Hydrogen Release Compound *HRC*®

How does Hydrogen in HRC finally get to the chlorinated hydrocarbons?

Background
Our customers sometimes ask about the convoluted process whereby electrons need to "run the gauntlet" relative to other electron scavenging reactions in the sub-surface – before "our electrons" can become available to do what is desired, i.e. achieve the destruction of chlorinated hydrocarbons by reductive dechlorination . To that end here is a brief synopsis of a complex issue.

Summary
In many ways this is a story we can think of as "the dance of the electrons". What we are trying to do is get electrons, using hydrogen as the carrier, to the chlorinated hydrocarbons; noting that in this case the hydrogen itself has value as the functional group that will replace chlorine on the contaminant molecules.

In nature, this process is not easily performed because there are other reactions that "sit on top of" reductive dechlorination in a hierarchy ruled by certain laws of physical chemistry. Sometimes these rules are described with reference to oxidation-reduction or redox potential, and sometimes people invoke the concept of Gibbs Free Energy or just free energy. Let's take a minute with these subjects first as they are seminal to the discussion to follow.

Oxidation – Reduction Reactions
The oxidation-reduction reactions are key chemical events in that they are about the net movement of electrons from one reactant to another. In describing this movement of electrons, oxidation describes a loss of electrons and reduction describes a gain of electrons. If the concept of reduction being a gain is counter-intuitive just realize that in an algebraic sense it is a gain of a negative charge and is therefore a reduction. These reactions always occur in couples so that if one compound is oxidized the other is reduced.

To further round out some terminology, the compound that is reduced (gains electrons) is seen as the oxidizing agent because some other compound was oxidized (lost electrons) in the process. An alternative way to express this is that oxidizing agents become reduced because they remove electrons (and thus gain them) whereas reducing agents become oxidized because they give up electrons (and thus loose them).

Redox potential is equivalent to ORP which stands for Oxidation Reduction Potential. It is a measurement of potential electron flow in a system and is a framework on which various oxidation-reduction couples are situated. A positive ORP, measured in millivolts (mV), is indicative of an

aerobic environment because oxygen is an electron acceptor – seeking electrons from other sources. If it is present then there is a potential for electron flow in its direction and the ORP of the system is positive. In the absence of oxygen there is an attenuated potential for electron flow and the ORP is therefore less positive and can actually be negative. We focus on oxygen in this case because of the aerobic –anaerobic context of the discussion, whereas an actual ORP measurement is not completely tied to oxygen dynamics (but tends to be dominated by it).

Free Energy
The use of the free energy concept runs in parallel here and sometimes forms the basis for describing the preference of how compounds will react (from a less stable high-energy state to a more stable low-energy state) .   For our purposes we will focus on the electron flow hierarchy, whereas "energy availability" relationships that are related to electron flow, are in the background. In some ways the energy issue is used when we bring the microorganisms into the discussion and call them the oxidizers or the reducers. They are, of course, trying to capitalize on the reactions in which electrons are flowing so they can capture the energy. This is an important part of the story, because as we will see, an organism that reduces nitrate is going to dominate an organism that reduces a chlorinated hydrocarbon because the nitrate sits above the chlorinated compound on the ORP scale (more positive) and has more free energy available.

So, to bring this all into focus for the purpose of the performance of HRC this is how it works. The major chemical species in the hierarchy and their "signature ORP value" are as follows:

	Chemical Species	"Midpoint" ORP in mV	
Environment is Aerobic			Higher Free Energy
	Oxygen	+820	

Environment is Anaerobic			Lower Free Energy
	Nitrate	>+740	
	Manganese	+520	
	Iron	-50	
	Sulfate	-220	
	Carbon Dioxide	<-240	

Now, we also must recognize that reductive dechlorination *occurs in a range* from about
-200 to -300, or slightly above sulfate and slightly below carbon dioxide.

We are putting HRC into solution where it is converted primarily to lactic acid and that will degrade by fermentation through a series of other organic acids (such as pyruvic and acetic) releasing hydrogen along the way. The hydrogen is a proton with one electron and this is why we call HRC an electron donor. It will donate electrons to the chlorinated hydrocarbon (so in fact it is a reducing agent that is being oxidized) while the chlorinated hydrocarbon becomes the oxidizing agent (that is being reduced). This reaction results in the dechlorination of the molecule - as the hydrogen and its electron are substituted for the chlorine which leaves (without its electron – hence CI); this is why we call it reductive dechlorination. Note that this is anaerobic metabolism and that in aerobic metabolism the roles are reversed. Oxygen is an electron acceptor and the contaminant

(an organic molecule such as a benzene or lactic acid) is the electron donor. Oxygen is reduced and the contaminant is oxidized.

Objective of HRC Application
The object of the HRC application is then to get this hydrogen/electron resource into the -200 to -300 range redox environment where it can be utilized in reductive dechlorination, but of course we have to run a gauntlet to get there if the initial ORP is above that point. All of the species that sit above our objective or target – the chlorinated hydrocarbons – are therefore considered to be Competing Electron Acceptors or CEAs, because that is exactly what they are from our perspective given our objective. We don't want competition for electrons, we want them to be used to reduce chlorinated hydrocarbons. Most of the time we are starting with an aerobic environment, so we are up in the oxygen range and have to take that on first.

Since we have oxygen in play we are in an aerobic environment. The lactic acid is seen as the organic electron donor and oxygen is consumed aerobically. Note that lactic acid has not gotten to the fermentation stage to make hydrogen yet, because fermentation is an anaerobic process. The lactic acid is just oxidized – but we are wasting resources that will never make hydrogen. The good news is that *there is very little oxygen to drive this wasteful process.* The irony of it is that when we are degrading petroleum hydrocarbons we complain that there is not enough oxygen, under the best of conditions in cold water it might be as high a 10 ppm. So, when we are going after chlorinated hydrocarbons we are looking to reduce them and the limited oxygen content of water works to our advantage.

When the oxygen is gone the microbes (now anaerobes) move onto nitrate. By this time we have made some hydrogen via fermentation and that will be consumed by nitrate reactions (by denitrifying microbes). Again, the good news is that with some rare exceptions that tie into fertilizer-mediated groundwater impacts, dissolved nitrate concentrations are also pretty low – only a bit higher than oxygen on average. After this step, we are really starting to get anaerobic.

We then confront manganese and while we should discuss it technically, it is a micro-constituent of most groundwater and is very inconsequential as a CEA. Moving onto iron, same thing; there is typically about as much iron as there is nitrate in a range that runs from the manganese levels (1 ppm or less) to levels that parallel nitrate when it is considered high (around 100 ppm). All in all, these combined CEA impacts are relatively minor, but when added up they should be accounted for and we do so in our design software. As a final note, these CEA neutralization reactions should be seen in a proper molar context. Consequently, one should realize that absolute weights (as in mg/L) may be easier to handle in light of the molar based stoichiometry calculations that determine the actual amount of HRC required to do the job.

This brings us to sulfate which is the only CEA of any real concern. Sulfate can range from trace levels on the order of a few ppm to as high as 7000 ppm (the worst we have seen) in highly alkaline desert environments which are clearly the exception. Even though sulfate can be of concern in some cases there is a lot of misconception about the degree to which it is a problem and, beyond that, how it can be fixed when it is a problem.

As we enter a discussion on sulfate bear in mind that we have already entered the reductive dechlorination zone. So in summary, even though we are in a realm where sulfate can scavenge electrons there are several important points to consider.

1) The reactions, sulfate reduction and reductive dechlorination are not necessarily mutually exclusive. Because of the overlap they can run simultaneously. So, while electrons can "get wasted" in the process, contrary to "common belief", sulfate reduction may not block reductive dechlorination. Basically, sulfate does not have to be eliminated in order to open up an opportunity for reductive dechlorination to occur. Further, for the most part sulfate is reduced by sulfate reducing bacteria and chlorinated hydrocarbons by reductive dechlorinators; two different populations, two different action centers.

2) Since monitoring wells are sampling across all intervals in their domain, sometimes high sulfate is confined to a certain strata (like one with a gypsum vein) and this is not where the contaminant is located. Only involved multi-level sampling can sort this out.

3) Most importantly, in light of the above, various researchers have been asking why there doesn't seem to be a problem with reductive dechlorination on some sites with high sulfate. This is not expected and fairly recently got some researchers thinking. The answer is that it is not about the sulfate *but rather the by-product of sulfate reduction which is sulfide.* In a word – sulfide is *toxic* to microorganisms- *unless* – it is precipitated by iron to form iron sulfide. So, sites with high iron convey an "immunity" to sites with high sulfate and that explains why we can't have a rigid rule about high sulfate inhibition in the field. In fact, we are aware of at least two sites in the Colorado desert, with 2500 and 4000 ppm of sulfate respectively, that are dechlorinating without prejudice; as you would suspect they have high iron. Regenesis is now working on a special variant of HRC, that is about to be field tested, that will contain an affordable time-release organic iron complex that will facilitate limiting the potential inhibitory effects of sulfate by tying up the sulfide.

So, at the end of the story we come to carbon dioxide which when reduced in the presence of hydrogen makes methane. Methane is not good to have and in fact, HRC provides a key advantage by virtue of its slow-release characteristics. The fact is that methane is generated by yet another class of microbes called methanogens and while they might be in the aquifer they only can make methane when hydrogen concentrations are high. In fact, it has been shown that the enzymes they produce to make methane are not activated until a certain partial pressure of hydrogen is achieved.

The injection of any easily flowing, readily soluble liquid organic material (such as a sugar solution) will promote too much methane production because fermentation will be accelerated (due to the higher surface area that accompanies the lower viscosity) and more hydrogen will form relative to a slow-release source (that has high viscosity and for the most part stays in place). Therefore, in the competition between reductive dechlorinators and methanogens, the methanogens can be kept at bay in the zone of ORP overlap by offering hydrogen at a rate that is sub-optimal for methanogens. HRC's slow release chemistry therefore offers a distinct advantage in this circumstance.