always the case. Some areas with sandy sediments or very low organic carbon concentrations may not have sufficient reducing capacity to naturally attenuate Cr(VI). It is unclear if the byproduct  $\text{MnO}_2$  can increase the attenuation capacity of these soils. Figure 3 shows treatability study results for two sites with differing attenuation capacities. For the fine-grained sediments, chromium

concentrations declined rapidly within 2 weeks. For the coarse-grained sediments, chromium concentrations remained elevated for the entire duration of the monitoring period (2 months). Thus, the attenuation capacity must be considered when planning  $\text{KMnO}_4$  remediation projects. If necessary, other methods to manage Cr(VI) such as chemical or biological reduction of the aquifer redox potential may be required.

### EFFECT ON SOIL PERMEABILITY

Various studies have indicated that  $\text{MnO}_4^-$  remediation can affect the permeability of the formation. Some bench and field studies indicate that  $\text{MnO}_4^-$  increases the permeability of the formation, while others show a decrease in overall permeability (Chambers, 2000; Reitsma and Marshall, 2000; Nelson et al, 2001). Changes in permeability may be due to geochemical reactions and/or physical changes in the matrix. Factors that appear to influence the effect of  $\text{MnO}_4^-$  on permeability include the geochemical composition of the formation, the initial permeability, the injected concentration, the rate of injection which drives mixing-dilution, the precipitation of  $\text{MnO}_2$ , and the type of  $\text{MnO}_4^-$  used (sodium versus potassium salt).

Two possible mechanisms that may reduce permeability are the precipitation of  $\text{MnO}_2$  and formation of  $\text{CO}_2$  gas. A high soil demand or the presence of DNAPL pools will result in a higher production of  $\text{MnO}_2$  and  $\text{CO}_2$  in these areas. Laboratory studies have shown that a  $\text{MnO}_2$  layer is formed over fine-grained sediments and DNAPL interfaces when high-concentration  $\text{MnO}_4^-$  is applied. Whether the precipitated  $\text{MnO}_2$  and  $\text{CO}_2$  gases migrate through the formation will depend on the size of the pore space and the hydraulic gradients. Precipitated  $\text{MnO}_2$  is initially colloidal in size, but may flocculate. The persistence of  $\text{CO}_2$  gas in the subsurface depends on the carbonate chemistry and pressure of aquifer. While free phase DNAPL pools are the exception to the rule, high SOD soils are common. Therefore, it is important to assess potential permeability alterations when treating finer-grained media.

Permeability increases have also been observed. For example, in one laboratory study the hydraulic conductivity increased by almost 1 order of magnitude after application of concentrated  $\text{KMnO}_4$ , but was practically unchanged when lower concentrations were used (Chambers, 2000). Permeability may increase due to removal of various oxidizable components of the soil or physical changes in the soil structure. For example, potassium ( $\text{K}^+$ ) (radius of 0.133 nm) is a large ion with a strong affinity for 2:1

silicate minerals, which may displace calcium (radius of 0.099 nm) and magnesium (radius of 0.080 nm), This may effectively increase the permeability of the formation. Other factors that could increase the permeability of the formation are the consumption of total organic carbon, DNAPL ganglia, and other oxidizable constituents such as soil carbonates.

Numerous sites have demonstrated significant rebound of the COCs after pilot testing. This rebound may be attributable to increased permeability, and therefore increased diffusion rates from areas of elevated concentrations. Partial oxidation of soil organic carbon may contribute to slight increases in permeability but also results in a reduction in the sorptive capacity of soil for hydrophobic COCs as described by the Karickhoff relationship.

### **ENGINEERING CHALLENGES TO $MnO_4^-$ SYSTEMS**

Although there are numerous designs for delivering  $MnO_4^-$  into the subsurface, two general approaches are commonly used. The first utilizes batch injections through temporary drive-point wells or permanent injection wells. The second delivery mode is hydraulic recirculation. Hydraulic recirculation has the benefit of enhancing the hydraulic gradients and containing displaced groundwater. Batch injections may achieve more uniform treatment by discrete injections but are limited by depth of application. Hydraulic analysis of batch injection processes becomes more difficult as pressure and flow rates are increased and dispersive and disruptive processes dominate over advection.

Byproduct formation must also be considered in assessing the appropriateness of  $MnO_4^-$  treatment. The potential byproducts associated with permanganate treatment include  $CO_2$  gas, partially oxidized products, chlorides, and  $MnO_2$  precipitates. The persistence of residual  $MnO_4^-$  and increases in total manganese may also be of concern. The importance of these issues depends on the permeability of the aquifer, regulatory agency concerns, the potential beneficial uses of the aquifer, and the migration potential of the byproduct.

The  $MnO_4^-$  mixing/delivery system should be designed with worker safety and the potential for clogging in mind. The authors have observed clogging of injection well screens, flow totalizers, and pump assemblies. If a recirculation system is employed,  $MnO_2$  may need to be filtered from extracted groundwater prior to reinjection. Careful design of the mixing/delivery system and evaluation of the make-up water composition reduces fouling problems and minimizes preventive maintenance.

Other factors to consider when developing field protocols for  $MnO_4^-$  remediation are safe handling of the  $MnO_4^-$ , neutralizing agents and management of the  $MnO_2$  wastes.  $MnO_4^-$  can cause serious injury if handled improperly. Use of high-rate feed systems will reduce the potential exposure of workers to  $KMnO_4$  dust while the use of proper personal protective equipment and engineering controls can not be overly stressed. Careful consideration of neutralizing agent thermodynamics and purchasing raw materials in dilute concentrations will reduce the potential for accidents.

### **CONCLUSION**

$MnO_4^-$  is an effective oxidant for the remediation of various chemicals. However, an adequate understanding of site-specific conditions and the interaction between  $MnO_4^-$

and the aquifer matrix is necessary to assess the appropriateness of this technology, and to design an effective treatment system.

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