

## Selecting Chemical Reagents for Green Remediation of Organic Contaminates

By

Laura J. Gimpelson, P.E.  
LG Environmental Engineering

The reagent selection process is mainly dependent on the contaminants present and the type of destruction process you wish to use. Once these two parameters have been identified, secondary issues such as health and safety concerns, permitting requirements and cost will narrow the choices to a preferred reagent and an alternative reagent.

Petroleum plumes are effectively destroyed by oxidation or biodegradation reagents. Examples of oxidation reagents include peroxides (provided by ERFS, Geo-Cleanse, or MAX-OX) or permanganates (Carus Corporation, Univar or Continental Chemicals). Companies such as Adventus, Bioremediation, Inc., Regensis, or ETEC provide biological reagents customized to your site's requirements.

Chlorinated solvents are effectively destroyed by using strong oxidizers such as persulfates (FMC or CL Solutions), chemical or biological reducing agents (ETEC) or natural or lab created biological agents (EOS, Micro-Bac, Terra Systems, or SiRem).

Less common contaminants such as dioxanes and pesticides have been treated to below cleanup targets levels in other states by proprietary products provided by EN-Rx, BIOX and Verutek.

Choosing the specific reagent depends on personal preference and secondary issues such as availability, possible cross-contamination, safety requirements and cost. At a site with a relatively shallow petroleum plume covering up to 12,000 square feet, hydrogen peroxide or potassium permanganate destroys the petroleum contamination in a shorter time frame than biological reagents do. These two chemicals are readily and cheaply available from chemical supply firms since neither is a proprietary or patented reagent.

However, these two chemicals generate inert gases and heat during the destruction process that could adversely affect the surface. Hydrogen peroxide obtained at typical commercial concentrations requires special handling permits from the TSA. Permanganates can turn the groundwater pink and add trace metals above their specific cleanup target level.

In addition, the naturally occurring chemicals in the soil and groundwater can react with these two chemicals before the oxidizers react with the plume. Due to their oxidizing potential, additional safety procedures are needed to prevent harm to human health and surface features during the storage, mixing and injection processes.

Biological reagents can be tailored to react only with the petroleum plume and more readily destroy the portion of the plume that has traveled down a utility corridor. Their slow reaction rate allows the injected reagents to form a barrier that can reduce the potential for off-site cross contamination.

The downside to using biological reagents is that the subsurface conditions may not support the biological degradation process without adding supplemental additives. The timeframe to reach the cleanup target level can be twice as long as the oxidation timeframe.

As the petroleum plume expands horizontally and vertically, a mix of oxidizers and biological reagents (bugs) should be used. The primary reagent is still the oxidizer especially in the source area with the

biological reagent used to treat the off-site portion of the plume or establish a barrier to minimize cross-contamination.

The oxidizers and bugs can be injected using the same injection system but on a different timeline. The oxidizing reagents are injected first and then every 90 days. The bugs should be injected 30 days after injecting the oxidizers to allow the aquifer water quality to stabilize. This injection schedule should be followed as needed until cleanup target levels are reached.

Using chemical injection to destroy chlorinated solvents balances quick destruction with unwanted side reactions. If naturally occurring bugs are present, enhancing the naturally occurring biodegradation of chlorinated solvents is preferred to using chemical dechlorination reagents.

Several companies provide bugs or other biodegradation additives that reduce the solvents to inert salts and gases. The supplemental bugs die off as they are consumed in proportion to the decrease in solvent and daughter product concentrations until cleanup target levels are reached. A pilot test is needed to provide optimal site-specific formulas, cost, and timeframes to reach cleanup target levels.

If the naturally occurring bugs are not present or biodegradation using lab-created bugs cannot destroy the plume, chemical dechlorination reagents should be used. Activated sodium or potassium persulfates destroy chlorinated solvents through reductive dechlorination but can increase sulfate, sodium and other trace metals concentrations above cleanup target levels.

Since the persulfates are strong corrosive chemicals before being activated, detailed safety plans and reviews are needed to minimize damage to the injection equipment during the injection step or to the local environment if a leak or spill occurs. Activated calcium persulfates can be used to minimize safety issues and addition of unwanted trace metals but limited case studies are available for review.

If caustic is used as the persulfates' activation chemical, the pH of the injected solution can create a corrosive aquifer, damage the injection equipment or increase the generation of anaerobic biological solids that clog recirculation or injection systems. If peroxides are used as the activation agent, the clogging is reduced but the chemicals can start reacting with the injection system equipment before the injected chemicals reach the contamination plume.

My preference is to use biological or food grade reagents whenever possible. Naturally occurring and sterile lab-grown bugs work well under the right aquifer conditions and within FDEP timeframes to destroy petroleum and chlorinated compounds. Unwanted byproducts or trace compounds are not a problem and there is minimal handling of hazardous products.

My next choice is peroxides, which can destroy most organic compounds but are more effective in destroying petroleum compounds especially within a short timeframe. As an added benefit, peroxides increased the dissolved oxygen concentrations that the naturally occurring petroleum destroying bacteria need to grow and multiply. Unwanted byproducts or trace compounds are not a problem but there are safety concerns in handling the peroxide solutions and dealing with an exothermic reaction.

Persulfates are preferred chemicals for destroying chlorinated solvents but need an activation agent to destroy the chlorinated solvents. Peroxides can act as the activation agent while minimizing the growth of anaerobic bacteria but will create an aerobic aquifer that can slow the reduction dechlorination process. Caustic is a more aggressive activation agent but has potential to introduce unwanted trace metals into the aquifer, increase generation of materials that clog equipment, and create safety issues during the injection process.

Selecting the reagent or reagents to use depends on technical and non-technical issues. Reviewing both will allow you to select a preferred choice for the client to approve.

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