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Overview of Cleanup Design Options and Treatability Testing for In Situ Remediation of Soil and Ground Water

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Treatability testing is an integral part of designing *in-situ* remediation of petroleum hydrocarbons, chlorinated solvents, “heavy” metals, and pH adjustment. After a series of geologic characterizations and an exposure pathway analysis have been performed, a detailed site conceptual model with boring logs, cross-sections, concentration maps, and mass calculations are typically developed. Following the preparation of a Corrective Action Plan (CAP) which summarizes the site conceptual model and reviews the various remediation options, treatability testing is the next logical step to define the best cleanup technologies using real laboratory data. Based on experience, if the treatment chemistry is not well understood or cannot be performed successfully under laboratory conditions using actual soil and ground water from the site, success in the field may be unlikely. Even though treatability studies can provide significant information regardless of the contaminant or specific remediation process, the studies are also frequently overlooked, undervalued, and misunderstood.

Most geologists are familiar with the challenges of bringing the field scale down to the laboratory bench top. Faults, ground-water gradients, subtle horizontal and vertical lithologic and associated permeability variations cannot be translated well into a treatability test setting. However, regardless of the contaminant, the specific chemical or biological reactions can be simulated quite well in the laboratory and the risks

and uncertainties as to the site specific chemical reactions and rate of contaminant reductions can be tested under ideal conditions. The main purpose of treatability testing is to evaluate the degradation potential of the treatment chemicals with the target compounds found on the site. The second purpose is to evaluate the potential to mobilize metals. This can occur as a result of the oxidation chemistry or changes in pH which can solubilize and mobilize transition metals (most notably chromium). Under neutral or near-neutral pH, once the chemical oxidant is consumed, the oxidized, more soluble, and potentially toxic Cr(VI) reverts back to Cr(III) and usually precipitates as chromium hydroxide $[\text{Cr}(\text{OH})_3]$. It is also possible to form some soluble $\text{Cr}(\text{OH})_2^+$.

In some cases, liquid treatment chemicals not only remediate ground water but they also can desorb contaminants from the soil matrix, creating what appears to be increases in ground-water concentrations while lowering soil concentrations. Treatability testing will help identify these issues prior to performing a pilot test in the field. In preparation for pilot testing and evaluation of the treatment chemical delivery methods in the field, treatability testing suggests the optimal chemistry and predicts the likelihood of field success.

Delivery of Treatment Chemicals

Delivery of the liquid treatment chemicals is accomplished by injection using pumps, or gravity feeding through exist-

ing and new monitoring wells at 40 psi to 100 psi or through small diameter (about 1-inch) probe rods at 100 psi to >3,000 psi. Depending on the reaction time of the treatment chemicals (minutes to months), surface spacing of injection ports or wells must be evaluated based on ground-water flow velocity, permeability, and other lithologic characteristics. Clays and silts, generally more challenging to remediate than higher porosity materials, typically require 0.91 m to 1.5 m (3 ft to 5 ft) injection or well spacing, whereas injection ports or wells for clean sand and gravels can be placed at 3.0 m to 4.6 m (10 ft to 15 ft) spacing or further. In some cases where the reaction time of the treatment chemicals is on the order of months and the contaminant target zone is shallow, soaker hoses in trenches or filter galleries can be an effective delivery method. For all types of in-situ treatments methods, chemical compatibility of the injection equipment, worker training, on-site supervision, personal protective equipment and safety procedures become critical with the injection of potentially dangerous chemicals including oxidizers, acids, bases, and other chemicals. Another consideration which can be evaluated in treatability testing is the effect and approximate volumes of gases that might be generated during the reaction. Reaction gas (such as oxygen or carbon dioxide, common in Fenton's Reagent processes) may greatly affect hydraulic conductivity of an aquifer, but usually only temporarily (Payne et al., 2008). Conductivity can also be reduced permanently with metal ion

precipitation, common among geochemical fixation processes. Observations of potential gas production or metal ion precipitation can be evaluated using treatability tests.

Dosage

Because many contaminants in soils are sorbed (both in the unsaturated zone and in the saturated zone) and owing to competing reactions that consume the treatment chemicals, higher stoichiometric dosages of treatment chemicals are generally required in the field. Treatability testing can help define the minimum treatment chemical dosage based on degradation rates per quantity of contaminant. Treatability testing is performed for a variety of processes.

Chemical Oxidizers

Chemical oxidation uses reagents to transform, degrade, or immobilize organic wastes. Chemical oxidizers have been used for decades in the waste-water industry for the treatment of carbon-containing (organic) compounds, such as petroleum hydrocarbons and chlorinated solvents, and numerous other contaminants. A summary of commonly used chemical oxidizers is presented in Table 1.

Oxidants commonly used for chemical oxidation processes	
Liquids:	Solids:
Hydrogen peroxide a source of hydroxyl radical	Note: solid peroxygens react with water (the O ₂ ²⁻ ion does not exist in water)
Peracetic acid	Sodium/calcium persulfate
	Sodium/calcium permanganate
	Potassium permanganate
Gases:	Sodium/calcium peroxide
Ozone	Sodium perborate
	Sodium percarbonate
	Magnesium peroxide

Table 1. Chemical Oxidation: Oxidizing Agents

The relative strength of various chemical oxidizers is presented in Table 2. Refer to the reference list for documentation of a variety of chemical oxidation processes, most notably Suthersan (2002), Suthersan and Payne (2005),

Payne et al. (2008), Watts et al. (1990, 1991, 1992 and 1994), and Jacobs and Testa (2003).

In Situ Chemical Oxidation Injection

In Situ Chemical Oxidation (ISCO) remedial process involves injecting an oxidizing agent, such as hydrogen peroxide (H₂O₂), activated sodium persulfate (Na₂S₂O₈), or other oxidant into the subsurface to destroy organic compounds. The by-products for complete mineralization of carbon-based compounds by most chemical oxidizers include carbon dioxide (CO₂), water (H₂O), and oxygen (O₂) as well as minor quantities of non-toxic ions, salts, and acids.

Hydrogen Peroxide and Fenton's Reagent

Hydrogen peroxide (H₂O₂) is one of the most powerful oxidizers known. A stronger oxidizer than chlorine (Cl₂), hydrogen peroxide is also a natural metabolite of many organisms that use oxygen, a by-product of the decomposition of the low concentration hydrogen peroxide. The autodecomposition can be represented overall as follows: 2H₂O₂ → 2H₂O + O₂. Pure hydrogen peroxide and its aqueous solutions are clear liquids resembling water. Unlike water, hydrogen peroxide has a slightly sharp

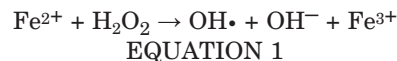
and distinctive odor. Low concentrations (1% to 3%) of hydrogen peroxide are sold in drug stores as a mild antiseptic. Hydrogen peroxide is available commercially at aqueous concentration as high as 80%.

In the presence of a transition metal such as iron or copper, hydrogen peroxide reacts much more vigorously and aggressively

than without the metal (acting as a catalyst). The reaction of iron-catalyzed hydrogen peroxide oxidation is called a "Fenton's Reagent" after its discoverer H.J.H. Fenton in 1894. Even after over 100 years of study and use in water

treatment, *in-situ* remediation methods were slow to use Fenton's Reagent, owing to safety concerns. For *in-situ* remediation applications, Leetham et al. (2002), describe gasoline and MTBE destruction using Fenton's Reagent. For *in situ* remedial applications, naturally occurring iron in the soil or fill materials dramatically increases the oxidative strength of hydrogen peroxide. This increase in oxidation power is attributed to the production of hydroxyl radicals (OH•). In addition, a chain reaction is initiated, forming more radicals, which are very reactive and destroy chemical bonds of organic compounds. The iron is not destroyed but rather cycles between the iron(II) and iron(III) oxidation states, yielding the hydroxyl radical and other by-products (Suthersan, 2002). Frequently, when natural concentrations of iron are too low in the field, iron salts such as iron(II) sulfate are added. Iron(III) also improves the oxidizing power of H₂O₂, albeit at a reduced rate. In addition, pH adjustment using a strong acid such as sulfuric acid (H₂SO₄) or hydrochloric acid (HCl) is common as reactions of classic Fenton's Reagent is more rapid and efficient under low pH conditions (pH 2 to 4 is optimal).

In presence of typical soil, residual hydrogen peroxide not used in the oxidative remediation process breaks down to water and oxygen in a matter of hours. In addition to the much simplified reaction described in Equation 1 there are also a large number of competing reactions including the free radical scavengers, most importantly, carbonate and hydrogen carbonate alkalinity that will greatly affect the overall reaction scheme. After the Fenton's Reagent has been completely depleted, the breakdown products of the spent hydrogen peroxide can serve as an oxygen source for microbes in the subsurface to enhance biodegradation of contaminants.



- Where,
- H₂O₂ = hydrogen peroxide
- Fe²⁺ = iron(II) ion
- Fe³⁺ = iron(III) ion
- OH• = hydroxyl radical
- OH⁻ = hydroxide ion

Classic Fenton's Reagent includes the use of a low to moderate concentration of hydrogen peroxide (1% to 30%), with iron addition at a pH of 2 to 4. Classic Fenton's Reagent is exothermic and can increase temperatures of aquifers, as

Species	Chemical Formula	Standard REDOX Potential, Eo (Volt)	Oxidants commonly used in chemical oxidation remediation
Fluorine	F ₂	3.0	No
Hydroxyl Radical	OH•	2.8	Yes – with acid or iron catalyst
Sulfate Radical	SO ₄ • ⁻	2.6	Yes – injected (persulfate)
Oxygen radical	O ₂ • ⁻ (superoxide radical)	2.4	No
Ozone	O ₃	2.2	Yes – sparged
Persulfate anion	S ₂ O ₈ ²⁻	2.1	Yes – injected
Hydrogen peroxide	H ₂ O ₂	1.8	Yes – see hydroxyl radical
Potassium Permanganate	KMnO ₄	1.7	Yes – mixed with water and injected
Hydrochlorous acid	HOCl	1.5	No
Chlorine dioxide	ClO ₂	1.5	No
Chlorine	Cl ₂	1.4	No
Oxygen	O ₂	1.2	No
Bromine	Br ₂	1.1	No
Iodine	I ₂	0.8	No
ACTIVATED OXYGEN SPECIES (Suthersan & Payne, 2005)	Formed by action of light on natural organic matter, peroxides or various inorganic catalysts		
Singlet Oxygen	¹ O ₂		
Protonated Superoxide	HO ₂ •		
Hydrogen Peroxide	H ₂ O ₂		
Hydroperoxide anion	H ₂ O ₂ /HO ₂ ⁻		
Hydroxyl Radical	OH•		
Ozone	O ₃		
Note: Fenton's Reagent	Hydrogen peroxide with an iron catalyst forms the hydroxyl radical		

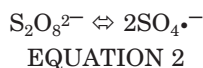
Table 2. Oxidizing Strength (Redox Potential) Of Various Oxidants

well as produce steam, reaction foam, and generate subsurface pressures in the treatment area capable of moving or cracking paved surfaces when used with hydrogen peroxide in the 10% to 12% concentration range. Deviation from the classic Fenton's Reagent, referred to as "modified Fenton's Reagent" includes the use of slurried solid peroxides and metallic or organo-metallic chelating catalysts, such as iron(II) EDTA to create a Fenton's Reagent at a neutral (pH 7) or higher pH.

Persulfate with Hydrogen Peroxide

Persulfate oxidation commonly uses sodium persulfate (Na₂S₂O₈) catalyzed by a chelated iron complex such as

iron(II) EDTA at a neutral pH to produce sulfate radicals (SO₄•⁻) that attack most petroleum hydrocarbons and selected chlorinated solvents. Liang et al. (2004) describe persulfate *in situ* remediation. The reaction mechanism (Equation 2) associated with the persulfate (S₂O₈²⁻) process is shown as follows:



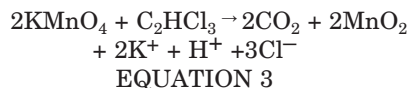
Where,
 S₂O₈²⁻ = persulfate ion
 SO₄•⁻ = sulfate radical

Heat, hydrogen peroxide (H₂O₂), and sodium hydroxide (NaOH) have also been used separately as activators for the persulfate. However, the by-product

generated by injecting activated persulfate is long lasting sulfate (SO₄²⁻). There is a secondary drinking water standard for sulfates of 250 mg/L.

Potassium permanganate(KMnO₄) lasts longer and can react in an environment with much higher pH compared to hydrogen peroxide. Permanganate has been well documented (Siegrist et al., 2001) for destruction of trichloroethene (TCE; C₂HCl₃) and other chlorinated solvents, but it is generally not used for petroleum hydrocarbons or methyl tertiary-butyl ether (MTBE) (Jacobs et al. 2000). For field use, potassium permanganate is shipped as a powder and is mixed with water creating a deep purple liquid. The solubility of potassium

permanganate is strongly influenced by temperature. At 30 °C, the solubility is more than 8%. The pH range is critical in being able to determine whether the oxidation reaction will be fast or slow. Equation 3 summarizes the permanganate reaction:



Ozone (O₃) is a powerful gaseous oxidizer that can be used to treat volatile organic compounds. Ozone is generated on-site because the gas is very difficult to store; therefore, all the ozone gas that is generated must be injected into the subsurface or destroyed using an ozone destruction unit on the ozone generator. The ozone gas can be bubbled into closely spaced injection ports that release the bubbles into the aquifer for remediation. The smaller the bubbles, the more surface area and the faster they can travel through small pore spaces. Pumping the ozone gas through specially designed ozone diffusers can produce micro-bubbles. Advanced oxidation processes refer to when ozone is catalyzed or enhanced by ultraviolet (UV) light, hydrogen peroxide, or other oxidizers, to increase the power of the ozone by producing more hydroxyl radicals. Treatability testing in the laboratory can evaluate the cost benefit of the different ozone enhancements prior to mobilizing into the field. Peroxone, a type of advanced oxidative process (AOP), uses hydrogen peroxide activated ozone to create the hydroxyl and perhydroxyl radicals (Equation 4). Ozone and hydrogen peroxide can mineralize most petroleum hydrocarbons and chlorinated solvents into water and carbon dioxide.



Where,

O₃ = ozone

OH· = hydroxyl radical

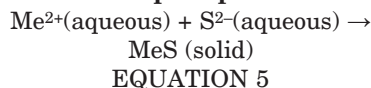
HO₂· = perhydroxyl radical

Heavy Metals Treatment

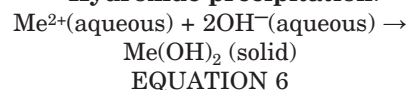
According to Suthersan and Payne (2005), the mechanisms that reduce heavy metals dissolved in ground water are transformation and immobilization, which use both abiotic and biotic pathways. Abiotic pathways include oxidation, reduction, hydration, sorption, and precipitation. Biotic pathways include oxidation, reduction, precipitation, bio-sorption, bioaccumulation, organo-metal complexation, and phytoremediation.

Precipitation is one of the most common *in situ* applications for treatment of soluble heavy metals in ground water or soil (Table 3). Dissolved heavy metals can be precipitated out of solutions to form insoluble sulfides, hydroxides, or carbonates. Suthersan and Payne (2005) note the following theoretical reactions (Equations 5 to 7) with a metal cation (Me²⁺):

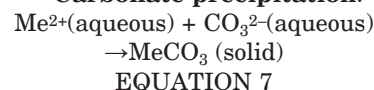
Sulfide precipitation:



Hydroxide precipitation:



Carbonate precipitation:



The solubility of a metal precipitate is a function of the pH of the water. Sulfide precipitation is particularly effective for copper [as Cu(I)], silver (Ag), mercury (Hg), cadmium (Cd), lead (Pb), and zinc (Zn). It is also important for the following transition metals: copper [as Cu(II)],

Species	Chemical Formula	Metal Precipitate*	pH
Sulfur Compounds			
Sodium sulfide	Na ₂ S	sulfide	Alkaline in solution
Sodium metabisulfite	Na ₂ S ₂ O ₅	sulfide	4.3 (1% solution)
Iron(II) sulfate	FeSO ₄	sulfide	3 to 5 (5% solution)
Calcium polysulfide	CaS ₅	sulfide	11.5 to 11.8
Alkaline Solutions (metals and pH adjustments)			
Calcium hydroxide (slaked lime)	Ca(OH) ₂	hydroxide	12.4 (saturated solution)
Potassium hydroxide Potash	KOH	hydroxide	13.5 (0.1 molar solution)
Sodium hydroxide (lye or caustic soda)	NaOH	hydroxide	13 to 14 (.05% solution)
Hydrogen or Hydrogen Producing Compounds (by fermentation)			
Hydrogen gas	H ₂	sulfide	7.0
Molasses	C ₁₂ H ₂₂ O ₁₁	sulfide	5.0
Corn syrup	C ₆ H ₁₂ O ₆	sulfide	5.0
Cheese whey	C ₆ H ₁₀ O ₅	sulfide	6.0 to 8.0
Vegetable oils	various	sulfide	Not water soluble**
Sodium lactate	C ₃ H ₅ O ₃ Na	sulfide	6.5 to 8.5
Other Reducing Reactions			
Elemental iron	Fe ⁰	sulfide	7.0

* Sulfide will precipitate if sufficient sulfur is available. Most “heavy” metals will insoluble form sulfides. However, Cr(VI) does not form insoluble sulfide but can form Cr(III) hydroxide.

** Vegetable oils are not soluble in water, so their pH can not be measured. Vegetable oils are typically very weak acids.

Table 3. Selected “Heavy” Metals Treatment

nickel [as Ni(I)], cobalt [as Co(II)], iron [as Fe(II)], and manganese [as Mn(II)]. With the exception of arsenic (As), most metal sulfide precipitates are much less soluble than the hydroxides (OH⁻) at the pH ranges encountered in most ground-water systems (Suthersan and Payne, 2005).

Geochemical stabilization of heavy metals can be performed easily in both soil and ground water. Some of the most common sulfur-based immobilizing agents include sodium metabisulfite (Na₂S₂O₅), iron(II) sulfate (FeSO₄), and calcium polysulfide (CaS₅). Hydroxide-based immobilizing agents include calcium hydroxide [Ca(OH)₂], commonly called slaked lime, and potassium hydroxide (KOH), commonly called potash, have also been used for geochemical stabilization projects.

Under reducing conditions, heavy metal cations can be removed from solution as sulfide precipitates, as long as sufficient sulfur is available (Suthersan and Payne, 2005). Some *in situ* remediation specialists use fermentable compounds that produce hydrogen. These types of compounds are carbon-rich solutions such as molasses, edible vegetable oils, sodium lactate, cheese whey, and corn syrup. The carbon-rich solutions ferment in a biotic, reducing (anaerobic) environment and ultimately produce hydrogen, an electron donor, that can be used to reduce the oxidation-reduction potential (ORP) in the aquifer to the point where heavy metals come out of solution and precipitate as sulfides, hydroxides, and carbonates.

Many heavy metals, such as copper, silver, lead, zinc, nickel, and cadmium precipitate as sulfides. At the same pH, with few exceptions, sulfides are an order of magnitude less soluble than the hydroxide forms, consequently, sulfide precipitation is preferred. However, a few metals such as chromium (Cr) do not precipitate as sulfides. Chromium changes from the soluble and more toxic form of chromium, Cr(VI), to Cr(III) and precipitates out as chromium hydroxide (Cr(OH)₃). Treatability testing using site specific soil and ground water allows for the testing of treatment chemicals and determining the length of time needed to complete the precipitation of the soluble metals. The number of pore volume flushings required for successful treatment of metals can be performed using a soil column test. Modifications of pH and concentration of treatment chemicals can be evaluated using treatability tests

to optimize site specific remediation options. Descriptions of various Cr(VI) treatability testing methods are included in Guertin et al. (2005).

For above-ground treatment of soluble metals in a water stream, such as Cr(VI), there are several options to consider. For low concentrations of heavy metals (1 µg/L to 10 µg/L), the least expensive passive options include bone-char carbon and specialized composite sorbents which contain a modified clay mineral and a modified fibrous carbon material. These techniques require sampling ports between the 136 kg (300 lb) or larger containers, so breakthrough does not occur. Bone char can remove about 0.82 kg (1.8 lb) of lead per 136 kg (300 lb) of bone char with about 1 minute of retention time. Treatability testing using soil columns with the proposed sorbents can be designed to determine the site-specific contaminant residence time required as well as the number of pore volumes of liquid that can be treated prior to breakthrough.

Other, more expensive, above-ground treatment options for soluble metals include various flocculating chemicals with mixing tanks, ion exchange resins, and reverse osmosis. As the technology becomes more complex, the price also increases significantly.

Anaerobic Treatments

A variety of carbon-rich compounds when fermented produce hydrogen as the end product. These compounds are used *in situ* to dehalogenate chlorinated solvents such as tetrachloroethene (PCE) and trichloroethene (TCE). This biotic fermenting process is also used for precipitating metals, such as chromium. Hydrogen gas in solution acts as an immediate electron donor without the fermenting stage. The chlorinated solvents (PCE and TCE) are electron acceptors. Recent studies by Leigh (2007) suggest that a combination of carbon-sources to ferment with high concentrations of dissolved hydrogen in the recirculation waters increased degradation of chlorinated ethenes. Other studies by Sheldon, et al. (2008) showed a 50% increase in PCE degradation when the edible micro-emulsion soy oil was combined with hydrogen gas infusion. All types of biological reactions (anaerobic, co-metabolic and aerobic) can be tested and optimized in the laboratory using microcosm studies to evaluate degradation pathways and biofeasibility

evaluations to evaluate biogeochemical conditions.

pH Adjustment Chemicals

For the neutralization of industrial acid pits, pH adjustment chemicals include the strong bases such as sodium hydroxide (NaOH at pH 13.5). Other bases, such as calcium polysulfide (CaS₅ at pH 11.5 to 11.8) are worth considering, especially when soluble metals are present owing to the low pH. Treatability scale testing helps in determining dose and to evaluate whether certain metals will be released as a result of changing the pH.

Free Product Removal

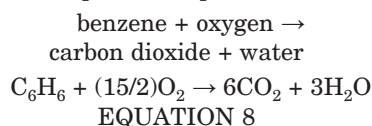
Treatability testing can be used for modeling active removal of freeproduct including, dense non-aqueous phase liquid (DNAPL) such as chlorinated solvents, or light non-aqueous phase liquid (LNAPL) such as fuel hydrocarbons. Active removal includes flushing with biosolvents, surfactants or dissolved carbon dioxide. These flushing methods lower the free product viscosity and increase mobility, where the vapors and free-product are removed using dual phase extraction equipment (Jacobs et al. 2008). Sand box models allow for easy viewing of the progress of the free-product removal process. Passive free-product removal using cloth sorbents or sphagnum moss in a steel, cloth, or plastic cage or sock can likewise be evaluated in the laboratory using a treatability test to determine the optimal removal material for the specific site.

Enhanced Bioremediation and Natural Attenuation

Bioremediation uses microorganisms to remove or reduce contaminants to effectively remediate a contaminated site. Some requirements for bioremediation include specific contaminant degrading microbes, moisture, macronutrients, appropriate pH, and a terminal electron acceptor (TEA) for cellular respiration.

For aerobic microbes, oxygen is the TEA and usually the limiting factor for biodegradation process. For every 0.45 kg (1 lb) of hydrocarbon that is degraded, about 1.4 kg (3 lb) of oxygen are required. This equation assumes that every molecule of oxygen present or infused into the aquifer is consumed in the degradation of the hydrocarbons. The theoretical amount of oxygen required to aerobically

biodegrade gasoline can be estimated. Since gasoline consists of thousands of compounds including benzene (C₆H₆), benzene is used in the example calculation. The equation (Equation 8) is:



	Benzene	Oxygen	Carbon Dioxide	Water
Moles	1	15/2 or 7.5	6	3
Mass (gram)	78	240	264	54

After Kuo (1999).

For each mole of benzene, 7.5 moles of oxygen are required, or for every 78 grams of carbon, 240 grams of oxygen are needed for complete mineralization, which is a ratio of (240/78) or 3.08. Therefore, a little more than 1.4 kg (3 lb) of oxygen are required to completely mineralize 0.45 kg (1 lb) of petroleum hydrocarbons. Owing to the complex geochemistry in aquifers with both solid and soluble oxygen demand, the amount of oxygen required for the biodegradation of the petroleum hydrocarbon contaminant is significantly higher. Depending on the oxygen demand, the ratio of oxygen to hydrocarbon consumed is more realistically 2.3 kg to more than 4.5 kg (5 lb to more than 10 lb) of oxygen per 0.45 kg (1 lb) of hydrocarbon destroyed.

For anaerobic microbes, nitrate, manganese(IV), iron(III), sulfate, and ultimately carbon dioxide are the TEAs. Biofeasibility treatability studies in the laboratory evaluate the types and concentrations of anaerobic microbes, often called bacterial enumeration. In addition, the presence and concentration of TEAs and macro-nutrients (measured as ortho-phosphate and ammonia as nitrogen) are evaluated. Other measurements include dissolved oxygen (DO), oxidation-reduction potential (ORP), total inorganic carbon (TIC), total organic carbon (TOC), solid, chemical and biological oxygen demand (BOD), and other biochemical parameters (Table 4).

To verify the effectiveness of bioremediation for compounds other than well-understood gasoline, a laboratory microcosm treatability study can be performed. Such a study would be contaminant-and-site specific. Effective microcosm studies can determine

whether biodegradation is occurring as opposed to volatilization, adsorption, photodegradation, or leaching of the contaminants from the soil or ground water. Control samples are sometimes used for quality control and comparison tests.

Collection of Representative Samples

Representative soil and groundwater samples are collected in the field. Typically 0.94 m to 1.2 m (3 ft to 4 ft) of 3.1 cm (2 in.) diameter soil tubes are enough for 3 case studies.

Unsaturated zone treatments use only soil and deionized water. For saturated zone treatment, about 11.4 L (3 gal) of water are needed for about 3 case studies. The samples are frequently spiked (addition of known quantity of contaminant) in the laboratory with the contaminant at a known concentration so that degradation rates can be measured more easily.

Treatability Testing Apparatus

There are several different ways of performing treatability tests, including using specially designed soil and groundwater test chambers which collect any gases produced during the reactions. In addition, soil column testing allows liquid reagents to percolate or be pumped through the soil column. Soil column tests are used to evaluate the number of pore volumes and time required for a specific degradation rate or result. For larger scale treatability tests, modified aquariums or sand box models are used for contaminant degradation studies.

Challenges

The main issue with treatability scale testing is whether the soil or groundwater samples collected from the field are representative of the site, given the frequent lithologic heterogeneity of many sites. For example, collecting at least 10 soil samples, and compositing them in the laboratory is a way to eliminate specific collection biases. Sometimes it is better to focus the treatability scale testing on the soil zones that are most likely to be remediated using the specific chemistry. But, if the contaminated soils are difficult to remediate

(typically clays), they can be treated and optimized in the laboratory to improve the chance of successful scaling to the pilot scale test or full scale remediation. In this way, unknowns about the specific treatment chemistry can be reduced. For *in situ* remediation, the intrinsic permeability (connected pores) of the soil or sediments should be greater than 9.3 x 10⁻⁴ m² (0.01 ft²) and hydraulic conductivity (K) should be greater than 3 x 10⁻⁷ m/s (10⁻⁶ ft/s) (US EPA, 2004).

The length of time for degradation of a particular contaminant can be difficult to assess by extrapolating from laboratory scale data into the field. Varying conditions in the subsurface (changes in temperature, pH, moisture content, etc.) also create discrepancies related to scaling problems between the treatability scale test and the field scale treatments. *In situ* treatments rely mostly on liquids, however gases (such as oxygen and hydrogen) and solids (magnesium peroxide and elemental iron) have been used successfully. Uniform delivery (vertically and horizontally) of the treatment chemicals into the subsurface target zone is frequently a challenge that can be evaluated by selecting a large number of soil samples for the treatability tests. Variations in laboratory treatability test results frequently provide insights into problem zones in the field.

Example Projects

Treatability scale testing can reduce overall project costs by identifying the most cost-effective remedial option. One recent case involved the use of a sulfur-based immobilizing chemical to precipitate Cr(VI). Although significant safety precautions were taken in the field, treatability tests were used with higher concentration of reactants than were used in the field to prove that hydrogen sulfide (H₂S) gas and sulfur dioxide (SO₂) gas would not be generated in the reaction chamber headspace. By matching the geochemical conditions in the laboratory closely with the field, the case results effectively lowered the risk of worker exposure to toxic gases in the field, which reduced the required level of worker protection and consequently, costs. In another case study, some heavy metals did not go into solution during treatability scale testing and these metals were not required to be analyzed during and after full-scale treatment, saving the owner laboratory costs. Other treatability test case studies have been used to support proposed cleanup goals

ANALYSIS	METER/LAB ANALYSIS
Contaminant	Laboratory analysis
<i>General Geochemistry</i>	
Oxidation Reduction Potential (ORP)	Meter
pH/temp/conductivity	Meter
Conductivity, temperature	Meter
Speciated alkalinity; CO ₂	Lab analysis
Total Organic Carbon (TOC)	Lab analysis
<i>Biological Assessment</i>	
Aerobic (or anaerobic) Heterotrophs	Biological laboratory
Specific Degraders	Biological laboratory
<i>Common Terminal Electron Acceptors (TEAs)</i>	
Dissolved Oxygen (DO)	Meter
Nitrate, manganese, and sulfate	Lab analysis
Iron(II) (soluble), total iron (soluble)	Field kit
<i>Macro-Nutrients</i>	
Orthophosphate	Lab analysis
Ammonia as nitrogen	Lab analysis
<i>Commonly Analyzed Heavy Metals</i>	
CAM 17 metals	Lab analysis
Cr(VI), bromate, selenium	Lab analysis
<i>Carbon</i>	
Speciated alkalinity; CO ₂	Lab analysis
Total Organic Carbon (TOC)	Lab analysis
Total Inorganic Carbon (TIC)	Lab analysis
<i>Total Solids</i>	
Total Dissolved Solids (TDS)	Lab analysis
Total Suspended Solids (TSS)	Lab analysis
<i>Miscellaneous</i>	
General mineral	Lab analysis
Soil moisture content	Lab analysis
DNAPL presence	Observation in field
Hydraulic conductivity	Determined in field
Mass of contaminant	Calculation
<i>Oxygen Demand</i>	
Biological Oxygen Demand (BOD ₅)	Lab analysis
Chemical Oxygen Demand (COD)	Lab analysis
Solid Oxidant Demand, by persulfate; (persulfate SOD), permanganate, etc.	Lab analysis (other chemical oxidizers can be used in SOD analysis)

Table 4. Summary Of Field And Laboratory Analysis For Enhanced Bioremediation And Chemical Oxidation Bench Tests

or provide data for the regulatory acceptance of field screening methods such as the use of spectrophotometers for initial field soil or water confirmation. In some cases the feasibility of certain processes can be evaluated as to success or failure, prior to performing pilot scale remediation projects, saving tens of thousands of dollars.

Summary

Treatability scale testing provides a scientific basis for the selection of remedial technology. The optimal concentrations of the treatment chemistry should be tested using treatability scale studies prior to the field work or the purchase of chemicals or equipment. With so many choices for remediation of petroleum hydrocarbons, chlorinated solvents, and "heavy" metals, treatability scale studies provide a low-cost method for choosing the most efficient, site-specific degradation pathway. This bench-scale method can be used with a variety of treatment process such as chemical oxidation, enhanced bioremediation, geochemical fixation, or pH adjustment. In sum, regardless of the contaminant, treatability testing is an important part of successful *in situ* soil and ground-water remediation projects.

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