

Nanoscale Iron Particles
Synthesis
Characterization
Applications

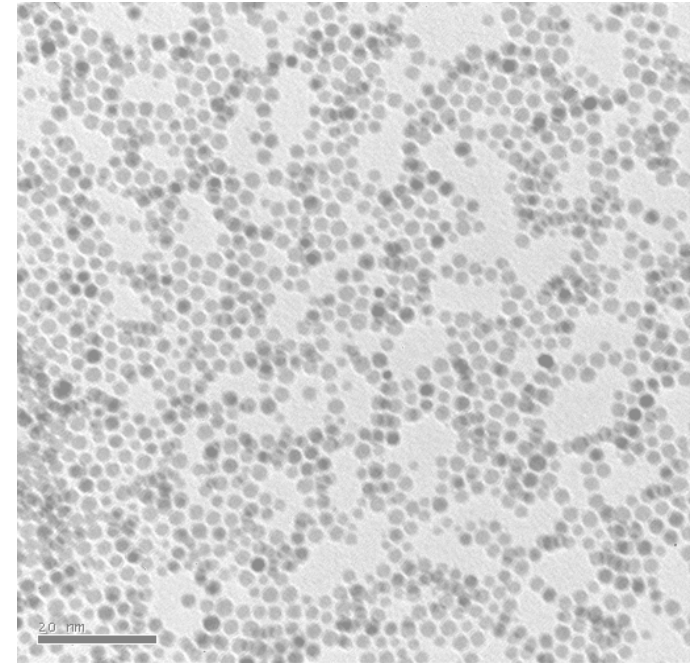
Nanotechnology for Hazardous Waste Site Remediation
Technical Workshop
October 20 - 21, 2005
Washington DC

Wei-xian Zhang



Nano Iron for Site Remediation

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

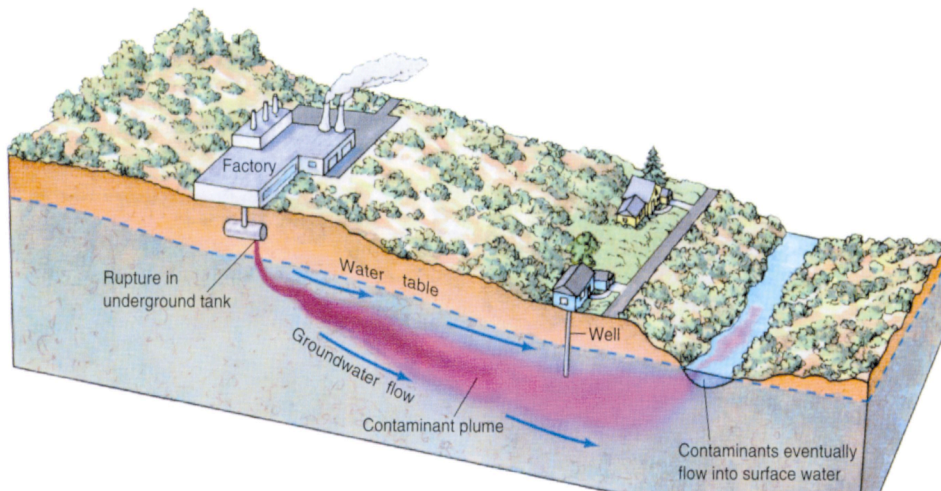


High reactivity

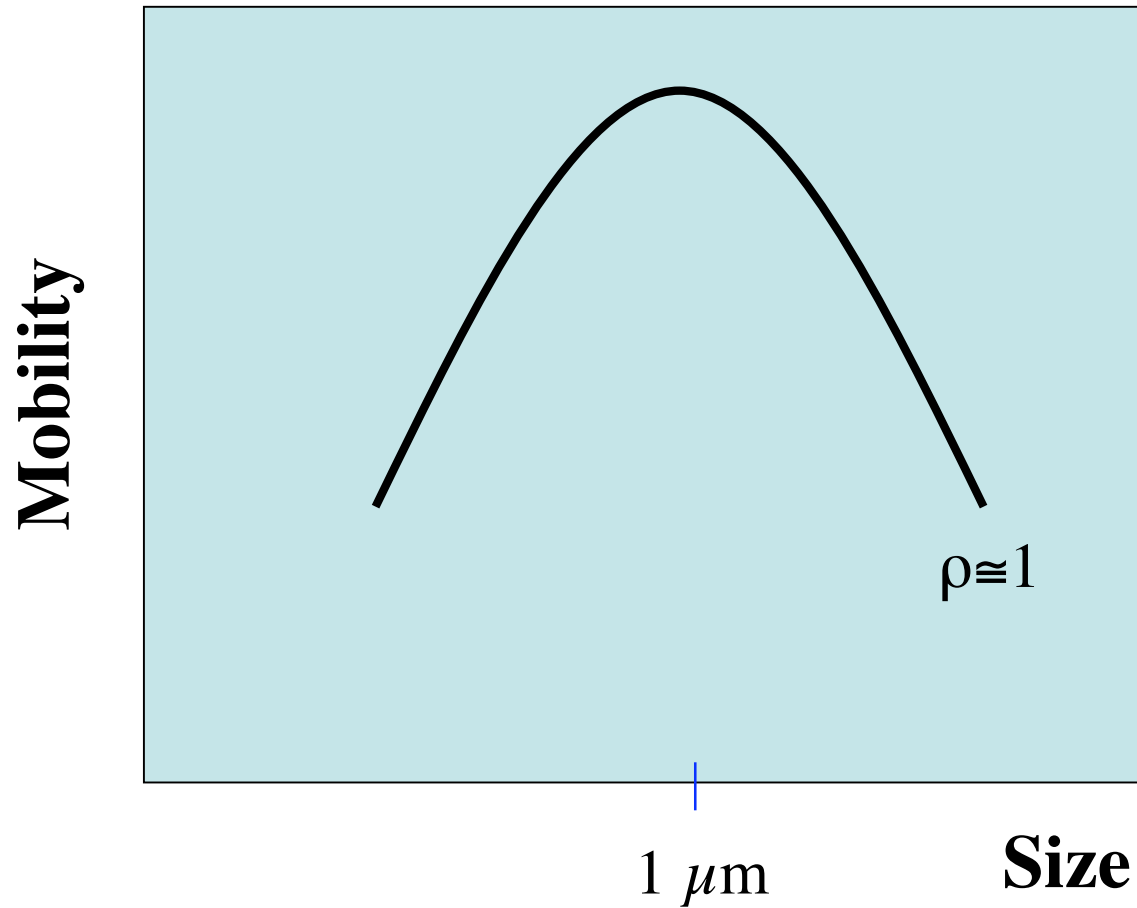
High mobility

Easy to use

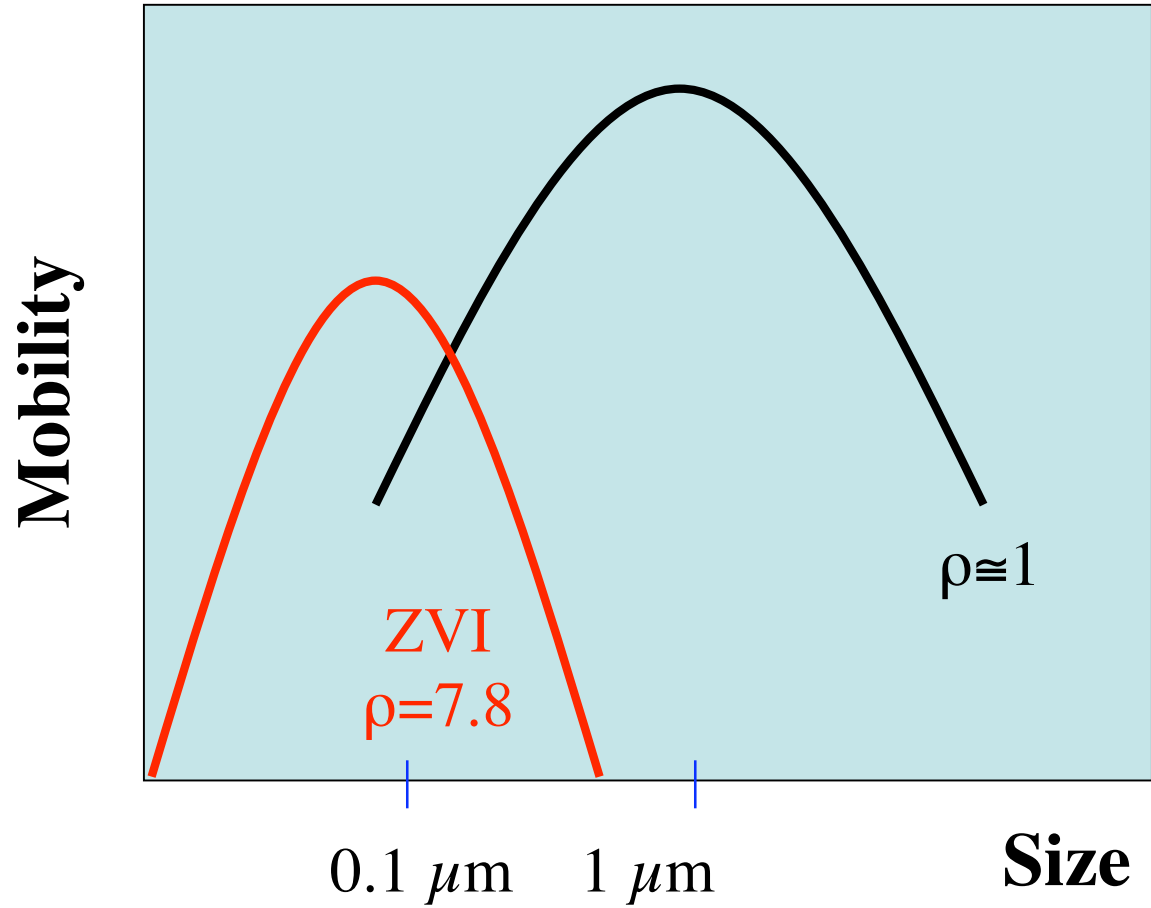
Low cost



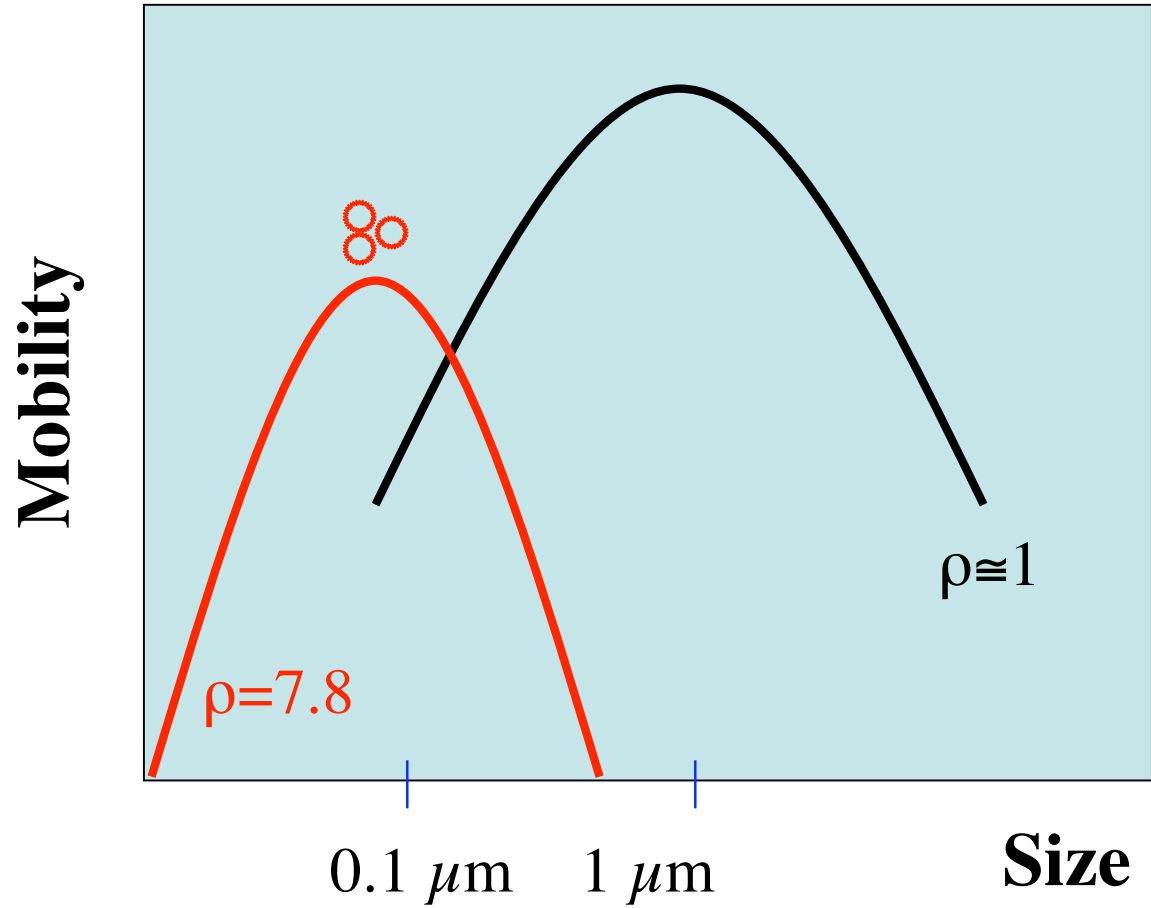
Particle Transport in Porous Media



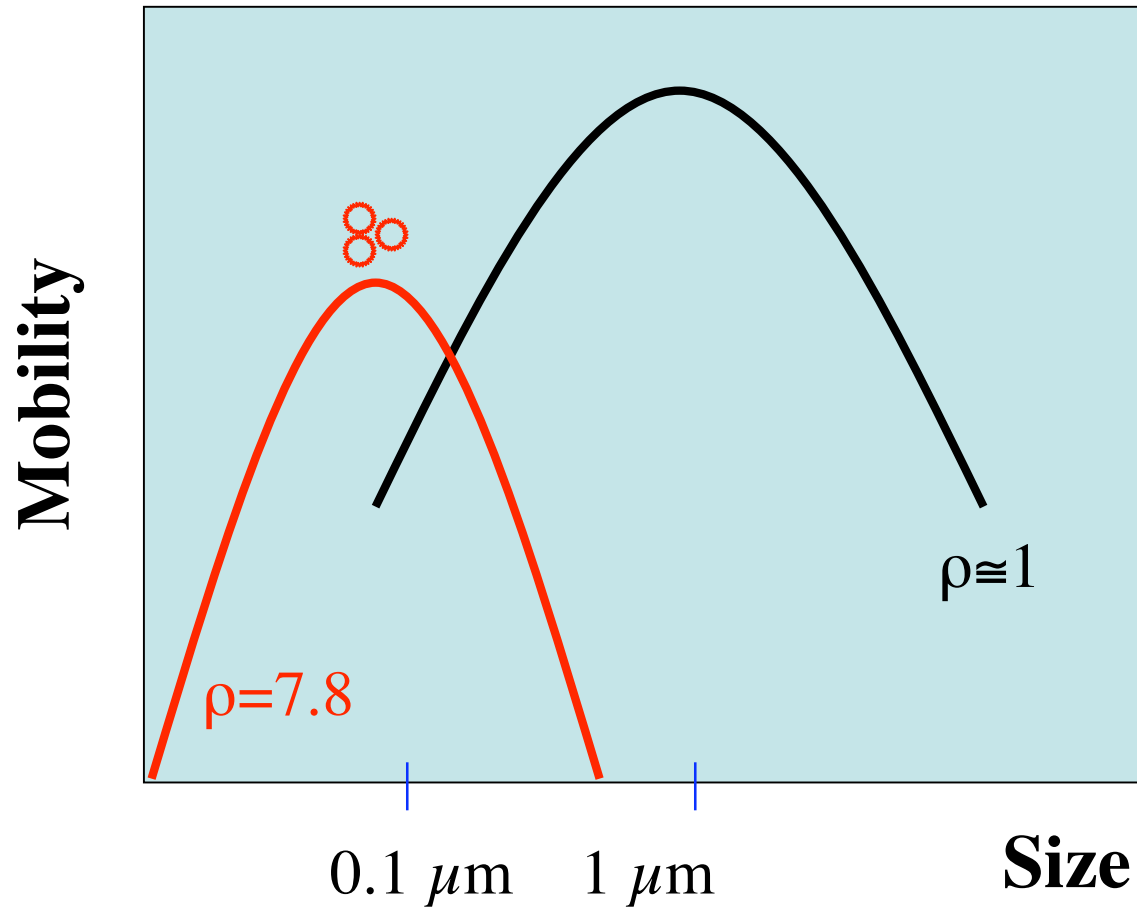
Size and Mobility



Size and Mobility



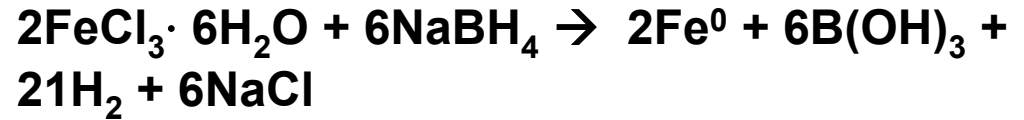
Need particles $\ll 100$ nm



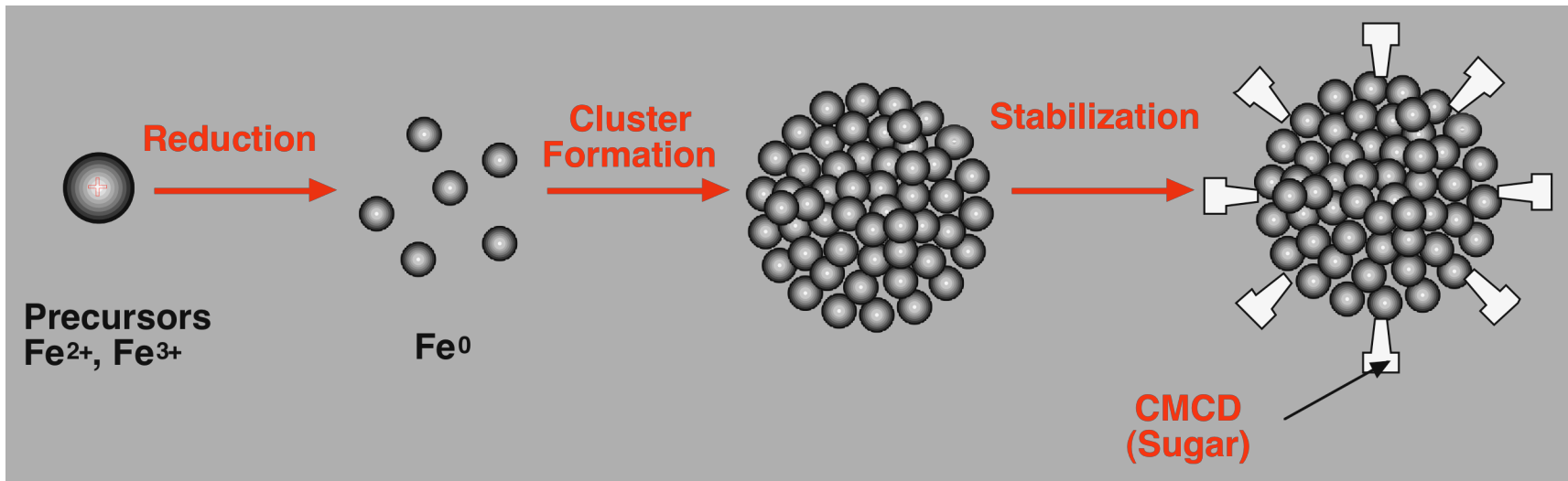
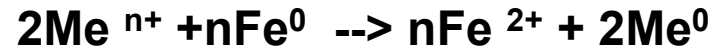
1. How to make nanoparticles?

Methods of Synthesis

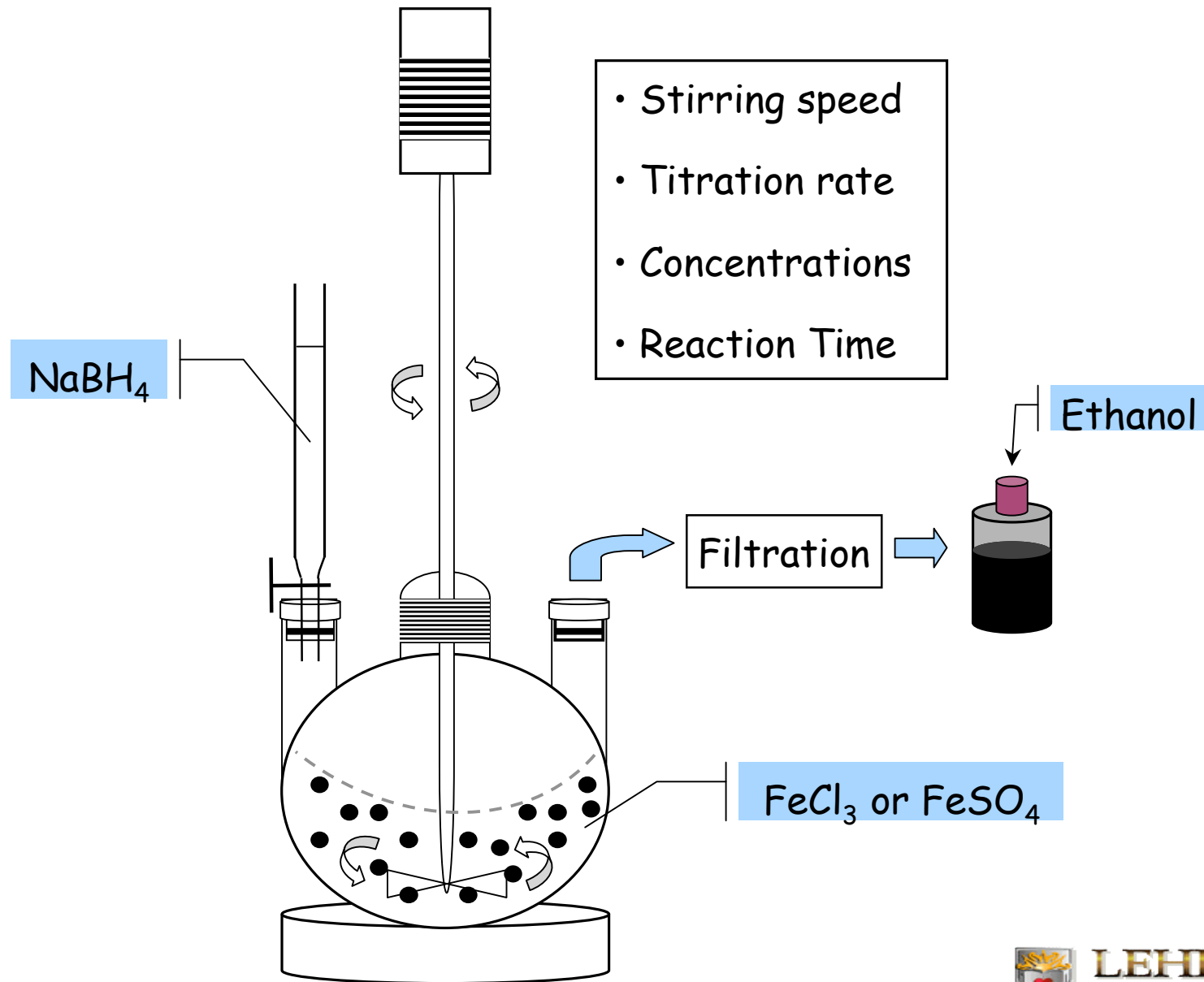
Step I - prepare nanoscale iron particles



Step II - deposit noble metal on iron

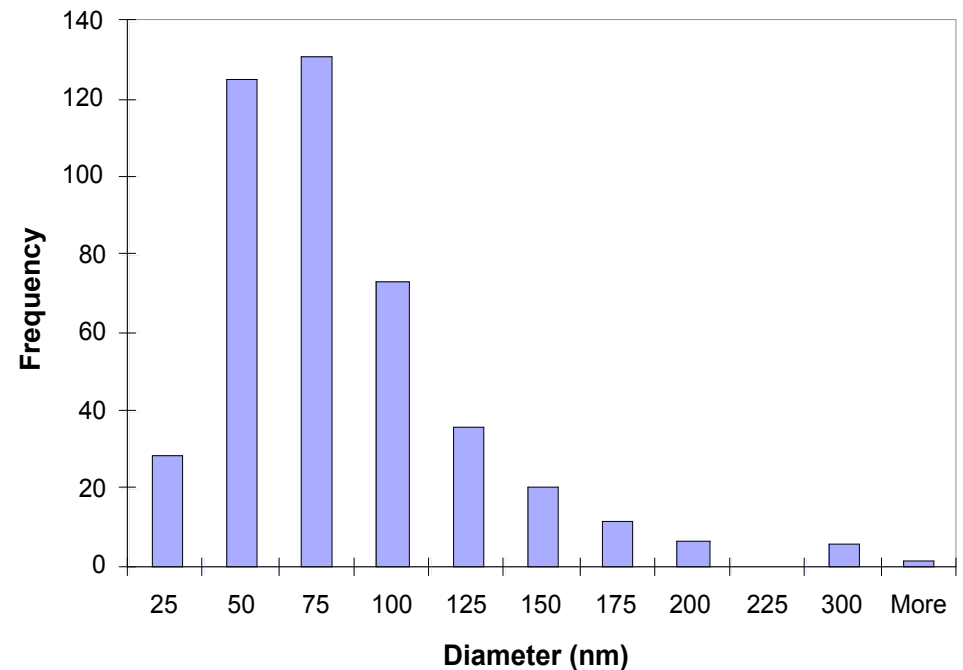
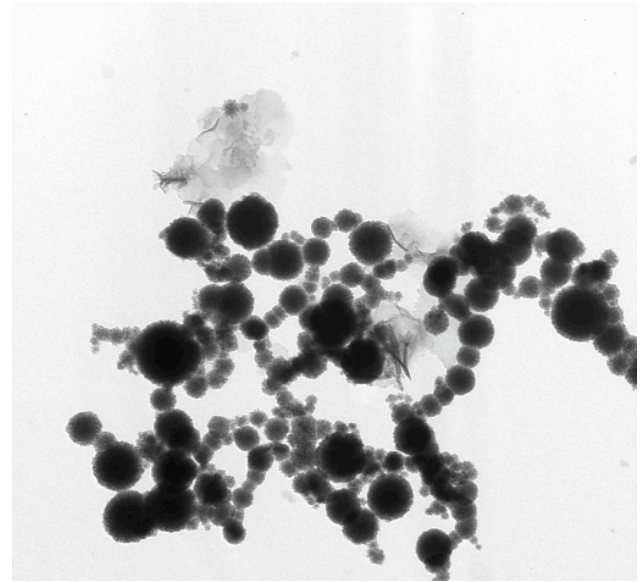


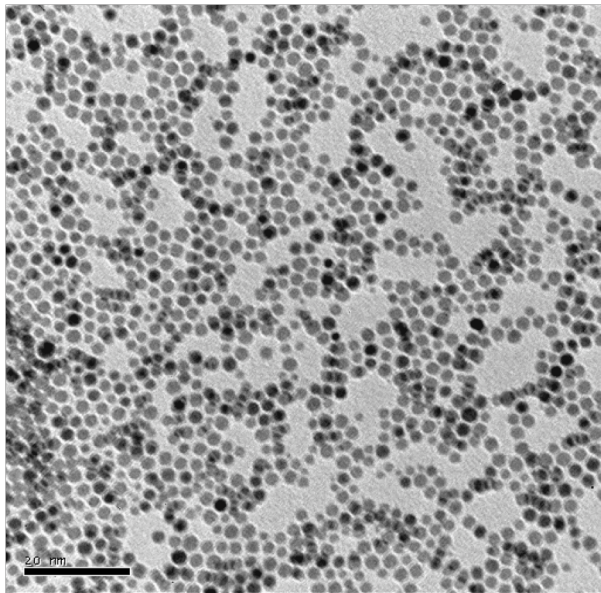
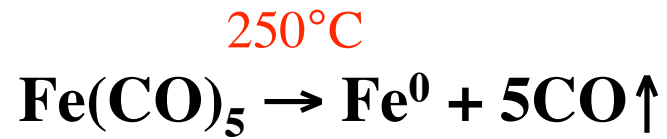
Synthesis of $n\text{Fe}^0$



Properties of nFe⁰

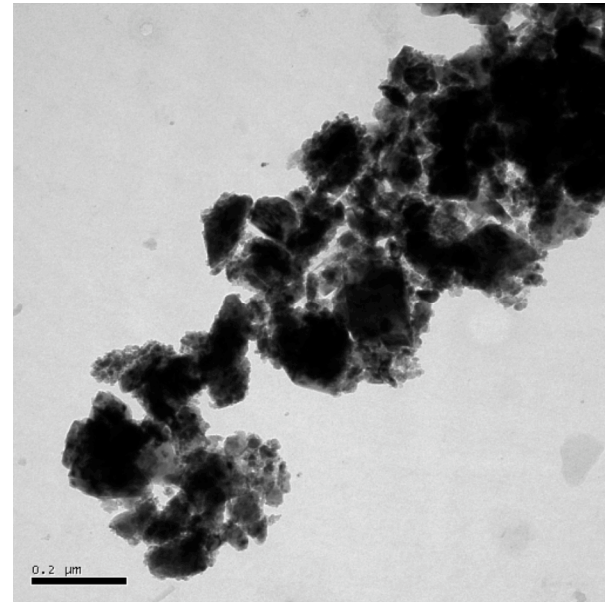
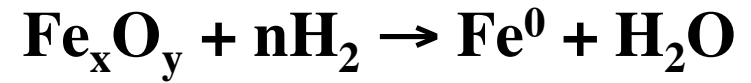
- **Size range:** 10-100 nm
- **Mean Size:** 50 ± 15 nm
- **Specific surface area**
 - 10-50 m²/g
- **ξ potential**
 - +10 to -10 mV





5 nm

Cao & Zhang, 2005

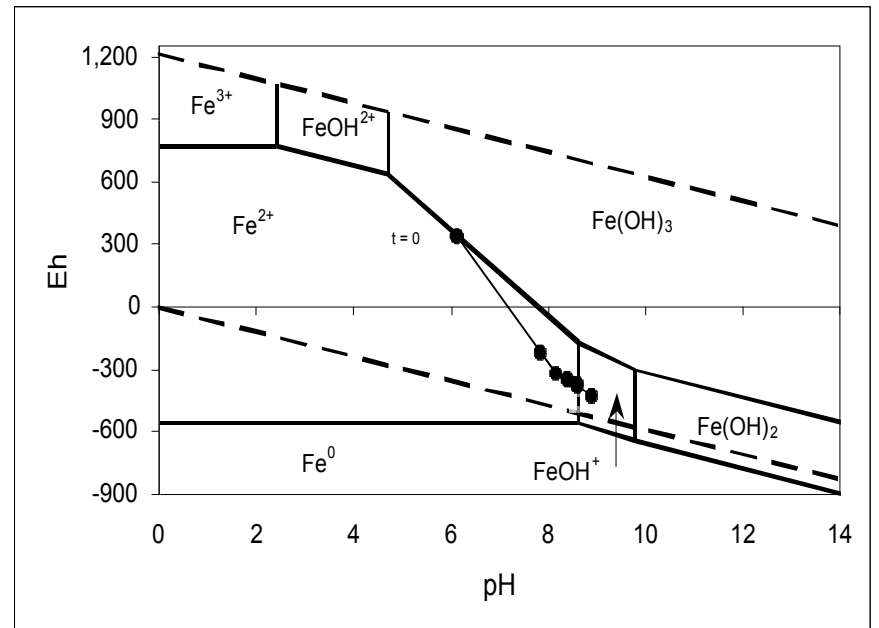
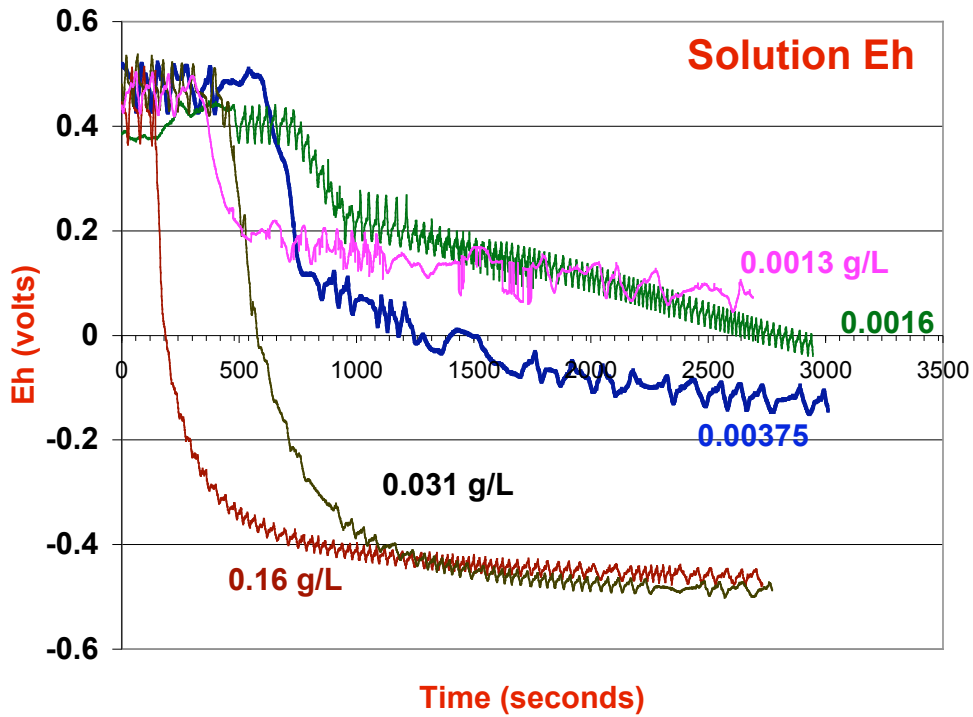


~200-300 nm

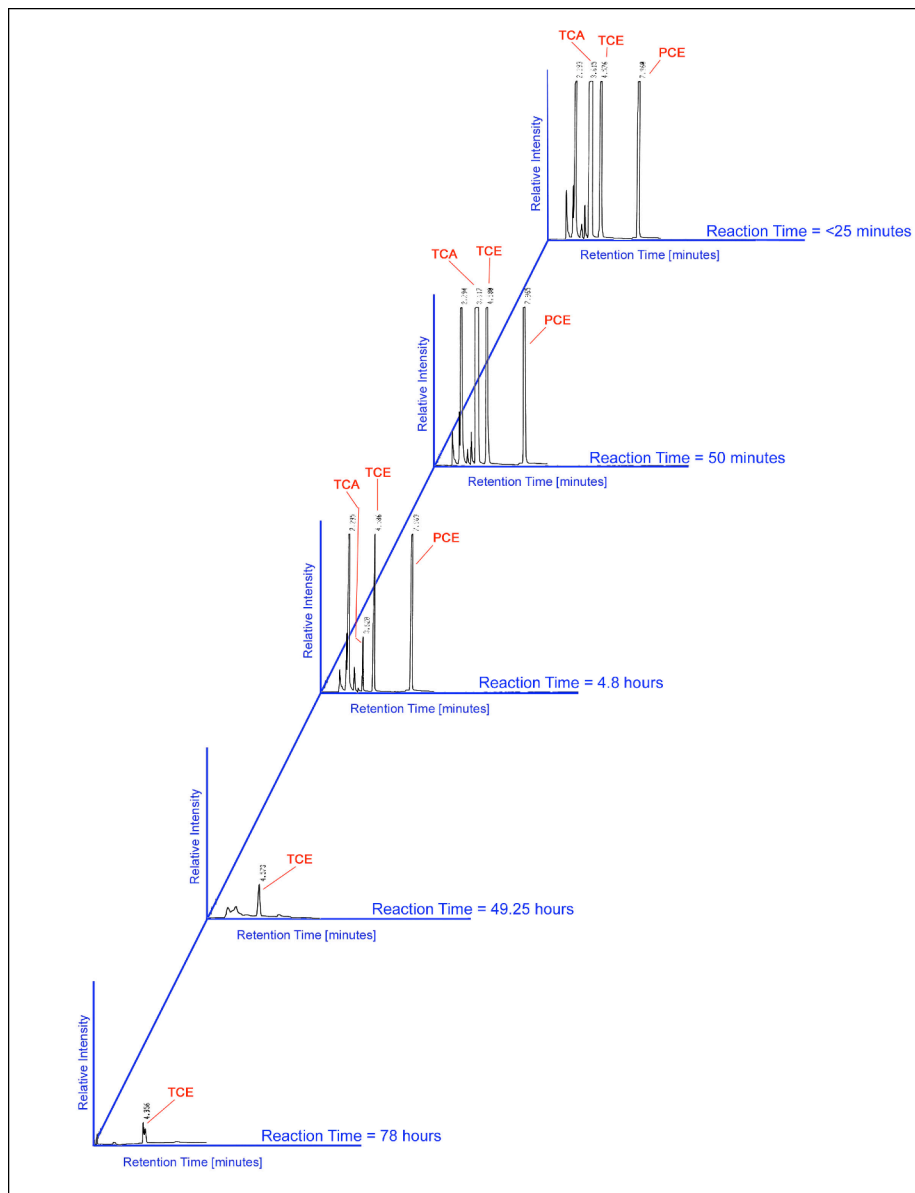
Cao & Zhang, 2004

Reactivity

Redox Chemistry

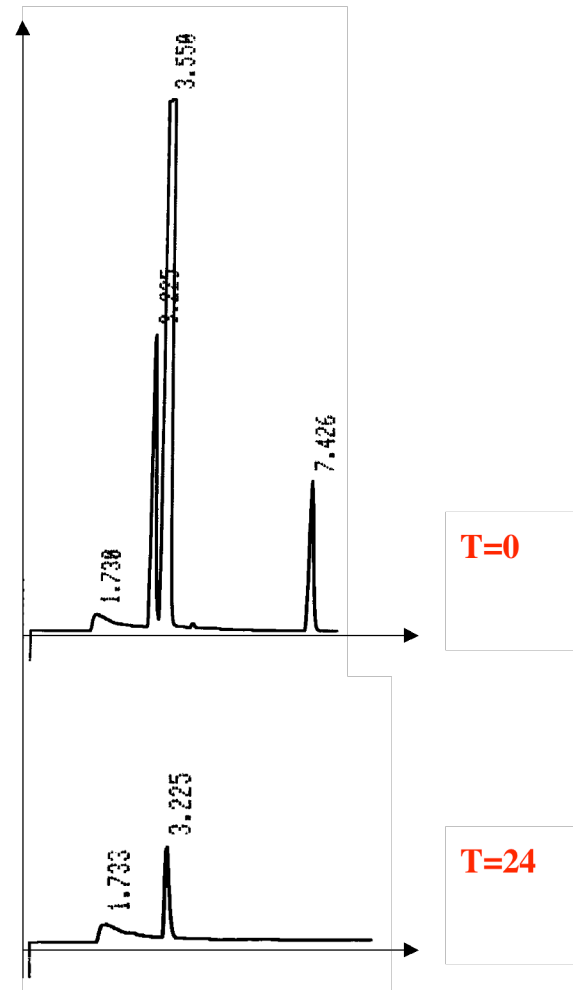
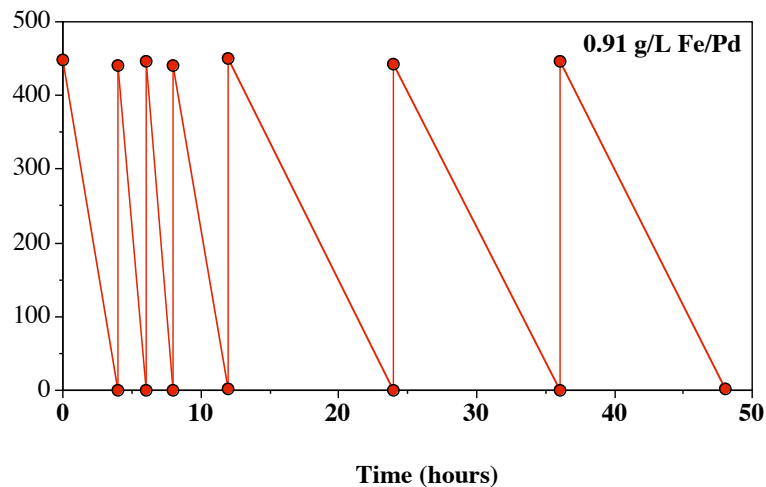


Transformation of Organic Solvents



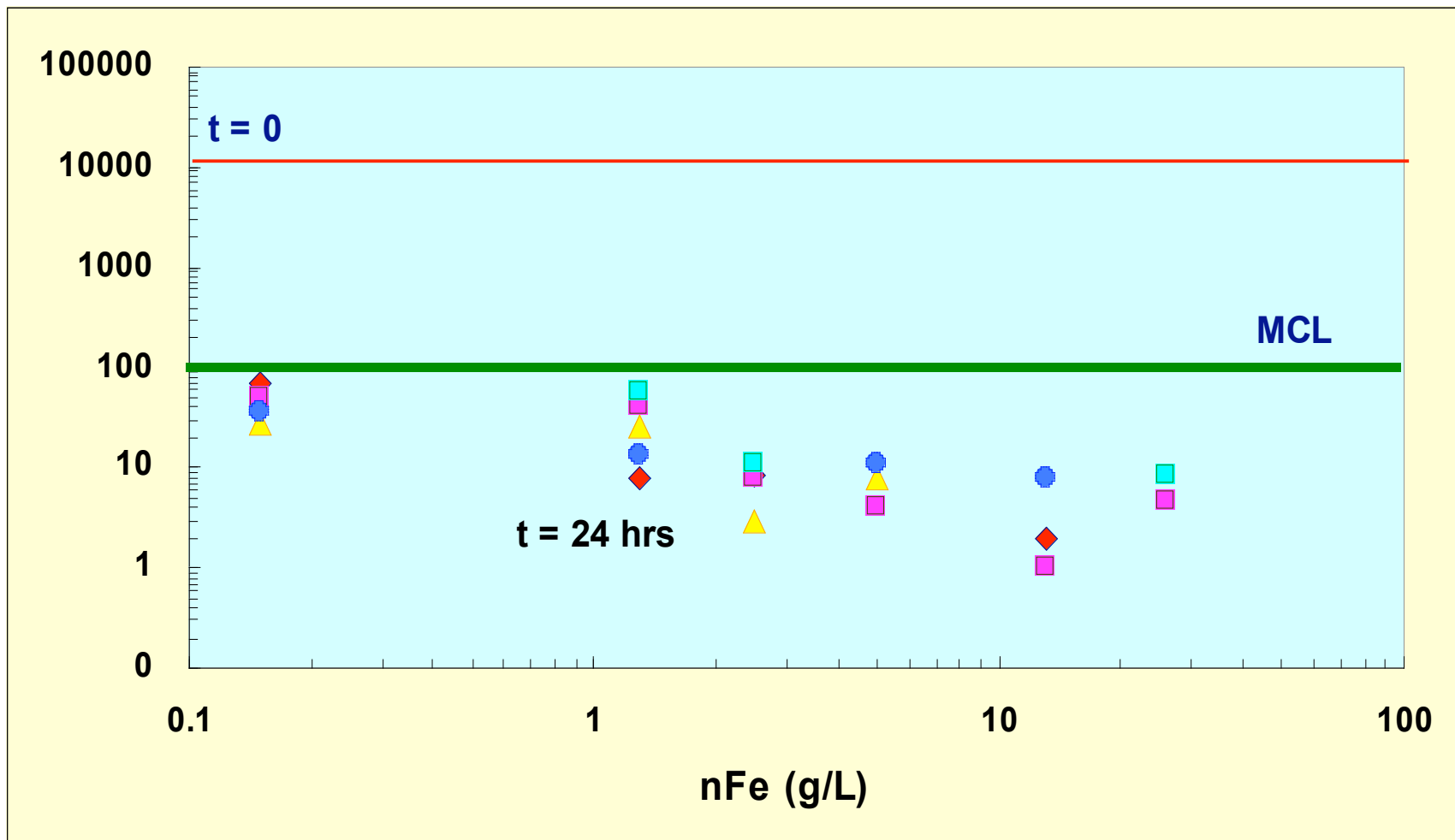
	Compound Name	Molecular Formula	K_{SA} (L/m ² /hr)
1	Tetrachloroethylene (PCE)	C ₂ Cl ₄	0.0122
2	Trichloroethylene (TCE)	C ₂ HCl ₃	0.0182
3	<i>trans</i> -Dichloroethylene (<i>trans</i> -DCE)	C ₂ H ₂ Cl ₂	0.0151
4	<i>cis</i> -Dichloroethylene (<i>cis</i> -DCE)	C ₂ H ₂ Cl ₂	0.0176
5	1,1-Dichloroethylene (1,1-DCE)	C ₂ H ₂ Cl ₂	0.0115
6	Hexachloroethane (HCA)	C ₂ Cl ₆	0.020
7	Pentachloroethane (PCA)	C ₂ HCl ₅	0.026
8	1,1,1,2-Tetrachloroethane (1,1,1,2-TeCA)	C ₂ H ₂ Cl ₄	0.021
9	1,1,2,2-Tetrachloroethane (1,1,2,2-TeCA)	C ₂ H ₂ Cl ₄	0.0088
10	1,1,1-Trichloroethane (1,1,1-TCA)	C ₂ H ₃ Cl 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 ₂ Br ₂	0.044
15	Dibromochloromethane (DBCM)	CHBr ₂ Cl	0.056

TCE Reduction (450 ppb, Trenton, NJ)

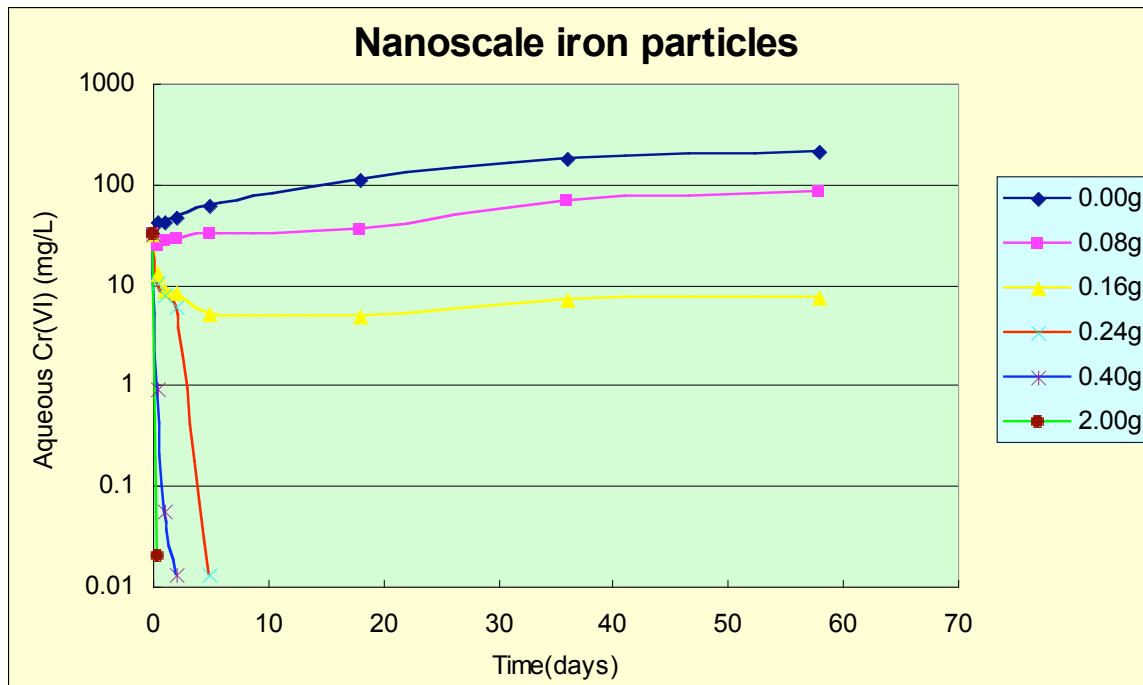
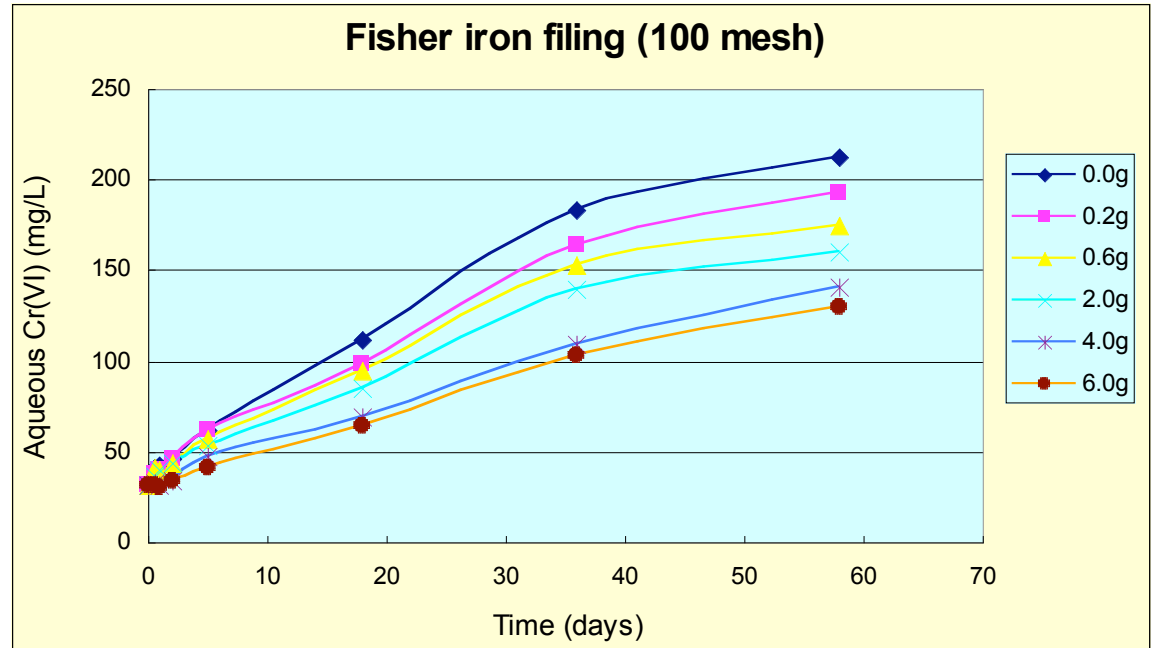


Carbon Tetrachloride
(CCl_4 , 14.5 ppm, S.
Charleston, WV)

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



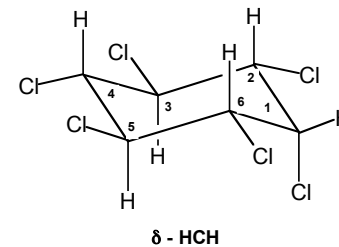
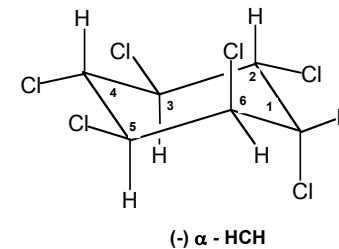
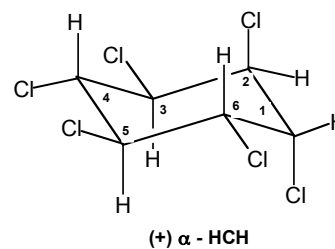
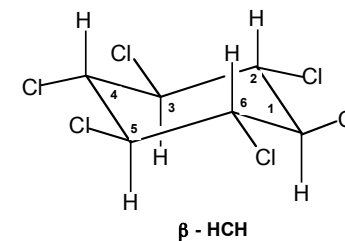
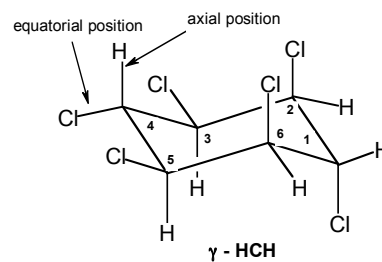
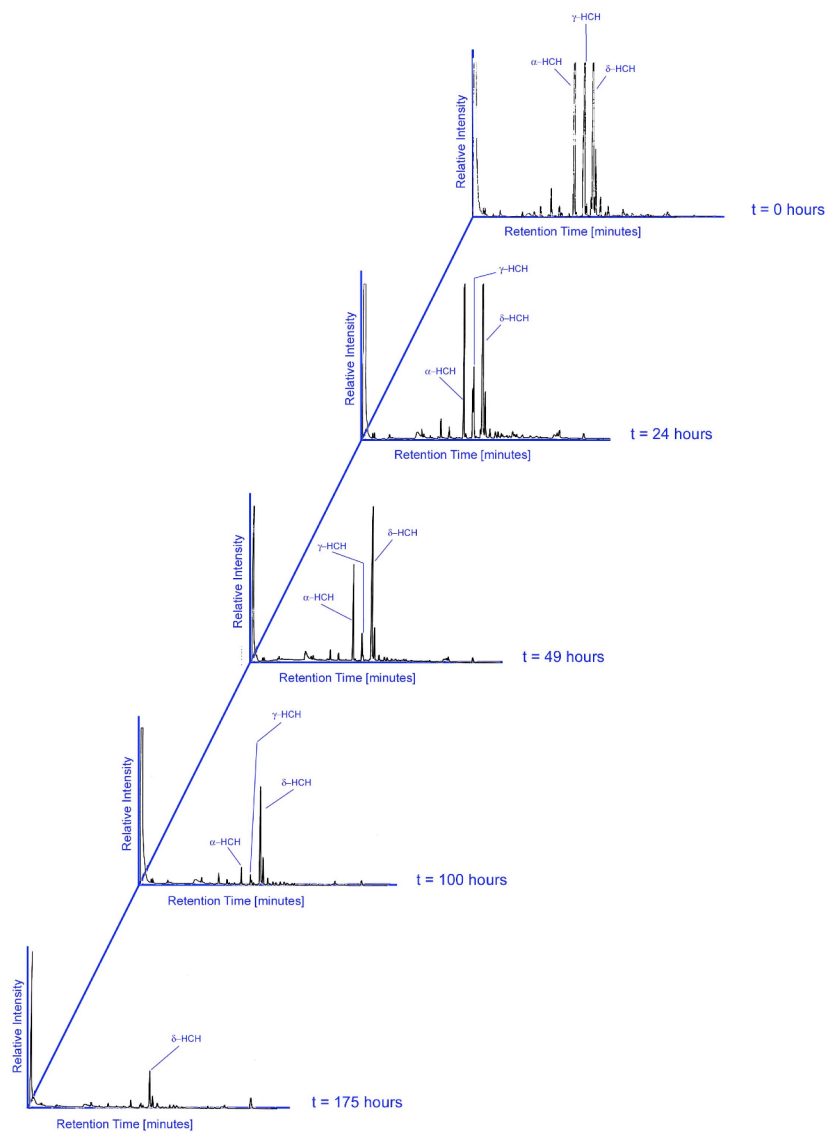
Immobilization of Cr(VI) in COPR ($>7,000$ mg Cr/kg)



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

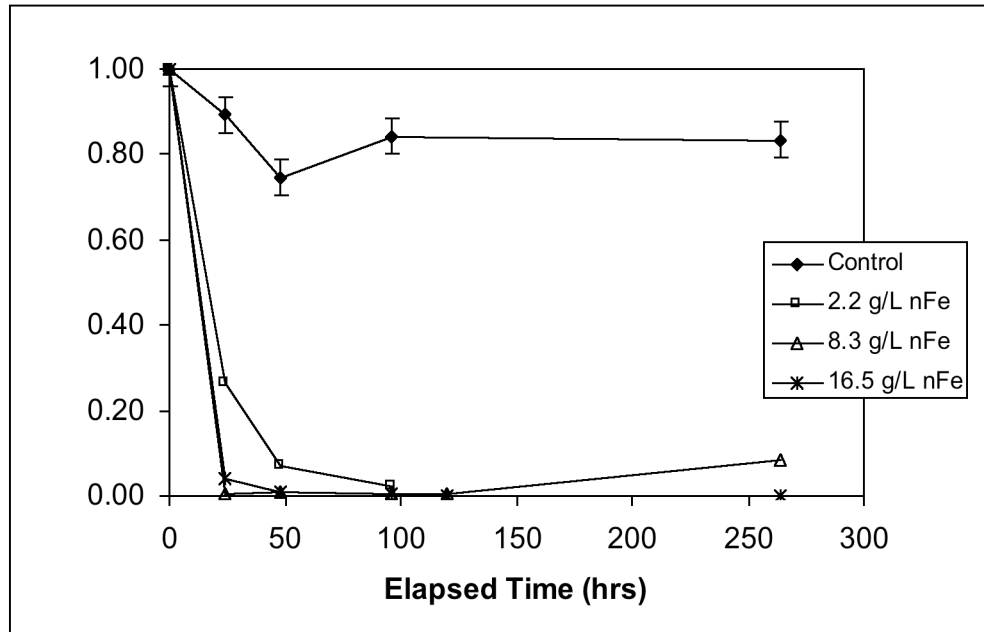
0.24 g **nFe** in 10 g COPR
(**2.4%**)

Treatment of Lindane

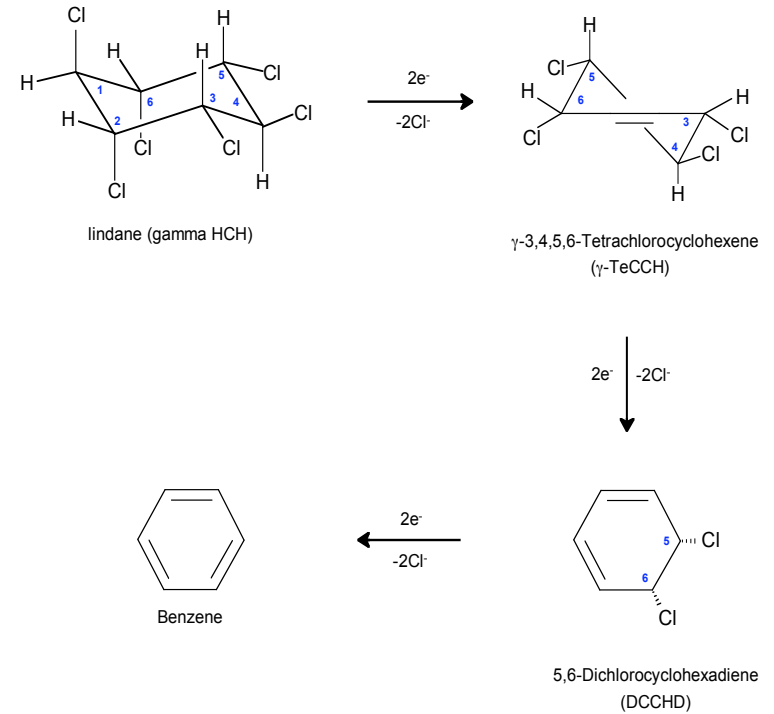


GW from a site in Jacksonville, FL

Dihaloelimination

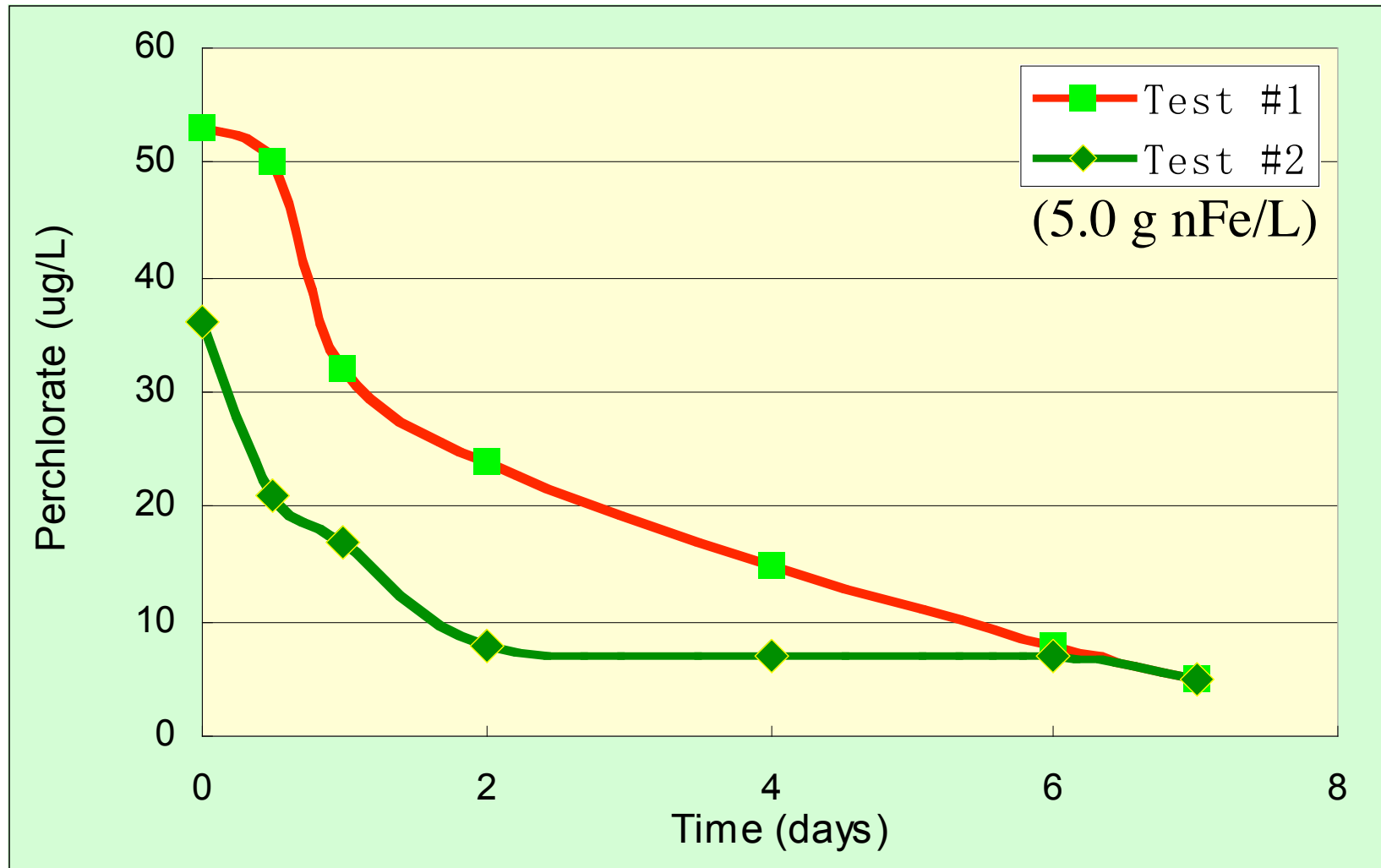


1,400 ppb HCHs



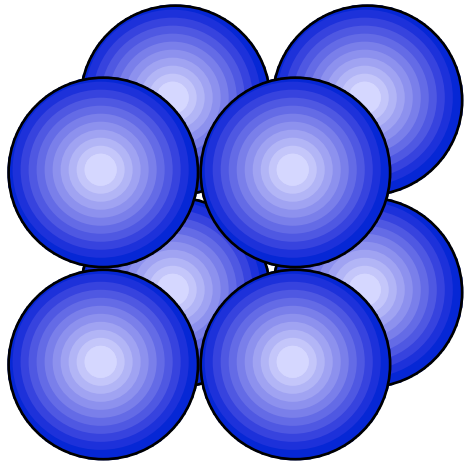
Reduction of Perchlorate (ClO_4^-)

(Samples from CA)

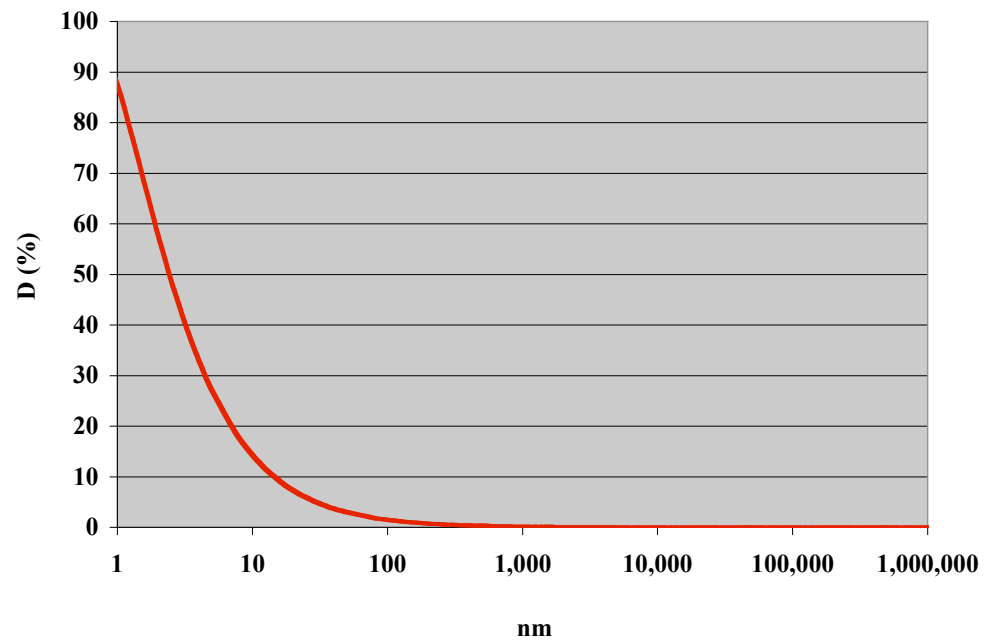
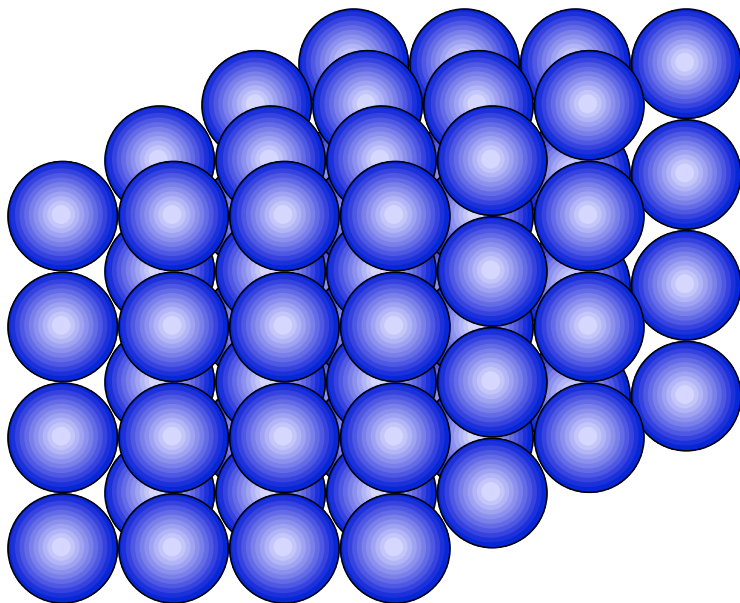


2. How to make better nanoparticles?

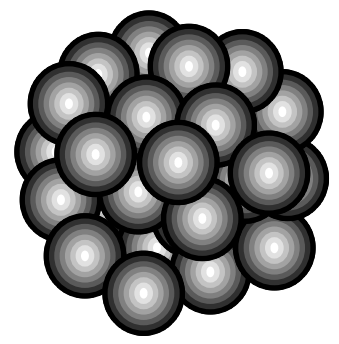
Fe on Surface



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

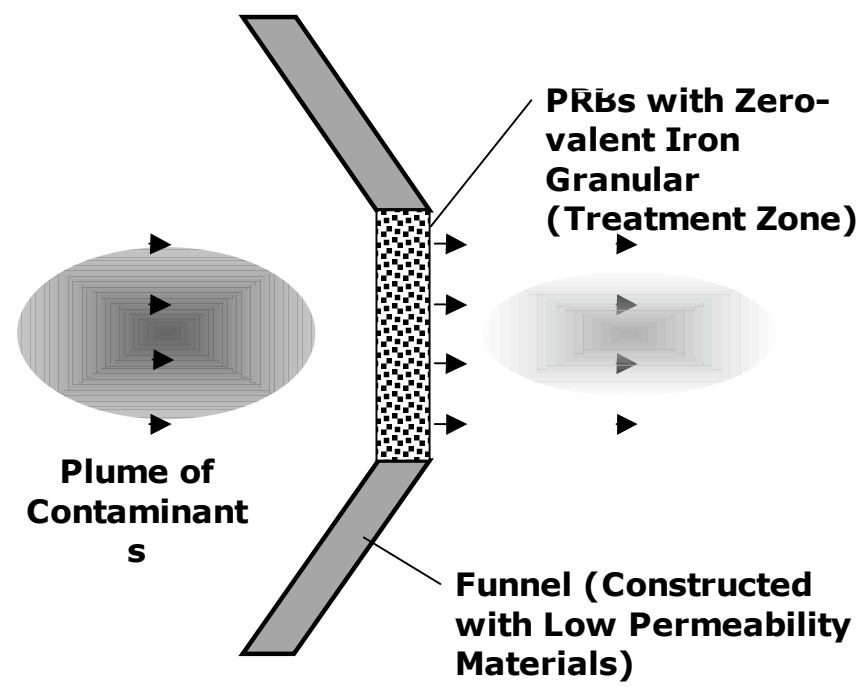


$n\text{Fe}^0$



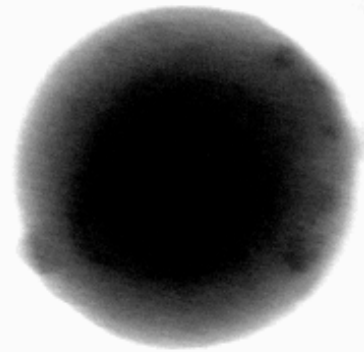
50 nm
~ 4% Fe on Surface

Fe in PRBs



0.5 mm
~0.0004%

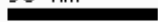
50 nm Fe



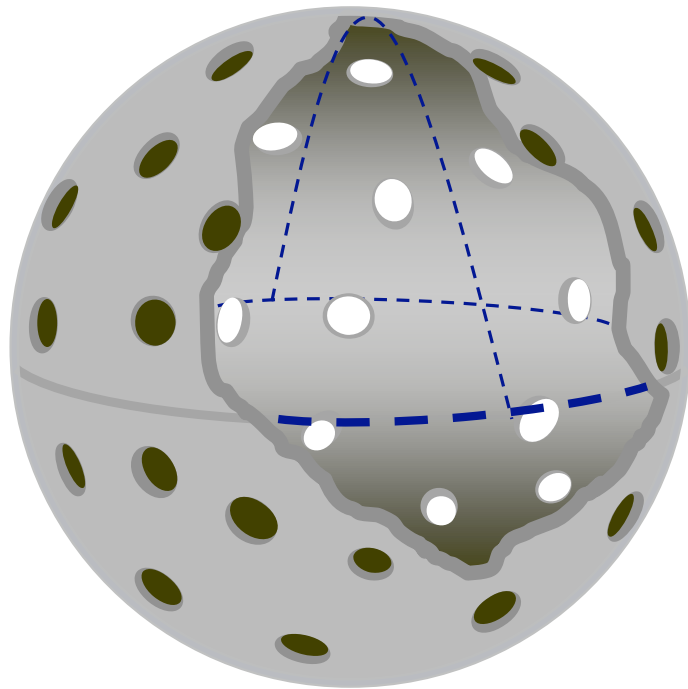
~ 4,000,000 atoms

Still a lot of room inside!

50 nm



Nano & Porous



~ 50 nm

Large surface area

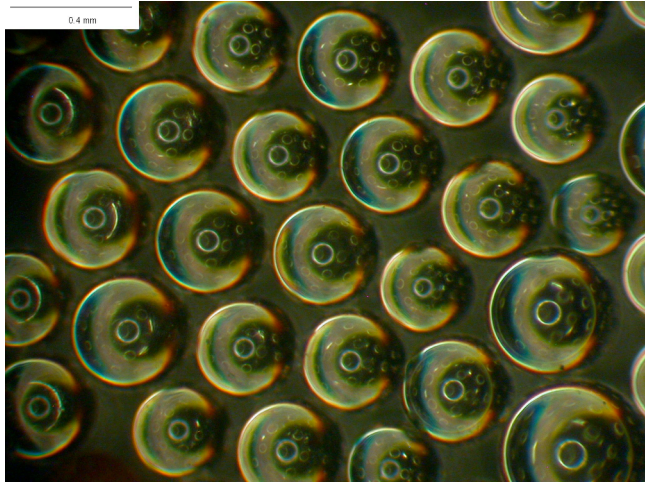
Better hydraulics

High reactivity

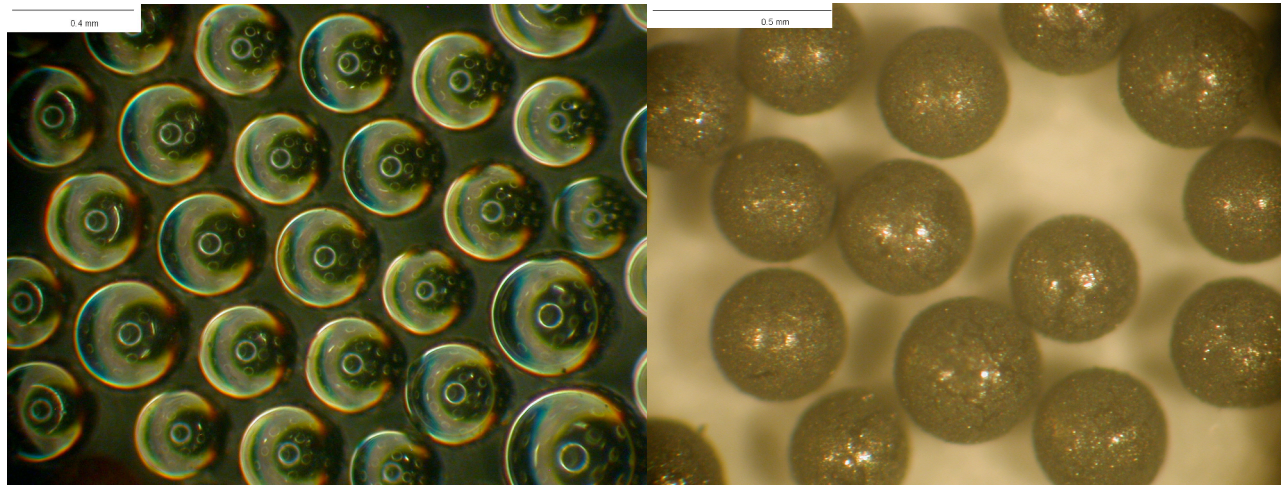
High mobility

Synthesis of Porous Fe

**0.4 mm
Resin**

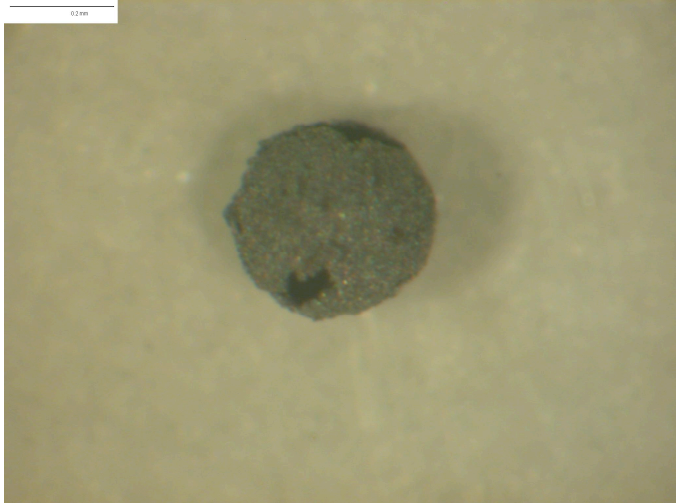
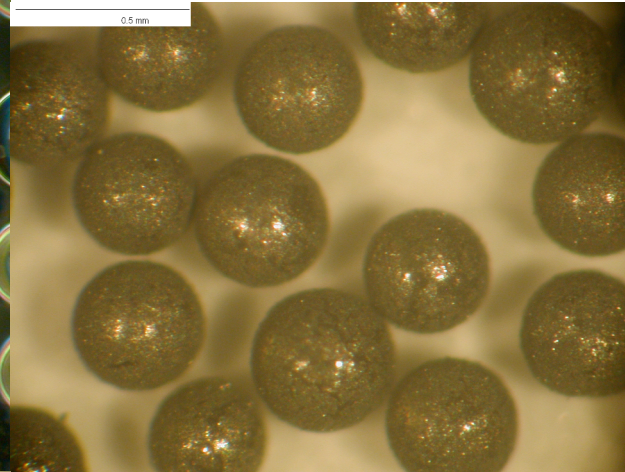
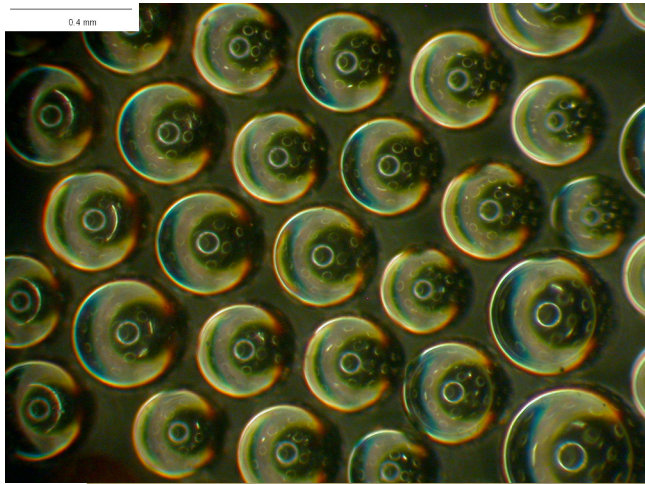


Synthesis of Porous Fe



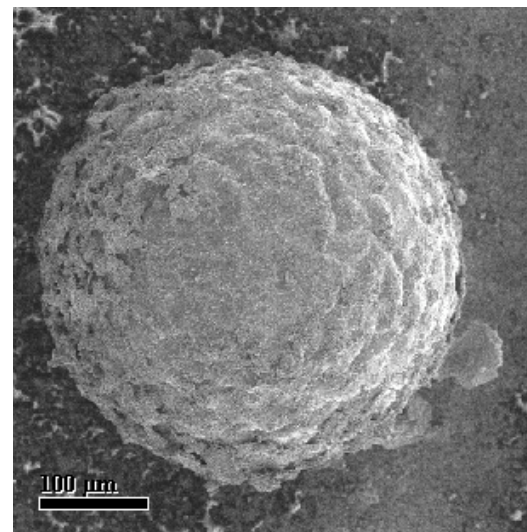
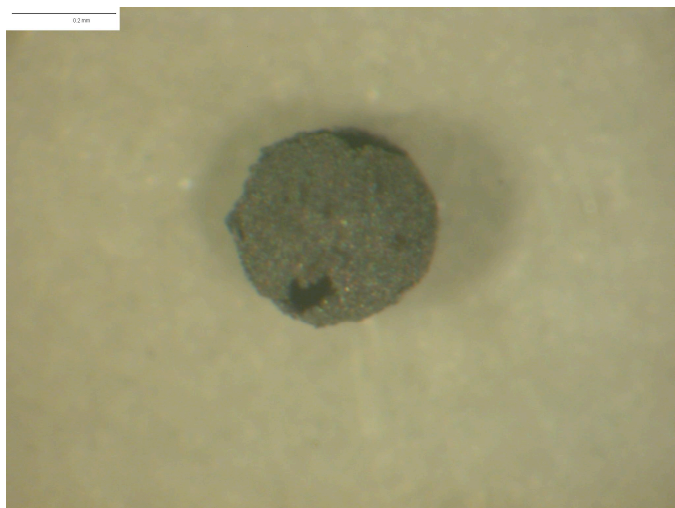
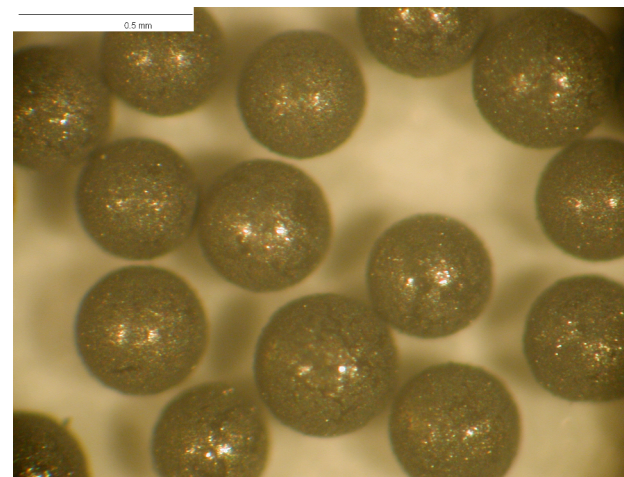
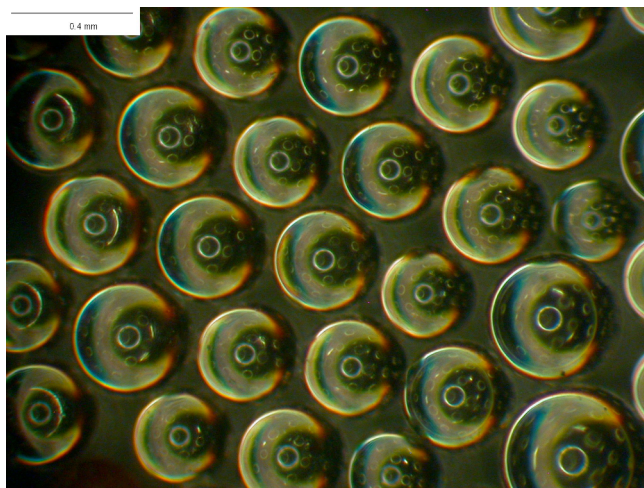
Coated with 50 nm Fe

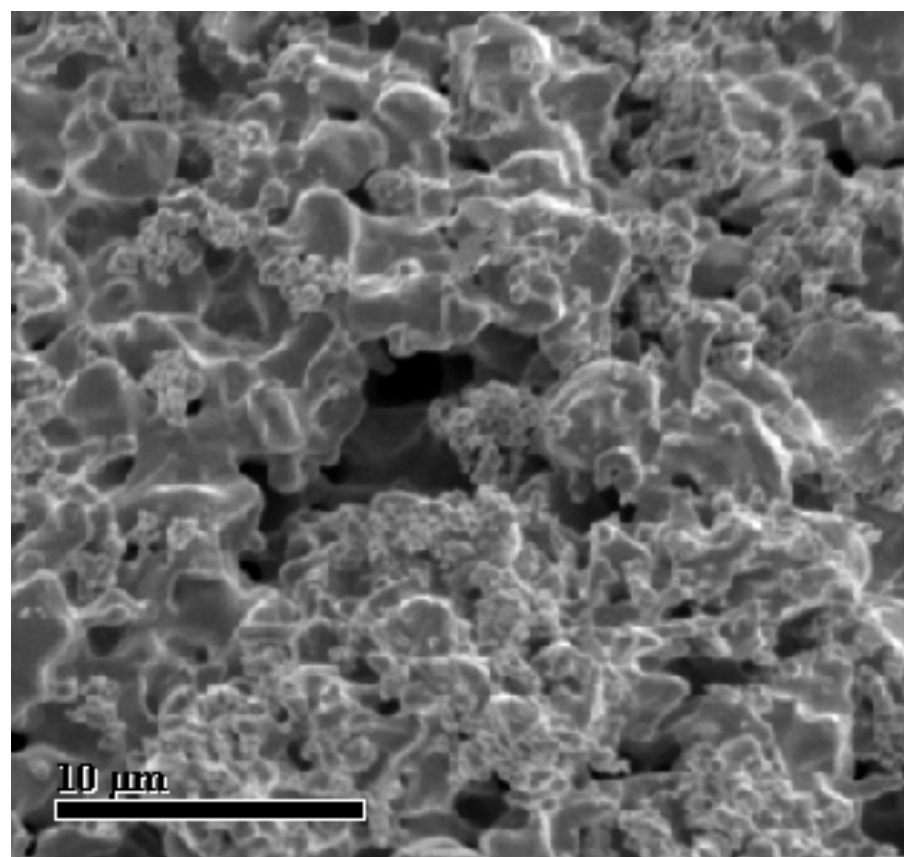
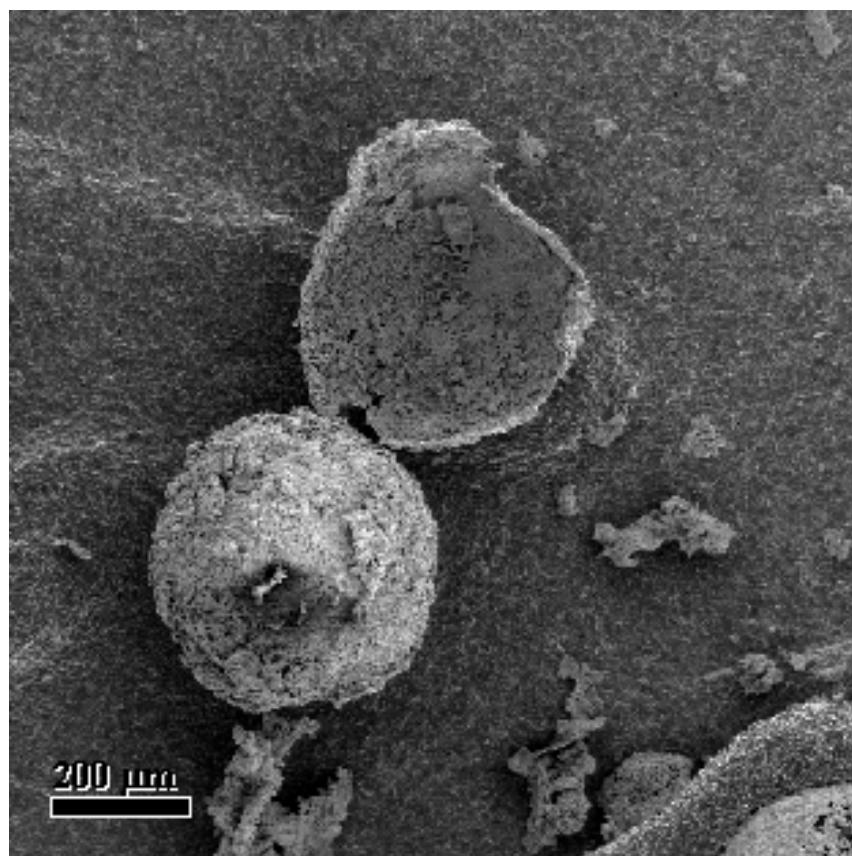
Template Directed Synthesis



Remove the core

Template Directed Synthesis





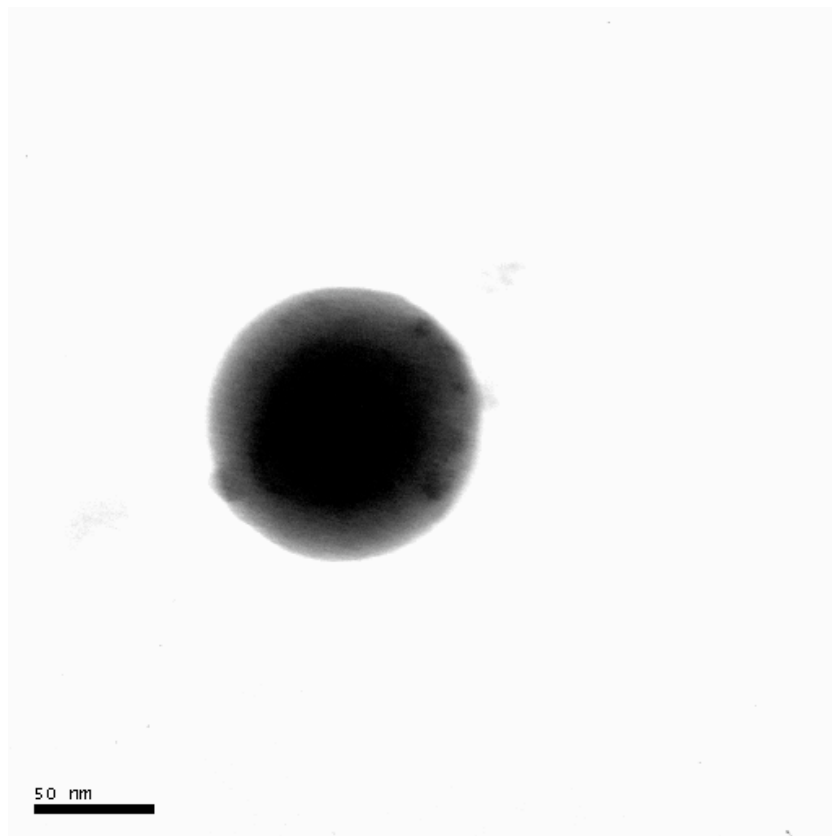
Specific Surface Area

	Size	BET area (m²/g)
Solid sphere (calculated)	0.4 mm	1.9

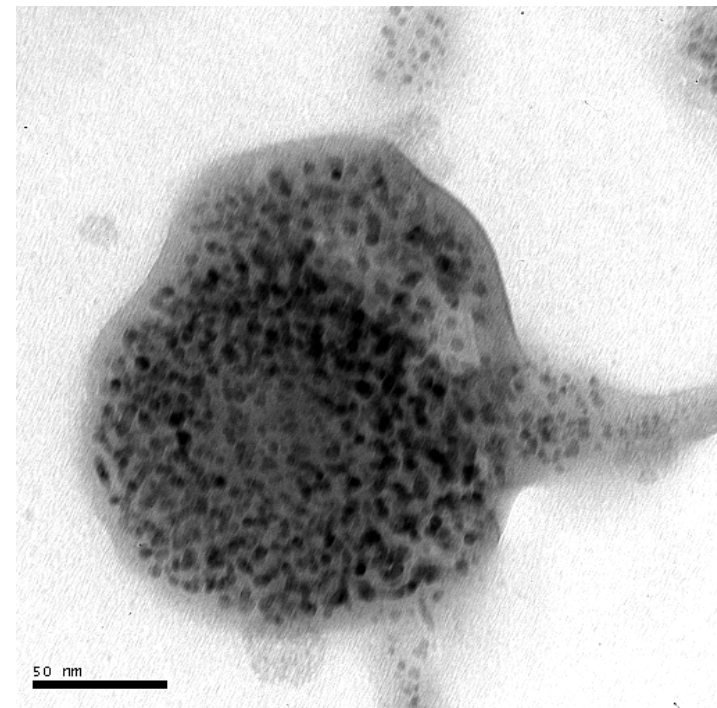
Specific Surface Area

	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 m²/g)

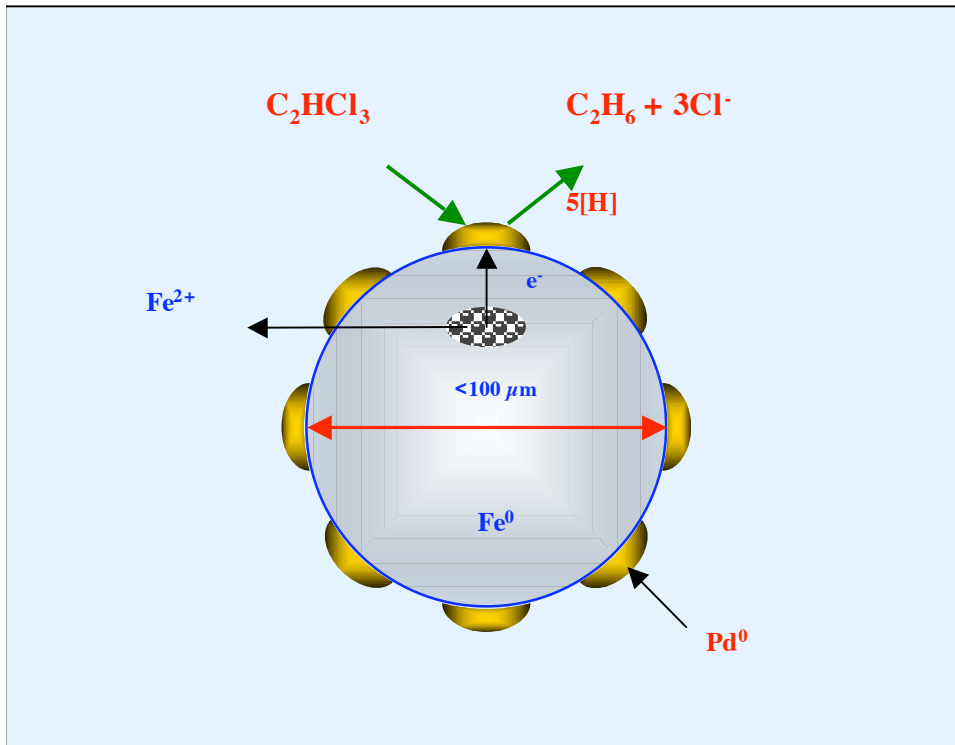


NanoPorous Fe
(150-250 m²/g)



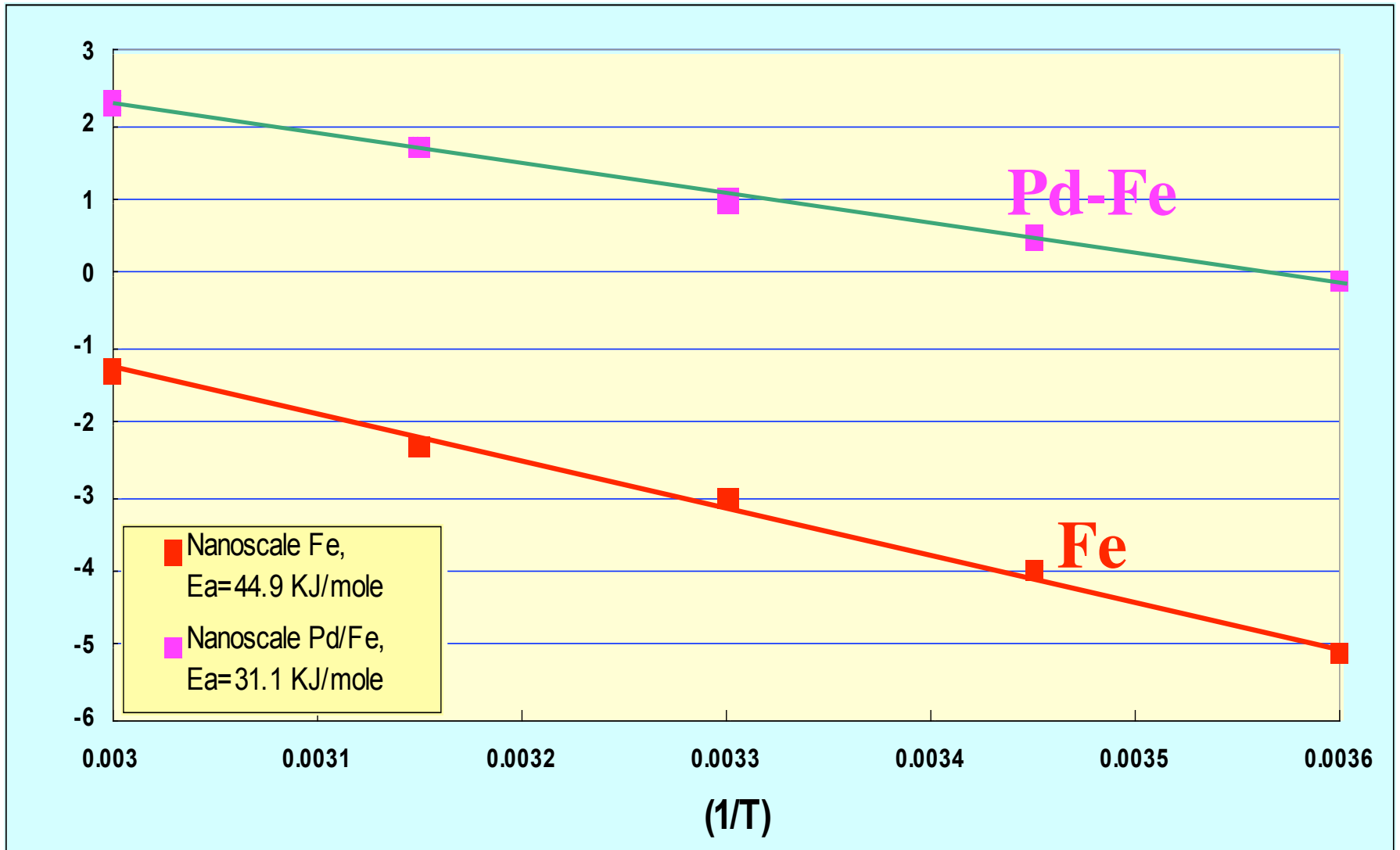
(Li and Zhang, 2005)

Bimetallic Structures



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

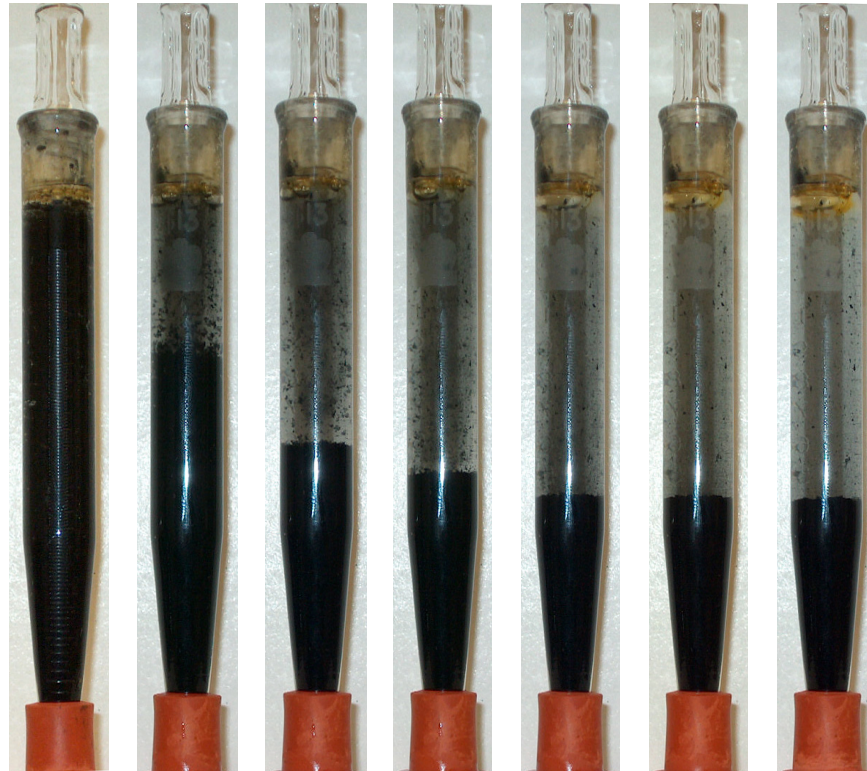
Fe vs Pd-Fe



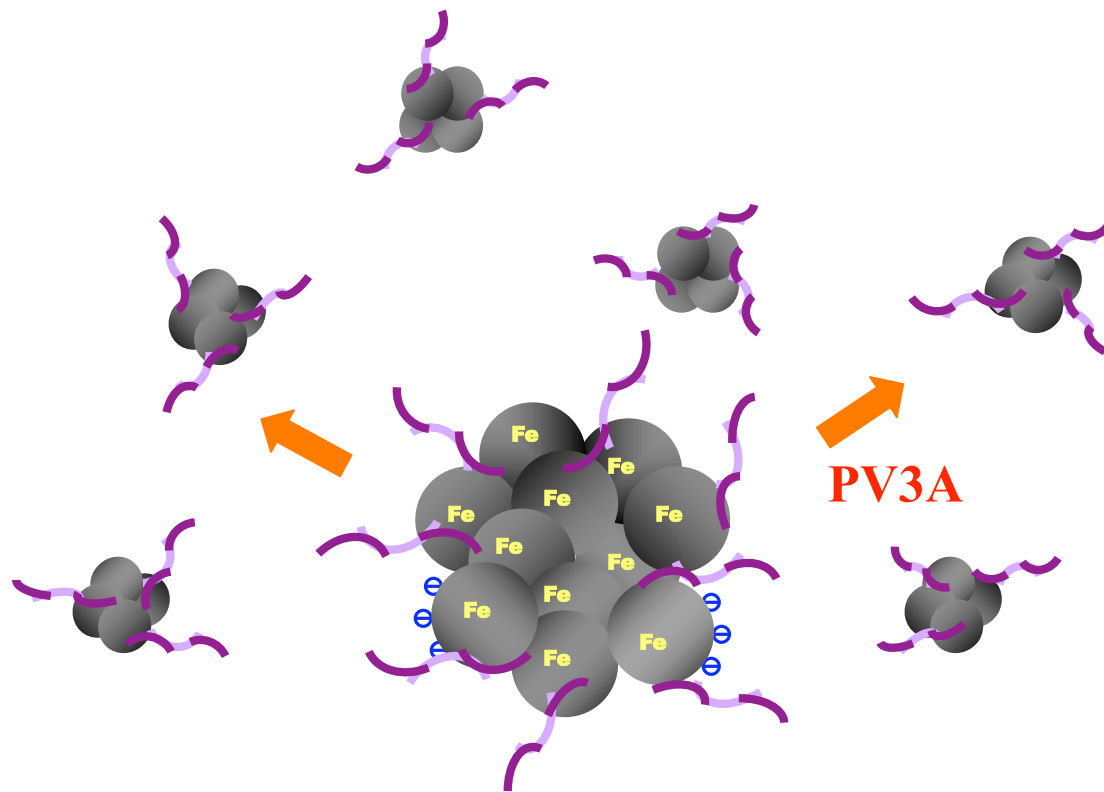
Dispersed nFe

Rapid Sedimentation

$n\text{Fe}^0$



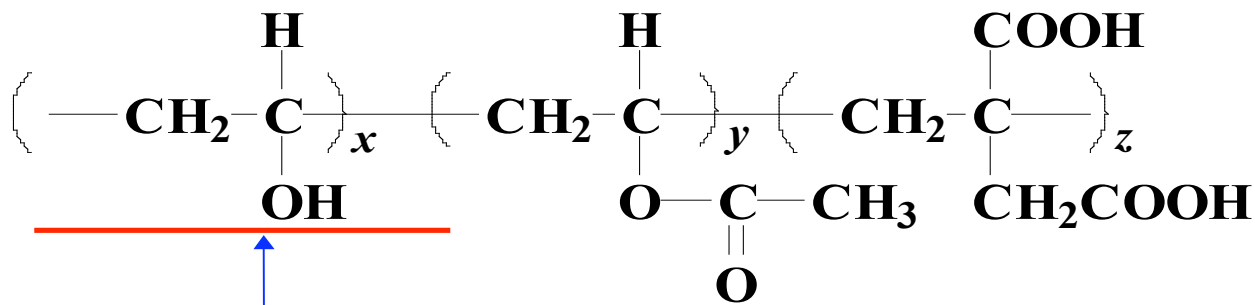
T (sec) = 0 20 40 60 120 300 1800



Dispersion of nano Fe

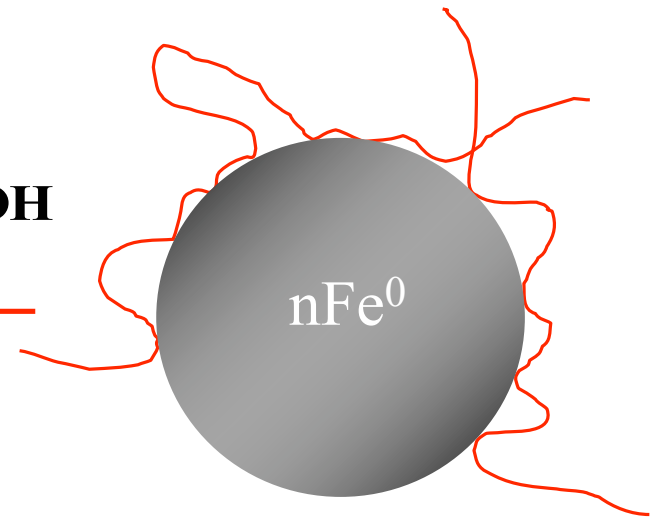
Dispersant

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

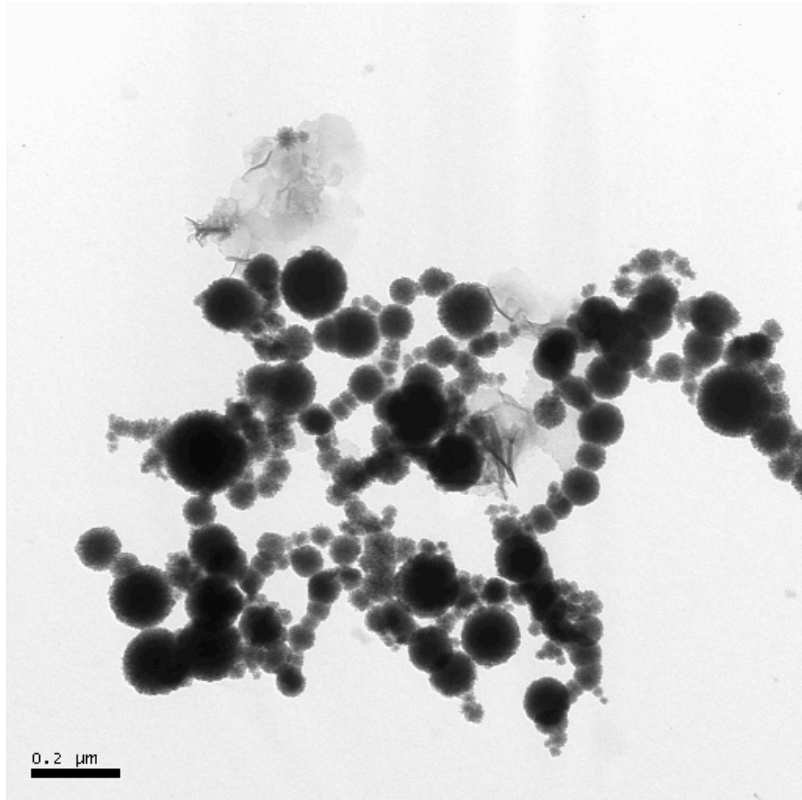


MW: 4,300~4,400
X:Y:Z = 97:2:1

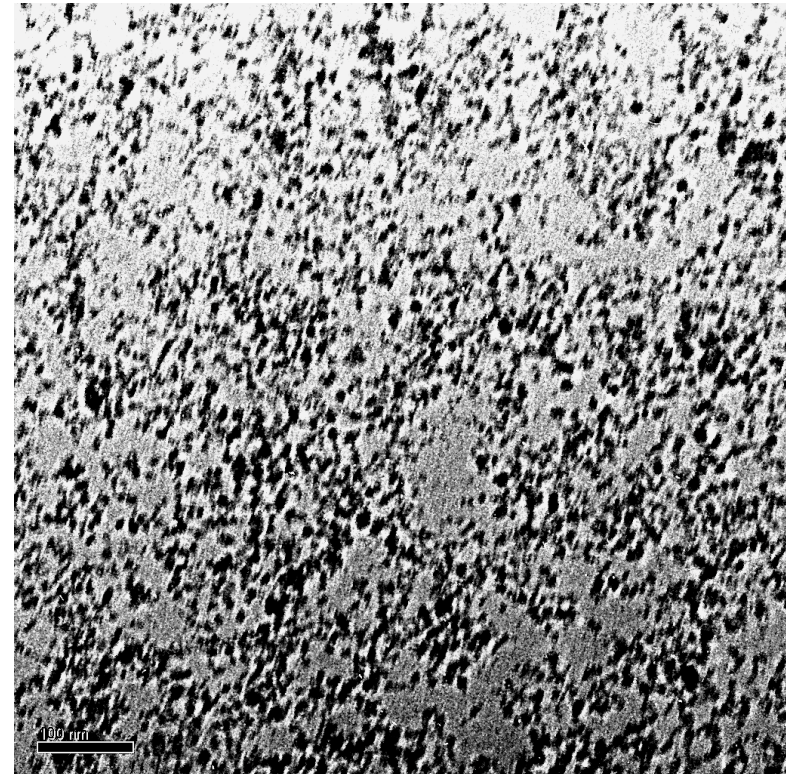
- Hydrophilic
- Stabilizing



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

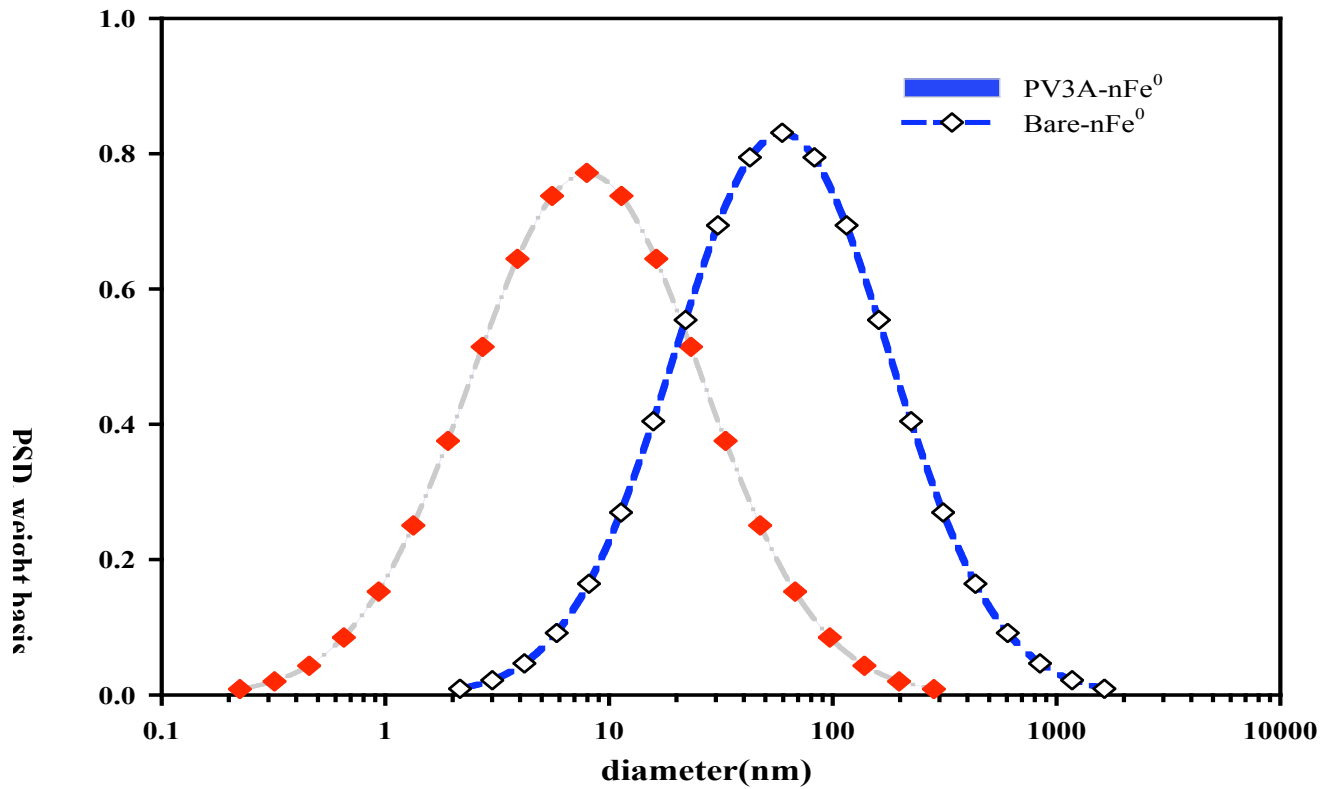


Before



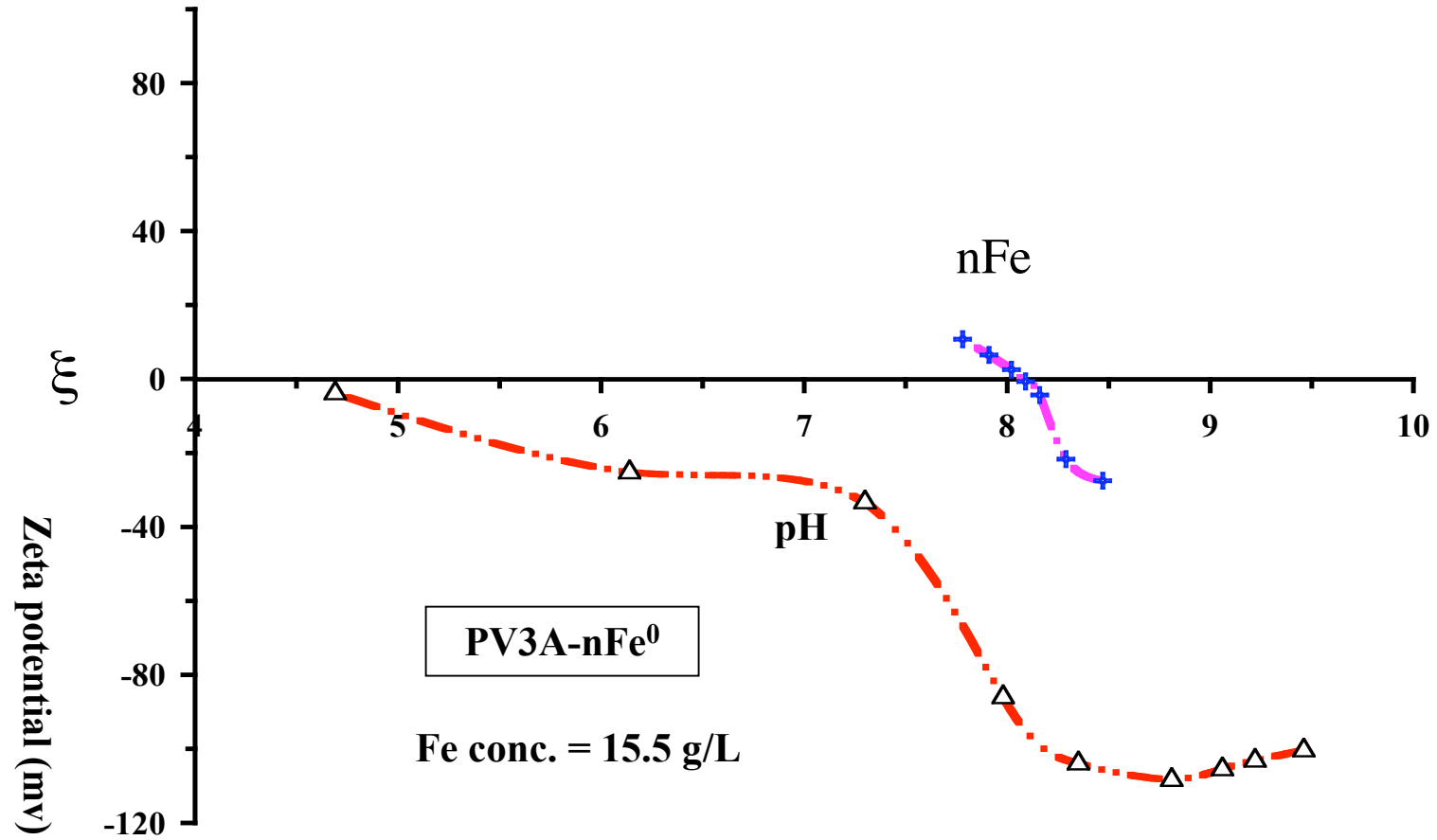
After

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

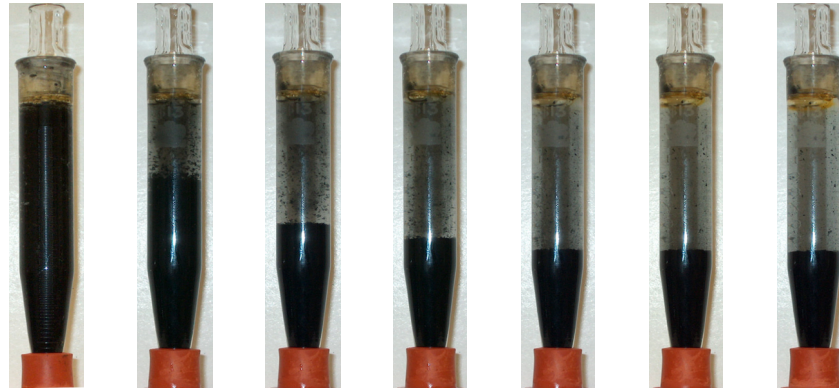


Particle Size

Surface Charge

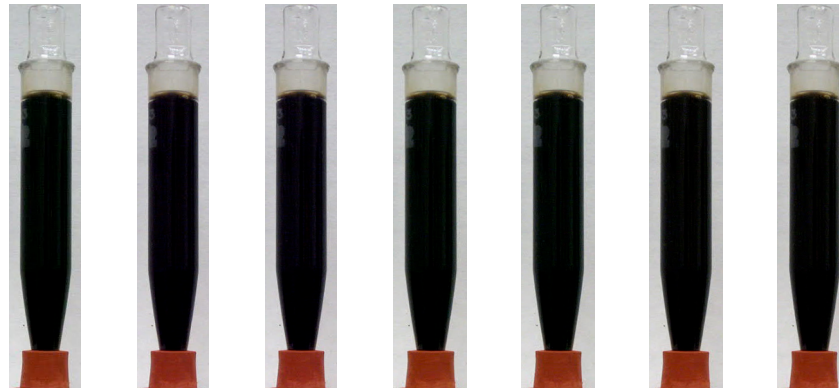


Stability Observations



Original-nFe⁰

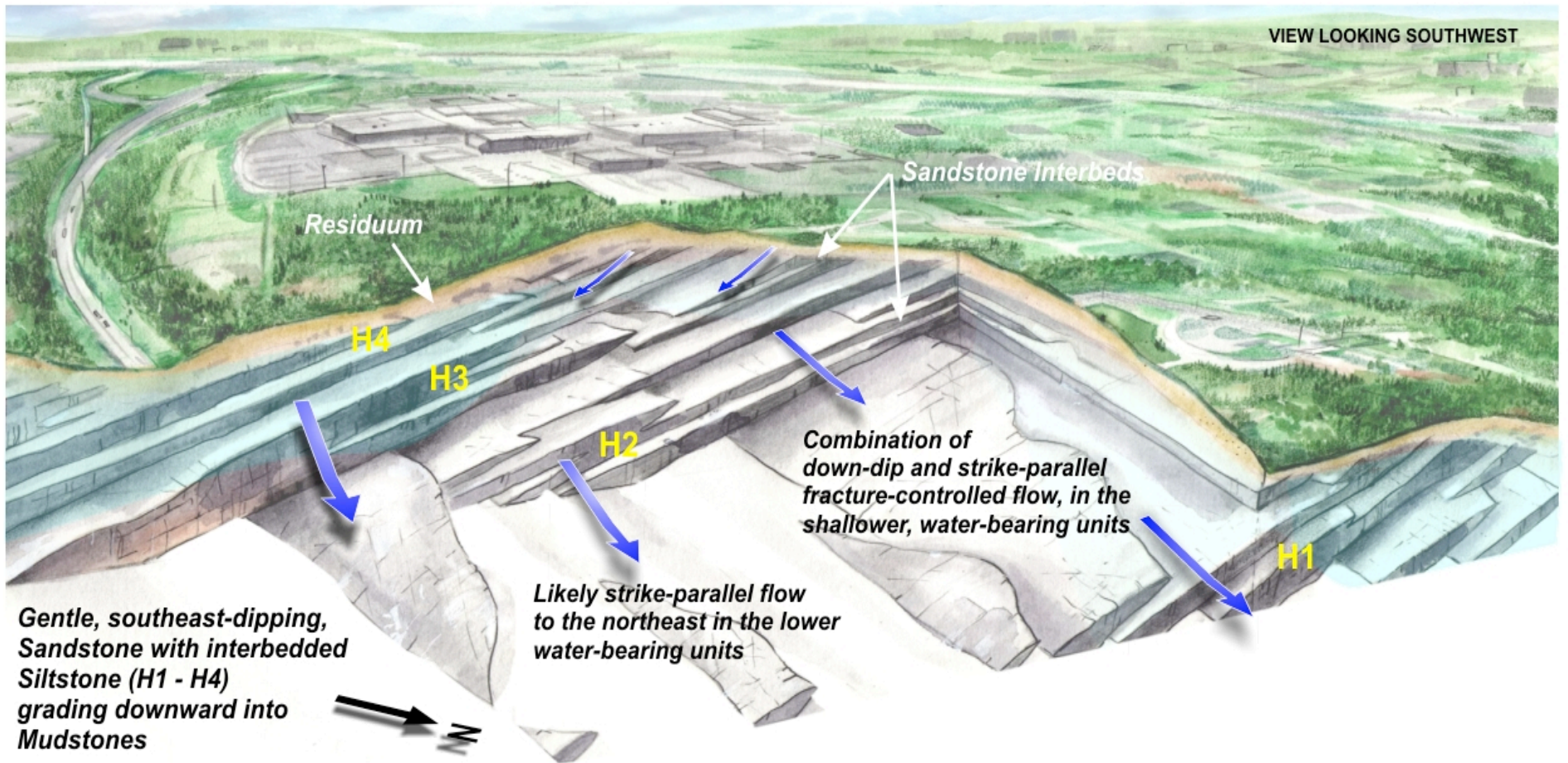
T (sec) = 0 20 40 60 120 300 1800



PV3A-nFe⁰

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

Applications

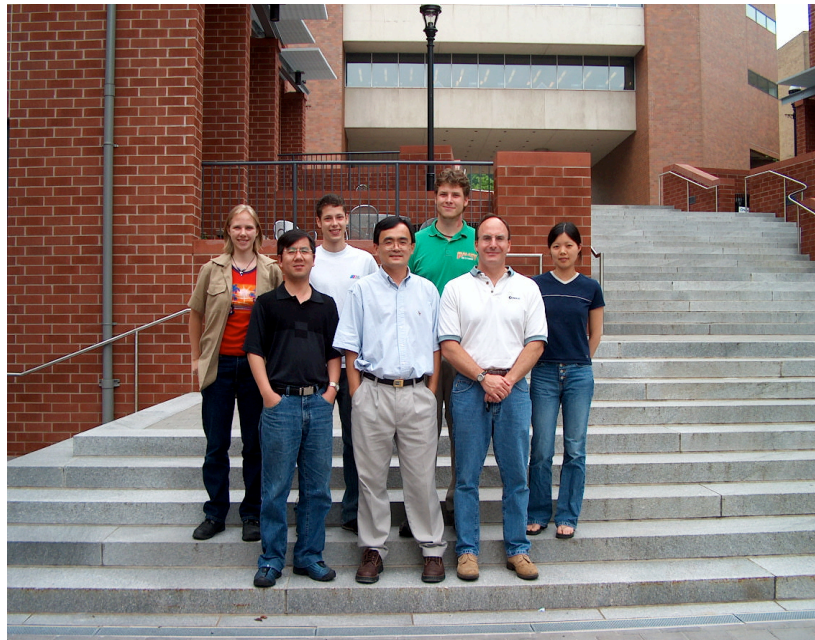


Acknowledgments

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