


# Recent Field Applications of Activated Persulfate Including Petroleum Sites

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**FMC Corporation**

KLOZUR™
Power. Stability. Versatility.

# Presentation Outline

- Brief Introduction to Persulfate Chemistry
- Activated Persulfate Treatment of:
  - BTEX
  - GRO
  - #6 Fuel Oil NAPL
  - MTBE

# Acknowledgements


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# Introduction to Persulfate Chemistry

## *Persulfate Oxidation Principles:*

**Persulfate Anion:** $E^0 = 2.12$ v

$$S_2O_8^{-2} + 2H^+ + 2e^- \rightarrow 2HSO_4^{-1}$$

**+ Activation**

**Sulfate-free radical:**

$$SO_4^{\bullet -} + e^- \rightarrow SO_4^{-2} \qquad E^0 = \sim 2.6 \text{ v}$$

- Activation Produces a Radical Which is More Powerful and Kinetically Fast
- Proper Activation Method is Based on Contaminant, Site Lithology, and Hydrogeology

# Introduction to Persulfate Chemistry

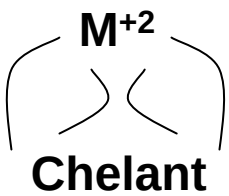
## Four Primary Methods to Activate Klozur® Persulfate

1. **Heat**

   $S_2O_8^{-2}$ + heat ➔ 2 $SO_4$•

   - kinetically fast
   - capable of destroying wide range of contaminants
   - 35 – 45 C

2. **Metal Chelates**




   - slower kinetics; longer lived
   - capable of destroying chlorinated ethenes, BTEX, PAHs, MTBE
   - target minimum 150 ppm F

3. **Hydrogen Peroxide**

   $S_2O_8^{-2}$ + $H_2O_2$ ➔ 2$SO_4$• + 2OH•

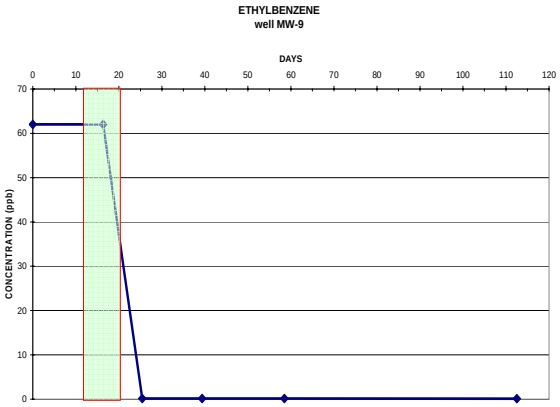
   - kinetically fast
   - capable of destroying wide range of organics
   - typical concentration: 5 moles peroxide / mole persulfate

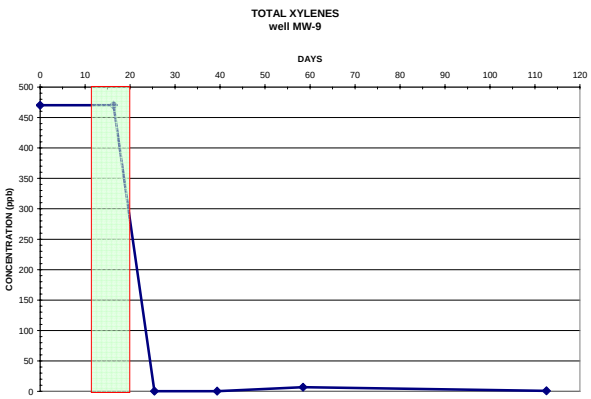
4. **High pH**

   - kinetically fast
   - capable of destroying wide range of organics
   - pH > 10.5

# *Ethylbenzene & Xylenes; chelated iron activation*

**Site:** former maintenance yard in Florida
**Contaminants:** ethylbenzene (130 ppb) and xylenes (1000 ppb)
**History:** one year of bioremediation prior to ISCO




## Application

**1800 gal of 20% Klozur® soln**
**297 gal of 2.5% Fe-citrate soln**
**Injected over 3 days**

## Conclusions

**GW contaminant concentration dropped below LMDLs within 7 days. Klozur® persulfate activated by Fe(II)-citrate effectively treated ethylbenzene and xylenes to meet the clean-up goals for this site with a single injection event targeting a limited impacted area.**

# Pipeline Release - BTEX;  Calcium Peroxide activation


**Site Information:**
- former pipeline release
- ave benzene in groundwater  is 4.7 ppm

Data courtesy of:

ORIN REMEDIATION TECHNOLOGIES

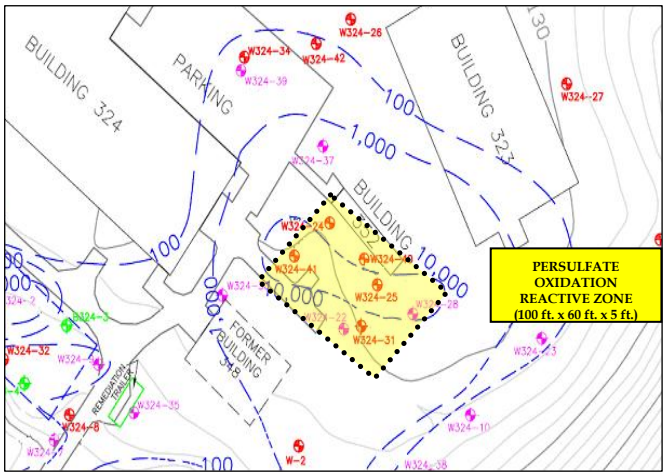
**Calcium Peroxide activation:**
- high pH activation (> 11)
- peroxide activation  Calcium peroxide generates hydrogen peroxide
- subsequent oxygen release over 9 months supports aerobic bioremediation
- generated sulfate supports long term anaerobic bioremediation

**Field Implementation:**
- 60,000 $ft^3$ plume treated
- 25 direct push points:  each received 50 gallons of Klozur persulfate + 100 gallons of PermeOx Plus
- 5 days of application time

**Results:**
- 4 months after application, benzene dropped from 4700 ppb to 3 ppb
- estimated cost savings over dig / haul and other chemistries: $28,000 - $50,000

# GRO former tank farm; Hydrogen Peroxide activation

Data courtesy of




TOTAL BTEX BASELINE CONCENTRATION ISOPLETH MAP WITH PERSULFATE OXIDATION REACTIVE ZONE.

## Site Information:

- Fort Belvoir, VA.
- former fuel tank farm with GRO, DRO
- silty sands with cobble and gravel deposits

## Field Implementation:

- 5,225 lbs of Klozur persulfate
- 1000 lb of 17.5% peroxide
- addition over a 5 day period

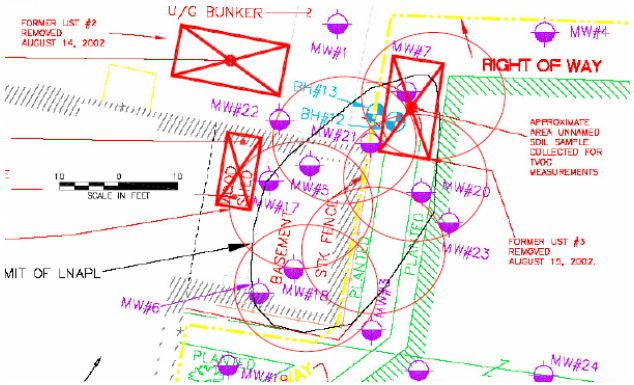
| | Sample Date | Benzene | Toluene | Ethylbenzene | Xylenes | Total BTEX |
|---|---|---|---|---|---|---|
| W324-22 | 9/27/2007 | <2.0 | <2.0 | 3.5 | 4.9 | 8.4 |
| | 9/7/2007 | <1.0 | <1.0 | 5.9 | 1.0 | 6.9 |
| | *Persulfate Oxidation Event (8-26-07)* | | | | | |
| | **4/2/1999** | **7,820** | **6,080** | **1,930** | **8,260** | **24,090** |
| | -- | -- | -- | -- | -- | -- |
| | -- | -- | -- | -- | -- | -- |

Example of results from one well

## Results:

- 1 month results indicate 88 – 99% reduction in total BTEX
- larger scale injection planned

# #6 Fuel Oil NAPL; hydrogen peroxide activation




Data courtesy of

MECX

## Site Information:

- historic building in MA
- leaking UST
- ave TPH in ground is 13,750 mg / kg
- NAPL thickness: 1 – 30 inches
- total NAPL: 2000 gallons
- target clean-up goal: < ½ NAPL on site

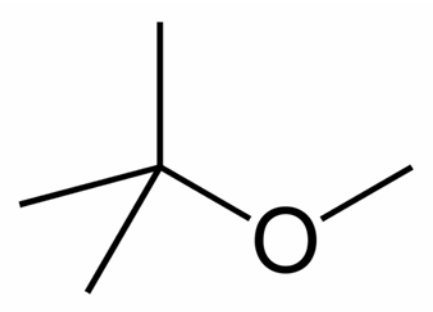
## Field Implementation:

- 2 weeks of hydrogen peroxide activated persulfate application
- sub-surface vapor extraction system

| Parameter | Pre-ISCO (Baseline) | Post-ISCO Value |
|---|---|---|
| Estimated NAPL volume | 2,000 gallons | 600 gallons |
| Average NAPL thickness | 1 to 30 inches | < ½-inch |
| Average TPH concentration in soils | 13,750 mg/Kg | 8,500 mg/KG |

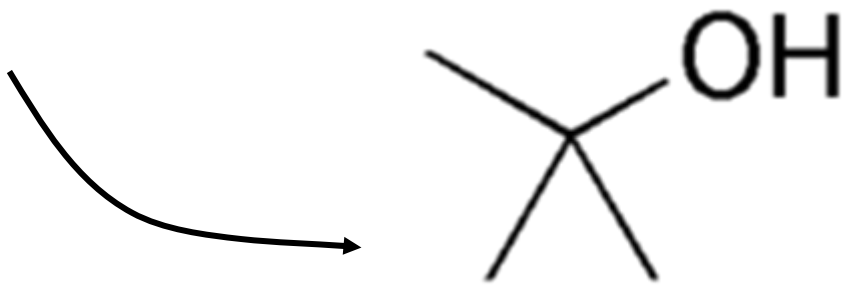
**Results a couple of weeks after implementation: site closure with deed restrictions**

# MTBE

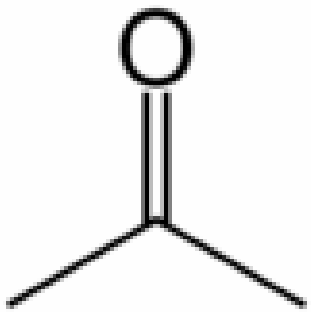



Structure of MTBE

- gasoline additive to enhance fuel burning
- over 20% of US drinking water supply contaminated by MTBE

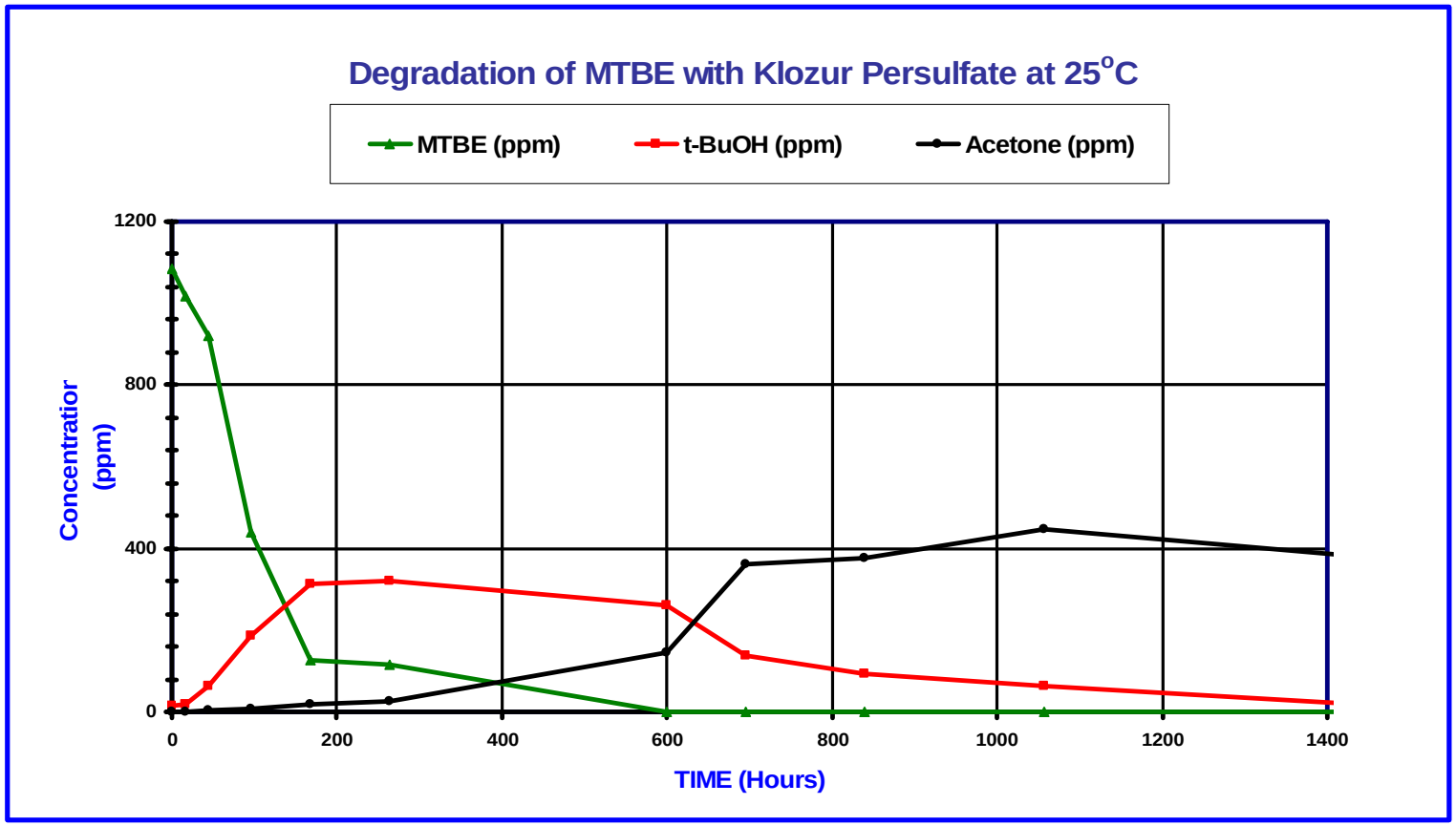



Structure of tert-butyl alcohol



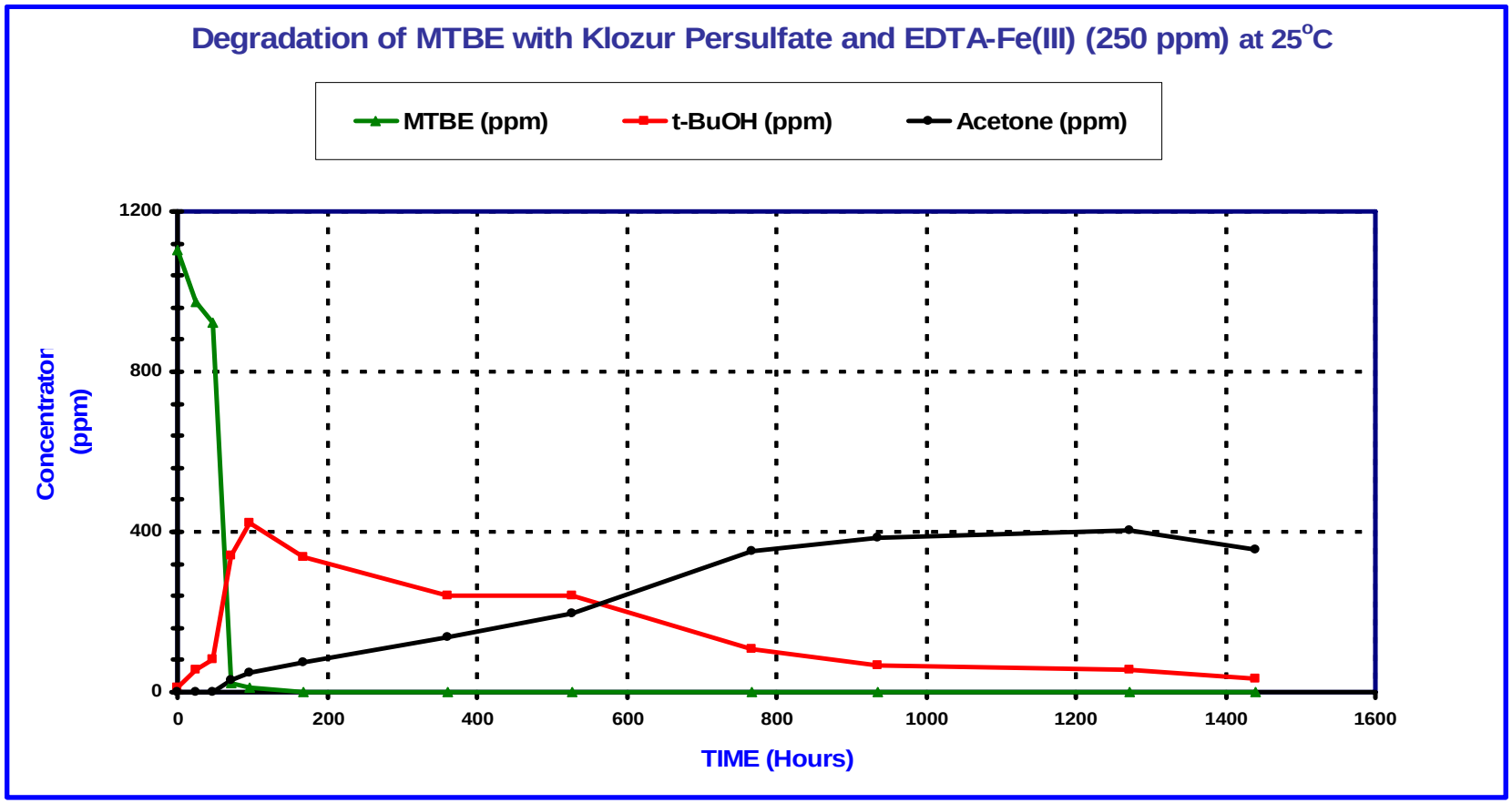

Structure of acetone

# MTBE



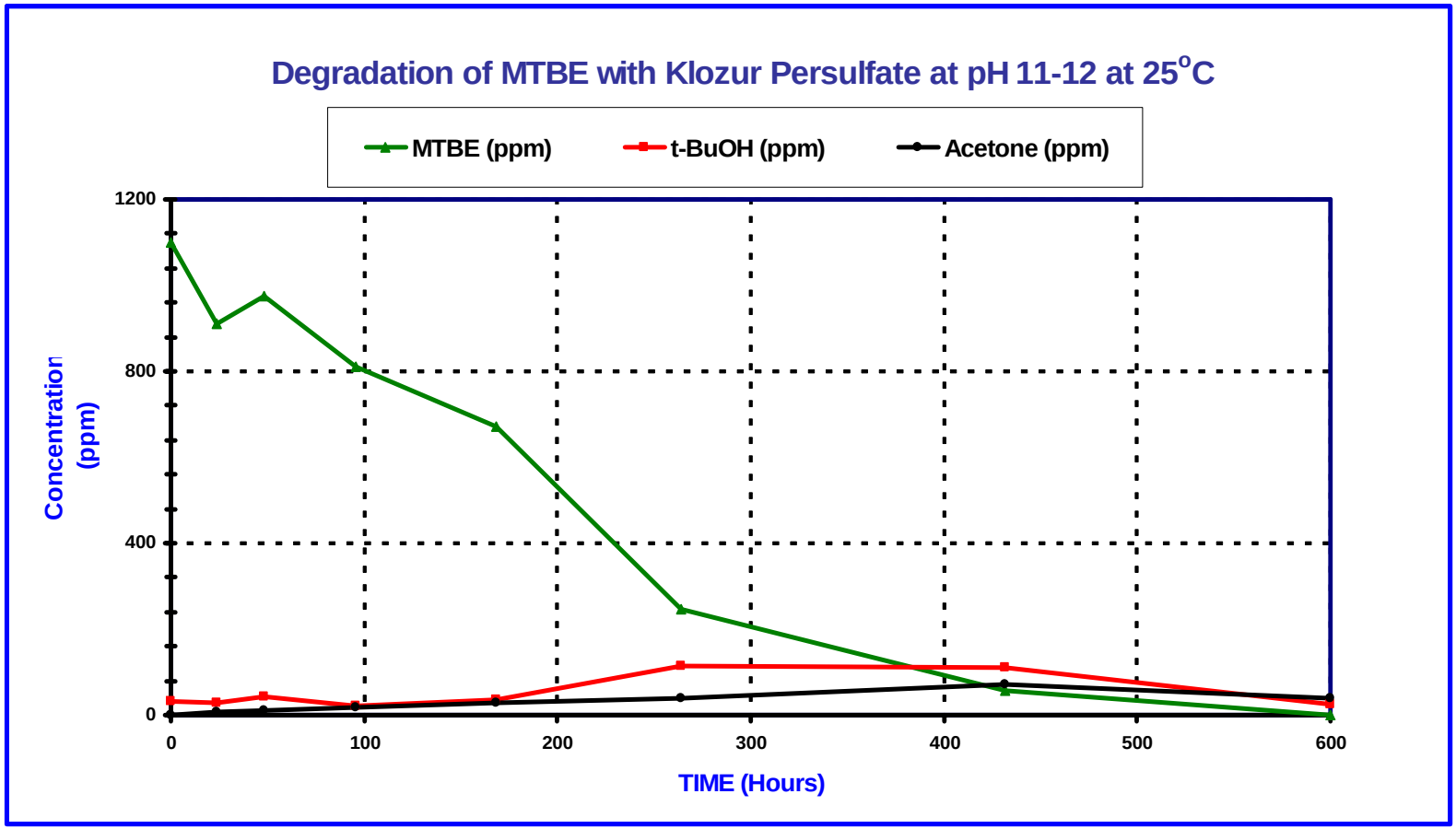

- **un-activated persulfate oxidation of MTBE can lead to significant formation of TBA and acetone**

# MTBE




- **FeEDTA persulfate rapidly destroys MTBE, but has much slower kinetics on TBA and acetone**

# MTBE




- **High pH activated persulfate oxidation of MTBE does not generate significant quantities of TBA and acetone.**

# Benzene / Naphthalene / MTBE; heat / high pH activation

## *Petroleum Hydrocarbons; Heat / Alkaline Activation*

Redox Tech, LLC

| Location | Contaminant (ug/L) | Pre-Injection Concentration (ug/L) | Post-Injection Concentration | % Reduction |
|---|---|---|---|---|
| Blackstone, VA | Benzene | 1,600 | 78 | 95.1% |
| Blackstone, VA | MTBE | 1,300 | 360 | 72.3% |
| Clayton, DE | Benzene | 519 | 7.4 | 98.5% |
| Clayton, DE | MTBE | 16,100 | 233 | 98.5% |

| Location | Contaminant (ug/L) | Pre-Injection Concentration (ug/L) | Post-Injection Concentration | % Reduction |
|---|---|---|---|---|
| Hagaman, NY | Xylene | 2,778 | 22 | 99.2% |
| Lexington, NC | Naphthalene | > 1,000,000 | < 1,000 | 99.9% |

# Summary

- Activated persulfate is effective at treating a range of TPH related compounds
  - BTEX
  - PAHs (ex: naphthalene, chrysene, anthracene, pyrene, etc)
  - GRO
  - DRO
  - ORO
  - Long chain alkanes
  - Fuel oxygenates: MTBE, TBA
- The choice of activation method is dependent on target contaminant and site lithology / hydrogolgy
- Activated persulfate can also effectively treat chlorinated solvents (ex: PCE, TCE, TCA, methylene chloride)

# Questions ?

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