Addressing Residual LNAPL Using Klozur Persulfate

PRESENTED BY:

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SOIL & GROUNDWATER
REMEDIATION

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ENVIRONMENTAL SOLUTIONS

Overview

Part I – Chemistry Overview

Klozur® Persulfate Chemistry

Residual LNAPL Treatment and Considerations

Klozur® Persulfate Dosing Considerations

Part 2 – Injection Approach

Free Product Removal (FPR) Strategy

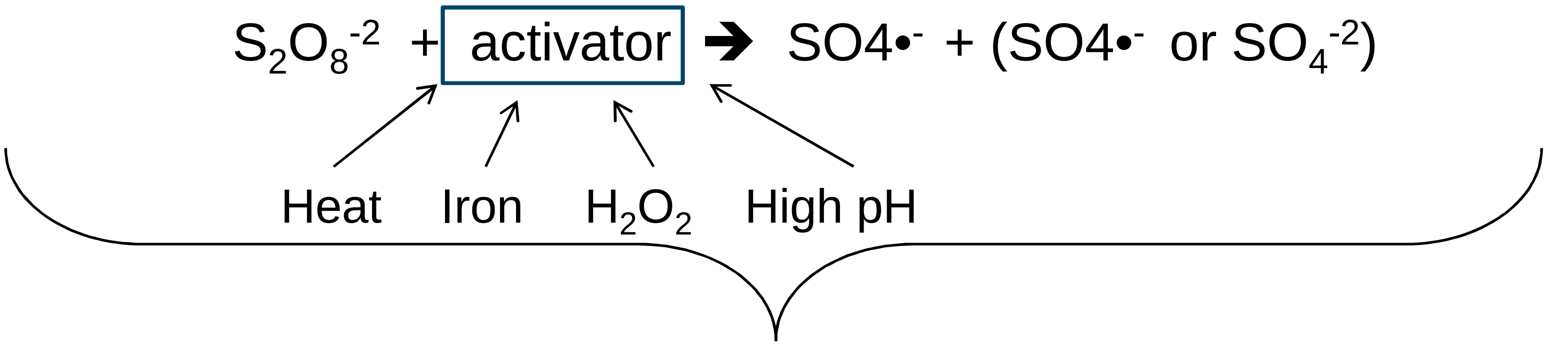
Flocculation by Klozur® and engineered Calcium Peroxide (PermeOx Plus)

Case Studies

Klozur® Persulfate Chemistry

Klozur® Activated Persulfate

- produces a radical which is powerful and very good kinetically
- **FMC always recommends using an activator**
- proper activation method is based on contaminant, site lithology, and hydrogeology



$$S_2O_8^{-2} + \boxed{\text{activator}} \rightarrow SO4^{\bullet -} + (SO4^{\bullet -} \text{ or } SO_4^{-2})$$

Heat Iron H_2O_2 High pH

Purchase of FMC's Klozur® Persulfate includes rights to practice the inventions covered by the patents in the purchase price of the product.

Sustainable Solution: Utilizes Hydroelectric Power

Klozur® Persulfate Chemistry

$$\underbrace{\text{Contaminants + Oxidant + Soil}}_{\text{Stoichiometry}} \rightarrow \underbrace{CO_2}_{\text{Mineralization}} + \underbrace{\text{oxidized soil components}}_{\text{Soil Oxidant Demand}} + \text{stable intermediates}$$

Stoichiometric Demand

- Contaminant demand is based on 2-electron transfer of persulfate anion

Decomposition

- Demand can be dependent upon activation chemistry

Soil Oxidant Demand (SOD)

- SOD arises from reactions with naturally occurring soil organics and reduced metals
- Average SOD = Can range from .5 to 3.0 g persulfate / kg soil, but will be site dependent

Note: It is important to account for SOD, or the oxidant will be under-dosed and will not meet the contaminant demand

Residual LNAPL Treatment - Key Data

Distribution

- GW and Soil, horizontal and vertical

Compounds

- Much more than just BTEX & SOD

What’s the driver?

- LNAPL itself?
- GW concentrations?
- Both or something else?
- Overall – Targeting a % removal or destruction goal

Klozur® Persulfate Dosing Considerations

Target Suitable Fraction of Residual LNAPL Mass

- % Reduction Needed » Remove residual LNAPL, target contaminant concentration, etc?

Identify Injection Approach

- Scenario 1 – high concentration, low volume injection (20 – 30 wt%)
- Scenario 2 – low concentration, higher volume injection (< 5 wt%)

Consider Multiple Injections if Required

Stoichiometric v Practical Loading

- Loading estimates are often based on 100% destruction
- Practical implementation plan/design

Free Product Removal (FPR) Strategy

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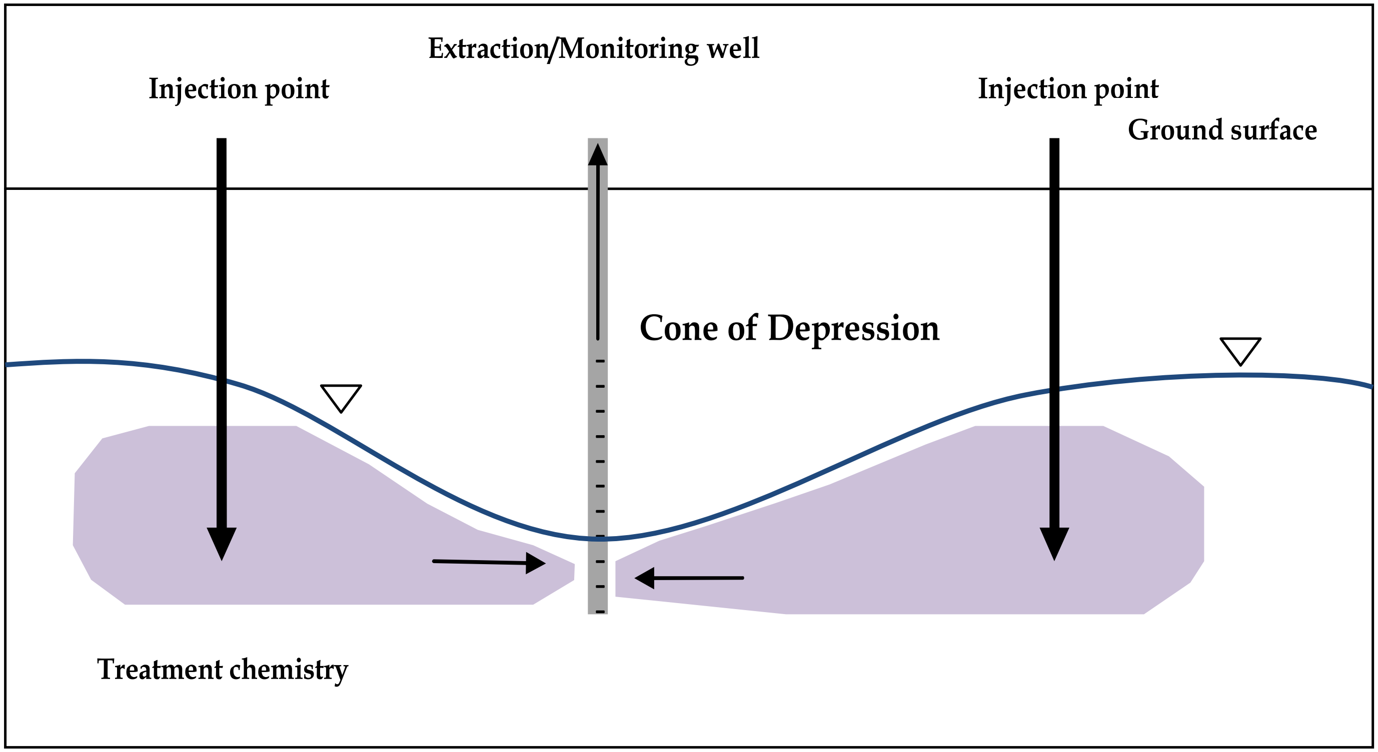
November 29, 2013

Extraction – In Conjunction with Injection

- Treatment chemistry mobilizes adsorbed contaminants
- Facilitates removal of contaminated groundwater and/or NAPL
- Less demand on the oxidant
- Assists in treatment chemistry distribution
- Hydraulic control

Example of Cone of Depression

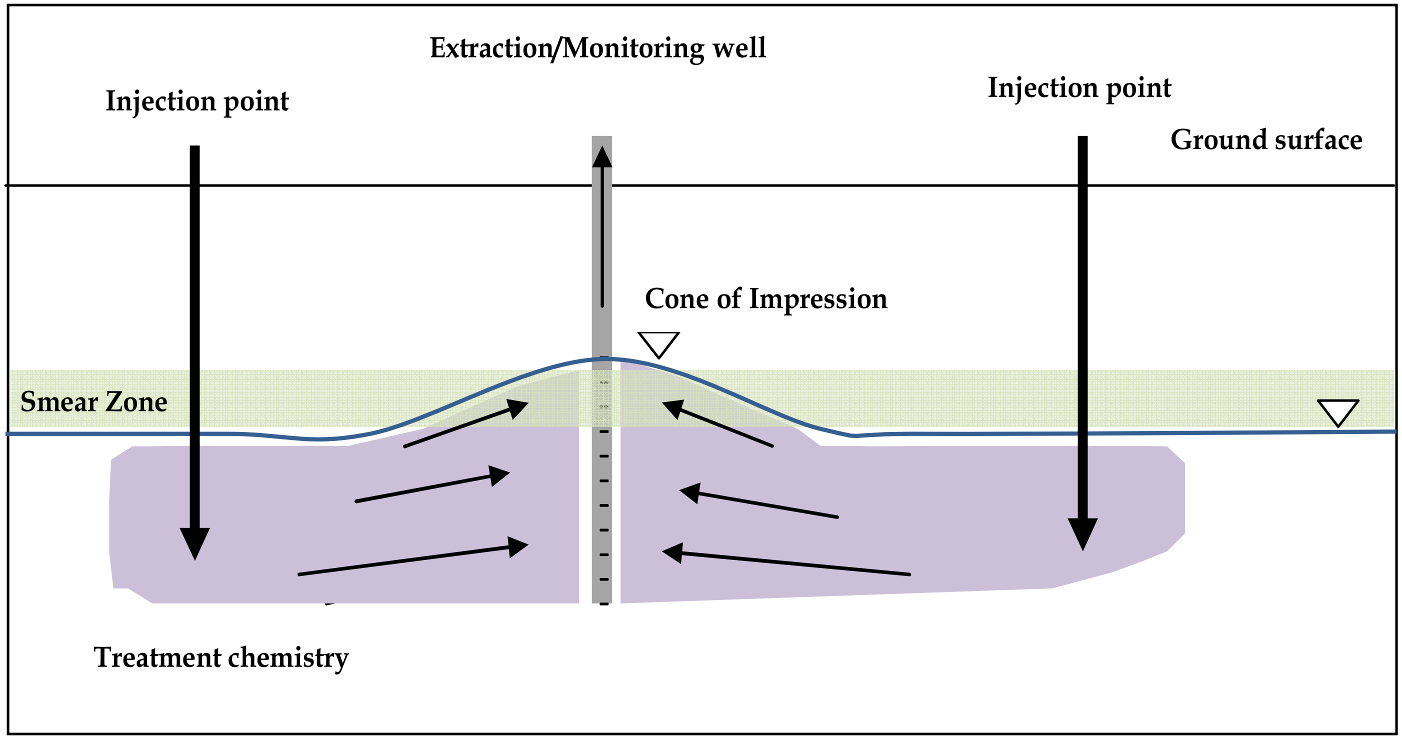
Injection and Extraction Cross Section



→ Hydraulic gradient ▽ Water table

Example of Cone of Impression

Injection and extraction cross section

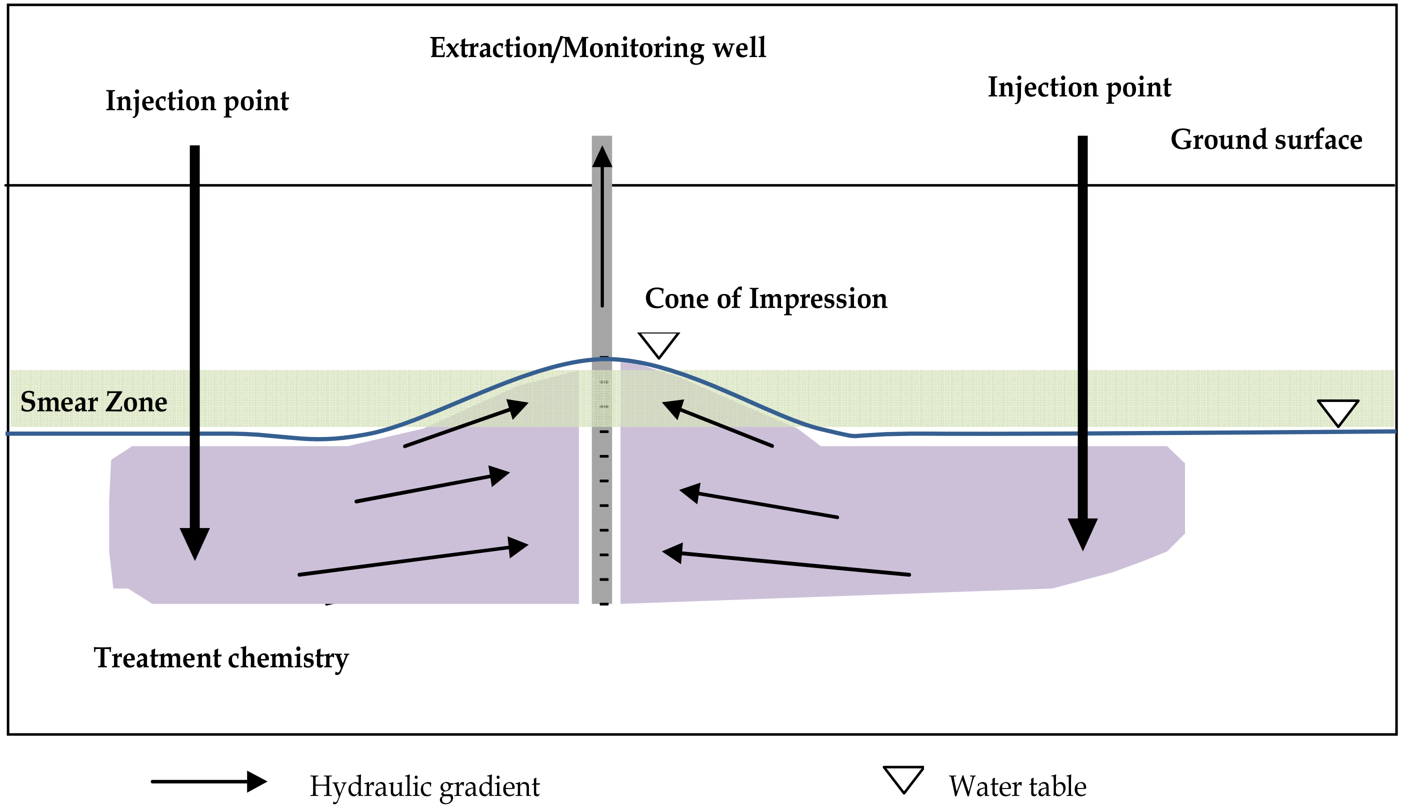


→ Hydraulic gradient

▽ Water table

Enhanced Product Recovery

Injection and extraction cross section



Extraction/Monitoring well

Injection point

Injection point

Ground surface

Cone of Impression

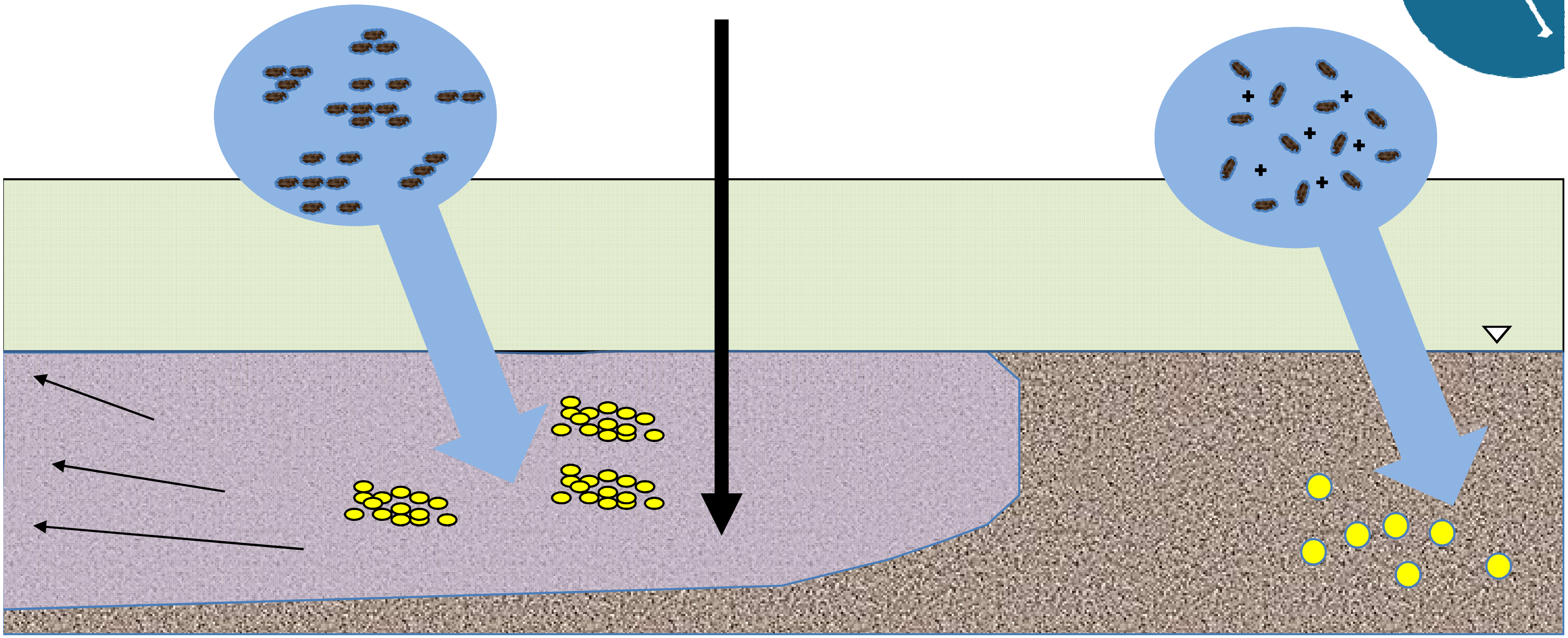
Smear Zone

Treatment chemistry

→ Hydraulic gradient

▽ Water table

Flocculated and Dispersed Particles



- ➢Clay and Silt particles change in the presence of cations
  - •Changing surface area for treatment chemistry contact
  - •Aids in “flushing” effect, and enhanced recovery

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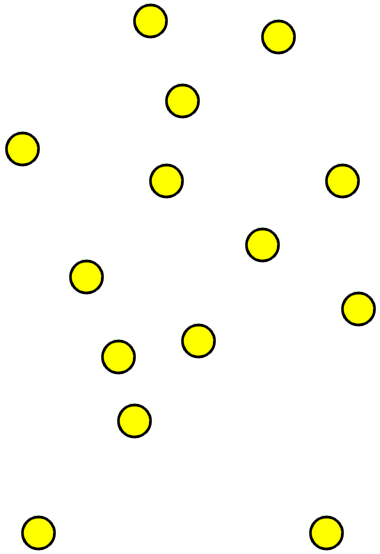
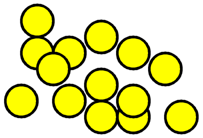
Clay and slit particles can be unattached to one another (*dispersed*) or clumped together (*flocculated*) in aggregates.

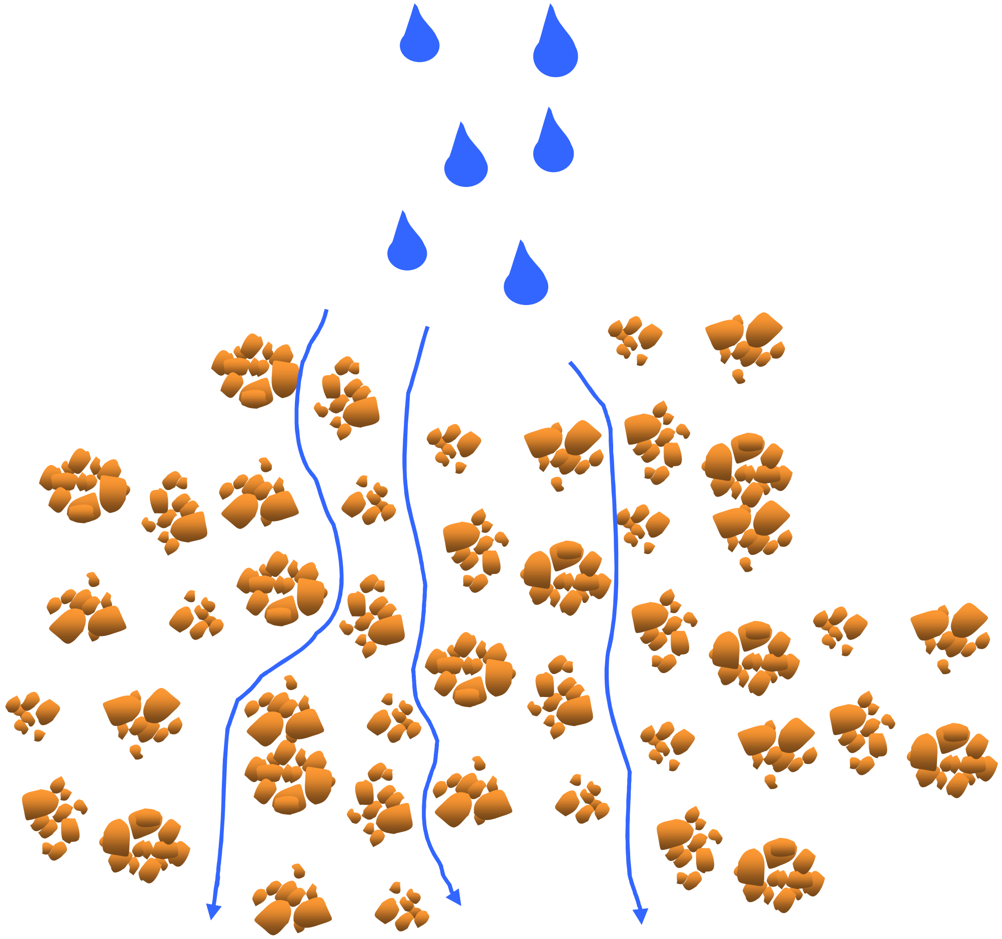
Dispersed Particles



Flocculated Particles



Flocculation is important because it allows contaminants and reagents to move more freely through the subsurface during the injection process.



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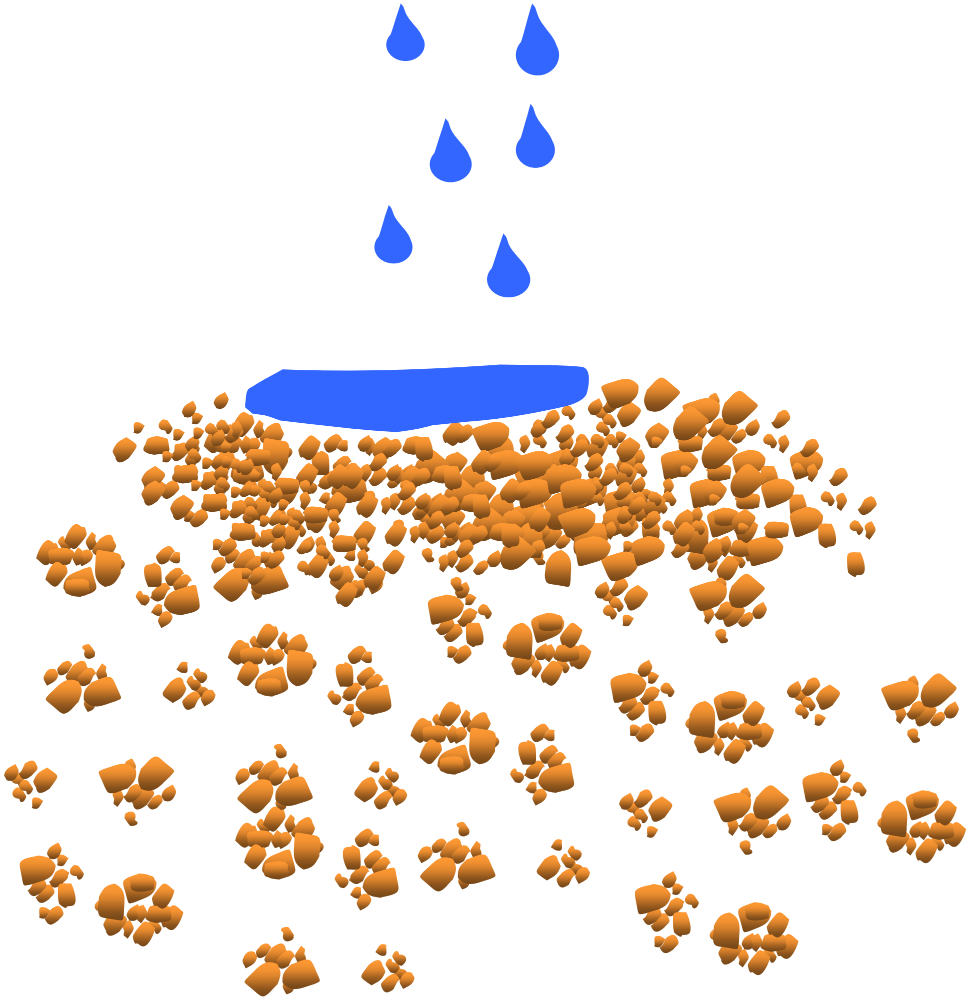
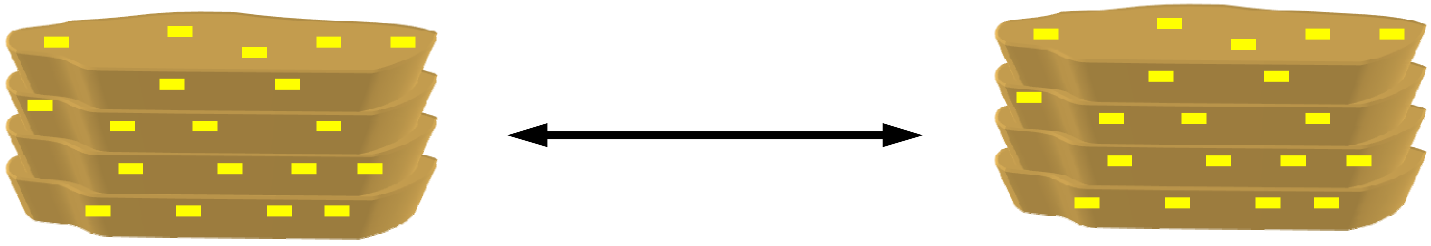
Dispersed clays and slits plug soil pores and impede flow through the sub surface.



Most clayey slit particles have a negative electrical charge. Like charges repel, so clay particles repel one another.

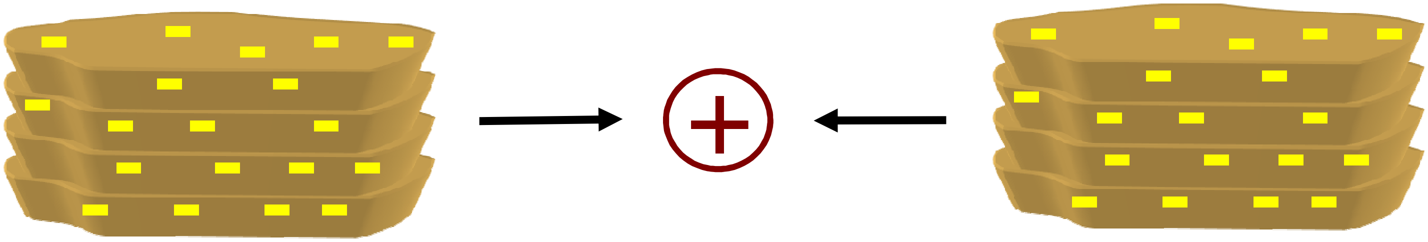


Negatively charged
clay particle

Negatively charged
clay particle

A cation is a positively charged molecule. Common soil cations include sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), and calcium (Ca^{2+}).

Cations can make clay particles stick together (flocculate).



Negatively charged clay particle

Negatively charged clay particle

Flocculating Cations

- We can divide cations into two categories
  - Poor flocculators
    - Sodium
  - Good flocculators
    - Calcium
    - Magnesium

Ion		Relative Flocculating Power
Sodium	Na^+	1.0
Potassium	K^+	1.7
Magnesium	Mg^{2+}	27.0
Calcium	Ca^{2+}	43.0

Sumner and Naidu, 1998

Enhanced Product Recovery

- Sodium persulfate oxidizes soil organics and LNAPL
    - Oxidation weakens bond between LNAPL and soil
- Caustic soda acts like a surfactant
    - Flushing effect mobilizes additional LNAPL
- Treatment chemistry flocculate soil particles
    - Increases treatment chemistry influence
- Mobilized product is recovered by vacuum extraction

Case Study

Active Gas Station Bamberg, South Carolina

In-Situ Chemical Oxidation w/ Vacuum Extraction

Free Product Removal

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General Information

Active Gas Station – Bamberg, South Carolina

- **Soil**: Clayey sand
- **Depth of contamination**: 8-16 ft bgs
- **Area:** Approximately 3000 sq feet
- **Contaminants**: 0.53 feet of Mobile LNAPL
- **Oxidant injected**: 15% Klozur® Sodium Persulfate activated with PermeOx Plus®
- **Number of injection points**: 34
- **Number of days of injecting**: 2

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Site Pictures

Site Pictures

Project Results

- 5.3 inches of LNAPL removed
- No free product returned with decreasing dissolve phase
- **Site Status**: No Further Action/Closed

Stoichiometric Loading based on oxidant demand (pounds)	Implementation cost utilizing Stoichiometric Demand chemical loading	ORIN's chemical loading strategy (pounds)	Implementation cost utilizing ORIN's chemical loading	Cost Savings
26,101	$141,000.00	7,295	$53,280.00	$87,720.00

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Case Study

Active Gas Station
Muscatine, Iowa

In-Situ Chemical Oxidation w/ Vacuum Extraction
Free Product Removal

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General Information

Active Gas Station – Muscatine, Iowa

- **Soil**: Silty Sand
- **Depth of contamination**: 9-15 ft bgs or 14-20 ft bgs depending on depth to groundwater
- **Area:** Approximately 6500 sq feet
- **Contaminants**: BTEX and 7.4 inches of LNAPL
- **Oxidant injected**: 17-20% Klozur® Sodium Persulfate activated with PermeOx Plus®
- **Number of injection points**: 51
- **Number of days of injecting**: 3

Site Pictures

Project Results

- 7.4 inches of LNAPL removed
- No free product returned
- **Site Status**: No Further Action/Closed

Stoichiometric Loading based on oxidant demand (pounds)	Implementation cost utilizing Stoichiometric Demand chemical loading	ORIN's chemical loading strategy (pounds)	Implementation cost utilizing ORIN's chemical loading	Cost Savings
28,462	$203,996.00	7,119	$74,220.00	$129,776.00

Case Study

Active Gas Station
Davidson, Michigan

In-Situ Chemical Oxidation w/ Vacuum Extraction

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General Information

Active Gas Station – Davidson, Michigan

- **Soil**: Clay and Silty Clay
- **Depth of contamination**: 4-8 ft bgs
- **Area:** Approximately 10,000 sq feet
- **Contaminants**: BTEX(LNAPL desorbed during injection activities)
- **Oxidant injected**: 17-20% Klozur® Sodium Persulfate activated with PermeOx Plus®
- **Number of injection points**: 47
- **Number of days of injecting**: 4

Site Pictures

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Site Pictures

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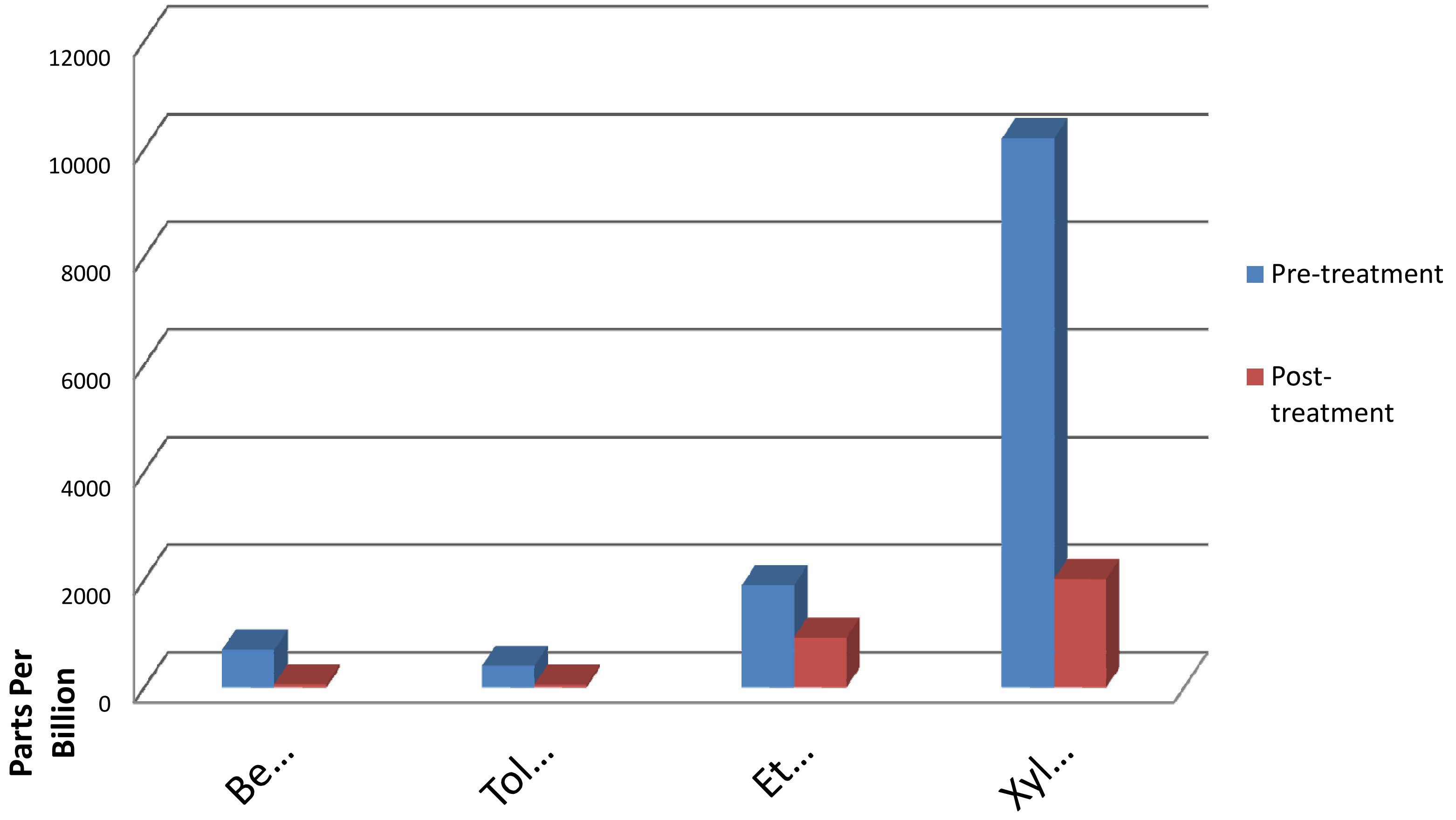
Groundwater Analytical Results

Most Contaminated Monitoring



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Project Results

- 8 inches of LNAPL removed
- No free product returned
- **Site Status**: No Further Action/Closed

Stoichiometric Loading based on oxidant demand (pounds)	Implementation cost utilizing Stoichiometric Demand chemical loading	ORIN's chemical loading strategy (pounds)	Implementation cost utilizing ORIN's chemical loading	Cost Savings
114,766	$475,000.00	4,500	$46,500.00	$428,500.00

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Case Study

Former Industrial Facility
Butler, Pennsylvania

In-Situ Chemical Oxidation w/ Vacuum Extraction
Free Product Removal

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General Information

Former Industrial Facility- Butler, Pennsylvania

- **Soil**: Clayey sand and gravel
- **Depth of contamination**: 6 to 10 ft bgs
- **Area:** Approximately 5500 sq feet
- **Contaminants**: BTEX, Waste Paint and 18 inches of LNAPL
- **Oxidant injected**: 18% Klozur® Sodium Persulfate activated with PermeOx Plus®
- **Number of injection points**: 30 drilled injection wells and 25 DPT locations
- **Number of days of injecting**: 3.5

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Site Picture

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Project Results

- 1.9 feet of LNAPL removed
- No free product returned
- **Site Status**: Applying for no further action

Stoichiometric Loading based on oxidant demand (pounds)	Implementation cost utilizing Stoichiometric Demand chemical loading	ORIN's chemical loading strategy (pounds)	Implementation cost utilizing ORIN's chemical loading	Cost Savings
220,007	$813,550.00	32,518	$206,325.00	$607,225.00

Any Questions?

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