

Enhanced Reductive Dechlorination through Biological Interactions with Zero-Valent Iron

Brian A. Wrenn

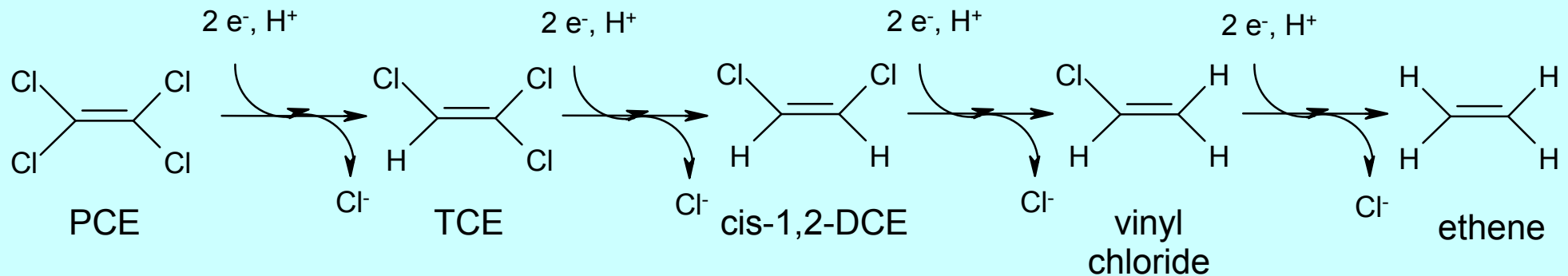
Environmental Engineering Science Program

Civil Engineering Department

Washington University

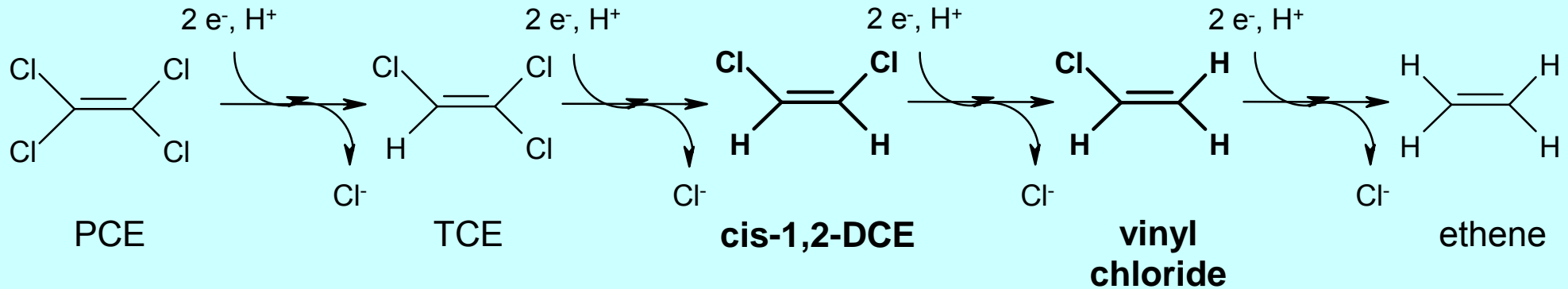
St. Louis, MO

Biological Reductive Dechlorination Pathway



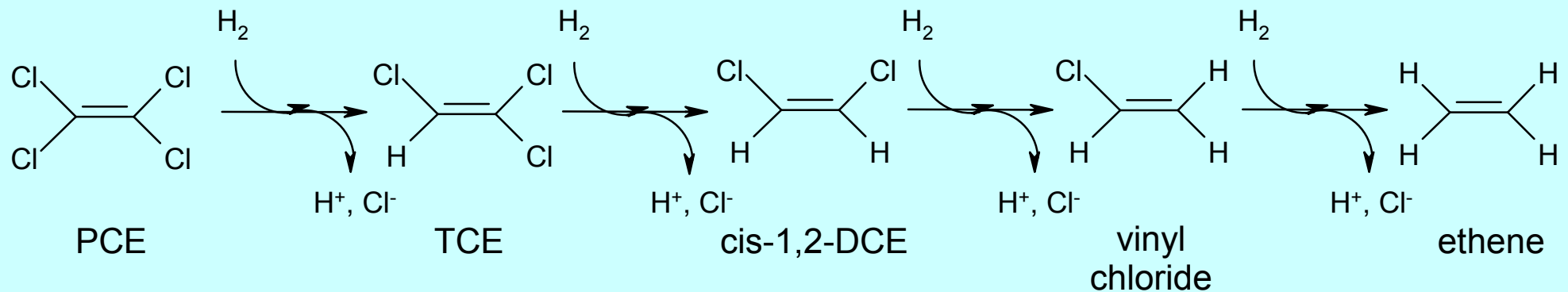
- sequential dechlorination mechanism
 - reaction rate is proportional to chlorine content
PCE > TCE > cis-1,2-DCE > vinyl chloride

Biological Reductive Dechlorination Pathway



- sequential dechlorination mechanism
 - reaction rate is proportional to chlorine content
PCE > TCE > cis-1,2-DCE > vinyl chloride
∴ accumulation of intermediates is a concern
 - vinyl chloride is known human carcinogen
- electron donor substrate is required as coreactant

Biological Reductive Dechlorination Pathway



- Hydrogen (H₂) is the preferred electron donor for biological reductive dechlorination
- Competition for hydrogen from methanogens, sulfate reducers, and Fe(III) reducers
 - Rapid turnover of hydrogen in subsurface
 - Limited transport away from site of production
 - ∴ Hydrogen must be produced close to its site of consumption

Competition for Hydrogen

TEAP	$\Delta G^{\circ'}$ (kJ/mol H ₂)	[H ₂] _{ss} (nM)
denitrification	224	<0.05 – 0.4
Fe(III) reduction	50	0.1 – 0.5
sulfate reduction	38	1 – 4.5
methanogenesis	34	2.5 – 24
PCE → TCE	112	0.6 – 0.9
TCE → DCE	102	0.6 – 0.9
DCE → VC	78	0.1 – 2.5
VC → ethene	93	2 – 24

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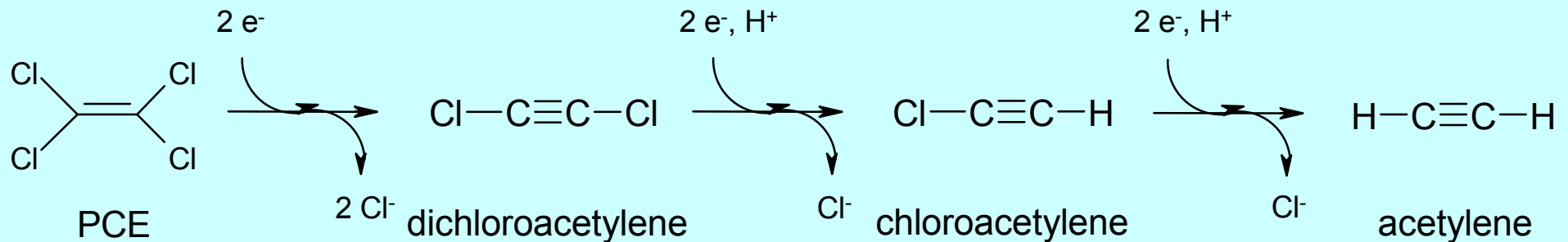
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Reductive Dechlorination by Zero-Valent Iron



Potential Reaction Mechanisms:

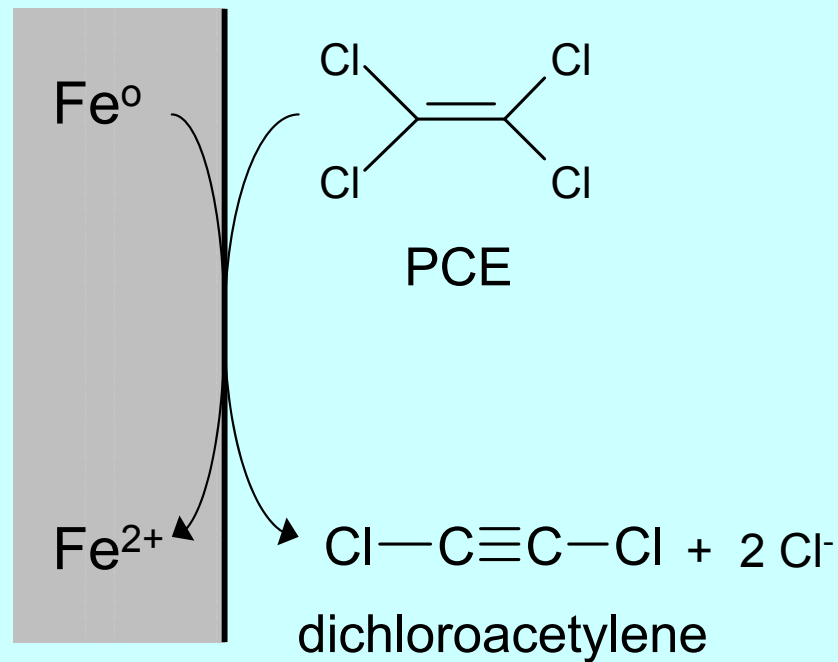
- direct reaction with Fe^0 at metal surface
- surface-mediated reaction with sorbed $\text{Fe}(\text{II})$

Competing Reactions:

- corrosion of Fe^0 surface by reaction with water
- passivation of reactive surfaces by accumulation of crystalline metal oxides (e.g., maghematite, magnetite)

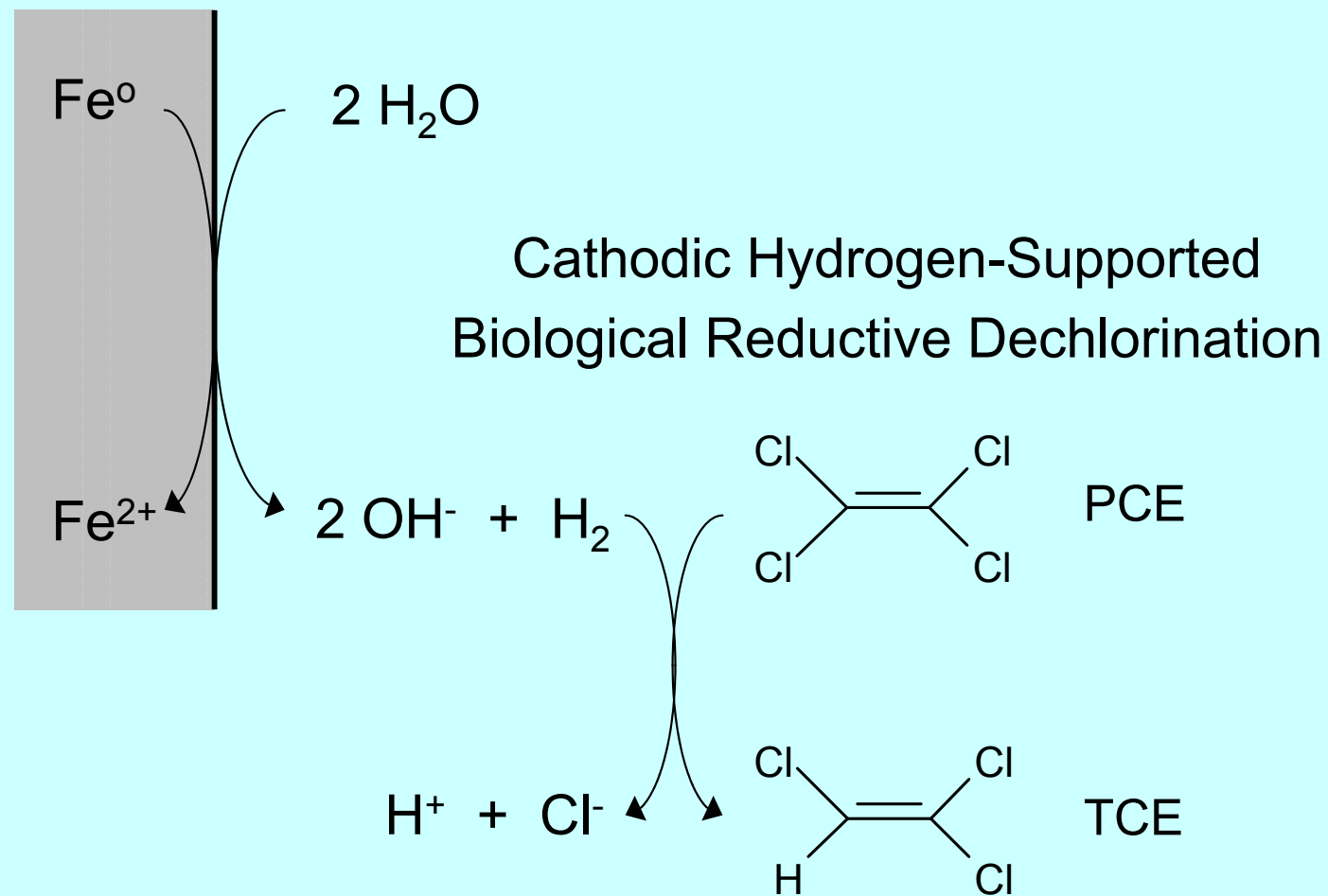
Zero-Valent Iron Reaction Mechanisms

Reductive Dechlorination: Direct Reaction with Fe^0



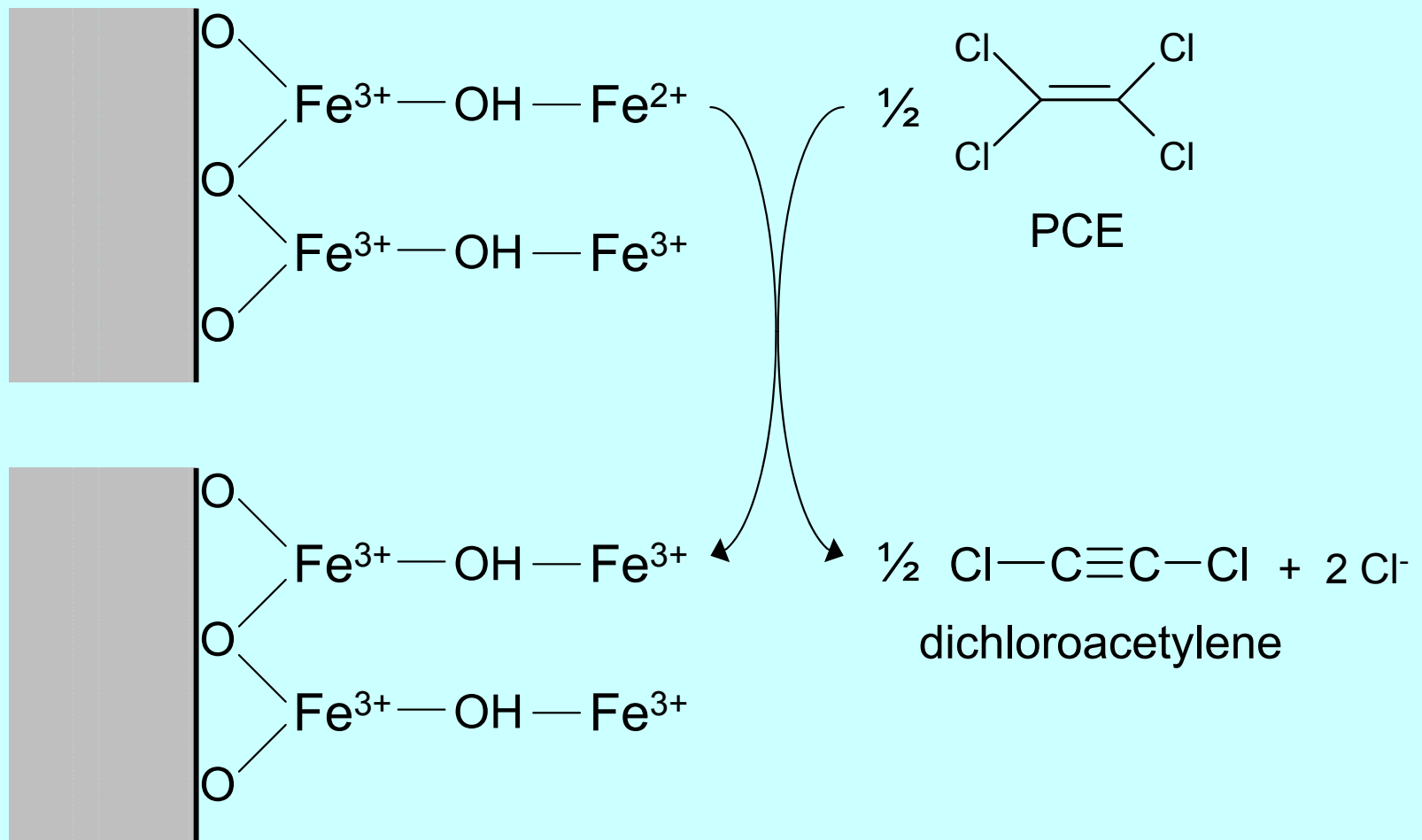
Zero-Valent Iron Reaction Mechanisms

Corrosion: Reaction with Fe^0 with Water



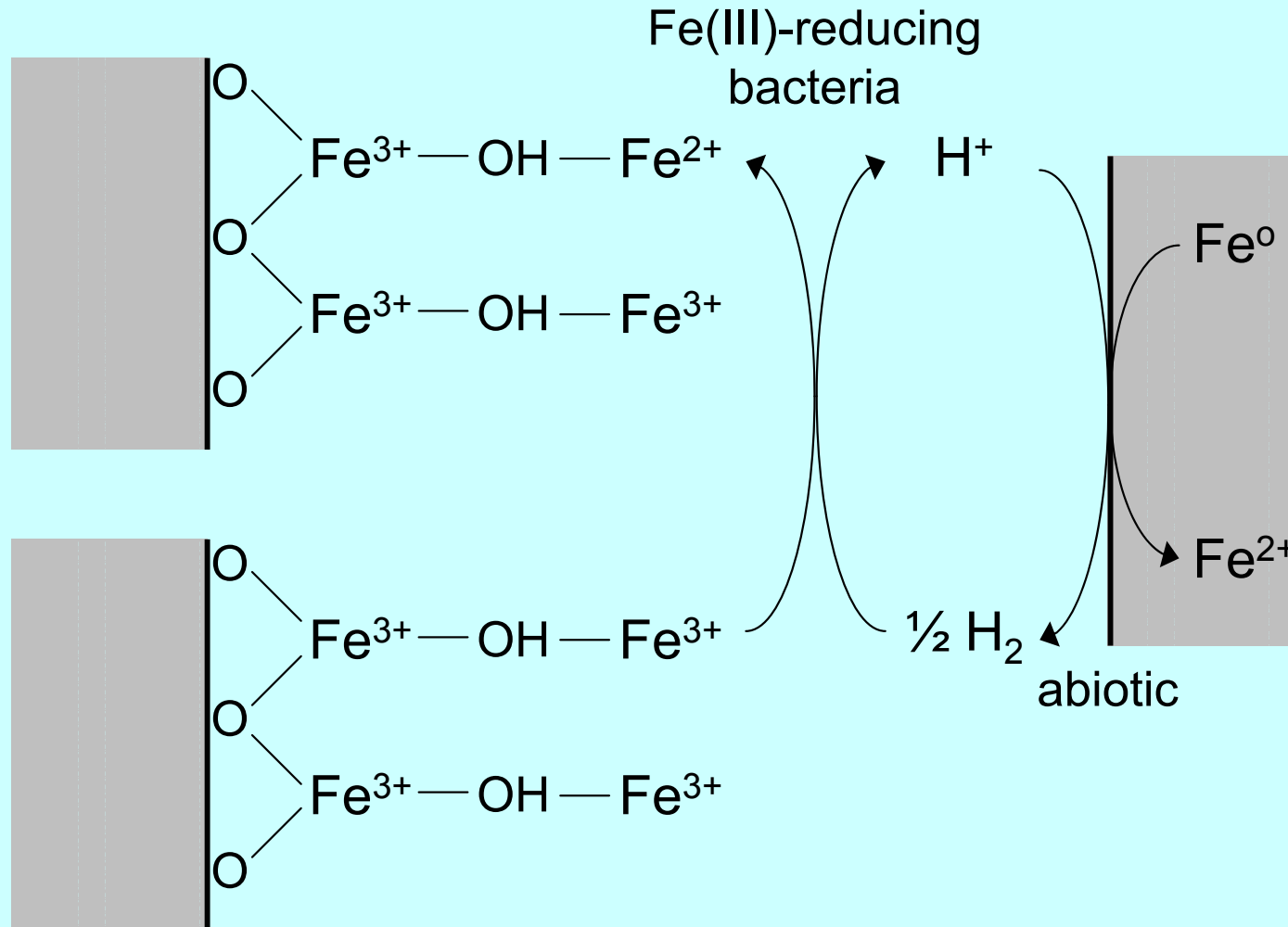
Zero-Valent Iron Reaction Mechanisms

Reductive Dechlorination: Reaction with Sorbed Fe^{2+}

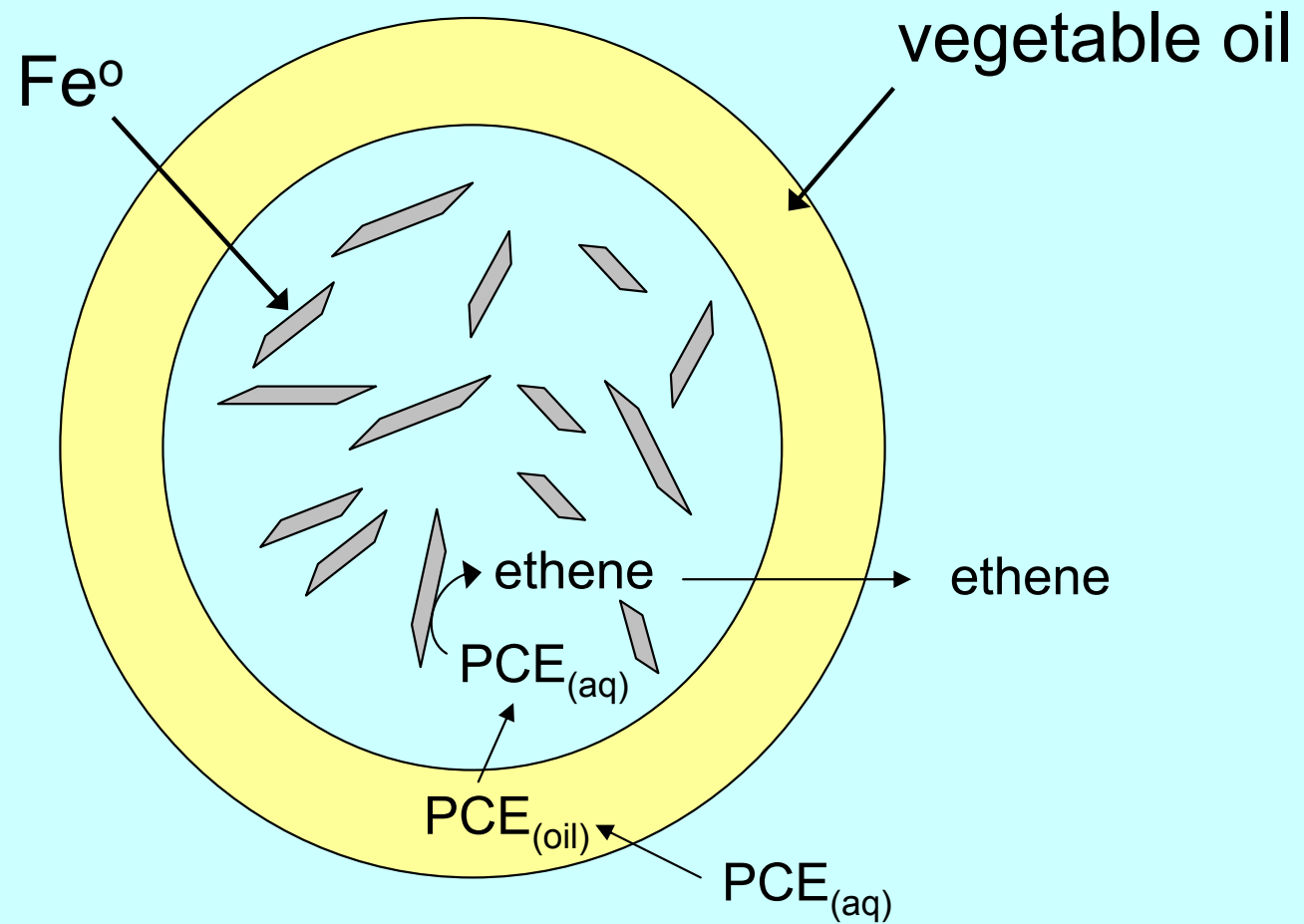


Zero-Valent Iron Reaction Mechanisms

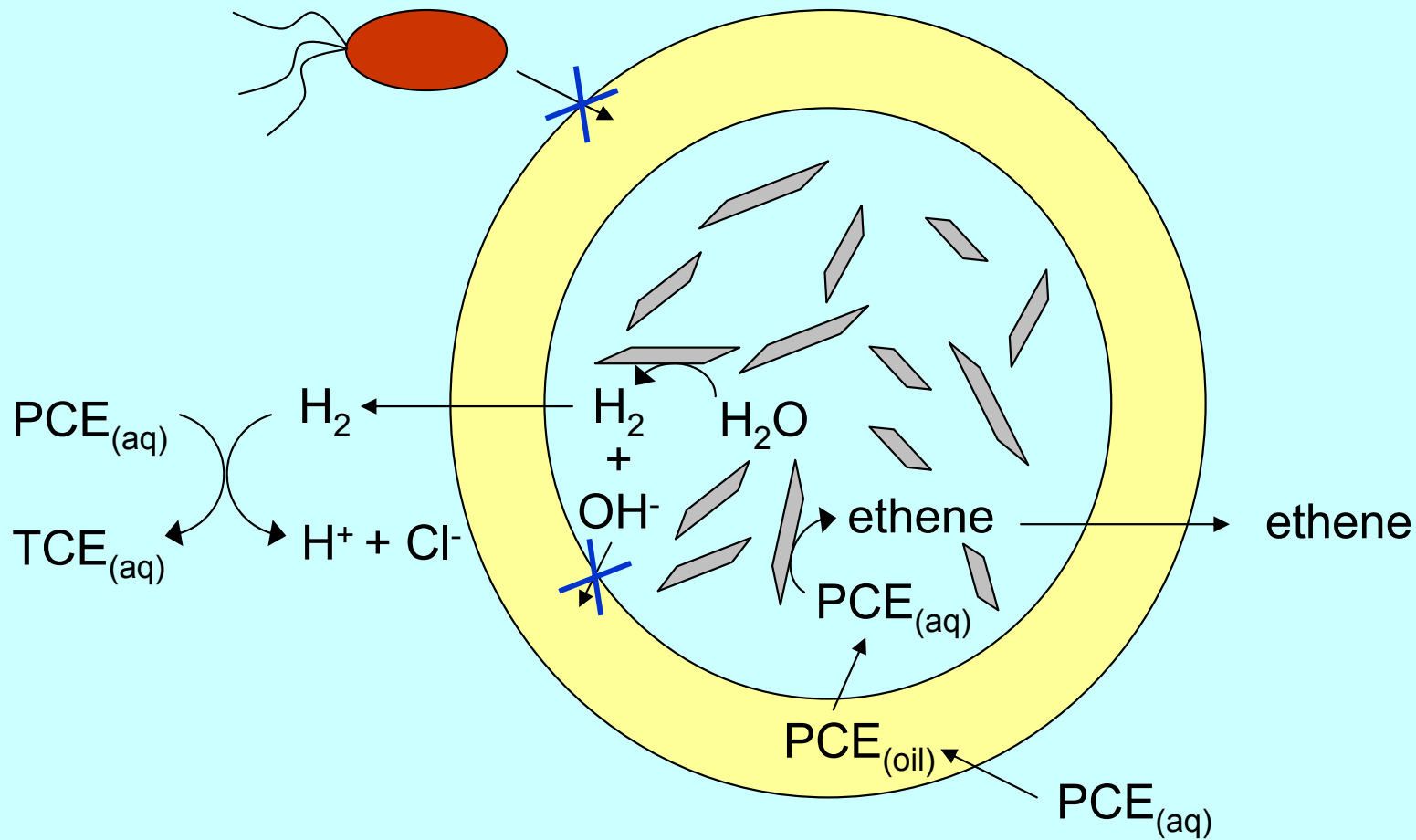
Biological Regeneration of Sorbed Fe^{2+}



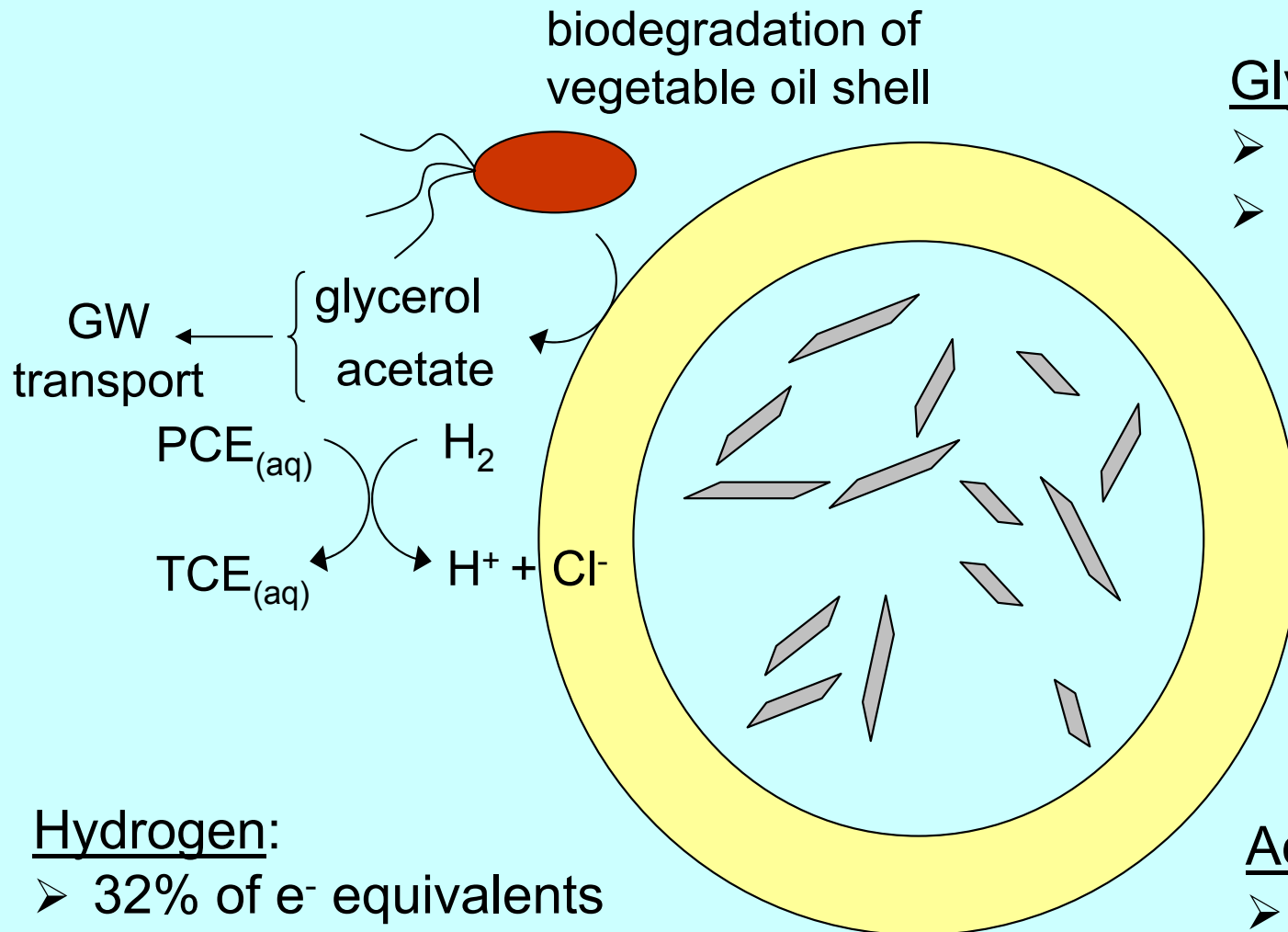
Biological Interactions with Emulsified Zero-Valent Iron



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Glycerol:

- 4% of e^- equivalents
- potential distant source of H_2

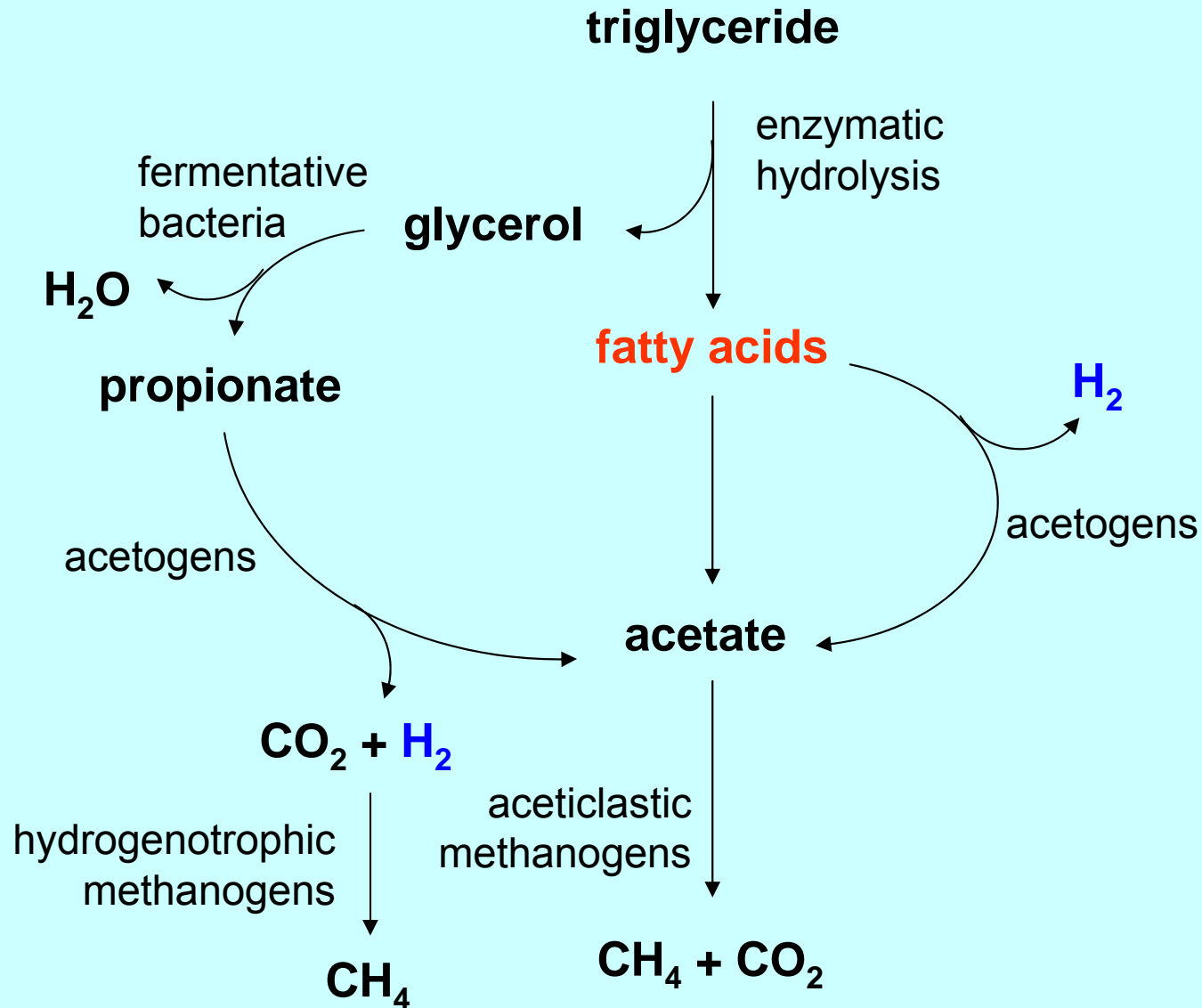
Hydrogen:

- 32% of e^- equivalents
- local production and consumption

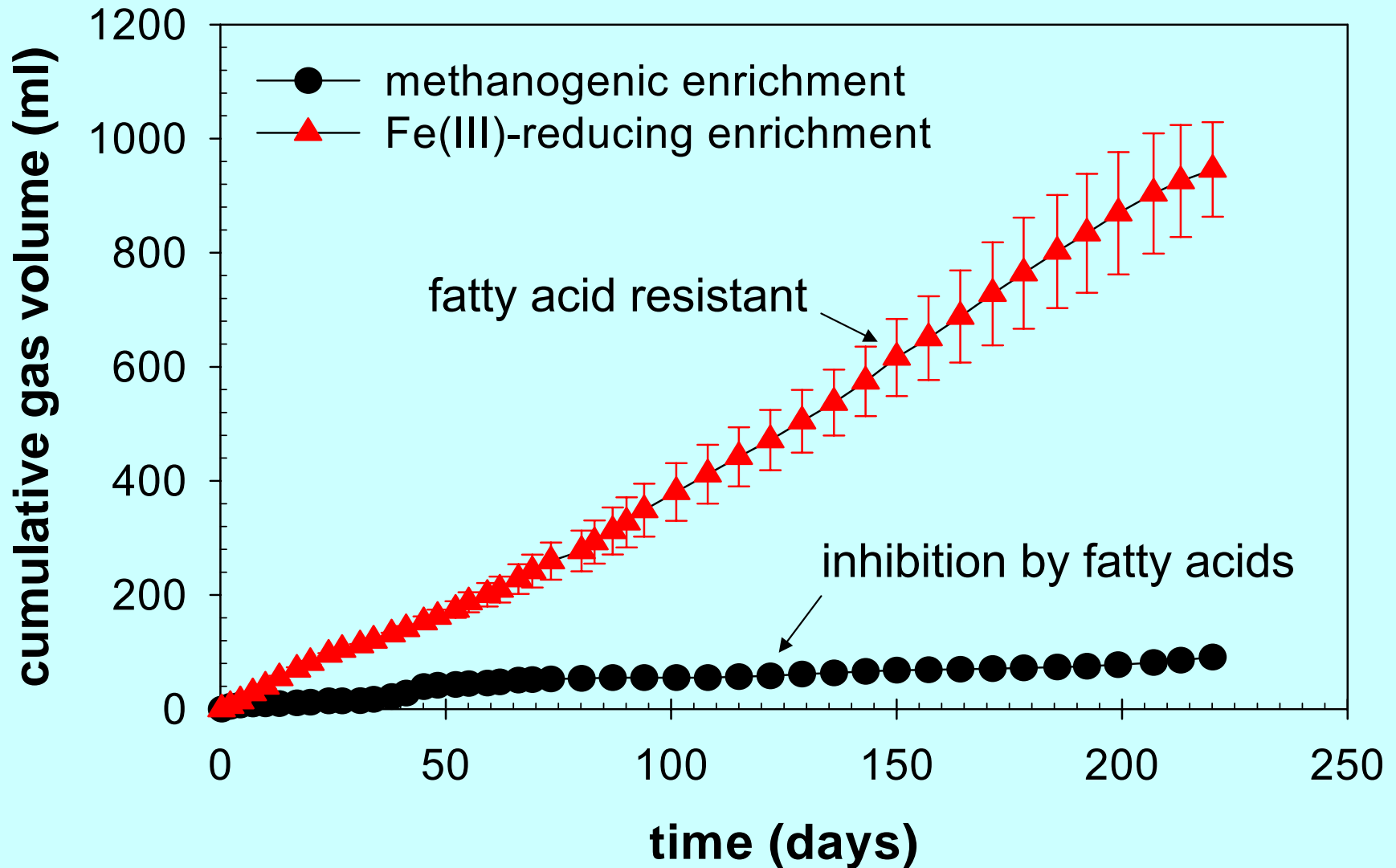
Acetate:

- 64% of e^- equivalents
- poor anaerobic electron donor

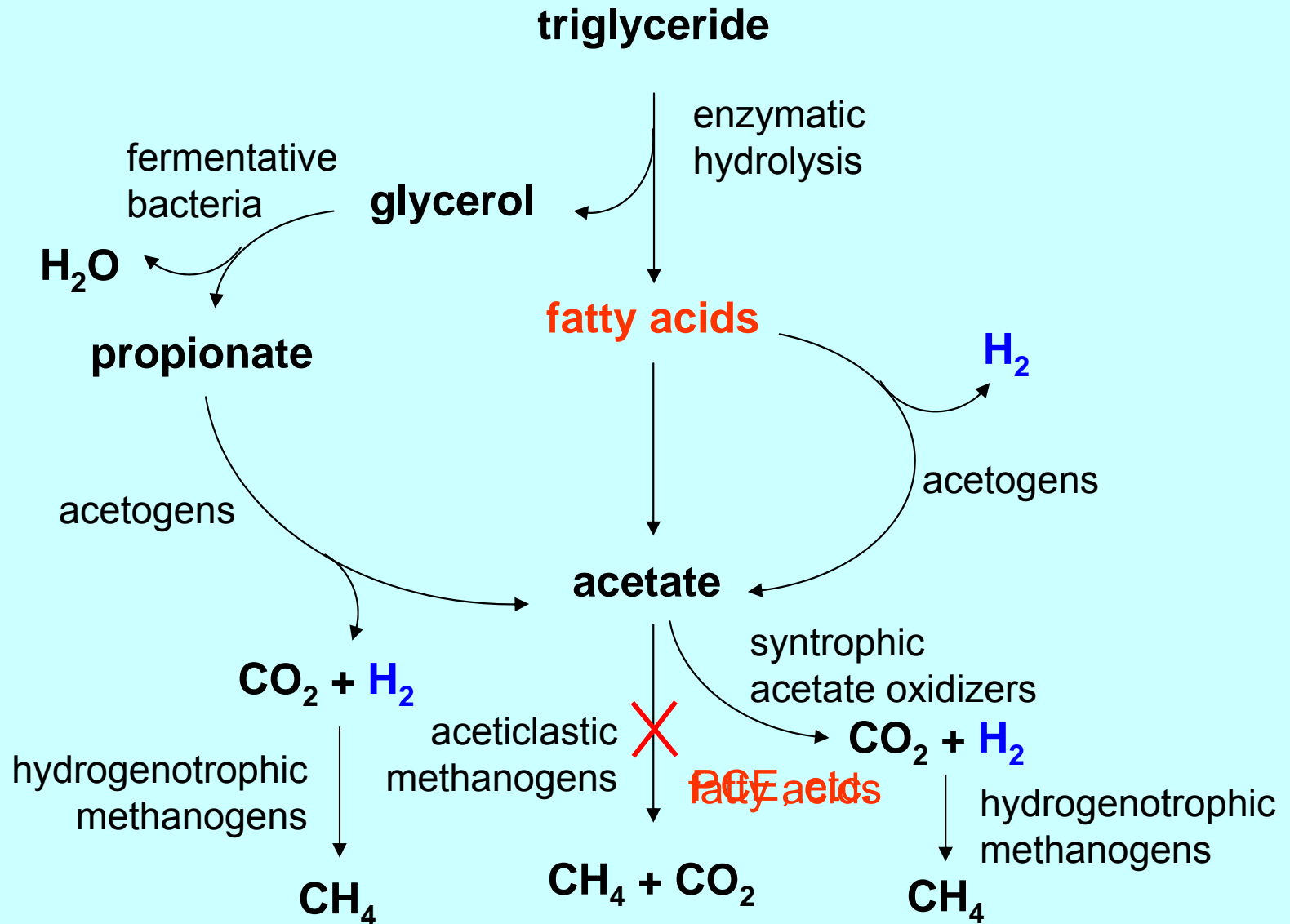
Anaerobic Biodegradation of Vegetable Oil



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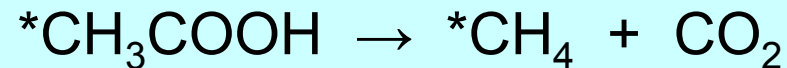


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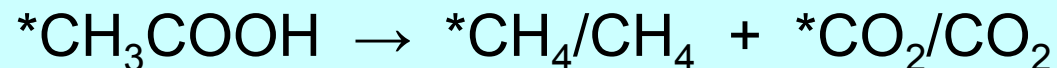
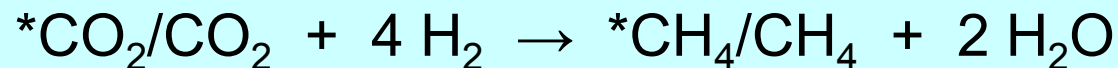
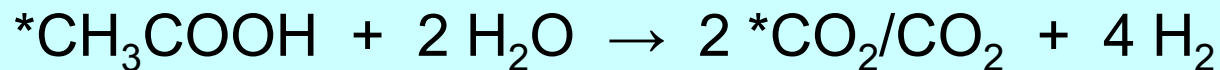


Fe(III) Effects on Fatty Acid Sensitivity

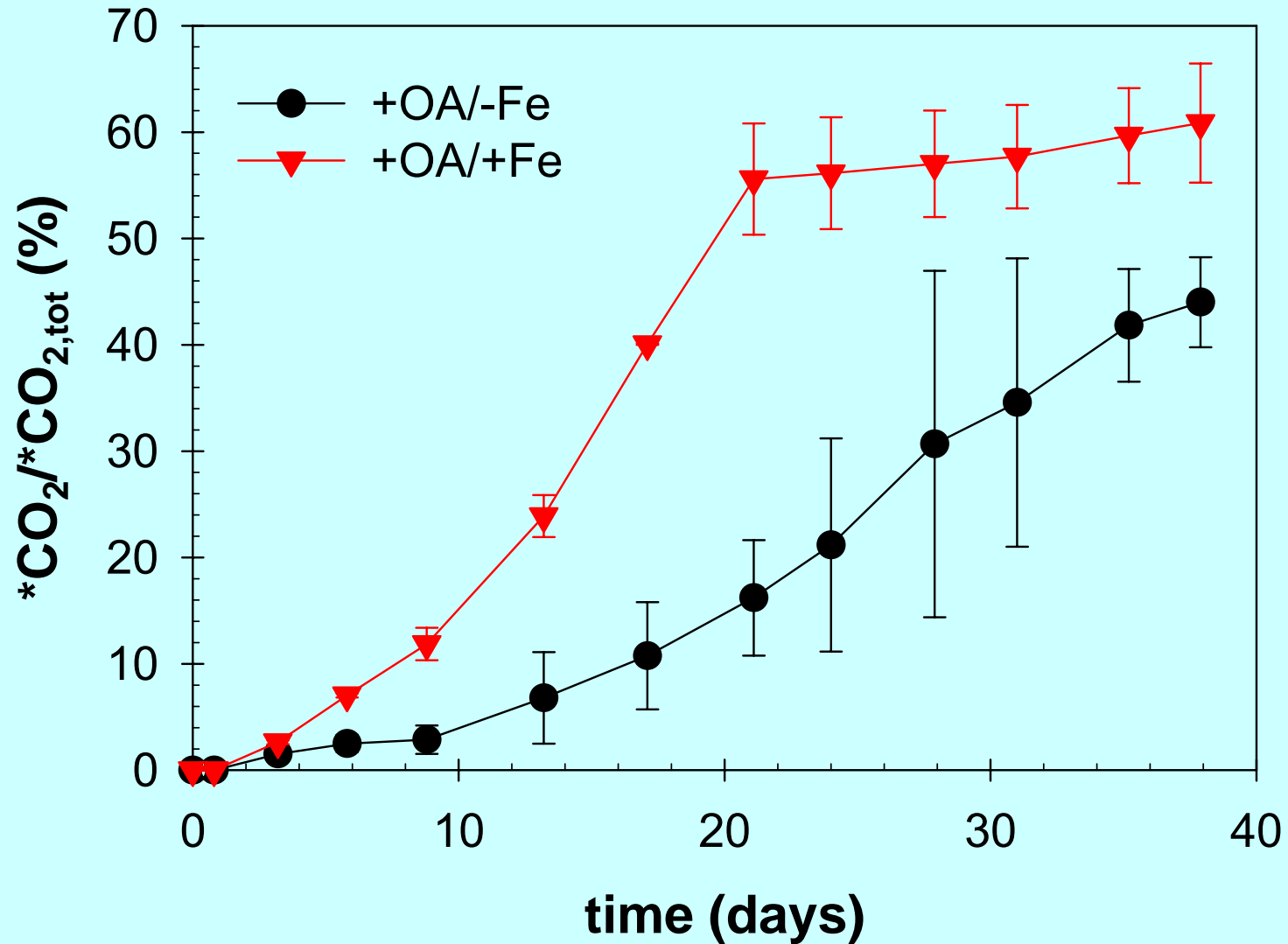
Known: Aceticlastic methanogens are very sensitive to inhibition by fatty acids.



Hypothesis: Acetate oxidizing Fe(III) reducers may be less sensitive to fatty acids. In the absence of bioavailable Fe(III), these organisms may grow as syntrophic acetate oxidizers with hydrogenotrophic methanogens.



Anaerobic Oxidation of $^{13}\text{C}_{\text{methyl}}$ -Acetate



Summary: Biological Interactions with Zero-Valent Iron

- Microbial activity can interact synergistically with zero-valent iron to enhance degradation rates of chlorinated aliphatic hydrocarbons (CAHs) in groundwater
 - Hydrogen produced by anaerobic corrosion of Fe^0 can support microbial reductive dechlorination
 - Fe(III)-reducing bacteria can reduce surface ferric oxides to generate sorbed Fe(II), which can reductively dechlorinate CAHs

Summary: Biological Interactions with Emulsified Zero-Valent Iron

- Microbial metabolism of vegetable-oil coat of emulsified zero-valent iron can support reductive dechlorination of chlorinated solvents in groundwater
 - The vegetable-oil shell prevents direct interactions of microorganisms with zero-valent iron particles
 - Anaerobic biodegradation of vegetable-oil fatty acids results in localized production of hydrogen, which can support biological reductive dechlorination of CAHs
 - Acetate may serve as a distant hydrogen source if syntrophic-acetate oxidizing (iron-reducing) bacteria are present