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EHC Technology Overview - Field Applications

EHC™ Technology Overview

EHC technology describes a family of remediation products used for the *in situ* treatment of groundwater and saturated soil impacted by heavy metals and persistent organic compounds such as chlorinated solvents, pesticides and energetics. The technology is a modification of our DARAMEND® technology which has been used since 1992 to treat over 550,000 tons of similarly effected soil and sediment. Both EHC and DARAMEND are the subjects of numerous patents owned by Adventus Intellectual Properties, Inc. (Adventus).

EHC comes in a variety of formulations to meet the requirements unique to each site (**Photo 1**). Standard **EHC** is a solid material available in pellets, granules or powders. **EMC-L™** is a liquid formulation provided as a suspendable solid or an aqueous solution for easy application to existing wells or other networks. **EHC-M™** is specially prepared for treatment of heavy metals. **EHC-O™** contains a slow-release oxygen source for rapid removal of petroleum hydrocarbons and other compounds that are amenable to aerobic biodegradation processes.

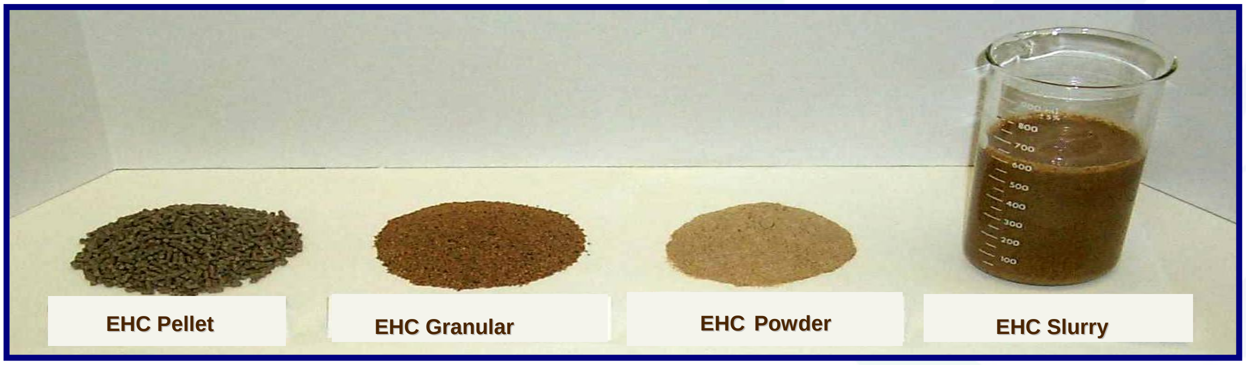

Photo 1. Pictures of various EHC Formulations.

How the EHC Technology Works

EHC is a unique combination of controlled-release carbon and reduced metal (*e.g.*, zero valent iron [ZVI], aluminum or zinc) used for stimulating reductive dechlorination and enhanced bioremediation in a subsurface environment. Following placement of EHC into the saturated zone, a number of physical, chemical and microbiological processes combine to create strong reducing conditions that stimulate rapid and complete dechlorination reactions. The organic component of EHC (fibrous organic material) is nutrient rich, hydrophilic and has high surface area; thus, it is an ideal support for growth of bacteria in a groundwater environment. As they grow on EHC particle surfaces, indigenous heterotrophic bacteria consume dissolved oxygen thereby reducing the redox potential, or Eh. In addition, as the bacteria grow on the organic particles, they ferment carbon and release a variety of volatile fatty acids (acetic, propionic, butyric) which diffuse from the site of fermentation into the groundwater plume and serve as electron donors for other microbes, including dehalogenators and halorespiring species. Finally, the small ZVI or other reduced metal particles provide substantial reactive surface area that stimulates direct chemical dechlorination and an additional decrease in the redox potential of the groundwater via corrosion of the iron and chemical oxygen scavenging.

For chlorinated organic compounds, these physical, chemical and biological processes combine to create an extremely reduced environment that stimulates chemical and microbiological dechlorination of otherwise persistent compounds. Redox potentials as low as –600 mV are commonly observed in groundwater after EHC application. At these Eh levels, the organic constituents of interest (COI) are chemically unstable and they physically degrade. Hence, the technology is biologically based in that we rely on indigenous microbes to biodegrade the EHC carbon (refined plant materials), but EHC does not require the presence or activity of special or otherwise unique bacteria (*i.e., Dehalococcoides* species are not required) for complete and effective remediation.

Potential Advantages of EHC Technology versus Other Potential Substrates

The unique combination of integrated controlled-release organic carbon and ZVI gives EHC powerful technical advantages over other materials that provide only carbon or only ZVI:

(1) Generation of significantly lowered reducing conditions leading to accelerated site closure ;

(2) Eliminates any requirement for specialty microorganisms or inoculants;

(3) Effective COI removal without accumulation of potentially problematic catabolites such as *cis*-1,2-dichloroethene (DCE), dichloromethane (DCM) or vinyl chloride (VC);

(4) Longer environmental life (from 12 to 60 months) as compared to other electron donors;

(5) Provision of plant-based major, minor and micronutrients that are essential to the activity of fastidious anaerobic bacteria involved in recognized dechlorination reactions; and

(6) Applicability to a wide range of target compounds (**Table 1**).

Composition of EHC

EHC products are available in a number of formulations specially selected for the unique situations found at every site. The primary active constituents of the EHC products are a combination of one or more of the following:

- controlled-release food-grade organic carbon (*e.g.* starches, cellulose, molasses, lecithin, soy, whey and /or other proteins). No animal products are used.
- oxygen-releasing compounds (*e.g.* calcium oxide or magnesium peroxide for EHC-O only).
- reducing compounds (*e.g.* zero valent iron, aluminum or zinc).

The proportion of each of these constituents depends on the type and concentration of the targeted COI. The MSDS for a typical EHC product is provided in **Appendix A**.

EHC-L is a water-soluble, liquid formulation specially designed for application to existing wells or hydraulic injection networks. Its unique mode of action does not require the presence of specialty microorganisms, nor will it result in the accumulation of potentially problematic catabolic intermediates (*e.g.,* DCE from PCE/TCE).

EHC-M is specially formulated for *in situ* immobilization of soluble metals via enhanced precipitation and adsorption reactions. The controlled-release feature of the carbon provides for extended longevity and greatly assists in maintaining very low redox conditions through simultaneous microbial consumption of the carbon and electron acceptors. Arsenic, for example, is precipitated through the production of iron arsenic sulfide minerals that are practically insoluble in groundwater.

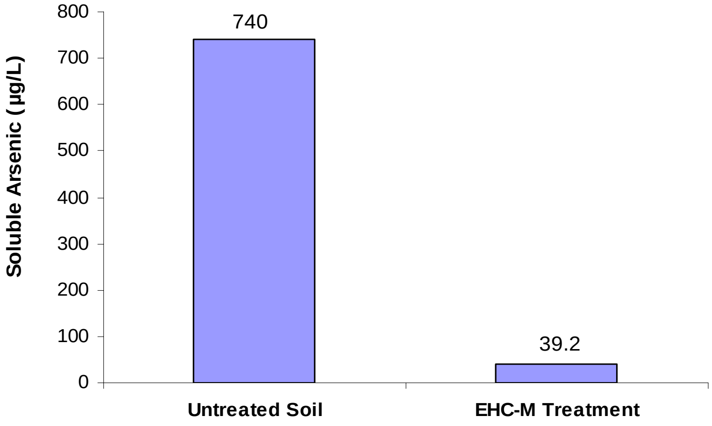

Figure 1. Reduced solubility of arsenic in soil as determined by TCLP analysis of treated soil.

EHC-M is well suited for treating environments co-impacted by heavy metals and chlorinated solvents

EHC-O contains an oxygen releasing component that provides a long-term source of dissolved oxygen. Native microorganisms utilize the dissolved oxygen as an electron acceptor, and the targeted contaminant serves as the electron donor resulting in its destruction. The organic carbon component of EHC provides trace micronutrients required for healthy growth and proliferation of the indigenous, naturally occurring microbial population.

Remedial Designs

EHC can be used for treatment of source areas and dissolved phase plumes. EHC has been employed at a number of sites to yield contiguous permeable reactive barriers (PRBs) as portayed in **Figure 2**. Injection of EHC into suspected source areas or dissolved plumes has also been performed to accelerate site remediation (**Figure 3**). The presence of any free phase hydrocarbon (LNAPL) or chlorinated hydrocarbon (DNAPL) is problematic; here alternative technologies such as *in situ* biogeochemical stabilization (ISBS) are likely more applicable to this problem (please see http://www.adventus.us/isbs.htm).

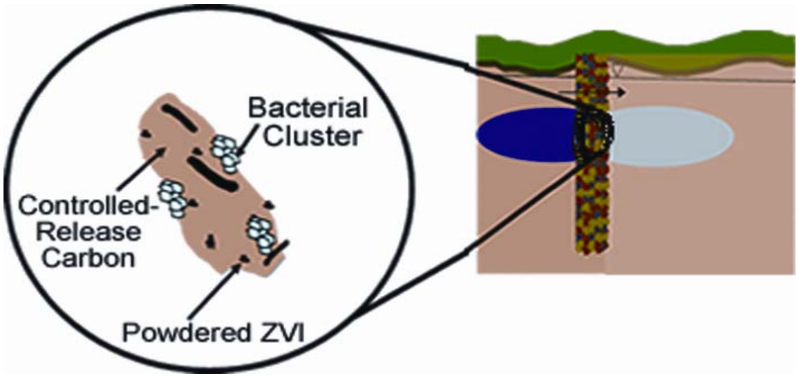

Figure 2. Schematic of PRB application.

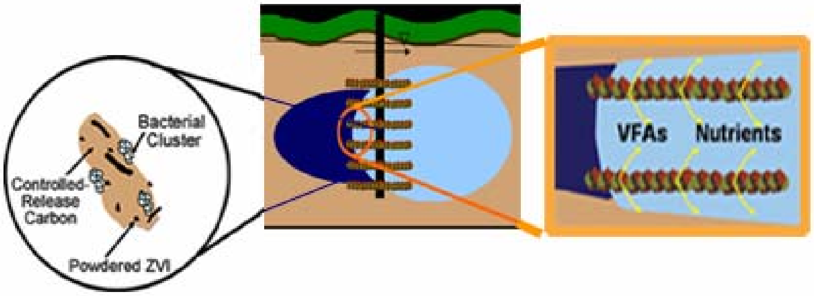

Figure 3. Schematic of source area treatment.

Implementation Methods

A variety of construction / implementation methods can be used to place EHC into a subsurface environment. The most effective delivery method will be determined by a number of site-specific lithological and hydrogeological features. Typical methods of subsurface installation are summarized below:

- backfill of a excavation
- backfill of a trench (*e.g.* PRB)
- injection from a direct-push drill rig
- injection using hydraulic fracturing
- injection using pneumatic fracturing and injection
- injection using high pressure jetting
- mechanical soil mixing

Excavation Fill

At a site in the southeast USA, EHC was mixed with sand (ratio of 9:1 by mass; *i.e.* 10% EHC) and placed in the bottom of an open excavation after most of the contaminated soils were removed (**Photo 2**). The EHC provided treatment of any residual contamination. An excavator was used to mix the EHC/sand and emplace the mixture into the opening. For larger scale excavations, pug mills and other mixing equipment could be used to mix the EHC and backfill material. Alternatively, the contaminated soil can be excavated, EHC can be mixed into the soils, and the soils amended with EHC can then be backfilled into the opening.

Photo 2. Picture of excavator leveling EHC and sand that were mixed together prior to placement into the excavated area

Permeable Reactive Barrier (PRB)

A PRB is a continuous, *in situ* permeable treatment zone designed to intercept and remediate a contaminant plume. A PRB is typically constructed from 0.3 m to 2 m wide, and from 2 m to 35 m deep, and it usually extends across the width of the plume. Over 200 PRBs have been constructed using a variety of construction techniques. For trenches that are typically less than 5 m deep constructed in competent soils such as tight clays, an excavator can dig the trench, and the EHC plus sand or gravel can be placed into it using a loader as shown in **Photo 3.** For deeper trenches, or trenches in less competent soils, a biopolymer slurry can be used where a mixture of water and guar gum is pumped into the open trench to hold up the sidewalls. The biopolymer exerts hydraulic pressure and prevents the collapse of the trench as it is excavated. Another method, which is applicable to depths of 10 m, is to use a continuous one-pass trencher where a cutting chain digs the trench and simultaneously backfills it with a mixture of sand plus EHC.

Photo 3. Backfilling PRB after installation of EHC and sand in the trench; southern USA.

Hydraulic Injection Using Direct Push Technology (DPT)

For DPT, hollow pipes, or ‘rods’ are driven into the ground using a vibration or hammering technique. A low viscosity, aqueous slurry of EHC is prepared on site using a tank and a mixer or a pump. The slurry is then injected into the subsurface using an appropriate pump (up to 500 psi). A number of variations on this methodology can be used. In some cases, an expendable tip is driven into the ground to the bottom of the desired injection depth. The rods are then retracted upwards leaving the metallic tip in the ground. The slurry is then pumped into the ground as the rods are incrementally lifted upwards. Another method uses a pressure-activated tip, where injection holes are revealed once the pressure of the slurry in the rods is increased by forcing a spring to compress. **Figures 4** and **5** show pictures of EHC being applied at a site in the southeast USA using direct push technology.

Photo 4. Overall picture of equipment used to perform direct injection of EHC. The DPT rig is on left; the mixing tank is on right. EHC can be injected from bottom of the targeted zone to the top, or vice versa depending on site lithology and COI distribution.

Photo 5. Close-up of rod connected to a hose that is delivering EHC slurry into the subsurface.

Hydraulic Fracturing

Hydraulic fracturing involves the injection of a slurry or gel of EHC mixed with guar gum. The slurry is injected into the ground through drilling rods. One of the primary differences between hydraulic fracturing and DPT is that a fracture initiation step precedes the injection. This step involves physically creating an opening or slot at the injection point that is roughly shaped like a disc (see Figure 3). This fracture initiation step helps to initiate a fracture along which the injected slurry can follow. This promotes the slurry reaching much greater distances from the injection location.

Photograph 6 shows a picture of a hydraulic fracturing rig; **Photograph 7** shows a soil core that was taken after EHC injection, revealing a thick layer of injected slurry located approximately 3 m radially from the point of injection.

Photo 6. Photograph of hydraulic fracturing rig.

Photo 7. Photograph of soil core showing green layer of injected slurry.

Pneumatic Fracturing and Injection

This process uses gas to inject either dry EHC or a slurry of EHC into the subsurface down an open borehole. Depending on the formation, the gas may be used to first fracture the formation (*e.g*. rock or clays). The EHC is then fluidized in a gas stream (nitrogen is used where reducing conditions are to be maintained) and injected under pressure. This process can be used to inject EHC into rock as the pressure of the nitrogen will open up existing fractures and allow the EHC to be injected into them. This process can also be utilized in tight soils such as clays, where a distinct fracture typically opens. If applied to less consolidated materials, pneumatic fracturing of EHC yields a more uniform zone of mixed EHC and aquifer material.

High Pressure Jetting

High pressure jetting consists of the injection of water and EHC at very high pressures (up to 5,000 psi for example) to erode soil in the subsurface and mix it with the injected EHC. This process will create soil returns at the surface because of the erosion process. This approach provides very good mixing of contaminated soil with EHC, and will be particularly useful for injection into layers that are not thick, but are very deep.

Soil Mixing

Soil can be mechanically mixed with a number of different tools such as excavators, (**Photo 8**), large diameter augers or the ‘Lang’ tool. These technologies provide very good contact between the soil and the EHC and are of particular use for shallow impacts. Shallow soil mixing equipment can be used for depths up to 12 m and deep soil mixing can be used fro greater depths. This method is more applicable to treatment of shallower source zone contamination where higher concentrations of the COI exist.

Photo 8. Mixing Adventus amendments into sediments impacted by explosives.

Typical Results

Critical redox (Eh) calculations have been performed which indicate that a majority of the targeted COIs listed in Table 1 will be degraded in an environment reduced to <450 mV (**Table 2**). At a site in the southeast USA, the *in situ* subsurface (*ca*. 40 ft bgs) redox was reduced to <500 mV at distances at least 10 ft from the point of injection (**Figure 3**).

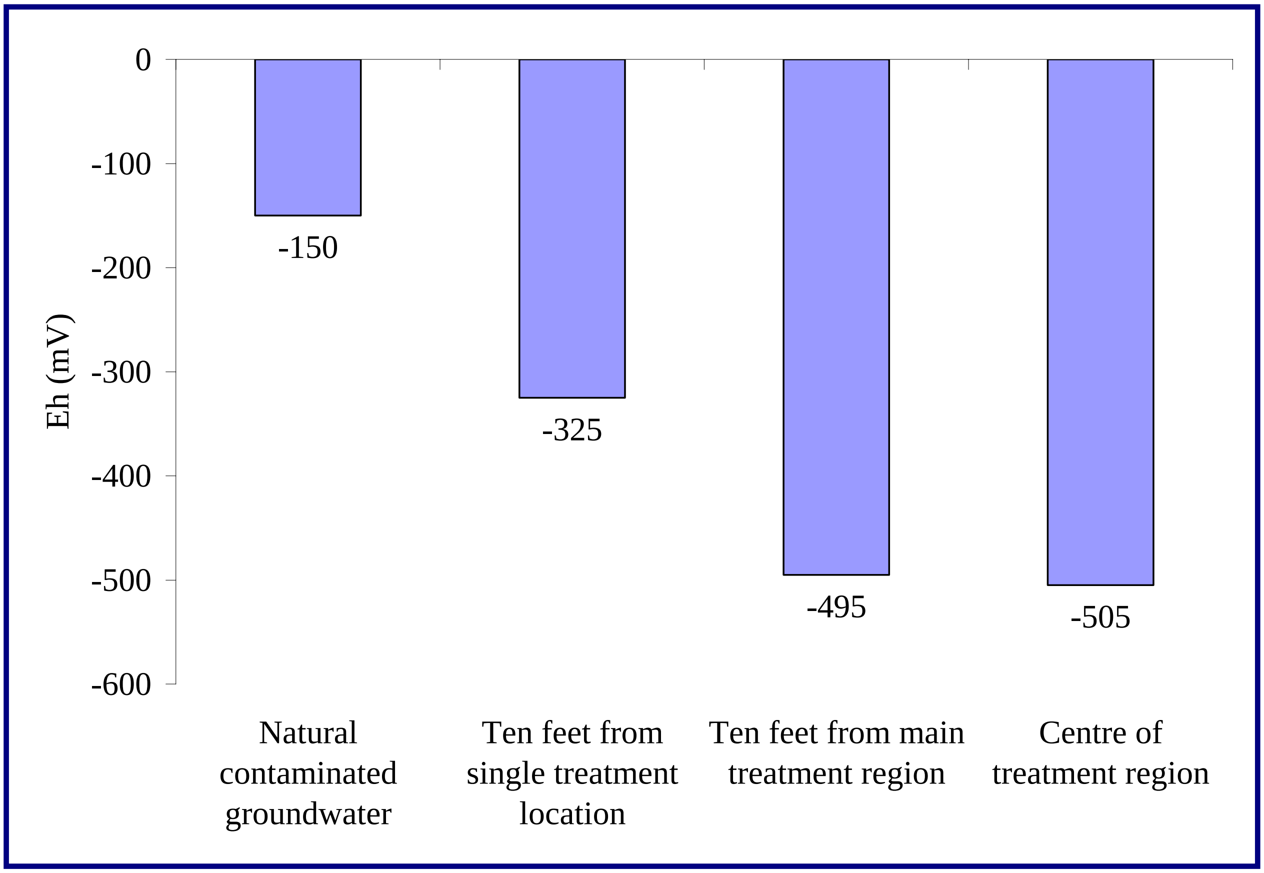

Figure 3. *In Situ* redox (Eh) following EHC injection

Because EHC creates such extremely reduced conditions, we do not observe the accumulation of potentially problematic intermediates such as DCE from PCE or TCE. Moreover, compounds typically resistant to biological or chemical reduction alone (*e.g.*, chloroethanes) are readily removed using the EHC technology **(Figure 4).**

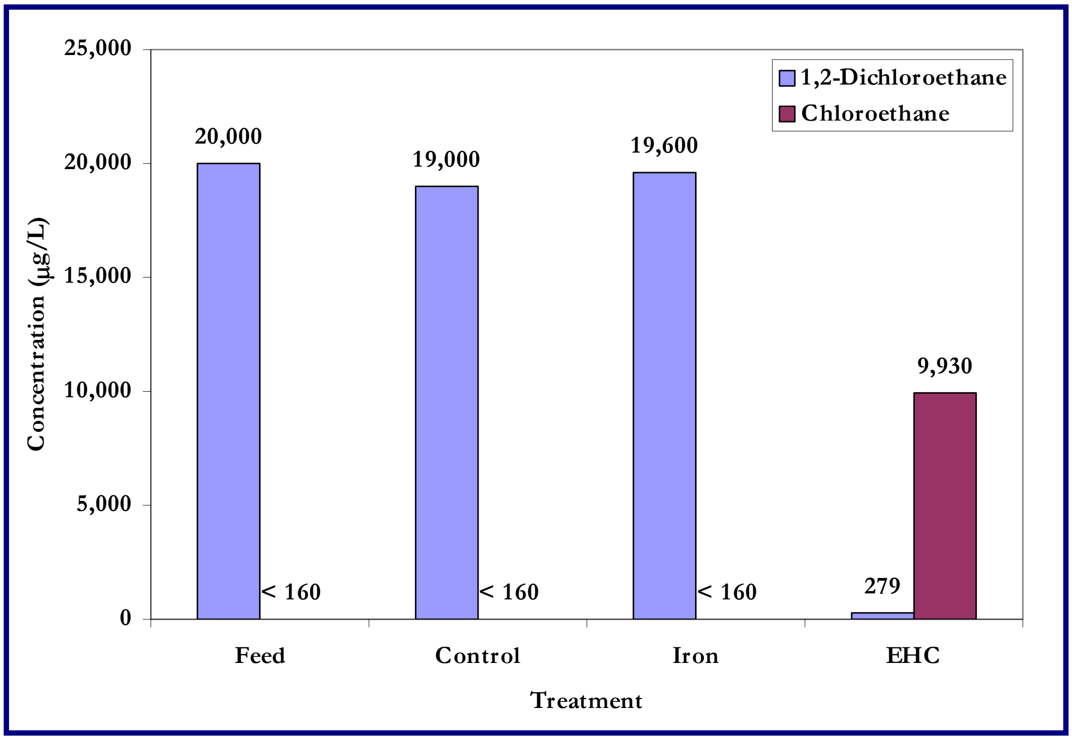

Figure 4. Effective removal of DCA during groundwater flow through a column packed with sand (control), iron and EHC.

NOTIFICATIONS:

The use of reduced metals for the purposes of treating organic contaminants in groundwater is the subject of numerous patents issued to the University of Waterloo and owned by Adventus Intellectual Property, Inc./ETI (www.eti.ca).

The combined use of an organic material plus reduced metals for the purposes of treating organic and inorganic contaminants in soil, sediment, water and groundwater is the subject of numerous patents issued to W.R. Grace & Company and owned by Adventus Intellectual Property, Inc. (www.adventus.us).

Adventus is obligated and committed to enforce its patent rights. The Patent Laws provide for punitive damages for the willful infringement of a patent in the form of treble damages and an assessment of the attorneys fees incurred by the patent owner in enforcing the patent (Title 35, United States Code, Section 284).

Adventus will continue to grant Patent licenses to end-users and installation contractors alike.

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TABLE 1 EHC TREATS THESE COMPOUNDS

Compound as Primary COI	**EHC and EHC-L**	**EHC-M**	**EHC-O**
Chlorinated Solvents			
Tetrachloroethylene (PCE)	X		
Trichloroethylene (TCE)	X		
cis 1,2-Dichloroethylene (*cis* DCE)	X		
trans 1,2-Dichloroethylene (*trans* DCE)	X		
1,1-Dichloroethene	X		
Vinyl Chloride	(x)		X
1,1,2,2-Tetrachloroethane (TeCA)	(x)		
1,1,1-Trichloroethane (TCA)	X		
Carbon Tetrachloride (CT)	X		
Chloroform (CF)	X		
Dichloromethane (DCM)	X		
Chloromethane (Methylene chloride)	X		
Pesticides			
Toxaphene	X		
Chlordane	X		
Dieldrin	X		
Pentachlorophenol	X		X
Energetics			
TNT	X		
DNT	X		
HMX	X		
RDX	X		
Perchlorate	X		
Heavy Metals		X	X
Petroleum Hydrocarbons			X

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Table 2 - Standard reduction potentials at 25°C and pH 7 of selected organic and inorganic redox couples

Electron Acceptor	Half-reaction of reductive transformations		$G^{o'}$ (kJ/electron)	$E^{o'}$ (mV)
1,1,1,2-TeCA	$CCl_3\text{-}CH_2Cl + 2e^-$	→ $(1,1\text{-})C_2H_2Cl_2 + 2Cl^-$	-93.4	968
TeCA	$CHCl_2\text{-}CH_2Cl_2 + 2e^-$	→ *cis*-$C_2H_2Cl_2 + 2Cl^-$	-90.1	933
TeCA	$CHCl_2\text{-}CH_2Cl_2 + 2e^-$	→ *trans*-$C_2H_2Cl_2 + 2Cl^-$	-87.9	911
1,1,2-TCA	$CHCl_2\text{-}CH_2Cl + 2e^-$	→ $C_2H_3Cl + 2Cl^-$	-79.8	827
O_2	**$O_2 + 4H^+ + 4e^-$**	**→ $2H_2O$**	**-78.7**	**816**
1,2-DCA	$CH_2Cl\text{-}CH_2Cl + 2e^-$	→ $C_2H_4 + 2Cl^-$	-71.3	738
CT	$CCl_4 + H^+ + 2e^-$	→ $CHCl_3 + Cl^-$	-65.0	673
MnO_2	**$MnO_2 + HCO_3^- + 3H^+ + 2e^-$**	**→ $MnCO_3 + 4H_2O$**	**-58.9**	**610**
	$CCl_3F + H^+ + 2e^-$	→ $CHCl_2F + Cl^-$	-58.7	608
	$CCl_2F\text{-}CClF_2 + H^+ + 2e^-$	→ $CHClF\text{-}CClF_2 + Cl^-$	-55.7	577
PCE	$C_2Cl_4 + H^+ + 2e^-$	→ $C_2HCl_3 + Cl^-$	-55.4	574
1,1,1,2-TeCA	$CCl_3\text{-}CH_2Cl + H^+ + 2e^-$	→ $CHCl_2\text{-}CH_2Cl + Cl^-$	-54.2	562
TCA	$CCl_3\text{-}CH_3 + H^+ + 2e^-$	→ $CHCl_2\text{-}CH_3 + Cl^-$	-54.1	561
CF	$CHCl_3 + H^+ + 2e^-$	→ $CH_2Cl_2 + Cl^-$	-54.1	560
TCE	$C_2HCl_3 + H^+ + 2e^-$	→ *cis*-$C_2H_2Cl_2 + Cl^-$	-53.1	550
1,1,2-TCA	$CHCl_2\text{-}CH_2Cl + H^+ + 2e^-$	→ $CH_2Cl\text{-}CH_2Cl + Cl^-$	-51.9	538
	$CCl_2F\text{-}CClF_2 + H^+ + 2e^-$	→ $CCl_2F\text{-}CHF_2 + Cl^-$	-51.2	530
TCE	$C_2HCl_3 + H^+ + 2e^-$	→ *trans*-$C_2H_2Cl_2 + Cl^-$	-50.9	528
TCE	$C_2HCl_3 + H^+ + 2e^-$	→ $1,1\text{-}C_2H_2Cl_2 + Cl^-$	-50.9	527
1,1,1,2-TeCA	$CCl_3\text{-}CH_2Cl + H^+ + 2e^-$	→ $CCl_3\text{-}CH_3 + Cl^-$	-49.9	517
1,1,2-TCA	$CHCl_2\text{-}CH_2Cl + H^+ + 2e^-$	→ $CHCl_2\text{-}CH_3 + Cl^-$	-49.8	516
TeCA	$CHCl_2\text{-}CHCl_2 + H^+ + 2e^-$	→ $CHCl_2\text{-}CH_2Cl + Cl^-$	-48.6	504
DCM	$CH_2Cl_2 + H^+ + 2e^-$	→ $CH_3Cl + Cl^-$	-47.6	493
CM	$CH_3Cl + H^+ + 2e^-$	→ $CH_4 + Cl^-$	-44.8	464
CA	$C_2H_5Cl + H^+ + 2e^-$	→ $C_2H_6 + Cl^-$	-44.6	462
	$CF_3\text{-}CCl_3 + H^+ + 2e^-$	→ $CF_3\text{-}CHCl_2 + Cl^-$	-43.6	452
VC	$C_2H_3Cl + H^+ + 2e^-$	→ $C_2H_4 + Cl^-$	-43.4	450
NO_3^-	**$NO_3^- + 2H^+ + 2e^-$**	**→ $NO_2^- + H_2O$**	**-41.7**	**432**
1,1-DCE	$(1,1\text{-})C_2H_2Cl_2 + H^+ + 2e^-$	→ $C_2H_3Cl + Cl^-$	-40.6	420
trans-DCE	*trans*-$C_2H_2Cl_2 + H^+ + 2e^-$	→ $C_2H_3Cl + Cl^-$	-40.5	419
cis-DCE	*cis*-$C_2H_2Cl_2 + H^+ + 2e^-$	→ $C_2H_3Cl + Cl^-$	-38.3	397
1,1-DCA	$C_2H_4Cl_2 + H^+ + 2e^-$	→ $C_2H_5Cl + Cl^-$	-38.3	397
1,2-DCA	$CH_2Cl\text{-}CH_2Cl + H^+ + 2e^-$	→ $C_2H_5Cl + Cl^-$	-36.2	375
$Fe(OH)_3$	**$Fe(OH)_3 + 3H^+ + 2e^-$**	**→ $Fe^{2+} + 3H_2O$**	**-11.4**	**118**
SO_4^{2-}	**$SO_4^{2-} + 9H^+ + 8e^-$**	**→ $HS^- + 4H_2O$**	**+20.9**	**-217**
HCO_3^-	**$HCO_3^- + 9H^+ + 8e^-$**	**→ $CH_4 + 3H_2O$**	**+23.0**	**-238**

Calculated on the basis of data from Thauer et al. (1977), Dolfing and Harrison (1992), Dolfing and Janssen (1994) and Dolfing (2003), for $[Cl^-]$ = 1 mM.

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Appendix A. MSDS for EHC 2007Fe50

MATERIAL SAFETY DATA SHEET: **EHC™ 2007Fe50**

1.	**PRODUCT IDENTIFICATION:**	EHC™2007Fe50
	PRODUCT USE:	Bioremediation Product

MANUFACTURER:

Adventus Remediation Technologies
1345 Fewster Drive
Mississauga, Ontario
L4W 2A5

EMERGENCY PHONE:

Office Hours:	905-273-5374
After Hours:	416-457-9491

TRANSPORTATION OF DANGEROUS GOOD CLASSIFICATION:
Not Regulated

WHMIS CLASSIFICATION:
Not Regulated

2. INGREDIENTS

CHEMICAL NAME:	**CAS#**	**TLV (mg/m3)**	**LD low (mg/Kg)**
Organic Amendment	N/D	N/E	N/E
Iron	1309-37-1	5 (as iron oxide fume)	N/E
Carbon	1333-86-4	3.5 (as carbon black)	N/E
Soy Oil Lecithin	8001-22-7	N/E	N/E

3. PHYSICAL DATA

Physical state	Solid	Melting point	1371-1480°F
Odour threshold	N/A	Boiling point	3000°C
Density	0.83 Kg/L	Vapour pressure (mm Hg)	1 @ 1787°C
pH	N/A	Vapour density (air=1)	N/A
Solubility in water	Insoluble	Evaporation rate	N/A
Coeff. of water/oil	N/A		
Appearance & odour	Odourless, Tan/Brown Flakes		

4. FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (Deg. C PMCC): N/A

	LOWER	**UPPER**
FLAMMABLE LIMITS IN AIR % BY VOLUME:	N/A	N/A
AUTO IGNITION TEMP (Deg. C):	N/A	

EXTINGUISHING MEDIA: Dry chemicals or sand or universal type foam.

SPECIAL PROCEDURES:
Firefighters should wear SCBA and protective clothing.

UNUSUAL FIRE AND EXPLOSION HAZARDS:

Dust can present fire and explosion hazards when exposed to fire, chemical reaction, or contact with powerful oxidizers.

5. REACTIVITY DATA

STABILITY (NORMAL COND.):
Stable: X **Unstable:**

CONDITIONS TO AVOID:	Contact with powerful oxidizers such as strong acids.
INCOMPATIBILITY (Materials to Avoid):	Powerful oxidizers such as strong acids.
HAZARDOUS DECOMPOSITION PRODUCTS:	Hydrogen, Carbon monoxide, Carbon dioxide.

6. TOXICOLOGICAL PROPERTIES

ROUTE OF ENTRY:
Inhalation
Ingestion (not likely)

HEALTH HAZARDS:

Acute overexposure may cause eye, nose, mouth and skin irritation.

Carcinogenicity:	No Information Available
Signs and Symptoms of Exposure:	No Information Available
Medical Conditions Generally Aggravated by Exposure:	No Information Available

7. PREVENTIVE MEASURES

PERSONAL PROTECTIVE EQUIPMENT:

Eye Protection: X Gloves: X Clothing:

RESPIRATORY PROTECTION:
Use dust mask in severe conditions.
Use good housekeeping practices to keep dust to a minimum.

VENTILATION REQUIREMENTS:
Not normally required.

SPILL AND LEAK PROCEDURES:
Sweep up and return to container.

WASTE DISPOSAL:
Sanitary landfill. Follow Federal, State and Local guidelines.

HANDLING PROCEDURES:
Wear safety glasses for normal use. Avoid generating excessive dust, wear dust mask in severe conditions.

STORAGE REQUIREMENTS:
Do not store near powerful oxidizers such as strong acids. Keep dry.

SPECIAL HANDLING INFORMATION:
Treat as a nuisance dust

8. FIRST AID MEASURES

INHALATION: Remove to fresh air. Seek medical attention.
INGESTION: Seek medical attention.
SKIN CONTACT: Brush off excess. Wash with soap and water.
EYE CONTACT: Flush with running water. Seek medical attention.

9. OTHER INFORMATION

None

10. PREPARATION INFORMATION

Prepared By:	K. Bolanos-Shaw	Date Prep./Rev.:	8/20/04
	Adventus Remediation Technologies	Print Date:	8/20/04
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	L4W 2A5		

Definitions:

N/D - No Data N/A - Not Applicable N/E - Not Established < - Less than
A= Oral rat LD50 B= Oral rat LD low C= Oral LD50/LD low other animal > - Greater than
D= Estimated 1000 E= Arbitrary 2000 F= Other route prefix
C= Ceiling limit