

The Chemical
Oxidation Experts



GEO-CLEANSE INTERNATIONAL, INC.

ISCO TECHNOLOGY REVIEW

Volume 4



Geo-Cleanse International, Inc.
400 State Route 34, Suite B
Matawan, NJ 07747
www.geocleanse.com

A New Approach Combining ISCO with Chemical Reduction to Destroy Carbon Tetrachloride DNAPL and Mixed Plumes

In-situ chemical oxidation with catalyzed hydrogen peroxide (CHP) or sodium persulfate (CSP) are generally optimized to produce oxidants such as hydroxyl radicals and sulfate radicals. Although these powerful oxidants are capable of destroying a wide range of contaminants, there are common soil and groundwater contaminants that cannot be oxidized. These contaminants, such as carbon tetrachloride (CT), must instead be *reduced* in order to be degraded. As a result, in-situ treatment of such compounds, particularly in the presence of DNAPL or as part of mixed plumes with compounds that can be oxidized, has presented a challenging problem.

CHP and CSP are known to produce superoxide radicals ($O_2^{\bullet-}$, a chemical reductant) as part of the chain of reactions associated with these reagents. Destruction of CT by CHP and CSP has been reported, however $O_2^{\bullet-}$ production generally appears to have been very inefficient. Recent reports have found that under certain conditions, hydrogen peroxide (H_2O_2) could be efficiently catalyzed to produce $O_2^{\bullet-}$, resulting in degradation of CT including DNAPL. In light of these results, Geo-Cleanse undertook extensive

research of catalysts to produce $O_2^{\bullet-}$ in response to a client seeking a rapid, cost-effective solution for a site impacted with CT and a suite of other compounds. The chemicals of concern included compounds that react well with oxidants (e.g., chlorobenzene and ethylbenzene), and compounds that cannot be oxidized or do not react well with oxidants (e.g., CT and related chloromethanes), including a DNAPL phase. The result of this effort is a new catalytic system for H_2O_2 , which produces both superoxide and hydroxyl radicals efficiently for in-situ destruction of a mixed contaminant plume and DNAPL.

Previous research by Watts and coworkers has shown that $O_2^{\bullet-}$ is produced by catalyzing H_2O_2 with Mn^{+4} at a pH of about 6.8 or higher. Applying this approach in the field, however, would be challenging because Mn^{+4} forms an insoluble precipitate (MnO_2) at circumneutral pH; thus application would require manipulating large pH shifts within an aquifer to maintain Mn in solution for distribution and subsequent precipitation of MnO_2 , or perhaps fracture emplacement of solid MnO_2 . Thus an approach was developed to more efficiently distrib-

ute the MnO_2 catalyst, and then controllably react the catalyst with H_2O_2 to produce $O_2^{\bullet-}$ in-situ. The approach developed by Geo-Cleanse comprises the following steps:

- (1) First inject sodium permanganate solution. Permanganate is an oxidant that can destroy certain organic compounds; but most importantly for this approach, the permanganate anion is reduced and manganese is precipitated throughout the aquifer as MnO_2 . The manganese in MnO_2 is predominantly in the Mn^{+4} valence state.
- (2) Permanganate reduction to MnO_2 preferentially occurs in zones with the highest organic mass, such as the portion of the treatment area impacted with DNAPL and associated highly elevated soil concentrations. Thus this catalyst is preferentially precipitated in the zones requiring treatment.



Inside this Issue of ISCO Technology Review

| | |
|---|---|
| Cover Story (continued) | 2 |
| Current GCI projects | 2 |
| State of the Art - Comparing Contaminant Oxidant Demand among ISCO Reagents | 3 |
| Upcoming Conferences | 3 |

Cover Story (Continued from Page 1)

- (3) A phosphate buffer at pH of 6.8 to 7.0 is injected next. The phosphate forms a ligand with colloidal MnO_2 and MnO_2 surfaces, thus stabilizing the very rapid catalytic reaction with H_2O_2 . The phosphate solution also buffers the pH within the desired range.
- (4) H_2O_2 solution is added next. The H_2O_2 reacts with MnO_2 to produce $O_2^{\bullet-}$. The $O_2^{\bullet-}$ degrades the CT and other chloromethanes.
- (5) The H_2O_2 solution also reacts with native iron in the formation, and/or with Mn^{+2} produced by manganese redox cycling, to produce hydroxyl radicals. This is important for degradation of other COCs such as ethylbenzene, which are destroyed by hydroxyl radicals but not reactive with $O_2^{\bullet-}$.

Laboratory bench tests were conducted with soil and groundwater from an industrial site in New Jersey. The soil and groundwater were impacted with CT, chloroform, methylene chloride, chlorobenzene, ethylbenzene, and methoxychlor, including a visible DNAPL phase. Batch reactor tests controlling all phases (soil, groundwater, and volatilization; volatilization was measured using absorbent cartridges) were performed to optimize and test the approach. Results for CT, chloroform, and chlorobenzene from a representative series of tests are shown in Figures 1 & 2. Results for the aqueous phase (Figure 1) show that baseline VOC concentrations were reduced by 99.99% for CT and chloroform, and 94.6% for chlorobenzene. The approach was also found to be extremely effective for the soil-sorbed and DNAPL phase; this was evaluated by calculating the total contaminant mass in each reactor. The contaminant mass results (Figure 2) show that VOC mass (excluding volatilized fraction) was reduced by very similar magnitudes, indicating destruction of soil-sorbed and DNAPL phases in similar proportions to the aqueous phase.

Experiments demonstrated that all of the compounds, including compounds destroyed only by reduction (e.g., CT) and compounds destroyed only by oxidation (e.g., chlorobenzene), were degraded effec-

tively. Overall destruction ranged from 84% to a nominal 100% relative to control samples. The compounds destroyed by $O_2^{\bullet-}$ reduction were destroyed slightly more efficiently than compounds destroyed by hydroxyl radical oxidation, but the efficient destruction of all compounds indicates that this approach can be used effectively for sites impacted with a wide range of oxidizable and reducible compounds. Analyses also included sampling for intermediate and final oxidation products to elucidate the degradation pathways. No hazardous intermediate or final compounds were detected, including negative analyses for phosgene (a potential reduction product of CT).

Based upon these results, a field pilot test is anticipated to be complete in the spring of 2010.

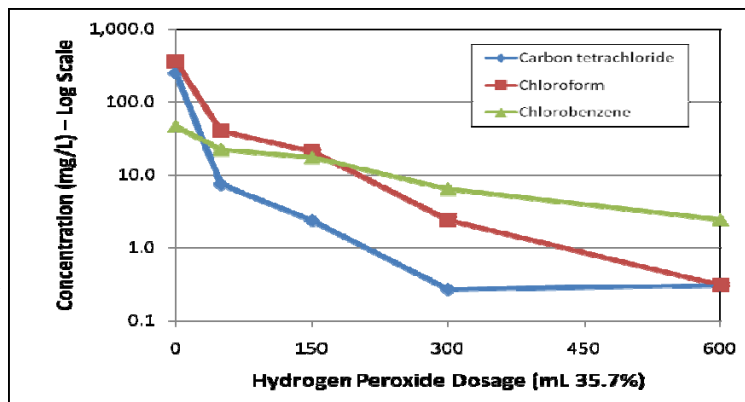


Figure 1. Aqueous VOC Concentrations

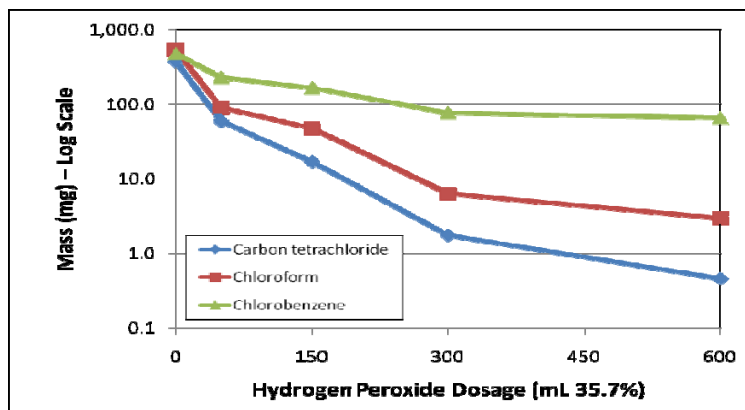


Figure 2. VOC Mass



Current Geo-Cleanse International, Inc. Projects

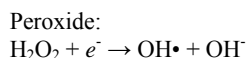
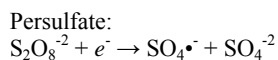
| Phase | Contaminants | Location |
|-------|--|--------------|
| Bench | Coal Tar | Confidential |
| Pilot | Carbon Tetrachloride | NJ |
| Pilot | 1,4-Dioxane | NC |
| Full | Petroleum / Coal Tar | FL |
| Full | Chlorobenzene | NJ |
| Full | Petroleum | GA |
| Full | 1,1'-Biphenyl, 1,4-Diphenyl Ether, Toluene | NJ |

State of the Art – ISCO Insights from GCI

Comparing Contaminant Oxidant Demand among ISCO Reagents

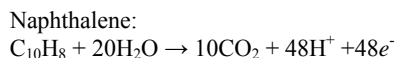
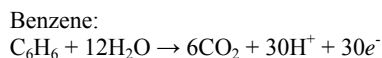
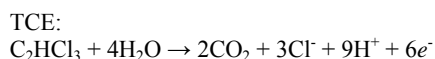
Many factors must be considered when evaluating a site and assessing potential ISCO approaches. One of the fundamental decisions to be made is which oxidant to utilize. An important factor in this decision, which is often overlooked, is how much oxidant is required to destroy target contaminant mass and the corresponding impact on cost. At sites with relatively low contaminant concentrations, the natural oxidant demand is usually larger than the contaminant oxidant demand; however at more heavily impacted sites, the contaminant oxidant demand is generally much larger than the natural oxidant demand. At sites with very high contaminant mass, such as coal tar or DNAPL sites, the overall project cost is heavily influenced by the cost of the oxidant required to destroy the contaminant. Thus the objective of this article is to show how contaminant oxidant demand can affect project costs.

For comparison purposes, oxidant demand is compared on a stoichiometric basis. The radical-initiating oxidation half-reactions for catalyzed persulfate and catalyzed peroxide are as follows:



The key observation is that, for both per-

oxide and persulfate, one mole of oxidant accepts one mole of electrons and produces one mole of radicals. The number of radicals required (or electrons removed) from a target contaminant can also be calculated from oxidation half-reactions. Reactions for several common contaminants are as follows:



Thus on a stoichiometric basis, oxidation of one mole of TCE produces six moles of electrons, or in other words requires six moles of radicals and, therefore, six moles of oxidant. Similarly, one mole of benzene requires 30 moles of oxidant, and one mole of naphthalene requires 48 moles of oxidant.

While the number of moles of peroxide or persulfate required to oxidize a contaminant is identical, the weight ratio (in terms of pounds of oxidant required per pound of

contaminant) is very different. This is because the formula weight of each oxidant is different. Sodium persulfate has a formula weight of 238 grams per mole, while hydrogen peroxide has a formula weight of 34.0 grams per mole. For example, oxidation of 1 mole of TCE requires 0.45 lbs of peroxide or 3.15 lbs of persulfate. Calculations for benzene and naphthalene are provided in Table 1. Due to the difference in oxidant formula weights, contaminant oxidation requires approximately 7 times more persulfate by mass than peroxide.

The oxidants also have a significant difference in cost. Hydrogen peroxide, on a 100% concentration basis and including ferrous iron catalyst, costs approximately \$1.10 per pound. Sodium persulfate, also on a 100% concentration basis and including caustic catalyst to overcome the oxidant and soil caustic demand, costs approximately \$2.25 per pound. The corresponding costs to destroy one pound of contaminant are shown at the bottom of Table 1.

Overall, persulfate costs about 14 times more than peroxide to destroy the same contaminant mass. The potential impact of the reagent cost on overall project cost will vary with the overall contaminant mass. At sites with low contaminant concentrations, the overall impact on cost may not be large, and other technical factors may have greater weight in determining oxidant choice. But at large sites with relatively high contaminant concentrations, such as a manufactured gas plant or DNAPL sites where contaminant mass is measured in tens of thousands of pounds or more, the difference in reagent costs can be tremendous. In these cases, catalyzed peroxide ISCO provides a much better choice from the perspective of reagent cost.

Table 1: Comparison of Oxidant Requirements and Cost

| Factor | TCE | Benzene | Naphthalene |
|--|--------|---------|-------------|
| Formula Weight | 131.4 | 78.11 | 128.2 |
| Moles of Oxidant Required to Destroy Contaminant | 6 | 30 | 48 |
| Pounds of H ₂ O ₂ per 1 mole of Contaminant | 0.45 | 2.25 | 3.60 |
| Pounds of Na ₂ S ₂ O ₈ per 1 mole of Contaminant | 3.15 | 15.74 | 25.19 |
| H ₂ O ₂ Cost per 1 lb (including catalyst; 100% basis) | \$1.10 | | |
| Na ₂ S ₂ O ₈ Cost per 1 lb (including caustic catalyst) | \$2.25 | | |
| H ₂ O ₂ Cost to Destroy 1 mole of Contaminant | \$0.49 | \$2.47 | \$3.96 |
| Na ₂ S ₂ O ₈ Cost to Destroy 1 mole of Contaminant | \$7.08 | \$35.42 | \$56.68 |

Upcoming Conferences

Come visit Geo-Cleanse at the following conferences:



20th Annual Conference on Soils, Sediments, Water, and Energy
San Diego, CA



TCEQ's Annual Environmental Trade Fair and Conference
Austin, TX



Remediation of Chlorinated & Recalcitrant Compounds Conference, Battelle
Monterey, CA



26th International Conference on Soils, Sediments, and Water
Amherst, MA



Geo-Cleanse International, Inc.

400 State Route 34, Suite B
Matawan, NJ 07747

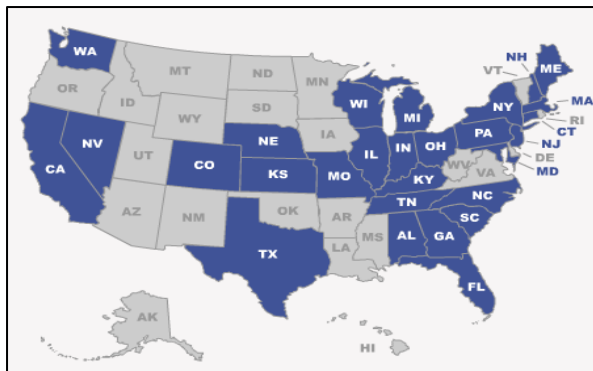
About Geo-Cleanse International, Inc.



Since 1995, Geo-Cleanse International, Inc. (GCI) has established a reputation as the premier in-situ chemi-

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.

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



GCI Field Experience (Blue States)

cal 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

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 to submit a site evaluation form.

We Adapt to the Site-Specific Conditions

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