ENVIRONMENTAL RESTORATION

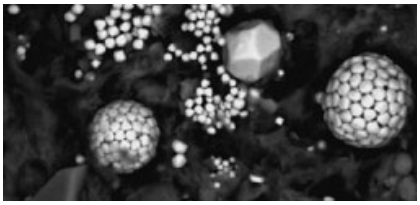
In Situ Biogeochemical Transformation Processes for Treating Contaminated Groundwater

Introduction

In situ biogeochemical transformation (ISBGT) processes result in the degradation of contaminants through combined biological, mineral, and chemical pathways. The contaminants are typically transformed abiotically by reduced iron (Fe II) minerals formed by microbial activity. However, the minerals may also be present naturally as part of the site geology. This fact sheet summarizes the application of ISBGT in treating groundwater contaminated with chlorinated solvents.

What Is the Reaction Chemistry?

This fact sheet focuses primarily on iron sulfide, mackinawite (FeS), as the reactive mineral. However, other iron sulfides (pyrite, greigite) and additional reduced iron(Fe II)-containing minerals such as magnetite, green rust, and phyllosilicate clays (biotite and vermiculite) are capable of abiotically transforming contaminants.



Framboid FeS (USGS, 2008)

The formation of iron sulfide species and the subsequent transformation of contaminants such as chlorinated solvents occurs through multiple steps (Figure 1). The first step is a biotic process. In a reducing environment, sulfate-reducing microbes generate HS^- by reducing naturally-occurring or amended sulfate, and Fe(II) is generated by the action of iron-reducing microbes on naturally-occurring Fe(III) oxyhydroxides (Step 1). The second step results in the rapid precipitation of loosely crystallized and reactive iron sulfide species (Step 2). The third step is an abiotic process. Contaminants in the presence of the reactive iron sulfide species are abiotically transformed as electrons are donated from the iron sulfide to the chlorinated solvent (Step 3).

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Step 1 Biotic		Step 2 Precipitation		Step 3 Abiotic
$SO_4^{2-} + 9H^+ + 8e^- = 8HS^- + 4H_2O$ $FeOOH + 3H^+ + e^- = Fe^{2+} + 2H_2O$	→	$HS^- + Fe^{2+} = FeS + H^+$	→	$C_2Cl_4 + FeS + 4H_2O = C_2H_2 + Fe^{3+} + SO_4^{2-} + 4Cl^- + 6H^+$
Days		Instantaneous		$t_{1/2} = 30 \pm 15$ days

Figure 1. Reaction Chemistry during ISBGT Processes (Courtesy of Battelle)

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Figure 2 shows the typical abiotic transformation pathways for chlorinated solvents by iron sulfides observed during ISBGT. The primary mechanism is a β-elimination pathway where chlorines are lost from both carbons at the same time to form a C-C bond. The traditional sequential formation of lower chlorinated transformation products is a minor abiotic pathway. Figure 3 shows a comparison of the typical pattern of ISBGT compared to biological transformation of chlorinated ethenes.

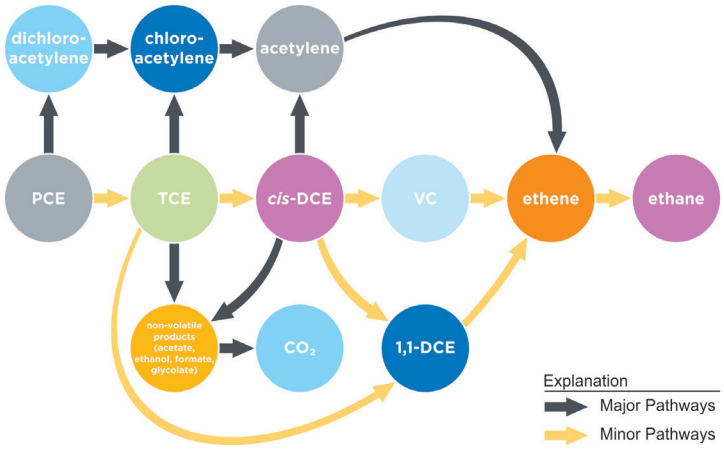

Figure 2. Chlorinated Ethene Abiotic Transformation Pathways
(Courtesy of Battelle)

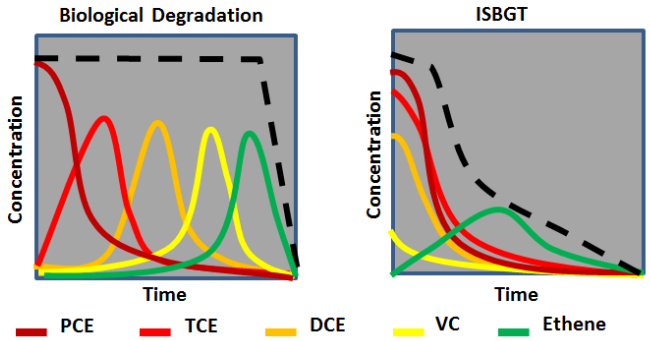

Figure 3. Biological vs. ISBGT Pattern of Degradation
(Courtesy of Battelle)

The transformation of chlorinated solvents by iron sulfide is the best understood mechanism. Although observed in the laboratory, the mechanisms for transformation by magnetite, green rust and phyllosilicate clays (such as biotite and vermiculite) are unclear. The transformation by magnetite has also been observed in the field and appears to be enhanced in the presence of dissolved Fe(II). Based upon these laboratory and field studies, several factors are known to influence the rate of reaction for ISBGT, including the mineral type, mineral surface area, groundwater pH levels and contaminant bond strength (Lebrón et al., 2010). In addition, the ratio of Fe(II) to Fe(III) present in the treatment area may also influence the rate of reaction. There has been some research on the cycling of Fe(II) and Fe(III) on the surface of the reactive metals as a contributing factor to the sustainability of the reaction.

What COCs Can Be Treated by ISBGT?

Table 1 can be used to determine if the contaminants at your site can be degraded by reduced iron minerals. The formation of sulfides fortuitously leads to precipitation and therefore the stabilization of metals such as lead and arsenic. However, caution must be taken when engineering biogeochemical transformation to precipitate metals as creating highly reducing conditions may lead to the mobilization of metals.

Table 1. Contaminants Transformed by Reduced Iron Minerals
(Courtesy of Battelle)

Contaminant Class	Iron Sulfides	Magnetite	Green Rust	ZVI
Chlorinated Hydrocarbons	✓	✓	✓	✓
Pesticides (Hexachlorocyclohexane)	✓			✓
Munitions Constituents (RDX)		✓		✓
Specific Metals (uranium, arsenic, etc.)	✓			

What Site Conditions Promote Biogeochemical Transformation Processes?

ISBGT processes may occur naturally at a site or a site could be a good candidate for engineered ISBGT. Some sites have specific site characteristics that promote biogeochemical processes such as:

- The presence of reduced iron minerals in the soil matrix shows potential for ISBGT. In laboratory microcosms with < 1 g/L of FeS, there was primarily microbial reduction, but column studies containing 6.6 g/L to 13 g/L FeS showed half of the trichloroethene (TCE) being degraded abiotically (Butler et al., 2013; Butler et al., 2009).
- Naturally available dissolved sulfate in groundwater.
- Naturally available dissolved Fe(II) in groundwater or solid Fe(III) in soil.
- Sufficient dissolved organic matter to maintain iron/sulfate reducing conditions.
- The presence of iron and sulfate-reducing microbes (typical soils contain as much as 10% iron predominantly as Fe(III), which can be converted to Fe(II) by iron-reducing microbes).
- Neutral to slightly elevated pH increases reaction rates.

If a site does not contain sufficient dissolved iron and sulfate levels, amendments can be added to the groundwater to promote ISBGT. However, if a site does not have an adequate population of iron and sulfate-reducing bacteria, especially in the presence of sufficient electron donor, it may not be a good candidate for ISBGT. Sites with very high organic matter may not be ideal for ISBGT, as highly reducing conditions can lead to competition between methanogens and sulfate-reducing bacteria therefore limiting sulfide production.

How Can ISBGT Be Engineered In Situ?

As shown in Figure 4, ISBGT is an innovative technology that has evolved over the last 15+ years through ongoing laboratory studies and field applications for the remediation of chlorinated ethenes in groundwater (Butler and Hayes, 1999, 2001; Butler et al., 2013). In the late 1990s, laboratory studies established that reduced iron enhanced the reaction between iron minerals and chlorinated ethenes. Further research indicated that microbially-generated iron sulfides had a higher surface area, making them more reactive than naturally-occurring reduced iron minerals (Environmental Security Technology Certification Program [ESTCP], 2008). This has led to several field-scale investigations in the past 10+ years designed to further study and/or engineer biogeochemical reactions in situ at groundwater remediation sites (see Figure 4).

Engineering ISBGT is accomplished by creating a reactive zone of iron sulfides for treatment of a contaminant plume. When engineering ISBGT, several factors must be considered. The engineered system must be able to generate the more highly reactive, high surface area form of iron sulfide. This is accomplished by ensuring a high volumetric sulfate loading rate, sufficient organic carbon, and the availability of iron oxide mineral surface area for constant formation and renewal of iron sulfides to sustain contaminant transformation. Sufficient hydraulic residence time is necessary to ensure amendments can react to form the reactive mineral and subsequently transform the contaminant.

Systems may need to be buffered, as a pH > 6 is more favorable for reactivity of the sulfides and amendments may cause a temporary decrease in pH.

The engineered systems used to enhance ISBGT include permeable reactive barriers (PRBs) and the injection of liquid amendments. PRBs are used to treat shallow contaminant plumes at typical trench depths of 25 to 35 ft below ground surface (bgs). The trench length for the PRB can vary from a few hundred feet to over a mile. The trench width for the PRB can be less than 6 ft because of the fast transformation reaction with iron sulfides. Injection of liquid amendments for engineering ISBGT typically occurs through installed injection wells or direct push points. Liquid amendments can be injected directly into the subsurface or recirculated by extracting and re-injecting the amended groundwater into the treatment zones. Injection wells are suitable for treating deep contaminant plumes and can remain in place for subsequent injections (more than one injection event is often needed). Table 2 lists some examples of solid and liquid amendments that can be employed in engineered ISBGT systems.

Table 2. Typical Amendments Used in Engineered ISBGT Systems (Courtesy of Battelle)

Sulfate	Iron	Organic Carbon	Buffer
Solid Amendments			
Calcium Sulfate	Hematite Magnetite	Mulch Cotton Gin	Limestone
Liquid Amendments			
Magnesium Sulfate Sodium Sulfate Iron Sulfate	Iron Sulfate Iron Chloride	Lactate Vegetable Oil Lecithin	Sodium Bicarbonate

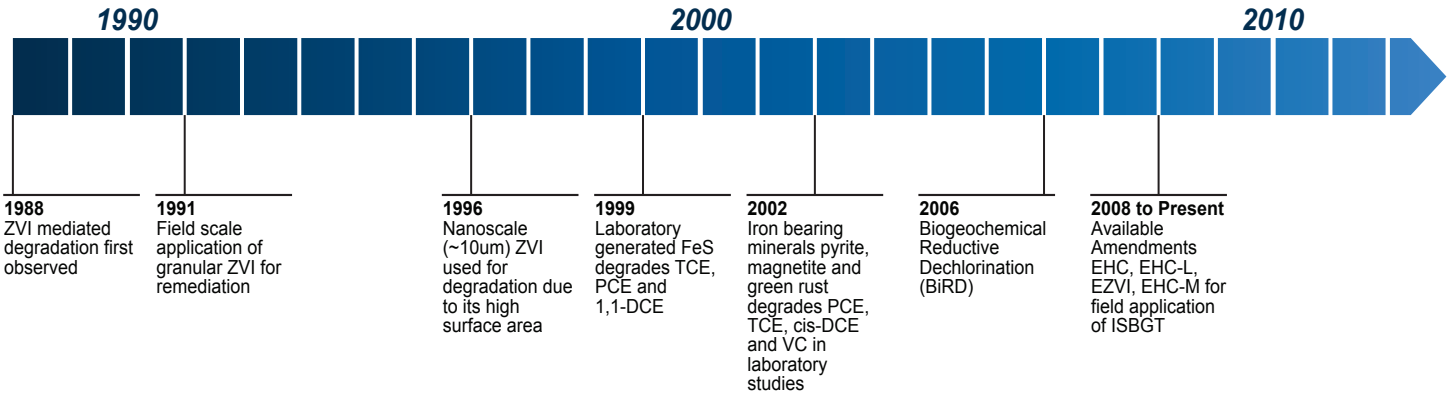

Figure 4. Technology Evolution from Abiotic to ISBGT Processes (Courtesy of Battelle)

What Parameters Should Be Monitored to Determine if ISBGT Is Taking Place?

A multidisciplinary approach must be taken when evaluating a site for ISBGT. This approach is necessary because ISBGT is a synergistic process of biological, geological, and chemical processes. Table 3 lists suggested parameters that should be measured (not including site-specific COCs).

Table 3. Multidisciplinary Approach to Evaluating ISBGT at a Site (Courtesy of Battelle)

Groundwater Geochemistry	Soil Analysis	Microbial Analysis
Dissolved Oxygen pH Oxidative Reductive Potential Dissolved/ Total Iron Sulfate Sulfide Methane Total Organic Carbon	Bioavailable Iron Mineral Surface Area & Grain Size Scanning Electron Microscopy of Mineral Surfaces Acid Volatile Sulfides Chromium Reducible Sulfides X-ray Diffraction Magnetic Susceptibility	Iron-Reducing Bacteria Sulfate-Reducing Bacteria Total Bacteria

In addition, contaminant concentrations should be monitored for a decrease in their concentrations and/or the presence of abiotic degradation products. The typical abiotic degradation products are chloroacetylene and acetylene, but these are short lived because they are both volatile and energetically favorable to use as food for microbes and therefore difficult to detect. They are most often detected in source areas where the contaminant concentrations, and therefore degradation product concentrations, are high. Monitoring carbon isotope ratios may provide information on transformation, but compound specific isotope analysis enrichment factors for abiotic transformation are often similar to those for biotic transformation. The visual presence of iron sulfides, (e.g, black precipitates) and a strong sulfide smell in the groundwater are typically reported during ISBGT.

Sampling methods suggested are low flow sampling via wells, as well as high resolution site characterization by electron microprobe. Geochemical models such as PHREEQC (PH [pH], RE [redox], EQ [equilibrium], C [program written in C]) can be used to determine the mineral phases that are present based on the geochemistry of the groundwater.

Has Engineered ISBGT Been Applied At the Field Scale?

Recent applications where ISBGT has been engineered at the field scale are described below.

- At Dover Air Force Base (AFB), a PRB was used to enhance the formation of iron sulfides to treat chlorinated solvents. The site groundwater contained low concentrations of both sulfate (~20 mg/L) and total organic carbon (~3 mg/L). Contamination was less than 35 ft bgs, so trench application of amendments was favorable. A trench was dug to ~25 ft and filled with tree wood bark to provide organic carbon, iron rich sand, crushed limestone for buffering and gypsum for sulfate. Within 150 days, the total chlorinated aliphatic concentrations decreased by 90% with no increase in daughter product concentrations (Kennedy, 2011).
- At Edwards AFB, chlorinated solvent contamination is present at 80 ft bgs in a mix of sandy and clayey soil. This site is aerobic with sulfate concentrations between 800 and 1,000 mg/L, low total organic carbon and dissolved iron. Bioavailable iron in the soil was around 1,500 mg/kg. Sulfate (magnesium sulfate) and electron donor (sodium lactate) amendments were recirculated into the treatment zone (60 to 80 ft bgs) by extracting groundwater from downgradient, mixing with the amendments, and reinjecting upgradient. Iron sulfide formation was evidenced by the formation of black precipitates in the groundwater and a strong sulfide odor. Within 90 days of recirculating the amendments, a 55% decrease in TCE concentrations was observed in the treatment area monitoring well with minor appearance of cis-DCE (Payne et al., 2013).
- At Joint Base Elmendorf-Richardson, amendments were direct injected by direct push technology into three test cells to enhance ISBGT. The most promising test cell received a direct injection of emulsified vegetable oil (EVO), calcium sulfate, and powdered iron hematite. At this site, 15 months after injection of the amendments, total chlorinated ethene (TCE and cis-DCE) concentrations decreased by 61%. Approximately 20 μg/L of vinyl chloride was formed. This indicates that ISBGT was the dominant transformation mechanism at this site (Parsons, 2012).
- At the Nike Battery Park Site PR-58 in North Kingstown, Rhode Island, a 144 gallons per day (gpd) treatment system is being installed to enhance biogeochemical transformation of chlorinated solvents. The system consists of three side by side in situ bioreactors each simulating a different remediation strategy for comparison. The three remediation strategies are: 1) a biogeochemical transformation bioreactor containing silica sand, mulch, vegetable oil, magnetite, and sulfate-amended groundwater; 2) injection of amendments to simulate biogeochemical transformation using native soil, vegetable oil, magnetite, and sulfate-amended groundwater; and 3) enhanced anaerobic bioremediation by adding silica sand, mulch, vegetable oil, and unamended groundwater. The system is currently installed and will be monitored

for water quality and geochemical parameters and contaminant concentrations. The hydraulic residence time, sulfate flux, buffer and electron donor may be modified to enhance performance (Smith et al., 2014).

Can ISBGT Processes Be Combined With Other Technologies?

ISBGT processes are rarely the sole mechanism of contaminant degradation at a site. To date, these processes have been primarily observed in tandem with another remediation approach or even occurring naturally at a site. A few examples provided below show where ISBGT processes have been fortuitously observed in the field where other remedial technologies were applied.

- At Altus AFB, the formation of FeS was observed in high sulfate groundwater where a TCE plume intersected with a benzene, toluene, ethylbenzene and xylene (BTEX) plume. At the point of intersection, TCE concentrations were depleted. Further investigation showed that FeS was formed because the BTEX served as an electron donor to iron and sulfate-reducing microbes (Kennedy et al., 2006).
- At Naval Weapons Station Seal Beach, enhanced in situ bioremediation (EISB) was carried out by injecting EVO and microbes into source area wells to treat a chlorinated ethene plume. FeS was formed in several of the wells and accompanied by removal of the chlorinated ethenes without sequential transformation of the daughter products (Darlington et al., 2010).
- ISBGT was observed at Alameda Site 26 and contributed to the rapid degradation of chlorinated ethenes to maximum contaminant levels (MCLs). A treatment train approach of iron activated persulfate followed by EISB with EVO and microbes was used. This led to the formation of FeS and abiotic transformation of the chlorinated ethenes. Sulfate and iron were abundantly available after the reduction of the iron-activated persulfate. Injecting EVO led to the immediate formation of FeS (Darlington et al., 2011).

What Are the Technology Limitations and Remaining Research Gaps?

ISBGT is a very promising technology for remediating anoxic sites contaminated with chlorinated solvents. However, ISBGT has limitations and because it is a fairly new technology there are still research needs.

- ISBGT appears to work best at sites where there is a constant flux of sulfate; limited sulfate prevents the formation of iron sulfide.
- No slow release form of sulfate is currently available for injection into sulfate-limited sites so frequent sulfate injections may be necessary at sulfate-limited sites.
- Competition between sulfate reducers and methanogens occurs when the site redox is methanogenic. This limits the production of sulfide causing biological degradation to be the dominant transformation mechanism. For contaminants such as chlorinated solvents, this may lead to the accumulation of vinyl chloride.
- Limited research is available on using ISBGT to precipitate metals. Care must be taken to not reduce the redox to conditions that cause dissolution of precipitated metals.

Resources

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