MAGAZINE



Simplify Science®

Carus Remediation Technologies continues to bring innovative solutions that help to Simplify Science without sacrificing quality or our commitment to excellent customer service

Carus Corporation



Since the 90s, Carus has been providing *In Situ* Chemical Oxidation (ISCO) technologies for the remediation industry across the world. We have been able to integrate our offerings with bioremediation and *In Situ* Chemical Reduction (ISCR) technologies to provide a wide variety of solutions for contaminated sites. In addition to products manufactured by Carus, we have partnered with four premier companies: Redox Tech, LLC, Solvay, Biorem Engineering and Directa Plus S.p.A. CRT (Carus Remediation Technologies) staff can support you in the feasibility and dose calculations for your sites. Please contact us with questions and for a free site review.

Challenges

Chlorinated Solvents Treatment

RemOx®, OBC™, ABC+, ABC® and CAP 18® family of products have been successfully used in hundreds of sites to chemically or biologically treat a wide range of chlorinated and halogenated contaminants. Since the 90s, RemOx® ISCO reagents have been used for chlorinated ethenes (PCE, TCE, DCE, VC) ISCO treatment.

Petroleum Hydrocarbons

Oxygen BioChem (OBC)™ is activated persulfate commonly used to treat ISCO sites impacted by petroleum hydrocarbons such as: TPH, DRO, GRO, BTEXs, PAH. Same contaminants can be biologically treated with IXPER® Calcium Peroxides, Oxygel, and Sulfate BioChem (SBC). RemOx® in some specific applications to treat aromatics (with exception to benzene), TPHs and PAHs.

Phenols, H_oS

RemOx® can effectively and quickly oxidize phenols and hydrogen sulfide (H₂S).

Low Permeability Soils

When it is difficult to inject reagents in tight soils you can consider our **SR** family of products for sustained release of oxidants. **RemOx® SR+** ISCO reagent and **Persulfate SR** ISCO reagent cylinders can be installed by direct push into the contaminated layer. Oxidants are distributed by concentration gradient over time, even in very tight matrixes. **CAP 18 ME®** and **Oxygel** can be used for remediation where small injection volumes are required.

Chemical Reactive Barriers

RemOx® SR+ and Persulfate SR cylinders have been developed for passive in situ treatment of dissolved plumes with chemical barriers. SR ISCO reagent is the first technology for long lasting oxidation release (years). SR ISCO reagent cylinders are installed to form a barrier using direct push technology or wells. The oxidant is slowly dissolved and released contacting contaminants as groundwater moves through the barrier, mitigating downgradient contamination.

Biological Reactive Barriers

CAP 18® and CAP 18 ME® anaerobic bioremediation products have been successfully used at sites contaminated by chlorinated ethenes (PCE, TCE, DCE, VC). Low volumes of CAP 18® are injected by direct push and the barrier effect is observed for 2-5 years with a single injection.

High Velocity Aquifers

In high velocity aquifers reagents can be quickly washed out by groundwater flow without allowing time for proper distribution and reaction. CAP 18® and CAP 18 ME® have demonstrated ability to remain in the aquifer and to release electron donors (carbon substrate) over a long period of time for long-term anaerobic bioremediation.

Free Phase

ABC+ (Anaerobic BioChem+) has been used for In Situ Chemical Reduction in sites with DNAPL. ABC®'s (Anaerobic BioChem) unique composition, including a natural solvent, enhances dissolution from Dense Non Aqueous Phase Liquid (DNAPL) allowing for Zero Valent Iron (ZVI) action in the aqueous phase. SBC (Sulfate BioChem) biostimulation product allows for very effective degradation by Sulfate Reductive Bacteria capable to remove residual free phase Light Non Aqueous Phase Liquid (LNAPL) in petroleum hydrocarbon impacted sites.

Chemistry and Biology

CRT products have been designed to synergistically work in treatment trains to increase effectiveness and sustainability. After OBC™ oxidation, some sulfates and dissolved oxygen remain available for bacteria for a second step of biological treatment. With only one application. ABC⁺ couples ZVI action along with electron donors supply to achieve ISCR and anaerobic bioremediation. RemOx® and CAP 18® have been jointly used in several sites: RemOx® lowers high chlorinated solvents concentrations to quickly reduce risk and toxicity for bacteria, and CAP 18® is used for a less invasive polishing to target levels.

Carus Remediation Technologies (CRT)

In Situ Chemical Oxidation (ISCO)

RemOx® S and **RemOx® L** ISCO reagents: remediation grade potassium and sodium permanganates.

Persulfate SR ISCO reagent and RemOx® SR+ ISCO reagent: solid sodium persulfate and solid potassium permanganate plus solid sodium persulfate.

OBC™: activated persulfate (Redox Tech).

In Situ Chemical Reduction (ISCR)

ABC+ (Anaerobic BioChem+): Zero Valent Iron (ZVI) based ISCR + bio reagent (Redox Tech).

Aerobic Bioremediation

IXPER® 75C Calcium Peroxide: for dissolved oxygen supply (Solvay). Oxygel: inorganic nanogel for dissolved oxygen supply (Biorem). Sulfate BioChem (SBC): proprietary blend for indigenous sulfate reducing bacteria long term biostimulation (Redox Tech).

Anaerobic Bioremediation

CAP 18®: is a proprietary blend of food-grade, long-chain fatty acids designed to be used in anaerobic bioremediation projects. Strong methane inhibition properties.

CAP 18 ME® and **ABC-Olé** (Redox Tech): are blend of soluble carbon substrate for anaerobic bioremediation, formulation can be based on site specific characteristics. Adding zero valent Iron (ZVI) to **ABC®** you have **ABC*** for a faster onset redox conditions potential decrease.

RemOx® Sand RemOx® LISCO Reagents

ISCO · Chlorinated Solvents · PCE · TCE · DCE · VC · PAHs

Chemical oxidation has been used for over 100 years in the water and wastewater treatment industries. *In situ* chemical oxidation (ISCO) is based on the *in situ* delivery of chemical oxidants to break the carbon bond of the organic contaminant to reduce mass, mobility, and/or toxicity of the contaminants therefore reducing them to their mineral components.

RemOx® S and RemOx® L

ISCO reagents provide the industry with highest remediation grade potassium and sodium permanganate in the industry. Permanganate chemistry does not require activation, does not produce appreciable gas evolution, does not dramatically shift pH, does not create heat and has lesser detrimental effects on bioremediation polishing compared to other oxidants.

RemOx® L and RemOx® S

ISCO reagents are used for soil and groundwater remediation by *in situ* or *ex situ* chemical oxidation and as active agent in subsurface reactive barriers for treatment of:

- Chlorinated Ethenes: PCE, TCE, DCE, VC.
- Phenolics-PCP, p-Cresol,
 2.3 Dichlorophenol, etc.
- Polyaromatic Hydrocarbons (PAHs): Naphthalene, Phenanthrene, Benzo(a)Pyrene, etc.
- Aromatics (excluding Benzene), TPHs, etc.
- TNT, RDX, HMX, etc.
- Some Pesticides

REACTIONS

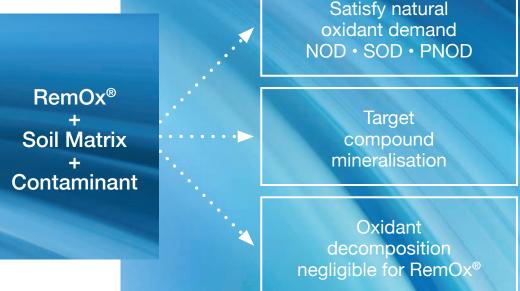
RemOx® ISCO reagent reacts with PCE, TCE, DCE, VC breaking the molecule without progressive dechlorination.

DOSE CALCULATION AND COMPETING REACTIONS

Similar to other oxidants RemOx® reacts with natural occurring reduced organic and inorganic matter Natural Oxidant Demand (NOD).

For a correct permanganate dose calculation it is important to evaluate the site soil for the Permanganate Natural Oxidant Demand (PNOD).

Carus offers PNOD testing at our laboratory located in the United States and follows ASTM method D7262-10.



CONTACT, CONTACT, CONTACT

In its simplest sense ISCO remains a contact process requiring the oxidant to physically contact the contaminant:

CONTACT = REACTION ■ SUCCESS

CONTACT = LIMITED REBOUND

Contact is facilitated by a variety of methods and techniques.

COLOR

Permanganate solutions show a typical purple color that can be detected also at very low concentrations up to 1 mg/l. This is a great advantage of ISCO with permanganate, as permanganate acts as a tracer to detect distribution in the subsoil. Instruments or chemical analyses are not needed to determine distribution.

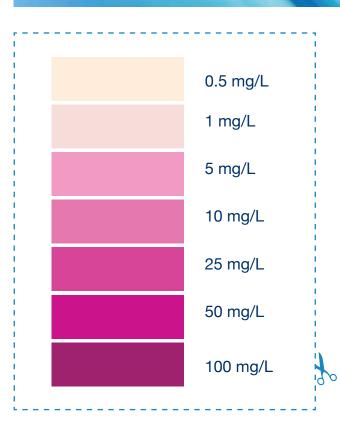
· PURPLE:

permanganate color indicates the product is active and chemical oxidation is still occurring.

• BROWNISH:

color indicates manganese dioxide (MnO₂) settling particles, permanganate is depleted. The reaction is complete and no further oxidation will occur.

Cut the picture below for field concentration evaluation.







Sustained Release

ISCO · Chlorinated Solvents · PCE · TCE · DCE · VC · PAHs · TPH · DRO · GRO · BTEX **MTBE** · Chemical Reactive Barriers · Low Permeability Soils

Sustained Release (SR) ISCO cylinders are a long-term, innovative, solution for passively treating contaminants in situ. This family of products includes:

Persulfate SR ISCO Reagent • RemOx® SR+ ISCO Reagent

The SR Products

include a solid paraffin wax matrix with:

- solid sodium persulfate (Persulfate SR)
- a blend of solid potassium permanganate and solid sodium persulfate (RemOx SR+)
- slowly release into groundwater over several months/years

SR ISCO Reagents

application may vary from direct push to in-well applications. These products can be used for source zone treatment. Emplaced cylinders can also be used as a reactive zone or barrier wall to prevent off-site contaminant migration.

SR cylinders can be utilized as a remedial alternative that is easy to implement, has low footprint, does not require the injection of liquids, and minimizes disruption of active facilities.

This technology is ideal for Brownfields, gas station and dry cleaner sites where passive in situ treatment could take place without aboveground equipment or infrastructure. Cylinders are manufactured as 18 inches in length (46 cm) and are currently available in 2.5 inch (5 cm) diameter suitable for use with standard DPT rod sizes.

LOW PERMEABILITY SOILS

When it is difficult to inject reagents in tight soils you can consider to use SR cylinders for sustained release of oxidants. SR cylinders can be installed by direct push into the contaminated layer and oxidants are distributed by concentration gradient over time even in very tight matrixes.

HSE

No need of dissolution and handling of powders or solutions. Reduced contact risk. No spills (it is a solid product). Minimal workers exposure.

Oxygen BioChem (OBC)™

ISCO · Chlorinated Solvents · PAHs · TPH · DRO · GRO · BTEX · MTBE

Redox Tech, LLC has formulated a mixture of sodium persulfate and calcium peroxide that can be employed for ISCO applications. The mixture in OBC[™] supports a two-fold mechanism for treating contaminants of concern.

OBC™ delivers one of the strongest chemical oxidants for shortterm ISCO, and also provides electron acceptors (oxygen and sulfate) for longer-term biological oxidation.

Rapid destruction of the contaminants of concern is possible with OBC[™] activated persulfate generating sulfate radicals.

Activated persulfate can remain available in the subsurface for few months providing a combination of power and stability.

The calcium peroxide imparts the alkalinity and peroxide needed to activate the persulfate and when mixed with water it provides a long-term, slow release source of hydrogen peroxide and calcium hydroxide.

The hydrogen peroxide that is slowly formed decomposes to oxygen and water, providing an extended oxygen source for subsequent bioremediation of petroleum hydrocarbons.

MAJOR ADVANTAGES ARE:

- · Works on a wide range of contaminants
- Oxygen content about 46% by weight
- Facilitates both chemical oxidant and bioremediation
- Typically 40% by weight solubility for the persulfate

CONTAMINANTS COMMONLY TREATED

- TPH
- 1,4-dioxane
- PCBs
- Pentachlorophenol
- Chloromethanes
- BTEX
- MTBE, ETBE
- PAHs
- Chlorinated Alkenes

ABC+ (Anaerobic BioChem+)

ISCR · Enhanced Reductive Dechlorination ERD · Anaerobic Bioremediation Zero Valent Iron ZVI · Chlorinated Solvents · Pesticides · Lindane · Chloromethanes Carbon Tetrachloride

ABC+ (Anaerobic Biochem+), is a mixture of our ABC® and ZVI (Zero Valent Iron). Formulated and mixed on a site-by-site basis, up to 75% by weight of ZVI can be added.

ZVI has been proven and widely accepted as an effective *in situ* remediation technology for treating chlorinated solvents. The degradation process using ZVI alone is comprised of several abiotic reductive dechlorination processes occurring on the surface of the granular iron, with the iron acting primarily as an electron donor (ISCR).

Details of the ABC® portion of ABC+ are discussed in the bioremediation section of this document.

The addition of ZVI to the ABC® mixture provides a number of advantages for enhanced reductive dechlorination (ERD).

The ZVI will provide an immediate reduction. The ABC® will provide short-term and long-term nutrients to support anaerobic bacteria growth, which also assists in creating a reducing environment.

In addition, the corrosion of iron metal yields ferrous iron and hydrogen, both of which are possible reducing agents.

The hydrogen gas produced is also an excellent energy source for a wide variety of anaerobic bacteria. Due to the presence of a natural co-solvent ABC+ can work where free phase is present.

ABC+ CAN BE SUCCESSFULLY USED ON:

chlorinated ethanes, chloromethanes, Lindane, pesticides, explosives and many other compounds susceptible of biotic and abiotic reduction.



Aerobic Bioremediation: IXPER® Calcium Peroxide, Oxygel, Sulfate BioChem (SBC)

Aerobic Bioremediation • TPH • BTEX • MTBE • ETBE • PAHs • Residual Free Phase • LNAPL

It has been well documented that aquifers contaminated by organic pollutants become rapidly depleted of oxygen due to the activities of aerobic heterotrophic microorganisms. Once oxygen is consumed, other electron acceptors must be readily available and requisite populations capable of utilizing these electron acceptors must be present, else further natural biodegradation processes cannot proceed. The depletion of electron acceptors is generally considered to be the primary factor that limits organic biodegradation *in situ*.

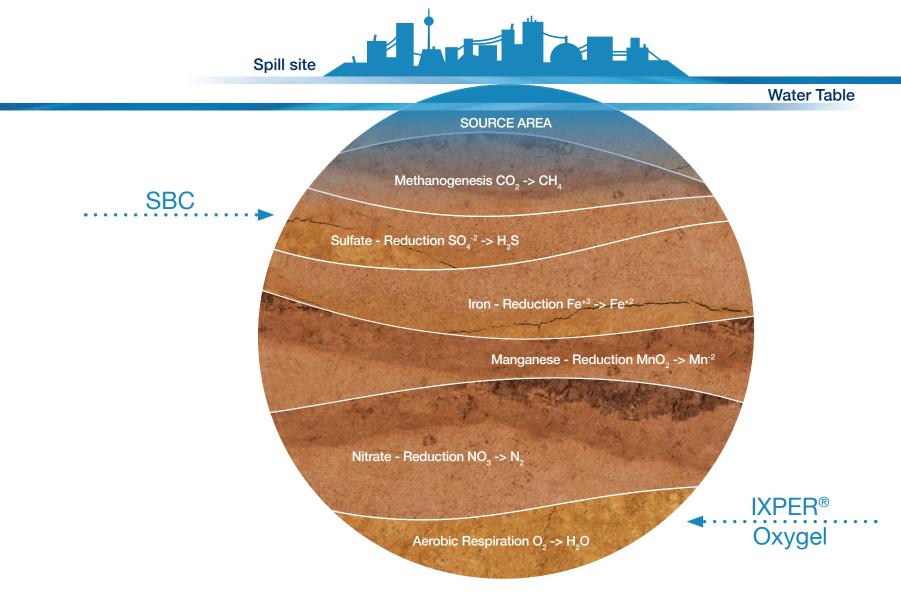
Oxygen has most often been added as the terminal electron acceptor in traditional *in situ* treatment schemes for hydrocarbons contaminated plumes. Carus can provide two different solutions to distribute oxygen into aquifers: IXPER® 75C from Solvay and Oxygel from Biorem Engineering.

In the last decade, it has been proven that other electron acceptors can bu used by bacteria for hydrocarbons biodegradations. Sulfate has been found to serve as an electron acceptor for hydrocarbons biodegradation. The advantage of injecting sulfate rather than oxygen to stimulate biodegradation is that high concentrations of

dissolved sulfate provide a substantially higher electron-accepting capacity relative to oxygen.

A recent study showed that intrinsic bioremediation of BTEX hydrocarbons in situ occurred predominantly under sulfate-reducing conditions, as sulfate was the only available electron acceptor present in sufficient quantity in the contaminated groundwater (Gieg et al., 1999).

Based on these findings, Redox Tech developed SBC a blend of sulfates and nutrients to support Sulfate Reducing Bacteria (SRB) bioremediation activities over the short and long-term.



IXPER®

IXPER® 75C Calcium Peroxide is a fine, odorless powder that contains primarily calcium peroxide. IXPER® 75C is mainly used for the enhanced natural attenuation of pollutants in soil and groundwater such as petrochemical spills and other aerobic biodegradable compounds.

Enhanced bioremediation with the use of IXPER® 75C Calcium Peroxide is achieved through the extended release of oxygen into the subsurface to supplement the rate limiting oxygen requirement by aerobic microorganisms.

IXPER® 75C FCC complies with the specifications of the Food Chemicals Codex for use in food industry.

Oxygel

Oxygel is a revolutionary inorganic gel that slowly produces oxygen over time, when in contact with water. Oxygel can stimulate aerobic biodegradation in anoxic aquifers and sediments (enhanced natural attenuation).

The oxygen-release of this gel continues for up to 6 months and allows biochemical oxidative degradation of a broad range of environmental pollutants. This product has been designed with ease of handling and application in mind, resulting in a pumpable liquid gel that can be applied in soil and sediment.

Oxygel was designed to be better dispersible in subsurface environments compared to powder-based products.

SAFER TO HANDLE





- Better control during application
- All our products are designed with ease of application in mind
- Improved stability: because of their semisolid character, products can remain on the spot of application

Sulfate BioChem (SBC)

Sulfate BioChem (SBC), previously called Oxygen BioChem+ (OBC+), works with naturally reducing conditions to promote long term aoxic biological oxidation of organic compounds. SBC contains several soluble sulfur salts each with a different purpose.

Magnesium sulfate provides the main source of sulfate electron acceptors as well as magnesium, which is essential for cell growth and function. Other sulfur compounds in the mixture help to achieve and maintain the proper redox conditions for anaerobic oxidation of petroleum compounds by sulfate reduction.

During anaerobic oxidation, the petroleum utilizes the oxygen on the sulfate to convert to harmless carbon dioxide and water.

SBC is ideally suited for sites that are already reducing and can be used in the treatment of BTEX, and MTBE, as well as naphthalene and other PAHs.

SBC does not include oxidants; $S^{=}$ from SO_{4} with metals to produce insoluble metal sulfides.



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Anaerobic Bioremediation: ABC®, ABC-Olé, CAP 18® and CAP 18 ME®

Anaerobic Bioremediation • Reductive Dechlorination • Dehalorespiration • PCE • TCE DCE • VC • Chloroethanes • Chloromethanes • Pesticides

In a biological context chlorine behaves similarly to other atoms in the halogen chemical series, and thus reductive dechlorination can be considered to fall within a somewhat broader class of biological reactions known as reductive dehalogenation reactions, in which the removal of a halogen substituent from an organic molecule occurs with a simultaneous addition of electrons to the molecule.



In many instances, microbiological reductive dechlorination, or halorespiration, of chlorinated organic molecules is important for bioremediation of polluted groundwater.

One particularly important example for public health is the organochloride respiration of the dry-cleaning solvent, PCE, and the engine degreasing solvent TCE by naturally occurring anaerobic bacteria, often members of the candidate genera Dehalococcoides.

Such reactions occurs under anaerobic conditions, close to methanogenesis when enough electron donor are available. CRT can provide several carbon sources, specifically engineered for anaerobic bioremediation/reductive dechlorination/halorespiration.

ABC®, ABC-Olé

ABC® (Anaerobic BioChem) is a patented mixture of lactates, fatty acids, alcohols and a phosphate buffer for slow and long term carbon release. ABC® includes a phosphate buffer and other alkaline materials, when necessary, to help maintain optimal pH.

The phosphates also serve as a micronutrient for bioremediation. Each component of ABC® can be altered to meet site specific needs.

ABC®, adds a "green" co-solvent. This serves as a solvent for sites that may have DNAPL, because solvates the DNAPL and promotes rapid treatment.

ABC-Olé is an emulsified fatty acid ester product designed for anaerobic bioremediation sites where emulsified vegetable oil (EVO) products are being evaluated. ABC-Olé is a modified blend of ABC® that contains fatty acid ester content ranging from 30 to 55%. ABC-Olé contains emulsified fatty acid esters, a phosphate buffer, and a small percentage of fast burning substrate.

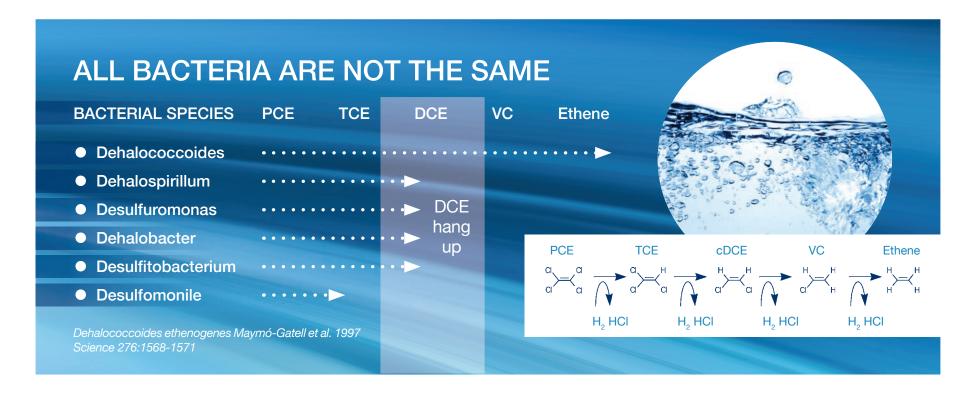
ABC-Olé is better suited for high permeability environments where groundwater flow constantly introduces hydrogen demand.

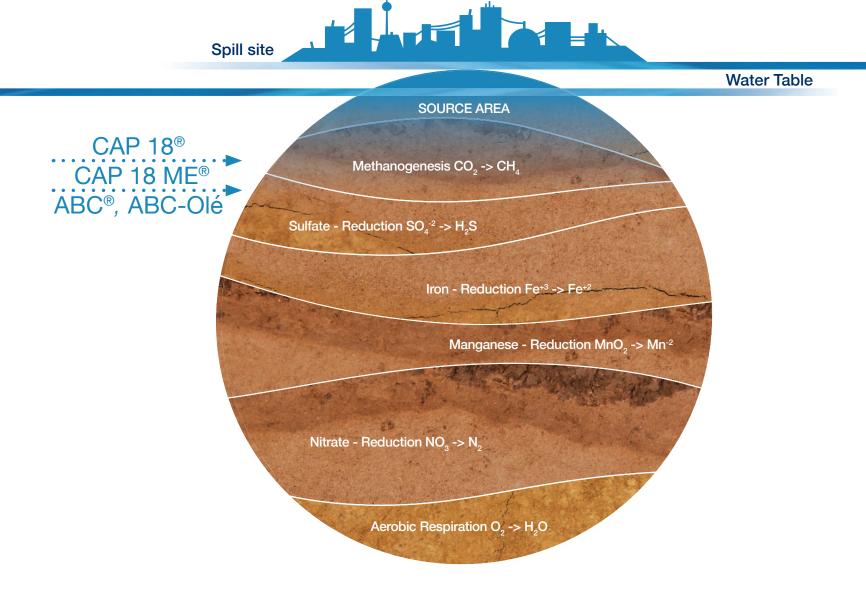
CAP 18® and CAP 18 ME®

CAP 18® anaerobic bioremediation product is a formulation of foodgrade, long-chain (C18) fatty acids, refined from natural vegetable oils, for environmental remediation solutions. CAP 18® can be used for cost-effective, rapid treatment of chlorinated solvents, perchlorate, nitrate, and explosives, found as contaminants in soil and groundwater. CAP 18® remediation is accomplished in-place without high capital costs, disruptive site activities, or complex engineered delivery systems. CAP 18® stimulates microbes to naturally degrade contaminants under anaerobic conditions.

The long-chain fatty acids are consumed via beta-oxidation, which establishes optimal anaerobic conditions for contaminant degradation, and produce hydrogen over a sustained period of time (many months to years).

CAP 18® inhibits microbial reduction of acetate to methane, thereby providing more substrate for hydrogen generation, and reducing microbial reduction of carbon dioxide with hydrogen. Different formulations of CAP 18® were tested to determine if the initial onset of strongly reducing conditions at sites treated with CAP 18® could be accelerated. This has been achieved by adding fatty acid methyl esters to prepare CAP 18 ME® anaerobic bioremediation product.







PRODUCT OVERVIEW

GRAFYSORBER™ (Directa Plus) is an innovative, ecological and effective solution, based on natural graphite and produced through a patented process, which is able to adsorb very quickly and with inimitable performances any type of oil and hydrocarbon from water, soil and air. GRAFYSORBER™ is usable as loose materials, within containment means and filtering systems (booms, pillows, pads, filters, etc.).

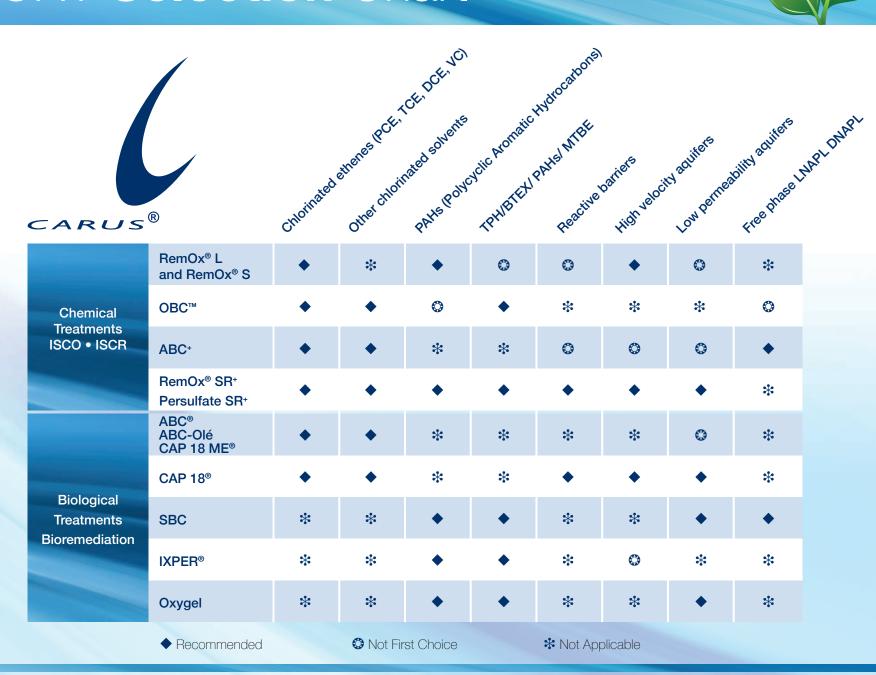
MAIN FEATURES

- SUPER PERFORMING MATERIAL: performs at least 5 times better than the other sorbents actually on the market and is able to remove hydrocarbons even at low concentrations, reaching a potability level.
- COST/EFFECTIVE: favours the recovery and the recycling of adsorbed oil, substantially limiting the production of waste. It can be produced directly on-site and on-demand.
- ECO-FRIENDLY: is completely ecologic as it's inert, not flammable, recyclable and doesn't contain toxic substances.
- UNIQUE and PATENTED: is produced by a unique Patented Plasma Super-Expansion Process (G+ Technology).
- APPROVED: it obtained the approval from the Italian Environmental Ministry for oil-spills clean-up.

CASE HISTORY - HYDROCARBONS DECONTAMINATION

- 30.000 m³ of hydrocarbons contaminated water (TPH concentrations range 300-60 ppm)
- Dose 5-10 g GRAFYSORBER™/m³
- 16 m³/h in 4 m³ batch
- Contact time: 10 minutes
- Total amount of GRAFYSORBER™: 120 kg
- Saving: >100 k€

CRT Selection Chart



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