Remediation of Contaminated Groundwater Using *In Situ* Chemical Oxidation

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INTRODUCTION

There are numerous chemicals associated with federal, commercial, industrial, and agricultural operations that are considered hazardous to humans, animals, plants, and the ecological environment. Groundwater becomes contaminated when hazardous chemicals leak into the ground and drain through the soil matrix into aquifers (see Exhibit 1). Once they reach the aquifer, chemicals either float or sink depending on their specific gravity (i.e., whether they are lighter or heavier than water). Gradually, the chemicals dissolve into groundwater and flow downgradient to impact additional aquifers, water reservoirs, land, and sea, expanding the risk to human health and the environment.

The location of initial impact to the environment is referred to as the "source area" (location of leaking drums in Exhibit 1). Free-phase contaminants at the source area, if not treated, continue to act as a source for dissolved-phase contamination for time periods ranging from a few years to potentially hundreds of years (depending on the chemical-specific properties).

Exhibit 1. Groundwater Contamination Process

The field of "Remediation" was developed to address the growing and ongoing problem of subsurface contamination of land and water by hazardous chemicals. An interdisciplinary approach is employed during the remedial process involving various branches of science, such as geology and hydrology, chemistry, and sound engineering methods. The remedial process typically involves:

- Site investigations to characterize the site geology and hydrology, geochemical conditions, and nature and extent of contamination.
- Laboratory testing to identify potential applicable remedial methods.
- Pilot-scale testing onsite to verify effectiveness of chosen remedial methods and identify optimal conditions for full-scale implementation.
- Full-scale remediation.

Remediation methods can generally be divided into *ex situ* (i.e., contamination is extracted and treated aboveground) and *in situ* (i.e., treatment in place, below ground) methods with the latter having evolved and developed extensively over the past decade to provide more effective and efficient solutions. One of the most well developed and widely used *in situ* remediation technologies for soil and groundwater contaminated with organic compounds is *in situ* chemical oxidation (ISCO).

IN SITU CHEMICAL OXIDATION

TECHNOLOGY DESCRIPTION

ISCO involves the delivery of chemical oxidants directly to the subsurface contamination source zones and downgradient groundwater contamination plumes. This is commonly achieved by either temporary injection points or permanent injection wells (see Exhibit 2). Upon direct contact with organic contaminants, a chemical oxidation reaction occurs, which mineralizes the contaminant compound and produces non-toxic end products such as carbon dioxide (CO_2), water, and in the case of chlorinated solvents (e.g., trichloroethene), inorganic chloride salts (Interstate Technology Regulatory Council [ITRC] 2005). The contaminants susceptible to chemical oxidation include total petroleum hydrocarbons (TPH)

Exhibit 2. Typical ISCO Injection

(i.e., fuels), polycyclic aromatic hydrocarbons (PAHs), oxygenates (e.g., MTBE), chlorinated solvents, phenols, and pesticides. The advantages and disadvantages of ISCO are presented in Exhibit 3:

Advantages	Disadvantages
▪ Relatively short remediation periods.	▪ Effectiveness dependant upon ability to disperse oxidant in aquifer.
▪ Non-toxic byproducts.	▪ Health and safety risk to workers handling oxidants.
▪ Minimized waste generation.	▪ Temporary mobilization of metals.
▪ Minimized site disturbance.	▪ Potential secondary drinking water impact (taste, odor).
▪ Cost effective for source areas and high-concentration plumes.	▪ Cost ineffective for low-concentration plumes.

Exhibit 3. Advantages and Disadvantages of ISCO

CHEMICAL OXIDANTS

Various chemical oxidants are commercially available. These oxidants have been tested under laboratory and field conditions, and have been the subject of numerous published studies and reports. The four major oxidants used for soil and groundwater remediation are: permanganate, persulfate, peroxide, and ozone. These oxidants differ in their oxidative strength; the stronger the oxidant, the more recalcitrant contaminants it can oxidize and the faster the reaction kinetics. However, this also translates to a shorter residence time in the subsurface and a limited area of treatment. Additional differences between the oxidants include the required oxidant dosage (mass and volume); location, number, and type of required injection points; logistics involved in mixing and delivering the oxidants to the subsurface; and health and safety considerations.

CASE STUDY

BACKGROUND

A pilot study was conducted at a site in Southern California, where underground storage tanks holding fuels and waste oils leaked to the subsurface in the 1970s. An interim remedial action using dual-phase extraction was implemented at the site from 1997 to 2007 and has mitigated the concentrations of organic contaminants in the site soils to levels where the future risk to human health and the environment is within acceptable limits. Large reductions were also achieved in the extent of free-product and dissolved-phase contamination at the site. The main contaminants of concern (COCs) present in groundwater prior to the study were residual free-product, TPH, BTEX (benzene, toluene, ethylbenzene, and xylenes), and cis-1,2-dichloroethene (DCE).

The purpose of the study was to evaluate the efficacy of ISCO using Klozur© persulfate for treating groundwater contaminated with free- and dissolved-phase petroleum hydrocarbons and chlorinated solvents. Klozur© persulfate is patented remediation-grade sodium persulfate, manufactured by FMC Corporation (USA).

Klozur© persulfate was chosen due to its reactivity with a wide range of organic contaminants including the COCs. The geology at the study site is alluvium, mainly clayey sands. Groundwater occurs at approximately 15 meters below ground surface.

The study was performed in two phases. During each phase, batches of persulfate were hydrated, mixed, and injected into the injection well (IW01). During Phase II of the study, air was continuously injected below the contaminated zone (i.e., air sparging) for the purpose of enhancing the distribution of persulfate in groundwater. Exhibit 4 shows the process flow diagram for the Phase II injection. A total of 3,800 kilograms of sodium persulfate were hydrated with 26,000 liters of water and injected into groundwater via the injection well.

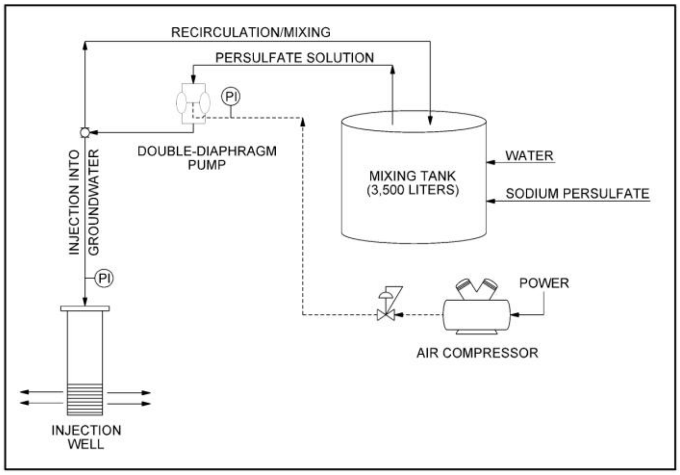


Exhibit 4. Injection System Process Flow Diagram

RESULTS

The performance and effectiveness of ISCO were measured by groundwater monitoring and sampling at the injection well (IW01) and three monitoring wells (MW01, MW02, and MW03), located 6 to 13 meters from the injection well (see Exhibit 5). Groundwater samples were analyzed for TPH and volatile organic compounds (VOCs). Exhibits 6, 7, and 8 show the concentrations of TPH, total BTEX, and cis-1,2- DCE, respectively.

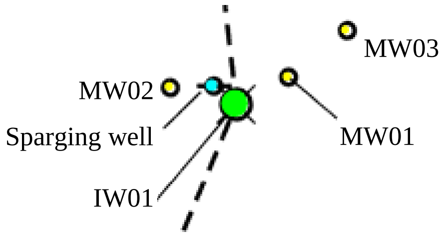
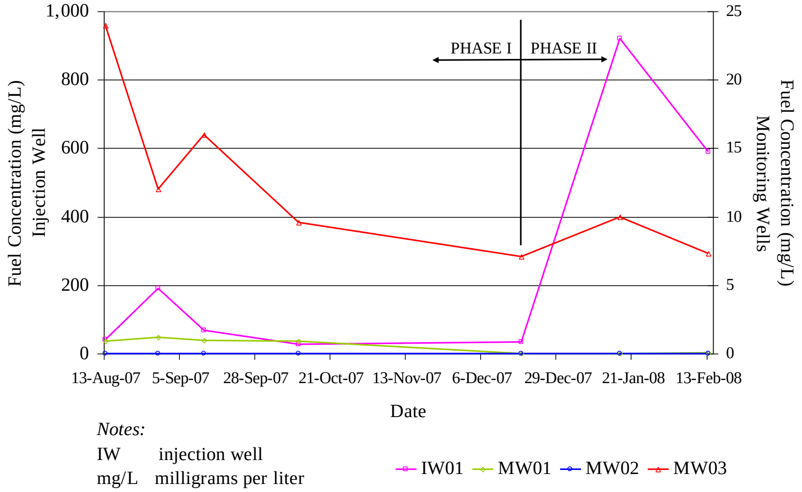


Exhibit 5. Pilot Study Layout

Total Petroleum Hydrocarbons

At the injection well, concentrations of TPH initially increased following the Phase I and Phase II injections and then decreased, indicating the dissolution of free-product into the dissolved phase followed by a reduction (oxidation) in dissolved-phase concentrations. This trend was significantly greater in Phase II, as compared to Phase I (see Exhibit 6) indicating that the addition of air sparging during Phase II enhanced the dissolution of free-product and subsequent oxidation of dissolved-phase contaminants.

At the monitoring wells, concentrations of TPH decreased in Phase I; however, other contaminants (benzene, trimethylbenzene, and cis-1,2-DCE) exhibited no meaningful changes and therefore these results do not conclusively indicate reduction in contaminant concentrations by persulfate oxidation.



Notes:

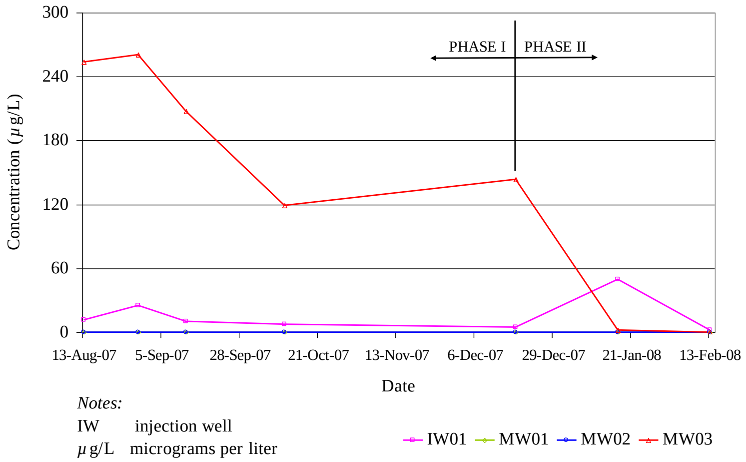
IW	injection well
mg/L	milligrams per liter
MW	monitoring well

Exhibit 6. TPH Concentrations Versus Time

Volatile Organic Compounds

At the injection well, total BTEX concentrations decreased during Phase I and Phase II. However, the decrease in Phase II was more significant (see Exhibit 7) and benzene concentrations, which were essentially unchanged in Phase I, were reduced to non-detect in Phase II. A similar trend was observed for cis-1,2-DCE (see Exhibit 8).

At the monitoring wells, BTEX and cis-1,2-DCE were only detected in Well MW03, the furthest well from the injection well. While BTEX concentrations decreased in this well in Phase I, other contaminants (benzene, trimethylbenzenes, and cis-1,2-DCE) exhibited no meaningful changes. During Phase II, concentrations of total BTEX, cis-1,2-DCE, and other VOCs decreased to non-detect. These results indicate that persulfate oxidation was conclusively occurring at Well MW03 during Phase II and therefore air sparging enhanced the radius of remediation by oxidation to greater than 13 meters.



Notes:

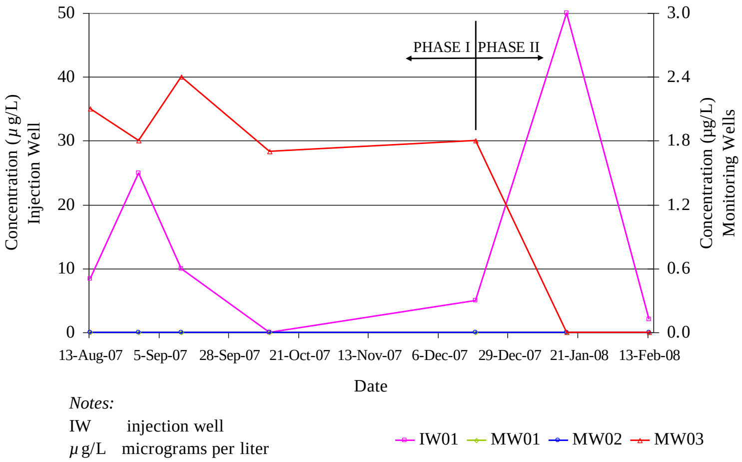
IW	injection well
μg/L	micrograms per liter
MW	monitoring well

Exhibit 7. Total BTEX Concentrations Versus Time

CONCLUSIONS

Results of Phase I of the persulfate pilot study demonstrated that a) persulfate was effective in promoting free-product dissolution and degradation at the injection well, b) persulfate oxidation was effective in degrading VOCs, and c) the radius of persulfate distribution was less than 6 meters.

Results of Phase II of the pilot study demonstrated that the addition of air sparging was effective in enhancing: a) the dissolution of free-product at the injection well and b) the radius of persulfate distribution from less than 6 meters to greater than 13 meters.



Notes:

IW injection well

μg/L micrograms per liter

MW monitoring well

Exhibit 8. Cis-1,2-DCE Concentrations Versus Time

REFERENCES

Interstate Technology & Regulatory Council. 2005. *Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater*, 2nd ed. ISCO-2. Washington D.C.: ITRC ISCO Team. Web link: http://www.itrcweb.org/gd_ISCO.asp.