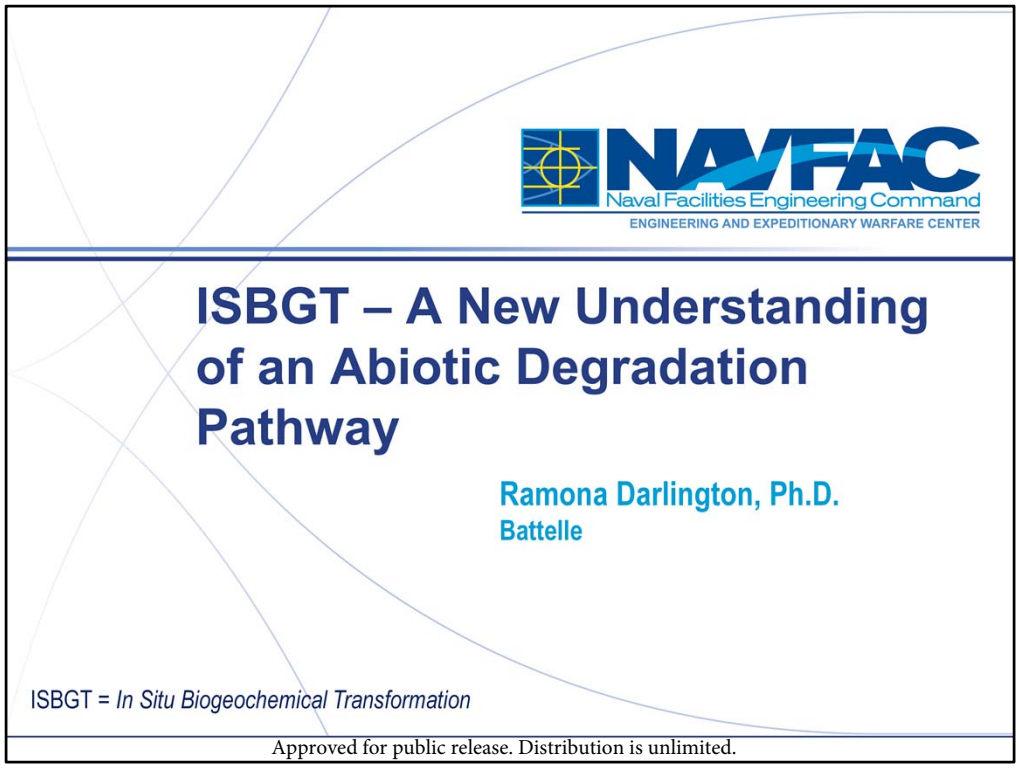


- Have been at Battelle 7 years
- First introduced to ISBGT during PhD research – one of the first studies looking at MNA of chlorinated ethenes by iron minerals.
- Member biogeochemical work group
- Author of Biogeo factsheet, Biogeohandbook

Where you have heard this before?

- Zero Valent Iron
- In Situ Chemical Reduction (ISCR)
- Abiotic Transformation
- Biogeochemical Reductive Dechlorination (BiRD)
- In Situ Biogeochemical (ISBG)
- Biologically Mediated Abiotic Degradation (BMAD)

2 RITS 2015: ISBGT

- Abiotic degradation by ZVI
- ISCR is opposite of ISCO – O for oxidation, R for reduction
- BiRD – specific to chlorinated solvents - reductive dechlorination
- Some of these technologies are related to ISBGT and not exactly ISBGT

Where you have heard this before? (cont.)

- September 2014 Biogeochemical Factsheet
- Zero Valent Iron Injection (ZVI) Tool, NAVFAC EXWC (Jan 2013)
- RITS Spring 2009 Emulsified Zero-Valent Iron (EZVI) Treatment of Chlorinated Solvents
- RITS Spring 2005 In Situ Treatment of Chlorinated Solvents using ZVI technologies
- Cost and Performance Reports on ZVI

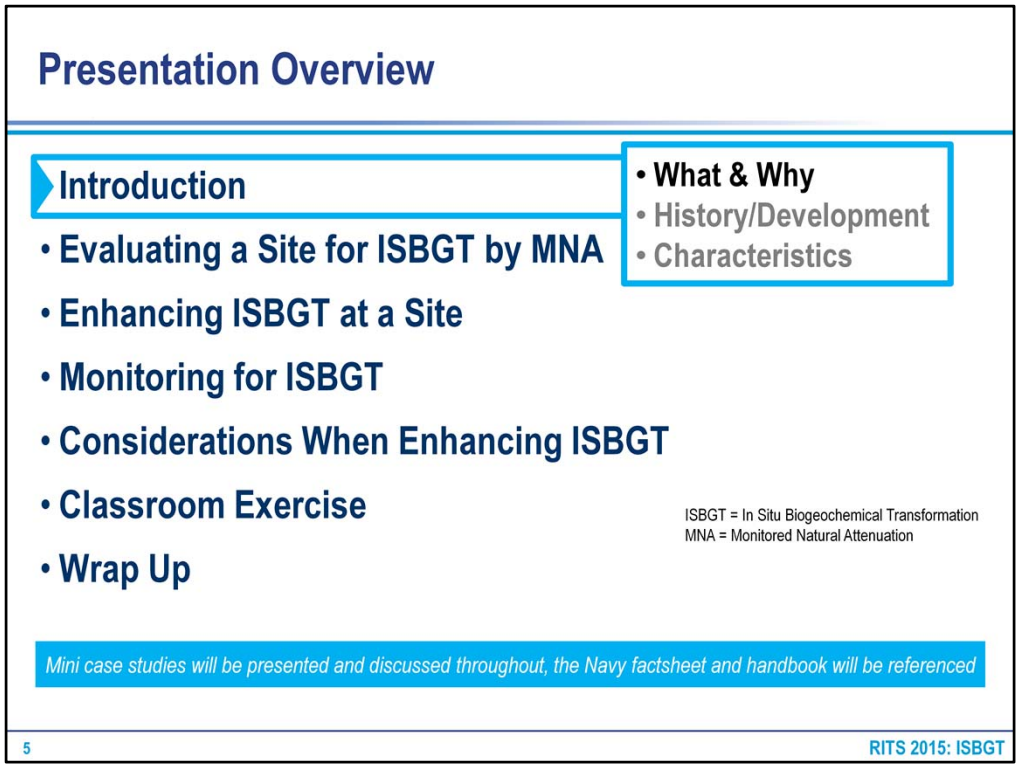
3 RITS 2015: ISBGT

- Promote Fact Sheet collaboration between Navy and AF
- Mention NAVFAC ER Website
- Cost and Performance reports can be found on the NAVFAC ERB Website

NAVFAC
In Situ Biogeochemical Transformation Processes Handbook

4 RITS 2015: ISBGT

- Handbook in draft
- Hold up draft copy
- Explain content of handbook – similar to this presentation – in question and answer format, covering topics like which contaminants can be transformed, how ISBGT contributes to MNA, how to investigate a site for MNA, appropriate conditions, engineering and design
- Look for an announcement in the T2 email Update (you can sign up by putting a checkmark next to your name on the sign in sheet)

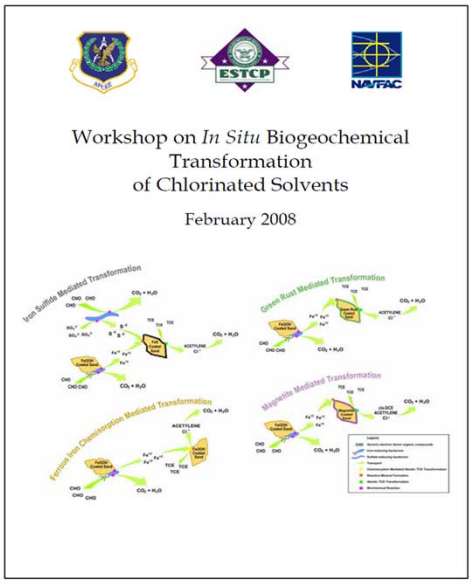


- Describe flow of presentation
- Here for 2.5 hours, 50 minutes, break (10 minutes) 45 minutes (break 10 minutes), class room exercise
- Go over outline of presentation – Take class on a journey – First understand what is ISBGT and how it was developed and what the characteristics are, Once we know the characteristics we will determine how to evaluate a site to see if it is happening. Then we will go through monitoring a site for these transformations and any considerations. Then wrap up with a classroom exercise so pay attention!

What are Biogeochemical Transformation Processes?

……..contaminants are degraded by abiotic reactions with minerals formed that are either naturally occurring or are biogenically produced in the subsurface…….

Biogeochemical Transformation Workshop
February 2008



6 Introduction – What & Why RITS 2015: ISBGT

- Here mention first work shop – point out that NAVFAC was involved
- Stress AF has spent $5M on ISBGT – multiple pilot studies
- NAVFAC and AFCEC partnered to prepare the factsheet and are partnering to prepare the handbook

Minerals Involved

Mineral	Formula
Iron sulfide (mackinawite)	FeS
Pyrite	FeS_2
Fougerite (green rust)	$Fe^{II}_4\ FE^{III}_2\ (OH)_{12}\ SO_4 \bullet yH_2O$
Hematite	Fe_2O_3
Magnetite	Fe_3O_4
Biotite	$K(Mg,Fe^{II})_3\ (Si_2Al)O_{10}\ (OH)_2$
Vermiculite	$Mg_{0.33}\ (Mg,Al,Fe^{II})_3\ (Si_2\ Al)O_{10}\ (OH)_2$

Reactivity : FeS >>> Magnetite >>> Green Rust

Key Point Iron sulfides are best understood and their formation can be enhanced in situ

7 Introduction – What & Why RITS 2015: ISBGT

- These minerals occur naturally as part of the site geology but iron sulfides can also be generated in situ
- Today we will talk about natural transformation by these minerals and also how to enhance their formation

Iron Sulfide Mineral Phases

Phase	Formula	Composition
Mackinawite	FeS_{1-x}	>63.5% Fe, >36.5% S
Pyrite	FeS_2	54% Fe 46.6% S
Marcasite	FeS_2	53.4% Fe, 46.6% S
Greigite	$Fe^{+2}Fe^{+3}{}_2S_4$	56.6% Fe 43.4% S
Pyrrhotite	$Fe_{1-x}S$	59.1 – 63.5% Fe, 36.5 – 40.9% S
Troilite	FeS	63.5% Fe, 36.5% S

- When we talk about iron sulfides we are referring to mackinawite and pyrite
- Marcasite exists in low pH areas
- Pyrrhotite and troilite in high temperature areas

Why Biogeochemical Transformation Processes?

- Typical aquifer mix has 0.1 to 10% Fe **Key Point**
- This iron is well dispersed and often has poorly crystalline grain coating
- Most native Fe minerals are Fe(III) or stable minerals

- Iron precipitates on the surface of other minerals like quartz
- Bottom line – there is a lot of iron available

Why Biogeochemical Transformation Processes? (cont.)

- Most native iron not reactive to chlorinated ethenes
- Possible to stimulate natural bacteria to convert native Fe to FeS minerals
- Combines low cost of bioremediation with effectiveness of ZVI
- AF has spent about $5M in pilot studies, ISBGT has been included in a ROD and will be implemented at NAS Mechanicsburg

Key Point Microbes can take this iron and convert it to reactive FeS

- FeS facilitates the complete reduction of chlorinated ethenes

Contaminants Transformed by ISBGT

- Chlorinated solvents
- Pesticides
  - DDT ($C_{14}H_9Cl_5$)
  - Lindane ($C_6H_6Cl_6$)
- Heavy metal ions
  - Mercury (Hg^{2+}), Uranium, Arsenic, Lead
- Munitions constituents
  - RDX

Discussed in more detail in handbook

- Chlorinated solvents are transformed by iron sulfide, magnetite and green rust to acetylene
- Pesticides are transformed by iron sulfides – mechanism of “reductive dechlorination” penta to tetra to tri to di
- Metals precipitate by iron sulfides as metal sulfides
- Munitions appear to be transformed by iron oxides/magnetite but unsure of transformation product
- Discussed in more detail in handbook

Presentation Overview

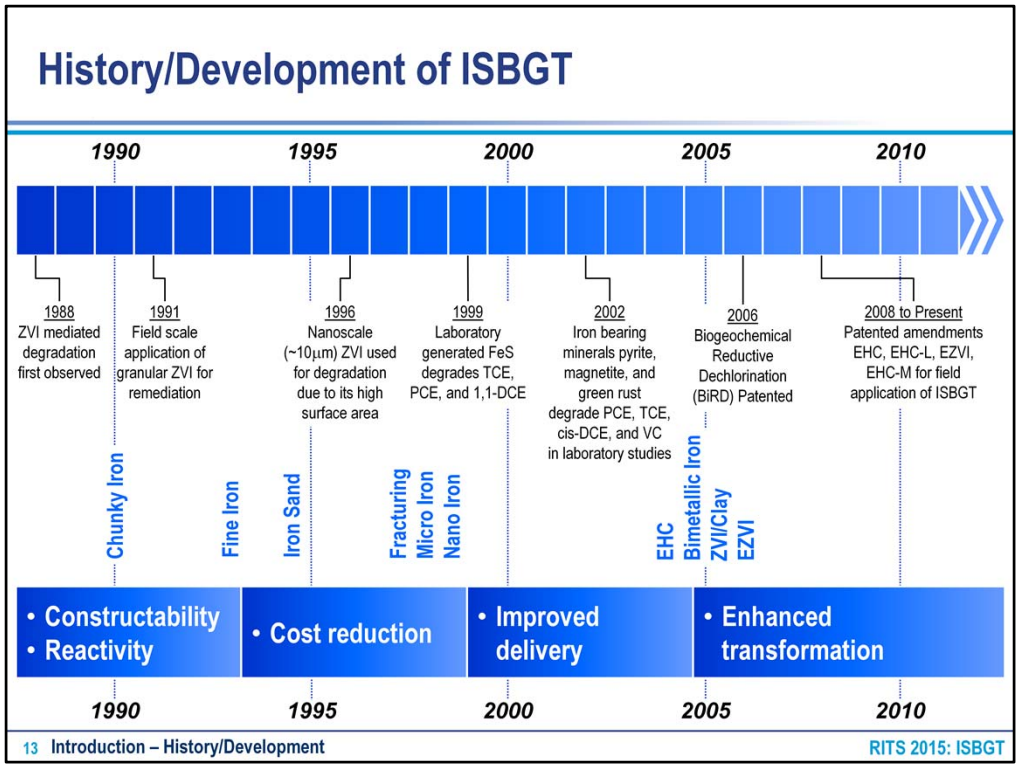
- Introduction
  - What & Why
  - History/Development
  - Characteristics
- Evaluating a Site for ISBGT by MNA
- Enhancing ISBGT at a Site
- Monitoring for ISBGT
- Considerations When Enhancing ISBGT
- Classroom Exercise
- Wrap Up

ISBGT = In Situ Biogeochemical Transformation
MNA = Monitored Natural Attenuation

(Mini case studies will be presented and discussed throughout, the Navy factsheet and handbook will be referenced)

12 RITS 2015: ISBGT

- Now we will discuss how biogeochemical transformation processes were discovered and how the technology has developed over time
- This will help you make the link between the well known zero valent iron and the more innovative ISBGT



- Walk though time chart – the research moved from first just being able to construct a system to get reactivity, to reducing cost, to enhanced delivery then to enhancing transformation
- Through these studies we learned a lot about the characteristics of abiotic transformations with iron sulfides
- Iron chunks, to micro scale to nano scale ZVI

History/Development – Zero Valent Iron

- Lab test with ZVI and halogenated aliphatics
- Chlorinated methanes, ethane and ethenes
- All degraded except for dichloromethane (DCM)
- Evidence of sequential dechlorination since low concentration of daughter products

- One of the first few studies in 1994 chlorinated methanes, ethanes and ethenes and ZVI
- concentration of TCE decreased in the presence of ZVI No decrease seen in the blanks
- drastic reduction in Eh to highly reducing conditions as ZVI is known to do and slight increase in pH to alkaline pH

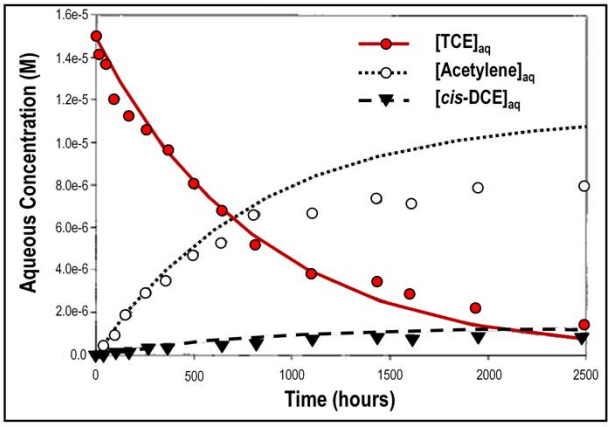
History/Development – Nanoscale Iron

- Nanoscale iron (10–100 nm)
  - Larger surface area
  - High surface reactivity
- Chlorinated organic solvents, organochlorine pesticides, and PCBs

- Development moved from using chunky iron to using iron of higher surface area to enhance reaction rates

History/Development – Synthetic Iron Sulfides

- **Transformation of TCE by FeS under alkaline conditions**

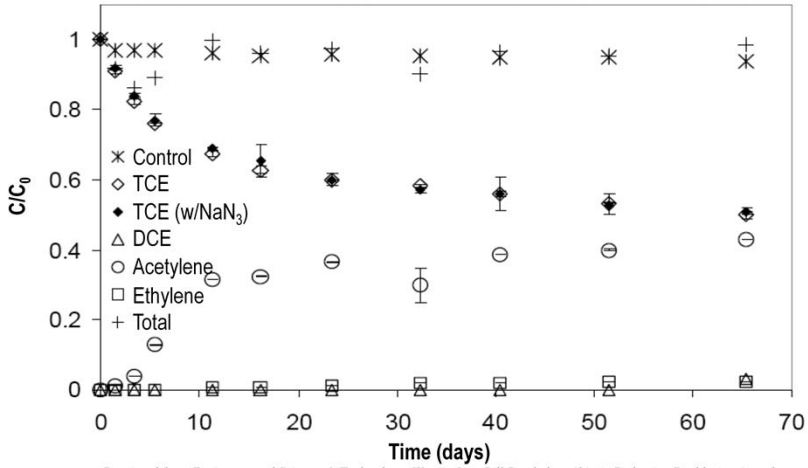


Reprinted from Environmental Science & Technology, Elizabeth C. Butler, Kim F. Hayes, Kinetics of the Transformation of Trichloroethylene and Tetrachloroethylene by Iron Sulfide, Copyright 1999 with permission from American Chemical Society

- Innovation moved to using synthetic FeS to treat chlorinated solvents
- This was born out of the observation that as ZVI reacted with contaminants it became oxidized and Fe(II) would precipitate on it's surface and that Fe(II) participated in the reduction reactions
- Led to the thought that iron (II) minerals could participate in transformation of contaminants
- During the reaction between FeS and TCE it was observed that acetylene was a major transformation product (first time) and minor amounts of reductive dechlorination degradation products
- Notice that stoichiometrically the products do not add up to the molar amount of TCE because there are other unknown abiotic degradation products

History/Development – Pyrite Minerals

- **TCE transformation by pyrite**

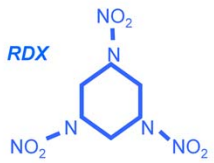


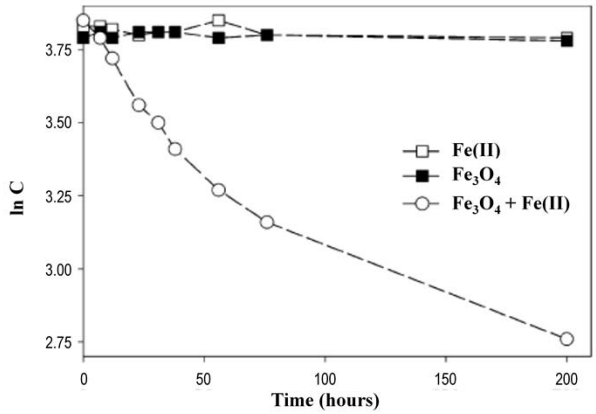
Reprinted from Environmental Science & Technology, Woojin Lee, Bill Batchelor, Abiotic Reductive Dechlorination of Chlorinated Ethylenes by Iron-Bearing Soil Minerals. 1. Pyrite and Magnetite, Copyright 2002 with permission from American Chemical Society

- Lee and Batchelor abiotic PCE and TCE by mineral pyrite. Similar degradation of TCE to acetylene in the treatment with sodium azide which kills microbes
- Notice that degradation happened then degradation stopped and concentrations plateaued off
- Here we learned that the transformation can stop once the mineral surfaces have changed

History/Development – Magnetite Minerals

- **RDX Reduction by Magnetite + Fe(II)**





Courtesy EPA

18 Introduction – History/Development RITS 2015: ISBGT

- Different mineral – magnetite and RDX. Removal enhanced in the presence of Fe(II)
- First-order plot for transformation of 47 mM RDX in the presence of 1.5 mM initial dissolved FE(II) and 44 m^2 L^{-1} magnetite at pH 7.0 (50 mM HEPES buffer)

Presentation Overview

- Introduction
  - What & Why
  - History/Development
  - Characteristics
- Evaluating a Site for ISBGT by MNA
- Enhancing ISBGT at a Site
- Monitoring for ISBGT
- Considerations When Enhancing ISBGT
- Classroom Exercise
- Wrap Up

ISBGT = In Situ Biogeochemical Transformation
MNA = Monitored Natural Attenuation

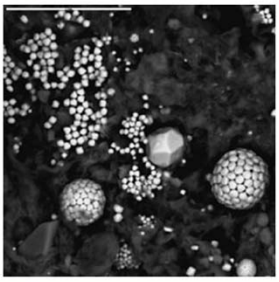
(Mini case studies will be presented and discussed throughout, the Navy factsheet and handbook will be referenced)

19 RITS 2015: ISBGT

- We have looked at the studies conducted during the development of this technology
- Now I'll summarize for you the characteristics that were observed during the studies and our level of understanding of the technology right now
- These laboratory studies and other research led us to understanding better ISBGT
- Understanding helps us be able to evaluate it and enhance it
- Based on the studies we now understand the main characteristics of ISBGT
- Discussion heavy on chlorinated solvents because studied the most and most well understood

Characteristics – Surface Catalyzed Reactions

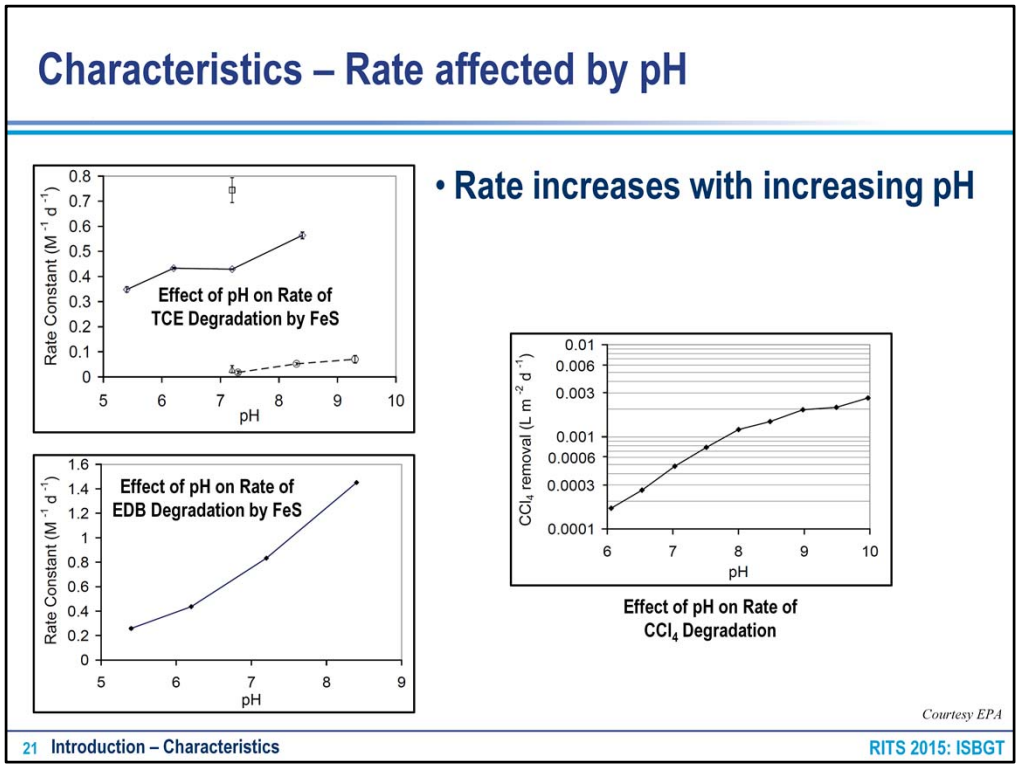
- **Rate constant – K (yr^{-1}) – varies with surface area**



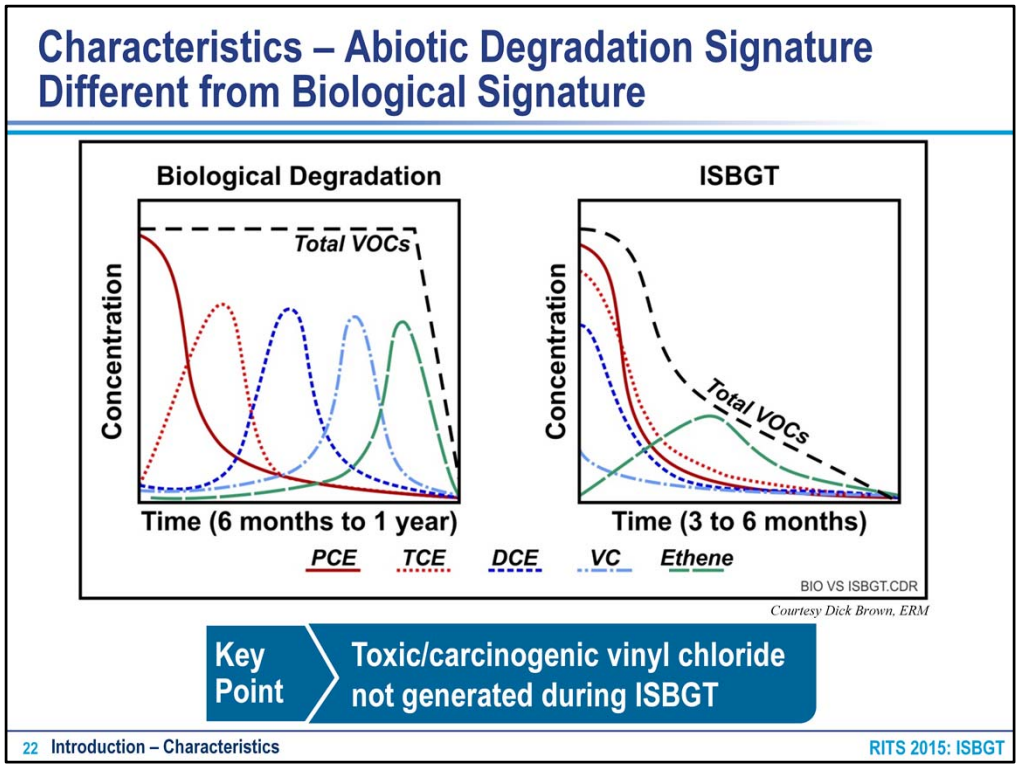
Courtesy USGS

Contaminant	Mineral Exposed to Porewater (g/L)	Rate (per year)
cis-DCE	25	0.82 ± 0.39
cis-DCE	29	0.73 ± 0.18
cis-DCE	47	2.29 ± 0.25

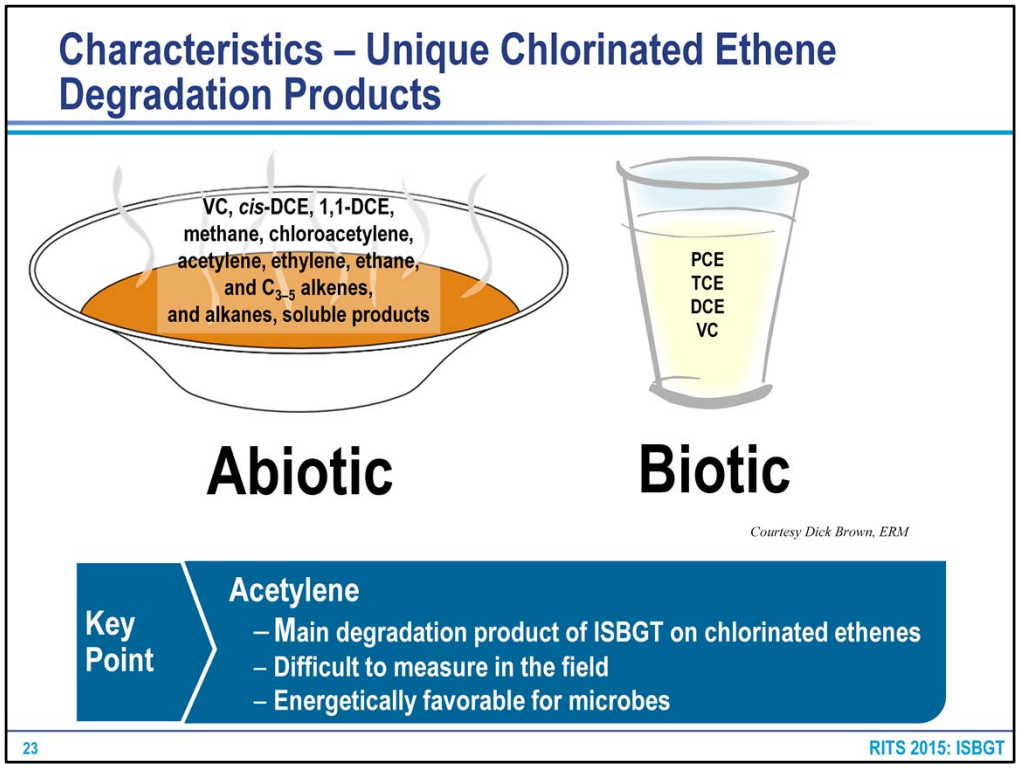
- Higher surface area, higher rate. Framboidal FeS has high surface area



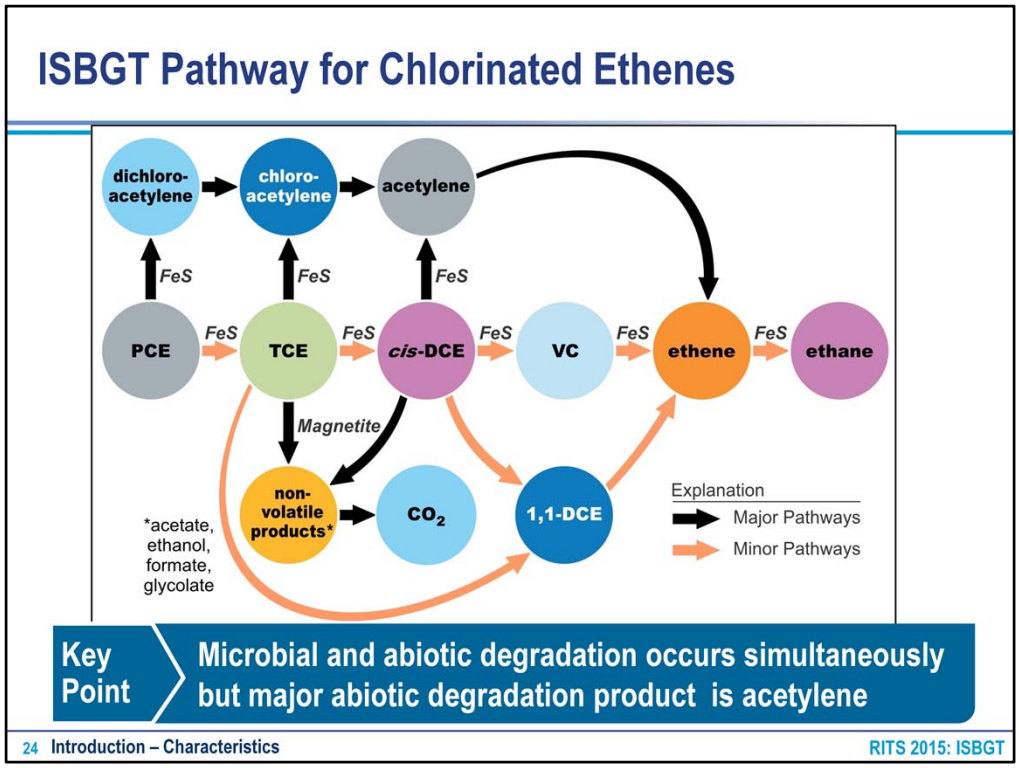
- Rate effected by pH
- This slide shows this phenomenon in three different contaminants TCE, EDB and Carbon tetrachloride



- Biological Degradation pattern sequential degradation of daughter products
- ISBGT parallel degradation of contaminant and daughter products



- Abiotic - several different degradation products
- Mainly chloroacetylenes to acetylene which are difficult to detect
- Acetylene is energetically favorable for microbes therefore quickly used up
- Also soluble products are formed from abiotic which are used quickly



- Reductive dechlorination minor degradation pathway. Major transformation pathway chloroacetylene to acetylene
- Iron sulfides are known to transform to acetylene and also the reductive dechlorination process
- Magnetite may lead to formation of non volatile products

Fast Reaction Rates

COC	Mineral	Products	Rate	Reference
PCE	Mackinawite (FeS)	TCE, cis-DCE, 1,1 DCE, Minor VC	1 to 7 x 10^{-2} d^{-1} 10^{-2} to 10^{-3} L/m^2d	Jeong and Hayes, 2007; Liang et al., 2007
PCE	Pyrite	TCE, acetylene, ethylene	(1.01±0.02) d^{-1} 1.97x10-5 L m-2 d^{-1}	Lee and Batchelor, 2002a
PCE	Magnetite	None measured	0.20 yr^{-1}	Ferrey et al., 2004
PCE	Green Rust	Conflicting reports	1.62x10^{-4} L m-2 d^{-1}	Lee and Batchelor, 2002b
TCE	Mackinawite (FeS)	Acetylene, cis-DCE, 1,1-DCE, Minor VC	(5.09±0.24)×10-2 d^{-1}	Jeong and Hayes, 2007
TCE	Pyrite	cis-DCE, acetylene, ethylene	(1.60±0.02) d^{-1} 2.53×10-5 L m-2 d^{-1}	Lee and Batchelor, 2002a
TCE	Magnetite	None measured	0.32 yr^{-1}	Ferrey et al., 2004
TCE	Green Rust	Conflicting reports	10^{-4} to 10^{-5} L m-2 d^{-1}	
TCE	Biological Degradation		3.5 to 7.0 x 10^{-4} d^{-1}	Ei et al., 1999; West et al., 1999.

- Rate can be represented as per day or per year or as a surface catalyzed reaction rate
- Notice FeS and Pyrite react faster than magnetite and green rust

Summary of Characteristics

- Surface Catalyzed Reaction
- Rate changes with pH
- Degradation signature for chlorinated solvents different from biological signature
- Fast reaction rates

Presentation Overview

- Introduction
- **Evaluating a Site for ISBGT by MNA**
- Enhancing ISBGT at a Site
- Monitoring for ISBGT
- Considerations When Enhancing ISBGT
- Classroom Exercise
- Wrap Up

Type of Site

- Reduction in contaminant concentration without appearance of degradation products
- Unable to close mass balance
- cis-DCE or VC stall appears to be occurring

28 Evaluating a Site for ISBGT by MNA RITS 2015: ISBGT

- Naturally occurring iron minerals degrade contaminants
- Sites where contaminant concentration is decreasing without appearance of traditional degradation products
- Or TCE to cis-DCE “stall” is occurring may be as a result of abiotic removal of cis-DCE

Frequently Asked Questions about Monitored Natural Attenuation in Groundwater (ESTCP 2014)

- **Emerging issue for evaluating MNA as a remedy:**

How do reactive mineral species contribute to attenuation?

"Reactive mineral species represent another means for promoting abiotic attenuation. Many of these minerals are naturally present in subsurface and anaerobic environments and may be contributing to natural attenuation in groundwater plumes."

29 Evaluating a Site for ISBGT by MNA RITS 2015: ISBGT

- 2014 Frequently asked questions on MNA addressed MNA by minerals as an emerging issue for evaluating MNA as a remedy

MNA Forum: The Case for Abiotic (Remediation 2007)

1. Plotting plume degradation patterns for the various chlorinated species
2. Conduct mineralogical analyses
3. Monitor for unique reaction products
4. Modifying and expanding microcosm study protocols to specifically examine abiotic reactions

Key Point Specific MNA protocol not available for ISBGT

- Early discussion on MNA by abiotic processes led to a forum with Dick Brown of ERM and John Wilson of EPA
- The conclusions of this forum were that abiotic processes have specific footprints similar to biological degradation
- The biotic footprint of MNA includes consumption of electron acceptors, presence of daughter products, and detection of metabolites, all of which are biologically derived

Plume Degradation Pattern

- **Plot the molar concentrations of the chlorinated compounds with distance from the source area**
  - **Biotic = divergence of contaminant concentration with distance**
  - **Abiotic = parallel decline in molar concentration**

31 Evaluating a Site for ISBGT by MNA RITS 2015: ISBGT

- RPM – When looking at data at your site you can evaluate the data in this way!
- One of the markers for abiotic attenuation is the loss of the parent compounds *without* the sequential production of mono-dechlorinated products. If one plots the molar concentrations of the chlorinated compounds with distance from the source area, one can differentiate between abiotic and biotic conditions. Biotic conditions are evidenced by a divergence of the contaminant concentrations with distance and often show a slower degradation or an accumulation of lesser chlorinated compounds. Abiotic conditions are evidenced by a parallel decline in molar concentrations with distance.
- Site A: The source area contained significant levels of petroleum hydrocarbons that "fueled" the biodegradation of 1,1,1-TCA to 1,1-DCA. The dissolved plume extends south from the source approximately 300 m, where it abruptly attenuates to chlorinated VOC concentrations < 0.01 mg/L. The dissolved plume outside the source area primarily occurs near the alluvium/bedrock interface at 30 to 60 m below ground surface (bgs). In descending order, the stratigraphic sequence includes fill, organic marine clay, silty sand alluvium, and fractured Franciscan Formation bedrock, an iron-containing serpentine rock. Abiotic degradation is most likely the primary attenuation process outside of the source area.
- Site B: The site is an industrial facility that has operated since the 1960s. Several distinct plumes of chlorinated solvents have been detected in groundwater at the site. The main plume is predominantly 1,1,1-TCA and its daughter products. A second plume contains PCE, TCE, and daughter products. On site, the plumes occur in a shallow aquifer composed of interbedded fine silts, clays, and peat to a depth of 3.5–5.0 m. Biodegradation is the primary process.

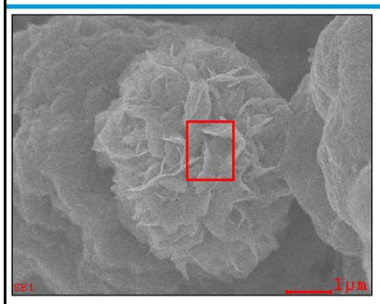
Mineral Analysis

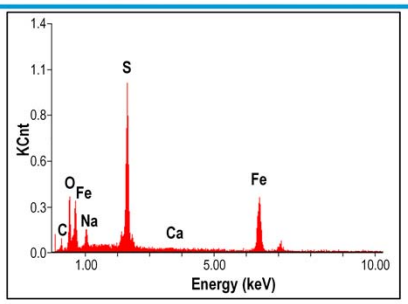
- **To identify active phases that promote transformation**

Analysis	Purpose
X-ray Diffraction	Crystalline phases in mineral
Magnetic Susceptibility	Measure of magnetite
Scanning Electron Microscopy – Energy Dispersive Spectroscopy	Elemental analysis
AVS CRS	Iron sulfide mineralogy

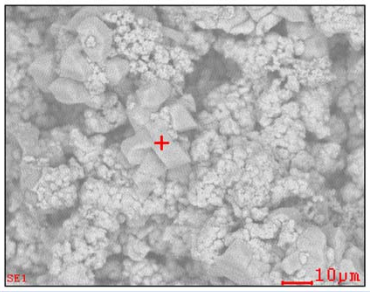
- Sediment analysis – identify and quantify active phases that promote transformation
- Collect samples and maintain anaerobic, minerals may be be present at low concentrations. Possible to concentrate based on density and size.
- Iron analysis can be done qualitatively by examining the color of soil samples. If the soil is a light gray or light cream color, it is probably devoid of iron. If it is red, brown, or orange, iron is present but it is oxidized. If the soil is dark gray, black, or green, there are potentially sufficient levels of reduced iron present to mediate abiotic reduction.
- X-ray diffraction – a bulk analysis technique used to determine the different crystalline phases (minerals) in a material. A portion of the rock core will be ground in an agate mortar and pestle and passed through a 400 mesh sieve before analysis by x-ray diffraction. This will detect any minerals present in the rock matrix above 1% by volume.
- Magnetic susceptibility – conducted to determine an estimate of the concentration of magnetite (a reactive mineral) in the core. This method is favorable because magnetite is the most abundant mineral in natural soils that exhibit a magnetic behavior. Therefore, magnetic susceptibility is a good estimate of the quantity of magnetite in an environmental sample.
- Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM-EDS) – thin sections of the core 30 µm in diameter will be prepared by an external laboratory, Spectrum Petrographics. The thin sections will then be sent to Battelle for viewing under a scanning electron microscope. EDS will be used during the evaluation of the thin section to determine elemental chemistry abundances for minerals in the core thin section. SEM-EDS data provide the atomic percent and weight percent of elements in the sample and therefore provide information to identify the different minerals present in the sample.
- Extractable iron analysis – used to determine the concentration of bioavailable iron present in the core sample. This bioavailable iron can be used by iron reducing microorganisms to produce iron(II), which forms reactive iron minerals by further reactions.

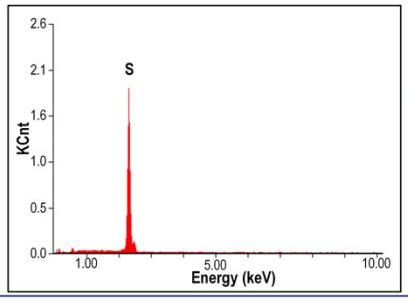
Scanning Electron Microscopy





Element	Wt%	At%
C	09.17	21.72
O	13.40	23.83
Na	05.91	07.31
S	27.91	24.76
Ca	00.86	00.61
Fe	42.75	21.78





Element	Wt%	At%
S	100.00	100.00

Courtesy Battelle

33 Evaluating a Site for ISBGT by MNA RITS 2015: ISBGT

- SEM analyzes surface of the mineral and determines the elemental composition of the surface
- The top figure is of iron sulfide and notice the mineral composition Fe 21% and S 24%
- Notice high surface area
- Atomic number Sulfur 16, Iron 26
- Molecular weight Sulfur 32 Iron 55.84

Typical for Natural Biogeochemical

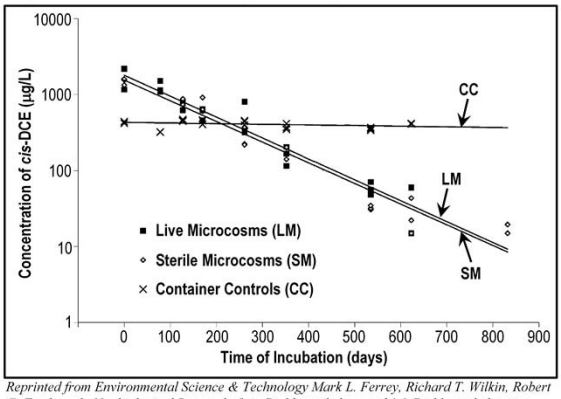
- **Magnetic susceptibility =** 1.6×10^{-6} m^3 kg-1
- **ORP = 0 to -250 mV**
- **Iron mineral = at least 1%**

Key Point Naturally occurring minerals participate in contaminant degradation

- Minimum of 1% needed for natural abiotic
- Transition by saying next we will look at a couple case studies where ISBGT was observed occurring naturally

MNA Microcosm Study

- Twin Cities Army Ammunition Plant
- Complete PCE and TCE degradation along the groundwater flow path
  - *cis*-DCE was detected, but not vinyl chloride or ethene
- Acetylene was not measured



Reprinted from Environmental Science & Technology Mark L. Ferrey, Richard T. Wilkin, Robert G. Ford, et.al., Nonbiological Removal of cis-Dichloroethylene and 1,1-Dichloroethylene in Aquifer Sediment Containing Magnetite, Copyright 2004 with permission from American Chemical Society

35 Evaluating a Site for ISBGT by MNA RITS 2015: ISBGT

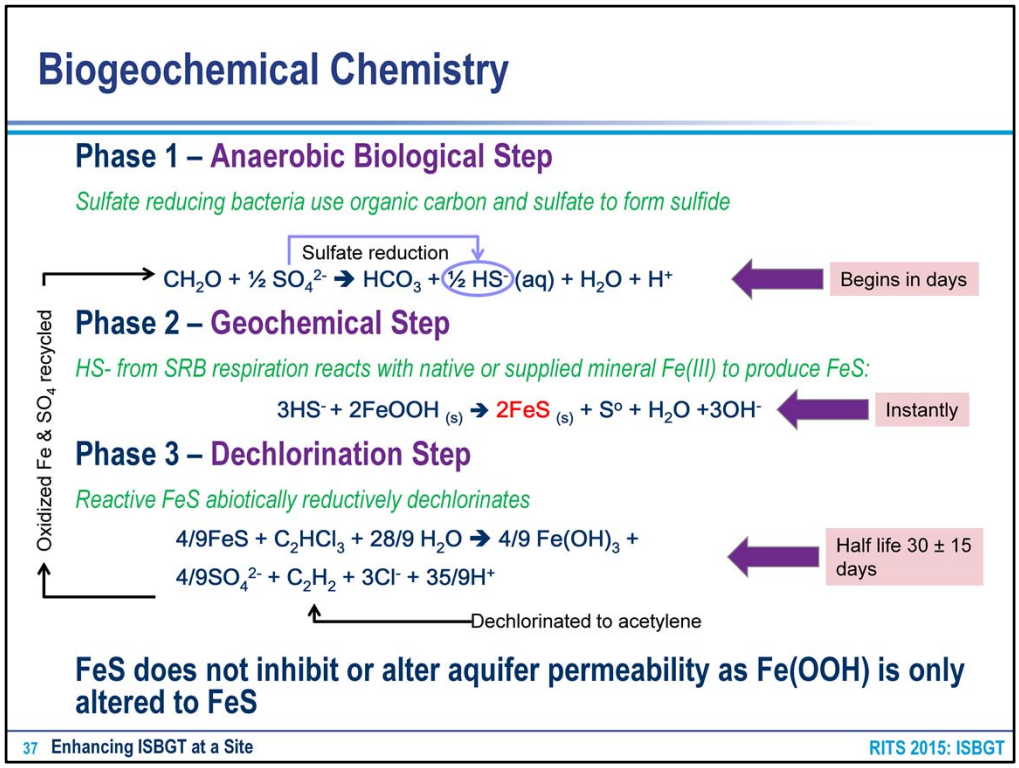
- In field-observed degradation of PCE and TCE, cis-DCE stall, no vinyl chloride, or ethene
- Laboratory study indicated same degree of degradation in live and abiotic microcosms indicating abiotic leading degradation mechanism for cis-DCE

Presentation Overview

- Introduction
- Evaluating a Site for ISBGT by MNA
- **Enhancing ISBGT at a Site**
- Monitoring for ISBGT
- Considerations When Enhancing ISBGT
- Classroom Exercise
- Wrap Up

36 RITS 2015: ISBGT

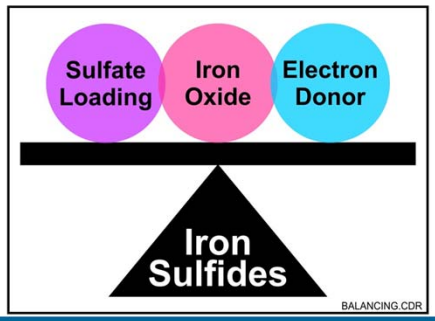
- ISBGT can occur naturally and through enhancement
- There are certain site characteristics that tell if a site is ideal for enhanced ISBGT
- This is information you find out during baseline sampling



- Simplified version of this is found in the factsheet as well as explanation

Determine Whether a Site is Amenable to ISBGT

- High sulfate loading rate
- Source of iron
- Source of electron donor



Key Point Enhancing ISBGT is a balance between sulfate, iron and electron donor

38 Enhancing ISBGT at a Site RITS 2015: ISBGT

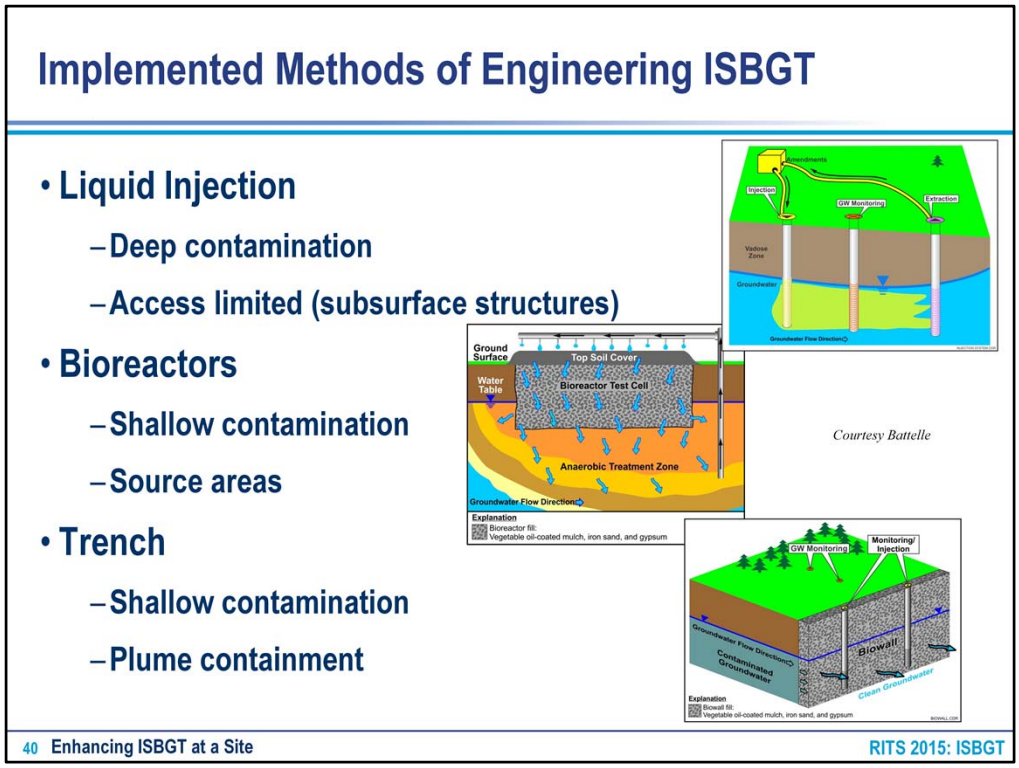
- Formation of iron sulfides is a balance between sulfate loading, iron present and electron donor
- Remember that sulfide and iron (II) is formed from the reduction of iron (III) and sulfate and it is this Fe and S that combine to form the reactive species FeS
- Need continuous source of sulfate to maintain sulfate reducing conditions, if sulfate become limiting can push conditions over to biological degradation
- Chemically quantify both the total iron and the reduced iron - Total iron is analyzed by EPA Method 200.7

Other Parameters to Consider

- **Presence of iron and sulfate reducing bacteria**
- **Anoxic to anaerobic geochemistry**
- **Neutral to alkaline pH**

Parameter	Typical for Biogeochemical
Sulfate (mg/L)	880 to 2,600
ORP (mV)	50 to -200
Organic Carbon (mg/L)	>20
Bioavailable iron	>0.5%
Presence of iron and sulfate-reducing bacteria	√

- Other important parameters – walk through slide
- Bioavailable iron is the iron that can be reduced by microbes
- Some irons are more highly complexed in the soil matrix and not available for microbial activity



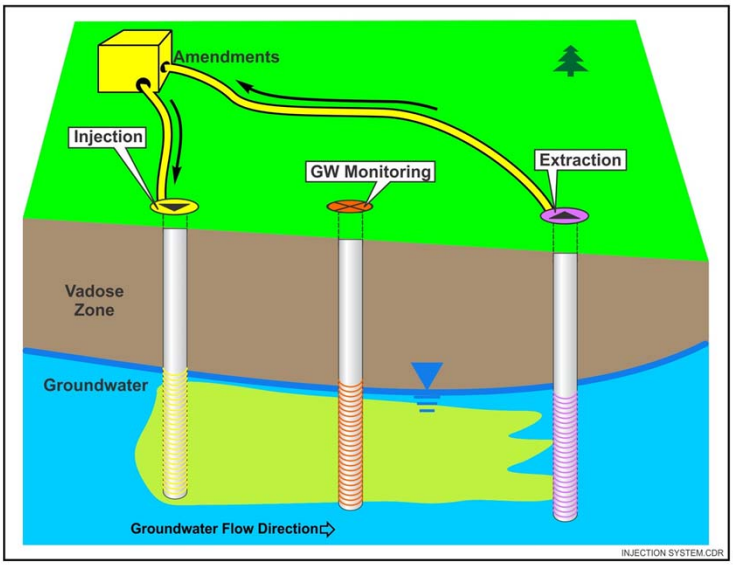
- Three main methods to engineer ISBGT – walk through slide, all info is there
- Trench and bioreactor can hold large amounts of amendments sustaining transformation
- Liquid injection may need to reinject amendments frequently

Amendments

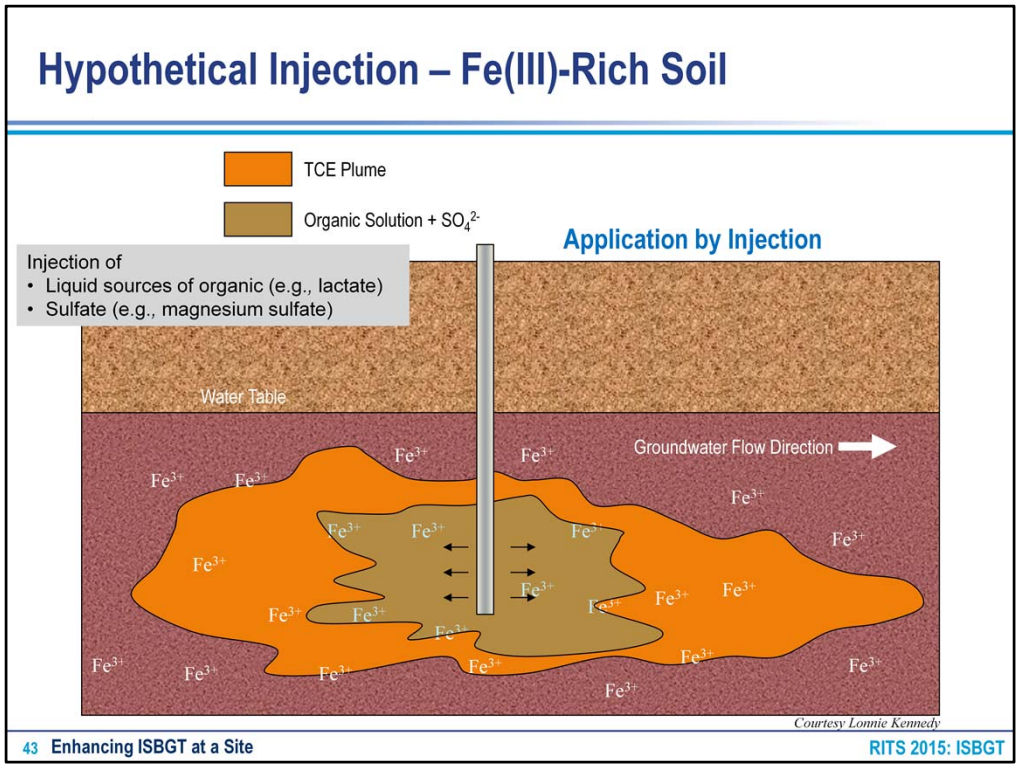
Component	Bioreactors and Trench Biowalls	Liquid injections
Iron	• Iron sand • Iron oxide (Hematite, magnetite)	• Iron sulfate • Iron chloride
Sulfate	Calcium sulfate (gypsum)	• Iron Sulfate • Magnesium sulfate (Epsom salts) • Sodium Sulfate
Electron Donor	• Tree Mulch • Cotton gin compost • Mulch coated with vegetable oil	• Sodium Lactate • Emulsified vegetable oil • Lecithin • Soybean oil
Additional Amendments	• Sand and/or gravel for permeability • Buffer (limestone)	Buffer (Sodium bicarbonate)

- Typical amendments – walk through slide – all info is there

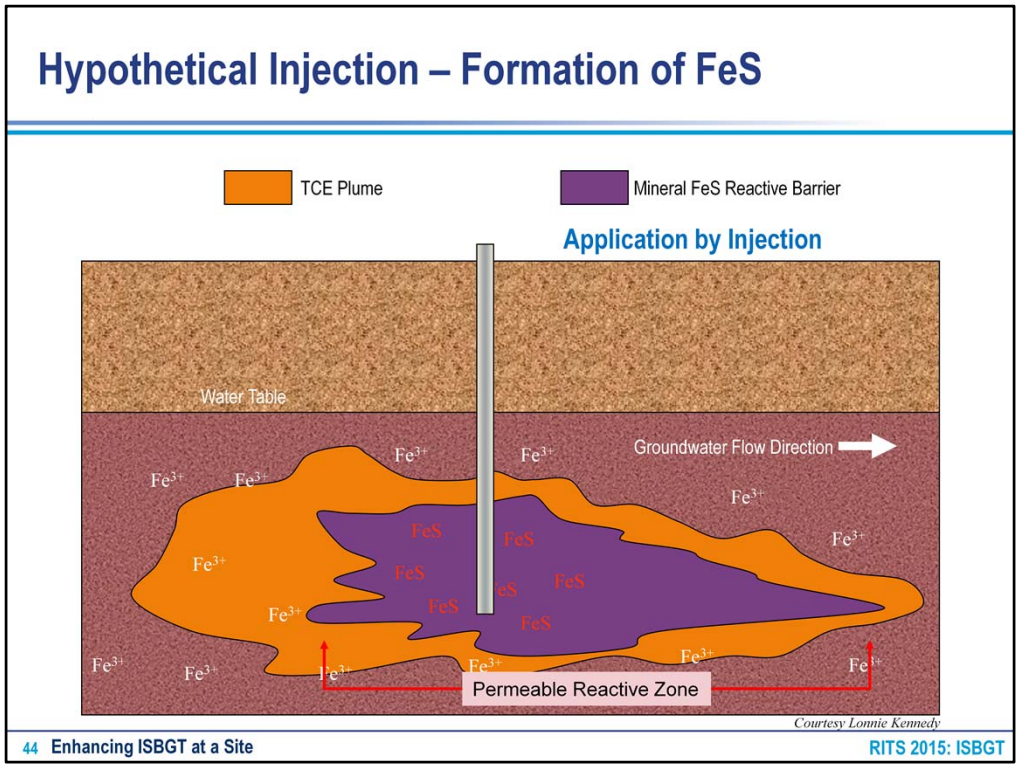
Hypothetical Injection



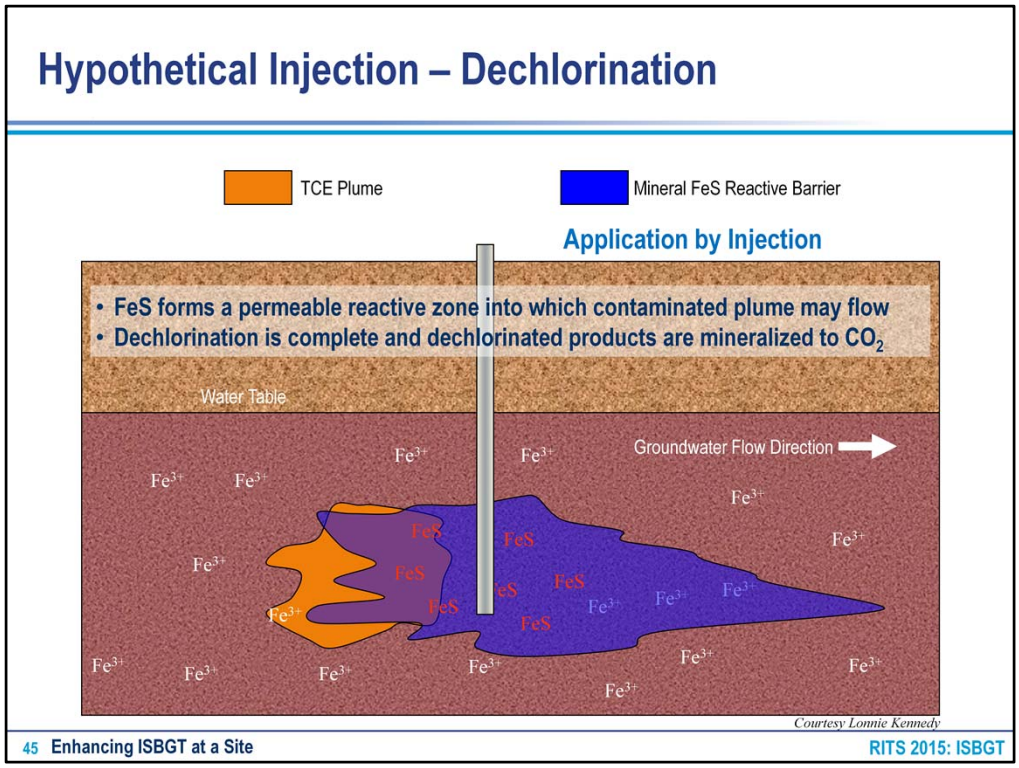
Courtesy Battelle



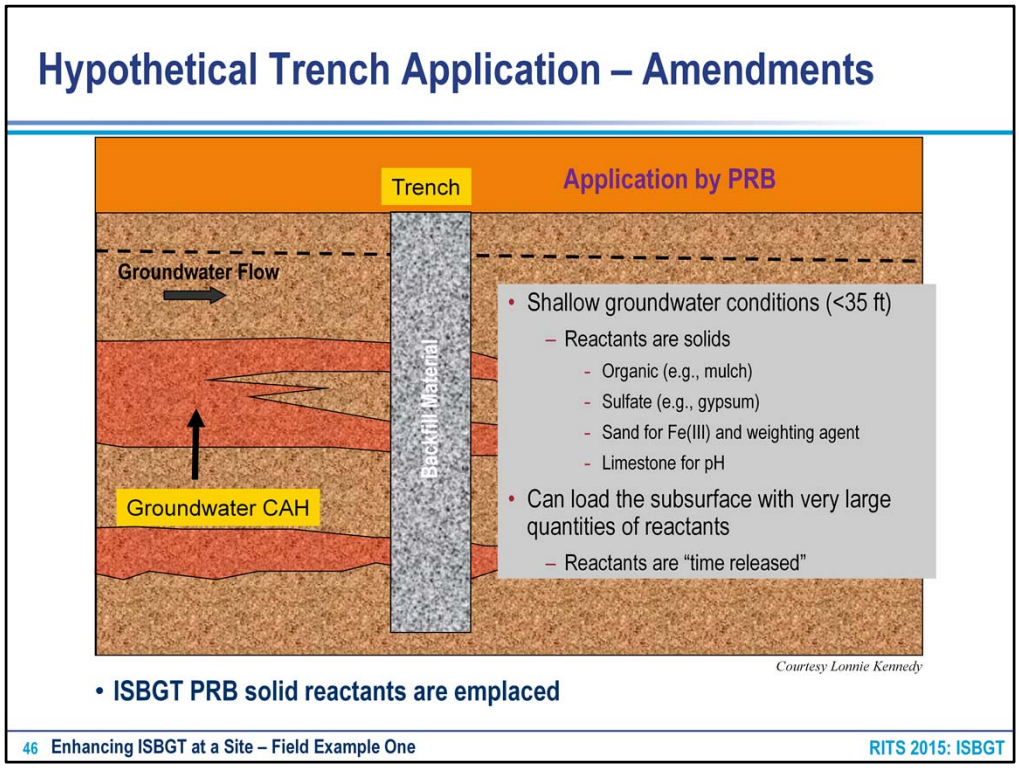
- Now we will go through each form of engineering ISBGT
- First a hypothetical injection system
- This TCE contaminated site is rich in Fe(III) but lacking in sulfate and organic carbon
- So amendments chosen are lactate and magnesium sulfate



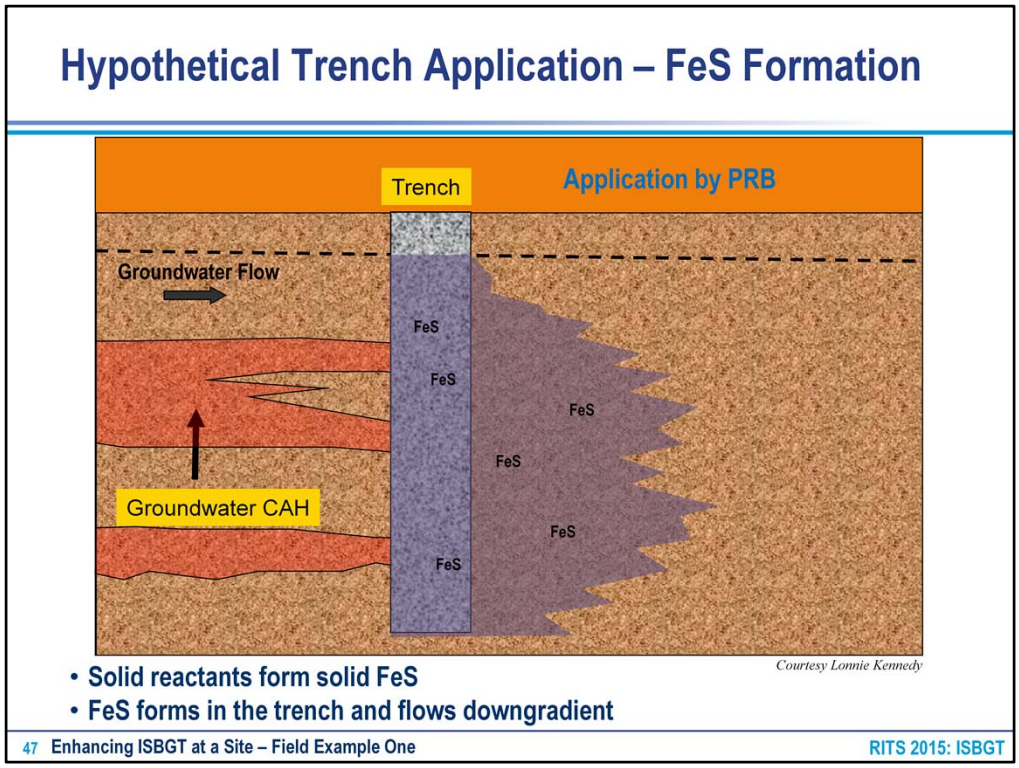
- Leads to precipitation of Fes creating a permeable reactive zone



- As plume flows through reactive zone TCE is degraded to acetylene by the FeS and acetylene is mineralized by microbes

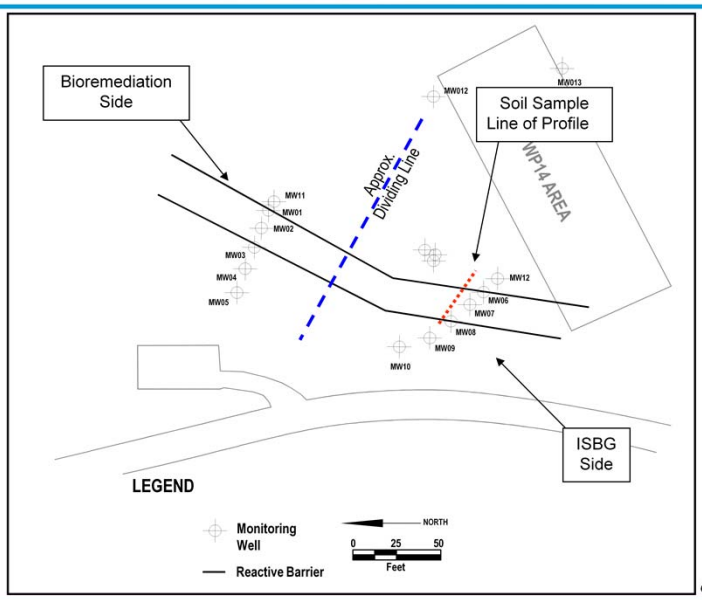


- Hypothetical trench
- Point out chlorinated solvent plume, typical depth <35ft
- Observe location of trench with groundwater flow i.e., perpendicular to GW flow
- Review typical amendments, mulch, gypsum, iron
- Mention sand/gravel used to control hydraulic retention time in barrier



- Iron sulfides precipitate in trench and amendments solubilize, flow short distances with groundwater and form iron sulfides slightly downgradient of trench

Trench Example – Dover National Test Site, WP14



Courtesy ESTCP

48 Enhancing ISBGT at a Site – Field Example Two RITS 2015: ISBGT

- Two trench side by side pilot studies
- One bioremediation, one ISBGT
- Two black lines represent trench width
- Monitoring wells perpendicular to trench length – includes upgradient, within trench and downgradient of trench wells

Trench Design

- Predesign ISBGT sediment and water analyses performed
- Bioremediation and ISBGT trenches
  - 450 cubic yards (yd^3) of finely ground, hardwood bark mulch
  - 375 yd^3 of iron rich sand
  - 45 yd^3 of crushed limestone
- The ISBGT trench also had 25 yd^3 crushed gypsum as a source of SO_4
- Sulfate balanced against soluble TOC in mulch with iron in abundance
- Post installation water and one sediment analyses done

49 Enhancing ISBGT at a Site – Field Example Two RITS 2015: ISBGT

- All info on slide
- Ask attendees to guess what the amendments would be
- 100 ft long

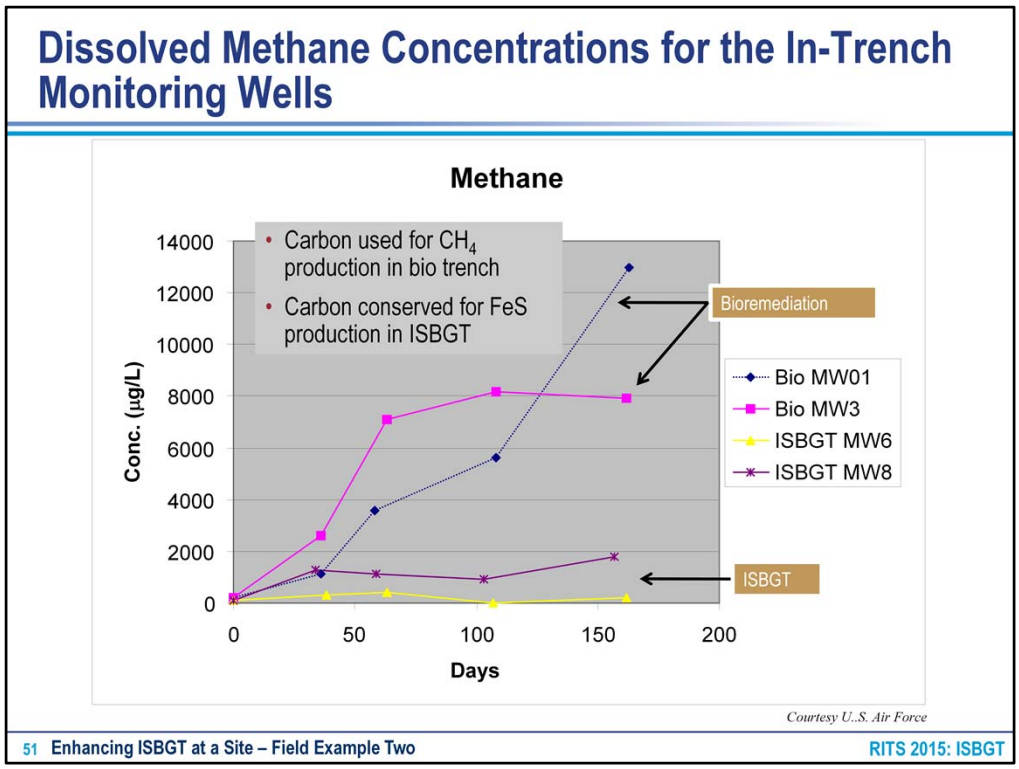
Photo of FeS Development in Trench Sediments

- Original mulch mixture
- Iron rich sand added to mulch
- Post-reaction ISBGT mulch mixture

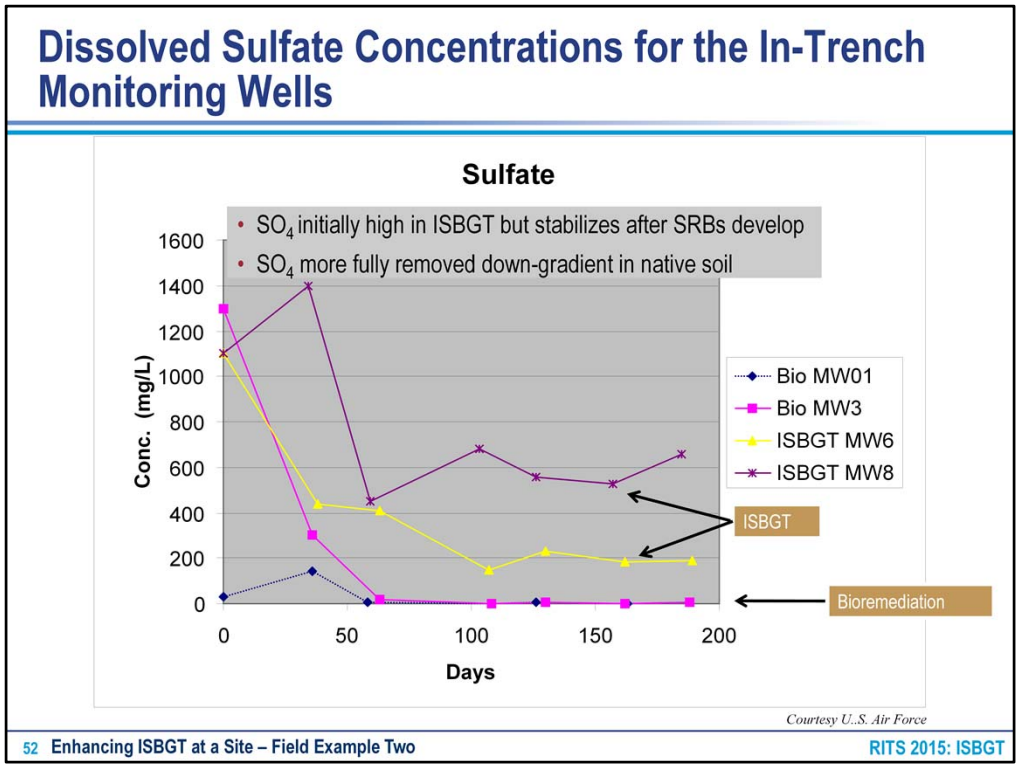
Courtesy U..S. Air Force

50 Enhancing ISBGT at a Site – Field Example Two RITS 2015: ISBGT

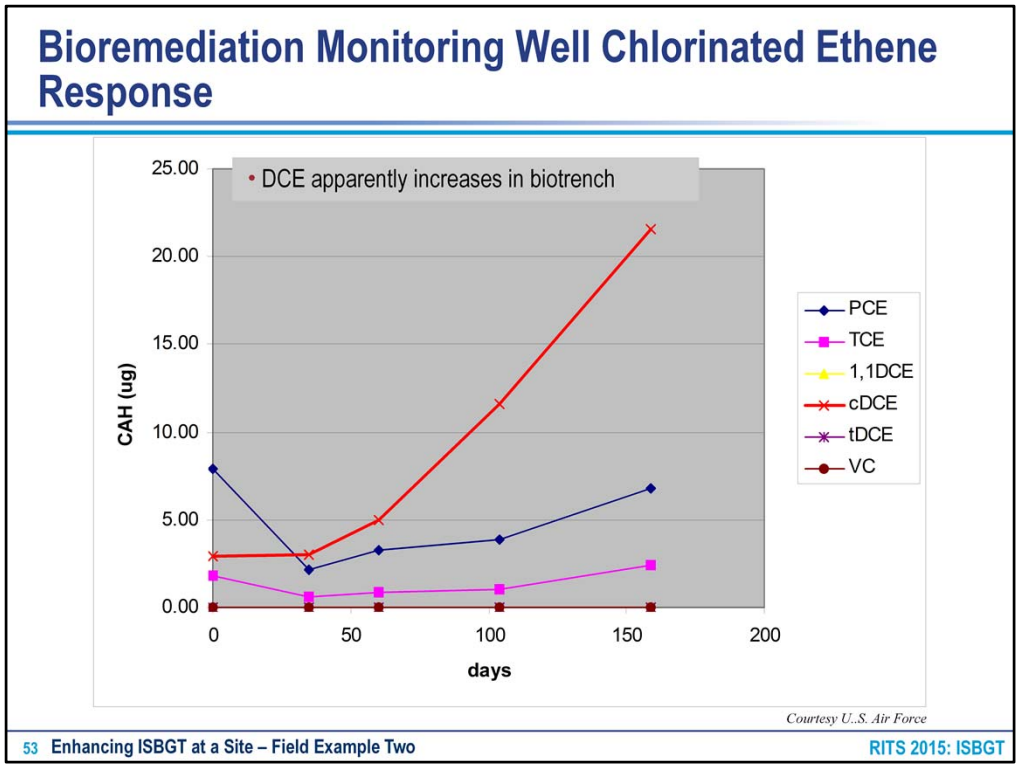
- Slide speaks for itself
- Point out the difference in the amendments and the trench material months after amendments were added to the trench



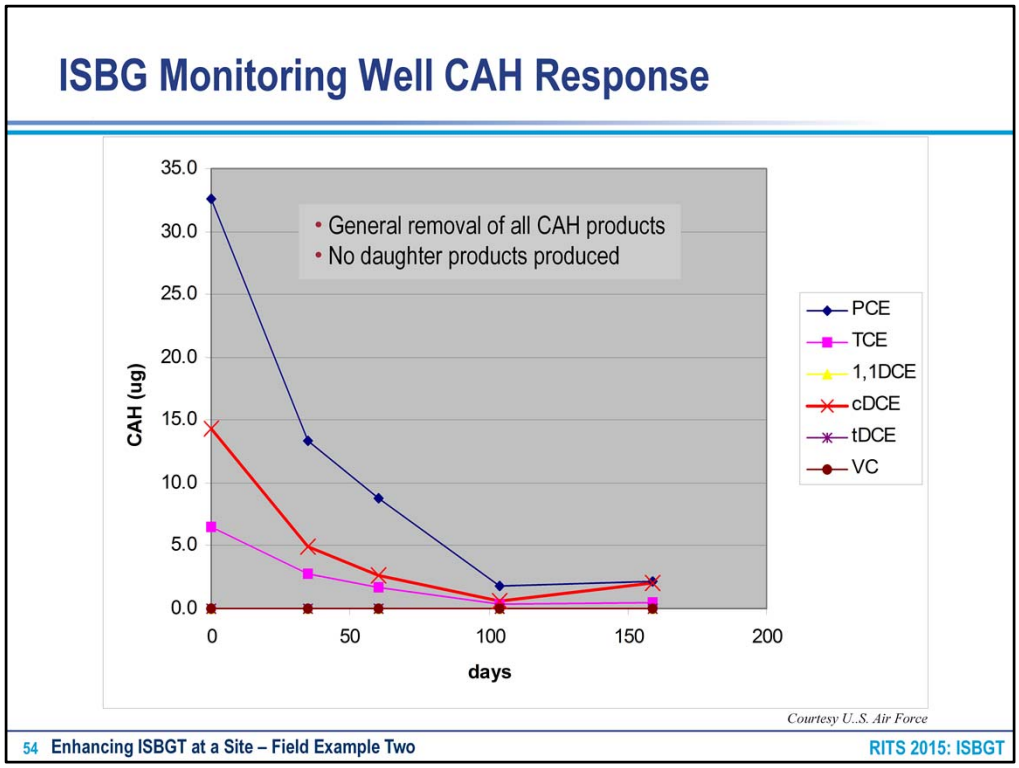
- Observe difference in methane production in bioremediation vs ISBGT trench
- In Bioremediation test plot, sulfate not in excess so methanogenic conditions exist
- In ISBGT test plot, little methane as trench remains in sulfate reducing conditions due to the excess sulfate



- Due to excess sulfate in IBGT test cell, sulfate concentrations remained slightly elevated in comparison to ISBGT test cell
- This matches the methane graph because for methanogenic conditions to exist, sulfate concentrations should be very low



- In bioremediation test plot as PCE concentrations decreased, TCE and cis-DCE concentrations also increased



- Characteristic of ISBGT parallel degradation of contaminants

Presentation Overview

- Introduction
- Evaluating a Site for ISBGT by MNA
- Enhancing ISBGT at a Site
- **Monitoring for ISBGT**
- Considerations When Enhancing ISBGT
- Classroom Exercise
- Wrap Up

55 RITS 2015: ISBGT

- Now we will discuss the parameters to be monitored after enhancing ISBGT to determine how effective the amendments and engineered system are

Monitoring Requires an Interdisciplinary Approach

- Groundwater Geochemistry – to understand electron accepting potential for microbes and active minerals
- Microbiology – identify specific bacteria that produce biogeochemically active phases
- Mineral Analysis – to identify active phases that promote transformation
- Isotope Analysis – to determine if degradation is taking place

56 Monitoring for ISBGT RITS 2015: ISBGT

- Multidisciplinary approach to monitoring for ISBGT. Similar to monitoring for Bioremediation
- Groundwater geochemistry – to understand the microbial potential for various electron accepting reactions and the electrochemical potential for production of certain active mineral phases
- Sediment analysis – identify and quantify active phases that promote transformation
- Microbiology – identify specific bacteria or enzymatic activities that use specific geochemical species and produce biogeochemcially active phases

Groundwater Geochemistry and Contaminant Concentration

Parameter	Purpose
DO, Fe(II), SO_4, CH_4	To determine dominant terminal electron accepting process
Chlorinated ethenes, methanes, ethanes, acetylene, ethene and ethane concentrations and Isotope fractionation	To determine degradation pathway
Electron donor – VFA, TOC, DOC, COD	Potential for sustained biological reduction
Water quality parameters	Further confirmation of redox condition, slightly alkaline pH best, low ORP

57 Monitoring for ISBGT RITS 2015: ISBGT

- Groundwater geochemistry – to understand the microbial potential for various electron accepting reactions and the electrochemical potential for production of certain active mineral phases
- DO, nitrate, ammonia, Fe(II), total iron, SO_4, sulfide, CH_4
- To determine dominant terminal electron accepting process
- For successful ISBGT there should be iron and sulfate reducing conditions
- Volumetric sulfate loading rate is an important factor in determining whether sufficient sulfate loading is adequate to promote rapid and on-going formation of fresh iron sulfide phases.
- Electron donor – VFA, TOC, DOC, COD
- Determines whether sufficient organic carbon is present to promote anaerobic conditions and active and sustained sulfate reduction
- pH, ORP, temperature, turbidity
- Further confirmation of redox condition
- Slightly alkaline pH increases rate of ISBGT
- Slightly cooler temperatures minimize biological reduction
- Turbidity could indicate presence of amendments in the monitoring wells and also presence of the iron sulfide particles
- Alkalinity
- This should be analyzed during baseline sampling to determine if the site has sufficient buffering capacity as some amendments may lower the pH of the groundwater, degradation of the contaminant may generate acidic conditions

Microbial Analysis

Analysis	Purpose
Microbial Analysis	
• Iron-Reducing Bacteria • Sulfate-Reducing Bacteria • Total Bacteria	• To identify microbial species that may be present

- Microbiology – identify specific bacteria or enzymatic activities that use specific geochemical species and produce biogeochemcially active phases
- Ideal microbial counts per ml should be >10^5

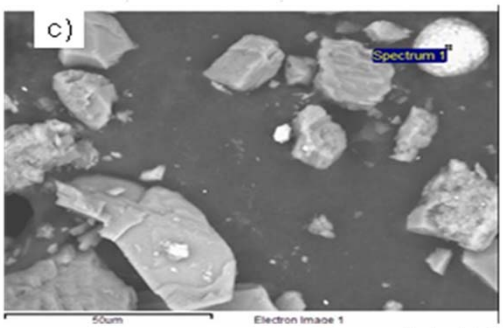
Mineral Analysis

Analysis	Purpose
X-ray Diffraction	Crystalline phases in mineral
Magnetic Susceptibility	Measure of magnetite
Scanning Electron Microscopy – Energy Dispersive Spectroscopy	Elemental analysis
Total Extractable Iron	Measure bioavailable iron
Geochemical Models	To identify mineral species that may be present
AVS CrS	Iron sulfide mineralogy

- Difference here from previous analysis of minerals vs. geochemical models and AVS, CrS
- AVS FeS
- CrS FeS2
- Geochemical models can tell the likelihood for precipitation of minerals

Mineral Analysis – Acid Volatile Sulfides (AVS)

- **Formation of FeS can be framboidal or crystal, framboidal better reacting**



Courtesy Battelle

- FeS formed can be framboidal or crystalline
- It is thought that quick formation of FeS minerals lead to the formation of smaller higher surface area framboidal FeS
- AVS tells whether FeS is present or not. AVS does not tell if the Fes is framboidal or crystalline. Therefore need analysis in addition to AVS to determine if the AVS present is reactive.

Geochemical Modeling and Thermodynamic Calculations

- Geochemical Modeling
  - Used to predict presence or absence of reactive minerals
  - Uses water chemistry measurements to determine minerals present
  - Collect multiple water samples over time
- Thermodynamic Calculations
  - Provide evidence for the potential occurrence of specific minerals
    - Based on measured concentrations of chemicals

61 Monitoring for ISBGT RITS 2015: ISBGT

- Modeling is a supporting line of evidence. Explain the definition of both types of modeling
- When modeling, have a specific question that you are trying to answer when running a model. Models can be run by contractors.
- Other available software to run geochemical models includes PHREEQ – chemical speciation will tell which species of Fe is present

Geochemical Modeling – Altus

- Measured Eh and sulfide in groundwater from a biowall
- Measured and characterized Fe and S minerals
- Minerals dominated by pyrite (FeS_2) and mackinawite (FeS)
- Eh and chemical activity of H_2S fell within range of pyrite and mackinawite
- Software used here: Geochemist Workbench

62 Monitoring for ISBGT RITS 2015: ISBGT

- Example of a model run on a biowall to determine if iron sulfides are precipitating in the trench biowall
- For this specific model, the objective was to determine if the iron sulfides are undersaturated, saturated, or oversaturated
- Undersaturated means in solution, oversaturated means precipitating

Geochemical Modeling – Altus – Model Inputs and Outputs

Field Data											
Well	pH	Eh_m	Na	K	Ca	Mg	Fe	Cl^-	SO_4^{2-}	DIC	ΣH_2S
	SU	mV	ppm	ppm	ppm	ppm	ppb	ppm	ppm	ppm	ppm
EPA110	6.58	-171	428	32	386	119	48.7	289	27	523	164
EPA109	6.77	-206	389	9.0	333	112	11.3	299	89	398	344
EPA108	6.81	-209	396	6.8	353	107	27.5	298	355	336	208
EPA107	6.60	-194	366	16.2	373	93.9	4.60	264	67	414	188
EPA106	6.64	-185	383	19.9	407	145	170	308	686	325	88
EPA105	6.73	-185	346	3.9	396	138	19.2	293	1030	229	121
EPA104	6.77	-230	383	21.2	444	152	291	289	389	352	210
EPA103	6.75	-196	370	11.9	406	158	53.0	253	806	311	190
EPA102	6.70	-195	379	27.6	447	156	68.2	269	319	493	178
EPA101	6.98	-70	398	4.9	395	155	11.2	301	1600	96	1

Model Outputs							
Well	Eh_c	Charge Balance	Pyrite	Mackinawite (crystalline)	Mackinawite (disordered)	Gypsum	Siderite
	mV	%	Saturation Index (SI)				
EPA110	-198	-8.4	9.42	-0.39	-0.87	-2.09	-2.46
EPA109	-210	-11.5	9.03	-1.00	-1.48	-1.60	-3.57
EPA108	-207	-6.8	9.37	-0.62	-1.09	-1.00	-3.06
EPA107	-197	-7.1	8.53	-1.41	-1.89	-1.67	-3.65
EPA106	-190	-3.3	10.0	0.13	-0.35	-0.71	-1.91
EPA105	-196	-6.4	9.19	-0.79	-1.27	-0.55	-2.99
EPA104	-202	-5.9	10.5	0.40	-0.08	-0.69	-2.02
EPA103	-200	-5.8	9.75	-0.34	-0.82	-0.65	-2.76
EPA102	-199	-7.5	9.77	-0.23	-0.72	-1.01	-2.61
EPA101	-199	0.1	7.03	-1.45	-1.93	-0.40	-2.39

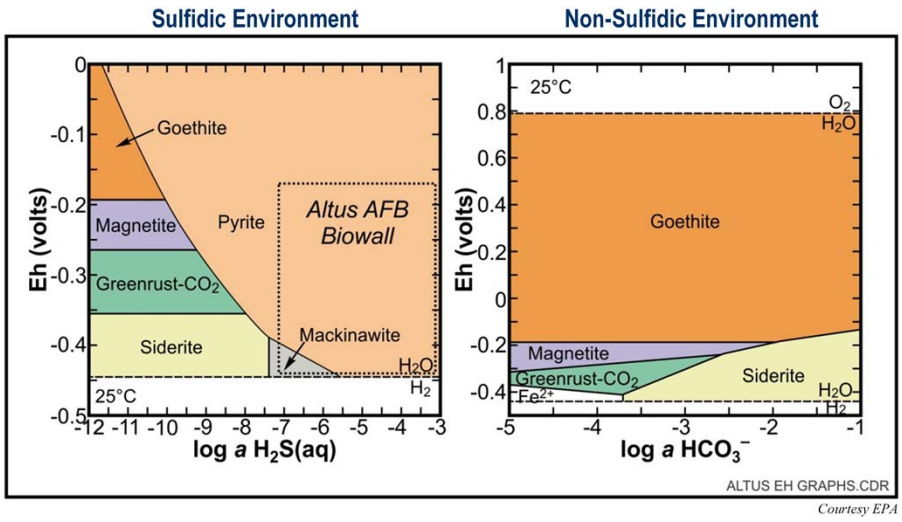
SI <0 = Undersaturated
SI >0 = Saturated

Courtesy EPA

63 Monitoring for ISBGT RITS 2015: ISBGT

- Field data compared to model output
- Very similar Eh values
- Pyrite is saturated
- FeS is present but undersaturated

Geochemical Modeling – Sulfidic vs. Non-Sulfidic



64 Evaluating a Site for ISBGT by MNA RITS 2015: ISBGT

- Assume equilibrium and slow nucleation reaction.
- Link geochemical conditions to minerals
- Conditions under which mineral is stable
- Non sulfidic – low dissolved sulfide
- Aerobic goethite (iron oxyhydroxide), Siderite low to medium Eh
- Carbonate forms of green rust
- And magnetite low Eh, medium to low sulfide ongoing sulfate reduction
- Fe is typically detrital. Dissolved by bacteria or chemically Fe(III) hydroxides.
- Understand primary controls
- More reactive Fe(III) oxide, goethite, iron bearing clays or sand and silt sized grains

Monitoring – Isotope Fractionation

- Carbon exists as two stable isotopes, ^{12}C and ^{13}C
- Natural isotopic abundances
  - ^{12}C about 99%, ^{13}C about 1%
- Hydrocarbon molecules mainly ^{12}C-^{12}C bonds; lesser ^{12}C-^{13}C bonds and even fewer ^{13}C-^{13}C bonds
- Stable isotopes ratios can change
  - Chemical process
  - Changes in the relative abundance of isotopes

Key Point Biotic and Abiotic mechanisms lead to a change in the carbon isotope ratio which can be measured

- Brief summary on isotopes
- Elements are made up of protons and electrons and neutrons
- Elements with different numbers of protons are isotopes
- Carbon has isotopes, two are stable and one is radioactive
- C12 and C13 are stable and C14 is radioactive
- When C is present in a compound both of its stable isotopes are present and it is possible to measure the ratio of these isotopes
- Bonds to 12C are easier during degradation processes to break and therefore there is an enrichment in the 13C in the original compound
- The enrichment can be measured and is usually represented by a –ve number per mil
- The bigger the number the greater the enrichment
- Microbes favor breaking lighter fractions, abiotic lighter bonds break easier

Contaminant Isotopic Fractionation

Transformation	Mineral	Enrichment	Microbial Degradation
Carbon Tetrachloride	Magnetite	−29 ± 3‰ (C-Cl bond)	
Carbon Tetrachloride	FeS	−15.9 ± 0.3‰	
PCE	FeS	−30.2 ± 4.3‰ (pH 7) −29.54 ± 0.83‰ (pH 8) −24.6 ± 1.1‰ (pH 9)	−1.39 ± 0.21‰ (BB1) −1.33 ± 0.13‰ (Sm) −7.12 ± 0.72‰ (BDI)
TCE	Green Rust	-23.00 ± 1.8‰	
TCE	Magnetite	-39 ‰ ± 12 ‰	
TCE	FeS	−33.4 ± 1.5‰ (pH 8) −27.9 ± 1.3‰ (pH 9)	−4.07 ± 0.48‰ (BB1) −12.8 ± 1.6‰ (Sm) −15.27 ± 0.79‰ (BDI)
cis-DCE	Magnetite	-0.60 ‰	
EDB	FeS_2	-20.2 ± 2.23‰	-5.7‰
TCE	Chloride Green Rust	-23 ± 1.8‰	

[Desulfuromonas michiganensis strain BB1 (BB1) and Sulfurospirillum multivorans (Sm)] and a bacterial consortium [BioDechlor Inoculum (BDI)].

66 Monitoring for ISBGT RITS 2015: ISBGT

- This slides shows enrichment factors
- Abiotic in general has a larger enrichment factor than microbial degradation
- Point out the larger numbers.

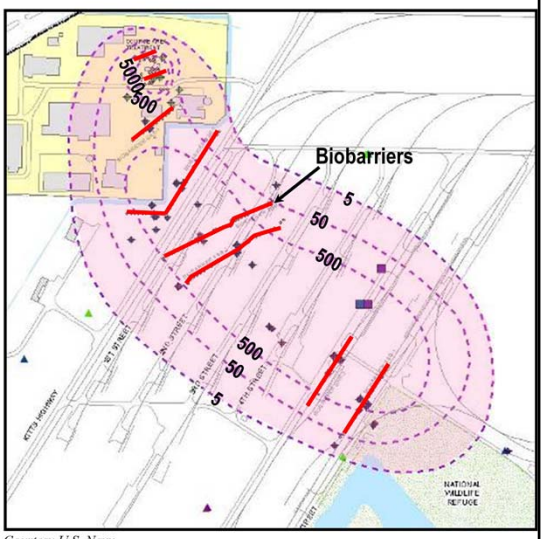
ISBGT with Other Treatment Processes

- ISBGT is often enhanced even when a different remedial process has been implemented
  - Enhanced In Situ Bioremediation
  - In Situ Chemical Oxidation

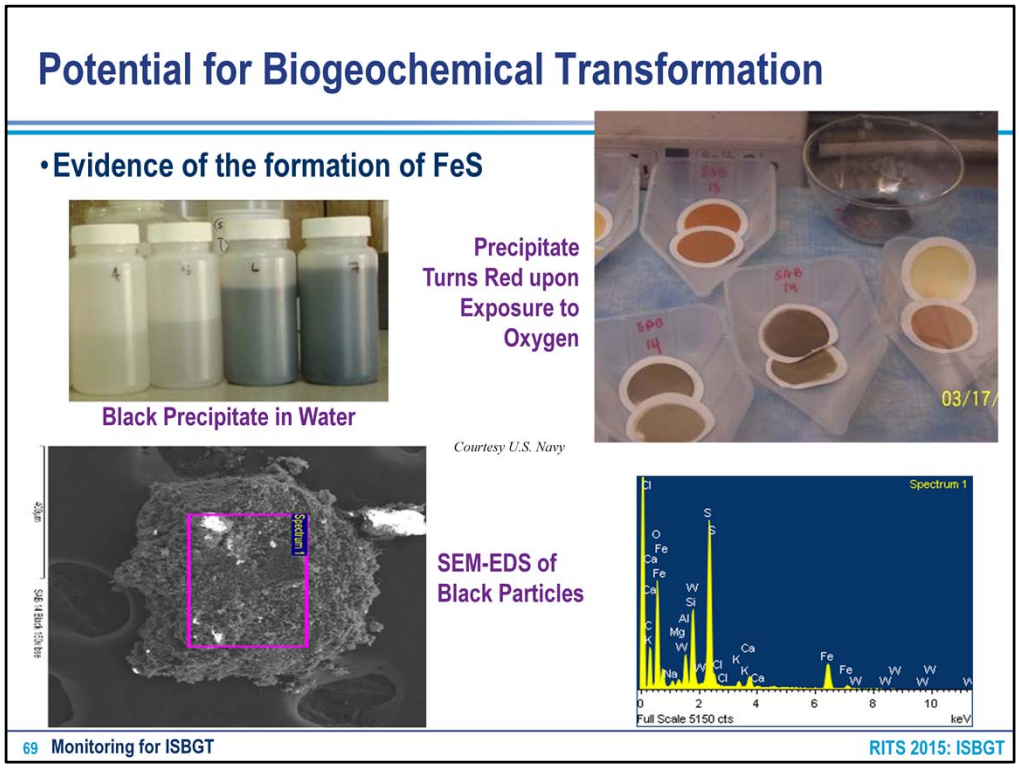
- Abiotic reactions have been occurring at sites “unaccounted” for and I will provide a couple examples of sites where ISBGT occurred when a different remedial approach was intended

Evidence of Biogeochemical Transformation

- Seal Beach
- Contaminant TCE 175 μg/L
- Sulfate 365 to 895 mg/L
- Iron 0.169 to 6.65 mg/L
- Biobarrier add KB1® and EVO

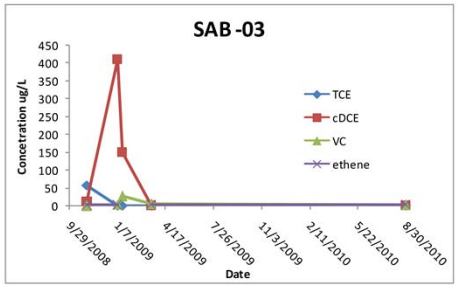


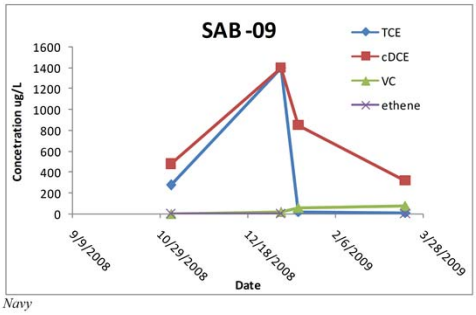
Courtesy U.S. Navy



- Notice color of groundwater from wells
- No cores taken
- So water samples filtered and precipitate analyzed by SEM/EDS

Evidence of Biogeochemical Transformation





Courtesy U.S. Navy

- **Black precipitate evidence of formation of reduced iron minerals**
- **Characteristics of precipitate suggest FeS present**
- **Simultaneous decrease in chlorinated solvents**

70 Monitoring for ISBGT RITS 2015: ISBGT

- Abiotic signature seen
- Further sampling needed to confirm this

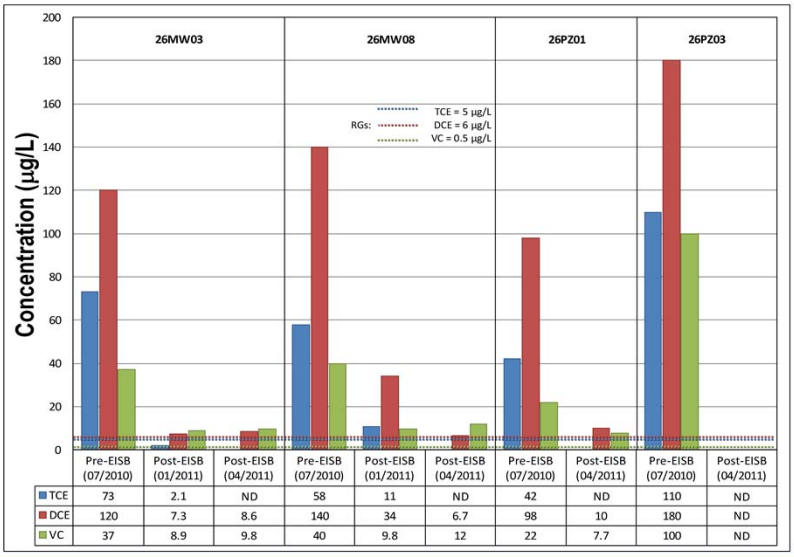
Alameda Site 26

- IR Site 26 is located in the central portion of Alameda Point, California
- Area of concern is ~550 m^2
- TCE, DCE, and VC are present in groundwater at concentrations as high as 700, 2,500, and 530 μg/L, respectively
- Remedy consists of ISCO followed by ISB

71 Monitoring for ISBGT RITS 2015: ISBGT

- ISCO site
- Persulfate
- Iron sulfate as activator
- Citrate to keep iron sulfate in solution
- When persulfate reacts it forms sulfate so site high in sulfate and also iron
- Electron donor added and reducing conditions created leading to the formation of iron sulfides

Alameda Site 26



	26MW03 Pre-EISB (07/2010)	26MW03 Post-EISB (01/2011)	26MW03 Post-EISB (04/2011)	26MW08 Pre-EISB (07/2010)	26MW08 Post-EISB (01/2011)	26MW08 Post-EISB (04/2011)	26PZ01 Pre-EISB (07/2010)	26PZ01 Post-EISB (04/2011)	26PZ03 Pre-EISB (07/2010)	26PZ03 Post-EISB (04/2011)
TCE	73	2.1	ND	58	11	ND	42	ND	110	ND
DCE	120	7.3	8.6	140	34	6.7	98	10	180	ND
VC	37	8.9	9.8	40	9.8	12	22	7.7	100	ND

Courtesy U.S. Navy

72 Monitoring for ISBGT RITS 2015: ISBGT

- Four wells
- First set of graphs after ISCO and before EISB
- 2nd and 3rd set of graphs post EISB
- No sequential formation of daughter products
- All degradation products have disappeared

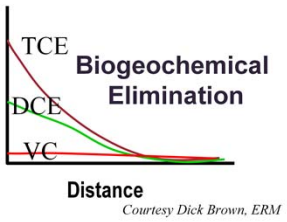
Mass Reduction

Monitoring Event	COC	Mass in Groundwater (lb)	Percent Reduction
			Mass
Baseline (Nov 07)	TCE	0.033	NA
	DCE	0.116	NA
	VC	0.021	NA
Pre-EISB Injections (Jul 10)	TCE	0.017	48%
	DCE	0.055	53%
	VC	0.012	43%
Post-EISB Injections (Jan 11)	TCE	0.0041	88%
	DCE	0.0069	94%
	VC	0.0031	85%

- Before EISB degradation in mass just 40 to 50 %
- Post EISB just three months degradation in mass 85 to 95%

Evidence of Biogeochemical Transformation

- Black precipitate evident in several wells during the January 2011 sampling event
- Decrease in chlorinated ethenes without subsequent increase in daughter products
- Further analysis done to determine contribution of biogeochemical transformation (April 2011)
  - XRD
  - SEM/EDS
  - AVS/CRS
  - Sulfide
  - Daughter products acetylene



Courtesy Dick Brown, ERM

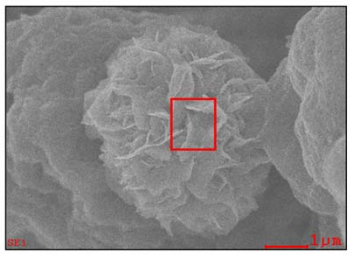
74 Monitoring for ISBGT RITS 2015: ISBGT

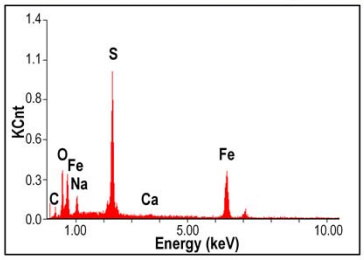
- Note the same methods discussed prior is what was used here

SEM/EDS

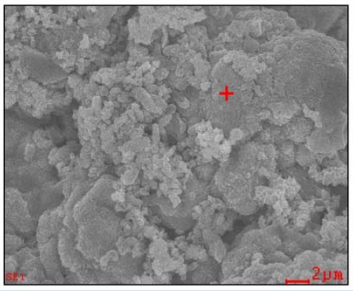
Courtesy Battelle

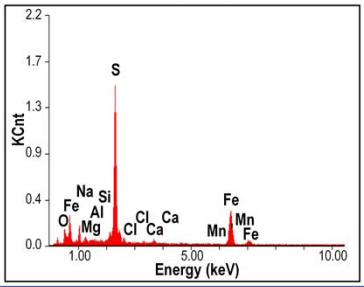
- **Provides detailed chemical information about crystalline precipitates**





Element	Wt%	At%
C	09.17	21.72
O	13.40	23.83
Na	05.91	07.31
S	27.91	24.76
Ca	00.86	00.61
Fe	42.75	21.78





Element	Wt%	At%
O	06.00	13.70
Na	05.64	08.95
Mg	01.33	02.00
Al	00.35	00.48
Si	00.00	00.00
S	35.65	40.62
Cl	01.30	01.34
Ca	01.43	01.31
Mn	00.67	00.44
Fe	47.63	31.16

75 Monitoring for ISBGT RITS 2015: ISBGT

- SEM EDS
- Note surface area of minerals
- Atomic percent
- Weight percent
- Larger spectra show mineral present

AVS/CRS

- **Determines the presence of FeS and FeS_2 respectively**

Sample	AVS, mmol/L	AVS mg/L	CRS, mmol/L
26MW08	2940	258.5	610
26MW08	3200	281.3	490
26PZ02	795	69.9	150
26PZ02	750	65.9	130
26PZ01	3460	304.2	640
26PZ01	1960	172.3	600
26MW03	5240	460.6	745
26MW03	4840	425.5	1000
26MW02	ND		30

- Studies shows 25mg/L threshold for abiotic to be dominant – here we have up to 425 mg/L
- Wow!

Conclusions from Combined Remedies

- ISBGT occurs simultaneously with other remediation technologies
- First line of evidence is usually the presence of iron sulfide precipitates in the groundwater
- Also reduction of contaminants without the presence of degradation products
- Further analysis of mineral confirm their presence

Presentation Overview

- Introduction
- Evaluating a Site for ISBGT by MNA
- Enhancing ISBGT at a Site
- Monitoring for ISBGT
- Considerations When Enhancing ISBGT
- Classroom Exercise
- Wrap Up

Challenges/Questions

- Difficult to track degradation product
- No field evidence of daughter products – regulatory acceptance??
- No official guidance
- Debate on whether aquifer clogging occurs
- Reactivity may stop when active sites used up
- No sustainable source of sulfate available
- Is hydraulic retention sufficient?

Key Point: Further research is being conducted to fill data gaps that will lead to official guidance

- Acetylene is degradation product of chlorinated ethene degradation – reason for other lines of evidence needed to ensure regulatory acceptance since difficult to close mass balance
- If using natural iron – no clogging – if adding iron clogging?
- Need sulfate – CDM currently injecting sulfate

How does ISGBT compare to other technologies?

	ISBGT	ISCO	EISB
Preferred Geological/Geochemical Conditions	Available iron mineralogy	• Low FOC (Permanganate) • Low Mn/FE (Peroxide) • Low Mn (Persulfate)	• Available natural organics • Low to moderate Fe/Mn (competitive metabolism)
Relative Rate of Treatment	Moderate to fast	Fast	Slow to moderate
Effect of Redox Conditions	• Works best in anoxic to anaerobic conditions • Not compatible with highly aerobic conditions	• Works best in oxic to aerobic conditions • Not compatible with highly reducing conditions	• Works best in highly anaerobic conditions • Not compatible with highly aerobic conditions
Amendments Needed	• Reducing agent • Available iron	Oxidant, and in some cases, a reaction catalyst (persulfate, peroxide)	• Carbon source • Inoculum • Nutrients
Compatibility with MNA	Very good	• Can transition to MNA	Very good if right bacteria present and properly maintained with multiple additions of substrate

80 Considerations When Enhancing ISBGT RITS 2015: ISBGT

- Go through slide slowly since lots of details

How does ISBGT compare to other technologies? (cont.)

	ISBGT	ISCO	EISB
Key Factors Limiting Success	• Available iron • Reduced iron	Stability/consumption of oxidant	• Requisite bacteria • Available carbon source
Residual Effect After Agent Spent	• Reduced iron may continue activity • Reapplication may be needed	• No reaction without oxidant • Reapplication may be required to meet goals	• No degradation without carbon • Reapplication required to meet goals
Secondary water quality impacts	• If Fe is limited sulfide may be elevated • Methane not as elevated as EISB • Secondary MCL for sulfate is 250 mg/L	• Mobilization of metals	• High methane
Sustainability	• All amendments biodegradable. • Environmental footprint similar to EISB	• Higher environmental footprint than EISB and ISCR	• Similar environmental footprint to ISBGT

81 Considerations When Enhancing ISBGT RITS 2015: ISBGT

- Mention cost similar to EISB, less than ISCO – using natural geochemical conditions to advantage

Presentation Overview

- Introduction
- Evaluating a Site for ISBGT by MNA
- Enhancing ISBGT at a Site
- Monitoring for ISBGT
- Considerations When Enhancing ISBGT
- Classroom Exercise
- Wrap Up

Classroom Exercise

- **Find classroom exercise sheet in the handbook at end of the presentation**

RITS 2015
In Situ Biogeochemical Transformation Processes
Classroom Exercise

Below you have site information for two sites (Site A and Site B). Form groups of 5 to discuss the data from both sites then answer the four questions below. Select one representative to report your group's conclusions.

Is abiotic transformation by minerals occurring naturally at Site A? Justify your answer

---

Is abiotic transformation by minerals occurring naturally at Site B? Justify your answer

---

Can ISBGT be enhanced at these sites? Justify your answer

Would you use an injection method or a reactive barrier method to enhance ISBGT at these sites and what amendments would you need to add?

Parameter	Units	Site A	Site B
ORP	mV	0 to 150	48
TOC	mg/L	9.1	3
Dissolved Fe	mg/L	0.5	0.1
Bioavailable iron in soil	%	0.1	5
Dissolved sulfate	mg/L	1,500 to 2,000	900 to 1,000
Volumetric sulfate loading	mg/L/d	167	130
IRB/SRB	cells/ml	10^3	10^2
TCE	µg/L	8,000	1,200 to 1,800
Geology/Hydrogeology			
Depth to contamination	ft	8 to 35	60 to 80
Depth to groundwater	ft bgs	5 to 8	30
Geology	ft	Weathered and fractured silty clays 25 to 50 ft	Alluvium to 100 ft
Hydraulic conductivity of soil	ft/day	8.7	7.6
Hydraulic gradient	ft/ft	0.003	0.007
Porosity		0.15	0.10
Iron minerals	%	0.002	0.5

83 Classroom Exercise RITS 2015: ISBGT

- Include the blank classroom exercise in the handbook and pass out the completed exercise with the answers as a handout

Presentation Overview

- Introduction
- Evaluating a Site for ISBGT by MNA
- Enhancing ISBGT at a Site
- Monitoring for ISBGT
- Considerations When Enhancing ISBGT
- Classroom Exercise
- Wrap Up

Advantages of ISBGT

- No need for bioaugmentation
- Conservation of reactants for CVOC treatment
- Inexpensive and easy to design
- No production of vinyl chloride from TCE
- Treats wide range of contaminants

Key Points and Take-Away Messages

- Iron sulfides are best understood and their formation can be enhanced in situ
- Typical aquifer matrix has 0.1 to 10% Fe
- Acetylene – main degradation product of ISBGT on chlorinated ethenes, difficult to measure in the field
- Specific MNA protocol not available for ISBGT
- Naturally occurring minerals participate in contaminants degradation
- Enhancing ISBGT is a balance between sulfate, iron, and electron donor

Look for T2 emails with info on handbook availability