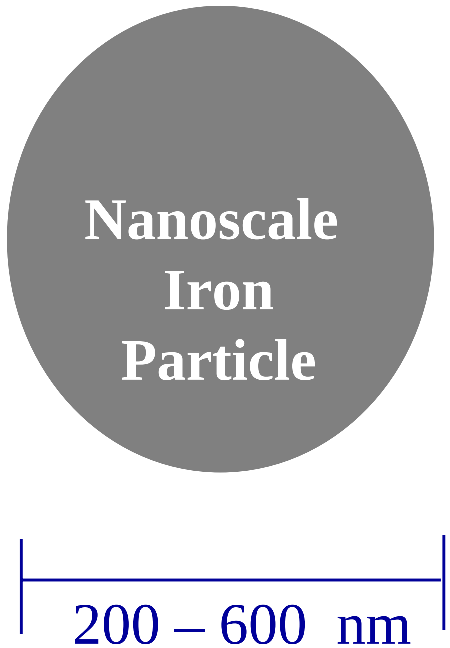


Evaluation of the Control of Reactivity and Longevity of Nano Scale Colloids by the Method of Colloid Manufacture

Nanotechnology for Hazardous Waste Site Remediation

Technical Workshop

Washington DC October 20-21, 2005

David Vance

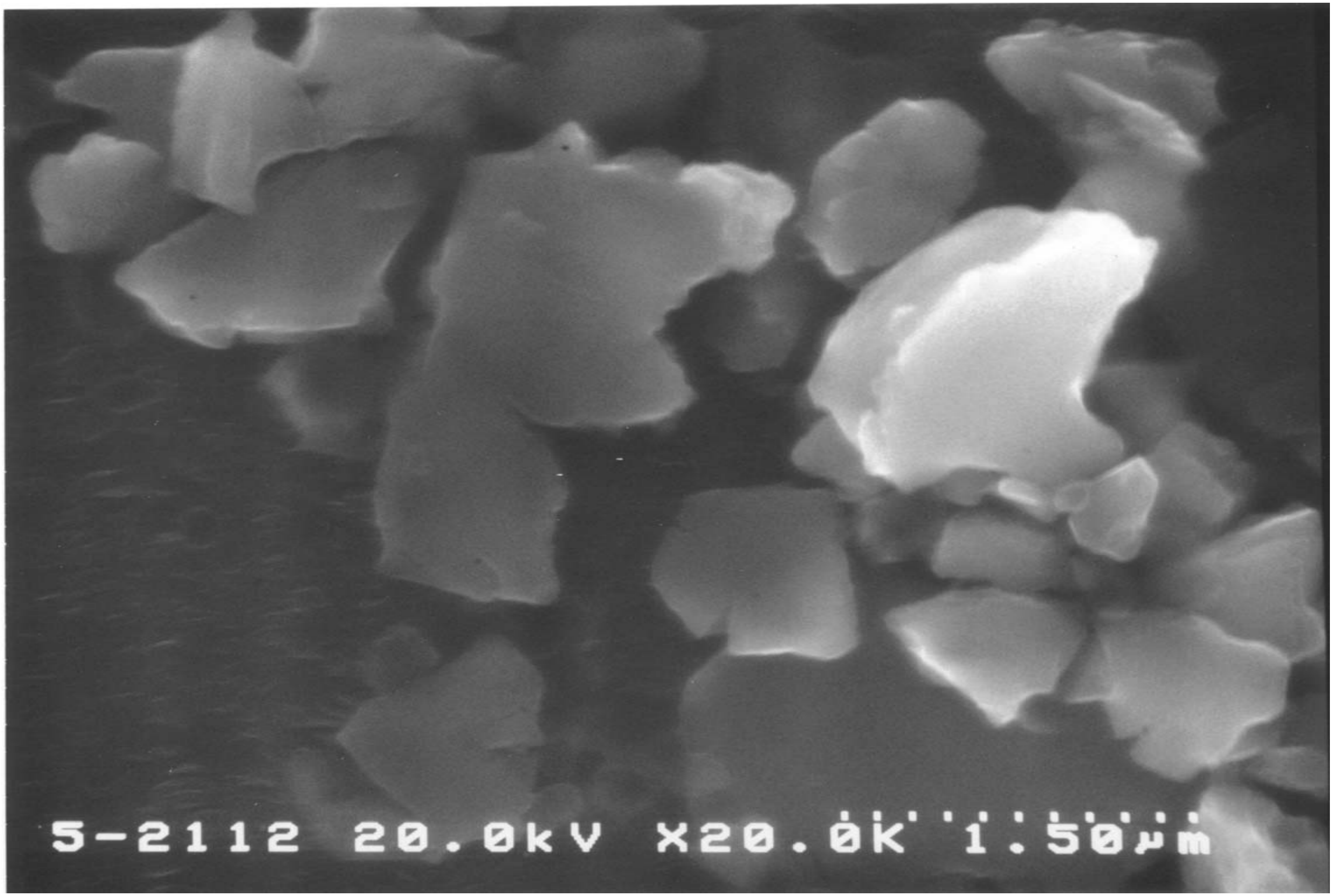
Current Practical Manufacturing Methods

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

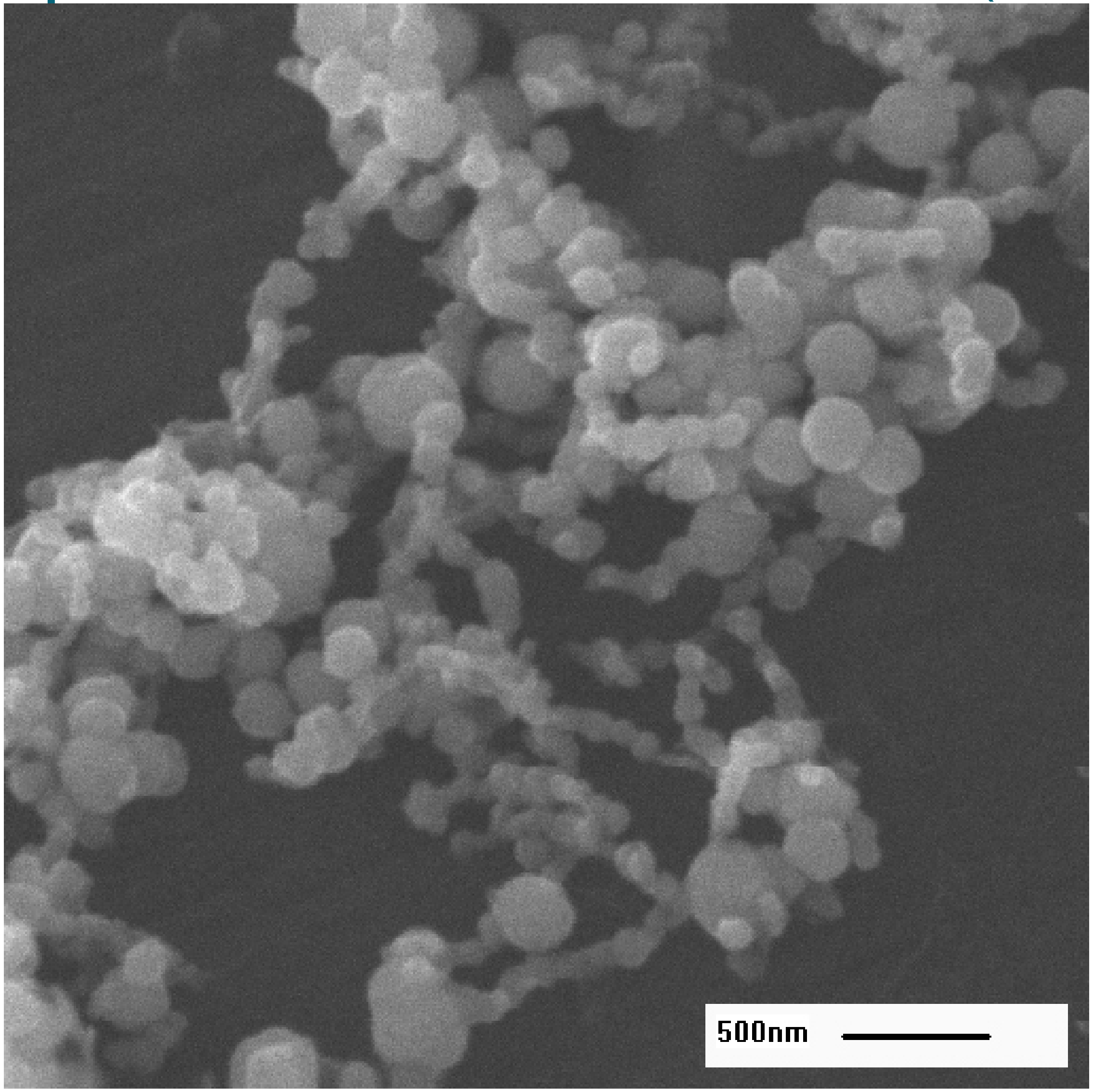
What Defines a Practical Manufacturing Technology

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

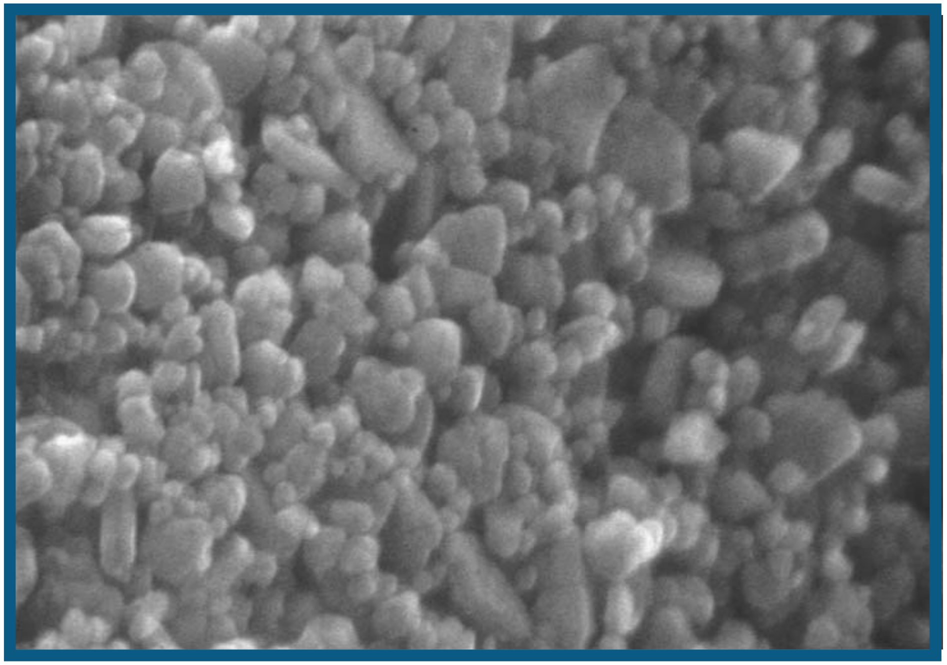
Top Down Nano-Scale Fe Colloids



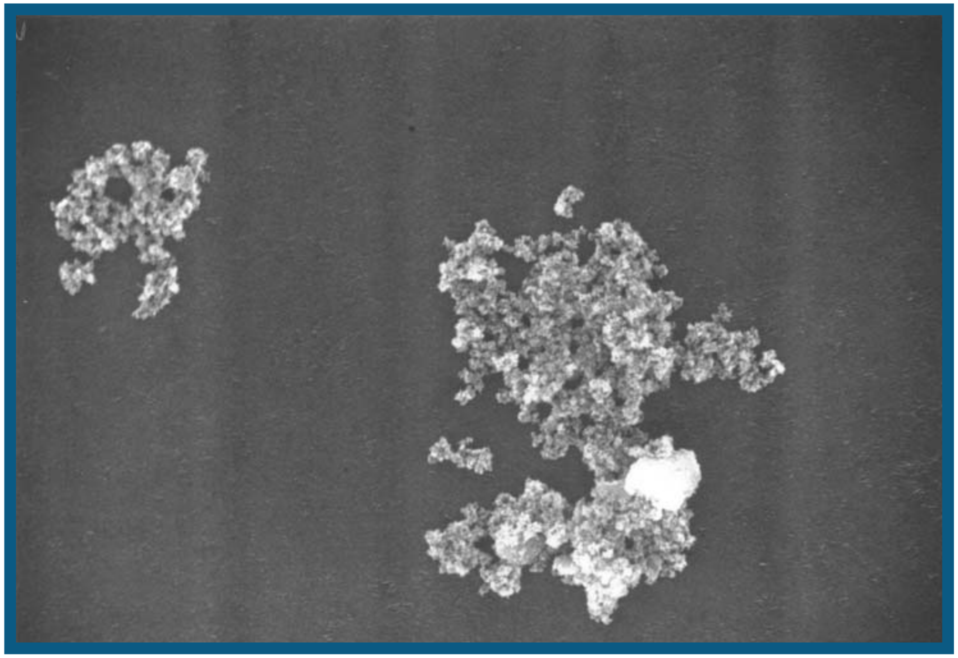
Bottom Up Nano Scale Fe Colloids (ARCADIS)



Another Bottom Up Iron



120 nm



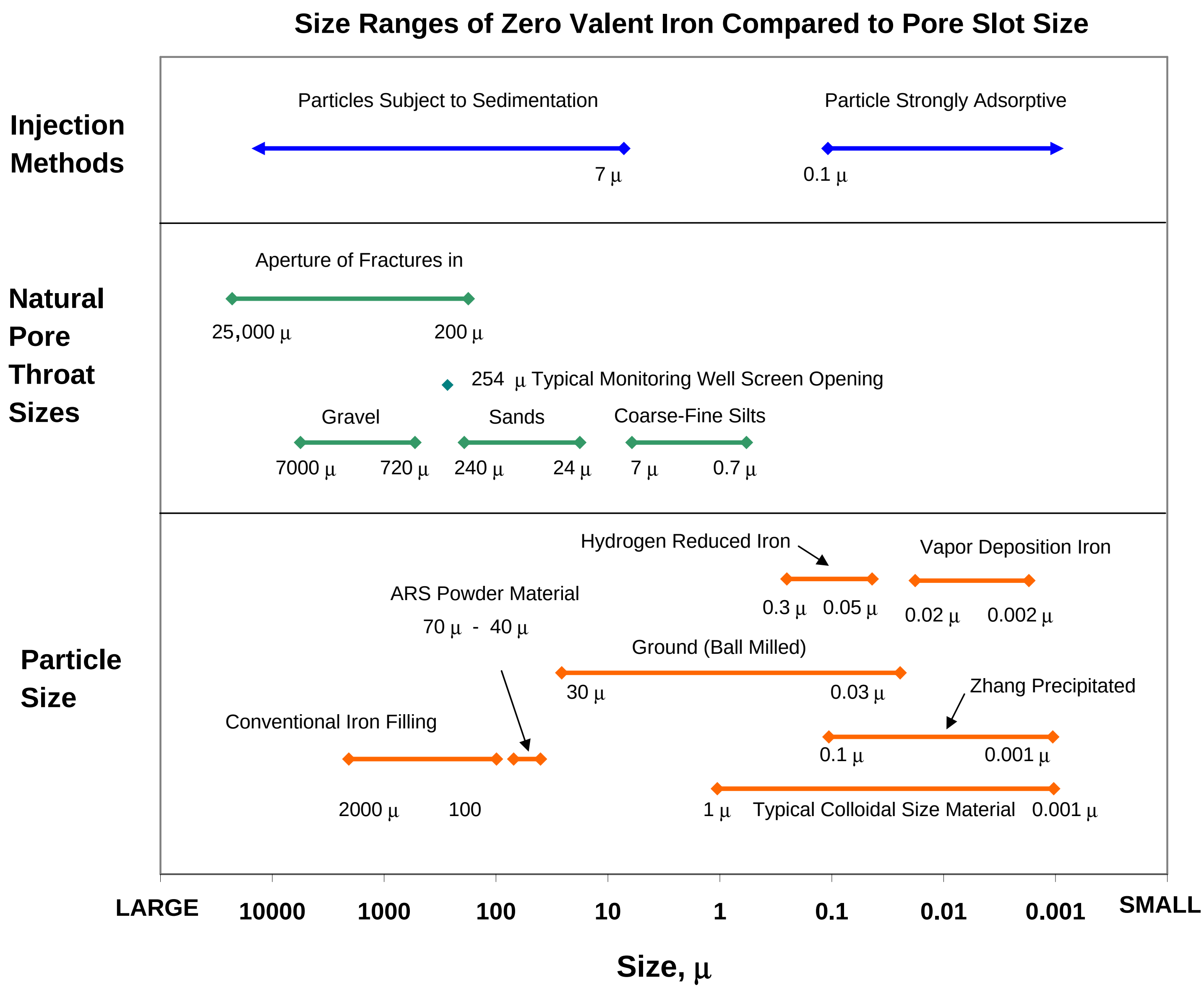
10 µm

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

Delivery

Nanoscale Iron Particle Size Comparison



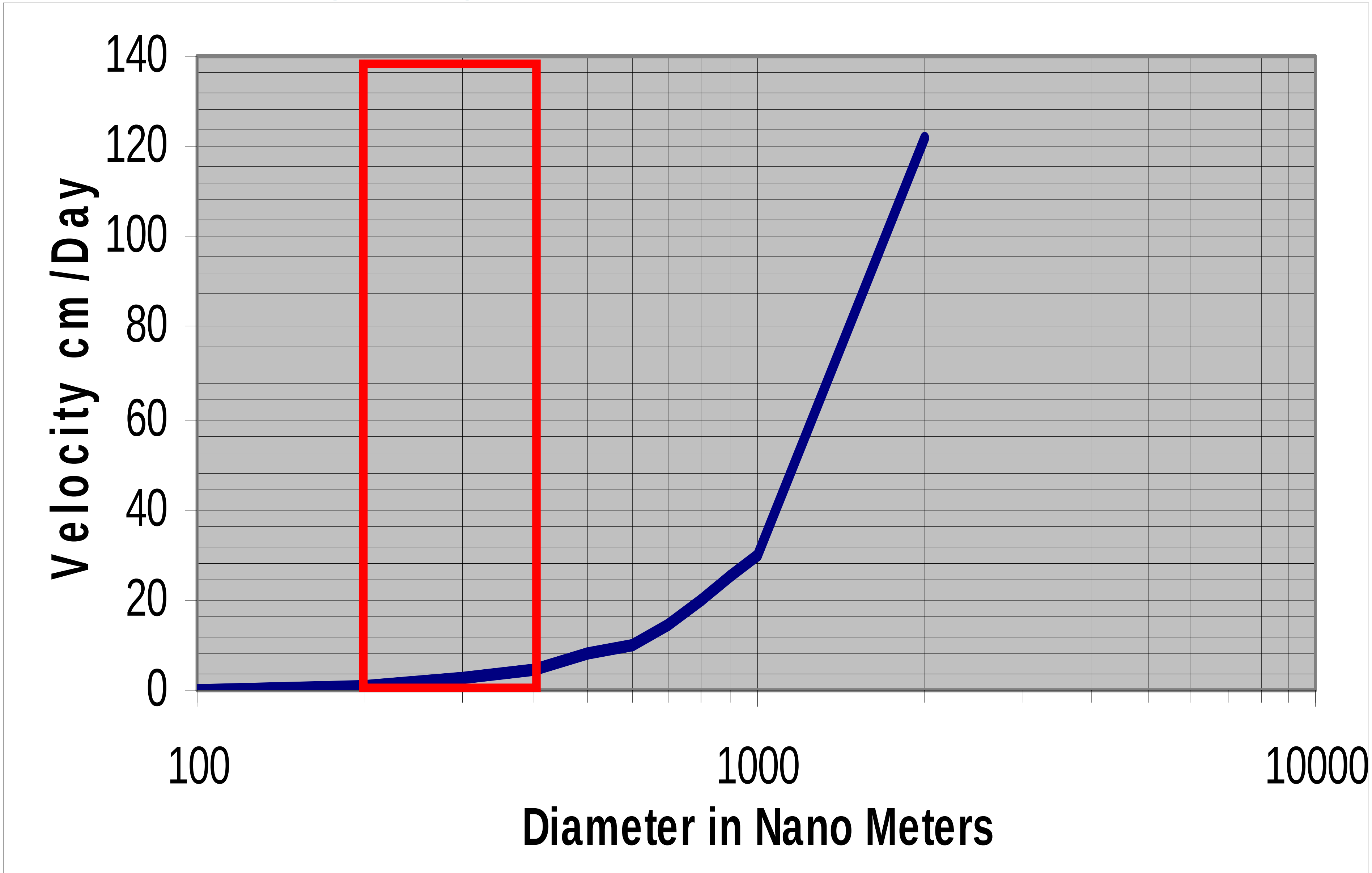
ARCADIS

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

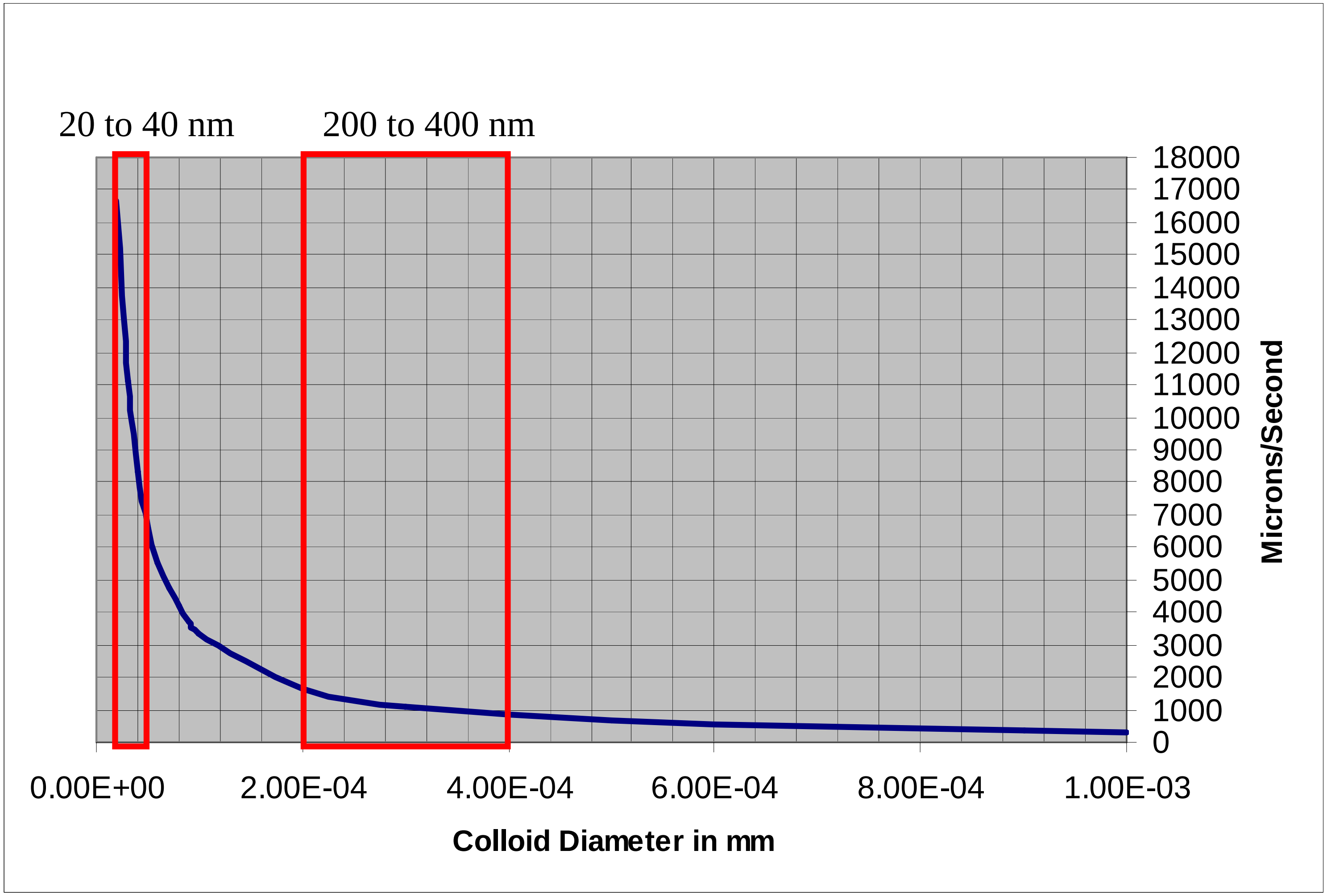
α-Al_2O_3	9.1	δ-MnO_2	2.8
α-$Al(OH)_3$	5.0	β-MnO_2	7.2
γ-AlOOH	8.2	SiO_2	2.0
CuO	9.5	$ZrSiO_4$	5
α-Fe_3O_4	6.5	Feldspars	2-2.4
α-FeOOH	7.8	Kaolinite	4.6
Fe_2O_3	8.5	Montmorillonite	2.5
$Fe(OH)_3$ (amorph)	8.5	Albite	2.0
MgO	12.4	Chrysotile	>10

ARCADIS

Stokes Settling Velocity Vs. Fe Colloid Diameter



Colloid Velocity Due to Brownian Motion



ARCADIS

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

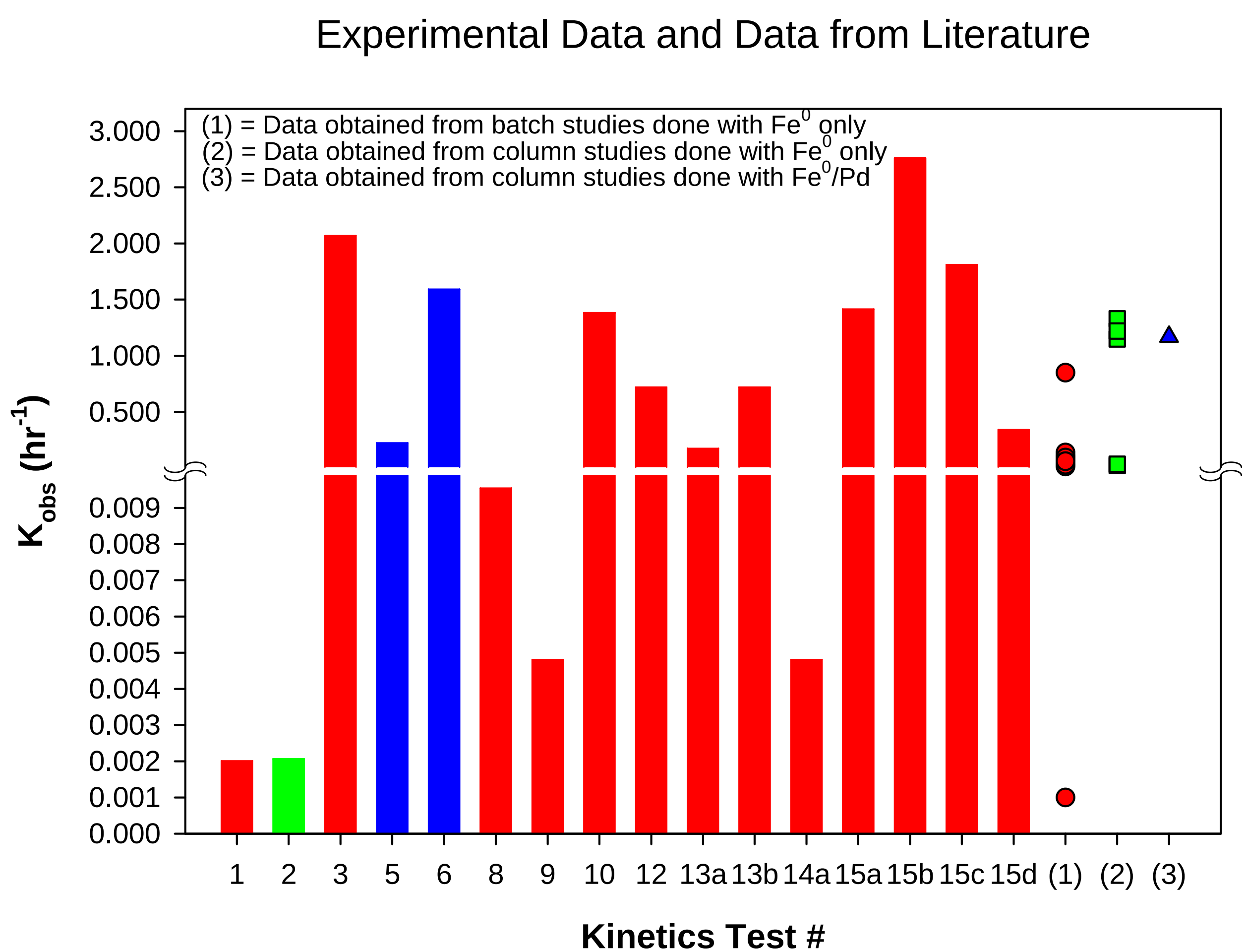
Intrinsic Controls on Colloid Longevity

- 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

ARCADIS

Kinetics Batch Test Results

(higher values indicate short half-lives)



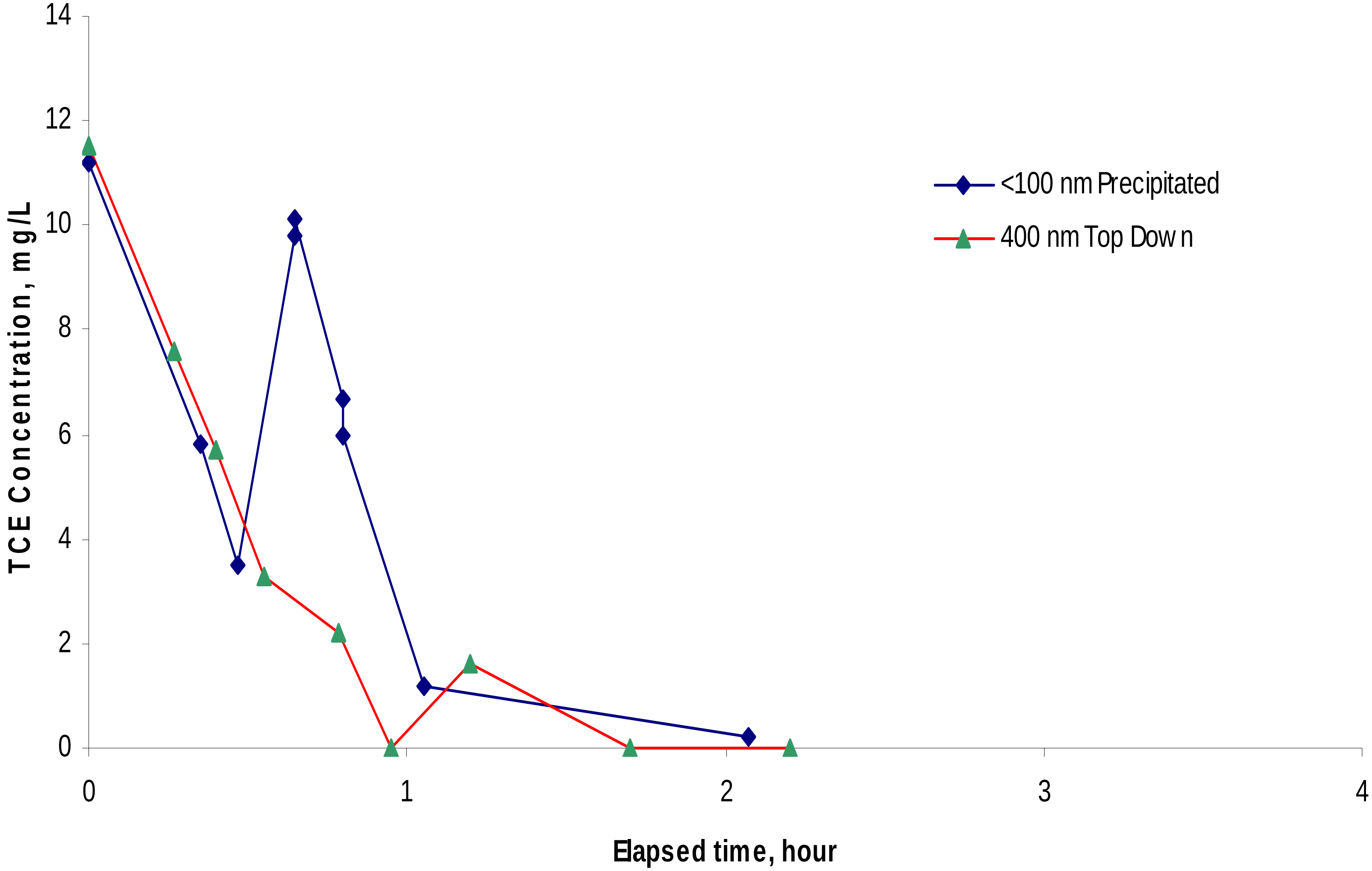
Red Bars are Vendor C Ball Milled

Green Bar is Vendor A Precipitated

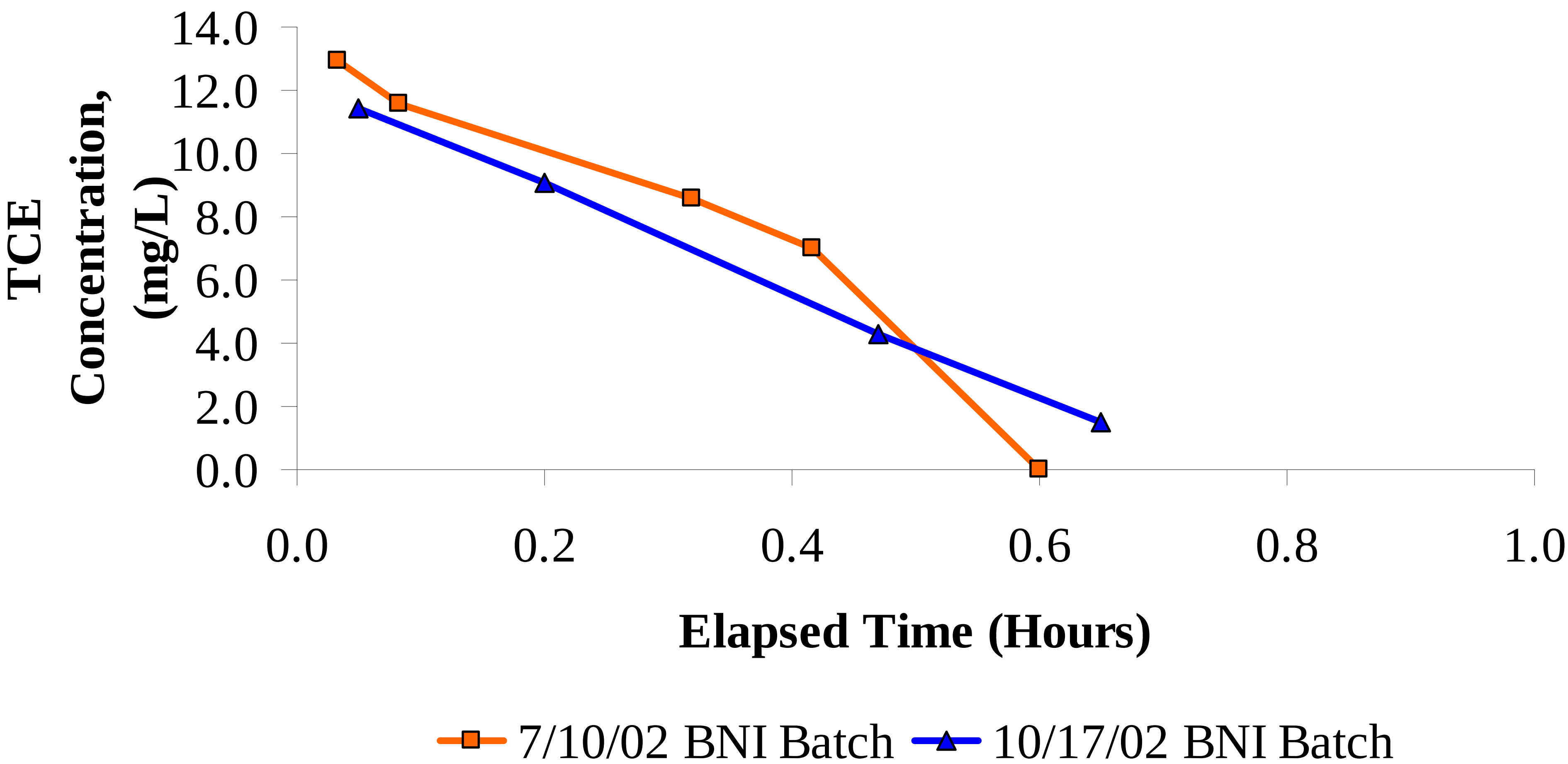
Blue Bars are Vendor B Precipitated

ARCADIS

Reactivity of Top Down Vs. Bottom Up Colloids

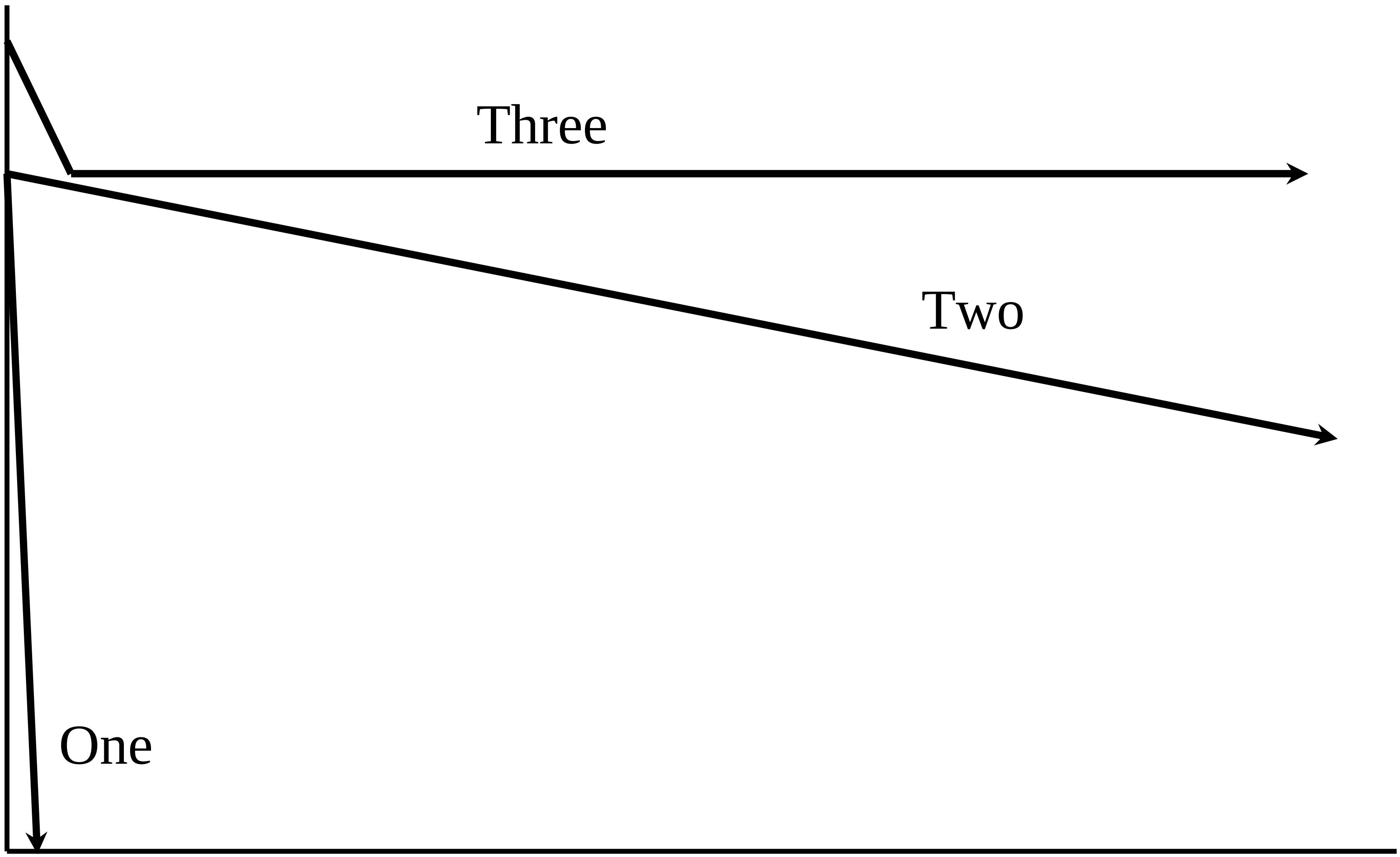


BNI TCE Dechlorination Kinetics Stability of Ball Milled Colloids



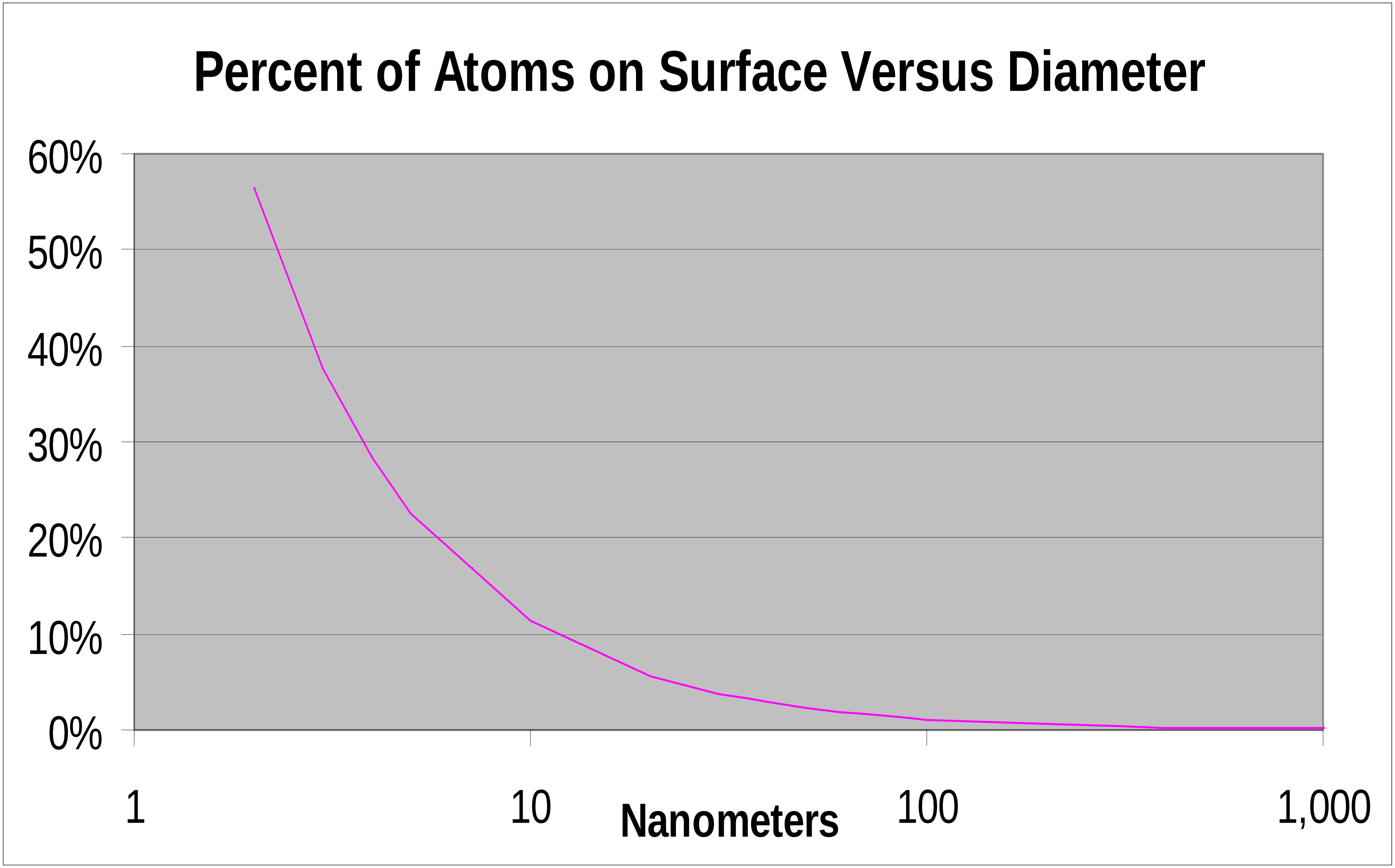
ARCADIS

Three Classes of Colloid Reaction



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


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

ARCADIS

Variations in Iron Colloid Response

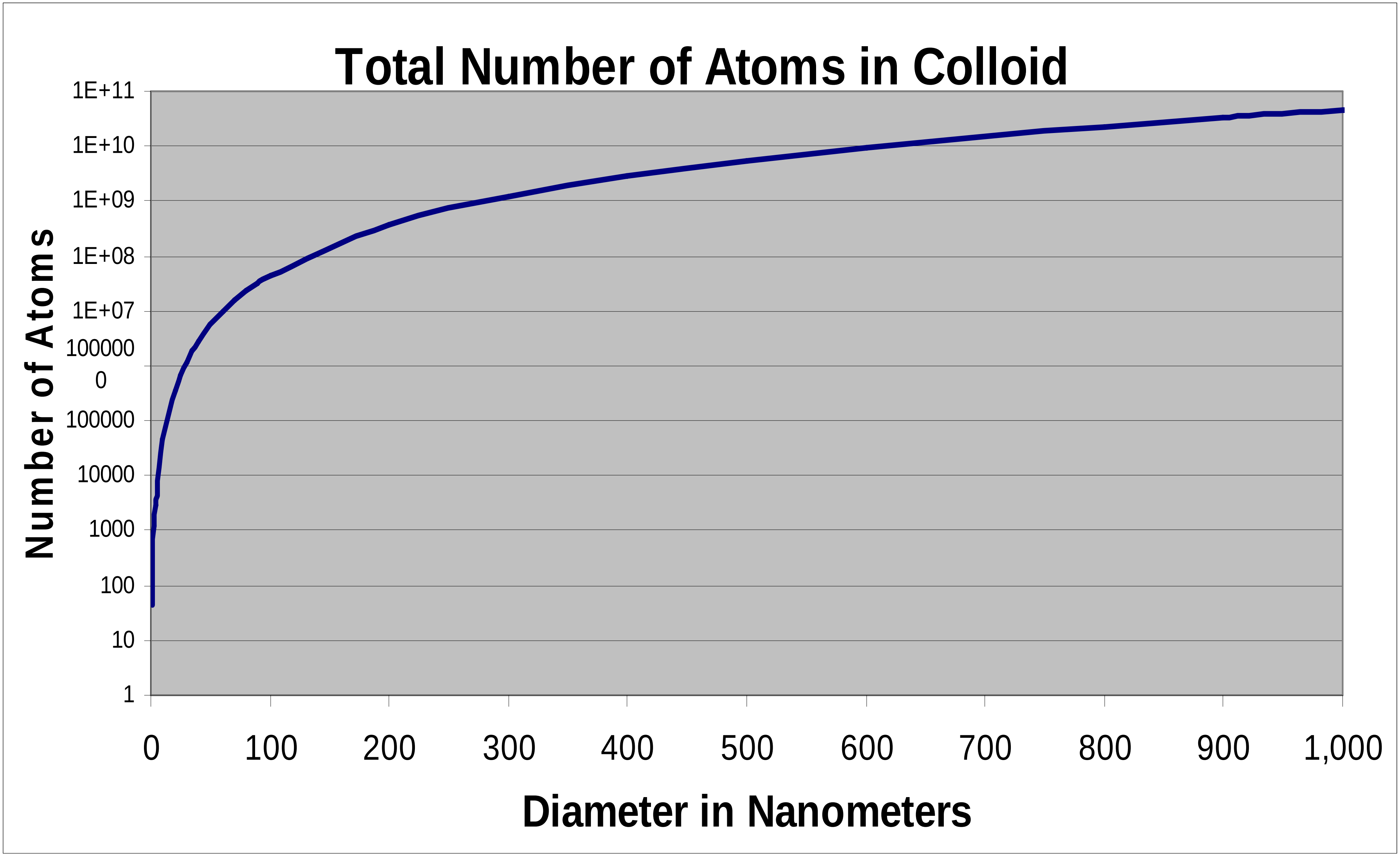
- Class One
  - Typical response from all early product runs
- Class Two
  - Effect due to size and chemical make up or structure – colloids from 100 nm to 2 Microns
  - Becomes class one with palladization
- Class Three
  - Acid pretreatment has no effect
  - Repeated testing by independent labs as 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
100000
0
100000
10000
1000
100
10
1
0
100
200
300
400
500
600
700
800
900
1,000
Diameter in Nanometers

ARCADIS

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

The Bottom Line

Make Assumptions at Your Own Risk