Catalyzed Peroxygens: Chemistry and Applications

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Presentation Outline

- Fenton's Reagent
- Modified Fenton's Reagent (Catalyzed H_2O_2 Propagations--CHP)
  - Unexpected Reactivity of Superoxide
  - Enhanced Contaminant Desorption and DNAPL Destruction
  - Stabilization of Hydrogen Peroxide
- Activated Persulfate
  - Activators
    - Proposed Mechanism: Base Activated Persulfate
    - Evidence for Organic-Activated Persulfate

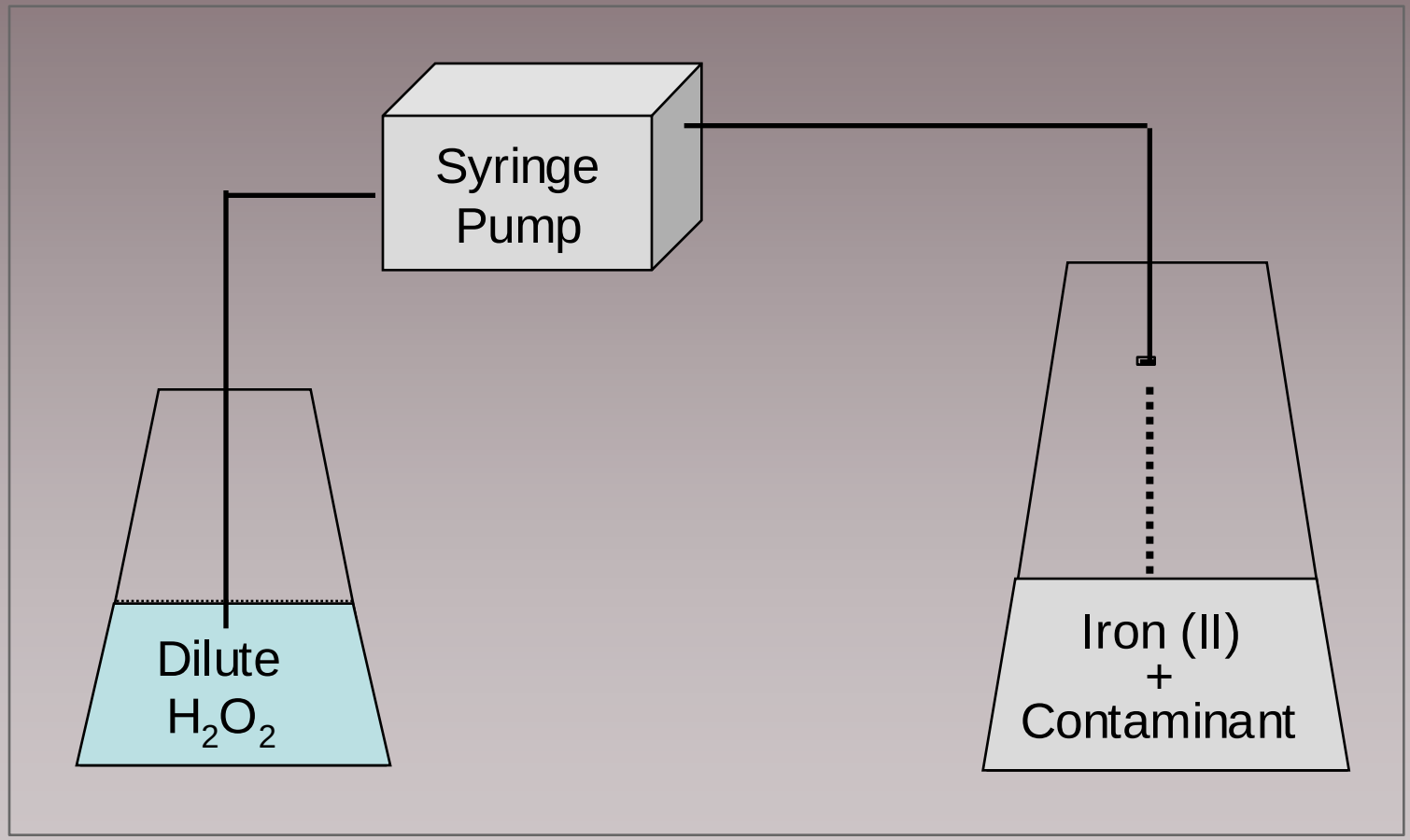
Peroxygens Used for In Situ Chemical Oxidation (ISCO)

- Peroxygens
  - Have a -O-O- moiety
  - Hydrogen Peroxide
    - H-O-O-H
  - Persulfate
    - $^{-}SO_3$-O-O-SO_3^{-}

Fenton's Reagent

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH\bullet + OH^-$$

Traditional Fenton's Reagent



Characteristics of Hydroxyl Radicals

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH\bullet + OH^-$$

$$OH\bullet + R \rightarrow ROH$$

- Strong oxidant
- Moderately nonselective
- Extremely short lived

Compounds Reactive With OH•

- Aromatics
  - BETX
  - Chlorophenols and Chlorobenzenes
  - PCBs and PCDDs
- Aliphatics
  - Alkanes and Alkenes
  - TCE, PCE
  - 1,4-Dioxane

Compounds Not Reactive With OH•

- Halogenated Alkanes
  - Carbon Tetrachloride
  - Hexachloroethane
  - Freons
  - Low Reactivity with TCA
- Keto Acids
  - Oxalate
  - Malate
  - Pyruvate
- Sorbed Contaminants and NAPLs

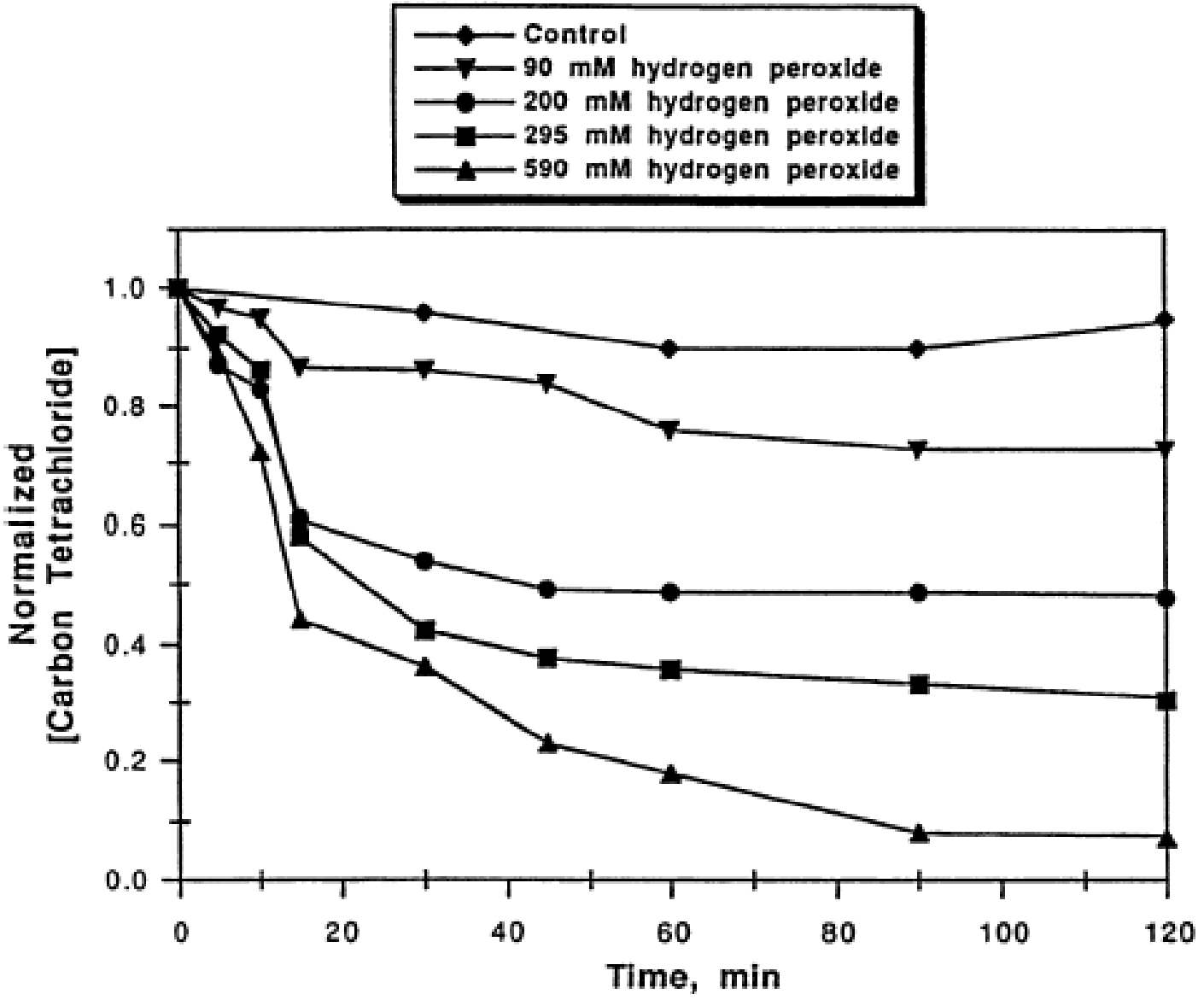
A Simple Propagation Reaction

$$OH\bullet + H_2O_2 \longrightarrow H_2O + O_2\bullet^- + 2H^+$$

- Propagation reactions are dominant
  - New name: Catalyzed H_2O_2 Propagations (CHP)
- Superoxide:
  - Weak nucleophile and reductant
  - Highly reactive when dissolved in organic solvents
  - Minimal reactivity in water

Unexpected Reactivity of Superoxide in CHP Systems

Carbon Tetrachloride Degradation with Increasing H_2O_2 Concentration



Unexplained Reactivity in CHP Systems

- Contaminants Unreactive with Hydroxyl Radical Rapidly Treated in CHP Systems
  - Carbon Tetrachloride
  - Hexachloroethane
  - 1,3,5-Trinitrobenzene
  - Sorbed Contaminants
  - DNAPLs

Consensus on Superoxide Reactivity in Water

"An intellectually curious species which is characterized by minimal reactivity in aqueous systems"

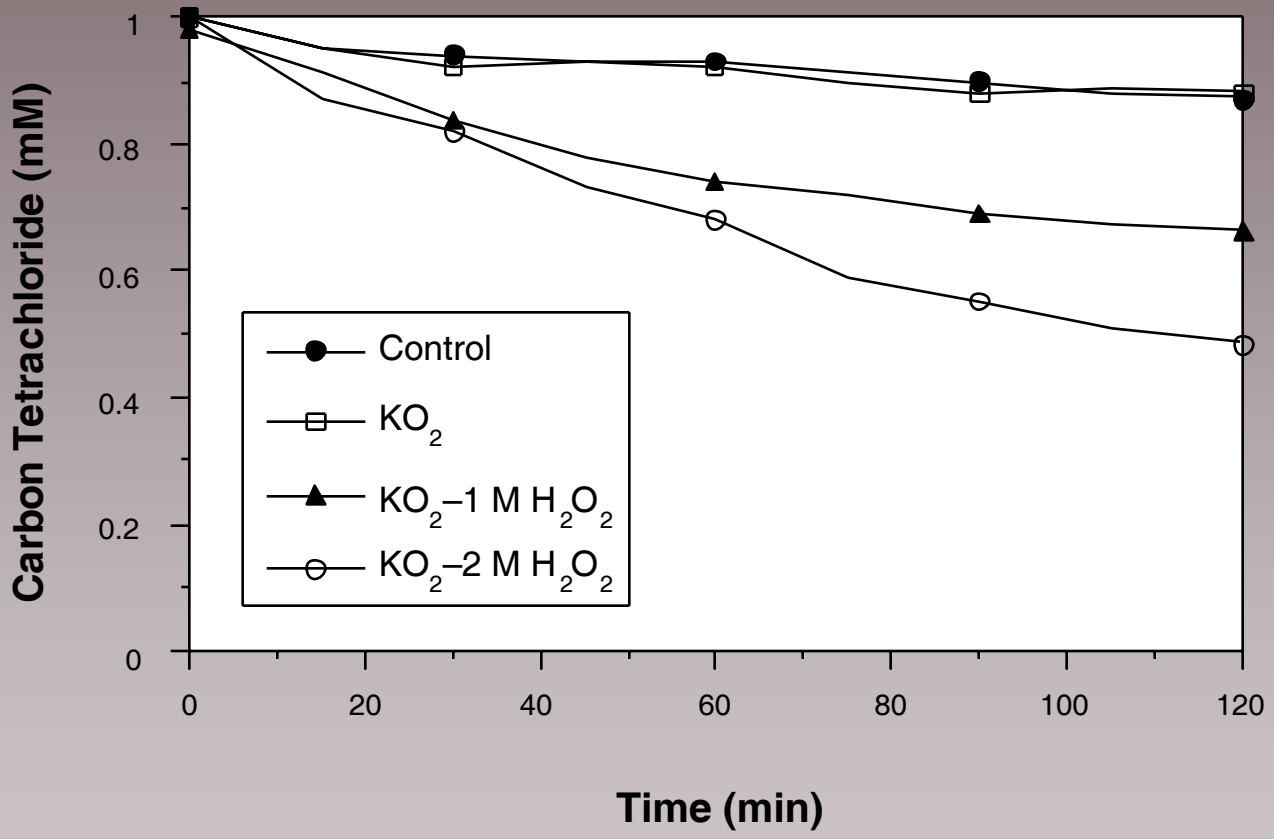
Sawyer, D.T., and J.S. Sullivan. How Super is Superoxide? 1971. *Acc. Chem. Res.* 14:393-400.

Solving the Superoxide Reactivity Puzzle

Idea: CHP reactions do not occur in pure aqueous systems, but in 2–12% hydrogen peroxide.

Hypothesis: Hydrogen peroxide, which is less polar than water, may be present in sufficient concentration to increase the reactivity of superoxide.

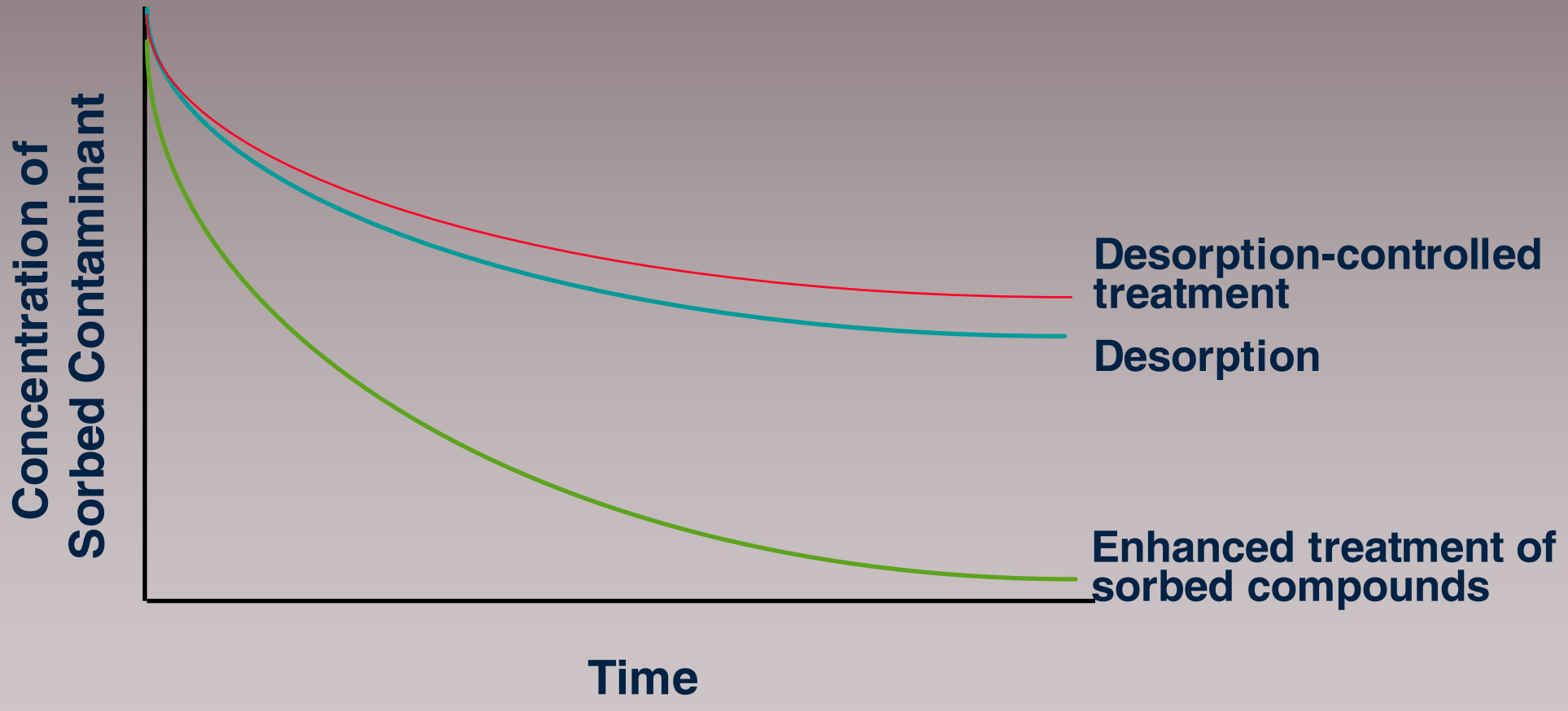
Effect of H_2O_2 on Superoxide Reactivity



Another Benefit of Superoxide:

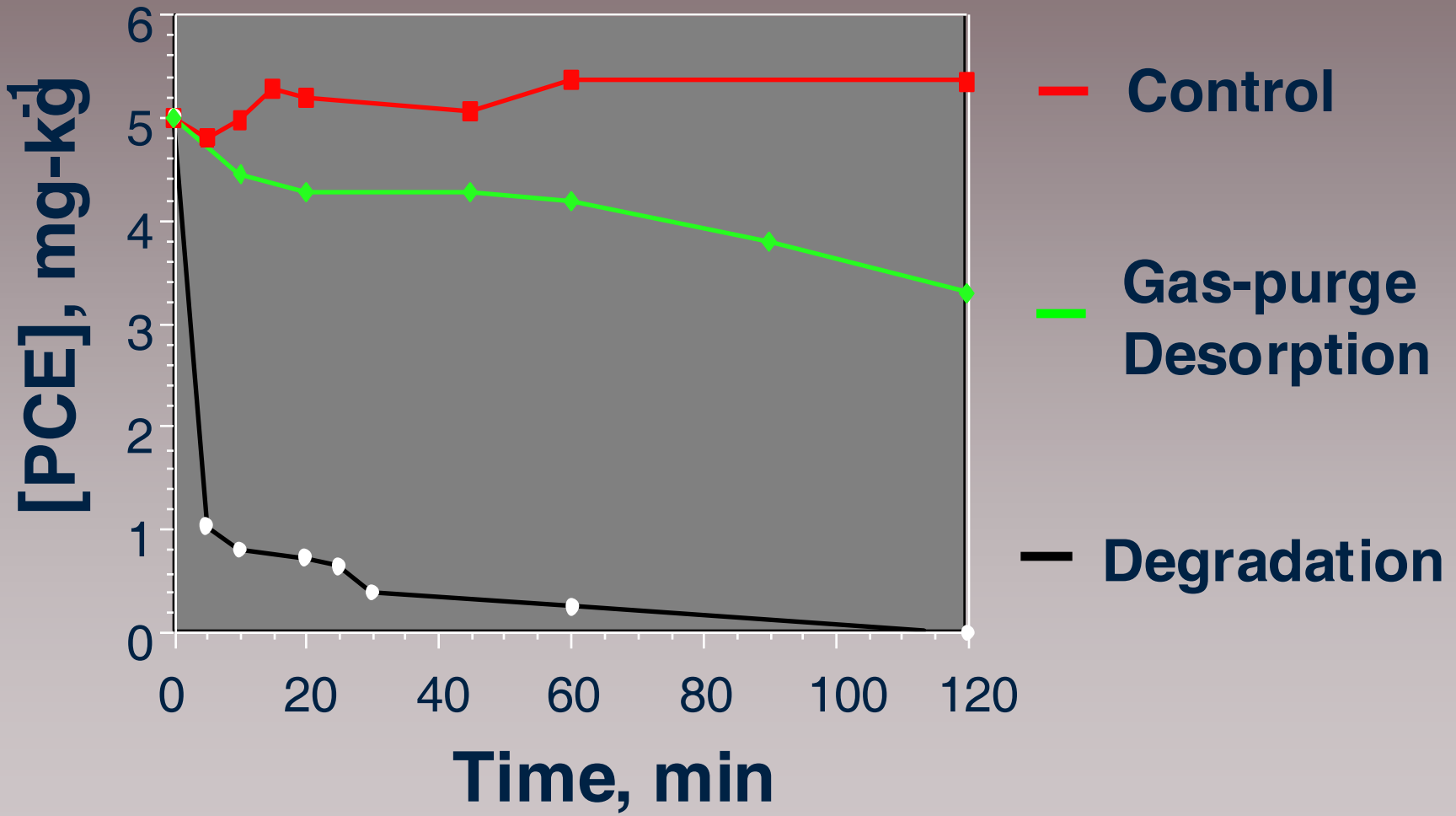
Enhanced Treatment of Sorbed Contaminants and DNAPLS

Desorption-Treatment Dynamics

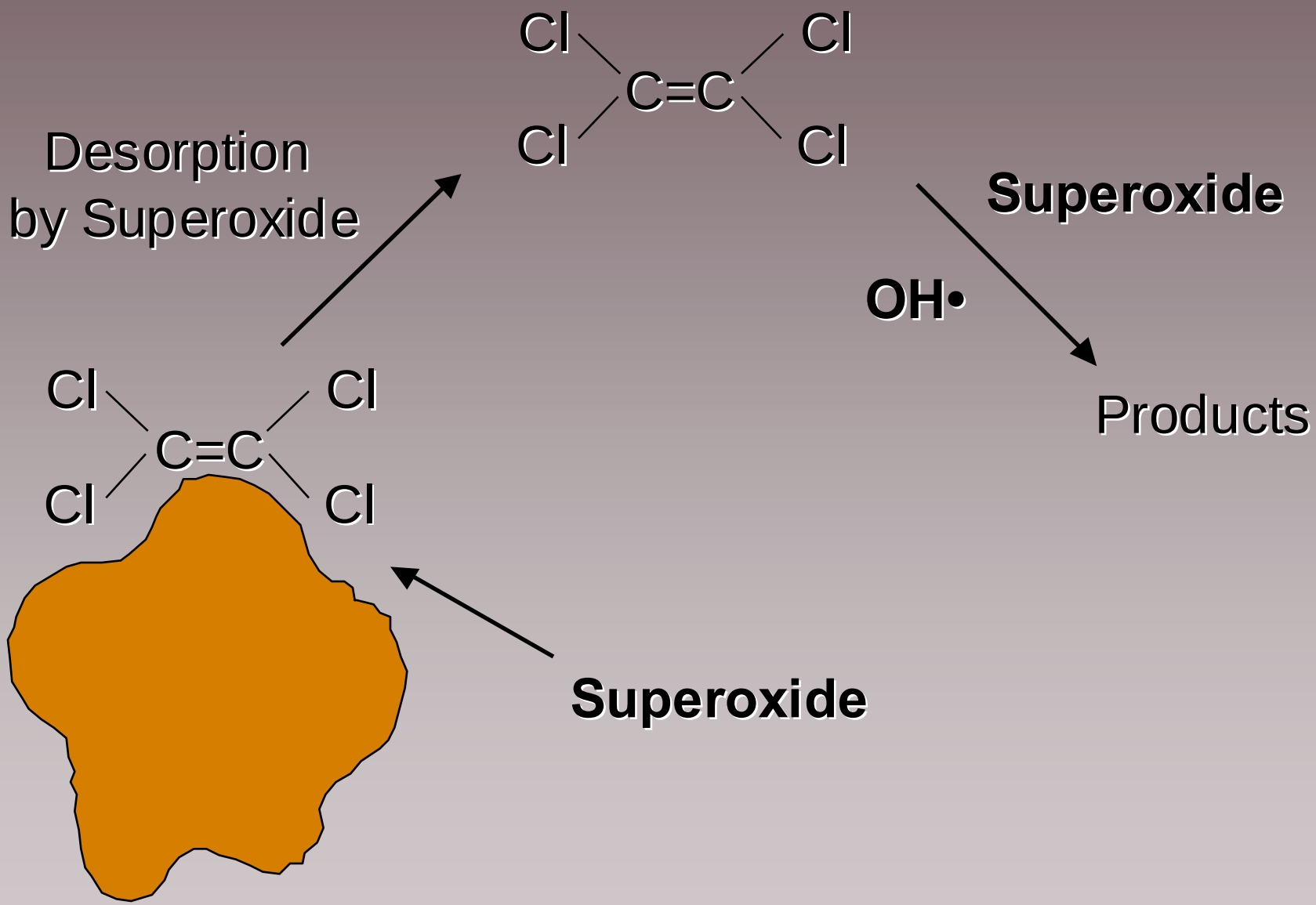


Degradation of PCE by CHP and its Corresponding Gas-purge Desorption

(Watts *et al.* 1999. *Environ. Sci. Technol.* 33:3432-3437)



Superoxide: The Species Responsible for Enhanced Contaminant Desorption



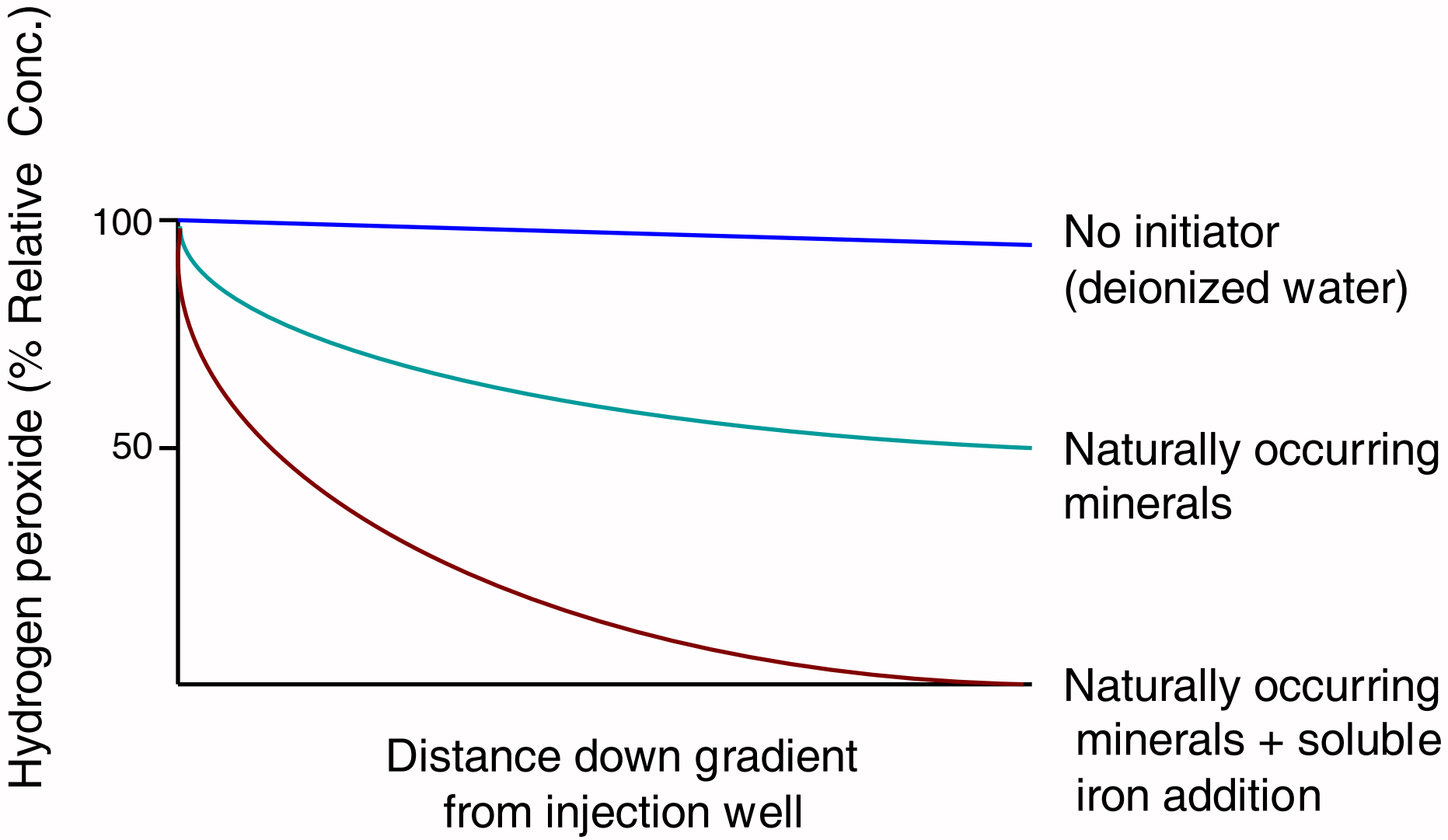
Increased Hydrogen Peroxide Stability in the Subsurface

CHP Initiators and Catalysts

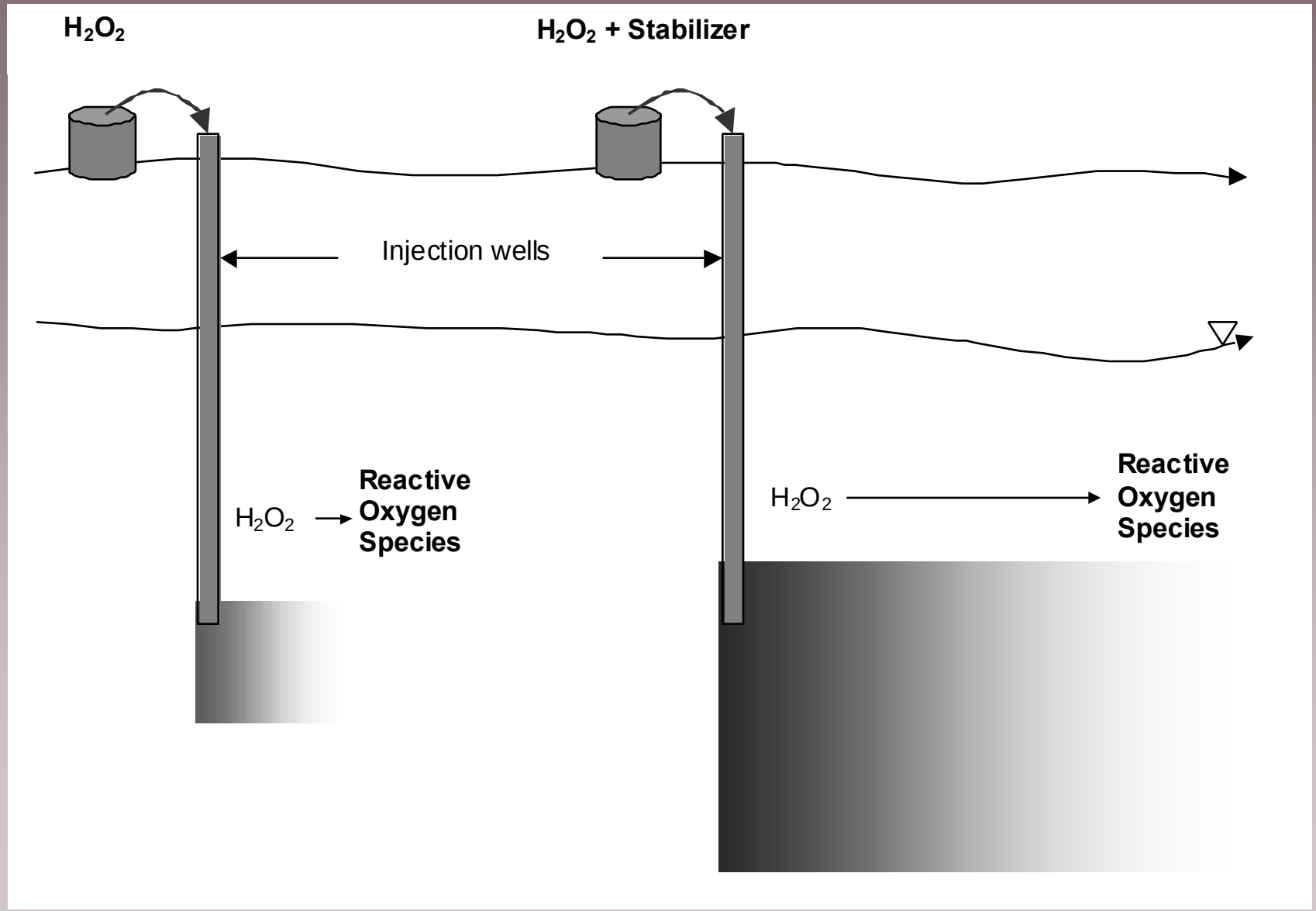
H_2O_2 + Initiator → Reactive Oxygen Species

- Naturally-occurring initiators
  - Iron oxide minerals
    - Goethite
    - Ferrihydrite
  - Manganese oxide minerals
- Initiators added for CHP ISCO
  - Iron (II)
  - Iron (III): Superoxide-driven reaction
  - Iron chelates

Effect of Iron Addition on Hydrogen Peroxide Decomposition Rate



Enhanced Delivery of H_2O_2

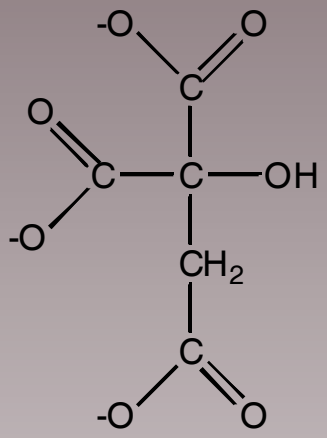


“Ineffective” Iron-Chelates

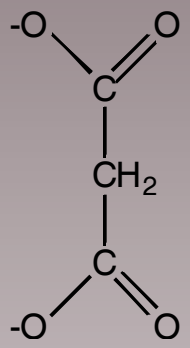
(Sun, Y., and J.J. Pignatello. 1992. *J. Agric. Food Chem.* 40:322-327)

- DTPA (Diethylenetriamine pentaacetic acid)
- Citrate
- Gallate
- Malate
- Malonate
- Oxalacetate
- Oxalate
- Pyruvate
- Phytate
- Succinate

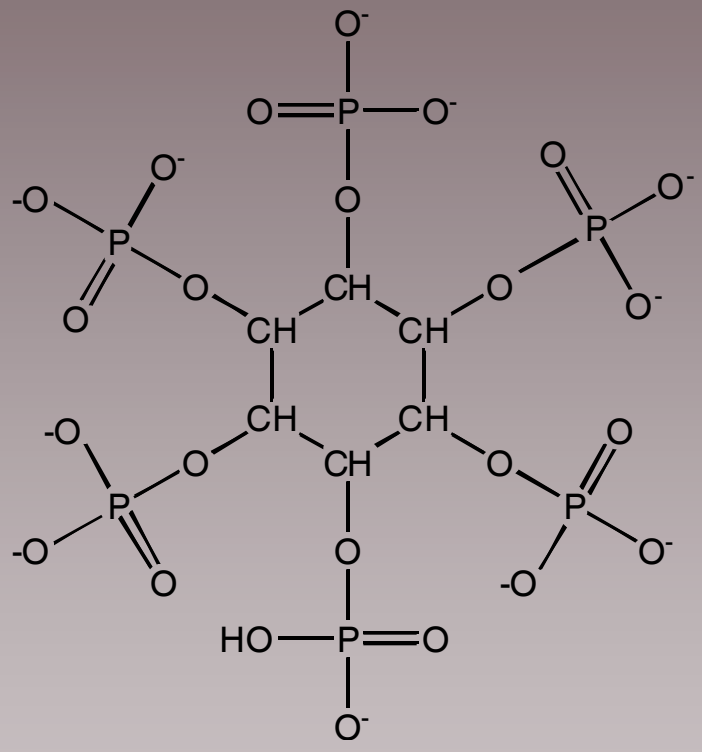
Most Effective Stabilizers



Citrate

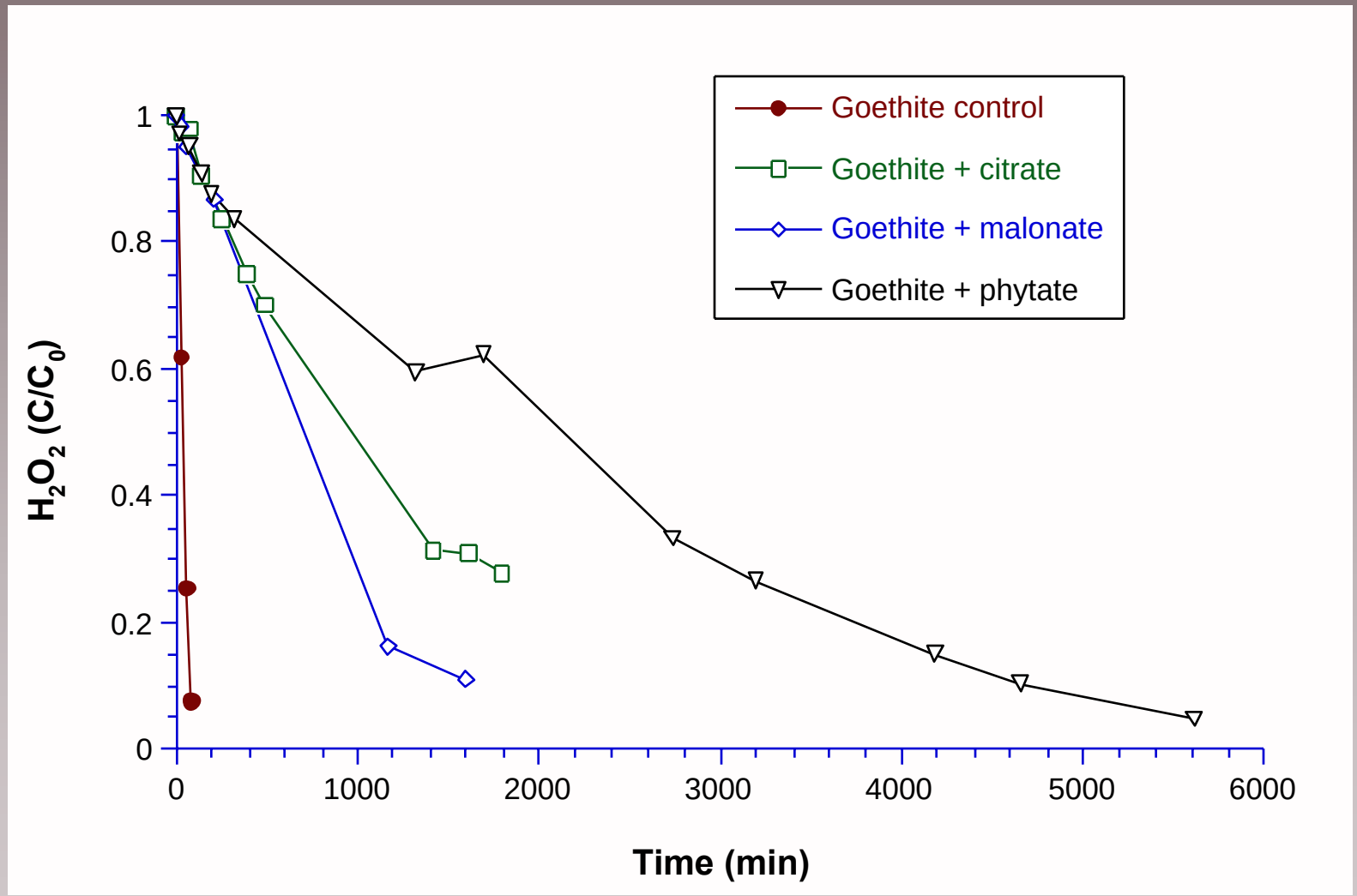


Malonate

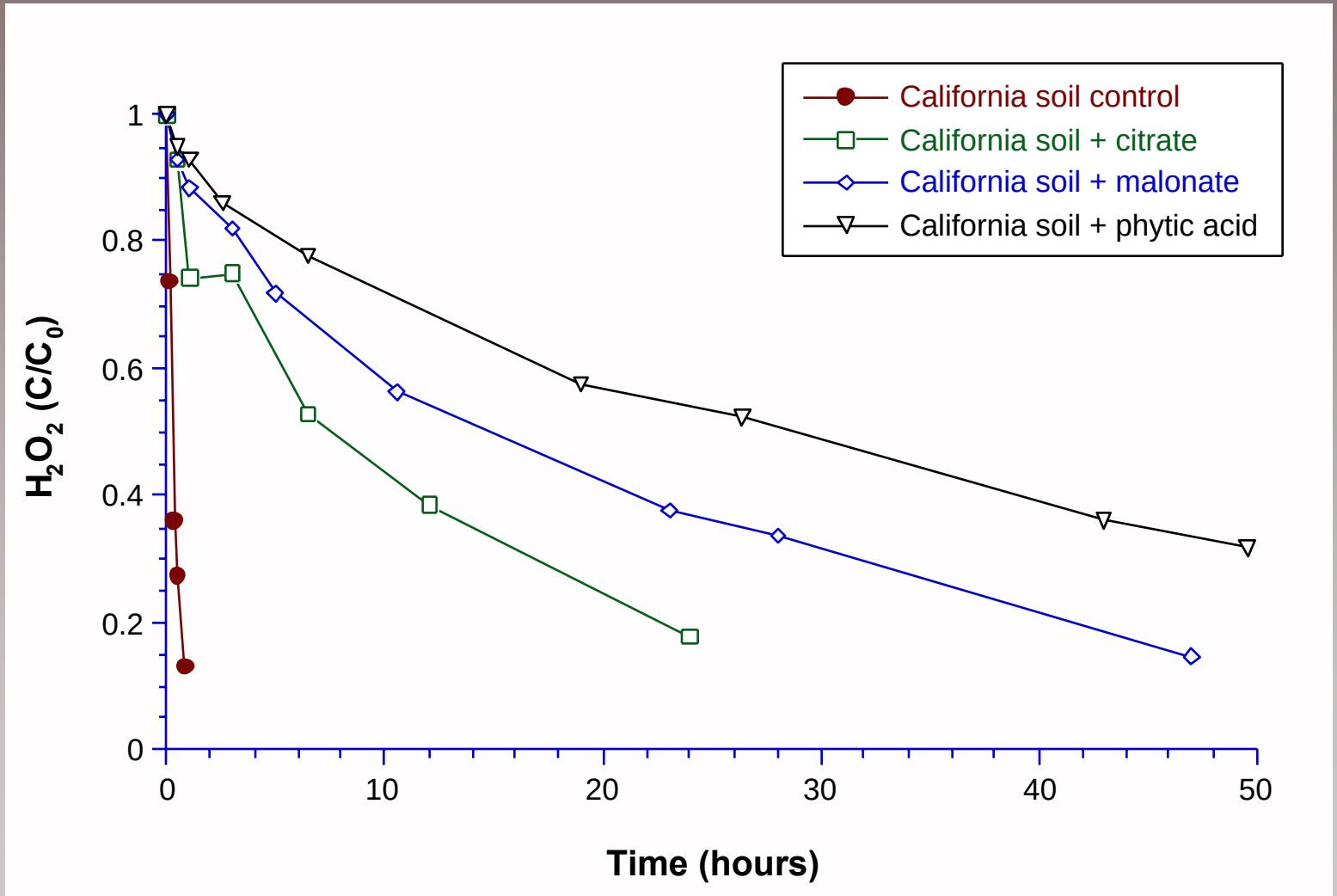


Phytate

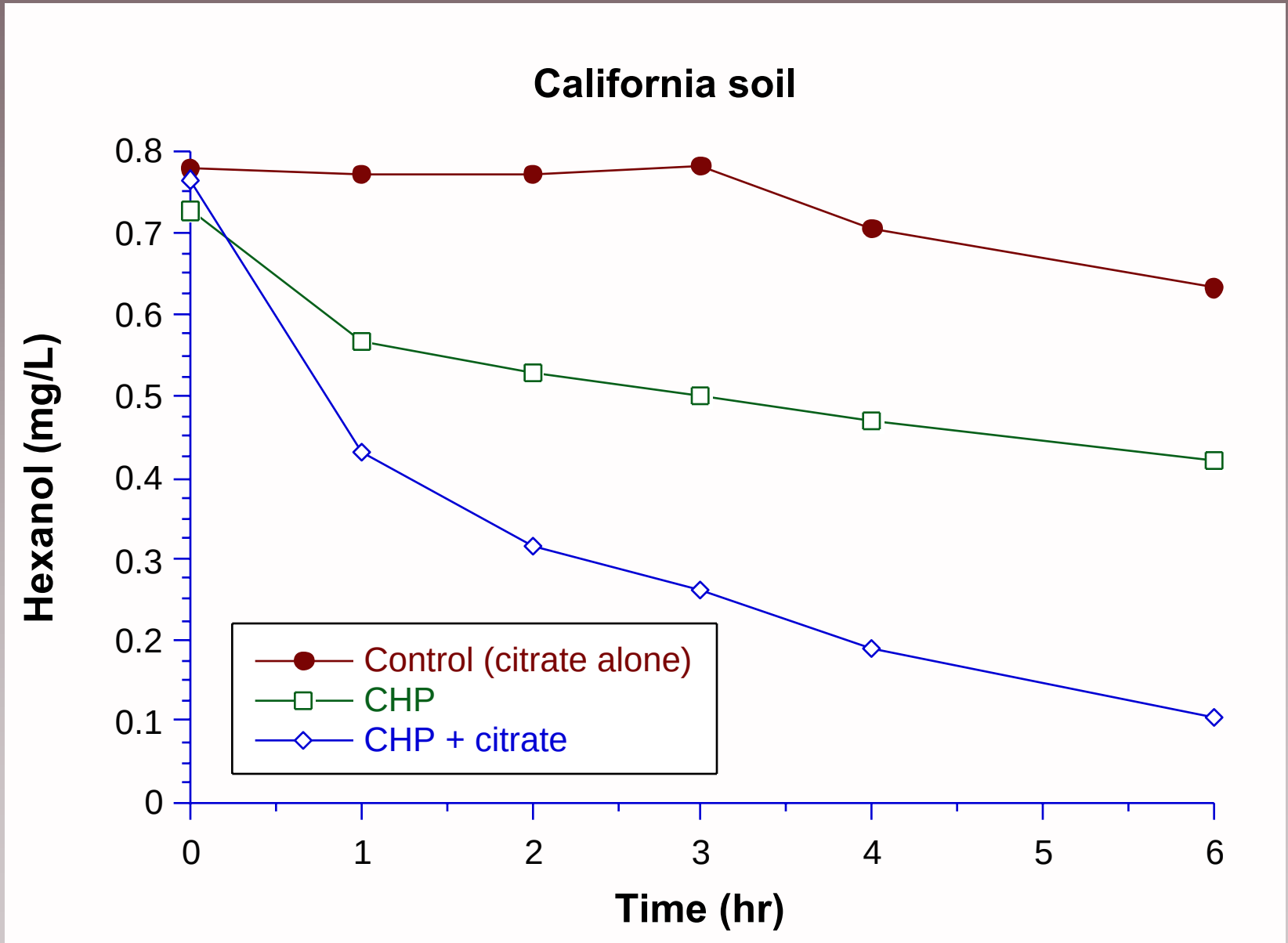
H_2O_2 Stabilization in Goethite Slurries



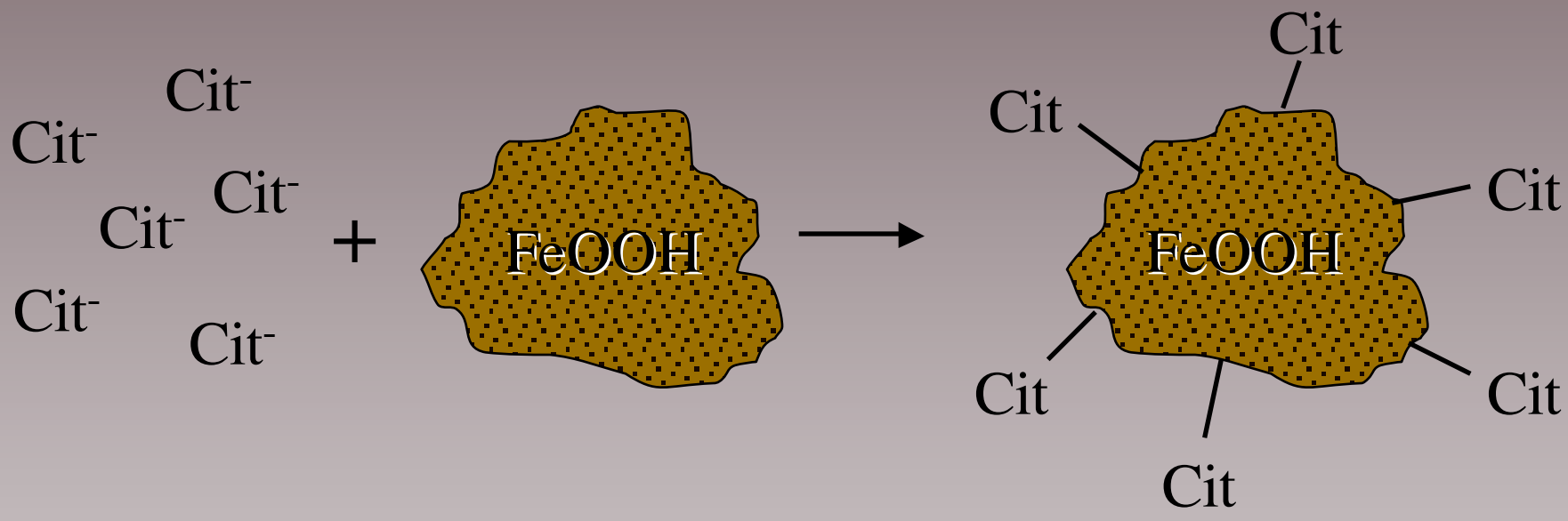
H_2O_2 Stabilization in the Presence of Subsurface Solids Collected from California



Effect of Stabilizer on OH• Generation



Possible Stabilization Mechanism: Binding to Mineral Surfaces



A New Research Challenge: Mechanisms of Persulfate Activation

Persulfate Activators

- Ultraviolet Light
- Heat
- Transition Metals
- Basic Conditions

Persulfate Activation by Transition Metals

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{\bullet -} + SO_4^{2-} + Fe^{3+}$$

$$\text{Contaminant} + SO_4^{\bullet -} \rightarrow \text{Products}$$

Proposed Mechanism: Base Activation of Persulfate

$$^{-}SO_3\text{-}O\text{-}O\text{-}SO_3^{-} + 2H_2O \xrightarrow{OH^-} H\text{-}O\text{-}O^{-} + 2SO_4^{2-} + 3H^+$$

$$H\text{-}O\text{-}O^{-} + {}^{-}SO_3\text{-}O\text{-}O\text{-}SO_3^{-} \longrightarrow SO_4^{-} + SO_4^{2-} + O_2^{-} + H^+$$

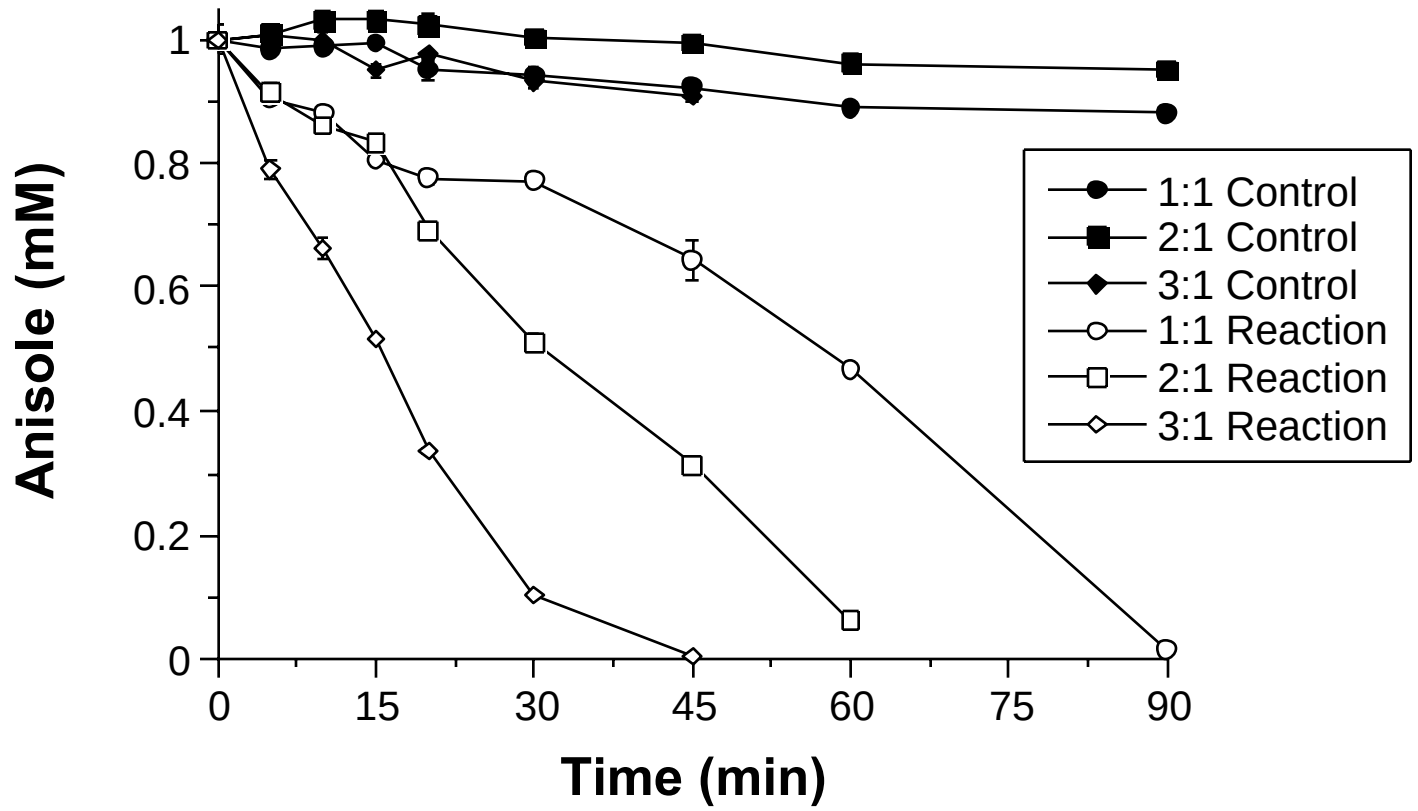
Primary Persulfate Propagation Reaction

$$SO_4^{\bullet -} + OH^- \rightarrow OH\bullet + SO_4^{2-}$$

Probes to Investigate Persulfate Mechanisms

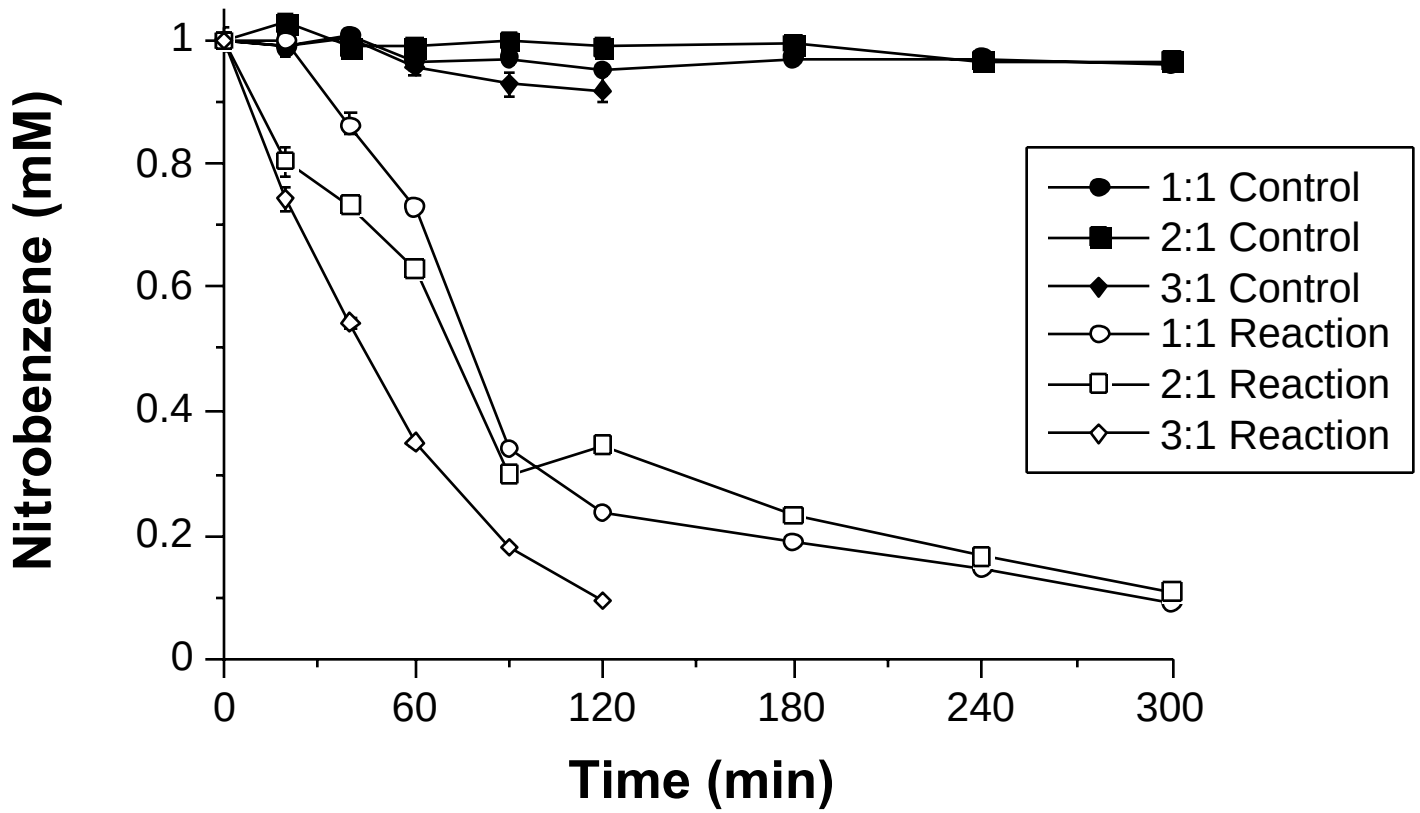
Anisole:	Reactive with Hydroxyl Radicals and Sulfate Radicals
Nitrobenzene:	Reactive with Hydroxyl Radicals
Hexachloroethane:	Reactive with Superoxide

Relative Rates of Sulfate + Hydroxyl Radical Generation



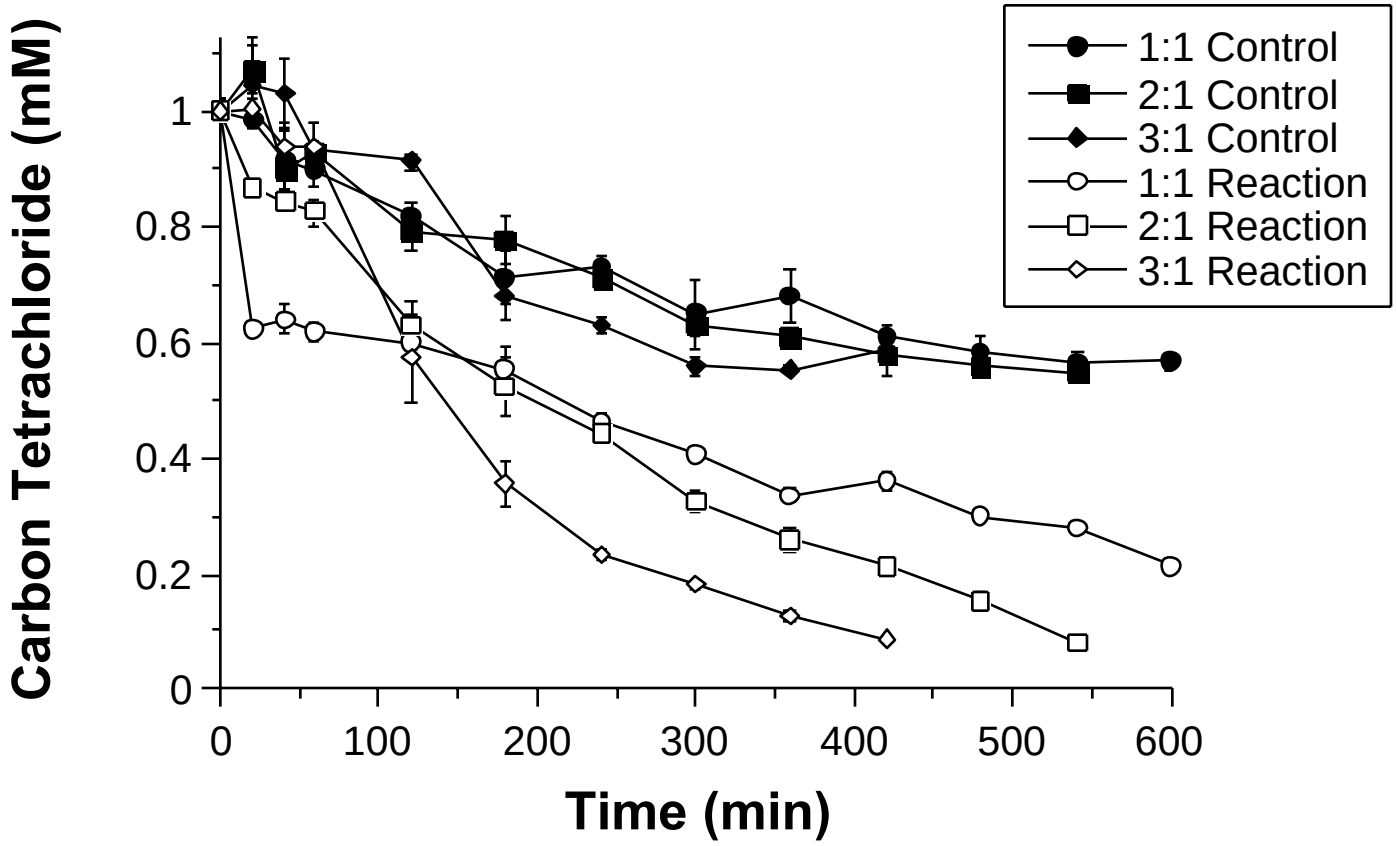
Relative rates of sulfate + hydroxyl radical generation measured by loss of the probe anisole under three hydroxide:persulfate molar ratios

Relative Rates of Hydroxyl Radical Generation



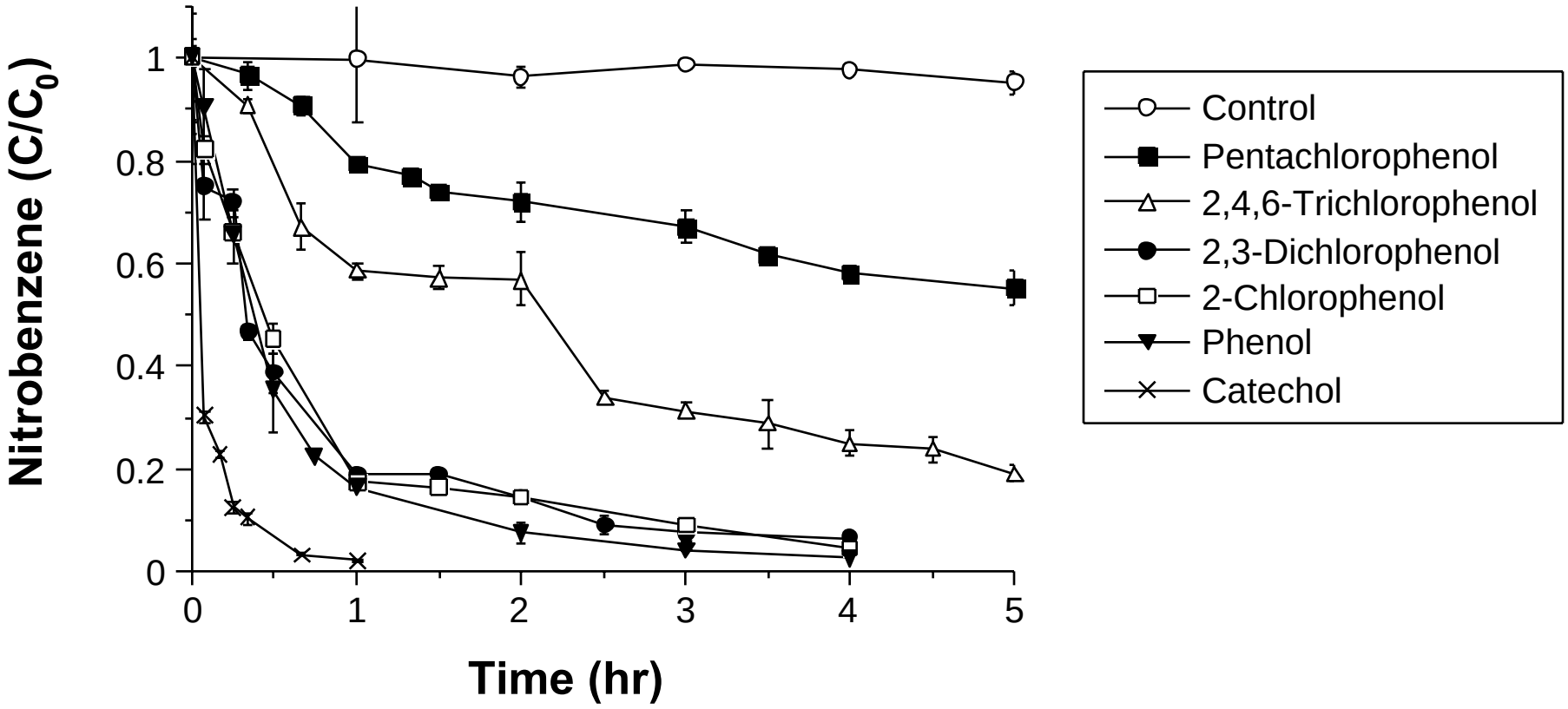
Relative rates of hydroxyl radical generation measured by loss of the probe nitrobenzene under three base:persulfate molar ratios

Relative Rates of Superoxide Generation



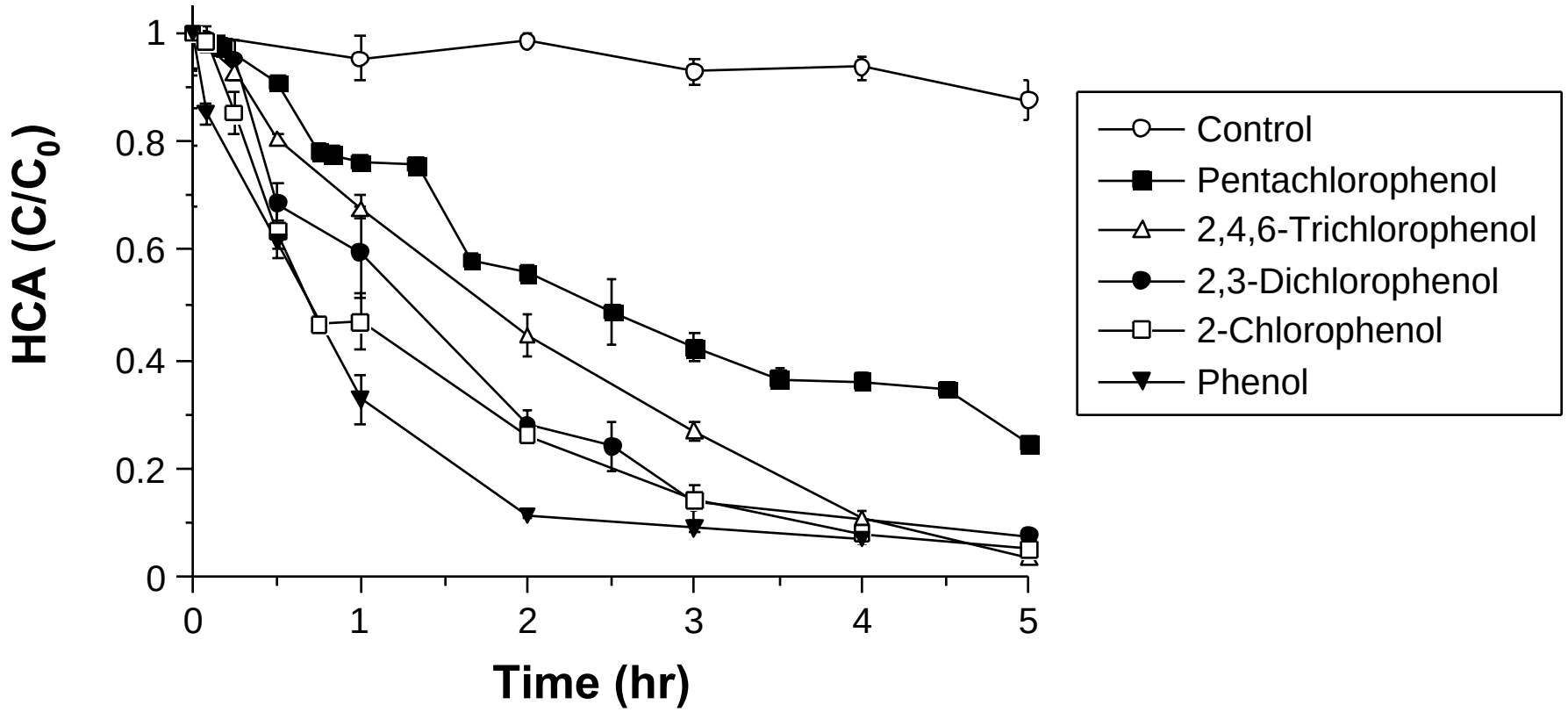
Relative rates of reductant generation measured by loss of the probe carbon tetrachloride under three hydroxide:persulfate molar ratios

Relative Rates of Reductant Generation through Phenoxide Activation



Relative rates of hydroxyl radical generation measured by loss of the probe nitrobenzene with activation by a series of phenoxides

Relative Rates of Hydroxyl Radical Generation through Phenoxide Activation



Relative rates of reductant generation measured by loss of the probe hexachloroethane with activation by a series of phenoxides

Current State of Knowledge on Activated Persulfate

CHP

- Factors affecting initiation known
  - Soluble transition metals
  - Minerals
- Reactive oxygen species known
  - Hydroxyl radical
  - Superoxide
  - Hydroperoxide
- Enhanced desorption and DNAPL destruction documented

Persulfate

- Factors affecting initiation better known
  - Soluble transition metals
  - Base
  - Some organics
- Reactive oxygen species better known
  - Hydroxyl radical
  - Sulfate Radical
  - Superoxide
  - Organic radicals (?)
- Enhanced desorption and DNAPL destruction unknown

Summary

- CHP will destroy just about everything, but is short lived in the subsurface.
- Enhanced contaminant desorption and DNAPL dissolution is promoted by superoxide.
- Hydrogen peroxide stability can be enhanced by the addition of citrate, malonate, or phytate.
- Activated persulfate is highly reactive and long lived in the subsurface, but its fundamental chemistry in the subsurface is only now being elucidated.

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