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Concepts of Chemical Oxidation vs. Chemical Oxygenation and Considerations for Engineered Remediation Design

REMTECH 2015

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AGENDA

- Feasibility and Challenges of Engineered Bio & Chemical Remediation Applications
- Reaction Kinetics: Oxidation vs. Oxygenation
- Selection and Engineering Design Factors and Applications for Oxidation
- Health and Safety Considerations
- Case Studies – Chemical Oxidation by Enhanced Hydrogen Peroxide at contaminated sites

Engineered Bio or Chemical Remediation

- Deep roots tracing to waste water / sewage treatment.
- Controlled vs. Natural Environment
- Technically feasible not financially viable in most cases.
- Perceptions vs. Reality
- Misunderstanding between Oxidation (Mineralization – Chemical Remediation) and Oxygenation (Aeration - Bioremediaton)

Chemicals for Oxidation vs. Oxygenation

Chemical Oxidants	Oxygen Release Chemicals
Enhanced Hydrogen Peroxide (H_2O_2)	Peroxide Compounds
Permanganate (MnO_4^-)	e.g. Calcium Peroxide (CaO_2)
Persulphate ($S_2O_8^{2-}$)	Commercially available ORC products
Ozone (O_3)	Raw Hydrogen Peroxide
To generate **Reactive Species**	To provide **Oxygen (aeration)**

Only successful chelation and activation of chemical oxidants can generate effective reactive species in the field applications!

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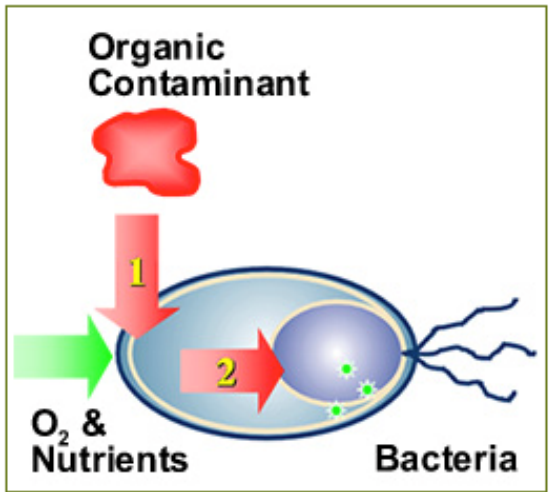
Reaction Kinetics - Oxygenation

- Part of stimulation of microbial activities in bioremediation.
- Process itself is not a contaminant mass removal process.
- A slow oxygen release compound is often misunderstood as a remediation agent.



Reference: ETEC, LLC

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Example - Oxygenation

- Calcium peroxide naturally decomposes very slowly to form calcium hydroxide and oxygen.
- Usage: Bioremediation and baking industry.

$$2CaO_2 + 2H_2O \rightarrow 2Ca(OH)_2 + O_2$$

or

$$CaO_2 + 2H_2O \rightarrow Ca(OH)_2 + H_2O_2$$

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

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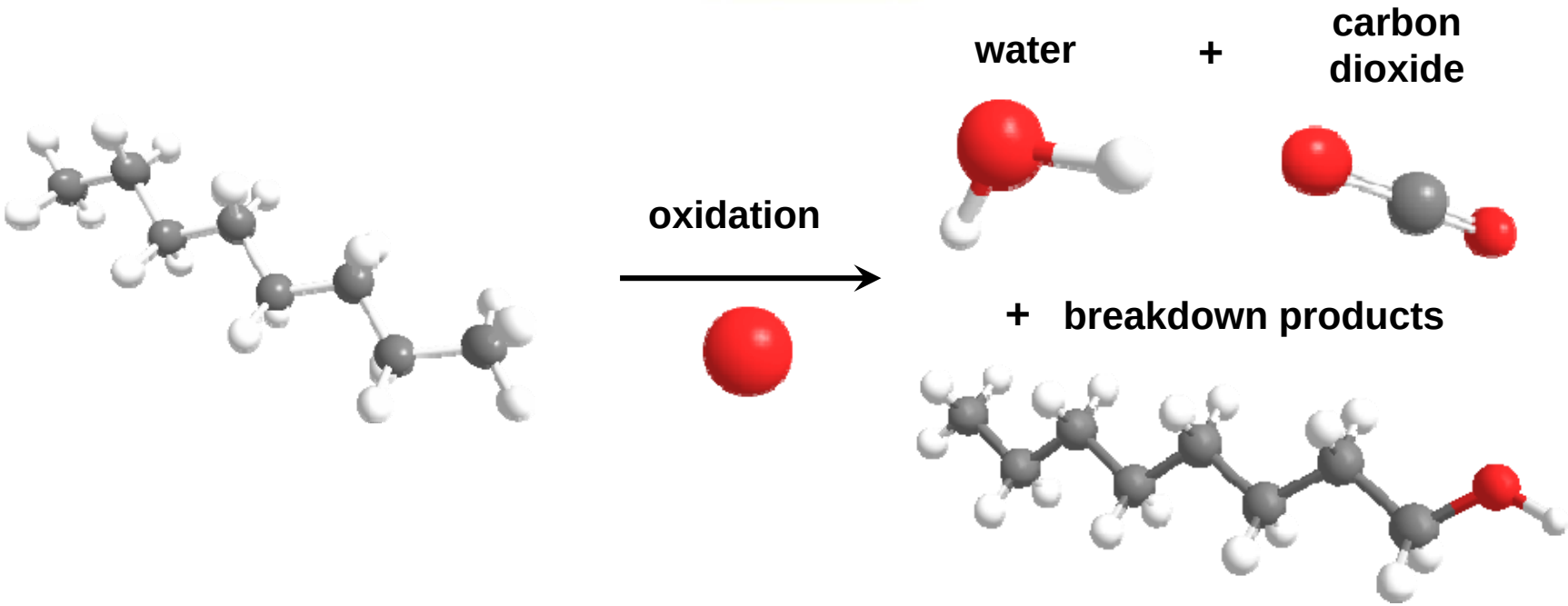
Reaction Kinetics – Oxidation by Enhanced Hydrogen Peroxide

Oxidation – Decomposition of Organic Compounds



Reaction continues to reduce original contaminants and breakdown products as it continues.

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Ex-situ Application- Oxidation by Enhanced Hydrogen Peroxide

- Unsaturated soils
- Shallow soils (<4 mbg)
- Typically fine grained
- Large volume treatment per day
- Remote or local access
- Rapid treatment (<3 days)
- Low input requirements
- Cost/Time/Safety/Sustainability

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In-situ Application- Oxidation by Enhanced Hydrogen Peroxide

- Groundwater (Vadose Zone)
- Dissolved phase impacts
- Deeper units (>3 mbg)
- High conductivity/bedrock
- Remote or local access
- Year round
- Low input requirements
- Cost/Time/Safety/Sustainability

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Design Basis and Parameters for Oxidation by Enhanced Hydrogen Peroxide

- Geological / hydrogeological characterization
- Background analytical parameters
- Partitioning in soil and groundwater
- Size of plume
- Oxidant demands – SOD & NOD
- Selection of a suitable oxidant
- Chelation / activation strategies
- Target timeframe and end points
- and etc.

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Heath & Safety Concerns

- Not a Routine Set-up
  - Regulation & supplier requirements
  - Client engagement & readiness (H&S, asset integrity, etc)
  - Project/stakeholder requirements
  - Controls – Administrative/Engineered/PPE/Competency

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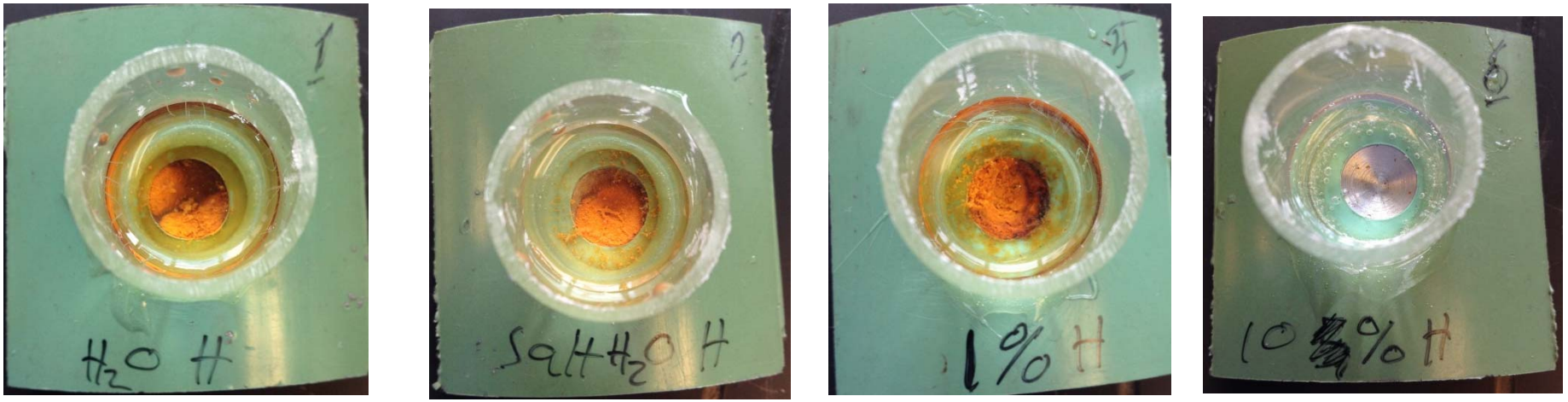
Corrosion Testing - Enhanced Hydrogen Peroxide
Surface observation (FBE)

- **Before exposure**

- **After 30 days**



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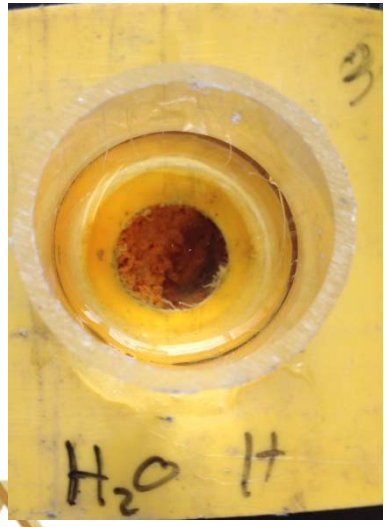
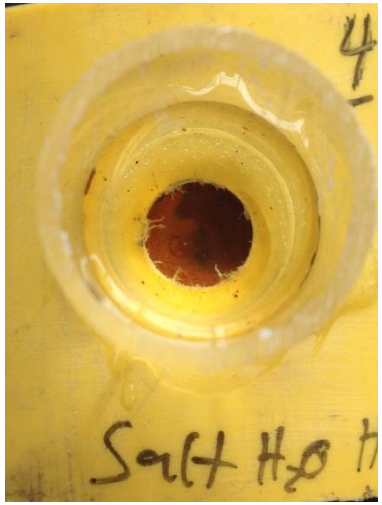
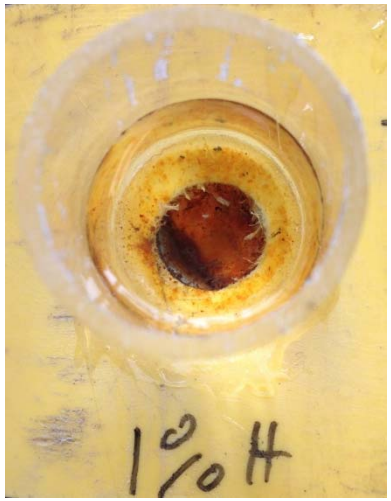
Corrosion Testing - Enhanced Hydrogen Peroxide
Surface observation (YJ)

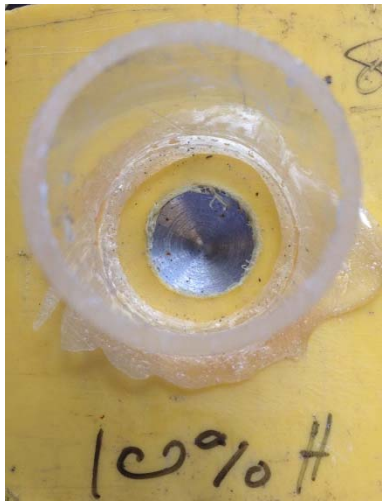
- **Before exposure**

- **After 30 days**









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Case Study 1
Ex- situ Chemical Oxidation

Optimized mixing for effective reactions

Generate aimed chemical oxidation reactions in fine grained soils

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Details

- Abandoned Pipeline – Alberta, Canada
- When: 2012 – 2013
- Contaminants of Concern: BTEX/F1-F4
- Impacted Media and Volume: >10,000 m^3 of Fine Grained Soil
- Tasks: Ground Disturbance and Proximity Arrangement, Field Screening, Procurement, Blending, Field Applications, Sampling
- Project Value - $1,300,000
- Completion - 100%

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The Problem

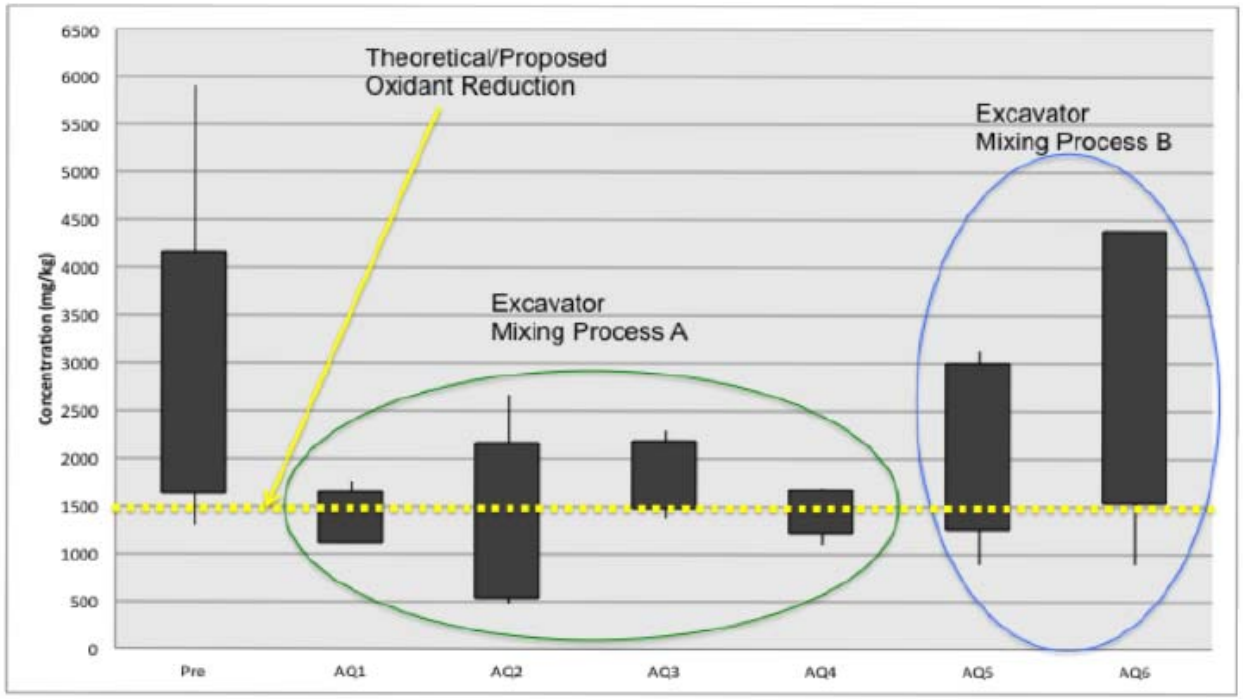
- Contaminated soil discovered by landowner when drilling fence posts
- Sandy silt/clay soils
- Minimal site disturbance required
- External stakeholder sensitivities
- Contamination:
  - BTEX: up to 7 mg/kg
  - PHC F1: up to 700 mg/kg
  - PHC F2: up to 950 mg/kg
  - PHC F3: up to 1400 mg/kg

The Approach - ChemOx®

- Ex-Situ Chemical Oxidation Program (EXCO®)
  - Direct application of 250,000 L of TRIUM's ChemOx® enhanced hydrogen peroxide over period of 10 weeks
  - Remediation Train® approach to supplement EXCO® with landfill program of 3,500 m^3 of highly impacted soils

The Results

- Samples collected within 24 hours of treatment completion satisfied de minimus remediation criteria (AENV Tier I, Agricultural Areas) or were below lab detection limits
- Cost savings versus complete landfill option
- Low footprint and program support by landowner
- Zero health and safety events

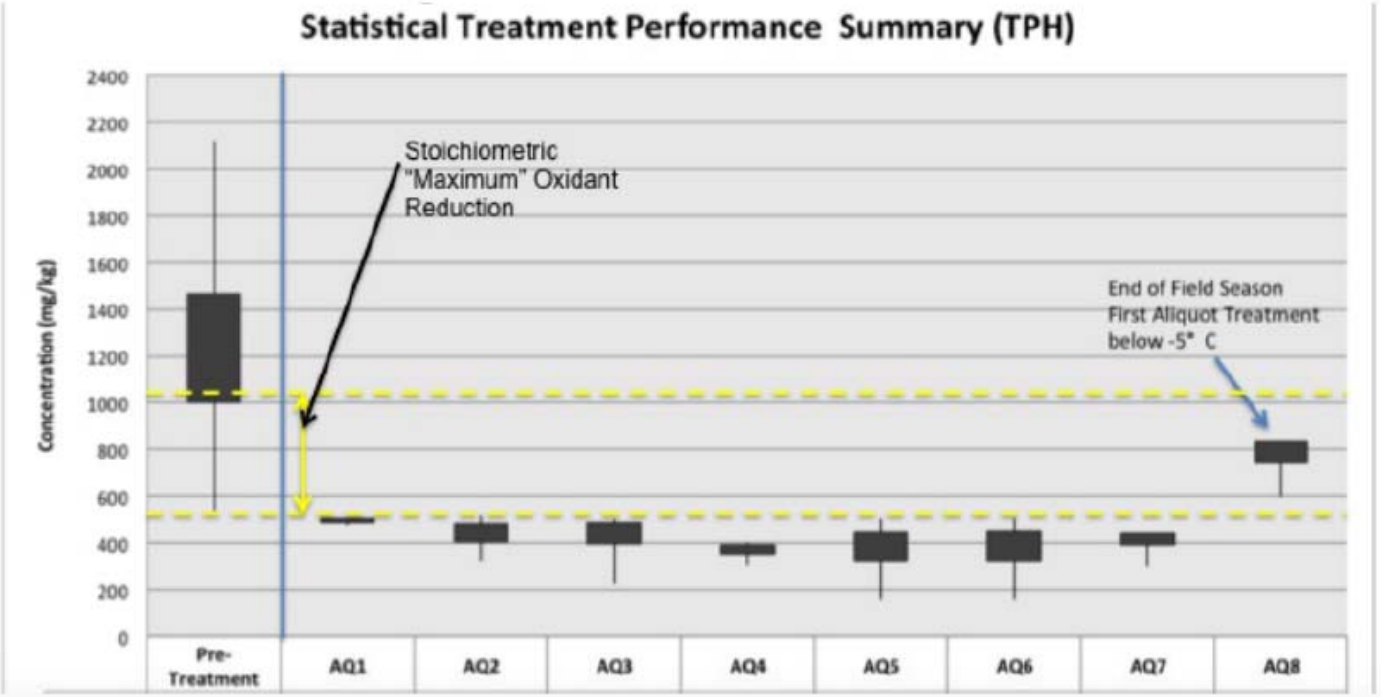


Excavator Process

- Increased variability
- Reduced reproducibility

Mulcher Process

- Reduced variability
- Increased reproducibility



Case Study 2
In-Situ Chemical Oxidation

Mass destruction to overcome residual impacts

Overcome rebounding and site closure within the target timeframe

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Detalls

- Active Retail Gas Station – Edson, Alberta
- When: 2013/2014
- Contaminants of Concern: BTEX
- Impacted Media and Volume: Groundwater, Discrete Point Source Treatment
- Tasks: Program Design, Injection Well Installation, Procurement, Blending, Field Applications, Sampling
- Project Value - $111,000
- Completion - 100%

The Problem

- Property sale pending, expedited results required
- High vehicle/pedestrian traffic area
- Minimal site disturbance and small footprint required
- Winter season
- Contamination from UST area
- Sitly Clay soils, shallow groundwater table (< 3 mbg)
- Contamination:
    - Groundwater
        - Benzene, ethylbenzene: Marginally impacted, exceeding site criteria by less than <1 mg/L
        - Bezene criteria - 0.005 mg/L
        - Ethylbenzene criteria - 0.0024 mg/L

The Approach - ChemOx®

- Pre and post treatment verification sampling
- In-Situ Chemical Oxidation Program (ISOTEC®)
    - Install 6 injection wells discretely within contaminated interval
    - Secure site for oxidant storage and exposure control
    - Conduct injection activities over night to avoid conflict with gas station operations
    - Heated injection units allow winter execution
    - Inject 7,600 L of TRIUM's ChemOx® enhanced hydrogen peroxide over 3 programs of <5 days each

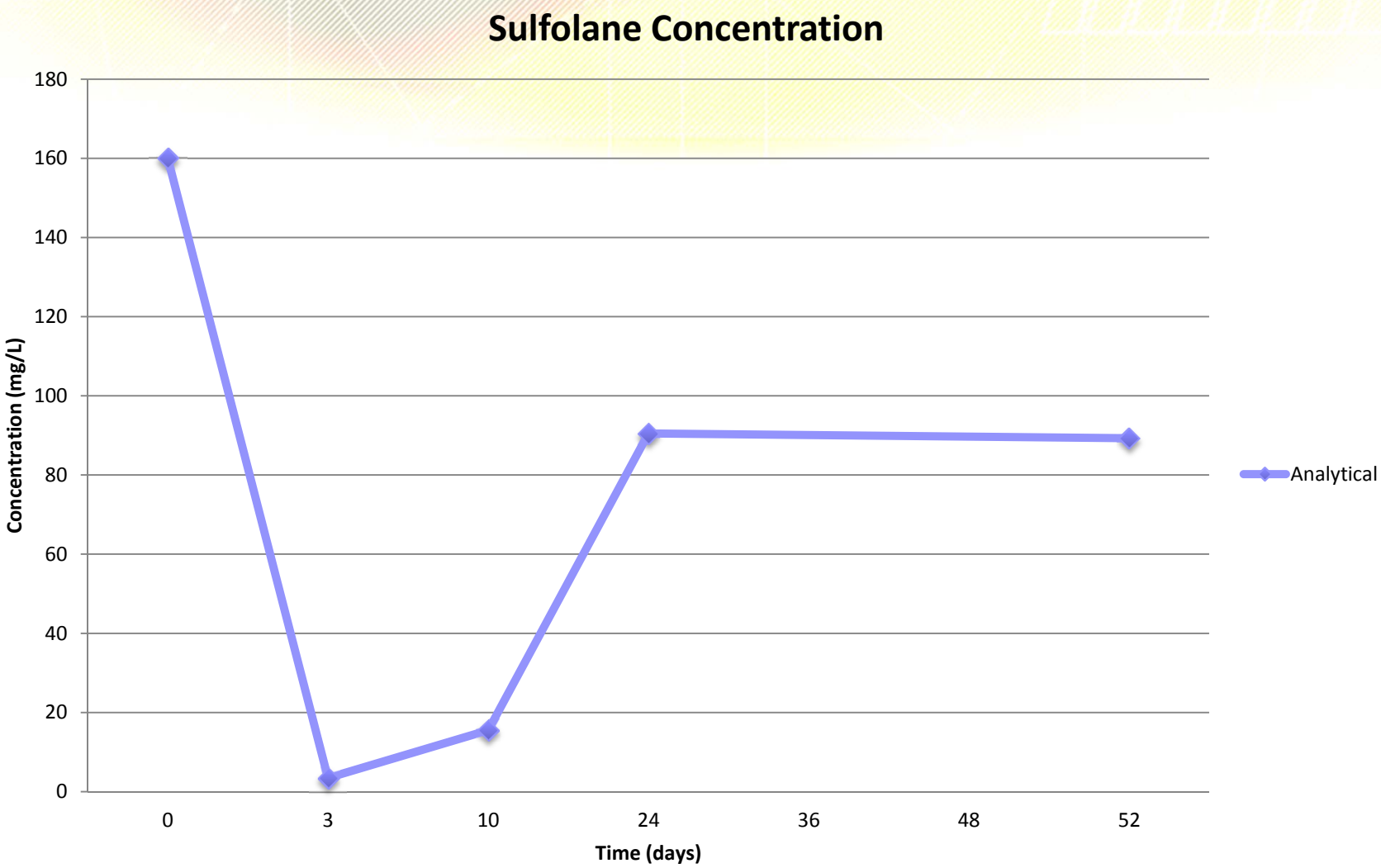
The Results

- Post treatment samples satisfied remediation target and allowed for approval of sale
- Real-time performance monitoring and reporting to client
- No on-site disturbance to site operations
- Zero lost time or first aid health and safety events

Case Study 3 – Sulfolane in GW

- Treatment at the most heavily impacted monitoring well location.
- Over 3 days of injections a total volume of 320L of 15% Enhanced Hydrogen Peroxide was administered.
- Four groundwater samples were taken 3, 10, 24 and 52 days from the beginning of the pilot.

Analytical Results for Field Pilot



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Proof of Concept

- Does not use dedicated monitoring wells as injection wells, as short term analytical results can be biased by various other injection related factors (i.e. dilution, dispersion, etc).
  - ✓ Closed system dilution
  - ✓ Closed system displacement
  - ✓ Groundwater flow/chemical diffusion
  - ✓ Open system diffusion
  - ✓ Open system hydraulic dispersion
  - ✓ Closed system mass destruction

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Summary

- The groundwater flow and open system dispersion models provide good correlation and evidence of the effects of “dilution” to the system.
- This extends up to the “24/52” day sampling events, where the linear relationships of the models deviate.
- This deviation could be considered reflective of reductions due to oxidation, with a potential reaction efficiency of up to 80% being observed.
- The 100 day sampling event is planned for early October

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www.chemox.org

Locations

Cochrane (HQ) / Edmonton / Drayton Valley

International

USA / S. Korea / Middle East / China

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Thank you

Acknowledgment

CHEMCO inc.

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