Remtech 2014

Slow Release Persulphate and MultiOx™ Cylinders for Passive, Long-term Treatment of Petroleum Hydrocarbon Contaminated Sites

Pamela Dugan, Ph.D., P.G.; Carus Corporation

Jean Paré, P. Eng.; Chemco Inc.

October 2014

CARUS®

CHEMCO inc.

Presentation Agenda

- Permeable Reactive Barrier - Definition & Usage
- Sustained-Release (SR) Technology Overview:
  - Permanganate Cylinder
  - Unactivated Persulphate Cylinder
  - Combinations of Reactants MultiOx™
- Experimental and Laboratory Validation:
  - Batch Kinetic Tests
  - 1-D Columns Experiments
- Engineering Design Tool Overview
- Questions

Permeable Reactive Barrier (PRB) Definition & Usage

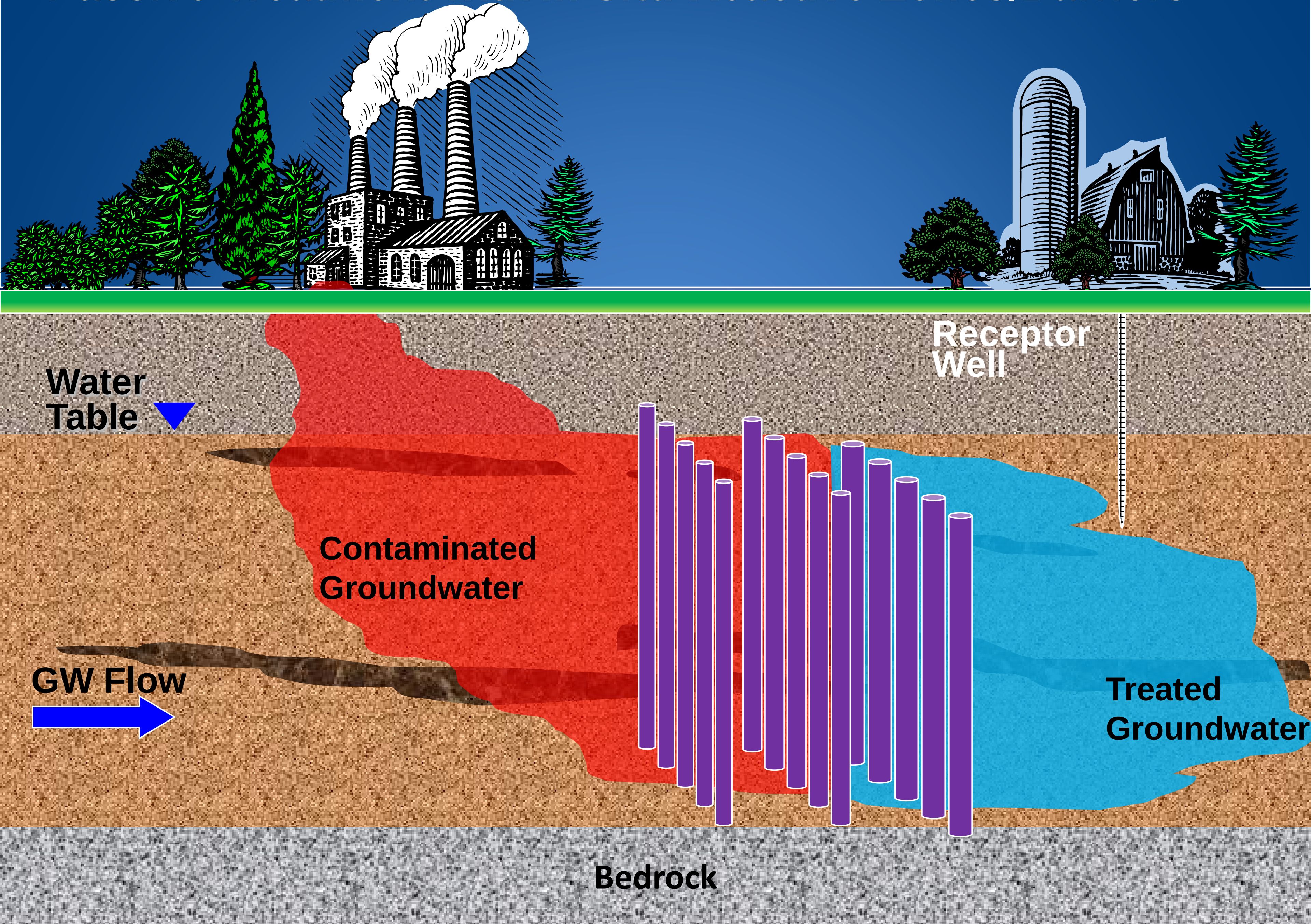
- PRB are used as an in situ permeable treatment zone designed to intercept and remediate a contaminant plume. PRBs have become an important component among the various technologies available to remediate groundwater contamination.

- PRB is an evolving technology with new and innovative reactive materials introduced to treat different contaminants as well as innovative construction methods. “New” reactive materials include mulch for treating chlorinated solvents, metals, and energetic and munitions compounds, zeolites for treating radionuclides and heavy metals.

- Sustained Release Technology (SR) allow the use of oxidants for organic contaminants and petroleum hydrocarbons control and removal.

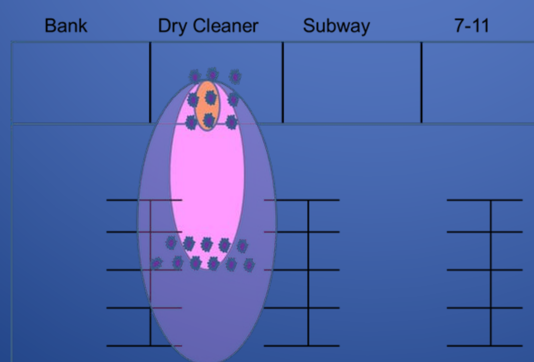
Source: ITRC - Permeable Reactive Barrier: Technology Update – June 2011

Passive Treatment with *In Situ* Reactive Zones/Barriers



Sustained-Release (SR) Technology Concept

- Can easily be coupled with many existing treatment technologies
- **Minimizes above-ground infrastructure at active sites**
- Long-term presence of oxidants can mitigate the impacts of **matrix diffusion (release can last up to 12 months)**
- Cost-effective, and can be implement as part of a **stepped-implementation** strategy
- Use **natural groundwater gradients** to deliver oxidants

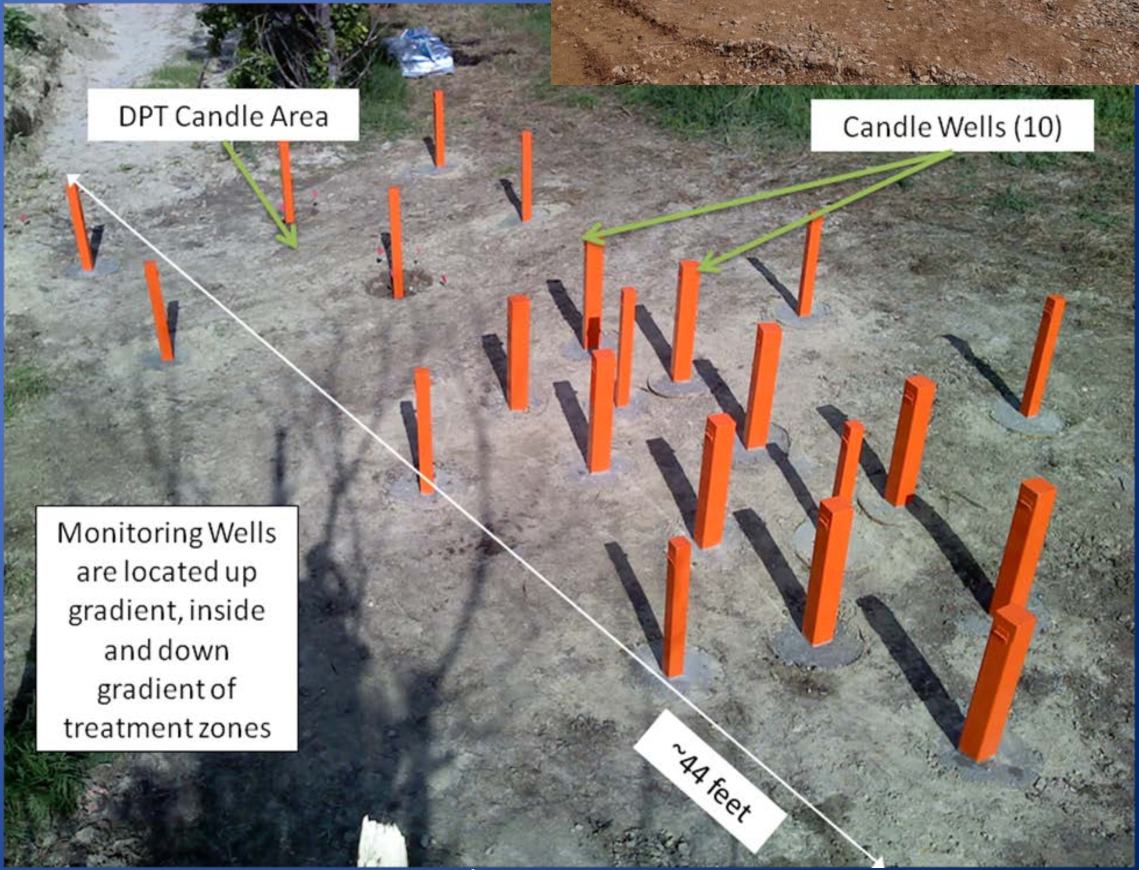


Minimizes Site Disruption

- Traditional ChemOx Permanganate Footprint

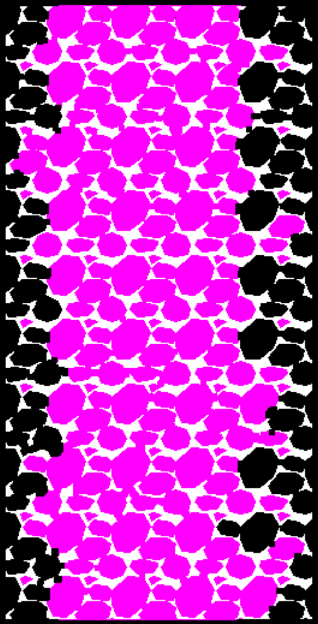
Minimizes Site Disruption

- Reduced Cylinder Site Impact



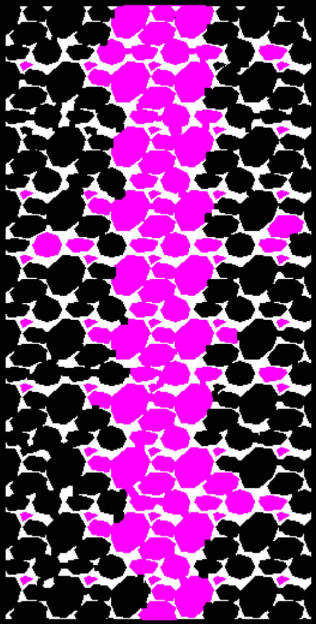
Christenson - 2010

Oxidant Release Mechanism



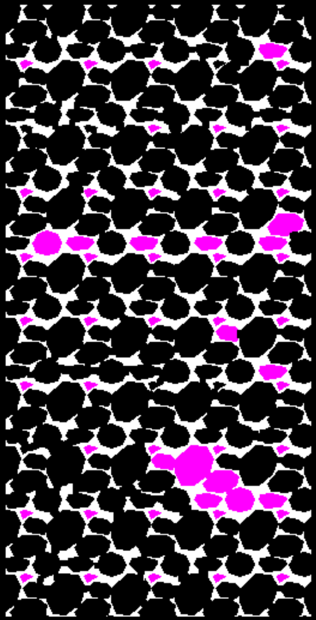
- As the oxidant solids dissolve void spaces are created

Oxidant Release Mechanism



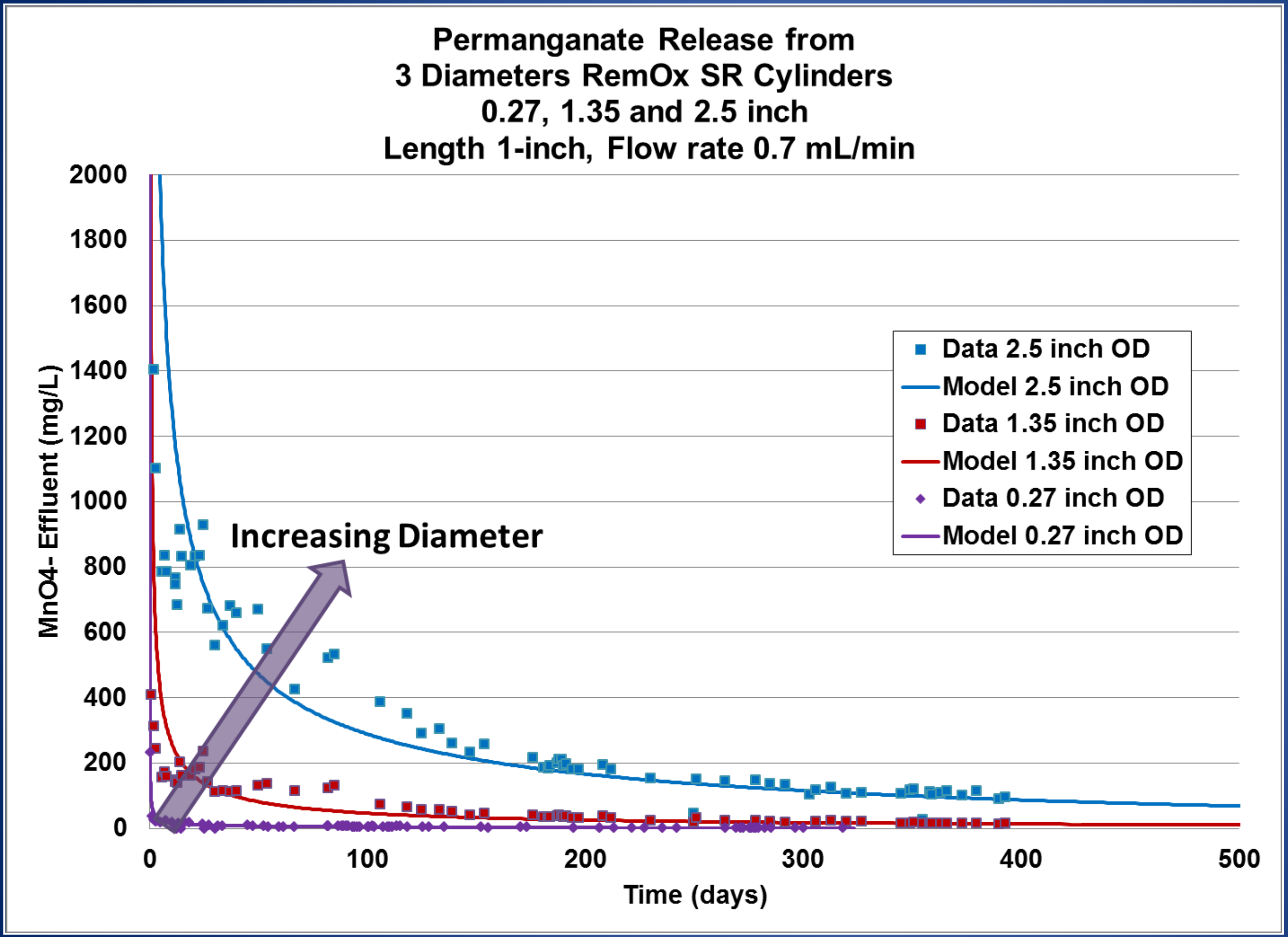
- Newly created void spaces expose additional oxidant solids for <u>dissolution and diffusion</u>
- Process occurs radially from the exterior of the cylinder to the inner core

Oxidant Release Mechanism



- Initial spike of permanganate in time
- Slower and lower release of permanganate at later times

Oxidant Release Characteristics - Permanganate



Permanganate Mini-Cylinder (80% w/w) running for ~6 months

$$Q' = \pi h A (r_0^2 - r^2)$$

$$\frac{r^2}{2}\ln\frac{r}{r_0} + \frac{1}{4}(r_0^2 - r^2) = \frac{C_s D_e t}{A}$$

Lee and Schwartz (2007)

Measured permanganate concentrations match model!

PERSULPHATE and OXYDANT BLEND MULTIOX™

(PERSULFATE +PERMANGANATE) CYLINDER TECHNOLOGY DEVELOPMENT

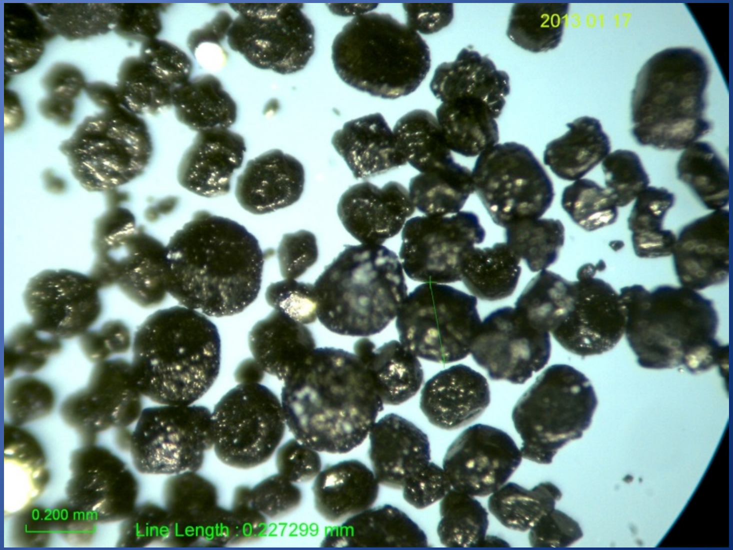
Physical Properties

Sodium Persulphate

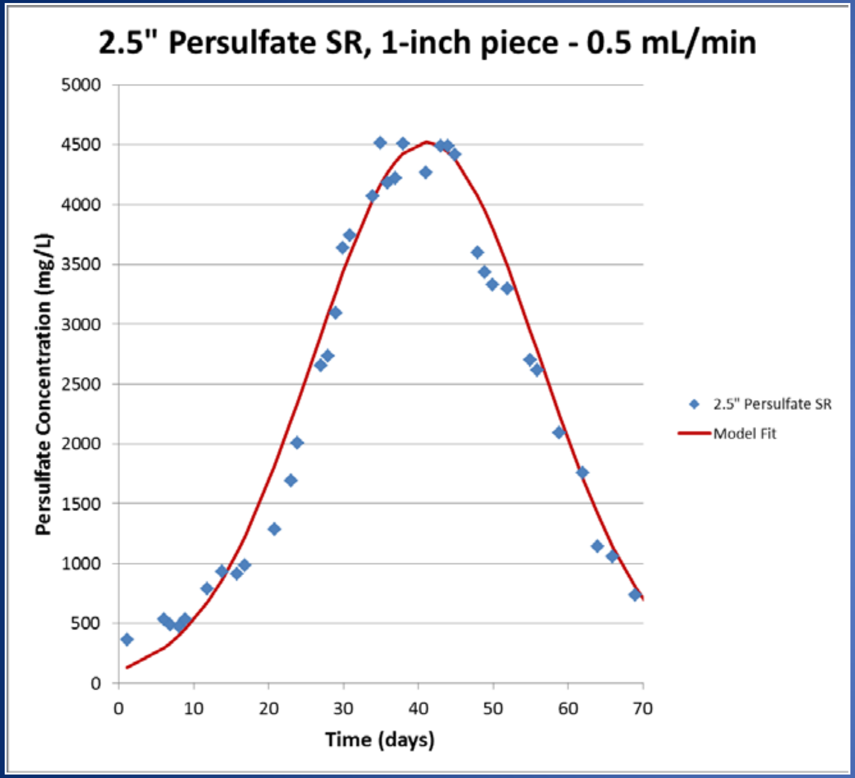
- Molar Mass: 238.10
- Density: 2.40 g/cm^3
- Solubility: 556 g/L

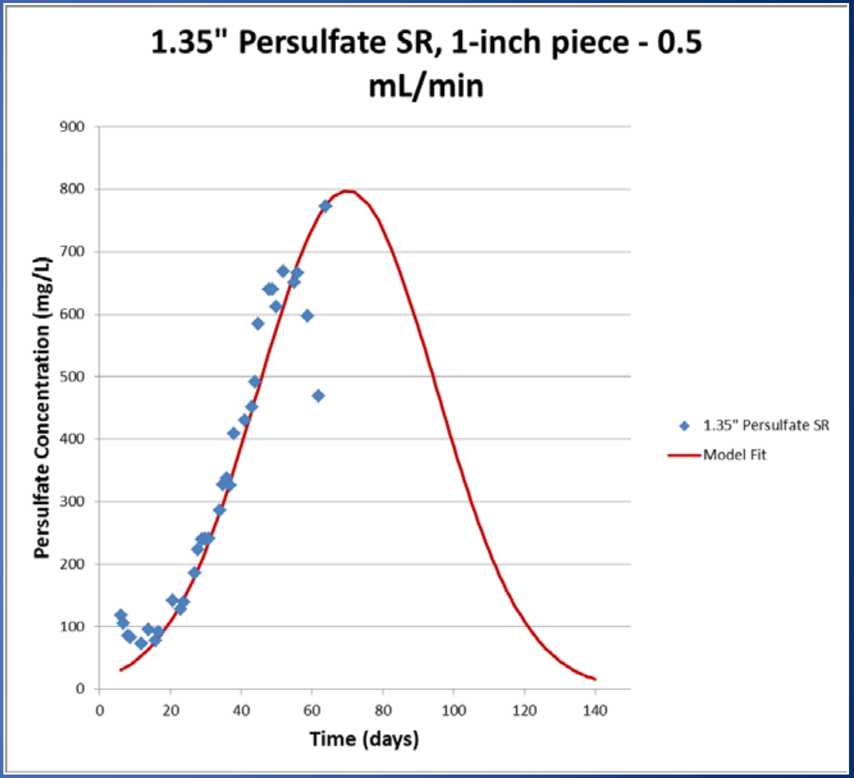
Potassium Permanganate

- Molar Mass: 158.03
- Density: 2.703 g/cm^3
- Solubility: 63.8 g/L



Oxidant Release Characteristics - Persulphate



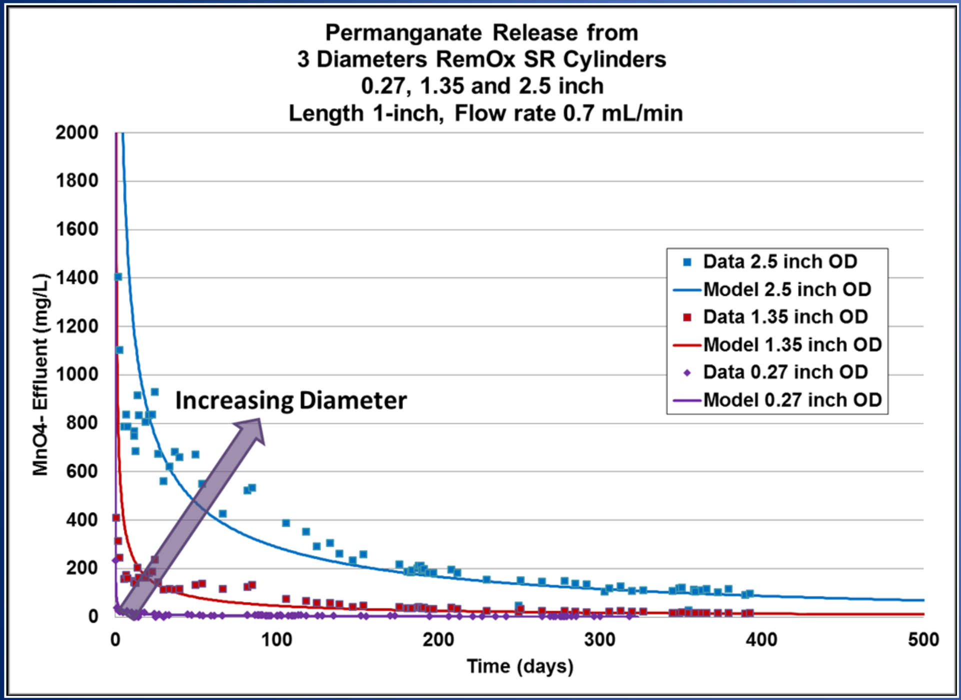


Release data was fit to simple Gaussian Distribution Model

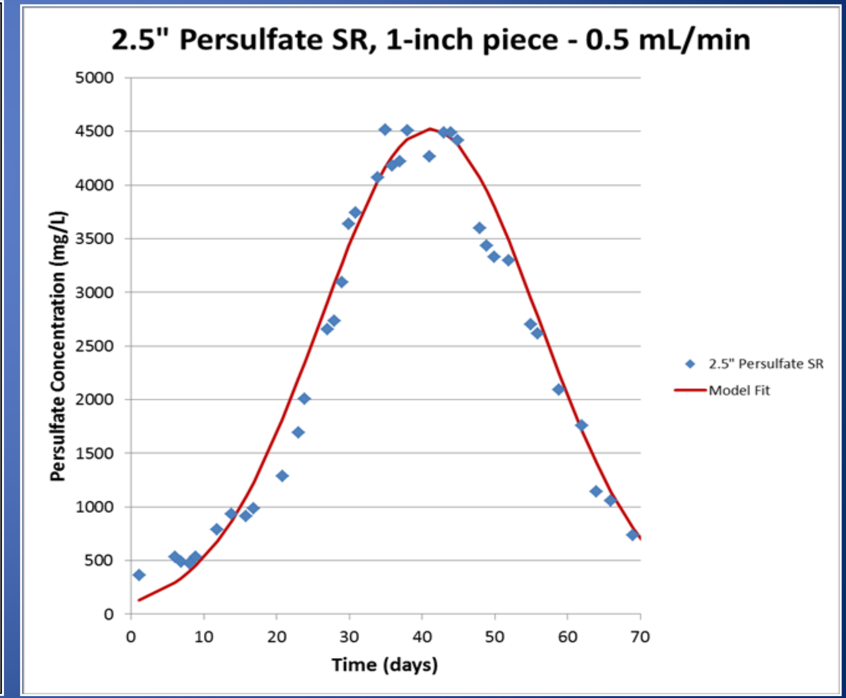
$$f(t) = A\frac{1}{\sigma\sqrt{2\pi}}e^{\frac{-(t-t_{max})^2}{2\sigma^2}}$$

Permanganate + Persulphate respective profile

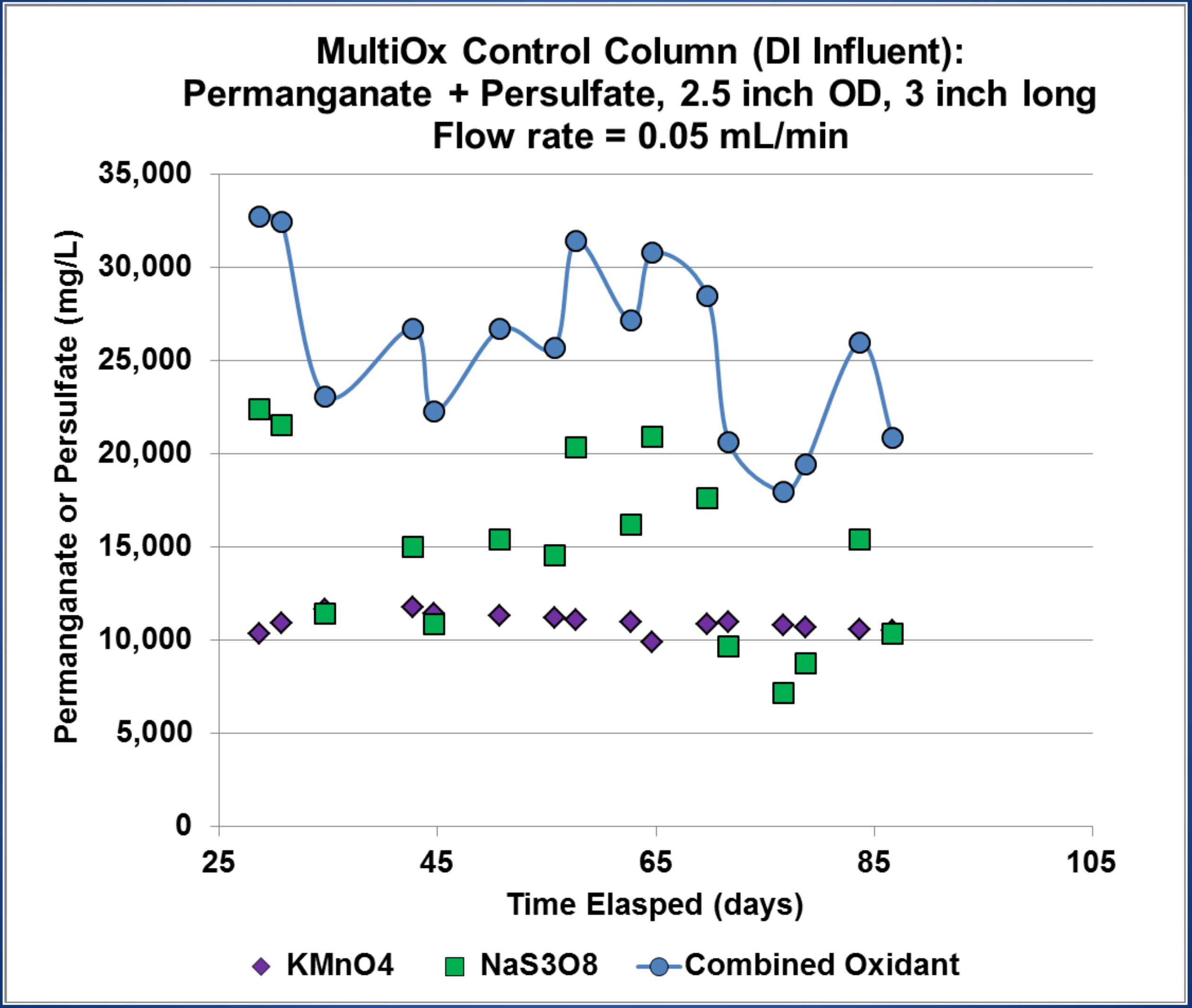
Permanganate



Persulphate



Oxidant Release Characteristics
MultiOx SR



US Patent Application PCT/US14/29247

Oxidant Release Conclusions

- Permanganate release is characterized by high initial concentration, followed by long-term and sustained release
  - ➢ Release rates can be modeled using an analytical solution
  - ➢ Release rates can be scaled and quantified
- Persulphate exhibits a different oxidant release profile than permanganate
  - ➢ Particle Size differences?
  - ➢ Crystalline packing differences?
  - ➢ Solubility
- The combination of persulphate and permanganate in MultiOx results in both:
  - ➢ Improved oxidant release characteristics and
  - ➢ Provides multiple oxidants for contaminant degradation

Laboratory Study - Unactivated Persulfate BTEX Batch Kinetic Tests

Batch kinetic experiments were performed to:

1. Determine the natural oxidant demand kinetics of unactivated persulphate
2. Determine the kinetic rate of contaminant degradation by unactivated persulphate
3. Use these results to design a 1-D column experiment

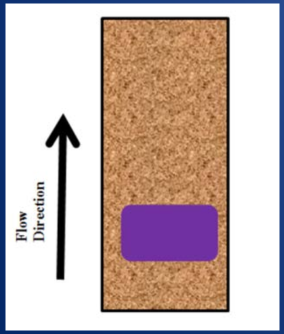
The experimental approach for batch kinetic experiments:

- Performed in sacrificial 40-mL VOA vials
- At each time point, duplicate vials were sacrificed and oxidant/COCs were measured
- BTEX/MTBE (~ 10 ppm) and unactivated persulfate or Multiox (100, 1000, and 10,000 ppm)

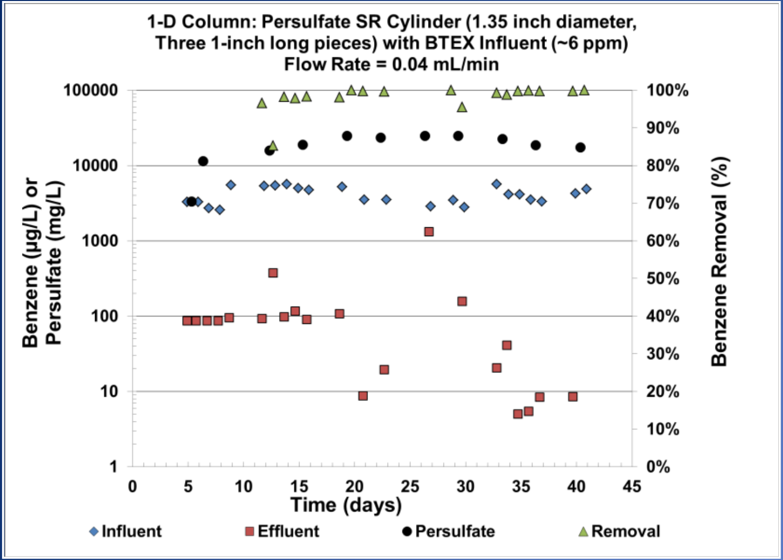
1-D Column Experimental Design

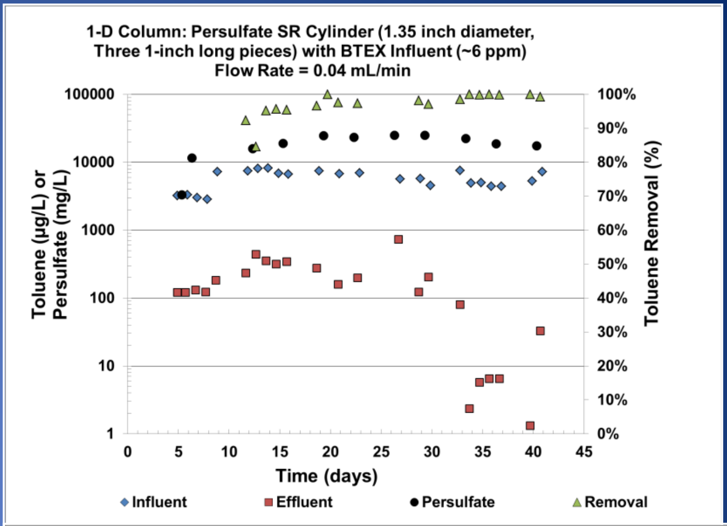
Experimental approach:

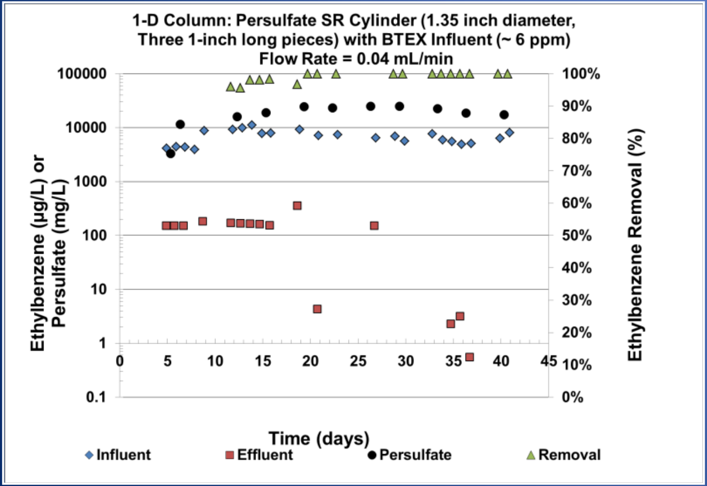
- 1-D Columns (2 inch ID x 48 inch length or 4 inch ID x 48 inch length)
- *Control columns* - DI water influent, packed with ASTM-graded silica sand or North Island Site soil (San Diego)
- *Treated columns* - BTEX influent prepared in deionized water (~6 ppm), packed with ASTM-graded silica sand or North Island Site soil
- Persulfate SR Permanganate SR or MultiOx SR cylinders - Three 1.35 inch diameter pieces,1 inch long pieces or One 3-inch diameter piece
- Flow rate (0.04 mL/min), seepage velocity (0.32 ft/day), ~5-8 day retention time (depending on column ID)

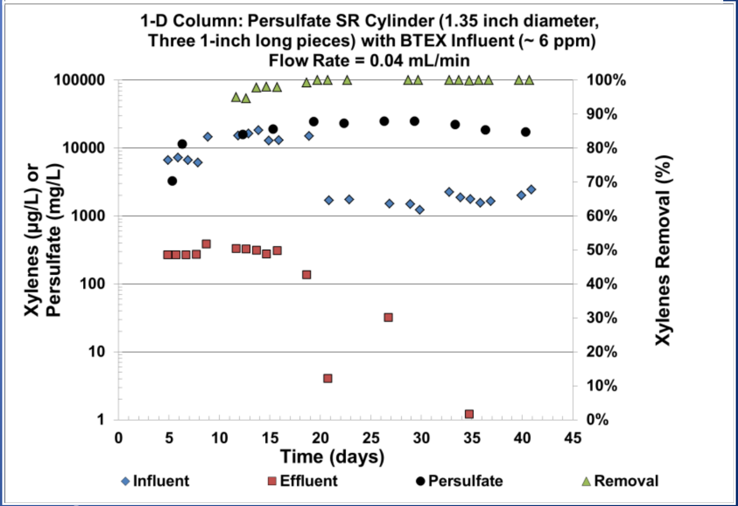


1-D Column Results–BTEX Removal – Persulphate SR





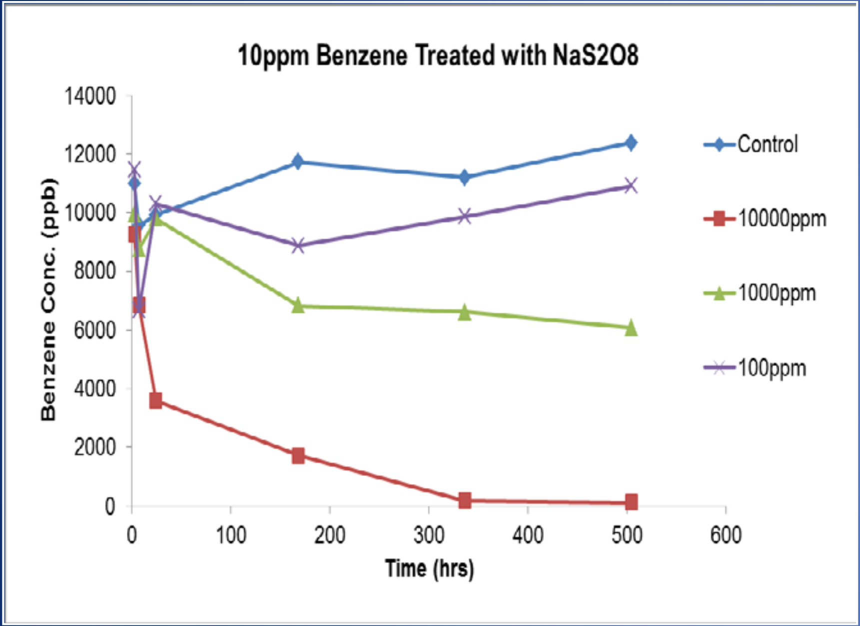




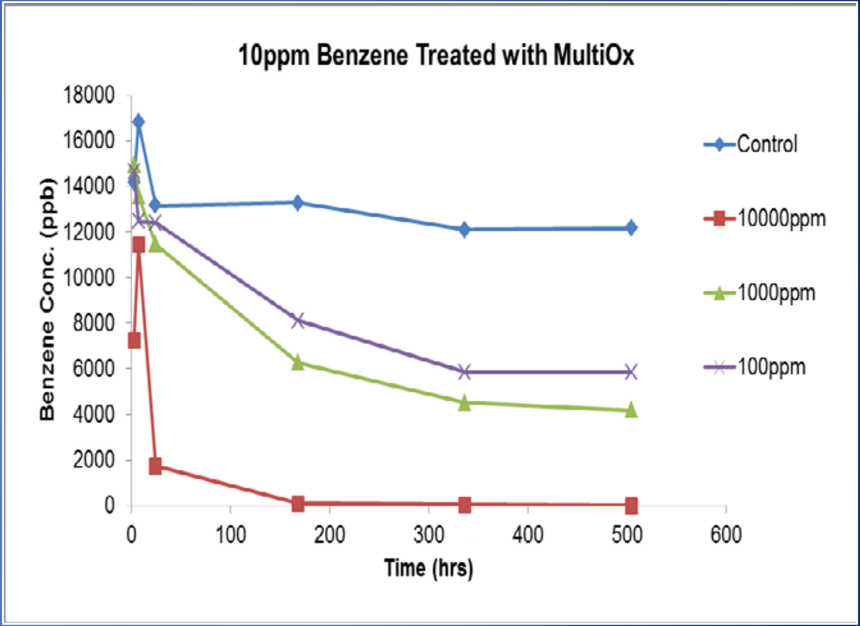
Removal Efficiencies: **Benzene**: 85.3%-98.3%, **Toluene**: 84.6%-96.6%, **Ethylbenzene**: 88.5%-98.3%, **Xylene**: 94.6%-99.3% over the 40-day experiment

Batch BTEX Oxidation Results

Persulphate Oxidation



MultiOx Oxidation



Second Order Oxidation Rate Constants ($M^{-1}s^{-1}$)			
	Permanganate	Persulfate	MultiOx
Benzene	Neglible	5.72E-5[2]	1.1E-4[2]
Toluene	5.74E-4[1]	5.63E-5[2]	3.2E-4[2]
Ethylbenzene	7.07E-3[1]	5.91E-5[2]	1.9E-3[2]
Xylene(s)	2.22E-3[1]	4.81E-5[2]	4.0E-3[2]
MTBE	8.82E-5[1]	Neglible	7.6E-5[2]

[1]ISCO-kin Database
[2]This study

Experimental Conclusions

- Persulphate
  - Exhibited sufficient reactivity with benzene, toluene, ethylbenzene, and xylene, dioxane and VOCs
- MultiOx
  - Increased reactivity with benzene, toluene, ethylbenzene, xylene, Dioxane and VOCs (not presented)
- 1-D columns validated the application of SR cylinders for remediation of BTEX, dioxane & VOCs
- Natural activation mechanisms (thermal, Fe, Mn, other transition metals) may enhance persulphate reaction kinetics

SR Cylinder Development

3 Type of SR Cylinder Available

- **Potassium Permanganate** - RemOx® SR ISCO Reagent: $KMnO_4$ based product dispersed in a solid matrix, (~80% w/w)
- **Sodium Persulfate SR**: NaS_2O_8 based product dispersed in a solid matrix (~73% w/w)
- **MultiOx SR**: Blend of permanganate and persulfate (***US Patent Application PCT/US14/29247***)
- 18 inches long (1.35 or 2.5 inch diameter)
- Borehole with sand
- holder (2 cylind
- via DPT or in we





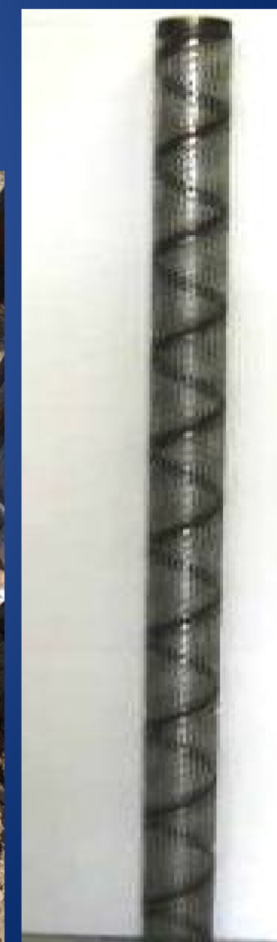
SR Cylinder Development

Cylinder Dimension Available

- 18 inches long (1.35 or 2.5 inch diameter) –
- Containing either 0.87 to 10.5 kg of oxidant per unit

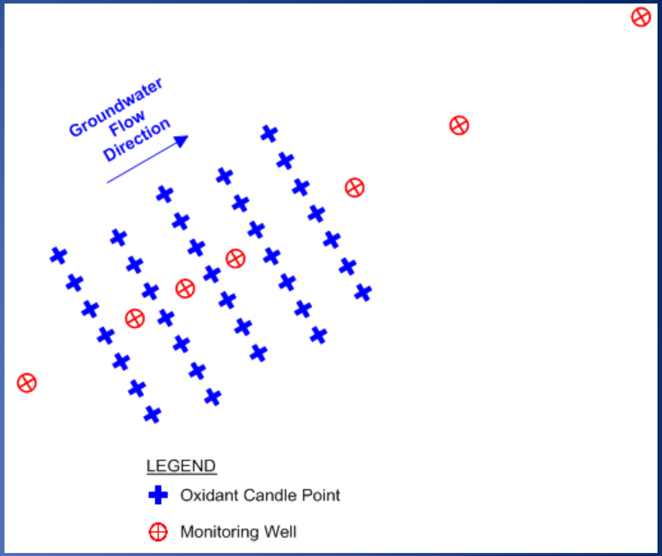
Site Positioning via

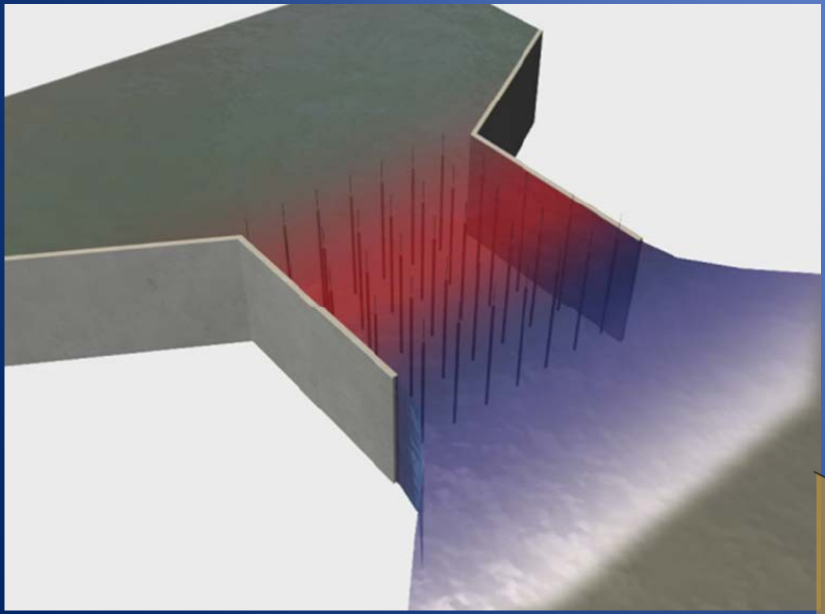
- Borehole with sand
- 3 feet long holder (2 cylinders)
- Deployed via DPT or in wells

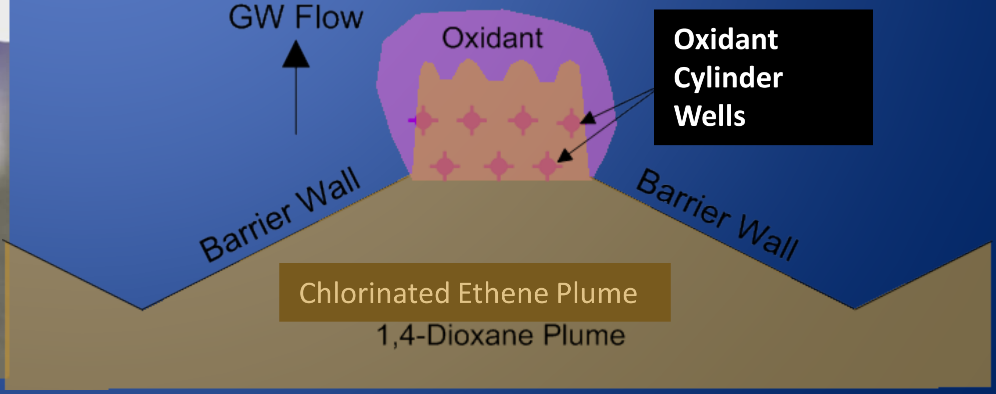


SR Deployment Strategies

- **Possible Configurations:**
  - ➢ Permeable reactive barrier (PRB)
    (1 to 3 feet radius offset recommanded)
  - ➢ Permeable reactive zone/grid (PRZ)
  - ➢ Trench
  - ➢ Funnel and gate







SR Engineering Design Tool
Design Factors

- Site characteristics (2nd Order NOD, groundwater velocity, porosity, type of contaminants and concentrations)
- Oxidant Type and Diameter
- Oxidant release rate(s)
- Contaminant Reaction Kinetics
- Treatment Objectives
- Tool will have costing information for cylinder site deployment either using DPT or wells

Note: Available for Permanganate SR , Persulfate SR and MultiOx SR to be released (possibly by end of the year)

SR Engineering Design Tool

GREEN cells = user must enter or choose values
YELLOW cells = output of interest for system design

Oxidant Release	Value
Oxidant	Persulfate
Cylinder Diameter (inches)	2.50
Cylinder Diameter (cm)	6.35
Initial Cylinder Radius (cm)	3.18
Oxidant solubility (g/cm^3)	0.03
Mass of Cylinder (g)	2794
Mass of Oxidant (g)	2236
% oxidant available	0.9
Mass of oxidant available (g)	2012
Effective diffusion coefficient (cm^{2}s^{-1})	4.E-07
Amount of available oxidant (g/cm^3)	1.39
Cylinder Height (cm)	45.7
Cylinder Volume (cm^3)	1447.9
Cylinder Density (g/cm^3)	1.9
Molecular Weight of Oxidant (g/mol or mg/mmol)	119

Site Characteristics	Value
Contaminant	Trichloroethene (TCE)
Contaminant Reaction Rate (L/mmol-day)	5.789E+01
Contaminant Reaction Rate (L/mg-day)	4.41E-01
Initial Contaminant Concentration (ug/L)	6000
Initial Contaminant Concentration (mg/L)	6.000
2nd order NOD rate (L/mmol-day)	0.001
2nd order NOD rate (L/mg-day)	8.40E-06
Hydraulic conductivity (cm/s)	1.00E-04
Hydraulic conductivity (cm/d)	8.64
Hydraulic gradient	0.0010
Porosity	0.25
Groundwater Velocity (cm/day)	3.46E-02
Cross Sectional Area of Flow (cm^2)	456
Groundwater Flow (L/day)	1.58E-02

Contaminated Volume and Treatment Goal	Value
Top of contaminated zone (feet bgs)	20
Bottom of contaminated zone (feet bgs)	44
Width of contamination (feet, perpendicular to flow of groundwater)	100
Length of contamination (feet, parallel to flow of groundwater)	500
Depth of contaminated zone (feet)	24
Volume of contamined zone (cubic feet)	1200000
Treatment Goal* **(see below)**	EPA MCLs or Recommended Values
EPA MCLs (ug/L)	5
Specific Contaminant % Reduction	
Other specified final concentration (ug/L)	
Desired final concentration (ug/L)	5

*The first step is to select the method for determining the treatment goal. Selecting EPA MCLs or Recommended Values means that the desired final concentration cell will populate with the concentration recommended by the EPA for that contaminant. Selecting Specific Contaminant % Reduction allows you to enter a percent (0-100) in the box to the right, and the desired final contaminant concentration cell will populate based on this percent reduction. The last option is to select Other Specified Value. If this option is selected, you can directly enter a final concentration into the cell to the right of the Other Specified Value cell. The desired final concentration cell will then populate with the same value as the one entered here.

Time and distance of interest** (see below)	Value
Time of Interest (days)	150
Time Step (days)	2
Downgradient Distance of interest (ft)	10

**Enter a time and distance of interest to generate figures of oxidant and contaminant concentration vs. time and distance to the right. The concentration vs. time figures are for the specified distance of interest. The concentration vs. distance figures are for the specified time of interest.

SR Engineering Design Tool

Cylinder Spacing* (see below)	Value
Spacing between cylinder rows (feet)	3
Time until contaminant concentration goes below desired concentration (days)	N/A
Change-out time (Days)	N/A
Contaminant concentration at change-out (ug/L)	N/A

*A change-out time listed as N/A indicates that additional rows are needed - continue to second row.

Second Row	Value
Would you like to use a second row? (autofills "yes" if one is not enough to achieve goal)	Yes
Would you like to enter the cylinder spacing or use the calculated minimum or maximum distance?	User Entered
User-specified spacing (feet)	5
Distance between first row and second row (feet)	5.0
Time until contaminant concentration goes below desired concentration (days)	
Would you like to override the automatically defined change out time and select the change out time? (days	Yes
User-specified change out time (days)	365
Change-out tIme (days)	1324
Concentration at change-out (ug/L)	6.00

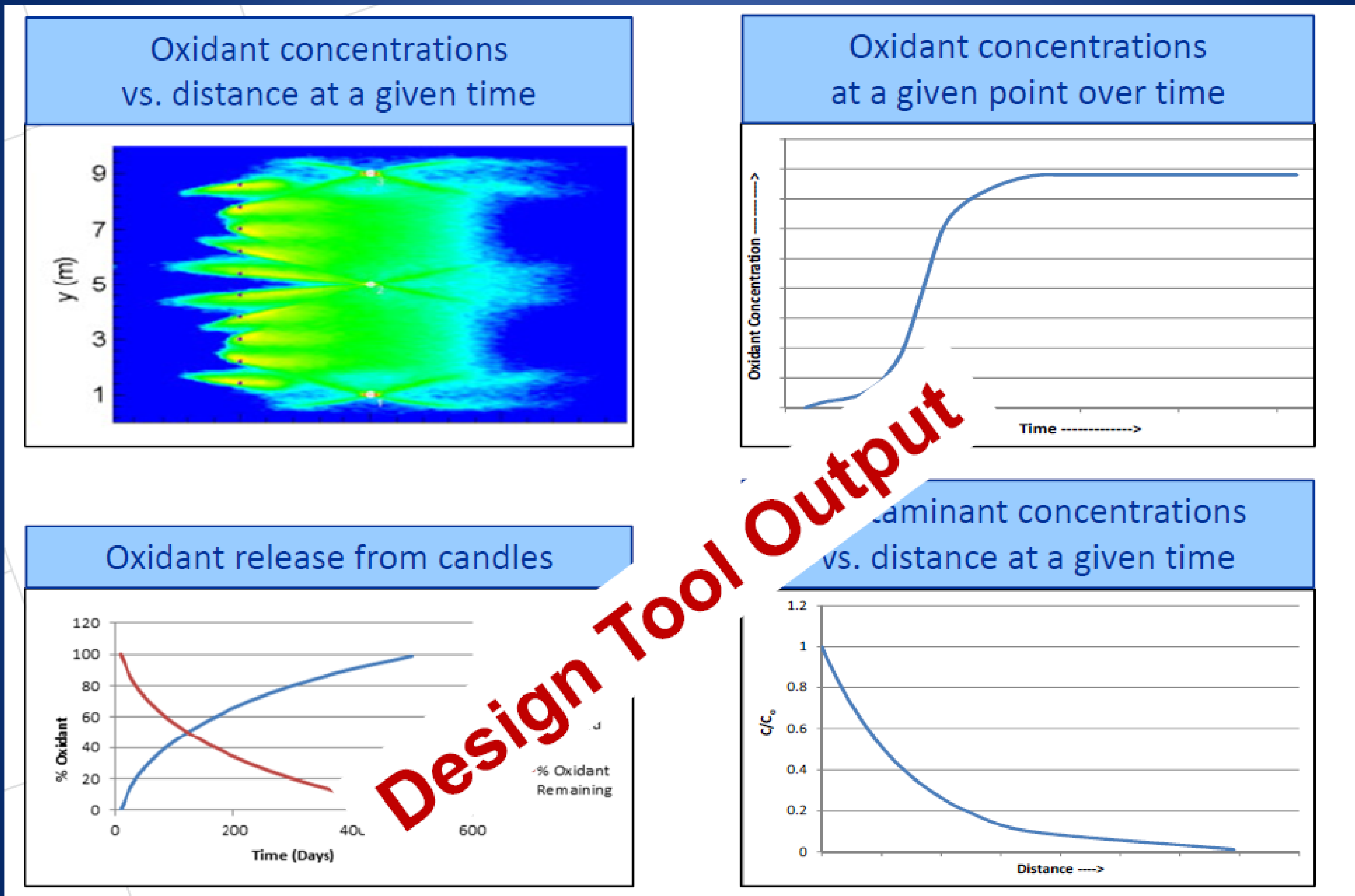
Third Row	Value
Would you like to use a third row? (autofills "yes" if two rows are not enough to achieve goal)	Yes
Would you like to enter the cylinder spacing or use the calculated minimum or maximum distance?	Minimum
User-specified spacing (feet)	
Distance between second row and third row (feet)	1.0
Would you like to override the automatically defined change out time and select the change out time? (days	No
User-specified change out time (days)	100
Change-Out Time (days)	1296.0
Contaminant concentration at change-out (ug/L)	0.05

Fourth Row	Value
Would you like to use a fourth row? (autofills "yes" if three rows are not enough to achieve goal)	Yes
Would you like to enter the cylinder spacing or use the calculated minimum or maximum distance?	Minimum
User-specified spacing (feet)	
Distance between third row and fourth row (feet)	100.0
Would you like to override the automatically defined change out time and select the change out time? (days	No
User-specified change out time (days)	100
Change-Out Time (days)	2034.0
Contaminant concentration at change-out (ug/L)	0.05

			Total Installation Fixed Costs ($)	11233.33
Site Information			**Total Installation Daily ($)**	4700
Top of cylinder interval	20	feet bgs	**Number of days per installation (days**	67
Bottom of cylinder interval	44	feet bgs	**Total Cost per Installation ($)**	326133.3
Installation Fixed Costs				
Prime contractor mobilization	500	$		
Subcontractor mobilization	2000	$		
Water supply	500	$		
Piping and other equipment needed for cylinder installation	2000	$		
Labor time required for set-up and removal	8	people-hrs		
Average labor rate	100	$/hr		
Labor cost for set-up and removal	800	$		
Number of cylinders needed	5333	cylinders		
Costs per cylinder	100	$		
Total cylinder cost	533333.3	$		
Total Installation Fixed Costs	11233.33	$		
Contractor Information and Costs				
Contractor personnel on-site everyday	1	people		
Labor rate of contractor personnel	100	$/hr		
Hours billed per person per day	10	hours		
Contractor labor costs	1000	$/day		
Per Diem (meals, housing, travel, etc)	200	$/day		
Additional expenses (consumables, H&S)	100	$/day		
Equipment rental costs	200	$/day		
Total daily contractor costs	1500	$/day		
Subcontractor Information and Costs				
Daily costs for DPT equipment and operator	3000	$/day		
Additional costs (material, IDW daily costs)	200	$/day		
Total daily subcontractor costs	3200	$/day		
Total Installation Daily Costs	4700	$/day		
Number ofcylinders that need to be installed	333			
Number of direct push installed points per day	5			
Number of days per installation	67			

Cost estimates for DPT or well emplacement

SR Engineering Design Tool



Conclusions

- MultiOx, Permanganate and Persulphate SR represent a novel delivery strategy for plume treatment
  - Effective at removing a variety of COCs (e.g., 1,4 Dioxane, BTEX, VOCs, phenols, PAHs, PHC F2-F4)
  - Sustained oxidant persistence can address "rebound" and back-diffusion
  - Active industrial/commercial facilities: passive *in situ* treatment without above ground equipment/infrastructure
- Unactivated persulphate kinetics may vary, so we recommend performing contaminant kinetic and NOD treatability tests
- Additional Contaminants Treatability Testing Data underway

About our Expertise, Products and Services

CHEMCO inc.
SOLUTIONS AND ENVIRONMENTAL PRODUCTS
WATER - SOIL - AIR

- **Training and Education:** technical transfer session, health and safety training;
- **Consulting and Technology Site Assessment:** technology support and selection (chemical oxidation and reduction, co solvent-surfactant soil washing and enhanced bioremediation);
- **Products supply, logistic and storage**: nutrients, bacterial preparations strains, oxidants, reducing agents, catalysts, oxygen and hydrogen release compounds, co solvent-surfactant blends
- **Laboratory Services and Analysis**: Groundwater Parameter Analysis, Tracer Study, Soil and Groundwater Oxidant Demand Evaluation (SOD), Bench Scale Treatability testing in saturated and unsaturated conditions.

CARUS®

CHEMCO inc.

SOLUTIONS AND ENVIRONMENTAL PRODUCTS
WATER - SOIL - AIR

Thank you for your attention !
Questions?

Contact information:
E-mail: jean.pare@chemco-inc.com // Pamela.Dugan@caruscorporation.com
Tel: 418-953-3480 // (815) 224-6870
Web site: www.chemco-inc.com // www.caruscorporation.com