Geo-Cleanse International, Inc.

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ISCO TECHNOLOGY REVIEW

Destruction of DNAPL during Pilot Leads to Full-Scale ISCO Program

A pilot-scale in-situ chemical oxidation program was performed at a confidential site in Northern Florida that was designed to address petroleum contamination,

TYPICAL SET-UP FOR PROCESS MONITORING

primarily benzene, ethylbenzene, toluene, and xylene (BTEX) and polycyclic aromatic hydrocarbons (PAHs). A PAH coal tar DNAPL phase was also present at the site. The primary goal of the pilot was to determine if the Geo-Cleanse® Process utilizing modified Fenton's reagent would be an effective remediation technology on the contaminants of concern at this site. Other goals of the pilot included refining geochemical and engineering design assumptions for a possible full-scale application.

The site is underlain to depths of greater than 28 feet below land surface (ft-bls) by a generalized, three-layered system. The first layer is located from land surface to approximately 12 ft-bls and consists of screened overburden material (SOM). The SOM is underlain by a layer of clean sand fill material with some fines to approximately 26 ft-bls. Both the SOM and sand fill material were backfilled after excavation of impacted vadose zone soil. The backfill material is underlain by a thick, continuous, native clay layer that is believed to serve as a basal confining unit for the source area.

The pilot test area was approximately 50-ft x 50-ft and included nine injection wells. The injection wells were installed in the treatment area in a grid-like pattern, spaced approximately 15 ft apart, and were installed to the depth of the confining clay layer. Approximately 18,260 gallons of 11.5% hydrogen peroxide and proprietary catalyst solution were injected across the pilot area over a 13-day period.

The soil data are most representative of the overall mass destruction as a result of the pilot due to the presence of DNAPL. The soil-sorbed fraction is estimated to represent over 99% of the total contaminant mass in the treatment area. Three of the nine injection locations were sampled by direct-push methods for baseline and post-treatment soil analysis. The samples were analyzed for BTEX, methyl tert butyl ether (MTBE), PAHs, and Florida Petroleum Range Organics (FL-PRO), which consists of organic compounds in the alkane C8-C40 range. The soil analytical data indicate that between 91% to a nominal 100% of the soil-sorbed contaminant mass was destroyed. The baseline and post-treatment soil analytical and percent reduction data are summarized in **Table 1**.

Application of the Geo-Cleanse® Process utilizing modified Fenton's reagent was proven highly effective on the contaminants of concern at this site as evident from the contaminant mass reductions achieved during the injection program. A full-scale treatment program is anticipated in 2008.

TABLE I: SOIL TREATMENT RESULTS

	Cumulative Contaminant Concentrations		
Sample Location	Baseline (mg/Kg)	Post Treatment (mg/Kg)	Reduction
IW-9	38,052	98	**99.7%**
IW-7	150,476	13,375	**91.1%**
IW-1	74,500	79	**99.9%**
Site-Wide Avg.	87,676	4,517	**94.9%**

TOP VIEW OF GROUNDWATER SAMPLES. VISUAL COMPARISON OF PRE- & POST-TREATMENT SAMPLES.

Impact of Persulfate Chemical Oxidation on Anaerobic Bioremediation

A common misconception in the remediation industry is that in-situ chemical oxidation (ISCO) essentially sterilizes the subsurface and eliminates microbial activity for a long period of time following an ISCO treatment. A second misconception is that the aquifer is so strongly oxidized following an ISCO treatment that re-establishing an anaerobic groundwater condition favorable to reductive dechlorination of chlorinated solvents is very difficult to achieve. Both misconceptions have been dispelled with numerous detailed studies, which have demonstrated conclusively that once the oxidants are consumed the impacted zone can return to anaerobic conditions and is rapidly repopulated by a diverse microbial fauna. As a result, stimulated bioremediation is commonly employed as a final plume management strategy following source reduction with ISCO. As leaders in the ISCO industry, GCI is often asked about the pros and cons of the various oxidants when utilized with this strategy. Each oxidant and catalyst system has different influences on the geochemical condition of the aquifer after treatment, which can impact microbial repopulation and the success of subsequent plume management strategies. This article focuses on the potential impact of persulfate ISCO on anaerobic bioremediation.

GCI'S PATENTED INJECTION DELIVERY STATION

Persulfate ISCO is commonly catalyzed to produce a persulfate radical as the active oxidant. Although several catalysis systems are available, two of the most commonly used catalysts are alkaline and transition metal systems. Alkaline systems typically utilize sodium hydroxide (NaOH) to temporarily establish a pH greater than 10.5, and must maintain that pH during the treatment period. Transition metal systems commonly utilize chelated iron (Fe-EDTA) to catalyze the persulfate. In either case, the catalyst reacts with the persulfate to generate a persulfate radical and sulfate anion:

$$S_2O_8^{-2} + \text{catalyst} \rightarrow SO_4^{\bullet -} + SO_4^{-2} \quad (1)$$

The persulfate radical or other derived species then oxidize organic compounds and release additional soluble sulfate to groundwater. For example, oxidation of one mole of trichloroethylene (HC_2Cl_3) requires six moles of persulfate radicals and releases six moles of sulfate:

$$HC_2Cl_3 + 6SO_4^{\bullet -} + 4H_2O \rightarrow 2CO_2 + 3Cl^- + 9H^+ + 6SO_4^{-2} \quad (2)$$

With respect to anaerobic bioremediation, the key concerns with persulfate ISCO are the pH shift (if alkaline catalysis is used), iron loading (if Fe-EDTA is used), and sulfate loading. Most aquifers have a naturally high buffering capacity, and thus groundwater pH shifts are typically relatively transient. Thus as long as a modest amount of pH amendment is applied, pH generally returns to circumneutral within a few weeks or months of the injection. However, the iron and sulfate may pose a more severe impact.

Approximately 80.7 lbs of sulfate are released to groundwater for every 100 lbs of sodium persulfate applied. If Fe-EDTA is utilized to catalyze the persulfate, a typical recommendation is to use sufficient Fe-EDTA to establish a minimum groundwater iron concentration of 150 mg/L. Approximately 13.3 lbs of Fe^{+3} are generated per 100 lbs of Fe-EDTA. For an example, a comparative case study considered using 48,137 lbs of sodium persulfate catalyzed with 9,873 lbs of Fe-EDTA in a 200 ft x 200 ft x 10 ft thick treatment area[1]. Approximately 38,800 lbs of sulfate and 1,300 lbs of Fe^{+3} may be released to groundwater by this application. Assuming a porosity of 30% and no advection out of the treatment area, the resulting concentrations to groundwater are up to approximately 5,200 mg/L sulfate and 175 mg/L iron.

The released iron and sulfate have a very negative impact on reductive dechlorination after the persulfate treatment, because iron- and sulfate-reducing bacteria more rapidly consume hydrogen than bacteria that reduce chlorinated solvents. The primary, bacteria-driven redox reactions in groundwater are:

Oxygen reduction:

$$O_2 + 2H_2 \rightarrow 2H_2O \quad (3)$$

Nitrate reduction:

$$2NO_3^- + 5H_2 + 2H^+ \rightarrow N_2 + 6H_2O \quad (4)$$

Iron reduction:

$$2Fe^{+3} + H_2 \rightarrow 2Fe^{+2} + 2H^+ \quad (5)$$

Sulfate reduction:

$$2SO_4^{-2} + 8H_2 + 3H^+ \rightarrow H_2S + HS^- + 8H_2O \quad (6)$$

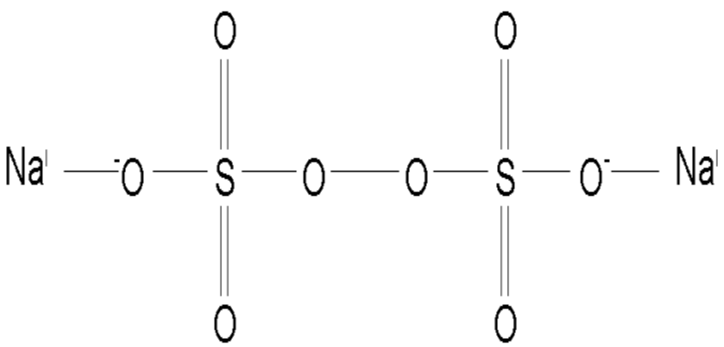
Methanogenesis:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (7)$$

Bacteria that reduce chlorinated solvents favor sulfate-reducing to methanogenic conditions, which can only be achieved after bioavailable oxygen, nitrate, iron and most of the sulfate have been reduced. The iron and sulfate introduced by the persulfate ISCO inhibit reductive dechlorination, therefore, by delaying or preventing establishment of strongly reducing conditions and resulting in poor bioremediation performance. Recognizing this issue, the USEPA has recommended that sulfate concentrations less than 20 mg/L are most favorable for reductive dechlorination[2] and the Air Force Center for Environmental Excellence recommends sulfate concentrations within the range of 20-50 mg/L or less[3]. The sulfate released by this example case study results in groundwater concentrations more than 100 times higher than these recommended ranges.

Carbon substrates are commonly utilized to generate strongly reducing conditions and to produce hydrogen for reductive dechlorination. Most ven-

Persulfate—continued from page 2.



Molecular structure of sodium persulfate

dors of such substrates utilize iron and sulfate concentrations (among other factors) to determine the volume of substrate that must be applied. Higher concentrations of Fe^{+3} and sulfate demand higher substrate dosage. For example, 270,000 to 350,000 lbs of *additional* CAP18® or HRC® would be required to overcome the additional demand from the iron and sulfate introduced by the persulfate ISCO in the case study above. This is over 10 times the baseline requirement without elevated sulfate or iron.

Establishment of strongly reducing conditions and successful implementation of stimulated anaerobic biodegradation have been demonstrated following catalyzed hydrogen peroxide ISCO with the Geo-Cleanse® Process. Although iron and sulfate are also commonly used in the Geo-Cleanse® Process, the mass utilized is far less than for persulfate. Alternative catalyst components can be utilized to reduce or eliminate sulfate altogether, and native iron liberated by the mildly acidic pH condition (typical pH range of 4-6) generated for the Geo-Cleanse® Process reduces the need for iron amendments. The pH shift is rapidly attenuated by the buffering capacity in most aquifer systems, and the oxidant lifetime is short (typically days). Therefore, the Geo-Cleanse® Process offers a more effective option when anaerobic bioremediation is an essential component of plume management following an ISCO treatment.

[1]P. Block and W. Cutler, *Klozur™ activated persulfate for site remediation: Comparative evaluation of treatment efficacy and implementation costs*, http://envsolutions.fmc.com/Klozur8482/ResourceCenter/tabid/356/Default.aspx.

[2]*Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water*, 1998, EPA/600/R-98/128.

[3]*Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents*, 2004.

Geo-Cleanse Completes Pilot Test at Belgian Industrial Site

Geo-Cleanse International, Inc. in collaboration with European Remediation Technologies (ERT) performed an in-situ chemical oxidation pilot test at an industrial site in Wervik, Belgium. The chemical oxidation methodology chosen was the Geo-Cleanse® Process, utilizing Fenton's reagent. The soil and groundwater at the industrial facility, is impacted with chlorinated volatile organic compounds (CVOCs), primarily perchloroethylene (PCE) and its degradation products.

The pilot test consisted of approximately six active injection days and included the injection of 17,896 liters (4,728 gal) of Fenton's reagent with peroxide concentrations of 10-12%. Eight injection wells and five vent wells were installed across the area found to be one of the most contaminated inside the active facility.

Injection system inside active facility

The conclusions that were drawn from the pilot test relate to the effectiveness of the engineering design, which achieved the appropriate geochemical conditions, distribution of oxidant, destruction of the CVOCs, and allowed for the potential coupling of technologies following the ISCO source reduction.

Current Projects

FR - Fenton's reagent SPS - Sodium persulfate
SP - Sodium permanganate

Scale	Oxidant	Contaminant	Location
Bench	FR	Dioxane	GCI's LAB
Pilot	FR / SP	TCE	NY
Pilot	FR	TCE	Belgium
Full	FR / SP	TCE	FL
Full	FR	Petroleum / Coal tar	FL
Full	FR	Petroleum	NJ
Full	FR	MGP	SC

Upcoming Conferences

Come visit Geo-Cleanse at the following conferences:

Environmental Trade Fair and Conference: May 1-3, 2008 in Austin, TX.

Remediation of Chlorinated and Recalcitrant Compounds: May 19-22, 2008 in Monterey, CA

Triad Investigations: New Approaches and Innovative Strategies: June 10-12, 2008 in Amherst, MA

Conference on Eastern Groundwater Issues: June 23-25, 2008 in Long Island, NY

International Symposium and Exhibition on the Redevelopment of MGPs: Sept. 23-25, 2008 in Mystic, CT

24th International Conference on Soils, Sediments, and Water: Oct. 20-23, 2008 in Amherst, MA.

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ABOUT GEO-CLEANSE INTERNATIONAL, INC.

Since 1995, Geo-Cleanse International, Inc. (GCI) has established a reputation as the premier in-situ chemical oxidation company. GCI consistently provides quality service and ensures that the goals of our treatment programs are achieved. We have the most experience of any chemical oxidation firm and were the first to commercially apply oxidants for a successful NAPL remediation. Our experience, together with independently published results of our work, and an experienced staff of professionals, keeps GCI at the top of the industry.

One of GCI's Treatment Vehicles

As the chemical oxidation field continues to evolve, GCI has expanded our services to incorporate the advances occurring within the industry, as well as our own proprietary technologies. GCI offers a variety of different chemical oxidation services to our clientele, including bench testing, pilot-scale applications, and full-scale applications. The Geo-Cleanse® Process can effectively treat a wide variety of contaminants in a range of lithologies. To date, GCI has field experience on over ninety sites in twenty-seven states, Canada, and Europe. GCI has experience remediating a wide variety of contaminants including chlorinated solvents, petroleum products, coal tar / MGP constituents, explosives and pesticides.

If you would like a free site evaluation, please contact us by phone, email, or by visiting our website at www.geocleanse.com.

Geo-Cleanse Services Include:

- Site evaluation and design
- Bench testing
- Pilot-scale injection
- Full-scale injection
- Vacuum extraction
- Field demonstrations
- Educational presentations
- Technology coupling

Oxidants:

- Fenton's reagent
- Sodium permanganate
- Potassium permanganate
- Sodium persulfate