

Provect-IR™ Antimethanogenic ISCR Reagent

Provect-IR is a unique mixture of reagents combined into a single product that optimizes the *in situ* reductive dechlorination of chemicals present in soil, sediment, and groundwater. It acts by promoting 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 promotes *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 (Brown *et al.*, 2009; Dolfig *et al.*, 2008; US Patent Office Scalzi *et al* 2012). Notably, Provect-IR is the only ISCR reagent to simultaneously inhibit the production of methane during the requisite carbon fermentation processes (US Patent Office Scalzi *et al*, 2013, 2014). This promotes more efficient use of the hydrogen donor (>30% more efficient which reduces amendment requirements) while avoiding negative issues associated with elevated methane (CH₄) in groundwater, soil gas, and indoor air.

LONGEVITY - HOW LONG DOES IT LAST?

One of the first questions asked regarding the efficacy of the (ISCR) technology is “How long does it last”? Circa 2003, scientists now at Provectus began working with an industrial client and others to develop answers these questions and there have been numerous laboratory and field study publications that have subsequently substantiated the following calculations and estimations.

For this example, groundwater at a hypothetical site contains 2 mg/L DO, 5 mg/L of TCE, 5 mg/L nitrate and 20 mg/L sulfate. The groundwater flow velocity is 0.10 m/day with an aquifer porosity of 0.25. An ISCR treatment zone was established 6 m wide by adding 0.5% (soil mass basis) Provect-IR which contains 90% carbon + 10% ZVI

Theoretical Considerations - Iron Consumption

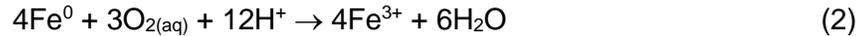
The potential rate of ZVI consumption was calculated using standard reactions with COIs and inorganic electron acceptors present at a hypothetical site (of course the same calculations can be made using site-specific data). The ZVI consumption calculations are based on a unit cell with a face surface area of 1 m² of the Provect-IR-amended zone, or a volume of 6 m³ of amended aquifer material, containing about 11 kg of ZVI. Here, the carbon electron donor was not included

in the electron acceptor consumption calculations. Water corrosion (oxidation) consumes the ZVI, resulting in the generation of ferrous iron, hydrogen gas and hydroxide ion production and an increase in pH and decline in Eh (Eq. 1):



Corrosion rates of various ZVI materials in water range between 0.1 to 0.6 mmol/kg Fe/day (Reardon, 2005). A corrosion rate of 0.3 mmol/kg Fe/day is applied to the particulate ZVI used in Provect-IR. In the field, the iron-water corrosion rate is independent of groundwater flow velocity. Based on the water corrosion rate of 0.3 mmol/kg Fe/day, the annual iron consumption due to water corrosion at this hypothetical site would be about 135 g/yr. This is equivalent to about 1.2% of the total ZVI present in the 6 m wide ISCR treatment zone.

Any dissolved oxygen will also corrode (consume) the ZVI (Eq.2):



Based on the above assumptions, the annual amount of DO (2 mg/L or 0.063 mmol/L) entering a unit cell of the ISCR treatment zone would be 18 g/yr (0.57 mole/yr). Since, four moles of iron are consumed for every three moles of DO, the annual iron consumption rate would be 43 g/yr (0.76 mol/yr). This iron amount represents about 0.4% of the total ZVI in the ISCR treatment zone.

Complete reductive dechlorination of TCE and the corresponding ZVI oxidation can be expressed by the following (Eq. 3):



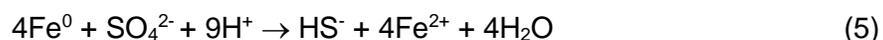
The annual amount of TCE (5 mg/L or 0.038 mmol/L) entering the unit cell of ISCR zone would be 46 g/yr (0.35 mole/yr). Since three moles of iron are consumed for every mole of TCE, the annual iron consumption rate would be 58 g/yr (1.04 mol/yr) or 0.6% of the available ZVI mass in the ISCR treatment zone.

If present, nitrate reduction by granular iron results in the production of ammonia/ammonium (Eq. 4):



Complete reduction of 5 mg/L of nitrate (0.08 mmol/L) by ZVI would result in consumption of an annual nitrate mass flux into the unit cell of the ISCR zone of 46 g/yr (0.74 mol/yr). Four moles of iron are consumed for every mole of nitrate; therefore the annual consumption rate would be equal to 165 g/yr (2.94 mole/yr) or 1.6% of the ZVI available.

Sulfate (SO_4^{2-}) in the presence of iron may undergo reduction to sulfide (Eq. 5):



If complete sulfate reduction occurred due via ZVI oxidation, the annual amount of sulfate (20 mg/L or 0.21 mmol/L) entering the unit cell of ISCR zone would be 183 g/yr (1.9 mole/yr). Since four moles of iron are consumed for every mole of sulfate, the annual iron consumption rate would be 426 g/yr (7.6 mole/yr) or about 4% of the ZVI available.

If electron acceptor reduction and VOC degradation do not compete with water corrosion of ZVI, the annual ZVI consumption rate would be about 7 or 8% of the ZVI available. This would result in a conservative ZVI lifetime in a Provect-IR ISCR treatment zone of about 13 to 15 years at this hypothetical site.

Theoretical Considerations - Carbon Consumption

The carbon component of Provect-IR is comprised in part of process plant materials, kelp/seaweed and other fibrous organic carbon particles. Because of the predominance of cellulose and hemicellulose in the particles, these particles will degrade more slowly (last longer) than more soluble forms of carbon such as lactates, oils, and other glucose based amendments.

Carbon consumption (decay) in the subsurface is often assumed to follow a first order model. Under aerobic soil conditions, cellulose has been shown to persist over several months (Cheshire 1979, Kassim et al, 1981) and will degrade more slowly under anaerobic saturated conditions. In other studies, a first order carbon decay constant (K) of $1.6E-3 \text{ day}^{-1}$ was obtained in cellulose columns used to promote denitrification exposed to a nitrate flux of about 70 to 75 mg/L nitrate-N at room temperature (Vogan 1993). This equates to a 50% loss of cellulose in about 300 days or 10 months. Lower rates of degradation (K of $5E-4 \text{ day}^{-1}$) were obtained in sawdust columns exposed to the same flux. Sawdust contains a relatively higher proportion of hemi-cellulose and lignin. *In situ* sawdust based denitrifying systems have operated for 15 years at field temperatures (Robertson et al, 2008).

Given that the carbon demand in the above conditions is far greater than that usually occurring in organic contaminant plumes these published carbon degradation rates indicate that the carbon component of Provect-IR should also last for > 5 years in the subsurface.

SUMMARY

Mathematical calculations under theoretical site considerations concluded that the ZVI component of Provect-IR will remain active in a subsurface aquifer environment for at least 10 years, and that organic carbon components will remain active in a subsurface aquifer environment for at least 5 years. Field data have shown longevity of over 4 years. There are many factors that can influence the actual longevity observed at a given site: temperature, groundwater flow velocity, electron acceptor demand, mass applied, installation method, and inorganic chemistry. But based on these factors, it appears that Provect-IR (containing 10% ZVI to 40% ZVI) will persist at least 5 years in most subsurface environments.

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CONTACT US FOR A COMPLIMENTARY SITE EVALUATION

PROVTECTUS ENVIRONMENTAL PRODUCTS, INC.

2871 West Forest Road, Suite 2 | Freeport, IL 61032

Tel: (815) 650-2230 | Fax: (815) 650-2232 | Email: info@ProvectusEnv.com

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