Successful Strategies for Integration of In-Situ Oxidation with Existing Technologies to Support Site Closure

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Closure of sites where groundwater is contaminated by chlorinated solvents often requires achievement of very low concentrations (low parts per billion). Lacking cost-effective technologies, site closures are often projected in terms of decades while pump and treat and/or hydraulic containment technologies are employed. IT Corporation developed PermOX-IT^{SM} as a cost-effective technology for performing *in situ* oxidation of contaminants in groundwater. To date, IT has worked with regulatory authorities to perform pilot tests of PermOX-IT^{SM} at over 40 sites and full-scale applications at 8 sites. In a diversity of hydrogeologic settings and with starting concentrations for chlorinated ethenes ranging from separate phase to low parts per million, PermOX-IT^{SM} has shown that it can be a cost-effective strategy as a stand-alone technique or integrated with other site activities to achieve closure in significantly reduced timeframes. This paper presents case histories for six different sites to illustrate differing closure strategies and regulatory approval processes. Specifically, IT's PermOX-IT^{SM} technology has been used as follows: to replace more costly and/or less effective technologies identified in a Superfund Record of Decision; to achieve source removal; to treat entire plumes; and to achieve more stringent cleanup standards than required by regulation to enhance property values and/or reduce liability.

Statement of Problem. Cleanup of groundwater to drinking water and/or risk-based standards has proven to take many years using pump and treat technologies and/or hydraulic containment. Even the recent acceptance of natural attenuation as an effective remediation technology requires many years to implement. Each year of ongoing remediation has operation and maintenance costs as well as related oversight and/or legal costs. In addition, risk management associated with long-term remediations has to consider potential changes in regulations, the potential for more stingent cleanup standards to be imposed, and/or changes in permit conditions, all of which carry potential financial liabilities. Long-term remediations may also restrict site use and development, or at a minimum create uncertainty for potential real estate transactions. Consequently, there is a great need for remediation technologies that shorten the time required to achieve closure, minimizing financial liabilities, improving risk management, and supporting the greatest range of site use/re-use alternatives. This need for innovation must be balanced with the concerns of federal and state regulatory agencies regarding the uncertainties associated with new technologies. This paper illustrates the concerns that regulatory agencies have identified with respect to implementation of our PermOX-IT^{SM} technology and the approaches used to gain regulatory approvals. This paper also illustrates how IT's PermOX-IT^{SM} can be integrated into a project in a variety of ways to reduce remediation durations.

PermOX-IT^{SM} Overiew. *In situ* oxidation is highly desirable as a remedial process because treatment is completed in-place, without the generation of additional wastes to be treated at the surface – contaminants are not displaced to the atmosphere, but are fully destroyed by chemical reaction. Oxidation treats a wide range of contaminant types, impacted media and concentrations. In general, the higher the oxidation potential of an oxidant, the more powerful the oxidant is, and the more reactive it is. While many oxidants are potentially usable, not all are environmentally acceptable. To be used for environmental remediation, oxidants have to be non-hazardous (both to the users and the environment), fully reactive, and not create undesirable by-products. The following oxidants, arranged in decreasing oxidation potential, are typically utilized: hydroxyl radical; ozone; persulfate; hydrogen peroxide; and permanganate. Successful oxidation requires that the oxidant come into contact the impacted media. This contact is controlled by the site hydrogeology, which impacts the ability to apply and distribute the oxidant, and the properties of the oxidant. IT research has shown that permanganate is a sufficiently strong oxidant to reduce a broad range of contaminants, including chlorinated ethenes. In addition, permanganate has several significant advantages over other oxidants: permanganate is safer to store, handle and apply; permanganate is more persistent in the subsurface allowing for more effective dispersion of the oxidant within the contaminated media; and permanganate is significantly less-expensive to deploy.

IT's PermOX-IT[SM] technology is an innovative and low cost remedial technology for destruction of VOCs in both unsaturated and saturated materials using permanganate solutions to facilitate remediation by direct and complete contaminant destruction. IT first began bench-scale and field pilot tests of PermOX-IT[SM] in 1997 at sites contaminated with chlorinated ethenes, which are oxidized to CO_2 and chloride ions. Our recent bench-scale and pilot tests have expanded to include other contaminant types. The most common sources of permanganate include potassium permanganate ($KMnO_4$) and sodium permanganate ($NaMnO_4$). $KMnO_4$ is purchased as a dark purple solid crystalline material, which is placed into a liquid solution (generally 1 to 2%). $NaMnO_4$ is purchased in liquid form, at a 40% concentration suitable for direct addition, or dilution and addition. Although more expensive than $KMnO_4$, $NaMnO_4$ is available at a much higher concentration, decreasing the volume of liquid to be added to achieve a given mass loading of oxidant.

Regulatory Concerns and Approaches for Approval. Each site presents unique concerns with respect to PermOX-IT[SM] applications. In general, the concerns can be categorized as the applicability of the technology (potential effectiveness), safety of implementation, by-products, and migration. Effectiveness has been addressed through the use of bench-scale studies and by presenting the results achieved from other, similar sites. The safety of the technology was an area that had to be demonstrated. IT developed specific procedures for material storage, handling, mixing and application. In particular, IT equips site personnel with neutralizing sprays to address spills. The issue of by-products needs to be addressed in a variety of ways. First, IT has developed data to show that residual concentrations of manganese will not be a concern. Second, IT has developed data to show that there are no harmful by-products from the oxidation process. Further, IT develops site-specific sampling plans to demonstrate that no harmful by-products result from the use of PermOX-IT[SM]. Migration is a site-specific issue and may involve a variety of areas such as migration of the oxidant in the subsurface to a nearby stream or wetland, or mobilization of a chemical species of concern at the site through the oxidation process. IT's experience has generated significant data on subsurface dispersion of the oxidant such that potential impacts due to oxidant spread can be anticipated. In addition, IT has generated data on a sufficient diversity of sites to be able to provide chemical data to show that any mobilization of chemical species (e.g., hexavalent chromium) is a temporary, short-lived phenomenon. Overall, IT's experience with PermOX-IT^{SM} has shown that the technology can be implemented with little or no harmful impact to the environment; this has been the basis of gaining regulatory support and approval.

Site Closure Strategies and Case Histories. IT will present case histories to illustrate the key factors that resulted in identification of PermOX-IT^{SM} as an applicable technology, and the approach and methodologies used to gain regulatory acceptance for its use. To date, IT has integrated PermOX-IT^{SM} into site closure strategies in a variety of ways, including the following: (1) replace remedies selected in Superfund Record of Decisions with a more effective technology; (2) perform source removal of chlorinated solvents from the unsaturated zone to support natural attenuation; (3) replace a groundwater pump and treat system to reduce projected cleanup from 30+ years to less than 10 years of site monitoring; and (4) perform additional remediation at commercial/insudatiral sites to achieve drinking water standards to promote increased real estate values for the properties.

An overview of data associated with some of our case histories is provided below. The goal of the presentation will be to show the diversity of approaches that can be used to integrate PermOX-IT^{SM} into site closure strategies, and the approaches for addressing regulatory concerns associated with implementation of this innovative technology.

Overview of Case Histories for PermOX-IT^{SM} Treatments (all concentrations in ug/L)

Site	Contaminated Media	Pounds Applied	Acres Treated	Primary Contaminants	Concentrations		Primary Oxidant Demand Factor
					Pre-	Post-	
Maine	Till and fractured bedrock aquifer	42,000	1.5	TCE DCE Xylene	1,000 2,000 1,000	40 20 20	Iron and solvents
Texas	Silt, Clay and weathered bedrock	1500	0.1	TCE DCE VC Chloroform	34,000 7,000 100 4,000	6 3 2 1,600	Humic material and solvents
North Carolina	Silt, Clay and weathered Bedrock	7000	1	Total VOCs	1,000 to 17,000	50-99% reduc-tion	Iron-soil demand, petroleum and solvents
Massachusetts	Till and fractured bedrock	4000	0.25	TCE	450,000	4	Iron and solvents
Connecticut	Sand	600	0.5	TCE	2,900	48	Soil matrix