

HOT-SPOT REMEDIATION USING IN-SITU JETTING TECHNOLOGY

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Abstract

Jetting technology using high-pressure, low to high volume injection of liquids into the subsurface using a small-diameter wand or lance driven into the subsurface has been widely used for several decades. Jetting technology, at its most basic, uses tree root feeder systems to inject liquids into the ground. The Remediation Injection Process (RIP®), an updated and more powerful, versatile and adaptable jetting delivery system has been used to efficiently implement, or augment, a variety of environmental remediation processes including chemical oxidation, bioremediation, pH adjustment and metals stabilization. Key to success for in-situ projects include a detailed bench or laboratory test, pilot-scale project and full scale remediation. These three steps are critical for significant cost savings can be made when appropriate chemical and/or biological information is designed into an in-situ project.

The hand-held RIP™ lances have been designed to use high-pressure liquid pumps to increase flow at the tip of the wand to pressures exceeding 5,000 psi. At these pressures, the lances are driven downward at velocities up to one foot per second. High pressure injection points placed on close spacing, such as 2 foot centers to 5 foot centers, allows for complete in-situ coverage, vertically and laterally. Radius of influence around injection ports has been documented to exceed 10 feet.

Jetting technology is used to remediate limited access areas such as underneath slabs, railways, and buildings, around tanks, pipelines and subsurface utilities; and into hillsides, excavation pits and stockpiles. The flexibility and accuracy of this injection delivery system provides distinct advantages over both conventional in-situ and ex-situ remediation systems. Hot spots can be effectively treated using this technology. As a result, the jetting technology can provide appreciable savings in cost and time over traditional remediation technologies.

Jetting uses chemical oxidizers to rapidly treat soils contaminated with toxic and persistent organic wastes. The two most common oxidizers used for jetting in soil and groundwater remediation are hydrogen peroxide and potassium permanganate to treat petroleum hydrocarbons (such as gasoline, diesel, motor oil, and jet fuel), volatile organic compounds, munitions, certain pesticides and wood preservatives. Aerobic biological degradation and natural attenuation of fuel hydrocarbons and selected other organic compounds have been remediated by jetting using liquid oxidants, nutrients and other amendments. Under the correct subsurface conditions, soluble metals, such as arsenic and chromium, have been stabilized using sulfide compounds, converting the toxic metals into a low solubility sulfide. Alkalinity, pH, and

organic content must be evaluated prior to any in-situ metals stabilization project. Injection ports are grouted with bentonite or neat cement. Case studies will be discussed summarizing the delivery capability in various soil conditions using oxidation and bioremediation technology featuring a variety of contaminants, including gasoline, diesel, tetrachlorethylene (PCE), trichloroethylene (TCE), dichloroethylene (DCE), and toluene.

INTRODUCTION

In-situ environmental remediation is optimized when geologic factors such as lithology, permeability, porosity, contaminant, soil and groundwater chemistry are fully evaluated and included in the design and implementation of a remediation program. Jetting is a remediation technology which uses a variety of liquids injected under high pressure to not only drive the jetting tool, but also to supply the liquids necessary to perform chemical or biological processes in the subsurface. After the liquids are injected and the jetting tool is removed from the subsurface, no pieces or parts are left behind. The injection holes are then sealed with cement grout or bentonite, as needed. Although jetting can be used in ex-situ applications, such as a treating a soil pile, this article is directed at subsurface applications.

The goal of in-situ remediation is to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater by adding liquids to oxidize, bioremediate, neutralize or precipitate contaminants in the subsurface without digging and handling of the soil or water. Jetting is usually a more economical and less disruptive to site activities than the more conventional approaches. The main benefits of in-situ remediation systems over conventional methods are the lower final cost for remediation, minimum cost for operations and maintenance, no moving parts that could break and no discharge permits or waste disposal of liquids for in-situ groundwater treatment.

Although groundwater monitoring wells and gravel-filled trenches or filter galleries have been used to saturate soil and groundwater with liquids designed for remediation, even vertical and lateral distribution of the remediation chemicals have been problematic due to the distances between injection ports. Remediation Injection Process (RIP®), proprietary non-reactive jetting equipment, uses high pressure injection technology placed on close spacing in the field, as close as 2 to 5 foot centers to solve this in-situ delivery challenge. The spacing design of liquid injection ports is directly related to permeability and porosity of the soil.

GEOLOGIC PRINCIPLES

A thorough understanding of subsurface conditions is critical in designing in-situ remediation processes and in determining the preferred flow pathways and subsequent transportation of contaminants in the subsurface. Geologic factors control the movement, distribution and quality of groundwater as well as contaminants through several physical, chemical, and biological processes. Fate and transport of contaminants in soil and aquifers are controlled by the lithology, stratigraphy, and structure of the geologic deposits and formations. (Testa, 1994).

The largest percentage of environmentally contaminated sites lie on alluvial and coastal plains consisting of complex interstratified sediments. A block diagram shows significant vertical and lateral variations in lithology over short distances in a meandering river system (Figure 1). The lithologic contacts, some abrupt and some gradational, significantly influence permeability, porosity and the preferred flow pathways in soil as well as groundwater and contaminants.

The majority of contaminated sites in the world have some component of impacted shallow soil or unconsolidated sediments. Shallow groundwater contamination can result from surface or near-surface activities including unauthorized releases or leaching from landfills, repositories, underground and above-ground storage tanks and pipelines, wells, septic systems, and accidental spills. Contamination can also occur from the application of agricultural chemicals to the land surface, or from nonpoint sources. Deeper soil or rocks may also become impacted due to preferred flow pathways along fault zones, a lack of a competent aquitard to stop migrating contaminants or unintended, but deeper conduits such as abandoned mines or improperly designed or abandoned wells (Testa, 1994).

Comprehensive understanding of the three-dimensional framework of geologic materials is essential to the assessment of groundwater vulnerability to contamination, the lateral and vertical extent or distribution of hazardous and toxic constituents in the subsurface, and design and monitoring of subsurface remedial systems since geology is the prime controlling agent for the movement of groundwater, thus, contaminants.

CONVENTIONAL REMEDIATION TECHNOLOGIES

The conventional remediation methods are summarized in Table 1. One of the most common remediation methods for shallow soil and groundwater contamination is excavation using a backhoe or excavator and relocation of the contaminated soils to a licensed landfill. This method, also called “dig and haul” removes the environmental liabilities from one site and transfers it to another property.

The conventional methods to remediate petroleum hydrocarbons and volatile organic compounds (VOCs) include, but are not limited to, excavation, incineration, bioremediation/natural attenuation and soil vapor extraction (SVE), and pump and treat. More information regarding various technologies are described in a variety of EPA reports (U.S. EPA, 1985, 1988, 1991a, 1991b). Metal contaminated soils have typically been remediated using the method of excavation, transfer and disposal.

IN-SITU REMEDIATION

In-situ remediation programs require detailed understanding of the lithology and hydrogeology of the subsurface. The typical timeline is broken into five main tasks. The first task is the characterization of the subsurface, typically using a direct push technology soil and groundwater sampling rig. During this phase of work, soil and water samples will be collected to evaluate the level of contamination. For remediation using an oxidation technique, chemical parameters such as contaminant concentrations in soil and groundwater, pH, alkalinity, iron content, total organic

compounds (TOC), vertical and horizontal porosity and permeability as well as other parameters would be evaluated. A specific chemical stoichiometry is determined in the laboratory to determine optimum contaminant treatment. If bioremediation is an appropriate remediation option, carbon dioxide levels, microbial counts, dissolved oxygen, and nutrient levels, as well as other parameters would be examined. An in-situ remediation program schedule is summarized in Table 2.

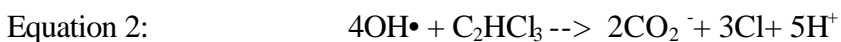
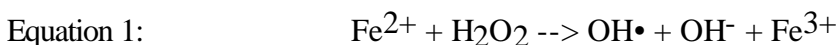
IN-SITU REMEDIATION TECHNOLOGIES

In-situ treatment technologies can be an attractive alternative when on-site activities or structure precludes more conventional remediation methods (Jacobs, 1995, 1996, 1997). The key to the injection of liquids for in-situ remediation of soil and groundwater is getting proper exposure of the treatment chemicals and amendments to the contaminated soil and groundwater, regardless of the delivery method used. Treatment chemicals can be injected for chemical oxidation, enhanced bioremediation, soil flushing, pH adjustment and metals stabilization.

OXIDATION

In-situ chemical oxidizers have the potential for rapidly treating soils contaminated with toxic and persistent organic wastes (Ho, et. al., 1995). In-situ oxidation uses contact chemistry of the oxidizing agent to react with petroleum hydrocarbons, volatile organic compounds, munitions, certain pesticides and wood preservatives. The two most common oxidizers used in soil and groundwater remediation are hydrogen peroxide and potassium permanganate. Table 3 shows how hydrogen peroxide and potassium permanganate relate to other oxidizers. A summary of the advantages and limitations of these two oxidizers is included in Table 4. Other oxidants are available, but are less commonly used due to cost or potential toxic by-products.

Fenton's Chemistry or Fenton's Reagent uses a transition metal catalyst to enhance the oxidation chemical reaction. The metal catalyst is usually provided by iron oxides within the soil or fill, or added separately as a solubilized iron salt, such as iron sulfate. Fenton's chemistry has been well documented for over 100 years and has been in use in water treatment plants for well over 50 years. The chemistry is well documented (Watts, 1991, 1992 and 1994) to destroy petroleum hydrocarbons and other volatile organic compounds. Hydrogen peroxide arrives in the field as a liquid store in poly drums. When chemical oxidant hydrogen peroxide (H_2O_2) is injected into the subsurface, it decomposes readily into reactive hydroxyl radicals ($OH\bullet$) and water. The hydroxyl radical ($OH\bullet$) in the subsurface can be used to rapidly mineralize hydrocarbon, solvent and other contaminants to water and carbon dioxide. This reaction is enhanced in the presence of iron. Iron is naturally occurring in soil and groundwater or can be added during the injection process, if needed. The reaction is based on the principle of Fenton's Chemistry where the iron and hydrogen peroxide react to form hydroxyl radicals and other by-products as shown in Equation 1 (Glaze, et. al., 1987). The oxidation reaction of trichloroethene (TCE) is shown in Equation 2 (Pignatello, 1992):

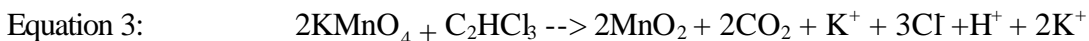


Any H_2O_2 not used in the oxidation process breaks-down to water and oxygen in a matter of hours. In addition to the reaction described in Equation 2, there are also a large number of competing reactions including the free radical scavengers, most importantly, carbonate and bicarbonate alkalinity, that will greatly affect the overall reaction scheme (Vella and Veronda, 199X). In addition, H_2O_2 can serve as an oxygen source for microbes in the subsurface to enhance biodegradation of contaminants.

Although handling hydrogen peroxide and other oxidants requires significant safety training and planning, the oxidant is effective at remediation and relatively inexpensive. The reaction time for hydrogen peroxide in the subsurface is usually within hours. Rise in temperatures in the subsurface illustrate the exothermic nature of the oxidation process. Increases in temperature beyond 140°F consumes the peroxide. Subsurface chemistry is important to evaluate for oxidation is optimal in lower pH settings, with lower alkalinity readings. In some cases, acids may be used to lower pH. The end products of oxidation are carbon dioxide, carbon monoxide and water. Trace chlorine from chlorinated compounds will likely combine with sodium or calcium ions to form salts or with hydrogen to form weak acids. Careful evaluation of the chemistry of the soil and water are required prior to the start of any injection process.

POTASSIUM PERMANGANATE

Although a much weaker oxidizer than hydrogen peroxide, potassium permanganate lasts longer in the environment and can react in an environment with much higher pH than hydrogen peroxide. 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 and at 30°C , the solution has slightly over an 8% concentration of KMnO_4 . The pH range is critical in being able to determine whether the oxidation reaction will be fast or slow. The chemical formula for chemical oxidation of TCE using potassium permanganate is shown below in Equation 3 (Nickelsen, et. al., 1992):



For example, remobilization of soluble metals such the creation of highly toxic Cr^{+6} from Cr^{+3} can be initiated by the injection of potassium permanganate into the subsurface under specific conditions. Chemical compatibility of the injection equipment components and safety procedures become critical with the injection of strong acids, bases, oxidants and other chemicals.

BIOREMEDIATION

Aerobic biological degradation and natural attenuation of fuel hydrocarbons and selected other organic compounds have been well documented (Rice, et. al., 1995, Mace, et. al., 1997). Supplying the appropriate amount of oxygen, nutrients and other amendments to the subsurface can enhance the biodegradation process, can significantly increase remediation effectiveness and decrease treatment time.

METALS STABILIZATION

Under the correct subsurface conditions, soluble metals, such as arsenic and chromium, can be stabilized using sulfide compounds, converting the toxic metals into a low solubility sulfide. Alkalinity, pH, and organic content must be evaluated prior to any in-situ metals stabilization project.

IN-SITU SOIL FLUSHING

Surfactants and other fluids, such as enzymes and water can be used to help disperse and transport previously immobile contaminants, such as heavy oils, providing that the remobilized chemicals are under active hydraulic control, from a trench or pumping well. The injected fluids can be used to increase saturation, provide pH adjustments and neutralization. This technique is not used much due to the potential for enhanced mobility of the contaminant and the possibility of escape.

JETTING TECHNOLOGY

The technology for high pressure, low to high volume injection of nutrients into the subsurface using a small-diameter wand or lance driven into the ground has been widely used for several decades. The jetting technology, at its most basic, uses tree root feeder systems to inject nutrients and other chemicals into the subsurface by means of a high pressure injector tip on the end of a small-diameter, 2 to 5 foot long steel wand.

The Remediation Injection Process (RIP®), a more powerful, versatile and adaptable jetting system has been used to efficiently implement, or augment, a variety of remediation processes including chemical oxidation, bioremediation, pH adjustment and metals stabilization. The RIP® also uses a hand held lance approach. The RIP™ lances have been designed to use high-pressure liquid pumps to increase flow at the tip of the wand to pressures exceeding 5,000 psi. At these pressures, the lances are driven downward at velocities up to one foot per second. High pressure injection points placed on close spacing, such as 2 foot centers to 5 foot centers, allows for complete in-situ coverage, vertically and laterally. The high pressures allow for the treatment liquids to be dispersed into the soil matrix, as well as into the groundwater.

After the reaction occurs, additional treatment events may be required to reduce contaminants to regulatory approved levels. Remedial chemicals can be accurately injected into the impacted areas to obtain direct contact with the target constituents. This precise injection of the treatment

solutions/slurries can expedite the remediation process to achieve substantial reductions in contaminant concentrations in a relatively short period of time. Two 1999 RIP® projects performed for a consultant indicated a radius of influence around injection ports exceeding 10 feet.

The hand-held RIP® injector wands can be used to remediate limited access areas such as underneath slabs, railways, and buildings, around tanks, pipelines and subsurface utilities; and into hillsides, excavation pits and stockpiles. Jetting technology has the capability to remediate a variety of constituents both in-situ or ex-situ including petroleum hydrocarbons, BTEX, chlorinated solvents, soluble inorganics, phenols, PCBs, PAHs, and other organic and inorganic contaminants. The flexibility and accuracy of this injection delivery system provides distinct advantages over both conventional in-situ and ex-situ remediation systems. As a result, the jetting technology can provide appreciable savings in cost and time over traditional remediation technologies.

RIP® CASE STUDIES

CASE STUDY # 1 - Based on previous site investigations, the soil and groundwater beneath a petroleum storage facility in northern California was found to be impacted with, free product consisting of TPH as diesel (TPH-d) and gasoline (TPH-g) range hydrocarbons. As part of a proposed pilot study, four soil borings were initially drilled using a direct push probe sampling rig. Soil samples were collected at 7 and 11 feet below ground surface (bgs) to provide pre-treatment data for the pilot scale test.

Groundwater samples were also collected as groundwater was encountered at about 7 feet bgs. The initial investigation detected free product, with concentrations of TPH-d as high as 6,500,000 micrograms per liter ($\mu\text{g/L}$) and TPH-g as high as 770,000 $\mu\text{g/L}$. The impacted soil extended to a maximum depth of approximately 15 feet bgs and generally consisted of fine sand, silts and clays.

Remediation Approach - The pilot study was designed to treat approximately 133 cubic yards or a 12-foot by 20-foot area. A grid pattern was established with 77 lance injection points spaced on 2 foot centers. After coring through the concrete and preparing the pilot study area, 495 gallons of 18% hydrogen peroxide were injected over 4.25 hours. The injection pressure at the lance tip ranged from 1,500 psi to 3,000 psi during the injection process.

Results - Significant reductions of diesel range hydrocarbons were found to occur in the groundwater. TPH-d was reduced in the groundwater from a maximum concentration of 6,500,000 $\mu\text{g/L}$ prior to the injection treatment down to a maximum detected concentration of 4,700 $\mu\text{g/L}$ following the oxidation process. No free product was detected after treatment. With only 4.25 hours of treatment, the overall average diesel concentration in the groundwater was reduced by greater than 99% and gasoline by greater than 50%.

CASE STUDY #2 - A manufacturing facility in Tumwater, Washington had soil contaminated with volatile organic compounds, including perchloroethylene (PCE), trichloroethylene (TCE), dichloroethylene (DCE) and toluene. The contaminants were reduced in the soil using high concentrations of hydrogen peroxide. The TCE, DCE and toluene were destroyed after one treatment event. Approximately 70 percent of the PCE in the soil was destroyed after two treatment events, enough to allow for site closure. The actual remediation cost was about eight percent of the alternative which was a dig and haul project with shoring, estimated to cost about \$500,000. Regulatory objectives were met and site closure, property transfer and redevelopment were accomplished.

Figures 1 and 2 (Photos and cross section, map view of injections)

Figure 3 and 4 (Results)

Case example - Based on previous site investigations, the soil and groundwater beneath a petroleum storage facility in northern California was found to be impacted with, free product consisting of TPH as diesel (TPH-d) and gasoline (TPH-g) range hydrocarbons. As part of a proposed pilot study, four soil borings were initially drilled using a direct push probe sampling rig. Soil samples were collected at 7 and 11 feet below ground surface (bgs) to provide pre-treatment data for the pilot scale test.

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Discussion - The concentrations of the lighter-end hydrocarbons such as TPH-g did not exhibit the same reductions and chromatograms from the laboratory analysis of pre- and post-treatment samples were distinctly different. Based on the chemistry of oxidation processes, longer chain aliphatics (C-12 to C-24) such as diesel tend to oxidize before lighter-end hydrocarbons, such

as gasoline. Therefore, upon injecting a strong oxidizing agent, such as hydrogen peroxide, into the subsurface where the soil is impacted with petroleum hydrocarbons, larger decreases to existing total organic carbon (TOC) and any oil or diesel range organics should initially be exhibited as these constituents are preferentially oxidized.

During the oxidation process, shorter-chain hydrocarbons are produced from the oxidation of the long-chain hydrocarbons, such as diesel. Some of these may appear as gasoline-range compounds and could explain the difference in chromatograms before and after treatment. It is also likely that various straight-chain acids, such as acetic acid, would be created during the chemical oxidation process; however, these mild acids are not a threat to groundwater. Both the gasoline range compounds and mild acids would ultimately break down to carbon dioxide and water with further exposure to hydrogen peroxide.

The significant reduction of diesel concentrations in the groundwater indicate the heavier-end diesel chains are being broken apart during the injection of the hydrogen peroxide. The likely by-products of the oxidation of diesel are gasoline-range petroleum hydrocarbons and straight-chain acids. With continued exposure to hydrogen peroxide, the diesel will be preferentially destroyed and the gasoline will start to be consumed at a faster rate.

For another case outside of Olympia, Washington, a manufacturing facility had soil contaminated with volatile organic compounds, including perchloroethylene (PCE), trichloroethylene (TCE), dichloroethylene (DCE) and toluene. The contaminants were reduced in the soil using high concentrations of hydrogen peroxide. The TCE, DCE and toluene were destroyed after one treatment event. Approximately 70 percent of the PCE in the soil was destroyed after two treatment events, enough to allow for site closure. The actual remediation cost was about eight percent of the alternative which was a dig and haul project with shoring, estimated to cost about \$500,000. Regulatory objectives were met and site closure, property transfer and redevelopment was accomplished.

CONCLUSIONS

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NOTES:

About the authors:

James A. Jacobs is a certified Hydrogeologist and has over 20 years of experience. He specializes in soil sampling methods and in-situ remediation systems.

Andrew Lehane is a professional engineer with over 11 years of experience in remediation design, site characterization, corrective actions, and environmental compliance.

Dan Ruslen is a project manager with over 6 years of experience in PCB sampling, remediation design, and in-situ oxidation projects.

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TABLE 1 – SUMMARY OF REMEDIATION METHODS

| CONVENTIONAL METHODS | TYPE | ADVANTAGES | DISADVANTAGES |
|---|---------|--|--|
| Excavation, Transfer and Disposal to landfill | Ex-situ | Effective at removal of shallow contaminants | Expensive, disruptive, relocates problem to another site (landfill) |
| Excavation and Incineration, Soil Washing | Ex-situ | Effective at removal of shallow contaminants | Expensive, disruptive |
| Bioremediation/Natural Attenuation | In-situ | Works well when conditions are right | Costly in monitoring and time consuming |
| Soil Vapor Extraction | In-situ | Works well when conditions are right | Costly in maintenance and time consuming |
| Pump and Treat | In-situ | Works well for free product removal and providing hydraulic control. | Generally ineffective at remediation, costly in maintenance and time consuming |
| | | | |
| UNCONVENTIONAL METHOD | | | |
| Remediation Injection Process (RIP™) | In-situ | Less costly than other methods and less time consuming, minimal disruption | Site specific design required related to site soil/water chemistry. |

Table 2 – An example schedule for an in-situ remediation program

| # | TASK | OBJECTIVE | W * |
|---|--|---|--------|
| 1 | Subsurface Investigation | Characterize lithology, hydrogeology, contaminant fate and transport | 2 |
| 2 | Bench-Scale Test | Under laboratory conditions, evaluate contaminated soil and groundwater to determine whether treatment will work. Design optimum specifications for contaminant destruction | 1 |
| 3 | Pilot-Scale Study | Perform a pilot study in the field to evaluate the treatment and contaminant destruction. | 3 |
| 4 | Full-Scale Remediation | Based on successful treatment procedures developed in the lab and during the pilot study, design distribution of treatment chemicals for full-scale remediation. | 6 |
| 5 | Confirmation Sampling and Site Closure | Collect adequate number of soil and groundwater samples to confirm successful remediation. Site closure by regulatory agency. | 2 |
| | Notes: * Example of timing in weeks (W) | | |

TABLE 3 – Comparative Oxidative Potentials

| Species | Volts |
|------------------------|-------|
| Fluorine | 3.0 |
| Hydroxyl Radical | 2.8 |
| Ozone | 2.1 |
| Hydrogen Peroxide | 1.8 |
| Potassium Permanganate | 1.7 |
| Hydrochlorous Acid | 1.5 |
| Chlorine Dioxide | 1.5 |
| Chlorine | 1.4 |
| Oxygen | 1.2 |

TABLE 4 – Summary of advantages and limitations of two common oxidizers.

| HYDROGEN PEROXIDE | H ₂ O ₂ | | POTASSIUM PERMANGANATE | KMnO ₄ |
|---|--|--|--|--|
| ADVANTAGES | LIMITATIONS | | ADVANTAGES | LIMITATIONS |
| Widely available | Special handling and safety precautions | | Stable and safe to handle | Purple staining |
| Inexpensive | Low pH (2-4) optimal; requires acidic environments with low alkalinity | | Reactive under neutral pH (7) | More expensive and less powerful oxidizer than hydrogen peroxide |
| Non-toxic by-products (CO ₂ , H ₂ O) | Non-selective oxidizer | | Non-toxic by-products (CO ₂ , H ₂ O) | Increased MnO ₂ can decrease permeability |
| Produces one of the most powerful oxidizers available (Hydroxyl radicals) | Short reaction period (minutes to hours) | | Long reaction time (hours to days) compared with hydrogen peroxide | Hexavalent chromium can be produced under specific conditions |