REACTIVE IRON SULFIDES

As reviewed by Fan *et al.*, (2017), multiple studies have shown that various reactive iron sulfide species can aid in the biogeochemical transformation of organic constituents of interest (COIs) such as halogenated organic solvents, and that they can be useful in precipitating inorganic COIs such as arsenic, chromium and mercury. This is most apparent with nanoscale or fine (*e.g.*, < 10 micron) zero valent iron (ZVI) particles because they have more surface area which can be quickly passivated, hence within a short period of time, they typically exhibit lower efficiency for dechlorination. In an effort to mitigate this phenomenon various formulations of sulfidated iron (S-ZVI) and other reactive iron sulfide species such as mackinawite *per se* have become available commercially as remedial amendments designed to be injected or otherwise applied directly to an impacted environment.

The reactive properties of S-ZVI adhere to classic corrosion chemistry principles governing the conditions under which sulfur attacks iron. Recognizing the potential distinctions between chemical sulfidation and natural sulfidation, an alternative means of harnessing the activity of reactive iron sulfides - instead of buying mackinawite alone (for example) - is to generate **multiple iron sulfide species, in place, and for free** as part of an engineered remedial amendment that integrates multiple synergistic biogeochemical reactions (see Mangayayam *et al*, 2019 for emerging insights into the actual value of buying and applying sulfidated iron products directly). In so doing the remedial actions occur where they are needed and not simply where the insoluble precipitates are directly emplaced.

As outlined below, this is what occurs with Provect-OX®/Provect-OX2™ *in situ* chemical oxidation (ISCO) / enhanced bioremediation amendments, Provect-IR® / Provect-IRM® (antimethanogenic) solid *in situ* chemical reduction (ISCR) amendments, and Provect-ERD-CH4+DVI Liquid ISCR amendment.

IN SITU FORMATION OF IRON SULFIDES

One of the most well-known redox-based inorganic precipitation reactions involves iron and sulfate (SO_4^{2-}) which is a common constituent in groundwater aquifers. At high redox potential (Eh), the stable form of sulfur is sulfate (SO_4^{2-}); at very low Eh sulfide (H_2S or HS^-) is the stable form, with HS^- being predominant at pH greater than 7 (Equation 1):

$$HS^- + 4H_2O \leftrightarrow SO_4^{2-} + 9H^+ + 8e^- \qquad \text{(Eq 1)}$$

Sulfate reduction in natural aquifer environments is biologically mediated via near-ubiquitous sulfate-reducing bacteria as they use the oxygen in sulfate to convert organic matter to bicarbonate as shown in Equation 2, which can be further transformed to carbon dioxide (CO_2) and methane (CH4).

$$SO_4^{2-} + 2C_{organic} + 2H_2O \rightarrow H_2S + 2HCO_3^- \qquad \text{(Eq 2)}$$

Sulfate can also be reduced by direct interaction with zero-valent iron (ZVI) or reduced iron. Given the low solubility of iron sulfide (FeS), the hydrogen sulfide produced precipitates out of solution (Equation 3). Hydrogen sulfide is slightly soluble in water and acts as a weak acid yielding the hydrosulfide ion HS^- ($pK_a = 6.9$) and the sulfide anion S^{2-} ($pK_a = 11.96$) per Equation 4.

$$Fe^{2+} + HS^{-} \rightarrow FeS_{(s)} + H^{+} \qquad \text{(Eq 3)}$$

$$H_2S \Leftrightarrow HS^{-} + H^{+} \Leftrightarrow S^{=} + H^{+} \qquad \text{(Eq 4)}$$

Over time, the precipitates yield a variety of reactive iron sulfide species including:

- Mackinawite (FeS), a (nano)crystalline or an amorphous form of black iron sulfide precipitate (Butler and Hayes, 1999; Dries *et al*., 2001; Fan *et al*, 2017).
- Greigite, an iron(II)/iron(III) sulfide mineral with formula Fe_3S_4 (Picard *et al.,* 2018), mostly upon oxidation of FeS (Bourdoiseau *et al*., 2011; Lennie *et al*., 1997) with conversion over time to Fe3S4 (Csakberenii-Malasics *et al*, 2012).
- Green Rust, a mixed iron(II)/iron(III) hydroxide layered combined with anions such as carbonate, chloride and sulfate (Christianson *et al*., 2009).
- Marcasite a polymorph of pyrite (Battelle, 2002; Yabusaki *et al,* 2001), and possibly Pyrite (FeS_2).

FREE MACKINAWITE and more…

Under ERD/ISCR Conditions

Provect-IR®/Provect-IRM® solid ISCR amendments and ERD+DVI liquid ISCR amendments are formulated on a site-specific basis. As such, the types and amounts of organic carbon and the grade, purity and amount of ZVI (and sulfur where needed) are optimized for both short- and long-term effectiveness. For example, a hypothetical site with a groundwater flow velocity of 0.3 m/day, an aquifer porosity of 0.3 and a sulfate concentration of 100 mg/L represents an annual 3,285 g/yr/m^2 (34.2 mol/yr/m^2) mass flux of sulfate. In the presence Provect-IR the amendment could form *in situ* an estimated 3,010 g/yr/m^2 of FeS or 2,462 g/yr/ft^2 of FeS_2. FeS formation continues only so long as reagents maintain anoxic conditions under continuous oxygen input, but assuming that all iron sulfides are eventually converted to marcasite and assuming a molar volume of FeS of 18.5 cm^3/mol, then the volume of precipitate formed would be equivalent to 632 cm^3/yr/m^2.

Provect-IR® Solid ISCR Amendment and Provect-IRM® are mixtures of reagents combined into a single product that optimizes the *in situ* reductive dechlorination of chemicals present in soil, sediment, and groundwater. It is engineered to create and sustain strongly reducing biogeochemical conditions through synergistic interactions between:

- Multiple hydrophilic, nutrient-rich organic carbon sources
- Zero-Valent Iron (ZVI)
- Chemical oxygen scavengers (dithionate and/or sulfite) - see Han and Yan, 2016
- Vitamin and mineral sources

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- Supplemental sulfur sources, where needed
- Optional natural antimethanogenic compounds (AMRs), where appropriate

Provect-ERD+DVI™ Liquid ISCR Amendment is a mixture of cold-water soluble reagents combined into a single product providing both fermentable carbon and supplemental Dual-Valent Iron (DVI) in the proper proportions so that the Fe^{+2} ions donate electrons and are oxidized to Fe^{+3} over several years. Where needed (*i.e.*, in the presence of low sulfate), additional source of sulfur is included in the product formulation. General physical parameters are as follows:

- Multiple hydrophilic, nutrient rich organic carbon sources at 60 to >85% weight basis (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
- Dual-Valent Iron water-soluble organic Fe content 5 to 10% weight basis
- Chemical oxygen scavengers (dithionate and/or sulfite)
- Vitamin and mineral sources
- Supplemental sulfur sources, where needed
- Optional natural antimethanogenic compounds (AMRs), where appropriate (two types typically at 4% to 8% weight of FC)

These distinctive, patented (US patents 7,129,388; 7,531,709; 7,828,974; 8,147,694; 9,221,699) combinations of natural and food-grade chemicals create and sustain ISCR conditions for fast and effective destruction of chlorinated solvents, organochlorine pesticides, and other halogenated compounds via combined abiotic and biotic processes (Brown *et al.,* 2009; Chen *et al*., 2014; Dolfing *et al.,* 2008; Scalzi *et al* 2013; Wei and Finneran, 2011). Notably, only Provectus ISCR reagents contain antimethanogenic reagents (AMRs) 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 – see Men *et al*., 2013; Mueller *et al.,* 2014) while avoiding negative issues associated with elevated methane (CH_4) in groundwater, soil gas and indoor air (Kram *et al*., 2019).

Under ISCO Conditions

Provect-OX® and Provect-OX2™ activate sodium and/or potassium persulfate using divalent and/or-trivalent metals such as Fe III (Scalzi and Karacharios, 2013a) which requires a lower activation energy than alternative mechanisms while not consuming the persulfate oxidant. The mechanism is believed to elevate the oxidation state of the iron transiently to a supercharged iron ion which also may act as an oxidant. The reactions that occur in the chemical oxidation include persulfate radicals and ferrate, as summarized below (Equation 4):

$$S_2O_8^{-2} + Fe^{+3} \text{ ---------> } Fe^{(+4\ to+6)} + SO_4^{2-} + SO_4^{2-\bullet} \qquad \text{(Eq. 4)}$$

As the supercharged iron cation is consumed, the resulting ferric species can act as a terminal electron acceptor for biological attenuation – which generates reactive iron sulfide species as noted above. Coincidentally, the generated sulfate ion from the decomposition of the persulfate provides a terminal electron acceptor for sulfate reducers which may further remediate the targeted compounds in the groundwater and soils.

1) Sulfate Residual

After an initial oxidative phase (weeks to months), an aquifer transition to a reducing environment in the presence of electron donor such as residual organic contaminant. After dissolved oxygen has been depleted in the treatment area, sulfate (a by-product of the persulfate oxidation) may be used as an electron acceptor for anaerobic biodegradation by indigenous microbes. This process is termed sulfidogenesis and results in the production of sulfide. Stoichiometrically, each 1.0 mg/L of sulfate consumed by microbes results in the destruction of approximately 0.21 mg/L of BTEX compounds. Sulfate can play an important role in bioremediation of petroleum products, acting as an electron acceptor in co-metabolic processes as well. For example, the basic reactions for the mineralization of benzene and toluene under sulfate reducing conditions are presented in Equations 5 and 6:

$$C_6H_6 + 3.75\ SO_4^{2-} + 3\ H_2O \text{ --> } 0.37\ H^+ + 6\ HCO_3^- + 1.87\ HS^- + 1.88\ H_2S^- \qquad \text{(Eq. 5)}$$

$$C_7H_8 + 4.5\ SO_4^{2-} + 3\ H_2O \text{ --> } 0.25\ H^+ + 7\ HCO_3^- + 2.25\ HS^- + 2.25\ H_2S^- \qquad \text{(Eq. 6)}$$

2) Ferric Iron

Ferric iron is also used as an electron acceptor during anaerobic biodegradation of many contaminants, sometimes in conjunction with sulfate. During this process, ferric iron is reduced to ferrous iron, which is soluble in water. Hence, ferrous iron may be used as an indicator of anaerobic activity. As an example, stoichiometrically, the degradation of 1 mg/L of BTEX results in the average consumption of approximately 22 mg/L of ferric iron (or “production” of ferrous iron) as shown below (Equations 7 – 9).

$$C_6H_6 + 18\ H_2O + 30\ Fe^{3+} \text{ -------> } 6\ HCO_3^- + 30\ Fe^{2+} + 36\ H^+ \qquad \text{(Eq. 7)}$$

$$C_7H_8 + 21\ H_2O + 36\ Fe^{3+} \text{ -------> } 7\ HCO_3^- + 36\ Fe^{2+} + 43\ H^+ \qquad \text{(Eq. 8)}$$

$$C_8H_{10} + 24\ H_2O + 42\ Fe^{3+} \text{ -------> } 8\ HCO_3^- + 42\ Fe^{2+} + 50\ H^+ \qquad \text{(Eq. 9)}$$

3) Formation of Mackinawite and other Reactive Iron Sulfides

While ferrous iron is formed as a result of the use of the ferric species as a terminal electron acceptor, residual sulfate is utilized as a terminal electron acceptor by facultative organisms thereby generating sulfide under these same conditions. Together, the ferrous iron and the sulfide promote the formation of iron sulfides as a remedial byproduct (Equation 3). This reaction combats the toxic effects of sulfide and hydrogen sulfide accumulation on the facultative bacteria, while also providing a means of removing targeted organic and inorganic COIs via precipitation

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reactions. Moreover, pyrite possesses a high number of reactive sites that are directly proportional to both its reductive capacity and the rate of decay for the target organics.

REFERENCES CITED

Blowes, D.W. and K.U. Mayer. 1999. An *in situ* permeable reactive barrier for the treatment of hexavalent chromium and trichloroethylene in ground water; Vol. 3, Multicomponent reactive transport modeling. EPA/6000/R-99/095c.

Bourdoiseau, J-A., M. Jeannin, C. Rémazeilles, R. Sabot and P. Refait. 2011. The Transformation of Mackinawite into Greigite studied by Raman Spectroscopy. J. Raman Spectroscopy 42(3):496-504. https://doi.org/10.1002/jrs.2729

Brown, R., J. Mueller, A. Seech, J. Henderson and J. Wilson. 2009. Interactions between Biological and Abiotic Pathways in the Reduction of Chlorinated Solvents. Remediation Journal Winter 2009, pages 9-20.

Butler, E.C. and K.F. Hayes. 1999. Kinetics of the transformation of trichloroethylene and terachloroethylene by iron sulfide. Environ. Sci. & Technol., Vol. 33, pp. 2021-2027.

Chen, S., D. Fan and P.G. Tratnyek. 2014. Novel Contaminant Transformation Pathways by Abiotic Reductants. *Environ. Sci. Technol. Lett. 1(10):*432-436. https://doi.org/10.1021/ez500268e

Christiansen, B.C., T. Balic-Zunic, K. Dideriksen and S.L.S. Stipp. 2009. Identification of Green Rust in Groundwater. *Environ. Sci. Technol.* (43): 3,436 - 3,441. https://doi.org/10.1021/es8011047

Csákberényi-Malasics, D., J.D. Rodriguez-Blanco, V.K. Kis, A. Recnik, L.G. Benning and M. Pósfai. 2012. Structural properties and transformations of precipitated FeS. Chem. Geol. 294-295:249-258. DOI: 10.1016/j.chemgeo.2011.12.009

Dries, J., Bastiaens, L., Springael, D., Diels, L. and Agathos, S.N., 2001. Kinetics of trichloroethene (TCE) reduction by zero valent iron: Effect of medium composition. Groundwater Quality: Natural and Enhanced Restoration of Groundwater Pollution (Proceedings of the Groundwater Quality 2001 Conference held at Sheffield, UK, June 2001). IAHS Publ. no. 275, 2002. Pages 397–402.

Dolfing, J., M. Van Eekert, A. Seech, J. Vogan and J. Mueller. 2008. *In Situ* Chemical Reduction (ISCR) Technologies – Significance of Low Eh Reactions. International Journal Soil & Sediment Contamination 17 (1): pages 63-74.

Fan, D., Y., Lan, P.G. Tratnyek, R.L. Johnson, J. Filip, D.M. O'Carroll, A.N. Garcia and A. Agrawal. 2017. Sulfidation of Iron-Based Materials: A Review of Processes and Implications for Water Treatment and Remediation. Environ. Sci. Technol. 51: pages 13070-13085.

Han, Y and W. Yan. 2017. Reductive Dechlorination of Trichloroethylene by Zero-Valent Iron Nanoparticles: Reactivity Enhancement through Sulfidation Treatment. Environ. Sci. Technol. 50: pages 12992-13001. https://doi.org/10.1021/acs.est.6b03997

Kram., M., B. Hartman and N. Clite. 2019. Automated Continuous Monitoring and Response to Toxic Subsurface Vapors entering Overlying Buildings: Selected Observations, Implications and Considerations. Remediation J. 29:31-38.

Lennie, A.R., S.A.T. Redfern, P. E. Champness, C.P. Stoddart, P.F. Schofield, and D.J. Vaughan. 1997. Transformation of Mackinawite to Greigite: An *in situ* X-ray powder diffraction and transmission electron microscope study. American Mineralogist, Volume 82, pages 302–309.

Mangayayam, M., J.P.H. Perez, K. Dideriksen, H. Freeman, N. Bovet, L.G. Benning, and D. Tobler. 2019. Structural Transformation of Sulfidated Zero Valent Iron and its Impact on Long-Term Reactivity. Environmental science. Nano. (00):1-9. DOI: 10.1039/C9EN00876D

Men, Y., P.K.H. Lee, K.C. Harding and L. Alverez-Cohen. 2013. Characterization of Four TCE-Dechlorinating Microbial Enrichments Grown with Different Cobalamin Stress and Methanogenic Conditions. Appl. Microbiol. Biotechnol. 97:6439-6450.

Mueller, J., A. Karachalios and T. Fowler. 2014. Controlling Methane Production during ERD and ISCR Applications. Pollution Engineering News, October pp 24-29.

Picard, A., A. Gartman, D.R. Clarke and P.R. Girguis. 2018. Sulfate-reducing Bacteria Influence the Nucleation and Growth of Mackinawite and Greigite. Gechemica et Cosmochemica (220):367-384.

Ropp, R.C. 2013. Chapter 3 – Group 16 (O, S, Se, Te) Alkaline Earth Compounds. In: Encyclopedia of Alkaline Earth Compounds, Pages 105-197. https://doi.org/10.1016/B978-0-444-59550-8.00003-X

Scalzi, M. and J. McGill. 2012. Method for the Treatment of Groundwater and Soils using Mixtures of Seaweed Kelp. US PTO No. 8,147,694 B2.

Scalzi, M. and A. Karachalios. 2013a. Chemical Oxidation and Biological Attenuation Process for the Treatment of Contaminated Media. US PTO 9,126,245.

Scalzi, M. and A. Karachalios. 2013 and 2014. Inhibition of Methane Production during Anaerobic Reductive Dechlorination. US PTO No. 9,221,699.

Wei, N. and K. Finneran. 2011. Influence of Ferric Iron on Complete Dechlorination of Trichloroethylene (TCE) to Ethene: Fe(III) does not always inhibit complete dechlorination. Environ. Sci. Technol 45, 7422–7430

Yabusaki, S., K. Cantrell, B. Sass and C. Steefel. 2001. Multicomponent reactive transport in an in-situ zero-valent iron cell. Environ. Sci and Technol., Vol. 35, pages 1493-1503.

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REVIEWER ACKNOWLEDGEMENTS

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John R. Hesemann, P.E., Burns & McDonnell – Kansas City, MO
jhesemann@burnsmcd.com

Bernd Rehm, ReSolution Partners, LLC. – Madison, WI
brehm@resolutionpartnersllc.net

CONTACT US FOR A COMPLIMENTARY SITE EVALUATION

PROVECTUS 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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