Nanoscale Iron Particles

Synthesis
Characterization
Applications

Nanotechnology for Hazardous Waste Site Remediation
Technical Workshop
October 20 - 21, 2005
Washington DC

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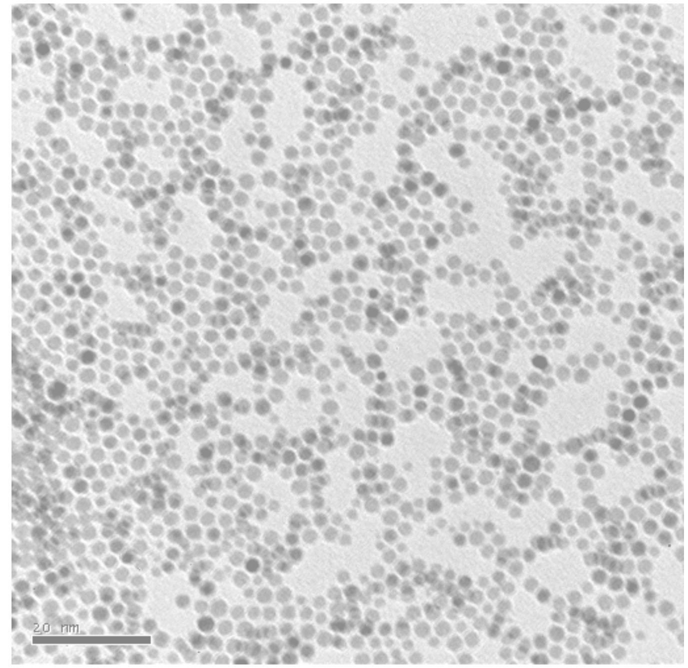
LEHIGH University

Nano Iron for Site Remediation

- Why nano?
- How to make nano
- Environmental chemistry
- What's next (better nano)

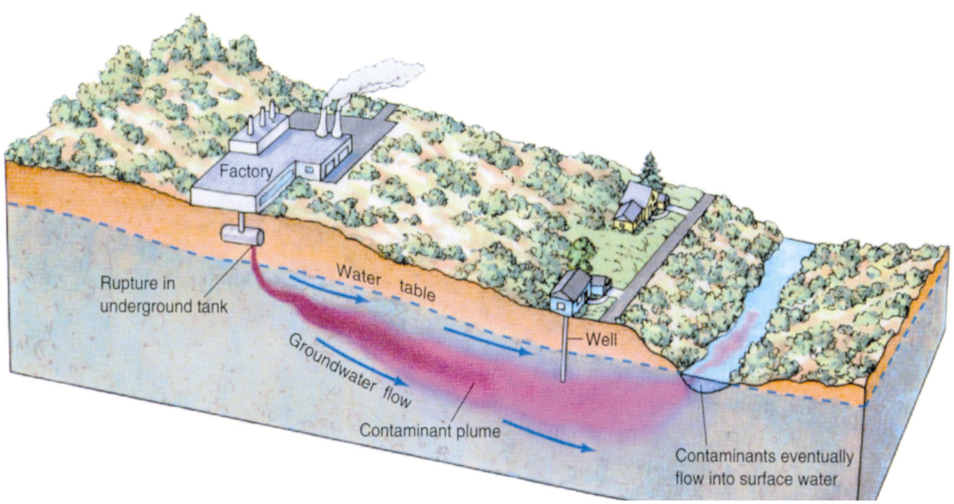


High reactivity

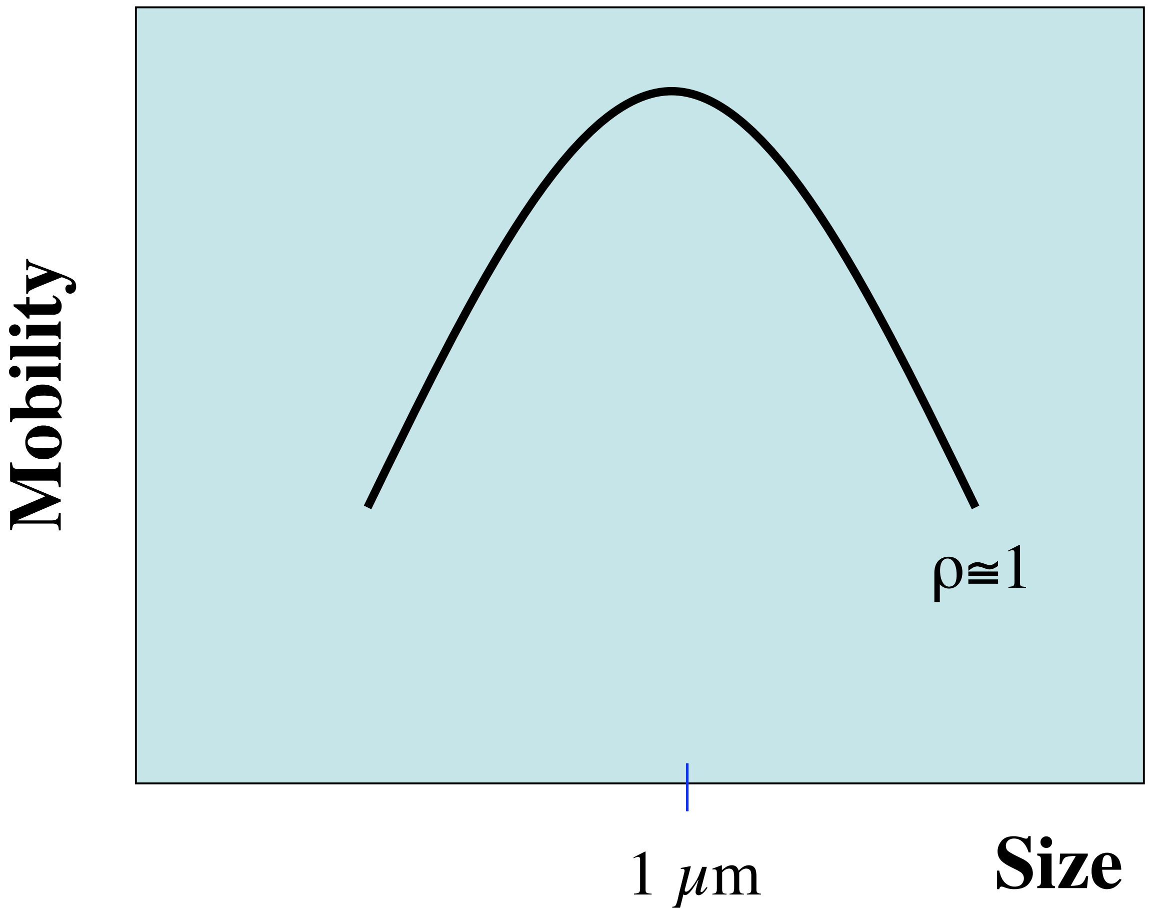
High mobility

Easy to use

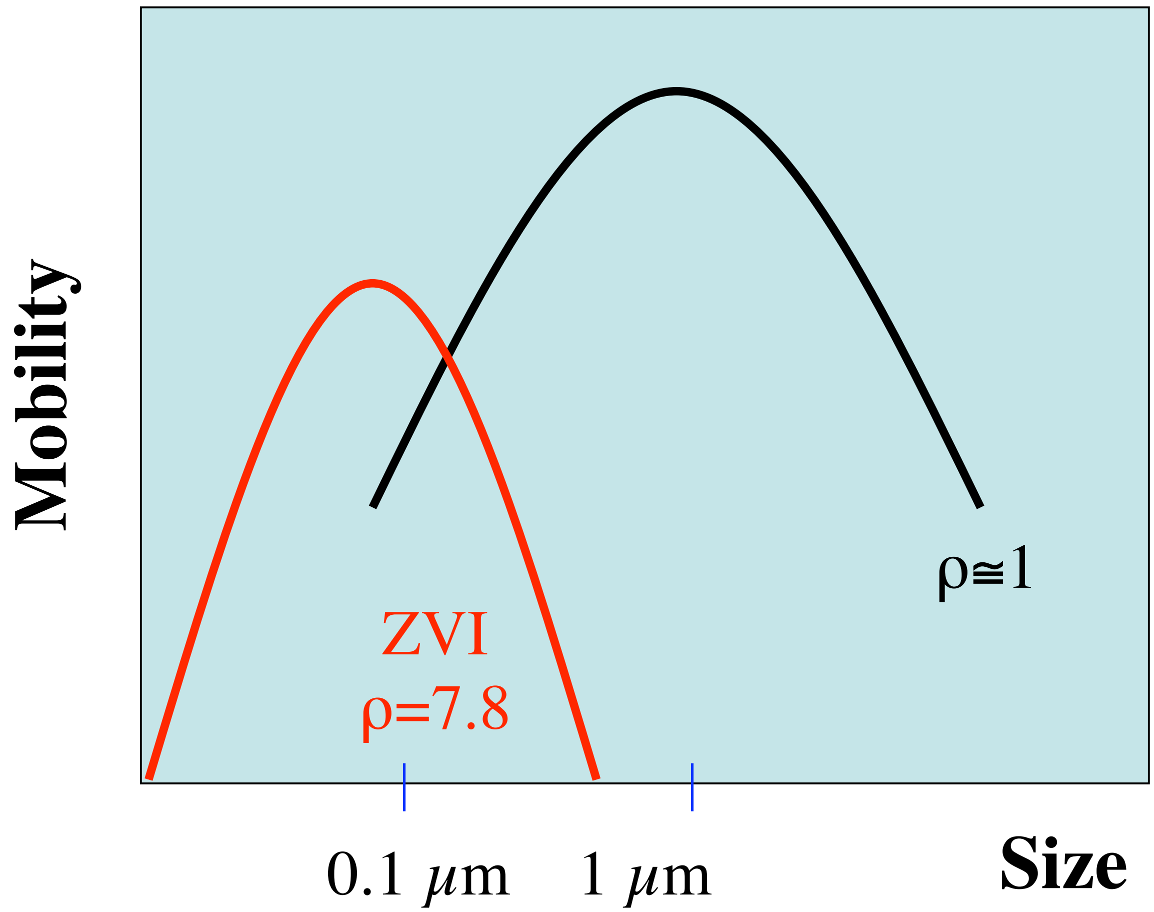
Low cost



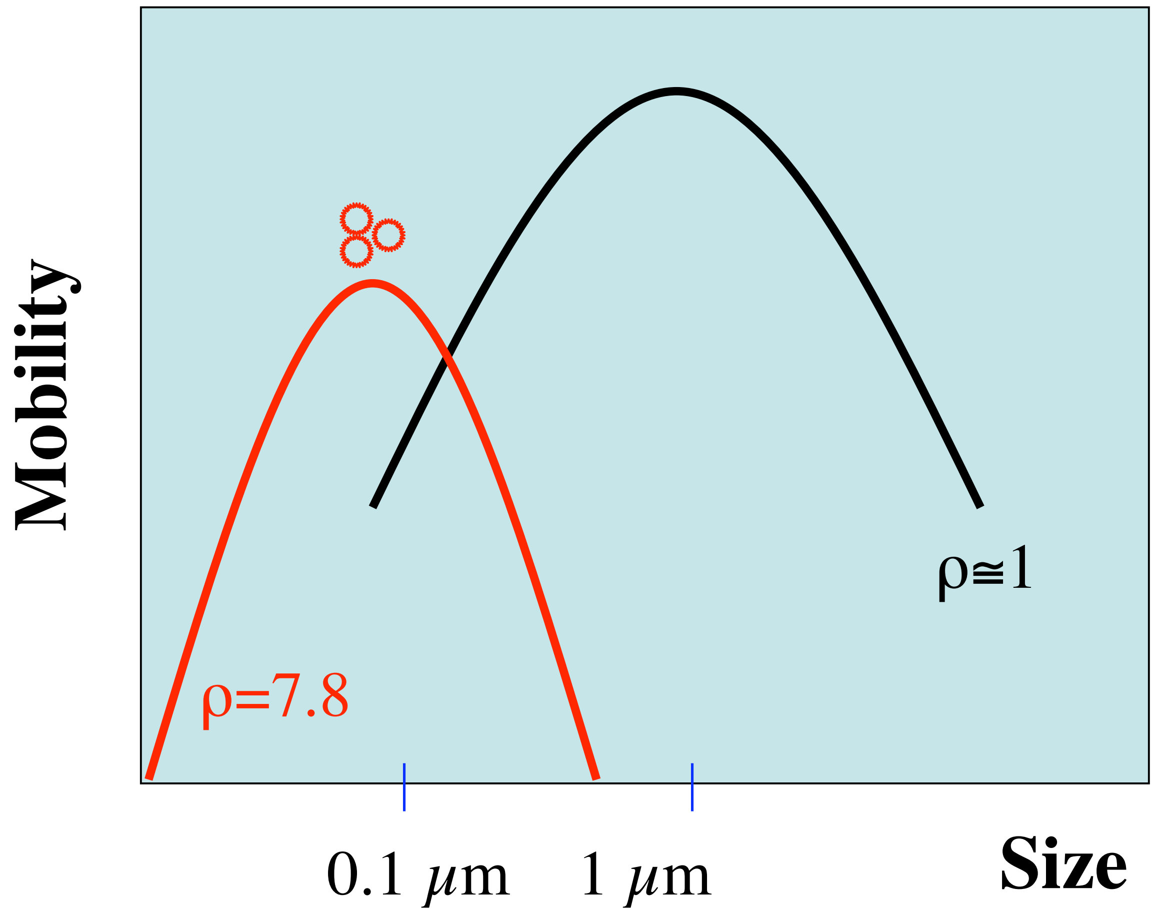
Particle Transport in Porous Media



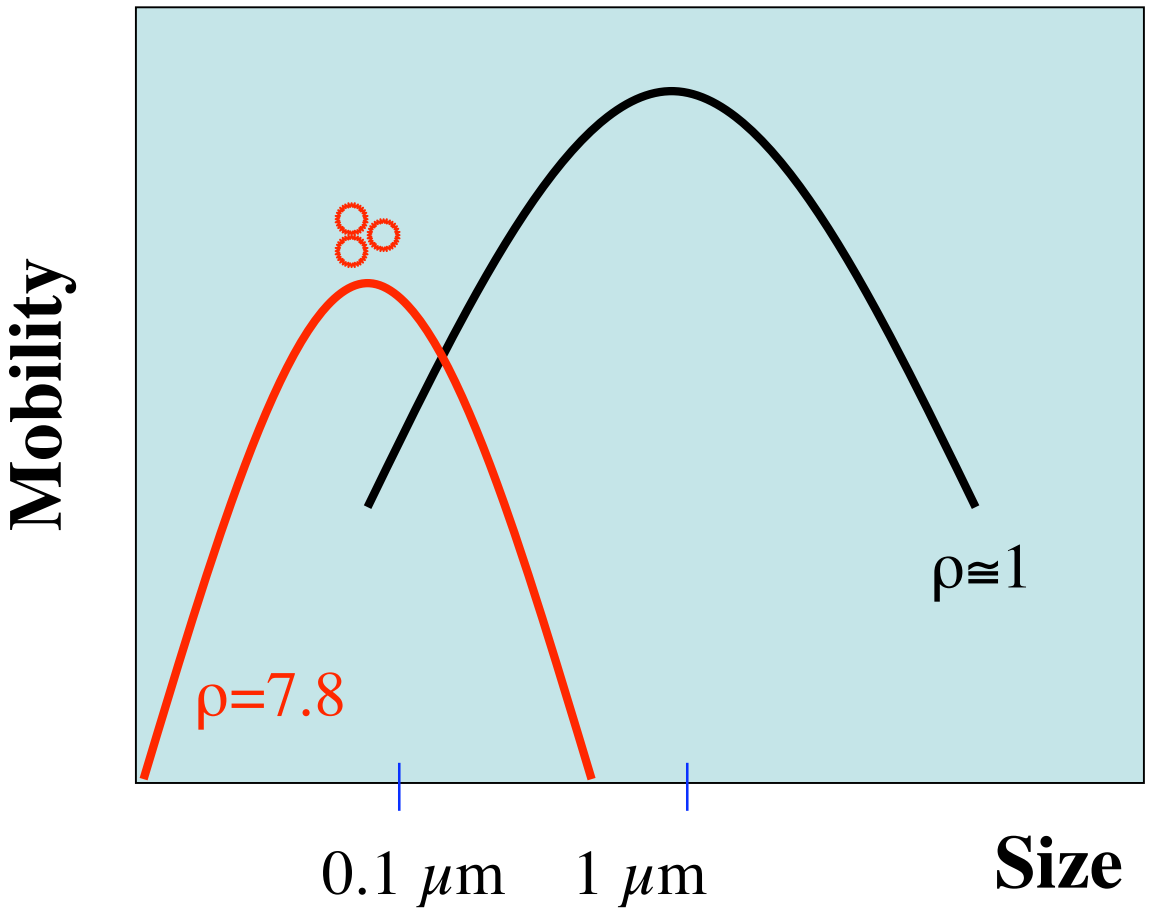
Size and Mobility



Size and Mobility



Need particles << 100 nm



1. How to make nanoparticles?

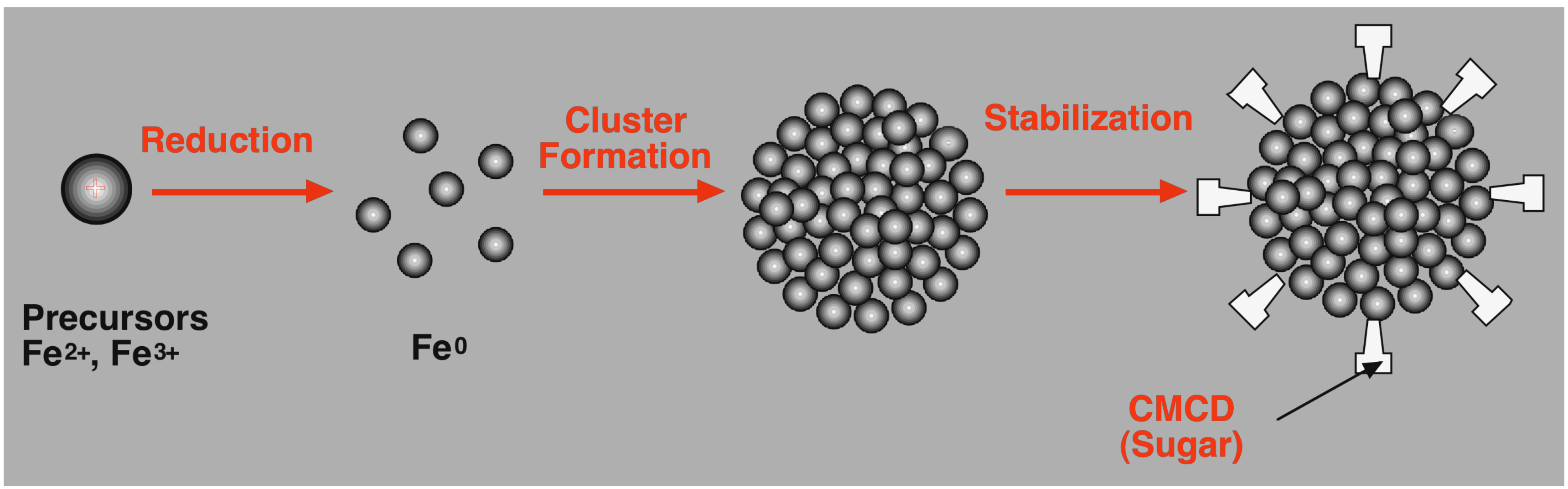
Methods of Synthesis

Step I - prepare nanoscale iron particles

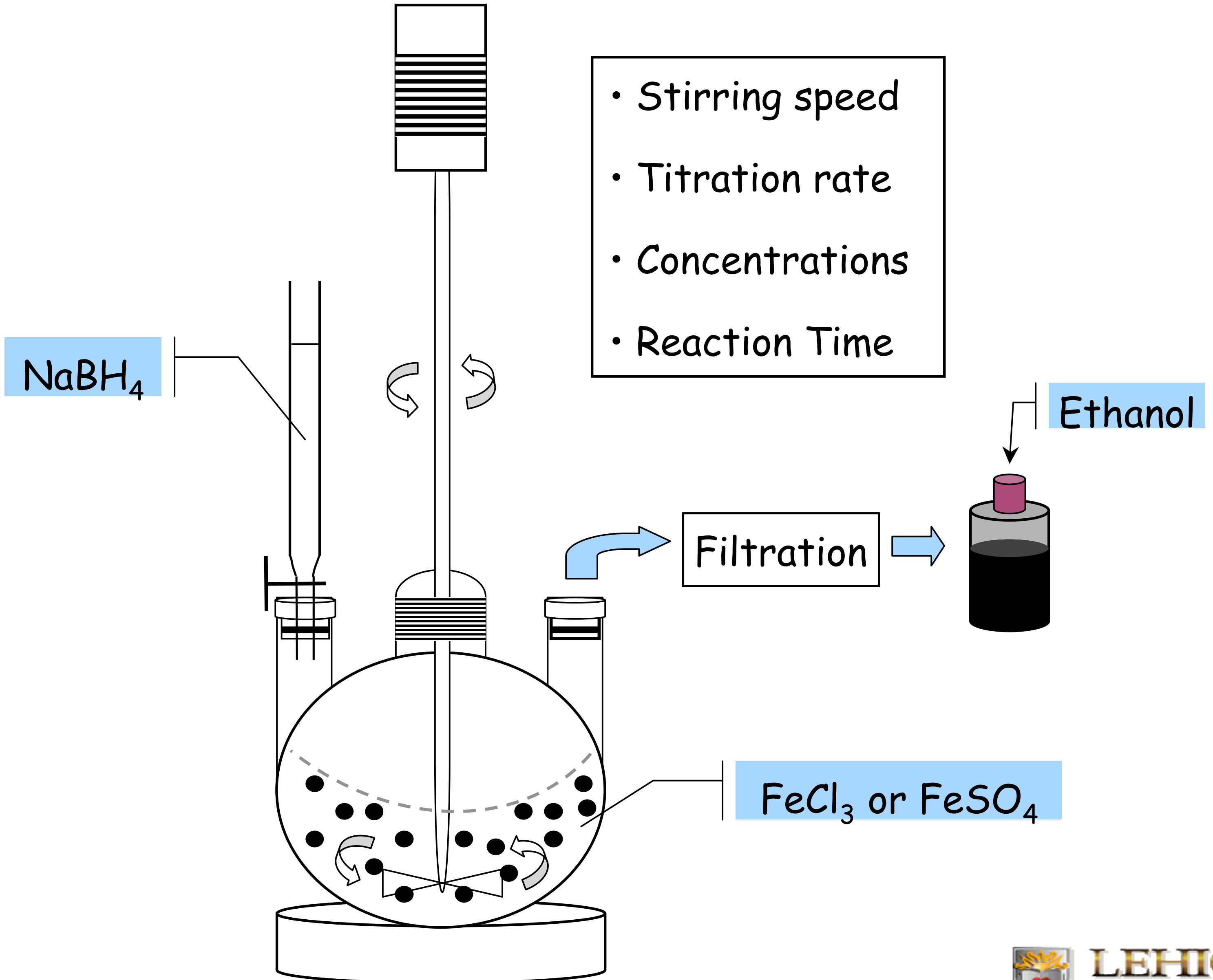
$2FeCl_3 \cdot 6H_2O + 6NaBH_4 \rightarrow 2Fe^0 + 6B(OH)_3 + 21H_2 + 6NaCl$

Step II - deposit noble metal on iron

$2Me^{n+} + nFe^0 \rightarrow nFe^{2+} + 2Me^0$



Synthesis of nFe^0



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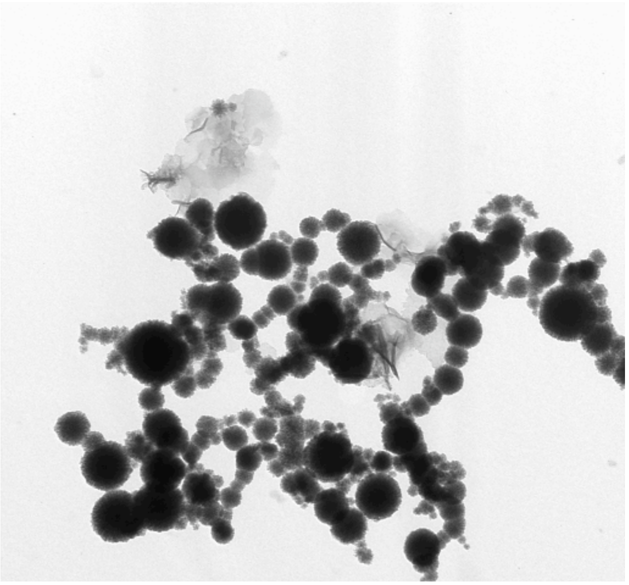
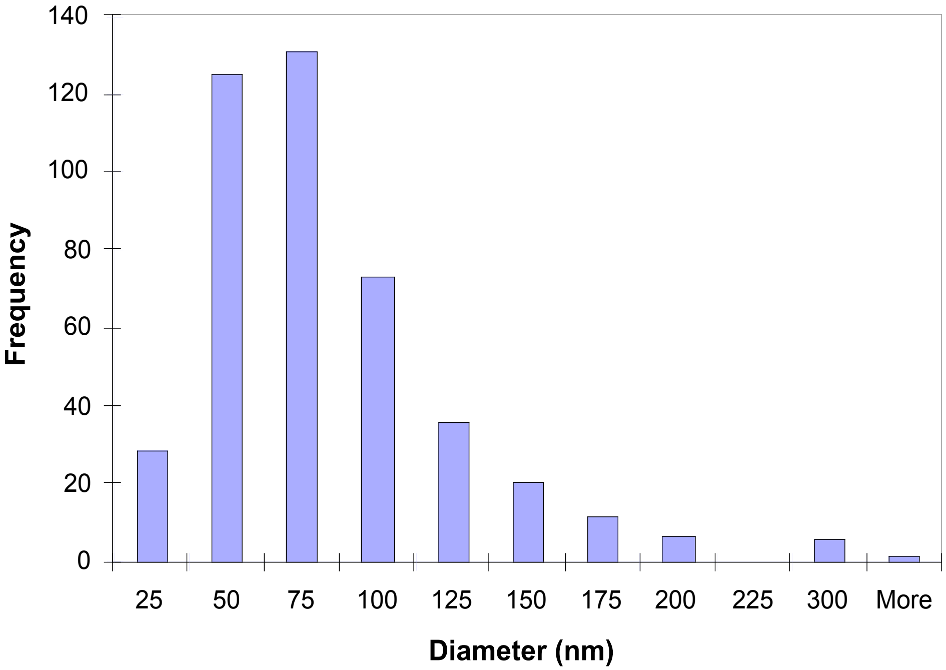
Properties of nFe^0

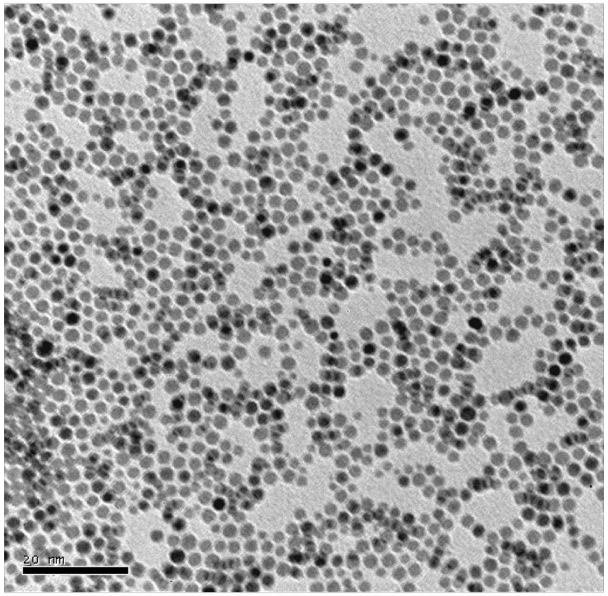
- **Size range**: 10-100 nm
- **Mean Size**: 50 ± 15 nm
- **Specific surface area**
  - 10-50 m^2/g
- **ξ potential**
  - +10 to -10 mV





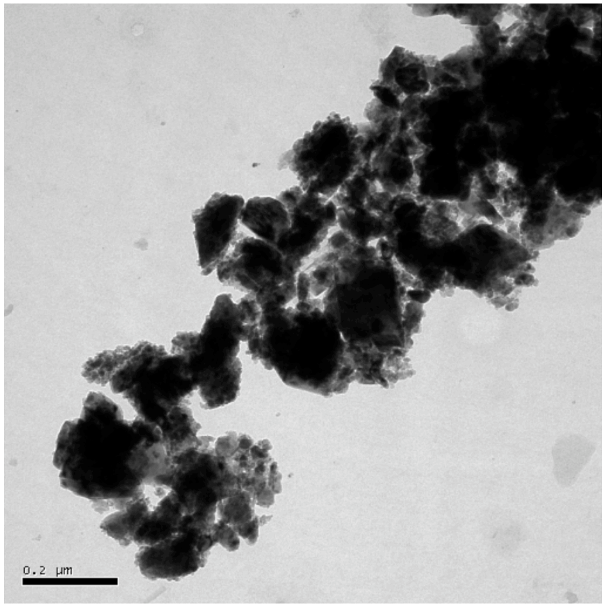
$$Fe(CO)_5 \xrightarrow{250°C} Fe^0 + 5CO\uparrow$$

$$Fe_xO_y + nH_2 \rightarrow Fe^0 + H_2O$$



5 nm

Cao & Zhang, 2005

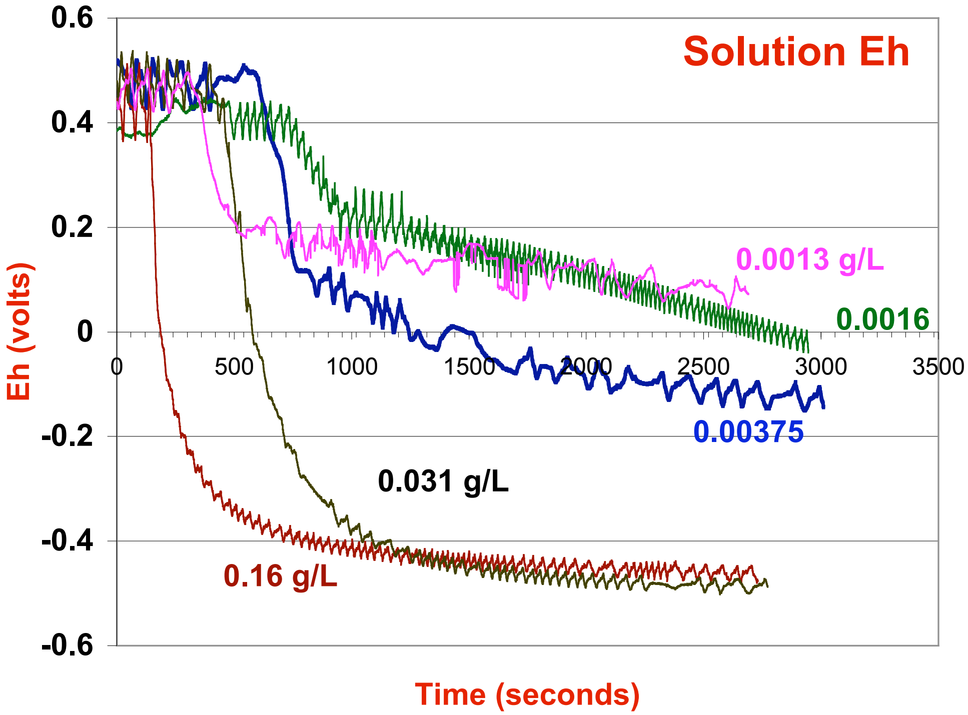


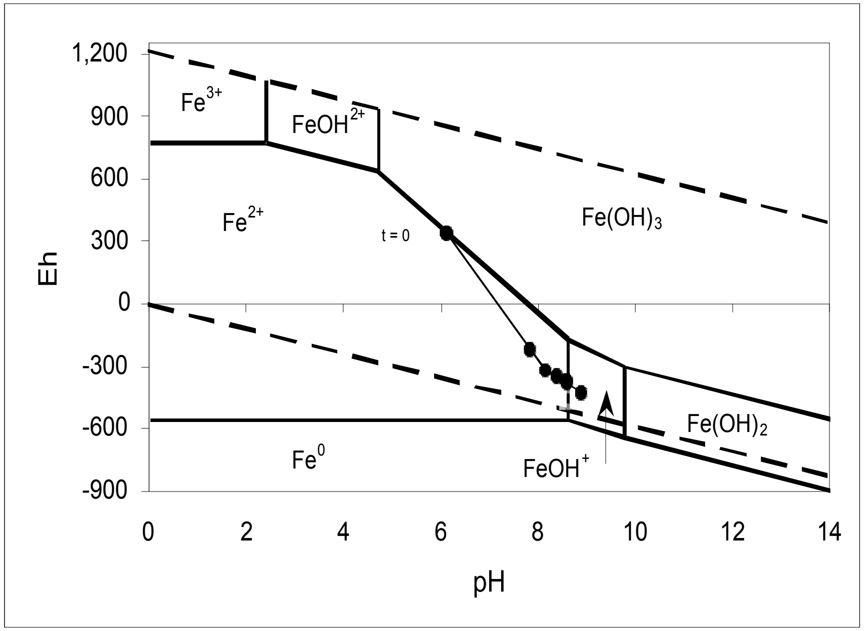
~200-300 nm

Cao & Zhang, 2004

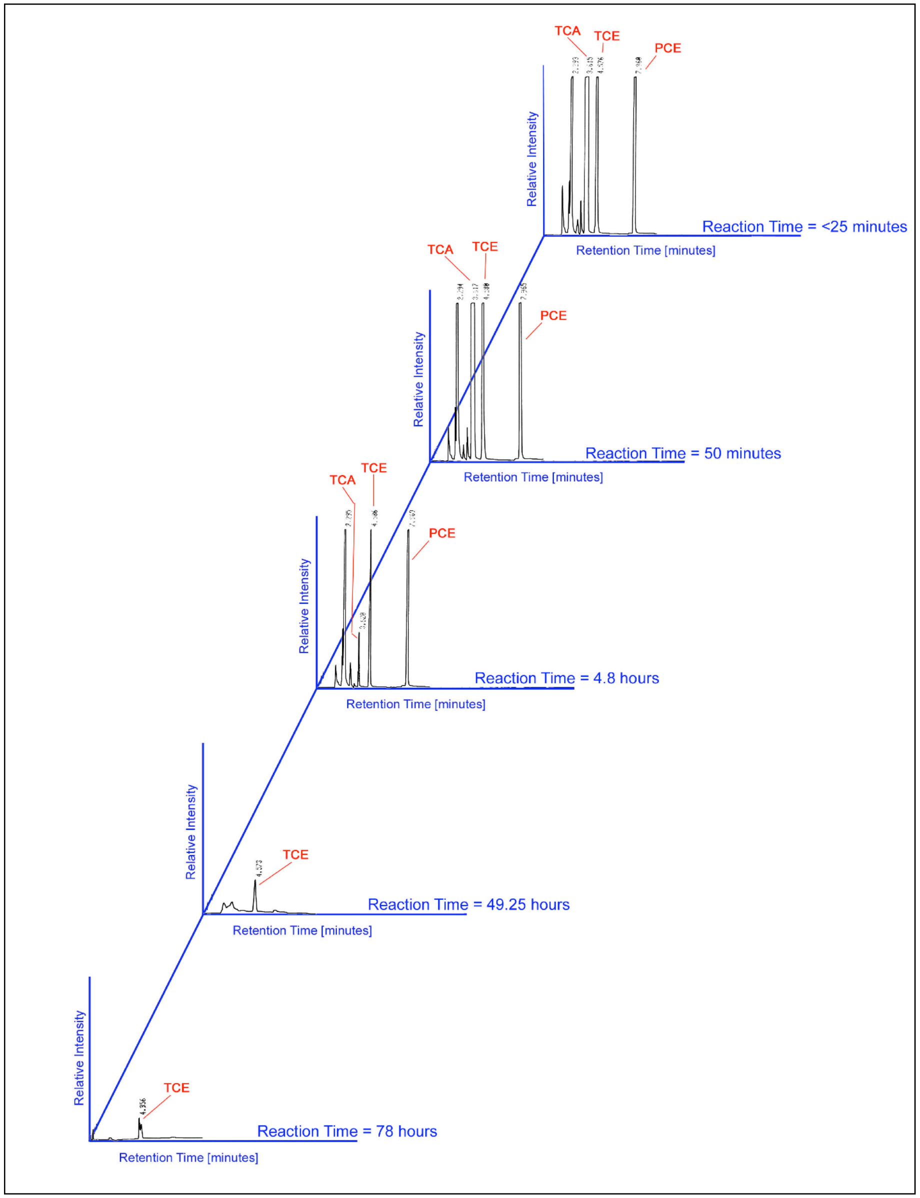
Reactivity

Redox Chemistry



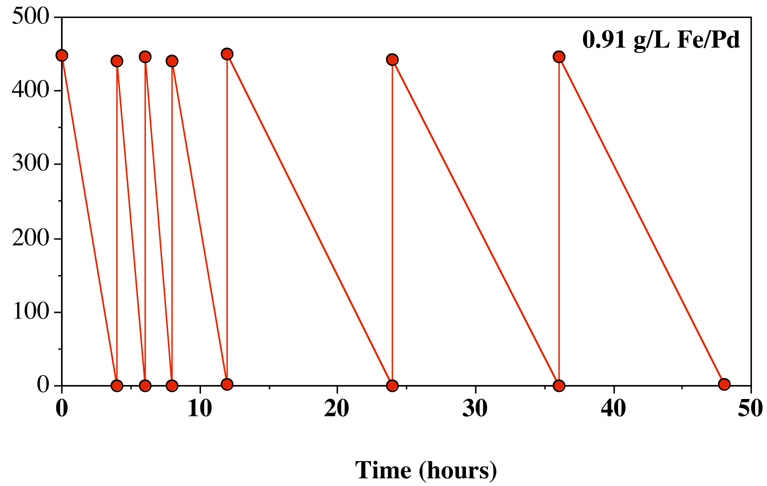


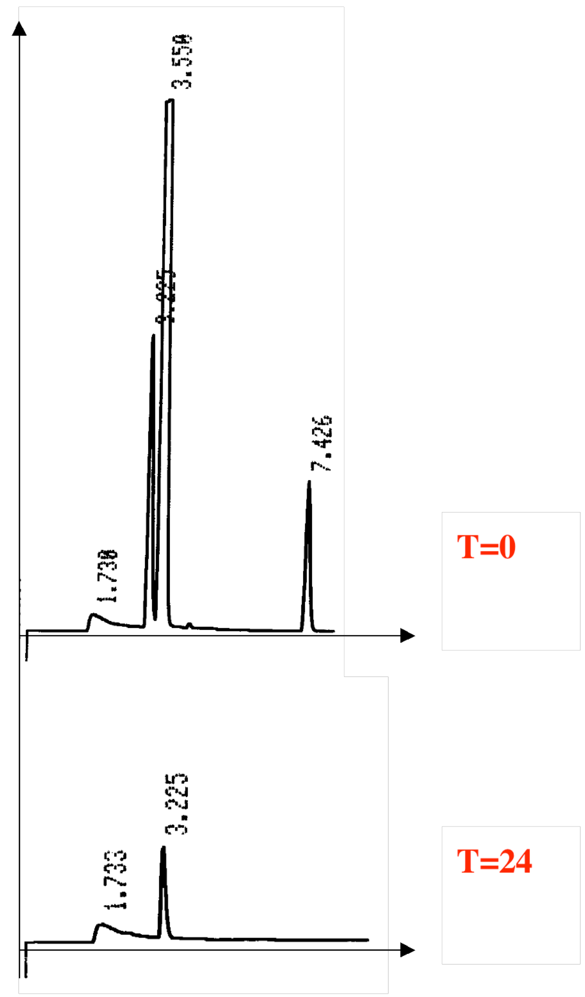
Transformation of Organic Solvents



	Compound Name	Molecular Formula	K_{SA} ($L/m^2/hr$)
1	Tetrachloroethylene (PCE)	C_2Cl_4	0.0122
2	Trichloroethylene (TCE)	C_2HCl_3	0.0182
3	*trans*-Dichloroethylene (*tans*-DCE)	$C_2H_2Cl_2$	0.0151
4	*cis*-Dichloroethylene (cis-DCE)	$C_2H_2Cl_2$	0.0176
5	1,1-Dichloroethylene (1,1-DCE)	$C_2H_2Cl_2$	0.0115
6	Hexachloroethane (HCA)	C_2Cl_6	0.020
7	Pentachloroethane (PCA)	C_2HCl_5	0.026
8	1,1,1,2-Tetrachloroethane (1,1,1,2-TeCA)	$C_2H_2Cl_4$	0.021
9	1,1,2,2-Tetrachloroethane (1,1,2,2-TeCA)	$C_2H_2Cl_4$	0.0088
10	1,1,1-Trichloroethane (1,1,1-TCA)	$C_2H_3Cl_3$	0.0054
11	Carbon Tetrachloride (CT)	CCl_4	0.009
12	Chloroform (CF)	$CHCl_3$	0.0065
13	Bromoform (BF)	$CHBr_3$	0.079
14	Dibromomethane (DBM)	CH_2Br_2	0.044
15	Dibromochloromethane (DBCM)	$CHBr_2Cl$	0.056

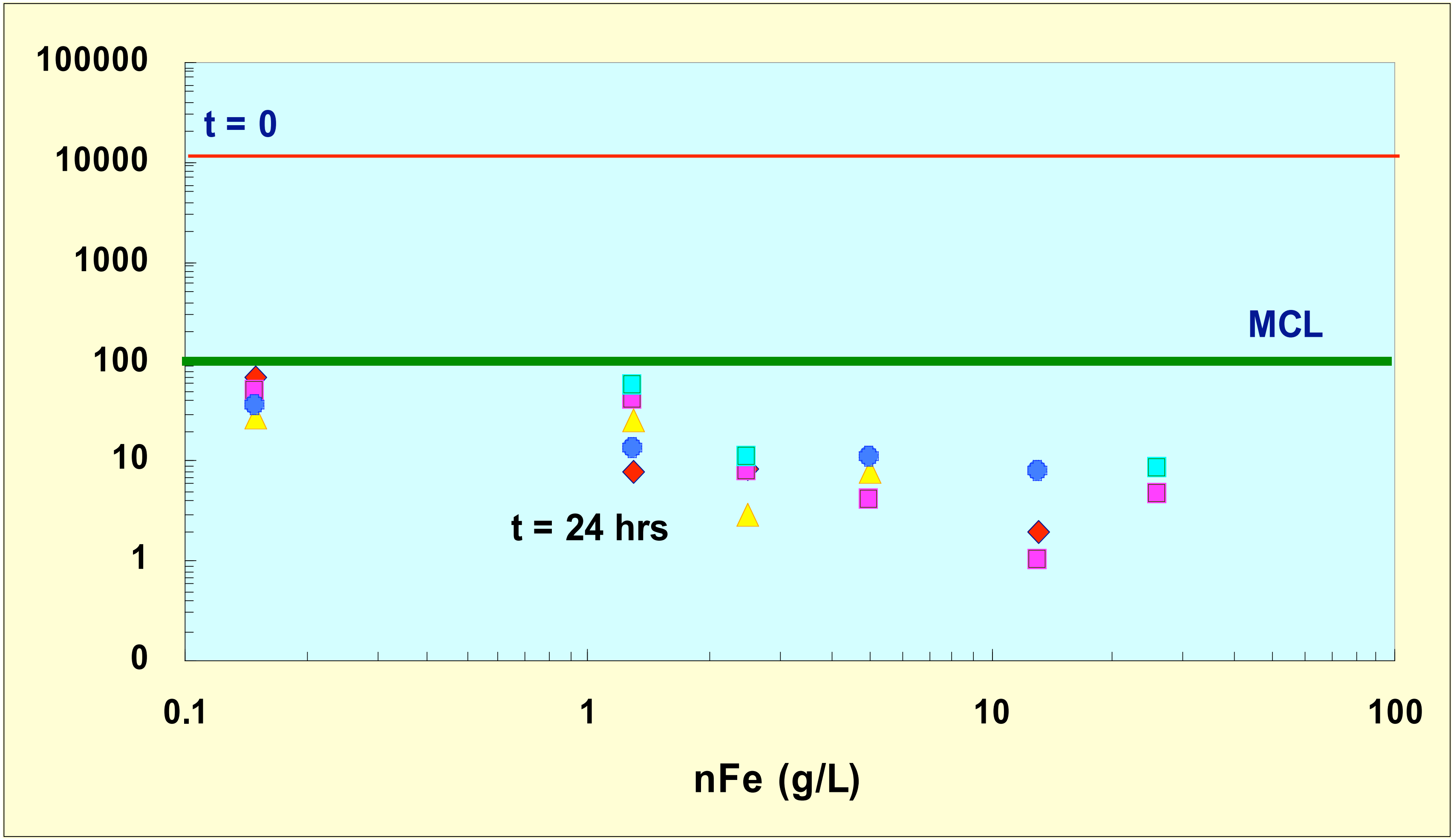
TCE Reduction
(450 ppb, Trenton, NJ)





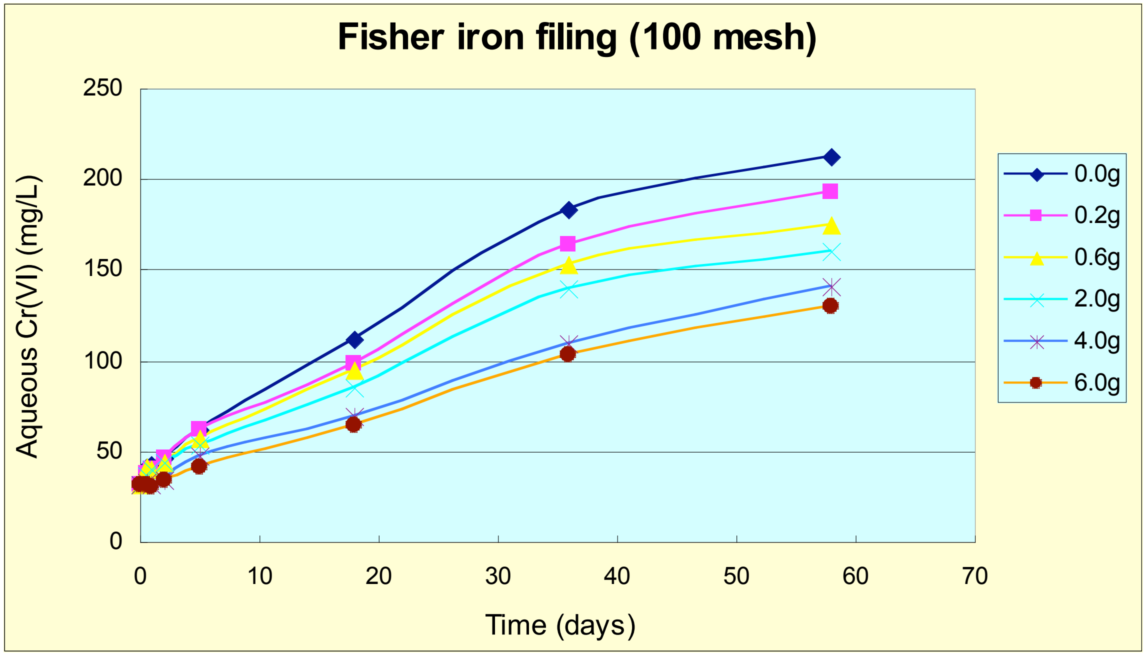
Carbon Tetrachloride
(CCl_4, 14.5 ppm, S. Charleston, WV)

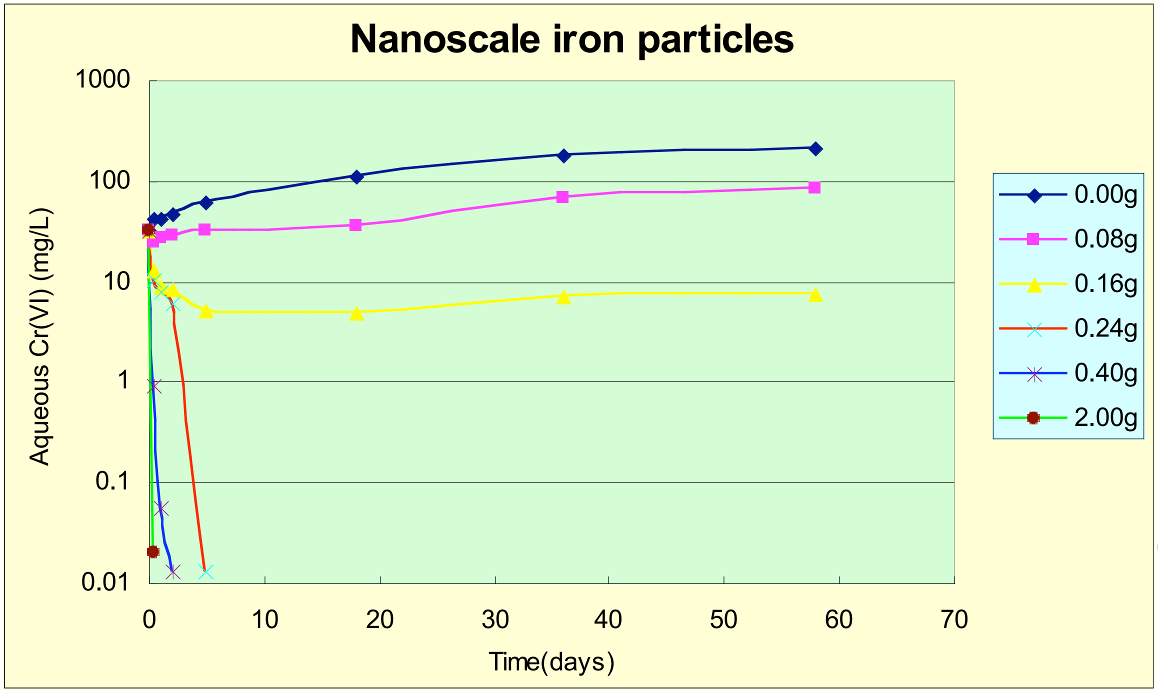
Reduction and Immobilization of Cr(VI) in COPR (Newark, NJ)



Immobilization of Cr(VI) in COPR

(>7,000 mg Cr/kg)

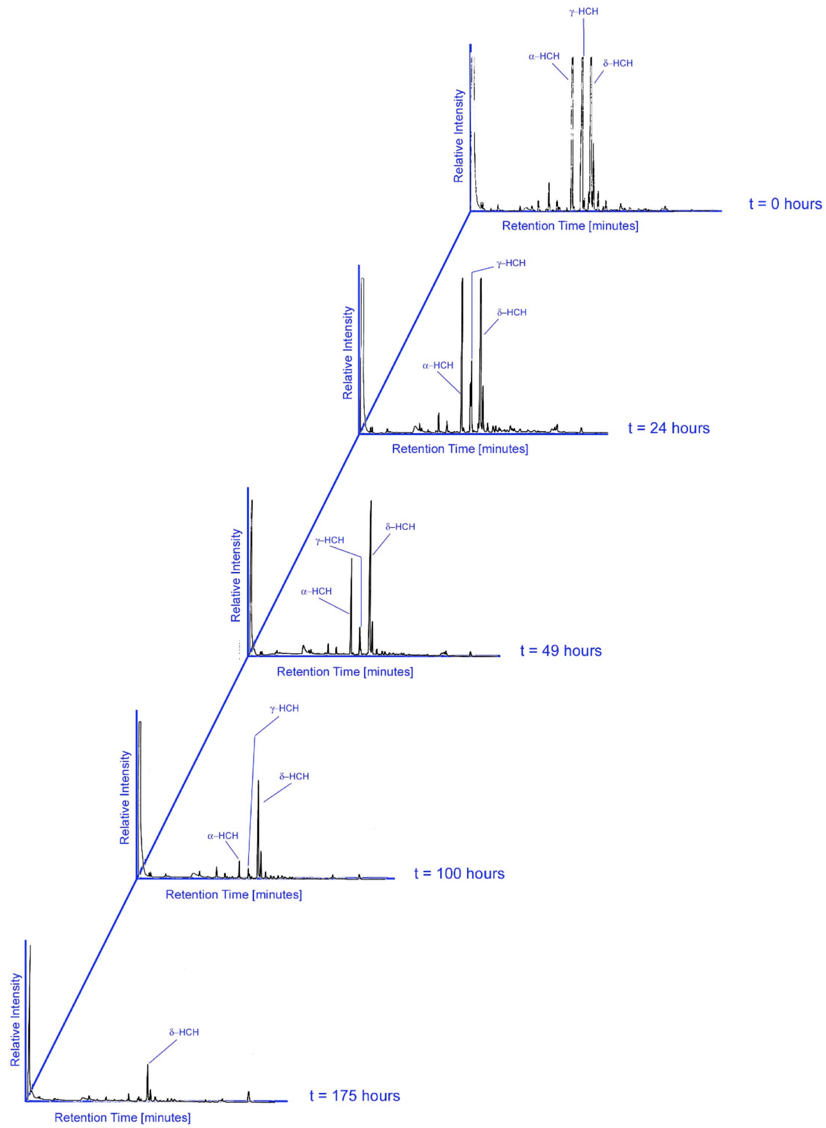


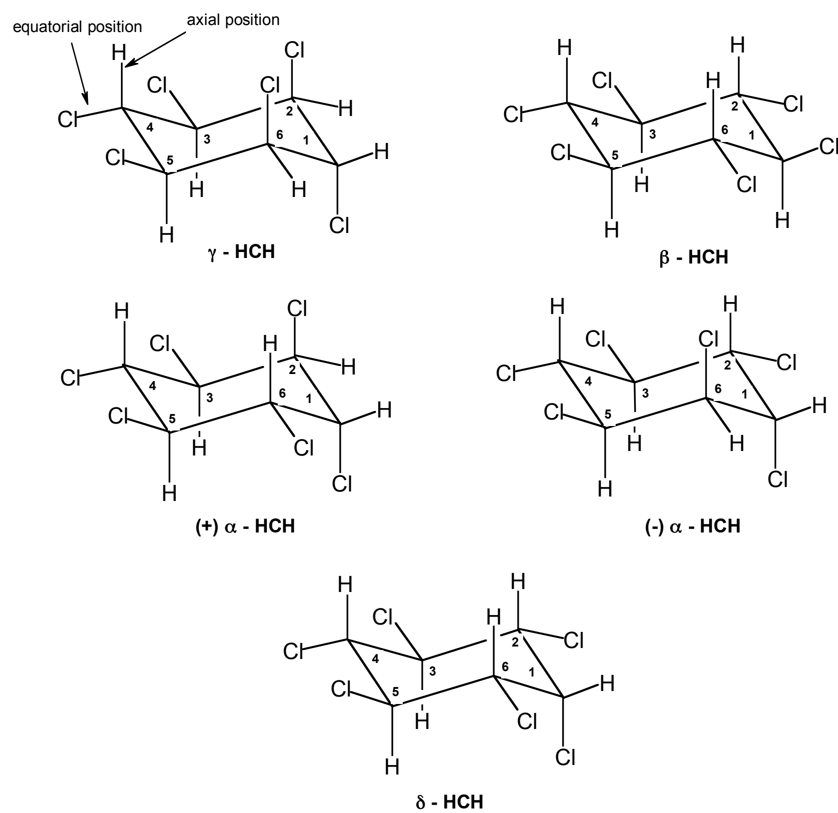


6 g **mFe** in 10 g COPR
(**1:1** Needed)

0.24 g **nFe** in 10 g COPR
(**2.4%**)

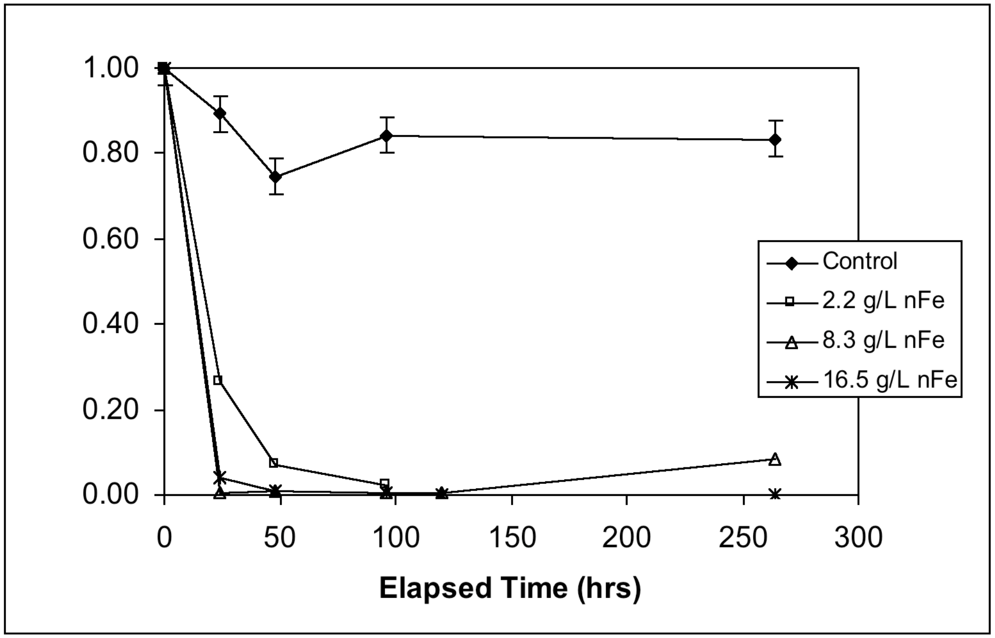
Treatment of Lindane



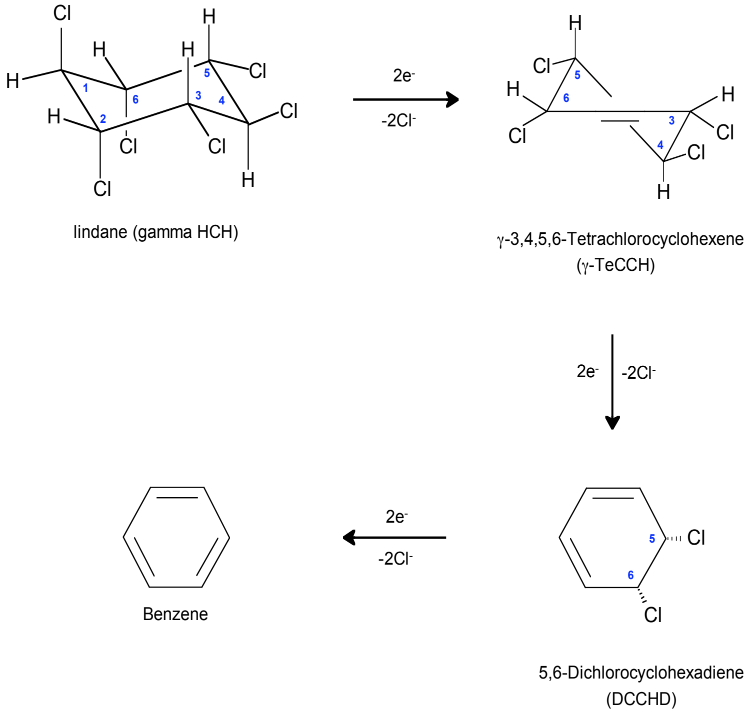


GW from a site in Jacksonville, FL

Dihaloelimination

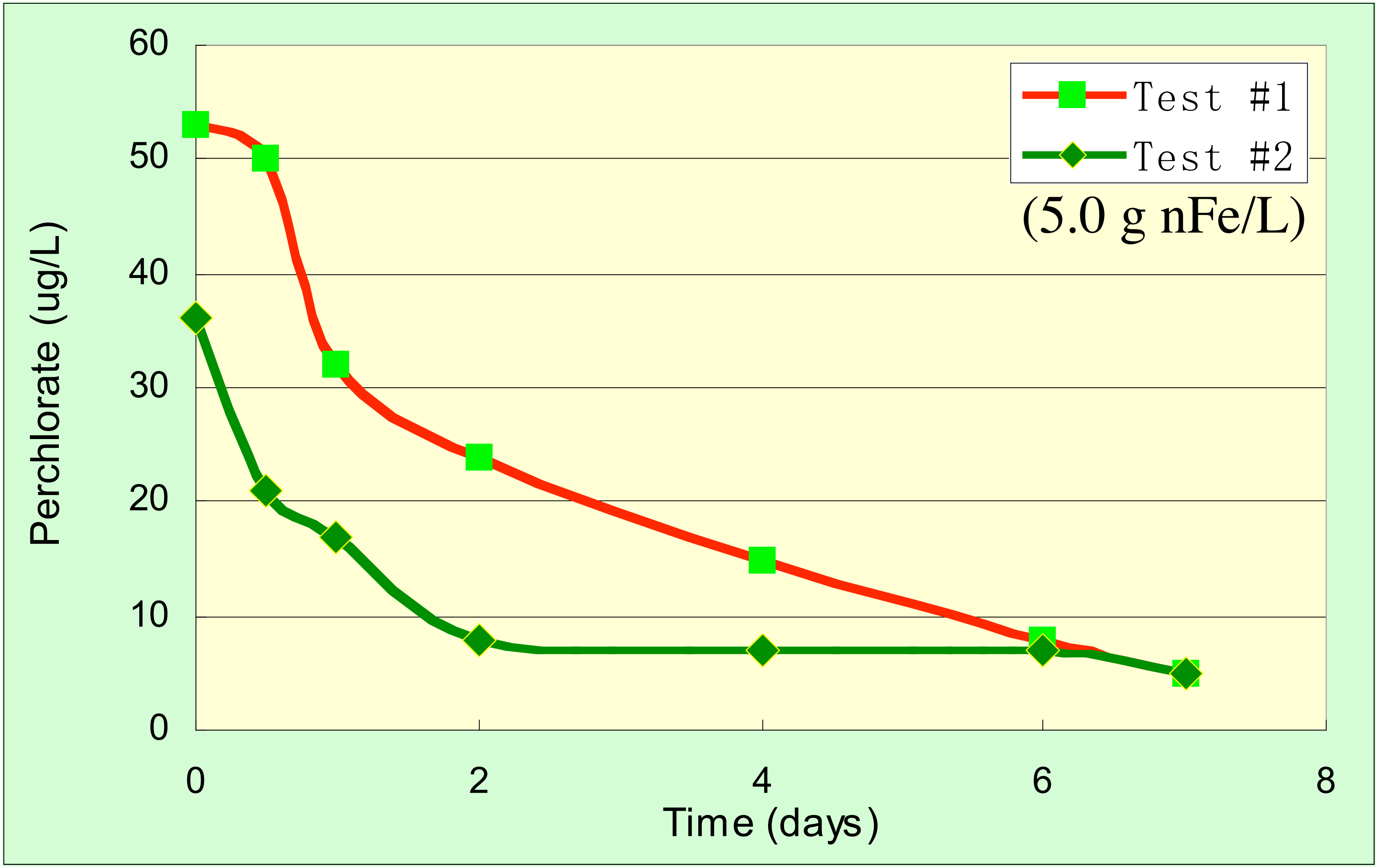


1,400 ppb HCHs



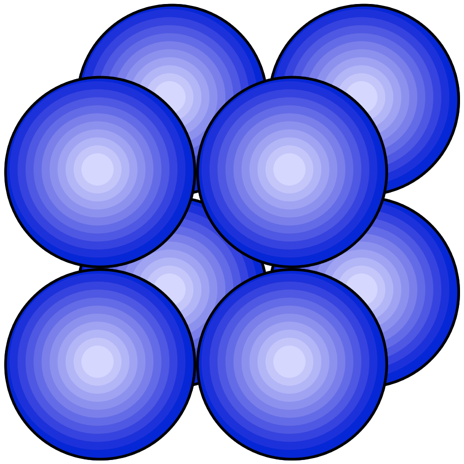
Reduction of Perchlorate (ClO_4^-)

(Samples from CA)

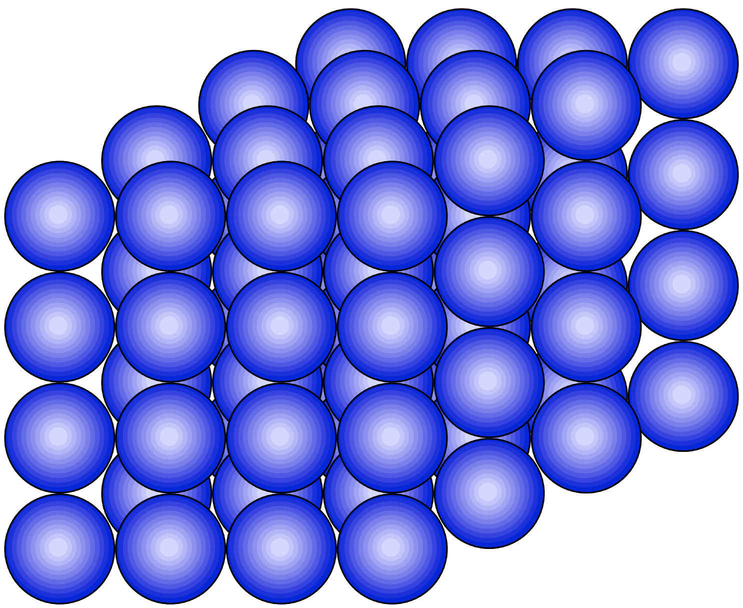


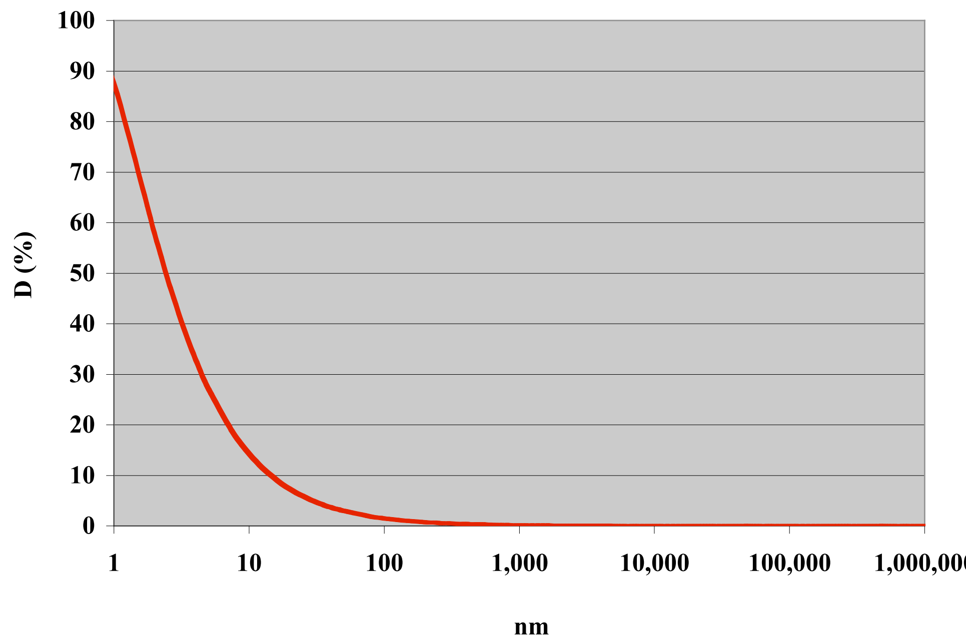
2. How to make better nanoparticles?

Fe on Surface

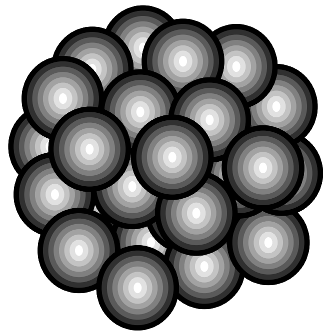


$$D = \frac{\text{number of surface atoms}}{\text{total number of atoms}} = \frac{2n^2 + (n-2)[n^2 - (n-2)^2]}{n^3} \cdot 100$$





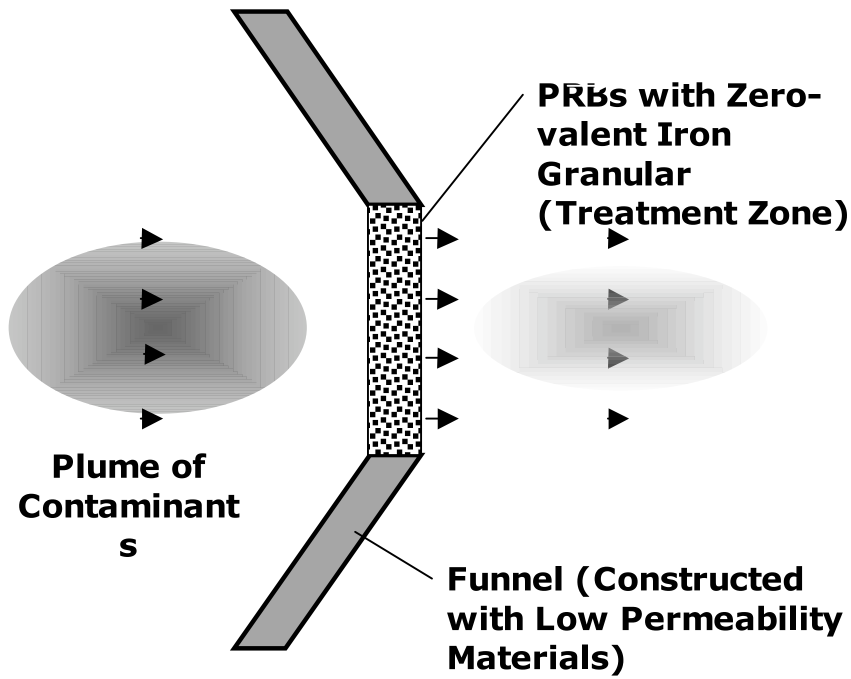
nFe^0



50 nm

~ 4% Fe on Surface

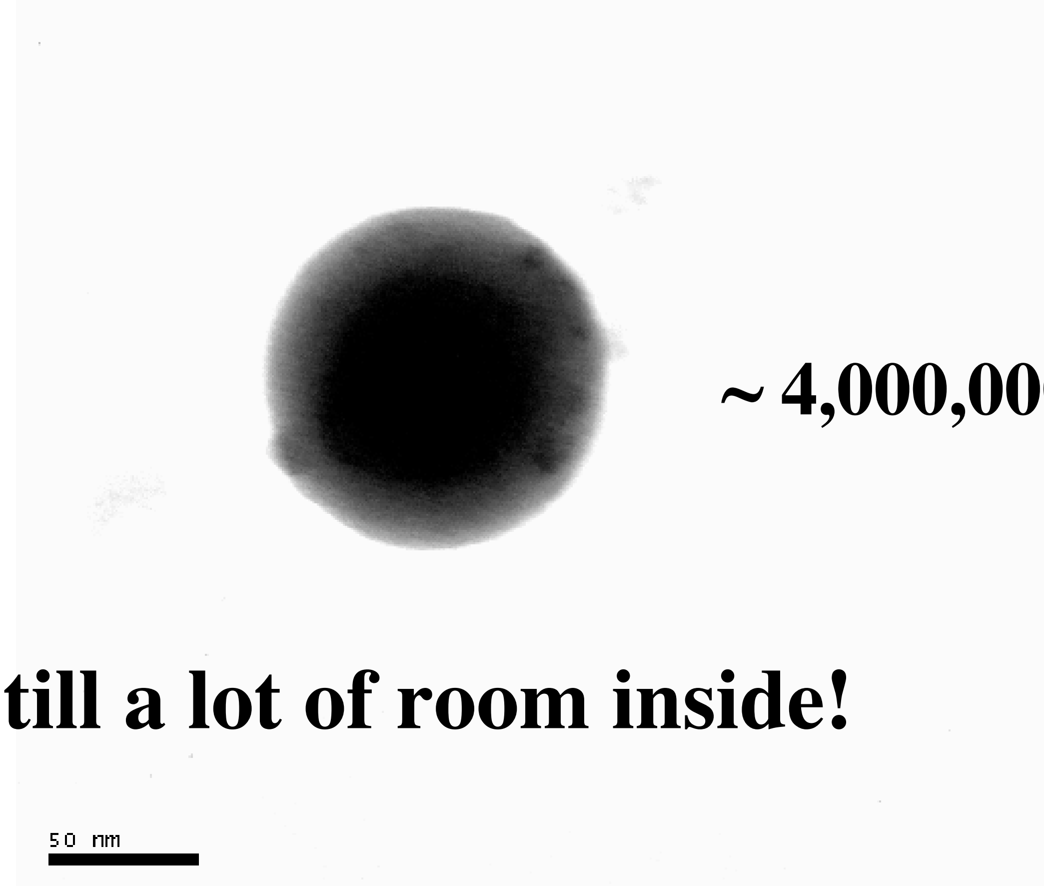
Fe in PRBs



0.5 mm

~0.0004%

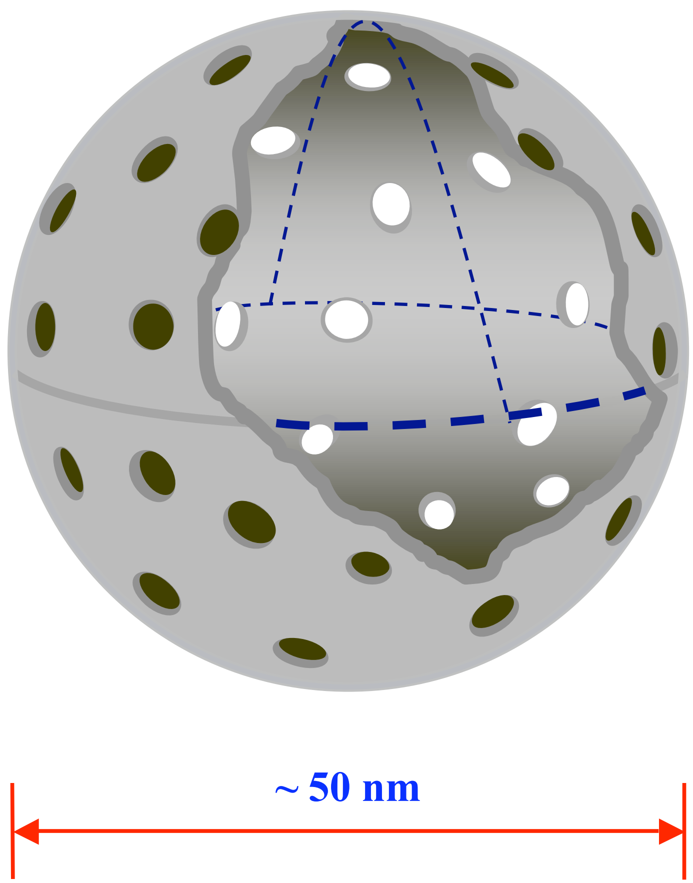
50 nm Fe



~ 4,000,000 atoms

Still a lot of room inside!

Nano & Porous



Large surface area

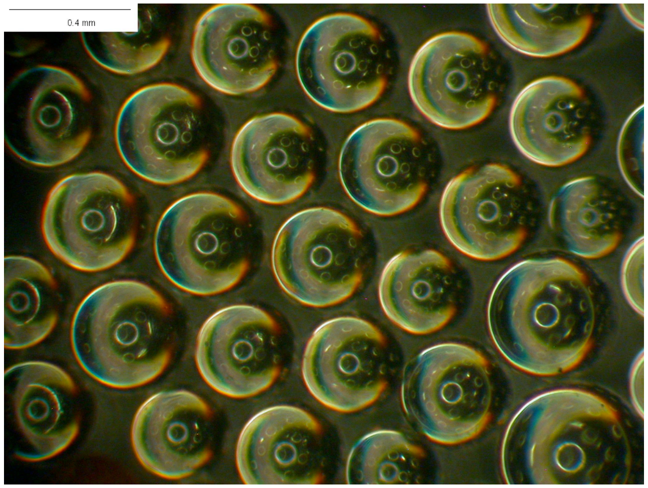
Better hydraulics

High reactivity

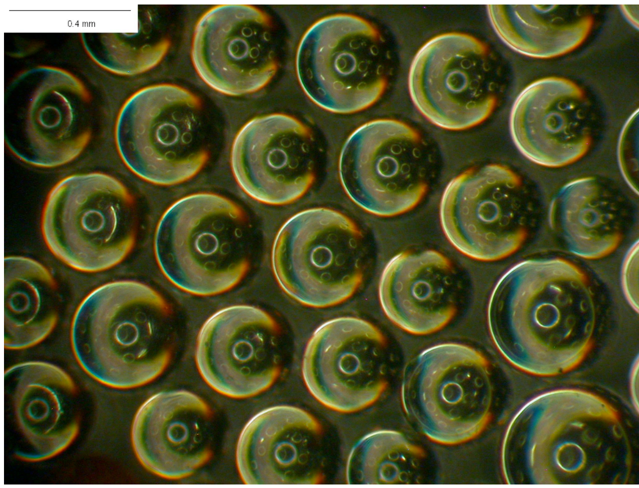
High mobility

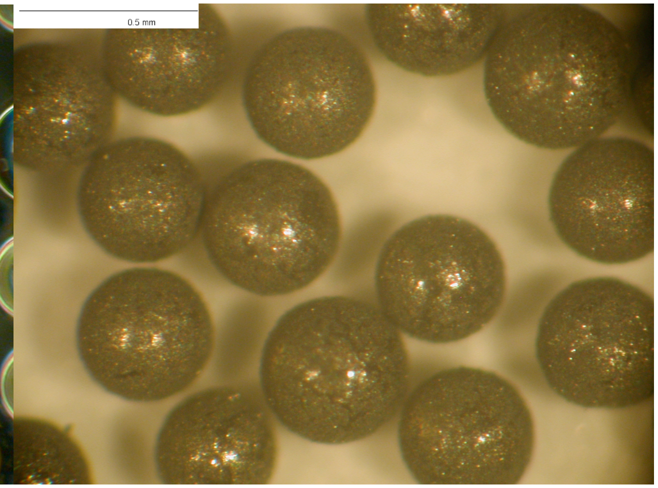
Synthesis of Porous Fe

0. 4 mm Resin



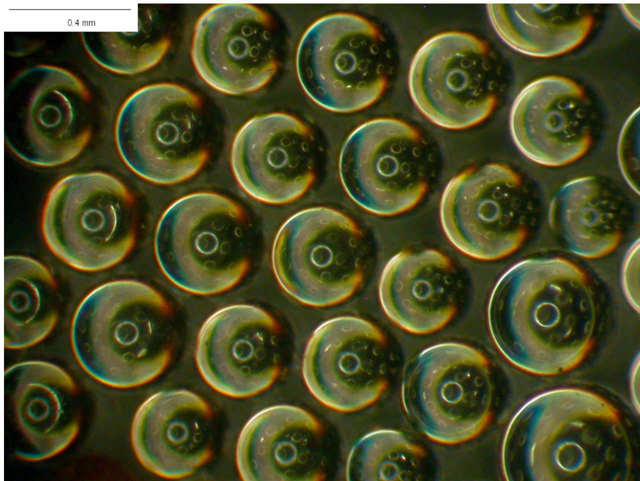
Synthesis of Porous Fe

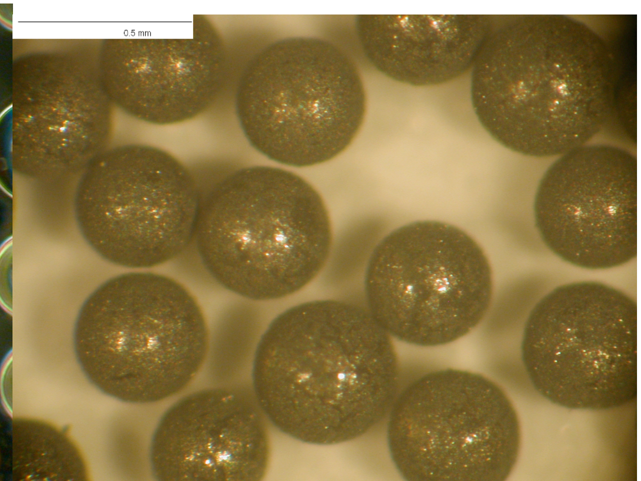




Coated with 50 nm Fe

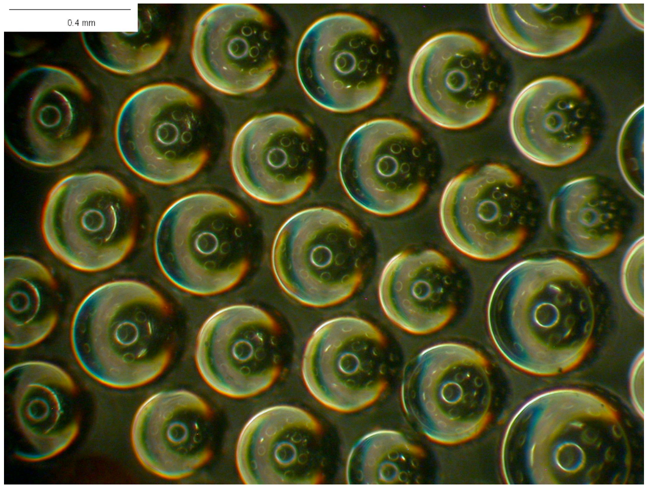
Template Directed Synthesis

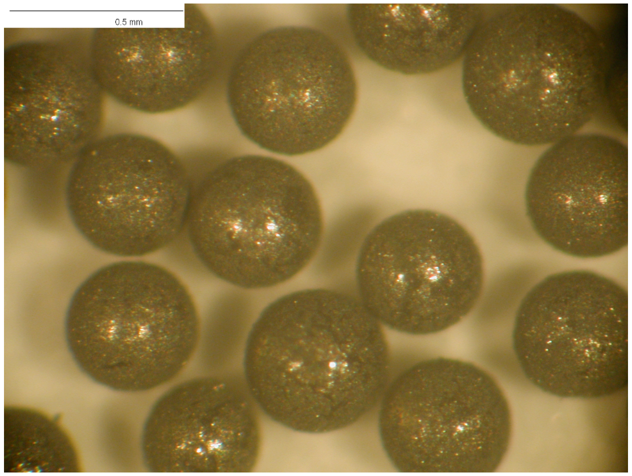


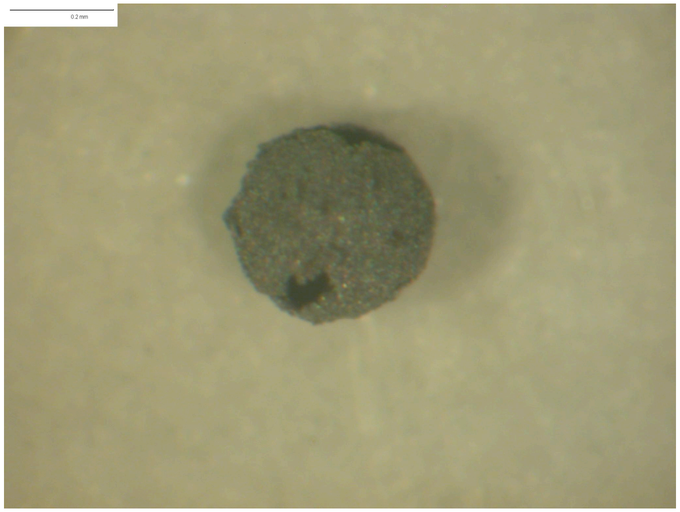


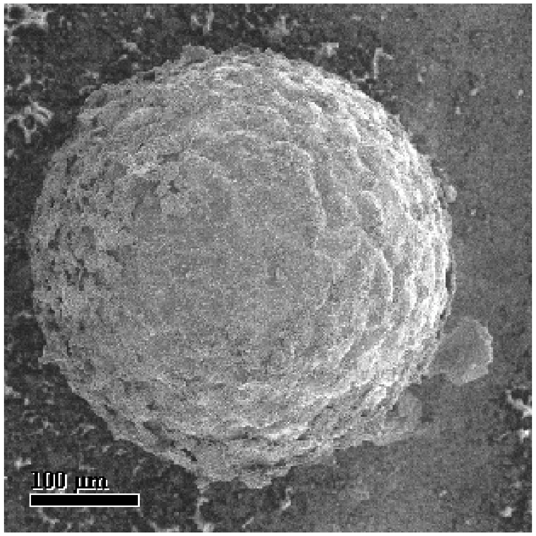
Remove the core

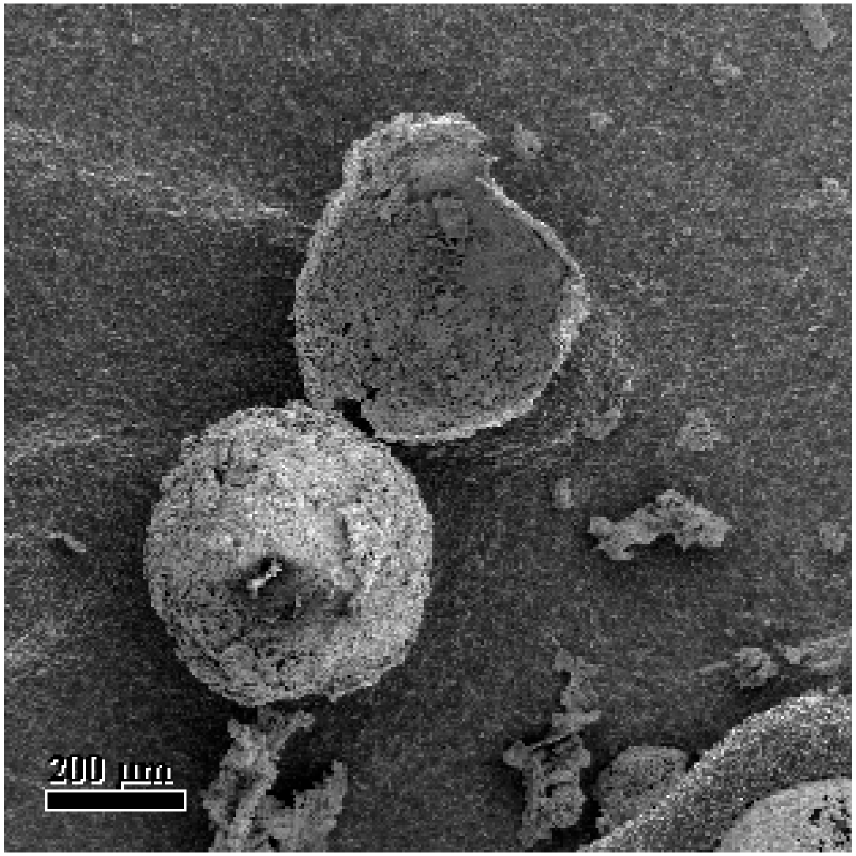
Template Directed Synthesis

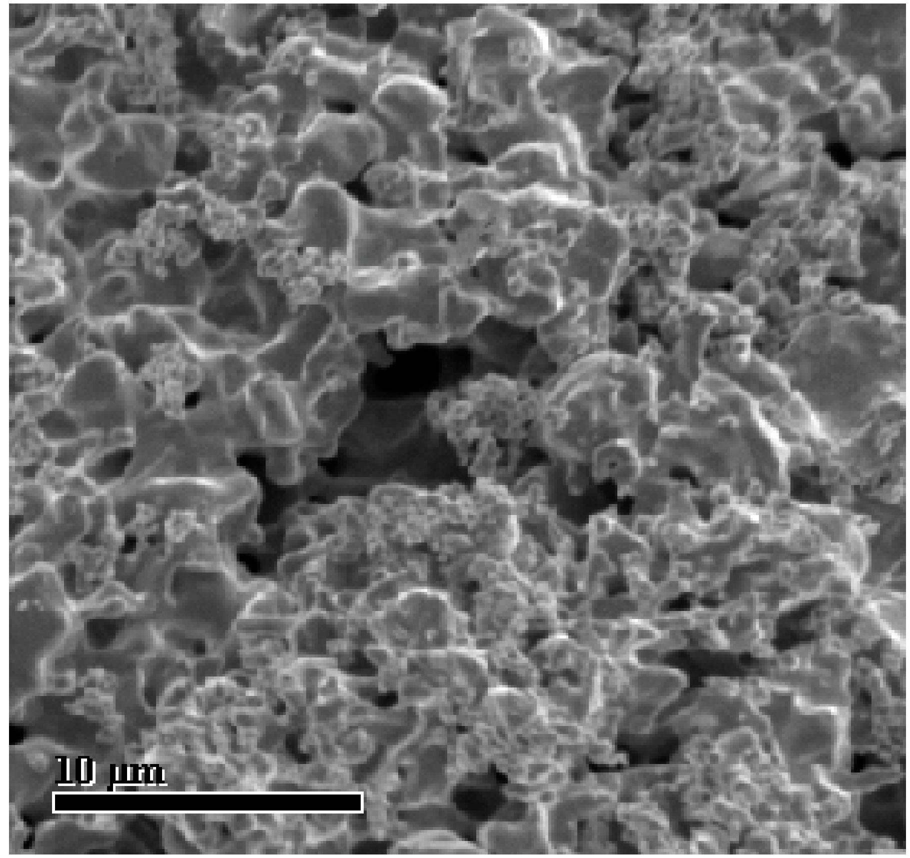









200 µm


10 µm

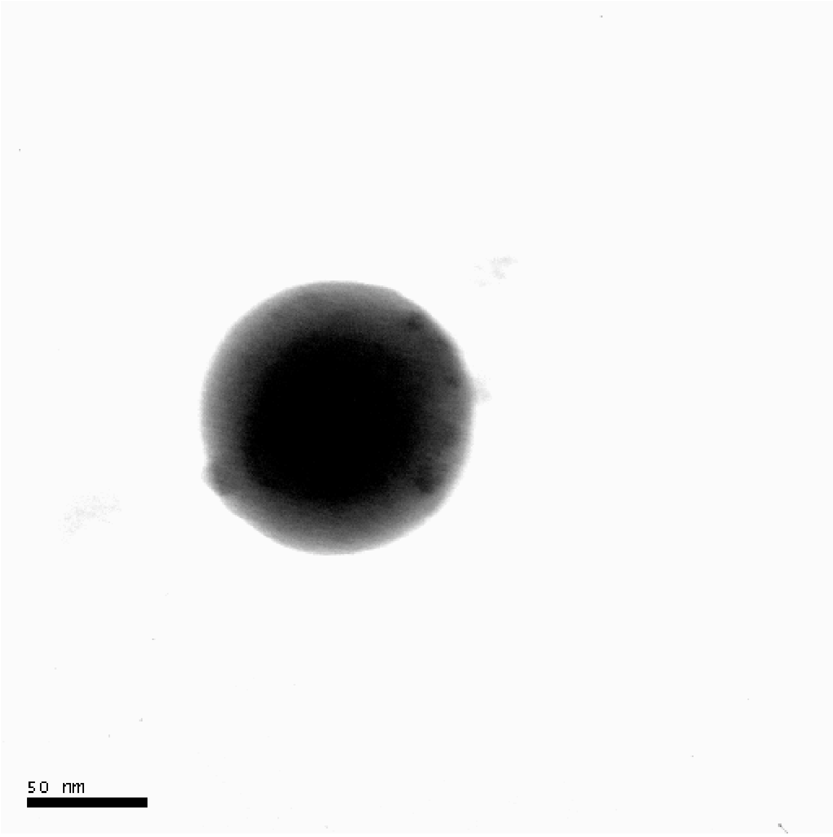
Specific Surface Area

	Size	BET area (m^2/g)
Solid sphere (calculated)	**0.4 mm**	**1.9**

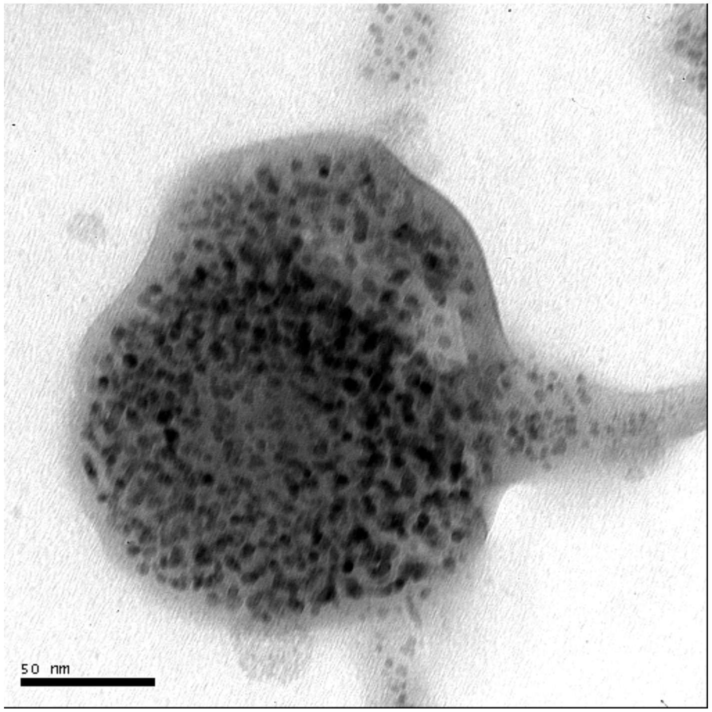
Specific Surface Area

	Size	Surface area (m^2/g)
Solid sphere (calculated)	0.4 mm	1.9
Porous sphere (synthesized)	0.4 mm	2,100

Solid nFe
(20-40 m^2/g)

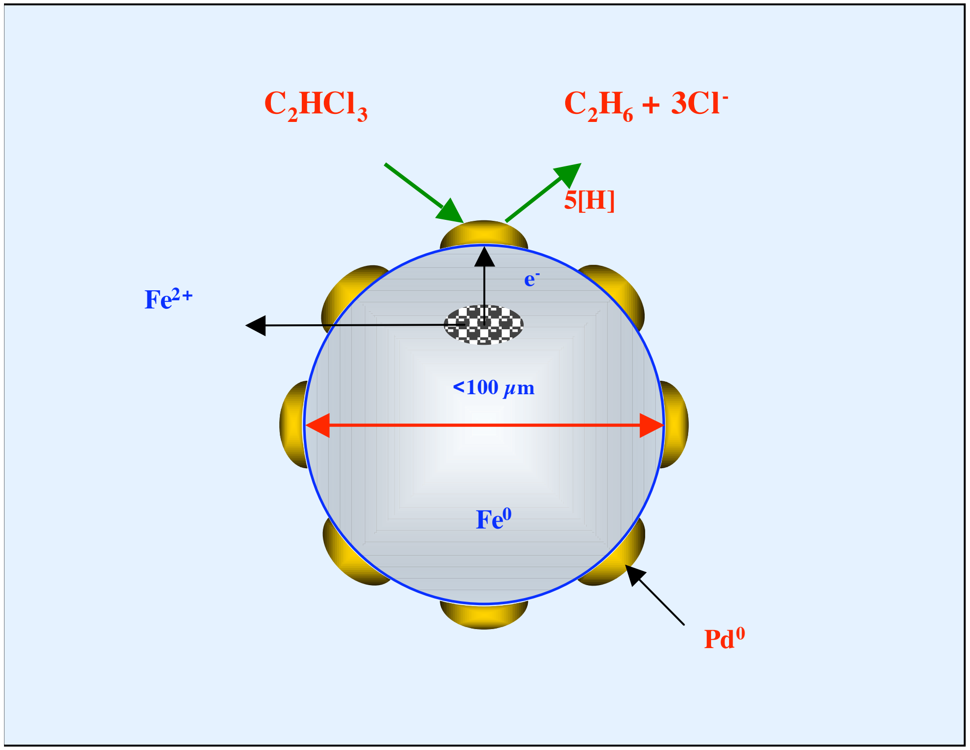


NanoPorous Fe
(150-250 m^2/g)



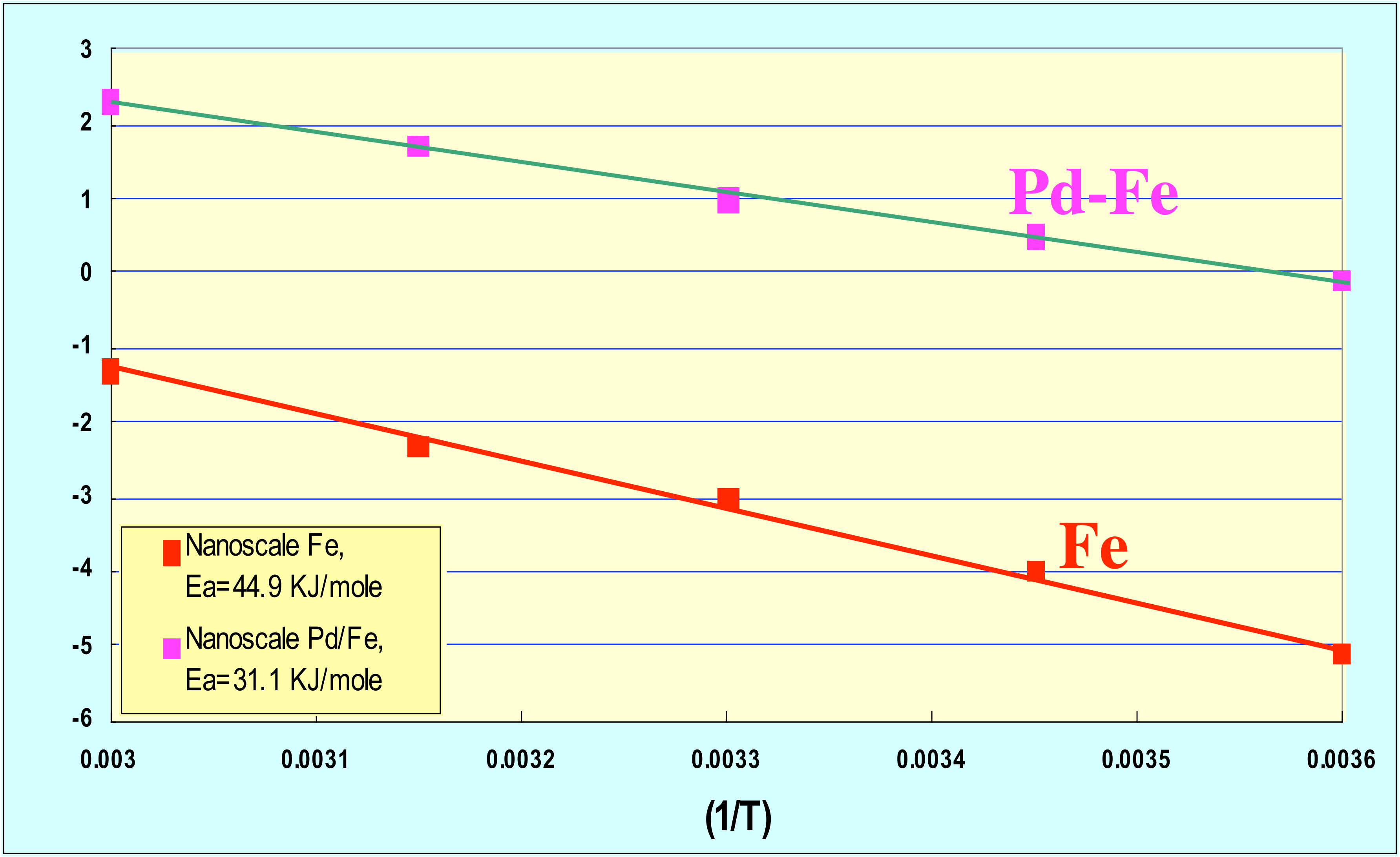
(Li and Zhang, 2005)

Bimetallic Structures



	E^0 (volts)
$Al^{3+} + 3\ e^- \Leftrightarrow Al$	-1.68
$Zn^{2+} + 2\ e^- \Leftrightarrow Zn$	-0.76
$Fe^{2+} + 2\ e^- \Leftrightarrow Fe$	-0.41
$Co^{2+} + 2\ e^- \Leftrightarrow Co$	-0.28
$Ni^{2+} + 2\ e^- \Leftrightarrow Ni$	-0.24
$Pb^{2+} + 2\ e^- \Leftrightarrow Pb$	-0.13
$Cu^{2+} + 2\ e^- \Leftrightarrow Cu$	0.34
$Ag^{+} + e^- \Leftrightarrow Ag$	0.80
$Pd^{2+} + 2\ e^- \Leftrightarrow Pd$	0.987

Fe vs Pd-Fe

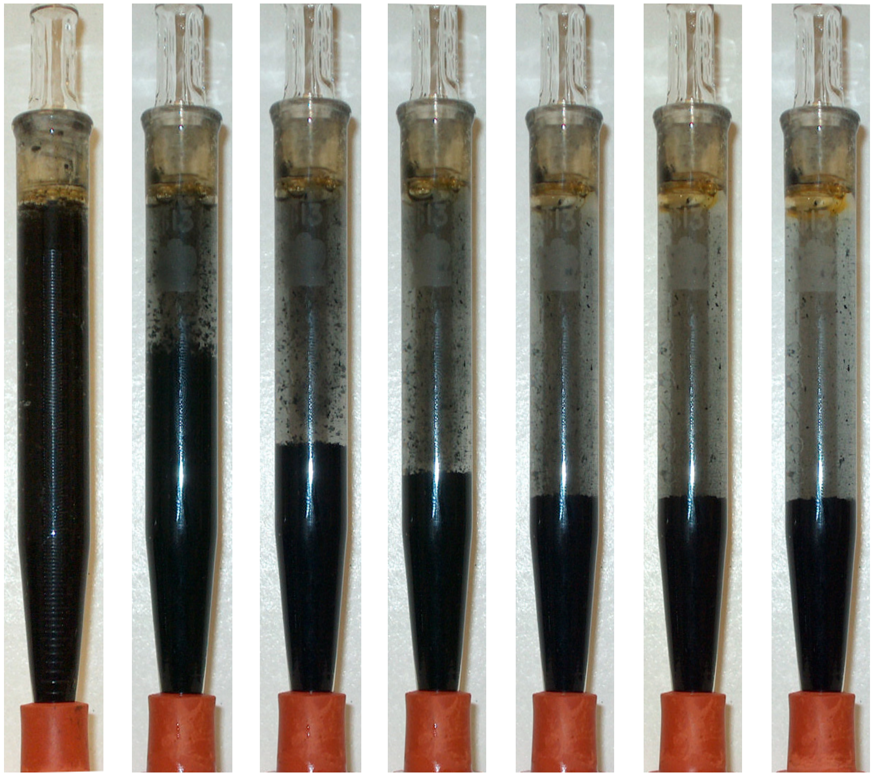


3
2
1
0
-1
-2
-3
-4
-5
-6
0.003
0.0031
0.0032
0.0033
0.0034
0.0035
0.0036
(1/T)
Pd-Fe
Fe
Nanoscale Fe,
Ea=44.9 KJ/mole
Nanoscale Pd/Fe,
Ea=31.1 KJ/mole

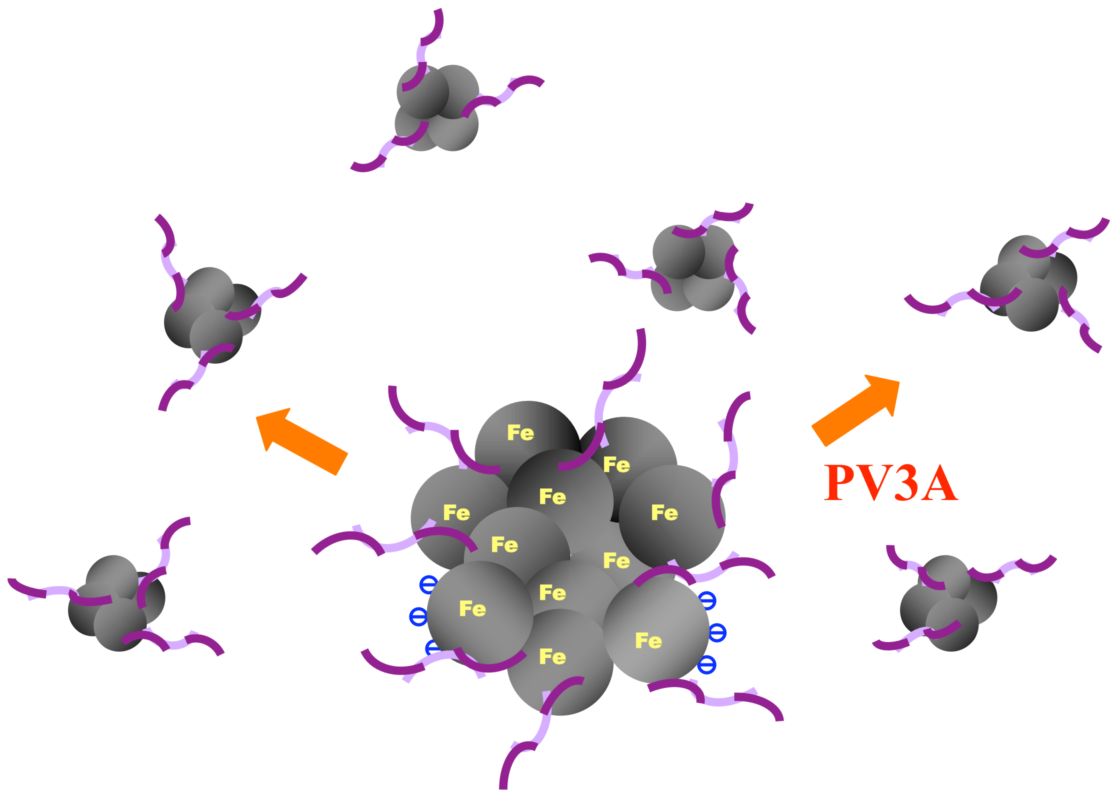
Dispersed nFe

Rapid Sedimentation

nFe^0



T (sec) = 0 20 40 60 120 300 1800



Dispersion of nano Fe

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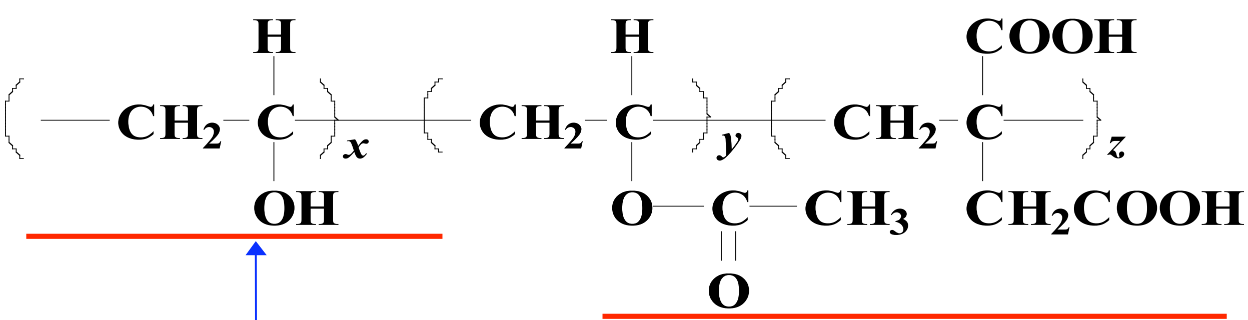
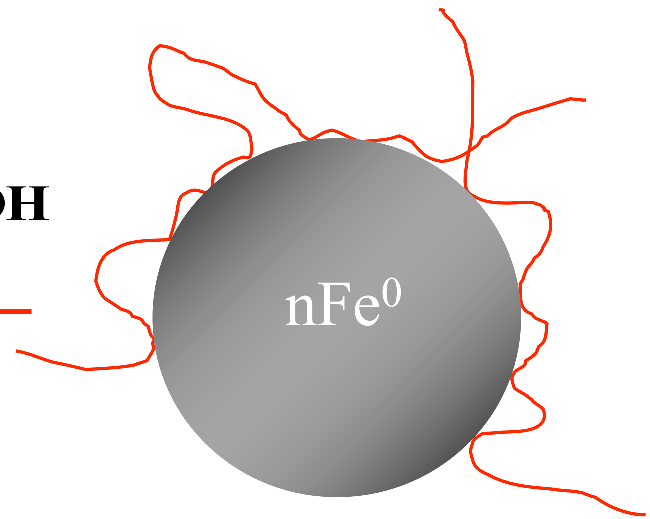
Dispersant

Poly(vinyl alcohol-co-vinyl acetate-co-itaconic acid)

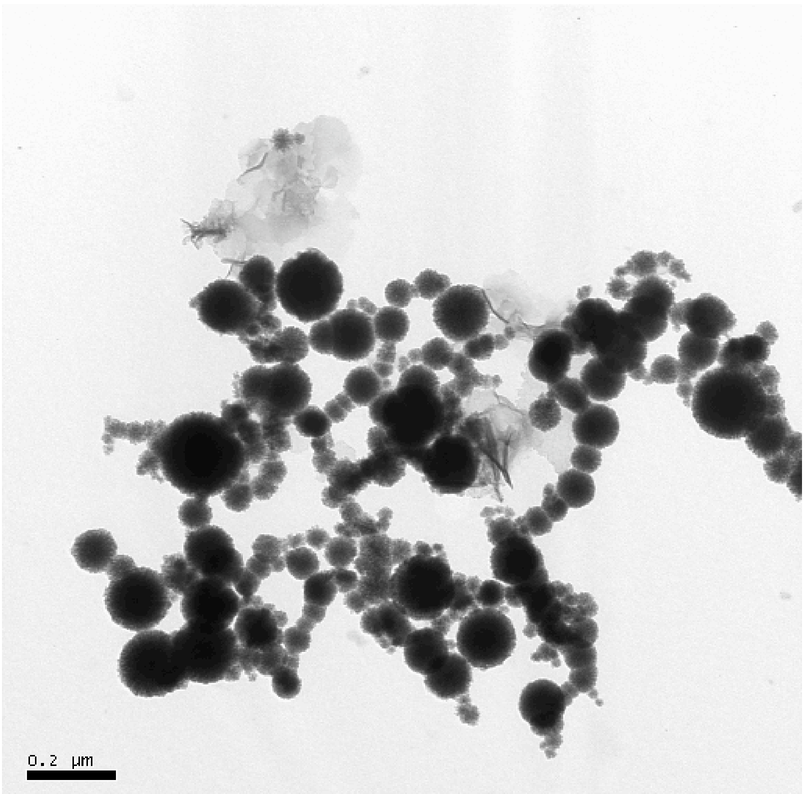




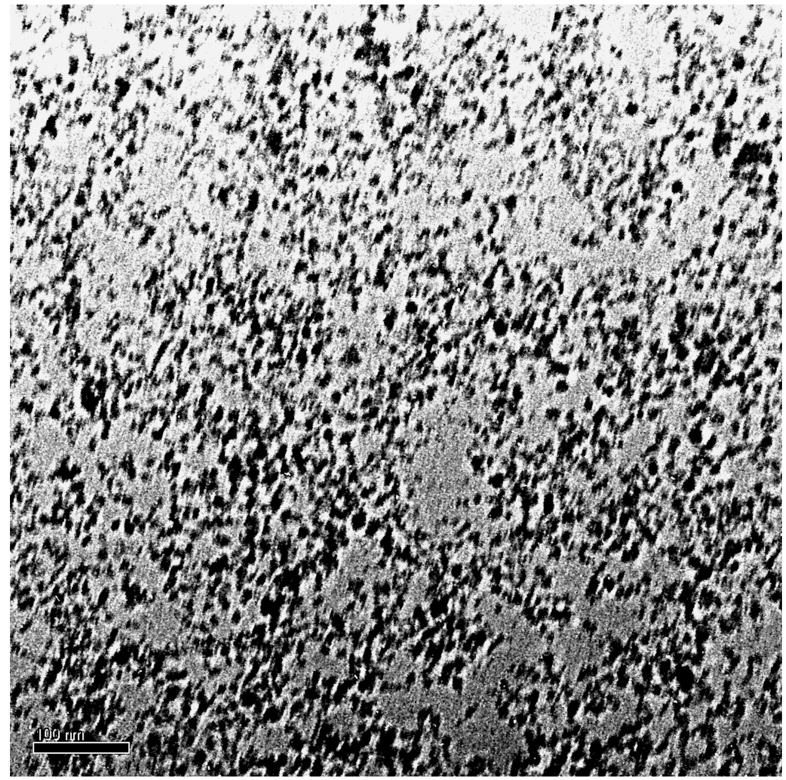
MW: 4,300~4,400
X:Y:Z = 97:2:1

- **Hydrophilic**
- **Stabilizing**

- **Hydrophilic**
- **Negative charge**
- **Anchoring groups (up to 4)**

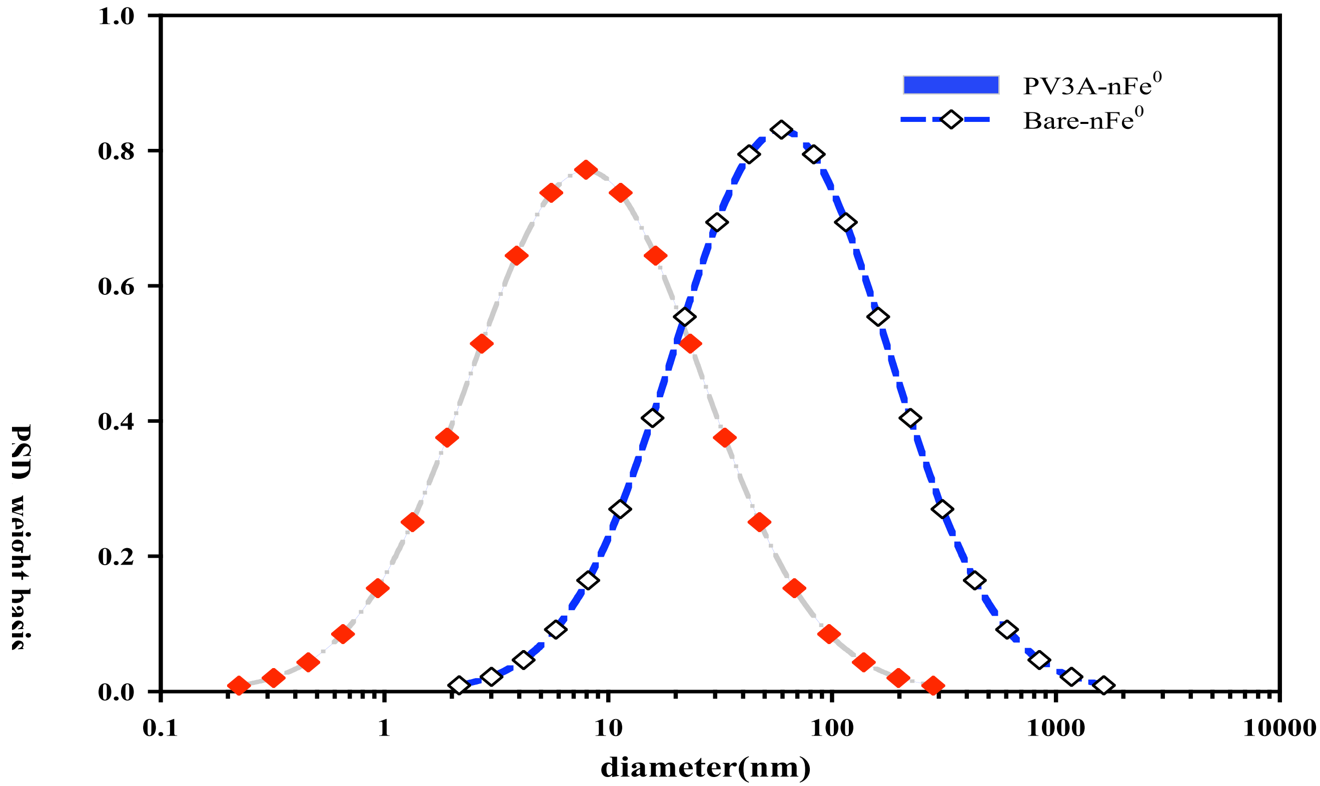


Before



After

	$d_{10\%}$ (nm)	$d_{50\%}$ (nm)	$d_{90\%}$ (nm)
A	15.8	*59.4*	223.7
B	1.9	*7.9*	33.2



Particle Size

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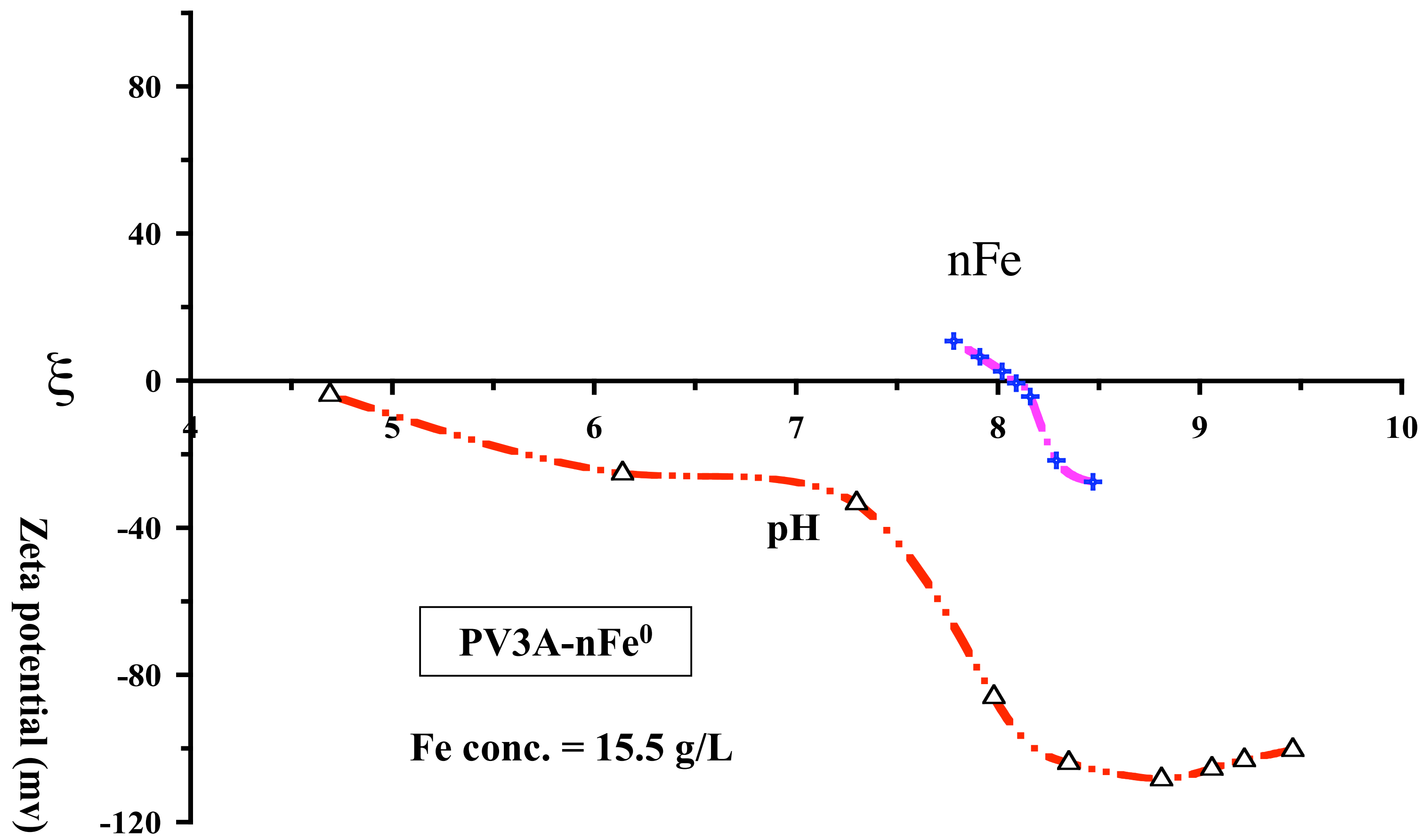
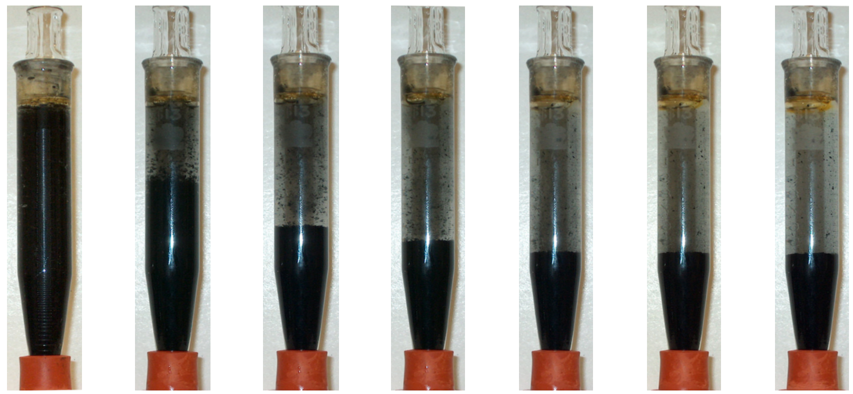
US EPA ARCHIVE DOCUMENT

Surface Charge

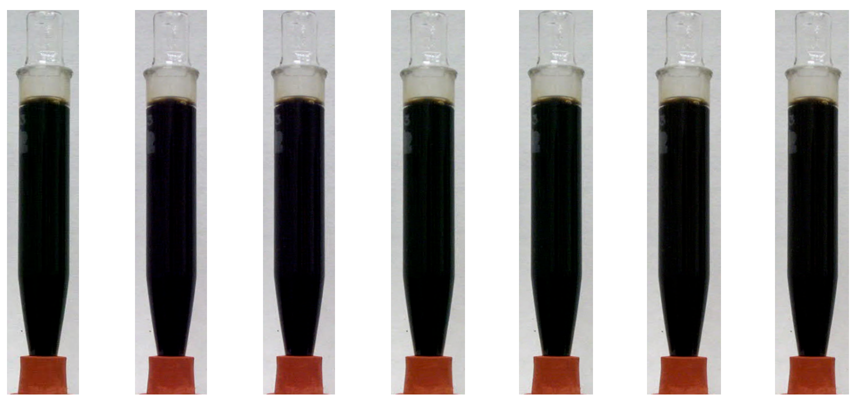


Stability Observations



T (sec) = 0 20 40 60 120 300 1800

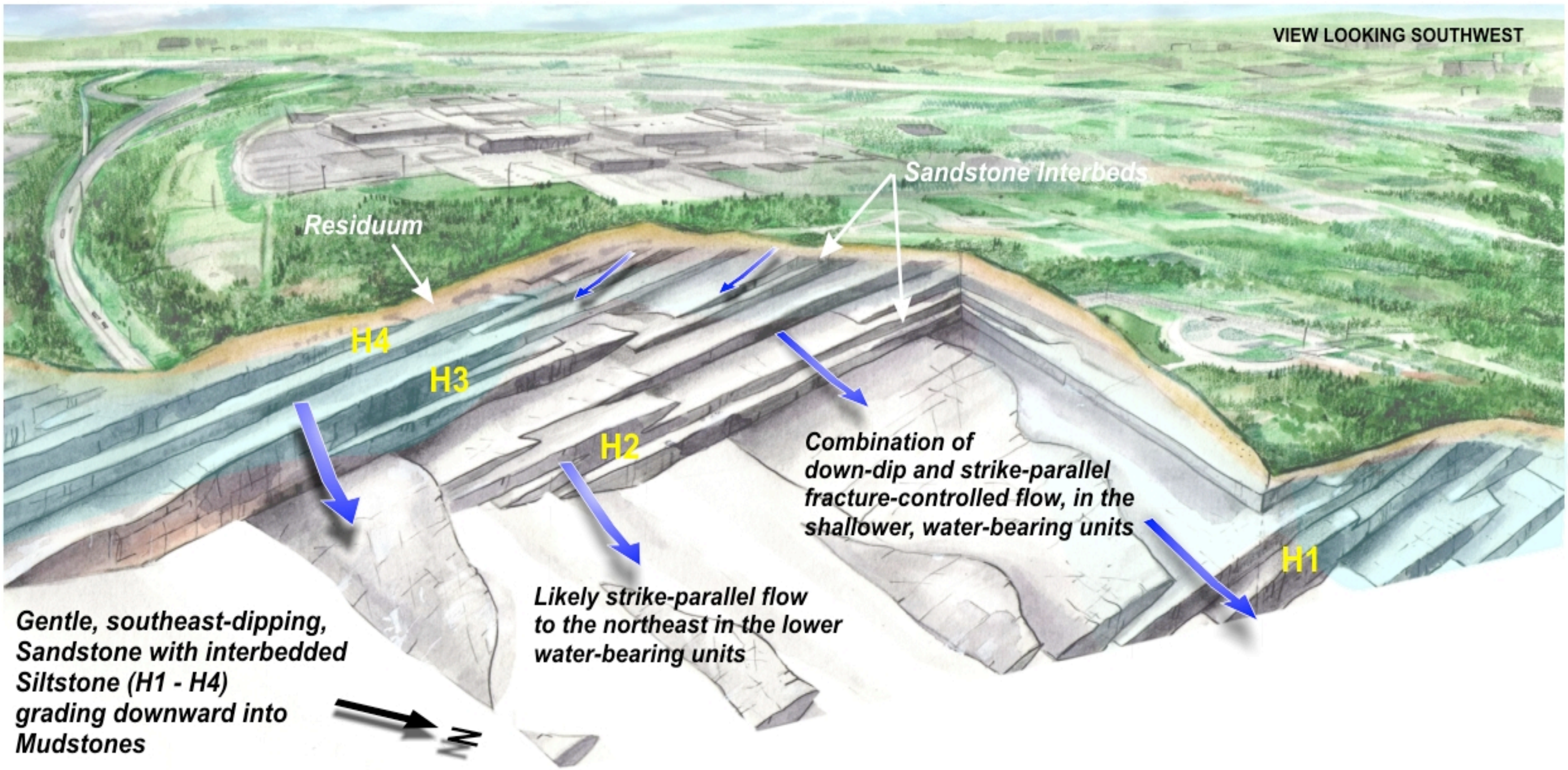
Original-nFe^0



T (month) = 0 1 2 3 4 5 6

PV3A-nFe^0

Applications



Acknowledgments

US EPA

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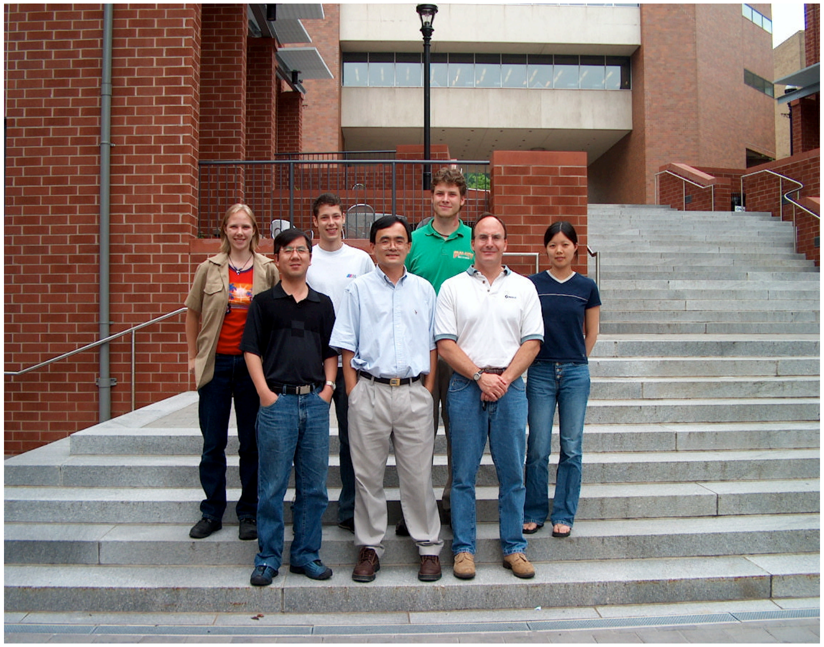

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