

Extended Release Potassium Persulfate: Laboratory and Field Results

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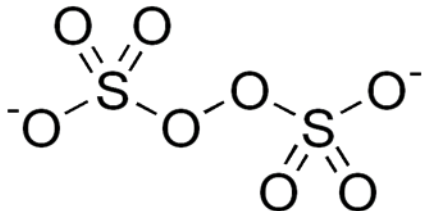
Presentation Outline

- Types of Persulfate
 - Batch tests
 - Column tests
 - Field Pilot
- Klozur KP
- Conclusions



Persulfates

- Klozur SP
 - Environmental grade sodium persulfate
- Klozur KP
 - Environmental grade potassium persulfate



Key Persulfate Characteristics:

- A strong oxidant
- Applicable across a broad range of organic contaminants
- Extended subsurface lifetime (weeks to months)
- Little to no heat or gas evolution
- Activation results in the formation of radicals

Klozur KP vs Klozur SP

- Different characteristics equals different opportunities
- Primary differences to sodium persulfate
 - Solubility
 - K⁺ vs. Na⁺

| Temperature (°C) | Klozur SP | | Klozur KP | |
|---------------------|-----------|-----|-----------|-----|
| | wt% | g/L | wt% | g/L |
| 0 | 36.5 | 480 | 1.6 | 17 |
| 10 | 40.1 | 540 | 2.6 | 29 |
| 20 | 41.8 | 570 | 4.5 | 47 |
| 25 | 42.3 | 580 | 5.7 | 59 |

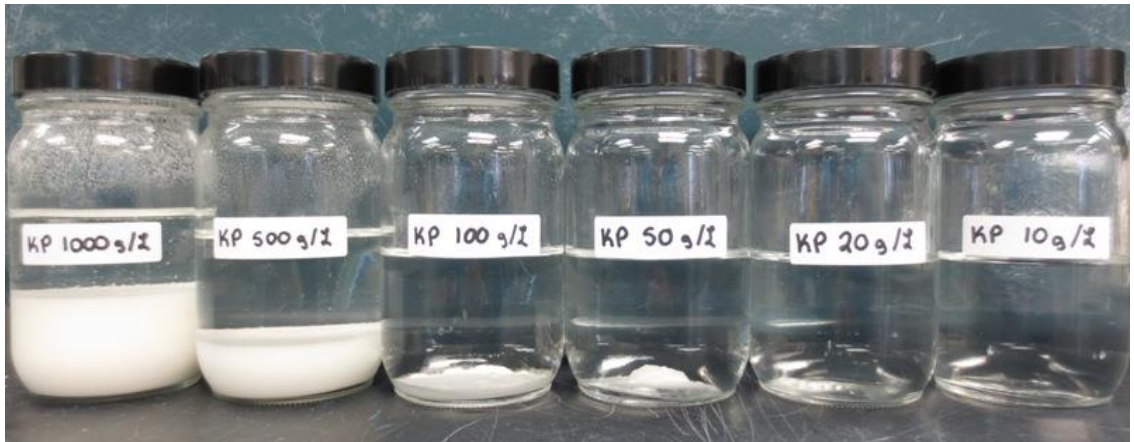
| Characteristic | SP | KP |
|---------------------------|---|--|
| Formula | Na ₂ S ₂ O ₈ | K ₂ S ₂ O ₈ |
| Molecular Weight | 238.1 | 270.3 |
| Crystal density (g/cc) | 2.59 | 2.48 |
| Color | White | White |
| Odor | None | None |
| Loose bulk density (g/cc) | 1.12 | 1.30 |

Potassium Persulfate: New Opportunities

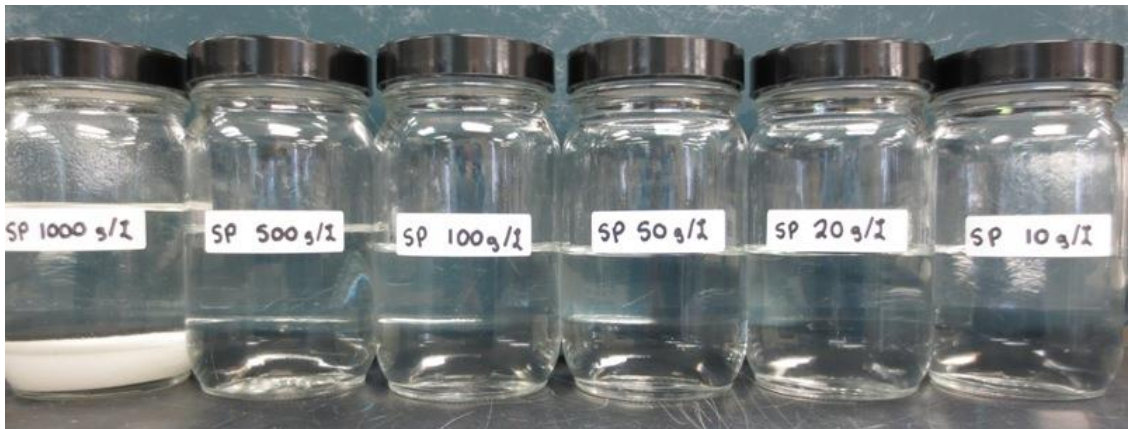
- Extended persistence of Klozur KP can help address some of the previous challenges and limitations:
 - Tight soils / clays – matrix diffusion
 - Permeable reactive barrier applications
 - Diffusive aqueous phase contaminants (plumes, aqueous phase contaminants, etc)

Solubility Limited Release Static System

Reactors at $\sim 20^{\circ}\text{C}$
Klozur KP Solubility
= 47 g/L

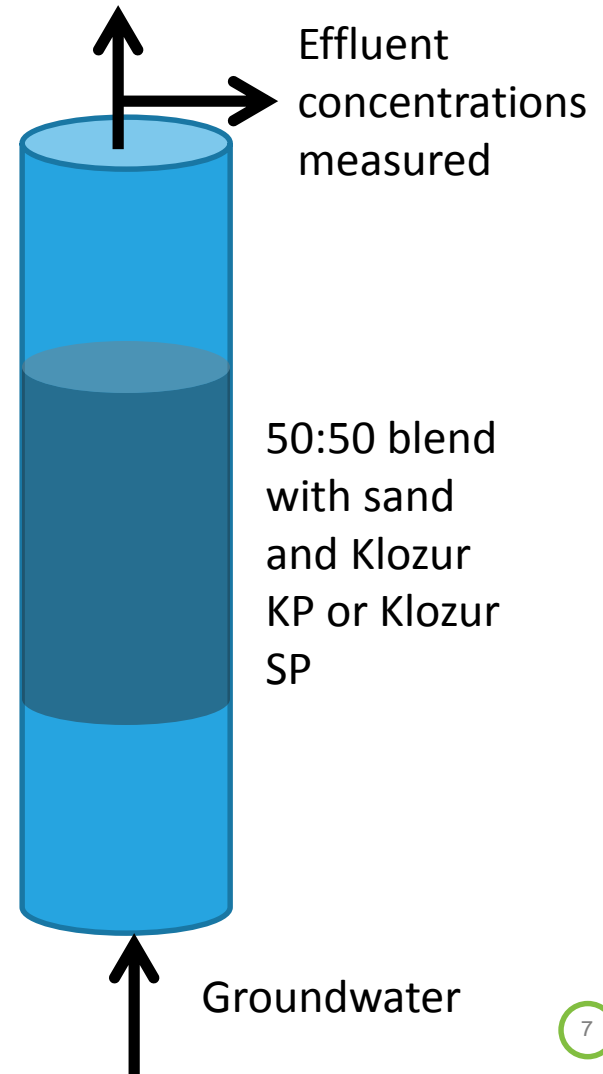


Reactors at $\sim 20^{\circ}\text{C}$
Klozur SP Solubility
= 570 g/L



Solubility Limited Release Dynamic System

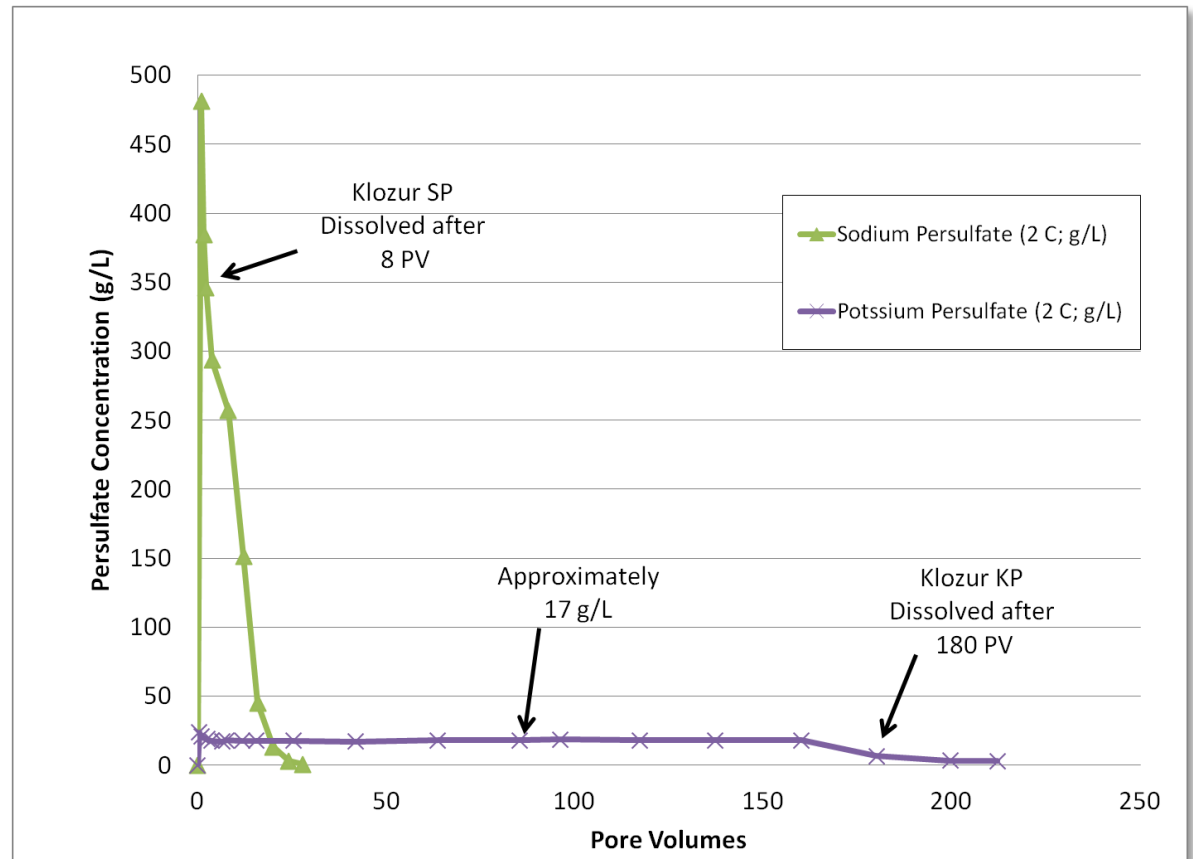
- Column Study:
 - 12 inch columns
 - 6 inch section of 50:50 blend of sand and either Klozur KP or Klozur SP
 - Targeting 300 g of oxidant
 - 3 inch sand above and below
 - Four columns
 - 2 °C :
 - Klozur SP
 - Klozur KP
 - 20 °C
 - Klozur SP
 - Klozur KP



Column Study (2°C)

Effluent Persulfate Concentration

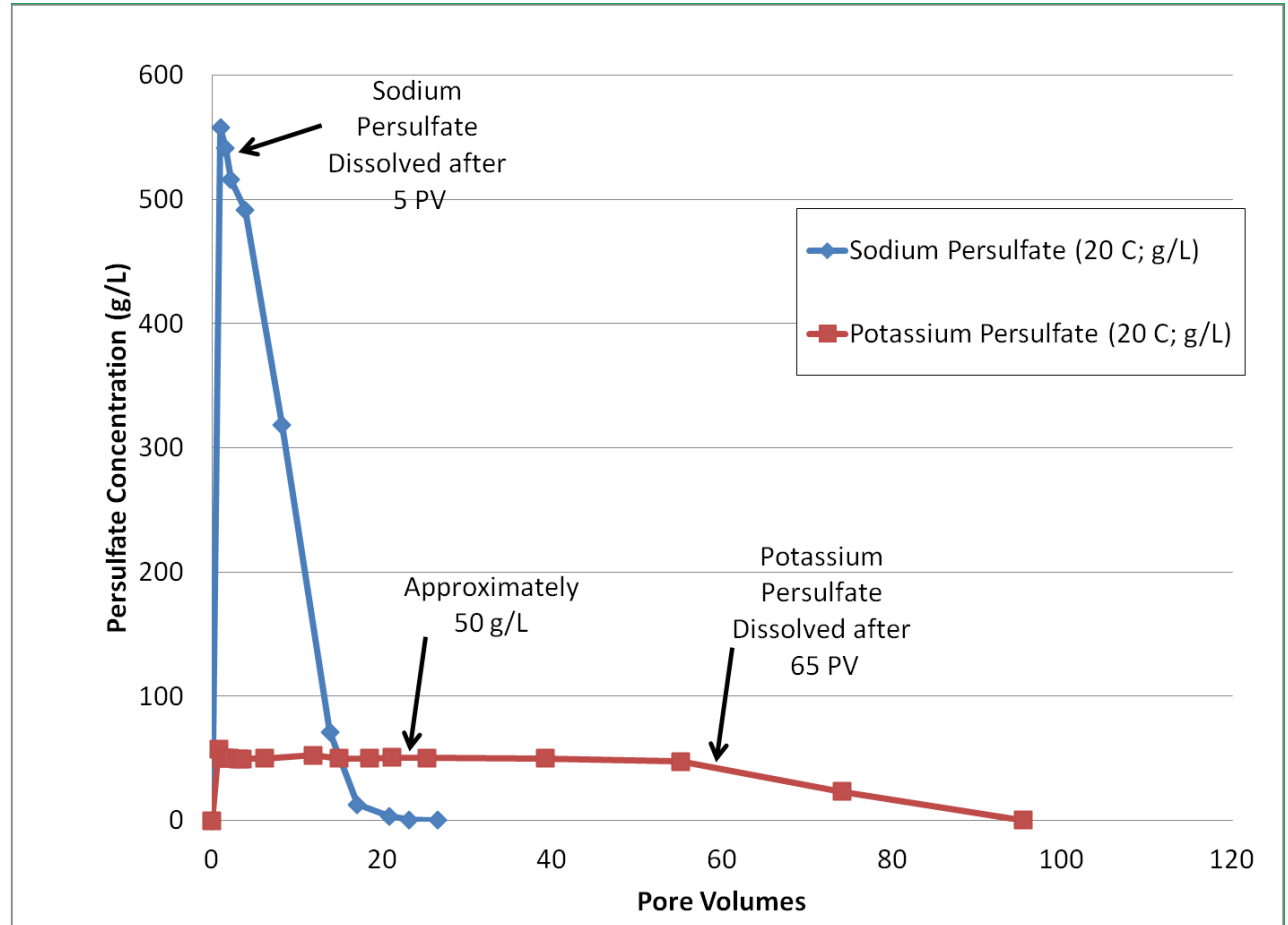
- Dissolution of Persulfate
 - 2 °C
- SP
 - Peak at theoretical maximum
- KP
 - Sustained at theoretical maximum



Column Study (20°C)

Effluent Persulfate Concentration

- Dissolution of Persulfate
 - 20-25 °C
- Klozur SP
 - Peak at theoretical maximum
- Klozur KP
 - Sustained at theoretical maximum



Dissolution Study Key Conclusions

- Klozur KP maintained theoretical maximum concentration for most of study
- Rate of release of Klozur KP linear with groundwater flux (pore volumes)
- Key variables for determining longevity of solubility limited release:
 - Ideal:
 - Mass of KP present
 - Volume of groundwater contacted
 - Groundwater flow velocity or flux
 - Temperature
 - Site factors:
 - Target and non-target demand
 - Decomposition

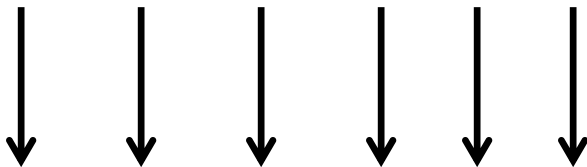
Conceptual Permeable Reactive Barrier

- Permeable Reactive Barrier (PRB)
- Conceptual Design of Gate
 - 20 m wide, 3 m high, and 1 m deep
 - 43,500 Kg of Klozur KP
 - 15% ePorosity

Conceptual Dissolution Only Persistence of the Extended Release KP

| | | Conceptual Klozur KP Persistence (years) | | | | | |
|-------------------------------------|-----|--|-----|-----|-----|-----|----|
| | | Temp (°C) | 5 | 10 | 15 | 20 | 25 |
| | | Solubility (g/L) | 22 | 29 | 37 | 47 | 59 |
| Groundwater Seepage Velocity (m/yr) | 3 | 73 | 56 | 44 | 34 | 27 | |
| | 10 | 22 | 17 | 13 | 10 | 8.2 | |
| | 20 | 11 | 8.3 | 6.5 | 5.1 | 4.1 | |
| | 30 | 7.3 | 5.6 | 4.4 | 3.4 | 2.7 | |
| | 60 | 3.7 | 2.8 | 2.2 | 1.7 | 1.4 | |
| | 150 | 1.5 | 1.1 | 0.9 | 0.7 | 0.5 | |

Groundwater Flow



KP PRB

Does not consider potential "site" factors

Activation of Persulfate

Sodium Persulfate:

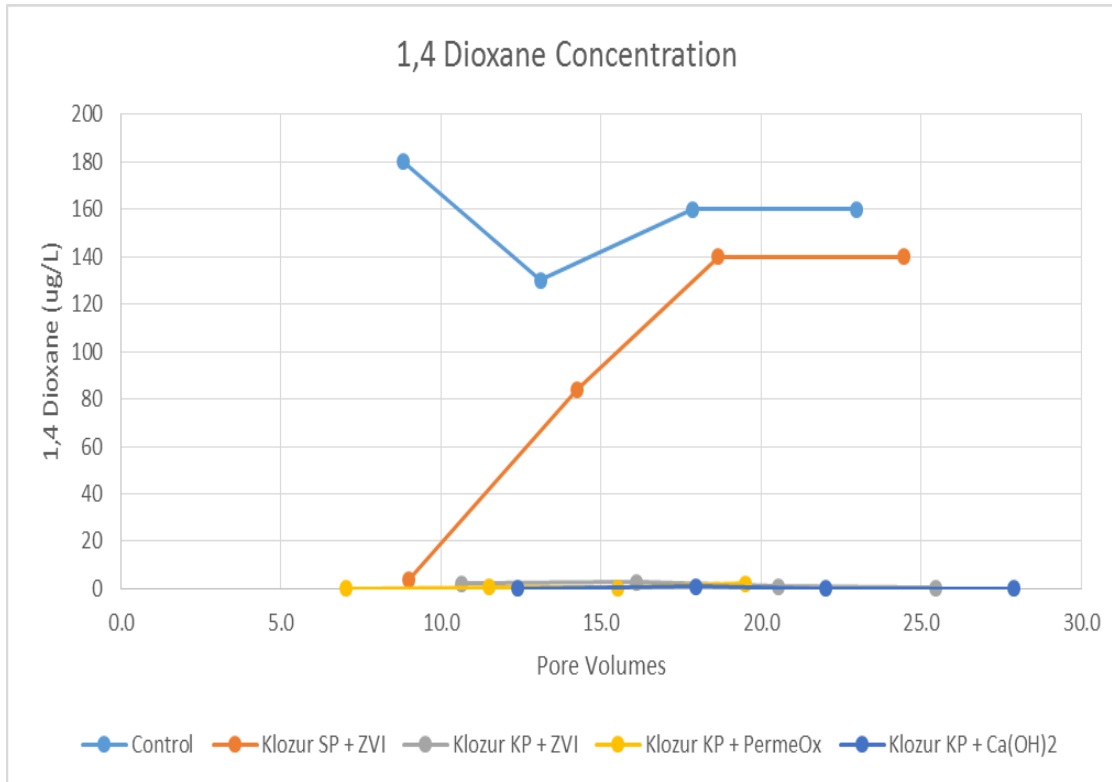
- Aqueous phase oxidant – aqueous phase activators
 - NaOH (alkaline)
 - Fe:Chelate
 - Hydrogen peroxide
 - Heat

Potassium Persulfate:

- Solid/extended release oxidant – **Solid/extended release activators**
 - Hydrated lime- Ca(OH)_2 (alkaline)
 - Zero Valent Iron (ZVI)
 - Separate trench (down gradient)
 - PermeOx Ultra (alkaline)

Purchase of Klozur persulfate includes with it the grant of a limited license under PeroxyChem's patents covering the use of Klozur persulfate for environmental applications at no additional cost to the buyer

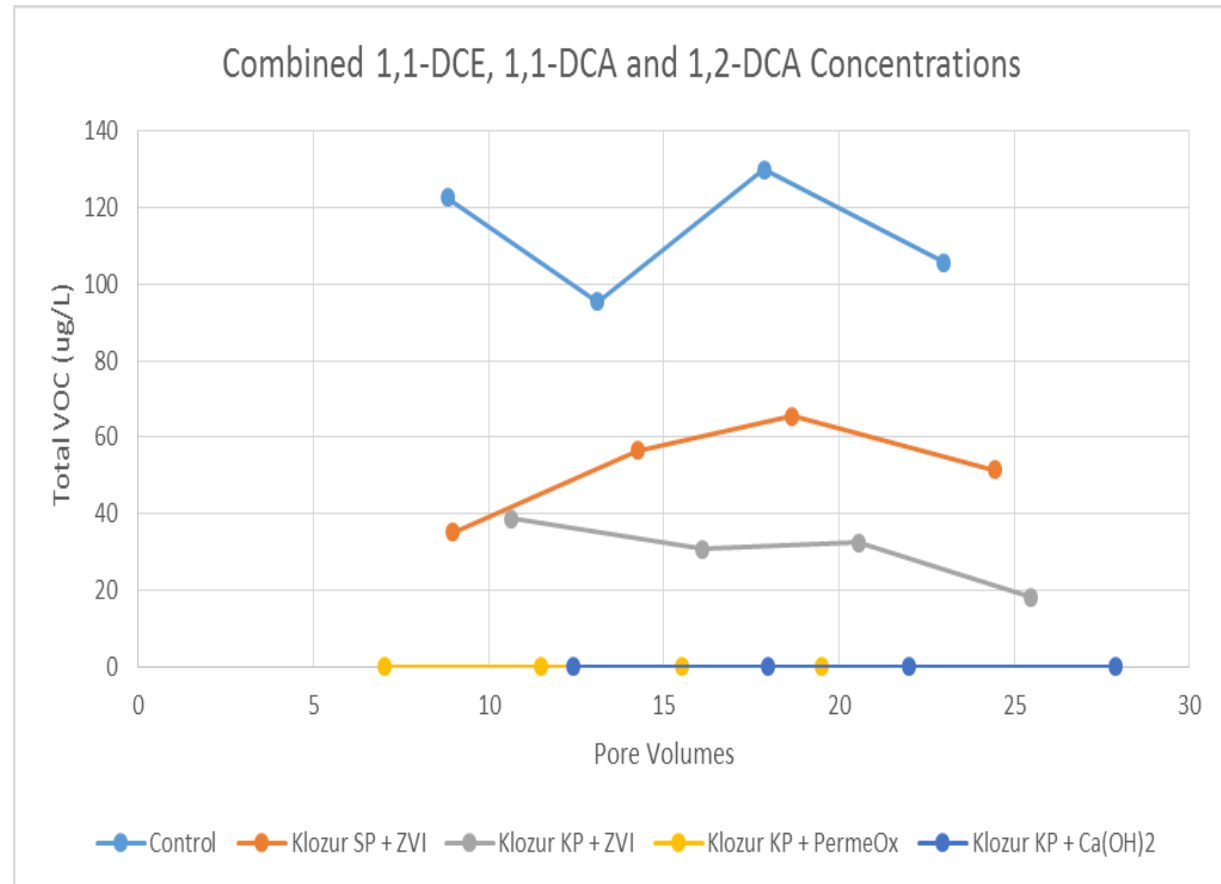
Treatment of 1,4-Dioxane



- All systems with KP treated 1,4-Dioxane to ND
- SP had breakthrough
- ZVI and hydrated lime lasted the longest

Treatment of CVOCs

- Alkaline activated KP treat cVOCs to ND
- ZVI activated KP-~75% treatment
- SP with ZVI- ~50% treatment



Case Study



Courtesy of Riskcom and Toterra

- Former industrial sites in Germany
- Former drum area
- Contaminants: cVOCs, Naphthalene and BTEX
- Contaminants mainly in low permeable sandstone up to 12 m bgs
- Pump & treat not practical and not possible for excavation
- Preferred approach was hydraulically placed ISCO technology

Case Study

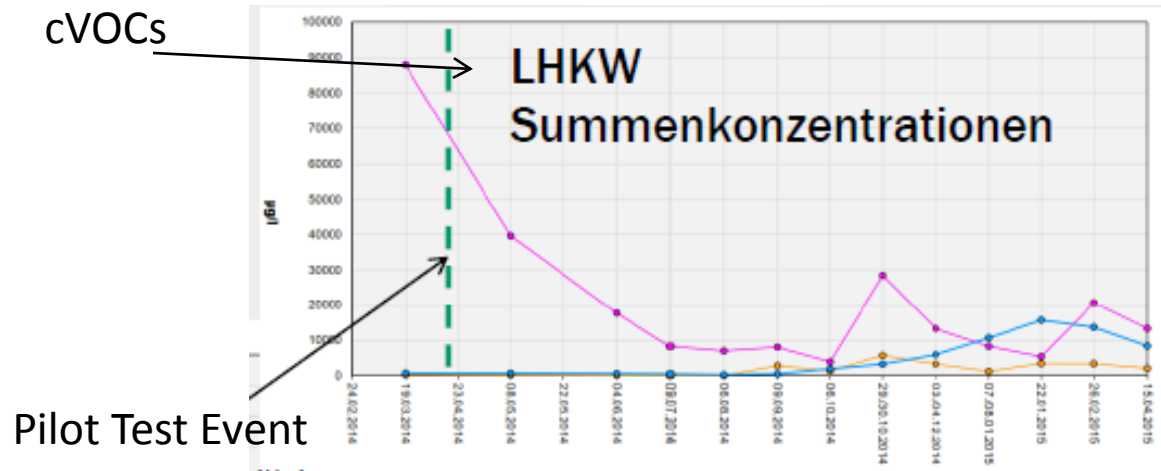


- Pilot Project:
 - Targeted 7 to 11 m bgs
 - Heavy GW impacts
 - Emplaced KP:
 - 3 injection location
 - 5 lifts per location
 - Total of 1,350 kg KP with 200 kg of ferrous lactate

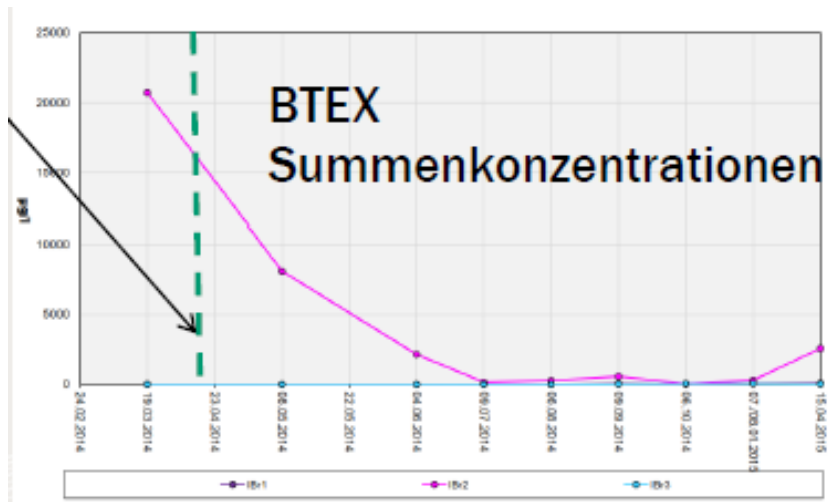
Tiltmeter Data

- Area of influence of the fractures
 - IBr-1
 - 125 m² (1,350 ft²)
 - 9.1 x 13.7 m (30 x 45 ft)
 - IBr-2
 - 111 m² (1,200 ft²)
 - 9.1 x 12.2 m (30 x 40 ft)
 - IBr-3
 - 127 m² (1,375 ft²)
 - 7.6 x 15.2 m (25 x 55 ft)
- If circular: 6.2 m ROI (~20 ft)
 - Observed to be more rectangular

Long Term Monitoring Results



Pilot Test Event



Courtesy of Riskcom

Results and Conclusions

- 1 Year Post Application Monitoring
- Successful distribution of KP and activator over a 200 m² area (2,152 ft²) with 3 injection locations
- Activated Klozur KP resulted in up to 99% treatment of Target COCs

| Date | Contaminant (mg/L) | | | | |
|-------------------|--------------------|--------|--------|--------|-------|
| | PCE | TCE | cDCE | BTEX | PAH |
| 3/19/2014 | 13,000 | 22,000 | 52,000 | 20,713 | 98 |
| 10/7/2014 | 8 | 23 | 3,800 | 47 | 5 |
| Percent Reduction | 99.9% | 99.9% | 92.7% | 99.8% | 94.5% |
| 4/15/2015 | 4 | 6 | 13,000 | 2,570 | 104 |
| Percent Reduction | 99.97% | 99.97% | 75.0% | 87.6% | -5.3% |

Courtesy of Riskcom

Potassium Persulfate Summary

- Extended Release
 - Target
 - Groundwater plumes
 - Low permeable soils
 - Potassium residual
 - Contaminants Treated
 - 1,4-Dioxane
 - MTBE
 - cVOCs
 - Petroleum hydrocarbons
 - Energetics
 - Pesticides, etc
- Critical Information:
 - Groundwater flux
 - Hydraulic conductivity
 - Hydraulic gradient
 - Aquifer temperature
 - Aqueous phase demand
 - Target
 - Non-target (COD, etc)
 - Depth to target interval

Conclusions

- Potassium persulfate (KP) offers an alternative to sodium persulfate (SP)
 - Both form the powerful oxidant persulfate anion
 - Different characteristics lend themselves to different field applications
 - Klozur SP: Source areas
 - Klozur KP: Extended release or when you want potassium residual
- Used to target:
 - Low permeable soils
 - Permeable reactive barriers
 - Soil mixing

Questions



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