



## SITE LOGIC

Evaluating Potential for Abiotic Degradation

Although not always fully considered, abiotic degradation can be a substantial or even the primary process for chlorinated hydrocarbon destruction at sites undergoing or transitioning to monitored natural attenuation (MNA). A variety of iron-bearing minerals including iron sulfides (mackinawite and pyrite), iron oxides (magnetite), green rust, and iron-bearing clays are capable of complete or nearly complete degradation of PCE, TCE, and carbon tetrachloride (He et al. 2009). Some iron-bearing minerals also catalyze the degradation of chlorinated ethanes and the lesser chlorinated ethenes cis-dichloroethene (DCE) and vinyl chloride. While the quantities and types will vary, these reactive iron minerals are frequently identified in subsurface environments under iron reducing and sulfate reducing conditions.

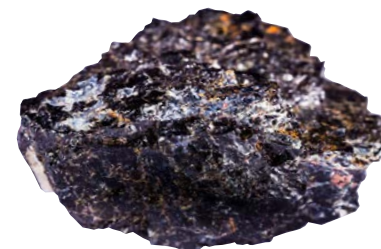
Brown et al. (2007) recommend four avenues for evaluating the role of abiotic processes in contaminant attenuation. First, examining contaminant concentrations along the flow path—decreasing parent compound concentrations with no evidence of accumulation of chlorinated transformation products like cis-DCE and vinyl chloride suggest abiotic degradation. Performing compound specific isotope analysis (CSIA) or monitoring for products unique to abiotic reactions such as acetylene can also provide a strong line of evidence. Microcosm studies with native sediment and killed controls can also be performed. Finally, Brown et al. (2007) suggest performing mineralogical analyses on aquifer sediment to characterize reactive minerals such as magnetite or iron monosulfides.

**Magnetic Susceptibility—Magnetite**

Magnetite ( $\text{Fe}_3\text{O}_4$ ) is a mixed valence iron mineral shown to react with PCE, TCE, and carbon tetrachloride. Furthermore, Ferrey et al. (2004) conclusively linked the observed degradation of cis-DCE at a former ammunition plant to magnetite in the subsurface. No direct chemical test is available for quantification of magnetite. However, magnetite is the most abundant mineral in natural sediments that exhibits magnetic behavior. Therefore, magnetic susceptibility provides an inexpensive and valuable estimate of the quantity of magnetite in environmental samples.

**X-ray Diffraction (XRD)—Mackinawite, Pyrite, Magnetite and Green Rust**

XRD is one of the primary techniques used to identify unknown crystalline materials. Most minerals are crystalline and will scatter X-rays in a regular, characteristic manner dependent on their crystal structure.



- Mackinawite is the most reactive of the iron-bearing minerals and a crystalline form (tetragonal  $\text{FeS}$ ) can be detected by XRD. Mackinawite will transform PCE and TCE primarily by elimination to acetylene. Carbon tetrachloride is transformed mainly to chloroform but carbon dioxide, formate, and carbon disulfide have also been detected. Finally, the more heavily chlorinated ethanes including hexachloroethane, pentachloroethane, and tetrachloroethanes react to form chlorinated ethenes which can be further degraded.
- Pyrite ( $\text{FeS}_2$ ) catalyzes beta elimination transforming PCE, TCE, and cis-DCE to acetylene and ethene. Vinyl chloride is transformed to ethene and ethane. Pyrite is also capable of degradation of carbon tetrachloride potentially forming a number of products including chloroform, carbon dioxide, carbon disulfide, and formate depending on reaction conditions.
- While not quantitative like magnetic susceptibility test, XRD can also detect magnetite when present at between 2% and 5% on a weight basis.
- Green rusts have been reported to transform a number of common chlorinated contaminants including cis-DCE, vinyl chloride, trichloroethanes, and tetrachloroethanes. While special sample care to prevent oxidation would be needed, XRD can be used to detect green rust.

**Percent Clay**

Clays have large surface areas, balanced by exchangeable cations, which can bind a large number of both organic and inorganic molecules impacting their availability and reactivity in the subsurface. While less well studied than the other iron-bearing minerals, various phyllosilicate clays have been shown to be capable of degradation of PCE, TCE, cis-DCE, vinyl chloride, and carbon tetrachloride.

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### Additional Analyses to Consider

- Dissolved Ferrous Iron ( $\text{Fe}^{2+}$ )  
Ferrous iron adsorbed to the surface of minerals including magnetite can increase contaminant degradation rates. Higher dissolved iron concentrations would indicate the potential for such sorption at the mineral surface.
- Acid Volatile Sulfide (AVS) and Chromium Reducible Sulfur (CrRS)  
AVS and CrRS are commonly used to estimate  $\text{FeS}$  and  $\text{FeS}_2$ , respectively.

### References

Brown, R. A., J. T. Wilson and M. Ferrey (2007). "Monitored natural attenuation forum: The case for abiotic MNA." *Remediation Journal* 17(2): 127–137.

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**Table 1 Abiotic Reactions of Chlorinated Compounds with Iron Bearing Minerals and Zero Valent Iron (ZVI).**

Summaries for iron bearing minerals are based on He et al. (2009) and references therein. He et al. available at <http://nepis.epa.gov/>

Summary of ZVI based on Liu et al. (2005) and (Song et al. 2005)

Contaminant	Mineral	Degradation?	Reported Degradation Intermediates and Products <sup>1</sup>
PCE	FeS	Yes	Acetylene, TCE, cis-DCE, 1,1-DCE, ethene
	Pyrite	Yes	TCE, acetylene, ethene
	Magnetite	Yes	Unknown <sup>2</sup>
	<sup>3</sup> GR(SO <sub>4</sub> )	Reports Differ	
	phyllosilicate clays	Yes	TCE, 1,1-DCE, vinyl chloride, 1,1,2-TCA, 1,1-DCA, chloroacetylene, acetylene, ethene, ethane
	ZVI	Yes	Ethene and ethane
TCE	FeS	Yes	Acetylene, cis-DCE, vinyl chloride, 1,1-DCE
	Pyrite	Yes	Acetylene, ethene, cis-DCE, (organic acids with DO present)
	Magnetite	Yes	Unknown <sup>1</sup>
	GR(SO <sub>4</sub> ), GR(CO <sub>3</sub> )	No	Only observed degradation when Cu(II) added
	phyllosilicate clays	Yes	cDCE, vinyl chloride, acetylene, ethene, ethane
	ZVI	Yes	Ethane, ethene, acetylene with minor amounts of DCE, VC depending on conditions
cis-DCE	FeS	No	None detected
	Pyrite	Yes	Acetylene, ethene
	Magnetite	Yes	Unknown <sup>2</sup>
	GR(SO <sub>4</sub> )	Yes	
	phyllosilicate clays	Yes	
	ZVI	Yes	Primarily acetylene and ethene but also much lesser amounts of ethane and VC and traces of methane, propane, propene, butane and butene
Vinyl chloride	FeS	Unknown	
	Pyrite	Yes	Ethene, ethane
	Magnetite	Yes	Unknown <sup>2</sup>
	GR(SO <sub>4</sub> )	Yes	
	phyllosilicate clays	Yes	
	ZVI	Yes	Ethene, ethane, (no evidence of acetylene)
1,1-DCA	FeS	Not Significant	None detected
1,1-DCA	GR(SO <sub>4</sub> )	Low conversion	Ethene and ethane (w/ Cu or Ag)
1,1-DCA	ZVI	Yes (low)	Ethane
1,2-DCA	FeS	Not Significant	None detected
1,2-DCA	FeS (Biogenic)	Yes	Not monitored
1,2-DCA	GR(SO <sub>4</sub> )	No	
1,2-DCA	ZVI	No	

**Table 1 Abiotic Reactions of Chlorinated Compounds with Iron Bearing Minerals and Zero Valent Iron (ZVI).**

**(Continued)**

Contaminant	Mineral	Degradation?	Reported Degradation Intermediates and Products <sup>1</sup>
1,1,1-TCA	FeS	Yes	1,1-DCA, ethene, 2-butyne
1,1,1-TCA	GR(SO <sub>4</sub> )	Yes	1,1-DCA, CA, ethene ethane
1,1,1-TCA	ZVI	Yes	1,1-DCA, ethane
1,1,2-TCA	FeS	Rate not significant	Small amounts of 1,1-DCE and vinyl chloride but rate not significant
1,1,2-TCA	GR(SO <sub>4</sub> )	Yes	Vinyl chloride, 1,1-DCE, ethene, ethane
1,1,2-TCA	ZVI	Yes	Ethane
1,1,1,2-TeCA	FeS	Yes	1,1-DCE
1,1,1,2-TeCA	GR(SO <sub>4</sub> )	Yes	1,1-DCE and minor (<1%) vinyl chloride, ethene, ethane
1,1,1,2-TeCA	phyllosilicate clays	Yes	1,1-DCE
1,1,1,2-TeCA	ZVI	Yes	TCE, 1,1-DCE
1,1,2,2-TeCA	FeS	Yes	TCE, cis-DCE, trans-DCE, acetylene
1,1,2,2-TeCA	GR(SO <sub>4</sub> )	Yes	TCE (major), cis-DCE, trans-DCE
1,1,2,2-TeCA	phyllosilicate clays	Yes	TCE
1,1,2,2-TeCA	ZVI	Yes	TCE, trans-DCE, cis-DCE
Carbon Tetrachloride	FeS	Yes	Chloroform, carbon disulfide, possibly methane, ethene, ethane
CT	Pyrite	Yes	Chloroform, CO <sub>2</sub> , carbon disulfide, formate (highly dependent on conditions)
CT	Magnetite	Yes	Chloroform, carbon monoxide, methane, formate (highly dependent on conditions)
CT	GR(SO <sub>4</sub> )	Yes	Chloroform and hexachloroethane; Chloroform, DCM, methane, ethene
CT	phyllosilicate clays	Yes	Chloroform
CT	ZVI	Yes	Chloroform, dichloromethane, methane (depending on conditions)

**Notes:** GR(SO<sub>4</sub>) sulfate green rust. GR(CO<sub>3</sub>) carbonate green rust. ZVI zero valent iron.

<sup>1</sup> Compilation of reported degradation products. Mass recovery of products typically low—additional undetected and unreported products are likely. Reported reaction products or proportions of reaction products were often a function of environmental conditions.

<sup>2</sup> No published studies that identify the transformation products of PCE, TCE, cis-DCE or vinyl chloride with magnetite. Ferrey et al (2004) analyzed for products of cis-DCE dechlorination including vinyl chloride, ethene, and ethane and did NOT find them. If Fe<sup>2+</sup> sorbed to magnetite stabilizes carbene ions, the ultimate degradation product of cis-DCE on magnetite would be CO<sub>2</sub>.