

REGEN



PRINCIPLES OF CHEMICAL OXIDATION TECHNOLOGY

For the Remediation of
Groundwater and Soil



Design and Application Manual V.4.0



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1.0 INTRODUCTION

1.1 Purpose

The intention of this manual is to serve as a reference point to allow the reader to understand the current “best practices” in chemical oxidation technology and more specifically the application of RegenOx®, the state-of-the-art remediation technology developed by REGENESIS. The first three sections of this manual (1-3) describe the basic chemical oxidation mechanisms and the technical attributes of chemical oxidation products. Then, Section 4- Biological Treatment Following Chemical Oxidation describes the coupling of chemical oxidation technology with accelerated bioremediation. The balance of the manual deals with technology application. Section 5- Expectations of Chemical Oxidation - deals specifically with setting realistic objectives for remediation and properly managing performance expectations. Sections 6 through 10 offer design and application guidance on successfully completing a chemical oxidation project. Lastly, Section 11 describes technical support available from REGENESIS to engineering firms for the design and application of chemical oxidation to treat subsurface contamination.

1.2 Chemical Oxidation - A Contaminant Mass Reduction Technology

The use of chemical oxidation technology as a form of *in situ* soil and groundwater remediation has been practiced for at least two decades. Early practitioners realized the potential for harnessing chemical oxidation processes employed in wastewater treatment to rapidly destroy organic contaminants in soil and groundwater. On the heels of this early work, a significant body of research has been accomplished elucidating many of the reactions that are involved with *in situ* applications of chemical oxidation technologies, and the many factors that influence the outcome of such projects. Valuable contributions have been made by researchers in academia as well as practitioners in the field regarding specific oxidative chemistries, the interactions of the oxidative species with native materials, and the requirements for successful delivery.

Further, it is now clear to many that chemical oxidation is best coupled with accelerated bioremediation for more successful site management. This is a program that REGENESIS is uniquely qualified to deliver within its range of expertise and products. Chemical oxidation has been used successfully to remove significant contaminant mass from soils and groundwater at numerous sites. Using a variety of oxidants, such as hydrogen peroxide, permanganate, persulfate, percarbonate, and ozone, some success has been seen on a majority of the Contaminants of Concern (COCs). Hydrogen peroxide has been shown to be effective for petroleum-based COCs and permanganate has been used for chlorinated solvents. Most researchers and practitioners believe that the technology has the ability to rapidly reduce large masses of contamination; however, the promise of chemical oxidation to rapidly and completely degrade target contaminants *in situ* has been overstated. Site owners or responsible parties have been disappointed as chemical oxidation has failed to meet their expectations of reaching low (ppb) contaminant concentrations within a short period of time. The requirement for direct oxidant- contaminant interaction, matrix interactions effects, contaminant desorption, plume distribution, and a range of other factors are now seen as inhibiting the simplistic view of complete and rapid treatment *in situ*.

These cumulative experiences have revealed that *in situ* chemical oxidation technology is a technically sound and potentially cost-effective approach for affecting a contaminant mass reduction in a relatively short period of time. However, following a single addition of an oxidant, rebound of dissolved contaminant concentrations is the norm. Most practitioners now realize that in order to reach low contaminant concentrations there is a requirement for multiple injections followed by engineered bioremediation. To emphasize this point, we present some very recent and seminal work which has emerged through SERDP/ESTCP funded research and asks hard questions

about source treatment and dissolved phase contaminant rebound. The following is an excerpt from a paper accepted for a peer reviewed publication and used herein with permission of the author C.J. Newell (McGuire, T.M., J.M. McDade, and C.J. Newell, 2005. Groundwater Monitoring and Remediation, in press). "The occurrence of rebound (i.e., an increase in groundwater concentrations following treatment completion) is another important factor in evaluating the success of source depletion technologies. Many case studies and literature reports document decreases in concentrations following source depletion activities. However, the data presented is typically of short duration and does not allow a complete assessment of whether or not the reduction achieved was permanent (Parsons 2004, USEPA 2004, USEPA 2001, ESTCP 1999, USEPA 1998). Of the few studies that have monitored concentrations for extended periods beyond completion of source depletion activities, several have observed some level of concentration rebound (ITRC 2004, ESTCP 1999).

In order to more accurately assess the occurrence of rebound, sites with concentration records including at least one year of post-treatment data were evaluated. Results of the rebound analysis are presented in Table 1-1. Rebound was analyzed for 43 wells at 20 sites (10 enhanced bioremediation sites, 7 chemical oxidation sites, 2 surfactant/co-solvent sites, and 1 thermal site). On an individual well basis, rebound was observed in 15% of wells at enhanced bioremediation sites, in 81% of wells at chemical oxidation sites, in 33% of wells at surfactant/co-solvent sites, and was not observed in one well at the thermal site. Concentrations in several wells at chemical oxidation sites rebounded by as much as 1 to 2 orders of magnitude throughout the post-treatment monitoring period. In fact, at 30% of the chemical oxidation rebound wells, rebound resulted in concentrations higher than pre-treatment conditions. For rebound wells at enhanced bioremediation and surfactant/co-solvent sites, the increased concentrations observed during the post-treatment period were still below pre-treatment concentrations."

Table 1-1: Evaluation of Rebound at Source Depletion Sites

Source Depletion Technology	Percent of sites with rebound at 1 or more well	Percent of sites with rebound at >50% of wells	Number of wells analyzed for rebound	Number of wells with rebound
Enhanced bioremediation	30	20	20	3
Chemical oxidation	88	57	16	13
Thermal treatment	50	0	1	0
Surfactant/co-solvent	0	0	6	0

Clearly, the respective costs of these treatments need to be considered as well. Thermal and surfactant treatments at smaller sites in particular would be problematic to justify relative to a chemical oxidation treatment. Our conclusion and that of many practitioners is that a coupled chemical and biological oxidation is the most cost-effective approach at most sites.

1.3 Chemical Oxidation Coupled to Accelerated Bioremediation

In situ bioremediation through the use of injectable controlled-release substrates (such as Oxygen Release Compound or Hydrogen Release Compound) has long been recognized as a very cost effective technology for achieving low contaminant concentrations when applied to dissolved phase contaminant plumes. Areas of high contaminant concentrations such as source zones within and above the aquifer have remained a challenge to these and other technologies due to the high contaminant demand. Thus, what has emerged is the integrated approach of coupling chemical oxidation technology to reduce the contaminant mass in high concentration areas with a follow up application of a controlled-release bioremediation substrate to treat the remaining contaminant concentrations over time.

1.4 Development of RegenOx®

Over the past decade, REGENESIS has been responsible for leading the development of innovative *in situ* remediation products. Initially this development focused on controlled-release bioremediation products. More recently, however, attention was given to the invention of a chemical oxidation product capable of rapidly removing contaminant mass while at the same time coupling seamlessly to *in situ* bioremediation. Our customers were looking for a product that was very active in reducing high concentrations (10 to 1,000 ppm) of contaminants, but also one that was easy to handle, non-detrimental to the environment, and very compatible with *in situ* bioremediation processes. In response, REGENESIS has developed RegenOx.

RegenOx is the new generation of chemical oxidation. RegenOx is a proprietary *in situ* chemical oxidation process using a solid oxidant complex (sodium percarbonate/catalytic formulation) and an activator complex (a composition of ferrous salt embedded in a micro-scale catalyst gel). RegenOx with its catalytic system has very high activity, capable of treating a very broad range of soil and groundwater contaminants including both petroleum hydrocarbons and chlorinated solvents. Additionally, RegenOx has significant longevity in the subsurface allowing for both the initial contaminant degradation and the continued treatment of contaminants desorbing from the matrix. Most importantly, RegenOx, when handled appropriately, is safe and easy to apply to the contaminated subsurface without the health and safety concerns and lingering environmental issues that have become associated with other chemical oxidation technologies.

2.0 CHEMICAL OXIDATION PRINCIPLES

In this Section, we discuss the fundamental chemical principles behind the usage of RegenOx. Even though sodium percarbonate provides molecules of hydrogen peroxide, the behavior and properties of a percarbonate solution is not the same as that of a hydrogen peroxide solution. This section will describe how the thermodynamics, the radicals formed, and the alkaline conditions generated by RegenOx differ from other chemical oxidation systems.

2.1 Chemical Oxidation Mechanisms

A chemical oxidation reaction involves the breaking of chemical bonds and the removal of electrons. The electrons are transferred from the contaminant to the oxidant. The contaminant is in turn oxidized and the oxidant, the electron acceptor, is reduced. All reactions are always paired in this way – hence the term oxidation-reduction reaction. We use the term “direct oxidation” for this simplest of mechanisms. With RegenOx however, there are other more complex mechanisms including catalyzed direct oxidation and free radical mechanisms that mediate contaminant degradation by both oxidation and reduction.

2.1.1 Direct Chemical Oxidation

A molecule of sodium percarbonate ($C_2H_6Na_4O_{12}$ or $2Na_2CO_3 \cdot 3H_2O_2$) dissolved in water yields sodium carbonate and hydrogen peroxide creating an alkaline, oxidative environment. One question that is probably emerging for the reader regards the difference between sodium percarbonate and hydrogen peroxide. As illustrated in the formula, sodium carbonate “carries” hydrogen peroxide in the same way as a molecule carries a “water of hydration”. This is a big advantage in that it makes it less immediately reactive. The direct oxidation of tetrachloroethene with sodium percarbonate would theoretically yield water and carbon dioxide as the standard oxidation end products per Equation 2-1.



RegenOx[®], by using sodium percarbonate, can directly oxidize a wide range of contaminants including:

- Fuel hydrocarbons from gasoline through the higher molecular weight compounds;
- Aromatic hydrocarbons such as the benzene, toluene, ethylbenzene and xylene (BTEX) compounds and the heavier polyaromatic hydrocarbon (PAH) compounds;
- Gasoline oxygenates such as methyl tertiary butyl ether (MTBE) and their derivatives;
- Petrochemically derived reagents such as phenols, aldehydes and ketones;
- Chlorinated solvents with emphasis on the common chlorinated ethenes perchloroethene (PCE), trichloroethene (TCE), chlorinated ethanes such as trichloroethane (TCA) and dichloroethane (DCA), and chlorinated methanes such as carbon tetrachloride and chloroform.

2.1.2 Surface-Mediated Chemical Oxidation

This is a variant of direct oxidation involving catalytic complexes. The RegenOx system employs a complex which includes a proprietary catalytic surface that provides a unique surface (activator complex) for both the contaminant and the RegenOx oxidizer complex to interface. When the contaminant, oxidizer complex and activator complex come together, rapid contaminant oxidation occurs. Reactions can still take place without the catalytic surface via direct oxidation; however, surface-mediated oxidation is more efficient. The advantages of surface-mediated reactions include:

- Increased efficiency -- brings oxidant and contaminant together isolating the oxidation reaction from soil matrix effects
- Adjustable reaction rates -- accomplished by varying oxidant to activator ratios
- Positional longevity -- activator mobility in the subsurface can be adjusted by injection design

2.1.3 Free Radical Mediated Oxidation and Reduction

In order to completely oxidize (mineralize) contaminants to carbon dioxide and water, all chemical oxidants must either supply oxygen from the oxidant itself or from reactions involving water. In addition to the oxygen provided by its oxidant, RegenOx is capable of promoting the propagation reactions that yield a mixture of free radicals. A free radical is a highly reactive molecule having an unpaired electron. Free radicals are generated by the decomposition of peroxide in the presence of metal salts such as a ferrous salt. Examples of free radicals that are formed by RegenOx include:

Perhydroxyl radical $\text{HO}_2\bullet$ (oxyhydroxyl or protonated superoxide)

The perhydroxyl radical is a species formed by a base catalyzed free radical mechanism. In the RegenOx system, the perhydroxyl radical is one of the predominant radical intermediates formed.



In addition, the hydroperoxide anion HO_2^- , the conjugate base of H_2O_2 , will form. The hydroperoxide anion is a reductant.



Hydroxyl radical OH•

The reaction of ferrous iron and hydrogen peroxide generates hydroxyl radicals. The hydroxyl radical can react with almost any hydrocarbon or chlorinated hydrocarbon. However, because of the alkaline conditions promoted by the RegenOx catalyst, hydroxyl radicals have only a minor role in the active mechanisms of this oxidative system.



Superoxide radical O₂•⁻

The superoxide radical is also a reductant which can break down highly oxidized compounds such as carbon tetrachloride and chloroform.



2.2 Oxidation Potential

The oxidation potentials of chemical oxidants are often ranked in terms of their electropotential. The electropotential is the electromotive force in units of volts (V) based on half-cell reactions. Theoretically, larger values indicate a greater potential for the half reaction to proceed.

Relative electropotentials: (Source: ITRC 2005)

Hydroxyl Radical	2.8 V
Ozone (Gas)	2.1 V
Sodium Persulfate	2.0 V
Sodium Percarbonate	1.8 V
Hydrogen Peroxide	1.8 V
Permanganate	1.7 V
Superoxide Ion	-2.4 V

Oxidation potentials (half-cell reactions) for oxidants, however, do not tell the whole story. They rate oxidants only against hydrogen and do not account for the chemistry needed to provide the oxygen for the oxidation reactions, provide the cation for the chloride, account for all electrons transferred, and provide the needed components for completely balanced equations (the contaminant side of a half-cell). Further, oxidation potentials tell us nothing about the speed of reactions. To understand the complete picture, one must evaluate the oxygen content of the oxidant, the thermodynamics and kinetics of the reaction.

2.3 Relative Oxygen Equivalence (Active Oxygen)

Having more oxygen in the oxidizer does not necessarily mean more oxygen will be used. To better understand each oxidant's provision of oxygen to oxidize, we can gauge the relative weight fraction of oxygen in each oxidant that can contribute to chemical oxidation. This is also known as % active oxygen (A.O.). Using this metric we have:

Hydrogen Peroxide	47% A.O.
RegenOx® Oxidizer Complex	15.3%
Potassium Permanganate	15.2%
Sodium Persulfate	6.7%

Thus on an Active Oxygen basis, RegenOx has 1/3 the electron equivalence of H₂O₂, approximately the same as permanganate, and over 100% more than sodium persulfate.

2.4 Thermodynamics

Thermodynamics tells us the likelihood or potential that a reaction will take place as well as to what extent the reversible reaction has proceeded when equilibrium is reached. Interpreting completely balanced equations in terms of the Gibbs Free Energy is a more valid approach for comparing reactions than one based on half-cell reactions alone. The Gibbs Free Energy (ΔG) is a measure of the amount of energy that is available from some process operating at constant pressure and is directly connected to voltage as expressed in Equation 2-2. The Gibbs Free Energy function is a convenient way to determine which way a reaction will go. If $\Delta G < 0$, that reaction will occur “spontaneously.” In the context here “spontaneously” means that the process, given a pathway, occurs spontaneously; it says nothing about the rate at which the process might occur. The voltage for the complete oxidation-reduction reaction (ϵ) is equivalent to the chemical change in Gibbs Free Energy (ΔG) divided by the number of electrons transferred (n) and a constant of nature termed Faraday’s Constant (F).

$$\epsilon = -\Delta G / nF \text{ (2-2)}$$

The lower the free energy (in other words, the more negative), the higher the voltage and the more likely the reaction will occur. The following are some common oxidation reactions using PCE as the contaminant and the common range of commercial oxidants. With reference to Dialogue Box 1 (next page) we can see two things.

1. The peroxide mediated reactions are the strongest based on the most negative ΔG . The calculations show the energetics of peroxide under basic conditions, as is done with RegenOx, are more favorable than for permanganate and persulfate under their use conditions.
2. When treating chlorinated contaminants, chloride is a terminal product of the oxidation, and we would prefer it not form a problematic chlorine species such as an oxide. By operating peroxide reactions under basic conditions, as is done with RegenOx, more benign chloride salts are formed. It is very important to note that not all reactions of chlorinated compounds lead to the formation of benign chlorine compounds. One example of problematic reactions with chlorinated compounds is as follows:
 - Formation of ClO₂ from the Peroxidation of PCE under Acidic Conditions



Dialog Box 1

RegenOx®	$\Delta G = -338 \text{ kcal/mol}$
$\text{C}_2\text{Cl}_4 + 2 \text{H}_2\text{O}_2 + 4 \text{NaOH} \rightarrow 2 \text{CO}_2 + 4 \text{NaCl} + 4 \text{H}_2\text{O}$	
Potassium Permanganate:	$\Delta G = -329 \text{ kcal/mol}$
$\text{C}_2\text{Cl}_4 + 4 \text{KMnO}_4 \rightarrow 2 \text{CO}_2 + 4 \text{MnO}_2 + 4 \text{KCl} + 2 \text{O}_2$	
Potassium Persulfate:	$\Delta G = -271 \text{ kcal/mol}$
$\text{C}_2\text{Cl}_4 + 2 \text{K}_2\text{S}_2\text{O}_8 + 4 \text{H}_2\text{O} \rightarrow 2 \text{CO}_2 + 4 \text{KCl} + 4 \text{H}_2\text{SO}_4$	
Hydrogen Peroxide:	$\Delta G = -261 \text{ kcal/mol}$
$\text{C}_2\text{Cl}_4 + 2 \text{H}_2\text{O}_2 \rightarrow 2 \text{CO}_2 + 4 \text{HCl}$	

The reader may note that the Energy of Activation is not considered in this discussion. The fact is that these reactions have been observed in practice, thus the required Energy of Activation is manifested.

2.5 Kinetics

Even if the reaction is thermodynamically favored, it is still governed by kinetics. In essence, thermodynamics addresses the probability of the reaction and kinetics tells us how fast the reaction will happen. If the reaction is fast, equilibrium calculations will predict the results of the reaction. If the reaction is not fast, then the only way to follow the course of the reaction is to measure the chemical composition as a function of time. (Robinson 1987).

The rate of reaction describes the destruction of the compound of interest over time as a function of the concentrations of the various species participating in the reaction. For chemical oxidation, the rate of reaction (with respect to the contaminant) for a contaminant A reacting with an oxidant B can be written as a function of both the concentrations of A and B with k as the rate constant, as per Equation:

$$-r_A = k (C_A / C_{A_0}) * (C_B / C_{B_0})$$

Where C_A is the final concentration of A and C_{A_0} is the concentration of A at time = 0, and C_B is the final concentration of B and C_{B_0} is the concentration of B at time = 0. Now if the concentration of oxidant B is in large excess compared to the concentration of contaminant A such that the concentration of oxidant B does not change much during the course of the reaction, then $C_B = C_{B_0}$. The above rate equation would then reduce to

$$-r_A = k (C_A / C_{A_0})$$

After integration $C_A = C_{A_0} e^{-kt}$. This equation would define a pseudo-first order reaction. A plot of the natural logarithm (ln) of C_A / C_{A_0} versus time should yield a straight line.

Half-life is commonly used as a measure of rate for first-order reactions. Half-life is the time required for the concentration of contaminant to reduce in half. Thus at time $t_{1/2}$ when $C_A = \frac{1}{2} C_{A_0}$, then

$$t_{1/2} = \ln 2 / k = 0.693 / k \quad (\text{Levenspiel 1972})$$

In the field the reaction rates will tend to be slower. However, practically speaking, the only way chemical oxidation is affordable is if the rate of the oxidation of the contaminant is faster than the rate of the interaction of the oxidant with the background oxidant demand of the aquifer.

In order to come up with an objective, scientifically-based comparison of the effectiveness of RegenOx with other oxidants, we compared the two properties of a chemical reaction that determines its effectiveness, thermodynamics and kinetics. The half-lives for several common contaminants treated with RegenOx and several other oxidants were experimentally determined in a laboratory (Source: Applied Power Concepts of Anaheim, CA). We calculated the Gibb's Free Energies for the same combinations of oxidant and contaminant. We normalize ΔG_r to the lowest ΔG_r of the group (the lowest ΔG_r is the most thermodynamically favorable reaction

$$(\text{normalized } \Delta G_r) = (\Delta G_r \text{ lowest} / \Delta G_r \text{ oxidant})$$

We added the normalized ΔG_r to a weighted half-life value to derive a score for effectiveness:

$$\text{Score} = (1/3)(\text{normalized } \Delta G_r) + (2/3)(\text{Contaminant half-life})$$

These calculations can be used to estimate comparative oxidant effectiveness as, for example, in these two tables:

Example Calculation Results 1:

PCE	ΔG_r	norm. ΔG_r	Half-life (hrs.)	Score	Grade
RegenOx [®]	-338	1.00	1	1.0	A
Persulfate	-271	1.03	2.3	1.9	B
Permanganate	-329	1.24	0.9	1.0	A

Example Calculation Results 2:

Toluene	ΔG_r	norm. ΔG_r	Half-life (hrs.)	Score	Grade
RegenOx [®]	-1416	1.06	0.8	0.9	A
Persulfate	-1505	1.00	1.25	1.2	B
Permanganate	-1056	1.43	7	5.1	D

Based on laboratory kinetic data, thermodynamic calculations and literature reports.

Oxidant Effectiveness Key:

A = Short half-life, low free energy (most energetically favored), most complete

B = Intermediate half-life, low free energy, intermediate degree of completion

C = Intermediate half-life, intermediate free energy, low degree of completion

D = Long half-life, high free energy (least favored), very low degree of completion

2.6 Longevity

The longevity of an oxidant after it is applied to the subsurface is important because it affects the radius of influence by affecting the distances the oxidant can travel in the subsurface and still be active. Increased longevity may be necessary to increase contaminant degradation that is limited by the desorption of contaminant from the soil matrix. Longevity varies as a function of a number of factors, including the concentration of oxidant used, the kinetics of the oxidant (including autocatalytic decomposition), temperature and pH of the aquifer, concentration of contaminants, and the composition and total oxidant demand of the groundwater and soils.

Laboratory studies of longevity have shown that RegenOx in water, with or without soil, lasts for weeks – or even months depending on how the catalytic complex is provided. Field studies have corroborated this where RegenOx indicated activity in excess of 25 days as measured by the presence of hydrogen peroxide. By comparison, Fenton's reagent using activated liquid hydrogen peroxide lasts seconds to days, persulfate lasts weeks to months, if not fully activated, and permanganate, a much milder oxidant, has been shown to persist from several months to over a year. It is also critical to note that longevity of organic free radicals and radical-producing compounds (like peroxyacids) generated by RegenOx[®] is beyond 30 days, and that these species are capable of degrading various contaminants.

2.7 The Advantages of Alkaline Chemistry

RegenOx uses a basic oxidizer complex and thus generates alkaline conditions (high pH) and does not rely on

operating under the acidic conditions (low pH) that are required when using standard catalyzed hydrogen peroxide (Fenton's chemistry). Fenton's reagent is typically conducted at low pH in order to maintain iron solubility; however, low pH may not be the most effective conditions for efficient peroxide consumption. This is because the production of perhydroxy and superoxide radicals is inhibited at acidic conditions.

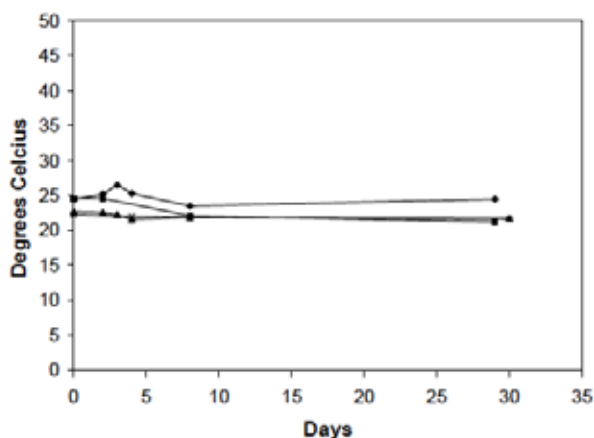
The formation of radicals is very different at high pH. None of the conventional logic associated with acid catalyzed reactions (where the hydroxyl radical is key) applies to the base catalyzed reactions of peroxide. The radical that is predominantly generated on the base side is the perhydroxyl radical ($\text{HO}_2\cdot$). This is well established from detergent technology and is the reason why detergent manufacturers "bleach" at high pH. Reactions under acidic conditions create more of the undesirable "chloro" compounds (rather than benign chloride salts) when chlorine is present either in the oxidant or the substrate. Under basic conditions carbonate scavenging is not a concern. In the solid state, the manner in which percarbonate "holds" hydrogen peroxide is by hydrogen bonding and crystal-packing forces. In solution, peroxide and carbonate dissociate and participate in many dynamic interactions including hydrogen bonding and acid-base equilibria. Although carbonate does react with the hydroxyl radical to produce a carbonate radical, this is one minor pathway in a group of many redox reactions taking place. It is important to note that the carbonate radical is also an oxidant, albeit a mild one.

2.8 Heat/Gas Production

Elevating the temperature at which the oxidation reaction occurs both activates and decomposes an oxidant. The rate of hydrogen peroxide decomposition doubles with every 10 °C rise in temperature. Thus, highly exothermic treatments (such as with the use of Fenton's reagents at high concentration) results in very short longevity of the oxidant and is often associated with high oxidant losses due to autocatalysis (the conversion of hydrogen peroxide to oxygen) (Vance, 2004). Thus less hydrogen peroxide is available for the desired oxidation reactions.

When high concentrations (greater than 15%) of liquid hydrogen peroxide are used (as in a Fenton's chemistry application), the exothermic breakdown of the peroxide generates heat which further accelerates decomposition and oxygen gas that tends to volatilize contaminants from the soil and/or groundwater. This rapid decomposition reaction with the evolution of heat and oxygen has the potential to create an explosive condition if used for treatment of flammable or combustible compounds (ITRC, 2005). RegenOx uses a solid peroxide oxidizer complex and does not generate excessive heat or gas. RegenOx is inherently easier to apply and is safer to use than oxidation technologies that employ liquid hydrogen peroxide. Therefore, RegenOx does not significantly increase groundwater temperature (Figure 1).

Figure 2-1: Monitoring Well Temperature profile after addition of 12% solution of RegenOx



3.0 CONTAMINANT MINERALIZATION VS. CHEMICAL OXIDATION

3.1 Generation of Partially Oxidized Intermediates

The chemical oxidation of contaminants in groundwater and soil is a process whereby the contaminant materials are converted into other chemicals with the addition of oxygen. The chemical reactions, in terms of the sequence of intermediate products involved, are similar to those involved in combustion (burning the chemicals in the presence of oxygen) or in aerobic bioremediation (biological oxidation). The time scale of chemical oxidation is between those two extremes of burning the chemicals in air which can occur in seconds or minutes and the biochemical oxidation reactions of bacteria which can take weeks or even months.

Like combustion and bioremediation the contaminants go through a series of reactions starting with the first step of changing the contaminant into a first “daughter product”. This daughter product is then further oxidized and the sequence continues with the potential of several side pathways until the ultimate state of complete oxidation occurs. In this final state we have only products of water (from hydrogen), carbon dioxide (from carbon) and comparable oxides or ionic species from other elements such as nitrogen, chlorine and sulfur when the contaminants contain these other elements.

To use a simple example consider the oxidation of the chemical toluene, one of the BTEX components. Complete or total oxidation would be written:



Therefore, it takes 18 oxygen atoms for each toluene molecule to completely oxidize toluene. This complete oxidation is sometimes referred to as “mineralization” since carbon dioxide is an inorganic material. The sequence of reactions to get from toluene to complete oxidation produces a series of reactions that has been well documented in the literature. The first step in the chain of reactions for a RegenOx® type of oxidation is conversion of toluene to benzyl alcohol:



The next step converts the benzyl alcohol to benzaldehyde which is then quickly converted to benzoic acid in the third step.



As illustrated in Figure 3-1:

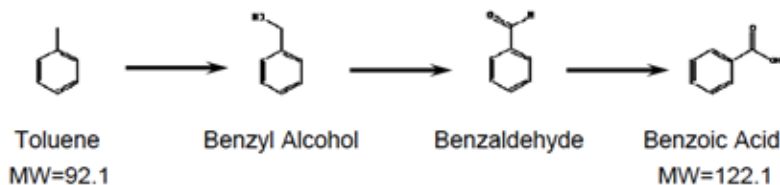


Figure 3-1: RegenOx® Oxidation Pathway for Toluene

However, the sequence of reactions to get from pentachlorophenol to complete oxidation may go through a series that includes chloranil, which is a suspected carcinogen (Figure 3-2):

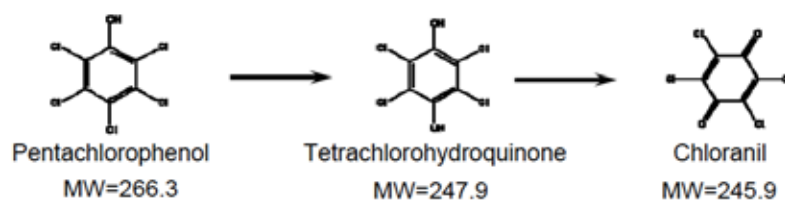


Figure 3-2: Potential Oxidation Pathway for Pentachlorophenol

This series continues until the reaction is completed or until one runs out of oxidant either by dilution or due to other reactions. Rarely are oxidations complete. As with internal combustion engines, there are always some residual unoxidized material such as carbon monoxide and some volatile organic compounds (VOCs).

3.2 Partially Oxidized Products are Readily Biodegradable

In site remediation it is critical to note that we are assisted by the fact that microbes in the aquifer can assimilate partially oxidized by-products. In fact, the oxidation by-products are likely to be much more biodegradable than the contaminants. For example, benzoic acid from toluene is much more water soluble and degradable than the toluene parent compound. While this may mean they are more readily transported, that is not necessarily bad as they can move into water with more available electron acceptors. Also, most of these compounds are not regulated. In the case cited, benzoic acid and derivatives are widely used in human food and personal care products.

In considering how much chemical oxidant is required to adequately treat a contaminated site, the ultimate objective of the remediation has to be considered. For example, highly contaminated sites will require multiple injections of contaminant. In very contaminated source areas it may be unrealistic or cost prohibitive to add enough oxidant to provide the oxygen required for total mineralization. In these cases, applying a lesser amount of oxidant that leads to a more readily degraded by-product that can be metabolized by microbes in the sub-surface may be a very successful and cost-effective strategy. As will be covered next, the RegenOx system was designed to work “seamlessly” with the subsequent bioremediation. By this we mean that the conventional mechanisms that may inhibit a smooth transition to bioremediation are minimized such as temperature and the presence of inorganic species that can be inhibitory to reductive dechlorination. Further detail on this can be found in Section 4.

The chemical literature provides vast amounts of information on the nature of oxidation reactions and the sequence of reactions. For example, the initial products of benzene are aromatic phenols such as catechol. The catechol is, therefore, naturally produced as part of the aerobic biodegradation of benzene and these compounds facilitate subsequent biological activity as an energy substrate even if they are not totally removed by the initial chemical oxidation. Likewise, the chlorinated solvents have been found to produce oxidation products that are similar to those found in bioremediation. For example, in PCE and TCE remediation, under reductive conditions, one expects to see DCE and VC – as well as compounds such as chloral and chloroacetic acid that are produced under more deeply methanogenic conditions. While these products can be quite toxic to humans, they have been shown to be readily biodegradable once they are produced. They are also produced under conditions of high energy chemical oxidation and likewise are readily biodegradable. This section illustrates that there is a

series of partially oxidized intermediates that can potentially be formed from some key target contaminants. It is very important to realize, however, that we cannot make a blanket statement for the benign or biodegradable nature of intermediates. What we can say is that in the area of the most common contaminants – the most ubiquitous petroleum hydrocarbons and chlorinated solvents – we seem to have a reasonable understanding of the by-products such that ordinary concerns are abated. Further, we must recognize that these intermediates have the potential to form under natural attenuation conditions and that it may be advantageous to make the conversions in a controlled area and process them through the system relying on biological mechanisms.

Others have addressed this issue at the regulatory level as well. The Interstate Technology Regulatory Council (ITRC) in its most recent treatment of chemical oxidation (ITRC 2005) offers this guidance in several different sections of the document. “In almost all cases, the intermediates that are produced in these reactions are more biodegradable when compared to the parent compound.”

“Measurement of the anaerobic microbial benefits of ISCO focuses on the post-oxidative effects of enhancing biological reductive dechlorination (e.g., halorespiration) of the chemical contaminant of concern. In many cases this post-oxidative effect acts as a “polishing” step to help bring contaminants below risk-based concentrations. The aquifer commonly reverts to pre-injection conditions within six months after the oxidant is consumed, which in many cases is an anoxic environment. The reduction of contaminant levels and the production of intermediates more biodegradable can enhance anaerobic degradation in the post-oxidation environment.”

“The remediation of groundwater contamination using ISCO involves injecting oxidants and potentially co-amendments directly into the source zone and downgradient plume. The oxidant chemicals react with the contaminants, producing innocuous substances such as carbon dioxide, water, and—in the case of chlorinated compounds—inorganic chloride. However, there may be many chemical reaction steps required to reach those end points, and some reaction intermediates, as in the case of polyaromatic hydrocarbons and organic pesticides, are not fully identified at this time. Fortunately, in most cases if an adequate oxidant dose is applied, the reactions proceed to completion, and the end products are reached quickly.”

“There are two main advantages of using chemical oxidation over other conventional treatment technologies: large volumes of waste material are not usually generated, and treatment is commonly implemented over a much shorter time frame. Both of these advantages often result in savings on material, monitoring, and maintenance.” In summary, the formation of a series of partially oxidized intermediates following chemical oxidation is to be expected. Complete chemical oxidation of the compounds of concern, especially in a complex aquifer, is not an expected result under normal and economically reasonable circumstances. Furthermore, the variation in what is produced can be a function of competing reactions within the aquifer, specific aquifer geochemistry and other physical and organic features. The good news is that intermediates produced are manageable with subsequent enhanced bioremediation. The combination of chemical oxidation treatments followed by the injection of controlled-release substrates for the stimulation of bioremediation is a practice that makes both technical and economic sense.

3.3 Intermediates as Performance Indicators

Lastly on the topic of intermediates, it should be noted that these compounds can be used as “tracking indicators” to follow the success of a remediation project employing chemical oxidation. In essence we are saying that if a source area is treated and experiences contaminant concentrations rebounding, the intermediates are a sign that mass was in fact removed – a fact that would otherwise be hidden by dissolution, desorption or an influx of new mass.

4.0 COMBINING CHEMICAL OXIDATION WITH BIOREMEDIATION

In the previous sections we have established that for most contaminated sites multiple chemical oxidation applications will be required. While RegenOx® has specific advantages over other available chemical oxidation technologies, one should still expect to apply multiple injections of the product in order to achieve significant mass reductions of contaminant in the subsurface (as is the case with all oxidants). As discussed in the previous section, complete and instant chemical oxidation of organic contaminants simply does not occur within the complex environment of the contaminated subsurface. Therefore, chemical oxidation is a sequential process taking the parent target contaminant through a series of partially oxidized intermediate daughter products on the path to complete mineralization. Also discussed in the previous section is the fact that the oxidized intermediates formed are generally more biodegradable than the parent. Based upon these facts, one can conclude that a logical strategy to achieve low contaminant concentrations on project sites with high contaminant mass would be the use of chemical oxidation technology to achieve initial mass reduction, followed by longer term stimulation of *in situ* bioremediation.

4.1 Indigenous Microbes Survive Chemical Oxidation

Over the past decade in which chemical oxidation technology has been applied there has been much debate over the topic of subsurface sterilization. It was thought by many that microbes indigenous to the subsurface would simply be wiped out by the application of harsh chemical oxidants. Today, this notion is now widely disregarded as an increasing amount of research and field experience has indicated the contrary. The ability for natural microbes to rapidly re-colonize the subsurface after chemical oxidation treatment is well documented in the literature (Azadpour-Keeley et al., 2004, Buyuksonmez et al., 1999, DeHghi et al., 2001, Miller et al. 1996). A full list of citations, separated by topic, can be found in the References.

Dr. Robert Norris, a widely respected peroxygen scientist and groundwater remediation expert, provided a useful and timely summary of the current industry perception on the viability of indigenous microbes following chemical oxidation. He stated, "Following *in situ* chemical oxidation, microorganisms in the treatment area may suffer but eventually will recover in periods measured in months. Downgradient reductive dechlorination is enhanced by the increase of electron donors generated from the native organics. Aerobic degradation appears not to be hurt, but increased oxidation potentials seem to be temporary and there is potential competition for electron acceptors from the newly formed soluble organic matter. The above seems to be true for ozone, permanganate and persulfate. Fenton's reagent using acidic conditions and lots of peroxide (temperature will play a part) may be more damaging. To me it seems that peroxide systems using lower temperatures and more neutral pHs will act more like the other oxidants". In this statement he is referring to the RegenOx oxidizer complex that is a more benign conveyor of hydrogen peroxide and basic chemistry. Today there is little doubt that indigenous microbial flora present prior to a chemical oxidation application will indeed rapidly re-colonize the treated area and will flourish in the presence of the right conditions.

4.2 RegenOx® is Designed to Transition to Bioremediation

In designing a chemical oxidation technology, REGENESIS sought to maximize not only the chemical oxidation potential of the product, but also to ensure maximum compatibility with *in situ* bioremediation. When developing the product, a main objective was to employ an oxidant within the formulation that would not negatively interfere with bioremediation processes that would occur after the oxidation was complete. Between the use of simple sodium percarbonate and the design of the REGENESIS two-part catalyzed activator complex technology, we have achieved this objective.

At present, with other chemical oxidation technologies, one risks leaving behind detrimental residuals such as manganese from permanganate or high levels of sulfate from persulfate applications. These compounds can interfere with reductive dechlorination by poisoning the redox reactions of the system in either manganese or sulfate reducing conditions at the expense of reductive dechlorination. Further, some minerals like manganese or hydrogen sulfide have been reported to be bacteriostatic and mutagenic which raise post-treatment water quality issues. The RegenOx system leaves behind very little residue, limited primarily to the innocuous carbonate and bicarbonate ions. These residuals do not have a negative effect or interfere with efficient natural attenuation or enhanced bioremediation and do not detrimentally impact the quality of the groundwater treated.

Figure 4-1 presents results of a study performed on the biodiversity of an environmental sample subjected to treatment by RegenOx. The biomass concentrations and microbial diversity was determined by Microbial Insights, Inc (www.microbe.com) before and after a RegenOx treatment. Biomass, as measure by phospholipid fatty acid analysis (PLFA), did not significantly change after treatment or rebounded rapidly. A more detailed look at the microbial community structure showed several things. The eukaryotes declined. The supposition is that the eukaryotes – whether unicellular or multi-cellular – are more complex and therefore more susceptible to oxidative stress. We also see a modest increase in fermentative organisms which also makes sense as the chemical oxidants make organic material more available and “pre-digested”. Then finally, if we have an increase in fermentative by-products such as hydrogen, the increase in some of the anaerobes makes sense as well. While much of this analysis is conjecture, it is clear that the microbial community present in the sample subjected to RegenOx was not radically harmed.

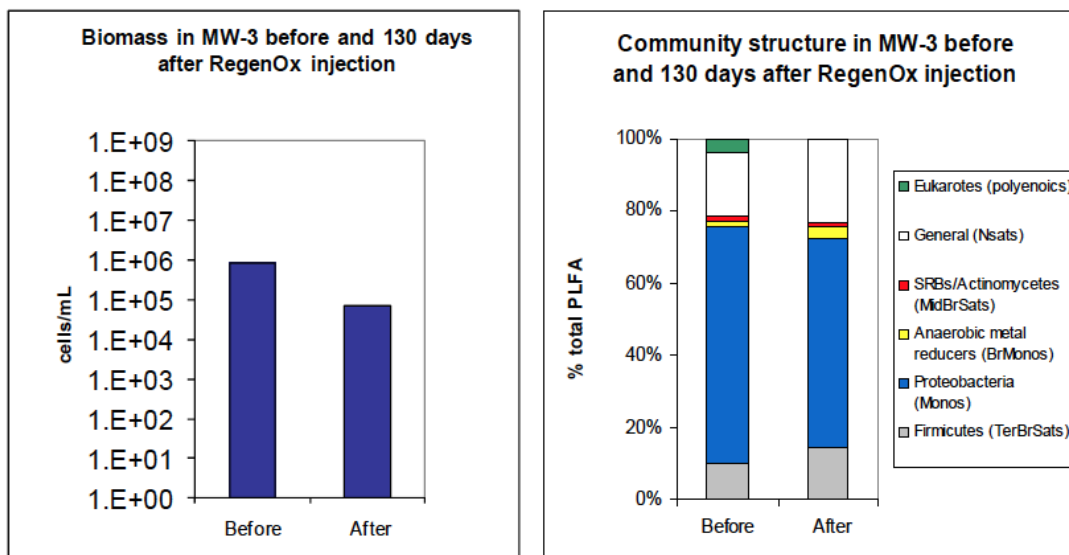


Figure 4-1: The Effect of RegenOx® on Biomass and Microbial Diversity

5.0 ESTABLISHING RATIONAL EXPECTATIONS FOR CHEMOX

It often bears repeating that chemical oxidation should not be viewed as a “silver bullet”. As with other remediation technologies, one hears of the failures of chemical oxidation as often as the successes. In order to increase the odds for success, it is imperative to understand the applicability of chemical oxidation.

5.1 Defining the Objective and Goals of the Remediation Plan

The first step in deciding whether or not to use chemical oxidation as a remediation technology is to have a clear definition of the overall objective of the treatment. Accompanying the objective should be a clear goal(s) that can be measured in order to determine if the objective has been met. Often the objective and goal(s) are established by the regulator, the responsible party, and/or the consultant. However, many times a remediation strategy is chosen prior to distinguishing site objectives and goals. If the goals have not been clearly articulated, then expectations for the technology and the definition of “success” may differ between the parties.

Let’s say the remedial objective at a hypothetical chemical oxidation project site is to “reduce contamination on the site so that the regulator can close the docket prior to land transfer”. All concerned parties may have agreed to this objective; however, no one established and agreed upon written measurable goals to determine whether the objective had been met. Nor under this scenario is there any agreed upon methodology to judge the performance of chemical oxidation.

Continuing with our hypothetical project, let’s say that over the course of six months, four injections of a chemical oxidant had reduced the mass of contamination by 90%. The consulting engineering firm viewed this as a success because their expectation was that the use of chemical oxidation would only reduce mass by 50% within a year. The property owner, however, viewed the use of chemical oxidation as a failure because he had expected one injection of the chemical oxidant to reduce the contaminants of concern to maximum concentration limits (MCLs) within two months time so as to allow for unrestricted use.

Thus one can see from this hypothetical scenario the need for all parties to agree beforehand on specific remediation goals. If the goal in this example was to meet MCLs in all site monitoring wells within 18 to 24 months, then a “successful” remediation plan may have included chemical oxidation to reduce contaminant mass by 70% in the first six months followed by bioremediation to meet MCLs over the course of the following year. The objectives and goals of a particular project have to realistically balance the performance criteria with the time constraints. Drinking water quality standards such as MCLs simply cannot be achieved in a short period of time by current remedial technologies including chemical oxidation. It has to be realized that either the time constraint has to be lifted or the performance goals have to be less stringent.

So before evaluating the use of chemical oxidation (or any remediation technology), the following questions should be addressed:

1. What are the objective and goal(s) of the remediation plan?
2. What is the expectation of chemical oxidation within this remediation plan?
3. How will the performance of chemical oxidation be measured?

Chemical oxidation is a useful remediation tool for removing contaminant mass and should be viewed in that light. Chemical oxidation can be used as the first or second step in a treatment-train approach to site cleanup. However, by itself, chemical oxidation may not be the most cost-effective solution to meeting MCL concentrations in the groundwater. Chemical oxidation’s role in the remediation strategy is bounded by its technical limitations and the life-cycle cost. A life-cycle cost analysis of the remediation strategy should be performed whereby input parameters are selected that can be monitored for the purpose of deciding when to switch to the next treatment component of the remediation plan (e.g., bioremediation).

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5.2 Contaminant Distribution in the Subsurface

As a basis for understanding how to best apply chemical oxidation to a site cleanup, it is worthwhile reviewing how contamination is distributed across a given contaminated project site after the initial contaminant release.

5.2.1 Non-Aqueous Phase Liquids

There has been much written on non-aqueous phase liquid (NAPL) and source remediation. The National Research Council recently issued the report *Contaminants in the Subsurface: Source Zone Assessment and Remediation* (NRC 2004). Other recent reports include *An Illustrated Handbook of DNAPL Transport and Fate in the Subsurface* (UK EA 2003) and *The DNAPL Remediation Challenge: Is There a Case for Source Depletion?* (US EPA 2003). The reader is directed towards these reports and others (ITRC 2002, US EPA 1998) for a broader discussion on the subject. The reports point out that often the site characterization, remedial technology selection, and metrics used to measure success are misaligned.

5.2.1.1 NAPL Movement and Distribution

In the case of NAPLs, “they flow (downward) through a vadose zone under the influence of gravity, until they encounter the capillary fringe. Since the water table typically rises and falls due to seasonal changes or precipitation events, the hydrocarbons become “smeared” across the capillary fringe and the water table. Much of this mass is occluded in interstitial and pore spaces as small droplets of NAPL, which can only be removed by dissolution in groundwater under normal conditions. This is a very slow process, and is limited by the constituents’ solubility, its diffusivity in water, and the velocity of groundwater movement. The amount of occluded NAPL is affected directly by the distribution of pore and particle sizes within the soil.”

“A portion of the hydrocarbons that come out of the solution below the water table will partition (sorption to soil) to natural organic carbon (expressed as total organic carbon). This can add to the depth of the “smear” zone, not uncommonly creating a zone eight to ten feet in thickness where most of the hydrocarbon is present, whether as small droplets of NAPL or sorbed to the soil. The amount of hydrocarbon actually dissolved in the groundwater is usually less than a few percent of the total hydrocarbon mass. Any process which solely treats the groundwater is thus required to wait for sorbed material or NAPL to dissolve” (US ACE 1997).

Likewise, “Dense non-aqueous phase liquid (DNAPL) can form pools in the subsurface, or they can exist as small globules or ganglia retained within the aquifer pores. Among the many distinguishing features of DNAPL sites is the fact that the distribution of DNAPL in the subsurface is typically sparse and highly heterogeneous. Once the contaminants are in the subsurface, processes such as dissolution, sorption, and biodegradation work to further affect contaminant distribution by redistributing mass locally among phases as well as carrying the contaminant away from the site of initial release. Depending on the hydrogeologic setting, a portion of the contaminant mass released to the subsurface as DNAPL may diffuse into stagnant zones as either sorbed or dissolved-phase contamination” (NRC, 2004).

5.2.1.2 Free Phase Product Mass

It's also imperative to have an understanding of the mass of free-phase NAPL that is present on site. In the case of light non-aqueous phase liquid (LNAPL), the thickness of the product is measured, but that measurement is typically not translated to the actual thickness or volume of LNAPL in the aquifer. When compared to the actual thickness in the aquifer, a 3-inch thickness of product measured in a monitoring well screened in clay is much more exaggerated than the same thickness measured in a well screened across sand. The relationship between the LNAPL thickness in a well and the volume of LNAPL in the aquifer is complex. American Petroleum Institute offers guidance on these types of calculations. See their website <http://api-ep.api.org/filelibrary/ACFE0.pdf> and Free-Product Recovery of Petroleum Hydrocarbon Liquids (Charbeneau 2000a,b).

The presence of free phase DNAPL is generally much less common. Historically, well gauging equipment has been used for measuring DNAPL thickness. More recently, however, newer methods have been introduced. Publications such as EPA's Site Characterization Technologies for DNAPL Investigations. US EPA 2004 and ITRC's Strategies for Monitoring the Performance of DNAPL Source Zone Remedies (ITRC, 2004) describe DNAPL characterization techniques using emerging tools such as Membrane Interface Probe (MIP) and Optical Spectroscopy. Other techniques such as Induced Polarization have also been used to characterize DNAPL in fractures within bedrock.

5.2.1.3 Sorbed Mass

Groundwater has a higher affinity than NAPL for soil, therefore, interfacial tension tends to hold the NAPL within the pores. According to API, "water and LNAPL coexist in the pores under different pressures. The difference in pressure between the LNAPL (non-wetting phase) and water (wetting phase) is defined as capillary pressure. The greater the pressure in the non-wetting (e.g., LNAPL) the more fully the pore space is filled (saturated) by the non-wetting phase" (API, 2003). Quite often the NAPL occupies only a small percent of the available pore space yet still provides a source for contaminants in the dissolved plume.

Similarly, DNAPL is generally the non-wetting phase in most saturated soils. In the vadose zone, the DNAPL is more often the wetting phase. Capillary barriers such as the water table and thin silt and clay lenses retard the migration of the DNAPL.

Estimating Sorbed Contaminant Mass Requires Soil Samples

The US Army Corp of Engineers Engineer Manual referenced earlier again offers that, "recognizing how the NAPL, both dissolved and sorbed, are distributed in the subsurface and how they can potentially be affected by the remedial technology are prerequisites to identifying the data collection needs. For most soil strata impacted by hydrocarbons, the majority of the hydrocarbon mass is sorbed to the soil particles or resides as NAPL within interstitial spaces. Soil concentrations provide the most useful assessment of how much material will actually require removal or degradation." This points directly to the need for sampling soils in the area of known or suspected NAPL so as to estimate the amount of contaminant bound to the soils. Simply sampling groundwater samples will grossly underestimate the contaminant mass to be treated.

5.3 Developing a Remediation Program

On most project sites with impacted groundwater, it is groundwater regulatory standards that drive the cleanup. This can be at the point of compliance or site wide. Since these regulatory standards are based on the concentration of contaminants in the groundwater, the site characterization and monitoring is focused on the mass in the dissolved phase. Thus, the overall objective set for a remediation plan is ultimately tied to reducing the con-

centration of contaminants in water. The remediation plan can, however, be composed of a sequence of treatment technologies (a “treatment train”) designed to meet this objective, but with individual goals for each phase or technology employed in the cleanup.

For example, consider a site with free-phase LNAPL.

Hypothetical Site Conceptual Remediation Strategy

First phase	Remove the volume of free-phase LNAPL
Second phase	Reduce the residual sorbed mass and high concentrations of dissolved phase
Third phase	Reduce the dissolved-phase concentrations to MCLs

Each of these sequences would have goals established and realistic timeframes within which to reach these goals. Now how does chemical oxidation fit into all of this discussion? At this hypothetical site, it would be unrealistic to expect chemical oxidation to take the site from free-phase LNAPL to MCLs. In fact, chemical oxidation is probably not a cost-effective selection for the first (also can be hazardous) or third treatment. However, chemical oxidation would be an excellent technology candidate for the second phase, reducing residual mass.

5.3.1 Treatment of Free Phase NAPL

It is generally more cost-effective to remove the free-phase NAPL first by other means prior to the use of chemical oxidation. The quantity of oxidant required to oxidize masses of recoverable free-phase NAPL will typically rule chemical oxidation as too expensive. In addition, there is a common misconception that chemical oxidation can be used to treat free-phase NAPL and “burn off” masses of contamination sorbed to the soils.

Chemical oxidants are not miscible in LNAPL or DNAPL so the contaminant oxidation occurs only in the aqueous phase, involving dissolved species of both the contaminant and the oxidant. Therefore, the solubility of the contaminant ultimately controls the rate of possible oxidation. The rate of mass removal is limited by the kinetics of the contaminant dissolution process rather than those of the chemical oxidation reaction (Vance, 2004).

5.3.2 Treatment of Residual/Sorbed NAPL

After the bulk of the free-phase NAPL has been removed, chemical oxidation makes sense as the second phase of treatment - to reduce the mass of residual NAPL. NAPL components are oxidized only as they dissolve into the aqueous phase with the first step generating more soluble oxidative intermediates. By mass action, contaminants are driven to the aqueous phase and oxidations at the water/NAPL interface proceed much faster and further. “Rebound” of contaminant concentrations within the groundwater is to be expected as the contaminant desorption proceeds between chemical oxidant injections. Again, this rebound is due to the desorption of contaminants from residual NAPL bound within the subsurface. If the contaminant binds tightly to the soil, then the rate of desorption can make the rate of dissolved phase reaction appear as though the oxidant-contaminant reaction is slow, when in fact the kinetics for this aqueous-phase reaction are quite high. This is due to the fact that the residual contaminant sorbed to the subsurface is serving as a reservoir for the release of dissolved phase. When this release occurs, it can manifest itself as “rebound”.

When the oxidant has been depleted, the dissolved phase contaminant concentrations may rebound to concentrations greater than were present initially. This phenomenon is due to the fact that the chemical oxidation process can often reduce the fraction of organic carbon bound to the mineral content of the soils, thereby reducing the adsorption capacity.

In addition, the elevation of pH can affect the solubility and chemical behavior of the contaminant. The end result of these phenomena is that a greater partitioning of contaminant in the aqueous phase is occurring after the treatment than before. This is a very positive result in that the chemical oxidation application has induced significant amounts of sorbed mass to move into the aqueous phase where oxidation can proceed.

Rebound is to be expected after an application of any chemical oxidation technology. The verification that mass has been reduced is found by taking a significant number of soil samples or using advance techniques, like Membrane Interphase Probes (MIPs), to map the subsurface concentration of contaminants. Monitoring the concentrations in the groundwater alone speaks only to the aqueous phase, ignoring the soil bound and generally greatest mass of contaminant.

After successive chemical oxidation treatments of the saturated subsurface, when the rate of removal starts looking asymptotic, there comes a point of diminishing returns where chemical oxidation no longer makes economic sense. As the mass of contamination is removed from the soils, the rate of overall mass transfer gets slower and slower to a point where the oxidant is being depleted by competing reactions in the absence of immediately available target contaminants. This point is generally well above low concentration standards such as MCLs. If, on a given project, the remediation objective is to attain low dissolved phase contaminant concentrations, then the goal of using chemical oxidation should be limited to rapidly removing contaminant mass down to a point where bioremediation can take over.

5.3.3 Treatment to Low Dissolved Phase Concentrations

The third phase of the hypothetical treatment train would be enhanced or accelerated bioremediation. Following the application of chemical oxidation, the subsurface will contain lower concentrations of original contaminants lower mass, less on soils, but not necessarily less in water, partially oxidized intermediates, and other organics generated from the soils themselves. A proven, effective, and low-cost approach to treating these constituents is the use of a passive, controlled-release compound to stimulate *in situ* biodegradation. REGENESIS' controlled-release compounds, such as ORC Advanced® or HRC®, as appropriate, can stimulate microbial populations in the subsurface environment to degrade contaminants and intermediates down to low concentrations.

Bioremediation is very effective at mineralizing the intermediates formed during the oxidation of otherwise recalcitrant compounds as discussed in Section 3. Because of its sustainability, the use of bioremediation can be the final cost-effective stage in achieving the overall objective of a groundwater restoration project. REGENESIS can help you with the life-cycle cost analysis of your remediation strategy by making the determination as to when it is both technically and economically favorable to switch from chemical oxidation to bioremediation (or in some cases even start overlapping chemical oxidation and bioremediation).

5.4 Other Factors in Determining the Applicability of *In situ* Chemical Oxidation

In addition to the concentration and distribution of contamination, there are other factors to consider when determining if chemical oxidation is applicable to your site conditions. These factors include the types of contaminants to be treated, the type of lithology and the lithology in which the contaminants are distributed, the time frame over which remediation will take place, and the surface/subsurface structures and impediments on the property.

5.4.1 Types of Contaminants to be Treated

The previous Section discussed the range of contaminants that RegenOx can treat. REGENESIS is currently

gathering information on other contaminants of concern. Please contact REGENESIS' Technical Services department for questions concerning contaminants not discussed here.

5.4.2 Soil Types/Lithology

The soil type and lithology of the subsurface will impact the effectiveness of chemical oxidation. The type of soil (sand, silt, clay, gravel) will largely determine the amount of water that the soil can hold (pore space volume) and the velocity thru which the groundwater can travel through the soil (permeability). Mass transfer of contaminant and oxidant in high permeability soils (e.g. sand) is dictated by dispersion/advection. Mass transfer of contaminant and oxidant in low permeability soils (clay) is dictated by diffusion. The length of time and plausibility that the oxidant will come in contact with the contaminant will be governed by the lithology. The oxidant will travel through sandy lenses quicker than clay lenses. Fractures provide preferential pathways that bypass pockets of contamination.

Clays and silts tend to bind contaminants to their surface tighter than sands. If this is not considered in the delivery design across heterogeneous lenses, the chemical oxidant will circumvent the low permeable clay and silt lenses in favor of the higher permeable sands. The oxidant will not make contact with the residual NAPL and the treatment will fail. If the lenses are well characterized, then the injection of the oxidant can be directly targeted to the tighter soils by use of special injection tools. However, it should be recognized that it is difficult to obtain adequate distribution of oxidant in clays without applying the oxidant in closely spaced, multiple injection points.

In addition, some aquifers and soils will have greater competing background or natural oxidant demand than others. Generally speaking the longer it takes the chemical oxidant to travel through the soil, the greater the oxidant will be consumed by competing demands. Furthermore, the tighter soils tend to have higher native organic content with which the oxidant might react. The special considerations given to fractured sedimentary rock and fractured clay such as saprolite are discussed later in this manual. The outcome is a function of how well the fractured areas containing sources can be identified and then how well those fractures are targeted. Channeling will occur through higher permeable fractures at the expense of lower permeable fractures.

5.4.3 Treatment Time-Frame

Realistic expectations need to be established for any remediation project. As stated before, when applying chemical oxidation technologies, more than one injection will usually be required. The cycling of injections will be driven by the rate of oxidation and the rate of desorption/diffusion.

Any perspective on time should consider that the degradation half-life is the same from 10 ppm to 5 ppm as it is from 100 ppm to 50 ppm. Often there is a misconception that a chemical oxidation treatment did not work as well at the lower concentrations, when in fact the rates were the same. Also, in dealing with lower concentrations there tends to be "noise in the data" and as part of this there are limitations in accuracy for the analytic techniques. An extended time period may be necessary to determine the trends in the data at the lower concentrations.

5.4.4 Site Structures/Impediments

Site infrastructure such as buildings and utilities need to be identified and evaluated when evaluating chemical oxidation. Utility corridors may serve as preferential pathways for oxidant delivery if not properly planned for. Safety considerations must be addressed when injecting oxidants under and around buildings and other structures particularly when treating shallow contamination. A geotechnical evaluation may be warranted prior to injecting

large volumes of solution directly underneath footings and foundations. Obviously, surface structures may also limit the feasibility of reaching all of the contamination, depending on the method of delivery chosen and hence the success of the project.

The alkaline chemistry of RegenOx is more chemically compatible with typical site infrastructure than most other chemical oxidants. As mentioned previously, Fenton's type chemistry and activated persulfate typically require acidic conditions that can be very corrosive. This is the main reason that Fenton's type remediation is not recommended near tanks or pumping islands of commercial gasoline stations.

6.0 DESIGN CRITERIA FOR A CHEMICAL OXIDATION PROJECT

The basis for any design of a chemical oxidation project can be reduced down to three principal factors (Dahmani 2004):

- Oxidant Selection
- Oxidant Loading
- Oxidant Delivery

Now let's evaluate RegenOx using the above ideal selection criteria.

6.1 Oxidant Selection

6.1.1 Rapid oxidation of target compounds

RegenOx activator provides for a proprietary micro-scale catalytic surface upon which the efficiency of the direct oxidation reactions is increased by 10- to 30-fold over that of percarbonate alone.

Unlike oxidants that can work only by direct oxidation (e.g. permanganates) RegenOx also generates free radicals, and therefore, has the energy to break saturated bonds (single bonds between carbon atoms as found in many hydrocarbons) in addition to unsaturated bonds (double bonds as found in chlorinated ethenes).

6.1.2 Production of Intermediates of Oxidation

As discussed in Section 3.0, all chemical oxidation reactions generate partially oxidized intermediate compounds. This is simply part of the oxidation process and is common to all chemical oxidation technologies available. However, the intermediates produced are manageable with subsequent enhanced bioremediation. The combination of chemical oxidation treatments followed by the injection of controlled-release substrates for the stimulation of bioremediation is a practice that is both technically feasible and cost-effective.

6.1.3 Toxicity of Oxidant and Oxidation Products in Groundwater and Soil

RegenOx will have minimal impact on water quality. The reagents injected into the subsurface and the post treatment residuals of these reagents are considered innocuous to the environment. Unlike permanganate and persulfate, RegenOx does not add compounds that will potentially have an adverse impact on water quality and bioremediation. Secondary drinking water standards exist for sulfate and manganese, and the use of these chemicals to treat groundwater jeopardizes the quality of the water after treatment.

With regard to shifting the geochemistry of the aquifer and the potential to increase the concentration of dissolved heavy metals, RegenOx generates basic conditions. Metals mobilization is less likely under basic conditions

than acidic conditions. Furthermore, mobilized metals are typically stabilized by the geochemical conditions of the aquifer. In most documented cases, metals naturally revert back to the reduced state after oxidation treatment is complete (ITRC 2004b).

6.1.4 Reactivity with Soil Organics and Inorganics

All oxidants will have some reactivity with soil organics and inorganics. Most important to an *in situ* chemical oxidation design, this reactivity can represent a considerable demand of the oxidant that must be added to any calculation of the amount of oxidant needed to remediate any site. This demand is referred to as the Soil Oxidant Demand (SOD), Natural Oxidant Demand (NOD) or Total Oxidant Demand (TOD). The order of importance of TOD to the amount of oxidant needed at a site is as follows:



This order is related inversely to the rate of auto-decomposition of the oxidants, which is as follows:



The reactivity of RegenOx is primarily driven by the activator complex. RegenOx tends to react less with background oxidant demand from natural organics and inorganics in the soil matrix. A more detailed description of reactivity with soil organics and inorganics is given in Section 6.2.

6.1.5 Oxidant Longevity and Oxidant Residual

The oxidative effect of RegenOx can continue in the subsurface for weeks and in some cases months depending on the quantity and placement of the activator as well as the soil and aquifer geochemistry. Again, the mere presence of an oxidant is only part of the story. Hence, RegenOx has significantly greater longevity than standard Fenton's reagent but does not persist in groundwater for the extensive period of time as seen with permanganate – where just observing the pale-purple color may not be relevant to product performance, but may classify the permanganate as a secondary groundwater contaminant.

6.1.6 Safe Application & Easy Materials Handling

RegenOx is a two-part product. Part A (the oxidizer complex) and Part B (the activator complex) each are separately packaged in easy to handle pails. Part A and Part B can be mixed together without concern of excess heat or gas generation. RegenOx does not require special injection tools or patented injection processes. The two part product is simply mixed together and pumped into the subsurface using easily-obtainable equipment standard to the remediation contracting and drilling industry.

6.2 Oxidant Loading

In order to determine the amount, or “load” of RegenOx required for your project, you will need to understand the oxidant demand of the contaminants of concern, as well as the dispersion and desorption processes in relation to the kinetics of contaminant degradation. Commonly available TOC and COD tests for site soil and groundwater are also valuable tools in RegenOx application design. In some cases, TOD (total oxidant demand) tests are used to estimate the oxidant loading. However, contaminant mass typically drives site design. Matrix effects are considered as modifiers to that basic strategy.

6.2.1 Oxidant Demand of Contaminants of Concern

The oxidant demand of contaminants of concern will come from several possible phases such as dissolved-phase contaminants, sorbed-phase contaminants, free-phase non-aqueous phase liquids (NAPL), and vapor-phase (limited to vadose zone). In order to estimate the oxidant demand of the contaminants, one must determine the total mass of each contaminant. The width, length, and depth of the source area must be approximated. Based on the type of soil (gravel, sand, silt, clay) assumptions are made as to the pore space volume available to groundwater within the volume and the bulk density of the soil.

The dissolved-phase mass can be approximated from the concentration of contaminants found in monitoring well data. The sorbed-phase demand can be estimated directly using concentrations of contaminants found in soil samples or indirectly from partitioning calculations. This is possible as the mass of contaminant sorbed to the aquifer is a function of the bulk density of the aquifer matrix, the fraction of organic carbon in the matrix (foc), and the contaminant-partitioning coefficient (Koc). Input values for the soil, the bulk density, and the foc can be measured or estimated based on soil types. The Koc value can be obtained for each contaminant from any number of published references (including REGENESIS software). Estimating the mass of free-phase NAPL is a bit more challenging. Methods have been developed by API and US EPA (API 2004, Charbeneau 2000a, Charbeneau 2000b, US EPA 2003).

After the mass has been calculated/estimated, the load of RegenOx to be applied is calculated based on the molar ratio of oxidant to contaminant(s) as dictated by the demand of the full oxidation-reduction calculations (mineralization). Contact REGENESIS for calculated stoichiometries for specific contaminants. The oxidant demand for each contaminant and each phase is summed to understand the load of RegenOx theoretically required to completely oxidize the contamination. To maximize the kinetics of the reaction, the actual load of RegenOx may need to be several orders of magnitude higher than the theoretical value.

6.3 Dynamics – Dispersion and Desorption/Diffusion Processes Versus the Reaction Kinetics

In addition to the previous discussion on comparing reaction kinetics, we also must consider the dispersion, desorption, dissolution, and diffusion processes that are affecting both the oxidant and the contaminant transport.

The transport of the oxidant through uncontaminated aquifer regions and its reaction with target contaminants is not entirely a function of the TOD alone but also a function of transport and reaction rates. The oxidant can either react with the contaminant, react with the NOD, or continue on to the next pore space. The relative rates of reaction and transport will determine what happens to the oxidant. If the rate of reaction between the oxidant and NOD is relatively slow, then more oxidant will be available for reaction with the target contaminant or transport to the next pore space. This also implies that since the entire NOD is not necessarily consumed, the next injection of the oxidant may encounter oxidant demand that was not consumed during the first injection (Mumford 2002).

Generally speaking the longer it takes the chemical oxidant to travel through a given distance in the soil, the greater the oxidant will be consumed by competing demands. Mass transfer of oxidant in high permeability soils (e.g. sand) is dictated by dispersion. Mass transfer of oxidant in low permeability soils (clay) is dictated by diffusion. Diffusion of contaminants also comes into play and thus concentration gradients.

Contaminant oxidation occurs only in the aqueous phase, involving dissolved species of both the contaminant and the oxidant. The solubility of the contaminant ultimately controls the rate of possible oxidation. There is interface mass transfer and then chemical oxidation. Generally in the subsurface, the rate of mass removal is limi-

ted by the kinetics of the contaminant dissolution process rather than those of the chemical oxidation reaction. On the other hand, there is also a strong driving force for the oxidant to diffuse into the deep soil pores and oxidize contamination. The oxidant will diffuse from higher permeability lenses into the lower permeability lenses and react with dissolved contaminants in the low permeability lenses and dead-end pores. The reaction leads to higher concentration gradients for both the oxidant and the contaminants. Since the oxidant is delivered in an aqueous solution, delivery is not inhibited by variation in soil capillary properties which is often the case for technologies relying on delivery of a gas phase (LaChance 1998, Watts 2003). The oxidant will move from the sandy zones into the silt layers via advective but advective flow is faster within the sand flow and diffusion (LaChance 1998, Watts 2003).

Chemical oxidants are insoluble in NAPL; therefore, the oxidation reaction takes place in the aqueous phase. Dissolution of DNAPL is a slow process limited by interphase mass transfer; however, oxidation can facilitate dissolution. Fenton's reagent reportedly enhanced DNAPL interphase mass transfer (Siegrist 2004a) and again, interphase mass transfer rate during oxidation treatment is greatly improved because chemical gradients are increased significantly for both the oxidant and the DNAPL.

6.4 Oxidant Delivery

Effective distribution of the oxidant is probably the most important factor in the success of an *in situ* chemical oxidation project. Chemical oxidation requires contact. The chemical oxidant has to come in direct contact with each molecule of contaminant in order to be effective.

The ultimate goal is to deliver enough oxidant to the majority of the pore volume in order to maintain first order kinetics with respect to the contamination until remediation goals are met. This requires knowledge of how the contamination is distributed laterally and vertically, the subsurface lithology, and the hydrogeology. Another factor to consider when choosing a delivery system is whether the contamination to be treated is located in the vadose zone or the saturated zone. It is also important to have knowledge of the location of surface structures and underground utility corridors.

Timely, Multiple "Paired" Injections

Most sites require 3-4 applications to ensure contact and minimize rebound. The 1st and 2nd applications in most designs do not overlap due to offsetting the injection points and together cover ~70-80% of the total treatment area. So, after "2" applications you accomplish one complete treatment.

Likewise, the 3rd and 4th treatments accomplish one complete treatment. Therefore, these "paired" injections should be done as soon as possible. On a small site (e.g pilot test) they should be done as a continuous injection event. On a large site, the first injection could be done one week and the second done the next week. Approximately, two weeks later the second paired injection (3 & 4) should be performed.

High Volume Injections

RegenOx injections are designed with relatively high volumes of 10 to 30 gallons per 1 ft. intervals. High volume injection ensures a sufficient emplacement volume (i.e. pore volume displaced by the injected liquid) to achieve good contact between the RegenOx solution and the soil contamination. RegenOx stays active for approximately 15 days (but can last up to a month). During that time advection and dispersion may increase its radius of influence (ROI) up to an additional 20 to 30% of the original emplacement volume. So, it is true that the larger the emplacement volume, the better the ROI, and the better the contact between RegenOx and the contaminants of concern. However, high volume injection can create greater subsurface hydraulic pressures that can

lead to short-circuiting and surfacing of fluids. If subsurface pressures are sufficiently high, asphalt and concrete cover can buckle. Although off-gassing from the chemical reaction can contribute to this pressure, the primary driver is the high liquid volumes that have been injected. To avoid the negative effects of high volume injections, make sure that you monitor the injection pressure at the wellhead with a suitable in-line gauge, and maintain the injection pressures below 20 psi. Additionally, the localized hydraulic head can be reduced by adequate spatial separation of installed injection points e.g DO NOT apply the material in a side-by-side fashion. Instead, move to the opposite side of the injection grid thus separating adjacent injection points with as much physical space and time as possible. At some sites, it may be necessary to stop injection for one to two hours to let the aquifer naturally dissipate the hydrostatic pressure.

Oxidant delivery is accomplished either by batch delivery or continuous delivery methods. Batch delivery methods include:

- Direct-push Injection
- Permanent Wells (vertical or horizontal)
- Temporary well points
- Lance – high-powered jet

Continuous delivery methods include:

- Open Ended Systems with injection wells, etc.
- Recirculating Systems with injection and recovery wells

Direct-Push Injection vs. Injection Point

Direct-push injections and high-pressure jetting rely on injecting into several points placed about 10-feet apart, depending on site-specific hydrology. Multiple injections are required to deliver enough oxidant. In the case of direct-push units, the drive rods are pushed to the desired depth and the chemical oxidant is pumped in while slowly pulling up the drive rods. The chemical oxidant can also be injected from the top down by using specially-designed injection rods. High-pressure jetting utilizes systems similar to tree root feeders to inject the chemical oxidant via steel wands that are pushed downward into the subsurface.

Direct-push injection is preferred because of the greater control, both vertically and horizontally, on where the injected fluids are placed. This method provides more field flexibility and adjustment to unanticipated field conditions. Typical direct-push applications use a grid injection pattern and inject a 3% RegenOx solution (i.e. 3% Part A and 3% Part B). To maximize the activity of the RegenOx in the aquifer, apply a solution volume that can be injected in ~1 hour (typically <200gals). A detailed description of the RegenOx® solution formulation procedure can be found in Section 9.0. Designs of continuous delivery through injection points generally rely on wells placed farther apart than batch systems. In the case of the recirculating systems, the hydraulic gradient is enhanced by the cone of depression created by the extraction wells. Permanent wells or recirculating systems in high TOD soils may not prove to be effective. Injection points are particularly conducive to vadose zone treatment where large volumes of solution are required to nearly saturate the soils. Further discussion on oxidant delivery is given in the upcoming section on full-scale design

Application through fixed well delivery points may be recommended if access to the treatment area is problematic or greater than 6 application events are warranted. For injection via a delivery well, the RegenOx concentra-

tion recommended is 3% and the Part A and the Part B materials are applied separately. A 3% solution of Part B and water is injected, followed by approximately 100 gallons of water (flush). This is followed by the application of the 3% solution of Part A, and finally, a second 100 gallon water flush. This injection plan prevents the RegenOx solution from clogging the well screen. Clogging does not occur in direct-push applications or in the aquifer in general because the flux area is greater than the flux area through the well screen.

Excavation Application

RegenOx can be applied in an excavation pit in a number of ways depending on the conditions. If the pit is dry, then RegenOx can be applied as an 8% solution (8% w/w Part A and 8% w/w Part B) and mixed into the first 1-2 feet of the bottom of the excavation pit. If the pit has standing groundwater, then Part B is applied as a 3:1 solution (3 gallons of Part B with ~1 gallon of water). This solution is mixed into the uppermost 1-2 feet of the excavation floor. Upon mixing, Part A is added as a powder, and mixed into the same uppermost 1-2 feet of the excavation floor. During this process care should be taken to minimize the dust from the Part A. All personnel in the Exclusion Zone should be wearing proper PPE to protect eyes, lungs and skin (see Section 10.2).

7.0 TESTING PARAMETERS & DIAGNOSTICS

7.1 Site Monitoring

Site monitoring testing is performed prior to designing a pilot test or full-scale system to assess conditions and provide a base line to compare to post treatment conditions. Site monitoring is also used to assess the performance of chemical oxidation after injection. It is recommended to collect soil samples in addition to groundwater samples. As discussed earlier in the manual, it is difficult to assess the reduction in mass of contamination without analyzing the extent of contaminant reduction in the soils. Optimally this will require a statistically significant number of soil samples. Analysis of soil samples immediately after an ISCO application may provide rapid feedback on the treatment performance.¹

In order to validate the effectiveness of the chemical oxidation treatment, we recommend conducting monitoring at selected locations as discussed below. A baseline round of sampling should be performed to identify the groundwater quality/conditions and soil concentrations prior to the injection of the chemical oxidant. Collection of groundwater levels before and during the application may give immediate indication of the radius of influence (ROI) for the treatment. The following Tables outline the parameters and methods that should be used to monitor the progress of an oxidant-based project as well as our recommended monitoring schedule.

Table 7-1: Recommended Field and Laboratory Monitoring Parameters and Frequencies

	<i>Analyte</i>	<i>Method</i>	<i>Baseline</i>	<i>Appr. two weeks after each injection</i>	<i>Four weeks after final injection</i>
Field	pH; dissolved oxygen (DO); oxidation/reduction potential (ORP); conductivity; GW Levels	Meter reading taken in flow-through cell (DO can also be measured with a Hach field test kit)	GW	GW	GW
	Contaminant of concern	Appropriate EPA method	GW Soil	NA	GW Soil

Groundwater Monitoring Locations for a RegenOx® Application

The following table outlines the suggested locations and significance of monitoring wells used to monitor the progress of an oxidant-based project.

Table 7-2: Recommended Monitoring Well Locations

Location	Significance
Upgradient of treatment zone	Provides a measure of contaminant flux entering treatment zone.
Inside treatment zone	Provides information on how the chemical oxidant is affecting the aquifer conditions and contaminant concentrations
Downgradient of treatment zone	Provides information on the effect the chemical oxidant is having on the degradation rates of contaminants and on aquifer conditions

7.1.1 Oxidant Testing

Testing of the RegenOx oxidant can be done in the field using specially prepared test kits. REGENESIS can direct you where to obtain and use these test kits.

7.2 Bench Testing

Although a field pilot test is the most meaningful indicator of RegenOx treatment feasibility for a given site, for some projects it may be required to conduct a bench scale test in order to demonstrate the feasibility of RegenOx to oxidize a specific contaminant under specific field conditions. The bench scale testing also provides a suitable method for calculating first-order degradation rates of both the contaminant and oxidant in the bench test. Note that these rates are independent, as the oxidant degradation rate depends on both the contaminant and soil demand, whereas the contaminant degradation rate depends solely on the oxidant.

The kinetic rates obtained in the lab should not be considered as an accurate prediction of contaminant and oxidant degradation rates in the field. The bench test will overestimate both the contaminant and oxidant degradation rates due to mixing and continuous contact in a closed system. However, rates obtained in the lab may provide useful information about relative contaminant degradation rates and the relative longevity of the oxidant. REGENESIS can provide the user with a recommended laboratory protocol for testing RegenOx. REGENESIS also continues to add to a large database of information of projects with both lab and field data. With this database and our growing knowledge of the use of this product, we can help you interpret the results of your lab test in a meaningful way.

7.3 Pilot Testing

For projects having unknown or challenging lithologies/hydrologies, REGENESIS advises conducting a pilot test on a 20 foot by 20 foot section of the site prior to going full-scale. This pilot test section should be close to the source and in an area that will not be immediately recontaminated by upgradient sources. Generally the pilot test should consist of at least three (3) injection events at a frequency of every one to two weeks. REGENESIS will assist the user in calculating the quantity of RegenOx that should be used for the pilot test and specifics of the application design.

Field measurements and laboratory samples as described above are collected for a baseline prior to injection. It is imperative to collect representative groundwater and soil samples as well. One should, whenever possible, have groundwater data for several pretreatment events so the typical fluctuations for that site are known. In

particular, you would like samples taken under the same water table conditions. Ideally, the injection of RegenOx during the pilot test would be performed using the same delivery system design anticipated for full-scale design to ensure compatibility of the delivery method (direct injection, temporary wells) with site lithology

One of the best methods to deliver RegenOx into the subsurface is to inject the material through direct-push rods using hydraulic equipment. This approach increases the spreading and mixing of RegenOx into the aquifer. This set of instructions is specific to direct-push equipment. For advice on other injection methods such as soil mixing, hydraulic and pneumatic fracturing, and vertical injection, please contact REGENESIS Technical Services directly. The installation of RegenOx should span the entire vertical contaminated saturated thickness, or in the case of vadose zone treatment the entire affected vadose zone targeted for treatment, and for hydrocarbons it is often critical to treat the capillary fringe.

Typical equipment used for a standard pilot test would include:

- Direct-push rig
- Drive Rods (typically 1 ½-inch O.D.) & Injection Tooling with fluid deliver sub-assembly
- Injection Pump rated for 5 gpm @ 200 psi for sandy formations and 800 psi for silt and clay formations (Geoprobe DP-800, Yamada, Moyno, Rupe Models 9-1500 and 9-1600, Wilden, etc.)
- Injection hosing and a pressure relief valve with a bypass
- Clear hosing between mixing tank/drum and pump
- Pressure gauges
- Power drill paint stirrer (3-inch diameter or smaller propeller tip)
- Plastic bucket lid puller tool/opener tool
- 5-amp sump pump (such as Little Giant) and hose
- Three to four 55-gallon drums or similarly sized mixing tanks for RegenOx mixing
- Sand, bentonite chips, granular bentonite, cement, hydraulic cement, and quick-set concrete for closing and sealing temporary injection holes
- Wood plugs or similar for temporarily sealing injection holes prior to grout sealing
- Access to water
- Access to electricity

Typical field instrument and groundwater sampling should occur after each injection. The frequency for the post-injection pilot test sampling is shown in Table 7-1. In addition, soil samples are collected during baseline sampling, between each injection, and after the final injection. The results of the bench test and/or pilot test are used to determine if full scale treatment is appropriate and, if so, to scale up the project and make modifications to procedures if necessary. Full-scale design is addressed in Section 8 of this manual.

8.0 FULL-SCALE DESIGN

8.1 Oxidant Load Calculations

As discussed previously, relying solely on the dissolved-phase concentration of contaminants in the groundwater will underestimate the load of oxidant. Many contaminants will partition onto the soil. In the case of many organic contaminants, the mass of contaminant sorbed to the soil is greater than the mass dissolved in the groundwater. It is best to use contaminant mass results obtained from soil samples collected from the site along with groundwater analyses to estimate the total mass of contamination. In the absence of these data, the mass

partitioned to the soil can be estimated using the method described in the earlier Section. First, it is important to calculate the mass of NAPL remaining in the area to be treated. In many cases NAPL is suspected but not found due to limited sampling. In these cases the practitioner is best to use his/her best professional judgment and assume an amount of NAPL if suspected.

As discussed earlier, a site with a large quantity of NAPL (recoverable amounts) will require more cost-effective measures to remove the NAPL prior to considering chemical oxidation as a treatment technology. However, in the absence of any recoverable NAPL layer, one must do their best to calculate the contaminant mass that will be contributed by any residual NAPL present. In order to calculate the proper amount of oxidant, it is important to quantify even a “sheen” of petroleum hydrocarbons into a mass calculation. Methods developed by API and others can be used to estimate the volume of free product. Also, seasonal variation in the apparent thickness of should be measured. Once arriving at a total mass of contaminants (in the groundwater, saturated or unsaturated soil, and free-product), the contaminant demand on RegenOx is determined by the amount of oxygen required to oxidize each of the contaminants. This stoichiometric ratio obviously varies for each of the contaminants of concern.

Next, consideration is given to including a high enough load of RegenOx to assure the best kinetics, assuming adequate delivery, for the reaction. As discussed in Section 2.5, if RegenOx is in great excess over the contaminant, then the reaction will be driven by first order or pseudo-first order kinetics. Under this condition, the reaction rate is independent of competing demands for the oxidant unless the oxidant is used before the contaminant is gone.

Example Discussion 1:

Let's consider an example where the target area to be treated is 50 feet by 50 feet and the vertical extent of contamination is 10-feet thick from 20 feet below ground surface (fbgs) to 30 fbgs. The volume of the aquifer is 50 feet by 50 feet by 10 feet or 25,000 cubic feet. For this example, the contamination is 40 ppm toluene in groundwater and 20 ppm in the saturated soil. If the porosity of the soil is 30 percent, then the pore volume within the treatment zone is 7500 cubic feet. The mass of toluene in groundwater in this example is then 19 pounds. The mass of toluene in the soil in this example is then 50 pounds (assuming a soil density of 100 pounds per cubic foot). The estimated total mass of toluene in the target area is thus 69 pounds.

The amount of oxygen (as O_2) to oxidize toluene to carbon dioxide is approximately 3 pounds O_2 to 1 pound toluene. A pound of RegenOx oxidant delivers 0.15 pounds of available O_2 (remember the discussion in the earlier section on what constitutes available O_2). Therefore approximately 20 pounds of RegenOx oxidant are required to oxidize one pound of toluene to carbon dioxide (if complete mineralization was possible). Since we have 69 pounds of toluene in our target area, 1380 pounds of RegenOx oxidant will be required.

Even if toluene was the only compound of concern, there exists other organics and minerals in the substrate which will place a demand on the oxidant. Site data such as COD, TOC, and/or TOD on soil and water can be used to estimated additional oxidant requirements. This information is used to determine how much oxidant is needed to maximize the oxidation of toluene. In this example a bench test was not performed, so we will estimate an additional 1 pound oxidant per 1000 pounds of soil or 1750 pounds of RegenOx oxidant.

We now have calculated that we theoretically need on the order of 1380 plus 1750 pounds of RegenOx oxidant or 3130 pounds to treat the target area. RegenOx should be applied over multiple applications. In most cases it

is more efficient to spread the oxidant load between injections. REGENESIS will assist you on how best to calculate the load for each injection.

8.2 Pore Space Requirements

The next step is to consider how much solution to add to the target area. In order to achieve mixing of RegenOx in the aquifer while minimizing displacement of the groundwater plume, the design should consider displacing on the order of 10 to 50% of the pore volume. So if the porosity is 30% of the aquifer, then the design would use 3 to 15% of the site volume to be treated in order to calculate the gallons of water to use when injecting RegenOx.

Example discussion 2:

Now if the target is the vadose zone, injecting generally at least 50% of the porosity is recommended. Actual volumes used will be subject to the proximity and potential impact to the underlying groundwater table.

Knowing how much oxidant is required and how much water is required, one can determine the volume and concentration of RegenOx solution that needs to be prepared. Generally, around a 3-5% solution of RegenOx oxidant complex is typically used. Depending on the demand, the percent of oxidant complex can be increased or decreased; however, to ensure complete mixing of the oxidant complex into solution, it is recommended that no more than a 10 percent solution be used.

Example discussion 3:

Back to our example, we want to add 3130 pounds of RegenOx oxidant to 11,200 gallons of water. Since the typical mix is 1:1 ratio of RegenOx Part A (oxidant complex) to RegenOx Part B (activator complex), we will also be adding 3,130 pounds of RegenOx Part B. In this case a 3% solution (3% of oxidant and 3% of activator or 6% total RegenOx) will provide approximately the injectate volume calculated above in discussion 2. The total 3,130 pounds of Part B and 3,130 pounds of Part A in 11,700 gallons of water produce approximately 12,300 gallons of the desired solution. In practice, solutions are prepared in a number of smaller batches. This 3% solution would mix with the groundwater at a 1:5 ratio, so the theoretical diluted post-injection oxidant concentration would be on the order of 0.6% or 6000 ppm.

8.3 Injection Spacing

After determining how much RegenOx is required and how much water to add to it, the next question to answer is the spacing of the injection points. Determining the optimal spacing is a balance between performance and cost. The closer the spacing the better the chances of coming into contact with the contamination; however, the cost of delivery increases as each injection point is added to the grid. For most sites a 10-foot spacing will suffice. Sites with clays will require closer spacing (5- to 8-foot centers) and sites with homogeneous sands can get away with larger spacing (15-foot centers). Note, because most RegenOx injection designs will incorporate multiple injections and the subsequent injection points will be offset from the original injection points, 10-foot spacing will effectively be only 5-foot spacing or less by the end of the project. The amount of water added during injection will determine the zone that will be immediately affected. If the groundwater velocity indicates sufficient travel velocity between zones (before the oxidant is depleted), then the downgradient influence will extend beyond the immediate zone of injection.

Example Discussion 4:

In the example scenario, the treatment zone is 50 feet by 50 feet or 2500 square feet. If we consider 10-foot centers for the injection points, we need 25 injection points. The 3% RegenOx solution of 12,700 gallons is then

spread between 25 points or 508 gallons per point. Since we are treating a 10-foot vertical interval, we would ideally inject 51 gallons of 3% RegenOx solution per foot. Alternatively, if we consider 8-foot centers for the injection points, we need 50 injection points and the injection would be 25 gallons of 3% RegenOx solution per foot.

8.4 Delivery System Design

There is more than one method of delivering RegenOx to the subsurface. These methods can generally be divided into direct injection and delivery wells. Over the years of use of our other products, REGENESIS has found that direct injection is typically the optimal approach for shallow soils to ensure thorough distribution across heterogeneous soils. Permanent or temporary injection wells could be used and may be a cost-effective delivery method where repeated injections are required in homogeneous sand. However, if there is a well that is screened across alternating lenses of sand and silts, most of the oxidant will be delivered to the sands because of their greater permeability and less will be delivered to the contamination bound to the silts that have a higher degree of adsorption capacity. With the use of a direct-push rig or sonic drilling rig, there is more control over the distribution of the oxidant. An injection tool can be used to deliver oxidant across each vertical foot of impacted aquifer. If a silt lens is the primary concern, then a higher concentration of oxidant can be directly pumped into that lens. The relative cost of direct injection also allows for closer spacing than can be achieved with the use of permanent wells.

As mentioned, if the site has NAPL, then the use of temporary injection wells may be cost-effective particularly if the wells are screened or nested solely across the NAPL interface. This would allow for repeated injection of oxidant for the purpose of knocking down the NAPL. After there is evidence that the NAPL has been treated, then direct injection can be used to treat the residual underlying the source.

8.5 Re-injection Requirements

It is important to recognize that most applications of chemical oxidation including those using RegenOx will require subsequent re-injections. This is obvious when the concentrations of contaminants are so high that the design calculations show it is impossible to meet the load of oxidant in the first injection. However, it is not readily apparent when the concentrations are low enough that the theoretical load of oxidant can be applied in the first injection. There is an efficiency factor that must be considered at each site that takes into account incomplete distribution of the oxidant and hence regions of incomplete contact of the oxidant with the contaminant molecules. Hence, despite how much oxidant is added, there will be regions in the target treatment area that are not treated. This geometry can be partly overcome by shifting the injection points within the treatment area at each re-injection event.

There is also a limitation on the amount of contaminant that can be oxidized in a given period of time based on the rate of partitioning of the contaminant from the adsorbed soil phase (or NAPL phase in the case of free product). The oxidant will initially oxidize the aqueous fraction of the contaminant. As the concentration of contaminant in groundwater decreases, the equilibrium between the aqueous phase and the sorbed-phase (or free-phase) will change, resulting in an increase in the rate of desorption of contaminant.

As the oxidant is consumed and soil organics are oxidized, the concentration of contaminant in the aqueous phase can increase. Monitoring of the site after injection sometimes shows an increase in the concentration of contaminant in the groundwater samples; however, if soil samples are also collected, they should show a corresponding decrease in mass of contaminant.

Estimating the number of injections, therefore, becomes a function of factoring in inefficiencies due to site geometry and partitioning of the contaminant mass.

REGENESIS uses several multipliers obtained from its experiential database of sites and combines them into an overall efficiency factor that can vary depending on the site conditions and the type of contamination. The efficiency factor also takes into account the predicted half-life of the contaminant(s). Again, performing a field pilot test would yield a greater understanding of the kinetics of the system and a better indication of the number of injections required.

With the exception of highly-concentrated sites and, especially, NAPL sites, each subsequent set (X3) of injections may require a lesser dosage of oxidant and/or activator thus the cost of each injection will typically be less than the previous sets of injection.

Example Discussion 5:

Using our example, if we assume that we had enough oxidant to start with and calculated a combined efficiency factor of 0.7, and applied it to 20 ppm toluene in the soil, then we estimate that after the first injection we would have $(1 - 0.7) * 20 \text{ ppm} = 6 \text{ ppm}$ toluene. Repeating this for each injection, we estimate that it will take at least 3 injections to decrease the concentration of toluene to less than 1 ppm. Alternatively, if the combined efficiency factor was 0.6, we would conclude that it will take at least 4 injections.

There is also the issue of waiting long enough between sets of injections to allow for equilibrium to be approached. It is also important to keep in mind that given an excess of oxidant, the time it takes to decrease contamination from 5 ppm to 2.5 ppm is the same as from 50 ppm to 25 ppm.

This assumes a well mixed system. There is often the perception that the oxidant is not working as well at lower concentrations as compared with higher concentrations. As long as the oxidant is in excess for each case, the oxidation of the contaminant will proceed under first order kinetics which is theoretically the same rate constant regardless of whether the concentration is 50 ppm or 5 ppm.

8.6 Transition to Bioremediation

Chemical oxidation is a useful tool for reducing the mass of contamination. As described throughout this manual, once the concentrations are reduced down to < 10 ppm (or perhaps higher depending on the contaminant's rate of biodegradation), it is often more cost-effective to switch to bioremediation. Of course, the opportunity to switch to bioremediation will be dictated by the time imposed to meet the remedial action objectives. Enhancing bioremediation is also timelier and potentially more cost-effective than relying on monitored natural attenuation to achieve low concentration goals as usually required for projects with the overall objective of regulatory site closure.

REGENESIS is dedicated to assisting environmental professionals in finding the most cost-effective solution of combining RegenOx with its bioremediation products such as ORC Advanced or HRC to meet treatment goals and project objectives.

Visit the REGENESIS website, www.REGENESIS.com, for more information on stimulating *in situ* bioremediation including design and usage.

9.0 INSTALLATION

9.1 Application Using Direct-Push Methods (Step-by-Step Procedures)

1. Prior to the installation of RegenOx®, any surface or overhead impediments should be identified as well as the location of all underground structures. Underground structures include, but are not limited to, utility lines; tanks; distribution piping; sewers; drains; and landscape irrigation systems. The planned installation locations should be adjusted to account for all impediments and obstacles. These considerations should be part of the SSHP or HASP.
2. Pre-mark the installation locations, noting any points that may have different vertical application requirements or total depth.
3. Set up the direct-push unit over each point and follow the manufacturer standard operating procedures (SOP) for the direct-push equipment. Care should be taken to assure that probe holes remain in the vertical.
4. For most applications, REGENESIS suggests using 1.5-inch O.D./0.625-inch I.D drive rods. However, some applications may require the use of 2.125-inch O.D./1.5-inch I.D. or larger drive rods.
5. Advance drive rods through the surface pavement, as necessary, following SOP.
6. Push the drive rod assembly with an expendable tip to the desired maximum depth. REGENESIS suggests pre-counting the number of drive rods needed to reach depth prior to starting injection activities.
7. After the drive rods have been pushed to the desired depth, the rod assembly should be withdrawn three to six inches. Then the expendable tip can be dropped from the drive rods, following SOP. If an injection tool was used instead of an expendable tip, the application of material can take place without any preliminary withdrawal of the rods.
8. In some cases, introduction of a large column of air prior to RegenOx application may be problematic because the air can block water flow to the treatment area. This is particularly the case in deep injections (>50 ft) with large diameter rods (>1.5-inch O.D.). To prevent the injection of air into the aquifer during RegenOx application, as well as to prevent problems associated with heaving sands, fill the drive rods with water, or the RegenOx mixture prior to dropping the expendable tip or exposing the injection tool.
9. The RegenOx® percent of the oxidizer in solution should range between 3% to 5%. Although solutions up to 8% may be used, this will likely increase the difficulty of injection due to reactivity. Solutions with greater than 8% oxidizer in solution will result in excess reaction and flocculation prior to injection and are not typically recommended.

Measure the appropriate quantity of RegenOx Oxidizer for one to four vertical feet of injection into a 55 gallon drum or mixing tank. The volume of water per injection location can be calculated from the following formula:

$$\frac{\text{RegenOx Oxidizer lbs/foot}}{(8.34 \text{ lbs/gal water})(\% \text{ RegenOx Oxidizer solids})} [1 - (\% \text{ RegenOx Oxidizer solids})]$$

Tighter formations (clays and silts), and even some fine sand formations will likely require higher oxidant percentages since less volume can be injected per location. The following are guides to various RegenOx mixing ratios based on the above equation.

- to make a roughly 3% oxidant solution for every 10 lbs of oxidant and 10 lbs of activator (20 lbs total RegenOx), use 38 gallons of water.
- to make a roughly 4% oxidant solution for every 10 lbs of oxidant and 10 lbs of activator (20 lbs total RegenOx), use 28 gallons of water.

- to make a roughly 5% oxidant solution for every 10 lbs of oxidant and 10 lbs of activator (20 lbs total RegenOx), use 22 gallons of water.
10. Pour the pre-measured quantity of RegenOx Oxidizer into the pre-measured volume of water to make the desired target % oxidant in solution. NOTE: always pour the Oxidizer into water, do not pour water into the Oxidizer. Mix the water and oxidant with a power drill and paint stirrer or other mechanical mixing device to ensure that the Oxidizer has dissolved in the water.
 11. Pour the applicable quantity of the pre-mixed RegenOx Activator into the oxidant:water solution. Mix the Oxidant and Activator using a power drill paint stirrer or other mechanical mixing device for at least 5 minutes until a homogenous mixture is formed. After mixing, the RegenOx mixture should be injected into the subsurface as soon as possible.
 12. Do not mix more RegenOx material than will be used over roughly 1 to 4 feet of injection so as to minimize potential above ground reaction/flocculation prior to injection. Transfer the contents of the mixing tank to the pump using gravity feed or appropriate transfer pump. (See Section 9.2: Pump Selection) For some types of pumps, it may be desirable to perform a volume check prior to injecting RegenOx.
 13. Connect the delivery hose to the pump outlet and the delivery sub-assembly. Circulate RegenOx through the hose and the delivery sub-assembly to displace air in the hose. NOTE: an appropriately sized pressure gauge should be placed between the pump outlet and the delivery sub-assembly in order to monitor application pump pressure and detect changes in aquifer backpressures during application.
 14. Connect the sub-assembly to the drive rod. After confirming that all of the connections are secure, pump the RegenOx through the delivery system to displace the water/fluid in the rods.
 15. Slowly withdraw the drive rods. Commonly RegenOx injections progress at 1-foot intervals. However, continuous injection while slowly withdrawing single lengths of drive rod (3 or 4 feet) is an acceptable option. The pre-determined volume of RegenOx should be pumped into the aquifer across desired treatment interval.
 16. Remove one section of the drive rod. The drive rod may contain some residual RegenOx. Place the RegenOx-filled rod in a clean, empty bucket and allow the RegenOx to drain. Eventually, the RegenOx should be returned to the RegenOx pump hopper for reuse.
 17. Monitor for any indications of aquifer refusal. This is typically indicated by a spike in pressure as indicated or (in the case of shallow applications) RegenOx “surfacing” around the injection rods or previously installed injection points. At times backpressure caused by reaction off-gassing will impede the pumps delivery volume. This can be corrected by bleeding the pressure off using a pressure relief/bypass valve (placed inline between the pump discharge and the delivery sub- assembly) and then resuming pumping. If aquifer acceptance appears to be low, as indicated by high back pressure, allow sufficient time for the aquifer to equilibrate prior to removing the drive rod.
 18. Repeat steps 13 through 23 until treatment of the entire contaminated vertical zone has been achieved. It is recommended that the procedure extend to the top of the capillary fringe/smear zone, or to the top of the targeted treatment interval.
 19. Install an appropriate seal, such as bentonite, above the RegenOx material through the entire vadose zone. Prior to emplacing the borehole seal, we recommend placing clean sand in the hole to the top of the RegenOx treatment zone (especially important in holes that stay open). Bentonite chips or granular bentonite should be placed immediately above the treatment zone, followed by a cement/bentonite grout to roughly 0.5 feet below ground surface. Quick-set concrete should then be used as a surface seal.
 20. Remove and clean the drive rods as necessary.
 21. Finish the borehole at the surface as appropriate (concrete or asphalt cap, as needed). We recommend a quick set concrete to provide a good surface seal with minimal set up time.

22. A proper borehole and surface seal assures that the RegenOx® remains properly placed and prevents contaminant migration from the subsurface. Each borehole should be sealed immediately following RegenOx application to minimize RegenOx surfacing during the injection process. If RegenOx continues to “surface” up the direct-push borehole, an appropriately sized (oversized) disposable drive tip or wood plug/stake can be used to plug the hole until the aquifer pressures equilibrate and the RegenOx stops surfacing. If wells are used for RegenOx injection, the RegenOx injection wells and all nearby groundwater monitoring wells should be tightly capped to reduce potential for surfacing through nearby wells.
23. Periodically compare the pre- and post-injection volumes of RegenOx in the holding tank or pump hopper using the pre-marked volume levels. Volume level may not be present on all tanks or pump hoppers. In this case, volume level markings can be temporarily added using known amounts of water and a carpenter’s grease pencil (Kiel crayon).
24. Move to the next probe point, repeating steps 8 through 29. We recommend that the next RegenOx injection point be as far a distance as possible within the treatment zone from the previous RegenOx injection point. This will further minimize RegenOx surfacing and short circuiting up an adjacent borehole. When possible, due to the high volumes of liquid being injected, working from the outside of the injection area towards the center will limit expansion of the plume.

9.2 Pump Selection

REGENESIS has evaluated a number of pumps and many are capable of delivering RegenOx to the subsurface at a sufficient pressure and volumetric rate. However, even though a number of the evaluated pumps may be capable of delivering the RegenOx to the subsurface based on adequate pressures and delivery rates, each pump has its own set of practical issues that may make it more or less difficult to manage in a field setting.

In general, REGENESIS strongly recommends using a pump with a pressure rating of 200 pounds per square inch (psi) in sandy soil settings, and 800 psi in silt, clay or weathered bedrock settings. Any pump under consideration should have a minimum delivery rate of 5 gallons per minute (gpm). A lower gpm rated pump may be used; however, they are not recommended due to the amount of time required to inject the volume of liquids typically associated with a RegenOx injection (i.e. 1,000 lbs of RegenOx [500 lbs Oxidant/500 lbs Activator] require roughly 1,100 gallons of water to make a 5% Oxidant solution).

Quite often diaphragm pumps are used for the delivery of chemical oxidants. Generally, these pumps operate pressures from 50-150 psi. Some of these pumps do not have the pressure head necessary to overcome the back pressure encountered in silt and clay lenses. In these cases the chemical oxidant thus ends up being delivered to the surrounding sands (the path of least resistance) and is not delivered to soil with residual adsorbed contamination. The use of a positive displacement pump such as a piston pump or a progressing cavity pump may be superior because these pumps have the pressure necessary to overcome the resistance of low permeability soils. NOTE: Be aware that application at pressures that are too high may over-consolidate the soil and minimize the direct contact of the oxidant. The key is to inject at a rate and pressure that maximizes the radius of influence without causing preferential flow. This can be achieved by injecting at the minimum pressure necessary to overcome the particular pressures associated with your site soil conditions.

Whether direct injection or wells are used, it is best to start by injecting RegenOx outside the contaminated area and spiral laterally inwards toward the source. Similarly, RegenOx should be applied starting vertically at the bottom elevation of contamination, through the layer of contamination, and a couple of feet above the layer of contamination. The reagents can be pushed out from the well bore with some water.

9.3 Installation Using Fixed Wells (Methods)

On some projects, it may be appropriate to apply RegenOx using fixed wells. This will allow the RegenOx to be reapplied multiple times and reduce a large mass of contaminant incrementally over time. Application of RegenOx via a series of fixed wells can be accomplished most effectively by separate application of RegenOx Part A and Part B via multiple separate application events. Most sites require 3-4 applications to ensure contact and minimize rebound. NOTE: For the purposes of this discussion, it is assumed that the hydraulic conductivity of this aquifer is sufficient to accept the volumes of material associated with this approach.

Well Installation:

It is critical that the delivery wells associated with this application are installed across the appropriate vertical application interval. These wells should be constructed using 2 or 4- inch diameter Schedule 80 PVC and preferably with the screened section composed of wire-wound PVC with a slot size >0.2 inch. The surrounding filter pack should be composed of an appropriately sized sand/gravel that is a reasonable match to the surrounding soil type. An adequate seal above the screen zone is critical. When possible we recommend a least a one-foot bentonite seal above the filter pack and an additional 3 feet or more or a cement-bentonite (<10%) grout to the surface.

Hydraulic Testing of Wells:

A hydraulic test should be performed prior to implementation of the RegenOx application. This testing consists of the injection of clear water at a volume equivalent to 1.3x the designed injection volume of the RegenOx Part A material. It is critical that you understand the hydraulic conductivity/volumetric limitation of the aquifer prior to installation of the RegenOx material. Each site's aquifer conductivity and capacity will directly affect the volume of RegenOx applied and the application rate.

Part A Estimation:

Using a designed application rate of 5,970 pounds of Part A material per event, a 5% solution will result in an application volume of 14,214 gallons of total fluids per event.

$$682 \text{ gal Part A} + 13,532 \text{ gal H}_2\text{O} = 14,214 \text{ gal of fluid}$$

Detailed steps for estimation of this volume are provided below. Using a five well application array results in an application volume of 2,843 gallons/well/event.

$$14,214 \text{ gal of fluid} / 5 \text{ wells} = 2,843 \text{ gal/well/event}$$

Hydraulic Test Volume Estimation:

The hydraulic test volume per well is estimated based on the above application rate (2,843 gallons) x (application factor of 1.3). This yields a total clear water test volume of 3,696 gallons/well.

RegenOx Application: Part B Application

This method is significantly different from a direct-push application. This method requires application of a solution of the catalyst material separately and prior to application of the Part A oxidant material. As discussed previously, application of Part B is typically installed at a low concentration, spread over two events and is followed by a clear water chaser equal to 1.5-3x the well's borehole volume.

Step 1:

Mix Part B at solution that is 3-8% by weight, see Table 1 for a volumetric estimation per bucket of material for each percentage solution. This range in volume is provided to allow for variations in aquifer types and specifically to adjust for each site's aquifer hydraulic conductivity and effective porosity. The aquifers hydraulic characteristics should dictate the solution percentage.

For example, Part B application in a fine grained aquifer (hydraulic conductivity of 10_{-5} to 10_{-6} cm/sec) should be mixed at approximately a 7% solution by weight while a coarse grained aquifer (10_{-2} to 10_{-3} cm/sec) should be mixed at approximately a 3% solution by weight.

TABLE 1.

No. of Buckets	Weight of Material (lbs.)	Desired Solution (%)	Volume of Water (gal.)
1	30	3	116
1	30	4	86
1	30	5	68
1	30	6	56
1	30	7	48
1	30	8	41

Example:

Based on application into a silty sand aquifer (10-4 cm/sec) the Part B solution should be mixed at 5%.

Using the previous example, this application will require a total of 5,970 pounds of Part B applied via two events of 2,985 pounds or 100 bucket/event

$$2,985 \text{ lb} / 30 \text{ lb /bucket} = 100 \text{ buckets}$$

Thus, for each of the two Part B applications, water volume necessary is calculated using the following equation:

$$100 \text{ buckets Part B} \times 68 \text{ gallons water/bucket} = 6,800 \text{ gallons of water}$$

This yields a total solution application per event estimation of:

$$(6,800 \text{ gal of H}_2\text{O} + 260 \text{ gal Part B}) / 5 \text{ wells} = 1,412 \text{ gal Part B Solution/well/event}$$

Step 2:

Clear Part B material from the injection well and surrounding well pack by application of a clear water chaser equivalent to the volume of 1.5-3x the borehole volume.

Example:

For a 2-inch diameter well with a 6-inch borehole diameter, a total depth of 20 feet (10 feet of blank and 10 feet of screen), a single borehole volume with an assumed sand pack void space of 30% would be the sum of the following:

Borehole Volume = (screened interval borehole volume + blank casing volume)

$$[(10 \text{ feet} \times 0.543 \text{ gal/ft}) + (10 \text{ feet} \times 0.163 \text{ gal/ft})] = 7 \text{ gal}$$

Using a clear water chaser application factor of 1.5-3x yields a total clear water chaser volume ranging from 11 to 21 gallons/well. For a 4-inch diameter well with a 8.25-inch borehole diameter, a total depth of 20 feet (10 feet of blank and 10 feet of screen). A single borehole volume using an assumed sand pack void space of 30% would be the sum of the following:

Borehole Volume = (screened interval borehole volume + blank casing volume)

$$[(10 \text{ ft} \times 1.23 \text{ gal/ft}) + (10 \text{ feet} \times 0.65)] = 19 \text{ gal}$$

Using a clear water chaser application factor of 1.5-3x yields a total clear water chaser volume ranging from 28 to 57 gallons/well.

Step 3:

Mix Part A at a solution of between 3-5%. As discussed previously the transmissivity and reactivity of a particular aquifer as well as hydraulic testing should be factored into the application volume decision. The stability of RegenOx Part A is optimal at approximately 3%. In coarse grained aquifers it is best to apply Part A at or near a 3% solution. In fine grained aquifers it may be necessary to decrease the water content to near a 5% solution.

NOTE: Do not apply a Part A that is >5% solution.

Example:

Based on application of Part A solution into a silty sand aquifer, the Part A solution should be mixed at 5%. As discussed previously this application is designed for application of 5,970 pounds of Part A per event via a 5 well application array. Using Table 1 the number of buckets of Part A required is estimated as follows:

$$5,970 \text{ lb Part A} / 30 \text{ lb/bucket} = 199 \text{ buckets}$$

The volume of water necessary to create a 5% Part A solution is calculated using Table 1 and this equation:

$$199 \text{ buckets Part A} \times 68 \text{ gallons H}_2\text{O/bucket} = 13,532 \text{ gallons of H}_2\text{O}$$

This yields a total solution application per event estimation of:

$$(13,532 \text{ gal of H}_2\text{O} + 682 \text{ gal Part A}) / 5 \text{ wells} = 2,843 \text{ gal Part A Solution/well/event}$$

Step 4:

Clear the Part A solution from the injection well and some of the surrounding well pack by application of a clear water chaser equivalent to the volume of 1.5-3x the borehole volume.

Example:

For a 2-inch diameter well with a 6-inch borehole diameter, a total depth of 20 feet (10 feet of blank and 10 feet of screen), a single borehole volume with an assumed sand pack void space of 30% would be the sum of the following:

Borehole Volume = (screened interval borehole volume + blank casing volume)

$$[(10 \text{ ft} \times 0.543 \text{ gal/ft}) + (10 \text{ ft} \times 0.163)] = 7.1 \text{ gal}$$

Using a clear water chaser application factor of 1.5-3x yields a total clear water chaser volume ranging from 11 to 21 gallons/well.

For a 4-inch diameter well with a 8.25-inch borehole diameter, a total depth of 20 feet (10 feet of blank and 10 feet of screen). A single borehole volume using an assumed sand pack void space of 30% would be the sum of the following:

Borehole Volume = (screened interval borehole volume + blank casing volume)

$$[(10 \text{ ft} \times 1.23 \text{ gal/ft}) + (10 \text{ feet} \times 0.65)] = 19 \text{ gal}$$

Using a clear water chaser application factor of 1.5-3x yields a total clear water chaser volume ranging from 28 to 57 gallons/well. Repeat the above series of steps as needed. As discussed previously the first two injection events will consist of application of Part B followed by Part A and thereafter as a series of Part A only injections.

Pumps:

It stands to reason that application of RegenOx via a series of wells is best accomplished using a pump that can deliver high volumes of fluids in a relatively low pressure setting. REGENESIS has evaluated a number of pumps that are capable of delivery of these volumes of RegenOx in a reasonably efficient manner. These pumps are typically the positive displacement pumps and the diaphragm pumps. The positive displacement pumps are generally a stader driven (auger) and are electrically driven via a generator while the diaphragm pump is composed of one or two diaphragms that use pneumatic pressure to drive the pump. Both of these types of pumps can provide a relatively high volume of reagent while allowing significant control of volume and pressure.

Pressure Gauge System:

It is critical that application of RegenOx be preformed with proper pressure gauge set up. The gauges used should be configured to read PSI at the pump effluent and either along the delivery line or at the well head. This provides on-site personnel with adequate information on the pumps working pressure as well as the well delivery pressure. The difference in the two is the result of line loss. It is critical that application of RegenOx not exceed the burst pressure of the application well casing.

9.4 Pump Cleaning

For best results, flush all moving parts and hoses with clean water at the end of the day. Flush the injection system with a mixture of water and biodegradable cleaner such as Simple Green.

9.5 Post-Treatment Performance Monitoring

After the injection, treatment progress should be monitored by collecting groundwater and/or soil samples and analyzing the parameters discussed earlier in Section 7.0. The sampling frequency is dictated by the anticipated half-lives of the contaminants. It is important to recognize that sufficient time is required to evaluate conditions after the site reaches a new, post-treatment equilibrium.

10.0 HEALTH AND SAFETY/HANDLING

10.1 Material Overview

RegenOx is packaged in two parts. Part A is the RegenOx Oxidizer complex and Part B is the RegenOx Activator complex. Part A and Part B are shipped in separate 5-gallon buckets and each bucket has a gross weight of

approximately 32 pounds (net weight of RegenOx material in each bucket is 30 pounds). The RegenOx Oxidizer complex is shipped as a fine white powder and the RegenOx Activator complex is shipped as a liquid gel. The Activator has a viscosity roughly equivalent to honey. It is common for stored RegenOx Activator to settle somewhat in a container, so it is imperative to adequately pre-mix the RegenOx Activator prior to mixing it with the RegenOx Oxidizer. Mixing the RegenOx Part B Activator with water at a ratio of roughly 1 gallon water per bucket of Activator makes the Activator pourable and easier to work with. A Material Safety Data Sheet for Part A (RegenOx Oxidizer) and for Part B (RegenOx Activator) is provided with each shipment..

10.1.1 Placarding/Labeling

RegenOx Part A (oxidizer complex) is an oxidizer. As such, it should be handled with care and only by personnel trained for handling and storage of hazardous materials. Shipping of this material is regulated under the Transport of Dangerous Goods Act.

RegenOx Part A carries the following designations:

D.O.T. Shipping Name:	5.1 Oxidizer N.O.S. UN Number: 1479
Hazard Class:	5.1
Labels:	5.1 (Oxidizer)
Packaging Group:	III

Part B (activator complex) is not regulated as a hazardous material.

10.1.2 Compatibility in Storage

Keep strong oxidants such as RegenOx Part A (oxidizer complex) away from combustible materials, reducing agents, acids, bases, and sources of heat (steam pipes, electrical appliances, heating vents). Store RegenOx Part A in an area separated from RegenOx Part B (activator complex). Store in a cool, dry area in closed containers. Follow NFPA 430 guidelines.

10.1.3 Compatibility with Underground Structures and Pipes

The use of RegenOx in proximity to underground tanks and pipes is not a concern. Underground tanks and pipes are installed to meet the relatively corrosive conditions of wet soil. Also, the advent of Fiberglass Reinforced Plastics (FRPs) has greatly diminished the overall concerns in this area. Both metal and FRP installations are normally exposed to fairly wide ranges of pH, oxygen saturated water and even corrosive mineral contents. Interactions with metals and plastics are an extremely complicated phenomenon that is dependent on time, temperature and concentrations. Given enough time, oxidizers and caustic solutions will slowly react with certain metals and plastics. RegenOx has a high oxidizing potential and a high pH; however, RegenOx is relatively short-lived in the subsurface (2-4 weeks). Because the high pH and oxidizing conditions are very localized and temporary, RegenOx will not affect most subsurface structures near the treatment zone. A detailed discussion of materials compatibility follows.

Metals

After RegenOx application, a pH increase is often observed in the treatment area. The actual pH values can range anywhere from 7-12, with pH values of 9-10 most common. Generally, pH values return to neutral or ambient levels within 4 weeks following the injection event. Iron corrosion rates drop at high pH (10-12), so a high pH may actually inhibit iron corrosion. However, as pH increases, corrosion rates increase for aluminum and zinc. If the pH remains high for an extended period of time, this may have implications for buried electrical conduit, which are frequently zinc coated iron or aluminum.

In order to summarize all the factors that may lead to metal corrosion, it is customary to use a grading system as an overall guide. In a corrosion index (Table 28-2) in the Chemical Engineer's Handbook (edited by Perry and Green, 1997), two categories apply to RegenOx: oxidizing media and alkaline solutions. This index is graded from 0-6 with a rating of 4-6 being good to excellent in terms of compatibility. A summary of the relevant information from this table is shown in Table 10-1. Materials rated a 4 or higher with oxidizing media and alkaline solutions include cast iron, ductile iron, mild steel, stainless steel, Incoloy 825 nickel-iron-chromium alloy, hastelloy alloy C-276 and Inconel 600. Materials receiving low ratings (unsuitable, poor or fair) with oxidizing media include aluminum brass, nickel-aluminum bronze, lead and silver. Caustic conditions may cause problems with silicon iron, aluminum, aluminum brass, nickel-aluminum bronze, lead, titanium and zirconium.

Plastics

A wide range of plastics and pipes or Fiberglass Reinforced Plastics (FRPs) may be used in underground service. Each type of plastic will have its own characteristic definition profile. These tanks and pipes are replacing metals due to their greater chemical resistance to corrosion. In many cases plastics can withstand significant concentrations of caustic chemicals. Overall, FRPs withstand a variety of harsh outdoor conditions where they are subjected to high temperatures, ozone and UV over long periods of time.

Table 10-1. General Corrosion Properties of Some Metals and Alloys (from Perry's Chemical Engineers Handbook, Table 28-2)

Table 10-1. General Corrosion Properties of Some Metals and Alloys (from Perry's Chemical Engineers Handbook, Table 28-2)

Materials	<i>Alkaline Solutions Caustic and mild alkalines</i>	<i>Oxidizing Media Neutral or alkaline solutions</i>
<i>Cast iron</i>	4	4
<i>Ductile iron</i>	4	4
<i>Mild Steel</i>	4	4
<i>Ni-Resist corrosion cast iron</i>	5	5
<i>Stainless steel</i>	4 – 5	6
<i>14% Silicon iron</i>	2	6
<i>Incoloy 825 nickel-iron-chromium alloy</i>	5	6
<i>Hastelloy alloy C-276</i>	5	6
<i>Hastelloy alloy B-2</i>	4	3
<i>Inconel 600</i>	6	6
<i>Copper-nickel alloys up to 30% nickel</i>	5	4
<i>Monel 400 nickel-copper alloy</i>	6	5
<i>Nickel</i>	6	5
<i>Copper and silicon bronze</i>	4	4
<i>Aluminum brass</i>	2	3
<i>Nickel-aluminum bronze</i>	2	3
<i>Bronze</i>	4	4
<i>Aluminum and its alloys</i>	0	0-4
<i>Lead</i>	2	2
<i>Silver</i>	6	2
<i>Titanium</i>	2	6
<i>Zirconium</i>	2	6

10.2 Personal Protective Equipment

Personnel working with or in areas of potential contact with RegenOx® should be required at a minimum to be fitted with modified Level D personal protective equipment:

- Eye protection – Wear goggles or a face shield
- Head – Hard hat when required
- Respiratory – Use dust respirator approved by NIOSH/MSA
- Hands – Wear neoprene gloves
- Feet – Wear steel toe shoes with chemical resistant soles or neoprene boots
- Clothing – Wear long sleeve shirts and long pant legs. Consider using a Tyvek body suit, Carhartt coverall or splash gear

10.3 On-Site Handling

Stainless steel 304 or 316 is recommended for mixing, conveyance and storage equipment. Other compatible materials include: polyvinyl chloride, polyethylene, Plexiglass, Teflon, Viton, stoneware and glass. Water should be readily available on site for dilution and eyewash.

RegenOx Part A (oxidizer complex) is soluble to a maximum concentration of about 12% in water. If you add it to soil with less than an 11 to 1 ratio of water to RegenOx Part A, there will be free salt which when partially wet may decompose to give off oxygen. Thus, if you treat a soil pile with only 22% water, you should only use up to 2% oxidant by weight to avoid off-gassing significant amounts of oxygen.

Do not apply directly onto a separate phase hydrocarbon layer within a well or open excavation. If spilled, follow the steps listed on the MSDS sheets to ensure proper cleanup.

Strong oxidizers that become waste material are classified as hazardous waste. An acceptable disposal method for spent RegenOx is to dilute with copious amounts of water and dispose via a treatment system. Any disposal method must be in compliance with all federal, state, and local agencies.

10.4 Permitting

10.4.1 Class V UIC permit

Wells for the injection of RegenOx may be considered Class V injection wells as per the federal Underground Injection Control (UIC) Program which falls under the federal Safe Drinking Water Act (SDWA) and are permitted by rule. Depending on the specific location of the project, State UIC programs may be delegated complete or partial enforcement responsibility (or primacy) by the USEPA. Class V wells regulated by specific state UIC programs may, however, require a permit. REGENESIS can assist you in determining permit requirements and filling out permit forms.

10.4.2 State and Local Agency Requirements

In most cases, state and local agencies view chemical oxidation treatment with RegenOx® as beneficial to aquifer quality. Prior to field application however, agencies may require information on the remediation plan. Examples of information that may be required include:

- The overseeing agency will most likely require a remediation plan,
- The zone of chemical oxidant discharge must be acceptable to the agency (and usually limited to within the

contaminant plume),

- The rate and volume of reagent injection must not cause undesirable migration of the reagents or of the contaminants already present in the aquifer,
- The remediation plan must address groundwater monitoring requirements associated with the use of the RegenOx technology based on site-specific hydrogeology and conditions.

11.0 REGENESIS SUPPORT

It is REGENESIS' goal to provide unmatched technical support and service to environmental professionals around the world. In order to achieve this goal REGENESIS has developed several levels of service available to interested parties. This includes a world-wide network of Field Technical Managers and a dedicated staff of Technical Service Representatives (experienced field scientists and engineers) that stand ready to assist in remediation design and cost estimation.

Additionally, reference documentation and case histories are available, as well as a library of technical documents published by third-party engineering firms and regulators on the use of REGENESIS' products to remediate contaminated groundwater and soils world-wide.

For more information please contact us or visit www.REGENESIS.com.

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