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# Enhanced Reductive Dechlorination

## It's A Matter of Give and Take

When scientists evaluate how to best cleanup groundwater that has been contaminated with chlorinated solvents, such as perchloroethylene (perc) from a drycleaner or trichloroethene from a manufacturing facility, the option of in situ treatment is considered. If the subsurface conditions are favorable, in situ (or in-place) remediation can have a lot of advantages to other remedial alternatives.

One of the most common in situ approaches is the use of bioremediation and reductive dechlorination. The advantages to using in situ bioremediation or reductive dechlorination technology are that a liquid can be injected into the subsurface using a small drilling rig while there is minimal business interruption. There is no need for an active treatment system involving a trailer or stationary shed with electrical pumps, compressors and treatment tanks. There is no trenching for conveyance lines and electrical wires. There are no costs for routine operation and maintenance, electrical power, or monitoring telemetry. Other advantages to using in situ bio-remediation are that the product is relatively inexpensive, readily available and it is safe and easy to handle. In situ treatment is particularly favorable when remediating a contaminated groundwater plume that has migrated away from the Site where the release occurred.

The bacteria that are involved in the biodegradation of chlorinated hydrocarbons in the subsurface are chemotrophs (bacteria that derive their energy from chemical redox reactions) and use organic compounds as electron donors and sources of organic carbon (organoheterotrophs). This naturally occurring process termed "reductive dechlorination" can occur when naturally occurring microbes dehalococcoides ethanogenes or dehalobacter are present in the groundwater under the correct geochemical conditions. These microbes strip chlorine atoms from the chlorinated solvent double carbon bonded molecule, replacing it with a hydrogen atom, creating daughter products. If the starting chlorinated solvent is perc or perchloroethylene (also known as tetrachloroethane), which hosts four chlorine atoms, and one chlorine atom is removed; trichloroethene

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is produced. Trichloroethene (three chlorine atoms) breaks down into dichloroethane (two chlorine atoms), which breaks down into vinyl chloride (one chlorine atom). When the final chlorine atom is removed from the vinyl chloride, the end point molecule is non-toxic ethane.

The dechlorinating microbes require two things to complete the reductive dechlorination reaction: electron donors (food) and electron acceptors (something to breathe). Electron donors typically consist of a carbon source that release hydrogen atoms, both natural and anthropogenic. Electron acceptors consist of naturally and commonly occurring molecules such as dissolved oxygen, nitrate, iron (as non dissolved species), sulfate and carbon dioxide that accept electrons and become a metabolic by-product (different chemical). Chlorinated solvents are also electron acceptors as they accept hydrogen atoms and expel chlorine.

To understand if your site is suitable for in situ bio-remediation and reductive dechlorination, the groundwater has to be analyzed for concentrations of key chemical parameters and bacterial population. Such chemical parameters include the concentrations of Chlorinated Aliphatic Hydrocarbons (CAHs) and daughter products (e.g. Perc, TCE, cis-DEC, vinyl chloride), oxygen content, pH, redox potential, iron, sulfates and nutrient concentrations. These parameters provide information about the baseline contamination and water quality at the site, to support biodegradation, and whether and how much intrinsic biodegradation (without enhancements) may be occurring at the site. Bacterial analysis further assists in assessing the potential for reductive dechlorination. Redox potential is being monitored to determine whether the subsurface environment is more reducing or more oxidizing.

There is a natural order in which the electron acceptors are used up in the microbial process. This order is shown as follows in order of increasing advancement (increasing reductive/anoxic conditions):

· Dissolved oxygen is depleted
· Nitrate is depleted
· Ferrous iron (non dissolved) is depleted
· Sulfate is depleted
· Carbon dioxide is depleted
· Chlorinated solvents begin to be depleted when sulfate reduction begins

When these processes are occurring, metabolic by-products are produced:

· Aerobic respiration of dissolved oxygen produces carbon dioxide
· Denitrification of nitrate produces nitrite
· Iron (III) reduction produces iron (II), which is soluble
· Sulfate reduction produces hydrogen sulfide; conditions are correct for solvent reduction
· Carbon dioxide reduction is caused by methanogenic bacteria triggered by highly reducing conditions and produces methane; conditions are optimal for solvent reduction

Commonly, solvent plumes are remediated utilizing this biogeochemical process; however, in most cases the microbes have the electron acceptors but not the electron donors (carbon source/food). Enhanced Reductive Dechlorination is accomplished by adding a carbon source to the saturated media that provides a means to complete the reductive dechlorination process in an expedited time frame.

These electron donors are typically a carbon source that must be introduced into the contaminated aquifer to act as a substrate and a food and energy source for the bacteria. During the microbial metabolic process, the carbon source is fermented releasing hydrogen, which acts as a preferred electron donor and bacteria reduce electron acceptors such as Chlorinated Aliphatic Hydrocarbons resulting in release of chlorine atoms. The carbon source can be any number of products from commercially made specialty products to commercial grade corn syrups, molasses, vegetable oil and even cheese whey.

While and before Enhanced Reductive Dechlorination is implemented, there are parameters that should be measured to determine the state of the biogeochemical system. They are as follows with rationale for collection:

· Dissolved oxygen - DO is toxic to the microbes that dechlorinate contaminants. Also, if results are lower than baseline sampling, aerobic respiration is occurring, which is the first of five target reductive states.
· Nitrate and Nitrite (individual, not combined) - If results are lower than baseline for nitrate or if nitrite is elevated, denitrification is occurring, which is the second of five target reductive states.
· Dissolved iron - This is the measure of iron (II), the reduced valence state of iron (iron III is the oxidized state). Iron (II) is soluble, iron (III) is not. If dissolved iron is detected, iron reduction is occurring, which is the third of five target reductive states.
· Sulfate - If results are lower than baseline, sulfate reduction is

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occurring, which is the fourth of five target reductive states. This also indicates correct conditions for reductive dechlorination.

· Methane/Ethane/Ethene - If methane results are elevated compared to baseline sampling, methanogenesis is occurring, which is the fifth and final of the target reductive states. This indicates optimal conditions for the reduction of chlorinated solvents. Ethane is the endpoint of the reductive dechlorination process. Detection of elevated ethane indicates replacement of all chlorine atoms on the molecule with hydrogen and the dechlorination is reaching finality.

· Biological Oxygen Demand - This parameter collected in the baseline sampling and in subsequent sampling will determine how much bioavailable carbon is present in the water. Bioavailable carbon is a measure of food available to the microbes. This parameter should elevate upon injection of electron donors (carbon source).

· Field parameters - DO/ORP/pH. These parameters are common parameters collected during routine groundwater sampling and help in understanding the pre and post remediation groundwater conditions. DO (as above). Oxidation Reduction Potential (ORP) is a rough measure of REDOX intensity. A negative ORP value indicates reductive conditions.

· Chloride - Chloride concentrations increase in groundwater as they are broken free from the chlorinated solvent molecule during dechlorination.

· Microbial Analysis (DHC) – This is a measurement of population of a specific group of microbes before and after the introduction of the carbon source. An increase in population is expected. The population can and should be analyzed by the individual genome groups that indicate that the correct strains of the microbe are there to push the dechlorination process to completion. Sometimes the population of microbes is low enough during baseline testing that microbes must be added to the groundwater with the electron acceptors.

In summary, in situ bioremediation and enhanced reductive dechlorination is an attractive remedial technologies because as a thick solution can be injected into the contaminated groundwater plume and the chlorinated solvents within the plume will degrade and breakdown. In situ bioremediation will not require a fixed or trailer mounted treatment system and will not require trenching, installing conveyance lines or long term Operation and Maintenance. The key is keep the groundwater anaerobic by reducing the oxygen content. Tests of the ambient water quality should be conducted in order to determine how much carbon source will need to be added to keep the groundwater in an anaerobic state. The transmissivity of the aquifer will need to be evaluated to ensure that a carbon source can be injected into the aquifer and to ensure the groundwater will come into contact with the carbon source, which will create the anaerobic environment. The groundwater will need to be monitored for the key parameters to ensure that it remains anaerobic or to determine when and if additional carbon source needs to be injected into the aquifer. The groundwater quality will also need to be monitored to determine the degradation of the volatile organic compounds.

***With 30 years of experience, Steve Henshaw holds professional geology registrations in numerous states. As President and CEO of EnviroForensics, Henshaw serves as a client and technical manager on projects associated with site characterization, remedial design, remedial implementation and operation, litigation support and insurance coverage matters. He has acted as Project Manager or Client Manager on several hundred projects. Henshaw has built a leading edge environmental engineering company that specializes in finding the funding to pay for environmental liabilities. By combining responsible party searches with insurance archeology investigations, EnviroForensics has been successful at remediating and closing sites for property owners and small business owners across the country, with minimal capital outlay from clients.***

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