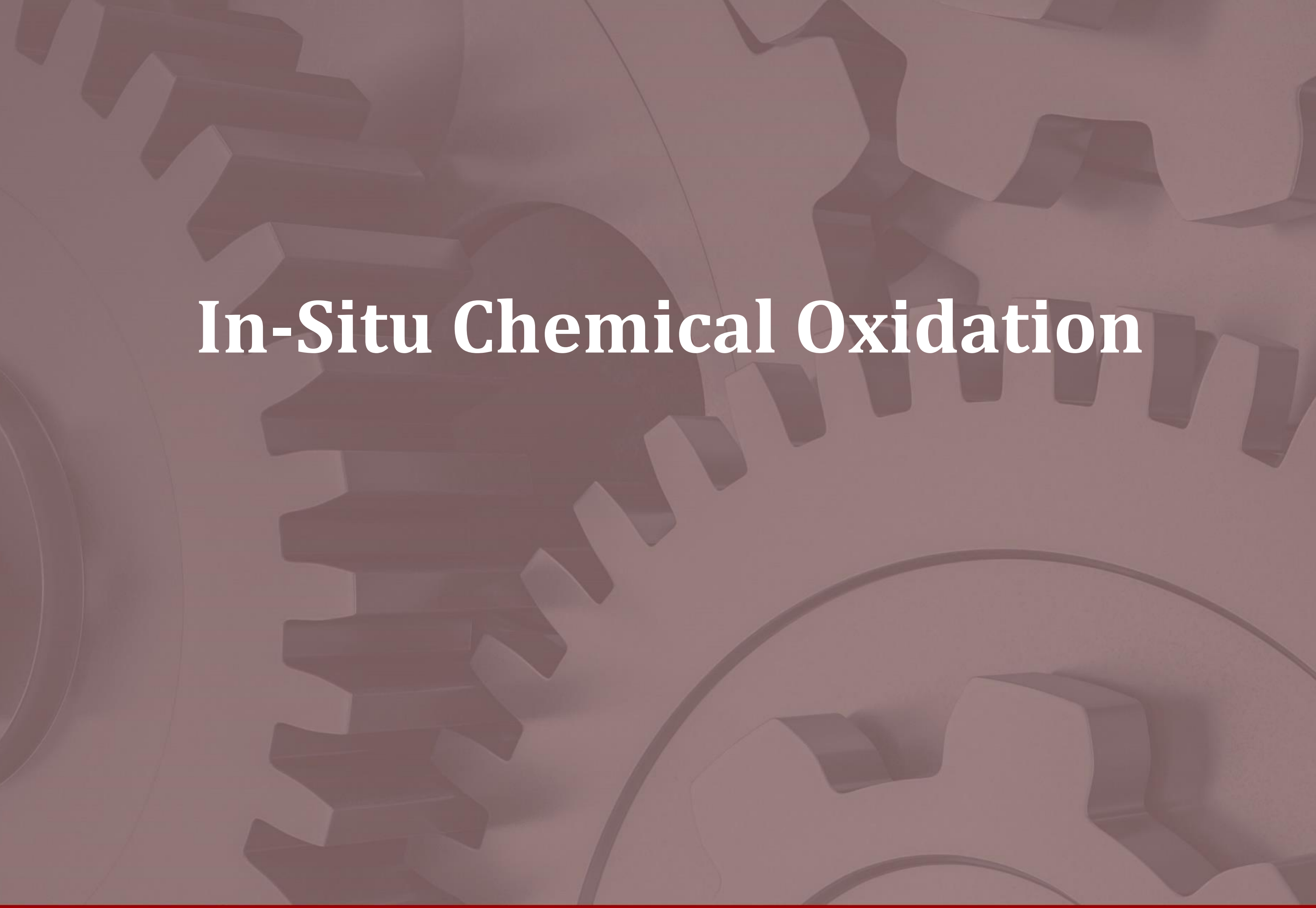

In-Situ Chemical Oxidation

An Online Continuing Education Course for Engineers

Course Number: EN-6005

Credit: 6 Hours / 6 PDH / 6 CPD

In-Situ Chemical Oxidation

I. INTRODUCTION

I.A. Background

In-situ chemical oxidation involves the introduction of a chemical oxidant into the subsurface for the purpose of transforming ground-water or soil contaminants into less harmful chemical species. There are several different forms of oxidants that have been used for ISCO; however, the focus of this course will be on the four most commonly used oxidants: permanganate (MnO_4^-), hydrogen peroxide (H_2O_2) and iron (Fe) (Fenton-driven, or $H_2O_2^-$derived oxidation), persulfate ($S_2O_8^{2-}$), and ozone (O_3) (Table 1). The type and physical form of the oxidant indicates the general materials handling and injection requirements. The persistence of the oxidant in the subsurface is important since this affects the contact time for advective and diffusive transport and ultimately the delivery of oxidant to targeted zones in the subsurface. For example, permanganate persists for long periods of time, and diffusion into low-permeability materials and greater transport distances through porous media are possible H_2O_2 has been reported to persist in soil and aquifer material for minutes to hours, and the diffusive and advective transport distances will be relatively limited. Radical intermediates formed using some oxidants (H_2O_2, $S_2O_8^{2-}$, O_3) that are largely responsible for various contaminant transformations react very quickly and persist for very short periods of time (<1 sec).

Table 1. Oxidant Form, Stability, Stage of Development and Oxidation Potential for Oxidants Used for In-Situ Chemical Oxidation

Oxidant	Reactive Species	Form	Persistence [(1)]	Stage of Development
Permanganate	MnO_4^-	powder/liquid	>3 months	developing
Fenton's	$\cdot OH, \cdot O_{2-}, \cdot HO_2, HO_2^-$	liquid	minutes - hours	experimental/emerging
Ozone	$O_3, \cdot OH$	gas	minutes - hours	experimental/emerging
Persulfate	$\cdot SO_4^{2-}$	powder/liquid	hours - weeks	experimental/emerging

Oxidant and Reactions	Electrode Potential (E_h) [(2)]	
Permanganate		
$MnO_{4-} + 4\,H^+ + 3\,e^- \longrightarrow MnO_2 + 2\,H_2O$	1.7 V (permanganate ion)	(1)
Fenton's (H_2O_2 Derived Reactants)		
$H_2O_2 + 2\,H^+ + 2\,e^- \longrightarrow 2\,H_2O$	1.8 V (hydrogen peroxide)	(2)
$2\,\cdot OH + 2\,H^+ + 2\,e^- \longrightarrow 2\,H_2O$	2.8 V (hydroxyl radical)	(3)
$\cdot HO_2 + 2\,H^+ + 2\,e^- \longrightarrow 2\,H_2O$	1.7 V (perhydroxyl radical)	(4)
$\cdot O_{2-} + 4\,H^+ + 3\,e^- \longrightarrow 2\,H_2O$	-2.4 V (superoxide radical)	(5)
$HO_{2-} + H_2O + 2\,e^- \longrightarrow 3\,OH^-$	-0.88 V (hydroperoxide anion)	(6)
Ozone		
$O_3 + 2\,H^+ + 2\,e^- \longrightarrow O_2 + H_2O$	2.1 V (ozone)	(7)
$2\,O_3 + 3\,H_2O_2 \longrightarrow 4\,O_2 + 2\,\cdot OH + 2\,H_2O$	2.8 V (hydroxyl radical, see rxn 3)	(8)
Persulfate		
$S_2O_8^{2-} + 2\,e^- \longrightarrow 2\,SO_4^{2-}$	2.1 V (persulfate)	(9)
$\cdot SO_{4-} + e^- \longrightarrow SO_4^{2-}$	2.6 V (sulfate radical)	(10)

1 Persistence of the oxidant varies depending on site-specific conditions. Durations specified here are based on general observations.

2 Reactive species in parentheses; reduction potential is negative.

Permanganate-based ISCO is more fully developed than other oxidants. Widespread use of in-situ permanganate oxidation involving a diversity of contaminants and geological environments under well-documented pilot- and field-scale conditions (in conjunction with long-term monitoring data and cost information) has contributed to the development of the infrastructure needed to support decisions to design and deploy permanganate ISCO systems. However, additional research and development is needed. Fenton-driven ISCO has been deployed at a large number of sites and involves a variety of approaches and methods involving the use of hydrogen peroxide (H_2O_2) and iron (Fe). In general, Fenton chemistry and in-situ Fenton oxidation is complex, involves numerous reactive intermediates and mechanisms, and technology development has been slower. Ozone (O_3) is a strong oxidant that has been used in the subsurface but in much more limited application than permanganate and Fenton-driven oxidation. Persulfate ($S_2O_8^{2-}$) is a relatively new form of oxidant that has mainly been investigated at bench-scale. However, considerable research and applied use of this oxidant at an increasing number of field sites is resulting in rapid development. The electrode (oxidation) potential of the oxidant and reactive species (Table 1) is a measure of the oxidizing strength of the reactive species, but is not a measure of the reaction rate with different organic compounds.

Site-specific conditions and parameters, in conjunction with oxidant-specific characteristics, must be carefully considered to determine whether ISCO is a viable technology for deployment relative to other candidate technologies, and to determine which oxidant is most appropriate. These issues and the advantages and disadvantages of each oxidant are discussed in detail.

The breadth of ground-water contaminants amenable to transformation via various oxidants is large. That is, many environmental contaminants react at moderately high rates with these oxidants. Therefore, a wide range of contaminant classes are amenable to chemical oxidative treatment (Table 2). Mixtures of contaminants may

Table 2. Assessment of the Amenability of Various Contaminant and Contaminant Classes to Oxidation Transformations

Contaminant	Oxidant																			
	MnO_4^-				Fenton's (H_2O_2/Fe)					$S_2O_8^{2-}$ (1)	$\cdot SO_4^-$ (Activated persulfate)[1]			Ozone				Ozone/ H_2O_2 (Peroxone)(2)		
	Rating sources																			
	a	b	c	d	a	b	c	d	e	a	a	b	c[3]	a	b	c	d	a	b	e
Petroleum hydrocarbons	G[4]				E[4]					G/E[4]	E[4]			E[4]						
BTEX		E[4]	E[4]	E		E	E[4]	E	E			E	E[4]		E	G[4]	E		E	E
Benzene	P[4]	G[4]	P[4]		E[4]		E[4]		E	G[4]	G/E[4]		E[4]	E[4]		G[4]				E
Phenols	G	E	E		E	E	E	E	E	P/G	G/E	E	E		E	E	E	E	E	E
PAHs	G	E	E	E	E	G	G	E	E	G	E	G	G/E	E	G	E	E		G	E
MTBE	G				G	E			E	P/G	E	E		G	E				E	E
tert-butyl alcohol						E			G			E			E				E	G
Chlorinated ethenes	E	E	E	E	E	E	E	E	E	G	E	E	E	E	E		E		E	E
Carbon tetrachloride	P	P	P		P/G	G	P		P	P	P/G		P/E	P/G	P				G	P
Chloroform		P	P			P	P		P				G/E		P				P	P
Methylene chloride			P			G	G		P				G/E		G				G	P
Chlorinated ethanes[5]	P			P	G/E			P	P	P	G/E			G			P			P
Trichloroethane[5]		P	P			E	P		P				P/E		P				E	P
Dichloroethane[5]			P			G	G		P				G/E		G				G	P
Chlorobenzene			P			E	E		E			E	E		E				E	E
PCBs	P	P	P	P	P	G	P	P	E	P	P	P	P/E		P	E	P	G	G	E
Energetics (RDX, HMX)	E				E					G	E			E						
Explosives		E	E			E	G					G	G/E		E	E			E	
Pesticides		G	G			P	P		G/E[6]			G	G/E		P	E			P	G/E[6]
1,4-dioxane[7]						E			E			E							E	E

Key: P = poor, G = good, E = excellent. While the different sources used slightly different terminology for rating the amenability, in general, they each used a three-tiered ranking represented here by the P, G, and E terminology.

Sources a, e:	P = poor, G = good, E = excellent
Source b:	P = recalcitrant, G = reluctant, E = amenable
Source c:	P = recalcitrant, no/low reactivity; G = reluctant, medium reactivity; E = amenable, high reactivity
Source d:	P = difficult to treat, E = susceptible

Notes:

[1] Persulfate/sulfate radical reactivity studies with 66 organic compounds and isomers under various conditions have been conducted elsewhere (FMC, 2005). (http://www.envsolutions.fmc.com/Klozur8482/ResourceCenter/tabid/356/Default.aspx).

[2] The reaction between O_3 and H_2O_2 produces $\cdot OH$. Therefore, the ratings from source (e) by Fenton's (H_2O_2/Fe) apply equally to the O_3/H_2O_2 (Peroxone) technology.

[3] Source (c) rated Fe-catalyzed and heat-catalyzed persulfate separately; the lower rating applies to Fe-activated and the higher rating applies to heat-activated persulfate.

[4] Benzene was rated separately from TEX or petroleum hydrocarbons; thus, the BTEX or petroleum hydrocarbons rating excludes benzene.

[5] TCA and DCA were rated separately by some sources; the other sources rated chlorinated ethanes as a class of contaminant.

[6] A detailed summary of second-order reaction rate constants between pesticides and $\cdot OH$ is reported in Haag and Yao (1992).

[7] Brown *et al.* (2004) present experimental results indicating that permanganate, Fenton's reagent, persulfate, and ozone are effective in oxidizing 1,4-dioxane.

Sources:

[a] Sperry, K.L., and J. Cookson, Jr. 2002. In Situ Chemical Oxidation: Design & Implementation. ITRC Presentation to New Jersey Department of Environmental Protection, October 30, 2002. http://www.state.nj.us/dep/srp/training/sessions/insitu200210c.pdf

[b] ITRC. 2005. Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater, Second Edition. Interstate Technology and Regulatory Cooperation Work Group, In Situ Chemical Oxidation Work Team.

[c] Brown, R.A. 2003. In Situ Chemical Oxidation: Performance, Practice, and Pitfalls. AFCEE Technology Transfer Workshop, February 24-27, 2003, San Antonio, TX. http://www.afcee.brooks.af.mil/products/techtrans/workshop/postworkshop03/Tuesday/pm/sourcezoneremediation/4_brown.pdf

[d] Siegrist, R.L., M.A. Urynowicz, O.R. West, M.L. Crimi, and K.S. Lowe. 2001. Principles and Practices of In Situ Chemical Oxidation Using Permanganate. 367 pp. Battelle Press, Columbus, OH.

[e] Rating based on the second-order reaction rate constants between contaminants and $\cdot OH$ reported in Buxton *et al.* (1988) and Haag and Yao (1992): Excellent (>10^9 L/mol-s), Good (10^8 - 10^9 L/mol-s), Poor (< 10^8 L/mol-s).

require treatment trains involving the sequential application of technologies to accomplish the treatment objective. Chemical oxidation can be deployed under a variety of applications, i.e., in either the unsaturated or saturated zones, or possibly above-ground, and under a variety of hydrogeologic environments. In this course, the focus is on ISCO. There are potential advantages and disadvantages of ISCO that should be assessed when considering the deployment of this technology.

Advantages:

- Applicable to a wide range of contaminants.
- Contaminants are destroyed in-situ.
- In-situ treatment may reduce costs incurred by other technologies such as pump and treat, MNA, etc.
- Aqueous, sorbed, and non-aqueous phases of contaminants are transformed.
- Enhanced mass transfer (enhanced desorption and NAPL dissolution).
- Heat from H_2O_2 reactions enhances mass transfer, reaction rates, and microbial activity.
- Potentially enhances post-oxidation microbial activity and natural attenuation.
- Cost competitive with other candidate technologies.
- Relatively fast treatment.

Disadvantages:

- Oxidant delivery problems due to reactive transport and aquifer heterogeneities.
- Natural oxidant demand may be high in some soil/aquifers.
- Short persistence of some oxidants due to fast reaction rates in the subsurface.
- Health and safety issues regarding the handling of strong oxidants.
- Potential contaminant mobilization.
- Potential permeability reduction.
- Limitations for application at heavily contaminated sites.
- Contaminant mixtures may require treatment trains.
- May have less oxidant/hydraulic control relative to other remedial technologies.

I.B. Definition

Chemical oxidation is a process in which the oxidation state of a substance is increased. In general, the oxidant is reduced by accepting electrons released from the transformation (oxidation) of target and non-target reactive species. Oxidation of non-target species, including reduced inorganics in the subsurface, also involves the loss of electrons; however, the main target during ISCO involves organic chemicals. Oxidation of organic compounds may include oxygen addition, hydrogen abstraction (removal), and/or withdrawal of electrons with or without the withdrawal of protons. The main objective of chemical oxidation is to transform undesirable chemical species into species that are harmless or nonobjectionable. For example, oxidation of trichloroethylene (TCE) and perchloroethylene (PCE) may produce reaction byproducts that include dichloroacetaldehyde and dichloroacetic acid, compounds with lower toxicity. Similarly, oxidation of phenolic compounds may produce an assortment of carboxylic acids (Huling et al., 1998) that are nontoxic. Oxidation of these byproducts to CO_2 and H_2O could be accomplished through additional oxidative treatment and expense, but may not be practical for economic purposes. These reaction byproducts may also serve as microbial substrate for natural attenuation processes.

I.C. Process Fundamentals

In oxidative treatment systems, numerous reactions could potentially occur, including acid/base reactions, adsorption/desorption, dissolution, hydrolysis, ion exchange, oxidation/reduction, precipitation, etc. In environmental systems there is a wide array of reactants and conditions that influence reaction rates and pathways that vary from site to site. Often, numerous reactions are required to achieve innocuous end products, and many of the reaction intermediates are never identified. The general reactions presented in this course represent a simplified set of reactions; however, a much broader and more complex set of reactions is expected under field conditions.

I.C.1. In-Situ Permanganate Oxidation

I.C.1.a. Chemical Reactions

Reaction 1 (Table 3) is the 3-electron half reaction for permanganate (MnO_4^-) oxidation under most environmental conditions (pH 3.5 to 12). One of the reaction byproducts is MnO_2, and in the pH range of 3.5 to 12 it is a solid precipitate. Under acidic conditions (pH <3.5), Mn in solution or in colloidal form may be present in different redox-dependent oxidative states ($Mn^{+2,\ +4,\ +7}$). Additionally, under strongly alkaline conditions, Mn may be present as Mn^{+6}. Under conditions where pH is <3.5 and >12, 5-electron and 1-electron transfer reactions occur, respectively (Table 3, half reactions 2 and 3). Reactions 1 to 3 illustrate the general permanganate reactions in the subsurface. Overall, permanganate oxidation potentially involves various electron transfer reactions (reactions 1 to 3), but is generally considered independent of pH in the range of 4 to 8.

Reactions 4 to 7 (Table 3) illustrate the oxidation of perchloroethylene (PCE), trichloroethylene (TCE), dichloroethylene (DCE), and vinyl chloride (VC), respectively. Examination of these balanced redox reactions indicate that the oxidant demand is inversely correlated with chlorine substitution. For example, the stoichiometric requirement for PCE, TCE, DCE, and VC is 1.33, 2.0, 2.67, and 3.33 mol $KMnO_4$/mol contaminant, respectively.

Although MnO_4^- will oxidize a wide range of contaminants, there are notable exceptions for co
are recalcitrant, including
1,1-dichloroethane (DCA)
chloroform (CF), methylen
zene (CB), benzene, some p
The rate of MTBE oxidation
orders of magnitude slower
cesses indicating that oxida
applicability of the process fo
al., 2002).

I.C.1.b. Reaction Rate

Contaminant oxidation by M
transfer rather than through the
radical attack characteristic of
relatively slow reaction rate of
tems offers advantages to perm
The slow rate of reaction allows
tances of MnO_4^- during injecti
and high permeability materials
sistence in the subsurface is proportional to the concentration of MnO_{4-} injected, and inversely proportional to the oxidant demand by the aquifer material and contaminant(s).

MnO_{4-} generally persists in the subsurface for months; however, persistence varies based on the concentration and volume of oxidant injected and from site to site. The long-term persistence of MnO_{4-} contributes to diffusive transport of the oxidant into low-permeability materials, such as silty clay (Struse et al., 2002a) and fractured shale (Parker, 2002). Consequently, this permits deeper penetration of the oxidant into aquifer materials that contain slow-moving contaminants.

I.C.1.c. Natural Oxidant Demand

A wide range of aturally occurring reactants other than
inant(s) also react with MnO_{4-} and
nd oxidant demand. The background
luces oxidation efficiency and is gen-
the demand imposed by the target
n-target reactants mainly include
reduced chemical species (e.g., fer-
lfidic species). In aquifer material
ities of organic carbon and reduced
ound oxidant demand can be low.
ghly reduced conditions and/or
naterials, the background oxidant
ggesting that the mass and cost of
reatment objectives will be high
A.3. Oxidant Demand).

alts

permanganate, potassium per-
nd sodium permanganate
grades of $KMnO_4$ are available from
chemical suppliers. The average prices of remediation grade $KMnO_4$ and $NaMnO_4$ are $1.80/lb and $6.50/lb ($2.50/lb aqueous 40% solution), respectively. $KMnO_4$ is available as a solid that must be mixed with water before injection and is soluble at approximately 60 g/L (6%). $KMnO_4$ concentrations are generally injected

Table 3. General Permanganate Oxidation and Related Chemical Reactions

$MnO_4- + 2 H_2O + 3 e- \longrightarrow MnO_2(s) + 4 OH-$	(pH 3.5-12)	(1)
$MnO_4- + 8 H+ + 5e- \longrightarrow Mn+2 + 4 H_2O$	(pH <3.5)	(2)
$MnO_4- + e- \longrightarrow MnO_4^{-2}$	(pH >12)	(3)
$4 KMnO4 + 3 C2Cl4 + 4 H2O \longrightarrow 6 CO_2 + 4 MnO_2 + 4 K+ + 8 H^+ + 12 Cl^-$		(4)
$2 KMnO_4 + C2HCl_3 \longrightarrow 2 CO_2 + 2 MnO_2 + 2 K^+ + H^+ + 3 Cl^-$		(5)
$8 KMnO_4 + 3 C_2H_2Cl_2 \longrightarrow 6 CO2 + 8 MnO_2 + 8 K+ + 2 OH- + 6 Cl- + 2 H_2O$		(6)
$10 KMnO_4 + 3 C_2H_3Cl \longrightarrow 6 CO2 + 10 MnO_2 + 10 K+ + 7 OH- + 3 Cl- + H_2O$		(7)