

RegenOx™

Advanced Chemical Oxidation

Increased Solubility Effects When Treating Total Petroleum Hydrocarbons

Chemical Oxidation Reactions with Petroleum Hydrocarbons

Complete chemical oxidation of petroleum hydrocarbons does not occur within the controlled and extreme environment of the internal combustion engine. So, it is unreasonable to expect that complete oxidation of organic molecules in the subsurface will result from the application of a chemical oxidant. In truth, the application of a chemical oxidant to the subsurface environment results in both complete oxidation and partial oxidation of the contaminants contacted.

When a chemical oxidant is applied to degrade an organic chemical, the initial reaction is “chemical activation,” where the long-chain alkanes ($\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-...CH}_2$) are converted to organic acids ($\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-...COOH}$). These organic acids are much more water soluble due to the polarity induced by the addition of oxygen.

Likewise the treatment of benzene, toluene, ethylbenzene, and xylenes (BTEX) and polyaromatic hydrocarbons (PAHs) by chemical oxidation is a series of reactions first activating the ring structures by the addition of oxygen resulting in greater solubility. The kinetic rate of BTEX and PAH oxidation is considerably faster than that of long-chain alkanes. Therefore, one should expect greater removal of these aromatic compounds when treating a mixed hydrocarbon-contaminated sample. In the case of both alkanes and aromatic hydrocarbons, further chemical oxidation results in stepwise conversions, ultimately resulting in carbon dioxide (complete mineralization).

Note that while reduced petroleum hydrocarbons are rather difficult to biodegrade, once made more soluble by chemical oxidation (activation) they are more easily biodegraded to carbon dioxide and biomass.

Impact of Partial Oxidation on Total Petroleum Hydrocarbon Analyses

In many remediation projects, performance is monitored by groundwater analyses. Often these analyses employ techniques used to measure total petroleum hydrocarbons (TPH), which is a simple measure of general hydrocarbon compounds. (The use of TPH analyses is the subject of RegenOx Technical Bulletin 10.0) Because of the very nature of the chemical oxidation process and its tendency to produce more water-soluble partial oxidation intermediates, one should expect to see an increase in dissolved-phase hydrocarbon species in the early stages of treatment. This is the direct result of a reduced amount of petroleum hydrocarbons bound to subsurface matrix (sorbed) becoming partially oxidized and moving into solution at the site. To distinguish between the dissolved, reduced petroleum hydrocarbon contaminant in the sample and the partially oxidized products, one can apply a silica gel filtration step in the analytical process (as described in RegenOx Technical Bulletin 10.0).

Before sampling to determine final chemical oxidation performance, it is important to allow for partially oxidized product to further biologically oxidize and to reestablish an equilibrium condition with the subsurface matrix material.

Contaminant Partitioning Challenges

Soil is a very complex mixture of numerous naturally occurring organic and inorganic chemicals. Many physical, chemical, and biological processes are occurring in soil, and all of these processes will be affected by chemical oxidation treatments, including RegenOx™. Understanding these effects and their interactions is important for predicting the effectiveness of RegenOx™ treatment in various situations, and to avoid unintended consequences.

In the typical model for the partitioning of organic matter to soil, the organic matter in most soil is intimately bound to clay as a clay-organic complex (Dragun, 1998). As a result, two major types of adsorbing surfaces are available to an organic chemical: clay-organic and clay alone. The relative contribution of organic and inorganic surface areas to adsorption depends on the extent to which the clay is coated with organic matter. The influence of clay on organic chemical adsorption can be significant, especially in soil with organic matter content below 1 percent. For example, the adsorption of polychlorinated biphenyls (PCBs) in clayey subsurface soil with an organic carbon content of 0.4 percent is greater than PCB adsorption to topsoil with an organic carbon content of 1.2 percent (Dragun, 1998). Subjecting these adsorptive surfaces to chemical oxidation can greatly effect the partitioning onto the surfaces, thereby shifting the equilibrium concentrations of dissolved versus sorbed contaminant mass.

Adsorption characteristics are specific to the chemical of concern, and are generally influenced by molecular size, hydrophobicity, and molecular charge. These chemical characteristics affect adsorption to soil by influencing adsorption mechanisms generally involving van der Waal's forces, hydrogen chemical bonds, and ionic interactions. Koc is typically used to describe the sorptive characteristics of a chemical. However, using Koc has many caveats (Dragun, 1998), Koc is an experimentally determined value, and the values reported in the literature for a given compound can vary widely. This creates large margins of error when using low groundwater concentrations to calculate the size of a large sorbed-phase contaminant mass. Therefore, real life adsorption systems are not easily modeled, and the effect of chemical oxidation cannot be predicted with any precision.

pH Effects

The addition of basic materials, like RegenOx™, to soil will have many different effects. Depending on the buffering capacity of the soil, base can dissolve base-soluble minerals, changing the absorptive capacity of the soil for organic materials. Under alkaline conditions, the surfaces of soil particles can acquire negative electrostatic charges giving them a lower affinity for charge-neutral hydrophobic species like petroleum hydrocarbons. In addition, alkaline conditions promote the saponification of fatty acids present from both chemical oxidation and naturally decomposing organic matter. The resulting carboxylates are surfactants that can shift the balance of hydrocarbon contamination from soil into the groundwater. One can consider this a kind of soil washing effect generated by the presence of newly formed surfactants.

Summary

Chemical oxidation (e.g., by RegenOx™) rapidly oxidizes many organic compounds and is a powerful tool for the remediation of contaminated soil and groundwater. However, it is important for the practitioner to make a realistic assessment of site characteristics and treatment objectives, and judge performance expectations accordingly.

The application of chemical oxidation technology to the subsurface will result in both complete oxidation of the contaminant of concern as well as partial oxidation. Partial oxidation will result in greater solubility of those hydrocarbons bound in the subsurface as sorbed mass. This can result in elevated dissolved-phase hydrocarbon measurements using some analytical methods. Additionally, the oxidation of the subsurface matrix itself, as well as pH effects imparted by the chemical oxidants, can result in elevated hydrocarbon concentrations in the dissolved phase.

References

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