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

Nanoscale Iron Particle

200 – 600 nm

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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

Size Ranges of Zero Valent Iron Compared to Pore Slot Size

- **Injection Methods**: Particles Subject to Sedimentation vs. Particle Strongly Adsorptive
  - 7 μ
  - 0.1 μ

- **Natural Pore Throat Sizes**
  - Gravel: 720 μ, 700 μ
  - Sands: 240 μ, 24 μ
  - Coarse-Fine Silts: 7 μ, 0.7 μ
  - 254 μ Typical Monitoring Well Screen Opening

- **Particle Size**
  - Conventional Iron Filling: 100 μ, 2000 μ
  - Hydrogen Reduced Iron: 30 μ, 0.3 μ, 0.05 μ
  - Ground (Ball Milled): 0.03 μ, 0.1 μ
  - Vapor Deposition Iron: 0.02 μ, 0.002 μ
  - Zhang Precipitated: 0.01 μ
  - Typical Colloidal Size Material: 0.001 μ

- **Additional Size Ranges**
  - 25,000 μ, 200 μ

**Legend**
- Green: Natural Pore Throat Sizes
- Orange: Particle Size
- Blue: Injection Methods

**Arrows**
- Green: Gravel, Sands, Coarse-Fine Silts
- Orange: Conventional Iron Filling, Hydrogen Reduced Iron, Ground (Ball Milled), Vapor Deposition Iron, Zhang Precipitated
Point of Zero Charge - $\text{pH}_{\text{pzc}}$

Binding or Dissociation of Protons

- $\alpha$-Al$_2$O$_3$ 9.1
- $\alpha$-Al(OH)$_3$ 5.0
- $\gamma$-AlOOH 8.2
- CuO 9.5
- $\alpha$-Fe$_3$O$_4$ 6.5
- $\alpha$-FeOOH 7.8
- Fe$_2$O$_3$ 8.5
- Fe(OH)$_3$ (amorph) 8.5
- MgO 12.4
- $\delta$-MnO$_2$ 2.8
- $\beta$-MnO$_2$ 7.2
- SiO$_2$ 2.0
- ZrSiO$_4$ 5
- Feldspars 2-2.4
- Kaolinite 4.6
- Montmorillonite 2.5
- Albite 2.0
- Chrysotile $>10$
Stokes Settling Velocity Vs. Fe Colloid Diameter

- Y-axis: Velocity cm/Day
- X-axis: Diameter in Nano Meters
Colloid Velocity Due to Brownian Motion

Colloid Diameter in mm

Microns/Second

20 to 40 nm

200 to 400 nm
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)

### Experimental Data and Data from Literature

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(1) = Data obtained from batch studies done with Fe^{0} only
(2) = Data obtained from column studies done with Fe^{0} only
(3) = Data obtained from column studies done with Fe^{+}/Pd

**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

![Graph showing reactivity comparison between different colloids](image)
BNI TCE Dechlorination Kinetics Stability of Ball Milled Colloids
Three Classes of Colloid Reaction

- One
- Two
- Three
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

The graph shows the percentage of atoms on the surface of a material versus its diameter in nanometers. As the diameter increases, the percentage of atoms on the surface decreases significantly, indicating a rapid decline in surface coverage with increasing size.
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

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

The Bottom Line
Make Assumptions at Your Own Risk