

Nanotechnology for Water Purification and Waste Treatment

Frontiers in Nanotechnology
US EPA Millennium Lecture Series
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LEHIGH
University

Acknowledgments

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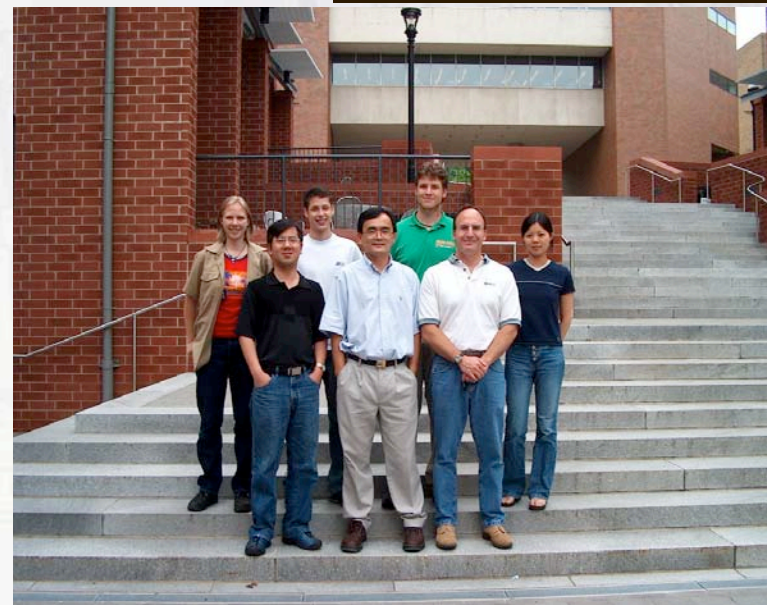
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Results (STAR) Program**

Grant # R829624

Nanotechnology is...

the art and science of manipulating matter at the atomic or molecular scale

Size

A billionth (10^{-9}) meter

Structure

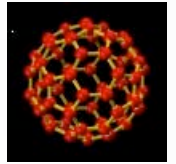
How things are put together -- arranged or assembled.

Novel properties

Novel and significantly changed physical, chemical, and biological properties

The ultimate goal of nanotechnology is to build essentially anything from scratch, atom by atom

C_{60}
(~ 1 nm)



Human
(~1 m)

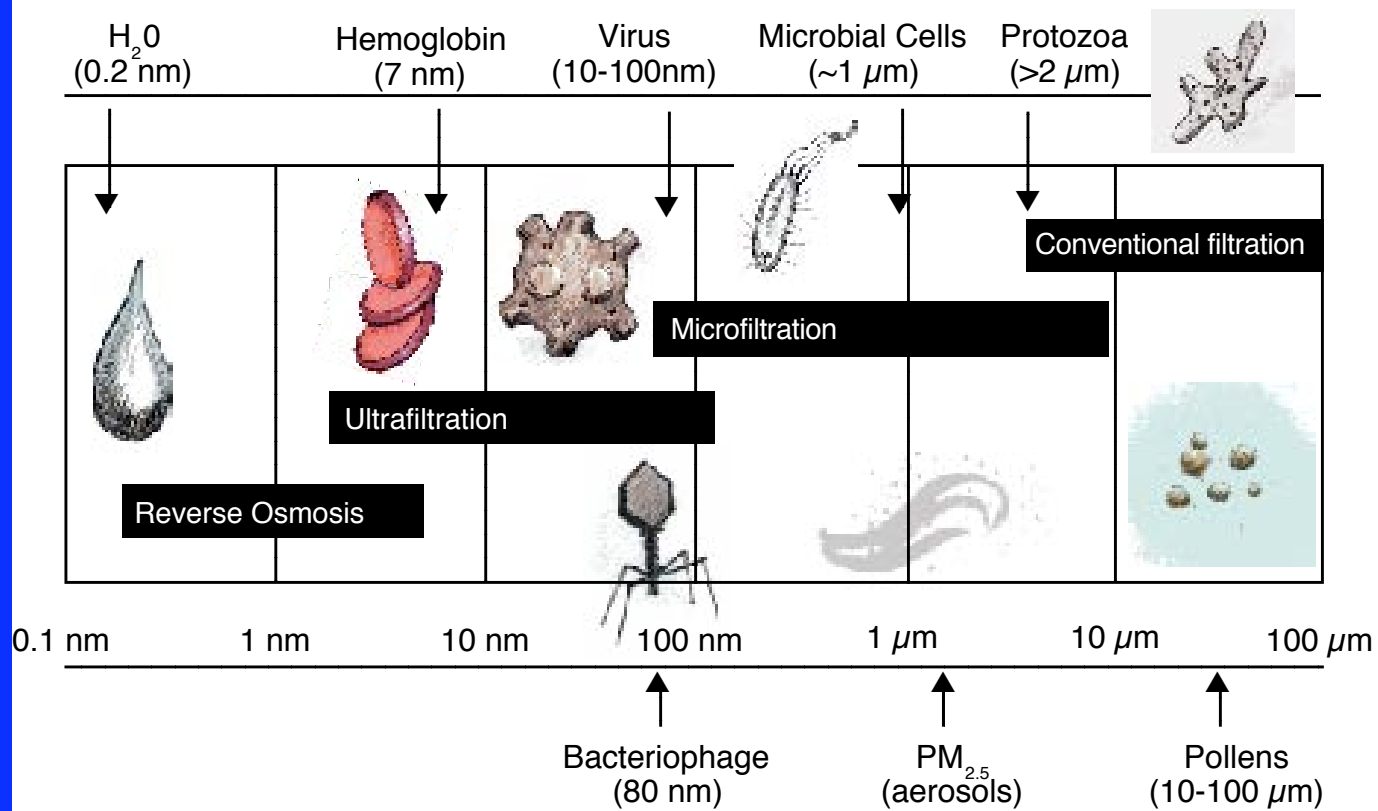


Moon orbit
(10^9 m)



Nanoscale has already been with our profession ...

Nanoscale Materials: Ultrafine Water and Air Contaminants?



Micropollutants

Nanopollutants

A Research Framework for NanoEnvironTech

Promote Applications
reactive to existing problems
or
proactive in preventing future problems.

Forecast Implications of
interactions of nanomaterials with the environment and
possible risks that may be posed by the use of
nanotechnology.

B.Karn, 2005, ACS

applications

- Sensors
- Treatment
- Remediation
- Green manufacturing
- Green energy

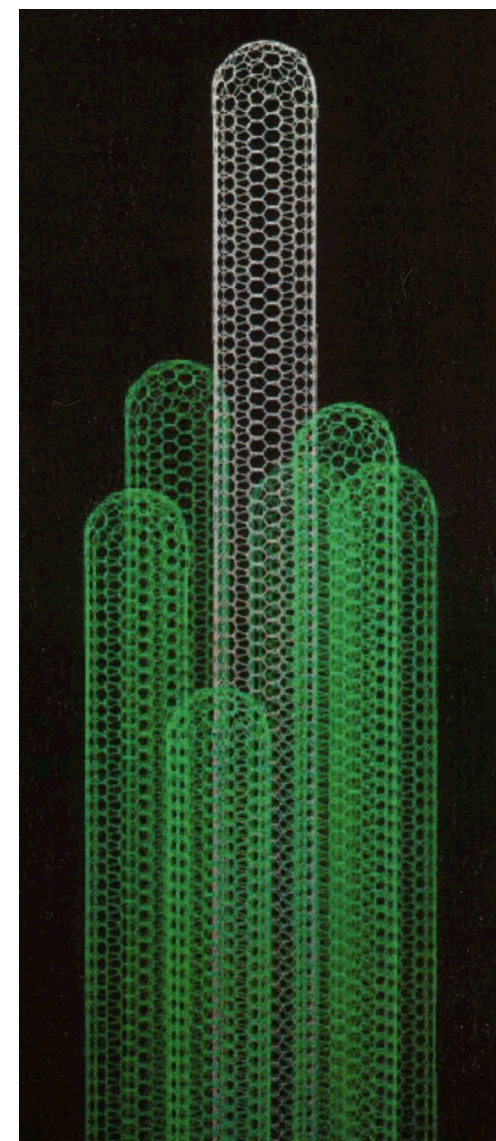
implications

- Natural nano processes
- Fate, transport, and transformation
- Lifecycle aspects
- Toxicology
- Exposure, bioavailability, and bioaccumulation

Nanotubes as SuperSorbent

SWNT for Dioxin Sorption (Long & Yang, 2001, JACS)

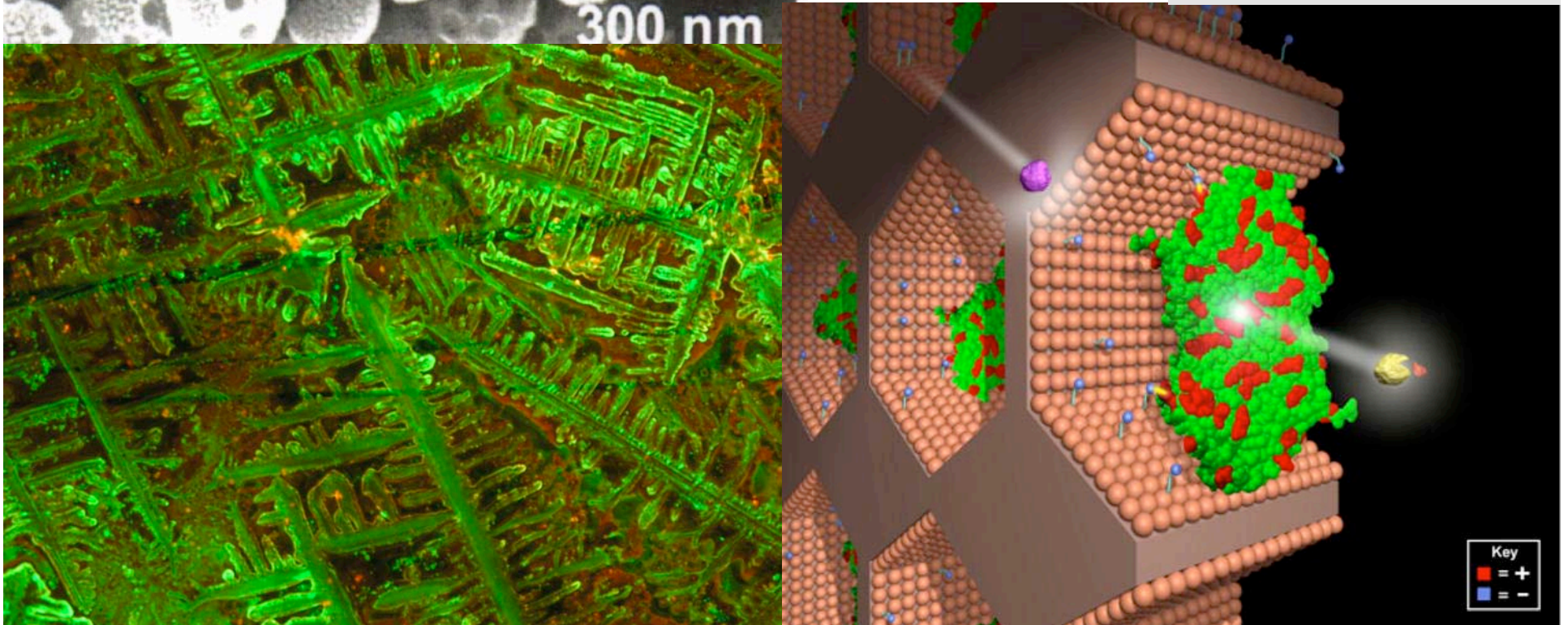
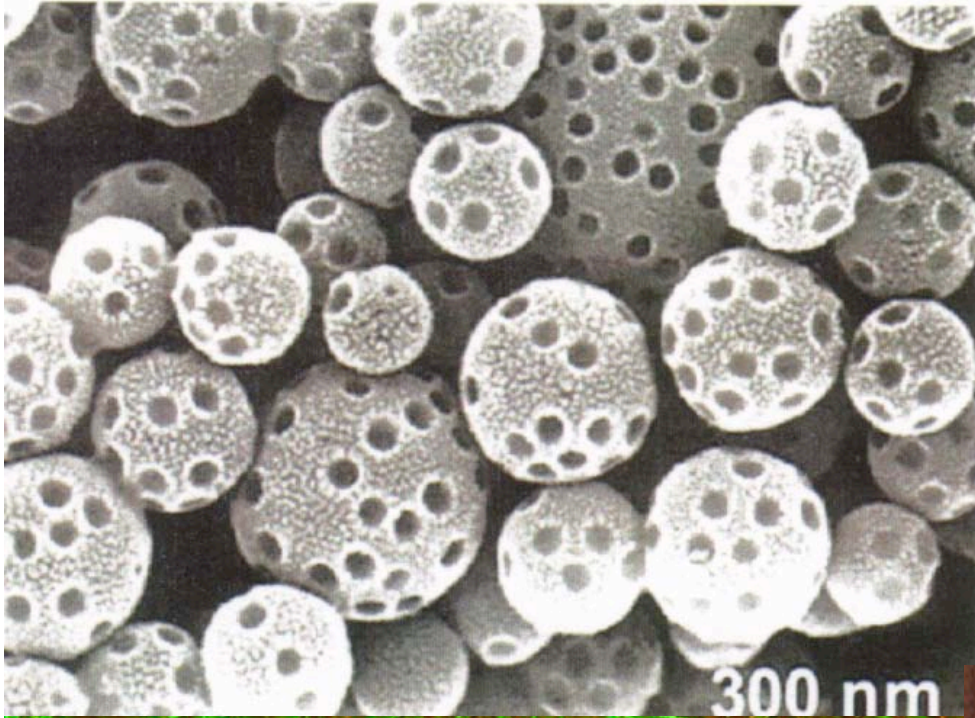
Sorbent	E (kJ/mol)	B (atm ⁻¹)
SWNT	315	2.7×10^{52}
Activated Carbon	119	1.3×10^{18}
γ -Al ₂ O ₃	47.9	4.5×10^5



Nanocomposites

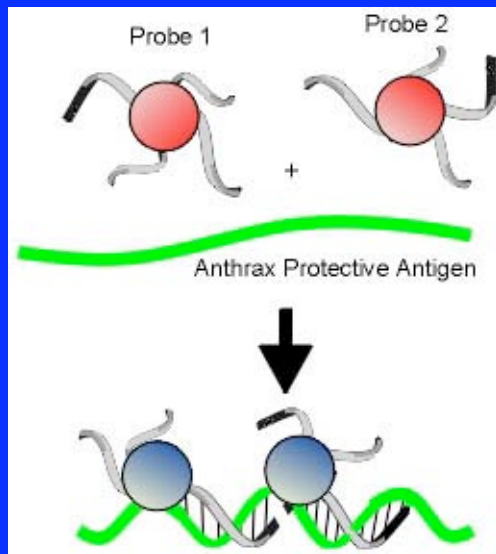
- Nanosorbents
- Nanoreactors

*Pacific Northwest
National Laboratory*

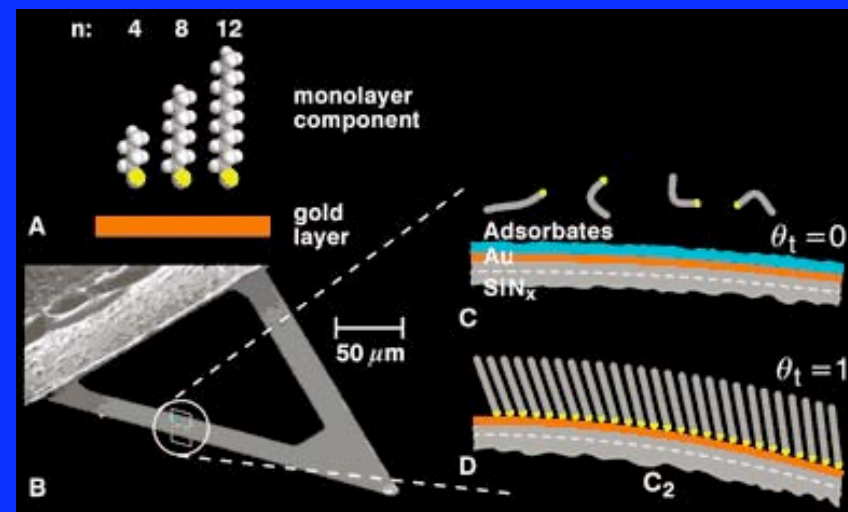


Sensing and Detection

Biological pathogens, heavy metals, organics, etc.



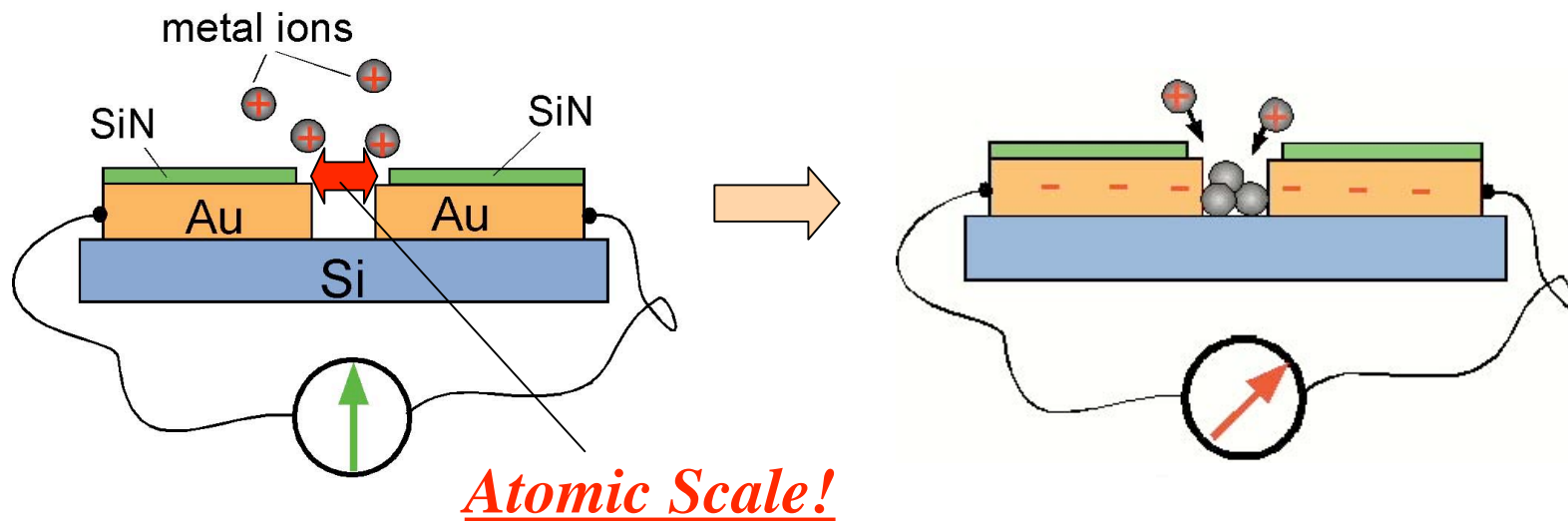
Chad Mirkin, Northwestern



IBM, Zurich

Nanocontact Sensor

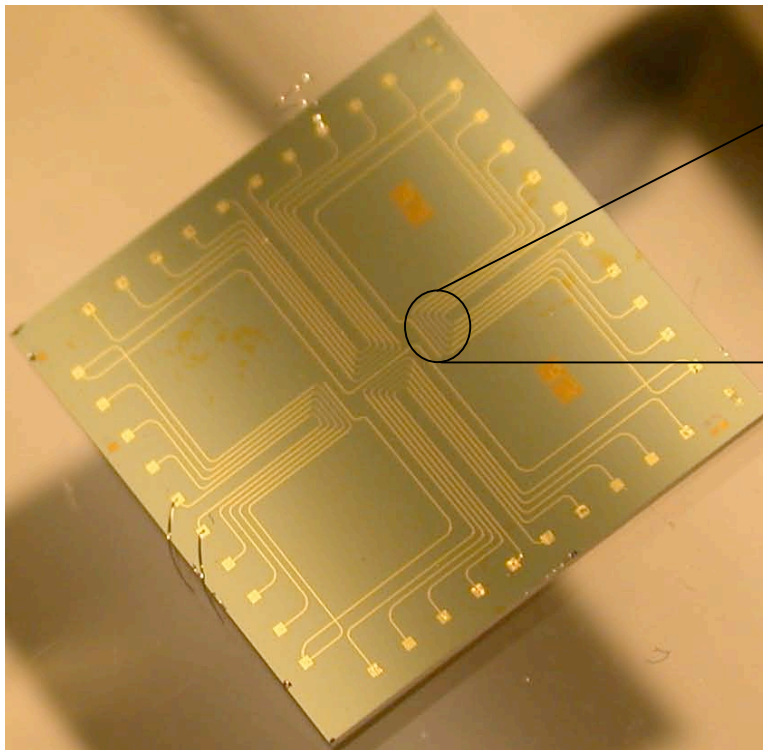
N.J. Tao (Arizona State)



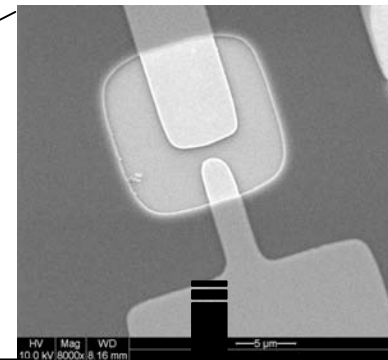
Sensitivity:

The electrodes are separated with an atomic-scale gap,
so **a few ions can be detected.**

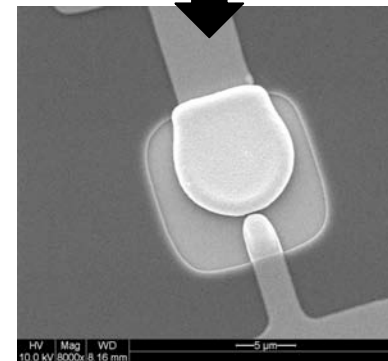
An Array of Atomic-Scale Gaps



$\text{Si}_3\text{N}_4 / \text{Au} / \text{SiO}_2 / \text{Si}$



before



after

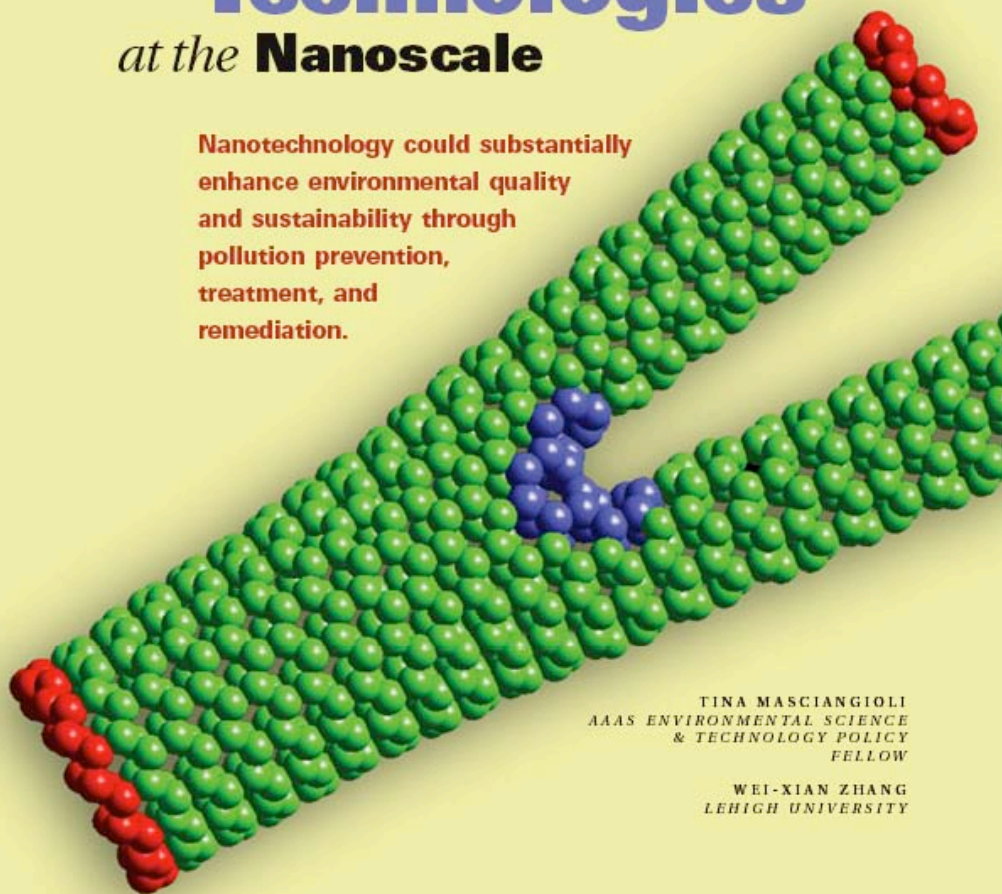
SEM images

N.J. Tao (Arizona State)

Environmental Technologies

at the **Nanoscale**

Nanotechnology could substantially enhance environmental quality and sustainability through pollution prevention, treatment, and remediation.

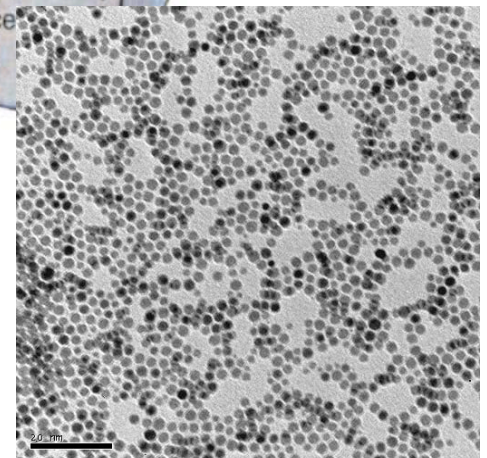
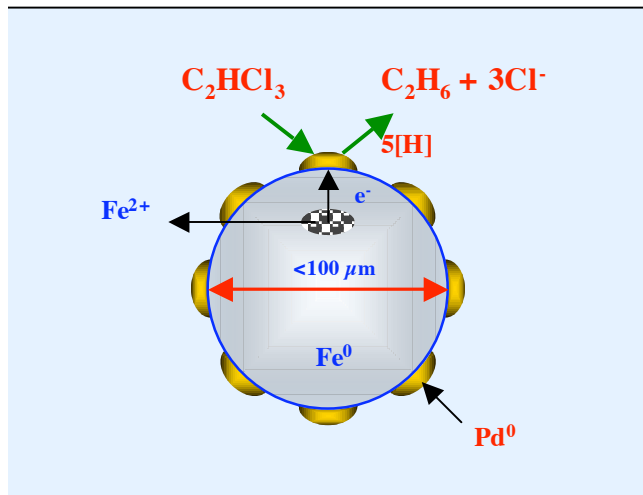
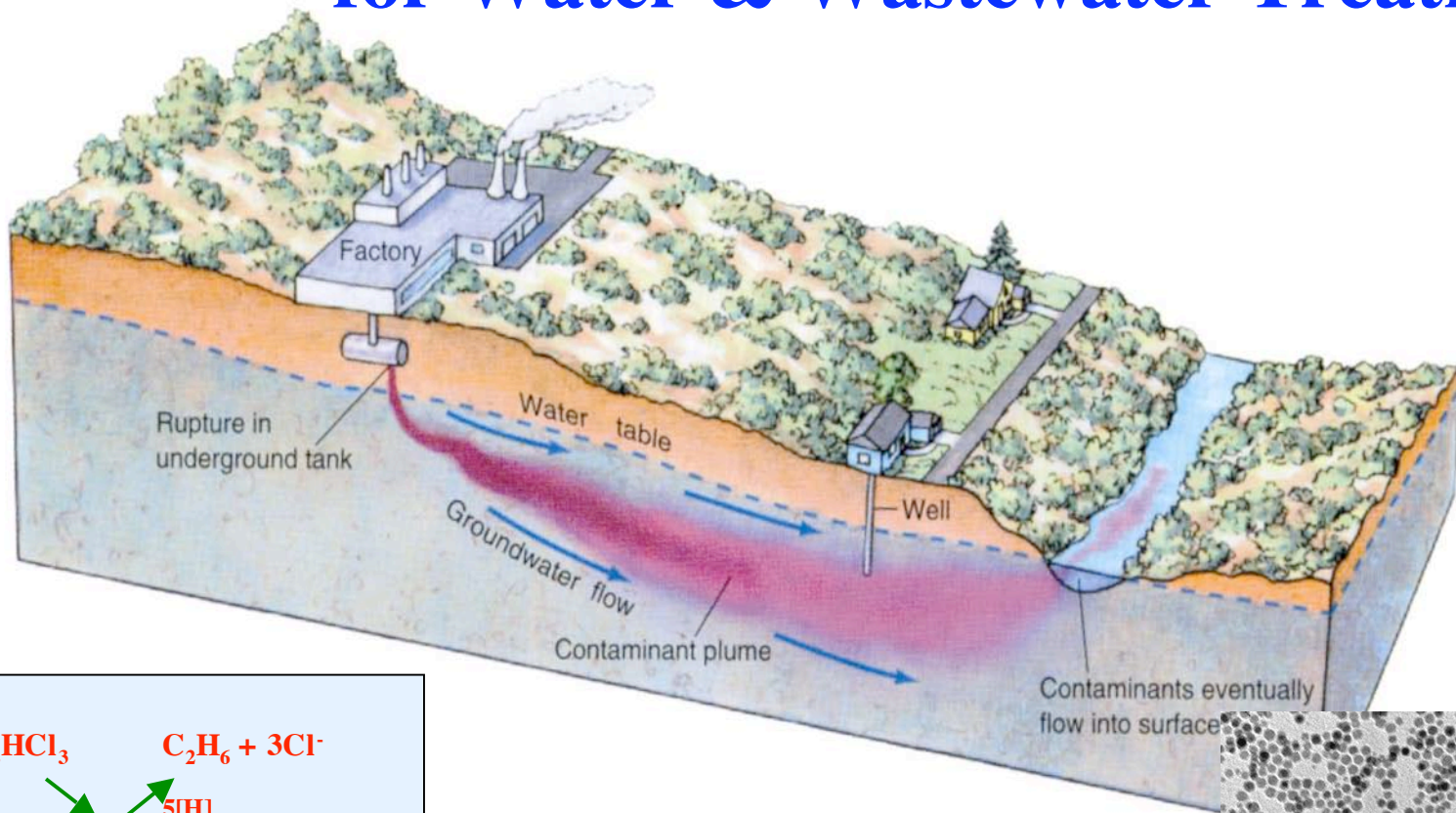


TINA MASCIANGIOLI
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FELLOW

WEI-XIAN ZHANG
LEHIGH UNIVERSITY

ES&T Feature Article
March 1, 2003
ES&T, 2003, 37 (5),
73A - 112A

Iron Nanoparticles for Water & Wastewater Treatment





A desk with a lamp, a ruler, and a pen over a blueprint. The background is a brick wall. The desk is white, and the blueprint is spread out. A lamp is in the top left corner. A ruler and a pen are in the bottom right corner. The text is in the center of the blueprint.

Advantages of Nano Remediants

Highly mobile

Highly Reactive

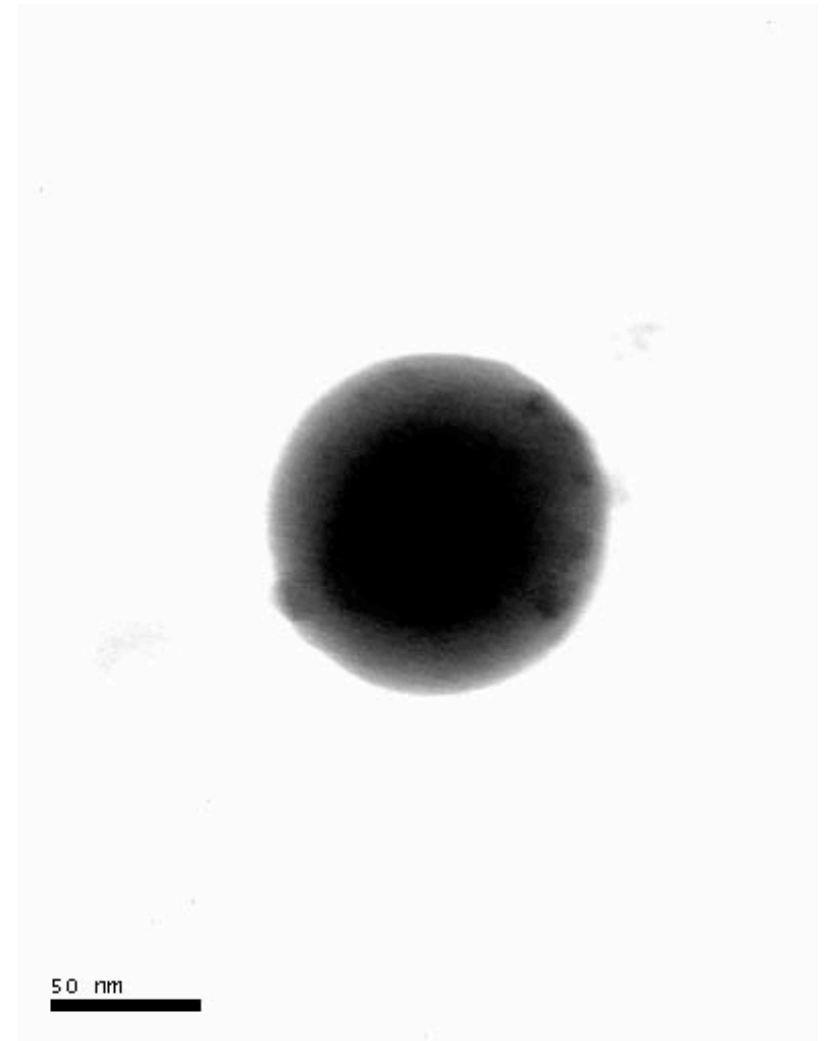
Shorter cleanup time & lower cost

A little history ...

- **Summer 1995 - original concepts**
- **July 1996 - Sodium borohydride method**
- **April 1997 - 1st paper (ES&T)**
- **Summer 2000 - 1st pilot test**
- **> 15 projects so far in U.S.**

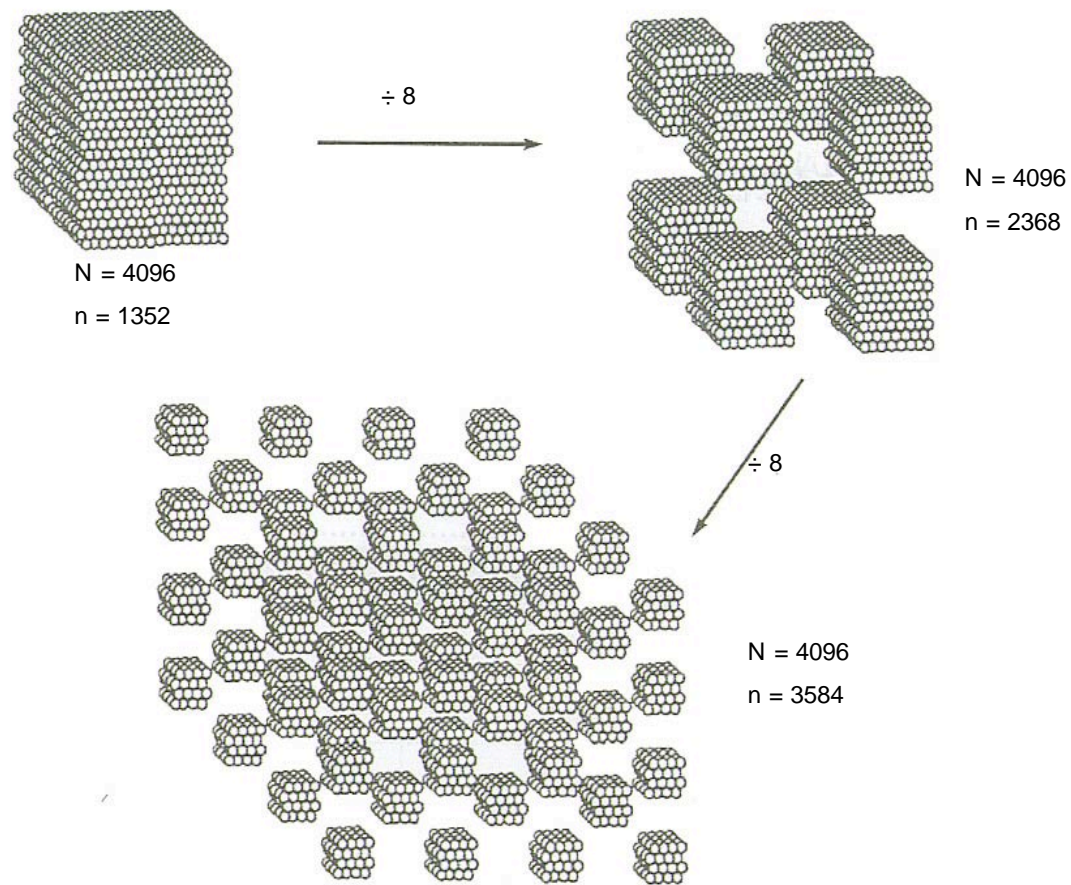
Nano Iron

- Effective reductant
- Widely used in PRBs
- Nontoxic
- Cheap

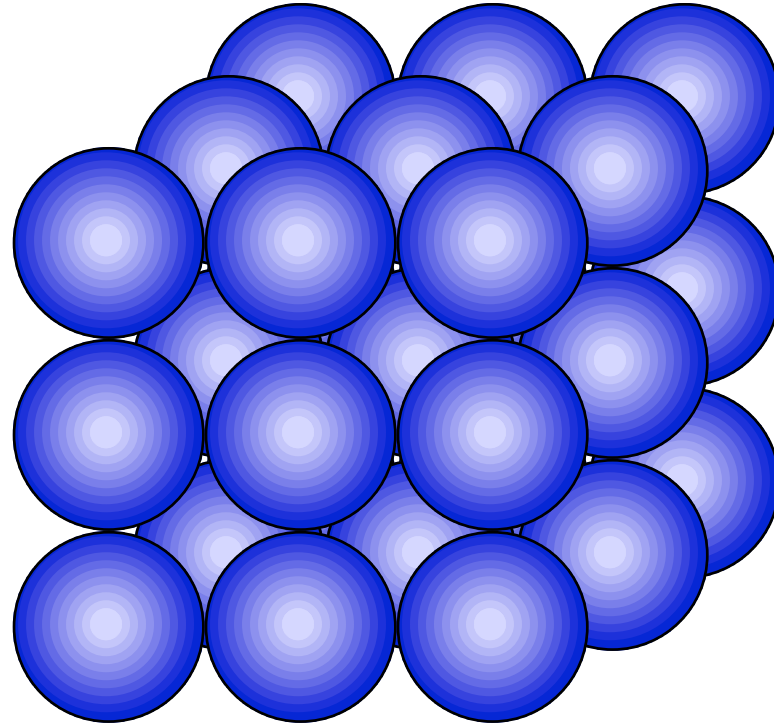


Key property - Efficient Electron Donor

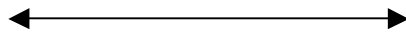
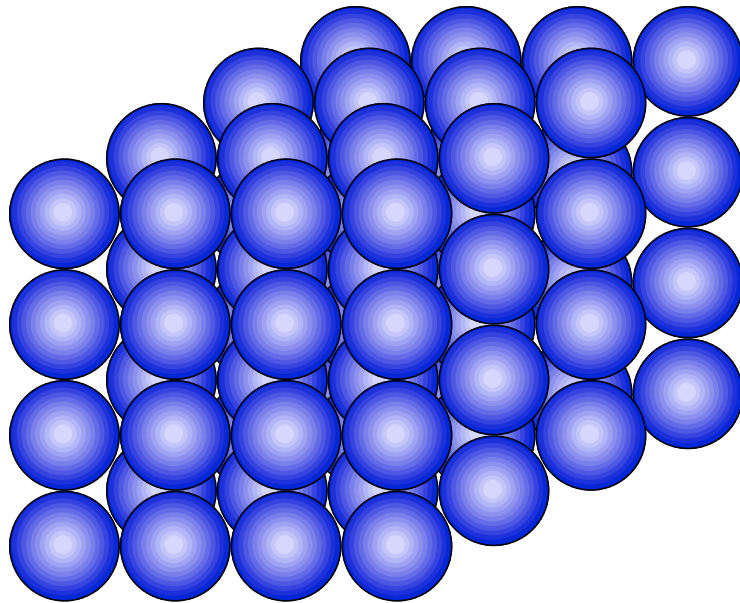




N: number of total atoms, n: number of surface atoms



27 Fe atoms - 26 (93.3%) on surface



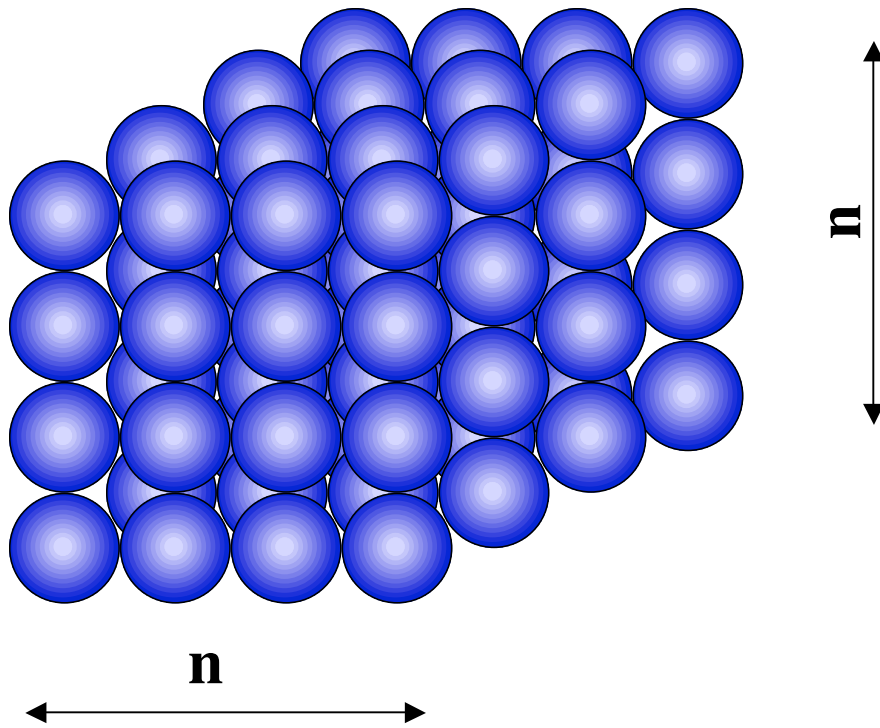
1 nm



1 nm

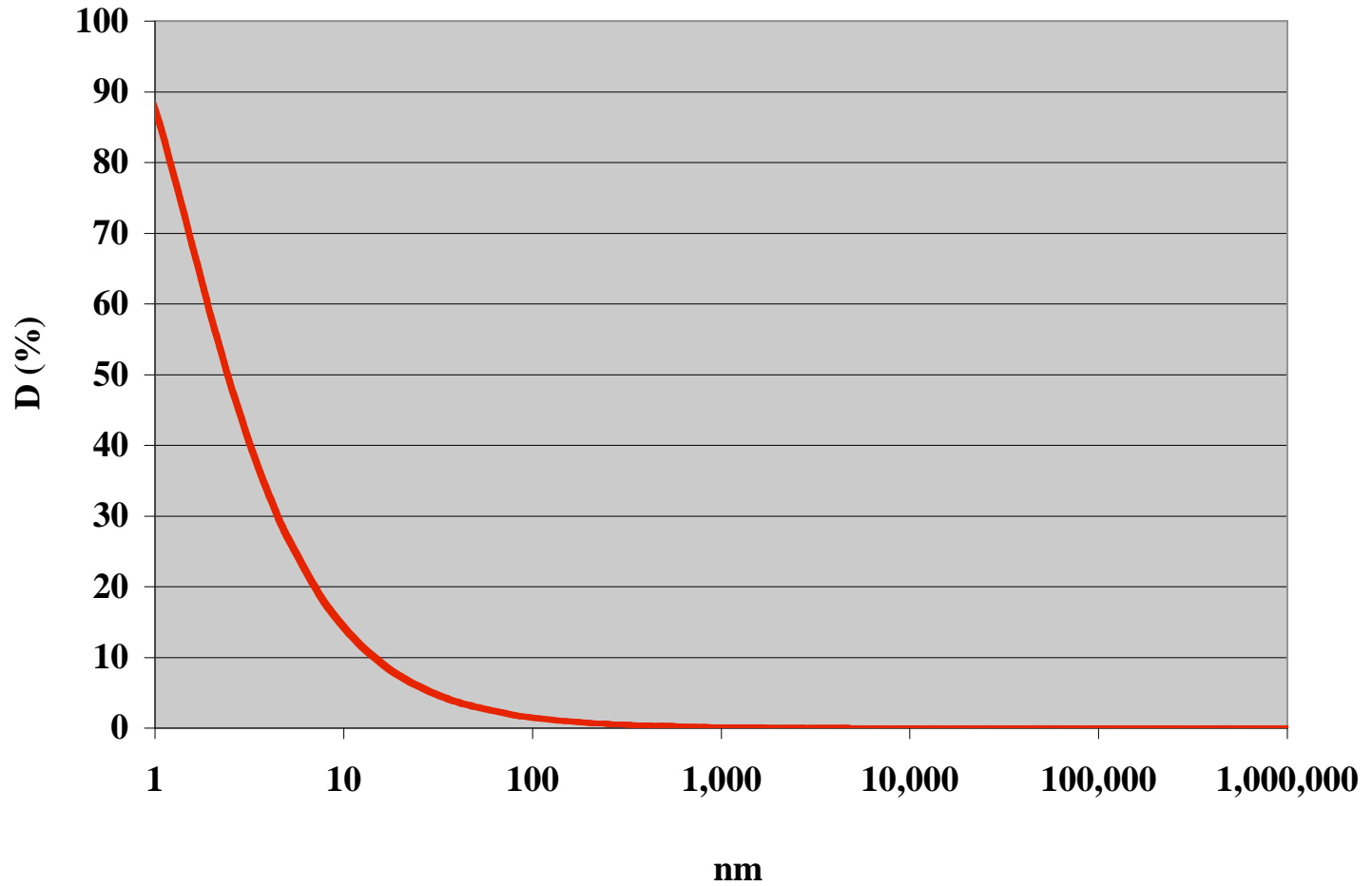
**A Cube of 64 Fe atoms
56 (87.5%) on surface**

Surface Atoms



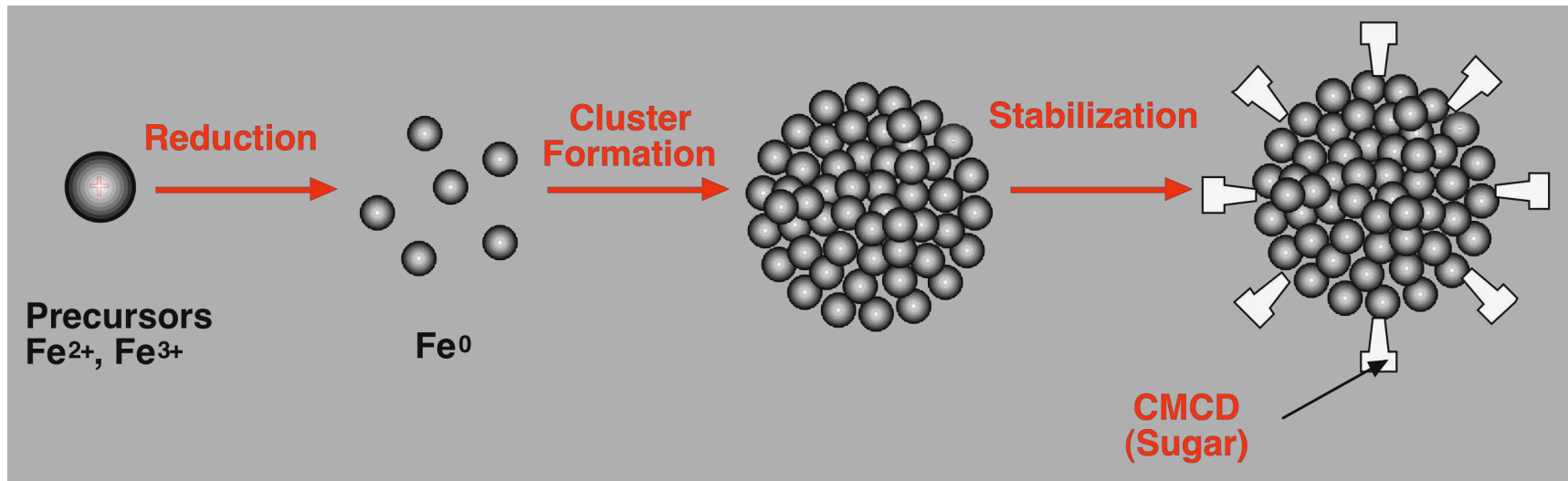
$$D = \frac{\text{number of surface atoms}}{\text{total number of atoms}} = \frac{2n^2 + (n-2)[n^2 - (n-2)^2]}{n^3} \cdot 100$$

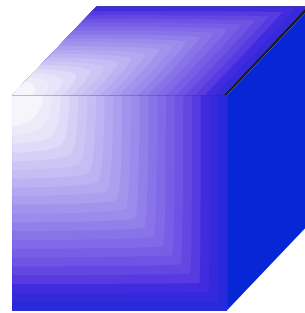
% Atoms on Surface



Calculations for Fe

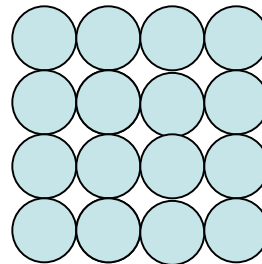
Methods of Synthesis





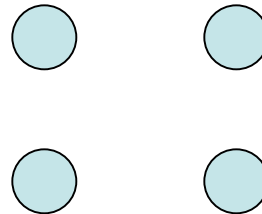
Block
materials

Top-down
↓



nanomaterials

Bottom-up
↑



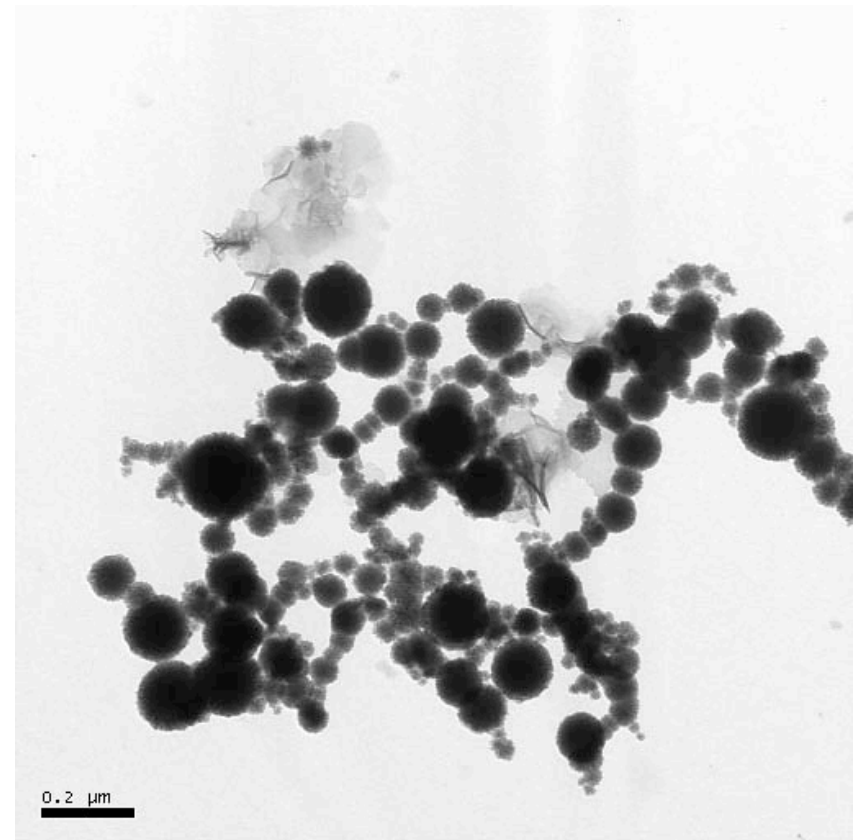
Atoms or
molecules

Nano Iron for Remediation

- Materials Chemistry
 - Synthesis
- Environmental Chemistry
 - Contaminant degradation
- Geochemistry
 - Fate and transport

Properties of Nano Fe

- **Size range:** 10-100 nm
- **Mean Size:** 60 ± 15 nm
- **Specific surface area**
 - 10-50 m²/g
- **Zeta potential**
 - 10 to -30 mV



Properties of Nano Fe

Nominal Reaction Rate (Ω)

0.1-1 mg TCE/g nanoFe/hour

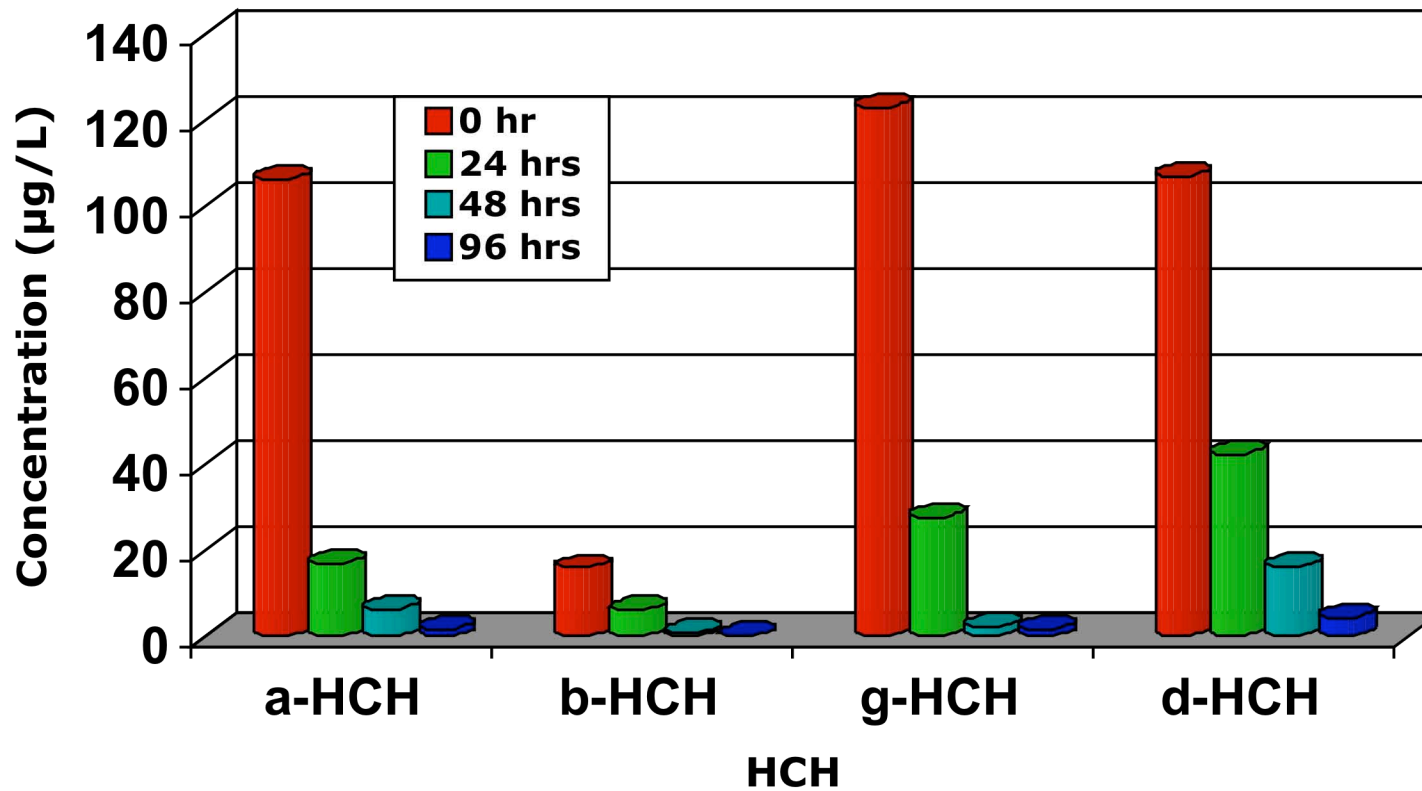
@ 22°C

@ 1-100 mg/L TCE

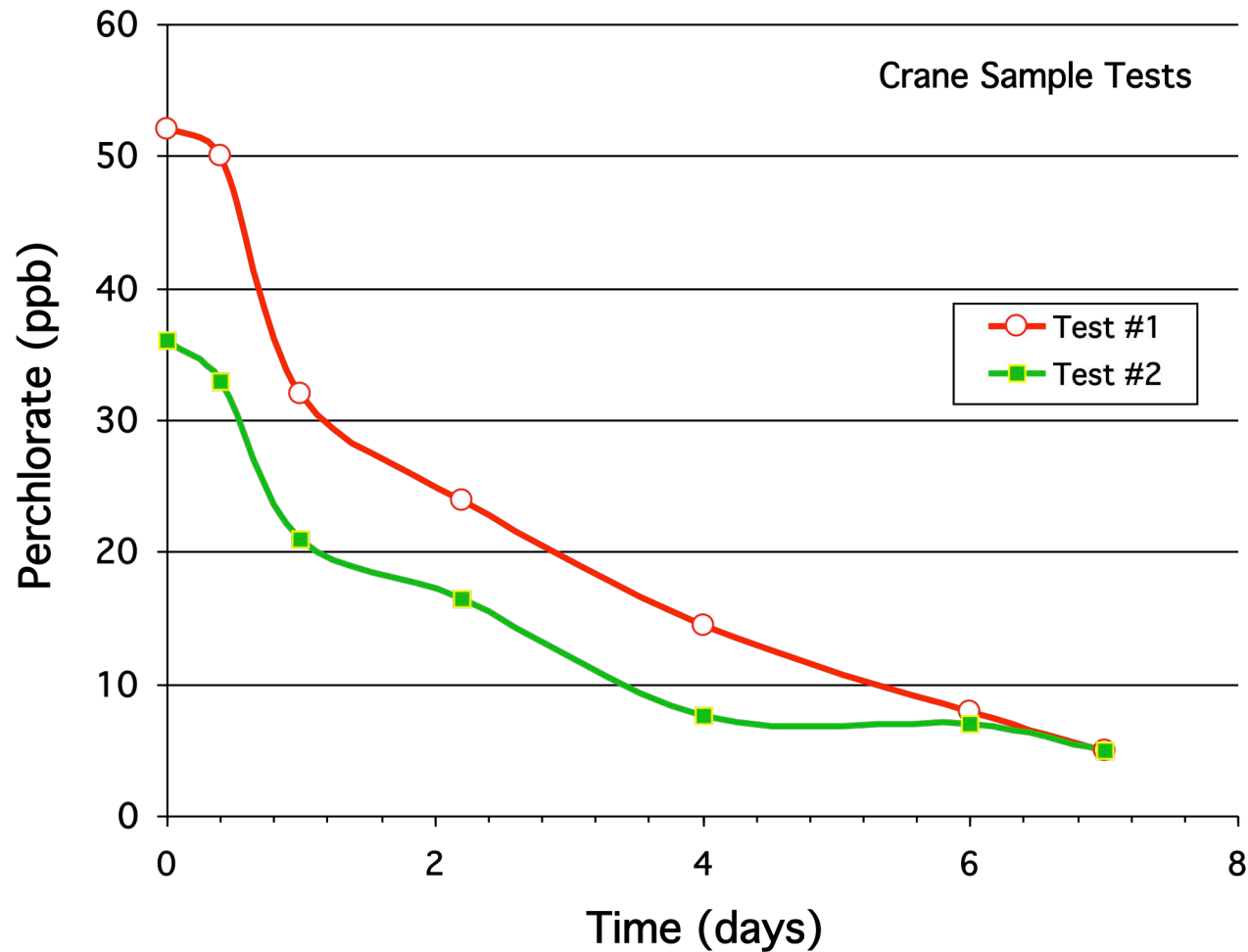
@ pH=7

Lindane (HCH, $C_6H_6Cl_6$)

(Sample from Jacksonville, FL)



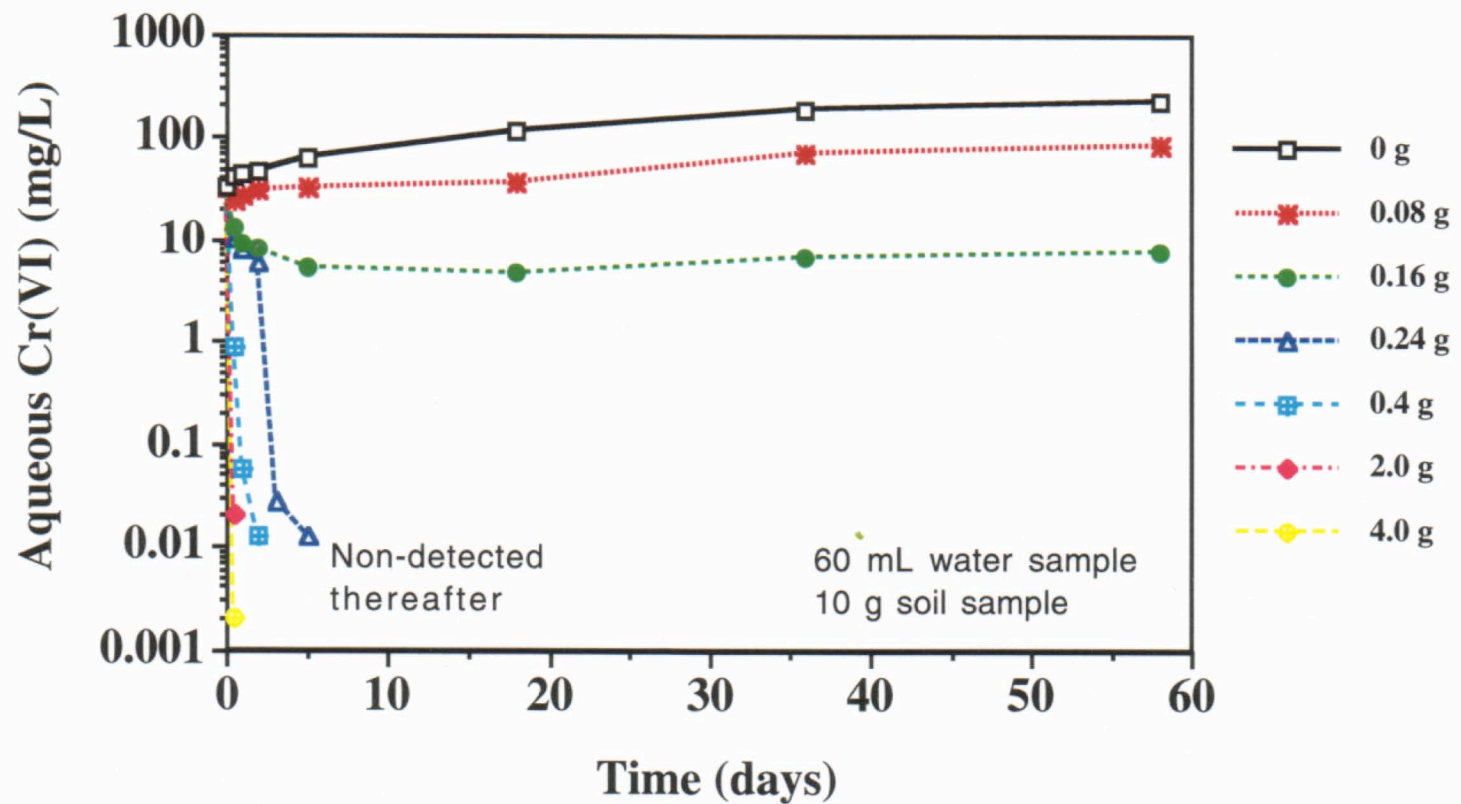
Perchlorate (ClO_4^-) (Sample from Phoenix, AZ)



Cr(VI) Reduction

COPR Samples from an industrial site in NJ

Aqueous Cr(VI) - 43.38 mg/L, Soil Cr_T - 7,725 mg/kg, pH = 11

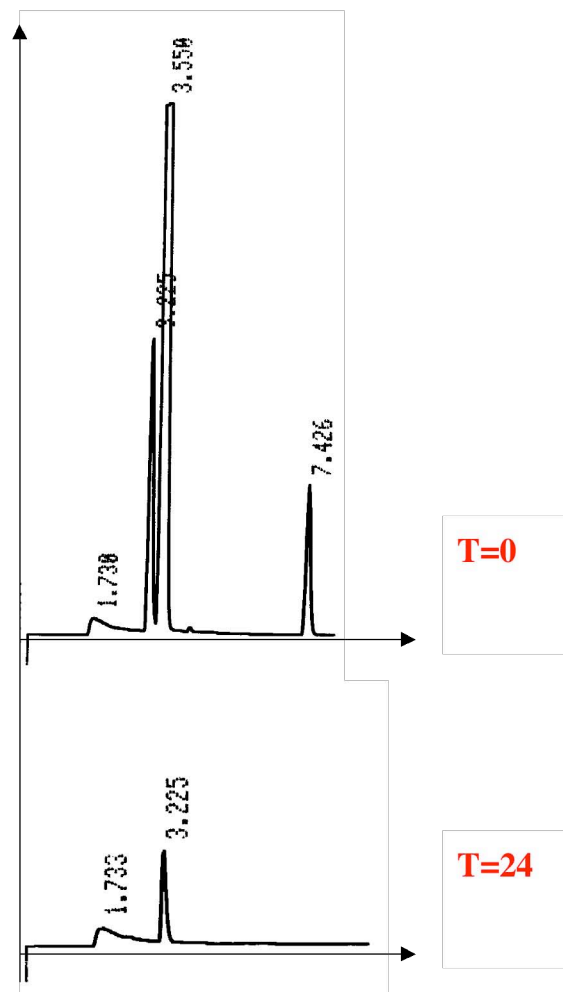


Cr(VI) Reduction/Immobilization

	Micro Fe (~10 μm)	Nano Fe (~50 nm)
Rate	0.0063 mgCr/m²/min	0.157±0.018 mgCr/m²/min
Capacity	1.53-1.75 mg Cr/g Fe	84.0-109.3 mg Cr/g Fe

Carbon Tetrachloride (CT)

(CCl₄, 14.5 mg/L, S. Charleston, WV)

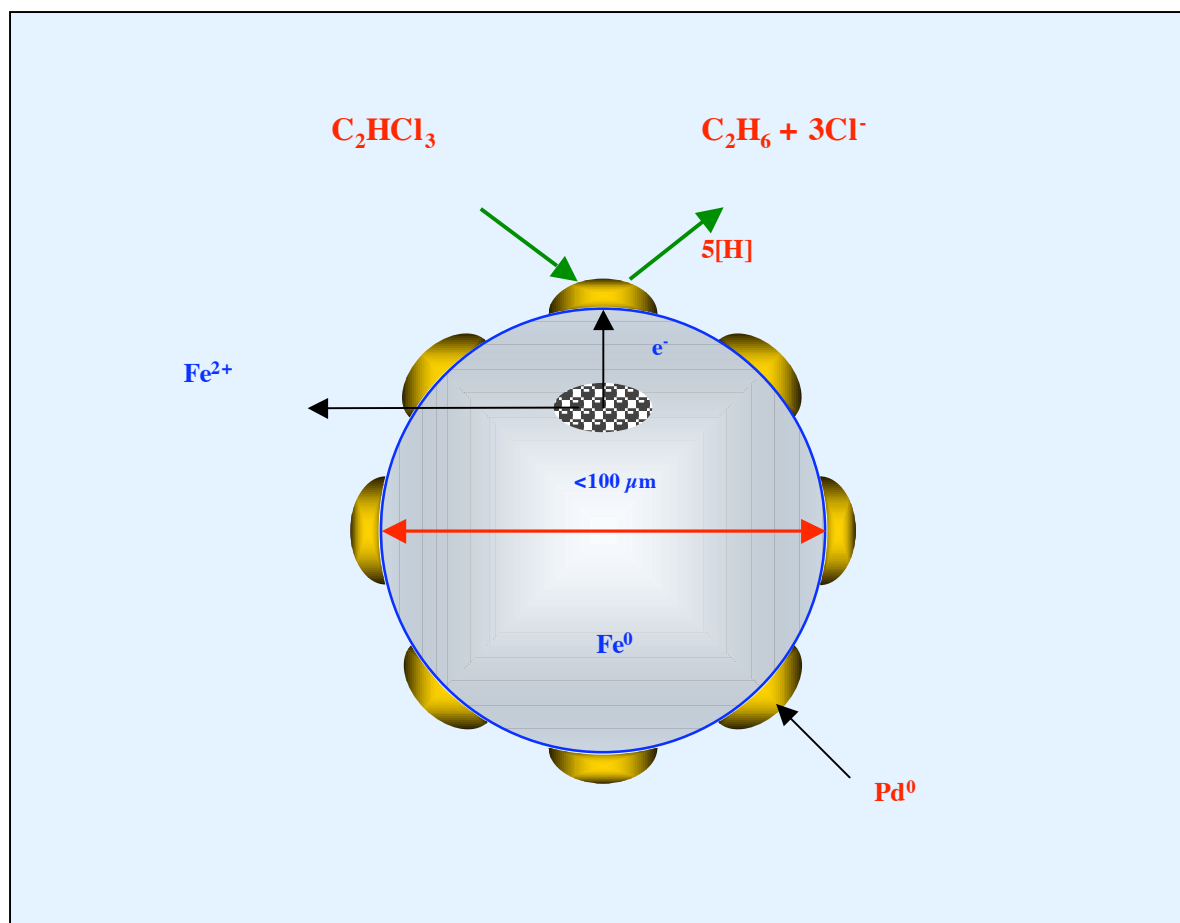


Contaminant Degradation

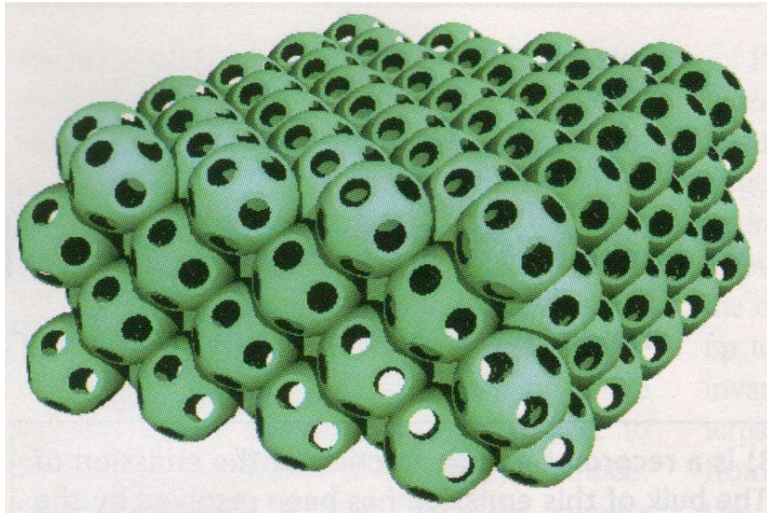
Chlorinated Methanes	Cr(VI)
Chlorinated Ethenes	Pb(II)
Chlorinated Ethanes	Ni(II)
Chlorinated Benzenes	Cd(II)
PCBs	Perchlorate
Lindane (HCHs)	As

> 100 compounds tested at Lehigh so far

Enhance Activity by Catalysts



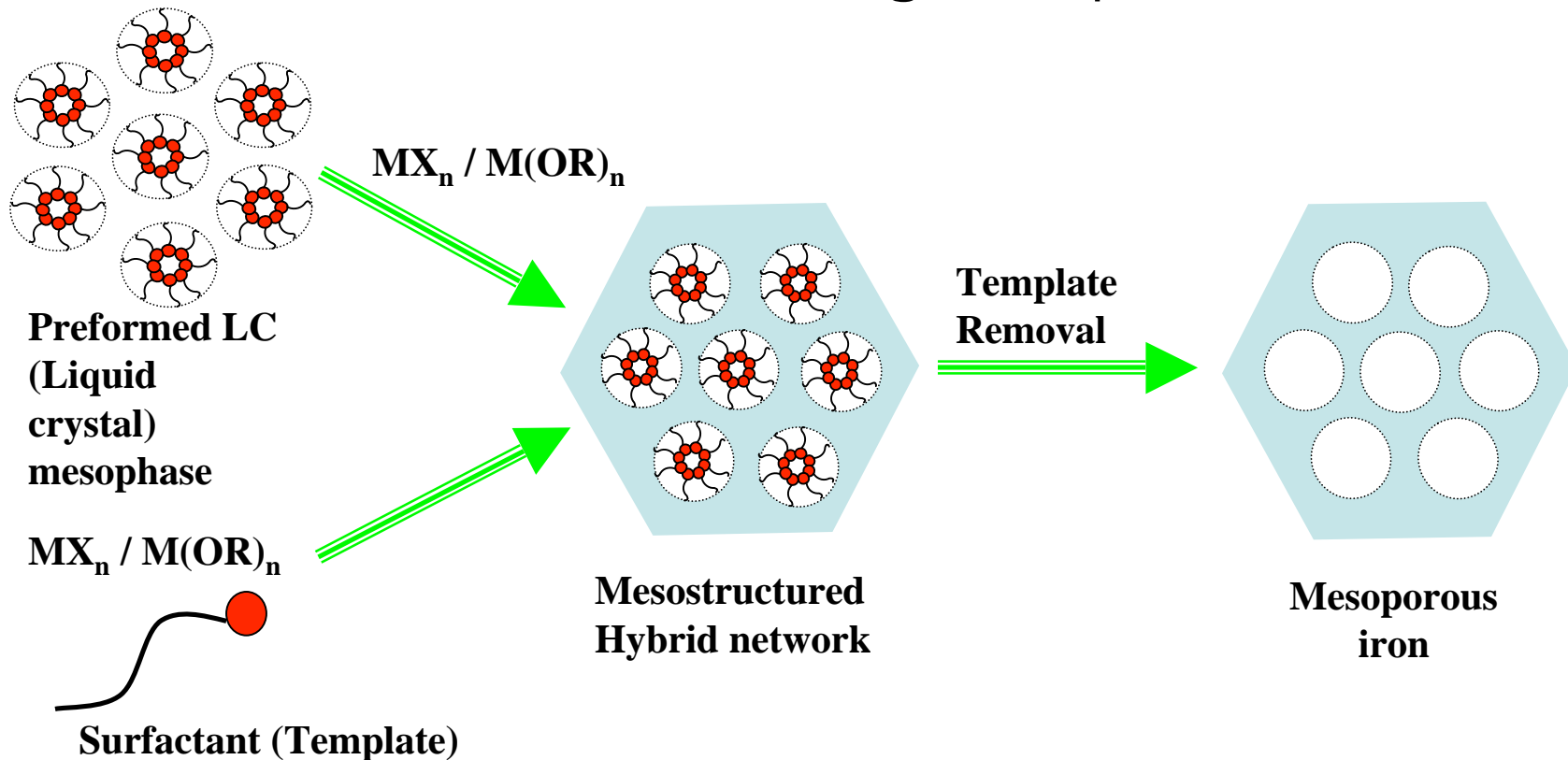
Enhance Activity by Porous Nanoparticles



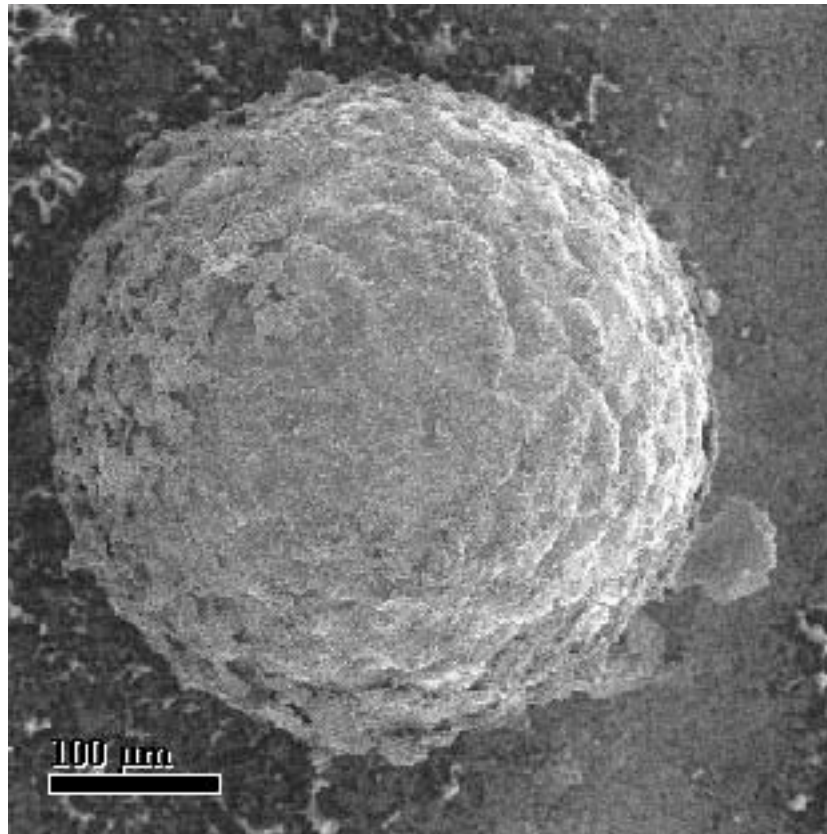
- Large surface area
- Better hydraulics
- High mobility

Synthesis of Porous Nanoparticles

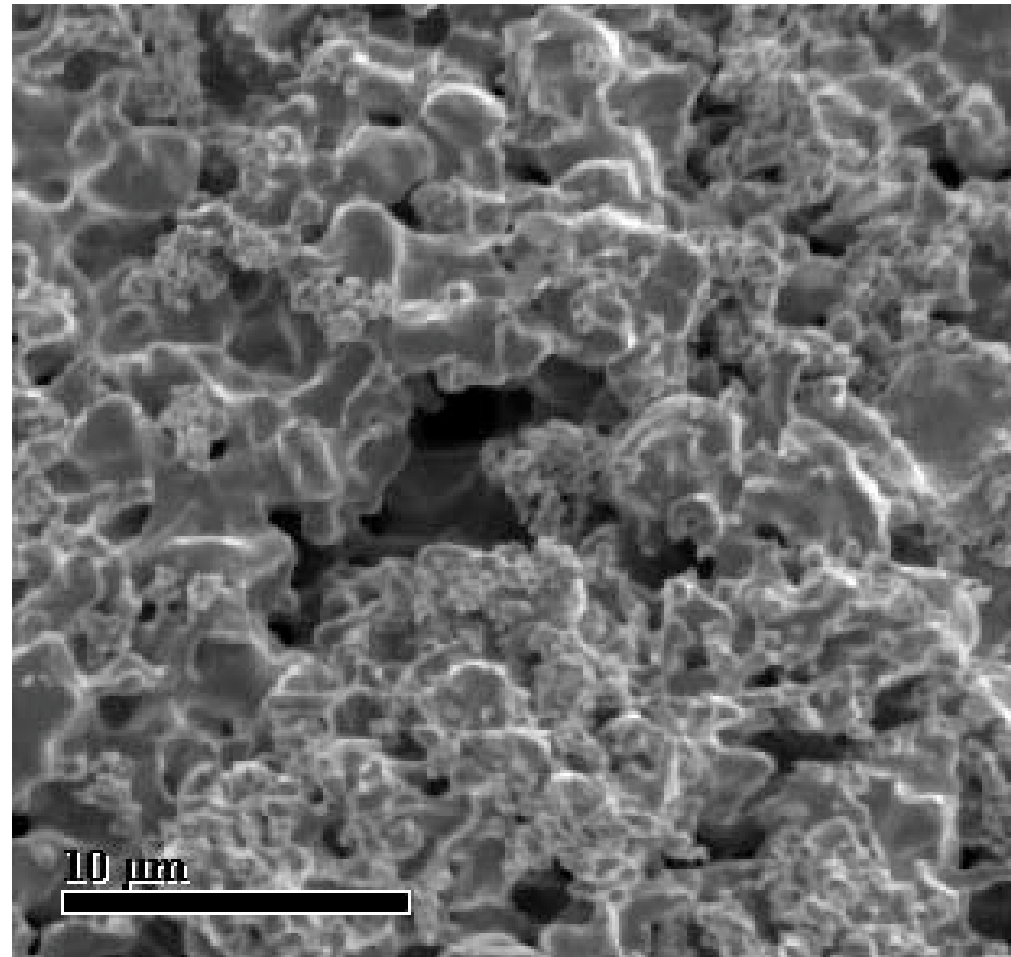
Self-assembling Template



Template-directed Synthesis



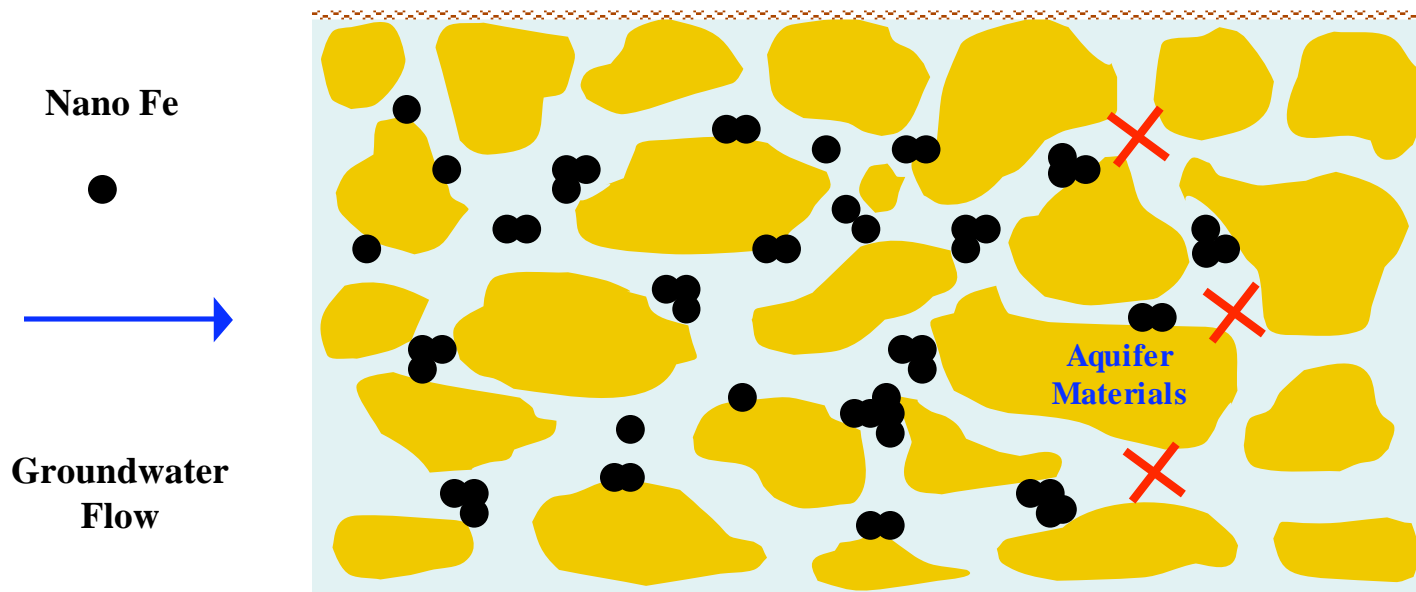
0.4 mm



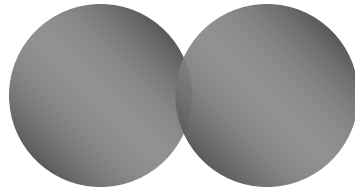
Surface Areas

Fe	SSA (m²/g)
Aldrich (~0.4 mm)	0.0012
BASF (~1 μm)	1.5
NanoFe (60 nm)	20-40
Nanoporous	142-250

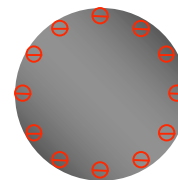
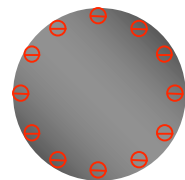
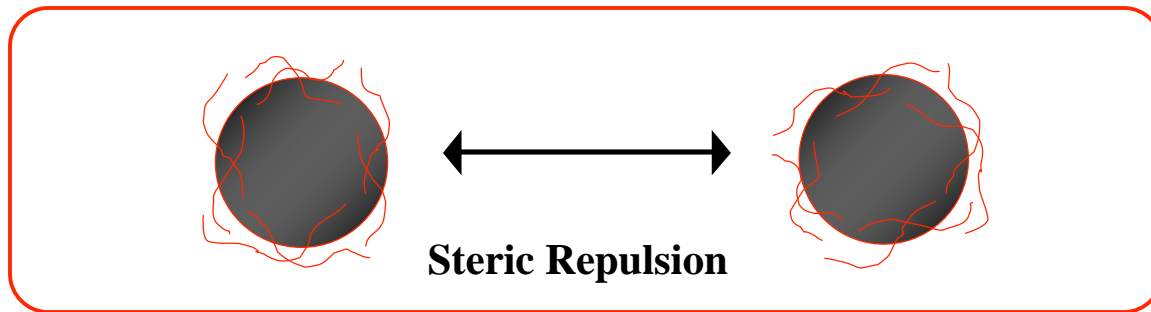
Manipulate Nanoparticle Mobility



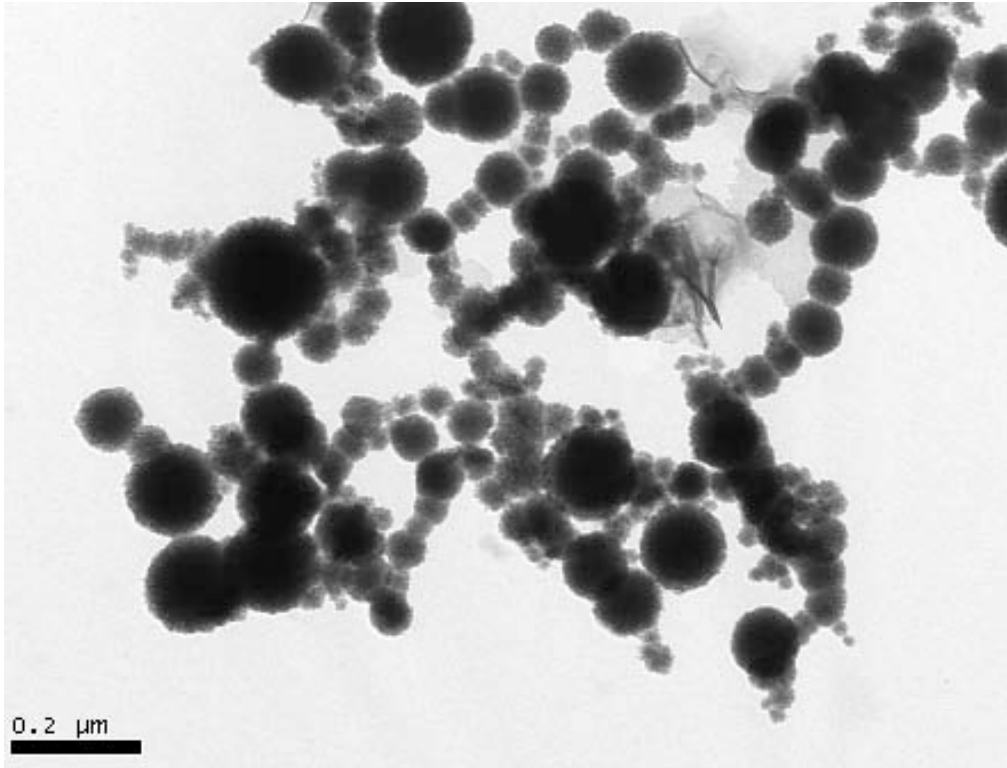
Dispersion



Attachment

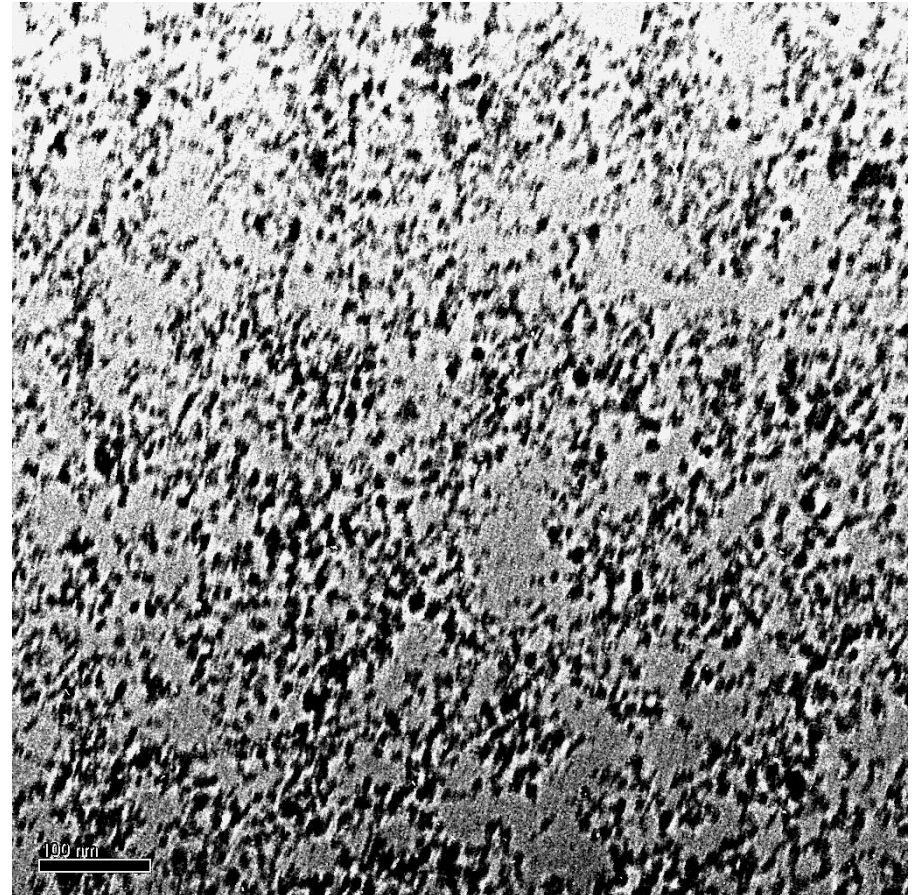


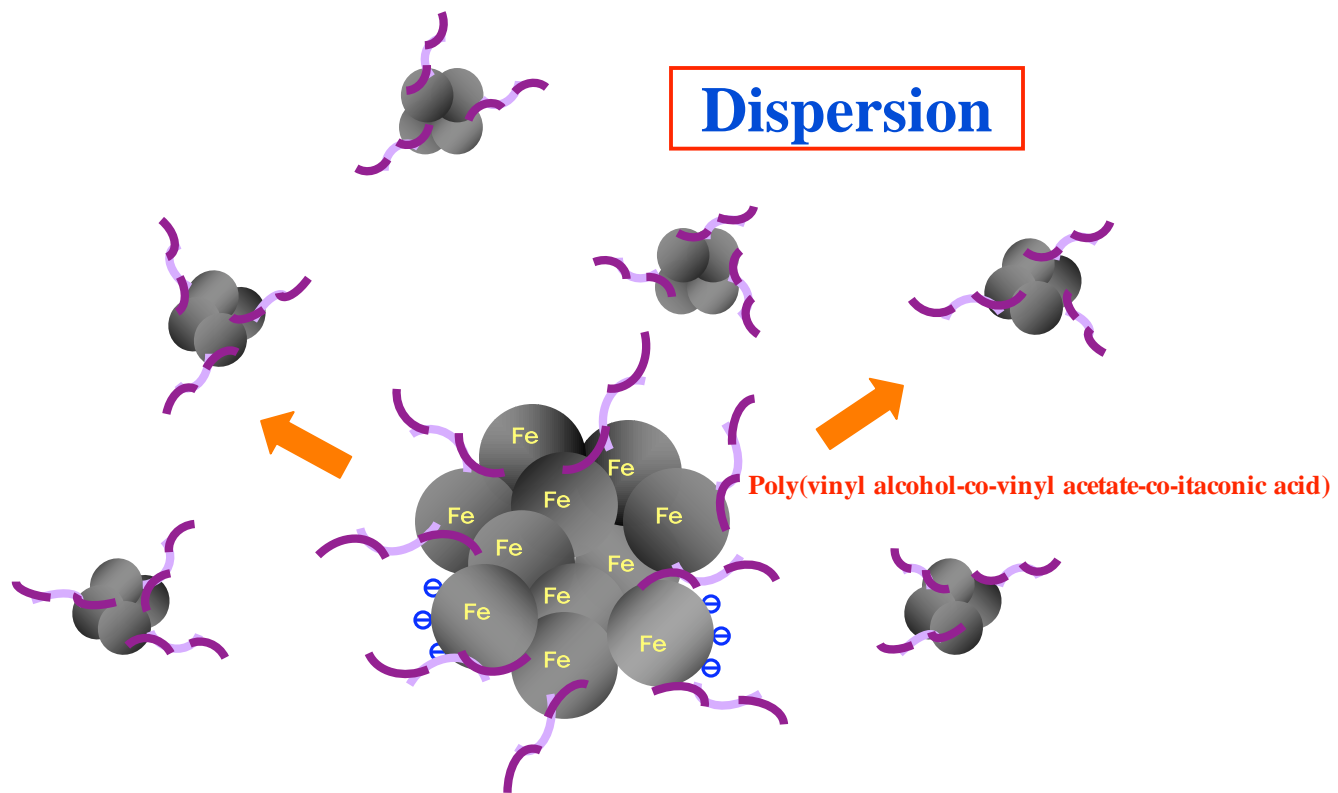
**Electrostatic
Repulsion**



**Original
Nanoparticle**

**Dispersed
Nanoparticle**





Iron Nanoparticle Aggregates

COSTS

Iron Filings
\$0.5/kg
<10 m ² /kg
<20 m²/dollar

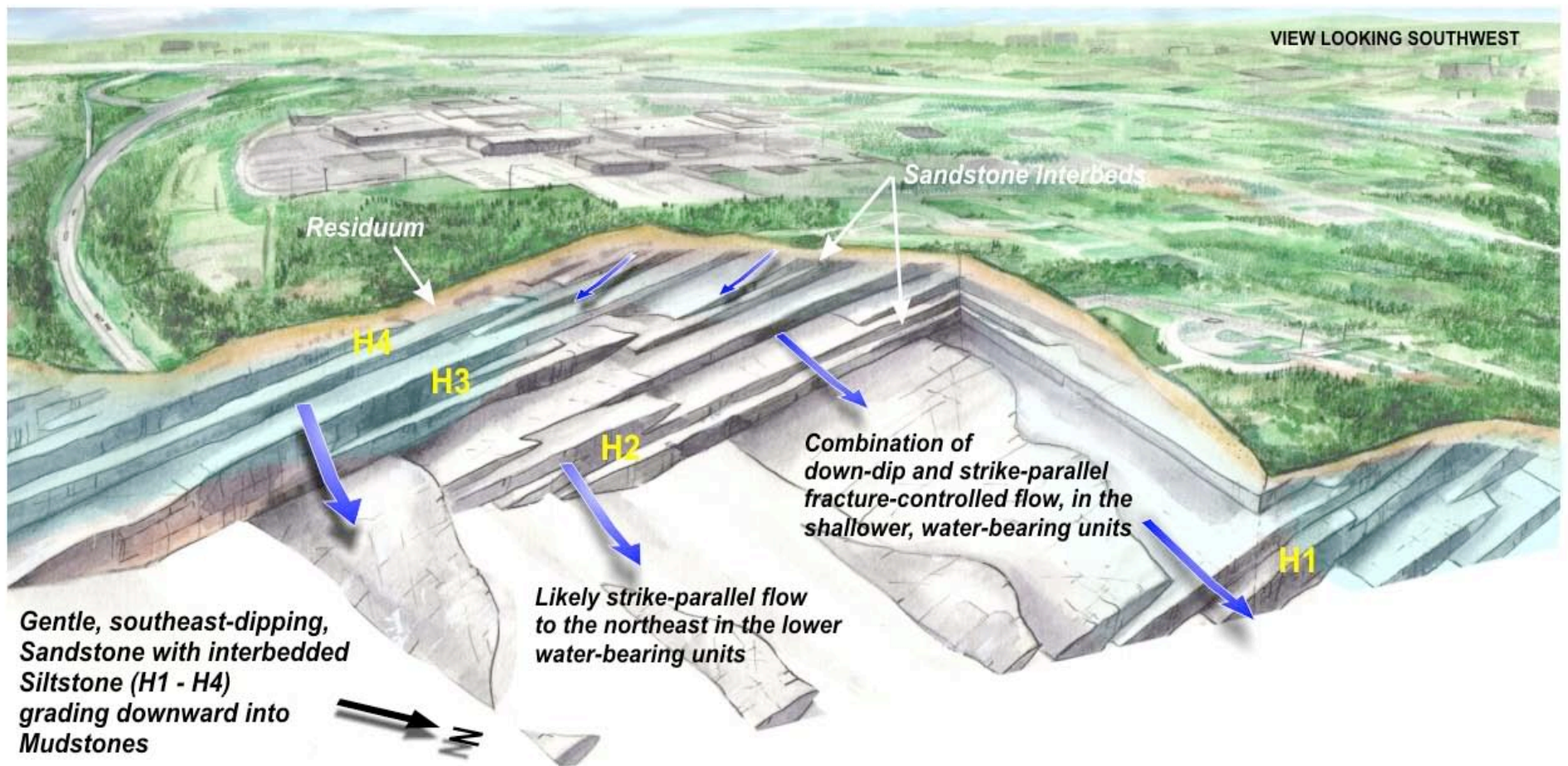
COSTS

Iron Filings	Nano Iron
\$0.5/kg	~\$25/kg
<10 m ² /kg	~25,000 m ² /kg
<20 m²/dollar	~1,000 m²/dollar

COSTS

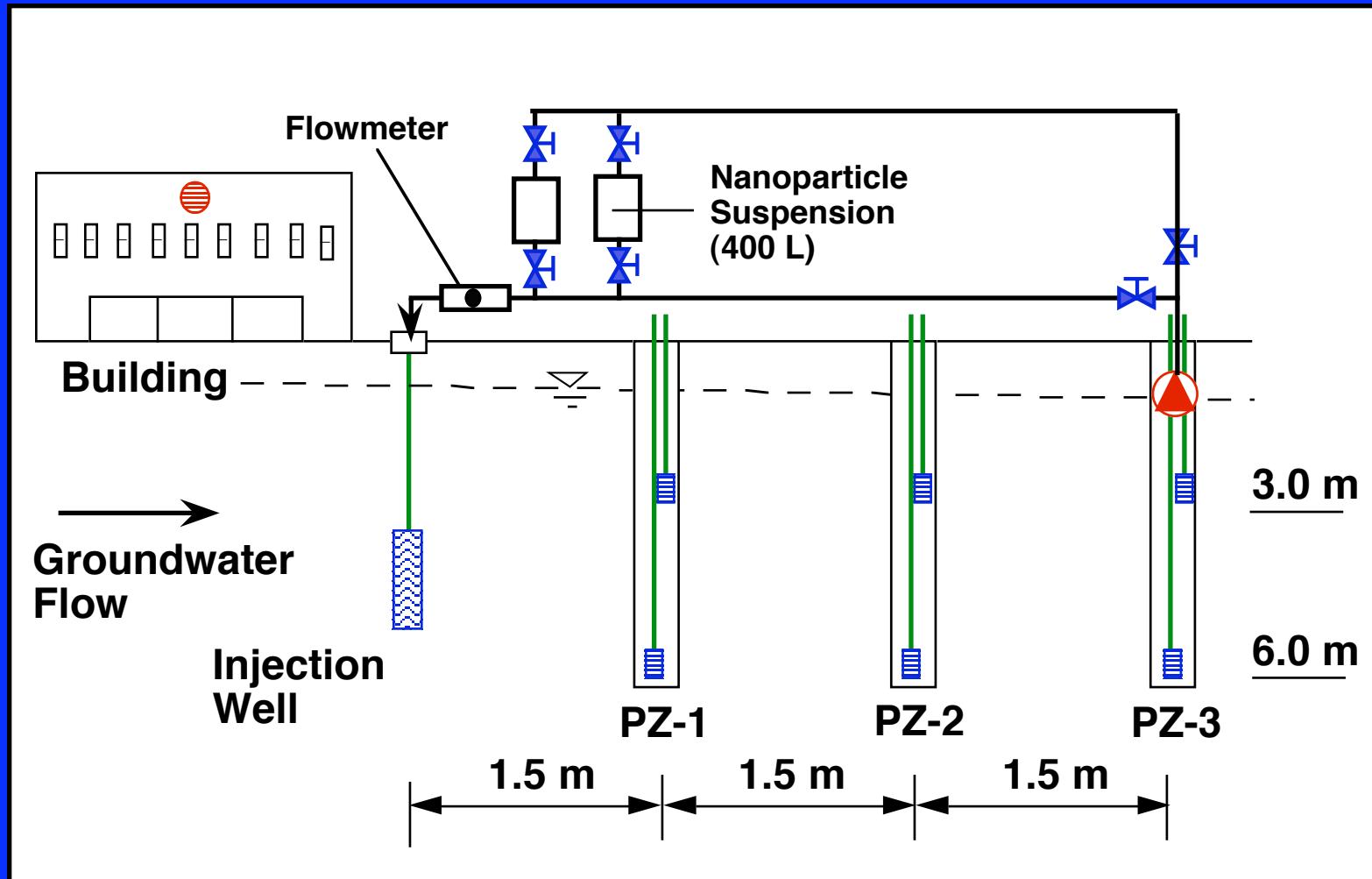
Iron Filings	Nano Iron	Porous Iron
\$0.5/kg	~\$25/kg	~\$50/kg
<10 m ² /kg	~25,000 m ² /kg	~200,000 m ² /kg
<20 m²/dollar	~1,000 m²/dollar	~4,000 m²/dollar

Conceptual Geologic and Hydrogeologic Model

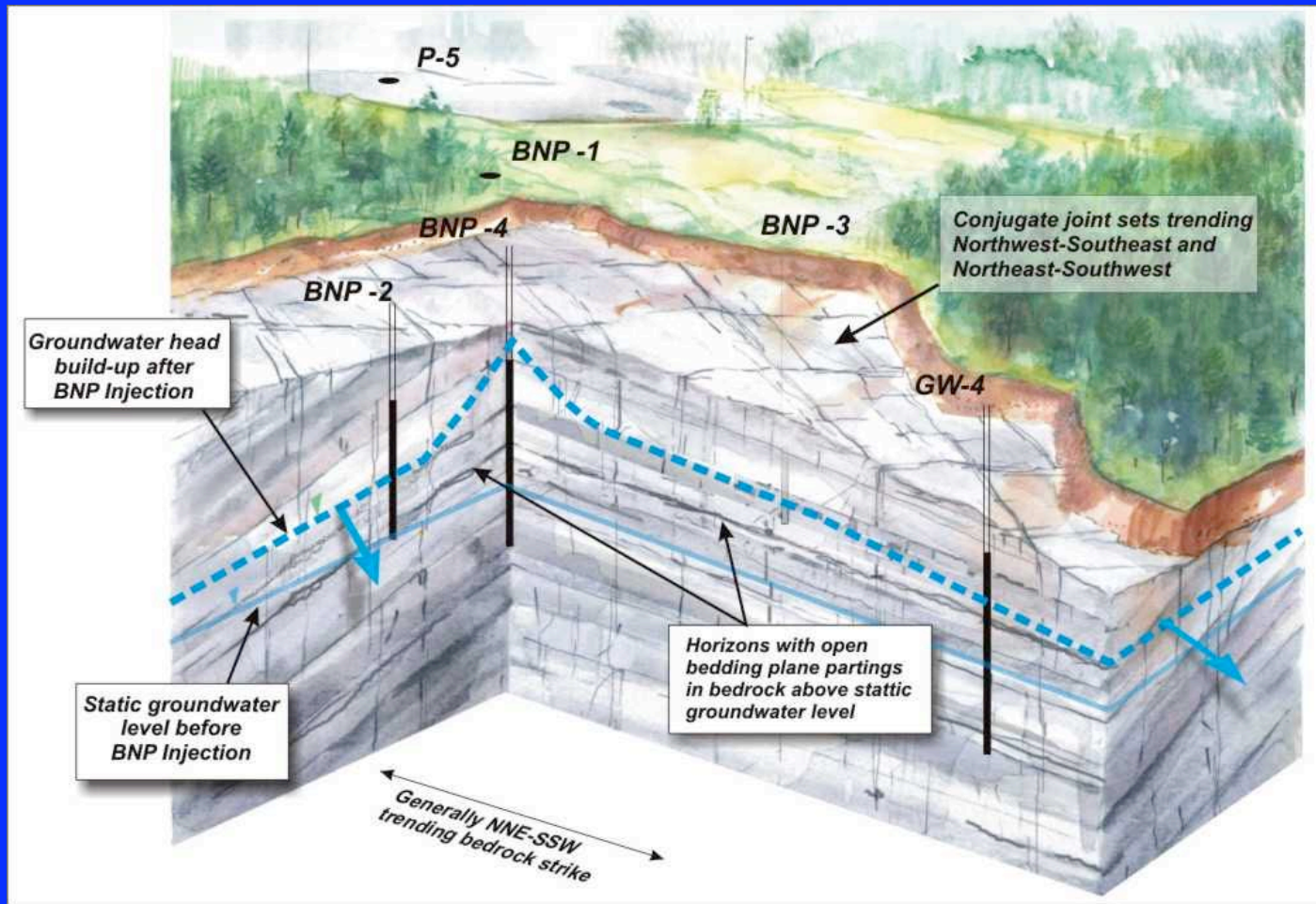


Field Applications

(11 projects so far, >10 Planned for 04')



Conceptual Model



The Nano Fe Slurry (1-2 g/L)

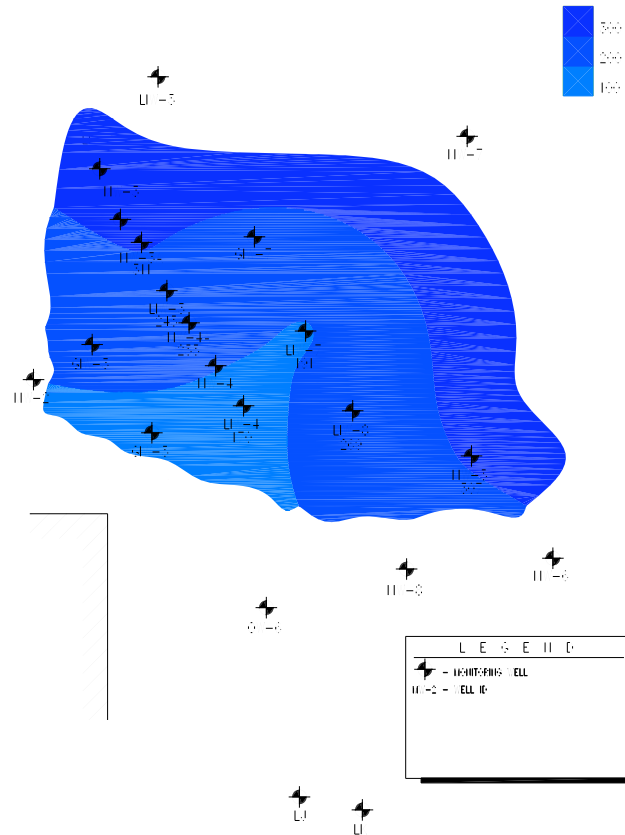


Test Set-up



ORP 2/4/02

**Before
Nano Fe
Application**

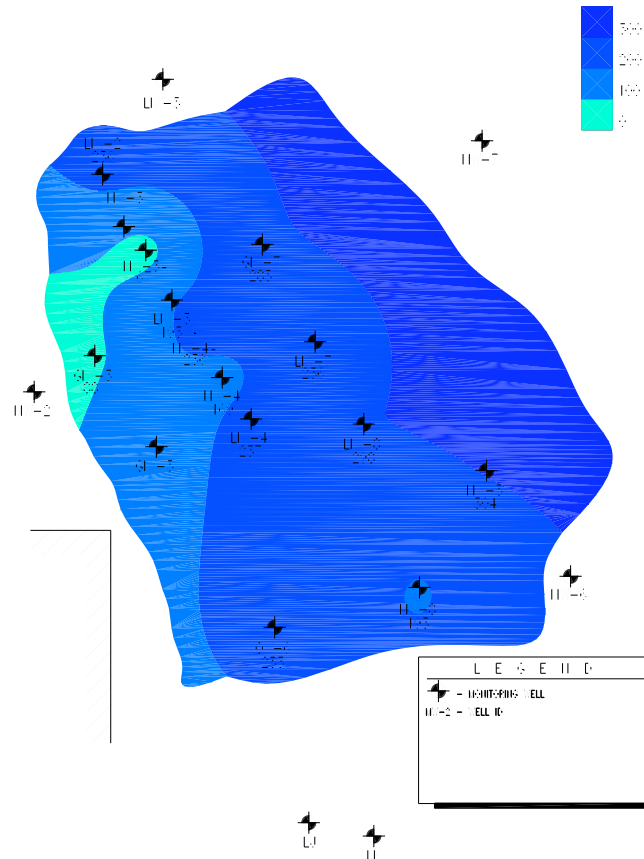


**Oxidative
Environment**

+100 to + 400 mV

ORP 2/11/02

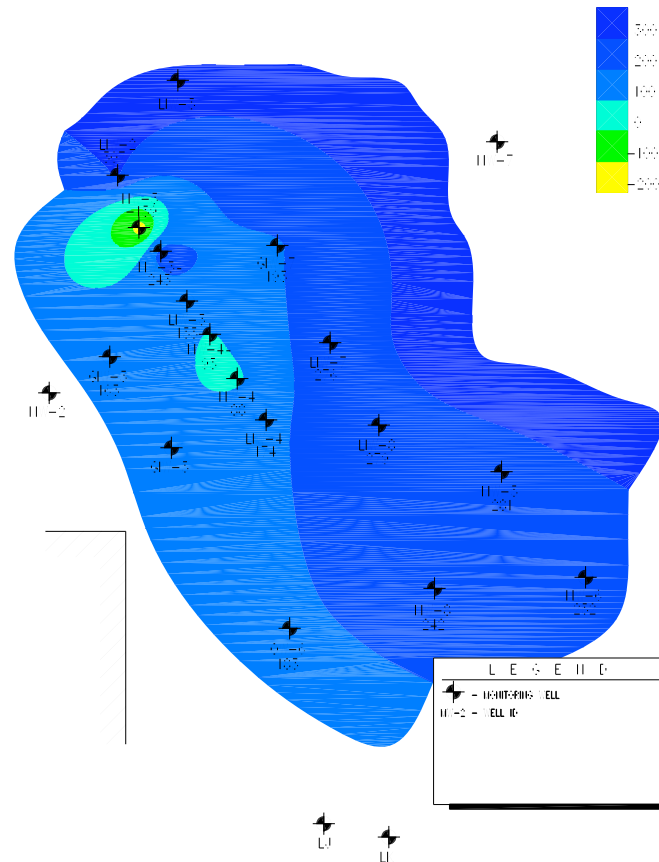
Right after
Nano Fe
Application



0 to + 400 mV

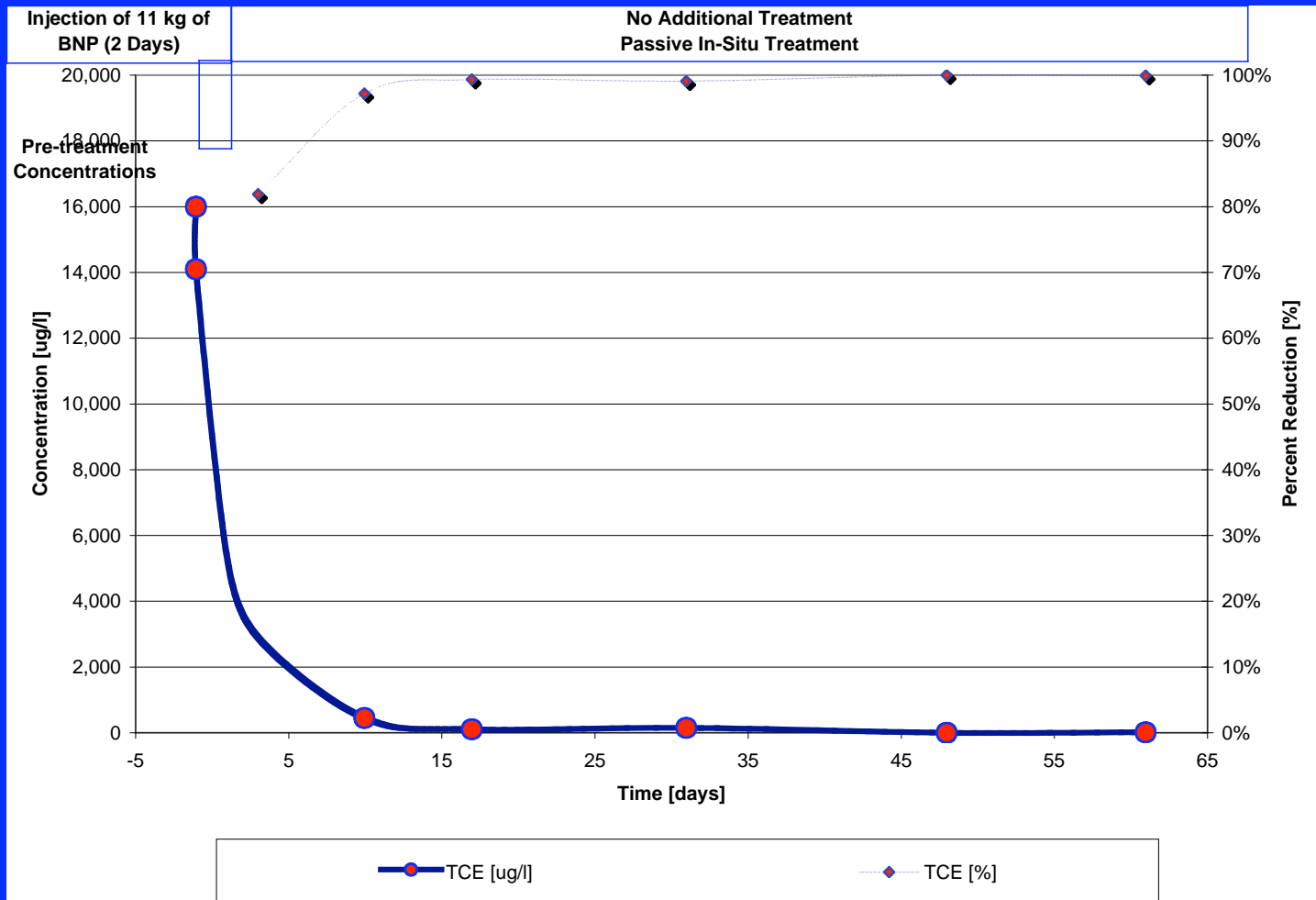
ORP 2/19/02

1 week after
Nano Fe
Application

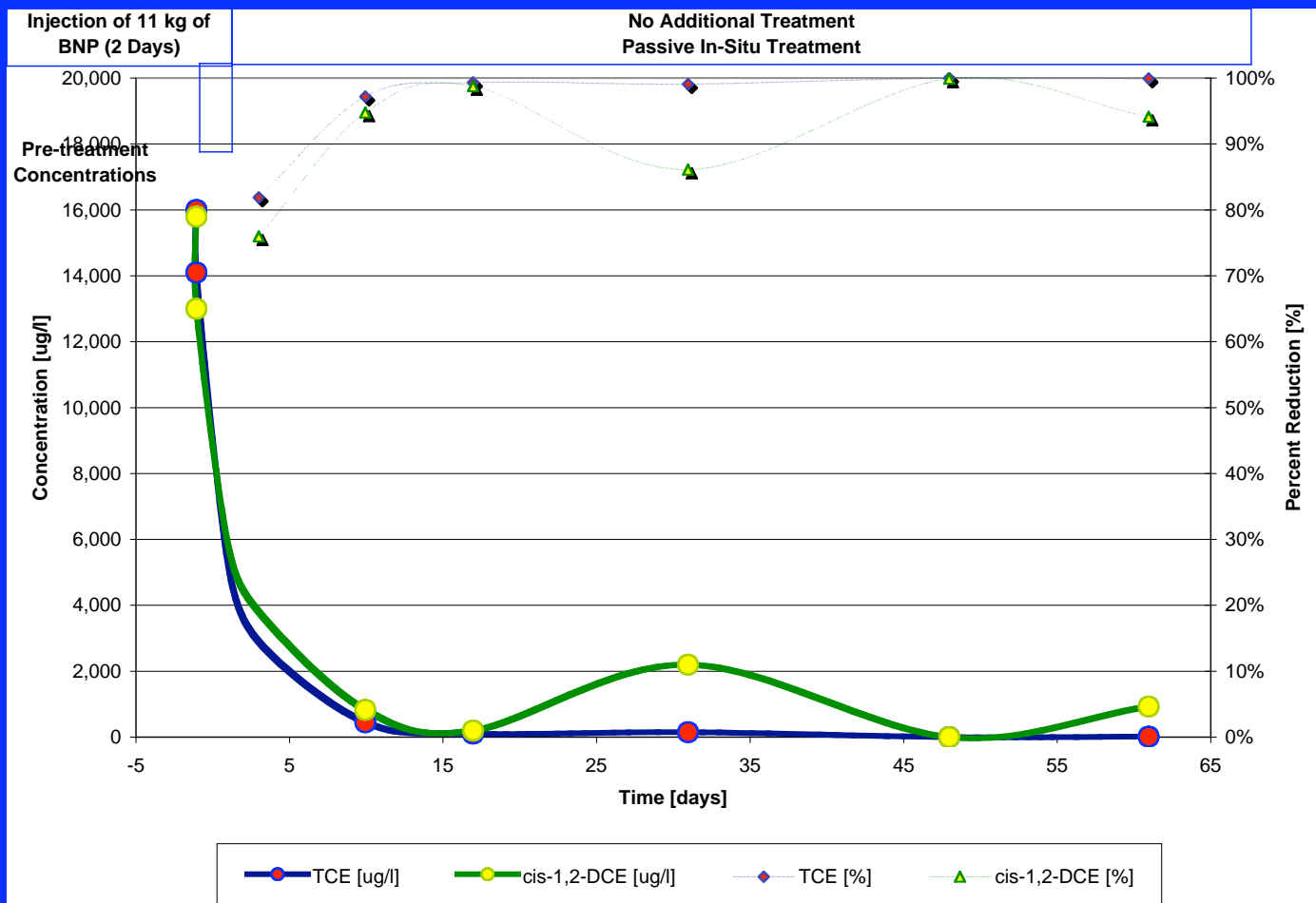


-200 to + 400 mV

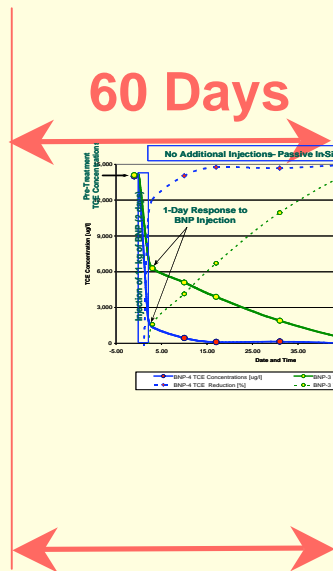
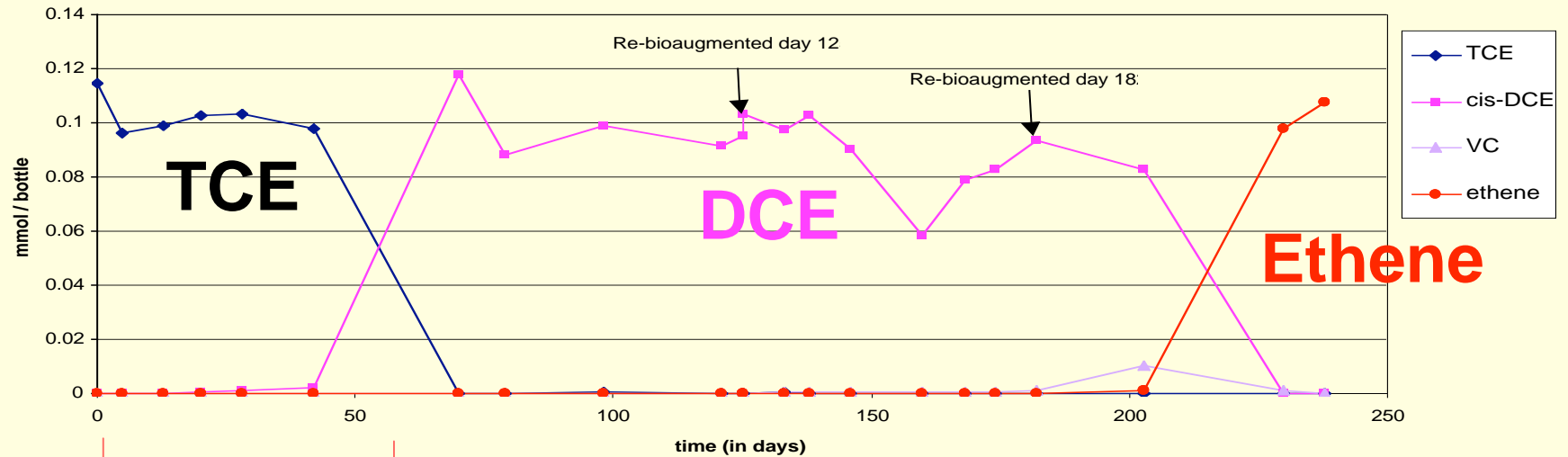
Sampling Results TCE - MW-4



Sampling Results TCE and cis-1,2-DCE at MW-4



Comparison: Bioremediation - and Nano Fe

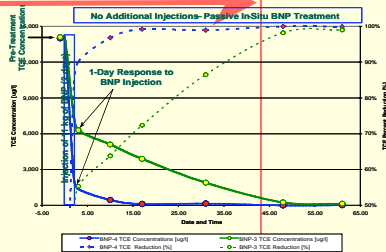


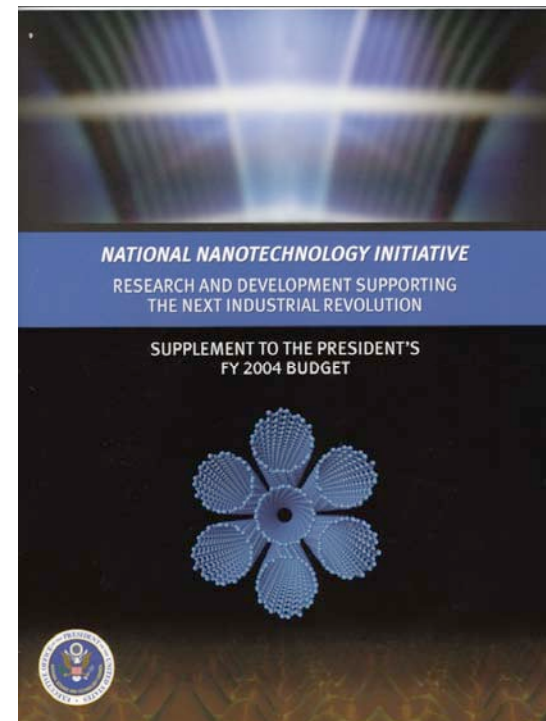
60 Days

Bioremediation

Nano Fe

60 Days





More on:

NY Times

USA Today

WSJ

>20 others



Thanks

Questions ?