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8 IN SITU REACTIVE ZONES

8.1 INTRODUCTION

The concept of *in situ* reactive zones is based on the creation of a subsurface zone where migrating contaminants are intercepted and permanently immobilized or degraded into harmless end products. The successful design of these reactive zones requires the ability to engineer two sets of reactions between (1) the injected reagents and the migrating contaminants and (2) the injected reagents and the subsurface environment to manipulate the biogeochemistry to optimize the required reactions, in order to effect remediation. These interactions will be different at each contaminated site and, in fact, may vary within a given site. Thus, the major challenge is to design an engineered system for the systematic control of these reactions under the naturally variable or heterogeneous conditions found in the field.

The effectiveness of the reactive zone is determined largely by the relationship between the kinetics of the target reactions and the rate at which the mass flux of contaminants passes through it with the moving groundwater. Creation of a spatially fixed reactive zone in an aquifer requires not only the proper selection of the reagents, but also the proper mixing of the injected reagents uniformly within the reactive zone. Furthermore, such reagents must cause few side reactions and be relatively nontoxic in both its original and treated forms.

When dealing with dissolved inorganic contaminants, such as heavy metals, the required process sequence in a pump and treat system to remove the dissolved heavy metals present in the groundwater becomes very complex and costly (Figure 8.1). In addition, the disposal of the metallic sludge, in most cases as a hazardous waste, is also very cost prohibitive. Therefore, *in situ* treatment methods capable of achieving the same mass removal reactions for dissolved contaminants in an *in situ* environment are evolving and gradually gaining prominence in the remediation industry.

The advantages of an *in situ* reactive zone to address the remediation of groundwater contamination are as follows:

- An *in situ* technology: eliminates the expensive infrastructure required for a pump and treat system; no disposal of water or wastes.
- Inexpensive installation: primary capital expenditure for this technology is the installation of injection wells.
- Inexpensive operation: reagents are injected at fairly low concentrations, and hence the cost should be insignificant; only sampling required is groundwater quality monitoring; management of large volumes of contaminated water without any disposal needs.
- Can be used to remediate deep sites: cluster injection wells can be installed to address deeper sites.
- Unobtrusive: once the system is installed, site operations can continue with minimal obstructions.
• In situ degradation of contaminants: organic contaminants can be degraded by implementing the appropriate reactions.
• Immobilization of contaminants: utilizes the capacity of the soils and sediments to adsorb, filter out, and retain inorganic contaminants.

8.2 TYPES OF IN SITU REACTIONS

Manipulation of the oxidation–reduction (redox) potential of an aquifer is a possible approach for in situ remediation of redox-sensitive groundwater contaminants. In addition, various microbially induced or chemically induced reactions also can be achieved in an in situ environment. As noted earlier, creation of spatially fixed reactive zones to achieve these reactions is very cost-effective in comparison to treating the entire plume as a reaction zone.

8.2.1 Heavy Metals Precipitation

The mechanisms that can be used to reduce the toxicity of heavy metals dissolved in groundwater are transformation and immobilization. These mechanisms can be induced by both abiotic and biotic pathways. Abiotic pathways include oxidation, reduction, sorption, and precipitation. Examples of biotically mediated processes include reduction, oxidation, precipitation, biosorption, bioaccumulation, organo-metal complexation, and phytoremediation. In this chapter, immobilization mechanisms induced by precipitation only will be discussed.

Dissolved heavy metals can be precipitated out of solution through various precipitation reactions shown below. A divalent metallic cation is used as an example in these reactions.

\[ \text{Hydroxide precipitation:} \quad \text{Me}^{\text{2+}} + 2\text{OH}^- \rightarrow \text{Me(OH)}_2 \downarrow \quad (8.1) \]

\[ \text{Sulfide precipitation:} \quad \text{Me}^{\text{2+}} + \text{S}^{\text{2-}} \rightarrow \text{MeS} \downarrow \quad (8.2) \]

\[ \text{Carbonate precipitation:} \quad \text{Me}^{\text{2+}} + \text{CO}_3^{\text{2-}} \rightarrow \text{MeCO}_3 \downarrow . \quad (8.3) \]

Theoretical behavior of solubility of these precipitation mechanisms is shown in Figure 8.2.
Hydroxide and sulfide precipitation of heavy metals have been used successfully in conventional industrial wastewater systems. Lime (Ca(OH)$_2$) or other alkaline solutions such as potash (KOH) are used as reagents for hydroxide precipitation. Sodium sulfide (Na$_2$S) is normally used as the reagent to form extremely insoluble metallic sulfide precipitates. Injection of these chemical reagents into the contaminated aquifers, to create a reactive zone, will precipitate the heavy metals out of solution. However, injection of a reactive, pH-altering chemical reagent into the groundwater may be objectionable from a regulatory point of view. Obtaining the required permits to implement chemical precipitation may be difficult. Furthermore, the metallic cations precipitated out as hydroxide could be resolubilized slightly as a result of any significant shift in groundwater pH.

Under reducing conditions, heavy metal cations can be removed from solution as sulfide precipitates if sufficient sulfur is available. The solubility pattern of heavy metals as a function of pH and redox potential is summarized for Cd, Ni, Zn, As, and Cr in Figure 8.3. In systems containing a sufficient supply of sulfur, neutral to mildly alkaline pH and low redox conditions are most favorable for the precipitation of many heavy metals. Chromium is insoluble under reducing conditions, as Cr(III) hydroxide, but only at neutral to mildly acidic and alkaline pH values.

Precipitation as sulfides is considered the dominant mechanism limiting the solubility of many heavy metals. Sulfide precipitation is particularly strong for “chalcophilic” metals exhibiting “B-character,” such as Cu(I), Ag, Hg, Cd, Pb, and Zn; it also is an important mechanism for transition elements such as Cu(II), Ni(I), Co(II), Fe(II), and Mn(II). Two situations can be distinguished in natural systems during sulfide precipitation conditions: the existence of a certain sulfide precipitation capacity (SPC), or (when exceeding the SPC) the accumulation of free sulfide (as H$_2$S or HS$^-$) in the aqueous phase. At excess sulfide concentrations, solubility of some metals can be increased by the formation of thio complexes. However, the stability of these complexes is still questionable.

The sulfide ions necessary to mediate sulfide precipitation can be directly injected into a reactive zone in the form of sodium sulfide (Na$_2$S). However, the sulfide ion (S$^{2-}$) is one of the most reduced ions and its stability within the reactive zone is short-lived. It will be converted to sulfate(SO$_4^{2-}$) very quickly in the presence of oxidizing conditions within the contaminated plume. Addition of a very easily biodegradable organic substrate, such as carbohydrates, will enhance the formation of reduced, anaerobic conditions by depleting the available oxidation potential. The presence of carbohydrates serves two purposes: microorganisms use it as their growth substrate by depleting the available oxygen, and use it as an energy source for the reduction of sulfate to sulfide.

Figure 8.2 Theoretical pathways for solubility of heavy metal cations.
Indirect microbial transformation of metals can occur as a result of sulfate reduction when anaerobic bacteria oxidize simple carbon substrates with sulfate serving as the electron acceptor. The net result of the process is the production of hydrogen sulfide ($H_2S$) and alkalinity ($HCO_3^-$). Sulfate reduction is strictly an anaerobic process and proceeds only in the absence of oxygen. The process requires a source of carbon to support microbial growth, a source of sulfate, and a population of sulfate-reducing bacteria. Dilute black strap molasses solution is an ideal feed substrate for this purpose, since typical black strap molasses contains approximately 20% sucrose, 20% reducing sugars, 10% sulfated ash, 20% organic nonsugars, and 30% water. The $H_2S$ formed in the reaction can react with many types of contaminant metals to precipitate metals as insoluble metallic sulfides. The process follows the reaction

\[ H_2S + Me^{2+} \rightarrow MeS \downarrow + 2H^+ . \]

As noted earlier, Cu, Ag, Cd, Pb, Zn, Ni, Co, in addition to Fe and Mn can be precipitated as metallic sulfides. Precipitated metallic sulfides will remain in an insoluble, stable form, unless the subsurface redox conditions change dramatically. The solubility products of various metallic precipitates are shown in Table 8.1. It can be seen from Table 8.1 that metallic sulfides are much more stable precipitates than hydroxides.

<table>
<thead>
<tr>
<th>Table 8.1 Comparison of Solubility Products for Various Metallic Precipitates</th>
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<td><strong>Metal</strong></td>
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The production of alkalinity from sulfate reduction reactions causes an increase in pH, which can result in metal precipitation through the formation of insoluble metal hydroxides or oxides. This process follows the reaction

$$\text{Me}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{Me(OH)}_2 + 2\text{H}^+.$$  (8.5)

### 8.2.1.1 Chromium Precipitation

**In situ** microbial reduction of dissolved hexavalent chromium Cr(VI) to trivalent chromium Cr(III) yields significant remedial benefits, because Cr(III) is less toxic, less mobile, and precipitates out of solution much more readily. In fact, it has been stated that the attenuation of Cr(VI) in the reduced Cr(III) from within an aquifer is a viable groundwater remediation technique.\(^4\)

*In situ* microbial reduction of Cr(VI) to Cr(III) can be promoted by injecting a carbohydrate solution, such as dilute molasses solution. The carbohydrates, which consist mostly of sucrose, are readily degraded by the heterotrophic microorganisms present in the aquifer, thus depleting all the available dissolved oxygen present in the groundwater. Depletion of the available oxygen present causes reducing conditions to develop. The mechanisms of Cr(VI) reduction to Cr(III), under the induced reducing conditions can be (1) likely a microbial reduction process involving Cr(VI) as a terminal electron acceptor for the metabolism of carbohydrates, by species such as *Bacillus subtilis*,\(^5\) (2) an extracellular reaction with by-products of sulfate reduction such as H\(_2\)S,\(^4\) and (3) abiotic oxidation of the organic compounds including the soil organic matter such as humic and fulvic acids.

The primary end product of Cr(VI) to Cr(III) reduction process is chromic hydroxide [Cr(OH)\(_3\)], which readily precipitates out of solution under alkaline to moderately acidic and alkaline conditions.\(^4\) To ensure that this process will provide both short-term and long-term effectiveness in meeting groundwater cleanup objectives, the chromium precipitates must remain immobilized within the soil matrix of the aquifer, and shall not be subject to Cr(OH)\(_3\) precipitate dissolution or oxidation of Cr(III) back to Cr(VI) once groundwater conditions revert back to natural conditions. Based on the results of significant research being conducted on the *in situ* chromium reduction process,\(^4\) it is readily apparent that the Cr(OH)\(_3\) precipitate is essentially an insoluble, stable precipitate immobilized in the soil matrix of the aquifer.

Contrary to the numerous natural mechanisms that cause the reduction of Cr(VI) to Cr(III), there appear to be only a few natural mechanisms for the oxidation of Cr(III). Indeed, only two constituents in the subsurface environment (dissolved oxygen and manganese dioxide) are known to oxidize Cr(III) to Cr(VI).\(^7\) The results of studies conducted on the potential reaction between dissolved oxygen and Cr(III) indicate that dissolved oxygen will not cause the oxidation of Cr(III) under normal groundwater conditions.\(^7,8\) Studies have shown that Cr(III) can be oxidized by manganese dioxides, which may be present in the soil matrix.\(^7\) However, only one phase of manganese dioxides is known to oxidize appreciable amounts of Cr(III), and this process is inversely related to groundwater pH.\(^7\) Hence, the oxidation of Cr(III) back to Cr(VI) in a natural aquifer system is highly unlikely.

The Cr(OH)\(_3\) precipitate has an extremely low solubility (solubility product \(K_{sp} = 6.7 \times 10^{-31}\)),\(^9\) and thus, very little of the chromium hydroxide is expected to remain in solution. It has been reported that aqueous concentration of Cr(III), in equilibrium with Cr(OH)\(_3\) precipitates, is around 0.05 mg/l within the pH range of 5 to 12 (Figure 8.4).\(^4\) The pH range of natural aquifer systems will be within 5 to 12, and hence the potential for the chromic hydroxide to resolubilize is unlikely. Furthermore, the potential for coprecipitation with ferric ions will further decrease the solubility of Cr(OH)\(_3\).

Dissolved Cr(VI) can be also precipitated as Cr(OH)\(_3\) in a reactive zone, also by the injection of ferrous sulfate solution into a reactive zone at appropriate concentrations. Cr(VI)
exists as chromate, $\text{CrO}_4^{2-}$, under neutral or alkaline conditions and dichromate, $\text{Cr}_2\text{O}_7^{2-}$, under acidic conditions. Both species react with ferrous ion:

**Acidic conditions**:  
$$\text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O} \quad (8.6)$$

**Neutral or alkaline conditions**:  
$$\text{Cr}_2\text{O}_7^{2-} + 3\text{Fe}^{2+} + 4\text{H}_2\text{O} \rightarrow \text{Cr}^{3+} + 3\text{Fe}^{3+} + 8\text{OH}^- \quad (8.7)$$

Both Cr(III) and Fe(III) ions are highly insoluble under natural conditions of groundwater (neutral pH or slightly acidic or alkaline conditions).

$$\text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{Fe(OH)}_3 \downarrow \quad (8.8)$$

$$\text{Cr}^{3+} + 3\text{OH}^- \rightarrow \text{Cr(OH)}_3 \downarrow \quad (8.9)$$

The addition of ferrous sulfate into the reactive zone may create acidic conditions, and hence the zone downgradient of the ferrous sulfate injection zone may have to be injected with soda ash or caustic soda to bring the pH back to neutral conditions.

### 8.2.1.2 Arsenic Precipitation

Soluble arsenic occurs in natural waters only in the pentavalent, $\text{As(V)}$, and trivalent, $\text{As(III)}$, oxidation states. Although both organic and inorganic forms of arsenic have been detected, organic species (such as methylated arsenic) are rarely present at concentrations greater than 1 ppb and are generally considered of little environmental significance compared with inorganic arsenic species. Thus, this discussion focuses exclusively on the behavior of inorganic arsenic.

Thermodynamics provides useful insight into the equilibrium chemistry of inorganic arsenic species. In oxygenated waters, $\text{As(V)}$ is dominant, existing in anionic forms of either $\text{H}_2\text{AsO}_4^-$, $\text{HAsO}_4^{2-}$, or $\text{AsO}_4^{3-}$ over the pH range of 5 to 12, which covers the range encountered in natural groundwater. Under anoxic conditions, $\text{As(III)}$ is stable, with nonionic ($\text{H}_3\text{AsO}_3$)
and anionic (H₂AsO₄⁻) species dominant below and above pH 9.22, respectively. In the presence of sulfides, precipitation of AsS (realgar) or As₂S₃ (orpiment) may remove soluble As(III) and exert considerable control over trace arsenic concentrations.

The thermodynamic reduction of As(V) to As(III) in the absence of oxygen could be chemically slow and may require bacterial mediation. As noted in the previous section, injection of dilute solution of blackstrap molasses will create the reducing conditions for As(V) to be reduced to As(III) and also provide the sulfide ions for As(III) to precipitate as As₂S₃. These reactions are described by the following equations.

Reduction of As(V) to As(III) under anaerobic conditions:

\[
\text{HAsO}_4^{2-} \rightarrow \text{HAsO}_2^-, \quad (8.10)
\]

In the presence of S⁻ under anaerobic conditions:

\[
\text{HAsO}_2^- + S^- \rightarrow \text{As}_2\text{S}_3 \downarrow. \quad (8.11)
\]

Within oxygenated zones in the aquifer, oxidation of ferrous ion (Fe(II)) and Mn(II) leads to formation of hydroxides that will remove soluble As(V) by coprecipitation or adsorption reactions. The production of oxidized Fe–Mn species and subsequent precipitation of hydroxides are analogous to an in situ coagulation process for removing As(V).

### 8.2.2 In Situ Denitrification

*In situ* denitrification can be accomplished by organisms belonging to the genera *Micrococcus, Pseudomonas, Denitrobacillus, Spirillum, Bacillus*, and *Achromobacter*, which are present in the groundwater environment. Denitrifying organisms will utilize nitrate or nitrite in the absence of oxygen as the terminal electron acceptor for their metabolic activity. If any oxygen is present in the environment, it will probably be used preferentially. The energy for the denitrifying reactions is released by organic carbon sources that act as electron donors. The microbial pathways of denitrification include the reduction of nitrate to nitrite and the subsequent reduction of nitrite to nitrogen gas.

\[
\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{N}_2 \uparrow. \quad (8.12)
\]

In biological wastewater treatment processes employing denitrification, a cheap, external carbon source such as methanol is added as the electron donor. It has long been known that NO₃⁻ can be converted to N₂ gas in anaerobic groundwater zones in the presence of a labile carbon source.

*In situ* microbial denitrification is based on the same principle as conventional biological wastewater treatment systems, except that it is carried out in the subsurface by injecting the appropriate organic carbon source. Since methanol could be an objectionable substrate from a regulatory point of view, sucrose or sugar solution is an optimum substrate to be injected.

It should be noted that in the hierarchy of redox reactions, NO₃⁻ is the most favored electron acceptor after dissolved oxygen. Hence, considerable attention should be focused in maintaining the redox potential in the optimum range, so that Mn(IV), Fe(III), sulfate reduction conditions, or methanogenic conditions are not formed in the subsurface. Furthermore, since denitrification is a reduction reaction, alkalinity and pH tend to increase in the aquifer. Since the end product N₂ gas will escape into the vadose zone, and hence the aquifer system is not a closed system, increased alkalinity will be observed in the groundwater. If the NO₃⁻ concentration is not very high, this concern will be short-lived.
8.2.3 Abiotic Reduction by Dithionite

The dithionite or hydrosulfite ion, $S_2O_4^{2-}$, may be conceptualized as two sulfoxyl (SO$_2^-$) radicals joined by a sulfur–sulfur bond. The S–S bond in S$_2$O$_4^{2-}$ is considerably longer (and hence weaker) than typical S–S bonds, and this weak link in the S$_2$O$_4^{2-}$ ion is the key to its chemistry, because the ion reversibly dissociates to form two SO$_2^-$ radicals that are strong and highly reactive reductants. Since the SO$_2^-$ radicals are extremely reactive, the dissociation of the S$_2$O$_4^{2-}$ is the slow and rate-limiting step in the reactions.

Injection of sodium thionite was found to reduce structural ferric ion in the soils, thus producing the reduced ferrous iron which remains available to react with soluble oxidized compounds present in the groundwater. Further experiments indicated that dithionite could abiotically reduce carbon tetrachloride (CCl$_4$) to achieve more than 90% removal. It was reported that the half life of dithionite ion is about 2 or 3 days and this half life is adequate for reducing the contaminants within the induced reactive zone, while ensuring that dithionite does not remain as a contaminant in the groundwater for an extended time.

8.2.4 In Situ Chemical Oxidation

During chemical oxidation of an organic compound, the compound is converted by an oxidizing agent into harmless end products, typically having either a higher oxygen or lower hydrogen content than the original compound. Typical oxidizing agents that have been used in the past under varying circumstances include chlorine dioxide (ClO$_2$), hypochlorite (either sodium (NaOCl) or calcium (Ca(OCl)$_2$)), hydrogen peroxide, and ozone. Recently potassium permanganate (KMnO$_4$) has been considered as a strong chemical oxidant to address chlorinated organic compounds. Injection of chlorine-based oxidants into a reactive zone may be objectionable from a regulatory point of view, due to the potential of forming various chlorinated by-products.

Hydrogen peroxide is a powerful oxidizing agent whose decomposition products, water and oxygen, are nontoxic.

$$H_2O_2 \rightarrow H_2O + \ddot{O} \quad (8.13)$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad (8.14)$$

Solutions of hydrogen peroxide are relatively safe, effective, and easy to use. Hydrogen peroxide can be a source of hydroxyl radicals, one of the most potent oxidizers known. The hydroxyl radical is second only to fluorine in oxidation potential among the common oxidants.

There are two main methods of producing hydroxyl radicals (OH$_x$) with hydrogen peroxide in an in situ reactive zone. In the first method, Fenton’s reagent can be used to enhance the production of hydroxyl radicals. Fenton’s reagent is a mixture of hydrogen peroxide and ferrous salts.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH_2 \quad (8.15)$$

Hydroxyl free radical (OH$_x$) generated as an intermediate reaction product is a very strong, nonselective oxidant for a wide range of organic compounds, in addition to being a very strong oxidant. The magnitude of the rate constant for the reactions between OH$_x$ and organic compounds generally lies within a range of $10^6$ to $10^{13}$ $M^{-1} s^{-1}$, which for practical purposes is an “instantaneous” rate for oxidation.

The second main method is by an advanced oxidation process involving the mixed injection of hydrogen peroxide and ozone into the reactive zone.
The emergence of in situ ozonation techniques for groundwater remediation is a direct result of advances made in air sparging technology in the last few years. For in situ ozonation, a properly designed air sparging system is an effective way to deliver ozone to the reactive zone. Furthermore, ozone can oxidize organic contaminants by direct oxidation in addition to the oxidation by free hydroxyl radical. Ozone as a direct oxidant is the third strongest oxidant after fluorine and hydroxyl radical.

Contaminants most amenable to oxidation by H$_2$O$_2$/O$_3$ injection include polynuclear aromatic hydrocarbons (PAHs), chlorinated ethenes such as trichloroethylene (TCE) or dichloroethylene (DCE), and petroleum-related compounds such as benzene, toluene, ethyl benzene, and xylenes.

Injection of H$_2$O$_2$/O$_3$ into a reactive zone may be integrated with other remediation technologies to achieve the highest possible treatment efficiencies. The amount of oxygen generated as a result of H$_2$O$_2$/O$_3$ injection will increase the dissolved oxygen content, and thus enhance the rate of aerobic biodegradation. Used as a pretreatment step before bioremediation, H$_2$O$_2$/O$_3$ injection can break down some complex organics, presenting simpler organic molecules that are more amenable to biodegradation. However, it should be noted that both H$_2$O$_2$ and O$_3$ at high enough concentrations or long enough residence times can act as sterilizing agents, killing the microbial population. Thus, when designing a system that integrates bioremediation and oxidation within the reactive zone, special consideration should be given to injection flow rate, concentration, and residence time.

Potassium permanganate (KMnO$_4$) is used as an oxidizing agent to control odor in sewage treatment plants and industrial wastewater treatment. Potassium permanganate is available either as granular or needle-shaped crystals, both of dark purple color. The solubility in water is strongly influenced by temperature, and at high concentrations the solution has a characteristic purple color.

Oxidations with permanganate can occur via several different reaction paths: 18 electron abstraction, hydrogen atom abstraction, hydride-ion abstraction, and direct donation of oxygen to the organic substrate. The pH of the system will determine whether the oxidation will involve one, three, or five electron exchange and whether the reaction will be fast or slow. It should be noted that oxidation potential increases with decreasing pH due to the capacity to accept a higher number of electrons.

Under extremely alkaline conditions (pH > 12), one electron is transferred:

$$\text{MnO}_4^- + e^- \rightarrow \text{MnO}_4^{2-}. \quad (8.17)$$

In the pH range of 3.5 to 12, three electrons are transferred:

$$\text{Acidic conditions : } \text{MnO}_4^- + 4\text{H}^+ + 3e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O} \quad (8.18)$$

$$\text{Alkaline conditions : } \text{MnO}_4^- + 2\text{H}_2\text{O} + 3e^- \rightarrow \text{MnO}_2 + 4\text{OH}^- . \quad (8.19)$$

Under more strongly acidic conditions (pH < 3.5), five electrons are transferred:

$$\text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} . \quad (8.20)$$

Besides pH, permanganate oxidation reaction rate and degree depends on temperature, time, and concentrations. Organic compounds that contain carbon–carbon double bonds,
primary alcohols, polynuclear aromatic hydrocarbons (PAHs), phenols, amines, and organic sulfur compounds can be potentially oxidized by KMnO₄ under optimum conditions in an in situ reactive zone. In situ chemical oxidation within a reactive zone may also oxidize compounds other than the target contaminants. Humic substances, carbonates, bicarbonates, organic content of the soil, and inorganic ions may also be oxidized in addition to the contaminants. Hence, efficiency of utilization of the oxidizing agent in targeting the contaminant mass may be significantly lower than stoichiometric predictions.

8.2.5 In Situ Microbial Mats

Inoculation of specialized microbial cultures for the in situ degradation of specific target compounds has been tried in the past. Usually, naturally occurring microbes are grown in surface bioreactors, separated from their growth medium, resuspended in groundwater from the site, and then reinjected into the reactive zone. The habitat for the inoculated microbial population can be the native soils or specially designed porous filters. Concentration of target contaminants is gradually increased in the surface bioreactor to enhance the acclimatization and species selection of the microbial population.

The microbial mat concept is based upon intercepting the migrating plume within the reactive zone. The survivability of the injected microbial culture with the highly specific species of microorganisms may not be long enough within the reactive zone. Thus, replenishment of the specialized, selective microbial culture should be accomplished by reinoculation.

The microbial mat concept can be implemented for various types of biodegradable contaminants. Both aerobic and anaerobic reactions can be accomplished within these reactive zones. However, it should be noted that this concept is still considered experimental and has to go through extensive field testing.

8.3 AQUIFER PARAMETERS AND TRANSPORT MECHANISMS

Redox processes can induce strong acidification or alkalinization of soils and aquifer systems. Oxidized components are more acidic (SO₄²⁻, NO₃⁻) or less basic (Fe₂O₃) than their reduced counterparts (H₂S, NH₃). As a result, alkalinity and pH tend to increase with reduction and decrease with oxidation. Carbonates are efficient buffers in natural aquifer systems in the neutral pH range.

Many events can cause changes in redox conditions in an aquifer. Infiltration of water with high dissolved oxygen concentration, fluctuating water table, excess organic matter, introduction of contaminants that are easily degradable, increased microbial activity, and deterioration of soil structure can impact the redox conditions in the subsurface. However, there is an inherent capacity to resist redox changes in natural aquifer systems. This inherent capacity depends on the availability of oxidized or reduced species. Redox buffering is provided by the presence of various electron donors and electron acceptors present in the aquifer.

An engineered in situ reactive zone has to take into consideration how the target reactions will impact the redox conditions within and downgradient of the reactive zone, in addition to degrading the contaminants with the available residence time. Furthermore, careful evaluation should be performed regarding the selectivity of the injected reagents toward the target contaminants and the potential to react with other compounds or aquifer materials. Careful monitoring, short-term and long-term, should be performed to determine whether the natural equilibrium conditions can be restored at the end of the remediation process. In some cases modified biogeochemical equilibrium conditions may have to be maintained over a long period of time to prevent the reoccurrence of contaminants.
8.3.1 Contaminant Removal Mechanisms

As noted earlier, the mechanisms used to reduce the toxicity of dissolved contaminants can be grouped into two major categories: transformation and immobilization. Examples of some of these mechanisms have been discussed in Section 8.2. Conversion of chlorinated organic compounds to innocuous end products such as CO₂, H₂O, and Cl⁻ either by biotic or abiotic reaction pathways is an example of transformation mechanisms. Precipitation of Cr(VI) as Cr(OH)₃ either by abiotic or biotic reaction pathways and subsequent filtration by the soil matrix is an example of immobilization mechanisms.

It can be assumed, in most cases, that the end products of transformation mechanisms will result in dissolved and gaseous species. It can also be assumed that the impact of these end products on the natural redox equilibrium will be short-term. If the impact is expected to be significant, it can be controlled by limiting the reaction kinetics and the transport of the end products away from the reaction zone. Dilution and escape of dissolved gases will also help in restoring the natural equilibrium conditions in the reaction zone.

Immobilization mechanisms, which include heavy metals precipitation reactions, in reality transform the contaminant into a form (precipitate) that is much less soluble. In addition, transport of dissolved heavy metals in groundwater should also be considered as a two-phase system in which the dissolved metals partition between the soil matrix and the mobile aqueous phase.

Metal precipitates resulting from an in situ reactive zone may move in association with colloidal particles or as particles themselves of colloidal dimensions. The term colloid is generally applied to particles with a size range of 0.001 to 1 µm. The transport of contaminants as colloids may result in unexpected mobility of low solubility precipitates. It is important to remember that the transport behavior of colloids is determined by the physical/chemical properties of the colloids as well as the soil matrix.

Metal precipitates may be pure solids (e.g., PbS, ZnS, Cr(OH)₃) or mixed solids (e.g., (Feₓ, Cr₁₋ₓ) (OH)₃, Ba(CrO₄, SO₄)). Mixed solids are formed when various elements coprecipitate or due to interaction with aquifer materials. The potential for many interactions of heavy metal cations in the aquifer matrix is shown in Figure 8.5.

Colloidal precipitates larger than 2 µm in the low flow conditions common in aquifer systems will be removed by sedimentation. Colloidal precipitates are more often removed mechanically in the soil matrix. Mechanical removal of particles occurs most often by straining, a process in which particles can enter the matrix, but are caught by the smaller pore spaces as they traverse the matrix.

Colloidal particles below 0.1 µm will be subjected more to adsorptive mechanisms than mechanical processes. Adsorptive interactions of colloids may be affected by the ionic strength of the groundwater; ionic composition; quantity, nature, and size of the suspended colloids; geologic composition of the soil matrix; and flow velocity of the groundwater. Higher levels of total dissolved solids (TDS) in the groundwater encourages colloid deposition.

In aquifer systems with high Fe concentrations, the amorphous hydrous ferric oxide can be described as an amphoteric ion exchange media. As pH conditions change, it has the capacity to offer hydrogen ions (H⁺) or hydroxyl ions (OH⁻) for cation or an ion exchange, respectively. Adsorption behavior is primarily related to pH (within the typical range of 5.0 to 8.5), and at typical average concentrations in soil, the iron in a cubic yard of soil is capable of adsorbing from 0.5 to 2 lb of metals as cations or metallic complexes. This phenomenon is extremely useful for the removal of As and Cr.

8.4 DESIGN OF IN SITU REACTIVE ZONES

The optimization of subsurface environmental conditions to implement target reactions for remediating groundwater plumes holds a lot of promise. Application and treatment
Efficiencies of these same processes in above-ground pump and treat systems were impacted by the required residence times and the infrastructure required to implement these processes. However, when dealing with slow-moving groundwater plumes, long available residence times can be utilized as an advantage to implement cost-effective remediation strategies.

*In situ* reactive zones can be designed as a curtain or multiple curtains to intercept the moving contaminant plume at various locations. An obvious choice for the location of an intercepting curtain is the downgradient edge of the plume. This curtain will act as a containment curtain to prevent further migration of the contaminants (Figure 8.6A). A curtain can be installed slightly downgradient of, or within, the source area to prevent the mass flux of contaminants migrating from the source (Figure 8.6B). This will shrink the size of the contaminant plume faster. If the duration of remediation is a critical factor, another curtain can be installed between the above two curtains for further interception at the middle of the plume (Figure 8.6C).

Another approach to designing an *in situ* reactive zone is to create the reactive zone across the entire plume. The injection points can be designed on a grid pattern to achieve the reactions across the entire plume. However, it should be noted that the cost of installation of injection wells constitutes the biggest fraction of the system cost, looking at both capital and operational costs. Hence, it becomes very clear that the reduction of the total number of injection wells will significantly reduce the system costs, and this leads to the conclusion that the curtain concept will be the preferred and most cost-effective approach to implement *in situ* reactive zones.

The three major design requirements for implementing an *in situ* reactive zone are (1) creation and maintenance of optimum redox environment and other biogeochemical parameters such as pH, presence or absence of dissolved oxygen, and temperature, etc., (2) selection of the target process reactions and the appropriate reagents to be injected to achieve these reactions, and (3) delivery and distribution of the required reagents in a homogeneous manner across the entire reactive zone, both in the lateral and vertical directions.

### 8.4.1 Optimum Pore Water Chemistry

The composition of interstitial water is the most sensitive indicator of the types and the extent of reactions that will take place between contaminants and the injected reagents in the aqueous phase. Determination of the baseline conditions of the appropriate biogeochemical parameters is a key element for the design of an *in situ* reactive zone. This evaluation will
give a clear indication of the existing conditions and the necessary steps to be taken to optimize the environment to achieve the target reactions. A potential list of the biogeochemical parameters is presented below:

- dissolved oxygen
- pH
- temperature
- redox potential
- total organic carbon (dissolved and total)
- total dissolved solids
- total suspended solids

Figure 8.6  *In situ* reactive zones based on the curtain concept. A. One curtain at downgradient edge. B. Two curtains at downgradient edge and at source area. C. Three curtains to remediate the plume faster.
- NO$_3^-$
- NO$_2^-$
- SO$_4^{2-}$
- S$	ext{---}$
- Fe (total and dissolved)
- Mn (total and dissolved)
- carbonate content
- alkalinity
- concentration of dissolved gases (CO$_2$, N$_2$, CH$_4$, etc.)
- microbial population enumeration (total plate count and specific degraders count)
- any other organic or inorganic parameters that have the potential to interfere with the target reactions.

It should be noted that the number of parameters that need to be included in the list of baseline measurements will be site-specific and will be heavily influenced by the target reactions to be implemented within the reactive zone. The above list is a universal list and should be used as a reference.

8.4.2 Reactions and Reagents

Based on the preliminary evaluation of the existing subsurface environment, appropriate reagents have to be selected to optimize the environment as well as to achieve the target reactions. The reactions and reagents and their interaction has been discussed in detail in Section 8.2. Injection of dilute blackstrap molasses solution is an example, where precipitation of metals can be achieved in an anaerobic environment due to the reaction between the heavy metal cations and the sulfide ions.

8.4.3 Injection of Reagents

Design of the reagents injection system requires an extensive evaluation and understanding of the hydrogeologic conditions at the site and specifically within the plume and the location of the reactive zones. This understanding has to include both a macroscopic, site-wide pattern and at microscopic levels between layers of varying geologic sediments. Specific geologic/hydrogeologic parameters required for the design of an in situ reactive zone are presented in Table 8.2.

As noted earlier, delivery, distribution, and proper mixing of the injected reagents is a key element to the success of remediation within an in situ reactive zone. Location and spacing of the injection wells and the placement of screens within each well (cluster) is critical to achieve the above objective.

Injection of reagents can be implemented in two ways: (1) gravity feed, and (2) pressure injection deeper into the well. Gravity feed is feasible only under conditions when the depth of contamination is very shallow (Figure 8.7). Under gravity feed conditions, injected reagents will tend to spread over the water table as a sheet flow, and the mixing within the reactive zone will be dominated by diffusion, rather than advective flow.

When the depth of contamination is deeper, multiple injection points may be required within a well cluster at each injection point (Figure 8.8). The reagent solution will have to be injected under pressure into the injection well. It is preferable to release the reagents at the bottom of each screen. If needed, mixing within each well can be provided by recirculating pumps placed in each well. Under this configuration, mixing within the reactive zone will be influenced by both advective and diffusional transport of the reagents. Concentration of the injected feed solution should be dilute enough to avoid any downward migration due to density differences between the reagent and groundwater.
Table 8.2 Impacts of Various Geologic/Hydrogeologic Parameters on the Design of an *In Situ* Reactive Zone

<table>
<thead>
<tr>
<th>Geologic/hydrogeologic parameter</th>
<th>Design impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth to water table</td>
<td>Injection well depth and screen locations</td>
</tr>
<tr>
<td>Width of contaminant plume</td>
<td>Number of injection wells</td>
</tr>
<tr>
<td>Depth of contaminant plume</td>
<td>Number of injection points within a well cluster</td>
</tr>
<tr>
<td>Groundwater velocity</td>
<td>Pressure injection vs. gravity feed</td>
</tr>
<tr>
<td>Hydraulic conductivity (horizontal and vertical)</td>
<td>Injection flow rate, residence time for the target reactions</td>
</tr>
<tr>
<td>Geologic variations, layering of various soil sediments</td>
<td>Dilution of end products</td>
</tr>
<tr>
<td>Soil porosity and grain size distribution</td>
<td>Mixing zones of reagents, extent of reactive zone</td>
</tr>
<tr>
<td></td>
<td>Number of injection points within a well cluster</td>
</tr>
<tr>
<td></td>
<td>Location of well screens within injection points</td>
</tr>
<tr>
<td></td>
<td>Removal of end products resulting from immobilization reactions (such as heavy metals precipitation)</td>
</tr>
</tbody>
</table>

**Figure 8.7** Gravity feed of reagents when the contamination is shallow.

**Figure 8.8** Multiple cluster injection points when contamination is deep.
During gravity feed of the reagents, the lateral spread of the injected solution will be significant due to the sheet flow effect. However, under pressure injection conditions, downgradient migration of the injected reagents and thus the mixing zone could be very narrow, depending on the hydrogeologic conditions within the reactive zone (Figure 8.9A). One way to overcome this problem is to install closely spaced injection points. This option, even though easier to implement, will significantly increase the cost of the system. Cyclic extraction and injection of adjoining wells, treated as a pair, will create a wider mixing zone downgradient of the injection wells, and thus will eliminate the need to install closely spaced injection points (Figure 8.9B). Extracted groundwater can be used as the dilution water to maintain the feed injection solution concentrations.

8.4.4 Laboratory Bench-Scale Studies

It is always preferable to perform a laboratory study to determine whether the proposed target reactions are achievable. The laboratory study can be used to obtain data on (1) reagent chemistry in the subsurface, (2) intra-aqueous redox kinetics and manipulation, (3) required residence times for the target reactions, (4) required acclimatization period for any microbially induced reactions, (5) need for any system enhancements during scale-up to the field scale, and (6) fate of end products and side effects of the reaction on the aquifer.

The best results from a laboratory study will be obtained when the test is run with samples collected from the proposed location of the reactive zone. Column studies performed with core, soil samples, and groundwater obtained from the site will yield the most reliable results.

8.5 REGULATORY ISSUES

In most cases, implementation of an in situ reactive zone requires injection of appropriate reagents and manipulation of the redox and biogeochemical environment within the reactive
zone. Injection of reagents, albeit innocuous, nonhazardous, and nonobjectionable, may raise some alarms regarding the short-term and long-term effects within the aquifer.

During immobilization reactions—for example, heavy metals precipitation—the contaminant is immobilized within the soil matrix below the water table. As noted earlier, under natural conditions, this immobilization will be irreversible in most cases. Hence, the cleanup objective for the dissolved contaminant will be based upon the groundwater standard (for example, Cr(VI) = 10 \( \mu \text{g/l} \)), and when the contaminant is immobilized in the soil matrix the cleanup standard will be based upon the soil standards (Cr(III) = 100 mg/kg). The huge difference in the two standards for Cr (10 ppb vs. 100 ppm) in the two phases is a significant benefit and provides a major advantage for achieving remediation objectives through an \textit{in situ} reactive zone.

In addition, consider a unit volume of the soil matrix below the water table, which has 1 l of water in its pore spaces (Figure 8.10). Assuming a porosity of 30\% and soil specific gravity of 2.6, the same cube will have about 6.0 kg of soil. If the dissolved Cr(VI) concentration within the cube is 5 mg/l (ppm) the pore water within the cube contains 5 mg of Cr(VI) mass. When all this chromium is immobilized within the soil matrix of the cube, the concentration of the Cr(III) in the soil is equal to 0.83 mg/kg (ppm) (i.e., 5 mg divided by 6.5 kg). It becomes very clear that in addition to the much less stringent standards, the concentration itself is reduced significantly during immobilization within a reactive zone.

\section*{8.6 Future Work}

The \textit{in situ} reactive zone is an innovative and emerging technology in the remediation industry. Furthermore, implementation and wide acceptance of this technology is still in its infancy, and thus the experience and knowledge of this technology is very much empirically based. Substantial amount of developmental work needs to be done on this technology before it becomes widely accepted.

Future work should be focused on

\begin{itemize}
  \item tools to design the appropriate specification of injection rates, durations, and concentrations to achieve optimal control at the field scale
  \item tools to predict/estimate and measure the target reaction kinetics in an \textit{in situ} environment
  \item tools to quantify reagent and pore water chemistry at the field scale
\end{itemize}
• reactive transport modeling tools to couple the microbial and chemical reactions to the physical transport processes
• better methods to measure the intra-aqueous redox and biogeochemical kinetics
• better understanding of the long-term fate of the immobilized contaminants.

8.7 CASE STUDY

8.7.1 Introduction

A field demonstration test was performed to evaluate an innovative groundwater remediation technique involving the \textit{in situ} reduction of chromium at an industrial facility in the midwestern U.S. To date, this evaluation has involved conducting a 6-month \textit{in situ} test near the source area at the site to determine the degree to which hexavalent chromium can be reduced and precipitated out within the aquifer due to the development of biologically induced reducing conditions. The test was developed to evaluate innovative, low-cost \textit{in situ} remediation techniques that could be used to potentially augment or replace the conventional groundwater pump and treat system which they currently operate at the facility. Although the existing pump and treat system provides containment of the chromium plume and a certain degree of chromium mass removal, the system is expensive to operate (hundreds of thousands of dollars annually) and does not provide any means for source reduction and active groundwater remediation. Thus, a low-cost \textit{in situ} remediation technique that would achieve source reduction and active groundwater remediation may provide a high degree of remedial benefits, either in conjunction with the continued operation of the existing pump and treat system or as a stand-alone remediation approach.

The field test required the installation of three injection wells and five monitoring wells. These wells augment the existing monitoring well network at the facility. The three injection wells have been installed within the vacant facility building and the five monitoring wells have been installed along the eastern edge of the facility building (Figure 8.11). The newly installed injection and monitoring wells are shallow monitoring wells screened over the approximate interval of 10 to 15 ft below grade.

To promote the \textit{in situ} biological reduction of hexavalent chromium Cr(VI) to trivalent chromium Cr(III), a dilute black strap molasses solution (which contains readily degradable carbohydrates and sulfur) has been periodically injected (at a batch feed rate of approximately 40 gal every 2 weeks per injection well) into the shallow portion of the impacted aquifer via the three injection wells. The carbohydrates, which consist mostly of sucrose, are readily degraded by the indigenous heterotrophic microorganisms present in the aquifer. This metabolic degradation process utilizes all of the available dissolved oxygen contained in the groundwater. Depletion of the available oxygen present in the groundwater causes reducing conditions to develop. Under the induced reducing conditions, the Cr(VI) is reduced to Cr(III). The actual mechanism of chromium reduction is likely a biotic oxidation–reduction process involving the Cr(VI) serving as a terminal electron acceptor for the catabolized carbohydrates. The primary end product of the Cr(VI) to Cr(III) reduction process is chroomic hydroxide [Cr(OH)$_3$], which readily precipitates out of solution under alkaline to moderately acidic conditions. These precipitates are then retained (i.e., filtered out) by the soil particles within the aquifer.

8.7.2 Injection/Monitoring Well System

As stated previously, a total of three injection wells and five monitoring wells were installed to facilitate implementation and assessment of the biological \textit{in situ} chromium reduction process. The three injection wells were installed within the former production area...
of the facility, while the five monitoring wells were installed just outside of the eastern edge of the existing facility building (Figure 8.11). The monitoring wells are positioned approximately 35 to 40 ft to the east of the injection wells. Each of the injection and monitoring wells were installed using the hollow stem auger method and consist of 4 in. diameter PVC casing and 5 ft long, 4 in. diameter, ten-slot PVC well screens. Each of the injection wells include a 1 in. PVC drop pipe for directing the injection solution to the middle of the screened interval. The installed injection and monitoring wells are shallow wells screened across a 1 to 3 ft thick sand seam at an approximate interval of 10 to 15 ft below grade. Although it is not known with certainty, it is assumed that this sand seam is continuous between the injection wells and the monitoring wells (Figure 8.12).
8.7.3 Solution Feed System

The solution feed system is designed to accurately and efficiently distribute the dilute water/molasses solution (200:1 dilution, by volume) to the three injection wells. The system components consist of a 300-gal polyethylene storage tank, approximately 100 ft of $\frac{1}{4}$ in. reinforced polyvinyl chloride (PVC) tubing with associated fittings to make the desired connections, and several PVC ball valves and stopcocks. The distribution tubing is connected to a hose barb fitting at each of the three injection wellheads. Each wellhead is equipped with a combination well seal/drop tube assembly through which solution is fed to the saturated zone.

Each month approximately 200 to 250 gal of water and 1 to 1.5 gal of molasses are added to the solution storage tank and mixed thoroughly. Biweekly batch feeding of 40 gal of solution to each injection well is performed (i.e., 80 gal per well per month). Each injection well is fed individually through the PVC distribution tubing system, and flow is controlled by manually adjusting the various ball valves and stopcocks.

8.7.4 Monitoring Events

Seven monitoring events were performed since system installation and start-up in December 1994. An initial monitoring event was performed in conjunction with system installation to determine baseline conditions. Subsequent to system start-up one monitoring event was performed each month for the first 6 months of the pilot study.

Monthly monitoring events included a series of measurements in each of the three injection wells and five monitoring wells to determine groundwater elevation, dissolved oxygen (DO) concentration, oxidation–reduction potential (ORP), pH, temperature, and hexavalent chromium [Cr(VI)] concentration. Depth to water measurements were performed to determine groundwater elevation and well water volume in each respective well. A YSI 6000 down-hole probe was used to measure DO, ORP, pH, and temperature in each injection well prior to bailing. Teflon bailers were used to bail three well volumes from each of the injection wells and monitoring wells in turn. Subsequent to the extraction of three well volumes from a respective well, the DO, ORP, pH, temperature, and Cr(VI) concentration were measured and recorded. A Hach Model CH-12 colorimetric test kit was used to determine hexavalent chromium concentrations in each well by mixing a 5 ml groundwater sample with a chromium reagent and comparing the sample to a concentration/color chart. Colorimetric field analysis results have agreed closely with laboratory analytical results. Groundwater samples were collected for laboratory analysis during the baseline monitoring event and then following the third month of system operation. These samples were analyzed for hexavalent chromium, total chromium, sulfate, sulfide, and total organic carbon concentrations.

Prior to initiating the in situ biological reduction pilot study, an initial microbiological enumeration task was performed. This initial assessment task was conducted to confirm that there is an adequate population of indigenous heterotrophic microorganisms present in the groundwater at the site. Groundwater samples were collected from existing monitoring wells and also from the influent to the existing groundwater treatment system. The collected samples were submitted for heterotrophic plate count (HPC) analyses. The results of the HPC analyses confirmed that there is an adequate population of heterotrophic bacteria indigenous to the aquifer and that it is possible to stimulate the microbial activity necessary to induce the required reducing conditions within the aquifer.

As mentioned earlier, monthly monitoring was performed to determine groundwater elevation, DO concentration, ORP, pH, temperature, and Cr(VI) concentration in each injection well. In addition, groundwater samples collected during the baseline monitoring event and then 3 months following process initiation were analyzed for hexavalent chromium, total
chromium, sulfate, sulfide, and total organic carbon concentration. Based on laboratory analysis, the initial Cr(VI) concentrations (baseline) in injection wells IW-1, IW-2, and IW-3 were 16, 1.2, and 0.02 mg/l, respectively. Field determined baseline Cr(VI) concentrations (15, 1, and <0.2 mg/l for IW-1, IW-2, and IW-3, respectively) agreed closely with the laboratory results.

The down-hole ORP data indicated that strong reducing conditions developed in and around the three injection wells within 1 month of process initiation and reached near steady-state conditions with 2 months of process initiation. Baseline ORP levels within the injection wells were within the range of +96 to +147 mV prior to initiating the carbohydrate solution injection process (indicating relatively moderate oxidizing conditions) and have been reduced down to a steady-state level of approximately −150 to −200 mV (indicating strong reducing conditions).

Because of the rapid inducement of reducing conditions, the concentration of hexavalent chromium in the injection wells decreased from a high of 15 mg/l to below 0.2 mg/l during the first month of process operation (Figure 8.13). The levels of hexavalent chromium measured in the injection wells (based both on field and laboratory analyses) remained below 0.2 mg/l through the first 6 months of monitoring. The laboratory analytical results for hexavalent chromium measured in the injection well samples collected 3 months following process initiation were all below the detection level of 0.05 mg/l. In these same samples, the levels of total chromium were slightly higher than the levels of hexavalent chromium but were still below the 0.2 mg/l groundwater cleanup objective for this site. This indicates that what chromium remains in the groundwater is in the trivalent form, rather than in the more toxic and mobile hexavalent form. In addition, it is important to note that the analytical data is based on unfiltered groundwater samples. Because only trace amounts of trivalent chromium have been detected in the unfiltered groundwater samples it is readily apparent that the chromium precipitates are being retained by the aquifer materials and are not subject to colloidal transport through the aquifer.

As expected based on the introduction of relatively high concentrations of carbohydrates and the development of strong reducing conditions, the levels of TOC have increased in the groundwater samples collected from the injection wells and the pH levels within the injection wells have decreased slightly since the start of the pilot study.

Figure 8.13 Graph of Cr(VI), DO, and ORP levels in injection well 1 (IW-1).
REFERENCES


