Nanotechnology and Oxidative Techniques for Remediation

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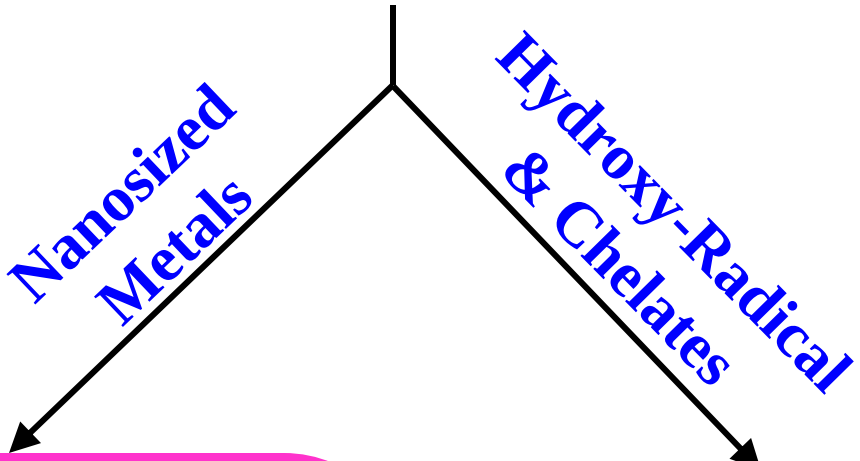
Presentation Overview

- Introduction to Oxidative and Reductive technologies for TCE and PCB removal (**D. Bhattacharyya**)
- Overview of reductive dechlorination involving bimetallic nanosystems (**D. Meyer**)
- Summary of laboratory studies involving Oxidation of TCE (**S. Lewis**)
- Concluding Remarks

Removal of TCE at Ambient Temperature



Reductive Dechlorination of TCE

$(nano)Fe^0 + TCE \rightarrow Fe^{2+} + Ethane + 3Cl^-$

$(Bulk)Fe^0 + TCE \rightarrow Fe^{2+} + intermediates + nCl^-$

Systems Used:
Zerovalent metals (**Fe**), Bimetallic systems (**Fe/Pd, Fe/Ni**), Supported Platforms

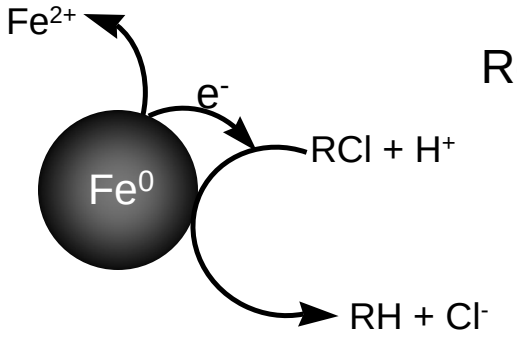
Oxidative Destruction of TCE

$TCE + OH^{\cdot} \rightarrow CO_2$ **, Organic Acids**

Systems Used:
Standard Fenton Reaction, Modified Fenton Reaction using **nontoxic chelate (citrate, gluconic acid) (L)** as a chelating agent (**FeL**).

Background (reductive dechlorination at room temperature)

Single Fe^0 system



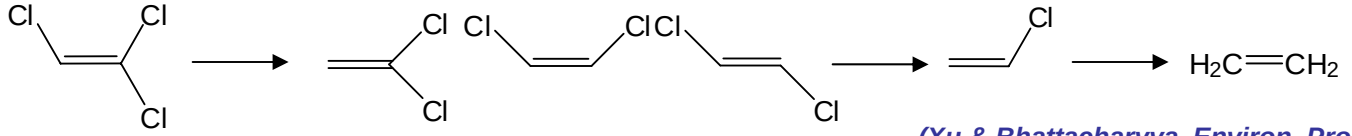
Reaction mechanism: electron transfer

$Fe^0 \rightarrow Fe^{2+} + 2e^-$

$RCl + 2e^- + H^+ \rightarrow RH + Cl^-$

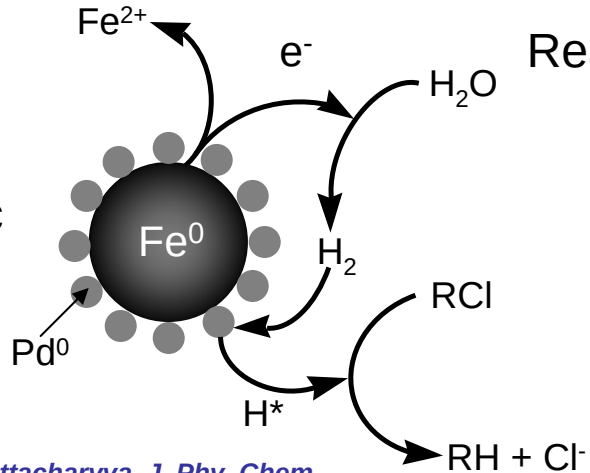
$RCl + Fe^0 + H^+ \rightarrow Fe^{2+} + RH + Cl^-$

(Matheson et al., Environ. Sci. Technol. 28, 2045-2053, 1994)



(Xu & Bhattacharyya, Environ. Prog., 24, 358, 2005)

Bimetallic system



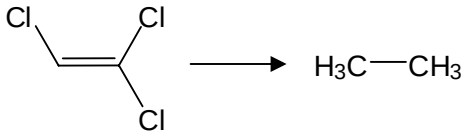
(Meyer and Bhattacharyya, J. Phy. Chem, 2007;Xu et al, J.Nanopar.Res. 7, 449-467, 2005)

Reaction mechanism: catalytic hydrodechlorination

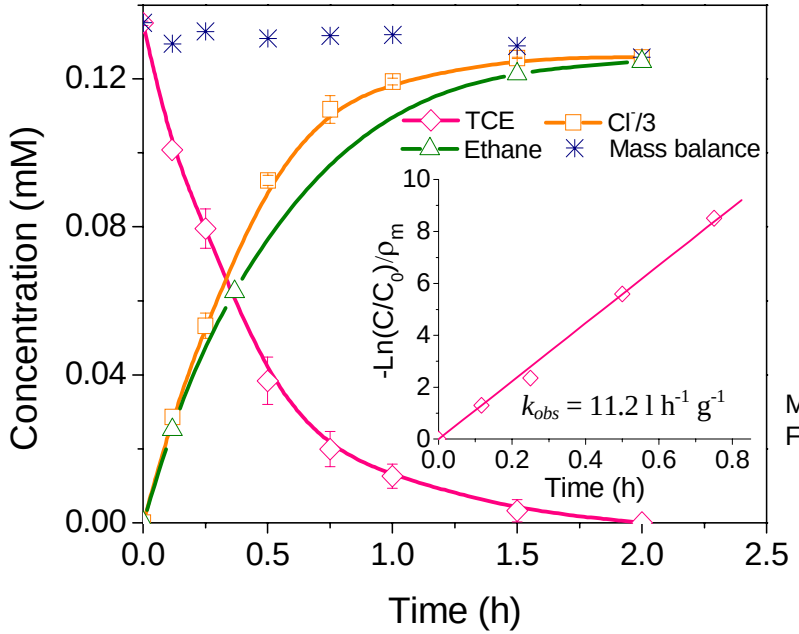
$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2$

$H_2 + Pd \rightarrow Pd\text{-}H + H^*$

$RCl + H^* \rightarrow RH + Cl^-$

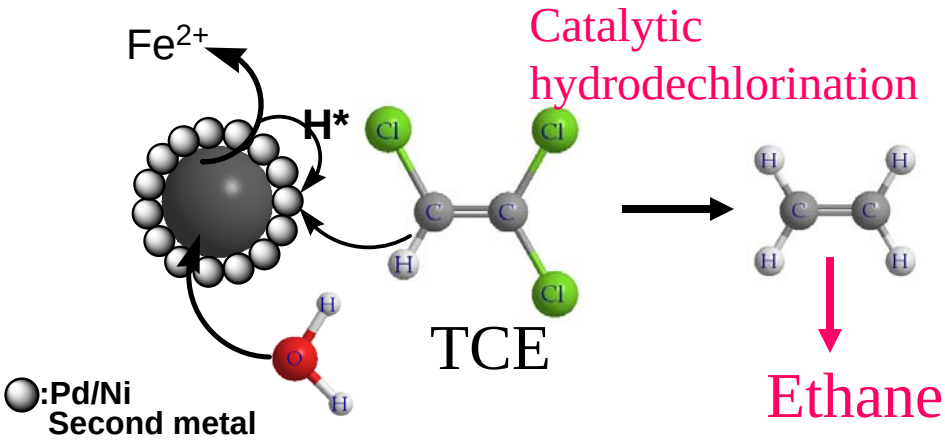


TCE Dechlorination by Membrane-based Bimetallic Nanoparticles



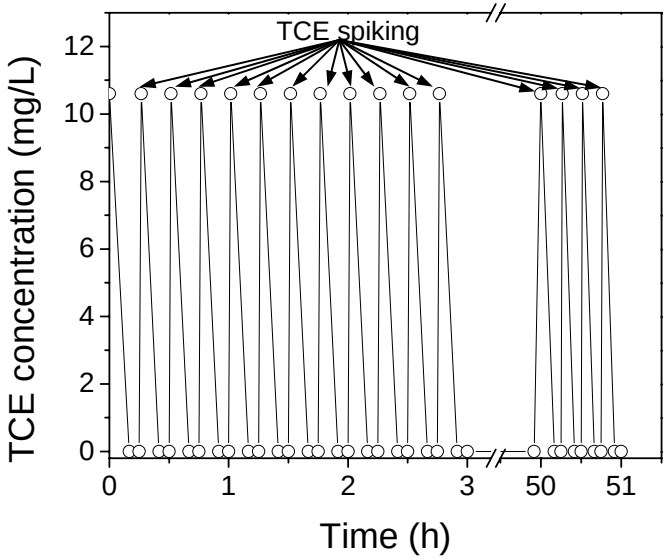
Fast and complete degradation

Metal loading:4.5mg/20mL
Fe/Ni (Ni = 25 wt%)



Catalytic hydrodechlorination

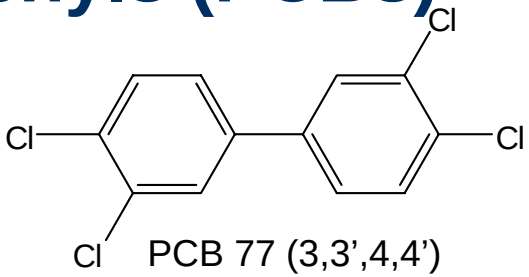
Ethane



- Fe/Ni (Ni =25 wt%) in PAA/PVDF membranes
- Metal loading: 0.08g/20ml
- 16 cycles of TCE dechlorination

Longevity of Fe/Ni Nanoparticle Reactivity

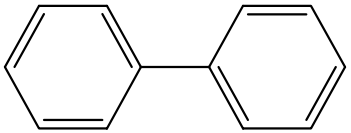
Dechlorination of Polychlorinated Biphenyls (PCBs)

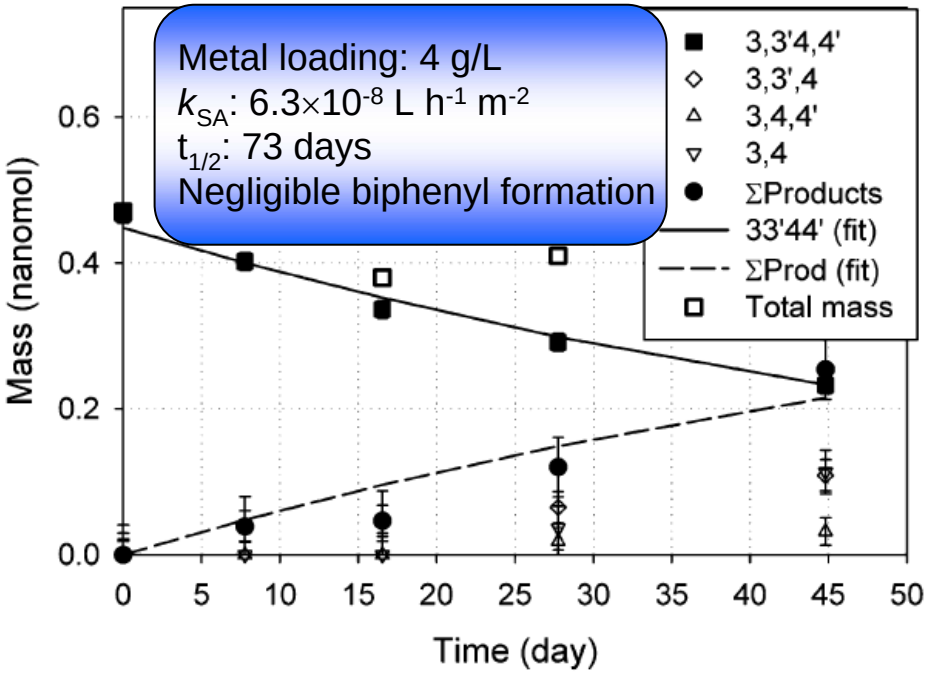


PCB 77 (3,3',4,4')

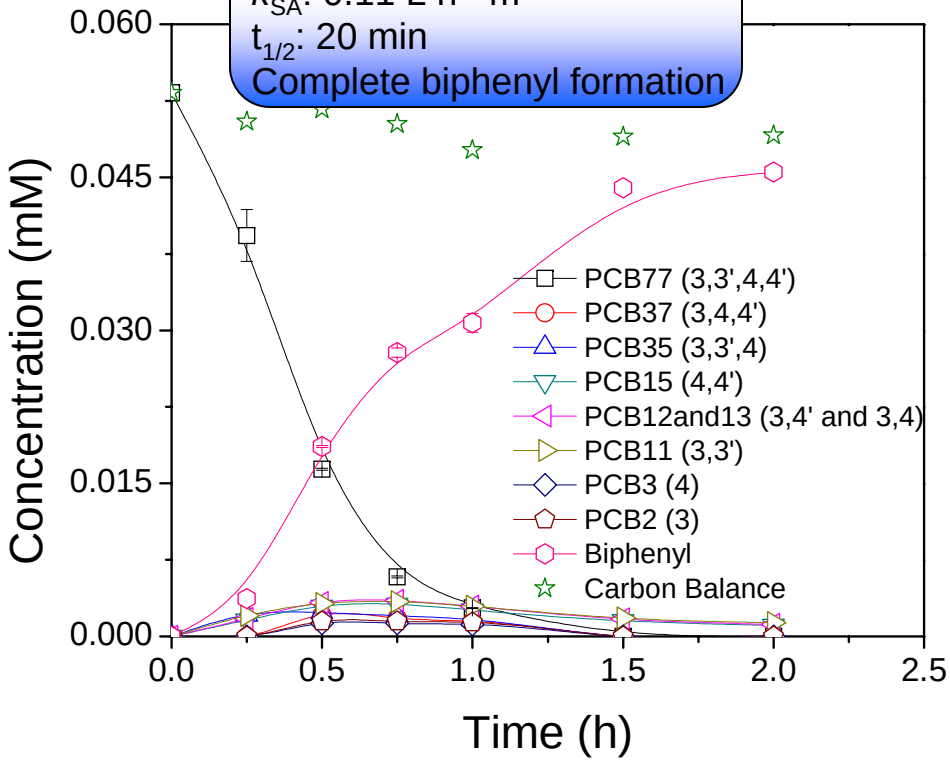
Room temperature

?





PCB 77 (3,3',4,4') dechlorination by Fe nanoparticles at room temperature (from ***Lowry, et al., Environ. Sci. Technol. 2004, 38, 5208***)



PCB 77 (3,3',4,4') dechlorination by membrane based Fe/Pd (Pd=2.3 wt%) nanoparticles at room temperature

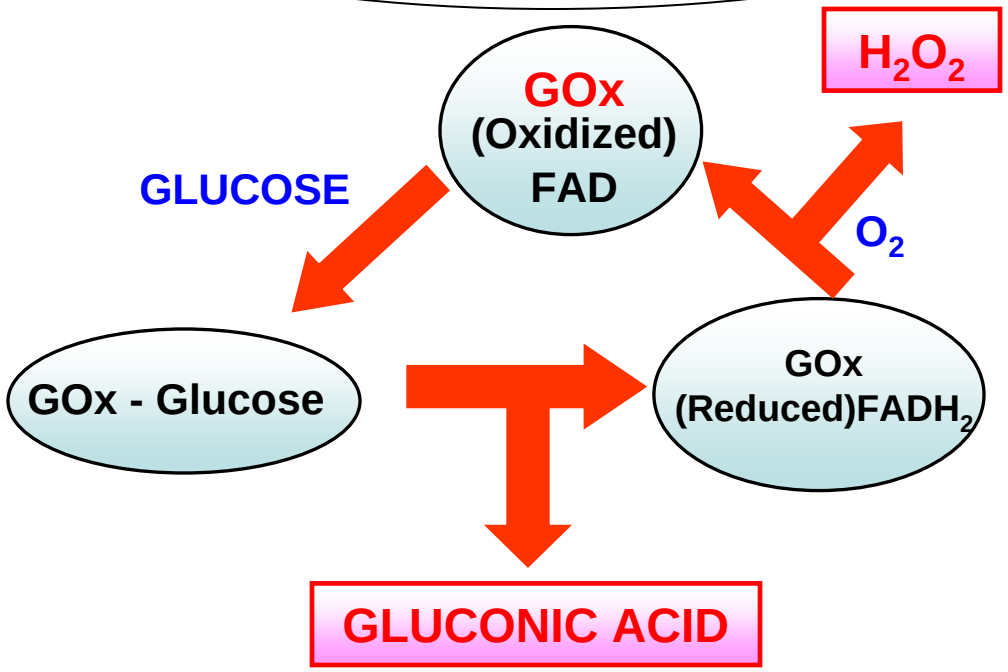
Technology Enhancement: On-site Generation of Chelate and H_2O_2

HYPOTHESIS

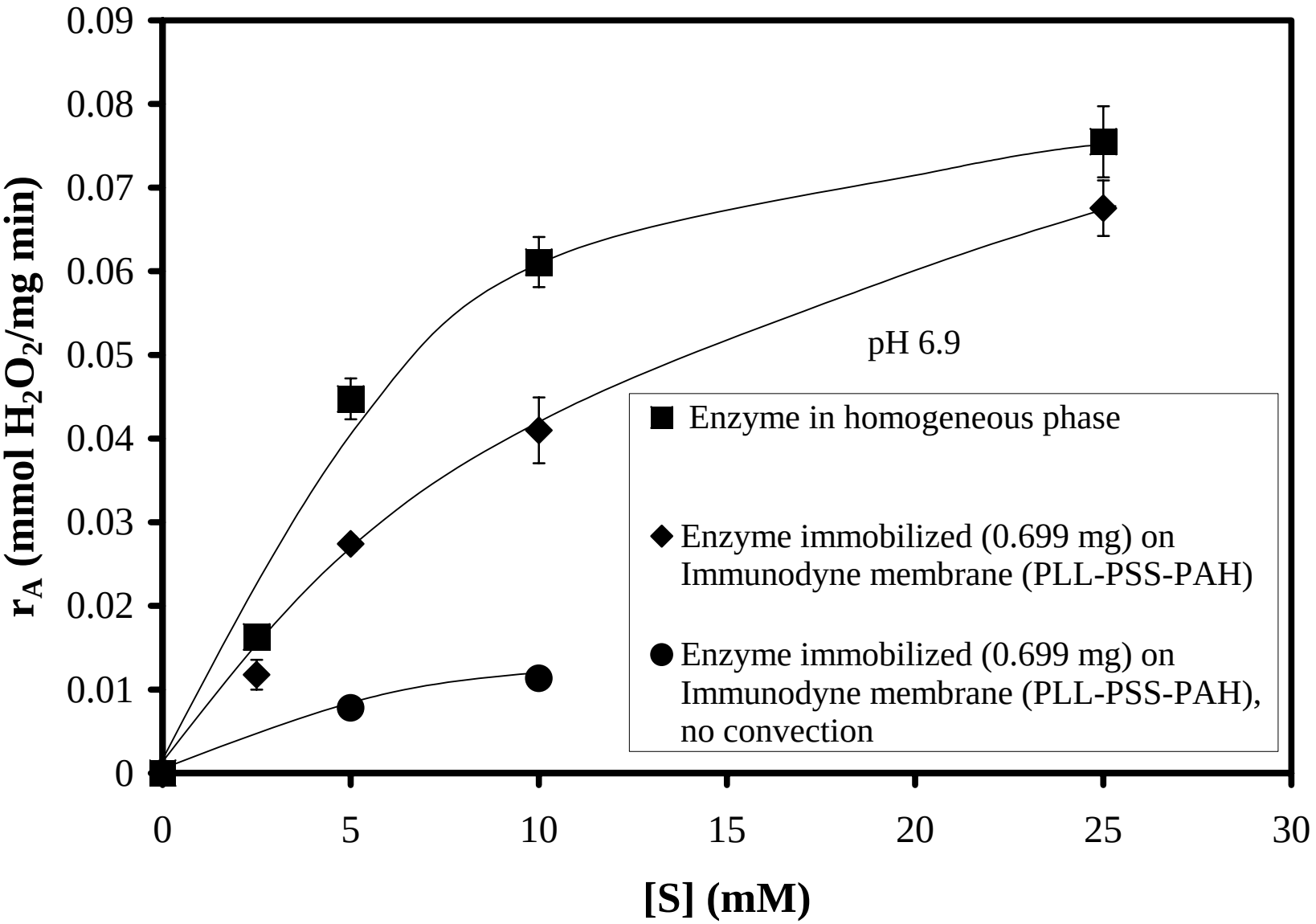
Gluconic acid produced by enzymatic reaction would act as a chelate in Fenton reaction, and thus allow degradation of TCE & PCBs near neutral pH

MOTIVATION

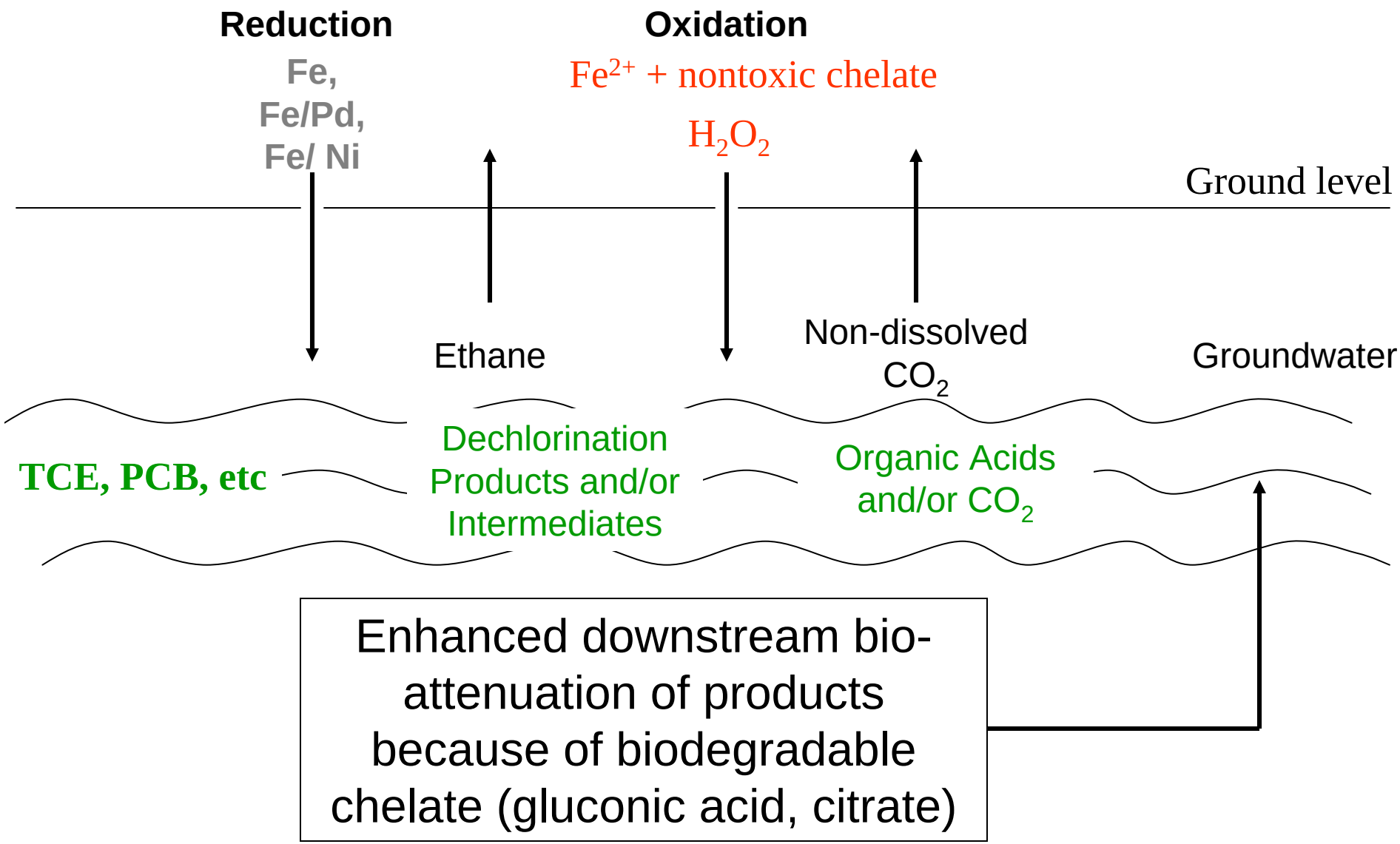
On-Site source of peroxide and chelate will eliminate the need for concentrated chemical Storage by using simple Glucose as a substrate



The Initial Rate of Glucose Oxidation Measured by H_2O_2 Formation at Different Substrate Concentrations



Groundwater Remediation Using Combined Strategies For Reduction and Oxidation



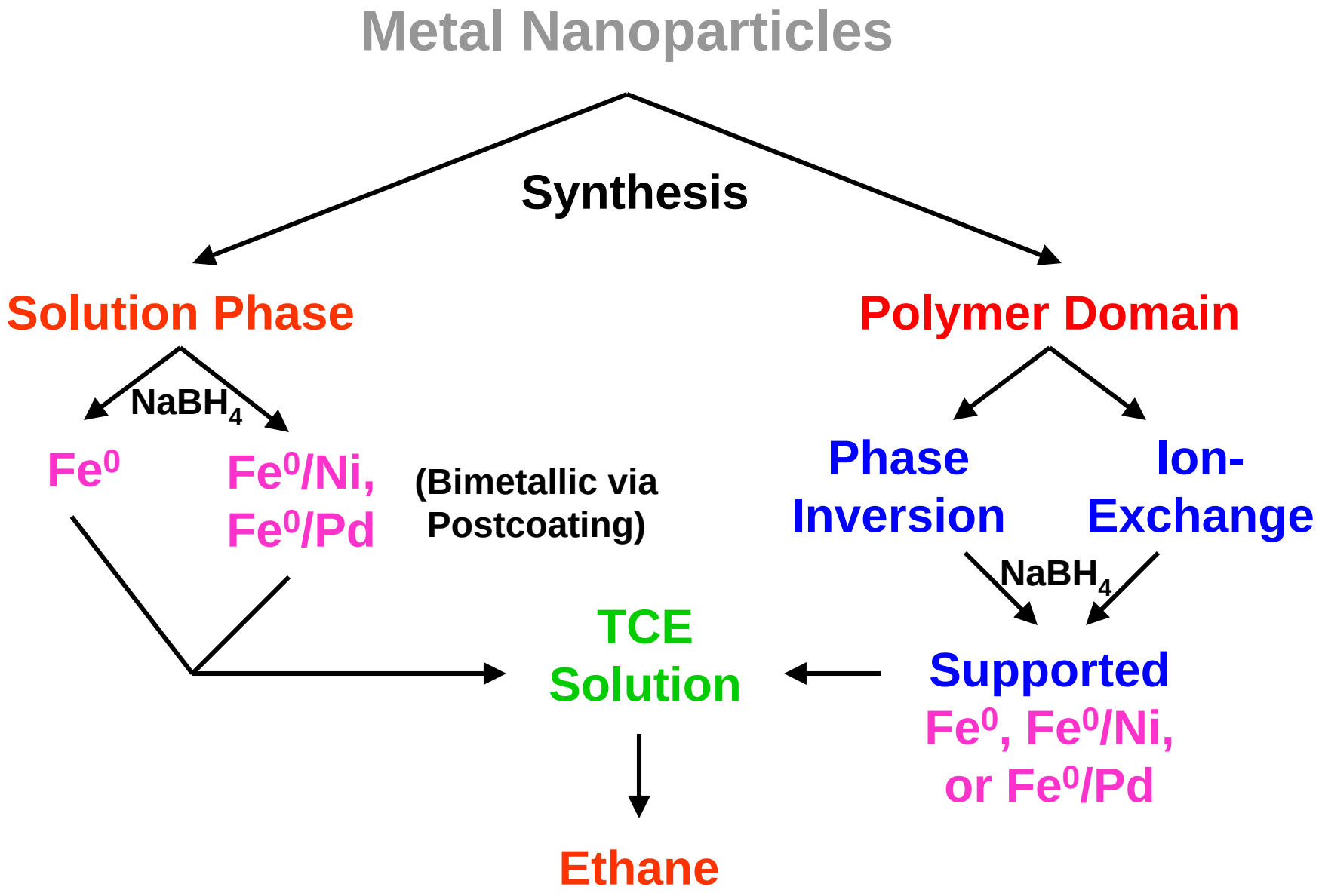
TCE Reduction Using Fe/Pd Nanoparticles

-Batch Studies of Matrix Effects

- Packed Column (Gravel) Studies

- In-Situ Injection Implications

Reductive Dechlorination of TCE

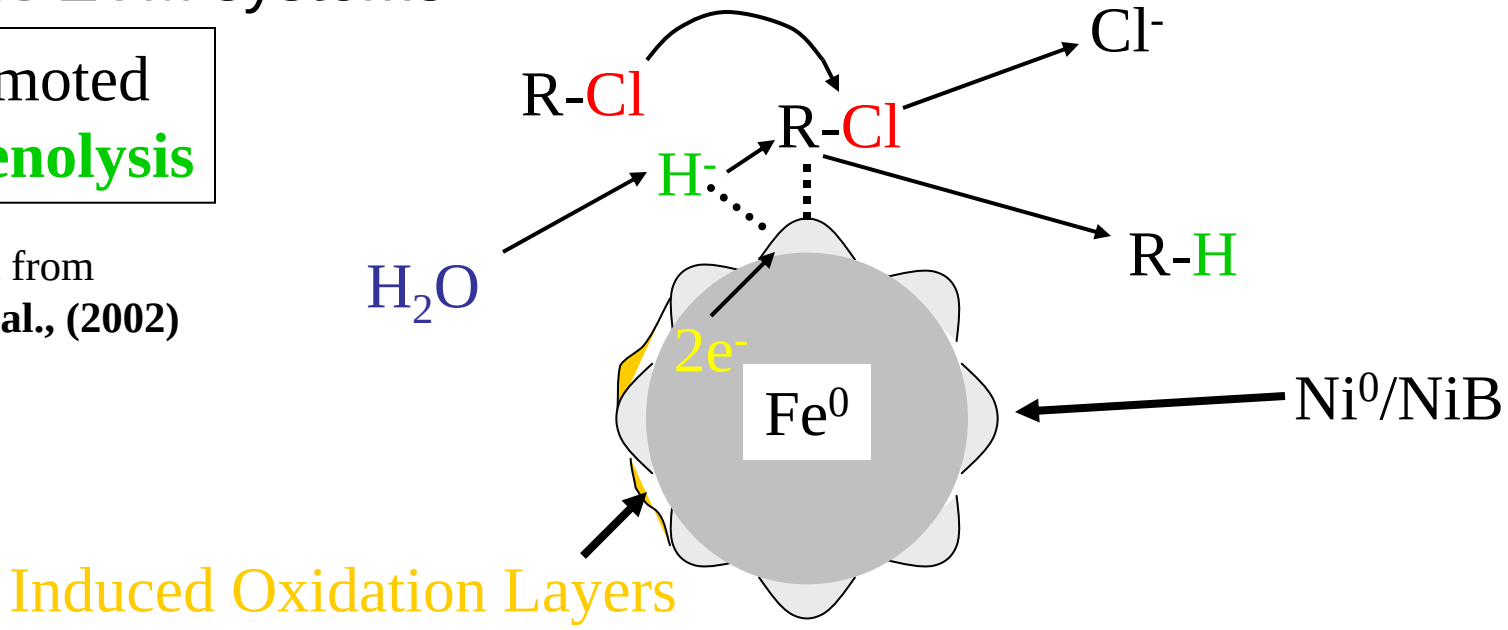


Reductive Dechlorination: Hydrogenolysis and Bimetallic Systems

- A catalyzed **Hydrogenolysis** mechanism is believed to exist for **bimetallic** ZVM systems.

Ni-Promoted Hydrogenolysis

Adapted from
Mallouk, et. al., (2002)

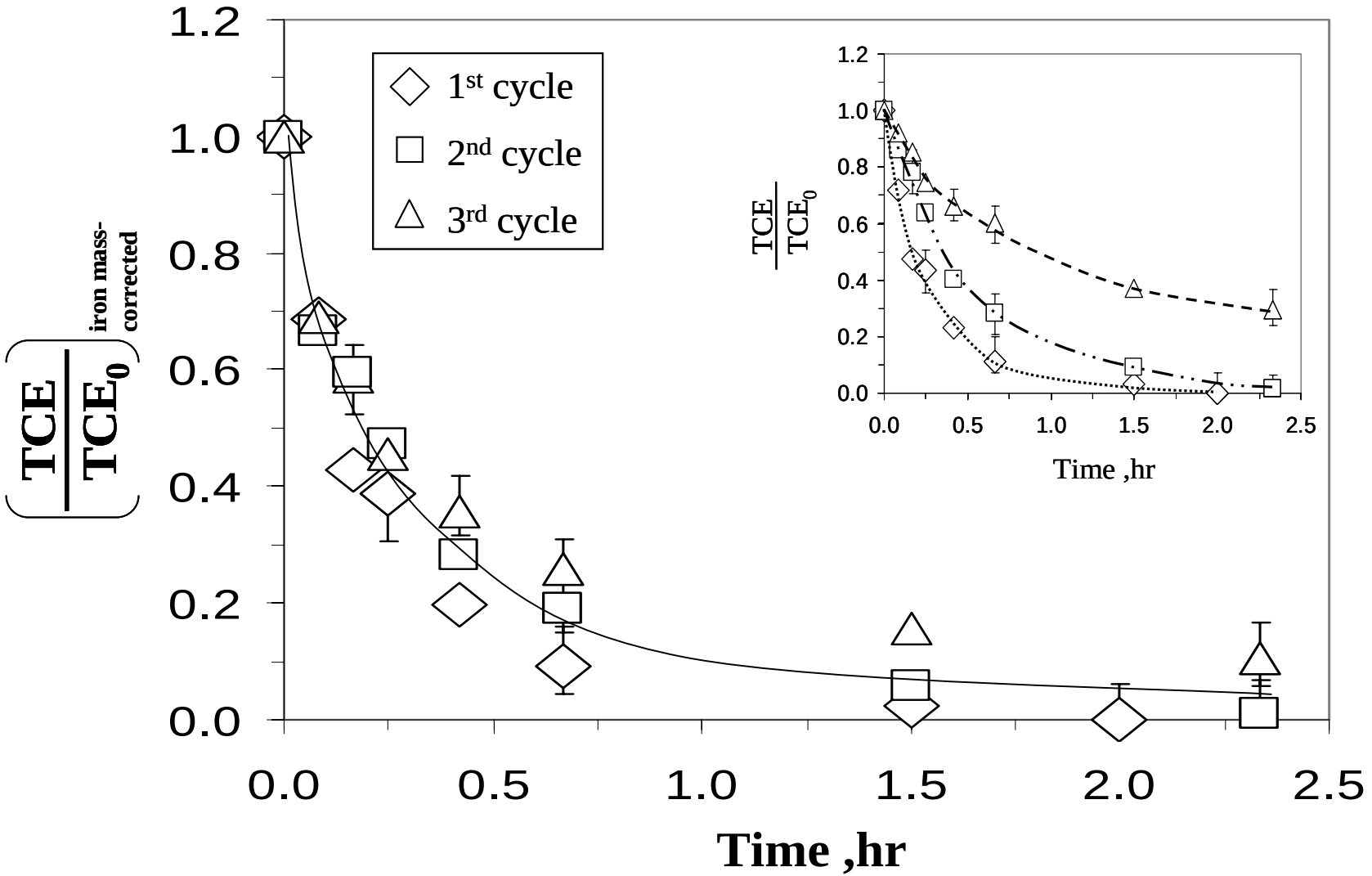


- This mechanism is supported by the fact that dechlorination rates increase as the H-promoting ability of the 2nd metal increases:

$$k_{Pt/Fe} > k_{Pd/Fe} > k_{Ni/Fe} > k_{Fe}$$

Batch Cycle Study for TCE Degradation by Ni/Fe (Ni = 20 wt%) Nanoparticles in Deoxygenated Water with Headspace:

Metal Loading = 2.5 g/L; pH = 6.5 ; TCE_0 = 10 mg/L

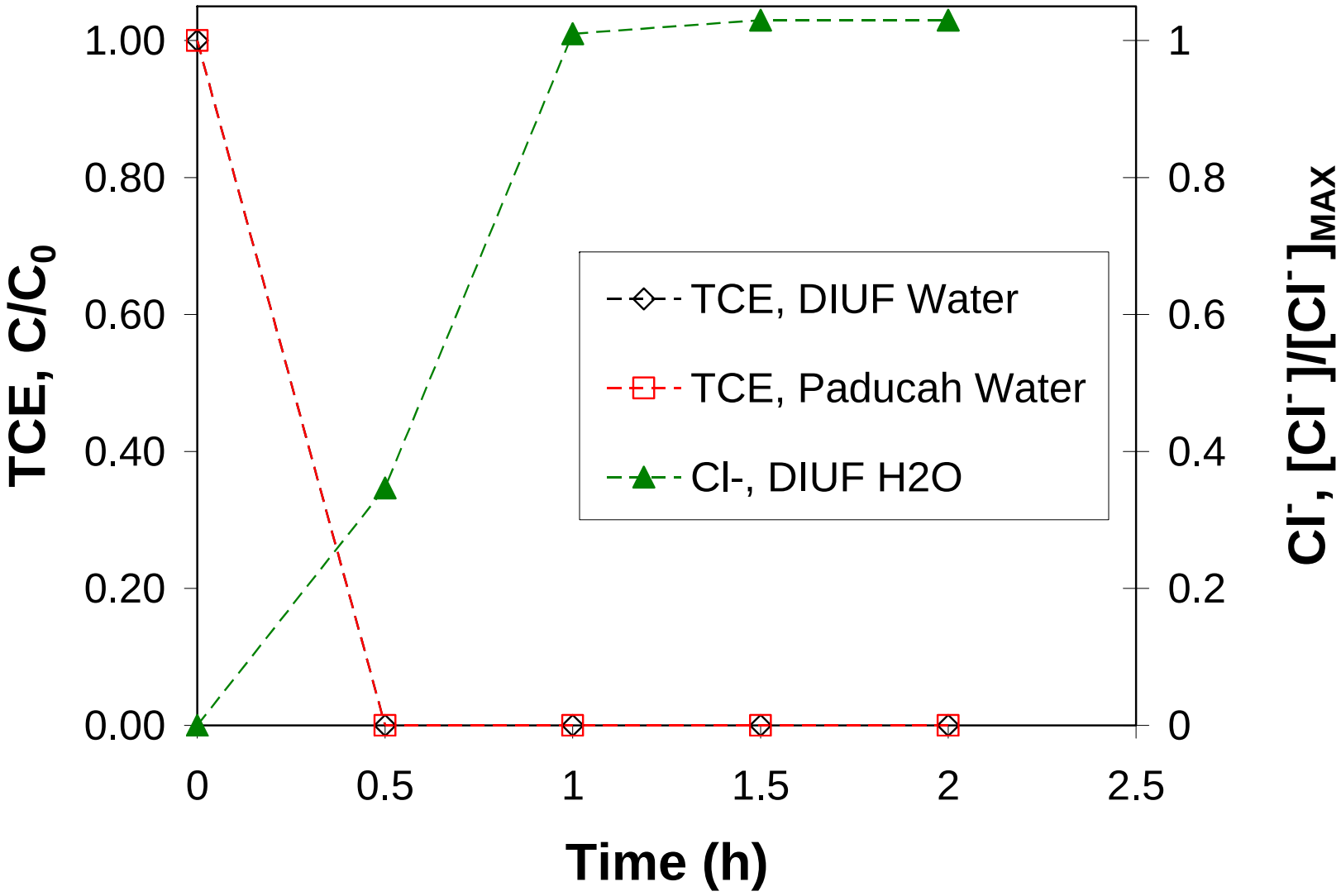


Aspects to Address for Successful TCE Dechlorination Using Direct Injection of Bimetallic Nanoparticle Systems

- What **composition** and **metal loading** are necessary for rapid and efficient TCE dechlorination? (**batch** data)
- Will the **presence of non-chlorinated chemical species** present in **Paducah groundwater and soil** alter the performance of Fe-based nanoparticle dechlorination systems? (**batch** and column experimental data)
- What impact, if any, will **dissolved oxygen** have on dechlorination kinetics? (**batch** data)
- What type of **mobility** will **nanoparticles** have while moving within plumes? (theoretical modeling)

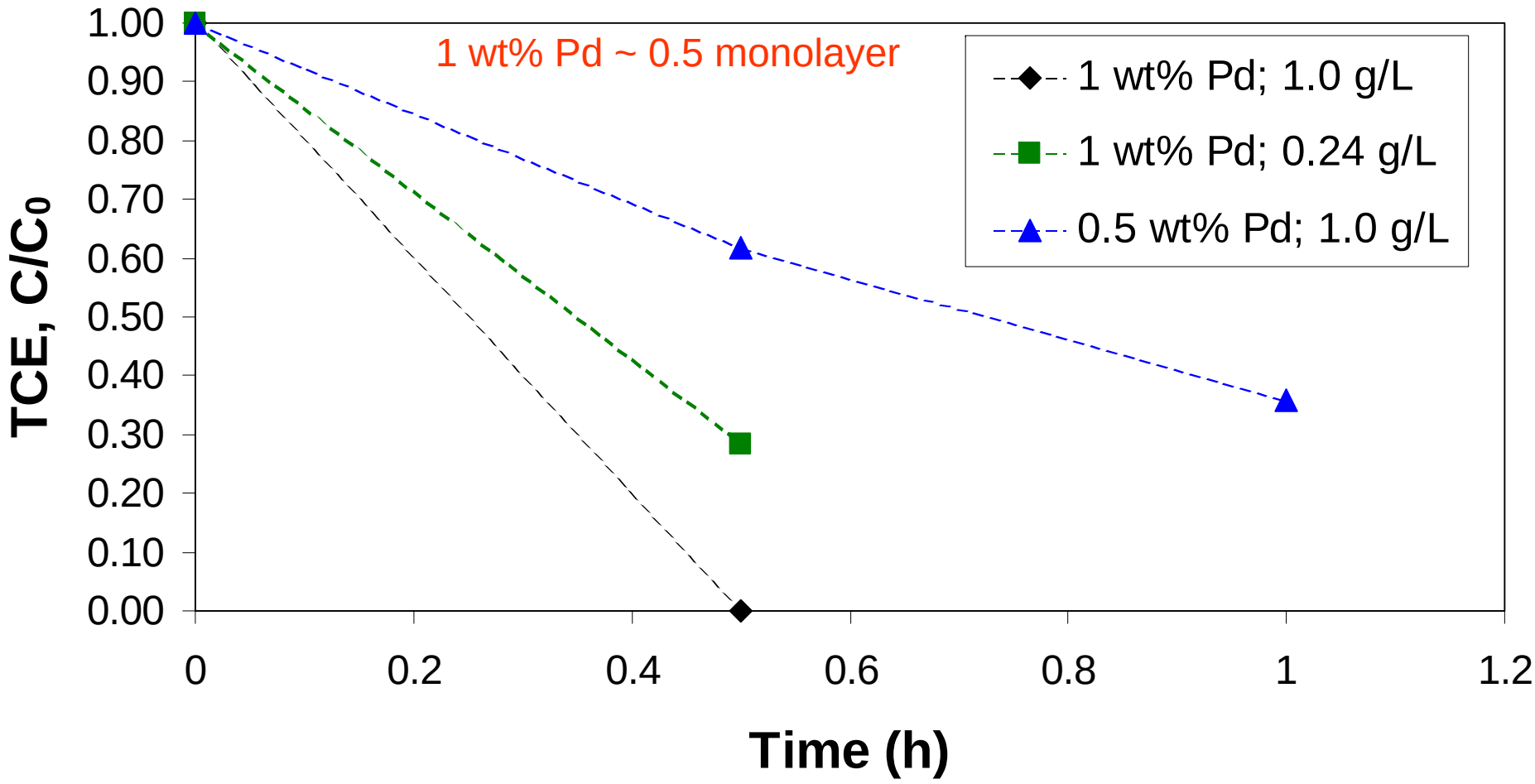
Dechlorination of TCE Using Fe/Pd Nanoparticles (1 wt% Pd) In Deoxygenated Water with Headspace:

Metal Loading = 1.0 g/L; pH = 6; C_0 = 16.6 mg/L TCE

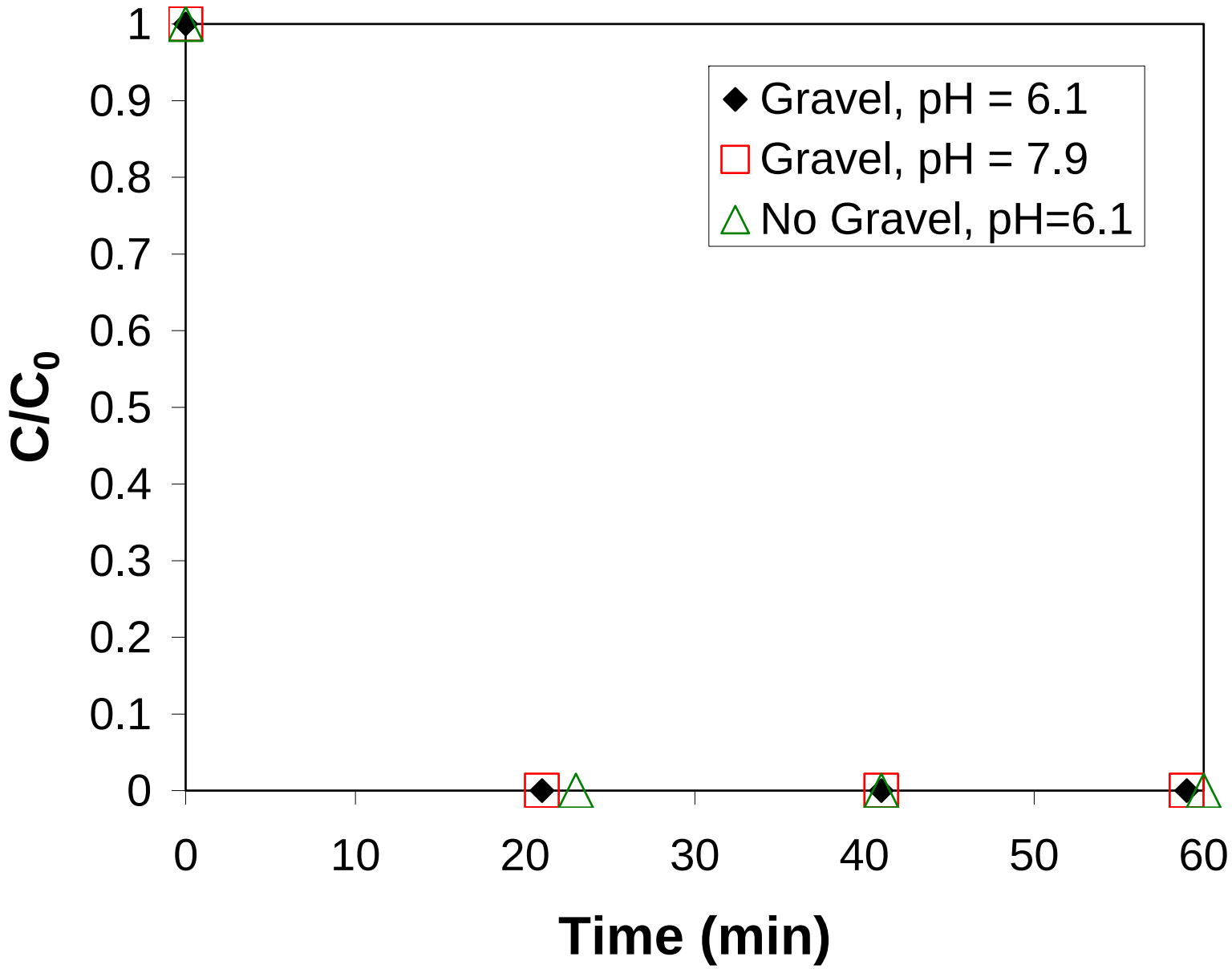


Dechlorination of TCE in Deoxygenated Paducah Water Using Fe/Pd Nanoparticles with Variable Metal Conditions:

C_0 = 20.5 mg/L; pH = 5

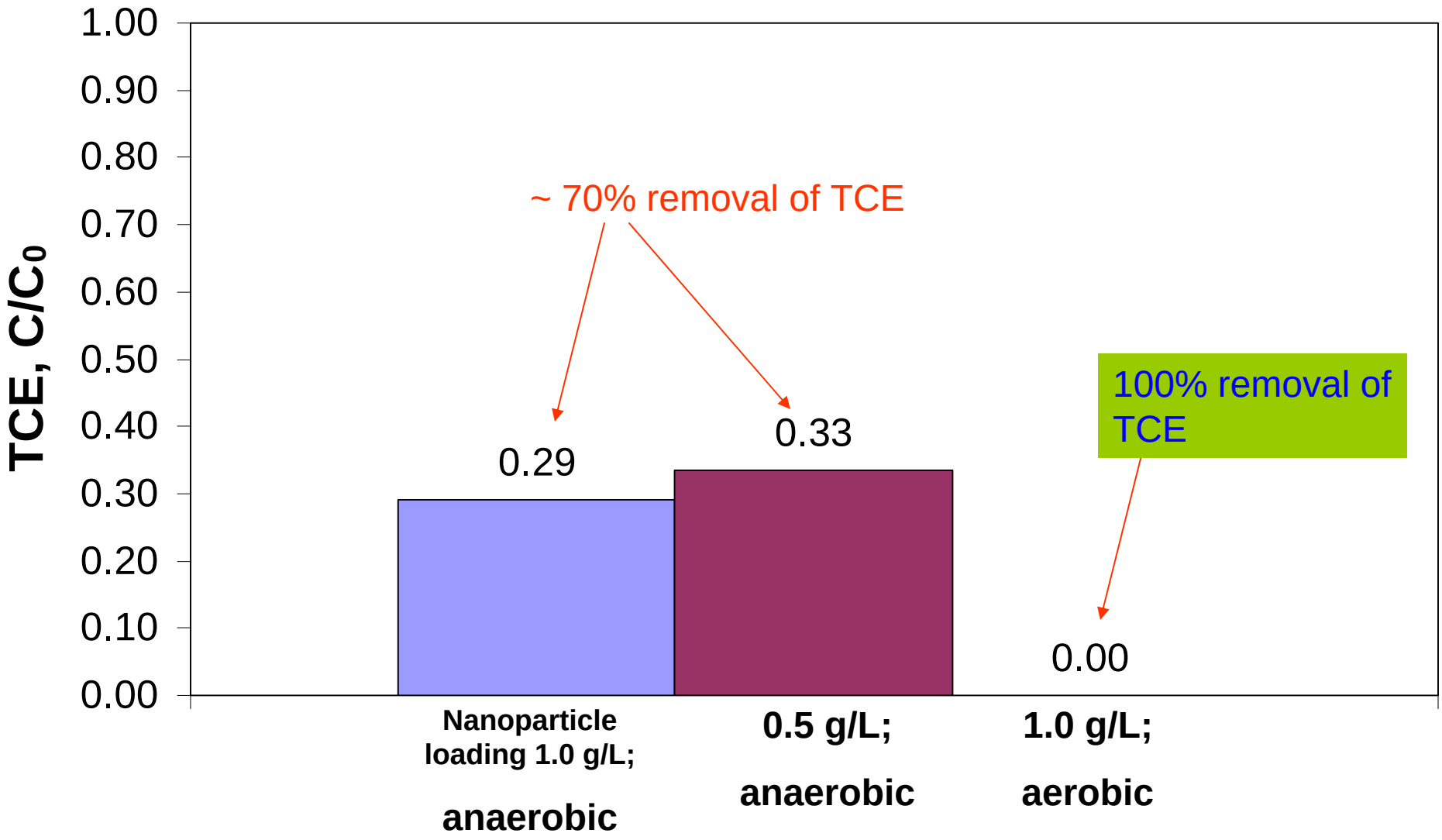


Reduction of a 20 ppm TCE Solution in Paducah Water Under Aerobic Conditions Using Fe Nanoparticles Post-Coated With 0.5 wt% Pd

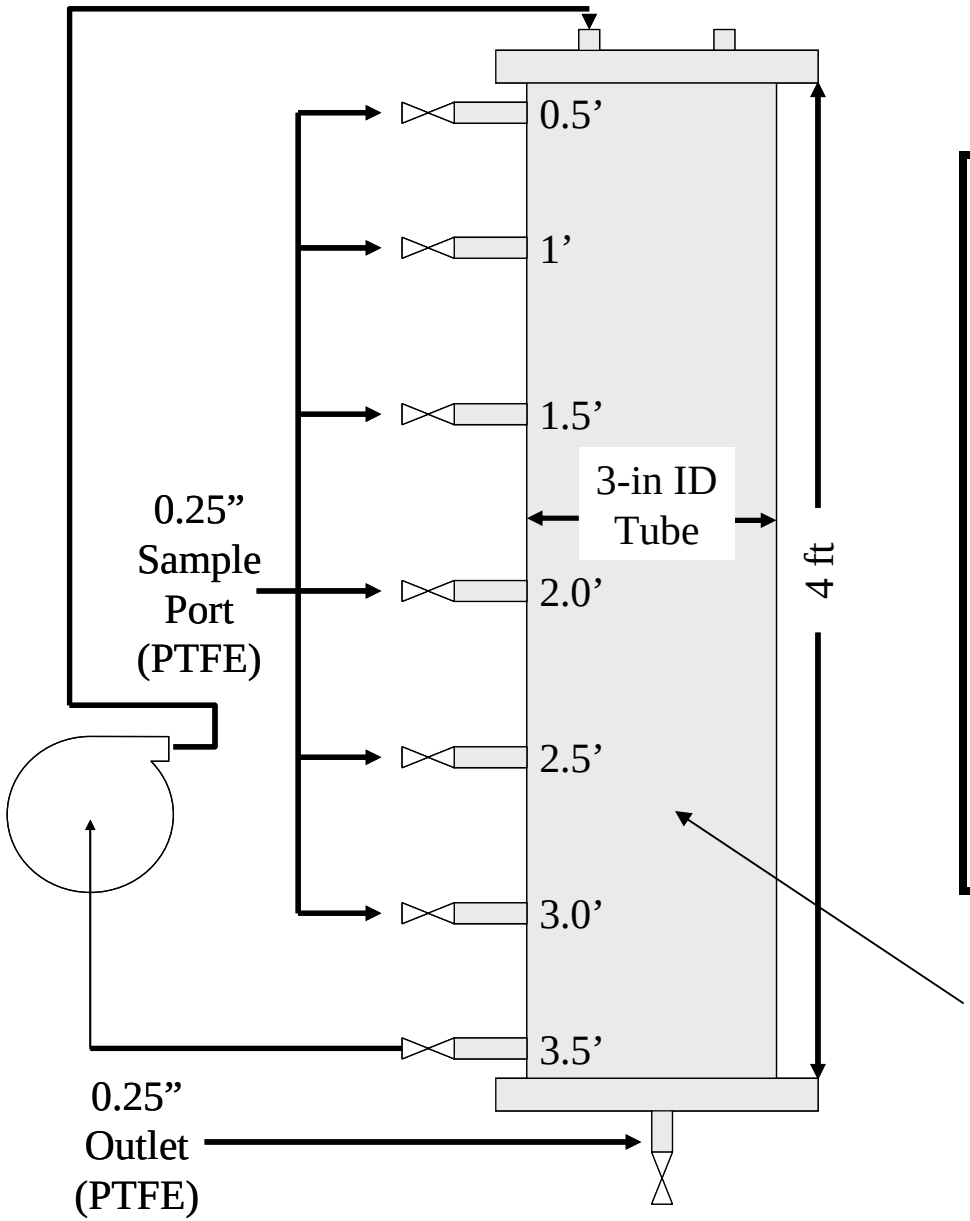


Dechlorination of TCE Using Fe/Pd Nanoparticles (1 wt% Pd) In Paducah Water with Gravel:

pH = 6; C_0 = 21.9 mg/L TCE, Reaction time = 0.5 hr



Packed Column Studies for Simulated Groundwater Injection



Preliminary Results

Column Flowrate = 260 ft/day

Liquid Volume = 2.25 L

Fe/Pd (0.5 wt%) = 0.4 g/L

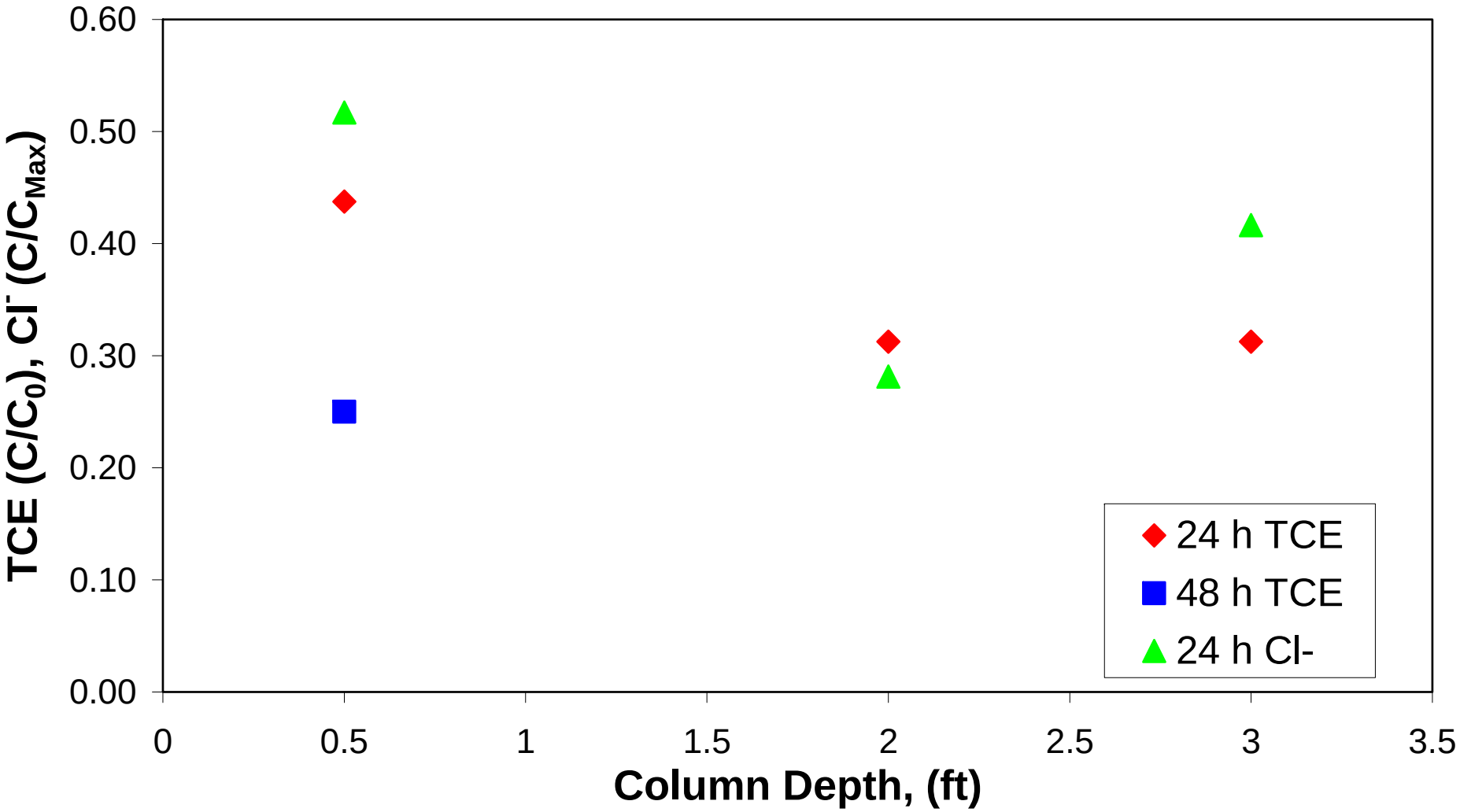
Initial TCE = 46 ppm

Circulation Time = 4 h

Column Depth (ft)	C/Co
0.5	0.185
2	0.080

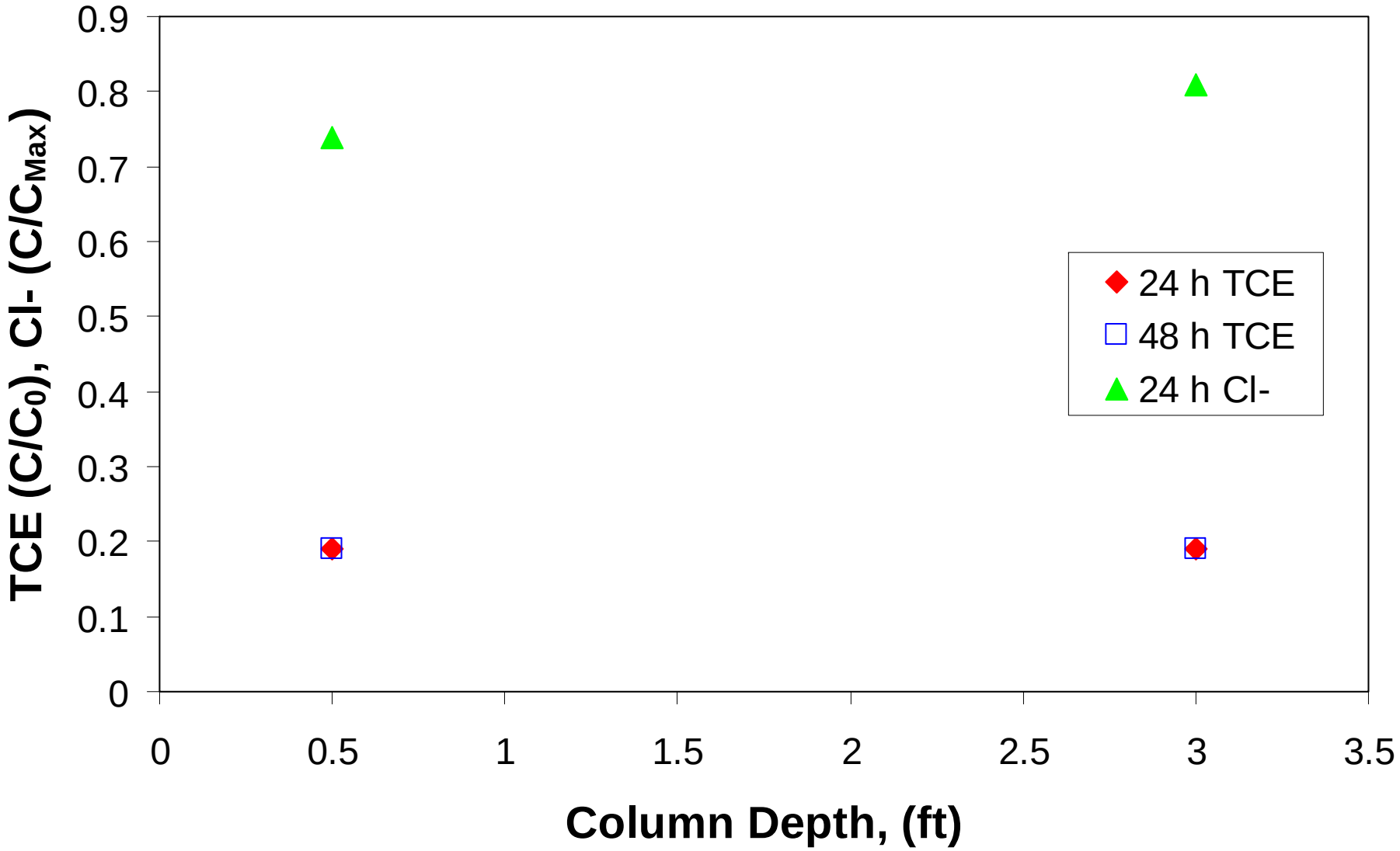
Packed Column Studies:

Flowrate = 73 ft/day; Metal Loading = **0.23 g/L** Fe/Pd (0.5 wt%);
C_0 = 25 ppm TCE; pH =7.0



Packed Column Studies:

Flowrate = 82 ft/day; Metal Loading = **0.46 g/L** Fe/Pd (0.5 wt%);
C_0 = 25 ppm TCE; pH =7.0



Examination of Material Usuage for the Reduction of 400 ppb TCE Using Fe/Pd Nanoparticles

Time Basis	24	**h**	**k_{SA}**	1.30E-01	**$L.m^{-2}.h^{-1}$ (Fe + 0.5 wt% Pd)**
Treatment Diameter	400	**ft**	**Fe/Pd loading**	0.25	**g/L**
Treatment Depth	20	**ft**	**mass Fe/Pd**	9,433	**g/h =** 20.753 **lbs/h**
Asssumed Porosity	0.4		**Surface Area**	30	**m^2 metal/g**
Treatment Area	125,664	**ft^2**	**Loading**	7.5	**m^2 metal/L**
Treatment Volume	2,513,274	**ft^3**			
Treatment C.S. Area	3,200	**ft^2**	**TCE**	400	**ppb**
Groundwater Velocity	10	**ft/day**			
	0.42	**ft/hr**	**C_{TCE} @ 1h**	0.000	**ppb**
Volume per hour	1,333	**ft^3/h**	**TCE reacted**	1.15E-01	**moles/h**
	37,733	**L/h**			

Fe:TCE ratio	4:1	
moles Fe consumed	4.59E-01	
mass Fe consumed	25.66	**g/h**
	0.056	**lbs/h**
Fe remaining	9,407.67	**g/h**
	20.697	**lbs/h unused**

Note: one can treat 38000 liters of water with 26 g of nano Fe particles

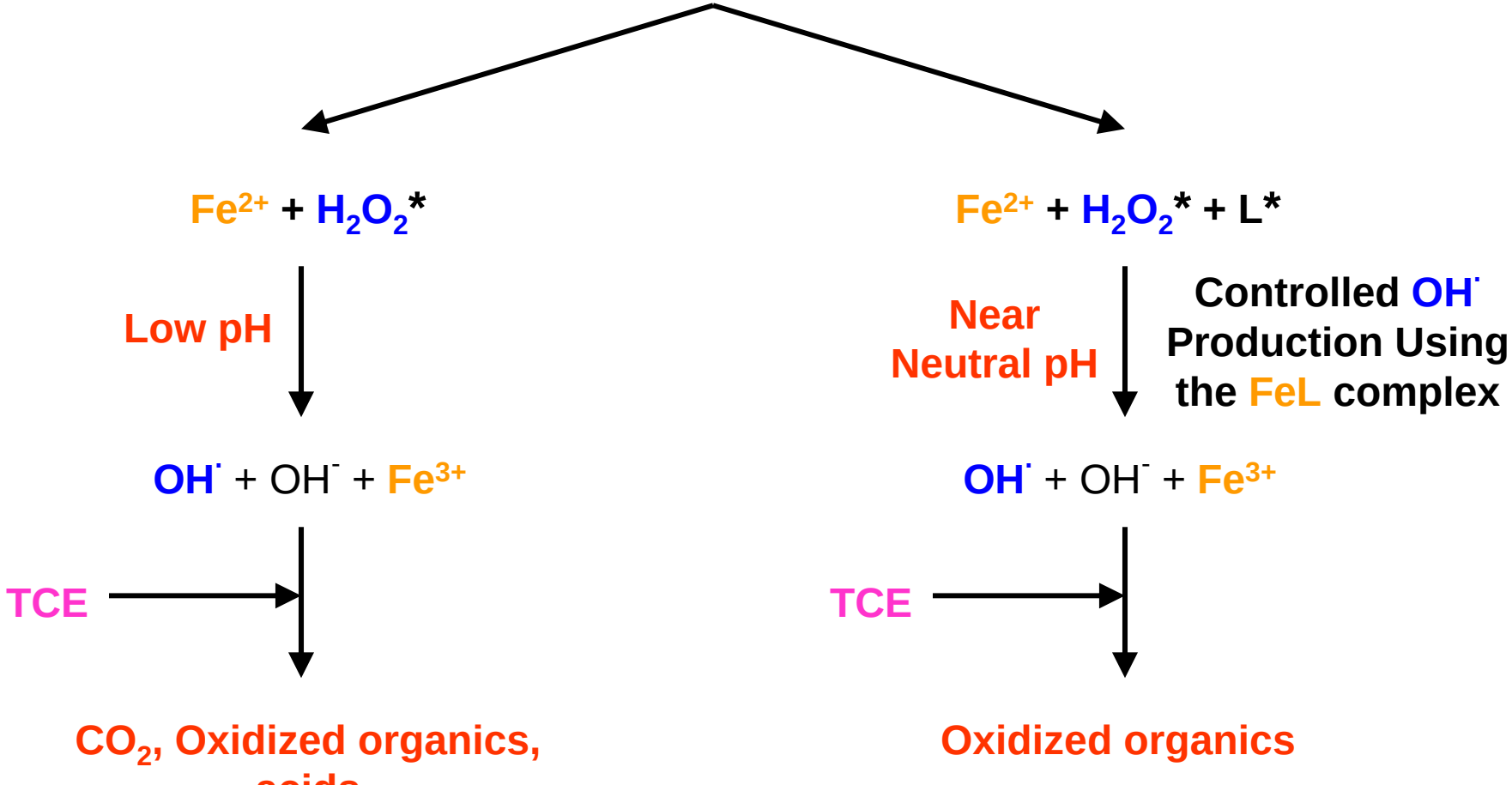
TCE Oxidation by Chelate-Based Modified Fenton Reaction

-Role of Surfactant Study

-Effect of Gravel on Reactivity

-H_2O_2 Decomposition by Ferrous and Ferric Iron

Oxidative Destruction of TCE Using $OH^{\cdot}$



***The potential exists for on-site production of both H_2O_2 AND a Chelate (L)**

At **near neutral pH**, the Fe^{2+} will undergo complexation as **FeL**. This slows $OH^{\cdot}$ production and prevents Fe(III) hydroxide pptn

Why Chelate-Based Modified Fenton's Reaction?

- Controlled release of Fe^{2+}
- Prevent Fe(II) oxidation
- At near neutral pH, prevent $Fe(OH)_3$ precipitate by complexing with Fe(III)
- Have a better H_2O_2 utilization during the reaction
- Hydroxy radical and superoxide* radical formation near neutral pH operation
- Potential biodegradation enhancement
- Chelate can also be immobilized in nano-particles

*Superoxide Radical Formation: $OH\bullet + H_2O_2 \rightarrow H_2O + HO_2\bullet$ $HO_2\bullet \rightarrow H^+ + O_2\bullet^-$

Required Materials for Chelate-Based Modified Fenton Reaction

Citrate

http://www.hort.purdue.edu/ext/senior/fruits/orange1.htm

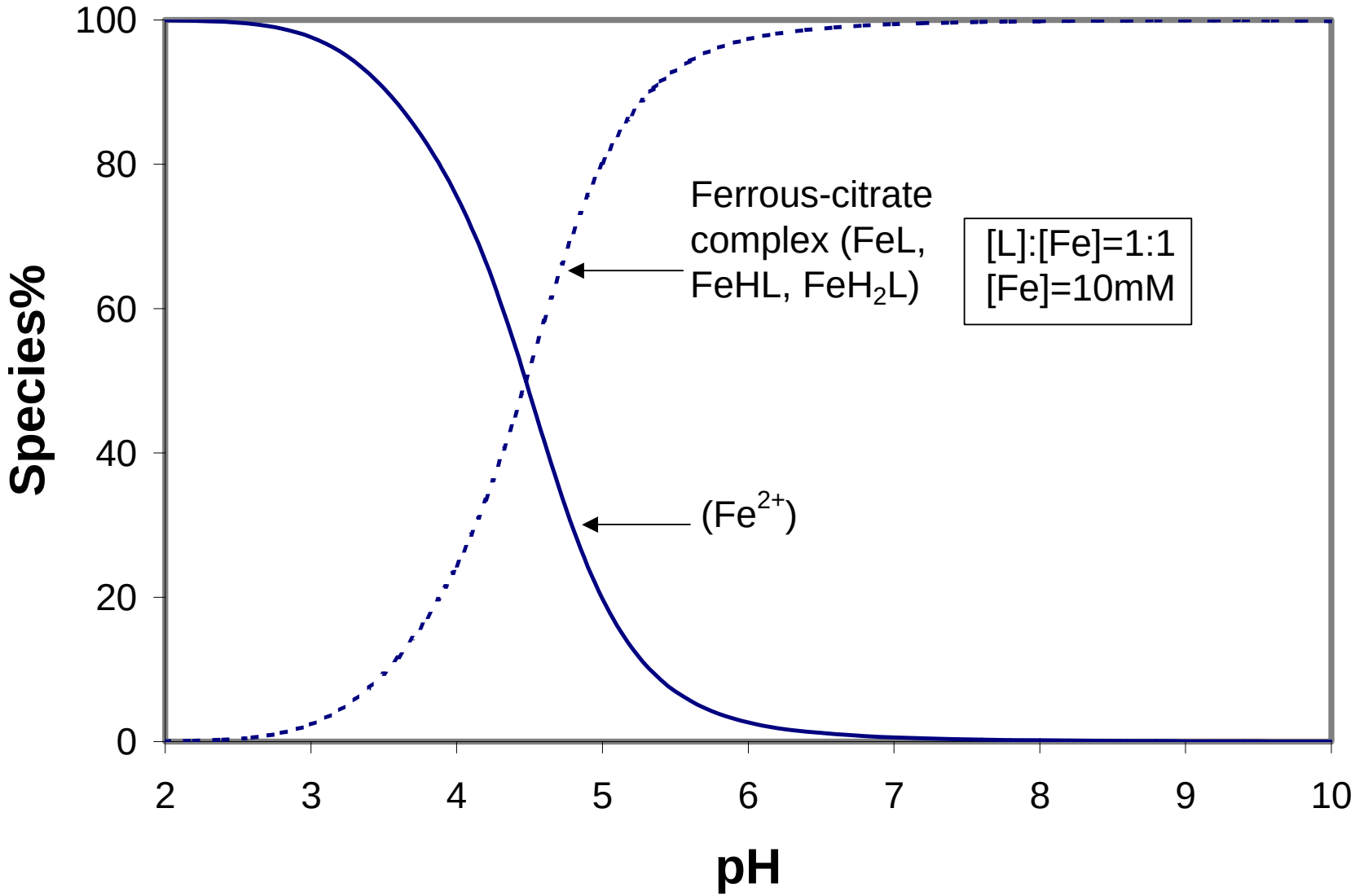
Ferrous Sulfate

http://www.drugstore.com/popups/largerphoto/default.asp?pid=77653&catid=39521&size=300&trx=29888&trxp1=77653&trxp2=1

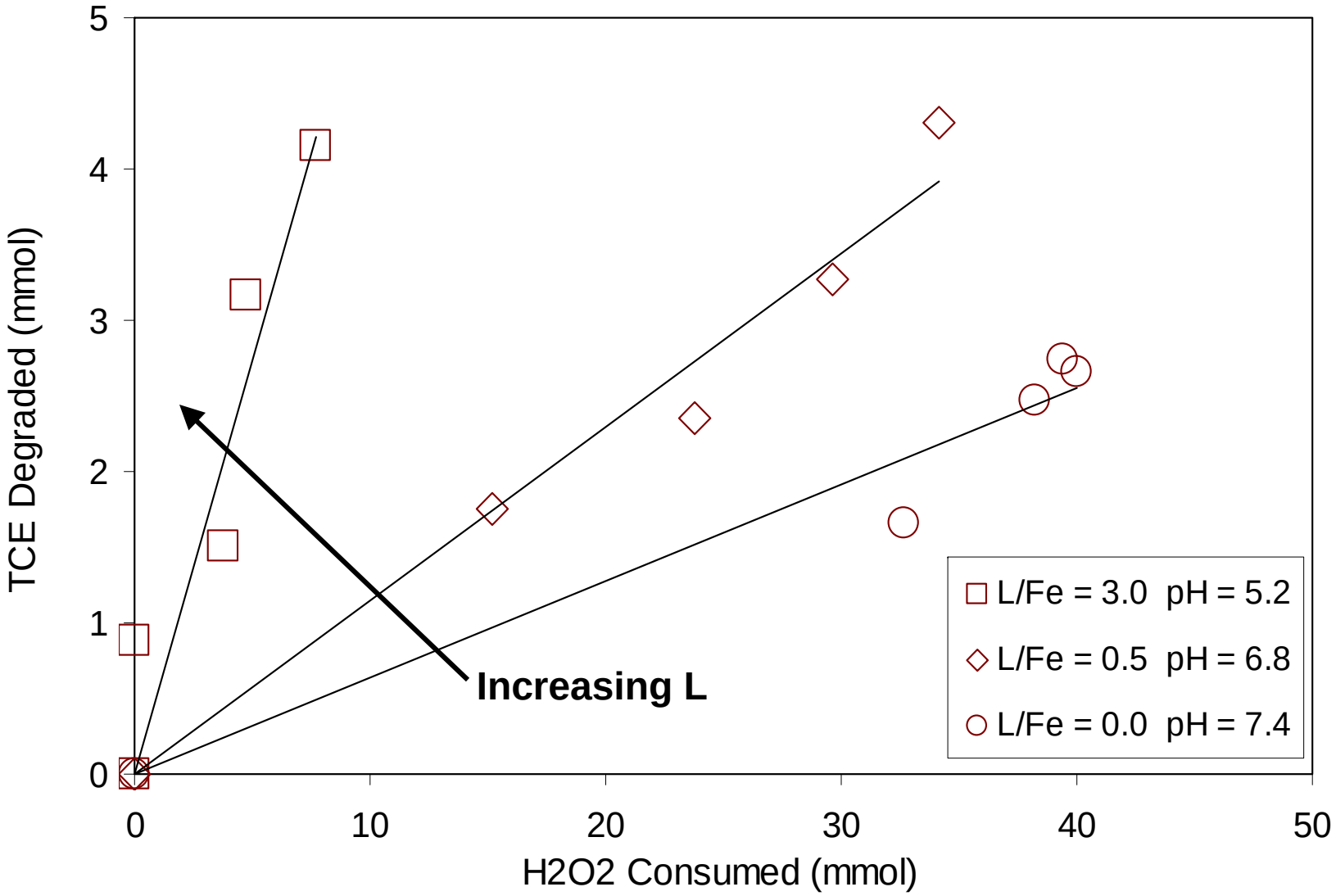
Hydrogen Peroxide

http://pics.drugstore.com/prodimg/73864/200.jpg

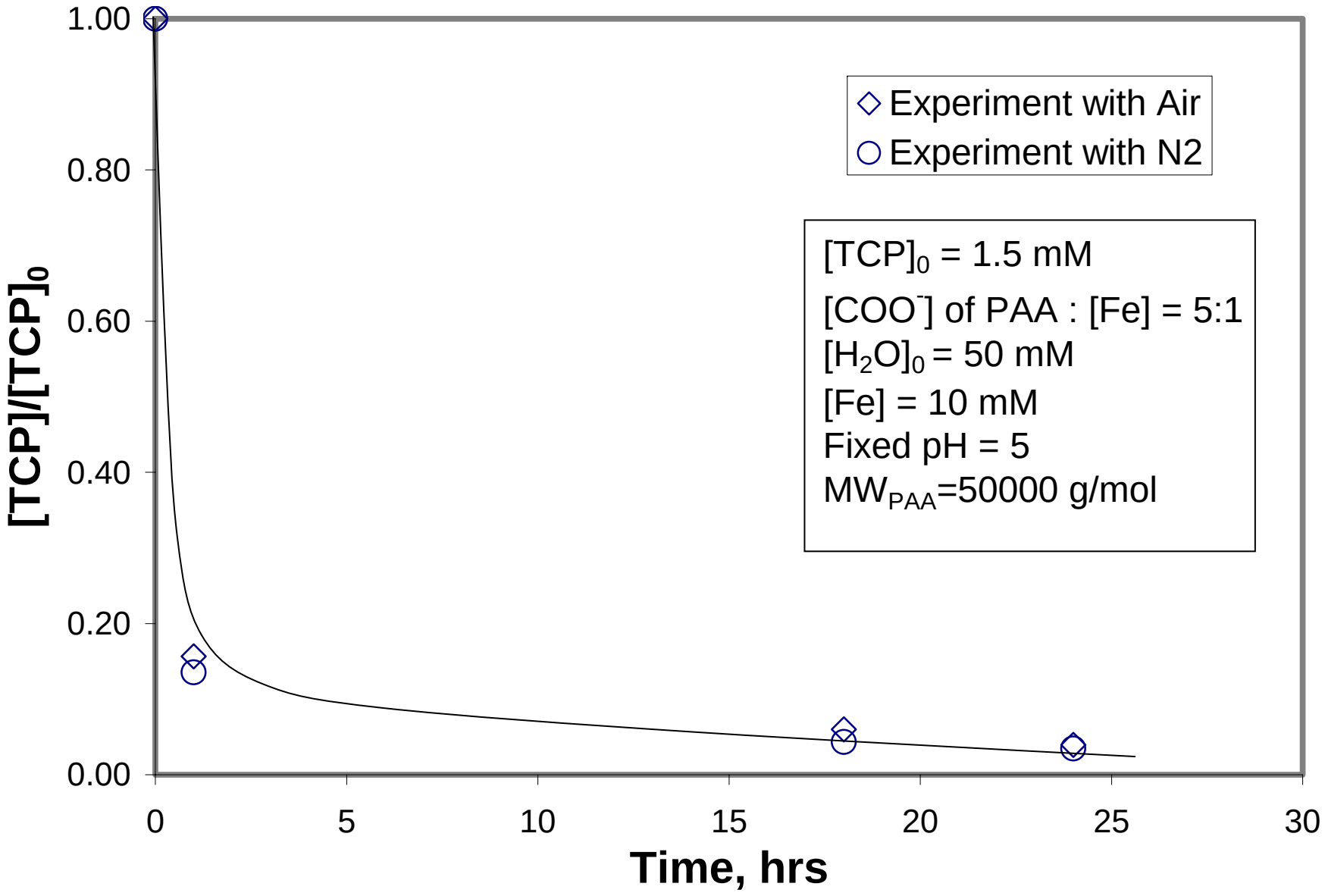
Iron-Citrate Species Distribution



TCE Degradation as a Function of **Peroxide Consumed** for **Varying Citrate (L)-to-Fe Ratios** Showing the **Potential Reduction in Peroxide Needs** for Chelate-Based Systems

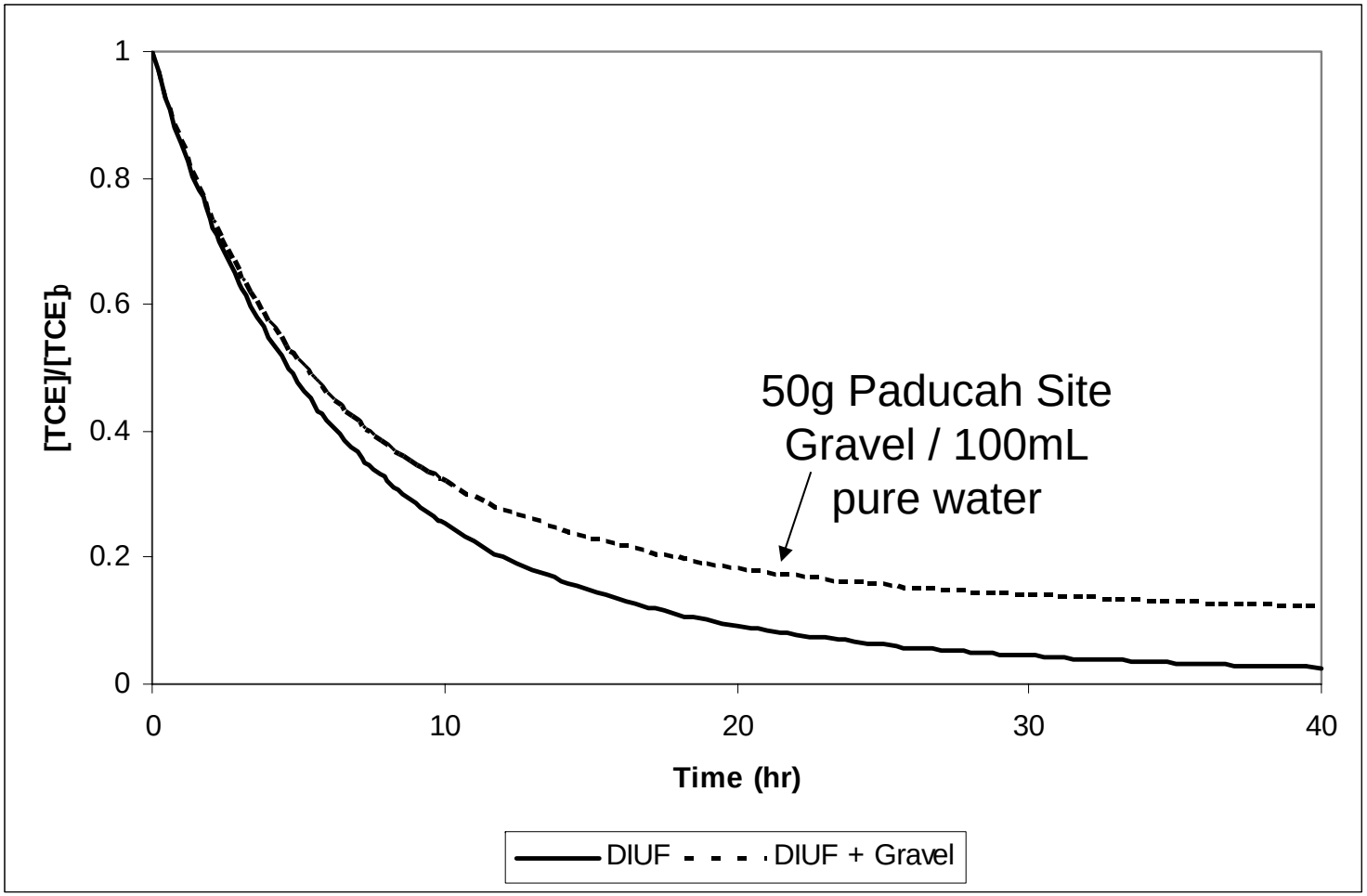


Effect of Dissolved Oxygen for TCP Oxidation by Fe^{2+} + PAA + H_2O_2 System (chelate modified system)

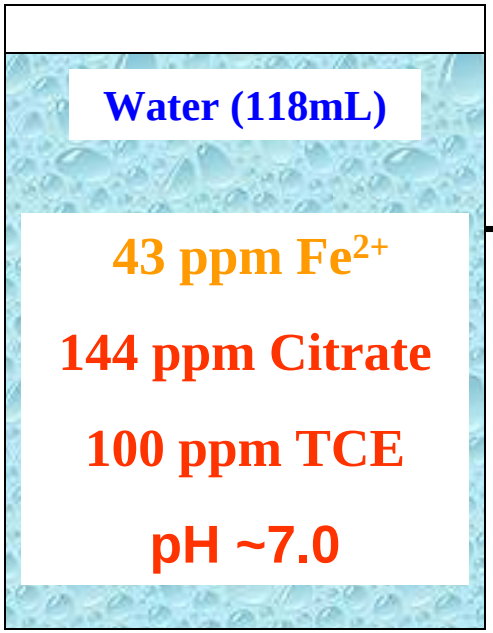


Effect of Gravel on TCE Destruction Using Chelate-Based Modified Fenton Reaction

TCE destruction model as a function of time for TCE:Fe:Citrate:H_2O_2 molar ratio of 1:1:1:8. Initial TCE concentration of 100ppm. Initial pH = 7.



Chelate-Based Modified Fenton Reaction (pH=7.0) Using Paducah Water With Varying Fe(II):H_2O_2 Ratio



100-mL Vial
(120-mL volume)

Add H_2O_2

Molar Ratios of
TCE:Fe:Citrate:H_2O_2
1:1:1:4
1:1:1:8

Reaction
Continuous pH Adjustment (pH~7)

Control Run
%TCE Remaining
87.5%

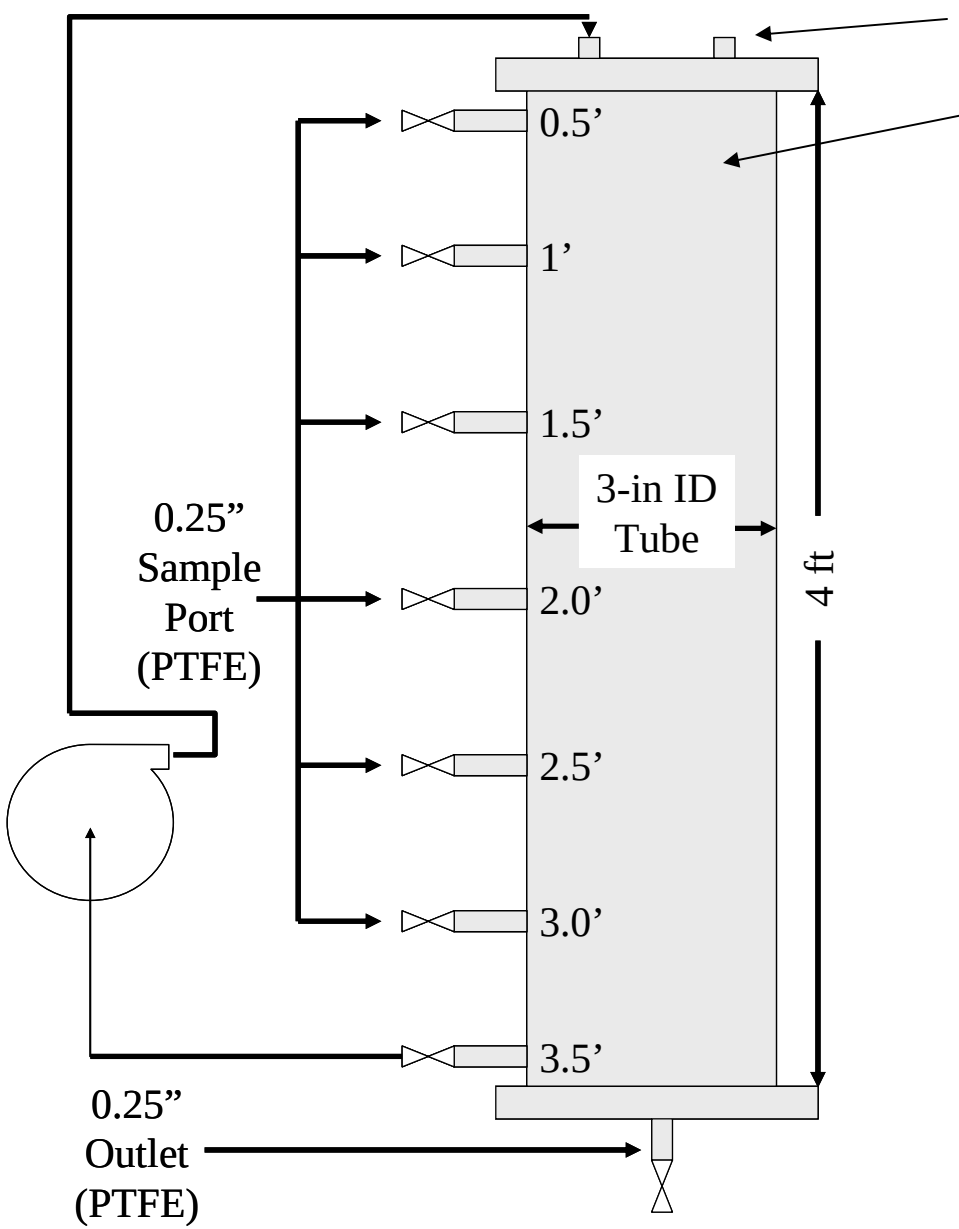
Paducah Water

TCE:Fe:Citrate:H_2O_2	%TCE Reacted at 40 hr
1:1:1:4	52%
1:1:1:8	87%

Distilled Water

TCE:Fe:Citrate:H_2O_2	%TCE Reacted at 40 hr
1:1:1:4	~64%
1:1:1:8	~100%

Packed Column Studies for Simulated Groundwater Injection



Preliminary Results

Column Flowrate = 2.5 ft/day
Liquid Volume = 2.25 L

Initial TCE = 54 ppm
85ppm Fe^{2+}, 290ppm Citrate

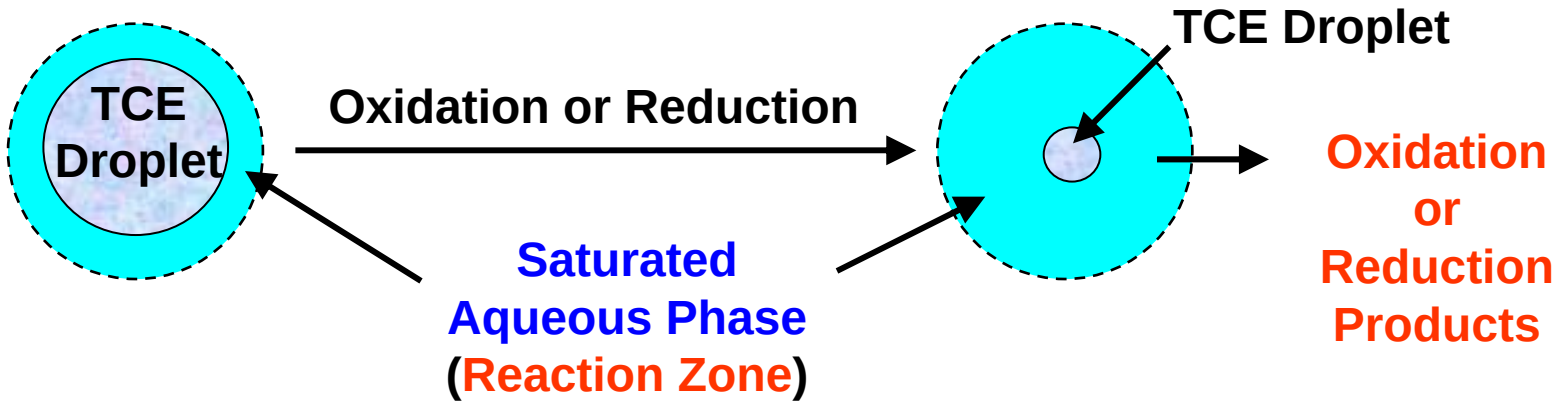
Peroxide Injections: 0hr, 24hr
2:1 H_2O_2:Fe molar ratio

	TCE/TCEo	
Column Depth (ft)	**24hr**	**48hr**
0.5	0.60	0.54
2.0	0.64	0.43
3.0	0.93	0.55*

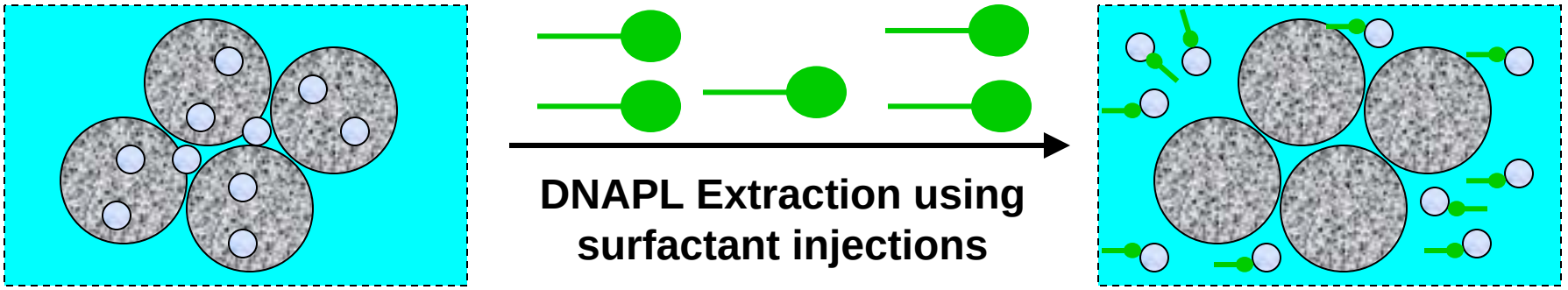
*TCE consumed → Cl^-

The Challenges of DNAPL

1.) TCE droplets dispersed in the aqueous phase will act as a source of TCE and shrink as mass is lost to the aqueous phase. The mass transfer between phases may have substantial impact on the observed reaction time for both oxidation and reduction.



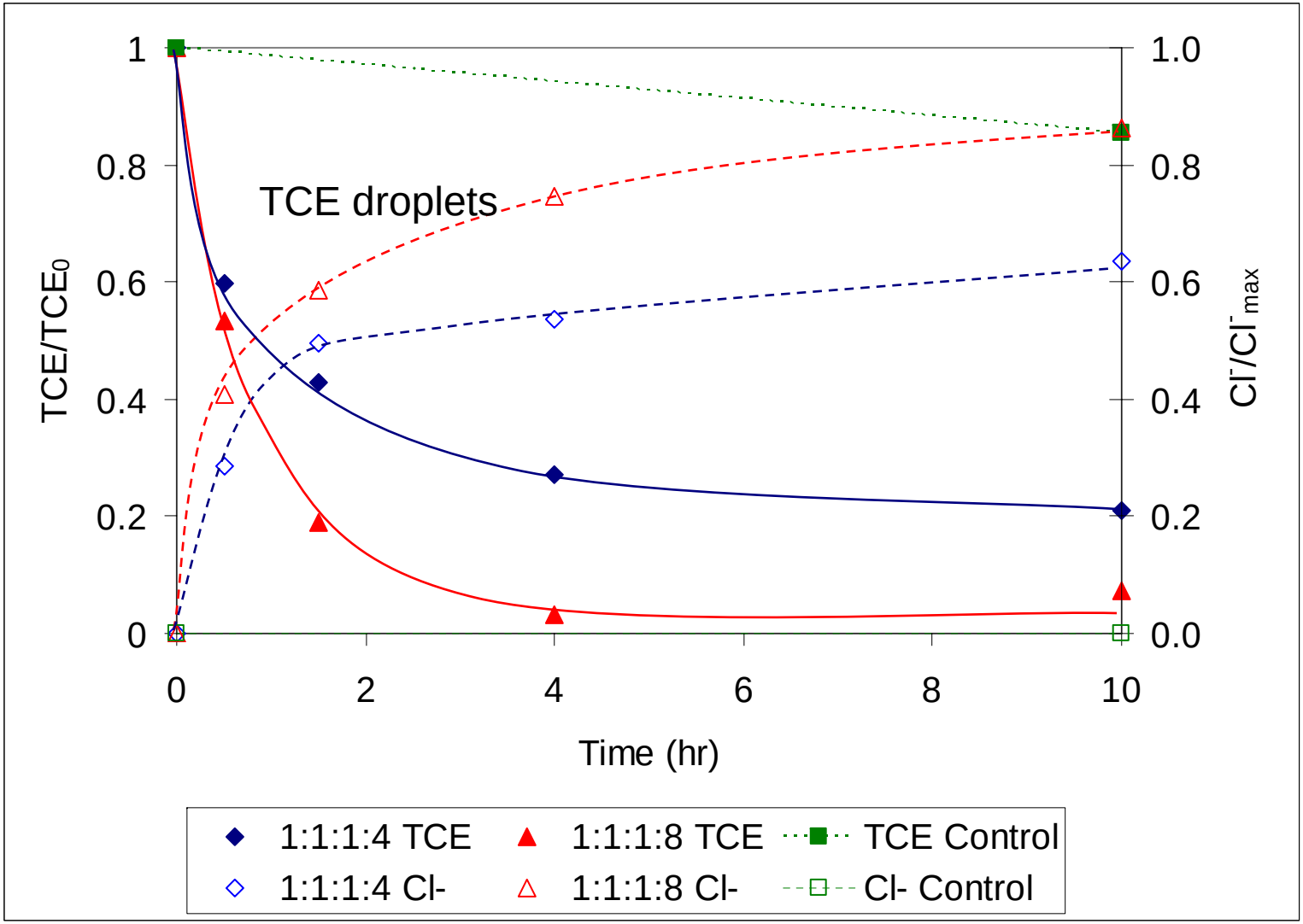
2.) If DNAPL droplets are dispersed within soil and rock, they may require much greater reaction times for direct treatment. To overcome this problem, surfactant addition can potentially be used to mobilize the DNAPL from the sediment. Laboratory packed columns operating under trickle-flow can be used to examine this phenomenon.



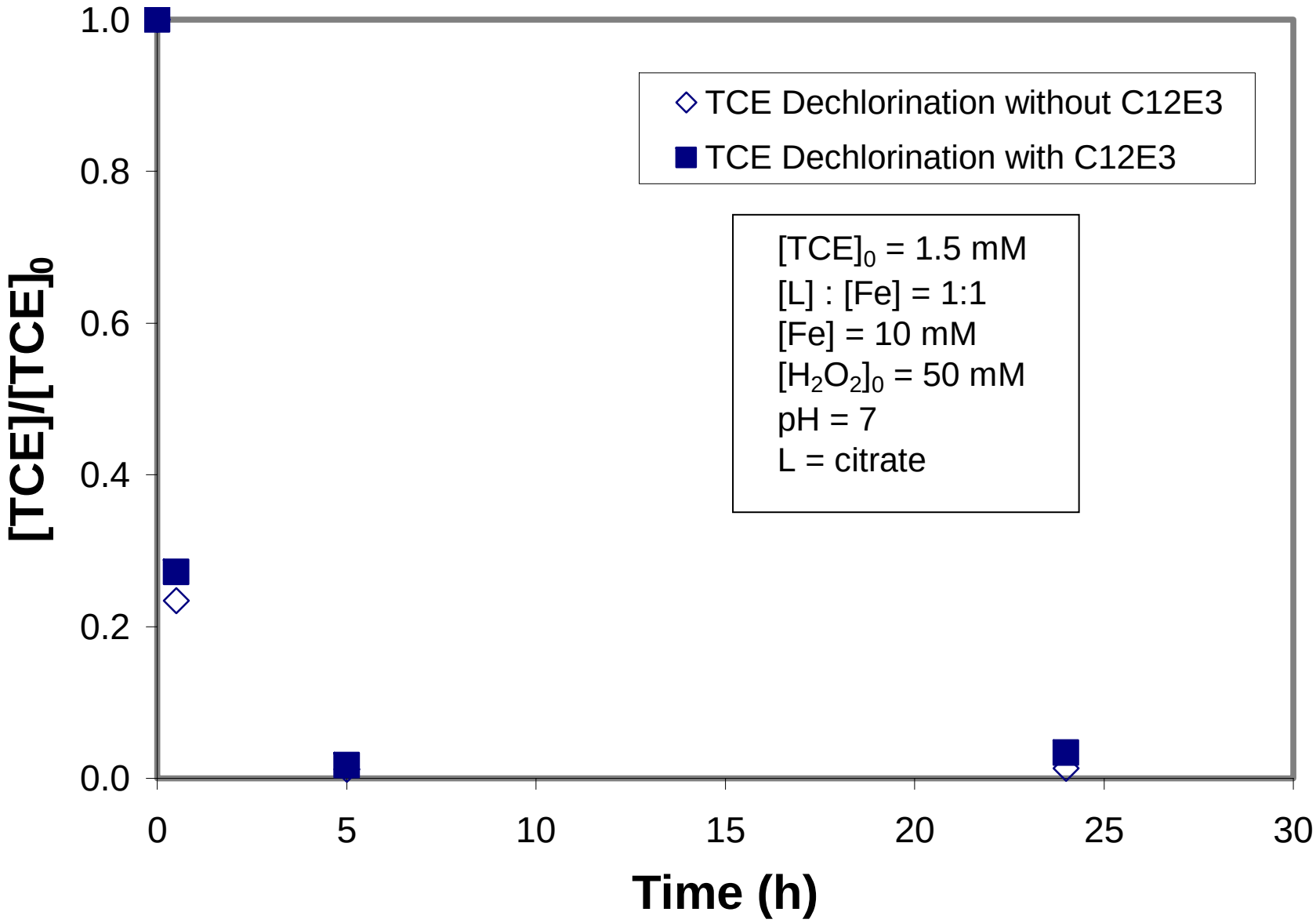
Dispersed DNAPL Droplets

Dispersed DNAPL Droplets

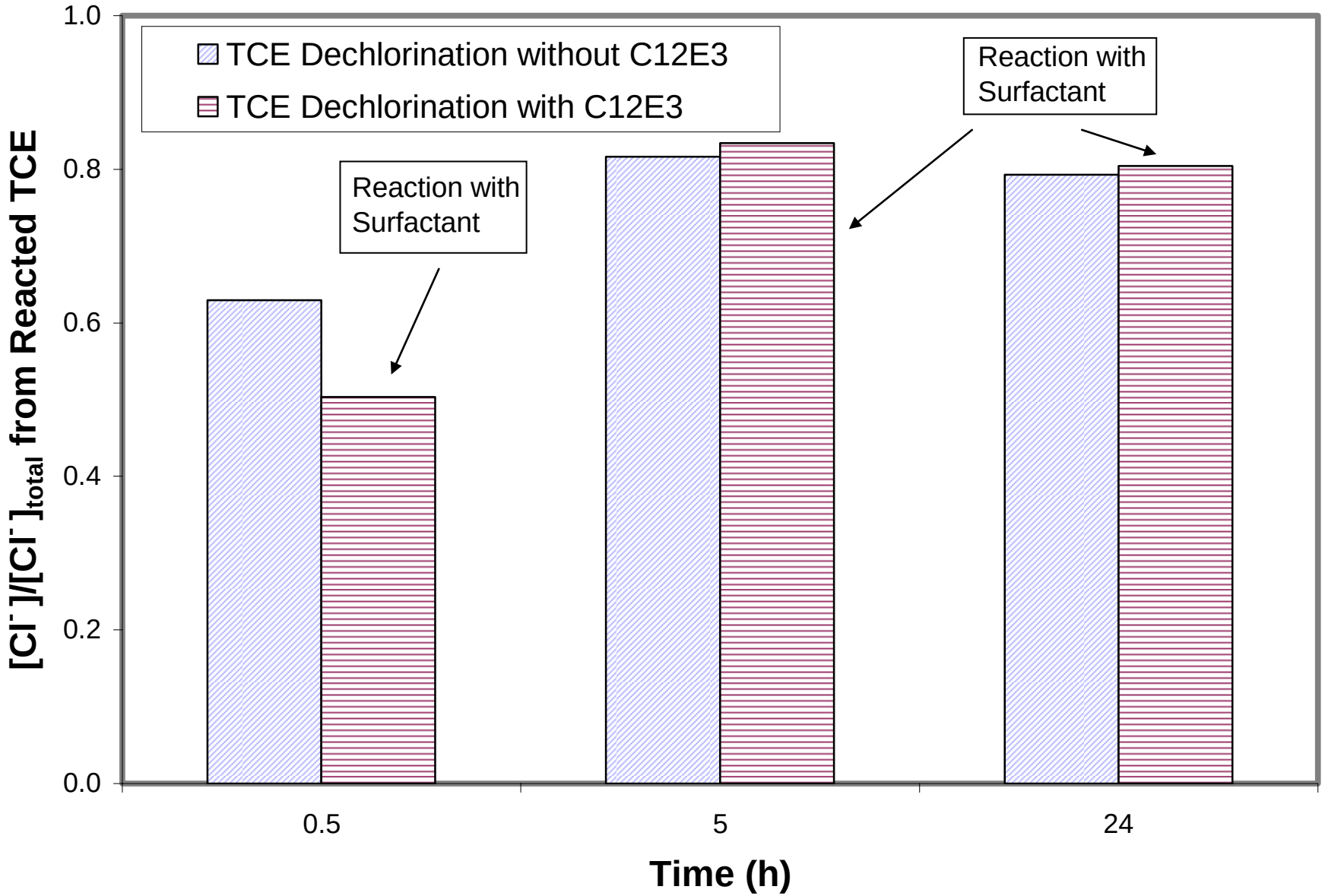
Chelate-Modified Fenton Reaction (initial pH=7.0, no further adjustments made) Using DIUF Water with DNAPL (2000ppm TCE) and Varying Fe(II):H_2O_2 Molar Ratio



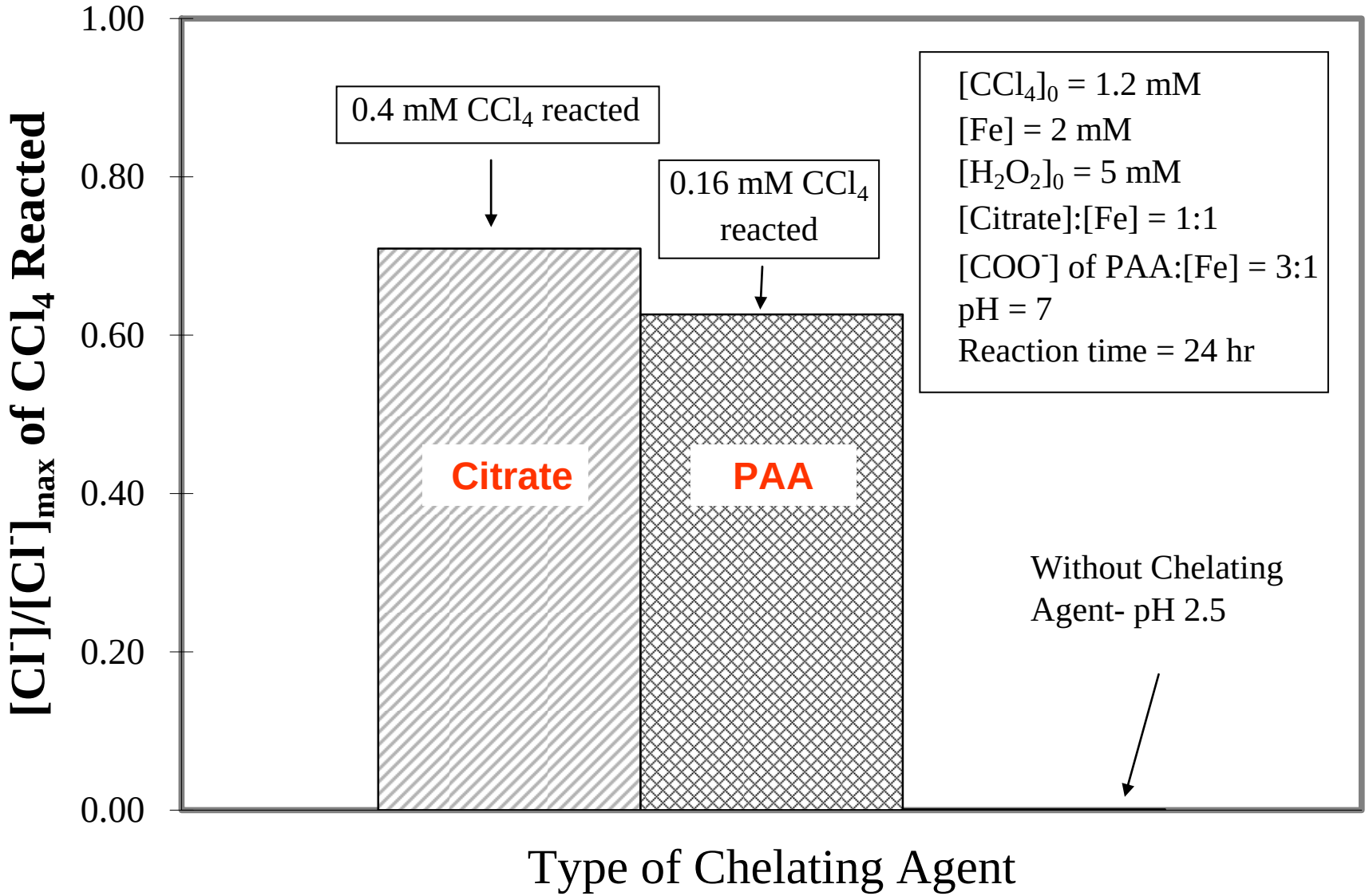
Effect of Surfactant for TCE Dechlorination by Fe^{2+} + Citrate + H_2O_2



Chloride Formation from TCE Dechlorination with and without Surfactant

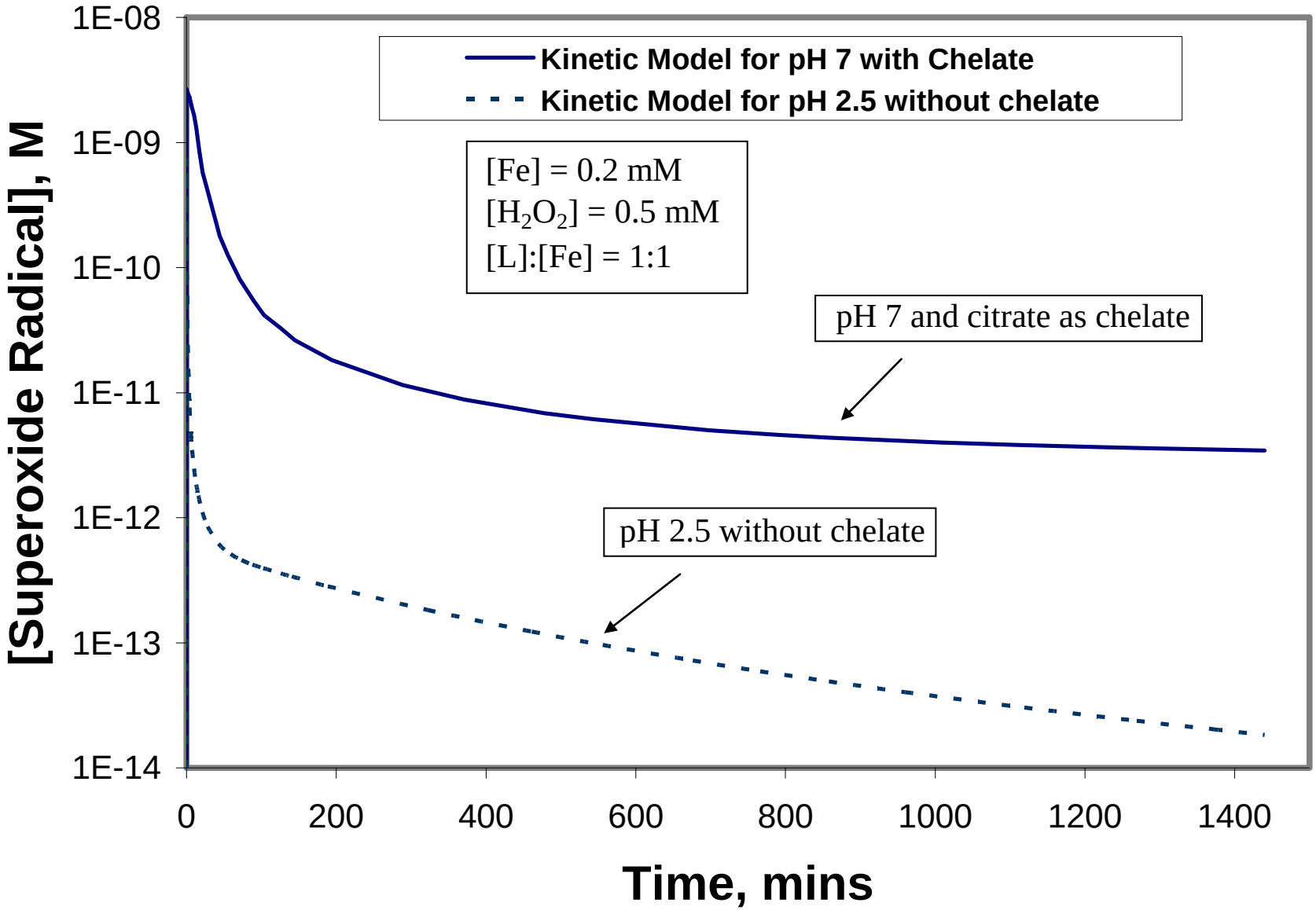


Chloride Formation During CCl_4 dechlorination under Standard and Chelate-Based Modified Fenton Reaction at 24 hr Reaction Time (role of superoxide radical)



Ref: Li, Bachas, and Bhattacharyya, I&EC Res (2007)

The Predicted Profiles of superoxide [$O_2^{\bullet -}$] for the Standard and Chelate-Based Modified Fenton Reactions



Ref: Li, Bachas, and Bhattacharyya, I&EC Res (2007)

Literature Results for Field Testing of Oxidative and Reductive Treatment Technologies

Site	Area	Agent	Initial TCE, Final TCE	# Injection Wells	Cost
Westinghouse Savannah River	50 ft x 50 ft (depth: ~110-140 ft)	$Fe(II)/H_2O_2$	**21**, **0.07** **(mg/L)**	4	$511K
Anniston Army Depot	2 acres (depth: ~8-26 ft)	$Fe(II)/H_2O_2$	**1760**, **Below detection** **(mg/L)**	255	$5,700K
Trenton, NJ Manufacturing Company*	15 ft x 10 ft (20 ft depth)	Nanoscale Fe^0/Pd	**0.445-0.800**, **0.016-0.028**** **(mg/L)**	1	NA

***Pilot test; site contained up to 4600 μg/L of PCE, DCE (cis and 1,1), VC, Chloroform, and Carbon Tetrachloride**

**** Values represent maximum removal achieved during initial injection period. Particles injections were reduced as part of testing to observe plume recovery.**

Conclusions

- Chlorinated organic destruction in modified Fenton reaction is same for both aerobic and anaerobic conditions
- Water from the Paducah area produces lower TCE destruction rates than deionized water due to the presence of hydroxyl scavengers (near neutral pH operation); will need slightly higher H2O2
- The complete dechlorination of TCE using Fe/Pd (1 wt% Pd) can be achieved in under 30 minutes using a metal loading of 1 g/L (or less) and is not affected by the presence of background chemicals in Paducah water.
- Batch dechlorination results obtained in the presence of Paducah gravel showed >70 % TCE removal in 1 h for 21.0 mg/L TCE using 0.5-1.0 g/L Fe/Pd (0.5 wt% Pd).
- Results for reductive dechlorination under aerobic conditions suggests that the presence of O_2 has minimal impact for the Pd-protected Fe nanoparticles.
- Both oxidative and nanotechnology-based treatments of TCE in a simulated groundwater column demonstrated > 50% TCE removal using minimal chemical dosing.

Acknowledgements

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