2.1.3 Chemical Oxidation

In-situ chemical oxidation is a relatively new technology used to treat organic contaminants in soil and groundwater. There are three viable oxidants that are currently commercially available – Permanganate (Potassium and Sodium forms – KmnO₄, NaMnO₄), Hydrogen Peroxide (H_2O_2), and Ozone (O_3).

The attractiveness of in-situ chemical oxidation is that it is a relatively fast process. For those contaminants that are amenable to oxidation, treatment can be done in relatively short order. Generally the oxidation products are CO_2 , water and chloride ion (if the contaminant contains chlorine). The end products for the oxidants are generally innocuous. Ozone and peroxide generate oxygen and water; permanganate generates Manganese Dioxide (MnO₂), an insoluble mineral. The permanganate also will leave the corresponding cation – potassium or sodium.

CBA has had tremendous success at using potassium permanganate for oxidation of chlorinated solvents, particularly trichloroethylene (TCE) and tetrachloroethylene (PCE). Other organics that are susceptible to oxidation by permanganate include Phenols, PAHs, and alkenes. Permanganate has been preferred as an oxidant over ozone and peroxide due to its resistance to auto decomposition and its effectiveness over a larger pH range. The stoichiometric reactions for the complete destruction of PCE and TCE utilizing potassium permanganate are as follows:

 $PCE: \ 4KMnO_4^{-} + 3C_2Cl_4 + 4H_2O = \ 6CO_2 + 4MnO_2 + 12CI + \ 4K^+ + 8H^+$

 $TCE: \ 2KMnO_4^- + C_2Cl_3 \ = \ 2CO_2 + 2MnO_2 + 3C\Gamma + 2K^+ + H^+$

The stoichiometry indicates that approximately 1.3 pounds of permanganate is required to completely oxidize one pound of PCE. The equation, however, ignores oxygen demand inherent in the site soils due to natural organic material (NOM) and other reductants. Therefore, using a factor of three to ten times the weight ratio noted above is not uncommon.

Although the reaction mechanisms involved with oxidizing organic compounds sorbed to soils are not fully understood, the key to successful application is ensuring the contact between the oxidant and the contaminant. Typically the rate of contaminant degradation in heterogeneous matrices is controlled by the concentration of the oxidant, and any surface or subsurface structures as well as lithological changes can impede the success of in-situ chemical oxidation.

However, CBA's patented MITU process is ideal for ensuring contaminant/reagent contact within vadose zone soils equating to appreciable contaminant degradation rates at lower than expected oxidant dosage rates. At a Wisconsin Hazardous Waste Site containing soils contaminated with chlorinated solvents, CBA used a combination of thermal treatment and chemical oxidation with potassium permanganate to achieve the required treatment objectives.



MITU-LVR mixing KMnO₄ with COC contaminated soil in Milwaukee, WI

Typically, permanganate is applied to contaminated media as a solution or as a slurry; however, CBA applied potassium permanganate in its dry crystalline form. This method has proven to be successful in vadose zone soils having an adequate moisture content (>17%) and also in saturated soil conditions. In this application, the MITU is utilized to mix the KMnO₄ directly into the soils. A water spray is typically used for dust control and to aid in the kinetics of the chemical oxidation.



MITU-12 mixing KMnO₄ with COC contaminated soil in Milwaukee, WI



Applying KMnO₄ in dry crystalline form Milwaukee, WI

Carus Chemical is the largest manufacturer of permanganate in the United States, and CBA has worked very closely with their research and development division to optimize the effectiveness of applying KMnO₄ with the MITU technology.

The MITU technology is ideal for introducing oxidizing agents or oxygen release compounds into vadose zone soils. The trenching action increases the available soil surface area and promotes the reagent-contaminant contact that is required for successful degradation of the contaminants.