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## **APPLICATION OF TIME RELEASE ELECTRON DONORS AND ELECTRON ACCEPTORS FOR ACCELERATED BIOREMEDIATION**

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### **ABSTRACT**

Currently, there are limited options for cost effective approaches to soil and groundwater contamination. One technology that has proven its potential involves the use of time release electron acceptors to accelerate the natural bioattenuation of aerobically degradable compounds and time release electron donors to accelerate the natural bioattenuation of anaerobic compounds. This technology enjoys its reputations as a sensible strategy for engineering accelerated bioattenuation, because it delivers results while 1) limiting or eliminating design, capital and management costs and 2) allowing for the engineering of a low-impact application and a subsequently invisible remediation process. Oxygen Release Compound (ORC<sup>®</sup>) is proprietary formulation of intercalated magnesium peroxide that releases oxygen slowly, for about a year, and facilitates the aerobic degradation of a range of environmental contaminants including petroleum hydrocarbons, certain chlorinated hydrocarbons, ether oxygenates and nitroaromatics. The history of ORC's introduction and acceptance represents a model for the evolution of an innovative technology. This statement comes by virtue of the fact that since 1994 ORC has been used on over 7000 sites worldwide and has been the subject of an extensive body of literature. Hydrogen Release Compound (HRC<sup>®</sup>) is also a proprietary polylactate ester that is food grade and, upon being deposited into the aquifer, is slowly hydrolyzed to release lactic acid and other organic acid derivatives for about one to two years. The organic acids are fermented to hydrogen, which in turn donates electrons that drive reductive bioattenuation processes. This is primarily directed at a wide range of chlorinated hydrocarbons, but can be applied to the remediation of metals by redox induced precipitation. HRC has now been used on over 220 sites, which we believe make it the most widely used electron donor for accelerating bioattenuation. ORC and HRC can be configured as a permeable reactive barriers, applied as a broader plume treatment or emplaced post-excavation as part of the back-fill. Many of these operations can be facilitated by commonly available push-point injection technology and these operations are well established. Also, it has long been suspected and is now known that bioremediation can facilitate

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desorption of residual, sorbed phase contamination. The role of ORC and HRC in facilitating this process has also been established.

Key words: contamination, bioremediation, electron acceptors, acceleration

### **Introduction to the Technology: The Chemistry**

Bioremediation has become a widely accepted protocol for the management of contaminated sites. One of the critical variables in the bioremediation process, whether natural or engineered, is the “electron status” of the system. The presence of electron acceptors is required for aerobic biodegradation and conversely, the presence of electron donors are required for anaerobic degradation.

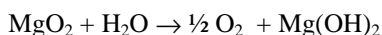
In engineered systems the rate of supply of these electron acceptors or electron donors can be an important variable in achieving cost effective remediation. An example of a commercially available time-release electron acceptor is Oxygen Release Compound (ORC<sup>®</sup>) and an example of a commercially available time-release electron donor is Hydrogen Release Compound (HRC<sup>®</sup>).

The following is a review of the chemical technology and engineering applications. Also, field performance is summarized herein and select examples (1-30) are referenced. In addition, numerous publications relating to field performance are available at [www.regenesis.com](http://www.regenesis.com).

#### *ORC:*

ORC is a source of oxygen, and oxygen is an electron acceptor - meaning that oxygen sits at the bottom of the mitochondrial electron transport chain and catches or accepts the “spent” electrons from contaminant molecules that are being degraded by microbes for energy and raw materials. A variety of oxygen containing compounds, specifically peroxides, can serve as time release electron acceptors, however, ORC is a proprietary formulation of magnesium peroxide that releases oxygen very slowly when hydrated.

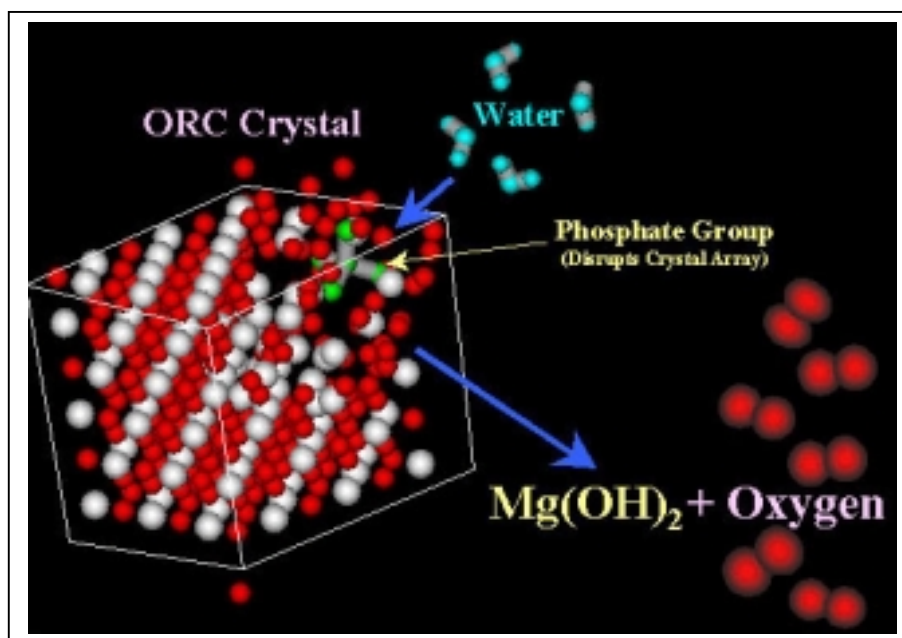
ORC is insoluble and releases its oxygen while being converted to ordinary magnesium hydroxide, which is also insoluble, in accordance with the following reaction:



Both magnesium peroxide and magnesium hydroxide are environmentally benign and actually safe enough to ingest. In fact, they are both recognized as medicinal antacids - the more common one being magnesium hydroxide, also known as Milk of Magnesia.

ORC is not simply magnesium peroxide, but rather a patented formulation of the compound intercalated with food-grade phosphate ions. This gives ORC the time-release properties that are critical in a passive, low-cost oxygen application system. The term intercalation defines the fact that the phosphates permeate the magnesium peroxide crystal, partially inhibiting the transmission of water into the structure. Controlling the rate of hydration of the crystal affects a “timed” oxygen release. The concentration of phosphate, and the manner in which it is reacted with and permeates the magnesium peroxide crystal, creates a product that is well matched to the needs of subsurface remediation. Finally, intercalation facilitates the release of all the oxygen by keeping a “hydroxide rind” from sealing up

individual particles during the hydration reaction. Intercalation also increases shelf life stability; ORC can be stored for several years without risking significant product degradation. Figure 1 illustrates intercalation and the reaction dynamics.



**Figure 1. ORC – An Intercalated form of Magnesium Peroxide**

Remediation experts, looking for a long-lasting oxygen source without incurring the cost of having to install continuous oxygen injection systems, or having to return to the field for multiple re-injections of other oxygen releasing chemicals that do not have slow-release capabilities, have employed ORC. ORC has been actively used for about 6 years and to date has been applied at over 6,500 sites in 50 states and 12 countries.

The ORC technology melds the intercalation concept with electron acceptor chemistry. We can therefore characterize the status of this technology as the development of a time-release electron acceptor for engineered, accelerated bioattenuation. This technology is a useful strategy insofar as the aquifer microorganisms involved in bioremediation are not present in very high numbers, in comparison to other environments, and they are often challenged with only a very small mass of contaminant fluxing through the system. Consequently, only a small amount of electron acceptor is necessary to drive bioremediation – but it must be present on a constant basis.

The first applications of ORC were for the treatment of benzene, toluene, ethylbenzene, and xylenes (BTEX) and other light petroleum hydrocarbon fractions. Use has now expanded to the treatment of heavier fractions such as heating oil and some of the polyaromatic hydrocarbons (PAHs). More recently, ORC has been used to bioremediate the highly mobile and problematic gasoline oxygenate methyl-tert-butyl-ether (MTBE) and has been applied to sites impacted with chloroaromatics, nitroaromatics and some of the lower-order chlorinated hydrocarbons that can be treated aerobically—most notably DCE and vinyl chloride.

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With regard to the lessons that have emerged from 7000 applications of ORC, a high level of success has been achieved at most sites when the site conditions are adequately understood and a proper design can be implemented. At one point, earlier in the technology development and roll-out process, the first thousand or so sites were implemented directly with Regenesys' oversight and 600 of those projects were subsequently tracked. In this population there were reports of 20 full technical failures – a rate of 3%. In a full technical failure we are referencing the complete inability for an ORC application to impact contamination at a site.

At present, many of the ORC applications are “automatic”, such that orders are received, product is shipped and the consultant is self-sufficient in the application either from past experience or through guidance from published information or the Regenesys web site. Consequently, no further efforts have been made to look at this metric of performance, however, 600 sites is a large population set and the 3% figure can be considered to be a fairly representative number. Also, there were lessons learned as to the reasons for the failures and, although it is low in comparison to other technologies, it was possible to implement these lessons to future customers. Therefore, if anything the rate full technical failure has probably decreased slightly and one marker of this is that we see very few customer complaints in this category. So, what were those lessons learned with regard to outright technical failures?

Technical failures, when they arise, can be classified as “intrinsic” and “non-intrinsic”. Intrinsic problems are related to conditions on the site that are independent of proper characterization of contaminant concentrations and locations. These are rare events and are essentially traced to very high levels of dissolved iron or natural organic matter in the system, i.e., unmanageable COD/BOD. Non-intrinsic problems are related to any one of a number of issues related to poor site characterization, such as unidentified and unremoved sources, poor understanding of groundwater flow dynamics and in rare cases a limiting biological and chemical background in the aquifer.

There is another class of problems that involve limited performance and we can classify those sites as having technical difficulties. This is invariably related to rebound and is often tied to a single application of ORC. Rebound is normally quite manageable with additional applications of ORC and, due to the low cost of an ORC treatment, even multiple applications if necessary can still be economically feasible with regard to the next available technology. The nature of rebound and its manageability is governed by the status of non-dissolved contamination, e.g., the nature of the source. Simple hydrophobically sorbed materials are highly manageable, whereas residual sorbed material (smear zone NAPL) is somewhat manageable as a function of total mass in the system, rates of desorption and availability and application rates of ORC. Free-product conditions are essentially beyond the scope of ORC to control.

On the use of ORC to manage plumes with rebound the following are some additional considerations. On sites with rebound it may take a while for a plume to regenerate and when it does it will be with less “vigor” than the previous event. In this circumstance a reasonable goal can be the pursuit of equilibrium between the rate of desorption and the rate of natural attenuation. Given the fact that many plumes are stable and shrinking, the objective of the clean-up exercise should be to work with this fact and strive to accelerate the process to a practical endpoint i.e., risk reduction. Investigations on several sites indicate give us a rough quantitative estimate with regard to the extent of accelerated natural attenuation upon application of ORC. In a range of 1X, representing no result, to

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1000X, representing extreme stimulation of a stalled anaerobic environment, applications of ORC will accelerate natural attenuation on average by a factor of 10X.

ORC has also proven to be a low cost diagnostic tool in that if it is applied and there is no or little response it means two things. The first is that a plan to rely on Monitored Natural Attenuation (MNA) is probably flawed, such that if providing electron acceptor is a futile exercise then how or why would one chose a severely open ended MNA approach. Secondly, such results would govern the choice to use more heroic modalities for clean-up at an earlier and more cost effective stage. It follows that success with ORC applications would evolve into a very sensible and economic site management strategy.

### *HRC:*

HRC is a source of hydrogen, and hydrogen is an electron donor – meaning it can provide required electrons that facilitate the degradation or “reduction” of certain contaminants like chlorinated hydrocarbons. The term reduction means that electrons, carrying a negative charge, are being added; the contaminant is reduced and the electron donor is oxidized. In aerobic reactions, such as with ORC, the contaminant is actually the electron donor (e.g., benzene, which gets oxidized) and oxygen is the electron acceptor (becomes reduced). In HRC, the electron acceptor can actually be the contaminant itself—most commonly a higher-order chlorinated hydrocarbon such as perchloroethylene (PCE) or trichloroethylene (TCE).

By example, we can look more closely at the microbially mediated, sequential destruction of chlorinated hydrocarbons such as PCE and TCE. This essentially translates to the removal, under anaerobic conditions, of various numbers of chlorine atoms from the molecule until it is rendered either benign or aerobically degradable, whichever comes first. Starting with PCE which has four chlorine atoms, if there is a source of electrons, under the right chemical and biological conditions, PCE is reduced to TCE (three chlorines), then to dichloroethene (DCE) (two chlorines), and then to vinyl chloride (VC) (one chlorine). The VC is still toxic and must then be reduced to the chlorine-free ethene skeleton that was originally filled with the four chlorines. The reactions from DCE on down can occur under both anaerobic and aerobic conditions. Usually the HRC application is enough, but sometimes a switch to ORC would be warranted.

Reductive dechlorination describes the anaerobic phase of the mechanism just described and can often bring the molecule to its full dechlorination. In reductive dechlorination, anaerobic microbes substitute both electrons and hydrogen for the chlorine in the molecule. In other words, hydrogen resulting from the breakdown of HRC serves as an electron donor, and the electrons are required to dechlorinate the contaminants.

HRC itself has as its active ingredient a proprietary, environmentally safe, food quality, polylactate ester specially formulated for the slow release of lactic acid upon hydration. The lactic acid is important because it produces hydrogen. Many organic substrates can serve as sources of hydrogen through fermentation reactions; however, lactic acid and related organic acids are some of the best substrates for reductive dechlorination.

Esters are compounds that are formed in a reaction between an organic acid and an alcohol. In this reaction a molecule of water drops out (condensation reaction), forming the ester linkage. When the water re-enters the molecule at the ester linkage (hydration), the alcohol and acid can separate once again. Glycerol polylactate, or GPL, is a polylactate ester in which the lactic acid, or in this special case a proprietary lactic acid complex, is esterified to an alcohol. In GPL, glycerol is used as the “alcohol backbone,” although historically

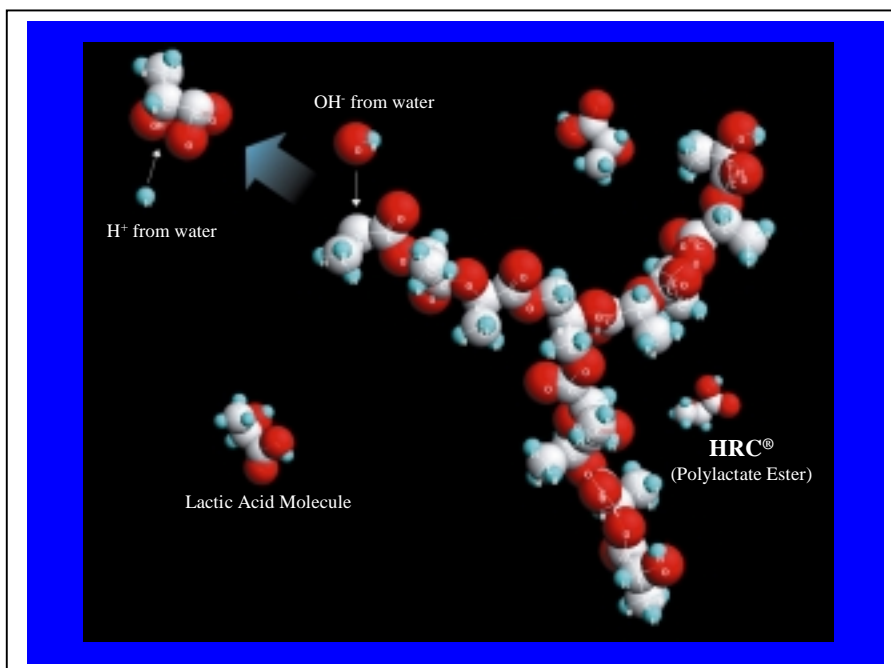
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sorbitol also has been used. Technically HRC contains glycerol polylactate ester or GPL, but early publications also make reference to SPL, which is the acronym for sorbitol polylactate ester.

One of the unique features of the polylactic acid complex is that lactic acid is esterified to itself. This is possible because lactic acid has both an OH and a COOH group. As a result tetramers of lactic acid and create a “polylactic acid complex” or “polylactate complex”, which is in turn esterified to the foundation OH donor as described. A representation of GPL is given in Figure 2.

A variety of organic substrates can serve as electron donors, what is necessary is that they be “fermentable” to hydrogen. However, not all fermentable substrates are created equal. Many issues such as longevity, efficiency and solubility need to be taken into account. HRC is a unique formulation of glycerol polylactate and has many of the desirable features just mentioned.

With respect to lessons learned we are somewhat earlier in the process with HRC than with ORC. At this writing, HRC has now been used on over 220 chlorinated hydrocarbon sites; which we believe make it the most widely used electron donor for bioattenuation. In fact, based on the condition that there are about 80 molasses applications and about half-that many applications of all other electron donors such as sugar, oils and biomass, we can say that more HRC has been applied as an electron donor than all other electron donors combined.



**Figure 2. Glycerol Polylactate – the Active Ingredient in HRC**

Of these applications, 42 were mature enough to be evaluated at this writing. From among these there were 9 sites that displayed exceptional results, defined as demonstrating very rapid and complete dechlorination (Type A). At 22 sites results are very positive,

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displaying accelerated degradation rates with varying degrees of daughter product formation depending on the age of the data set (Type B). Finally, 9 sites show moderately accelerated or mixed rates of dechlorination with varying degrees of daughter product formation depending on the age of the data set (Type C), and 2 of the sites were not responding at all after a single application (Type D).

There are a number of studies in the literature, and which have been presented at conferences, that indicate reductive dechlorination can “slow-down” at DCE during bioremediation efforts. This trend is reflected in the data summary presented above. The following should be considered as factors that may act alone or in combination and a “solution” to the problem in each case is offered.

*More Time Needed:* The data presented is based on sites that were between 3 months and 2 years old with an average age of about 9 months. Based on HRC longevity of a year or longer, on many of the sites there is still “reducing power” available. In a major government undertaking, funded by ESTCP, the RABITT protocol was developed. The protocol was a treatability test for evaluating the potential applicability of the Reductive Anaerobic Biological In-Situ Treatment Technology. One of the reports states that assuming 1 month for electron acceptor depletion, 2 months for acclimation and 3 months for treatment, the total time required for a RABITT treatability test under ideal conditions would be 6 months. Realistically, significant reductions of all chloroethenes, including VC, at full-scale could take several years”. Solution: Give the system more time to react and add more electron donor if economically feasible relative to alternatives.

*Desorption and Kinetic Disparity:* Basically DCE and VC degrade more slowly under anaerobic conditions than parent materials. This is why they accumulate. This can actually be a positive sign, especially when the levels of DCE and VC actually exceed the levels of their sources – because it points to the fact the desorption may be in process. The hypothesis is that DNAPL is being desorbed and is degrading relatively instantaneously as it slowly becomes available. As a result, the intermediates with slower degradation rates will keep escalating – while an increase in the parents from the source being removed is not apparent. In essence, a combination of stimulated desorption and kinetic disparity can account for the observed accumulations of DCE and VC. Also, the fact that sorption decreases and solubility increases as one goes down the daughter product sequence will also contribute to the elevated daughter product concentration in a water sample. Solution: Add more electron donor if economically feasible. If the system is completely recalcitrant as a function of excess mass, the relatively low-cost HRC treatment can be seen in retrospect as having been a sensible diagnostic tool. In essence, if natural attenuation cannot be accelerated to a point that is acceptable in a short-term electron donor mediated process, a course of monitored natural attenuation could be criticized.

*Accumulation of Dissolved Iron:* When an aquifer is reduced it can generate elevated levels of dissolved iron ( $Fe^{++}$ ). This in turn can “block” DCE biodegradation from a free energy perspective. In examining a number of Regenes data sets, which is the focus of paper by Patrick Evans of CDM (Evans and Koenigsberg, 2001), the theory gained further support and it was also shown that the blockage is more often than not a transient phenomenon. Solution: Wait for the dissolved iron to drop and for DCE and VC degradation to accelerate – a phenomenon which, as stated, has been observed frequently. Also, it is important to note that DCE and VC can be degraded four ways (anaerobic, co-metabolic, anaerobic oxidative and aerobic), in comparison to TCE which only goes the first two ways and PCE which only goes the first way. Therefore, turning PCE or TCE into the intermediates increases the possibilities for degradation even if the rates may slow down.

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Finally, if feasible, the system can be converted to aerobic conditions for degradation DCE and VC at faster rates.

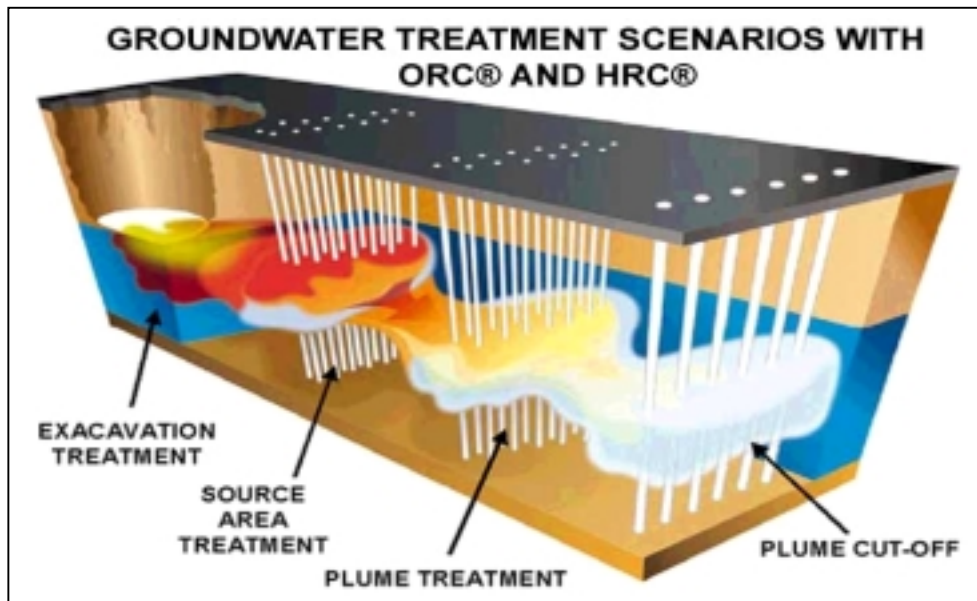
*Need for Specific Microbial Degraders:* A recent theory that has gained some support is that certain microorganisms must be present to facilitate complete dechlorination. The focus of this effort is Dehalococcoides etheneogenes and related species and the theory holds that if they are not present in sufficient numbers that dechlorination will stall at DCE. Solution: Consider bioaugmentation as a solution if available gene-probe work indicates a microbial deficiency is present.

In summary, since oxygen is an electron acceptor and hydrogen is an electron donor, we can characterize the Regeneration strategy as the development of time-released electron donors and electron acceptors for accelerated natural attenuation. This technology is differentiated in that it can provide the optimum level of substrate (i.e., oxygen or hydrogen) on a constant basis. It really doesn't matter if the contaminant is the electron acceptor or the electron donor—as long as it is destroyed in the process

### **Introduction to the Technology: The Engineering**

#### *Methods of Product Delivery*

The availability of time-release electron acceptors and electron donors has a direct impact on the successful engineering of passive treatment systems rather than active treatment. Figure 3 illustrates some of the delivery options for the slow release compounds.



**Figure 3. Methods of Applying ORC or HRC.**



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## *ORC*

Since ORC is an insoluble powder, it can be packaged in socks composed of a specially designed filter fabric. These “filter socks” are contacted with contaminated groundwater via an array of wells or trenches. ORC is also mixed directly with water to form a slurry for permanent injection in the saturated zone. Finally, ORC can be used as a slurry or dispersed in powdered form for the in-situ or ex-situ treatment of soil. All of these methods help accelerate the natural bioremediation of aerobically degradable compounds.

The ORC can be installed as an “oxygen barrier” to create a permeable reactive barrier across a plume, thereby cleaning the groundwater as it passes through. A partial treatment, at lower cost, can significantly reduce contaminant mass and bring the control point of the plume back toward the source and reduce risk. An array of treatment points, in which ORC is injected or backfilled into borings, has also been shown to be an effective dissolved phase plume (source) treatment or a method of establishing a barrier. The points can be implemented with low-cost, small-bore, push-point or standard auguring technologies to achieve full remediation or risk reduction objectives. One option that has emerged is a reusable injection point that can generate even more cost-effective treatments. ORC powder or slurry is applied several ways into biopiles or into the floor of tank pit excavations. In the latter case, the objective is to address residual hydrocarbons and the recharge of new contaminated water into clean fill.

## *HRC*

HRC can be manufactured as a thick syrup that can be pressure injected using various direct-push technologies or as a very thick gel that can be used to implant borings or, when placed in canisters, applied to wells. Depending on site conditions, the liquid formula can facilitate anaerobic remediation for six months to a year or more, and the thicker gel can provide many years of continuous release. In either formulation, HRC can enhance the remediation of a variety of contaminants by providing a long-lasting, time-released hydrogen source. By increasing the amount of hydrogen in the subsurface, HRC significantly increases the rate of biodegradation.

When HRC is applied to an aquifer, the water can hydrate the ester linkage and separate the polylactic acid complex from the glycerol. The release of the polylactic acid complex is a moderately slow process depending on the size and nature of the microbial population in the vicinity of the HRC. Polylactic acid release is the first part of a multi-step slow-release hydrogen mechanism. When the polylactate complex is released, it takes even more time to be turned into individual lactic acid molecules. Then, when there is finally some free lactic acid, it can be fermented by indigenous anaerobic microbes. In the fermentation reactions, the lactic acid is converted to several other organic acids and produces hydrogen along the way. The resulting hydrogen can then be used by reductive dehalogenating microorganisms, which are capable of dechlorinating contaminants as previously discussed. Viscosities in a range around 20,000 cP are necessary for deposition into an aquifer, by direct injection or pumping into boreholes, however, buckets of higher viscosity materials (200,000 cP range) can be made pumpable using an ordinary hot water bath. These uncut materials can last about twice as long. Other formulations, which have been synthesized for experimental purposes, such as Sorbitol Polylactate (SPL) with a viscosity of 1,000,000 cP, have the potential for many years of longevity.

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## Passive Treatment Systems versus Active Treatment Systems

The various limitations of active mechanical solutions for *in situ* remediation, such as pump-and-treat or sparging, are well documented. The focal point should not be the limitations of these systems, but rather the merits of engineered bioremediation. Given that bioremediation is a viable option for the accelerated natural attenuation of contaminated sites, the following are some advantages of using slow-release compounds in performing this in a passive mode.

### *1. Low Capital, Design, and O&M Costs:*

Since the slow-release compounds are part of a passive, *in situ* approach, substantial design, capital, and operations/maintenance (O&M) costs are avoided. Actively engineered systems such as pump-and-treat or air sparging with soil vapor extraction are expensive, time-consuming, and often burdened with costly and extensive design considerations. Sometimes even the design costs alone of mechanical systems will approach or exceed the costs of an ORC or HRC treatment.

### *2. Environmental Safety:*

Besides oxygen, the only by-product of the reaction of ORC and water is magnesium hydroxide (Milk of Magnesia) and a trace of food-grade phosphate that can also serve as a nutrient. With respect to HRC, the ester simply degrades into two naturally occurring, safe compounds—glycerol and lactic acid, from which hydrogen is derived.

### *3. Minimal Site Disturbance:*

ORC and HRC offer the potential for *in situ* treatment without the requirement for aboveground equipment after initial injection, thereby allowing remediation without disrupting normal business or commercial activities. Applying these slow-releasing substrates to the subsurface is fast and easy. After application, there are no aboveground indications that the product has been applied because it works silently below ground. The disadvantages of visible and active systems are self-evident with respect to aesthetics, safety, and theft.

### *4. Safe Application and Treatment:*

The controlled rate of oxygen released by ORC avoids the potential hazards of hydrogen peroxide and Fenton's Reagent. With respect to hydrogen, the use of slow-release compounds prevents the over-saturation of water with hydrogen and subsequent off gassing. Hydrogen is an explosive gas and requires attention when used as a sparging gas—as well as in its subsequent transport and fate in the vadose zone.

### *5. Applicability at Difficult to Manage Sites:*

Slow-release compounds are ideal for sites where geological or physical conditions make active systems inappropriate. Particularly in clay soils, where pumping is difficult and sparging promotes channeling, the slow release of diffusible materials has advantages.

### *6. Reduced Risk and Potential Liability:*

If left unchecked, a migrating plume can pose significant financial and health risks. Slow-release compounds can be strategically and discretely applied to remediate contaminants around the plume's perimeter to abate plume migration and avoid the potential liability associated with unmanaged natural attenuation.

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*7. Elimination of Long-term Monitoring Costs Associated with Natural Attenuation:*

By accelerating the rate of natural attenuation, the use of slow-release compounds decreases the time to site closure. This eliminates the cost of the periodic monitoring that might normally be required in unassisted natural attenuation.

*8. Enhanced Desorption:*

Any contaminants that are sorbed to the surfaces of the aquifer media will desorb at a certain natural rate. This rate is determined by a complex array of physical and chemical parameters. An overriding factor in this dynamic is biological activity, which is enhanced by ORC and HRC. As microorganisms are stimulated to bioremediate the dissolved phase plume, a concentration gradient is established that facilitates desorption from contaminated surfaces.

*9. Limited Disturbance of the Contaminant Plume:*

Any mechanical action in the aquifer has the potential to distort the dynamics of a contaminant plume—usually not to the benefit of the project. Sparging is of particular concern in this regard. Injections of ORC and HRC are minimally invasive and limit site disturbance.

*10. Usefulness at Remote Sites:*

Slow-release compounds are ideal at geographically remote sites, particularly in regions such as Alaska and Canada that have a limited window of opportunity for remediation due to freeze/thaw cycles. Sites may also be considered remote because of the lack of available utilities with which to operate mechanically based systems.

*11. Constant and Persistent Source of Electron Acceptor/Donor:*

ORC and HRC will remain where emplaced and generate diffusible active agents slowly over time. Particularly in the case of chlorinated hydrocarbons, since plumes are difficult to locate, a continuous source of diffusible materials increases the effectiveness of contact, containment, and remediation.

## **Performance Features of ORC and HRC**

In evaluating the merits of a time release electron acceptor or electron donor, in conjunction with engineering a passive system, one should be concerned with features such as longevity and distribution.

*ORC Longevity:*

ORC-mediated oxygenated zones have been shown to generally last from four months to over a year as a function of contaminant flux. This is illustrated in Figure 4. The average lifetime for an ORC application in the field is in excess of six months. Usually only one application is necessary depending on rebound and regulatory demands.

*ORC Distribution:*

The potential for the diffusion of oxygen from ORC is not great due to the limited average concentration, as the driving force, at the interface between a mass of ORC and the aquifer. Theoretically diffusion can allow oxygen to migrate about 10 feet per year but under actual

field conditions this figure would be reduced. The movement of oxygen must be considered highly dependent on groundwater flow.

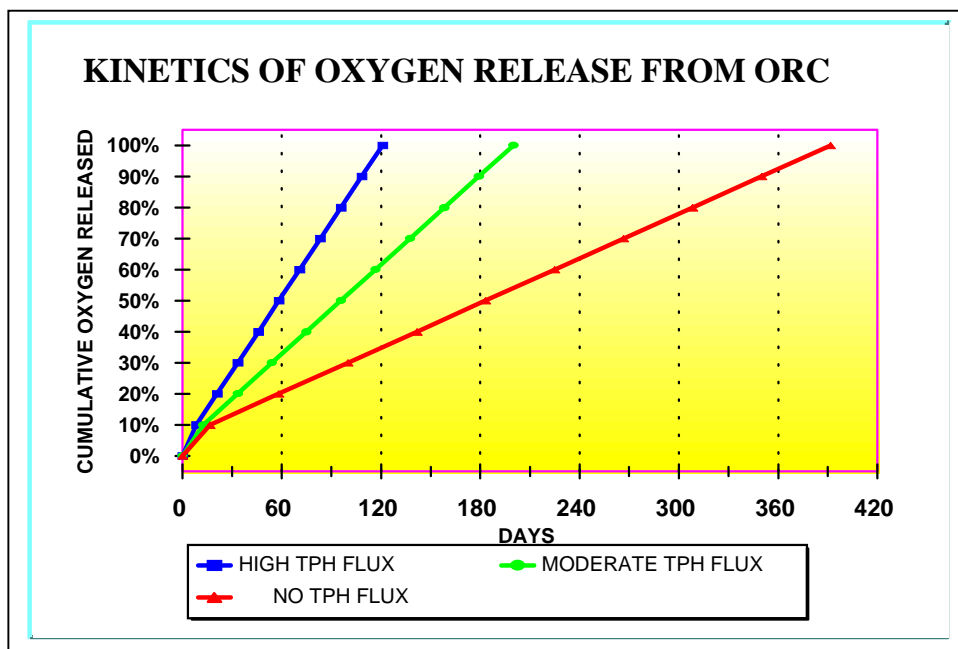


Figure 4. ORC Longevity as a Function of Aquifer Characteristics

*HRC Longevity:*

HRC is specifically defined as a formulation of Glycerol Polylactate (GPL), diluted about fifty percent with an agent like glycerol to a viscosity of 20,000 centipoise (cP). In this formulation the product can stimulate reductive dechlorination within the aquifer for about 12 months. Some of the modulators of longevity include viscosity and aquifer microbiology.

The degree of complexity and esterification of the molecule controls its viscosity and hence a major component of its reactivity. This in turn controls product longevity under a uniform set of conditions. Viscosity becomes a dominant issue in longevity because it is a measurement of resistance to flow. As a result, viscosity controls the evolution of surface area over time and the speed at which HRC becomes soluble in water. Therefore, if a polylactate formulation becomes less viscous it will spread more, thus exposing more sites to chemical and biological attack. In essence, “thicker lasts longer”, which one would intuitively gather for the reaction of any solute with a solvent. With respect to aquifer microbiology, the relative concentration of microorganisms present in the system can affect the rate of HRC hydrolysis and longevity.

*HRC Distribution:*

If we consider diffusion from a point source we have

$$C(x,t) = C_0 [ \text{erf } c(x / 2*(D*t)^{0.5}) ]$$

Where C is the final concentration at distance x in cm. Co is the initial concentration, erf c is the complementary error function, D is the diffusion coefficient in cm<sup>2</sup>/sec and t is time in seconds. This can be used to show that theoretical calculations show that to achieve a lactic acid concentration of 20 ppm, starting with an initial concentration of 5000 ppm, (provisionally enough to treat about 1 ppm of chlorinated hydrocarbon), sources can be as far apart as 56 feet as two 28 foot radii converge between application points. This is in a non-consumptive environment with no path length tortuosity and in a one dimensional diffusion situation. As we will see the more exact result, which is connected to an actual experimental measurement of the diffusion coefficient and involves tortuosity and consumption, values are presented that are about 40 percent of those presented in the above analysis. The point of this simple exercise is to emphasize that “diffusion matters”. Essentially, because the driving force is substantial at 1,000 ppm (versus, say, oxygen at 25 ppm), we can document a fairly vigorous movement of lactic acid and its breakdown products. Diffusion is actually a major driving force in low to moderate flow environments (noting that 0.1 ft/day = 36.5 ft/yr). It is also a valuable force in actually achieving contact between contaminant and substrate, because diffusion is an excellent way to distribute materials in the sub-surface relative to the injection of liquids – an activity that creates preferential flow paths and mixing problems.

In contrast to the previous treatment of diffusion we have here an actual experimental result. Since the diffusion is for a cylinder of HRC rather than a point source we refer to a different equation.

$$0.6 = \frac{Dt}{r^2} \quad [1]$$

Where D is the diffusion coefficient in cm<sup>2</sup>/sec, t is time in seconds and r is the radius of diffusion in cm. This is for a cylinder where we want the concentration to be 2% of the source, e.g. 20 ppm if the source is 1,000 ppm. Fitting the data and converting to the English System, using an average value from the experiments of 1 foot in 3 days, gives an effective diffusion coefficient of 0.2 ft<sup>2</sup>/day and thus a fairly straightforward and usable diffusion rule is derived:

$$t = 3 x^2 \quad [2]$$

Where t is the time in days it takes the front to move out a distance x in feet. Thus, it takes about 300 days to move 10 feet or about 11 feet per year. If a higher concentration is used at the source, the time will decrease. We cannot really project exact amounts at various distances from the data because it is difficult to gauge bacterial utilization rates and localized substrate concentrations. What we do get is a sense of diffusional movement as a function of time at a level quite adequate for project design purposes.

Ultimately the point of all this is to determine injection point spacing. A highly detailed answer depends on the bacterial activity and product viscosity, but nominally it appears that diffusion alone will drive the lactic acid out several feet in two months. The data suggest that 10 ft points will work if coverage is desired in two to three months. The distance between 10 ft points where coverage occurs is where the two fronts meet at a 5 ft distance from both injection points. Placing 5 for x in equation [2] results in a time of 75 days. If injection wells were placed 20 feet apart they would meet at a distance of 10 feet from each point. This would occur in 300 days according to equation [2]. In a year the distance increases to 11 feet. Note that this assumes no advection whatsoever. The motive force is simply diffusion.

With respect to field results, the data in Table 1 provide an excellent cross section of results across 10 sites. The sites have a range of groundwater velocities from essentially static (Site 1) to moderate flow rates of about 128 ft/yr. (Site 5). All of these sites were treated with 20,000 cP HRC injections, noting that an “injection” is not a process that sends material as far from the injection point as might happen with thin liquids. Therefore, the movement as measured is due to the net mass transport forces of advection, dispersion, diffusion, retardation and consumption. Overall it seems that HRC applied to an aquifer can move quite readily.

**Table 1. Movement of Organic Acids in the Field.**

ID	Distances and Days to Wells	GW Velocity (ft/yr)	Potential Yearly Movement (ft)
Site 1	8 in 89 days (CW-201-S)	0.15	33
Site 2	20 in 32 days (MW-8, 23 and 27)	110	228
Site 3	16 in 35 days (MW-31)	110	167
Site 4	15 in 154 days (MW-3)	27.4	36
Site 5	32 in 31 days (IMP-6)	128	377
Site 6	5 in 70 days (MW)	14.6	26
Site 7	5 in 33 days (TMM-B)	< 36.5	55
Site 8	20 in 30 days (MW-26)	102	243
Site 9	140 in 140 days (MW-9)	< 36.5	365
Site 10	25 in 120 days (RW-68)	73	76

## References

### Oxygen Release Compound

- 1) Bianchi-Mosquera, G.C., R.M. Allen-King and D.M. Mackay. (1994). Ground Water Monitor. Rem. (Winter). pp. 120-128.
- 2) Kao, C.M., and R.C. Borden. (1994). Hydrocarbon Bioremediation, (Eds. R.E. Hinchee and B.C. Alleman), Boca Raton, Florida. pp 262-266. Lewis Publishing.
- 3) Abou-Rizk, J.A.M., Leavitt, M.E. and D.A. Graves. (1995). Applied Bioremediation of Petroleum Hydrocarbons, (Eds. Hinchee, R.E., Kittel, J.A. and H.J. Reisinger), Vol. 3(6): pp 175-183. Battelle Press, Columbus, OH.
- 4) Odencrantz, J., Johnson, J. and S. Koenigsberg. (1996). Remediation (Fall) Vol 6:4. pp. 95-109.
- 5) Bohan, D. and W. Schlett. (1997). In-Situ and On-Site Bioremediation. Vol 5, pp. 475-480, (Eds. B. Alleman and A. Leeson), Battelle Press, Columbus, OH.
- 6) Byerley, B.T., Chapman, S.W., Smyth, D.J.A. and D.M. Mackay. (1997). Ground Water Monitor. Rem. (Spring) pp. 93-105.
- 7) Koenigsberg, S. (1997). Environmental Protection. November 1997, pp. 26-28
- 8) Koenigsberg, S. (1998). Eighth Annual West Coast Conference on Contaminated Soils, Oxnard, CA. March pp. 9-12.

- 
- 9) Koenigsberg, S. (1998). ATV Conference on Groundwater Remediation. March 10-11, Bilund, Denmark.
  - 10) Lewis, R.F., Dooley, M.A., Johnson, J.C. and W.A. Murray. (1998). Designing and Applying Treatment Technologies, (Eds. G.B. Wickramanayake and R.E. Hinchee), Vol. 1(6): pp. 1-7. Battelle Press, Columbus, OH.
  - 11) Hicks, P., Eshbaugh, G. and C. Sandefur. (1999). In-situ Bioremediation of Petroleum Hydrocarbon and Other Organic Compounds, (Eds. A. Leeson and B.C. Alleman), pp. 277-282. Battelle Press, Columbus, OH.
  - 12) Hicks, P. and G. Kubal. (1999). Bioremediation of Nitroaromatic and Haloaromatic Compounds, (Eds. A. Leeson and B.C. Alleman), Battelle Press, Columbus, OH, pp. 123-127.
  - 13) Koenigsberg, S.S., Sandefur, C.A. (1999). The Use of Oxygen Release Compound for the Accelerated Bioremediation of Aerobically Degradable Contaminants: The Advent of Time-Release Electron Acceptors. *Remediation Journal*. 10(1): pp.1-30.
  - 14) Koenigsberg, S.S., Sandefur, C.A., Mahaffey, W.R., Deshusses, M. and N. Fortin. (1999). In-situ Bioremediation of Petroleum Hydrocarbon and Other Organic Compounds, (Eds. A. Leeson and B.C. Alleman), Battelle Press, Columbus, OH, pp. 13-18.
  - 15) Oudijk, G., Duffy, B. and D. Ochs. (1999). In-situ Bioremediation of Petroleum Hydrocarbon and Other Organic Compounds, (Eds. A. Leeson and B.C. Alleman), pp. 271-276. Battelle Press, Columbus, OH.

#### Hydrogen Release Compound

- 16) Dooley, M., Murray, W., Koenigsberg, S. (1999). In: Leeson, A., Alleman, B.C. (eds.), *Engineered Approaches for In Situ Bioremediation of Chlorinated Solvent Contamination*, pp. 121-127. Battelle Press, Columbus, OH.
- 17) Farone, W.A., Koenigsberg, S.S., Hughes, J. (1999). In: Leeson, A., Alleman, B.C. (eds.), *Engineered Approaches for In Situ Bioremediation of Chlorinated Solvent Contamination*, pp. 287-292. Battelle Press, Columbus, OH.
- 18) Kallur, S., Koenigsberg, S. (1999). In: Leeson, A., Alleman, B.C. (eds.), *Engineered Approaches for In Situ Bioremediation of Chlorinated Solvent Contamination*, pp. 181-184. Battelle Press, Columbus, OH.
- 19) Koenigsberg, S.S., Farone, W. (1999). In: Leeson, A., Alleman, B.C. (eds.), *Engineered Approaches for In Situ Bioremediation of Chlorinated Solvent Contamination*, pp. 67-72. Battelle Press, Columbus, OH.
- 20) Koenigsberg, S.S., Sandefur, C.A. (1999). The Use of Hydrogen Release Compound for the Accelerated Bioremediation of Anaerobically Degradable Contaminants: The Advent of Time-Release Electron Donors. *Remediation Journal*. 10(1): pp. 31-53.
- 21) Sheldon, J.K., Koenigsberg, S.S., Quinn, K.J., Sandefur, C.A. (1999). In: Leeson, A., Alleman, B.C. (eds.), *Engineered Approaches for In Situ Bioremediation of Chlorinated Solvent Contamination*, pp. 61-66. Battelle Press, Columbus, OH.
- 22) Wu, M. (1999). In: Leeson, A., Alleman, B.C. (eds.), *Engineered Approaches for In Situ Bioremediation of Chlorinated Solvent Contamination*, pp. 177-180. Battelle Press, Columbus, OH.

- 
- 23) Anderson, D. (2000). In: Wickramanayake, G.B., Gavaskar, A.R., Chen, A.S.C. (eds.), *Bioremediation and Phytoremediation of Chlorinated and Recalcitrant Compounds*, pp. 213-219. Battelle Press, Columbus, OH.
  - 24) Boyle, S.L., Dick, V.B., Ramsdell, M.N., Caffoe., T.M. (2000). In: Wickramanayake, G.B., Gavaskar, A.R., Chen, A.S.C. (eds.), *Bioremediation and Phytoremediation of Chlorinated and Recalcitrant Compounds*, pp. 255-262. Battelle Press, Columbus, OH.
  - 25) Dooley, M., Murray, W. (2000). In: Wickramanayake, G.B., Gavaskar, A.R., Chen, A.S.C. (eds.), *Bioremediation and Phytoremediation of Chlorinated and Recalcitrant Compounds*, pp. 287-294. Battelle Press, Columbus, OH.
  - 26) Farone, W.A., Koenigsberg, S., Palmer, T., Brooker, D. (2000). In: Wickramanayake, G.B., Gavaskar, A.R., Chen, A.S.C. (eds.), *Bioremediation and Phytoremediation of Chlorinated and Recalcitrant Compounds*, pp. 101-106. Battelle Press, Columbus, OH.
  - 27) Lodato, M., Graves, D., Kean, J. (2000). In: Wickramanayake, G.B., Gavaskar, A.R., Chen, A.S.C. (eds.), *Bioremediation and Phytoremediation of Chlorinated and Recalcitrant Compounds*, pp. 205-211. Battelle Press, Columbus, OH.
  - 28) Schuhmacher, T., Bow, W., Chitwood, J. (2000). In: Wickramanayake, G.B., Gavaskar, A.R., Chen, A.S.C. (eds.), *Bioremediation and Phytoremediation of Chlorinated and Recalcitrant Compounds*, pp. 15-22. Battelle Press, Columbus, OH.
  - 29) Sheldon, J.K., Armstrong, K.G. (2000). In: Wickramanayake, G.B., Gavaskar, A.R., Chen, A.S.C. (eds.), *Chemical Oxidation and Reactive Barriers: Remediation of Chlorinated and Recalcitrant Compounds*, pp. 347-352. Battelle Press, Columbus, OH.
  - 30) Zahiraleslamzadeh, Z.M., Bensch, J.C. (2000). In: Wickramanayake, G.B., Gavaskar, A.R., Chen, A.S.C. (eds.), *Bioremediation and Phytoremediation of Chlorinated and Recalcitrant Compounds*, pp. 237-244. Battelle Press, Columbus, OH.