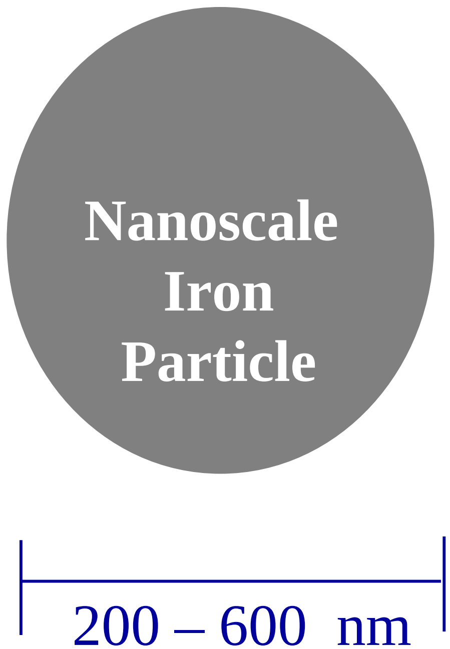

Evaluation of the Control of Reactivity and Longevity of Nano Scale Colloids by the Method of Colloid Manufacture

Nanotechnology for Hazardous Waste Site Remediation

Technical Workshop

Washington DC   October 20-21, 2005

David Vance

Current Practical Manufacturing Methods

- Bottom Up – Precipitation
  - Dominant Known Technology is Sodium Borohydride Reduction
  - Others ?
- Bottom Down – Attrition via Ball Milling
- Bottom Down Iron Oxides then Hydrothermal Reduction

What Defines a Practical Manufacturing Technology

- Cost
- Capacity to be produced in ton lots
- Capacity to be produced in relatively short time frames

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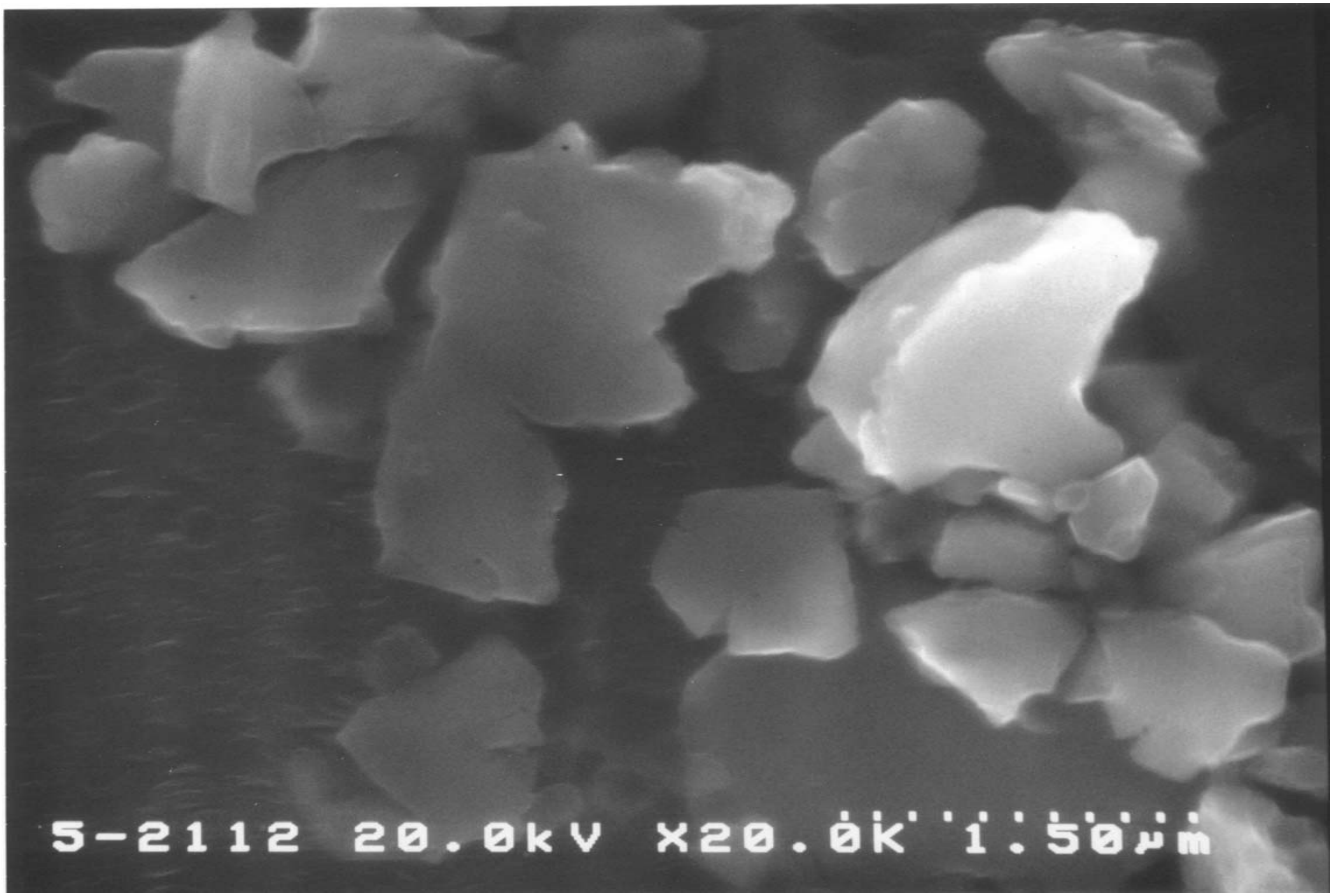
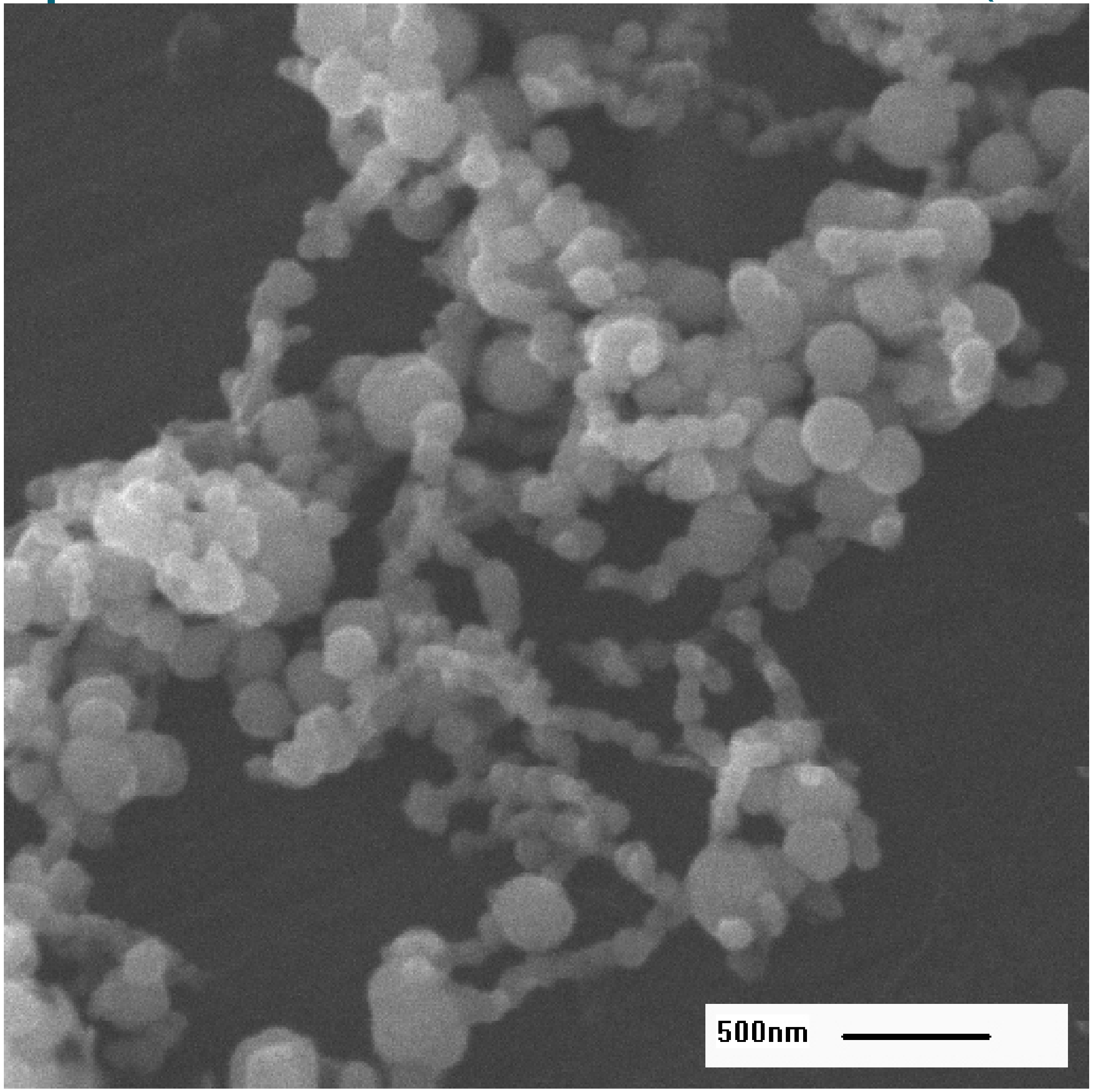
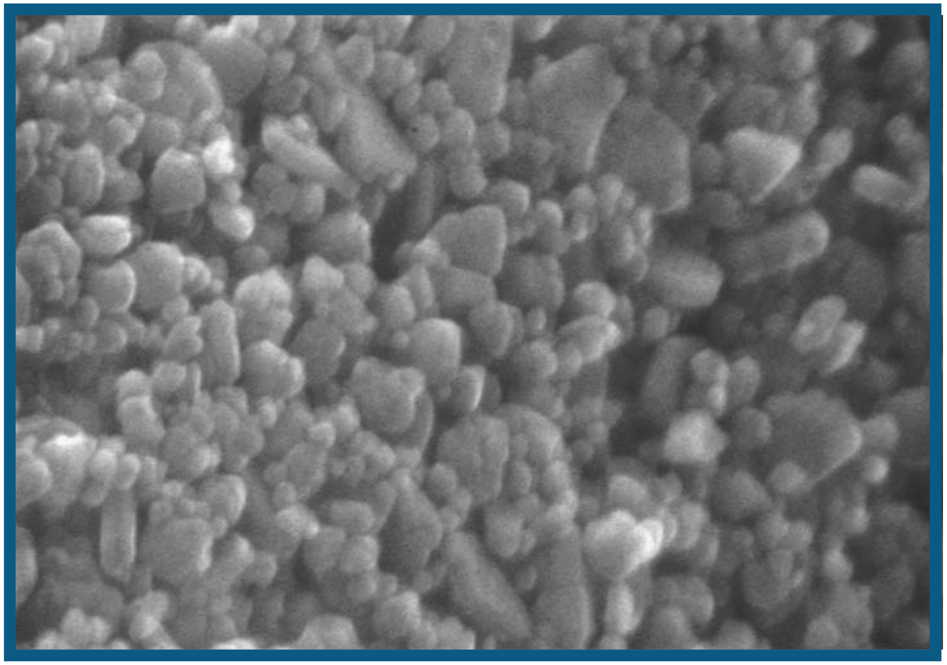
Top Down Nano-Scale Fe Colloids



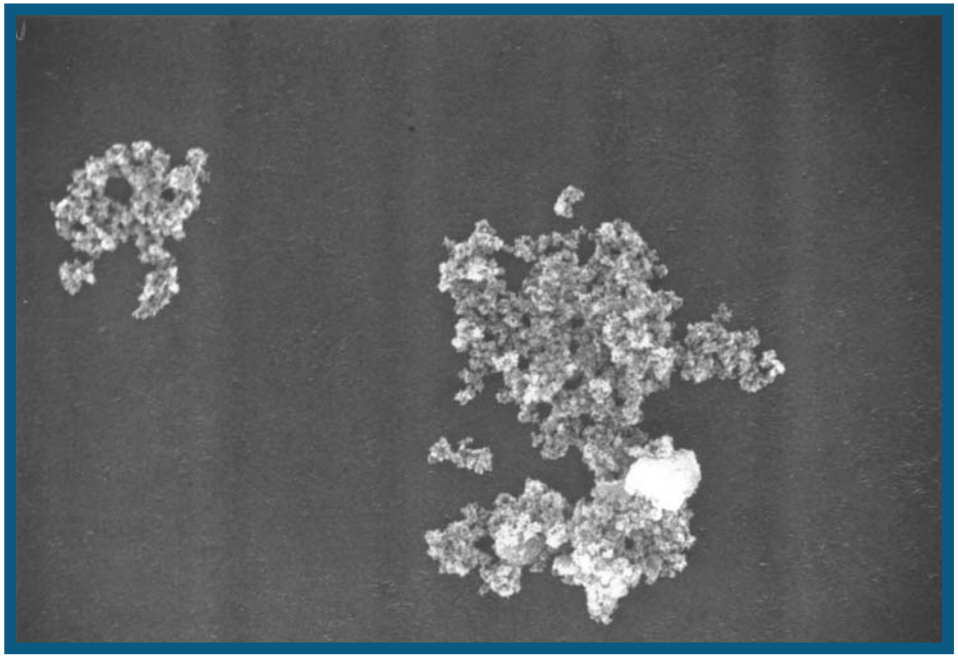
Bottom Up Nano Scale Fe Colloids (ARCADIS)



Another Bottom Up Iron



120 nm



10 µm

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Key Performance Issues

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

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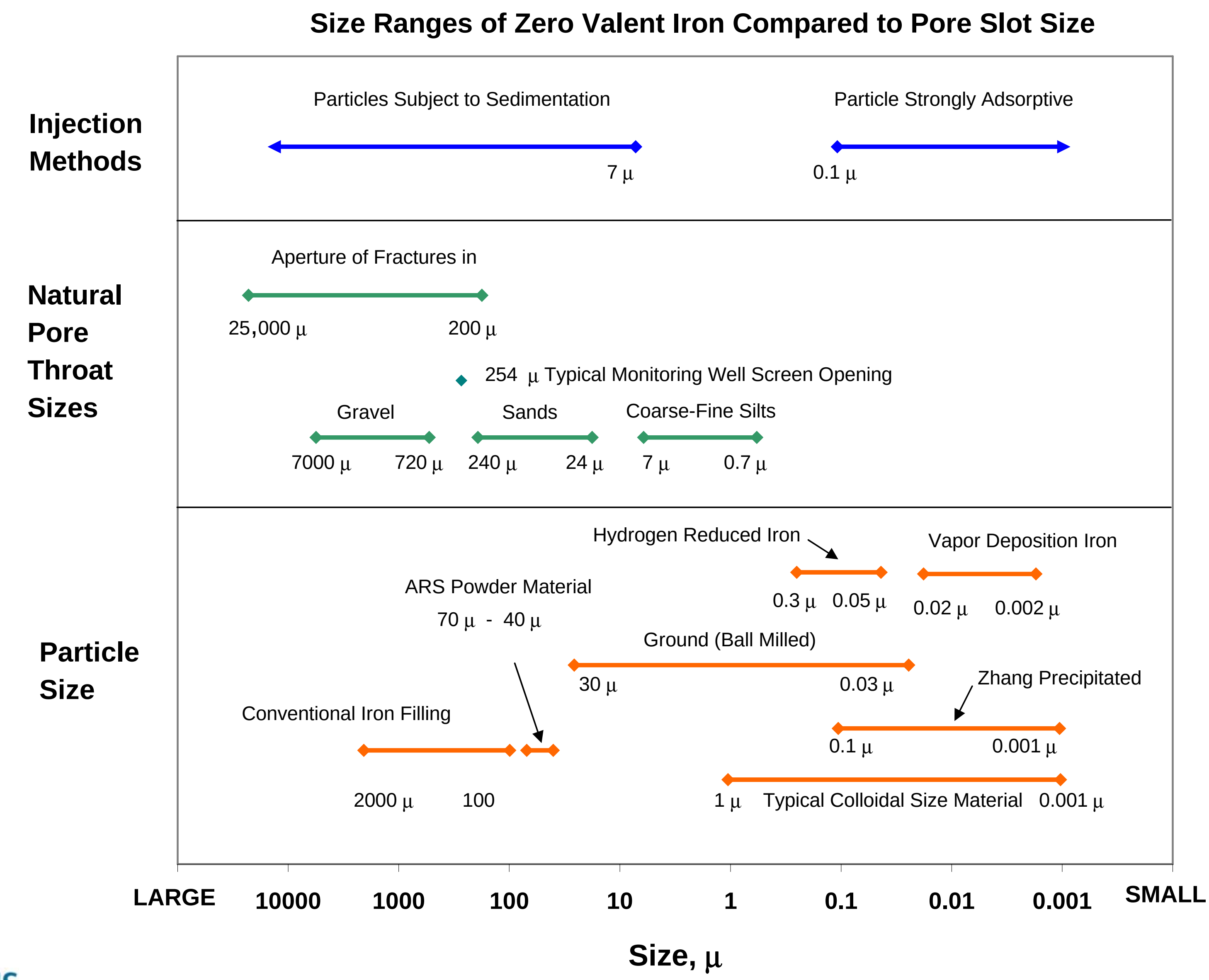
Delivery

Nanoscale Iron Particle Size Comparison



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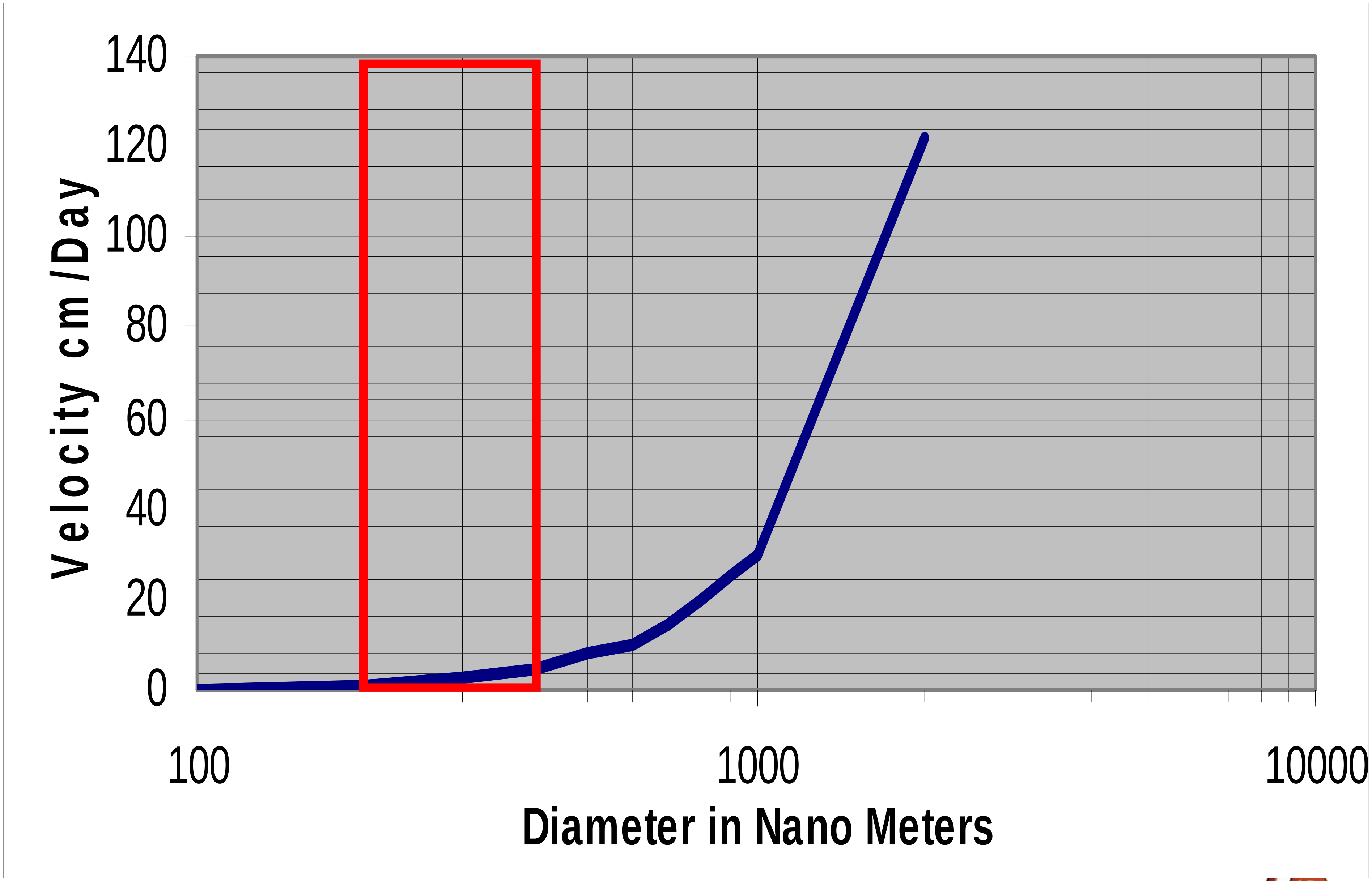
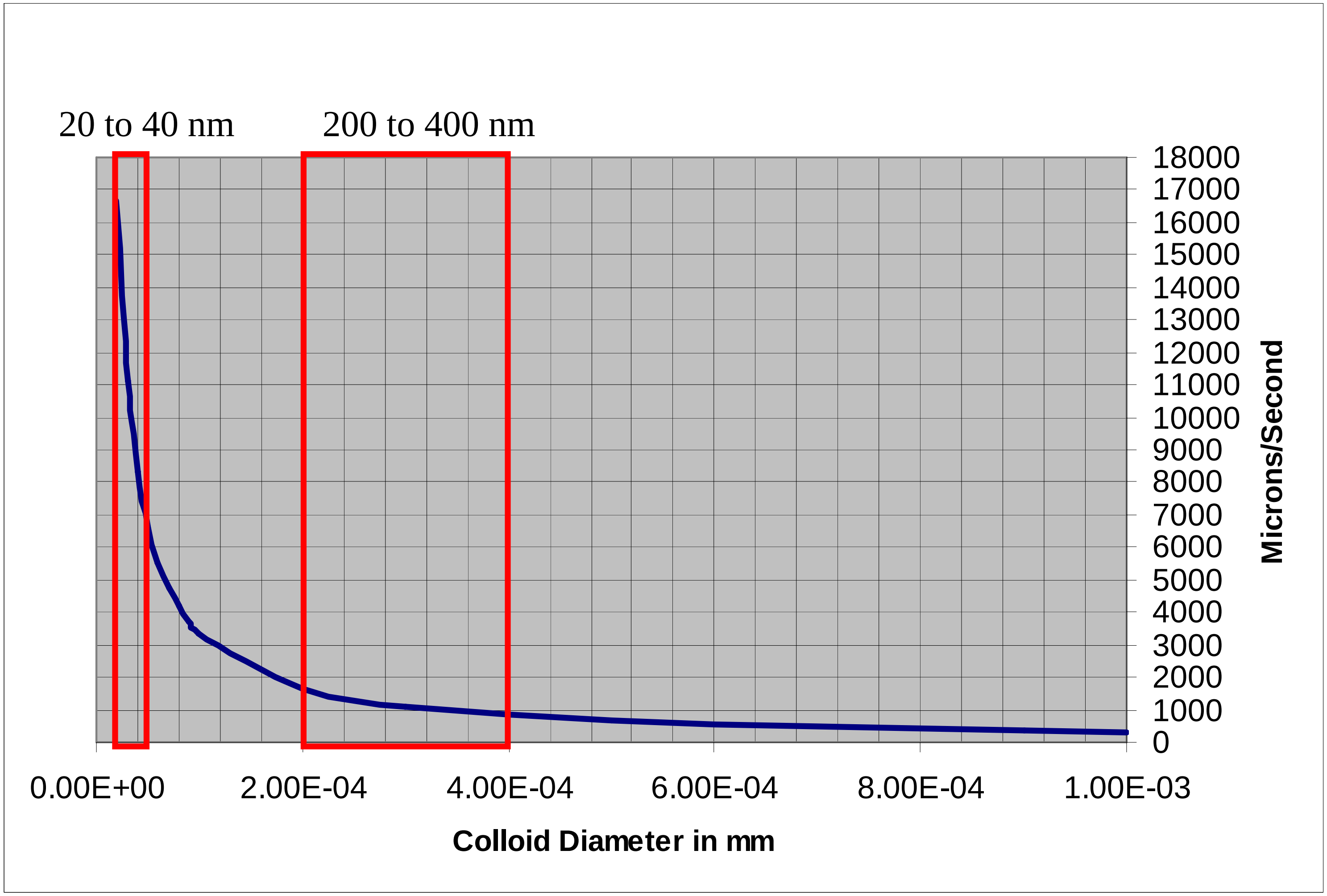
Point of Zero Charge - pH_{pznpc}
Binding or Dissociation of Protons

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



Colloid Reactivity and Longevity

Environmental Impacts on ZVI Longevity

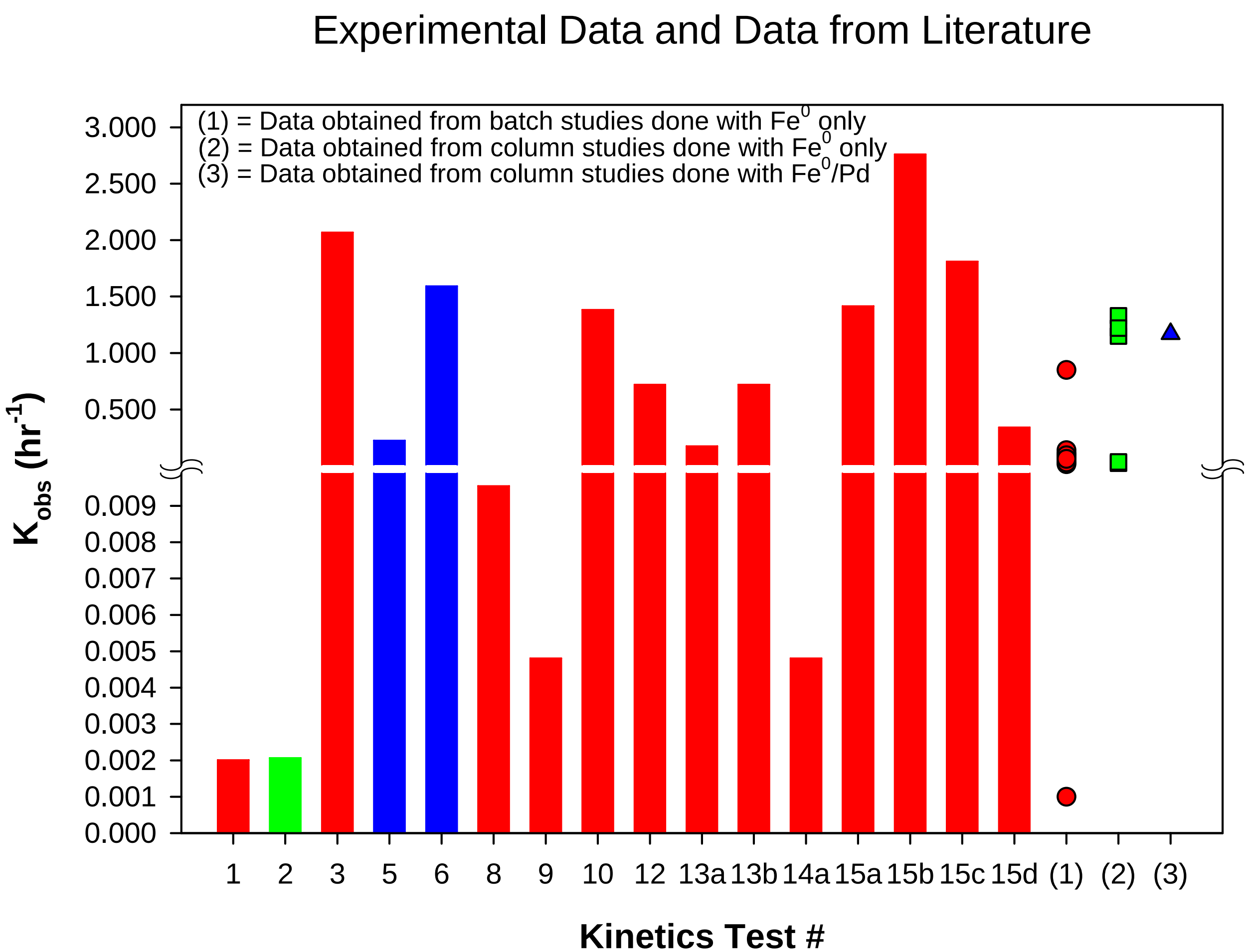
- Effect of high TDS
  - Sulfate and Soluble Carbonates
- Effect of water dissociation
- Effect of CVOC reactions

Intrinsic Controls on Colloid Longevity

- Colloid structure
  - Particle morphology – shape, pits
  - Particle crystal structure – size of crystal domains, kinks, amorphous zones
- Control composition - Secondary constituents in colloids
  - Catalysts
  - Manufacturing byproducts
- Modification of the colloid surface
  - Catalysts
  - Inorganic inhibitors
  - Polymers

Kinetics Batch Test Results

(higher values indicate short half-lives)

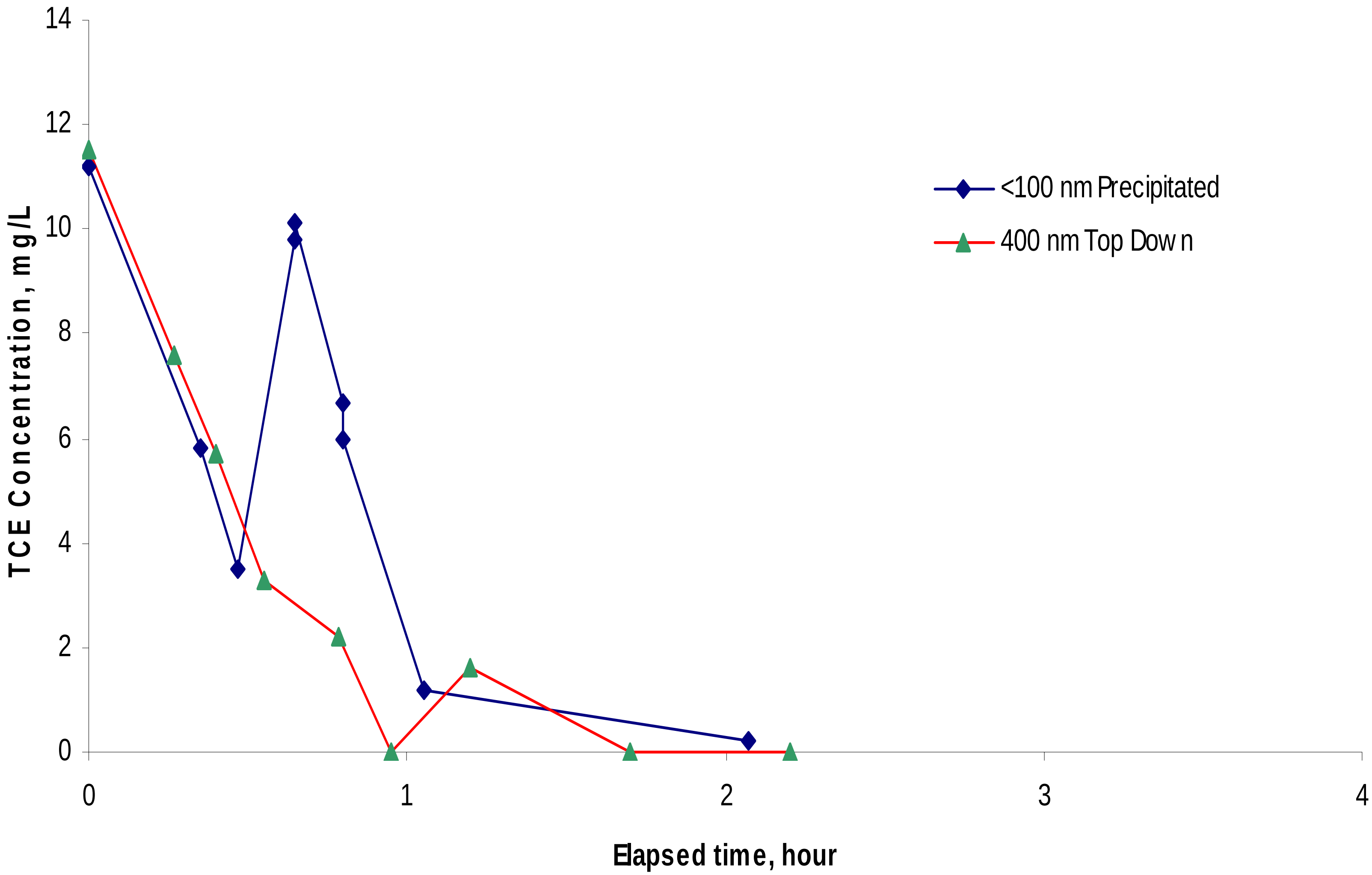


Red Bars are Vendor C Ball Milled

Green Bar is Vendor A Precipitated

Blue Bars are Vendor B Precipitated

Reactivity of Top Down Vs. Bottom Up Colloids



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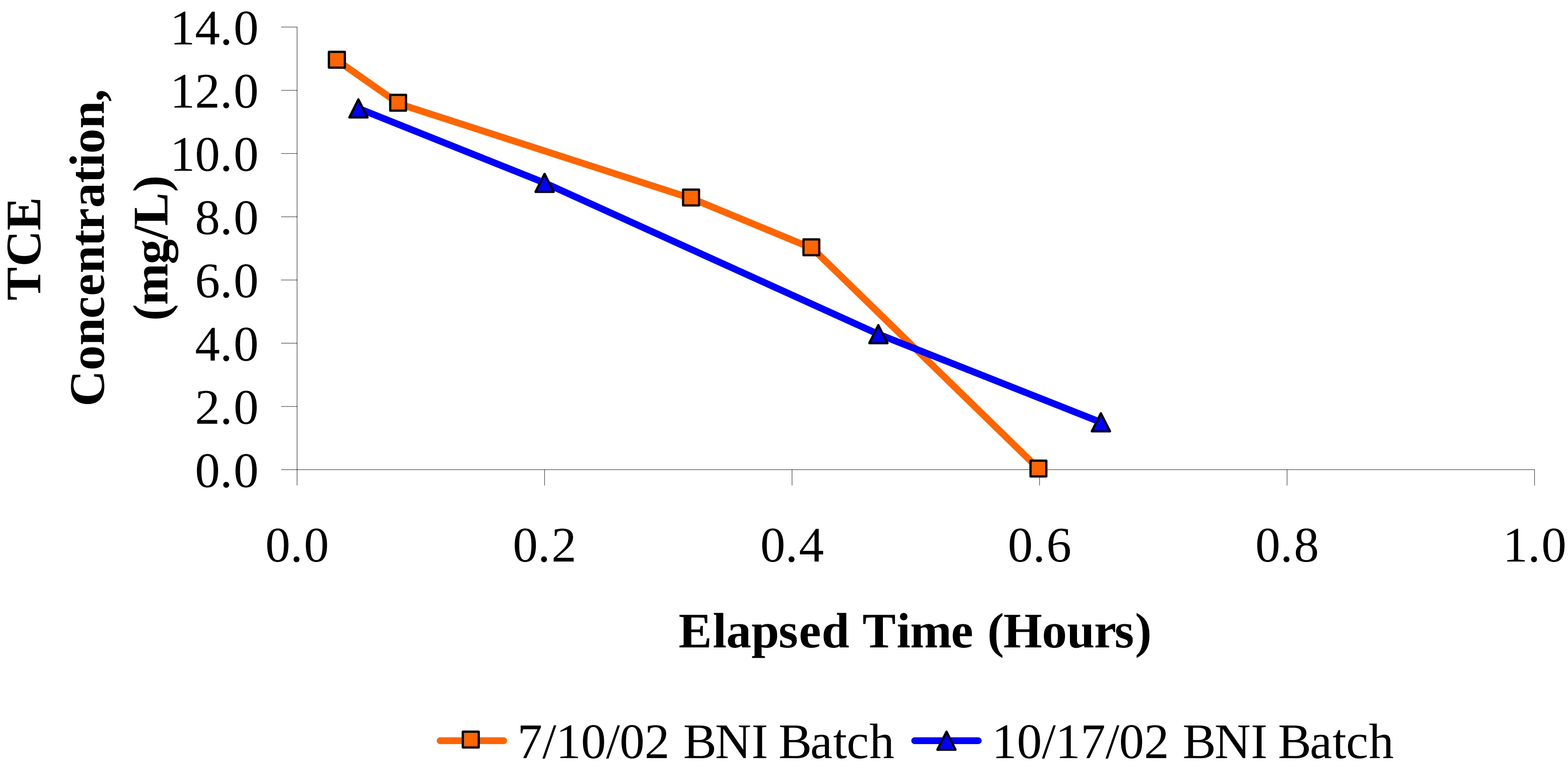
BNI TCE Dechlorination Kinetics Stability of Ball Milled Colloids



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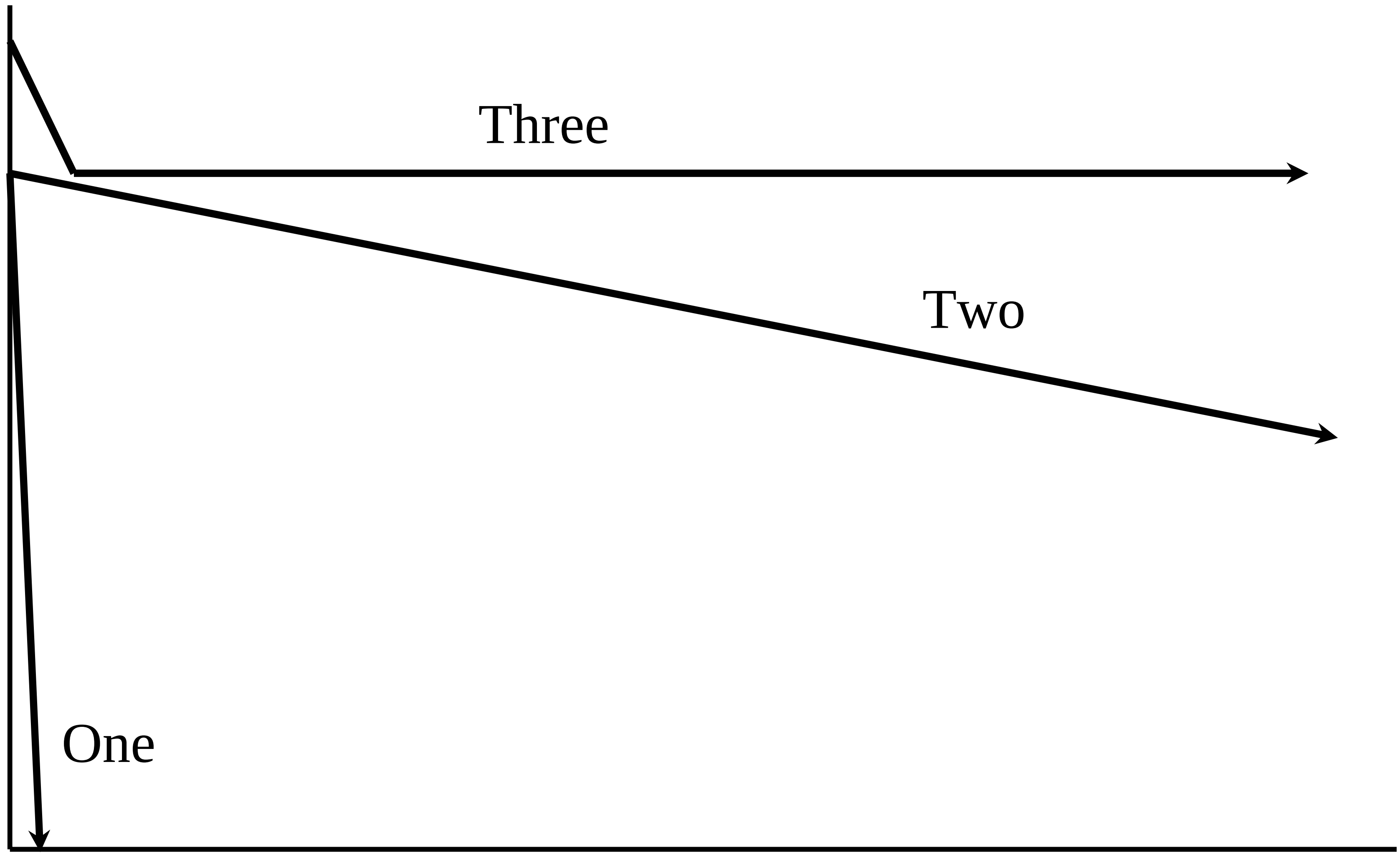
Three Classes of Colloid Reaction



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What Causes Type Three Behavior?

- Oxidation during shipment or handling, surface coatings
  – Acid treatment does not remove effect
- The presence of by products from the manufacturing process that interfere with electron transfer
  – Borohydride leaves % concentrations of boron in the colloid
- Structural changes
  – Annealing or Ostwald Ripening
- Palladization restores reactivity

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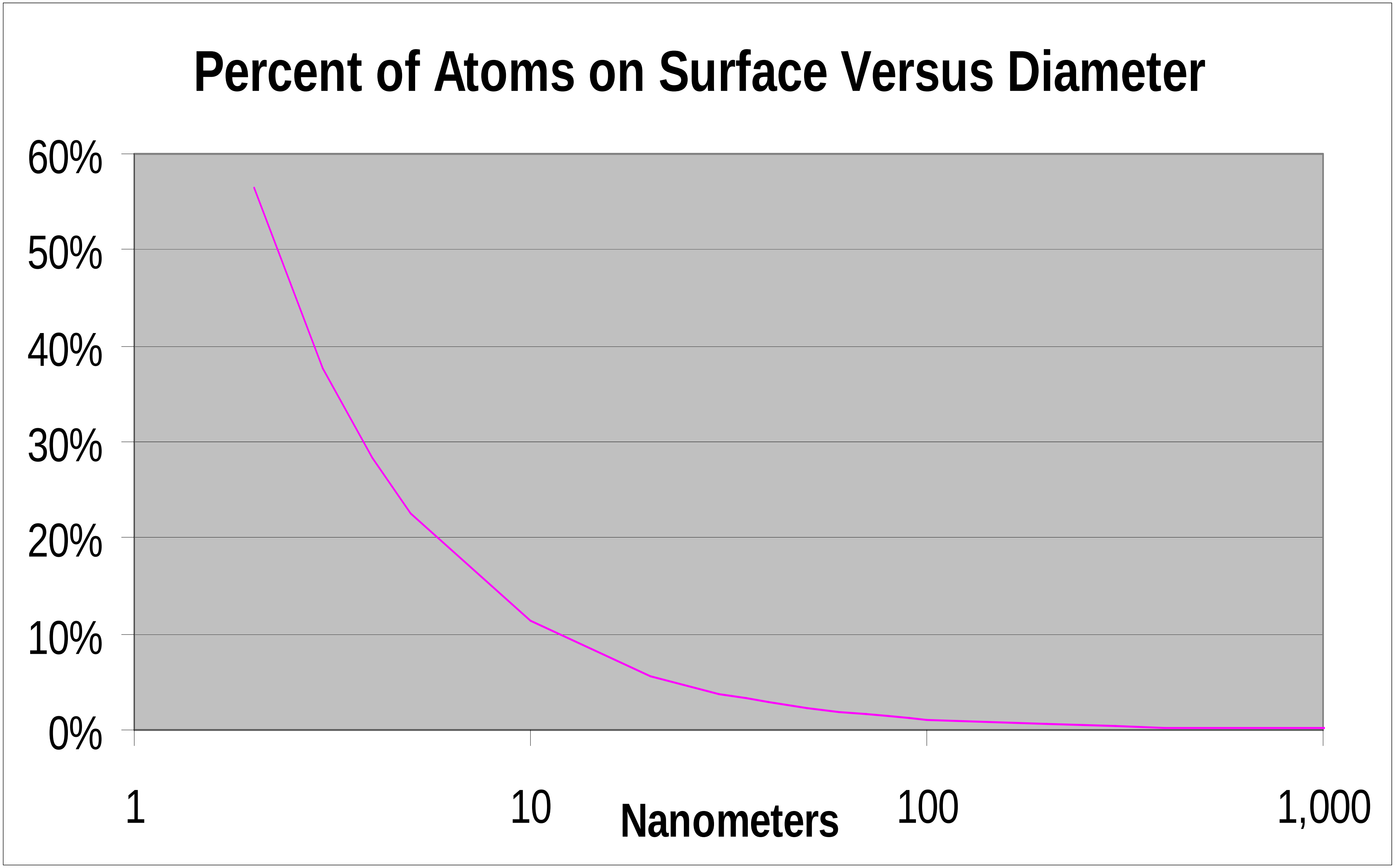

Percent of Atoms on Surface Versus Diameter
60%
50%
40%
30%
20%
10%
0%
1
10
100
1,000
Nanometers

Variations in Iron Colloid Response

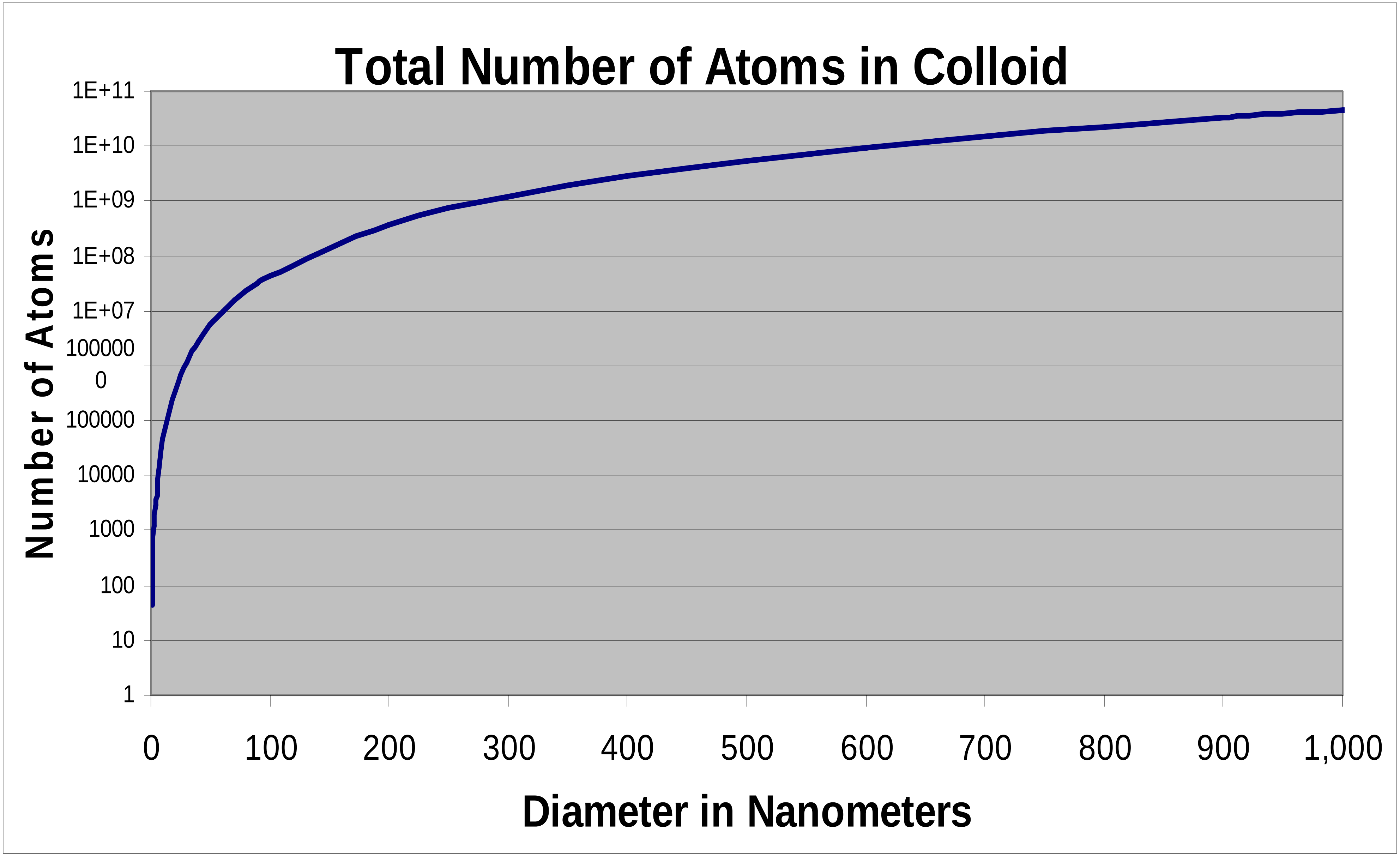
- Class One
  - Typical response from all early product runs
- Class Two
  - Effect due to size and chemical make up or structure – colloids from 100 nm to 2 Microns
  - Becomes class one with palladization
- Class Three
  - Acid pretreatment has no effect
  - Repeated testing by independent labs as well
  - Becomes class one with palladization

The Good News
Type One and Type Two Each Have a Valuable Niche

- Type one colloids are of value for treatment of DNAPL or high concentrations of adsorbed CVOC
  - Think of reductive version of chemical oxidation
  - The “Champaign effect” is observed with the most extreme examples
- Type two colloids are of value for use in reactive walls for the long term treatment dissolved CVOCs under natural flow conditions

A New Technology with Unique Potential Problems

- We understand how to manipulate isolated molecular systems, chemical oxidation for example
- Efficient bacterial enzymatic pathways have been developed over several billion years
- Nano scale colloids are large assemblages of molecules subject to atomic forces with complex structure and a behavior that is in the process of definition


Total Number of Atoms in Colloid
Number of Atoms
1E+11
1E+10
1E+09
1E+08
1E+07
1000000
100000
10000
1000
100
10
1
0
100
200
300
400
500
600
700
800
900
1,000
Diameter in Nanometers

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“Reality is that which,
when you stop believing in it,
does not go away”

The Bottom Line

Make Assumptions at Your Own Risk

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