Geosyntec consultants

Manganese Activated Persulfate (MnAP) for the Treatment Recalcitrant Organics: Development and Commercialization

PRESENTED BY | **Bruce Marvin, P.E.** Geosyntec Consultants, Oakland, California
Pamela Dugan, Ph.D. Carus Corporation, Peru, Illinois
Michelle Crimi, Ph.D., Clarkson University, Potsdam, New York

On-Going Innovations in ISCO

- New Delivery Strategies
- Improved handling and integrated persulfate activators
  - Calcium Peroxide & Sodium Persulfate
    - *Klozur® CR*
  - Sodium Persulfate & Basic Silica
    - *PursulfOx™*
  - Sodium Persulfate & Ferric Iron
    - *Provect-OX™*
  - Sodium Permanganate &/or Sodium Persulfate
    - *RemOx ® SR*
- New Activator Systems
  - Sodium Persulfate & Ascorbic Acid
  - Sodium Permanganate & Sodium Persulfate (PMPS)
    - Manganese-activated Persulfate

Presentation Outline

- Background and Literature
  - Matrix Activation
  - Novel Anthropogenic Activators
- Field Application at the MEW CERCLA Site
  - Two Phase of Laboratory Trials
  - Field Pilot and Maintenance
- Recalcitrant Contaminants
- On-going Research and Development
  - Carus Corporation
  - Clarkson University and University of California
  - SiREM and PRIMA Environmental

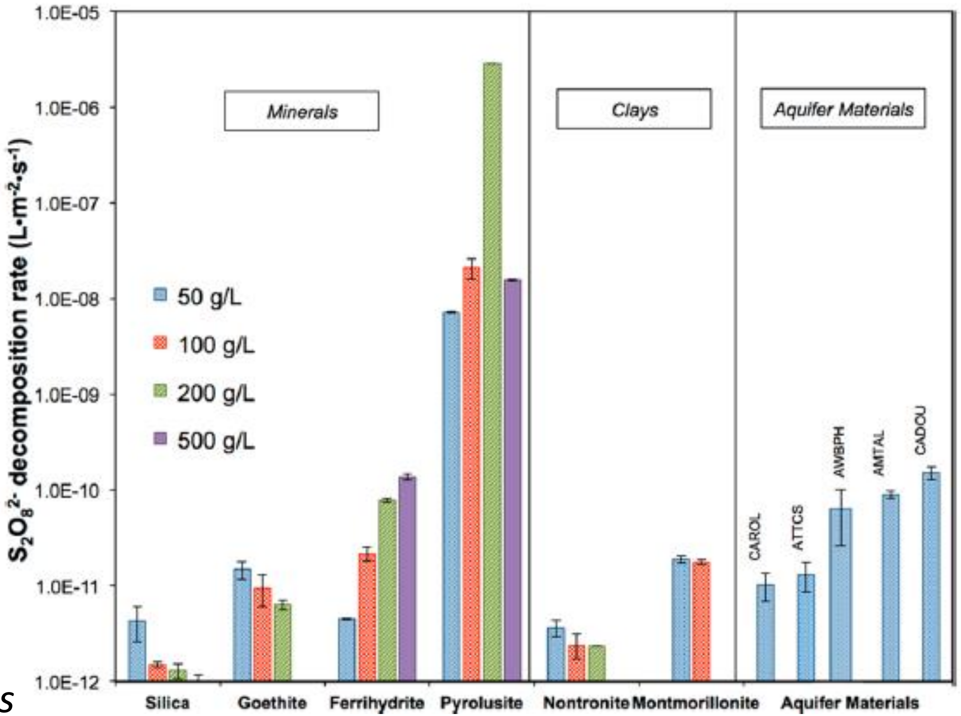
Combining Permanganate and Persulfate

- Why combine oxidants?
  1. Permanganate injections are simple and persulfate often requires anthropogenic activators
  2. Permanganate is more expensive than persulfate on a mass basis
  3. High doses of permanganate produce manganese oxides than can coat environmental media
  4. High doses of persulfate produce substantial sulfate and acidity
  5. Permanganate and persulfate have unique decomposition kinetics

- Hypothesis - *Mixed manganese oxides from permanganate decomposition and iron oxides formed in-situ can activate persulfate and enhance ISCO treatments.*

Research into Matrix Activation of Persulfate

- Ahmad et al 2010 found that birnessite (MnO_2) induced higher rates of persulfate decomposition than four iron oxides
- Teel et al 2011 examined natural minerals
  - Four (cobaltite, ilmenite, pyrite, and siderite) of 13 natural minerals
- Liu et al 2014 found that Fe(III) and Mn(IV) induced decomposition of persulfate produced sulfate and hydroxyl radicals



Environ Sci Technol. 2014 Sep 2; 48(17): 10330–10336.

"When persulfate encounters a zone that is rich in iron- or manganese-oxides or clay, its half-life can decrease substantially."

Fresh and Anthropogenic Activators

- Heterogeneous activation of persulfate by metal oxides has been reported to produce radicals
  - Zero-Valent Iron (Oh et al. 2009 Liang et al. 2010)
  - Mixed Iron and Manganese Oxides (Furman et al. 2009 Do et al. 2010 Jo et al. 2014)
  - Subsurface minerals including birnessite (d-MnO_2) and goethite (FeOOH) (Ahmad et al. 2010).
  - Iron Oxides (Fang et al. 2013; Yan et al. 2011)

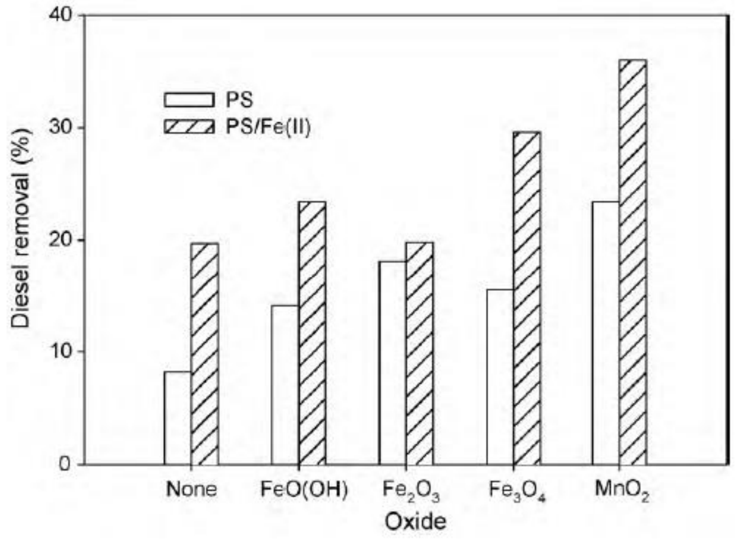
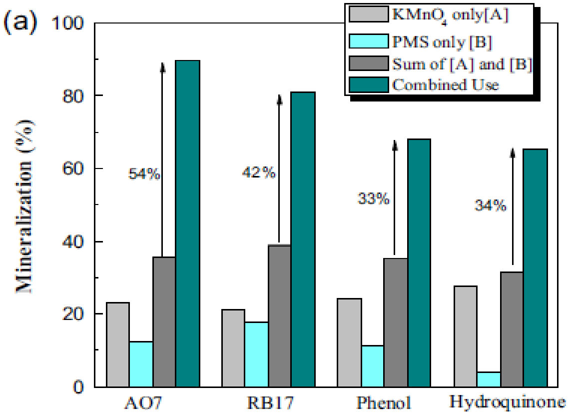


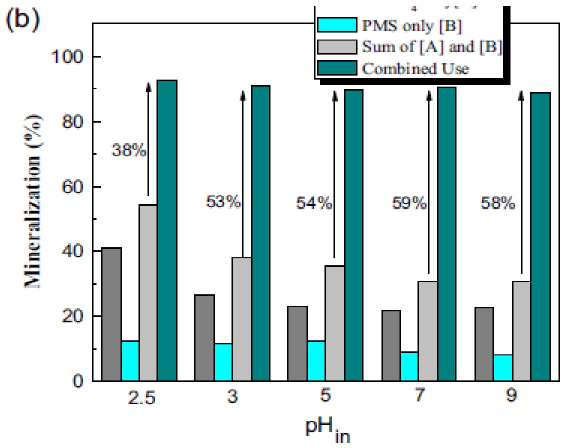
Fig. 2. The effects of metal oxides on the reactivity of persulfate with/without Fe(II) to degrade diesel on sand at pH 3.

S.-H. Do et al. / Journal of Hazardous Materials *182 (2010) 933–936*

Dual Oxidants and Synergy



S. Gao et al. / Separation and Purification Technology 144 (2015) 248–255

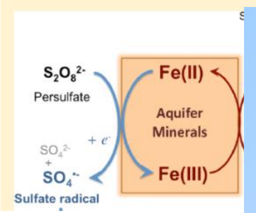


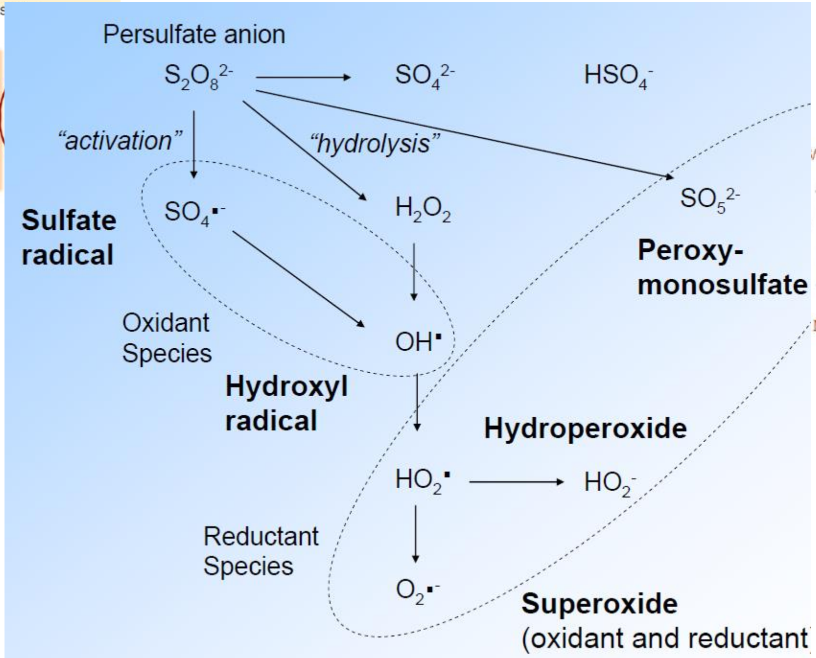
- Peroxymonosulfate (PMS) and Potassium Permanganate
  - Most experiments did not include a solid phase and had pH control
  - Nanostructure of the amorphous MnO_2 plays a significant role
  - Transition of Mn^{4+}/Mn^{3+} involving a single electron transfer is responsible for catalytic reaction (Saputra et al 2013)
- Mechanism of Base Activation of Persulfate

Environ. Sci. Technol. **2010,** *44,* 6423–6428 2013

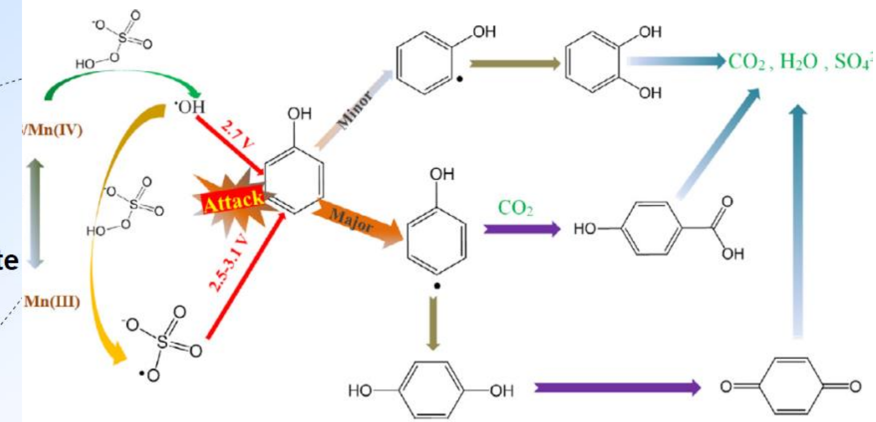
Iron and Manganese Initiation of Radical Chain Reactions

Environ. Sci. Technol. 2016, 50, 890−898





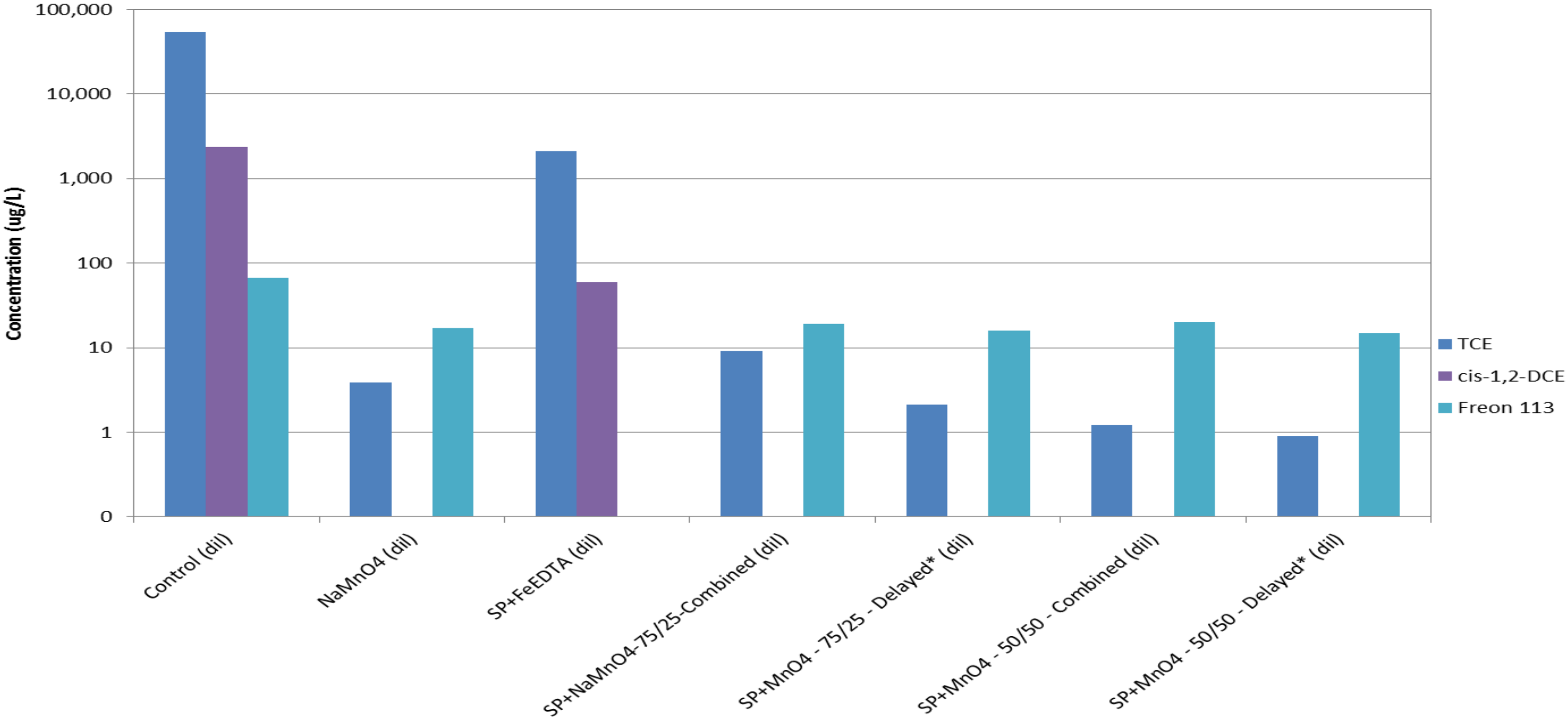
Y. Wang et al. / Chemical Engineering Journal 266 (2015) 12–20



Middlefield-Ellis-Whisman (MEW) Treatability Studies

1. Evaluate traditional ISCO and the potential of MnAP
2. Evaluate use at a residual DNAPL source area
    a. TCE concentrations from 300 to 3 mg/L
    b. Freon 113 is a non
3. Evaluate dual oxidant and sequential application
4. Assess secondary effects including pH, sulfate, chromium and manganese

Phase I – 14 Day Laboratory Trial



Phase II and Phase III Laboratory Trials

- Speciation of the natural iron and manganese in solid phase
- Evaluate a range of mass ratios of sodium permanganate to sodium persulfate
  - Simultaneous addition
  - Delayed addition
  - Stalled addition of sodium persulfate
- pH adjustment
- Extended duration to 29 days

Middlefield Ellis Whisman Study Area Source Zone

Dosage – 10 g/kg-soil

- Permanganate – 10 g/L
- Persulfate – 30 g/L

Target radius of treatment

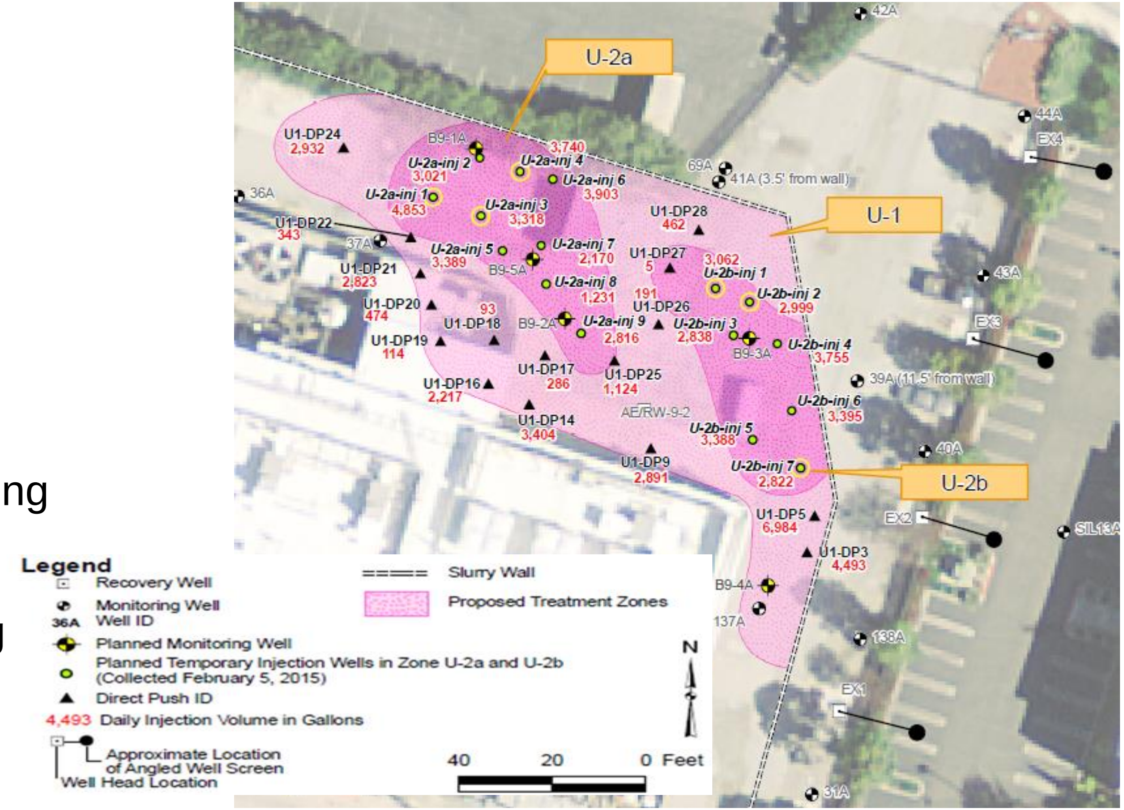
- 10 feet

Total of 318,000 liters

- 2/3 wells and 1/3 temporary boring

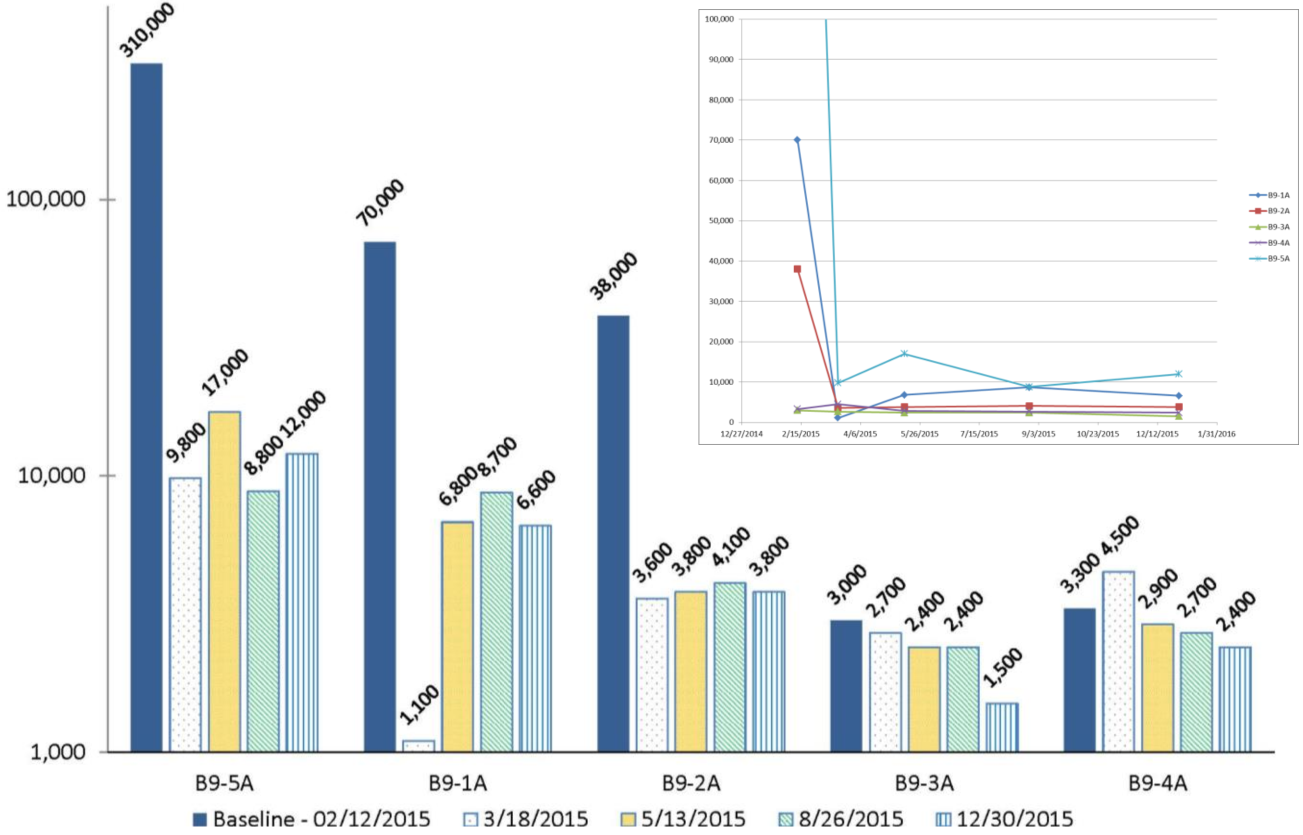
Total Mass Injected

- Sodium Permanganate 3,168 kg
- Sodium Persulfate 9,505 kg



TCE Treatment at Ten Months

- Mass Removal was Equivalent to 25 years of Pump and Treat
- Applied Dosage was Lower
  - 5 g/kg-soil
  - 84,000 gallons
- Dec 2015 Maintenance injections
  - 3,000-5,000 GAL
- Dec 2016 Maintenance injections
  - 15,000-20,000 GAL



Oxidant Consumption and Longevity

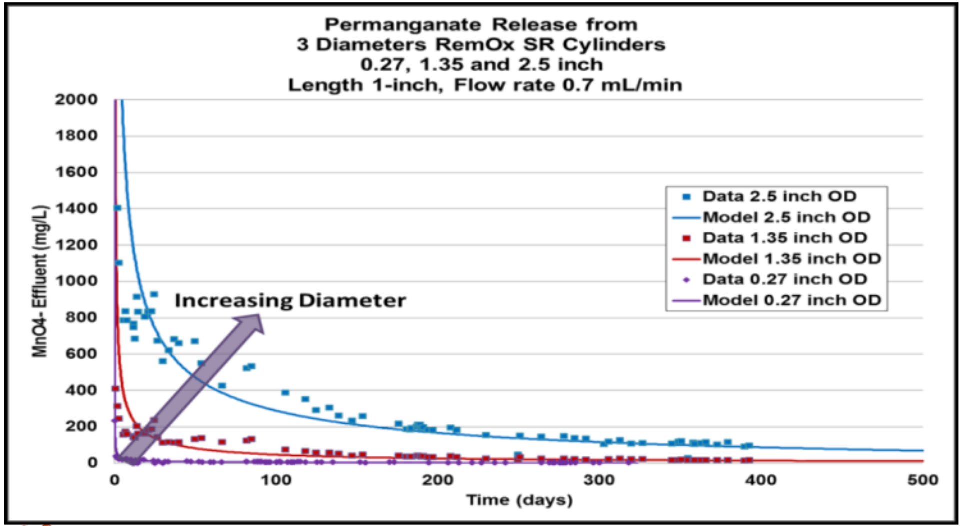
- Thirteen day Injection Event
  - Monitored permanganate until consumed and then measured persulfate concentration
- Permanganate at 55-75% of Co at 15 days
  - 2-4 day half-life
  - 10-30 days of longevity
- Persulfate at 10-95% of Co at 21 days
  - 19-25 day half-life
  - 90-100 days of longevity

Collaboration with Carus Chemical and Universities

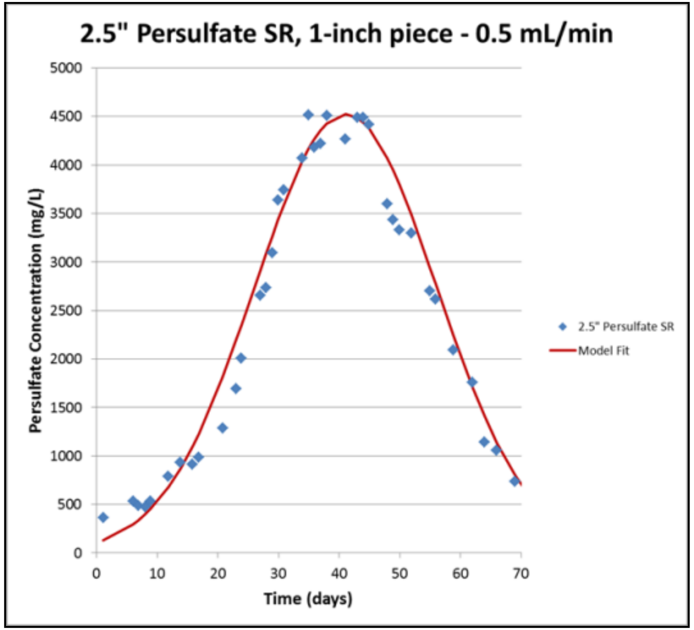
- Collaborative development goals in 2015
  - Treatability of compounds recalcitrant to direct oxidation by permanganates
    - Which radical species are formed?
  - Controlled genesis of key mixed oxide species
  - Development of a method to accurately measure $S_2O_8^-$ and MnO_4^- in homogeneous solutions
- Commercialization Goals in 2016
  - Expand on treatability data – more compounds and media
  - Evaluate impact of elevating the pH of the injected solution
  - Develop site screening protocol

Carus Corporation – Sustained Release (SR) Technology

Permanganate

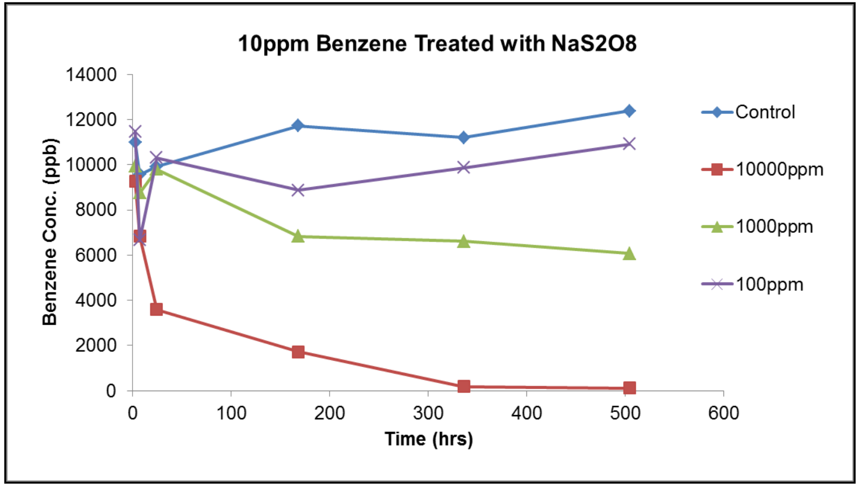


Persulfate

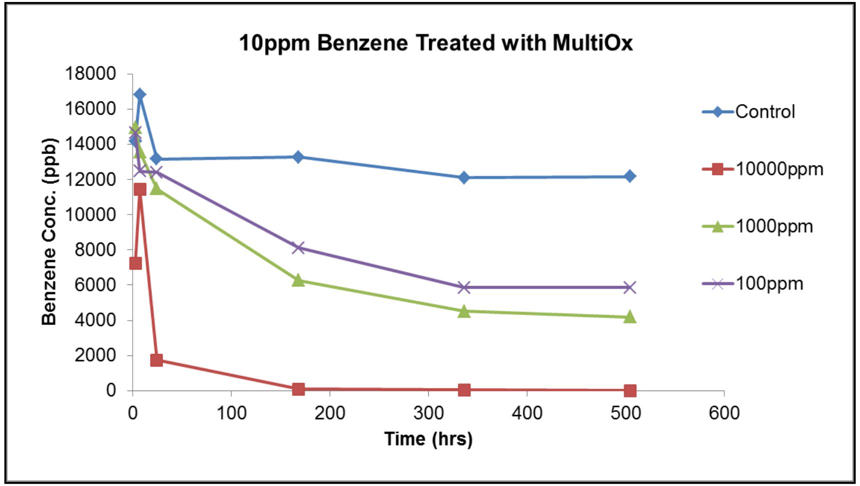


BTEX Oxidation Synergistic Results

Un-Activated Persulfate



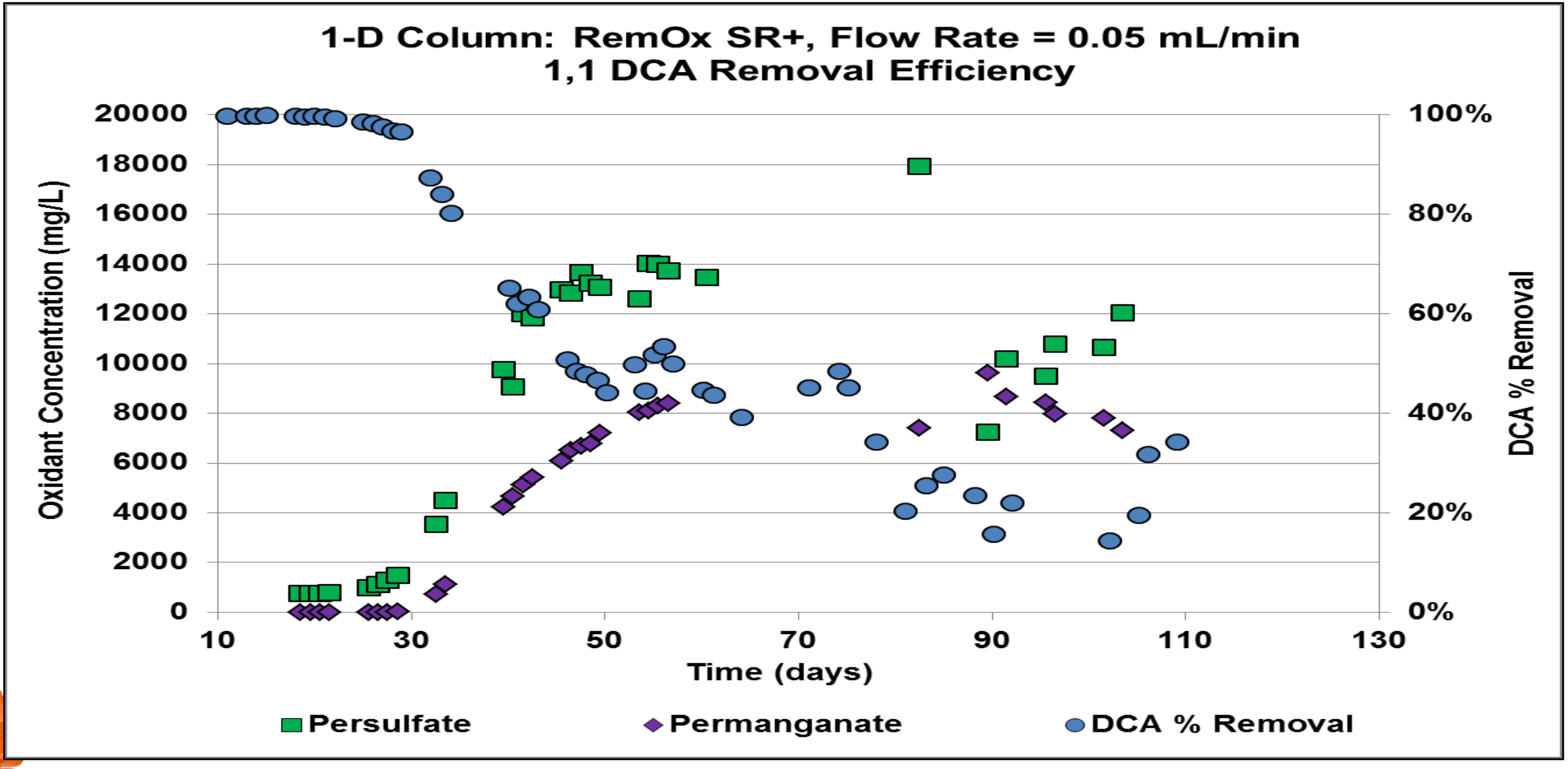
RemOx SR+



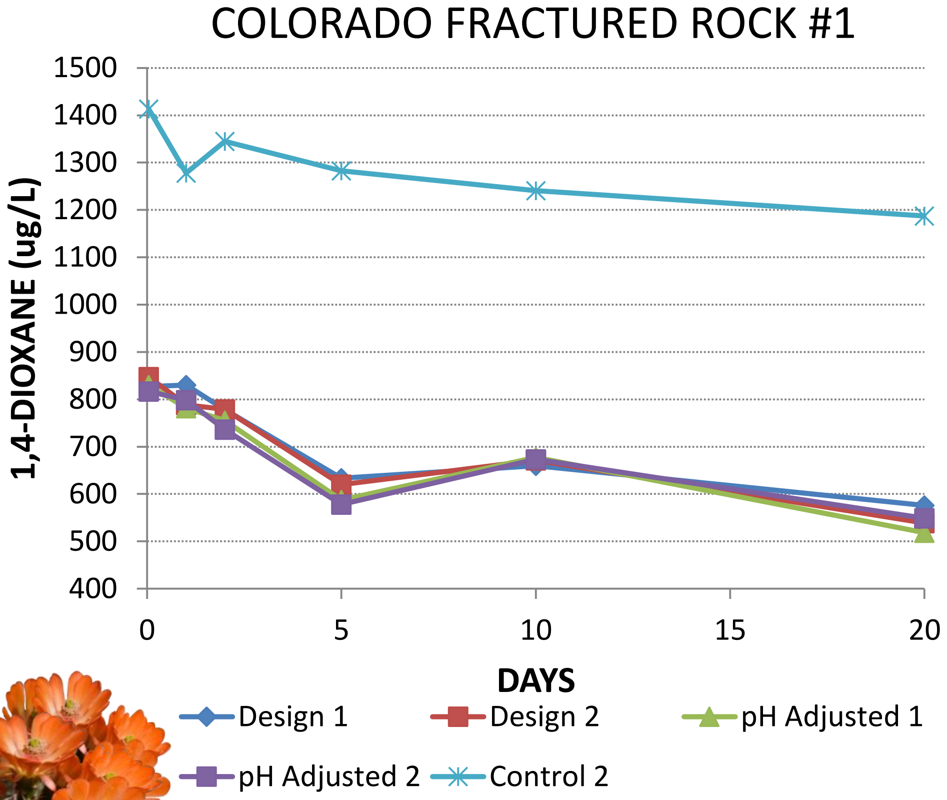
Second Order Oxidation Rate Constants ($M^{-1}s^{-1}$)			
	Permanganate	**Persulfate**	**MultiOx**
Benzene	Neglible	5.72E-5[2]	1.1E-4[2]
Toluene	5.74E-4[1]	5.63E-5[2]	3.2E-4[2]
Ethylbenzene	7.07E-3[1]	5.91E-5[2]	1.9E-3[2]
Xylene(s)	2.22E-3[1]	4.81E-5[2]	4.0E-3[2]
MTBE	8.82E-5[1]	Neglible	7.6E-5[2]

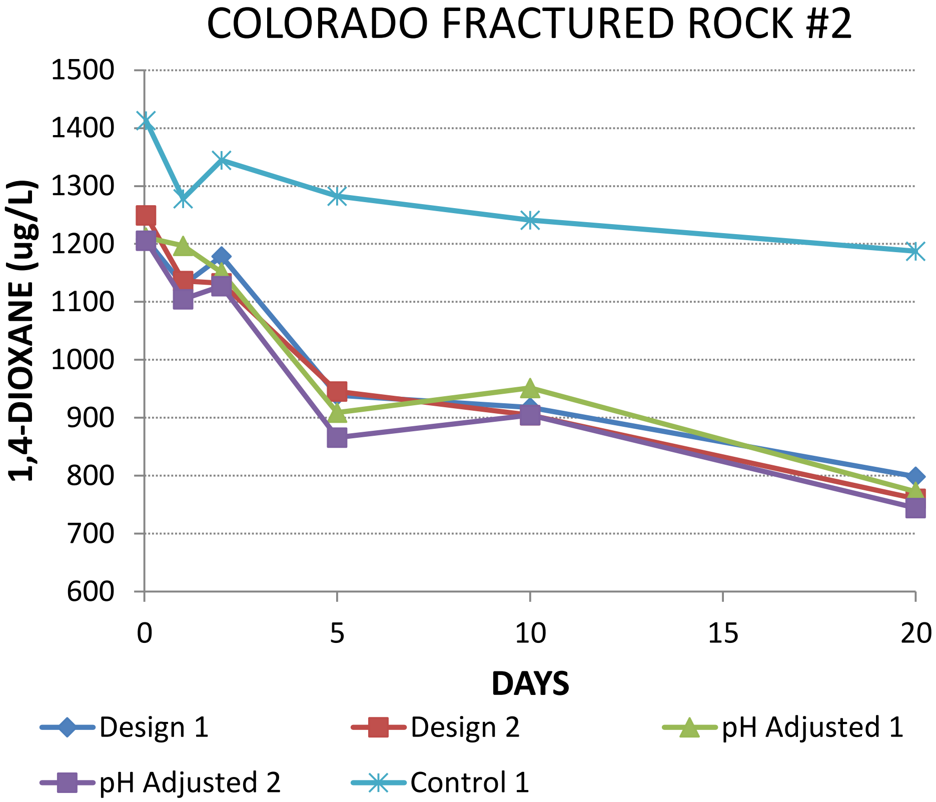
[1]ISCO-kin Database
[2]This study

1,1 Dichloroethane Oxidation over Time



1,4-Dioxane Oxidation over Time





Next Steps

MnAP Projects

- Southern California: Solvents
- Colorado: Vapor Degreaser
- Northern California: API Sludge

On-going R&D

- Role of Base Addition
- Minimum Oxidant Concentrations
- Performance by Media Type

Continued Collaboration

- Clarkson University
- Carus Corporation
- SiREM
- University of California

Treatability of Recalcitrant Compounds

- Freon and 1,2- DCA
- 1,4-Dioxane
- Benzene and TPH
- Perfluoroalkyl compounds (PFCs)

QUESTIONS?

Bruce K Marvin, P.E.
Geosyntec Consultants, Inc.
1111 Broadway, 6th Floor
Oakland, California 94607
01 510 285 2753
bmarvin@geosyntec.com