In-Situ Chemical Reduction and Oxidation of VOCs in Groundwater

Groundwater Treatability Studies

NASA
Marshall Space Flight Center
Huntsville, Alabama
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Located within Redstone Arsenal.

Marshall listed on the NPL (as a Superfund Site) - May 31, 1994.

65-70 sites are Marshall’s responsibility.
Marshall Center
Quick Facts

- Originally used for manufacturing munitions during WWII.
- 1949: RSA mission to develop rocketry and guided missile systems.
- 1960: Civilian rocketry and mission activities transferred to NASA.
  - Mercury through Apollo Program
  - Space Shuttle Main Engine Development
  - X-33 Program
  - International Space Station
Site Conceptual Model (Epikarst and Karst System)

**Contaminant Migration Pathway**

Vertical movement within preferential paths, given sufficient driving force. Lateral movement limited due to conditions.

Lateral movement largely to downgradient wetlands and surface waters. Some lateral and vertical interchange within groundwater systems possible. Contaminants subject to natural attenuation.

**Primary Flow Direction & Thickness**

- Residual (Clays, with lenses of Silts, Gravel and Sand)
- Rubble Zone (Gravelly, Cherty Clays)
- Fusscumbia Limestone (Karst Most Prevalent in Upper 50 Feet)
Marshall Center CERCLA Groundwater Strategy

- Identify Potential Exposure Locations
- Eliminate / Reduce Rubble Zone Source Areas.
- Monitor to Verify Effectiveness of Treatment Actions.
- Monitor to Verify Continued Compliance With ARARs
- Contingency Plan for Spring (GW discharge points) in Case of Risk Exceedance
Treatability Studies

- Treatability Results Will be Used to Prepare a Feasibility Study (late 2002)

- Proposed In-Situ Groundwater Treatment Technologies Include
  
  - Chemical Reduction (FeroxSM)
  - Chemical Oxidation (Fenton Reagents, Permanganate, and Persulfate)
  - Thermal (Dynamic Underground Stripping, Six-Phase Heating)
Source Area 2
Site Description

- **SA-2 (MSFC-005)** is a pond that received TCE from engine cleaning operations.

- **TCE** is no longer used at the site; no continuing source.

Dissolved phase TCE and DCE reported in the groundwater.
Source Area 2 Groundwater and Subsurface Characteristics

UXO is potentially buried beneath the surface

The highest reported TCE concentration in the rubble zone groundwater is 72,800 μg/L

TCE was not detected in the vadose zone clays

Depth to bedrock varies from 22 ft to 34 ft

Rubble Zone Groundwater Characteristics
  Groundwater velocity is 0.14 ft/day
  Groundwater is aerobic (DO 5-7 mg/l)
  Groundwater ORP is 130 mV
Source Area 2 Pilot Test Approach

Pneumatic Fracturing of the rubble zone and soil capillary zone

ZVI (Ferox™) injections in accessible TCE “Hot Spots”

Create a ZVI permeable reactive zone downgradient from the “Hot Spots”
Source Area 2 FeroxSM Chemistry

Catalyzed reaction involving TCE, Ethene, Chloride, Hydrogen, Hydroxyl Ion, and Water.

Note: Equation not stoichiometrically balanced.
Source Area 2 Ferox$^\text{SM}$ Injections

Nitrogen and Fracture Trailer

Iron Slurry
Source Area 2 Ferox™ Injections (continued)

Injector System Set Up

360° Injection Nozzle and Packer
Source Area 2 FeroxSM Injections (continued)

Gravity Feed Injection

Atomized Injection

Note: Flow rate 5 gpm for both injections
Source Area 2 Pilot Test Results

- 11,000 lbs of ZVI was injected

- An Iron to TCE ratio of 200:1 was established (from bench scale study)

- Radius of influence was 20 to 60 ft

- Iron impregnated the subsurface treatment zone

- Average fracture initiation pressure was 120 psi

- Average fracture propagation pressure was 60 psi
Source Area 2 Pilot Test Results - TCE Reduction, cis-1,2-DCE and Chloride Ion Formation

SA-2 Source Well VOC and Cl Concentrations vs Time

- Injections
- K = 0.011 / day
- 99% removal in 455 days (predicted)
Source Area 2 Pilot Test Results - Aquifer Reducing Conditions

MW00-213 In-Situ Troll Data

Note: Well was purged on 2/16/01 and Sampled on 2/27/01

Ph, DO, and Temperature

Date

8-Feb 13-Feb 18-Feb 23-Feb 28-Feb 5-Mar 10-Mar 15-Mar 20-Mar

ORP (mV)

-500 -400 -300 -200 -100 0 100 200

• pH

■ DO (mg/l)

° Temp (°C)

x ORP (mV)
Source Area 12 Pilot Test

SA-12 - Degreasing Operations Conducted

TCE concentrations up to 500,000 µg/l

Unexpected DNAPL Conditions

Rubble Zone Groundwater Characteristics
Groundwater velocity is 0.04 ft/day
Groundwater is aerobic (DO 5-7 mg/l)
Groundwater ORP around 130 mV
Source Area 12 Pilot Test Approach

- Pneumatic Fracturing of the rubble and vadose zone and ZVI injections
- Create a ZVI reactive zone 10 ft by 50 ft in the "Hot Spot" to treat the TCE

- Monitoring Well 2-inches
- Monitoring Well Cluster - Upper and Lower Rubble Zone
A total of 4,500 lbs of iron was injected in the subsurface

An Iron to TCE ratio of 100:1 was established

Radius of ZVI influence was about 20 ft

Iron impregnated the subsurface soil

Average fracture initiation pressure was 130 psi

Average fracture propagation pressure was 60 psi
Source Area 12 Pilot Test Results - TCE Reduction

The graph shows the TCE (ug/l) and Cl (mg/l) levels from August 1999 to April 2001. There are three lines on the graph:

- MW00-305 TCE (solid square line)
- CW03-082 TCE (solid circle line)
- MW00-305Cl (crossed line)

Injections are indicated on the graph.
Source Area 12 Pilot Test Results - Aquifer Reducing Conditions

In-Situ Troll Data MW00-305

Note: Well was purged and sampled on 2/28/01

- pH
- DO (mg/L)
- Temp (°C)
- ORP (mV)

Date
Feb-01 Feb-01 Feb-01 Feb-01 Feb-01 Mar-01 Mar-01 Mar-01 Mar-01
Source Area 12 TCE DNAPL Bench Scale Results

SA-12 TCE Mass vs. Time in Microbatch Reactor

- Control (no ZVI)
- 0.2 g ZVI
- 1 g ZVI
- 5 g ZVI
- 2 g ZVI

Day

Mass (µg)
Source Area 12 TCE DNAPL Bench Scale Results (continued)

Comparison Between Rate Constants vs Weight Ratios for Contaminants Partitioned to the Groundwater and Soil Phase

- Adsorbed TCE
- Dissolved TCE

Iron Ratio

Kinetic Rate Constar
Source Area 13 Pilot Test

SA-13 Characteristics

- SA-13 is located in the Northwest portion of MSFC
- Depth to bedrock ranges from 33 to 37 feet
- TCE concentrations up to 300,000 µg/l

Pilot Test Approach

- Establish a 30 ft by 30 ft treatment area
- Inject Fenton's reagents in the subsurface to oxidize TCE in vadose and rubble zone
Source Area 13 Pilot Test Results - TCE Concentration

TCE vs. Time in the Deep Rubble Zone

TCE Concentration (ppb)

Date

May-99 Jul-99 Aug-99 Oct-99 Dec-99 Jan-00 Mar-00 May-00 Jun-00 Aug-00

CW03-011
CW03-021
CW03-031
CW03-041
CW03-051
MW00-304
Source Area 13 Pilot Test Results - TCE Concentration

TCE vs Time in the Shallow Rubble Zone

Date

TCE Concentration (ppb)

May-99 Jul-99 Aug-99 Oct-99 Dec-99 Jan-00 Mar-00 May-00 Jun-00 Aug-00

CW03-012
CW03-022
CW03-032
CW03-052
Questions & Discussion