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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 activated sodium persulfate (ASP) 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 ASP are known to produce superoxide radicals $(O_2^{\bullet}, a \text{ chemical reductant})$ as part of the chain of reactions associated with these reagents. Destruction of CT by CHP and ASP has been reported, however O₂•⁻ 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 O2., 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 H₂O₂ 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 (MnO₂) 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 MnO₂, or perhaps fracture emplacement of solid MnO_2 . Thus an approach was developed to more efficiently distribute the MnO₂ catalyst, and then controllably react the catalyst with H₂O₂ to produce O₂• 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 MnO₂ 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.
- (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.



Figure 1. Aqueous VOC Concentrations



- (4) H₂O₂ solution is added next. The H₂O₂ reacts with MnO₂ to produce O₂•. The O₂• degrades the CT and other chloromethanes.
- (5) The H₂O₂ 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 O₂•.

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 soilsorbed 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 effectively. 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 was completed in 2010, and the full-scale application is scheduled to be complete by the end of 2014. Furthermore, Geo-Cleanse received <u>U.S. Patent No. 8,556,537</u> for Manganese-Mediated Redox Processes for Environmental Contaminant Remediation for this novel technology.









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 rela-

tively 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:

Persulfate: $S_2O_8^{-2} + e^- \rightarrow SO_4^{-2} + SO_4^{-2}$ Peroxide: $H_2O_2 + e^- \rightarrow OH^{-1} + OH^{-1}$

The key observation is that, for both peroxide 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 halfreactions. Reactions for several common contaminants are as follows:

TCE: $C_2HCl_3 + 4H_2O \rightarrow 2CO_2 + 3Cl^- + 9H^+ + 6e^-$

Benzene: $C_6H_6 + 12H_2O \rightarrow 6CO_2 + 30H^+ + 30e^-$

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 Destory 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

Naphthalene:

 $C_{10}H_8 + 20H_2O \rightarrow 10CO_2 + 48H^+ + 48e^-$

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 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



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

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.

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About Geo-Cleanse International, Inc.



Geo-Cleanse International, Inc. (Geo-Cleanse) is a full-service remediation firm, dedicated to the design and implementation of in-situ chemical remediation technologies. Since 1995, we have completed hundreds of field-scale remediation programs across the United States, Canada and Europe. As leaders in our industry, our field experience includes the first successful in-situ chemical remediation treatment programs to address chlorinated solvent dense, non-aqueous phase liquids, manufactured gas plant constituents, energetics, and chloromethanes. Our completed projects include several of the largest sites remediated utilizing chemical remediation technologies, as well as high-profile Superfund and Brownfield projects.

Geo-Cleanse has consistently provided innovative remedial solutions to our diverse clientele network, and we continue to expand our services to incorporate the advances occurring within the industry. Our extensive field experience, together with independently published results of our work and our knowledgeable staff of professionals, ensures that Geo-Cleanse continues to be one of the world's top environmental remediation firms.



Services Site Evaluation and Design Bench Testing/Lab Studies Field-Scale Programs Field Demonstrations Technology Coupling Educational Resources Contaminants Coal Tar Chlorinated Solvents Petroleum Hydrocarbons Diesel Fuels/Fuel Oils Chloromethanes Pesticides PAHs/MAHs NAPLs VOCs/SVOCs Energetics GRO/DRO/TPH/EPH



<u>Reagents</u> Catalyzed Hydrogen Peroxide (*Fenton's Reagent*) Potassium Permanganate Sodium Permanganate Sodium Persulfate Zero Valent Iron

