ORC TECHNICAL BULLETIN #2.2.2.3

Oxygen Release Compound, ORC®

Remediation of Vinyl Chloride

Vinyl Chloride and ORC

Vinyl chloride (VC) is a common groundwater contaminant usually associated with higher order chlorinated aliphatic hydrocarbons (CAHs) such as perchloroethylene (PCE), trichloroethylene (TCE), and dichloroethylene (DCE). The presence of oxygen stimulates the degradation of vinyl chloride and is the basis upon which ORC has been shown to effectively treat this contaminant.

### Aerobic Metabolism of Vinyl Chloride

The metabolism of vinyl chloride in the presence of oxygen may proceed via two possible mechanisms. In one pathway, VC serves as a primary substrate for oxygen-dependent microbial growth and is degraded completely to carbon dioxide and water (Davis and Carpenter, 1990). This process occurs intracellularly and unlike co-metabolic (aerobic) remediation, no oxygenase-inducing compounds, such as methane are required for VC metabolism in this oxidative pathway. The use of ORC can thus stimulate vinyl chloride degradation without any additional treatment amendments or technologies.

The direct, intracellular metabolism of vinyl chloride proceeds via oxidation to an intermediate compound (chlorooxirane) which ultimately degrades to carbon dioxide and water (Hartmans and DeBont, 1992). The chlorooxirane, an unstable epoxide intermediate, degrades further into various fragments (such as formic acid and oxyglycolic acid) which, in turn, are transformed to CO_2 and H_2O. This results in a net energy benefit to the microbe. The proposed mechanism of intracellular aerobic metabolism of VC is illustrated in Figure 1:
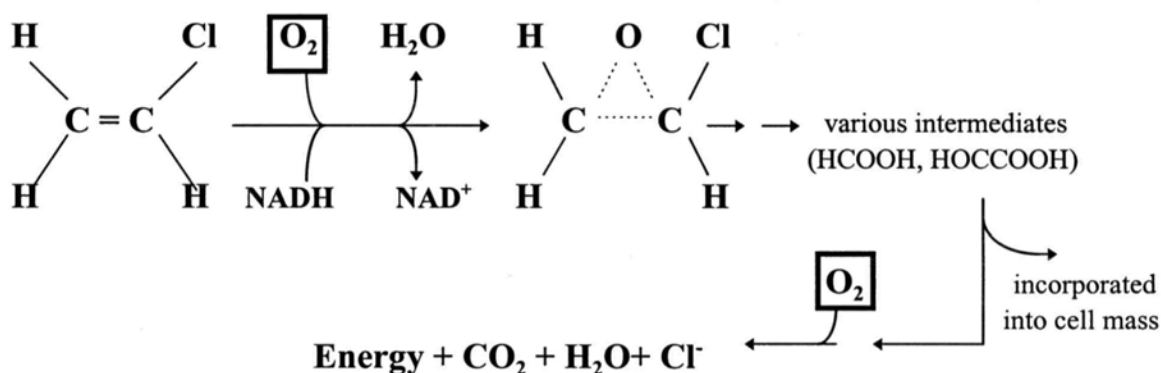
Figure 1: VC intracellular degradation pathway: Net energy benefit to degrading organism.

Others have suggested a second possible pathway that involves methanotrophs capable of destroying vinyl chloride extracellularly through co-metabolism (McCarty, 1994). In co-metabolism, the formation of the chlorooxirane intermediate requires an enzyme-inducing substrate (in this case methane) that is apparently not required in intracellular aerobic VC metabolism. When co-metabolic VC degradation occurs, methanotrophs produce oxygenases, for example methane monooxygenase (MMO), that leak out of the cell and fortuitously degrade VC extracellularly with no net energetic benefit to the microbe. This co-metabolic degradation pathway may proceed according to the reactions shown in Figure 2:
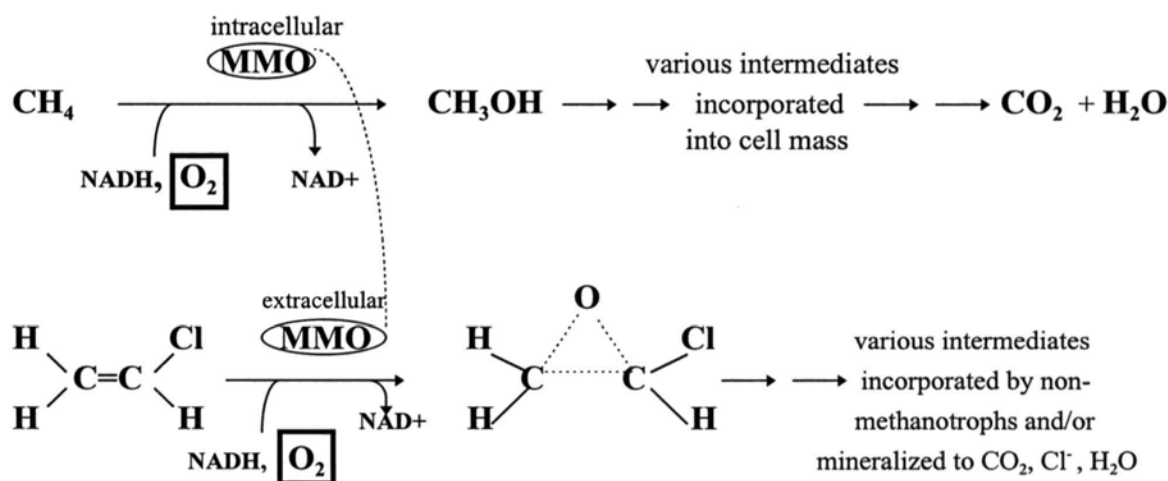
Figure 2: VC extracellular, co-metabolic degradation pathway: No net energy benefit to MMO producing methanotroph.

Both of the proposed mechanisms of VC biodegradation are oxygen-demanding processes that will benefit from ORC treatment. In addition to the requirements of aerobic respiration, oxygen plays an integral role in both intracellular and extracellular enzymatic reactions. The application of ORC can thus aid in the sustenance of the relevant microbial populations and enhance the rate of aerobic dechlorination of vinyl chloride.

ORC Treatment of Vinyl Chloride

Results from controlled laboratory studies and field applications support the ability of ORC to effectively enhance the biodegradation of vinyl chloride.

1. In a recent study conducted on groundwater and soils from an industrial site, VC was shown to degrade very rapidly ($T_{1/2}$ = 5 days) with ORC addition as the only applied treatment technology (Bell, P. et.al, 1997).

2. In another field demonstration of ORC conducted on a New York State Superfund site, ORC treatment resulted in significant degradation of vinyl chloride (Martinovich and Putscher, 1997; see also TB 3.1.1). Concurrent laboratory studies corroborated the field results using materials from the site.

3. At an industrial site in Massachusetts, project engineers sought to remediate chlorinated compound contamination in the property's groundwater. Treatment options were confined to the following limitations: the treatment was to be non-invasive and operate within limited available space; facility operations were to remain undisturbed; all possible air and water (both surface and subsurface) health hazards were to be considered and monitored for exposure to contamination. The particular remediation objectives of this site prompted project engineers to design an inventive dual phase strategy to remediate chlorinated compounds *in situ.* The strategy is engineered as follows:

   💧 A groundwater recirculation system extracts water from three wells and re-injects the water into three injection wells upgradient:

   💧 **Phase one:** addition of organic acids stimulates anaerobic conditions in the recirculation system, allowing microbial dechlorination of highly chlorinated compounds (PCE, TCE, DCE).
   💧 **Phase two:** ORC socks are placed in an injection well to generate *aerobic* conditions and bacteria begin to degrade the vinyl chloride that accumulates in phase one.

   💧 Preliminary results indicate that vinyl chloride concentrations decreased as dissolved oxygen levels increased.
   💧 During the aerobic phase, the co-metabolic substrate methane was also introduced into the system. Addition of methane further accelerated degradation of vinyl chloride.

These results suggest that both of the possible metabolic processes for aerobic vinyl chloride degradation may be occurring simultaneously within this system.

As of early 1997, ORC has been applied to degrade VC at several sites across the U.S. This passive approach to remediation of chlorinated compounds presents a cost-effective method of treating both leachate contaminated landfills and industrial solvent contaminated sites. Investigations to further establish the role of ORC in vinyl chloride biodegradation are currently underway.

ORC Installation Design Parameters

The theoretical mass ratio of oxygen to vinyl chloride required for the aerobic metabolism of VC is relatively low at 1.3:1. Thus, for every pound of vinyl chloride to be degraded, at least 1.3 pounds of oxygen are required.

The sorption coefficient (K_{oc}) for vinyl chloride is 57 (ml/g), indicating that its tendency to sorb to the aquifer matrix is approximately equal to that of benzene (K_{oc} = 83 ml/g). Therefore, in ORC application designs, when using dissolved vinyl chloride data from groundwater samples one can use additional demand factors usually associated with BTEX remediation projects as an acceptable approximation.

References

Bell, P., K Casper and P. McIntire. 1997. Treatability Evaluation of In-Situ Biodegradation of Chlorinated Solvents in Groundwater. Proceedings from Air & Waste Management Association 90th Annual Meeting & Exhibition. Toronto, Canada.

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