Soil, Sediment, Bedrock and Sludge

Chemical Oxidation

Introduction:

Oxidation through chemical means alters hazardous contaminants to less toxic compounds that typically are more stable, less mobile, and inert. Oxidising agents commonly used include ozone, permanganate, hydrogen peroxide, chlorine, and chlorine dioxide.

Description:

Chemical oxidants are able to cause the rapid and complete destruction of many toxic organic chemicals. Typically, oxidants have been able to achieve high treatment efficiencies (> 90 percent) for unsaturated aliphatics such as trichloroethylene (TCE) and aromatic compounds such as benzene, with fast reaction rates (90 % destruction within minutes). Field applications have affirmed that matching the oxidant and delivery system to the contaminants of concern (COCs) and the condition of the site are key to the successful implementation of the process.

Ozone addition

Ozone gas is able to oxidise contaminants directly or through forming hydroxyl radicals. Ozone reactions are most effective in systems that have an acidic pH. The reaction is extremely fast - pseudo first order kinetics. Due to such high reactivity and instability, O_3 needs closely spaced delivery points (e.g. air sparging wells). *In situ* decomposition of the ozone can result in beneficial oxygenation and improved biostimulation.

Peroxide

Oxidation using liquid hydrogen peroxide (H_2O_2) in the presence of ferrous iron (Fe^{+2}) brings about Fenton's Reagent, which yields free hydroxyl radicals (OH^-). These are strong, non-specific oxidants, which are capable of rapidly degrading numerous organic contaminants. Fenton's Reagent oxidation is more effective under extremely acidic pH conditions (e.g., pH 2 to 4) and is ineffective under moderate to strongly alkaline pHs. These reactions are also extremely rapid, following second-order kinetics.

Permanganate

Due to its multiple valence states and mineral forms, Mn can participate in several reactions. The reactions proceed at a slower rate than the previously mentioned reactions, according to second order kinetics. The reaction can include destruction by direct electron transfer with free radical advanced oxidation permanganate reactions being most effective over a pH range of 3.5 to 12.

Applicability:

The rate and degree of degradation of a COC are driven by the properties of the chemical itself and its susceptibility to oxidative degradation as well as the condition of the matrix, most notably the pH, temperature and concentration of oxidant. Due to the indiscriminate and rapid rate of reaction of the oxidants with reduced substances, the delivery system and distribution throughout a subsurface region of the soil of great importance. Delivery systems regularly use vertical or horizontal injection wells and sparge points with forced advection to swiftly push the oxidant into the subsurface. Permanganate is more stable and persistent in the subsurface; and as a consequence it can migrate by means of diffusive processes. Consideration must be given to the effects of oxidation on the system. All three oxidation reactions can decrease the pH if the system is not buffered in an appropriate manner. Other potential effects can include colloid genesis leading to reduced permeability, mobilisation of redox-sensitive and exchangeable sorbed metals, potential formation of toxic by-products, evolution of heat and gas and possible biological perturbation.

Limitations:

- Handling of large quantities of hazardous oxidising chemicals due to the oxidant demand of the target organic chemicals and the unproductive oxidant consumption of the formation.
- Some COCs are resistant to oxidation.
- Potential exists for process-induced detrimental effects. Further research and development is ongoing to advance the science of this process to improve its overall cost effectiveness.

Data Needs:

In situ chemical oxidation must be done with great attention being paid to the reaction chemistry and transport processes involved. It is also vital that attention be paid to worker training and safe handling of processes of the chemicals, in addition to ensuring proper management of wastes. The design and implementation process should rely on an integrated effort that includes screening level characterisation tests and reaction transport modelling, in conjunction with treatability studies at both lab and field scale.

Performance Data:

The possible benefits of *in situ* oxidation include the rapid and extensive reactions with various COCs applicable to numerous bio-recalcitrant organics and subsurface environments. The process can also be tailored so it's site-specific and implemented with relative ease. Some limitations do exist such as the requirement for handling large quantities of hazardous oxidising chemicals and the fact that some COCs are resistant to oxidation. Additionally there is potential for process-induced detrimental effects.

Cost:

No costs figures are currently available.