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# **NAVFAC RPM Tech Update: In Situ Biogeochemical Transformation**

# Presentation Overview

- Introduction
- ISBGT Reaction Chemistry/Pathways
- Target Contaminants
- Site Conditions
- ISBGT Amendments
- Monitoring Approach
- Case Studies
- Conclusions




**ENVIRONMENTAL RESTORATION**

## In Situ Biogeochemical Transformation Processes for Treating Contaminated Groundwater

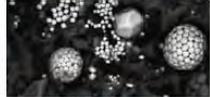
### Introduction

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.

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<sup>-</sup> 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



Framboid FeS (USGS, 2008)

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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What COCs Can Be Treated by ISBGT?

What Site Conditions Promote Biogeochemical Transformation Processes?

How Can ISBGT Be Engineered In Situ?

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

Has Engineered ISBGT Been Applied At the Field Scale?

Can ISBGT Processes Be Combined With Other Technologies?

What Are the Technology Limitations and Remaining Research Gaps?

Resources

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<b>Step 1 Biotic</b> $SO_4^{2-} + 9H^+ + 8e^- = 8HS^- + 4H_2O$ $FeOOH + 3H^+ + e^- = Fe^{2+} + 2H_2O$ Days	<b>Step 2 Precipitation</b> $HS^- + Fe^{2+} = FeS + H^+$ Instantaneous	<b>Step 3 Abiotic</b> $C_2Cl_4 + FeS + 4H_2O = C_2H_2 + Fe^{2+} + SO_4^{2-} + 4Cl^- + 6H^+$ $t_{1/2} = 30 \pm 15 \text{ days}$
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Figure 1. Reaction Chemistry during ISBGT Processes (Courtesy of Battelle)

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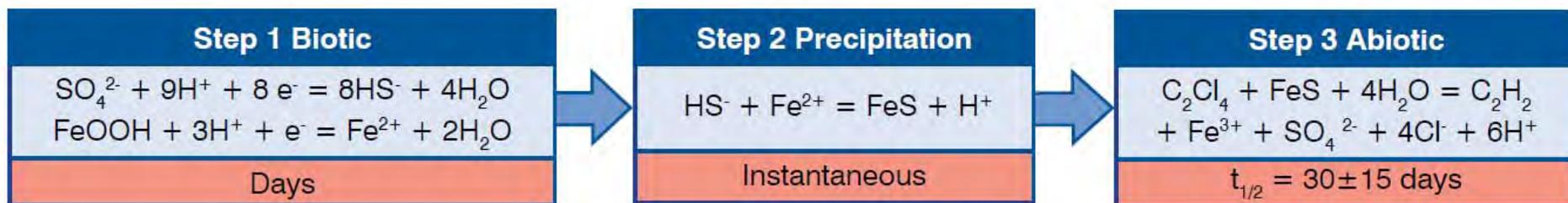
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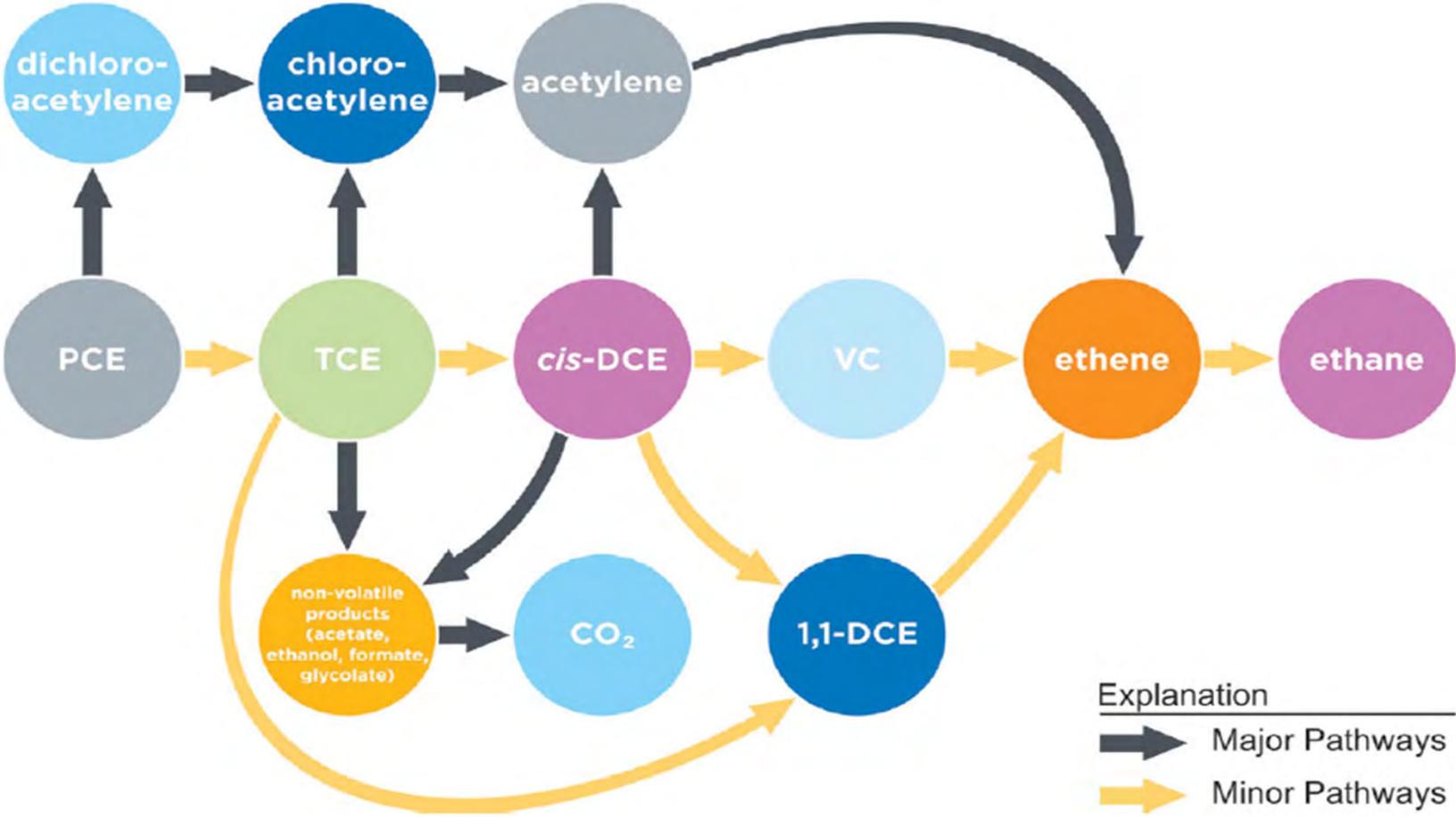
## In Situ Biogeochemical Transformation (ISBGT)

- Contaminants are transformed abiotically by reduced iron (Fe II) minerals formed by microbial activity
- Minerals may be present naturally as part of the site geology

# ISBGT Reaction Chemistry



# Chlorinated Ethene Abiotic Transformation Pathways



# Target Contaminants

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

# Favorable Site Conditions

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Presence of reduced iron minerals in the soil matrix

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

Presence of iron and sulfate-reducing microbes

Neutral to slightly elevated pH increases reaction rates

# Typical ISBGT Amendments

Sulfate	Iron	Organic carbon	Buffer
<b>Solid Amendments</b>			
Calcium Sulfate	Hematite Magnetite	Mulch Cotton gin	Limestone
<b>Liquid Amendments</b>			
Magnesium Sulfate Sodium Sulfate Iron Sulfate	Iron Sulfate Iron Chloride	Lactate Vegetable Oil Lecithin	Sodium Bicarbonate

# Monitoring Approach

Groundwater Geochemistry	Soil Analysis	Microbial Analysis
<ul style="list-style-type: none"><li>• DO</li><li>• pH</li><li>• ORP</li><li>• Dissolved/Total Iron</li><li>• Sulfate</li><li>• Sulfide</li><li>• Methane</li><li>• TOC</li></ul>	<ul style="list-style-type: none"><li>• Bioavailable iron</li><li>• Mineral Surface Area and Grain Size</li><li>• Scanning Electron Microscopy of Mineral Surface</li><li>• Acid Volatile Sulfides</li><li>• Chromium Reducible Sulfides</li><li>• X-Ray Diffraction</li><li>• Magnetic Susceptibility</li></ul>	<ul style="list-style-type: none"><li>• Iron-Reducing Bacteria</li><li>• Sulfate-Reducing Bacteria</li><li>• Total Bacteria</li></ul>

# Field Scale Applications

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## Dover Air Force Base (AFB)

- PRB used to enhance the formation of iron sulfides to treat chlorinated solvents

## Edwards AFB

- Chlorinated solvent contamination at 80 ft bgs
- Sulfate and electron donor were recirculated.

## Joint Base Elmendorf-Richardson

- Amendments was directly injected using DPT into three test cells

## Nike Battery Park Site PR-58

- A 144-gal-per-day treatment system installed to enhance ISBGT of chlorinated solvents

# Conclusions

- Visit the ERB Web site to download the ISBGT Factsheet
- Share with your team
- Goal is to support innovative technology implementation
- ISBGT Handbook by ARTT will be published in 2015



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Step 1 Biotic	Step 2 Precipitation	Step 3 Abiotic
$\text{SO}_4^{2-} + 9\text{H}^+ + 8\text{e}^- = 8\text{HS}^- + 4\text{H}_2\text{O}$ $\text{FeOOH} + 3\text{H}^+ + \text{e}^- = \text{Fe}^{2+} + 2\text{H}_2\text{O}$	$\text{HS}^- + \text{Fe}^{2+} = \text{FeS} + \text{H}^+$	$\text{C}_2\text{Cl}_4 + \text{FeS} + 4\text{H}_2\text{O} = \text{C}_2\text{H}_2$ $+ \text{Fe}^{2+} + \text{SO}_4^{2-} + 4\text{Cl}^- + 6\text{H}^+$
Days	Instantaneous	$t_{1/2} = 30 \pm 15$ days

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