The Chemical Oxidation Experts

GEO-CLEANSE INTERNATIONAL, INC.

ISCO TECHNOLOGY REVIEW

Innovative Coupling of ISCO Technologies Proves Successful in Orlando

Soil and groundwater contaminated by chlorinated solvents posed a potential delay to construction of the Orlando Events Center, the future home of the Orlando Magic basketball team. Rapid remediation of a perchloroethylene (PCE) source area was required in order to prevent construction delays. After a competitive public bid, the City of Orlando contracted Geo-Cleanse International, Inc. (GCI) to provide turnkey in-situ chemical oxidation (ISCO) remediation at site. GCI subcontracted MACTEC Engineering and Consulting, Inc. to provide local support, including acting as regulatory liaison for the project team, securing approval of a Limited Scope Remedial Action Work Plan from the Florida Department of Environmental Protection (FDEP), and overseeing certain field construction activities. Challenges to be addressed as part of the treatment program were:

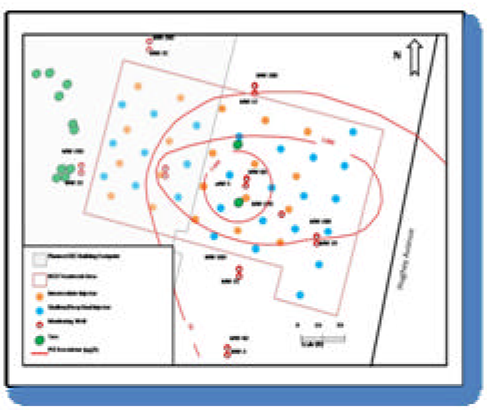

Figure 1: *Treatment Area Map*

- Very short time frame – Nov. 2007 award to July 2008 completion, including six months of post-remediation groundwater monitoring.
- Presence of potential dense nonaqueous phase liquid (DNAPL) source, with groundwater concentrations greater than 14,000 µg/L of PCE.
- Basal clay aquitard – could pose rebound problem with back-diffusion of PCE into groundwater.
- Pay for performance contract - The City of Orlando was not obligated to make payments over the initial 50% of contract unless GCI achieved and maintained Cleanup Target Levels (CTLs) of 3 µg/L PCE, 3 µg/L of trichloroethylene (TCE), and 70 µg/L of cis-1,2-dichloroethylene (DCE) in groundwater, and soil leachability criteria of 0.03 mg/kg for PCE.

After careful review of the site background investigation data, GCI designed a phased treatment program to meet the CTLs in the timeframe necessary to avoid development delays. The remediation program incorporated a "treatment train" consisting of three remediation phases:

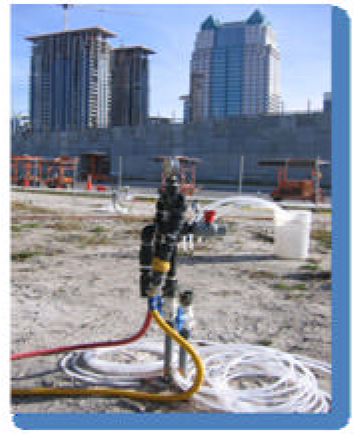

Figure 2: *GCI's Patented Mixing Head*

- Phase 1 consisted of injection of catalyzed hydrogen peroxide (CHP) for primary source reduction.
- Phase 2 consisted of injection of sodium permanganate to achieve the CTLs and prevent back-diffusion from the underlying clay aquitard.
- Phase 3 consisted of excavation of shallow vadose zone soil impacts.

The ISCO component called for 72 injection wells installed across three depth intervals between approximately 10-40 feet below grade, in an approximate 130 feet x 80 feet area (Figure 1). The aquifer lithology consists of sand to silty sand with an underlying clay aquitard at a depth of 40

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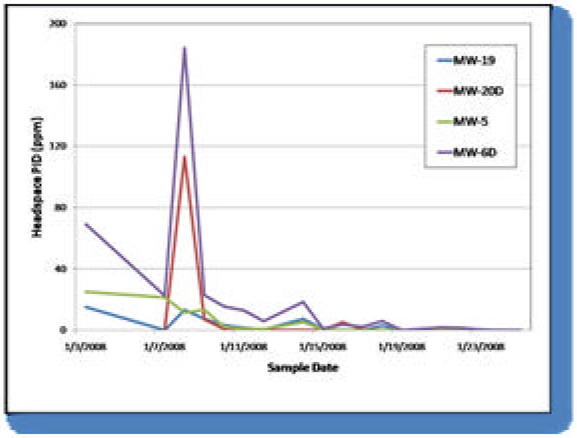

Figure 3: *Monitoring Well Headspace PID*

feet. Injection well installation was completed during the period of November 27 to December 15, 2007. The injection wells were then allowed to cure for two weeks.

The first phase of remediation consisted of injecting 85,000 gallons of CHP solution over the period from January 2-26, 2008 (Figure 2). GCI conducted intensive groundwater and offgas sampling to ensure appropriate geochemical conditions for an effective CHP injection existed in the treatment area, and to evaluate treatment progress. Measurements of volatile organic compounds (VOCs) in the headspace over a groundwater sample, as taken with a photoionization detector (PID), provide a semi-quantitative measure of VOC concentration in the groundwater. Figure 3 is a chart of the PID readings of groundwater samples from the four monitoring wells in the source area. The PID readings show an initial spike in headspace PID measurements related to desorption of VOCs from the aquifer matrix, followed by subsequent degradation of the PID measurements to non-detectable levels over the treatment period. These data confirm that the CHP component was complete, and the next remediation phase was initiated.

One week was allowed for residual hydrogen peroxide to degrade after completing the CHP injection before beginning the permanganate injection. The same network of injection wells installed for the CHP injection was also utilized for the permanganate. This second phase of remediation consisted of injecting 21,000 gallons of 4% sodium permanganate solution over the period from February 4-10, 2008. Field monitoring for sodium permanganate injection consisted of collecting groundwater samples for visual analysis to ensure uniform distribution of the permanganate reagent. Permanganate (recognized by its characteristic purple color) was found throughout the treatment area following the injection. The post-injection groundwater monitoring period began after completion of the permanganate injection.

The third phase of remediation consisted of soil removal from two areas at which PCE was detected at concentrations exceeding the soil leachability criterion of 0.03 mg/kg. A total of approximately 94 tons of soil was removed from two areas over the period from February 25-27, 2008. During the removal action, a PVC pipe attached to an apparent floor drain system was discovered at the site (Figure 4). The pipe was found to contain residual sludge and exhibited elevated PID readings, and was located directly over the groundwater source areas, and thus is the presumed source. The piping and associated bedding was, therefore, also removed from accessible portions of the site. After receipt of post-excavation sampling results, the excavation was backfilled on March 7, 2008.

Figure 4: *Presumed Source of PCE Contamination*

The post-treatment performance sampling program consisted of three groundwater sampling events, conducted on February 14, 2008 (4 days after injection), April 23, 2008 (73 days after injection), and July 23, 2008 (164 days) after injection, with a supplemental sampling event on August 5, 2008 (177 days after injection). With one exception, the VOC concentrations in all five of the performance monitoring wells have been reduced to below the CTLs. The total VOC concentration (consisting of the summed PCE, TCE and DCE concentrations) is plotted in Figure 5 for the two monitoring wells exhibiting the highest pre-injection VOC concentrations. During the July 23rd event, PCE was detected at 11 mg/L in MW-5 and was confirmed with a second analysis. MW-5 is a shallow well located adjacent to the soil excavation area, thus the VOC detection is likely associated with the soil removal. Additional treatment was focused in the area of MW-5, and a new sample was collected on August 5, 2008. All VOCs were below CTLs. The injection and monitoring wells were then abandoned in accordance with Florida regulations by August 8, 2008 to allow construction.

This treatment program was successful in obtaining Florida CTLs for the target compounds and was completed in a timeframe in order to avoid delays in construction. All pre-construction permitting and field work to achieve the CTLs in all media, including LSRAP submittal, regulatory approval, drilling, injection, soil removal, and backfill, was completed by March 7, 2008, approximately 4.5 months after contract execution. The FDEP has approved the results and construction has begun. This project demonstrates how DNAPL sites can be successfully remediated with a "treatment train" approach utilizing ISCO. Rarely can one single technology provide a complete remedy. As this case study demonstrates, GCI has the experience and capability to couple technologies, and to undertake innovative approaches, to achieve cleanup goals.

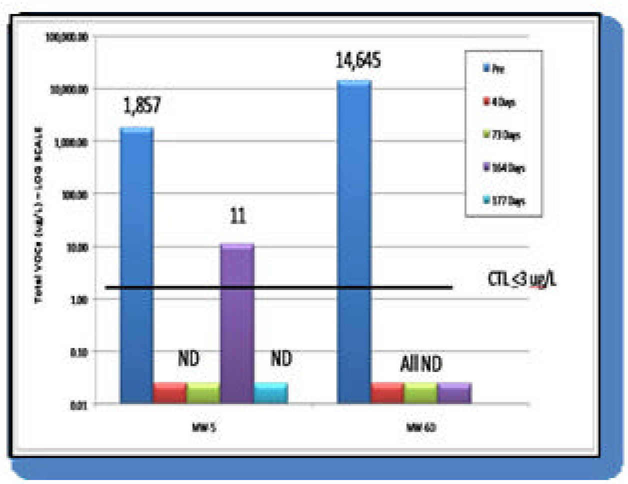

Figure 5: *Post-Treatment Groundwater Results*

Acidification during Catalyzed Hydrogen Peroxide ISCO

There are many choices today regarding selection of oxidants and catalytic systems. Catalyzed hydrogen peroxide (CHP) is arguably the most versatile oxidant, and an important question to be addressed during system design is whether acidification is necessary as part of the treatment. Studies of classical Fenton's reagent systems found that treatment was generally most effective at acidic pH conditions, typically at a pH of 3-4. Some practitioners try to differentiate themselves as using "neutral" or "cool" CHP as opposed to an "acidified" CHP approach, and claim more efficient treatment than an acidified approach. However the answer to the "which is best?" question lies with consideration of site-specific conditions and treatment objectives. This article explores some of the advantages and disadvantages of acidification as part of CHP ISCO.

Hydroxyl radicals (which are the primary reactants with CHP) can be generated at nearly any pH. Thus important considerations are how pH affects, or is affected by, (1) lithology of the soil and aquifer matrix, (2) the catalyst system, and (3) scavengers that affect treatment efficiency. These factors are interrelated, and should not be considered independently.

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The advantages of an acidic pH catalyst system over a circumneutral pH catalyst system include:

- Transition metals are required to catalyze peroxide to produce hydroxyl radicals. Under acidic conditions, transition metals are kept in solution rather than precipitating as oxyhydroxides. Naturally occurring transition metals are also released from the aquifer matrix, thus the amount of transition metals that must be added is reduced under acidic conditions.
- Bicarbonate interference is reduced. Hydroxyl radicals react with dissolved bicarbonate in groundwater. The reaction rate of the hydroxyl radical with a bicarbonate is slower than for reaction of hydroxyl radical with common contaminants; however, if dissolved bicarbonate is present at relatively high concentrations (200 – 400 mg/L), then radicals may be hundreds or thousands of times more likely to react with bicarbonate than with the contaminants, and thus may significantly reduce treatment effectiveness. Bicarbonate is eliminated at a pH of about 5.4, thus the hydroxyl radicals are utilized more efficiently for contaminant destruction under mildly acidic pH conditions.

At circumneutral pH, transition metals are typically added in a chelated form. This offers both advantages and disadvantages:

- Treatment can be accomplished in carbonate-rich aquifers. Under heavily impacted (NAPL) conditions, the contaminant concentrations are typically high enough that bicarbonate interference is less significant. This may remain as an advantage until dissolved contaminant concentrations are reduced (for example, to the 1-10 mg/L range), and bicarbonate interference again becomes significant.
- Chelating agents react with hydroxyl radicals. Thus when a chelated metal is added, often at a concentration much higher than the target contaminant, the chelating agent becomes a hydroxyl radical scavenger and contaminant treatment efficiency is reduced. At neutral pH, radical scavenging from dissolved bicarbonate and chelators will significantly reduce treatment efficiency.
- Many commonly used chelating agents may also be considered environmental hazards if not fully destroyed by the catalyzed peroxide. For example, EDTA does not readily biodegrade in groundwater, and has been linked to mobilization of metals; and NTA is a suspected carcinogen.
- Transition metal injection must be sustained throughout the treatment. At circumneutral pH, once the chelating agent is destroyed and the transition metal has reacted with peroxide, the metal is oxidized and will precipitate as an insoluble oxyhydroxide. Additional transition metal injection is therefore required in order to continue to catalyze the peroxide.

"Our goal is to provide the most effective treatment, and will always optimize the catalyst to best fit the site-specific conditions and treatment objectives."

The decision to utilize an acidic pH catalyst system or a circumneutral, chelated metal catalyst system requires consideration of site-specific issues. Both catalyst systems have advantages and disadvantages, and there is no "best" catalyst system applicable to all sites. GCI has considerable experience with both acidic and circumneutral catalyst systems. Our goal is to provide the most effective treatment, and will always optimize the catalyst to best fit the site-specific conditions and treatment objectives.

Current GCI Projects

Scale	Oxidant	Contaminant	Location
Bench	FR	Carbon Tetrachloride	NJ
Bench	FR	Coal Tar	NJ
Pilot	FR	TCE, BCEE	NJ
Pilot	FR	Dioxane	NC
Full	FR	Petroleum / Coal tar	FL
Full	FR	Chlorobenzene	NJ
Full	FR	Petroleum	NJ

Upcoming Conferences

COME VISIT GEO-CLEANSE AT THE FOLLOWING CONFERENCES:

Remediation Technology Summit
March 3-5, 2009
in Atlanta, GA.

Conference on Soil, Sediments, and Water
March 9-12, 2009
in San Diego, CA

Environmental Trade Fair and Conference
May 12-14, 2009
in Austin, TX.

11th Annual Florida Brownsfield Conference
2009 TBD

Florida Remediation Conference
October 15-16, 2009
in Orlando, Fl

25th International Conference on Soils, Sediments, and Water Oct. 19-22, 2009 in Amherst, MA.

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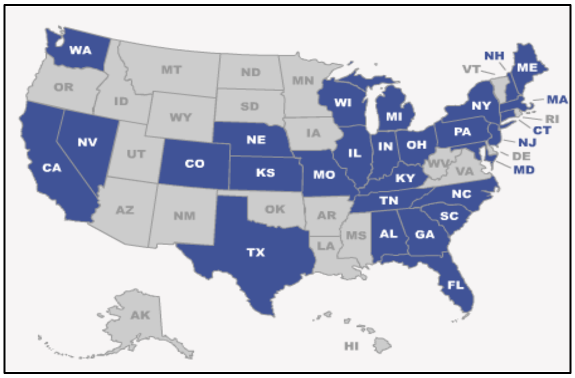
The Chemical Oxidation Experts

About GCI ...

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.



GCI Field Experience (Blue States)

As the chemical oxidation field continues to evolve, GCI has expanded our services to incorporate the advances occurring within the industry. The Geo-Cleanse® Process can effectively treat a wide range of contaminants and has successfully been applied in many different lithologies. To date, GCI has field experience on well over 100 sites in 28 states, Canada, and Europe.

Visit the GCI website at www.geocleanse.com to view our case studies or for a free site evaluation.

We Adapt to the Specific Site Conditions

- **Oxidants:** *Peroxide, Permanganate, Persulfate*
- **Additives:** *Surfactants, Chelating Agents, Stabilizers*
- **Novel Application Methods**
- **In-Situ Reduction**
- **Coupling with:**
  - *Bioremediation*
  - *Extraction*
  - *Other Technologies*