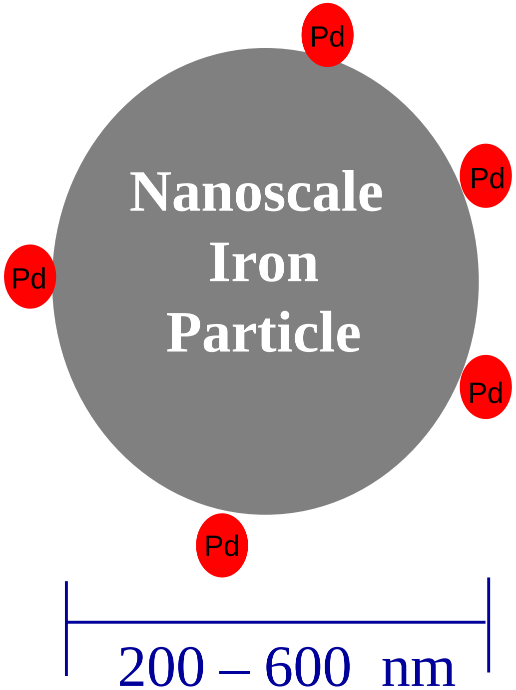


Developments in Nanoscale Iron Technology for the Treatment of CVOC Source Areas

RTDF Permeable Reactive Barriers (PRB) Action Team Meeting

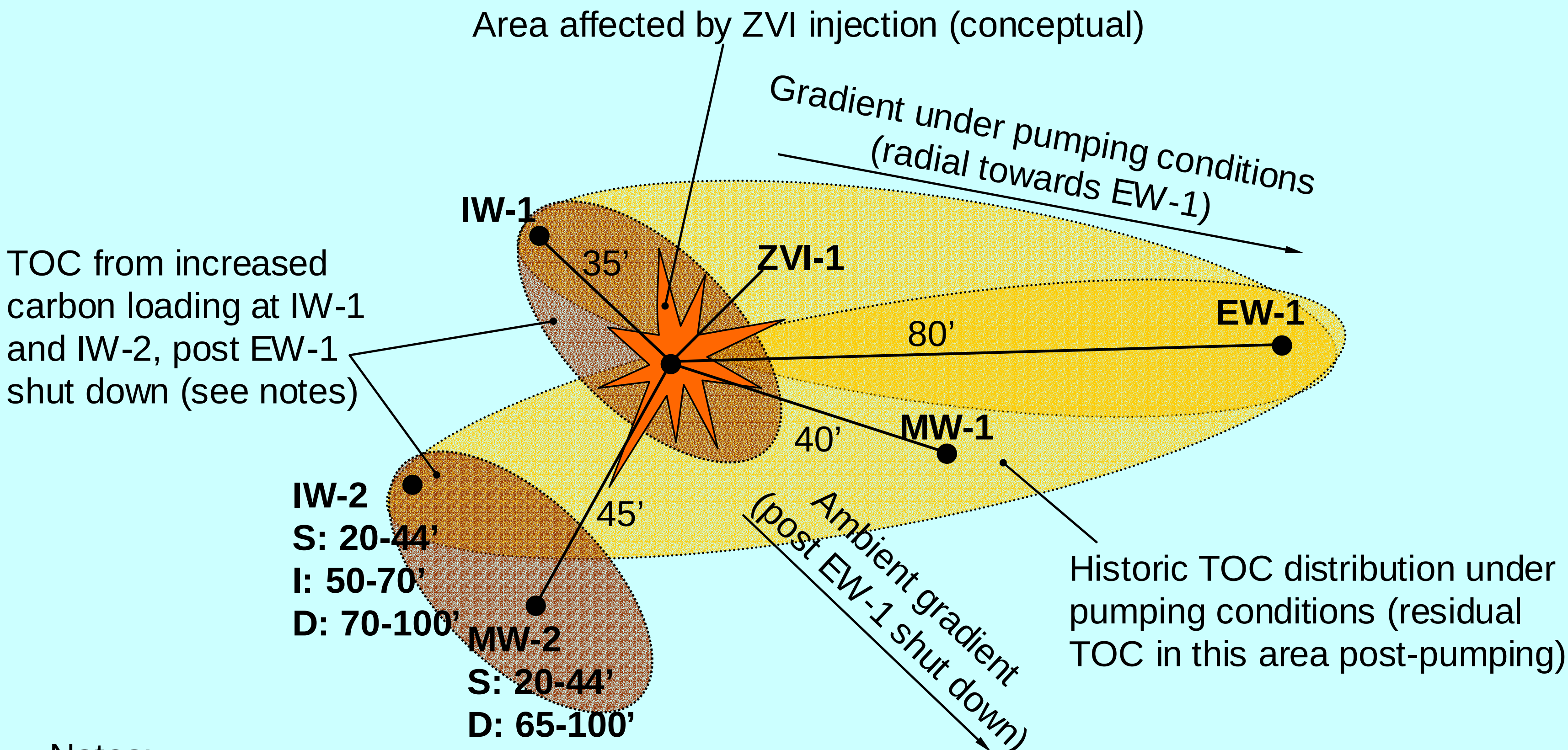
Albuquerque, New Mexico October 26-27, 2004

David Vance, David Liles, Chris Lutes

ARCADIS

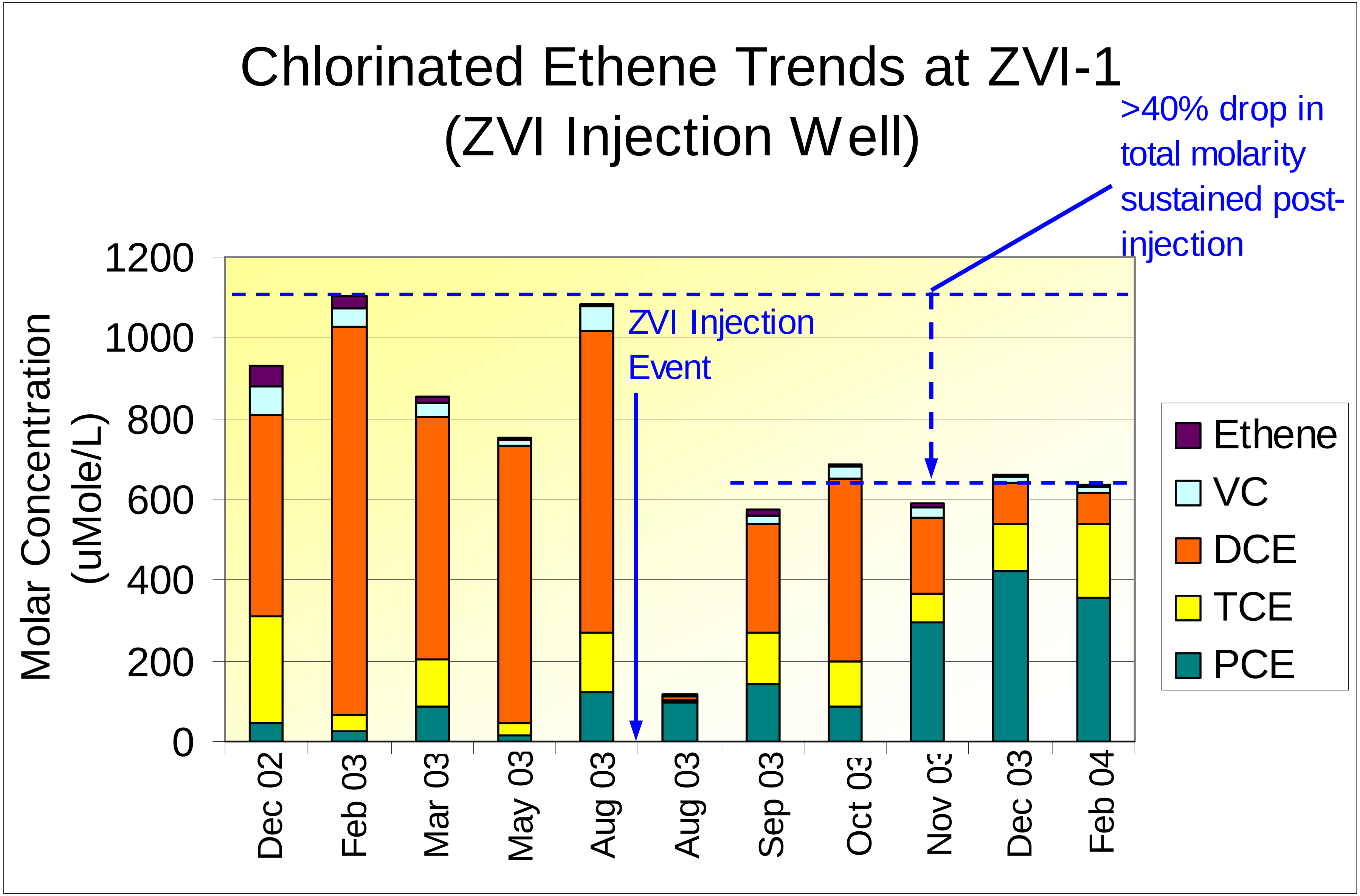
Nanoscale ZVI Field Pilot

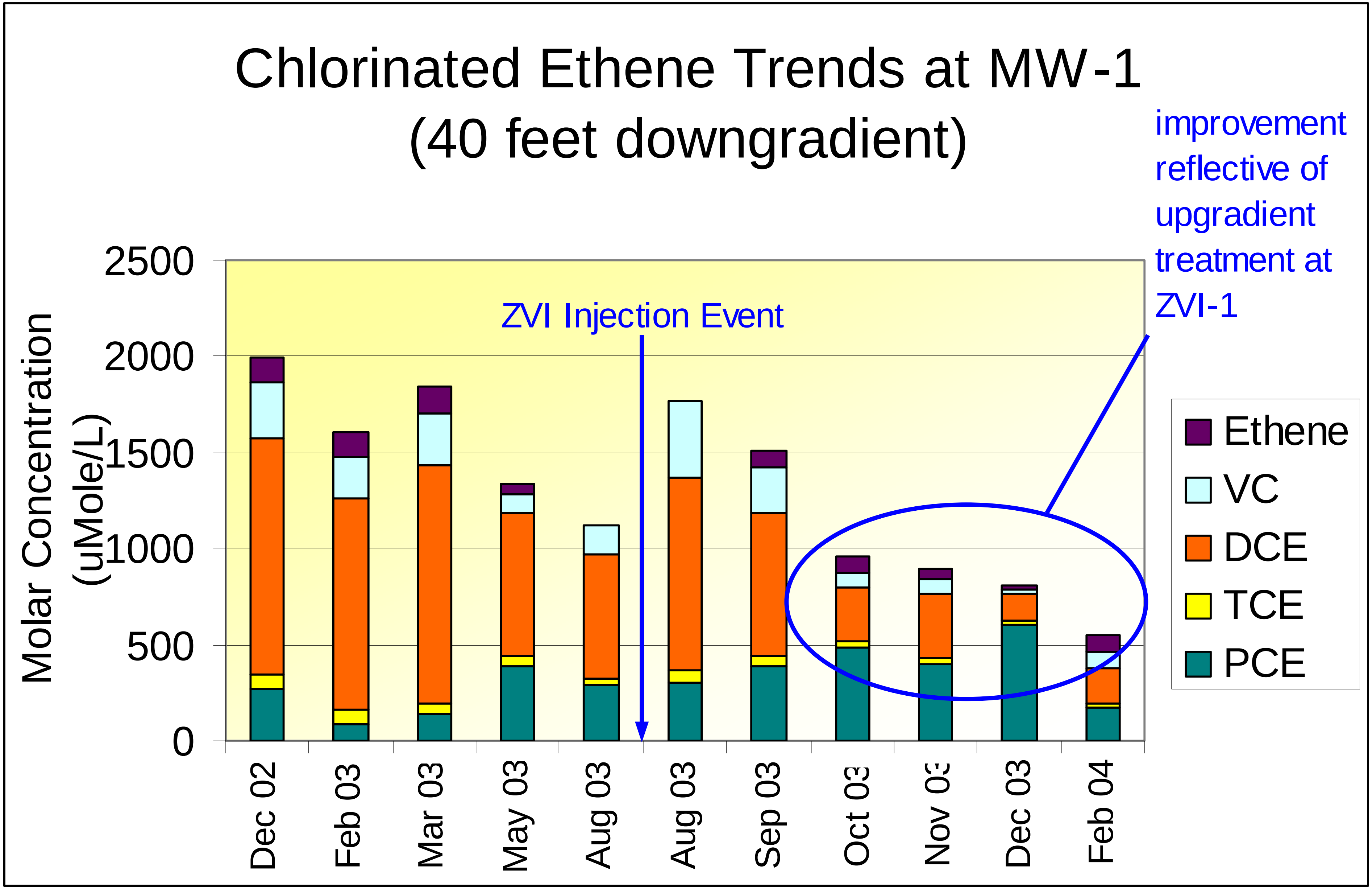
- New Jersey Fractured Bed Rock Site
- Untreated dissolved PCE approximately 130 mg/L
- After 30 months of molasses injection still seeing rebound due to trace DNAPL
- Injected 100 pounds of Crane Polyflon Polymetallix™ precipitated iron colloid
- John Horst, Frank Lenzo, David Liles, Jennifer Martin,



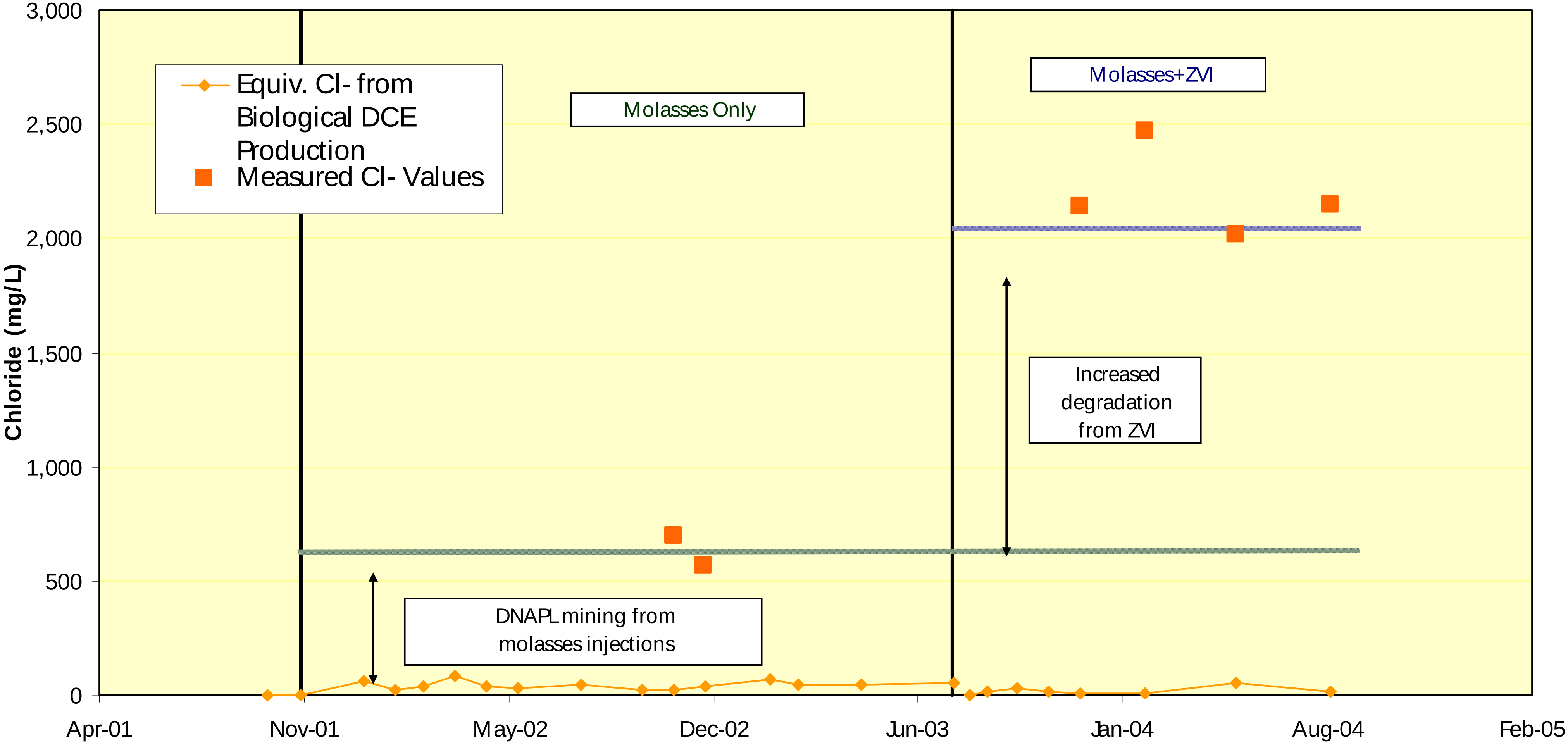
Notes:

- IW-1 and IW-2 = enhanced reductive dechlorination (ERD) injection wells
- Pumping at EW-1 previously helped to distribute TOC from IW-1 and IW-2
- EW-1 shut down nine months prior to ZVI injection
- Carbon loading increased at IW-1 three months prior to ZVI injection; TOC breakthrough observed at ZVI-1 one month after ZVI injection
- Carbon loading increased at IW-2 one month after ZVI injection; TOC breakthrough observed at MW-2 (D) four months after ZVI injection


Chlorinated Ethene Trends at ZVI-1
(ZVI Injection Well)
>40% drop in
total molarity
sustained post-
injection
ZVI Injection
Event
Molar Concentration
(uMole/L)
1200
1000
800
600
400
200
0
Dec 02
Feb 03
Mar 03
May 03
Aug 03
Aug 03
Sep 03
Oct 03
Nov 03
Dec 03
Feb 04
Ethene
VC
DCE
TCE
PCE


Chlorinated Ethene Trends at MW-1
(40 feet downgradient)
improvement reflective of upgradient treatment at ZVI-1
ZVI Injection Event
Molar Concentration (uMole/L)
2500
2000
1500
1000
500
0
Dec 02
Feb 03
Mar 03
May 03
Aug 03
Aug 03
Sep 03
Oct 03
Nov 03
Dec 03
Feb 04
Ethene
VC
DCE
TCE
PCE

ARCADIS



3,000
2,500
2,000
1,500
1,000
500
0
Chloride (mg/L)
Equiv. Cl- from Biological DCE Production
Measured Cl- Values
Molasses Only
Molasses+ZVI
Increased degradation from ZVI
DNAPL mining from molasses injections
Apr-01
Nov-01
May-02
Dec-02
Jun-03
Jan-04
Aug-04
Feb-05

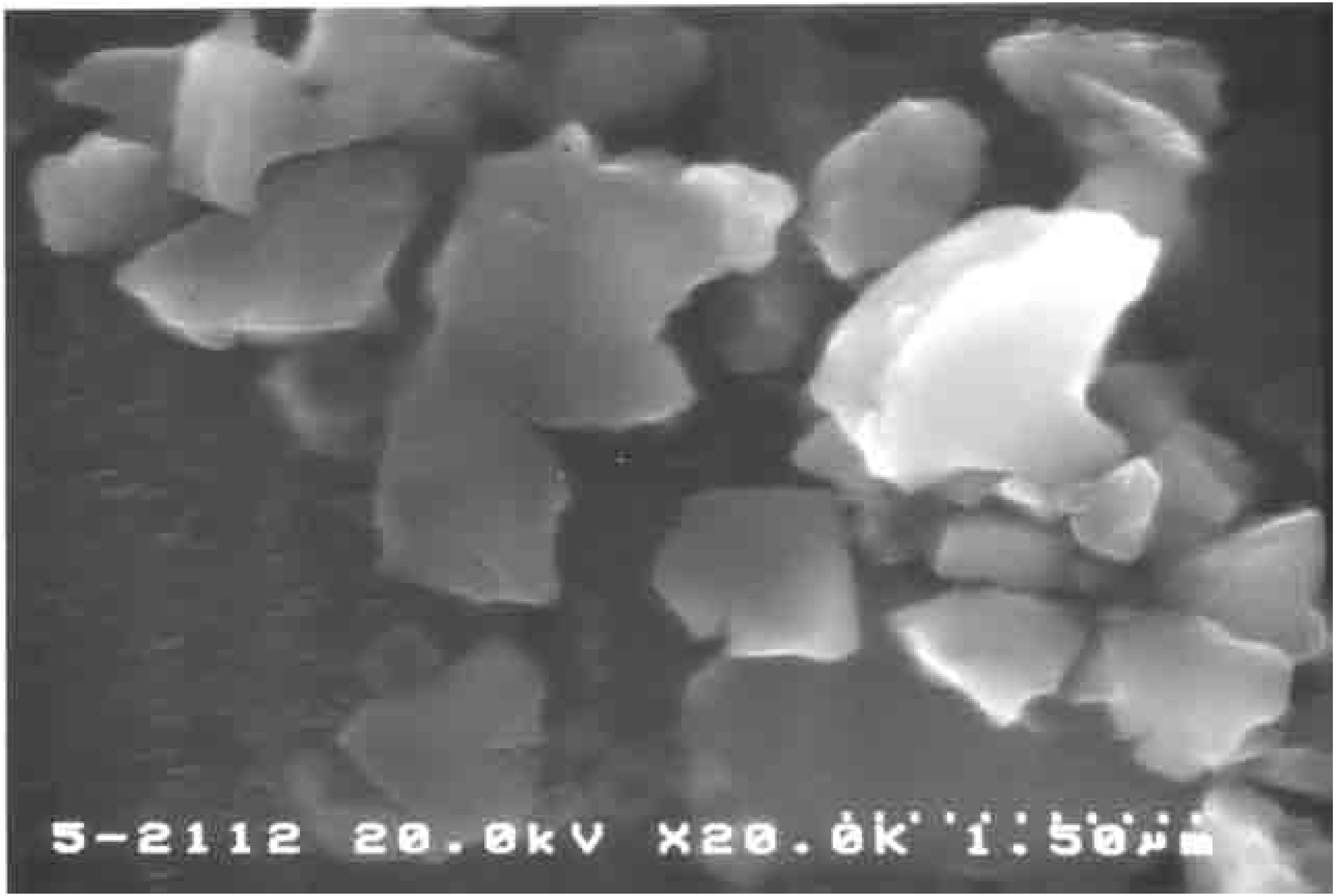
Nanoscale ZVI Technology Review

- Reactive Properties
- Delivery
- Going Forward

Nanoscale ZVI

Reactive Properties

Top Down Nano-Scale Fe Colloids (OnMaterials)



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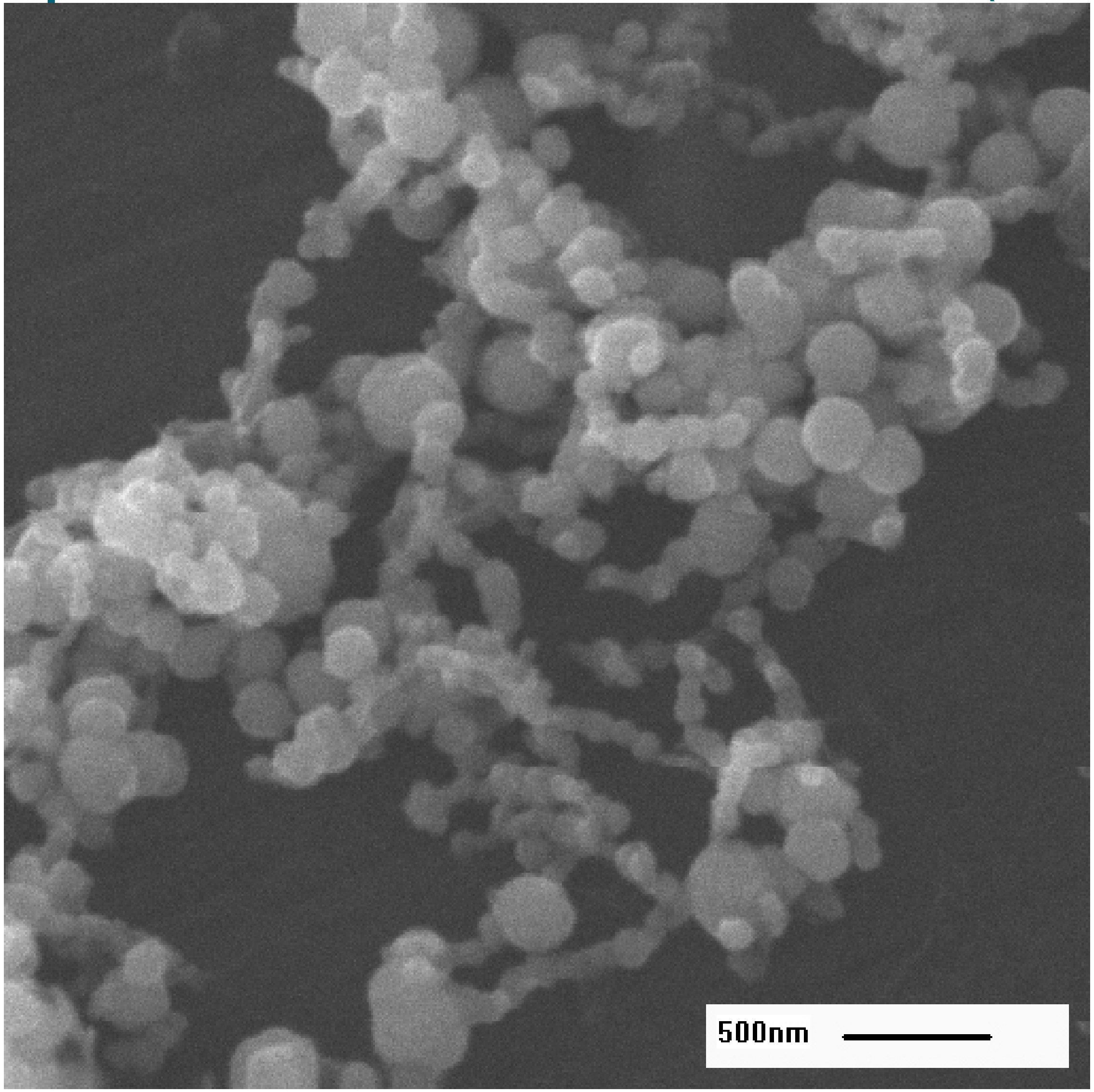
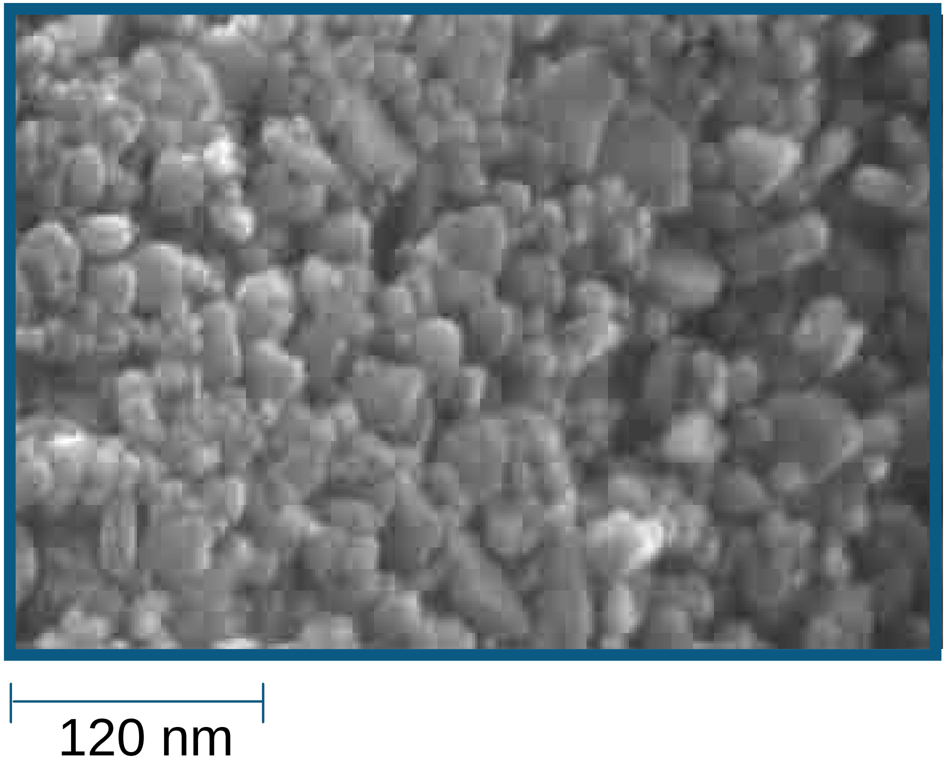
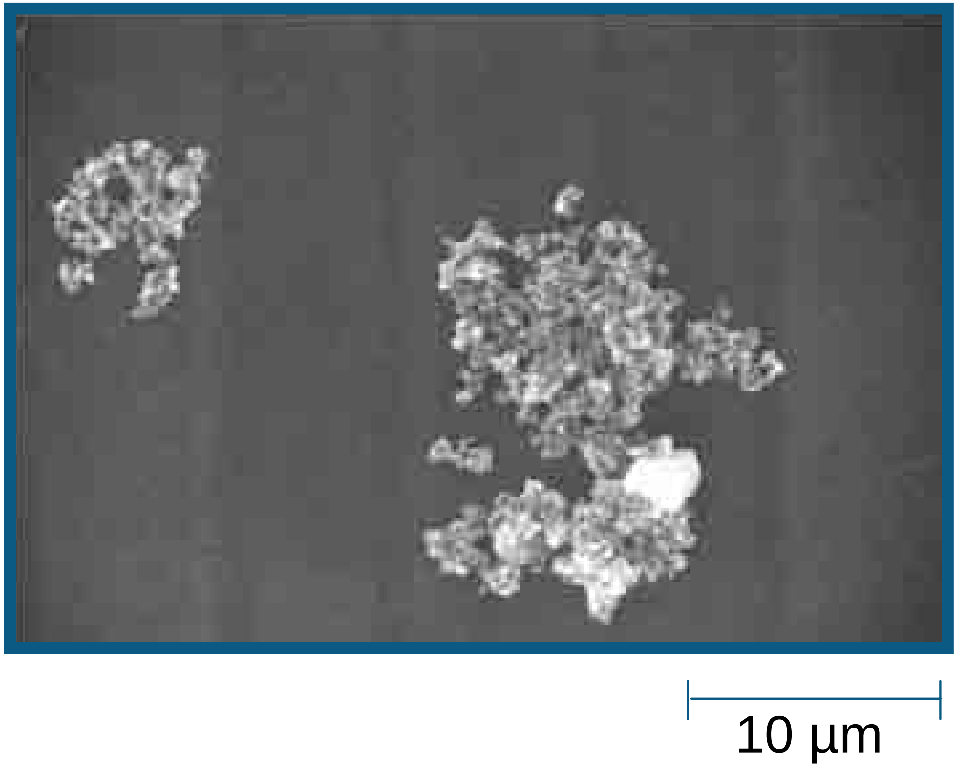
Bottom Up Nano Scale Fe Colloids (ARCADIS)



Another Bottom Up Iron (Crane Polyfon PolyMetaqllix™



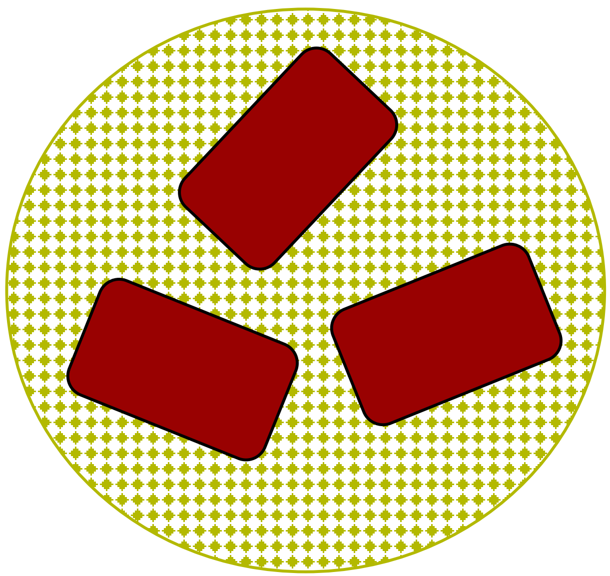


Controls on Reactivity

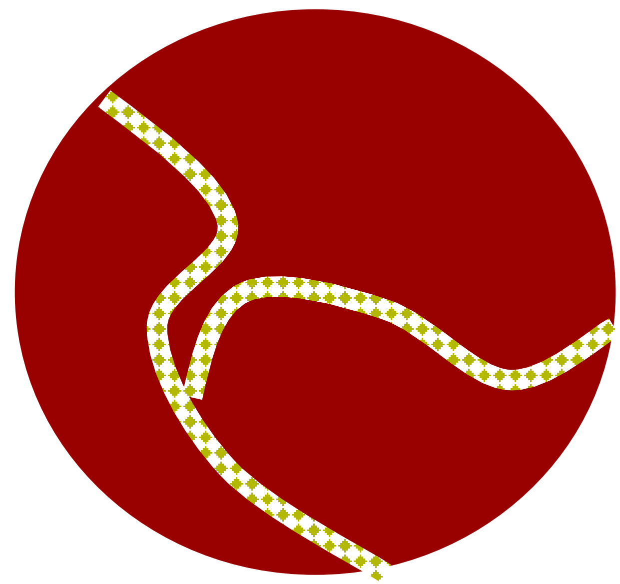
- Particle size
- Reactive Surface Area
- Presence or Absence of Hydrogenation Catalyst
- Method of Manufacture
- Particle morphology – shape, pits
- Particle crystal structure – size of crystal domains, kinks, amorphous zones
- Impurities (good in some cases) and coatings
- Acid Washing
- Aqueous geochemistry

ARCADIS

Control of Colloid Reactivity

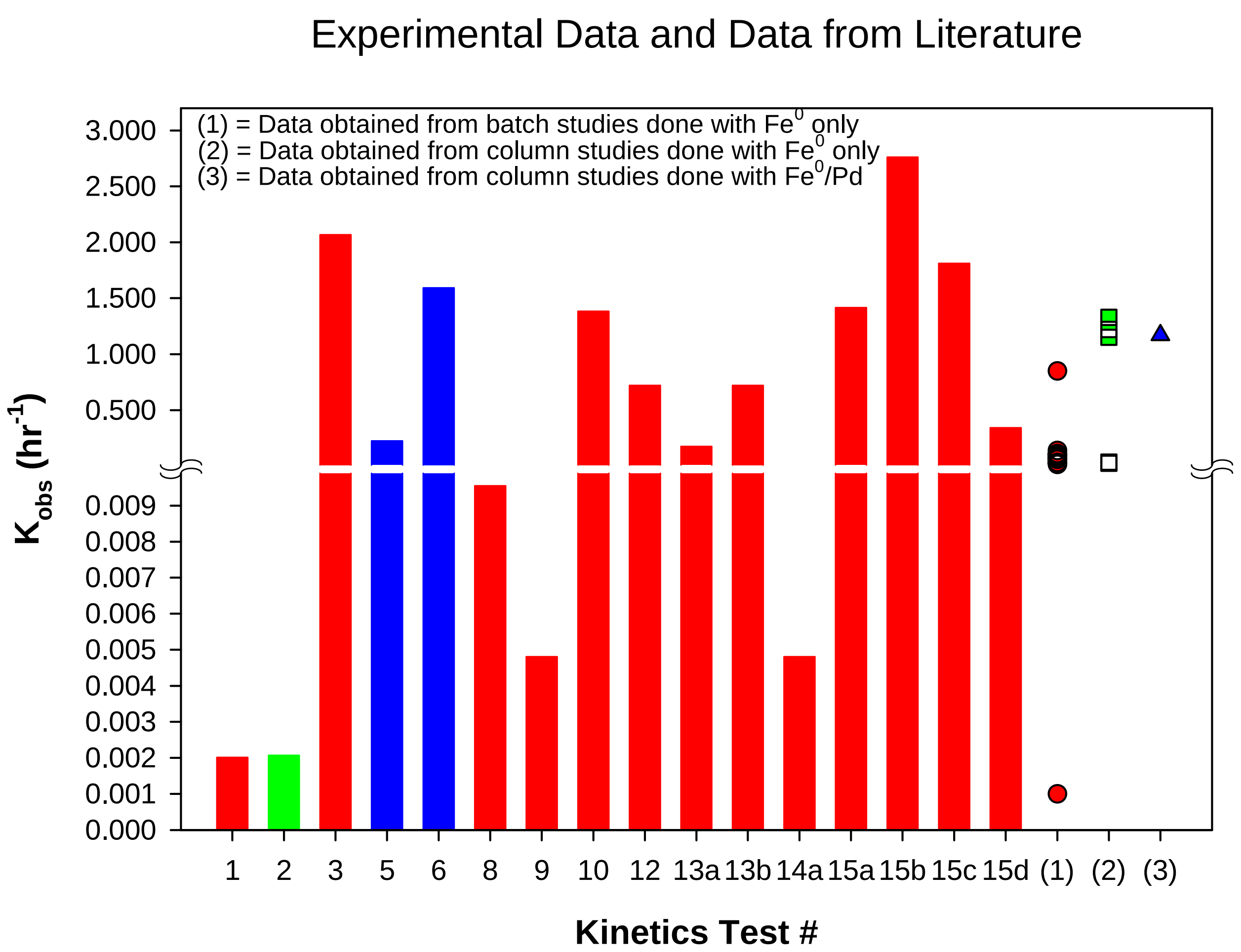


Top Down
Ball Milled



Bottom Up
Precipitated

Kinetics Batch Test Results
(higher values indicate short half-lives)



Red Bars are Vendor C Ball Milled

Green Bar is Vendor A Precipitated

Blue Bars are Vendor B Precipitated

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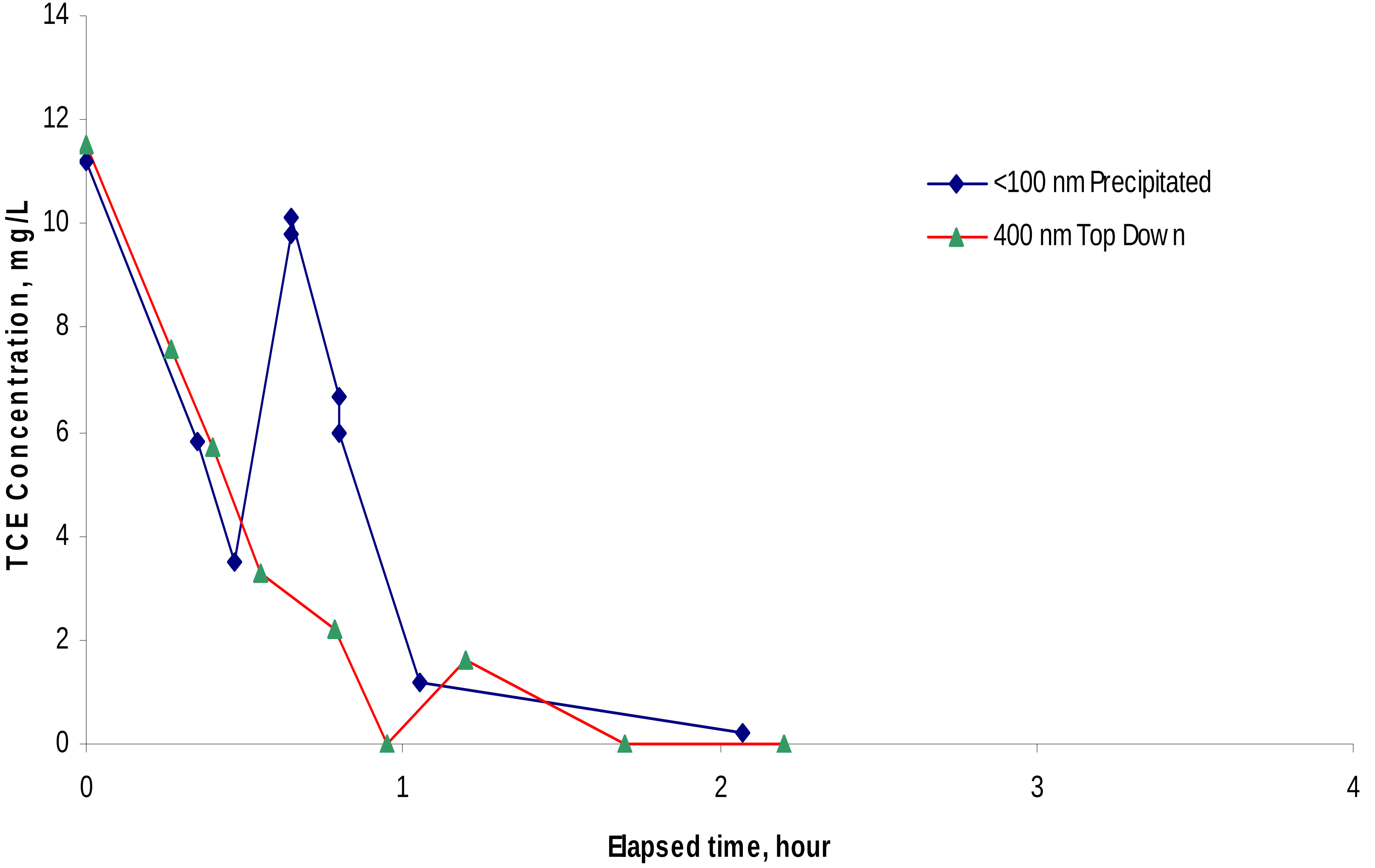
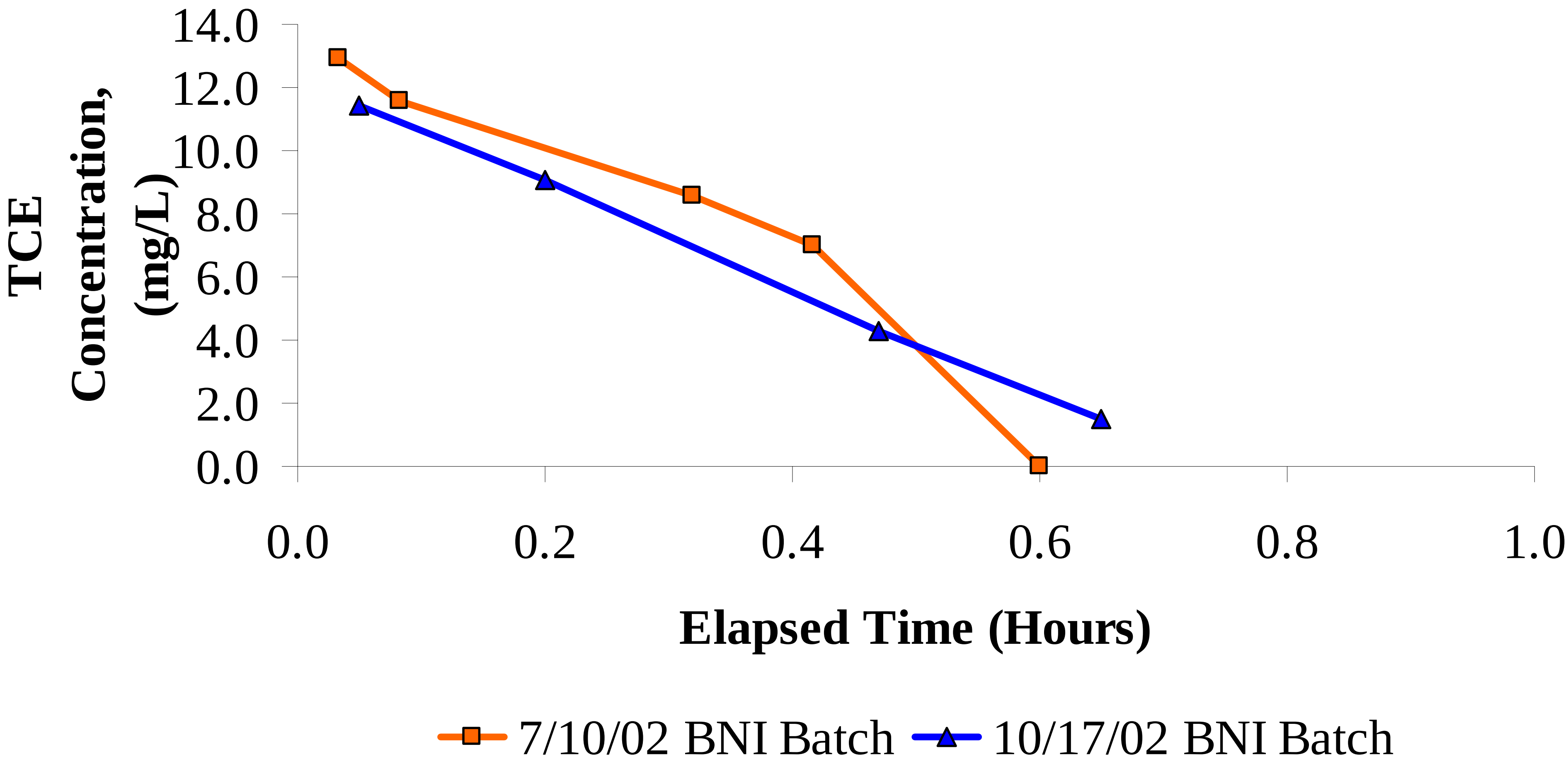
Reactivity of Top Down Vs. Bottom Up Colloids



BNI TCE Dechlorination Kinetics Stability of Ball Milled Colloids



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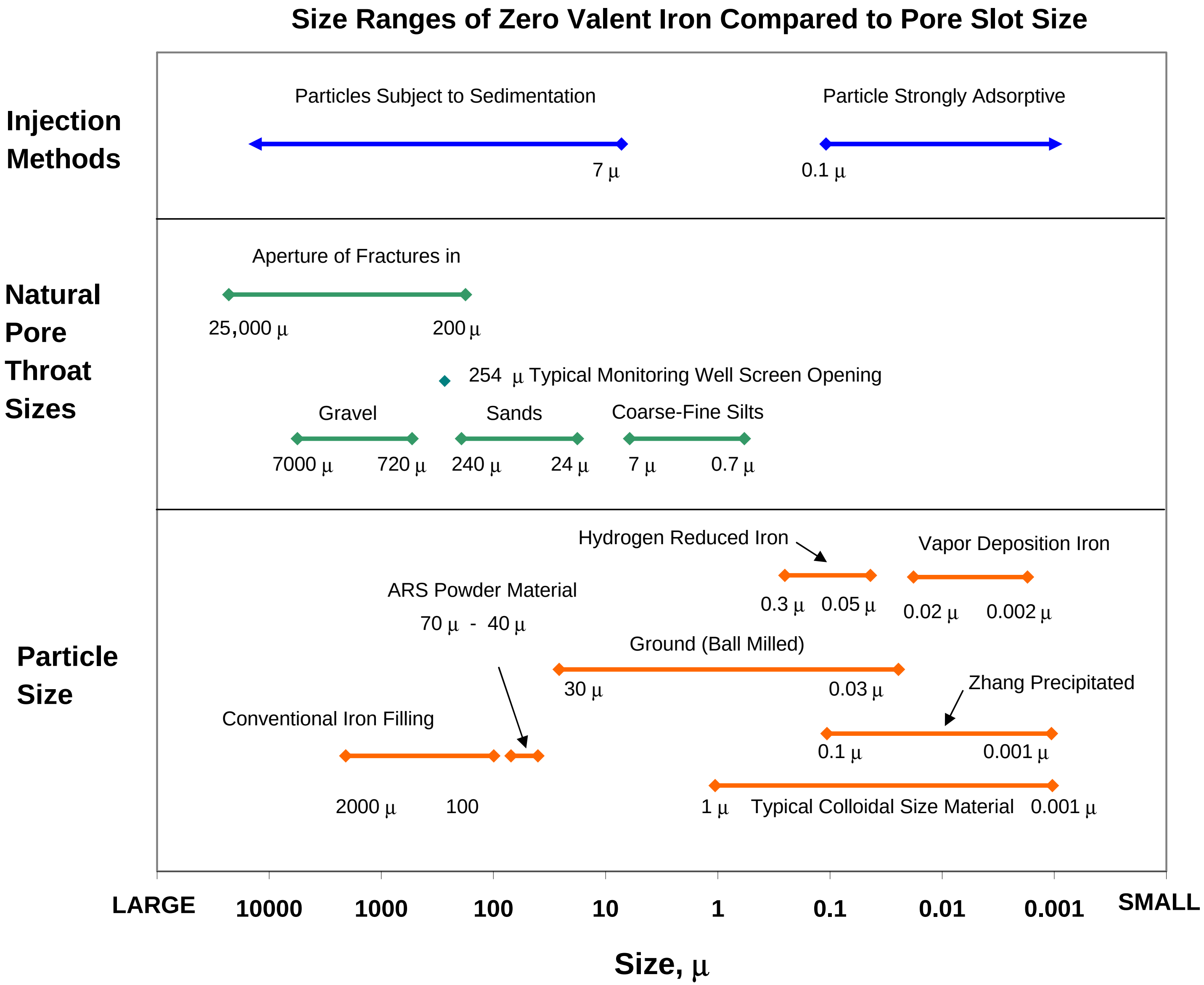
Key Batch Testing Results as Compared to Literature

Characteristic	Literature Effect	Our Observed Effect
Surface area	Roughly linear	Roughly linear
Hydrogenation catalyst	3-100X improvement	7x with precipitated iron, 500x with ball milled iron
Acid washing effect	0.1-10x improvement	Up to 490X
Impurities/surface defects	Can have either positive or negative effects	Dramatic differences between the the ductilely deformed, ball milled and the crystalline, precipitated materials

Nanoscale ZVI

Delivery

Nanoscale Iron Particle Size Comparison



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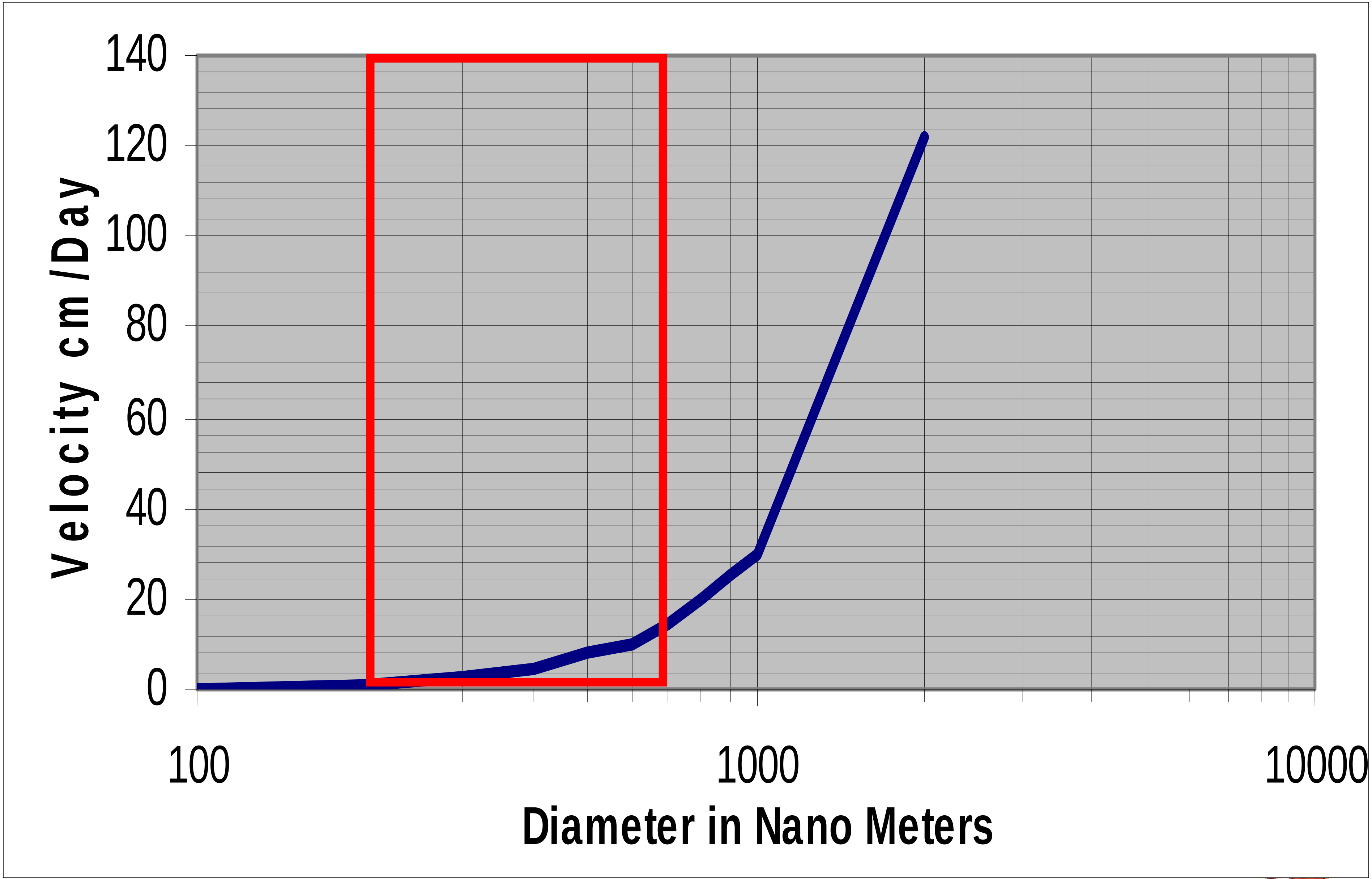
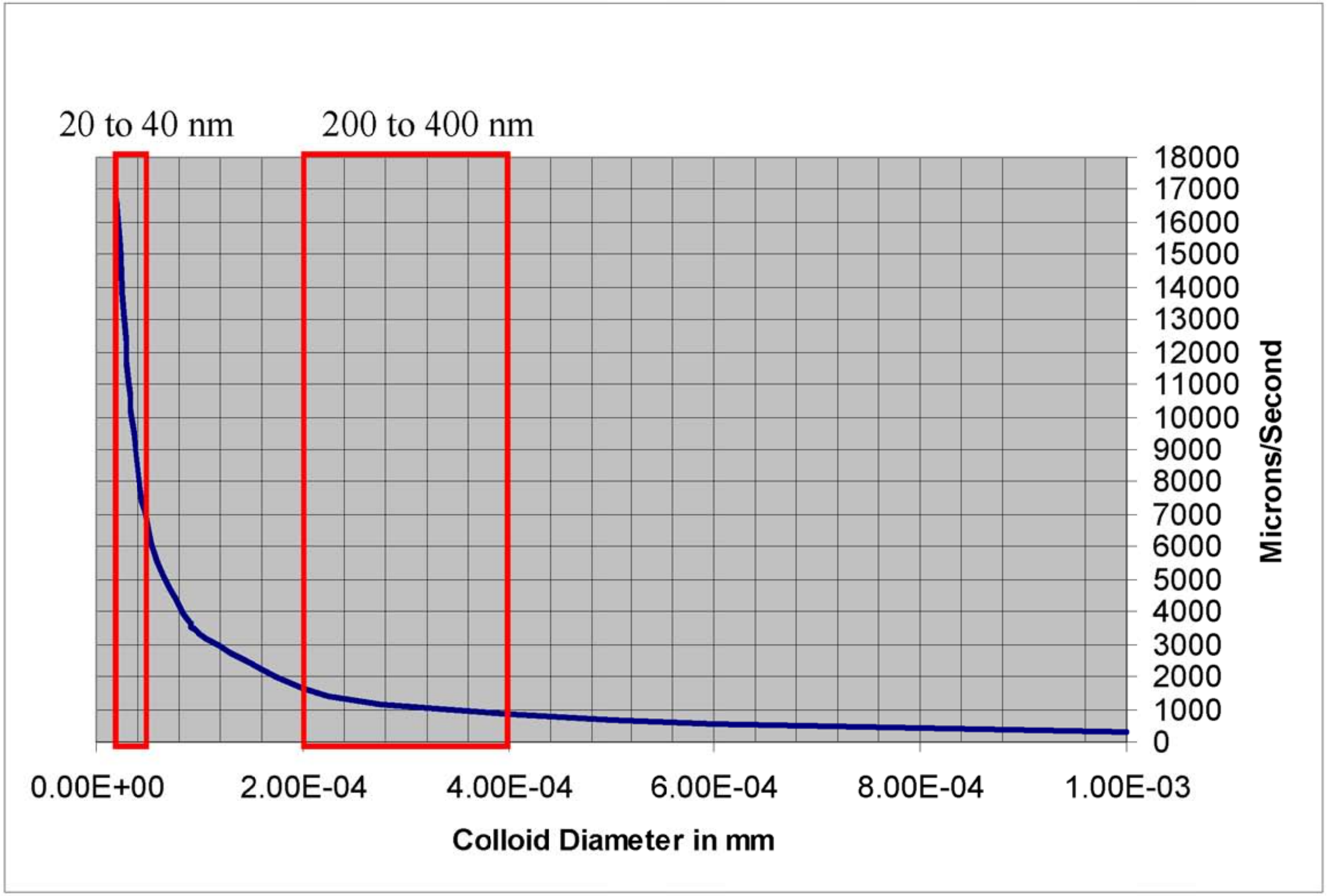
Point of Zero Charge - pH_{pznpc}
Binding or Dissociation of Protons

α-Al_2O_3	9.1	δ-MnO_2	2.8
α-$Al(OH)_3$	5.0	β-MnO_2	7.2
γ-AlOOH	8.2	SiO_2	2.0
CuO	9.5	$ZrSiO_4$	5
α-Fe_3O_4	6.5	Feldspars	2-2.4
α-FeOOH	7.8	Kaolinite	4.6
Fe_2O_3	8.5	Montmorillonite	2.5
$Fe(OH)_3$ (amorph)	8.5	Albite	2.0
MgO	12.4	Chrysotile	>10

Stokes Settling Velocity Vs. Fe Colloid Diameter



Colloid Velocity Due to Brownian Motion



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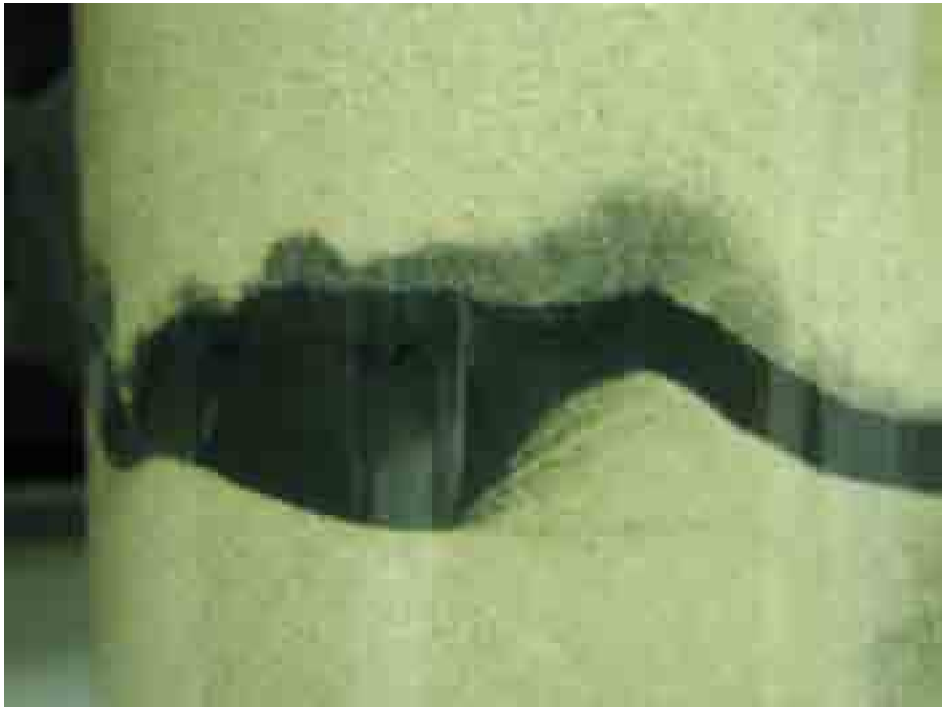
Colloid Delivery

- Since movement of the colloids takes place primarily during the actual injection event only -- A good grasp of the site hydrodynamics is required
- Management of interfacial forces may require attention, but in most cases will be secondary to hydrodynamics

Column Study Injection without Pressure Pulse



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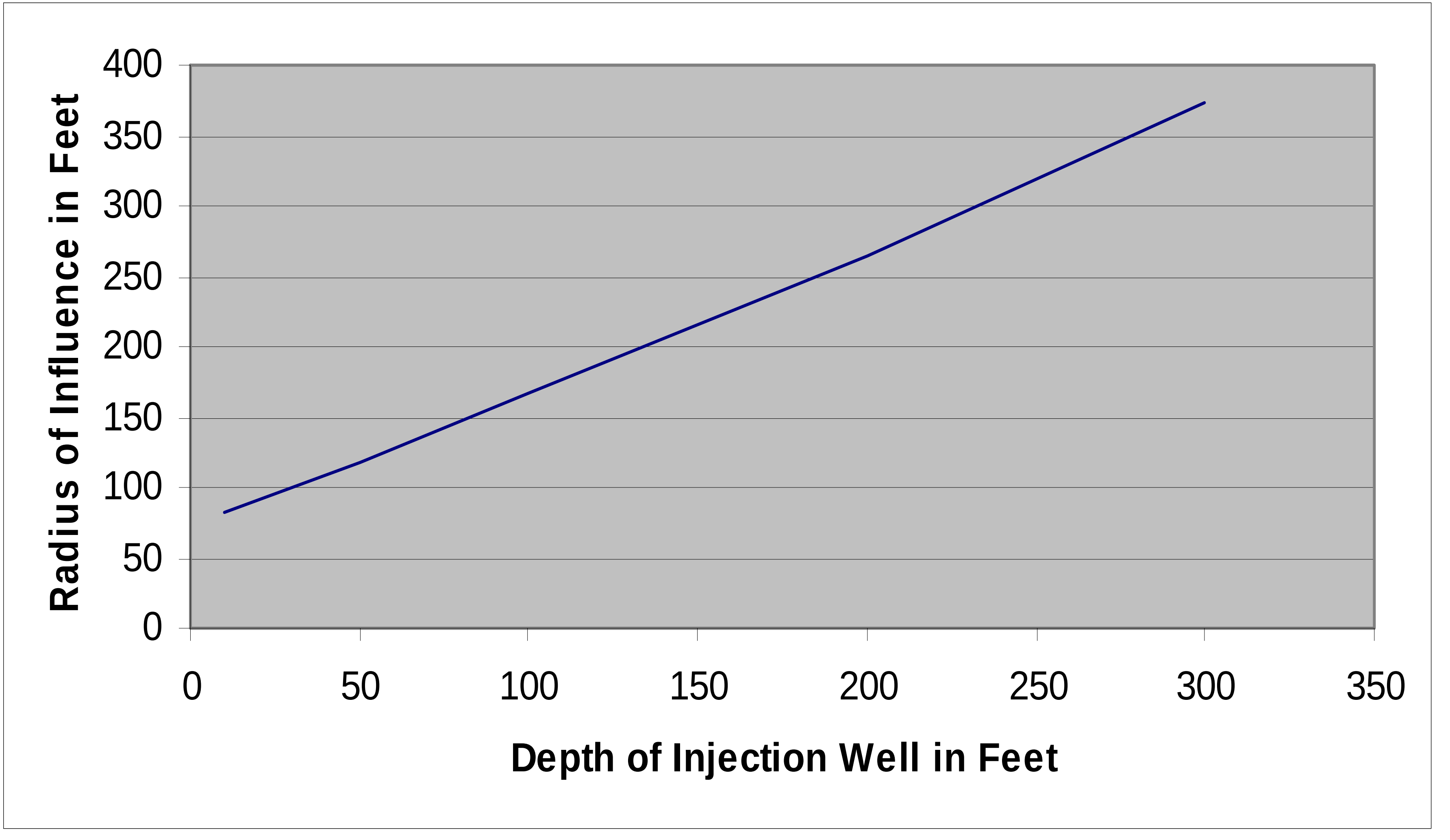
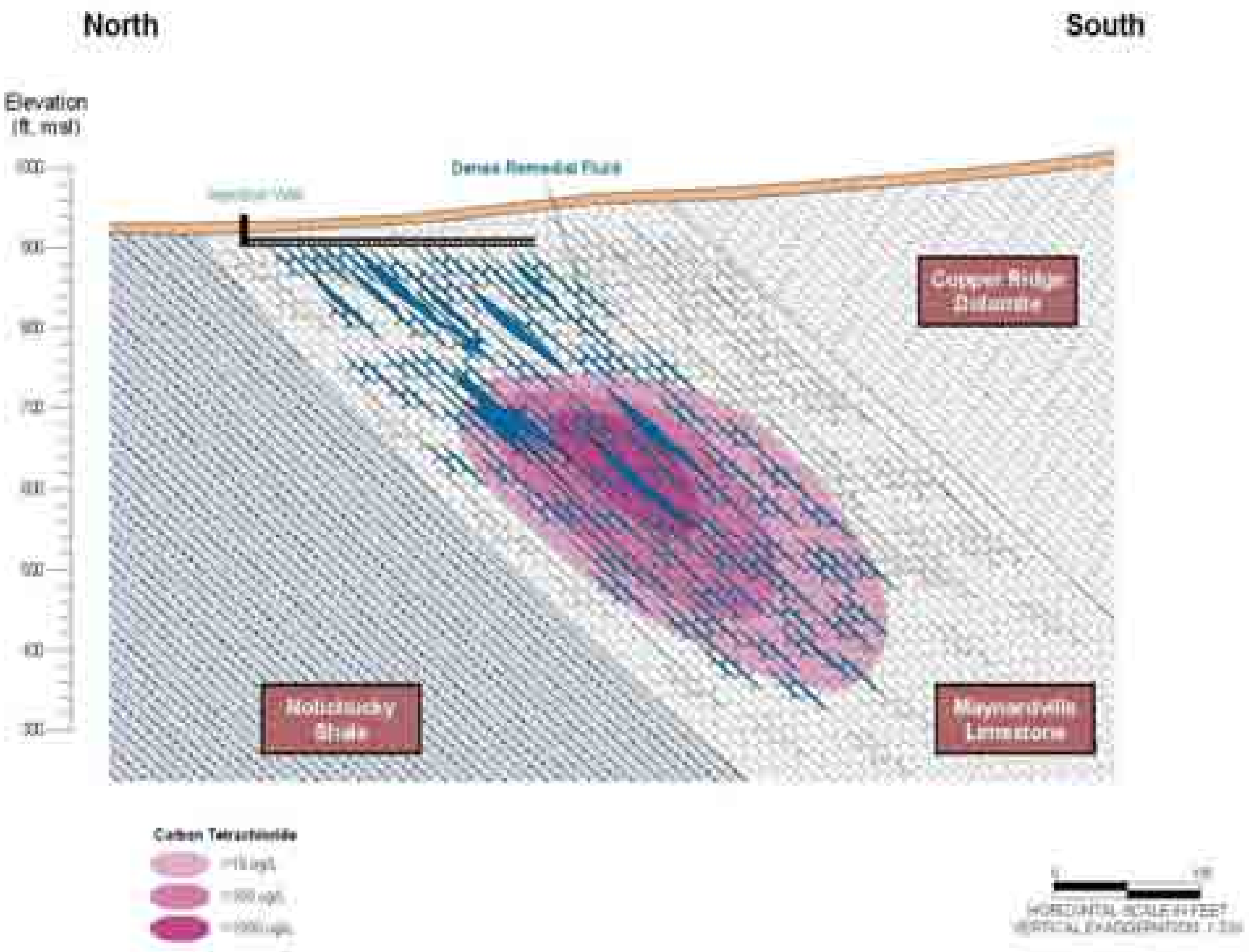
Column Study with Pressure Pulse

PPT Radius of Influence Enhancement



Reagents can be Designed to Follow Original DNAPL Contaminant Pathways

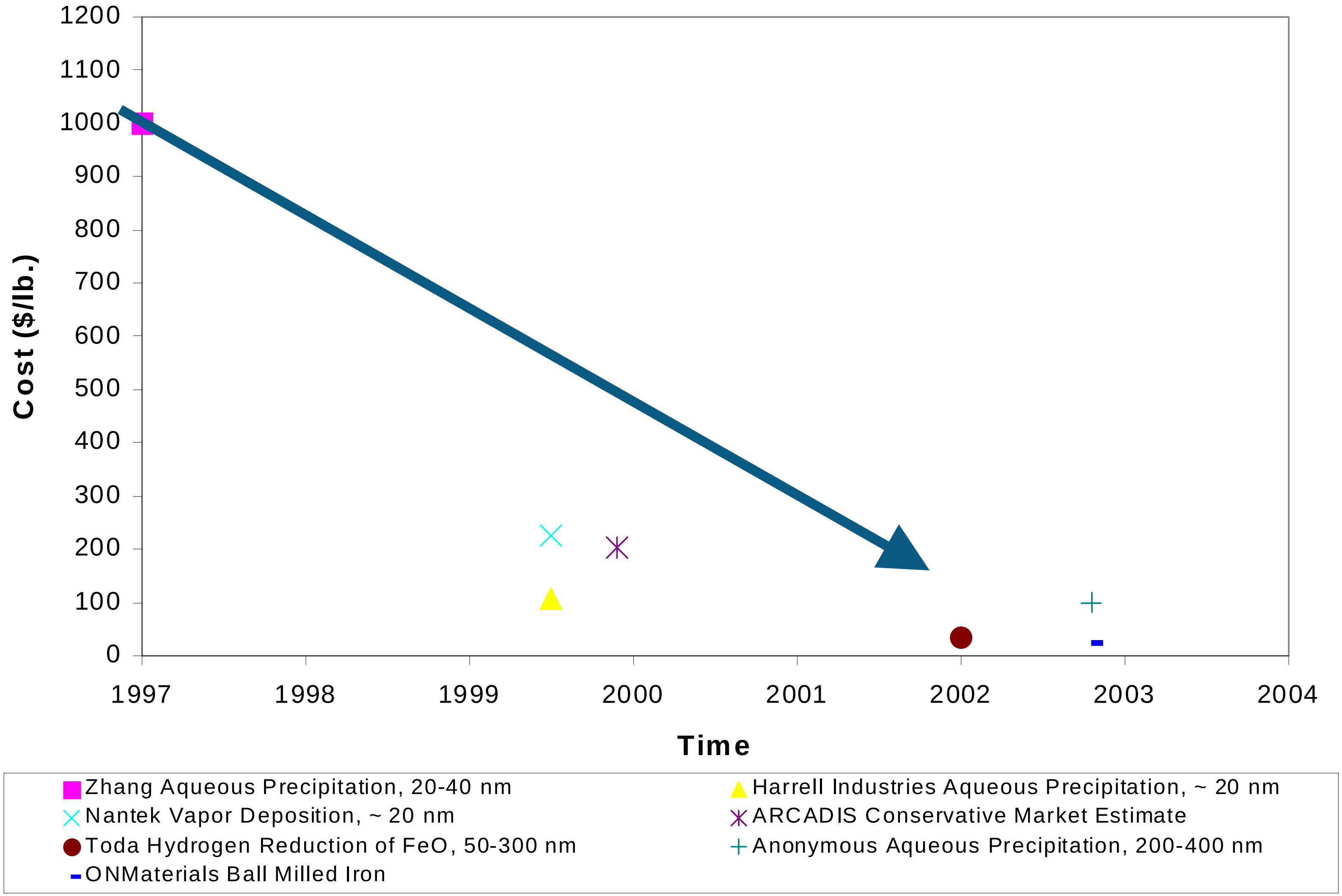


A Bedding Plane Surface of a Permian Limestone.

Nanoscale ZVI

Going Forward

Trend in Nanoscale Iron Price



Key Performance Issues

- Colloid Longevity
  - – Passivation by dissolved inorganics
  - – Unproductive hydrogen generation
- Transport Issues
  - – Size – the balance between gravitational settling and attractive forces – 200 to 600 nm ideal

Impacts on ZVI Longevity

- Effect of high TDS
  - Sulfate and Soluble Carbonates
- Effect of water dissociation
- Effect of CVOC reactions

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Controls on Colloid Longevity

- Control colloid structure
- Control trace constituents in colloids
  - Catalysts
  - Inorganic Inhibitors
- Modification of the colloid surface
  - Catalysts
  - Inorganic Inhibitors
  - Polymers

Colloid Longevity and DNAPL

- The positive effect of chloride as a corrosion promoter
  - Accelerate electron generation and transport
  - Create new reactive sites
  - Overcome passivation effects
  - See ES&T Vol. 38, pp 5157-5163 Hernandez et al
- Exploitation of colloid structure and composition

Evaluation of Colloid Longevity

- Three types of colloid
  - Hydrogen Reduced (Toda)
  - Precipitated (Polyfon)
  - Ball Milled

The Use of Palladium

- Cost will contribute 5 to 20% of total cost
- Concern is regulatory driven by the toxicity of palladium or other metals

Resolving Regulatory Issues

- Presence of the hydrogenation catalyst (Pd, Pt, Sn, Ni, Ag) is likely to be the object of regulatory scrutiny
- Many of these metals used historically in ways that foster human oral exposure such as dentistry, and food preservation
- Geochemistry literature analysis shows that Pd or Pt introduced into the environment through the application of BNI will remain insoluble rather than dissolving and migrating downgradient
- Pd has been used during another TCE remediation program in California