

# **Provect-IR® Antimethanogenic ISCR Reagent**

Provect-IR is a unique, patented mixture of reagents combined into a single product that optimizes the *in situ* reductive dechlorination of chemicals present in soil, sediment, and groundwater (US patents 7,129,388; 7,531,709; 7,828,974; 8,147,694; 9,221,699). It is engineered to create and sustain strongly reducing biogeochemical conditions through synergistic interactions between:

- Natural antimethanogenic compounds
- Multiple hydrophilic, nutrient rich organic carbon sources
- ♦ Zero-Valent Iron (ZVI)
- Chemical oxygen scavengers
- Vitamin and mineral sources



This distinctive, patented combination of natural and food-grade chemicals creates and sustains *In Situ* Chemical Reduction (ISCR) conditions for fast and effective destruction of targeted constituents of interest (COIs) such as chlorinated solvents, organochlorine pesticides, and other halogenated compounds via combined abiotic and biotic processes (Brown *et al.*, 2009; Dolfing *et al.*, 2008; Scalzi *et al* 2013). Notably, Provect-IR is the only ISCR reagent to simultaneously inhibit the production of methane during the requisite carbon fermentation processes. This promotes more efficient use of the hydrogen donor (>30% more efficient which reduces amendment requirements and time/labor associated with their application) while avoiding negative issues associated with elevated methane (CH4) in groundwater, soil gas, and indoor air.

### HYDROGEN EQUIVALENTS ANALYSIS

Under some circumstances it is desirable to compare remedial amendments based on their theoretical  $H_2$  production. One limitation to such efforts is the uncertainty in values assigned to various carbon sources, and the rates of hydrogen release which is dependent on the site-specific conditions and groundwater quality. Nevertheless, the following calculations can be presented.

<u>Carbon Moiety</u>: The multiple, complex, hydrophilic organic components of Provect-IR can be viewed simply (although not accurately) as cellulose and hemicellulose which may therefore undergo hydrolysis to yield glucose. Hydrogen gas is produced during glucose fermentation via several enzymatic pathways, depending on site conditions and microbial assemblages:

$Glucose + 6H_2O \rightarrow 6CO_2 + 12H_2$	(1)
Glucose + $2H_2O \rightarrow 2$ Acetate + $2CO_2 + 4H_2 + 2H^+$	(2)



As summarized below, the maximum amount of  $H_2$  that can be generated from a carbon source is about 0.18 moles  $H_2/g$  substrate or 0.36 g  $H_2/g$  substrate (**Table 1**).

Anaerobic Fermentation							
	Atoms	per Mole Sub	ostrate	Average	H₂ Released	Moles H₂ released	
	С	н	Ο	Molecular Weight	per mole Substrate	per gram substrate	
Acetate	2.0	4.0	2.0	60.1	4.0	0.0666	
Lactate	3.0	6.0	3.0	90.1	6.0	0.0666	
Glucose	6.0	12.0	6.0	180.2	12.0	0.0666	
Soybean	56.3	99.5	6.0	873.1	156.5	0.1792	
Corn	56.3	99.9	6.0	873.5	156.6	0.1793	
Cottonseed	55.5	99.3	6.0	862.8	154.7	0.1792	
Palm	54.2	100.8	6.0	848.5	152.8	0.1800	
Peanut	56.8	102.7	6.0	881.4	158.9	0.1803	
Olive	56.2	102.7	6.0	875.0	157.8	0.1804	
Canola	57.1	102.3	6.0	884.6	159.3	0.1801	
Butterfat	50.2	94.0	6.0	793.4	141.4	0.1782	
Lard	55.2	102.4	6.0	862.4	155.6	0.1804	
Beef Tallow	55.1	102.9	6.0	862.2	155.8	0.1807	

# Table 1.Average Composition of Edible Oils and Electrons Released during their<br/>Anaerobic Fermentation

<u>ZVI Moiety</u>: Provect-IR also contains ZVI which corrodes in water and produces hydrogen and hydroxide resulting in an increase in pH and decline in redox potential (Eh):

$$Fe^{\circ} + 2H_2O \rightarrow Fe^{2+} + H_{2(aq)} + 2OH^{-}$$

(3)

Hydrogen gas evolution from ZVI will occur independently of the presence of organic compounds in the site water. Approximately 0.036 g H<sub>2</sub> (1/56) will be released from ZVI itself. Using the parameters and assumptions presented in **Table 2**, various ISCR reagents will exhibit total H<sub>2</sub> production or Hydrogen Equivalents ranging from a high of 0.32 g H<sub>2</sub>/g for Provect-IR + 15% ZVI (standard formulation) to as low as 0.12 g H<sub>2</sub>/g.



# Table 2. Comparative Analysis of Provect-IR Antimethanogenic ISCR Reagent and Other Amendments (Martinson, *et al* 2008; 2011).

▼ Component	Average MW	Moles of H <sub>2</sub> per mole	g of H <sub>2</sub> per g substrate	
LACTATE	90	6	0.12	
EHC <sup>®</sup> with	ZVI = 56	1	0.12*	
40% ZVI	C component = 180	12	0.12	
Emulsified Soybean Oils	873	156	0.18**	
HRC <sup>®</sup> + unknowns	956	212	0.22***	
Provect-IR <sup>®</sup> with 15% ZVI	ZVI = 56	1	0.32	
	C component = 873	156	0.32	

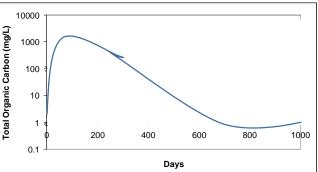
\* As reported (2008; 2011), not substantiated via the scientific literature or vendor.

\*\* Assumes suspension of 50% oil

\*\*\* As calculated and reported, but not substantiated via the scientific literature or vendor.

### HYDROGEN AND CARBON (DOC) RELEASE RATES

When supplying hydrogen for reductive dehalogenation reactions, the <u>rate</u> of release of the hydrogen is as important as the total amount of hydrogen provided. Provect-IR is engineered with multiple sources of organic hydrogen donors that are designed to provide short, medium and long-term hydrogen release profiles. These specially selected carbon sources are



designed to maintain >20 ppm TOC over an estimated 3 to 5 year period of time.

To quickly establish reducing conditions via biological stimulation, the readily biodegraded calcium propionate provides a fast release rate and will liberate high amounts of TOC (>1,000 ppm) for an estimated 100 to 200 days. Next, the relatively more biodegradable components of the kelp and organic plant materials will liberate moderate levels of TOC (>200 ppm) for the next ca. 400 days. Subsequently, the more slowly degraded carbon moieties will liberate lower levels of TOC (*e.g.* >50 ppm) over the following 800+ days. Based on the AFCEE recommendation to maintain at least 20 ppm TOC to support reductive dechlorination reactions, this is sufficient to maintain effective treatment as the contaminant concentrations decrease and the TOC demand is lowered.

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# **ZERO VALENT IRON ANALYSIS**

Customized formulations of Provectus products are always available based on site-specific needs. Our standard Provect-IR product material has 15% (weight basis) ZVI which is of premium grade, optimal particle size to balance reactivity and longevity, and very high in terms of purity and reactive surface area. As described above, Provect-IR also contains multiple, complex, hydrophilic carbon sources. Hence, with improved carbon and *ca*. 5x the ZVI surface area of older, conventional (*i.e.*, no methane control) ISCR reagents, the overall reactivity and performance of Provect-IR is much greater than what we have seen over the past 15+ years with any other conventional ISCR products, even if they might contain more ZVI on a product weight basis.

In terms of practical longevity and reactive life of the ZVI particles in an aquifer, ZVI "a" lasts just as long as ZVI "b" in other ISCR reagents (*ca.* 4 to >7 years is what we have experienced over the years, and yes, longevity is very site specific). When large ZVI granules are used in PRB type applications, it can last decades (AFCEE estimates), but there are emerging issues associated with the overall reactivity, or lack thereof, of these large ZVI PRB's, as the ZVI surface becomes encrusted/occluded and increasingly inert over time. Once any ZVI particle has been exhausted, the ISCR treatment zones still contains reduced iron sulfide precipitates and other reactive minerals (*e.g.*, green rusts, BiRD process, *etc.*) that can help maintain active treatment over an extended period.

# SUMMARY – SO WHAT'S IN THE BAG?

The Provect-IR product is purposefully designed to be the most effective ISCR reagent available, it is the next generation of ISCR chemistry. Therefore, when comparing Provect-IR Antimethanogenic ISCR reagent to seemingly similar alternatives on the simple basis of "What's in the Bag?" the benefits and technical attributes of Provect-IR are very clear (**Table 3**):

- 400% to 500% more ZVI surface area (reactivity)
- Longevity of *ca*. 4 to >7 years
- 100% more hydrogen provided

And

- Multiple hydrophilic, nutrient rich organic carbon sources
- ZVI and other reagents
- Active methane control
- Guar for easy field use
- Chemical oxygen scavengers
- Vitamin and mineral sources



# Table 3. What's in the Bag? Comparative Analysis of Provect-IR® Antimethanogenic ISCR Reagent and other Older, Conventional ISCR Materials.

▼Component	Provect-IR 15% ZVI "a"	Other 15% ZVI "b"	Provect-IR 40% ZVI "a"	Other 40% ZVI "b"	Provect-IR 60% ZVI "a"	Other 60% ZVI "b"
% ZVI in Product	15	15	40	40	60	60
Pounds of ZVI in a 50 lb bag	7.5	7.5	20	20	30	30
ZVI surface area in a 50 lb bag	1,658 ft <sup>2</sup>	330 ft <sup>2</sup>	4,420 ft <sup>2</sup>	1,240 ft <sup>2</sup>	6,630 ft <sup>2</sup>	1,860 ft <sup>2</sup>
% Organic Hydrogen Donor (OHD) in Product	85	85	60	60	40	40
Pounds of OHD in a 50 lb bag	42.5	42.5	30	30	20	20
H Equivalents (50 lb bag)	7,264 g H₂	4,086 g H <sub>2</sub>	5,128 g H₂	2,884 g H <sub>2</sub>	3,418 g H₂	1,923 g H <sub>2</sub>

#### Footnotes:

Calculations based on Provect-IR Average ZVI average particle size of 17.5 microns.

Calculations based on Other Average ZVI particle size of 62.5 microns.

▼ ZVI MATERIAL	Provectus ZVI "a" (see footnotes)	Other ZVI "b" (see footnotes)
Particle size range	5 to 75 micron	40 to 150 micron
Average particle size	15 to 20 micron	50 to 75 micron
General Reactivity	High	Medium
Typical Longevity (site specific)	<i>ca.</i> 4 to >7 years	<i>ca</i> . 5 to >7 years

Footnotes:

Provectus ZVI "a" = specifications based on supplier technical data sheets

Other ZVI "b" = based on internal analyses, public documents including publications/proposals, TDS for commercial ZVI sources, and other assumptions, but not verified by vendors.

# **SUMMARY**

# **Hydrogen Equivalents:**

There are many site-specific factors that will influence the actual  $H_2$  release kinetics and longevity. In general, the standard formulations of Provect-IR and Provect-IRM containing 10% to 40% ZVI (weight basis) will have a hydrogen equivalence of 0.23 g  $H_2/g_{provect-IR40}$  to 0.32 g  $H_2/g_{provect-IR15}$ . This exceeds the amount of H<sub>2</sub> liberated from older formulations of conventional ISCR amendments while uniquely offering the safety and economic benefits of antimethanogenic ISCR treatment. The TOC release characteristics are very favorable, maintaining >20 ppm TOC over a 3 to 4 year period.

About 2x or 100% more hydrogen than other ISCR reagents (no methane control)

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# ZVI Surface Area, Content and Reactivity:

Our standard "Provect-IR15" product material has 15% ZVI which is of premium grade, optimal particle size to balance reactivity and longevity, and very high in terms of purity and reactive surface area. Of course, customized formulations of Provectus products are always available based on site-specific needs. Comparing Provect-IR to seemingly similar ISCR reagents, it has:

- About 4x to 5x or 400% to 500% more ZVI surface area (reactivity)
- Longevity of *ca*. 4 to >7 years (site specific)

## **Other Important Issues:**

Provect-IR represents the evolution of the ISCR process, as it contains high quality, reactive ZVI powders, plus a combination of hydrophilic carbon sources that are rich in vitamins and nutrients and designed for tiered, sustained hydrogen release profiles uniquely in conjunction with actively controlled methanogenesis.

- Active Methane Control
- Easy Handling
- Safer to Use
- Less Expensive
- More Efficient
- Better Performance

A critical analysis of Provect-IR yields a very compelling story, and shows that it is simply a better product. As originators of the technology, our staff know Provect-IR is a better ISCR reagent, which echo the immortal words of the former owner of Remington (Norelco) Razors - Mr. Victor Kermit Kiam II (1926-2001):

"I liked the shaver so much, I bought the company!"



# **References Cited:**

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