ABC-CH4™

Liquid, Antimethanogenic ERD Reagent

TECHNOLOGY DESCRIPTION

In 2003, Redox Tech, LLC introduced Anaerobic BioChem (ABC®) as a patented (Rice *et al,* 1999) mixture of hydrogen donors, nutrients, and buffer to accelerate the anaerobic biodegradation of halogenated solvents in groundwater. Since then, millions of pounds of ABC have been used on hundreds of sites throughout the world. Over time the essential ingredients of ABC have been refined, and the materials formulated specifically for the unique geochemistry, biology, and hydrogeology of a given site.

ABC-CH4™ represents the most significant technology advancement in over a decade: it combines the proven chemistry of ABC with the power of the Provect-CH4™ methanogen inhibitors to yield a truly unique liquid, antimethanogenic ERD reagent that contains 60% water soluble carbon:

- Provect-CH4™ methanogenic inhibitor
- Glycerin as fast-release H donors
- Soluble lactic acid as mid-release H donors
- Ethyl lactate as a green solvent and H donor
- Dissolved Fatty acids as long-term release H donors
- Dipotassium Phosphate for micronutrients and pH buffering
- Potash or bicarbonate for pH control

ABC-CH4™is only liquid ERD reagent designed **to actively control the production of methane** in a safe, reliable and predictable manner (US Patent Office Scalzi *et al*, 2013, 2014). In addition to the safety issues, associated with elevated methane in groundwater, soil gas, and indoor air, this effect also promotes more efficient use of the hydrogen donor.

WHAT IS THE PROBLEM WITH METHANE?

There are recognized benefits to methanogens and of limited methanogenesis. For example, i) methanogens are known to play important roles in synergistic microbial ecology, ii) their metabolic activity can help maintain anoxic conditions in treatment zones (through seasonal changes), and iii) the activity of methane mono-oxygenases and other enzymes can stimulate co-metabolic activity of TCE/DCE/VC in redox-recovery zones. Hence, limited production of methane is part of a healthy ERD/ISCR application. However, excessive methane production can be dangerous and represents a costly waste of amendment.

Cost and Efficiency Issues: Production of methane is a direct indication that hydrogen generated from the electron donor amendments was used by methanogens instead of the target microbes (*e.g., Dehalococcoides spp.*), substantially reducing application efficiency. **Table 1** (below) presents a site example where hydrogen demand is calculated for a highly aerobic and oxidized source area measuring approximately 1,850 cubic yards. Hydrogen demand for complete dechlorination of all PCE and TCE mass to ethene within this source area example, including both adsorbed and dissolved contaminants, is less than the amendment consumed to generate 20 mg/L of methane. The same is true of reducing all dissolved oxygen, nitrate, sulfate, and bio-available iron and manganese competing electron acceptors within the hypothetical treatment zone. So, even though this example site is highly oxidized with relatively high total concentrations of PCE and TCE, generating just 20 mg/L of methane constitutes greater than 33% of the total amendment consumption based on moles of H2.

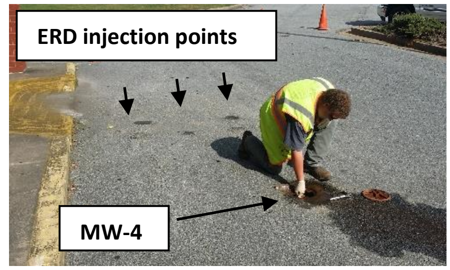
Table 1. H Demand for Complete Dechlorination of PCE/TCE in Hypothetical Source Area

Constituent	Groundwater Concentration (mg/L)	Molecular Weight (g/mol)	Moles of H_2 to Reduce Mole Analyte	Moles of H_2 Acceptor In Treatment Area
Contaminant Electron Acceptors (To End Product Ethene)				
Tetrachloroethene (PCE)	10.0	165.8	4	1,393
Trichloroethene (TCE)	7.0	131.4	3	364
cis-1,2-Dichloroethene (cDCE)	0.0	96.9	2	0
Vinyl Chloride (VC)	0.0	62.5	1	0
			Complete Dechlorination (Soil+Groundwater) Subtotal	**1,757**
Native Electron Acceptors				
Dissolved Oxygen	9.0	32	2	199
Nitrate (as Nitrogen)	9.0	62	3	682
Sulfate	50.0	96.1	4	736
Fe^{+2} Formation from Fe^{+3}	20.0	55.8	0.5	63
Mn^{+2} Formation from Mn^{+4}	10.0	54.9	1	64
			Baseline Geochemistry Subtotal	**1,745**
Hydrogen Waste for Methane Formation				
Methane Formed	20.0	16	4	**1,769**
			Initial Treatment Area Hydrogen Usage	**5,271**

<u>Potential Health and Safety Issues</u>: Methane is considered to be a major greenhouse gas. It is explosive, with an LEL of 5% and an UEL of 15%. As a result of the microbial fermentation process, methane will be produced in most situations following the addition of any conventional ERD or ISCR amendment. Excessive and extended production of methane can result in elevated in groundwater concentrations (as high as 1,000 ppm have been reported) which can lead to accumulation in soil gas subsequently impacting indoor air. While this is perhaps more relevant in urban settings where methane can accumulate in basements, under slabs/foundations and/or migrate along utility corridors, excessive methane production has also been observed in more rural settings and other open spaces.

<u>New and Emerging Regulatory Issues</u>: State specific regulations for methane in groundwater have been promulgated, with others pending for soil gas and indoor air. For example, current regulations for methane in groundwater vary from *ca*. 10 to 28 mg CH_4/L (Indiana Department of Environmental Management, 2014). Notably, several ERD projects which intended to use liquid carbon (emulsified oils) sources have failed to receive regulatory approval due to issues associated with excessive production of methane during previous technology applications (Personal Communication - State of California; State of Minnesota). As a result, many remedial practitioners proactively design contingencies for conventional ERD/ISCR implementation in the event that methane exceeds a threshold level ranging from 1 to 10 ppm groundwater. These contingencies often entail expensive and extensive systems for treating methane in soil gas/vapor captured via SVE systems.

ABC-CH4™ PROOF OF CONCEPT – FIELD CASE STUDY:



In August 2014, ABC-CH4 was added proximal to existing monitoring well MW-207s to treat groundwater at an active shopping mall in Georgia, USA that was impacted by PCE and its catabolites (TCE, DCE and VC) from a former dry cleaning operation. At the same time, the same amount of a standard ERD amendment (no methane inhibitors) was added proximal to existing monitoring well MW-4 which was located ca. 200 feet cross gradient.

Prior to amendment application, baseline groundwater analysis were conducted for dissolved methane and COIs. Six weeks post application, groundwater samples were collected for similar analysis. At that same time, analysis of the head space gases in MW-4 and MW-207s was conducted by Field Environmental Instruments (Pittsburgh, PA) using both a Thermo/Foxboro TVA-1000B PID/FID Analyzer (PID sensitive to 2,000 ppm CH4; FID sensitive to 50,000 ppm CH4) and a LandTec GEM5000 Landfill Gas (LFG) Meter (infrared detector calibrated to 15% methane). Well head space gases were analyzed from top of the well heads immediately upon opening the well caps with readings recorded every minute for 5 minutes.

As summarized in **Table 2,** the MW-4 (water depth 11.9 ft bgs; pressure 0.11 in) treated with an ERD substrate only had over 30% CH4 in the headspace gas as measured by the GEM5000 LFG meter (note – TVA detectors exceeded their level of sensitivity and shut down). By comparison, the well headspace gas in MW-207s (water depth 18 ft bgs; pressure 0.24 in) had only 0.5% CH4 (**Table 2a**). Dissolved methane concentrations were reduced by about 60% in the presence of the methane inhibitors (**Table 2b**). After ca. 6 months, both systems effectively removed site COIs without excessive accumulation of Catabolites (some data not shown)

Table 2a. Well Head Gas Analysis at a Former Dry Cleaner Site in Georgia (6 weeks post ERD application).

Well Location	CH4 PID (ppm)	CH4 FID (ppm)	CH4 TGA %	CO2 %	O2 %	Balance (N) %
MW-4						
0 min	297	>50,000	34.8	65.2	0.0	0.0
5 min	439	>50,000	35.6	61.0	0.2	3.2
MW-207s						
0 min	82	Out of range	0.5	1.0	12.7	85.8
5 min	41	1,599	0.4	0.7	20.2	78.7

Table 2b. Dissolved Gas Analysis at a Former Dry Cleaner Site in Georgia (Method RSK 175).

Well Location	Pre-Injection (ppm)		6-Wks Post-Injection (ppm)		6-Months Post-Injection (ppm)	
	CH4	PCE	CH4	PCE	CH4	PCE
MW-4	13.7	170	10.2	Lost	5.6	<0.01
MW-207s	11.8	1,200	4.2	Lost	7.9	<0.03

ABC-CH4™ PRIMARY FEATURES:

ABC-CH4™ is the only ERD Reagent that includes Provect-CH4™ to rapidly improve remedial performance while simultaneously minimizing the production of methane. The benefits are notable:

- More Efficient = More Cost Effective: Production of methane is a direct indication that the hydrogen generated from the organic carbon amendments was used by methanogens and the amendment has been wasted because it was not utilized by acetogens or dehalorespiration. By inhibiting the growth and proliferation of methane producing Archaea, chlororespiring bacteria can become the more dominant bacterial populations and **at least 30% less ERD amendment can be applied**.
- Safer: Methane is explosive with an LEL of 5% and an UEL of 15%. Production of methane will result from the addition of any conventional ERD or ISCR amendment: excessive and extended production of methane can result in elevated in groundwater concentrations (as high as 1,000 ppm have been reported) which can lead to accumulation in soil gas subsequently impacting indoor air. State specific regulations for methane in groundwater have been promulgated, with others pending for soil gas and indoor air.
- Green and Sustainable Technology: Formulated with byproducts from "green" energy processes, so it is better for the environment.
- Patented Technologies: Technology end users and their clients are fully protected from all Patent and other legal issues.
- Ease of Use:
    - Completely soluble in water hence no need for extensive and time consuming "water chase".
    - No need to emulsify the product with specialize tooling and equipment
    - No laborious material transfers and dilutions
    - No worry about an emulsion breaking.
    - Lower injection pressures
    - No soap formation from bringing pH up too high
    - ABC-CH4 is formulated for each site specific application
    - Avoids cost and need for contingency planning to manage excessive methane production (SVE/AS off gas treatment)
- Longevity (> 2 years): Contains C14 to C18 fatty acids that have been shown in the field to last for over two years. Emulsified oils eventually break down into bioavailable C18 fatty acids through hydrolysis, so we are essentially using the same long-lived components of emulsified oils without having to emulsify or wait for hydrolysis to occur.
- Natural Co-Solvent: Through a license with Oregon State University, ABC-CH4™ includes ethyl lactate which is a "green" co-solvent. This helps dissolve fatty acids, and it also serves as a solvent for sites that may have DNAPL, because the ethyl lactate solvates the DNAPL and promotes rapid treatment.
- Cost Competitive: At a list price of $1.85/lb (Volume Discounts will Apply) for ABC-CH4™ containing 60% carbon + methane inhibitor, this is the most cost efficient way of procuring the combined technologies. When all factors are considered ABC-CH4™ is an excellent value.
- Saves on Least 10% When Compared to ERD Alone: Using the site scenario summarized below, 67,500 lbs of ABC-CH4™ (which includes the methane inhibitors) cost $121,500 which is an excellent value when compared to a cost of $135,000 for 90,000 lbs of a conventional ERD amendment that does not include methane inhibitors.

ABC-CH4™ What Does it Cost?

Treatment Zone Dimensions		
Width of targeted zone (perpendicular to gw flow)	266	ft
Length of targeted zone (parallel to gw flow)	266	ft
Depth to top of treatment zone	20	ft
Depth to bottom of treatment zone	45	ft
Treatment zone thickness	25	ft
Calculated Volume	1768900	ft3
Methane Inhibitor Calculations		
Estimated Porosity	30	%
Calculated impacted liquid	530,670	ft3
Targeted RYR Conc in GW	50	ppm
Methane Inhibitor for Project	1,656	lbs
ROUND TO 55 lb units (25 kg drums)	30	
Unit Price as ERD Supplement (VOLUME DISCOUNTS APPLY)	$35/lb	1,650 lbs
TOTAL (excludes shipping)	**$57,750**	

- Calculated at least 30% less ERD Amendment required = cost offsets.
  - 90,000 lbs ERD required x $1.50/lb = $135,000
  - Can use 30% less ERD = 67,500 lbs x $1.50/lb = $101,250 (saves $33,750)
  - ERD Plus 1,650 lbs Provect-CH4 x $35/lb = $57,750 → $159,000 (adds $24,000 or ca. 15%)
  - 67,500 lbs ABC-CH4 x $1.80/lb = $121,500 **($13,500 less than ERD alone)**
- Avoids need for contingency planning; Safety and Efficacy assurance

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APPLICATION GUIDELINES:

We calculate the theoretical hydrogen demand of a subsurface system based on the redox equations specified in Stumm and Morgan (1996) using site-specific data for the parameters that participate in redox reactions: dissolved oxygen, nitrate, sulfate, ferrous hydroxide, manganese dioxide, contaminant species (*e.g.,* PCE, TCE, *et cetera*), as well as pH and redox potential. From our experience, this value is usually a significant underestimate of the amount of hydrogen required for the system, nevertheless it provides a lower boundary for the range of hydrogen that should be applied to the target volume.

Factors that increase the required hydrogen dose over the theoretical dose include compound concentration heterogeneity (both ambient species and contaminant species), relevant bacteria heterogeneity (presence, viability and density), dynamic conditions (groundwater recharge and flow), application limitations (inherently non uniform distribution of hydrogen due to access methods like injection), hydrogen conversion inefficiencies (hydrogen in a molecule of amendment is rarely converted with 100% efficiency), and others. From our experience of successfully applying enhanced reduction (both biological and abiotic) at hundreds of sites, we have developed an application range that incorporates site specific analytical data as well as knowledge of successful application rates from similar sites under similar conditions. Typically our successful application dose ranges from approximately 0.05 to 0.15 lbs of amendment per cubic foot of aquifer for injections.

- Viscosity = 10 cP at 20 C
- Specific Gravity = 1.14

ORDERING:

All orders for ABC-CH4™ are processed through Redox Tech, LLC at the following address:

REDOX TECH, LLC
"Providing Innovative In Situ Soil and Groundwater Treatment"

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Literature Cited:

Rice *et al,* 1999. *In Situ* Anaerobic Dehalogenation, US Patent 6,001,252.

Scalzi, M. and A. Karachalios. 2013 and 2014. Inhibition of Methane Production during Anaerobic Reductive Dechlorination. US PTO 13/ 785,840 and CIP 14/268,637.

Stumm and Morgan, 1996 (Aquatic Chemistry, 3rd Ed. pp 464-498).

CONTACT US FOR A COMPLIMENTARY SITE EVALUATION

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