

Calcium Sulfate

(Biogeochemical Reductive Dechlorination - BiRD)

1. Submitted by Gary Cronk, JAG Consulting Group, Inc.
2. Calcium sulfate is a white powder product commonly called Gypsum. It has a chemical formula of CaSO_4 (often hydrated with water molecules). It is used to stimulate the growth of sulfur reducing bacteria and promote anaerobic conditions in the subsurface environment as part of the Biogeochemical Reductive Dechlorination (BiRD) process.
3. MSDS - See attached file
4. Number of Field Applications: 200 (estimated)
5. Case Studies - See attached files
6. Technical Summary: Calcium sulfate is used to promote growth of sulfur reducing bacteria and anaerobic conditions in the subsurface. Calcium sulfate is normally delivered in 50 pound or 1,000 pound bags. The addition of sulfate and carbon into groundwater will stimulate naturally occurring sulfate reducing soil bacteria to produce hydrogen sulfide (HS^-) (a biological process). The hydrogen sulfide produced then reacts with naturally occurring ferric iron in the soil (or supplied ferric iron) to produce ferric sulfides (FeS) (a geochemical transformation). Then, the ferric sulfides reductively dechlorinate chlorinated contaminants in a final abiotic process. The Biogeochemical Reductive Dechlorination (BiRD) process can be used to build an in-situ geochemical barrier targeting specific ground water flow paths for maximum treatment

Calcium sulfate (Gypsum) is a naturally occurring mineral in the environment (with low toxicity). Respiratory and eye protection from dust particles should be provided by use of proper PPE.

Magnesium Sulfate

(Biogeochemical Reductive Dechlorination - BiRD)

1. Submitted by Gary Cronk, JAG Consulting Group, Inc.
2. Magnesium sulfate is a white powder product commonly called Epsom salts. It has a chemical formula of $MgSO_4$ (often hydrated with water molecules). It is used to stimulate the growth of sulfur reducing bacteria and promote anaerobic conditions in the subsurface environment as part of the Biogeochemical Reductive Dechlorination (BiRD) process.
3. MSDS - See attached file
4. Number of Field Applications: 200 (estimated)
5. Case Studies - See attached files
6. Technical Summary: Magnesium sulfate is used to promote growth of sulfur reducing bacteria and anaerobic conditions in the subsurface. Magnesium sulfate is normally delivered in 50 pound or 1,000 pound bags. The addition of sulfate and carbon into groundwater will stimulate naturally occurring sulfate reducing soil bacteria to produce hydrogen sulfide (HS^-) (a biological process). The hydrogen sulfide produced then reacts with naturally occurring ferric iron in the soil (or supplied ferric iron) to produce ferric sulfides (FeS) (a geochemical transformation). Then, the ferric sulfides reductively dechlorinate chlorinated contaminants in a final abiotic process. The Biogeochemical Reductive Dechlorination (BiRD) process can be used to build an in-situ geochemical barrier targeting specific ground water flow paths for maximum treatment

Magnesium sulfate (Epsom salt) is a naturally occurring mineral in the environment (with low toxicity). Respiratory and eye protection from dust particles should be provided by use of proper PPE.

Ferric Oxide (Hematite)

(Biogeochemical Reductive Dechlorination - BiRD)

1. Submitted by Gary Cronk, JAG Consulting Group, Inc.
2. Ferric oxide has a chemical formula of Fe_2O_3 . It is also commonly found naturally as a mineral called Hematite (also called iron ore).
3. MSDS - See attached file
4. Number of Field Applications: 20 (estimated)
5. Case Studies - See attached files
6. Technical Summary: Ferric oxide is used to induce a geochemical transformation of hydrogen sulfide to ferric sulfides in the subsurface environment as part of the Biogeochemical Reductive Dechlorination (BiRD) process. Then, the ferric sulfides reductively dechlorinate chlorinated contaminants in a final abiotic process. The BiRD process can be used to build an in-situ geochemical barrier targeting specific ground water flow paths for maximum treatment

Ferric oxide (Hematite) is a naturally occurring mineral in the environment (with low toxicity). Respiratory and eye protection from dust particles should be provided by use of proper PPE.

Depending on the specific geologic source of Hematite, it may contain elevated levels of trace metals (i.e., arsenic and chromium) that may be undesirable to local groundwater resources. Therefore, if Hematite is proposed for use, the Water Board should require that a full metals analysis be provided for review to ensure that it is acceptable for protection of groundwater quality.

Evaluation of Biogeochemical Reductive Dechlorination for Inclusion in the General WDR Permit

By: Gary Cronk, P.E.

JAG Consulting Group, Inc.

November 30, 2013

Introduction to Biogeochemical Reductive Dechlorination

- Includes all types of Biogeochemical Reductive Dechlorination Processes including the patented BiRD™ process
- BiRD Process involves the addition of non-specific sources of sulfur, iron, and organic carbon to help stimulate the growth of sulfur reducing bacteria and subsequently the abiotic formation of iron sulfide minerals in the subsurface environment (causing reductive dechlorination).
- BiRD process can used effectively used to treat VOCs, hexavalent chromium and arsenic in soil and groundwater

BiRD: Three Phases of Development

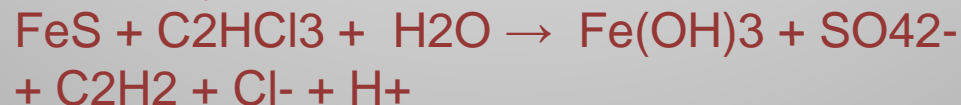
- Phase 1: Biological Step: Addition of sulfate and carbon source stimulate common sulfate reducing soil bacteria:



- Phase 2: Geochemical Step: HS⁻ from SRB respiration reacts with native or supplied mineral Fe³⁺ to produce FeS:



- Phase 3: Dechlorination Step: Reactive FeS reductively dechlorinates CAH abiotically:



- The formation of FeS does not inhibit or alter aquifer permeability.
- Typical Fe oxides, for example hematite (Fe₂O₃), are actually transformed to FeS minerals rather than “precipitating” out of solution.
- BiRD builds an in-situ geochemical barrier targeting specific ground water flow paths for maximum treatment

BiRD Reaction Times

- Generating sulfate reducing conditions is rapid (within days) because O₂ and NO₃ concentrations in ground water are typically low
- Nearly all native sediments and aquifers have existing sulfate-reducing bacteria.
- Fe and HS⁻ react quickly to form FeS minerals
- FeS reaction with CAH typically approximates first order kinetics facilitating half lives in the range of a few weeks to a month
- BiRD takes much less time than Bioremediation to achieve significant VOC reductions

Commonly Used BiRD Minerals

- **Iron Minerals**
 - Hematite (ferric oxide, Fe_2O_3) – iron ore
 - Iron Rich Sand
- **Sulfur Minerals**
 - Gypsum (Calcium Sulfate)
 - Epsom Salt (Magnesium Sulfate)
- **Carbon Sources**
 - All food grade Carbon products in the Authorized List of Amendments
- Iron and Sulfur minerals are naturally occurring and considered to be of low toxicity

Injection/Application Methods

- Injection wells are used for liquid sources of organic and sulfate. Injection is useful in deeper aquifer environments or in areas where access is limited by surface structures.
- Emplacement of solid organic and sulfate into a Permeable Reactive Barrier. The PRB approach can load the subsurface with very large quantities of reactants (lasting for years). The application is best suited for open areas of relatively shallow ground water, typically <35 feet bgs.
- BiRD process used at two dozen sites across the U.S. (primarily at Air Force Bases)

Advantages of BiRD versus Bioremediation

- BiRD chemicals are inexpensive and readily available, including bulk minerals, agricultural soil products and common food grade organics and/or waste materials (mulch)
- CAH treatment is complete with no daughter products generated or degradation stall at 1,2-DCE
- Contaminant treatment half-lives are short, usually <1 month
- BiRD takes much less time than Bioremediation to achieve significant VOC reductions

Health & Safety Issues

- Because naturally occurring minerals are often used for the BiRD process, few health & safety issues occur.

Case Study No. 1 – Dover Air Force Base, Delaware

- Pilot Test using Direct injection of Epsom Salts (MgSO_4) and Sodium Lactate (Carbon Source) into 5 injection wells
- Sediments sampled 8 months after injection and showed significant development of iron sulfide minerals in the sandy aquifer matrix.
- Achieved 95% reduction in PCE, TCE, and cis 1,2-DCE in 225 days (no VC generated)
- Acetylene (C_2H_2) was the primary end product of CAH dechlorination
- Performed for AFCEE (Air Force Center for Environmental Excellence, San Antonio, Texas) Enhanced In Situ Bioremediation (EISB) Initiative.

Case Study No. 2

Use of Permeable Reactive Barrier at Dover AFB Site

- PBR Installed at Dover National Test Site WP-14
- Two parallel emplacement trenches measured 25 feet deep by 556 feet in length
- One-half of barrier was designed for BiRD and one-half designed for Bioremediation
- Native groundwater was low in sulfate and soil was low in iron
- Bioremediation trenches backfilled with finely ground mulch (bark), iron rich sand, and crushed Limestone (to maintain pH levels)
- BiRD trenches had the same as the Bio trenches but also had crushed Gypsum (as a sulfur source)

Case Study No. 2

VOC Reductions in PRB, Dover AFB

- For BiRD trenches, PCE and TCE were completely destroyed within 150 days and no daughter products formed.
- For Bioremediation trenches, PCE showed limited treatment, TCE no treatment but mostly biotransformed into 1,2-DCE (complete treatment was not achieved).

Case Study No. 3 – Altus Air Force Base, OU-1, Oklahoma

- EPA sponsored Treatability Testing to identify optimal use of sulfate and iron supplemental sources for BiRD Technology Permeable Reactive Barrier installation
- The first PRB was constructed with mulch (pine bark), sand, and Gypsum (sulfur source)
- The 2nd PRB was constructed with the same materials as No. 1 PRB but also included crushed Limestone (CaCO_3) as a pH buffering agent.
- The 3rd PRB was constructed with the same materials as No. 1 PRB but also included Hematite as a supplemental iron source

Case Study No. 3 – Results: Pilot Test, Altus AFB, OK

- Pilot Test was run for over one year
- While sulfur was consumed in all PBRs, much larger quantities of sulfur were consumed in the limestone and hematite supplemented RBRs, suggesting an improved environment for sulfur reducing bacteria.
- Formation of FeS minerals was greatly increased in the supplemented PBRs. Increased FeS produced faster degradation of CVOCs.
- TCE levels were reduced from 2,000 $\mu\text{g/L}$ to 3 $\mu\text{g/L}$ (99.9%)in the supplemented PBRs within 6 months. No Vinyl Chloride was generated. Very little DCE was generated.
- Although BiRD processes occurred naturally, it could have been promoted to a higher efficiency using engineering design (i.e., adding gypsum and iron)

Case Study No. 4 – Buckley Air Force Base, Denver, CO

- Treatability and Pilot Testing at Buckley AFB evaluating Epsom Salts vs. Gypsum (as sulfur sources) and Sodium Lactate vs. Chitin (as carbon sources)
- Aquifer sediments are Weathered Denver Formation, a siltstone and sandstone formation.
- Chemical emplacement by pneumatic fracturing in open boreholes to increase permeability of formation and dispersion of chemicals
- Achieved significant TCE reductions (over 90%) within 90 days. The combination of Epsom salts and Chitin achieved slightly better TCE destruction. It is likely that the improved performance was due to the higher solubility of Epsom salts in water

Case Study No. 5 – Hickham AFB, Oahu, Hawaii

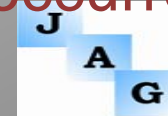
- Pilot Test performed using BiRD chemical supplements, specifically Epsom Salts (MgSO_4) and sodium lactate (Carbon source).
- Aquifer sediments were primarily sand contaminated with over 500,000 $\mu\text{g/L}$ of TCE and 9,000 $\mu\text{g/L}$ of DCE.
- Reducing conditions generated within 7 days and formation of FeS minerals within 30-60 days.
- TCE levels reduced to 40 $\mu\text{g/L}$ (99% reduction) within 120 days and DCE reduced to 4,000 $\mu\text{g/L}$ (40% reduction).

Case Study No. 6 – Elmendorf AFB, Alaska

- Sandy aquifer contaminated with TCE (215 µg/L) and 3,500 µg/L of DCE.
- Pilot Test performed using powdered Gypsum (CaSO₄) and Emulsified Vegetable Oil (Carbon source).
- TCE levels reduced to 3 µg/L (99% reduction) within 6 months and DCE was reduced to 1,300 µg/L (63% reduction).
- No vinyl chloride generated

Case Study No. 7 – Hill AFB, Utah

- Sand and gravel aquifer contaminated with high levels of TCE
- Pilot Test performed using two treatment zones using direct push injection of Epsom Salts ($MgSO_4$), Hematite (Fe_2O_3), and Emulsified Vegetable Oil (Carbon source).
- TCE levels were significantly reduced after 6 months, although mostly due to biological degradation.
- Over-stimulation of biological processes occurred due to a large imbalance in the amount of EVO injected (over 100 mg/L of DOC). Generation of iron sulfide minerals was suppressed and little abiotic dechlorination occurred as a result.



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Field-scale demonstration of induced
biogeochemical reductive dechlorination
at Dover Air Force Base, Dover, Delaware

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Field-scale demonstration of induced biogeochemical reductive dechlorination at Dover Air Force Base, Dover, Delaware

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Abstract

Biogeochemical reductive dechlorination (BiRD) is a new remediation approach for chlorinated aliphatic hydrocarbons (CAHs). The approach stimulates common sulfate-reducing soil bacteria, facilitating the geochemical conversion of native iron minerals into iron sulfides. Iron sulfides have the ability to chemically reduce many common CAH compounds including PCE, TCE, DCE, similar to zero valent iron (Fe^0). Results of a field test at Dover Air Force Base, Dover, Delaware, are given in this paper. BiRD was stimulated by direct injection of Epsom salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and sodium (L) lactate ($\text{NaC}_3\text{H}_5\text{O}_3$) in five injection wells. Sediment was sampled before and 8 months after injection. Significant iron sulfide minerals developed in the sandy aquifer matrix. From ground water analyses, treatment began a few weeks after injection with up to 95% reduction in PCE, TCE, and cDCE in less than 1 year. More complete CAH treatment is likely at a larger scale than this demonstration.

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Keywords: Biogeochemical reductive dechlorination; TCE; FeS; Reduced minerals

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1. Introduction

The bioremediation of chlorinated aliphatic hydrocarbons (CAHs), including perchloroethylene (PCE), trichloroethylene (TCE), trichloroethane (TCA), has generally focused on direct microbially facilitated oxidation/reduction reactions (Bouwer, 1994; Wiedemeier et al., 1998). Both natural and enhanced bioremediation of CAH compounds normally requires the presence of labile organics and special chlororespiring bacteria, which facilitate the oxidation of the organic through the complimentary reductive dechlorination of the targeted CAH. The bioremediation of CAH compounds is typically stepwise with highly chlorinated compounds (e.g., PCE or TCE) biotransformed to intermediate, less chlorinated, daughter products (e.g., DCE or VC). Active CAH bioremediation is often recognized by the generation of these daughter products. In some instances, if these are not further biodegraded, they can persist in the environment.

Biogeochemical reductive dechlorination (BiRD) is a new approach to CAH treatment (Kennedy, 2005). Under certain natural or stimulated conditions, native sulfate-reducing soil bacteria have the ability to significantly modify the mineralogical composition of their environment, inducing the rapid authigenic formation of mineral iron sulfides. FeS minerals are strongly reduced and facilitate the autoreduction of CAH compounds similar to exposure to elemental iron. Synthetic FeS has been documented to dechlorinate a wide range of chlorinated compounds including PCE, TCE, PCA, CT, PCA, and others (Butler and Hayes, 1998, 1999, 2000; Gander et al., 2002). Lee and Batchelor (2002) also found good dechlorination rates for PCE, cDCE, and VC by reaction with pyrite (FeS₂).

FeS forms in many natural subsurface environments and has also been documented to occur in sediment contaminated with labile organics, including landfill leachate and fuel hydrocarbons (Howarth and Jorgensen, 1984; Morse et al., 1987; Kennedy et al., 1998a,b; Kennedy et al., in press). By stimulation, high concentrations of FeS and FeS₂ have been developed in just a few weeks under controlled conditions simulating natural aquifers in typical sediment (Kennedy and Everett, 2001). BiRD can be stimulated through the addition of sulfate and a labile organic in the presence of natural or supplemented Fe (typically mineral).

There are several theoretical advantages to BiRD. Sulfate bacteria are ubiquitous and sulfate reduction is simple and rapid to stimulate. The formation of iron sulfide minerals during sulfate reduction is almost instantaneous. Reaction half-lives for dechlorination by iron sulfides range from only hours to weeks. CAH treatment via BiRD results in the generation of comparatively little daughter products. BiRD is also inexpensive, requiring only the addition of sulfate salts, manufactured for agricultural purposes, and any of a number of organic materials, such as lactate or plant mulch.

The demonstration project presented here is the first to stimulate the formation of FeS under field conditions for the purpose of CAH remediation. The project was located in a chlorinated solvent plume at Dover Air Force Base, Dover, Delaware (DAFB). DAFB is a National Test Site, and multiple treatment technologies have been evaluated there. The BiRD treatment area is located 160 ft cross-hydraulic gradient to a bioremediation test site performed as a separate effort (Lee, 2002) so that CAH treatment response could be compared. Both field tests were conducted as part of the Air Force Center for Environmental Excellence (Brooks City-Base, San Antonio, Texas) Enhanced In Situ Bioremediation (EISB) Initiative.

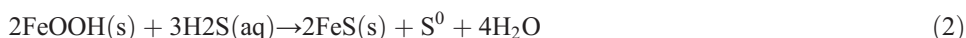
2. BiRD background

BiRD can be divided into three parts: (1) biological sulfate reduction, (2) geochemical mineral formation, and (3) dechlorination. To facilitate the biological phase, a soluble labile organic (e.g.,

lactate) is added to the aquifer with sufficient SO_4^{2-} to facilitate the desired end treatment parameters. These amendments are added to stimulate sulfate-reducing bacteria (SRBs). SRBs are ubiquitous in most subsurface environments so bioaugmentation is normally not required. Oxidation of the organic by SRBs initially produces hydrogen sulfide (H_2S) according to the reaction:



In the geochemical phase, iron sulfide minerals develop in response to geochemical perturbations induced in the preceding biological step. Most sediment contains high concentrations of available Fe^{3+} oxide/hydroxide minerals. Surveys of multiple sites contaminated with fuel oils and/or chlorinated solvents show mineral Fe normally ranging from 1000 to 20,000 mg/kg (Kennedy et al., 1998a,b, 2003, 2004a, 2006). Assuming normal soil densities, a large mass of mineral Fe ranging from 1.6 to 32 kg/m³ normally exists which could be available for geochemical conversion to FeS minerals. Native iron minerals provide a strong chemical sink for H_2S , forming iron sulfide minerals as, for example, with Fe(III) as goethite:



Alternatively, H_2S reaction with Fe(II) as iron hydroxide can be expressed as:



Sulfide reactions with Fe are almost instantaneous. Iron sulfides form as microfine minerals of high surface area. Preexisting iron minerals are converted to iron sulfides so matrix permeability is not affected significantly. With time some FeS may be converted to FeS_2 as:



Microcosm studies were conducted by Kennedy and Everett (2001) to observe the development of mineral iron sulfides in native sandy sediments. Sand was amended with a mixture of fatty acids, for carbon, and sulfate. Organic and sulfate consumption and mineral iron sulfide precipitation was monitored. Concentrations of over 150 and 20 mg/kg of S as FeS and FeS_2 , respectively, developed in just 12 weeks.

The reductive dechlorination step occurs spontaneously and may be expressed, for TCE as:



From laboratory studies with pure minerals, acetylene is the primary end product of CAH dechlorination (Butler and Hayes, 1998, 1999, 2000; Gander et al., 2002; Lee and Batchelor, 2002). However, acetylene may not be useful as an indicator of abiotic dechlorination in live systems as it is labile and certainly transient. The pseudo half-life for reactive CAH compounds can be measured in days to weeks. Many partial oxidation products for Fe and S may be possible.

In contrast to microbial reductive dechlorination, CAH treatment via BiRD is difficult to observe in the field because few, if any, partially dechlorinated daughter products are formed. However, it has been suggested that iron sulfide minerals could be more important than microorganisms under some conditions (e.g., sulfate reducing conditions) in affecting the fate of chlorinated ethylenes (Lee and Batchelor, 2002). Fe and S mineralogical investigations of sites where sulfate reduction is dominant suggest this may be the case (Kennedy et al., 2004b). Finally, the reactions in Eqs. (1)–(5) are straightforward to induce, facilitating BiRD by engineering design.

3. Methods and experimental design

3.1. BiRD field site

The study site at DAFB is known as Target Area 1. Contaminants originated from surface impoundments that received hazardous waste from 1963 to 1984. The plume is approximately 183 m wide and 1158 m long. A monitoring well network was established during the characterization phase, and ground water, monitored for many years, consistently shows significantly elevated concentrations of chlorinated compounds.

As shown in Fig. 1, the BiRD treatment array consisted of five injection wells (ESI1–ESI5) and six monitoring wells (ESM1–ESM6). The injectors were positioned 3 m apart and perpendicular to the prevailing ground water flow direction. Monitoring wells ESM1 through ESM5 were aligned perpendicular to the central injection at distances of 0, 0.9, 2.1, 3.6, and 5.6 m and intended to be down-flow gradient with respect to the prevailing ground water flow direction. ESM6 is located 7.9 m west northwest of the injection system, up-flow gradient relative to the prevailing ground water flow direction.

The injectate was prepared in batches in two 1900 l tanks using ground water pumped from a nearby recovery well (Fig. 1), approximately 21 m from INJ3 and within the contaminant plume. Monitoring well sampling before and after injection was made specifically to demonstrate the affects of injection water on the system. Those analyses show that concentrations fluctuated near the injectors for a few days then returned to near original concentration. A total of 450 kg Epson salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and 318 kg of 60% sodium (L) lactate ($\text{NaC}_3\text{H}_5\text{O}_3$) was injected. Each well received 10,000 l of amended ground water/injectate. The resulting concentrations of SO_4^{2+} and lactate in the injectate were 3500 and 3000 mg/l, respectively. Sulfate and lactate were mixed in a ratio of approximately 1:1.25 according to the following stoichiometry:



It is desirable to fully consume all added sulfate during the biological phase. Therefore, slightly more than the stoichiometric amount of organic was added.

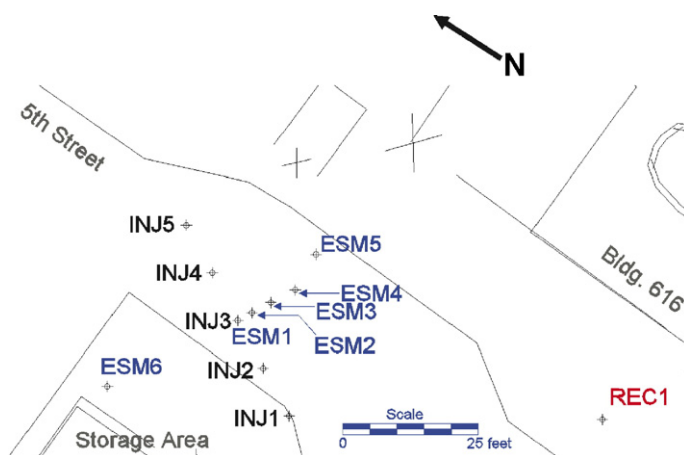


Fig. 1. BiRD injection and monitoring array.

The number and location of injection wells used at a BiRD remediation will depend on site conditions and the goals of treatment. In this case, as the goal was only to demonstrate that BiRD can be engineered, not to treat the entire plume, a short line of injection wells was located within the plume. To allow comparison with the bioremediation test, BiRD injection wells were located at cross-hydraulic gradient. A 3 m separation between wells was deemed to be close enough to allow the zones of influence of the injection wells to overlap, given the volume of injectate introduced to each well. The concentration of SO_4^{2+} and lactate resulting about each injection well should not produce sulfide in excess of the local supply of iron, but should produce enough iron sulfide mineral to destroy any contaminant entering the zone for a sufficiently long time. In the case presented here, the concentrations were more than sufficient, considering the relatively short duration of the test.

The potentiometric surface for the study site is rather flat with ground water flow generally towards the east northeast. Based on water level data collected during the field demonstration, there was a ground water flow reversal during the last third of the test, which influenced observations as described below. The ground water flow reversal is documented in Fig. 2, which is used to present the change in ground water elevation difference between monitoring wells ESM1 and ESM6. The change in flow direction that occurred during the demonstration made data interpretation more complex, but not impossible.

3.2. Sediment analyses

At the BiRD field site, sediment was sampled two times for Fe and S mineral constituents, once before the injection (August 2003) and 8 months after the injection (April 2004). Borings were located at or adjacent to the monitoring wells and were full-hole cored from surface to total depth (0 to 12.2 m). Sediment samples were acquired in intervals between 0.6 and 1.8 m. Cores were inspected and the lithology described. Sediment sampling and analyses methods were used as per Kennedy et al. (2000). Briefly, sediment were acquired anoxically and preserved under N_2 headspace. Total Fe and Fe^{2+} are measured using Hach Methods 8146 and 8147, respectively, adopted from Standard Methods for Water and Wastewater (Eaton et al., 1995). Sulfide is

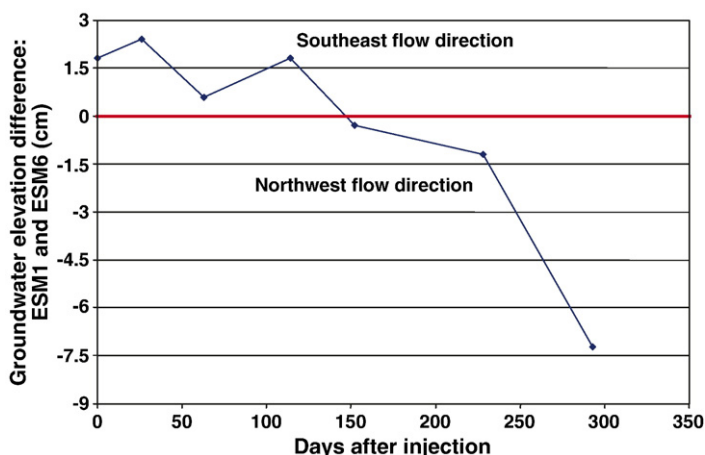


Fig. 2. Ground water flow gradient between ESM6 and ESM1 with respect to time. A positive gradient indicates flow from ESM6 towards ESM1 (the injector) while negative indices indicate the reversal in ground water flow.

measured using Hach Method 8131, which is EPA approved. Mineral sulfides are volatilized from sediment using a sequential extraction process. Initially, the sediment sample is subjected to 6 N HCl for 72 h to extract monosulfides, e.g., FeS. The same sediment is subjected to 1 N Cr^{2+} and 12 N HCl for an additional 72 h to extract sulfides from FeS_2 and S^0 . For both extractions, sulfides are trapped in a zinc acetate solution and analyzed using Hach Method 8131. The 6 N acid solution from the first extraction is analyzed for Fe(II) and Fe Total to measure bulk Fe in the sediment. Bulk iron is the total amount of Fe(II) and Fe(III) found on sediment particles. Bulk Fe (III) is determined by subtracting Fe(II) from Fe Total. Some forms of iron, e.g., magnetite, are resistant to extraction by 6 N HCl. If the presence of resistant iron minerals is suspected, and a complete iron extraction required, a stronger extractant can be used, e.g., 12 N HCl. Sediment analyses were performed at Rowan University, Glassboro, NJ.

3.3. Aqueous sampling

Water from monitoring wells was sampled before and immediately after injection, then periodically (approximately each month). Water samples were collected from all monitoring wells for laboratory analyses of PCE, TCE, cDCE, and VC using gas chromatography (EPA Method 8021), and total organic carbon (TOC) and SO_4^{2-} using a TOC analyzer (EPA Method 415) and ion chromatograph (EPA Method 300), respectively. Chlorinated compound analyses were performed by the Dover National Test Site Research Laboratory, Dover AFB, Dover, DE. TOC and Sulfate analyses were performed at Rowan University, Glassboro, NJ.

3.4. Microcosm methods

Sediment samples from the BiRD field site were obtained for microcosm testing 8 months after the injection treatment. Samples were acquired next to ESM1 from a depth of 11.6 to 12.2 m in a sand layer which had visible darkening (an indication of FeS minerals). Upon retrieval, the core was immediately placed into a field portable anaerobic glove bag which had been quadruple purged with ultrapure N_2 gas. Approximately 10 g sediment was placed into serum tubes filling them to approximately 3/4 the bottle volume. Each bottle was sealed with a rubber stopper secured with an aluminum seal. The bottles were then removed from the glove bag, triple vacuum purged, and refilled with N_2 gas in the field. Half the bottles were sterilized by irradiation to kill any chlororespiring bacteria which may have been present. Irradiation was selected as the sterilization technique as it does not adversely affect FeS mineral reactivity as, perhaps, autoclaving or chemical bactericides. Each bottle was then filled with 2500 $\mu\text{g/l}$ TCE in deoxygenated deionized water. Water in the microcosm had <0.1 mg/l organic carbon, removing any carbon source and further inhibiting bioremediation from occurring. Sample bottles from both the killed and live systems were sacrificed in duplicate and periodically analyzed for TCE, cDCE, and VC using gas chromatography.

3.5. Bioremediation field cell

The bioremediation treatment cell was a separate effort and is reported here as a standard for comparison with BiRD Field Cell (Lee, 2002). Bioremediation was stimulated using edible vegetable oil (VegOil) as an organic substrate. The treatment cell is located approximately 49 m south of the BiRD test site and is laterally positioned with respect to ground water flow. Similar injection and monitoring arrays were used for both the bioremediation and BiRD test sites. The

bioremediation treatment array consisted of four injectors on 1.5 m spacing and a series of ground water monitoring wells ranging from 0.6 to 4.3 m down-flow gradient. A total of 830 l of soybean oil, 83 l of lecithin (an emulsifier), and 30,300 gal of ground water were injected.

4. Results

In this section results from the BiRD field site are presented first. This is followed by results from the microcosm test on sediment from the BiRD field site. Finally, results from the BiRD field site are compared with results from the nearby bioremediation study.

4.1. Lithology

Sediment lithology, and by extension its hydraulic characteristics, affected the distribution and migration of injectate and subsequent treatment. The mineral concentration profiles that follow are superimposed onto a lithology cross-section. The sedimentary sequence includes fine silts grading to sands with underlying gravel to approximately 12.2 m. That sand sequence rests on a low conductivity clay confining layer. As shown below, injectate moved preferentially through conductive sand and gravel layers underlain by clay.

Prior to injection, sediment was orange or yellow brown in color at the level where wells were screened. This color indicated abundant iron oxide mineral coating on grains of quartz sand or gravel. Post injection, there was a distinct change in sediment color which became medium to dark gray, indicating the presence of black colored mineral iron sulfides. This was confirmed by laboratory analysis.

4.2. Mineral iron

Figs. 3–5 show results from sediment analyses along the line of the monitoring wells. Fig. 3 shows a concentration profile of total mineral iron (Fe(II) + Fe(III)) through the monitoring wells, as measured before the injection. Variations in total iron are the result of historical events at the site, from the deposition of sediment to the sampling event. The results indicate that Fe was naturally leached from sediment above approximately 3.4 m (gleying) resulting in lower concentrations (250 and 2000 mg/kg, respectively). Below the leached boundary, iron concentrations are higher, ranging from 2000 to 21,000 mg/kg. Concentrations of iron were adequate for FeS development. Sulfate reduction is not normally a prominent microbial respiration pathway at this site as ground water has less than 25 mg/l sulfate. Prior to injection the sediment had no measurable concentrations of mineral FeS or FeS₂.

Post injection FeS and FeS₂ concentrations are shown through the monitoring well profile in Figs. 4 and 5, respectively. FeS concentrations increased significantly after injection in all borings, attaining a maximum of 112 mg/kg at ESM2. FeS₂ distribution mirrors that of FeS in profile but extends slightly higher in the sediment section with slightly higher concentrations (maximum = 174 mg/kg at ESM2). The distribution of iron sulfide minerals follows local flow pathways that dictated injectate distribution and conformed to conductive sand/gravel layers immediately above clay layers. As with any treatment technology relying on injection, it was not possible to generate iron sulfide minerals throughout the entire injection interval, as defined by the injection well screens. Because the plume has been present for a year, contaminants have penetrated beyond local flow pathways. Therefore, contact between the generated iron sulfide minerals and with entire plume is not possible. However, as the majority of the contaminants

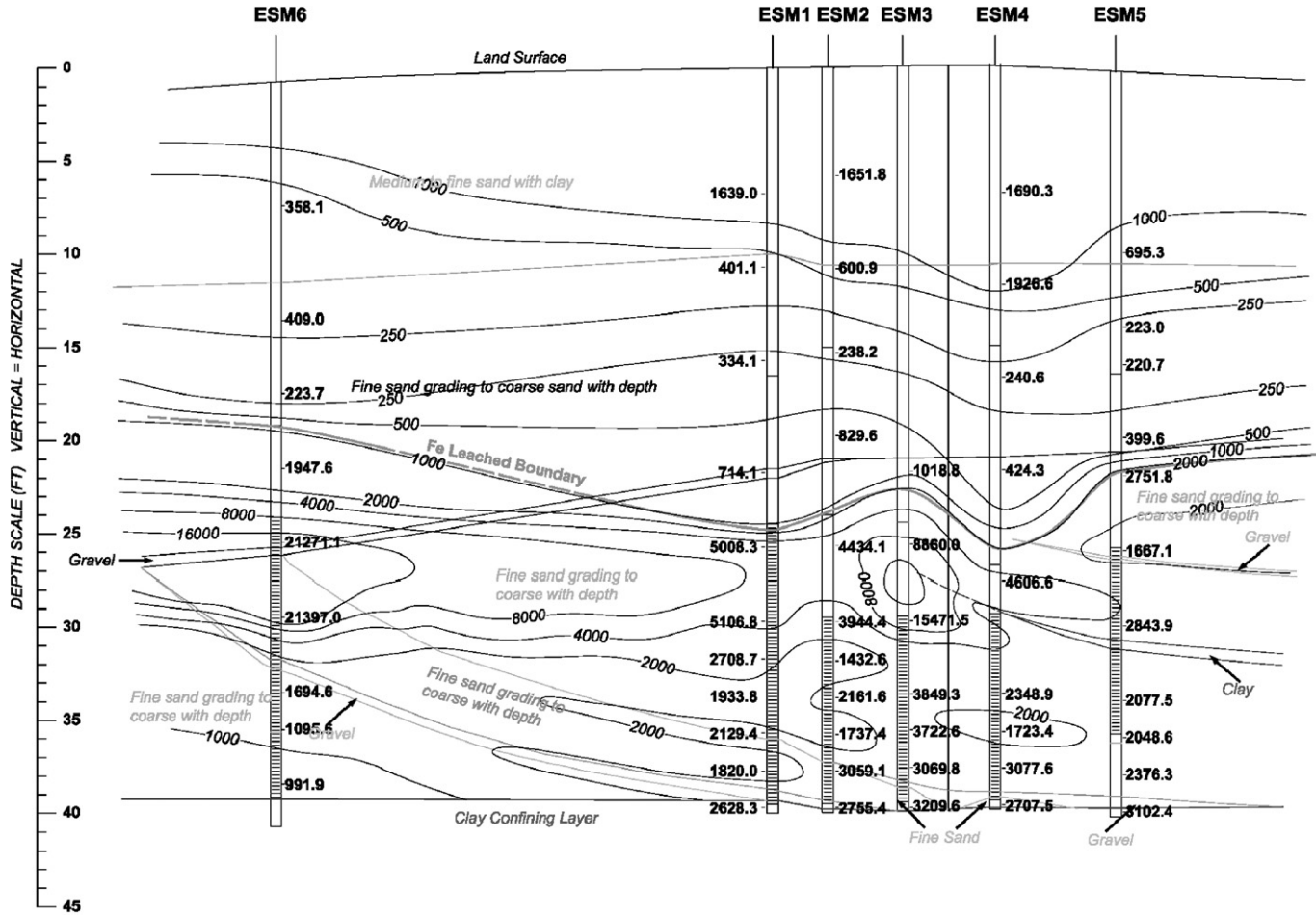


Fig. 3. Total iron, mg/kg (sediment collected before injection).

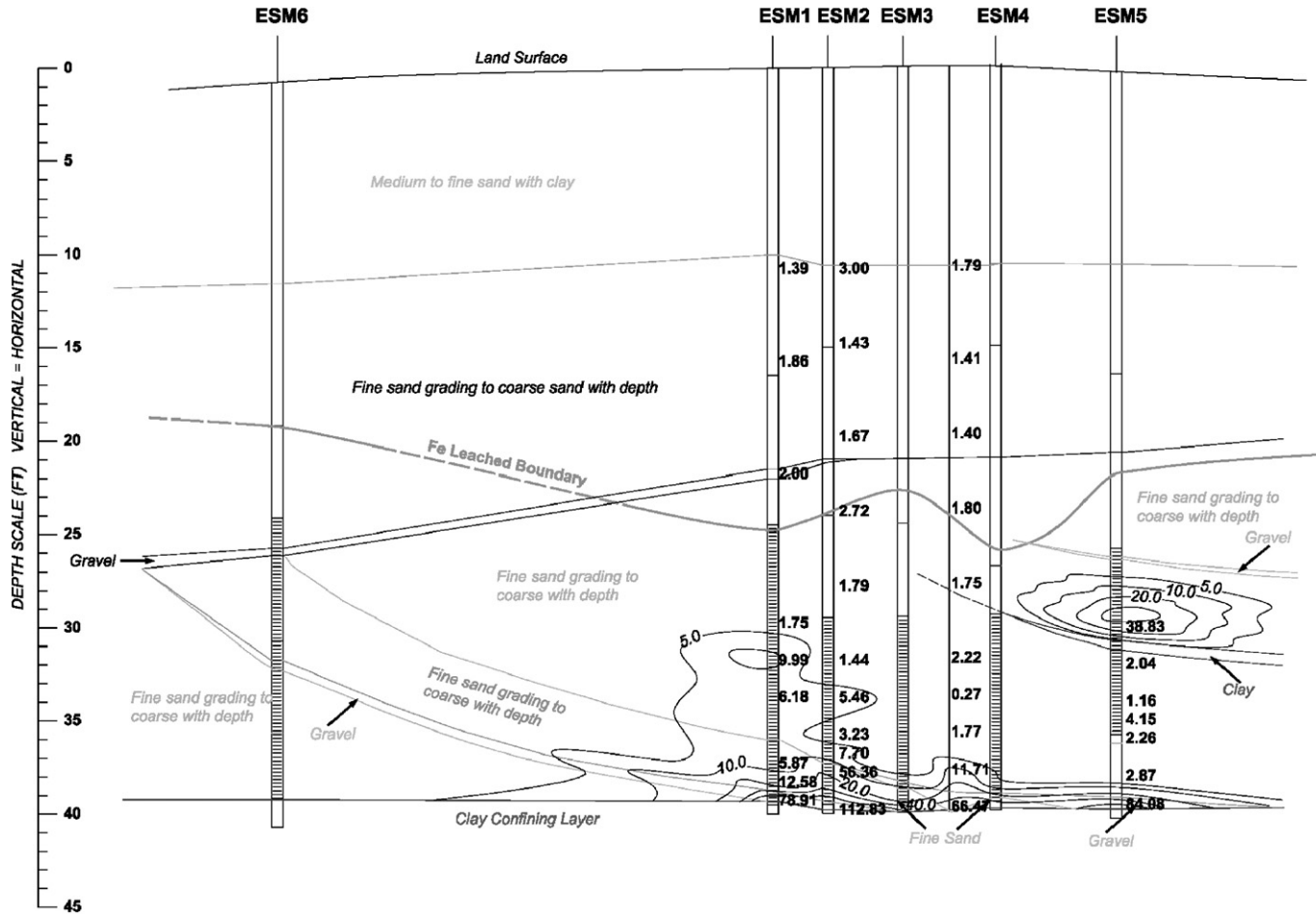


Fig. 4. FeS, mg/kg (sediment collected 9 months after injection).

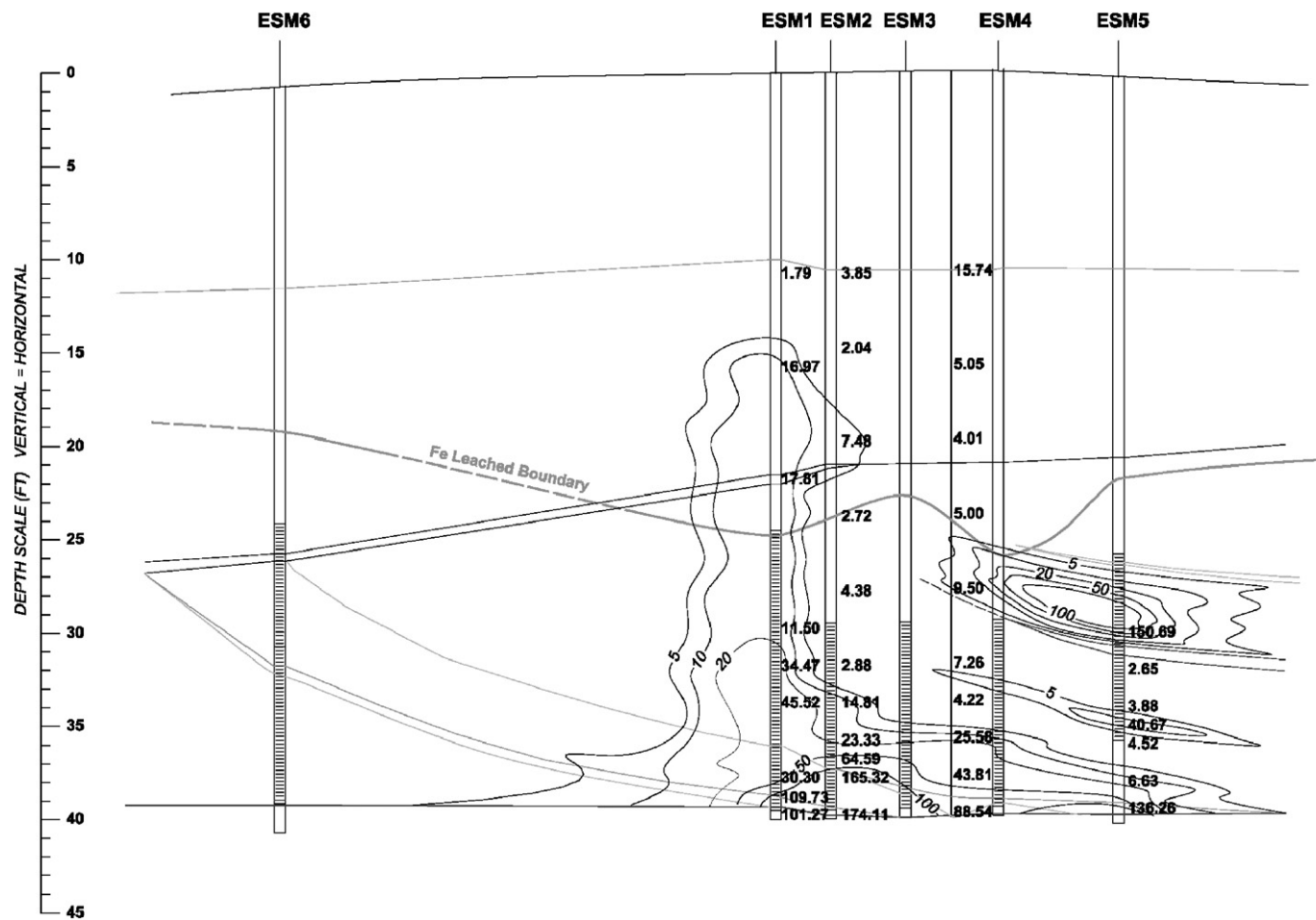


Fig. 5. FeS₂, mg/kg (sediment collected 9 months after injection).

move through these local flow pathways, a large portion of the contaminants can be treated; thus, the treatment can be effective.

Most FeS was found about 12.2 m below the ground surface, near the base of the sand and top of the lower clay confining layer. However, FeS was found much higher at ESM5, at about 9.1 m, in an isolated conductive sand channel bound by an underlying clay lens. This channel sand is evidently oblique to the monitoring well array, essentially connecting ESM5 to the injectors. Evidently, injectate was preferentially conducted to ESM5 via this upper channel sand layer resulting in more FeS development and faster treatment at this well compared to monitoring wells that were closer to the injectors but less hydraulically connected.

4.3. Aqueous observations

Concentrations with respect to time for ESM1 to ESM6 are shown in Figs. 6–11. Post injection, concentrations of both SO_4^{2-} and TOC declined rapidly near the injectors (ESM1 and ESM2) due to biological consumption and advection. Small transient quantities of injectate were observed over time in the intermediate monitoring wells. Little SO_4^{2-} or TOC was observed at ESM5.

Contaminated ground water from the site was used for the injectate so CAH concentrations were little perturbed by actual injection. CAH removal began to occur rapidly after injection, especially in the most up-gradient observation points (ESM1 and ESM2) and in the most down-gradient monitoring point, ESM5. Treatment for the intermediate observation points (ESM3 and ESM4) was slightly delayed. Treatment response was influenced by hydraulic heterogeneities in the aquifer media. All wells ultimately responded favorably with marked decreases in both TCE and DCE. VC was not generated. Concentrations of PCE for the observations wells are plotted separately (Fig. 12). Most of the monitoring wells showed decreases in PCE, averaging approximately 120 $\mu\text{g/l}$ before injection and 20 $\mu\text{g/l}$ during the final monitoring event.

ESM6 was designed to monitor up-gradient background conditions. CAH concentrations were generally stable at ESM6 during the early part of the demonstration, when ground water flow was towards the east and CAH was decreasing in ESM1 to ESM5. However, when the ground water flow direction reversed, both TCE and DCE concentrations decreased rapidly at ESM6 as well. Small quantities of sulfate were also observed late in the test for this well further indicating the reversal in ground water flow direction.

The largest decline in CAH concentrations were observed in ESM5 which is logical as the treatment time through the reaction front increases with distance down-flow gradient. At this point, TCE was reduced to 6% of its original concentration and DCE was treated to 3% of its original concentration. Maximum treatment was achieved 228 days after injection. At the end of the test, CAH concentrations increased slightly at ESM5 due to the ground water flow reversal.

4.4. Microcosm results

Sediment used for microcosm construction was determined to have 59 mg/kg FeS and 134 mg/kg FeS_2 and was characteristically dark gray in color when obtained. Concentrations of TCE with respect to time for the live and killed microcosms are shown in Fig. 13. TCE was removed from both the live and killed systems at the same rate demonstrating that abiotic processes dominate treatment. Overall, TCE was treated to approximately 17% of its original concentration during 76 days with an apparent half-life of approximately 30 days. DCE was mostly not detectable; however, transient concentrations up to 0.17 mg/l were occasionally observed. VC was not generated.

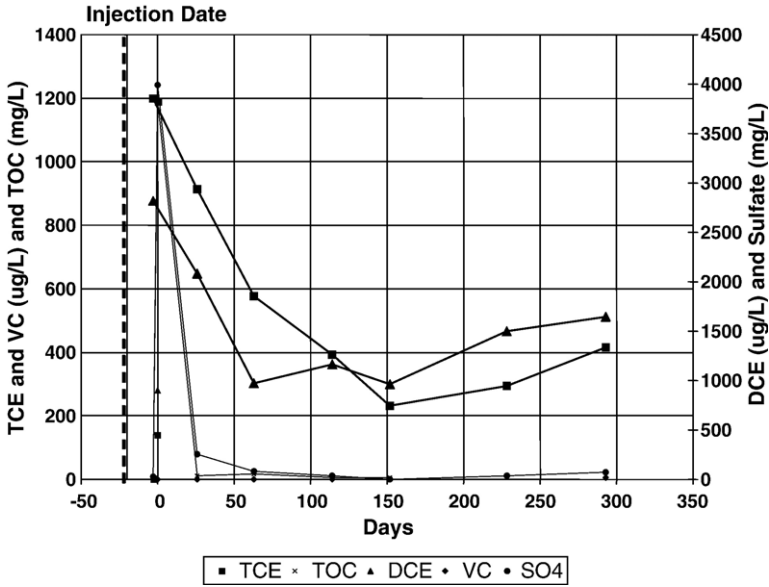


Fig. 6. ESM1 aqueous CAH and injectate concentrations with respect to time.

4.5. Comparison with VegOil bioremediation

Comparisons were made between the VegOil bioremediation and BiRD test cells at DAFB for the most up-gradient and down-gradient observation points for both systems. VegOil bioremediation resulted in significant decreases in TCE; however, there were also equivalent

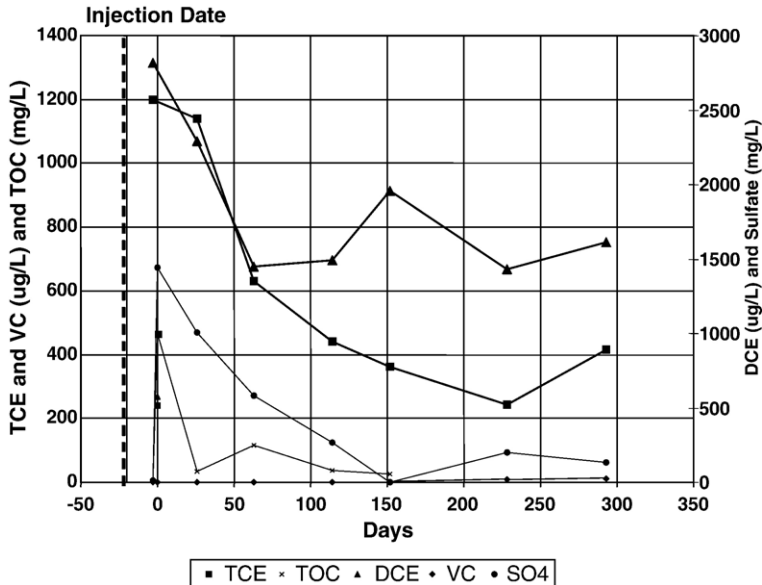


Fig. 7. ESM2 aqueous CAH and injectate concentrations with respect to time.

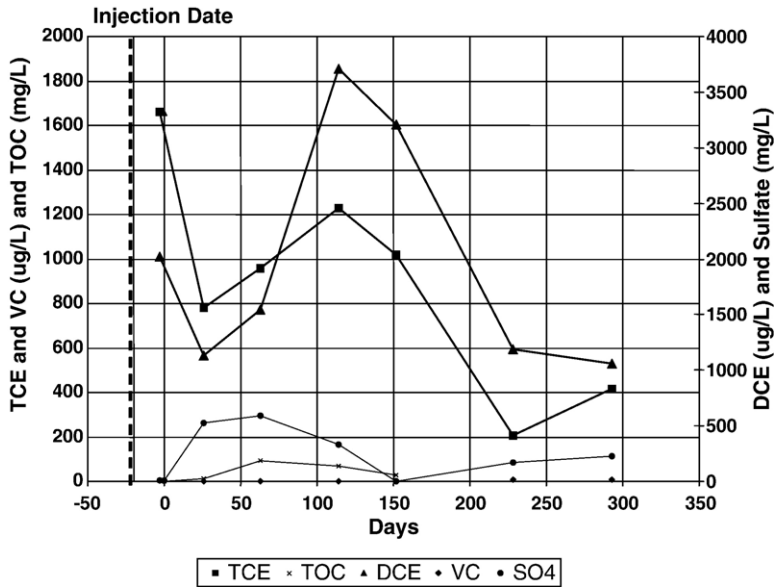


Fig. 8. ESM3 aqueous CAH and injectate concentrations with respect to time.

increases in daughter products, principally cDCE and to a lesser extent VC. Initial concentrations of TCE and cDCE for ESM1 and ESM5 (BiRD) and comparably positioned wells in the VegOil bioremediation test cell were normalized to 1.0 to permit direct comparison (Figs. 14 and 15). As shown, both BiRD and VegOil bioremediation resulted in TCE reduction; however, significant

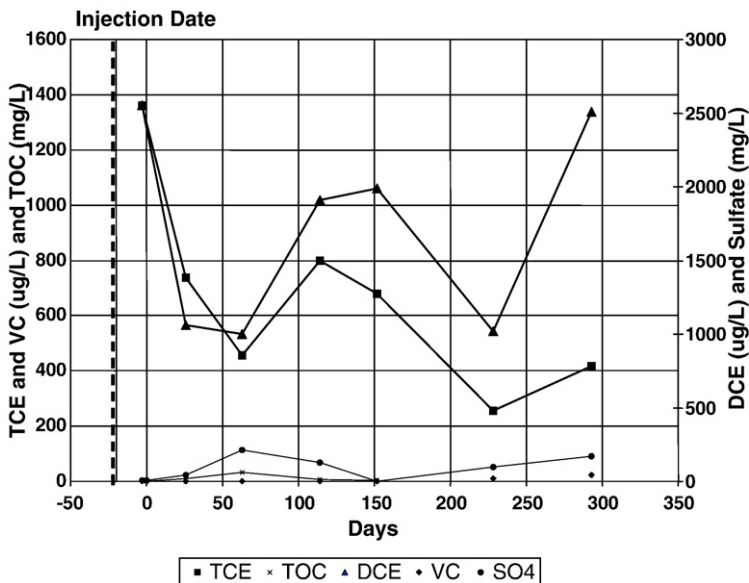


Fig. 9. ESM4 aqueous CAH and injectate concentrations with respect to time.

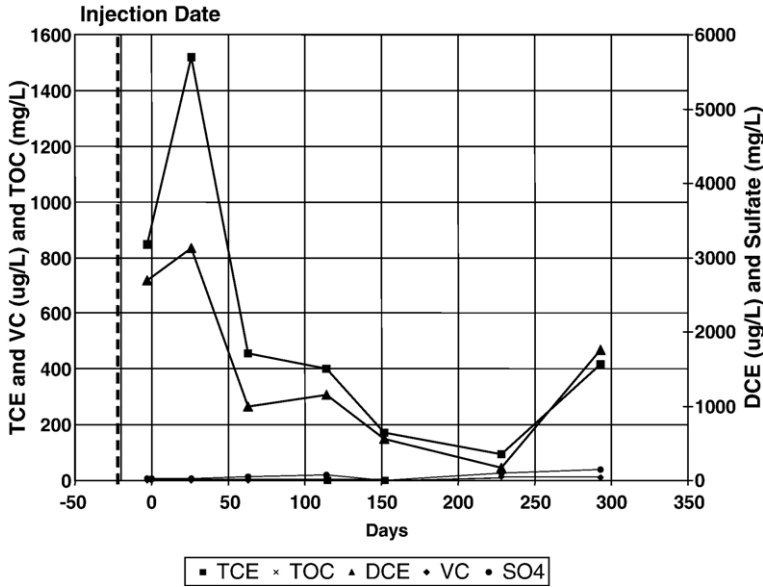


Fig. 10. ESM5 aqueous CAH and injectate concentrations with respect to time.

differences between the remediation plots were observed with respect to cDCE. For the bioremediation plot, cDCE experienced a two-fold increase but for the BiRD plot DCE was not produced and pre-existing cDCE was reduced up to 97%. However, more monitoring should be conducted to determine the longevity of both remediation methods.

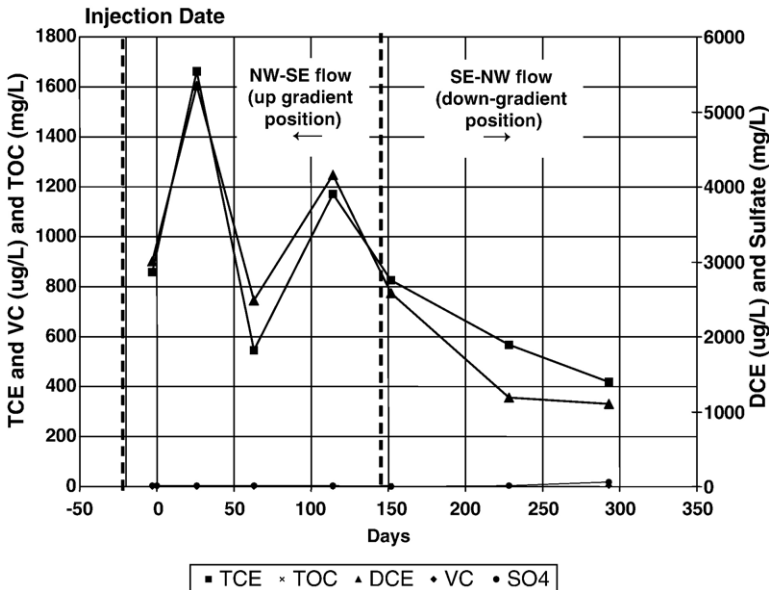


Fig. 11. ESM6 aqueous CAH and injectate concentrations with respect to time.

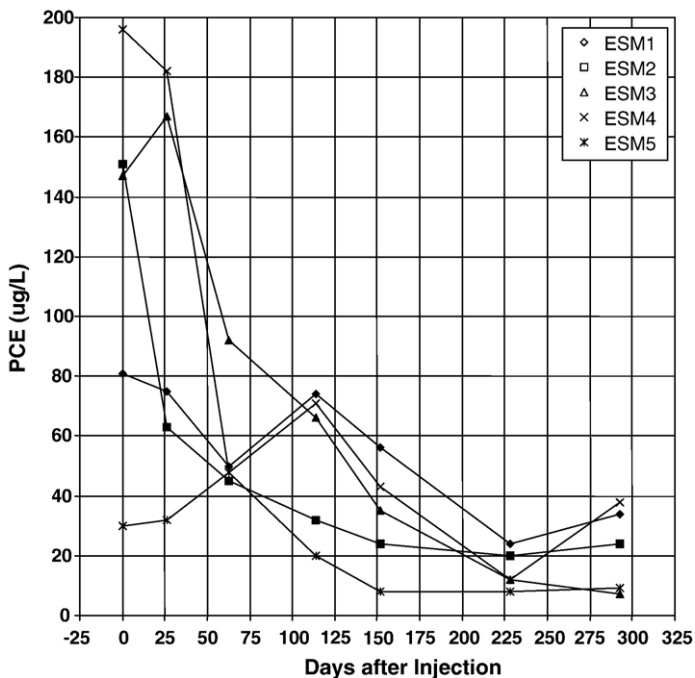


Fig. 12. PCE concentrations for monitoring wells ESM1 and ESM5.

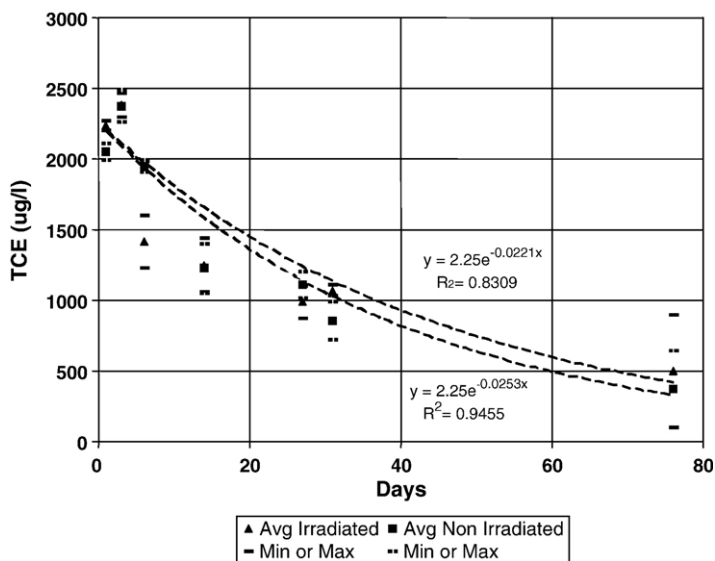


Fig. 13. TCE concentrations for the live and killed microcosms. Dashes are maximum and minimum values. Triangles and squares are average of three values.

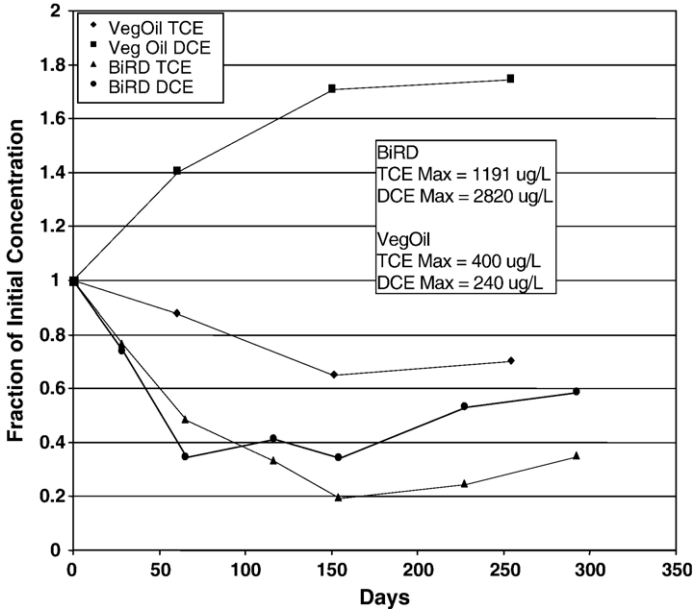


Fig. 14. TCE and DCE concentrations for the BiRD and bioremediation sites for monitoring points closest to injection. Initial values normalized to 1.0.

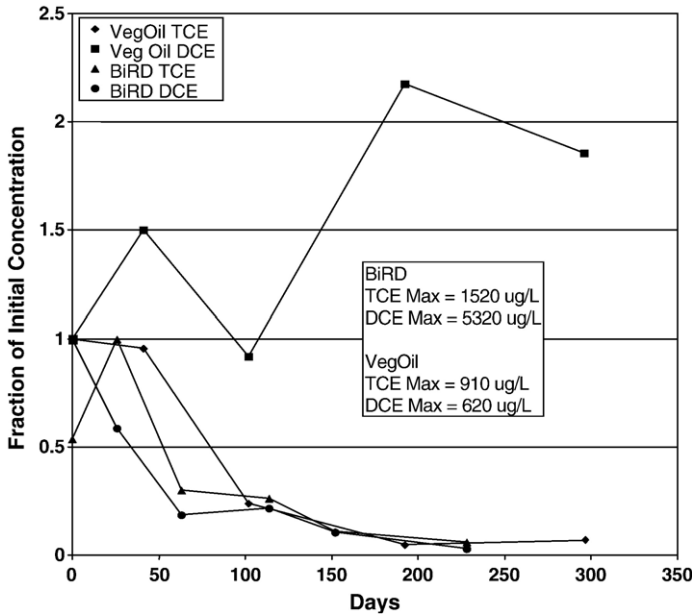


Fig. 15. Comparison of TCE and DCE concentrations for BiRD and bioremediation sites for most down-gradient monitoring points. Initial values normalized to 1.0.

5. Conclusions

Biogeochemical Reductive Dechlorination (BiRD) was successfully tested at the Target Area 1 site at DAFB. DAFB was a good test site as the ground water had very low naturally occurring concentrations of SO_4^{2-} and bioremediation had been tested nearby. Therefore, as BiRD would not have occurred naturally at the DAFB site, a direct comparison between biostimulation and BiRD could be made.

The native sediment contained, as is typical, adequate quantities of native iron for mineral iron sulfide formation. Biogeochemical stimulation required the addition of both organic and sulfate which resulted in the generation of significant quantities of FeS and FeS_2 via biogeochemical processes. This demonstrates that the in-situ formation of iron sulfides can be stimulated by design. The treatment was simple to apply and, compared to the VegOil bioremediation plot, required only the addition of a soluble organic (sodium (L) lactate) and a common sulfate salt (magnesium sulfate, also known as Epsom salt) which is used as a cattle feed additive and soil amendment.

CAH treatment response was observed within a few weeks of injection indicating a very short lag period. PCE, TCE, and DCE concentrations were all reduced and VC was not generated. The generated iron sulfides apparently formed a flow-through reactive treatment zone. Therefore, maximum treatment generally occurred at the most down-gradient observation point (ESM5) where the original concentrations of TCE (1520 $\mu\text{g/l}$) and DCE (5320 $\mu\text{g/l}$) were reduced by 95% or more. The microcosm tests performed using FeS bearing sediment from the site demonstrated that abiotic processes were responsible for TCE treatment. The observed TCE half-life was approximately 30 days which is acceptably rapid. It should be noted that although encouraging results were observed, the test was quite limited both in aerial extent and in the quantity of injectate added. More conclusive results may have been achieved by monitoring the site for a longer period of time or by developing a larger treatment area with higher concentrations or volume of injectate. TCE was also treated in the bioremediation test plot but equivalent concentrations of persistent cDCE, with lesser amount of VC, daughter products were generated.

It is likely that iron sulfides reduce CAH at many sites where sulfate and organics occur naturally or as a result of human impact; however, BiRD has been overlooked because (a) investigators were not looking for it and (b) no distinct daughter products are generated. This demonstration project indicates that BiRD can be stimulated in aquifers that lack necessary organic and/or sulfate. These may be added by injection in soluble form, the method employed in the project described in this paper, or by placement in permeable reactive trench as solids. Future research should explore the use of permeable reactive trenches.

There are several theoretical advantages related to stimulating BiRD for the purpose of destroying contaminants. Sulfate-reducing bacteria are ubiquitous in the subsurface and are easy to stimulate. The necessary amendments for BiRD are readily available and inexpensive. The problems associated with subsurface mixing are diminished as highly soluble injectates are used, and native sediment is essentially transformed into a permeable reactive zone. Finally, CAH treatment via BiRD may be more complete with few daughter products. BiRD may be a viable and economic alternative method for chlorinated solvent remediation combining the beneficial attributes of bioremediation and chemical treatment. Further demonstrations are needed, of longer duration and treating larger aquifer volumes.

It is unlikely that BiRD could be used to completely remove a contaminant source. Thus, other technologies should be used to remove the source. BiRD can be used to disconnect a source from its plume, by creating a treatment zone in the up-gradient portion of the plume. Of course, this

would only be needed if the source cannot be removed. BiRD can also be used to stop down-gradient movement of plume, by creating a treatment zone in the down-gradient portion of the plume. Finally, BiRD can be used to treat any portion of a plume, by locating injection wells appropriately. However, long-term maintenance of any treatment zone will require periodic reinjection if the outer layer of iron sulfide minerals, the layer most in contact with contaminants, become oxidized over time. Reinjection will convert the oxidized outer layer once again to iron sulfide minerals.

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PILOTS TO ENHANCE TRICHLOROETHENE REDUCTIVE DECHLORINATION AND FERROUS SULFIDE ABIOTIC TRANSFORMATION

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ABSTRACT: Two field pilots are being conducted at Altus Air Force Base (AFB), Oklahoma in areas with high levels of sulfate and iron. An edible oil emulsion was injected into these pilots to promote biological reductive dechlorination of trichloroethene (TCE) and to stimulate ferric sulfide and ferric disulfide production and the abiotic reaction with TCE. Within the injection zone of the larger SS-17 pilot, TCE declined from 9.9 μM to $<0.043 \mu\text{M}$ after 13 months with decreases in cis-1,2-dichloroethene (cDCE) [26%] and sulfate (99%), and increases in vinyl chloride (VC) to 0.75 μM and methane to 16.3 mg/L. In a well 7.6 m downgradient, TCE declined from 12.6 μM to $<0.043 \mu\text{M}$ with decreases in cDCE (92%), and sulfate (42% to 247 mg/L). Increases in VC to 28 μM , ethene to 18.2 μM , and methane to 15.2 mg/L were observed at 13 months in this well. Although ferric sulfide and ferric disulfide were produced in the treatment zone by microbial activity, acetylene (an abiotic reaction product from ferric sulfide and ferric disulfide) was not detected at appreciable concentrations. Biological reductive dechlorination processes appeared to predominate in this area. A second smaller pilot was conducted in the OU1 plume with 1,700 mg/L of sulfate, but with no evidence for the presence of dechlorinators. In one injection well, TCE decreased from 43 μM to 0.33 μM after 13 months, cDCE increased to 7.1 μM , and little VC was detected. Both ethene and ethane were detected at high concentrations after 5 months, but then declined to trace levels at 13 months. Although acetylene was not detected, the abiotic pathway for TCE removal appeared to be favored because of the low levels of cDCE and VC that were produced. The results from these field pilots demonstrate that dechlorination of TCE can be stimulated by biological and abiotic process in areas with high sulfate and iron levels.

INTRODUCTION: Biological reductive dechlorination of TCE to cDCE, VC, and ethene or ethane has been demonstrated at a number of sites (Ellis et al. 2000, Lee et al. 1998). The activity of dehalorespiring organisms such as *Dehalococcoides ethenogenes* is promoted by the addition of an electron donor to generate anaerobic conditions and provide electrons for the reductive dechlorination process (Maymo²-Gattell et al. 1999). *Dehalococcoides ethenogenes* have been found at many sites where ethene was detected (Hendrickson et al. 2002). However, it was not found at sites where cDCE was the final degradation product. The dehalorespirers typically operate under methanogenic conditions and are inhibited by high levels of sulfate (Harkness et al. 1999). In contrast, Drzyga et al. (2002) conducted column studies under sulfate-reducing conditions fed

methanol, lactate, and sulfate. Ethene and ethane were detected in each column effluent along with sulfate levels in excess of 200 mg/L.

When a biodegradable organic substrate is present in an aquifer with ferric iron and sulfate, sulfate and iron reduction occurs (Kennedy and Everett 2001). Bacteria generate several forms of ferrous sulfide including amorphous iron sulfide, mackinawite ($\text{Fe}_{0.995-1.023}\text{S}$), greigite (Fe_3S_4), and pyrrhotite ($\text{FeS}_{1.1}$). Upon further reaction with elemental sulfur, pyrite (FeS_2) can be formed.

Butler and Hayes (2000 and 2001) have demonstrated that ferric sulfides and ferric disulfides such as mackinawite and pyrite can promote the abiotic dechlorination of TCE. In one lab study with 10 g/L freshly synthesized mackinawite, TCE was transformed to 11% cDCE, 76% acetylene, and 12% residual TCE at pH 7.3 with an observed half-life of 1,690 days. Lee and Batchelor (2002) reported a transformation rate of 1.59 day^{-1} for TCE with pyrite yielding 3.3% cDCE, 43 % acetylene, 2.2% ethene, and 50% TCE after 32 days. VC was not produced from TCE, but was generated when cDCE was treated with pyrite. Gander et al. (2002) reported enhanced degradation of 1,1,1-trichloroethane in a system containing ferric sulfide and a methanogenic culture over that achieved by the ferric sulfide or methanogenic culture alone.

Two pilots were initiated at Altus AFB to evaluate the potential for an emulsion of soybean oil to promote reductive dechlorination and abiotic transformation of the TCE found in the groundwater. The edible oil substrate or EOSTM was developed as inexpensive, long-lasting carbon source that can be easily distributed from the point of injection (Borden and Lee 2002).

SITE DESCRIPTION: Historical solvent releases of degreasing agents at Altus AFB resulted in a 1,520 m-long chlorinated solvent plume with TCE concentrations reaching 78,000 $\mu\text{g/L}$ in the source area. The geology at the site consists of reddish-brown, moderately plastic, sandy clay to a depth of roughly 4.6 m, underlain by fractured clayey shale with occasional gypsum layers. The depth to ground water is 2.4-3.1 m below ground surface (bgs). Most ground-water flow and contaminant transport appears to occur through a series of weathered shale fractures located immediately beneath the surficial clay and within a thick gypsum layer approximately 10.7 m below grade. The soil and groundwater contain high levels of ferrous iron and sulfate.

SS-17 PILOT: Groundwater at the SS-17 site was impacted by TCE and a fuel release which had led to the development of a microbial population capable of partial dechlorination of TCE to cDCE, trans-1,2-dichloroethene (tDCE), VC, ethene, and ethane, and removal of some of the sulfate. Sulfate levels prior to the addition of the emulsified substrate ranged from 107 to 2,000 mg/L with lower levels in wells impacted by the fuel release.

An emulsion of soybean oil, surfactant, yeast extract, and lactate was prepared and injected into six injection wells spaced 1.5 m apart in a barrier configuration to intercept the groundwater plume at the SS-17 site approximately 76 m downgradient from the source area (Figure 1). The wells were screened from 2.4 to 5.5 m below ground surface to achieve maximum distribution of the treatment mixture in the upper weathered fracture zone.

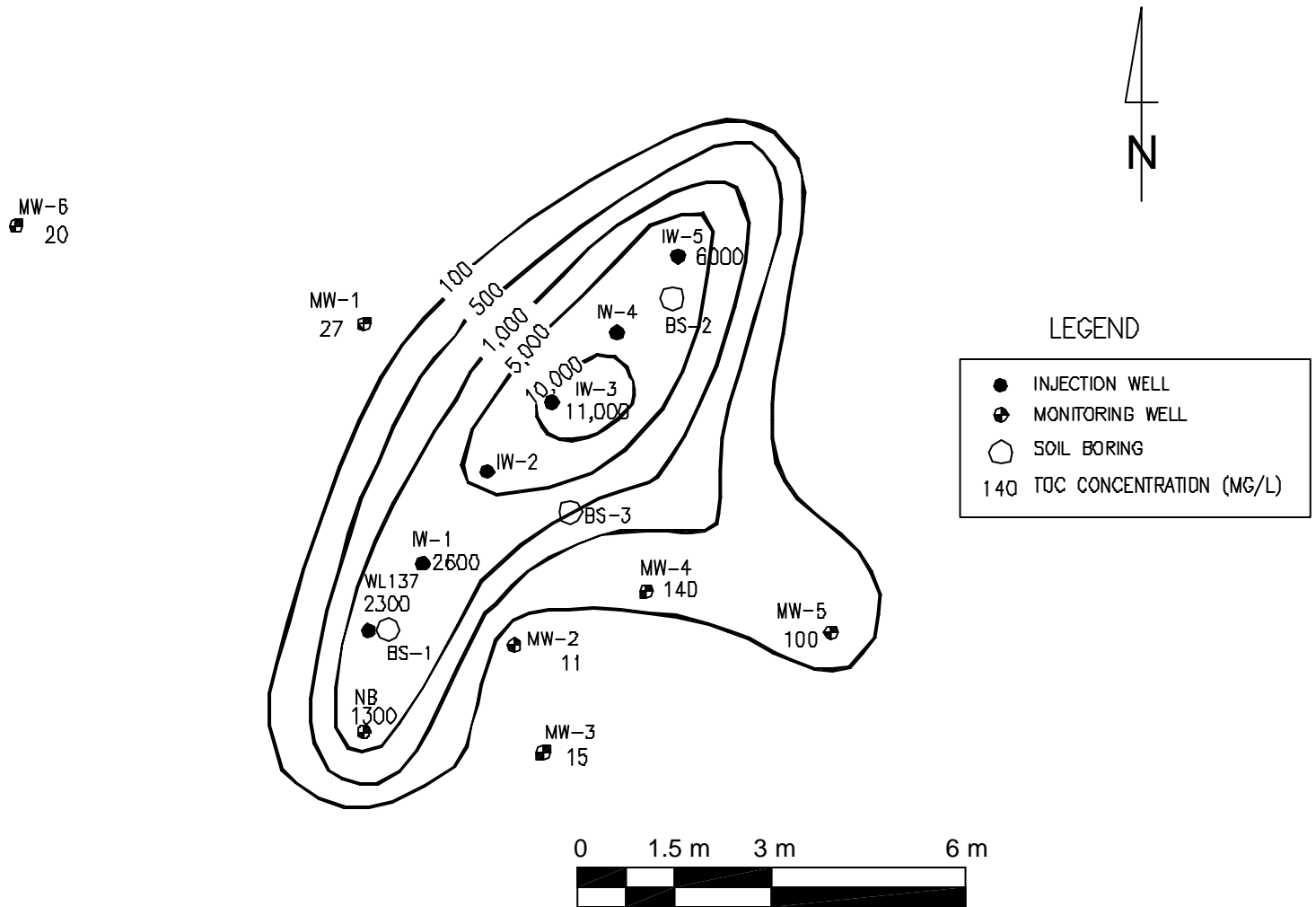


FIGURE 1. SS-17 test plot and TOC distribution (mg/L) on 4/2/02.

Table 1. Volatile contaminants, sulfate, methane, and TOC for SS-17 pilot wells IW-3 and MW-5

IW-3	Units	11/14/01	12/18/01	4/24/02	7/31/02	1/16/03
Ethene	μM	<0.046	<0.046	0.43	1.9	<0.046
Ethane	μM	<0.043	0.43	0.83	5.3	<0.043
Acetylene	μM	<0.046	<0.046	<0.046	<0.046	<0.046
VC	μM	<0.090	<0.090	0.12	0.77	0.75
cDCE	μM	1.0	<0.058	0.096	1.6	0.76
tDCE	μM	0.25	<0.058	<0.058	0.15	<0.056
TCE	μM	9.9	0.43	0.26	0.75	<0.043
Total CE	μM	11.2	0.86	1.7	10.4	1.5
Sulfate	mg/L	1623		100		1.6
Methane	mg/L	0.24	0.023	0.83	7.5	16.3
TOC	mg/L	5.1	33000	11000	7300	2900

MW-5	Units	11/15/01	12/17/01	4/23/02	7/30/02	1/17/03
Ethene	μM	0.25	0.43	3.9	3.3	18.2
Ethane	μM	0.083	0.37	0.14	0.11	0.070
Acetylene	μM	<0.046	<0.046	<0.046	<0.046	<0.046
VC	μM	7.0	13.3	12.6	19.0	28.3
cDCE	μM	9.3	10.8	0.071	1.0	0.75
tDCE	μM	0.46	0.25	<0.058	0.42	0.14
TCE	μM	12.6	4.0	<0.043	0.15	<0.043
Total CE	μM	29.8	29.2	16.8	24.0	47.5
Sulfate	mg/L	424		558	103	247
Methane	mg/L	1.5	5.4	3.4	4.5	15.2
TOC	mg/L	5.5	2200	100	74	15

Monitoring of adjoining wells during the injection process showed that EOSTM reached monitoring well MW-5 located 7.6 m from the injection wells, but several closer wells in less permeable zones received little substrate as measured by Total Organic Carbon or TOC (Figure 1). TOC levels four months after EOSTM injection ranged from 11 to 11,000 mg/L. In injection well IW-3, TCE concentrations dropped immediately after injection due to sorption to the oil (Table 1). However by August 2002 (7.5 months after injection), total ethenes (molar concentration) in this well had recovered to over 90% of the pre-injection concentration indicating that sorption to the oil was no longer significant. After 13 months, TCE declined from 9.9 μM to <0.043 μM with decreases in cDCE (26%) and sulfate (99%), and increases in vinyl chloride (VC) to 0.75 μM and methane to 16.3 mg/L. In well MW-5, 7.6 m downgradient, TCE declined from 12.6 μM to <0.043 μM after 13 months with decreases in cDCE (92%), and sulfate (42% to 247 mg/L). Increases in VC to 28 μM, ethene to 18.2 μM, and methane to 15.2 mg/L were observed after 13 months. Acetylene (an abiotic reaction product from ferric sulfide and ferric disulfide) was not detected.

Biological reductive dechlorination processes resulting in the production of VC, ethene, and ethane appeared to predominate in the SS-17 area in zones impacted by the injection of the edible oil substrate. In addition to biological mechanisms, the contribution of abiotic transformation mechanisms was evaluated. Samples were taken from three cores near the injection zone (BS-1, BS-2, and BS-3 on Figure 1) with a fourth core from a background location. Samples were analyzed for bioavailable ferrous iron (Fe^{II}), bioavailable total iron, completely extracted ferrous iron, completely extracted total iron, sulfide from ferrous sulfide, and sulfide from ferrous disulfide (Kennedy and Everett 2001). The bioavailable ferrous and total iron were extracted with a mild acid, 0.5 N HCl. Completely extracted ferrous and total iron were extracted with 6N HCl.

Table 2 shows the results on analysis of soil samples collected from six different depths in three soil cores installed within the SS-17 pilot barrier and one background location in July 2002, approximately eight months after injection of the edible oil substrate. Samples collected from below 2.4 m below ground surface were in the saturated zone. Bioavailable ferrous and completely extracted ferrous iron were elevated beneath the water table in the three borings near the injection wells compared to the background locations and the shallow samples which were not impacted by the emulsion injection. While some samples from the beneath the water table in the injection zone showed elevated bioavailable and completely extracted total iron, there was no clear pattern. Both forms of sulfide (FeS and FeS_2) were elevated in the saturated zone and were generally higher than those seen in the background location. The vegetable oil has stimulated both iron and sulfate reduction and the production of ferric sulfide and ferric disulfide.

TABLE 2. Bioavailable and total extractable iron and sulfide with depth for cores from SS-17 Pilot in July 2002.

Well	Depth (m)	6N Fe II (mg/Kg)	6N Fe T (mg/Kg)	S-FeS (mg/Kg)	S-FeS ₂ (mg/Kg)	0.5 N Fe II (mg/Kg)	0.5N Fe T (mg/Kg)
BS1	0.8	364	19735	0.00	2.24	15	3095
BS1	1.5	265	20359	0.47	1.01	60	2738
BS1	2.4	562	21168	0.97	48.11	941	2917
BS1	3.0	392	23504	15.94	54.84	950	2935
BS1	3.8	987	41492	9.72	38.56	1044	3806
BS1	4.6	1253	29044	1.51	19.39	424	5796
BS2	0.8	282	18315	0.28	0.78	167	3607
BS2	1.5	295	28469	0.21	1.28	79	4849
BS2	2.3	512	19635	2.35	154.86	719	2386
BS2	3.0	718	39607	0.51	35.31	428	2681
BS2	3.0	828	29532			566	3620
BS2	3.0	923	38502	2.18	25.39	507	3718
BS2	3.8	1667	29749	5.65	11.59	909	4260
BS2	4.6	630	15573	0.26	1.91	229	1454
BS3	0.8	103	21317	0.23	1.89	79	3814
BS3	1.5	444	25562	0.41	1.29	67	4159
BS3	2.0	387	19180	24.77	39.15	1097	3344
BS3	2.3	637	21100	9.17	36.68	1107	3705
BS3	3.0	761	50373	0.43	49.44	764	3157
BS3	3.8	762	49339	1.01	41.31	1040	5711
BS3	4.6	833	25344	0.87	35.61	613	2380
Background	0.8	176	19425	0.36	2.07	54	3443
Background	0.8	166	22352	0.14	8.54	62	3881
Background	1.5	89	9563	0.91	4.30	144	4786
Background	2.3	92	9691	0.91	4.10	47	3142
Background	3.0	116	13894	0.64	3.61	38	2583
Background	3.7	225	18208	0.73	3.41	75	2862

6N Fe^{II} = ferrous iron extracted with strong acid (6N HCl). 6N Fe T = total iron extracted with strong acid (6N HCl). S-FeS – Sulfide in the form of ferrous sulfide. S-FeS₂ – sulfide in the form of ferrous disulfide. 0.5 N Fe^{II} – bioavailable ferrous iron extracted with weak acid (0.5 N HCl). 0.5 N Fe T = bioavailable total iron extracted with weak acid (0.5N HCl).

OU-1 PILOT: A second, smaller pilot was conducted near a landfill in the OU-1 plume at Altus AFB. TCE levels of up to 10,400 µg/L were found in a high sulfate groundwater with between 1,560 and 2,110 mg/L sulfate. The emulsified soybean oil was injected into two wells. As shown in Table 3, TCE levels have fallen in injection well IW-6 from 43 µM to 0.33 µM, cDCE increased from 4.4 to 6.1 µM, and VC has increased from <2 µM to 0.12 µM after 13 months. Maximum ethene and ethane levels of 28.2 µM and 24.7 µM were found after four months. Sulfate fell from 1,717 mg/L to 26 mg/L while methane increased from non-detect to 10 mg/L. Although acetylene was not detected, the

low levels of cDCE and VC that were produced, suggest that the abiotic pathway for TCE removal appeared to be favored at this location.

TABLE 3. Volatile contaminants, sulfate, methane, and TOC in OU-1 pilot well IW-6

IW-6	Units	11/14/01	12/18/01	4/24/02	7/31/02	1/17/03
Ethene	μM	<1.1	0.15	28.2	0.50	<0.046
Ethane	μM	<1.0	0.32	24.7	0.37	0.057
Acetylene	μM	<1.0	<0.42	<0.42	<0.046	<0.046
VC	μM	<2.0	<0.090	<0.80	0.50	0.12
cDCE	μM	4.4	9.7	4.4	7.5	6.1
tDCE	μM	<1.3	<0.058	<0.52	<0.058	<0.058
TCE	μM	43.0	45.7	3.8	4.3	0.33
Total CE	μM	47.4	55.8	61.1	13.2	6.6
Methane	mg/L	<0.016	<0.066	0.89	3.9	10.0
Sulfate	mg/L	1717		100	518	26
TOC	mg/L	3.2	19000	11000	3400	2400

SUMMARY: Field pilot-scale projects were conducted at two locations at Altus AFB. At SS-17, the injection of EOSTM into the shallow aquifer resulted in the rapid establishment of conditions to support and promote anaerobic reductive dechlorination. After only nine months, significant decreases in TCE were observed with concomitant increases in cDCE, VC, and ethene observed in several monitoring wells downgradient of the permeable reactive barrier production. Although biological reduction of iron and sulfate resulted in the accumulation of ferric sulfide and ferric disulfide within the treatment zone compared to an untreated location, the abiotic transformation mechanism appeared to be a minor contributor to the removal of TCE within this area of the aquifer. At the OU-1 pilot site, there was a substantial decrease in the concentration of TCE without substantial increases in cDCE and VC that would be expected from biological reductive dechlorination. Although the abiotic by-product acetylene was not detected at appreciable levels, the loss of TCE and sulfate suggest that the transformation at this location was primarily due to abiotic processes with the biological component providing a measurable, but minor contribution.

Degradation of TCE can be stimulated by biological and abiotic process in areas with high sulfate and iron levels. Injection of a soluble or long-lasting substrate can promote reductive dechlorination of TCE and stimulate the reduction of sulfate and iron that can then abiotically react with TCE.

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U.S. EPA Contaminated Site Cleanup Information (CLU-IN)

CLU-IN | Databases | Remediation Technology Demonstration Project Profiles | [In Situ Biogeochemical Reductive Dechlorination \(BiRD\) at Altus Air Force Base, Oklahoma](#)

Remediation Technology Demonstration Project Profiles

In Situ Biogeochemical Reductive Dechlorination (BiRD) at Altus Air Force Base, Oklahoma

- [Home](#)
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- [Disclaimer](#)

Last Updated: September 7, 2004

Site Identifying Information

Site Name, Location: Altus Air Force Base, Altus, Oklahoma, United States (EPA Region 6)

Cleanup Program: Not Specified

Entity Responsible for Cleanup: Air Force

Site Type: Aircraft Degreasing Operations

Government Affiliation: Federal

Project Information

Project Name: In Situ Biogeochemical Reductive Dechlorination (BiRD) at Altus Air Force Base, Oklahoma

Project Status: Complete

Contaminants Treated:

Chemical Name	Conc.	Units	Comment
Trichloroethene			

Media Treated:

Media	Quantity	Units	Basis for Quantity
Ground Water			

Demonstration Technology and Type: Monitored Natural Attenuation (In Situ Biological)

Geology and Hydrogeology: Three important geologic layers were identified and included a red clay alluvium, red shale, and blue green to redsiltstone, which extend from approximately 0 to 15 ft, 15 to 39 ft, 39 ft to bit refusal (39 to 47 ft) respectively. Layers of sulfate-rich

mineral gypsum ($\text{Ca}(\text{SO}_4) \cdot 2\text{H}_2\text{O}$) were often found in the shale and siltstone layers. The aquifer is in the clay and shale layers beginning about 12 ft bgs. Ground water flow is towards the south-southwest. Iron concentrations, found in all the stratigraphic layers but especially in the upper clay zone, exceed concentrations of 2,000 mg/kg. The ratio of Fe^{2+}/Fe total shows Fe^{2+} is <10% in background clays but approaches 100% in the hydrocarbon impacted clay zone due to direct or indirect microbial reduction. Elevated Fe^{2+} in the siltstone layer is not biological in origin but instead is caused by concentrations of chlorite rich clays giving it a blue green color. Sulfate concentrations are significantly depleted in the fuel impacted clay zone and there are correspondingly high concentrations of mineral FeS and FeS_2 .

Demonstration Year: 2003

Year of Publication: 2003

Goal of the Demonstration: To describe a method for assessing biogeochemical treatment for natural attenuation and engineered in situ bioremediation (Biogeochemical Reductive Dechlorination [BiRD]) in the treatment of TCE-contaminated site.

Design and Operations: This project involved evaluation of natural attenuation processes for TCE in a sulfate-rich environment, referred to by the vendor as BiRD. Eighteen soil borings (A-1 through A-18) were cored using a hollow stem auger rig to depths to 40 feet. Sediment samples were collected approximately every 2.5 feet and evaluated for mineral Fe and S species and for chlorinated solvents and fuel compounds using EPA Method 8260. Bore hole geophysics were run in each boring. Geostatistical modeling was performed in 3D using GridStat (2000). The attribute profiles shown on successive figures are vertical slices through their respective three-dimensional models developed by interpolating the spatial data for all borings simultaneously. All attribute profiles are taken along line of section crosses the ground water flow gradient and includes both the TCE and fuel source areas. A batch study, using live and killed microcosms, was also performed to determine if ERD or BiRD was occurring at this site.

Performance Data Relevant to Demonstration Goals: At the Altus AFB, high concentrations of both iron and SO_4^{2-} are naturally present. Supplied organic (released fuel) stimulated SO_4^{2-} reducing bacteria to produce iron sulfides and reduced iron minerals. Technically, the observed mass of FeS from the small fuel release site is sufficient to dechlorinate all of the TCE found in the clay aquifer but the mineral is not uniformly distributed. In the vertical profile, TCE was found to be predominantly in the clay/shale interface and in the high porosity shale layer at 23 feet. TCE was removed from the iron sulfide release area and no significant daughter products were produced. In map plan, TCE is almost completely removed in the clay layer in the fuel-impacted area but was present everywhere in the underlying shale.

Interesting Aspects or Significance of the Demonstration: Treatment of Recalcitrant Compounds

Other Interesting Aspects or Significance of the Demonstration: Abiotic biogeochemical treatment of chlorinated solvents

Lessons Learned: Significant benefits can be realized by engineered remediation by supplying a source of labile organic and/or sulfate (SO_4^{2-}). The process has a number of advantages over enzymatic reductive dechlorination including: (1) Reservoir permeability is not affected (2) Use of substrate for methanogenesis is inhibited by electron acceptor competition with SO_4^{2-} . High SO_4^{2-} environments augment rather than impede the process (3) Sulfate reducing bacteria are ubiquitous and common, so bioaugmentation is not necessary (4) The rate of FeS production is rapid (5) The experimental rate of dechlorination is very quick (6) The requirement for subsurface mixing is minimized (7) Deleterious byproducts (such as vinyl chloride) are not produced

Other Demonstration Information (such as cost data, if available): At Altus Air Force Base, Building 506 was identified as the source for a chlorinated solvent release principally consisting of TCE. A fuel release is also located near Building 506 at an area known as OWS-506. The source of the fuel includes an oil water separator, underground storage tanks for fuel, and possibly associated fuel distribution lines. This fuel release site is located down and

cross-gradient of the chlorinated solvents release area. From the outset the sediment was suspected to be high in mineral Fe³⁺ and it was known that ground water contained very high concentrations of naturally occurring SO₄²⁻. Thus, the site "naturally" contained all the elements (organic, Fe³⁺, and SO₄²⁻) in a TCE impacted area necessary to examine BiRD under field conditions. In vertical profile, TCE was predominantly found in the clay/shale interface and in the high porosity shale layer at 23 feet. TCE is absent in the iron sulfide-rich sediment zone.

Other Comments about the Demonstration:

Abiotic processes may be important to dechlorination. Mineral iron sulfides can fully dechlorinate TCE and PCE without elevated vinyl chloride. Abiotic dechlorination is spontaneous and rapid. The biotic process occurs via reductive dechlorination, and involves direct enzymatic processes in heterotrophic bacteria that can use TCE and PCE as electron acceptors in the presence of an electron donor substrate. BiRD theory: This approach is biogeochemical because it is a sequential process beginning with a microbiological step followed by mineralogical/geochemical interactions resulting in reductive dechlorination. Of special interest to BiRD are sulfur/iron mineral complexes induced by microbial sulfate reduction. Oxidation of an organic by sulfate-reducing bacteria produces hydrogen sulfide (H₂S) according to the general reaction: (1) CH₂O + 0.5 SO₄²⁻ => HCO₃⁻ + 0.5 H₂S (g). Equation 1 is the biological step in BiRD. Sediments normally have available Fe³⁺ oxide/hydroxide minerals that provide a chemical sink for H₂S, forming various iron sulfide minerals as: (2) 2FeOOH (s) + 3 H₂S (aq) => 2FeS (s) + So + 4H₂O. Equation 2 is abiotic, spontaneous, and almost instantaneous. One mole of sulfide in H₂S is oxidized to elemental sulfur to facilitate the reduction of two moles of Fe³⁺ to Fe²⁺ resulting in the formation of two moles FeS. With time FeS is converted to more stable pyrite (FeS₂) as: (3) FeS (s) + So => FeS₂. Therefore, equations 1 and 2 show that 66% to 50% of the reduced SO₄²⁻ should precipitate as FeS with the remaining 33% to 50% as either So or FeS₂. The suggested chemical reaction for TCE dechlorination via FeS oxidation is: 4/9 FeS + C₂HCl₃ + 28/9 H₂O => 4/9 Fe(OH)₃ + 4/9 SO₄²⁻ + C₂H₂ + 3 Cl⁻ + 35/9 H⁺

Vendor(s) or Consultant(s) Associated with the Demonstration:

Earth Sciences Division, Oklahoma City, OK
Rowan University, Glassboro, NJ
Air Force Center for Environmental Excellence

Information Source(s) for the Demonstration:

Biogeochemical Treatment for the Engineered and Natural Attenuation of Chlorinated Solvents, Paper H-16, in: V.S. Magar and M.E. Kelley (Eds.), In Situ and On-Situ Bioremediation - 2003. Proceedings of the Seventh International In Situ and On-Site Bioremediation Symposium (Orlando, Florida, June 2003). ISBN 1-57477-139-6, published by Battelle Press, Columbus, Ohio.
<http://www.battelle.org/bookstore#>

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US006884352B1

(12) **United States Patent**
Kennedy

(10) **Patent No.:** **US 6,884,352 B1**
(45) **Date of Patent:** **Apr. 26, 2005**

(54) **TREATING TOXIC SOLVENTS AND HEAVY METAL CONTAMINANTS IN GROUNDWATER AND SOIL USING IRON SULFIDES MICROBIAL GEOCHEMICAL TREATMENT ZONE**

(76) Inventor: **Lonnie G. Kennedy**, 3233 NW. 63rd St., Oklahoma City, OK (US) 73116

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 160 days.

(21) Appl. No.: **10/367,461**

(22) Filed: **Feb. 14, 2003**

Related U.S. Application Data

(60) Provisional application No. 60/362,521, filed on Mar. 7, 2002.

(51) **Int. Cl.⁷** **C02F 3/00**

(52) **U.S. Cl.** **210/610; 210/747; 210/912**

(58) **Field of Search** **210/610, 631, 210/747, 912-914, 170**

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* cited by examiner

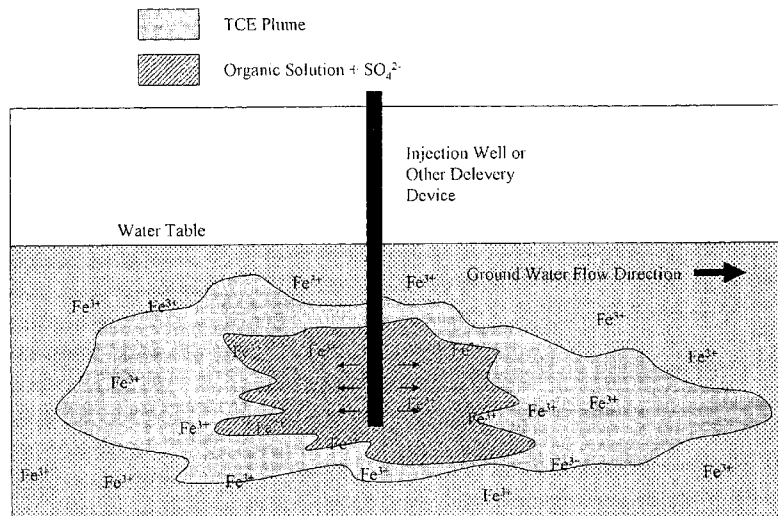
Primary Examiner—Chester T. Barry

(74) *Attorney, Agent, or Firm*—Randal D. Homburg

(57) **ABSTRACT**

A method a process involving the application of a labile organic substrate, with supplied sulfate as needed, to a soil and ground water supply for the express purpose of stimulating sulfate reduction to facilitate the formation of mineral iron sulfides or other reduced reactive minerals, abiotically treats soil contaminants, including chlorinated solvents, and hexavalent chromium, with an iron monosulfide microbial geochemical treatment zone. Other iron sulfide compounds, or generally Fe_xS_y, may also comprise the treatment zone in addition to iron monosulfide. The process also includes, in some cases, the supplementation of sulfate to ground water where insufficient natural supply exists, wherein a solution of organic and dissolved reactive sulfate introduced to the soil and ground water, the introduction of sulfate tailored to the individual site conditions to meet contaminant mass constraints.

10 Claims, 6 Drawing Sheets



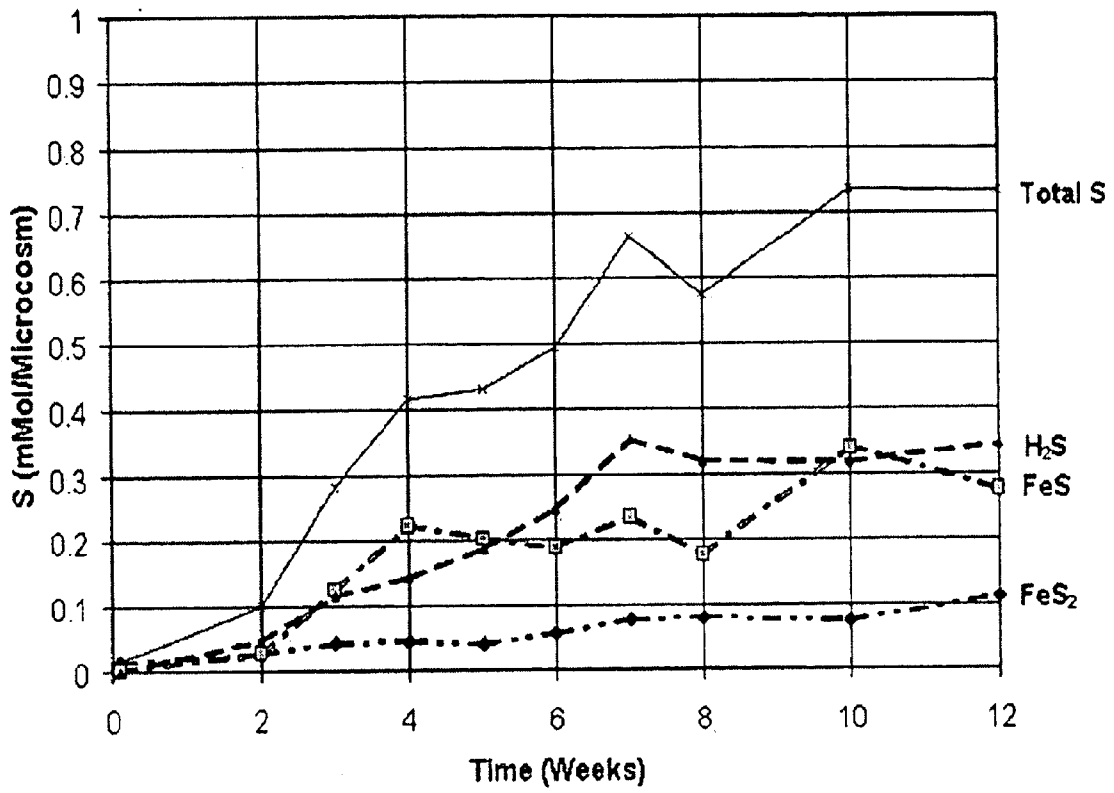


Figure 1

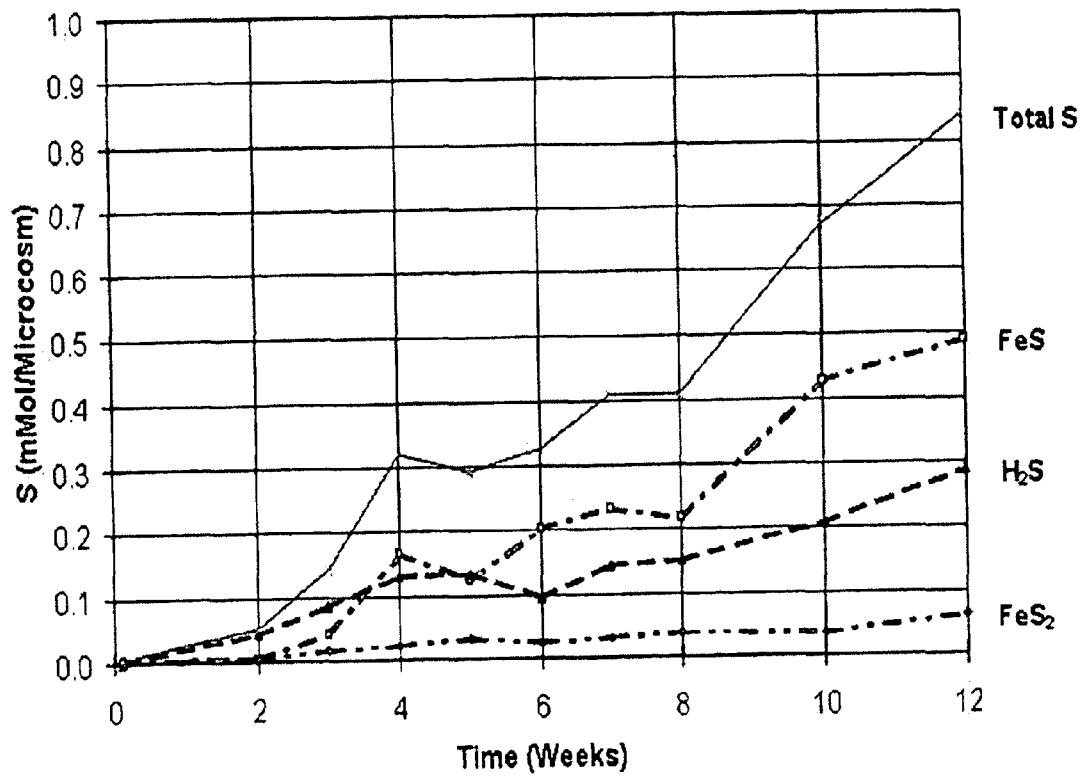


Figure 2

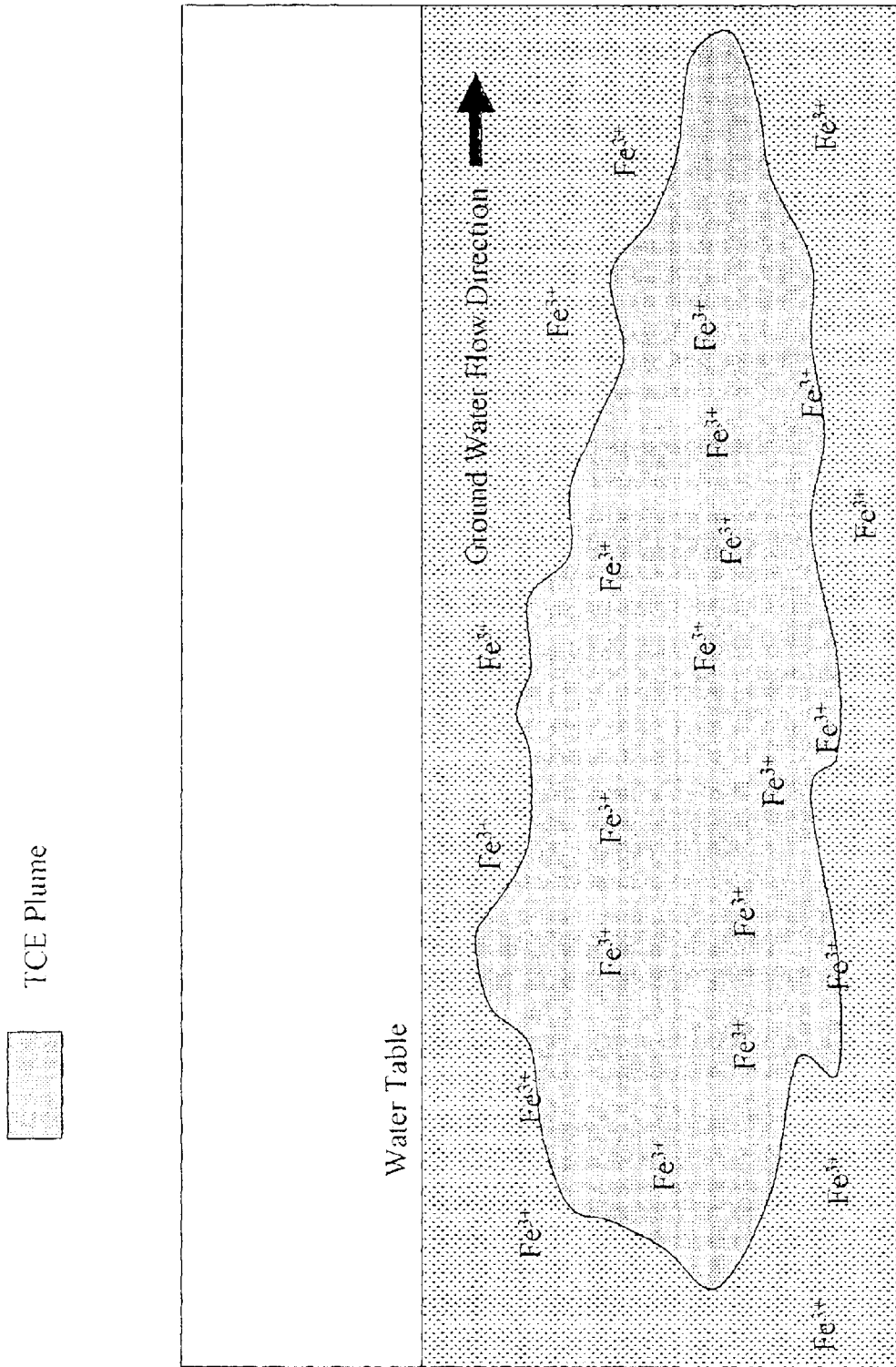


Figure 3

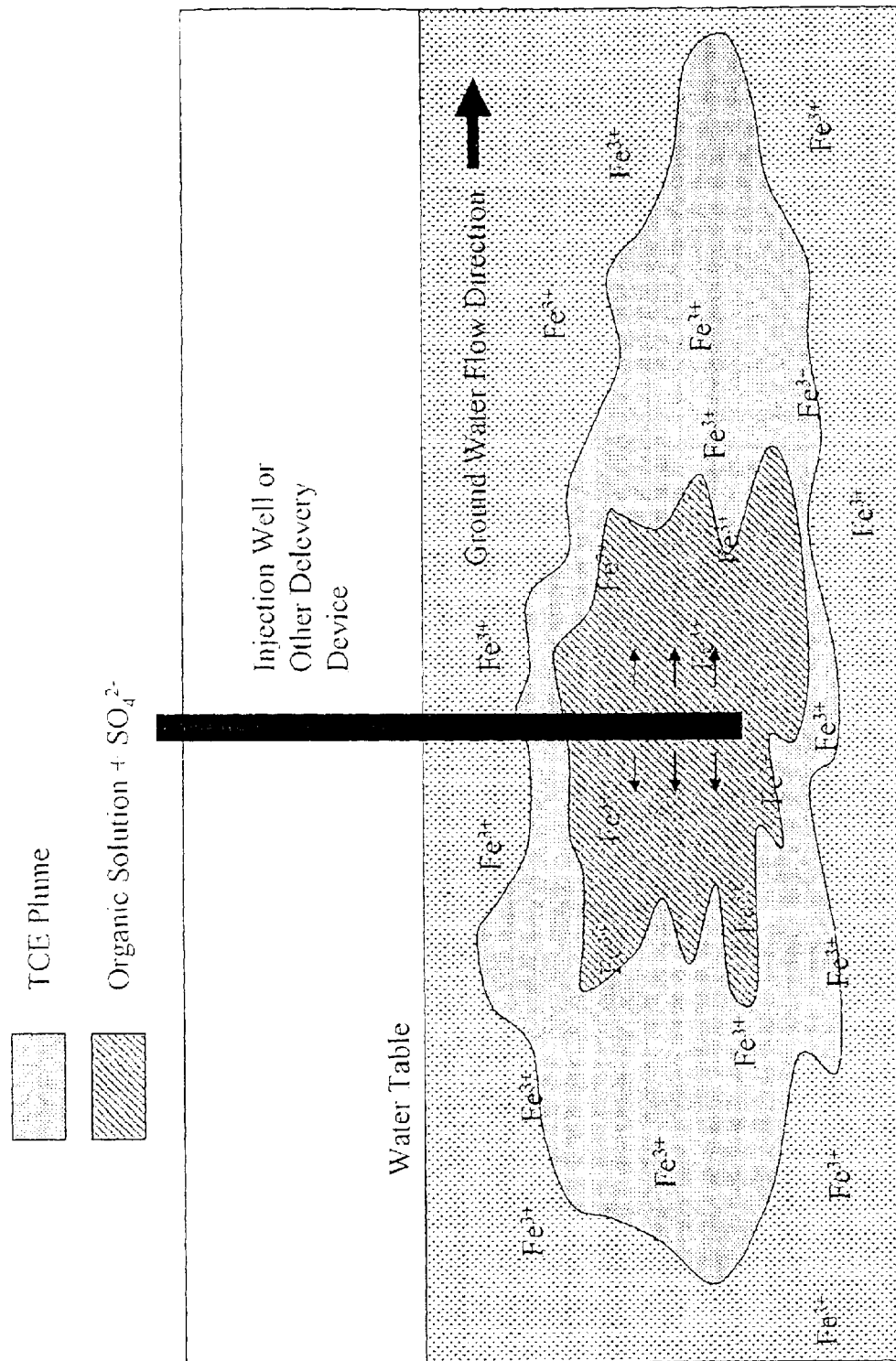


Figure 4



Figure 5

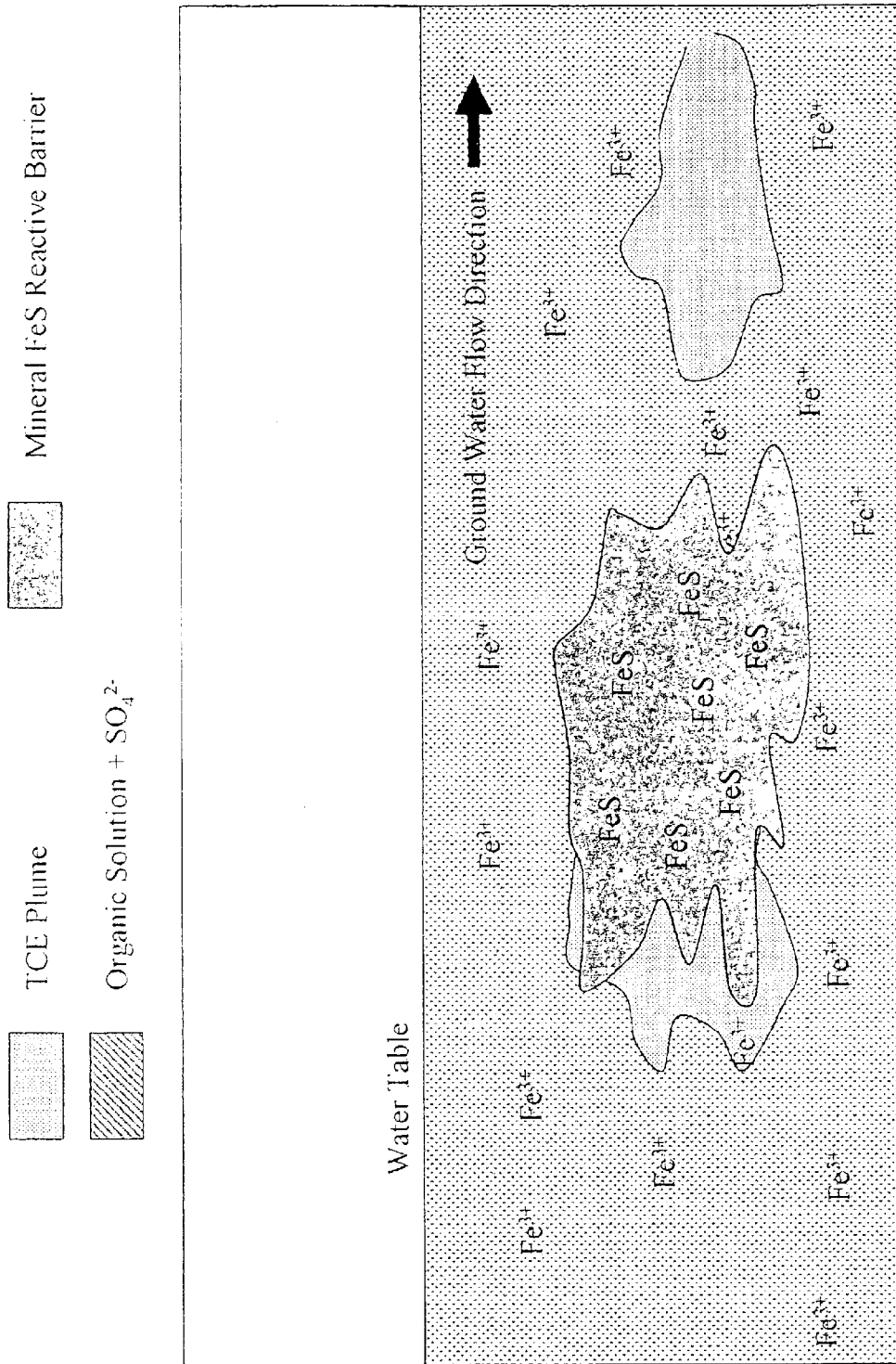


Figure 6

1

**TREATING TOXIC SOLVENTS AND HEAVY
METAL CONTAMINANTS IN
GROUNDWATER AND SOIL USING IRON
SULFIDES MICROBIAL GEOCHEMICAL
TREATMENT ZONE**

**CROSS REFERENCE TO RELATED
APPLICATIONS**

Applicant claims the benefit of the provisional patent application Ser. No. 60/362,521 filed on Mar. 7, 2002.

BACKGROUND OF INVENTION

1. Field of the Invention

A method a process involving the application of a labile organic substrate, and optionally sulfate, to a soil and ground water supply for the express purpose of stimulating reactive sulfate reduction to facilitate the formation of mineral iron sulfides that abiotically treats soil contaminants, including chlorinated compounds, and hexavalent chromium or other oxidized or partially oxidized organic and inorganic contaminants, with an iron sulfide microbial geochemical treatment zone. Other iron sulfide compounds, or generally Fe_xS_y , may also comprise the treatment zone in addition to iron monosulfide including activated iron or other metals which may be formed by microbial geochemical processes. The process also includes, in some cases, the supplementation of reactive sulfate to ground water where insufficient natural supply exists, wherein a solution of organic and dissolved reactive sulfate introduced to the soil and ground water, the introduction of reactive sulfate tailored to the individual site conditions to meet contaminant mass constraints.

2. Description of Prior Art

The following United States patents are identified and disclosed herein. Several devices are disclosed relating to the chemical treatment of ground and water contaminants, but none of them are or may be adapted to define the stated method or process of the current invention, nor do they utilize the same chemicals, reactions and process a does the current invention.

In U.S. Pat. No. 5,362,402 to Haitko, a method for the dehalogenation of halogenated hydrocarbons using metallic iron in the presence of citric acid, primarily in aqueous solutions. Addition of agitated iron particles in an aqueous solution containing hexavalent and trivalent chromium forming an insoluble precipitate is the objective of the disclosed method of U.S. Pat. No. 5,380,441 to Thornton, and also the relative subject matter of U.S. Pat. No. 5,427,692 to Thornton, but including the use of barium nitrate.

Use of iron powder and a water soluble weak acid inorganic compound which does not contain nitrogen or phosphorus to decontaminate soil infused with a halogenated organic compound is disclosed in U.S. Pat. No. 6,068,777 to Kimura, which is adapted primarily for the treatment of groundwater. Hexavalent chromium is the target contaminant in the method and process in U.S. Pat. No. RE 36,915 to Suci, which uses the addition of a ferrous ion and a sulfide ion to a stream of waste water prior to disposal reducing the hexavalent chromium to trivalent chromium, which forms a precipitate in the waste water creating a sludge, the process also including the addition of a flocculating polymer to induce the formation of the precipitant.

Also disclosed are three articles, the first co-authored by the inventor, indicated as follows. In a first article, (Kennedy, L. G. and Everett, J. W., 2001. Microbial degra-

2

5 dation of simulated landfill leachate: Solid iron/sulfur interactions; Applied Environmental Research, Vol. 5, No. 2, pgs. 103–116.) the focus of the article dealt primarily with the formation of reduced iron and sulphur minerals to assess organic contaminant degradation due to Fe^{+3} and SO_4^{2-} microbial reduction process, but did not disclose any resultant method or process dealing with chlorinated solvent reduction in the soil or groundwater.

10 In the article by Butler, E. C. and Hayes, K. F., 1999. Kinetics of the transformation of trichloroethylene and tetrachloroethylene by iron sulfide; Environmental Science Technology, Vol. 33, No. 12, pgs. 2021–2027, laboratory process for the degradation of PCE an TCE are discussed, but without disclosure of a method or process for naturally forming the iron sulfide using the disclosed process creating the iron sulfide barrier as a microbial geochemical treatment zone. Another collaterally related scholarly article is found in the article, Parker, T. and Mohr, T., Symposium on natural attenuation of chlorinated solvents in groundwater—a summary; Hydro Vision Online Newsletter, Volume 5, No. 4, Winter 1996; www.grac.org/winter96/rnapaper.htm, dealing with chlorinated solvent plume movement, migration and activity.

25 In Applicant's article, See Kennedy, supra., preliminary research and testing is documented dealing with the use of solid electron acceptors, including $CaSO_4^{2-}$ and $Fe(OH)_3$, to promote carbonate and sulfide mineral formation to control greenhouse gas production, including carbon dioxide and methane, with the suggestion that the Fe and S mineral could also be used to assess organic contaminant degradation occurring due to Fe^{3+} and SO_4^{2-} microbial reduction processes for natural attenuation studies. The current invention is a result of such studies, and is the method for creating an iron monosulfide (FeS) microbial geochemical treatment zone for areas having previously experienced soil and ground contamination with toxic chemical solvents and by-products.

SUMMARY OF THE INVENTION

40 The primary objective of the invention is to create a soil retentive barrier of iron sulfides to reductively dechlorinate polychlorinated hydrocarbons through an abiotic chemical reaction by the formation of an iron sulfide or iron monosulfide microbial geochemical treatment zone.

45 The secondary objective of the invention is to provide a naturally occurring sulfate reducing heterotrophic soil bacteria oxidizing the organic while reducing the reactive sulfate, which, in turn causes a liberated reactive hydrogen sulfide combining with iron, to form iron sulfides which oxidizes chlorinated chemicals including solvents to form non-toxic by-products.

50 A third objective of the invention is to apply this process to toxic metallic compounds, including hexavalent chromium, to form non-toxic by-products from the redox reactions with FeS or, in general, Fe_xS_y .

DESCRIPTION OF THE DRAWINGS

60 The following drawings are informal drawings submitted with this provisional patent application.

FIG. 1 is a graphic representation of a first laboratory tests involving native sediment amended with acetate and sulfate showing the generation of FeS along with a nonreactive mineral form FeS_2 and some associated non-reacted H_2S .

65 FIG. 2 is a graphic representation of a first laboratory tests involving native sediment amended with acetate and sulfate

showing the generation of FeS along with a nonreactive mineral form FeS₂ and some associated non-reacted H₂S.

FIG. 3 is a diagram of an aquifer at pre-injection with TCE contamination and native mineral Iron (III), with or without sufficient quantity of sulfate.

FIG. 4 is a diagram of the injection of the organic and sulfate into the contaminated aquifer.

FIG. 5 is a diagram of the removed injection and the formation of the Iron Sulfide created by the oxidation of the organic with the Sulfate, the Iron Sulfide produced from the reactive Hydrogen Sulfide and the Iron (III).

FIG. 6 is a diagram of the TCE oxidized by the Iron Sulfide, indicating the formed geochemical treatment zone, severing the TCE contamination from the source, the remaining source TCE swept into the barrier by ground water advection and dechlorination.

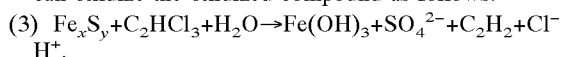
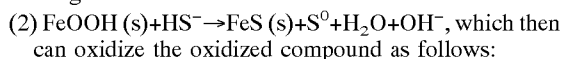
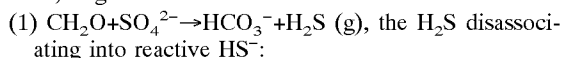
DESCRIPTION OF THE PREFERRED EMBODIMENT

Chlorinated solvents and other ground and water contaminants, including toxic heavy metals, have become increasingly known public hazard. Both public and private corporations, having become aware of such hazards have searched for methods and technology to abate the contamination to soil and water recently, which had been improperly or inadvertently introduced to the soil, seeping into the ground water, lakes and streams and public drinking supplies. These water contaminants most noted are often oxidized compounds and more specifically chlorinated solvents, including perchlorate, perchloroethylene (PCE), trichloroethylene (TCE), and dichloroethylene (DCE), which are recalcitrant to microbial degradation. Also, as recently come to light, heavy reactive metals, including hexavalent chromium, are know health hazards, resulting in cancer, soft tissue disease and birth defect. These chemicals tend to persist in an aqueous environment, primarily due to their being a poor substrate for heterotrophic bacteria that conserve chemical energy, such as ATP redox reactions oxidizing a reduced organic (aliphatic compounds) and reducing an external electron acceptor (oxygen).

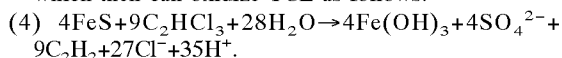
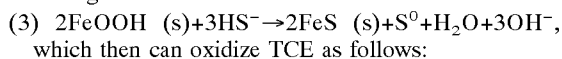
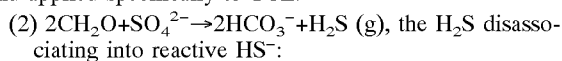
In order to treat and reduce this contamination, the invention consists primarily of a method and process for the creation of a reduced mineral barrier, or specifically, an iron sulfide microbial geochemical treatment zone using sulfide reducing bacteria to treat toxic and harmful contaminants in groundwater and in the soil. Although direct microbial degradation of the contaminants of concern is difficult, sulfate reduction is relatively simple to stimulate in the subsurface and the resulting activated minerals arising from microbial geochemical reactions can then treat the contaminants by largely abiotic chemical reactions. This process, as shown in FIGS. 3-6, involves locating a contamination zone in soil and ground water containing a target contaminant, introducing a quantity of labile organic compound to the contamination zone, potentially adding a sulfate reducing heterotrophic soil bacteria to the contamination zone, oxidizing the organic while reducing a naturally occurring sulfate present within the soil and ground water, adding additional sulfate to the contamination zone, if needed, to complete the redox reactions where the naturally occurring sulfate is insufficient, producing a quantity of HS within the contamination zone, which in turn reacts with a naturally occurring iron (III) present within the contamination zone forming a deposit of iron monosulfide (FeS) within the contamination zone, the iron sulfides oxidizing the target contaminant while creating an iron sulfide microbial

geochemical treatment zone further oxidizing any target remaining contaminant which may pass through or present itself within the iron sulfide microbial geochemical treatment zone swept into such treatment zone via ground water advection, dispersion, or molecular diffusion.

The general chemical equations below indicates the chemical reaction occurring during the above disclosed process as related to the treatment of a polychlorinated solvent, in general is as follows:



In the below example, wherein iron monosulfide is utilized and applied specifically to TCE:



[Full or partial oxidation of the iron monosulfide; full or partial reduction of the polychlorinated hydrocarbon.]

Typical soils and shallow aquifers contain substantial quantities of mineral iron (III) or Fe³⁺ including ferrhydrate, iron hydroxide, goethite, hematite and others. The liberated sulfides, from equation (1) can combine with the mineral Fe³⁺ to form the FeS as per equation (2). It should be noted that a wide range of reduced metals and metal sulfides can be created by reaction with the hydrogen sulfide which will vary in their reactive properties. Biologically generated FeS or other reduced minerals can then oxidize the chlorinated solvent or other oxidized contaminants similar to equation (3). The chlorinated solvents contemplated for reduction by this process include primarily, oxidized compounds, perchlorate, vinyl chloride, perchloroethylene (PCE), trichloroethylene (TCE), and dichloroethylene (DCE), but may also include other less identified and problematic chlorinated solvents or oxidized metals.

Laboratory testing results, as shown in FIGS. 1 and 2 of the drawings, verify the formation of the iron monosulfide (FeS) and other iron sulfides from the above disclosed process, such laboratory tests performed in using native sediments from two locations within the State of Oklahoma, amended with simple organic acids and sulfate. The charts show the generation of iron monosulfide (FeS), along with a less mineral form iron disulfide (FeS₂) and some associated hydrogen sulfide (H₂S) that did not fully react in the small containers within which the tests were performed.

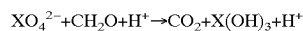
Precipitation of Fe_xS_y is similar to the creation of a permeable reactive wall, but using geomicrobiological processes. Generated Fe_xS_y resides in the aquifer as a permeable, chemically reactive zone in mineral solids. This zone can then capture and treat chlorinated solvents that may be swept into the treatment area via ground water advection, dispersion, or molecular diffusion.

Iron monosulfide (FeS) have been demonstrated to react with chlorinated solvents including trichloroethylene (TCE) and tetrachloroethylene (PCE) to facilitate complete dechlorination. See Butler, E. C., Kinetics of the transformation of trichloroethylene and tetrachloroethylene by iron sulfide, supra. As stated within that article, iron monosulfide (FeS) chemically reacts with these chlorinated solvents to form ~75% acetylene and ~ethane, ethane or other C₂-C₆ com-

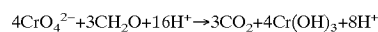
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pounds. Noteworthy is the absence of vinyl chloride (VC) produced in this reaction, nor is there any accumulation of dichloroethylene (DCE) in this reaction, as the suggested pathway for trichloroethylene (TCE) oxidation is via cis dichlorovinyl radical directly to acetylene. In previous test conditions, trichloroethylene (TCE) was degraded in this manner according to pseudo first order decay with a rate of $1.49 \text{ E}-3 \text{ h}^{-1}$ of 0.036 d^{-1} . This rate equates to a half life of approximately 19 days, which is comparably and obviously quite rapid.

It is also predicted that this process will also effectively remove dangerous and hazardous heavy metal contaminations (X), as follows:



As applied to reactive hexavalent chromium (Cr VI) the following chemical equation would be:



[wherein the hexavalent chromium (Cr VI) is reduced by the iron monosulfide (FeS) found within the iron monosulfide microbial geochemical treatment zone.]

Under some conditions, dissolved sulfate (SO_4^{2-}) can be supplemented to ground water during the addition of the labile organic, where insufficient quantities of naturally occurring sulfate (SO_4^{2-}) exists. The quantities of organic and sulfate (SO_4^{2-}) must be tailored to individual contamination zones to meet contaminant mass constrains. The determination of such quantities of organic and sulfate (SO_4^{2-}) may be determined by pre-application soil testing or by continual soil testing and monitoring after the process has been performed within the contamination zone until the contamination zone is eradicated of the involved contaminants.

Although the embodiments of the invention have been described and shown above, it will be appreciated by those skilled in the art that numerous modifications may be made therein without departing from the scope of the invention as herein described.

I claim:

1. A process for the creation of an iron sulfide microbial geochemical treatment zone to treat toxic and harmful contaminants in ground water and in the soil, the process comprising the steps of:

- (A) locating a contamination zone in soil and ground water containing a target contaminant;
- (B) introducing a quantity of labile organic compound to the contamination zone;
- (C) adding a sulfate reducing heterotrophic soil bacteria to the contamination zone, oxidizing the organic while reducing a naturally occurring sulfate present within the soil and ground water;
- (D) adding additional sulfate to the contamination zone to complete the redox reactions where the naturally occurring sulfate is insufficient, producing a quantity of HS within the contamination zone, which in turn reacts with a naturally occurring iron (III) present within the contamination zone;
- (E) forming a deposit of an iron sulfide (Fe_xS_y) within the contamination zone;
- (F) oxidizing the target contaminant; and
- (G) contemporaneously creating an iron sulfide microbial geochemical treatment zone further oxidizing any target remaining contaminant which may pass through or present itself within the iron sulfide microbial

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geochemical treatment zone swept into such treatment zone via ground water advection, dispersion, or molecular diffusion.

2. The process of claim 1, wherein said process is applied to chlorinated solvents comprising the general chemical series equations of:

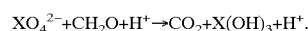
1. $\text{CH}_2\text{O} + \text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + \text{H}_2\text{S (g)}$, the H_2S disassociating into reactive HS^- ;

2. $\text{FeOOH (s)} + \text{HS}^- \rightarrow \text{FeS (s)} + \text{S}^0 + \text{H}_2\text{O} + \text{OH}^-$, which then oxidizes a chlorinated solvent as follows:

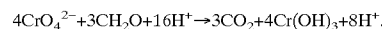
3. $\text{Fe}_x\text{S}_y + \text{chlorinated solvent} + \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + \text{SO}_4^{2-} + \text{C}_2\text{H}_2 + \text{Cl}^- + \text{H}^+$, with full or partial oxidation of the Fe_xS_y , and full or partial reduction of the chlorinated solvent.

3. The process of claim 1 wherein said target contaminant is selected from the group consisting of perchlorate, perchloroethylene (PCE), trichloroethylene (TCE), and dichloroethylene (DCE).

4. The process of claim 1, wherein said process is applied to reduce heavy metal (X) contaminations within the soil and ground water, resulting in the following general chemical reaction:



5. The process of claim 1, wherein the resultant iron sulfide (FeS) forming the iron sulfide microbial geochemical treatment zone reduces a hexavalent chromium (Cr VI) per the general chemical equation of:



6. A process for the creation of an iron monosulfide microbial geochemical treatment zone to treat toxic and harmful contaminants in ground water and in the soil, the process comprising the steps of:

- (A) locating a contamination zone in soil and ground water containing a target contaminant;
- (B) introducing a quantity of labile organic compound to the contamination zone;
- (C) adding a sulfate reducing heterotrophic soil bacteria to the contamination zone, oxidizing the organic while reducing a naturally occurring sulfate present within the soil and ground water;
- (D) adding additional sulfate to the contamination zone to complete the redox reactions where the naturally occurring sulfate is insufficient, producing a quantity of HS within the contamination zone, which in turn reacts with a naturally occurring iron (III) present within the contamination zone;
- (E) forming a deposit of an iron monosulfide (FeS) within the contamination zone;
- (F) oxidizing the target contaminant; and
- (G) contemporaneously creating an iron monosulfide microbial geochemical treatment zone further oxidizing any target remaining contaminant which may pass through or present itself within the iron monosulfide microbial geochemical treatment zone swept into such treatment zone via ground water advection, dispersion, or molecular diffusion.

7. The process of claim 6, applied to chlorinated solvents comprising the general chemical series equations of:

(4) $2\text{CH}_2\text{O} + \text{SO}_4^{2-} \rightarrow 2\text{HCO}_3^- + \text{H}_2\text{S (g)}$, the H_2S disassociating into reactive HS^- ;

(5) $2\text{FeOOH (s)} + 3\text{HS}^- \rightarrow 2\text{FeS (s)} + \text{S}^0 + \text{H}_2\text{O} + 3\text{OH}^-$, which then oxidizes TCE as follows:

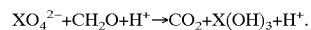
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(6) $\text{FeS} + \text{chlorinated solvent} + \text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_3 + \text{SO}_4^{2-} + \text{C}_2\text{H}_2 + \text{Cl}^- + \text{H}^+$, with full or partial oxidation of the FeS and full or partial reduction of the chlorinated solvent.

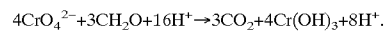
8. The process of claim 6 wherein said target contaminant is selected from the group consisting of perchlorate, perchloroethylene (PCE), trichloroethylene (TCE), and dichloroethylene (DCE).

9. The process of claim 6, wherein said process is applied to reduce heavy metal (X) contaminations within the soil and ground water, resulting in the following general chemical reaction:

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10. The process of claim 6, wherein the resultant iron monosulfide (FeS) forming the iron monosulfide microbial geochemical treatment zone reduces a hexavalent chromium (Cr VI) per the general chemical equation of:



* * * * *

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Biogeochemical Iron Reduction for Dechlorination of Chlorinated Solvent Plumes - Status of the Practice Shift from Biotic to Abiotic Degradation Pathways

James E Studer and Lonnie Kennedy, InfraSUR

The introduction and commercialization of novel subsurface remediation technologies is a significant driver in the evolution of the practice of environmental remediation. With respect to remediation of subsurface plumes containing chlorinated aliphatic hydrocarbons (CAH) such as PCE, TCE, TCA, and the like, a popular approach to in-situ treatment is represented by biological reductive dehalogenation. However, abiotic reductive dehalogenation is gaining ground with variations based on zero valent iron (ZVI) being perhaps the most popular at this time. An intermediate iron-based approach has been under development for the last decade and is now set to enter the remediation professionals practice as a highly attractive technology option. This new approach is referred to as Biogeochemical Iron Reduction for Dechlorination or BiRD and has recently been shown in multiple government-sponsored demonstrations to achieve desirable technology and economic performance metrics relative to biological, ZVI, and ZVIbiological hybrid approaches. Discriminating benefits of BiRD include: rapid degradation of a wide range of chlorinated compounds; no production of undesirable transformation products cis-1, 2 DCE and vinyl chloride (and therefore avoidance of accumulation of these products); greatly reduced conversion of carbon to methane; and highly robust process that can be reliably implemented using low-cost treatment materials and trench-based or direct injection tactics.

BiRD is an engineering process based on amplification of naturally occurring biogeochemical and geochemical reactions where solid-phase iron sulfide minerals are generated in-situ and en masse as a permeable reactive barrier (PRB). Indigenous and ubiquitous sulfate reducing bacteria are relied upon for a short period of time to generate the iron sulfide minerals but then the resulting CAH treatment is an abiotic reaction with the reactive mineral matrix. Groundwater containing CAHs passes through the PRB and CAHs are abiotically transformed to achieve treatment end-points of regulatory and otherwise practical significance. In some cases, biological reductive dehalogenation reactions have been shown to take place alongside the abiotic

reactions. These biological reactions are generally considered to offer insignificant treatment benefit and have the potential to generate cis-1, 2 DCE and/or VC transformation products.

BiRD is currently being tested and implemented at commercial scale as an alternative to biological and hybrid technologies based on both biological and abiotic treatment pathways. There is a growing base of evidence that points to the desirability of strict abiotic and biogeochemical strategies based on ZVI and BiRD for many situations involving CAH contamination of soils, sediment, bedrock, and groundwater. The presentation will describe the salient features of the spectrum of treatment technologies ranging from biological to biological-abiotic (ZVI-based hybrid) to strict abiotic and will introduce the BiRD technology. A case study involving the side-by-side demonstration of biological dehalogenation and BiRD will be presented to illustrate the differences (and similarities) between the technologies and the features and benefits of BiRD.

James E Studer, M.S., P.E

James E. Studer is managing principal of InfraSUR LLC located in Albuquerque, New Mexico, USA. InfraSUR is a small specialty consulting practice and lead organization of the InfraSUR Team. The InfraSUR Team is comprised of highly skilled remediation professionals with special difficult-to-find expertise. The InfraSUR Team provides technical support services to consulting firms and contractors of all sizes and reach. Mr. Studer's 25-year professional career has focused on development and delivery of solutions involving advanced technology applications for cost-effective remediation of soil and groundwater. Technologies include advanced subsurface characterization technologies, in-situ chemical oxidation and reduction, surfactant and polymer enhanced remediation, and advanced aerobic and anaerobic bioremediation technologies. Mr. Studer holds two engineering degrees from the University of Missouri-Rolla (recently renamed Missouri University of Science and Technology) and is a registered professional engineer in the United States.



2710 Wycliff Road
 Raleigh, North Carolina 27607
 919-781-4550

MATERIAL SAFETY DATA SHEET

Effective Date: 5-08
 Replaces: 12-05-2000

I – PRODUCT AND COMPANY IDENTIFICATION		
CHEMICAL NAME Gypsum	CHEMICAL FORMULA CaSO ₄ • 2H ₂ O	MOLECULAR WEIGHT 172.2
TRADE NAME Gypsum		
SYNONYMS Calcium(II) sulfate dihydrate, Gypsum stone, Hydrated calcium sulfate, Mineral white		DOT IDENTIFICATION NO. None

II – COMPOSITION/INFORMATION ON INGREDIENTS				
COMPONENT(S) CHEMICAL NAME	CAS REGISTRY NO	% by weight (approx)	MSHA/OSHA PEL	ACGIH TLV-TWA
Calcium Sulfate, Dihydrate	13397-24-5	49-99.9	(T) 15 mg/m ³ , (R) 5 mg/m ³	(I) 10 mg/m ³

(T) =total dust (R)= respirable dust (I)= Inhalable fraction

III – HAZARDS IDENTIFICATION	
White powder or colorless, crystalline solid [Note: May have blue, gray, or reddish tinge]. Odorless.	
Health Effects: The information below represents an overview of health effects caused by overexposure to one or more components in gypsum. The individual effects are described in Section XI.	
Primary routes(s) of exposure:	<input checked="" type="checkbox"/> Inhalation <input type="checkbox"/> Skin <input checked="" type="checkbox"/> Ingestion
EYE CONTACT:	Direct contact with dust may cause irritation by mechanical abrasion.
SKIN CONTACT:	Direct contact may cause irritation by mechanical abrasion.
SKIN ABSORPTION:	Not expected to be a significant route of exposure.
INGESTION:	If ingested, intestinal obstruction may occur if the material hardens, especially in the pyloric region.
INHALATION:	Dusts may irritate the nose, throat, and respiratory tract by mechanical abrasion. Coughing, sneezing and shortness of breath may occur following exposures in excess of appropriate exposure limits.
MEDICAL CONDITIONS AGGRAVATED BY EXPOSURE	
Inhaling respirable dust may aggravate existing respiratory system disease(s) and/or dysfunctions.	
Exposure to dust may aggravate existing skin and/or eye conditions. Smoking and obstructive/restrictive lung diseases may also exacerbate the effects of excessive exposure to this product.	

IV – FIRST AID MEASURES

EYES:	In case of contact, immediately flush eyes with plenty of water for a minimum of 15 minutes. Warm water is recommended, but cold water may be used.
SKIN:	In case of skin contact, immediately rinse skin with plenty of water. Cover the irritated skin with an emollient. Remove contaminated clothing and shoes. Wash clothing before reuse. Thoroughly clean shoes before reuse. Get medical attention if irritation persists..
INGESTION:	Do not induce vomiting. If conscious, have person drink plenty of water. Seek medical attention or contact poison control center immediately.
INHALATION:	If a person breathes large amounts of this product, move the exposed person to fresh air at once. Other measures are usually unnecessary.

V – FIRE FIGHTING MEASURES

FLASHPOINT Not flammable	FLAMMABLE LIMITS IN AIR Not flammable
EXTINGUISHING AGENT None required	
UNUSUAL FIRE AND EXPLOSION HAZARD None	

VI – ACCIDENTAL RELEASE MEASURES

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED
Sweep or vacuum spilled material into waste container for disposal. Avoid creating excessive dust. Wear approved respirators if necessary. Do not wash down drains, this material may plug drains.

None of the components in this product are subject to the reporting requirements of Title III of SARA, 1986, and 40 CFR 372.

VII – HANDLING AND STORAGE

Be sure proper ventilation, and respiratory and eye protection are used under dusty conditions. Dew point conditions or other conditions causing presence of moisture will harden gypsum during storage. Excessive particulate concentrations in work place air must be avoided even though it is inert and non-toxic.

VIII – EXPOSURE CONTROLS/PERSONAL PROTECTION

ENGINEERING CONTROLS
Ventilation: Use local exhaust, general ventilation or natural ventilation adequate to maintain exposures below appropriate exposure limits. If a person breathes large amounts of this material, move the exposed person to fresh air at once; other measures are usually unnecessary.

EYE/FACE PROTECTION
Safety glasses with side shields should be worn as minimum protection. Dust goggles should be worn when excessively (visible) dusty conditions are present or are anticipated. If product contacts the eyes, immediately wash the eyes with large amounts of water, occasionally lifting the lower and upper lids. Get medical attention immediately. Contact lenses should not be worn when working with this material.

SKIN PROTECTION
Workers should wear close-fitting working clothes of dust-tight material.

RESPIRATORY PROTECTION

Respirator Recommendations:

NIOSH/MSHA approved respirator for nuisance dust.

Emergency or planned entry into unknown concentrations or IDLH conditions: Any self-contained breathing apparatus that has a full-face piece and is operated in a pressure-demand or other positive-pressure mode or any supplied-air respirator that has a full-face piece and is operated in a pressure-demand or other positive-pressure mode in combination with an auxiliary self-contained positive-pressure breathing apparatus.

Escape from unknown or IDLH conditions: Any air-purifying, full-face piece respirator with a high-efficiency particulate filter or any appropriate escape-type, self-contained breathing apparatus.

GENERAL HYGIENE CONSIDERATIONS

There are no known hazards associated with this material when used as recommended. Following the guidelines in this MSDS are recognized as good industrial hygiene practices. Avoid breathing dust. Avoid skin and eye contact. Wash dust-exposed skin with soap and water before eating, drinking, smoking, and using toilet facilities. Wash work clothes after each use.

IX— PHYSICAL AND CHEMICAL PROPERTIES

APPEARANCE AND ODOR

White powder or colorless, crystalline solid [Note: May have blue, gray, or reddish tinge]. Odorless.

SPECIFIC GRAVITY.

2.17 – 2.32

BOILING POINT

Not applicable

VAPOR DENSITY IN AIR (AIR = 1)

Not applicable

VAPOR PRESSURE

Not applicable

% VOLATILE, BY VOLUME

0%

EVAPORATION RATE

Not applicable

SOLUBILITY IN WATER

0-.2% @ 40C

X – STABILITY AND REACTIVITY

STABILITY

Stable

CONDITIONS TO AVOID

Items listed in Incompatibility

INCOMPATIBILITY (Materials to avoid)

Aluminum (at high temperatures), diazomethane

HAZARDOUS DECOMPOSITION PRODUCTS

When heated to high temperatures gypsum may emit toxic fumes of oxides of sulfur and calcium.

XI – TOXICOLOGICAL INFORMATION

Calcium Sulfate, Dihydrate:

Exposure route: Inhalation, skin and/or eye contact

Target Organs: Eyes, skin, respiratory system

Acute Effect: Calcium sulfate dust has an irritant action on mucous membranes of the respiratory tract and eyes. There have been reports of conjunctivitis, chronic rhinitis, laryngitis, pharyngitis, impaired sense of smell and taste, bleeding from the nose and reactions of tracheal and bronchial membranes in exposed workers. .

Chronic Effect: N/A

XII – ECOLOGICAL INFORMATION

No data available.

XIII – DISPOSAL CONSIDERATIONS

WASTE DISPOSAL METHOD

May be disposed of as an inert solid in sanitary landfill or by other procedures in accordance with all federal, state, and local regulations. May be used as a supplement on land and on some agricultural products.

XIV – TRANSPORT INFORMATION

DOT HAZARD CLASSIFICATION

None

PLACARD REQUIRED

None

LABEL REQUIRED

Label as required by the OSHA Hazard Communication standard {29 CFR 1910.1200(f)}, and applicable state and local regulations.

XV – REGULATORY INFORMATION

FDA: Product is manufactured for use as building construction material, agricultural applications, or other industrial applications. As such, FDA regulations are not deemed applicable.

XVI – OTHER INFORMATION

ACGIH: American Conference of Governmental Industrial Hygienists
CFR: US Code of Federal Regulations
DOT: US Department of Transportation
IARC: International Agency for Research on Cancer
IDLH: Immediately Dangerous to Life and Health
NIOSH: National Institute for Occupational Safety and Health, US Department of Health and Human Services
NTP: National Toxicology Program
OSHA: Occupational Safety and Health Administration, US Department of Labor
PEL: Permissible Exposure Limit
SARA Title III: Title III of the Superfund Amendments and Reauthorization Act, 1986
TLV: Threshold Limit Value
TWA: Time-weighted Average
FDA: Food and Drug Administration

FOR FURTHER INFORMATION

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HOURS; 8 AM – 5 PM (EST)

DATE OF PREPARATION 5/08

NOTICE: Martin Marietta Materials believes that the information contained on this Material Safety Data Sheet is accurate. The suggested precautions and recommendations are based on recognized good work practices and experience as of the date of publication. They are not necessarily all-inclusive or fully adequate in every circumstance as not all use circumstances can be anticipated. Also, the suggestions should not be confused with nor followed in violation of applicable laws, regulation, rules or insurance requirement. However, product must not be used in a manner which could result in harm.

NO WARRANTY, EXPRESSED OR IMPLIED, OF MERCHANTABILITY, FITNESS FOR A PARTICULAR PURPOSE OR OTHERWISE IS MADE

MSDS 3600-002

Trade Name: **Epsom Salt, Magnesium Sulfate, U.S.P.**

Date Prepared: **07/24/06**

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1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

Product name: **Epsom Salt, Magnesium Sulfate, U.S.P.**
Product description: **Magnesium sulfate, heptahydrate**
Manufacturer: **PQ Corporation**
P. O. Box 840
Valley Forge, PA 19482 USA
Telephone: **610-651-4200**
In case of emergency call: **610-651-4200**
For transportation emergency
Call CHEMTREC: **800-424-9300**

2. COMPOSITION/INFORMATION ON INGREDIENTS

<i>Chemical and Common Name</i>	<i>CAS Registry Number</i>	<i>Wt. %</i>	<i>OSHA PEL</i>	<i>ACGIH TLV</i>
Magnesium sulfate, heptahydrate; Epsom salt	10034-99-8*	100%	Not Established	Not Established

* Under the Toxic Substances Control Act (TSCA), hydrates are considered as mixtures of their anhydrous salt and water. Accordingly, the CAS Numbers 7487-88-9, 7732-18-5 are used for purposes of TSCA.

3. HAZARDS IDENTIFICATION

Emergency Overview: **White or transparent crystalline odorless powder. Noncombustible. At very high temperatures, magnesium oxide, sulfur dioxide, and sulfur trioxide may be generated. Causes mild eye irritation.**

Eye contact: **Causes mild irritation to the eyes.**

Skin contact: **No known adverse effects.**

Inhalation: **Causes nausea, vomiting, abdominal cramps, and diarrhea.**

Ingestion: **Causes nausea, vomiting, abdominal cramps, and diarrhea.**

Chronic hazards: **No known chronic hazards. Not listed by NTP, IARC or OSHA as a carcinogen.**

Physical hazards: **Spilled material can be slippery.**

4. FIRST AID MEASURES

Eye: **In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Get medical attention if irritation persists.**

Skin: **Not applicable.**

Inhalation: **Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.**

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Ingestion: **If large quantities of this material are swallowed, call a physician immediately. Do NOT induce vomiting unless directed to do so by a physician. Never give anything by mouth to an unconscious person.**

5. FIRE FIGHTING MEASURES

Flammable limits: **This material is noncombustible.**

Extinguishing Media: **This material is compatible with all extinguishing media.**

Hazards to fire-fighters: **See Section 3 for information on hazards when this material is present in the area of a fire.**

Fire-fighting equipment: **The following protective equipment for fire fighters is recommended when this material is present in the area of a fire: chemical goggles, body-covering protective clothing, self-contained breathing apparatus.**

6. ACCIDENTAL RELEASE MEASURES

Personal protection: **Wear chemical goggles, See section 8.**

Environmental Hazards: **Sinks and mixes with water. No adverse effects known. Not a listed toxic chemical under SARA Title III, §313 40 CFR Part 372. Not a CERCLA Hazardous Substance under 40 CFR Part 302.**

Small spill cleanup: **Sweep, scoop or vacuum discharged material. Flush residue with water. Observe environmental regulations.**

Large spill cleanup: **Keep unnecessary people away; isolate hazard area and deny entry. Do not touch or walk through spilled material. Sweep, scoop or vacuum discharged material. Flush residue with water. Observe environmental regulations.**

CERCLA RQ: **There is no CERCLA Reportable Quantity for this material.**

7. HANDLING AND STORAGE

Handling: **Avoid breathing dust. Promptly clean up spills.**

Storage: **Keep containers closed. Protect from extremes of temperature and humidity during storage. Recommended storage conditions 68-110° F and 54-87% relative humidity.**

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Engineering controls: **Use with adequate ventilation. Safety shower and eyewash fountain should be within direct access.**

Respiratory protection: **Use a NIOSH-approved dust respirator where dust occurs. Observe OSHA regulations for respirator use (29 C.F.R. §1910.134)**

Skin protection: **Wear gloves if abrasion or irritation occurs.**

Eye protection: **Wear chemical goggles.**

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9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance: **Crystalline odorless powder.**
Color: **White or transparent.**
Odor: **Odorless.**
pH: **Approximately 6-7**
Specific gravity: **1.76 g/cm³, Bulk Density Approximately 1.05 g/cm³**
Solubility in water: **71g/100 ml at 20° C, 91g/100 ml at 40° C**

10. STABILITY AND REACTIVITY

Stability: **This material is stable under all conditions of use and storage.**
Conditions to avoid: **None.**
Materials to avoid: **Metal hydrides and other water reactive materials.**
Hazardous decomposition products: **At very high temperatures, magnesium oxide, sulfur dioxide, and sulfur trioxide may be generated.**

11. TOXICOLOGICAL INFORMATION

Acute Data: **When tested for primary irritation potential, this material caused mild eye irritation. RTECS reports Oral TDLo= 428 mg/kg in man 351 mg/kg in women**

12. ECOLOGICAL INFORMATION

Eco toxicity: **Data not available.**
Environmental Fate: **This material is not persistent in aquatic systems and does not contribute to BOD. It does not bioconcentrate up the food chain.**
Physical/Chemical: **Sinks and mixes with water.**

13. DISPOSAL CONSIDERATIONS

Classification: **Disposed material is not a hazardous waste.**
Disposal Method: **Landfill according to local, state, and federal regulations. Disposed material is not a RCRA Hazardous waste.**

14. TRANSPORT INFORMATION

DOT UN Status: **This material is not regulated hazardous material for transportation.**

15. REGULATORY INFORMATION

CERCLA: **No CERCLA Reportable Quantity has been established for this material.**

Trade Name: **Epsom Salt, Magnesium Sulfate, U.S.P.**

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SARA TITLE III:

Not an Extremely Hazardous Substance under §302. Not a Toxic Chemical under §313. Hazard Categories under §§311/312: Acute

TSCA:

All ingredients of this material are listed on the TSCA inventory.

FDA:

Magnesium sulfate is an FDA GRAS substance pursuant to 21 CFR 184.1443.

16. OTHER INFORMATION

Prepared by:

John G. Blumberg

Supersedes revision of:

03/07/05

THE INFORMATION ON THIS SAFETY DATA SHEET IS BELIEVED TO BE ACCURATE AND IT IS THE BEST INFORMATION AVAILABLE TO PQ CORPORATION THIS DOCUMENT IS INTENDED ONLY AS A GUIDE TO THE APPROPRIATE PRECAUTIONS FOR HANDLING A CHEMICAL BY A PERSON TRAINED IN CHEMICAL HANDLING. PQ CORPORATION MAKES NO WARRANTY OF MERCHANTABILITY OR ANY OTHER WARRANTY, EXPRESS OR IMPLIED WITH RESPECT TO SUCH INFORMATION OR THE PRODUCT TO WHICH IT RELATES, AND WE ASSUME NO LIABILITY RESULTING FROM THE USE OR HANDLING OF THE PRODUCT TO WHICH THIS SAFETY DATA SHEET RELATES. USERS AND HANDLERS OF THIS PRODUCT SHOULD MAKE THEIR OWN INVESTIGATIONS TO DETERMINE THE SUITABILITY OF THE INFORMATION PROVIDED HEREIN FOR THEIR OWN PURPOSES.



Material Safety Data Sheet

Hematite

MSDS Number 450-30

Section 1: Product and Company Information

Product Name(s) Hematite

Product Number(s)

Company Natural Pigments LLC
PO Box 112
Willits, CA 95490
United States of America

Technical Phone 707-459-9998

Fax 408-516-9442

Section 2: Composition / Information on Ingredients

Product Name Hematite is a natural mineral from Russia

Synonyms anhydrous iron oxide, English red, ferric oxide, Indian red, iron (III) oxide, iron sesquioxide, jeweler's rouge, Mars red, red iron oxide, red iron trioxide, red ochre, rouge, specular iron

Colour Index Pigment Red 101

Component Name	CAS No.	% Composition Range	OSHA PEL mg/m ³		ACGIH TLV mg/m ³		DFG-MAK mg/m ³	
			TWA	STEL	TWA	STEL	TWA	STEL
Chemical Formula								
Ferric Oxide, Iron Sesquioxide Fe ₂ O ₃	1309-37-1	Varies	10	N.E. ¹	5	N.E.	1.5 ²	N.E.
1) N.E. = None Established 2) Respirable fraction								

Section 3: Hazards Identification

Emergency Overview No unusual fire or spill hazard. Low health risk by inhalation.

Potential Health Effects

Eyes May cause mechanical irritation.

Skin None

Inhalation Low health risk by inhalation. Treat as a nuisance dust.

Oral LD₅₀ Greater than 10g/kg (rat)

Section 4: First Aid Measures

After Inhalation Remove to fresh air. If breathing is labored or stopped, give artificial respiration. Get immediate medical attention.

After Skin Contact	Wash area of skin with soap and water.
After Eye Contact	Flush eyes with plenty of water for at least 15 minutes. Seek medical attention if irritation develops or persists.
After Ingestion	If victim is conscious and alert, give large quantities of water to induce vomiting. Seek medical attention immediately.

Section 5: Fire Fighting Measures

Fire	Not considered to be a fire hazard. Not flammable.
Explosion	Not considered to be an explosion hazard.
Extinguishing Media	This material is not combustible and is not anticipated to react with commercially employed extinguishing media. Use appropriate extinguishing media for surrounding fire.

Section 6: Accidental Release Measures

Spill Procedures	Protect against identified hazards through use of prescribed personal protection equipment, proper work and hygiene practices. Limit foot and vehicular traffic to minimize mechanical agitation and dispersion. Employ a vacuum, equipped with HEPA (High Efficiency Particulate Air) filter, for clean-up of the spill material. If no vacuum is available, use a broom and shovel to collect excess powder in the area. Recover uncontaminated material for use. Vacuum or sweep remaining material keeping dust to a minimum. Residual material should then be cleared, utilizing the process of wet sweeping, to avoid dust generation.
Containment Techniques	This is a solid material and will not travel far from the spill location unless mechanically agitated.
Spill Response Equipment	The following equipment is recommended for spill response: <ul style="list-style-type: none"> • vacuum, equipped with a HEPA filter • broom, wet mop • dustpan, shovel, or scoop • bags, drums or sacks for collection
Personal Protective Equipment	All personnel should utilize the following protective equipment when performing spill response activities: <ul style="list-style-type: none"> • gloves (rubber or leather) • safety glasses or goggles • respiratory equipment as recommended in Section 8

Section 7: Handling and Storage

Storage	A moderately dry, well-ventilated area is considered adequate for handling and storage. Usual precautions for nuisance dust should be followed.
Handling	When handling this product, all personnel are directed to: <ul style="list-style-type: none"> • Wear all specified elements of PPE, as directed by this document, or under location specific requirements, whichever is more conservative. • Avoid creating dust, where possible.

Section 8: Exposure Controls / Personal Protection

Engineering Controls	Use with adequate ventilation to meet exposure limits listed in Section 2.
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Respiratory Protection Use NIOSH-approved dust respirator, if overexposure exists.

Skin Protection Leather or rubber gloves.

Eye/Face Protection Safety glasses, goggles or face shield are recommended.

Work Hygiene Practices

- To control potential exposures, avoid creating dust.
- Do not eat, drink, smoke, or perform other hand-to-mouth activities in product use or handling area.
- Wash thoroughly after handling this product.

Section 9: Physical and Chemical Properties

Earths are natural products. Technical data varies or are not measurable.

Physical State: Solid
Appearance Color: Red to reddish brown
Form: Powder

Odor Odorless

Section 10: Stability and Reactivity

Stability Stable under ordinary conditions of use and storage.

Hazardous Decomposition Products None

Hazardous Polymerization Products None

Incompatibilities Iron oxides are not compatible with hydrazine, calcium hypochlorite, performic acid and bromine pentafluoride.

Conditions to Avoid None

Section 11: Toxicological Information

Ingestion There are no known dangerous acute or chronic effects associated with the use of this product. The acute oral toxicity LD₅₀ (rat) for Fe₂O₃ is greater than 10g/kg (rat).

Skin No known dangerous acute or chronic effects.

Eye If dust intrudes into the eyes, a slight eye irritation can occur.

Section 12: Ecological information

No harmful effects known other than those associated with suspended inert solids in water.

Section 13: Disposal Considerations

Recommended Disposal Method Collect in containers, bags or covered dumpster boxes. Whatever cannot be saved for recovery or recycling should be managed in an appropriate and approved waste disposal facility. Processing, use or contamination of this product may change the waste management options. State and local disposal regulations may differ from federal disposal regulations. Dispose of container and unused contents in accordance with federal, state and local requirements.

Section 14: Transportation Information

U.S. DOT Not regulated for domestic transport by land, rail or air. Enter the proper freight classification on the shipping documents, "MSDS Number" and "Product Name" for shipping purposes.

Canadian TDG Hazard Class and PIN Not regulated

Section 15: Regulatory Information

SARA 313 Title III Section 311/312 Hazardous Categories: None
Section 313 Toxic Chemicals: None

OSHA Status This product is not considered hazardous.

TSCA Status Components of this product are listed in the TSCA Inventory.

California Proposition 65 Not listed

CERCLA Reportable Quantity None

International Regulations Canadian Ingredient Disclosure List: Components are listed.
Canadian WHMIS: This material is not a controlled substance under WHMIS.
European Community: This material is not subject to classification according to EEC Directive 67/548/EEC.

Section 16: Other Information

Date 1 August 2007

The above information is believed to be correct but does not purport to be all inclusive and shall be used only as a guide. The information in this document is based on the present state of our knowledge and is applicable to the product with regard to appropriate safety precautions. It does not represent any guarantee of the properties of the product. Natural Pigments, LLC shall not be held liable for any damage resulting from handling or from contact with the above product.
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