Materials Science Perspectives of Injectable Zero Valent Metals and Alloys

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Thanks to EPA for Phase II SBIR

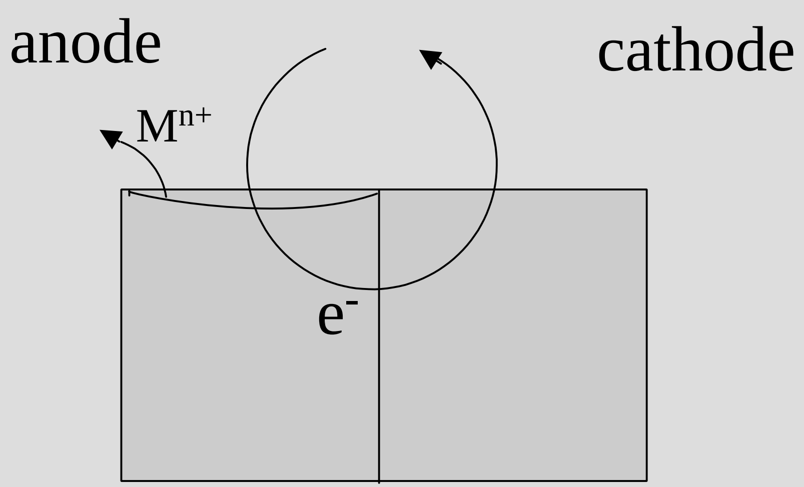
Injectability Premise

- even the most reactive material can only degrade contaminant that comes into contact
- requires a balance between reactivity, mobility, and cost
- application scenarios
  - biocompatible in situ remediation
  - infrastructure limitations
  - subsurface limitations

Transition Metal Reactivity

- Iron
  - thermodynamically unstable
    - no native iron deposits
    - must be synthesized
  - corrosion
    - bimetallic
    - compositional variation
    - microstructual/phase variation
    - pit/crevice
    - stray currents
    - dislocations/strain
    - morphologic
      - flake
      - turnings
  - enhanced corrosion occurs when a potential difference results between neighboring areas

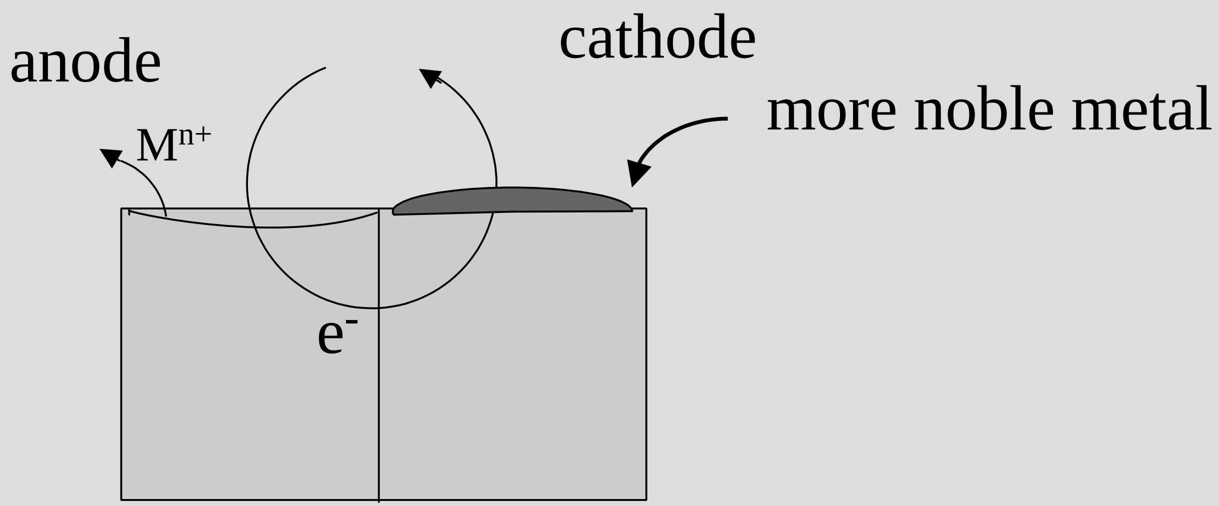
Macroscopic Corrosion



$M + OH_2$ <==> $MOH + H_2$
$MOH(surf)$ <==> $MO^-(surf) + H^+(sol)$

$H_3O^+ + e^-$ --> $H_{ads} + H_2O$
$H_{ads} + H_{ads}$ --> $H_2(gas)$
preferably protonation
CCl_4 --> CH_4

Bimetallic Corrosion



– bimetallics
  - create enhanced corrosion at the anode by increasing the corrosion potential

Transition Metal Reactivity

- anodic - electron loss by metal

  $M + OH_2 <==> MOH + H_2$ (K_1)

  $MOH(surface) <==> MO^-(surface) + H^+(solution)$ (K_2)

$$PZC = \frac{pK_1 + pK_2}{2}$$

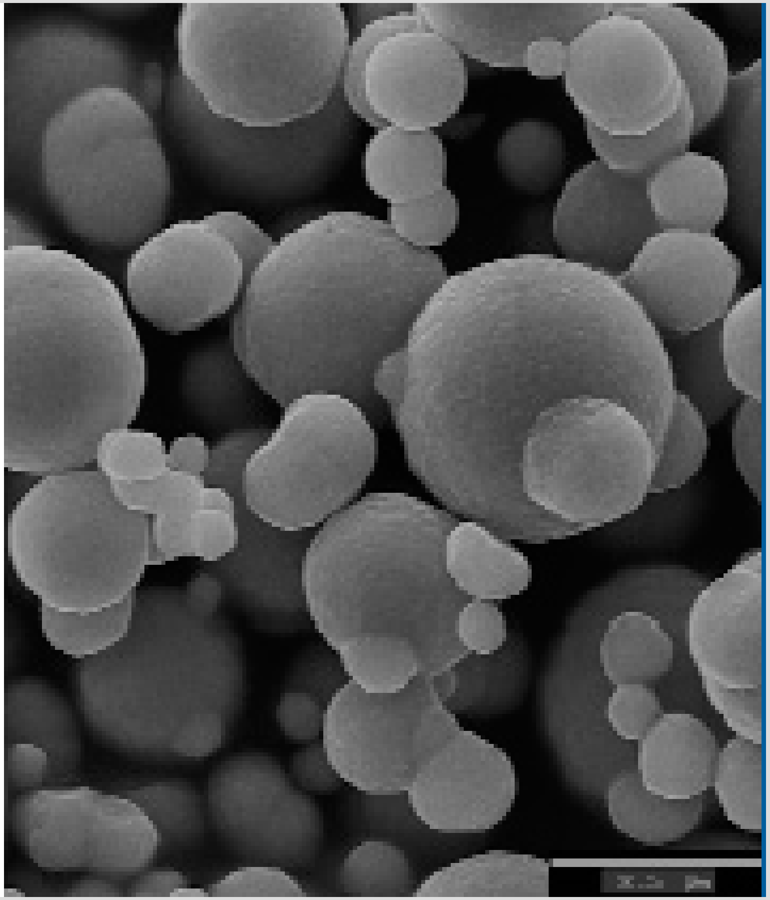
- cathodic

  $H_3O^+ + e^- --> H_{ads} + H_2O$

  $H_{ads} + H_{ads} --> H_2(gas)$

Synthesis

- Synthesis
  - build up
    - vapor
    - chemical precursors
      - carbonyl iron powder
      - with reduction
  - break down
    - mechanical energy
      - ductility
      - cryogenic
  - chemical reduction
    - electrolysis
    - hydrogen
    - sodium borohydride



BASF OM CIP
d50 4 µm   d90 9 µm

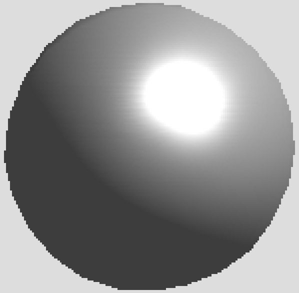
Characterization

Reaction occurs at the Solid/Liquid interface

- What do we need to know about the material?

- chemical reactivity
  - bench
  - column
- specific surface area
  - N_2 BET
    - ESD
    - not all surface area is beneficial – oxide passivation
- morphology
- composition
- colloidal stability

Equivalent Spherical Diameter



$$SSA = \frac{6}{\rho * d}$$

- Model the sphere

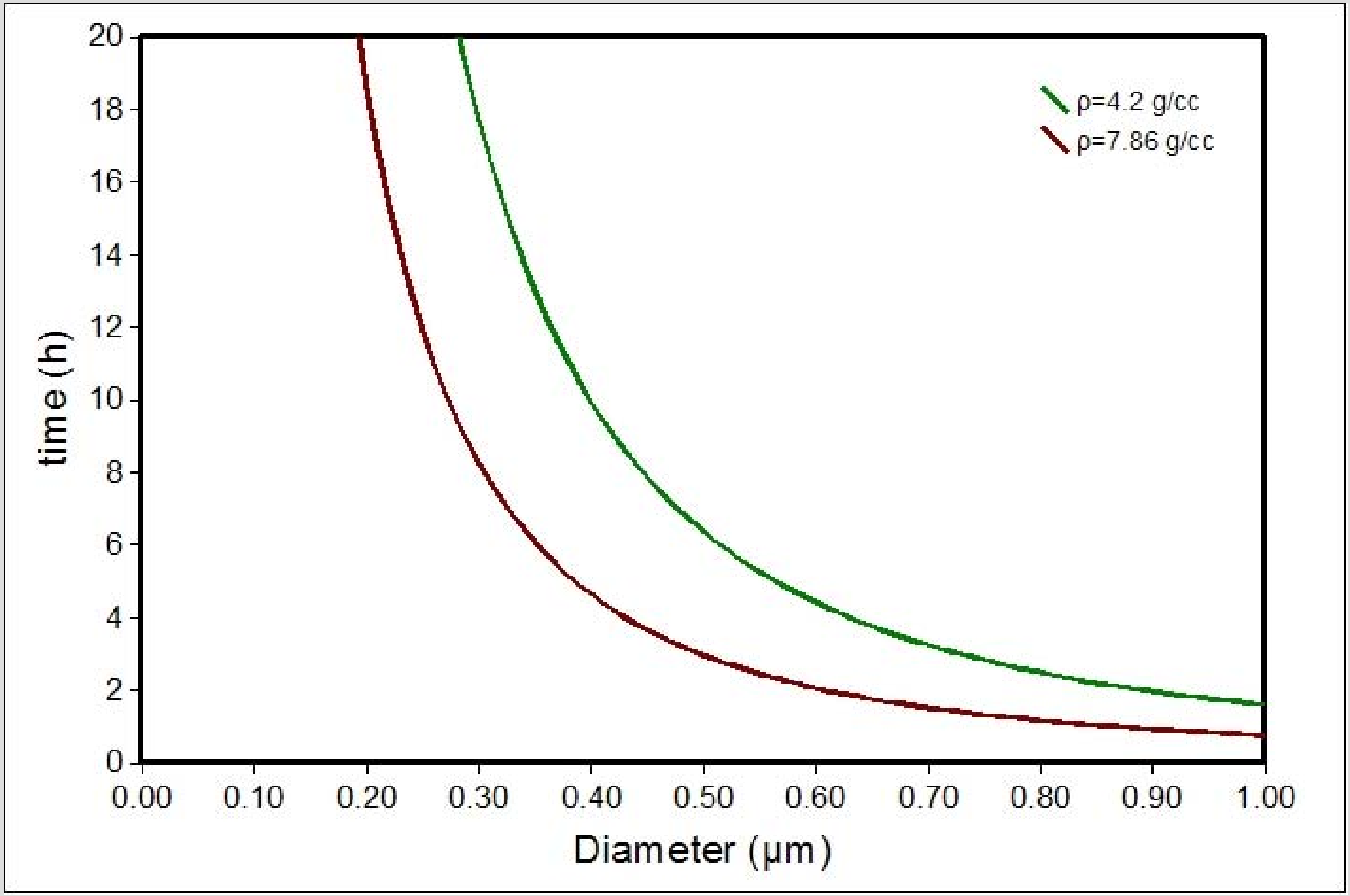
$$SSA \equiv specific\ surface\ area$$

$$\frac{A}{mass} = \frac{A}{\rho * V}$$

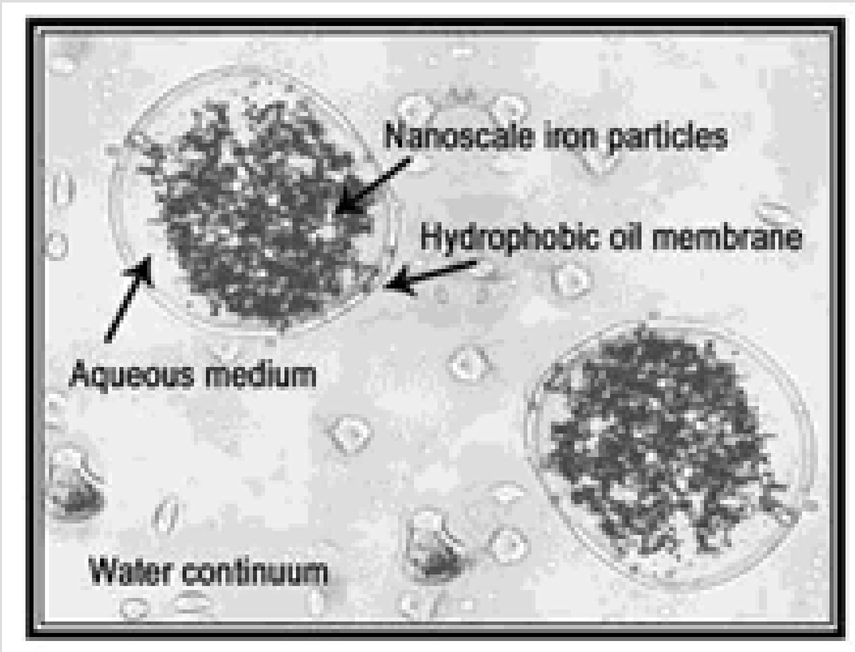
$$\frac{A}{\rho * V} = \frac{4\pi\left(\frac{d}{2}\right)^2}{\frac{4}{3}\pi\left(\frac{d}{2}\right)^3}$$

$$SSA = \frac{6}{\rho * d}$$

Stokes Settling



Morphology

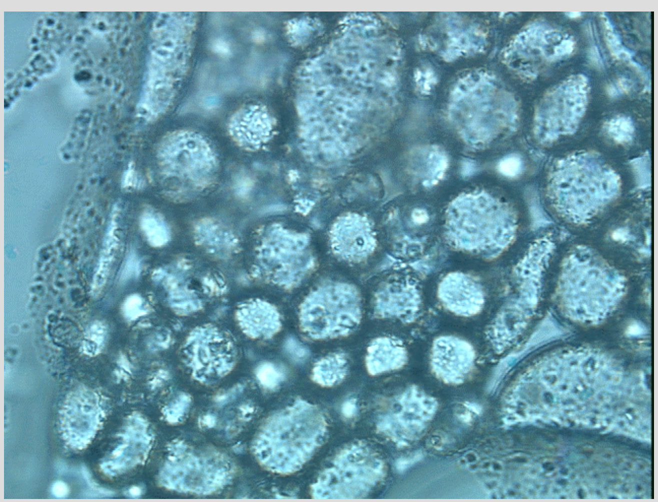


- shape
- aggregation
- microscopy
  - resolving limit
  - micron scale

    see D.J. Shaw *Introduction to Colloid and Surface Chemistry*
- *electron microscopy*

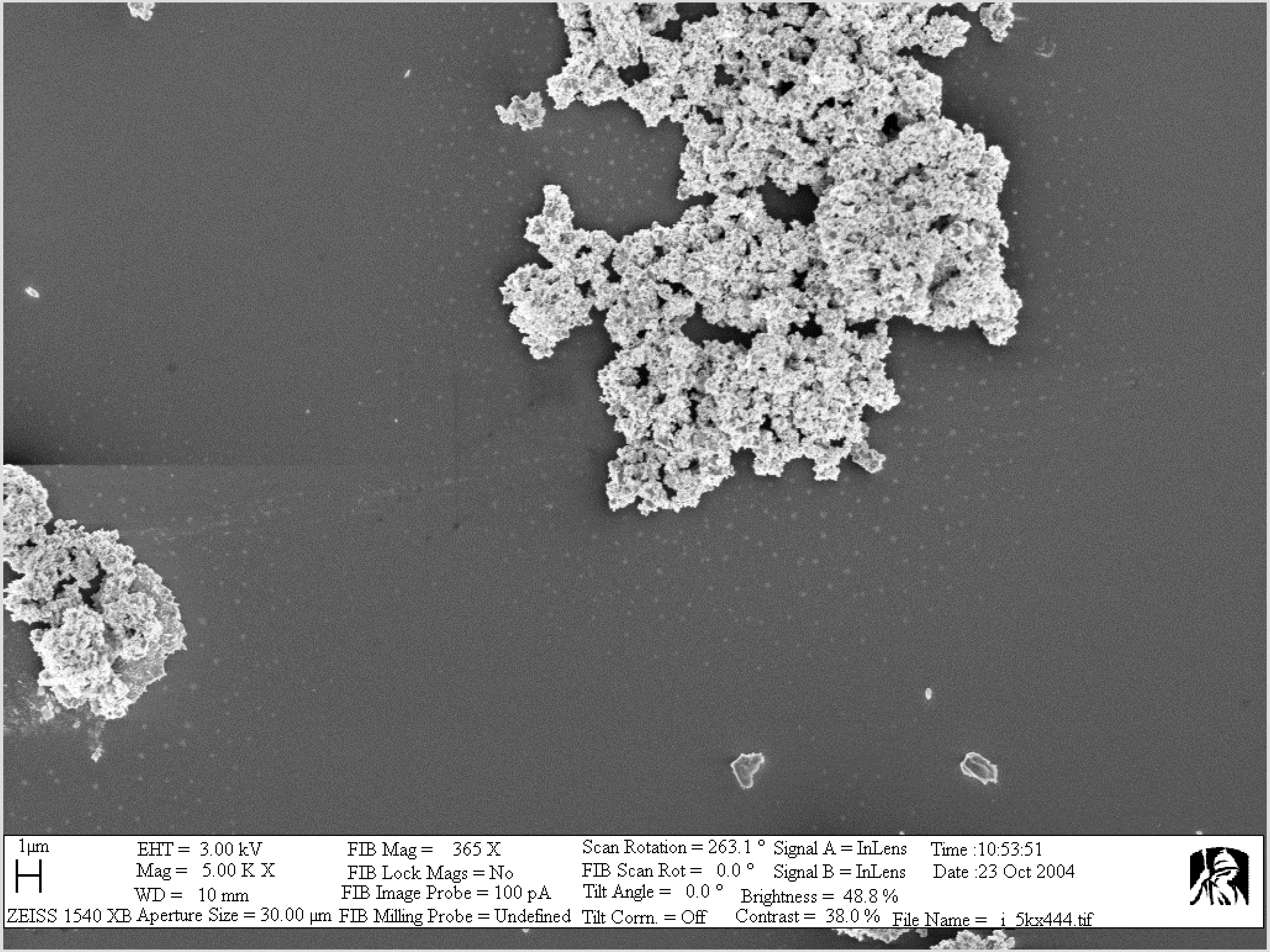
  thanks to Prof. Thiel @ SUNY Albany
  College of Nanoscale Science and Engineering

NASA EZVI

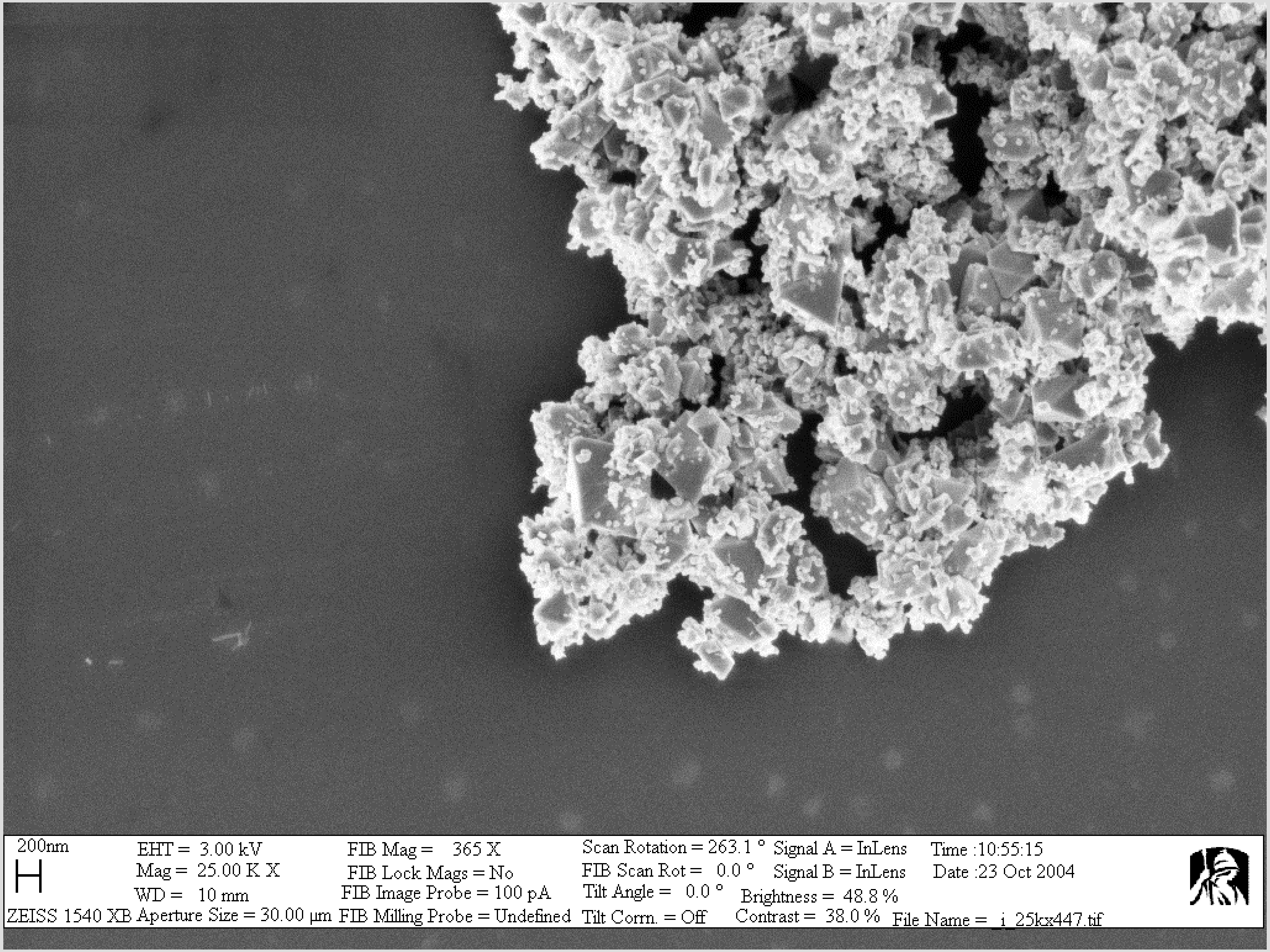


ASAT EZVI

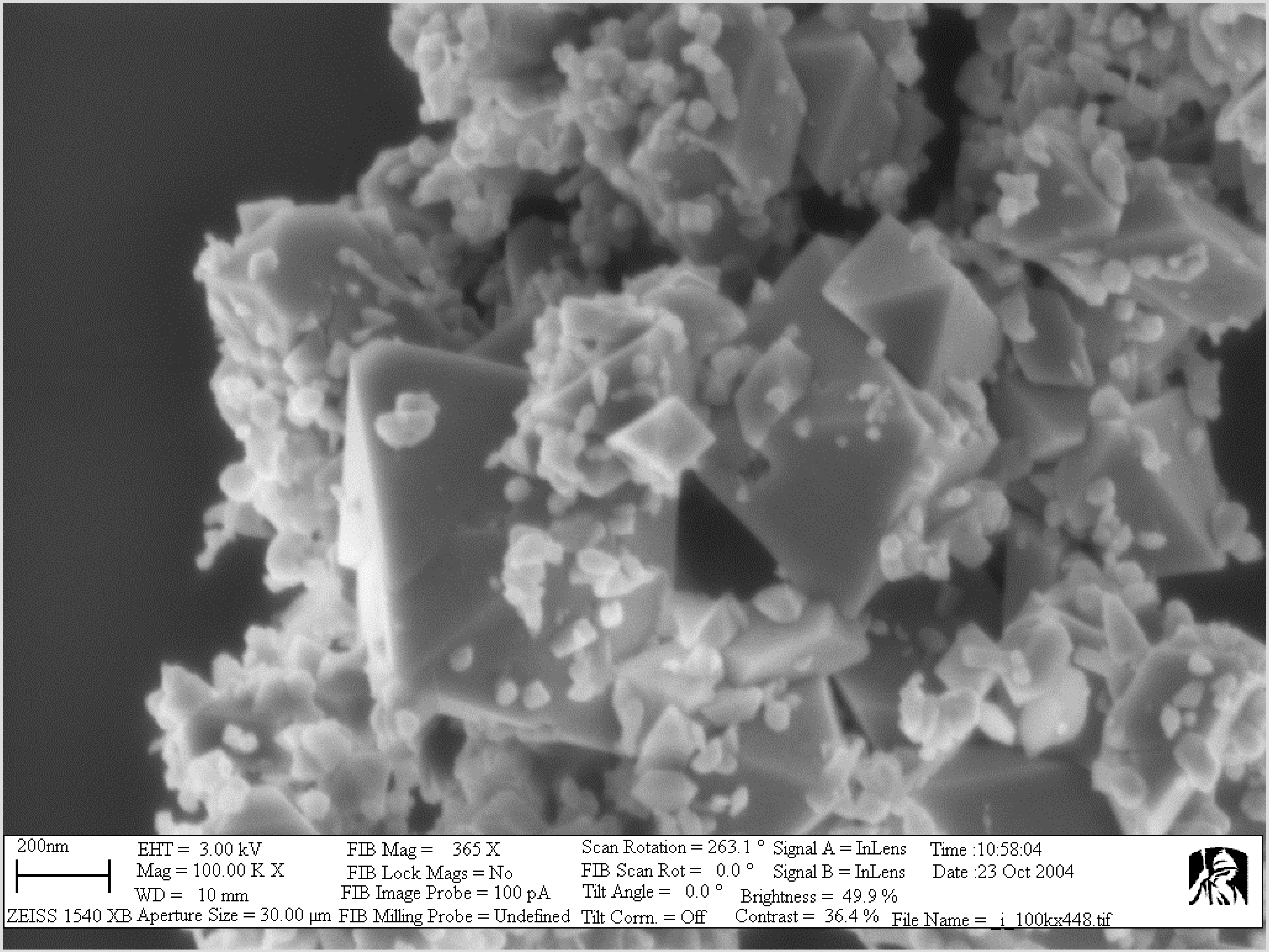
Competitor


1μm
EHT = 3.00 kV
Mag = 5.00 K X
WD = 10 mm
ZEISS 1540 XB Aperture Size = 30.00 μm
FIB Mag = 365 X
FIB Lock Mags = No
FIB Image Probe = 100 pA
FIB Milling Probe = Undefined
Scan Rotation = 263.1 °
FIB Scan Rot = 0.0 °
Tilt Angle = 0.0 °
Tilt Corrn. = Off
Signal A = InLens
Signal B = InLens
Brightness = 48.8 %
Contrast = 38.0 %
Time :10:53:51
Date :23 Oct 2004
File Name = i_5kx444.tif

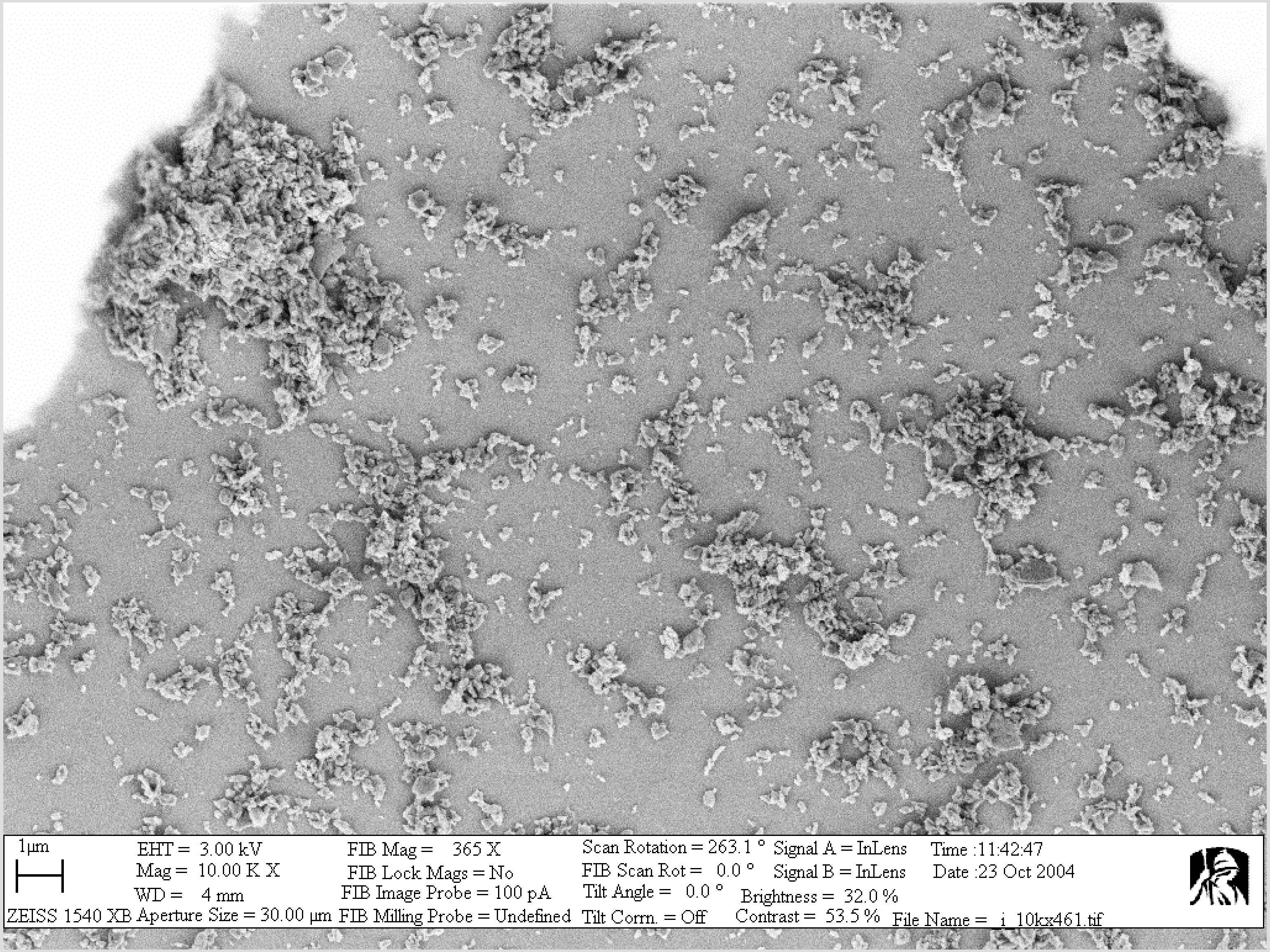
Competitor 25K



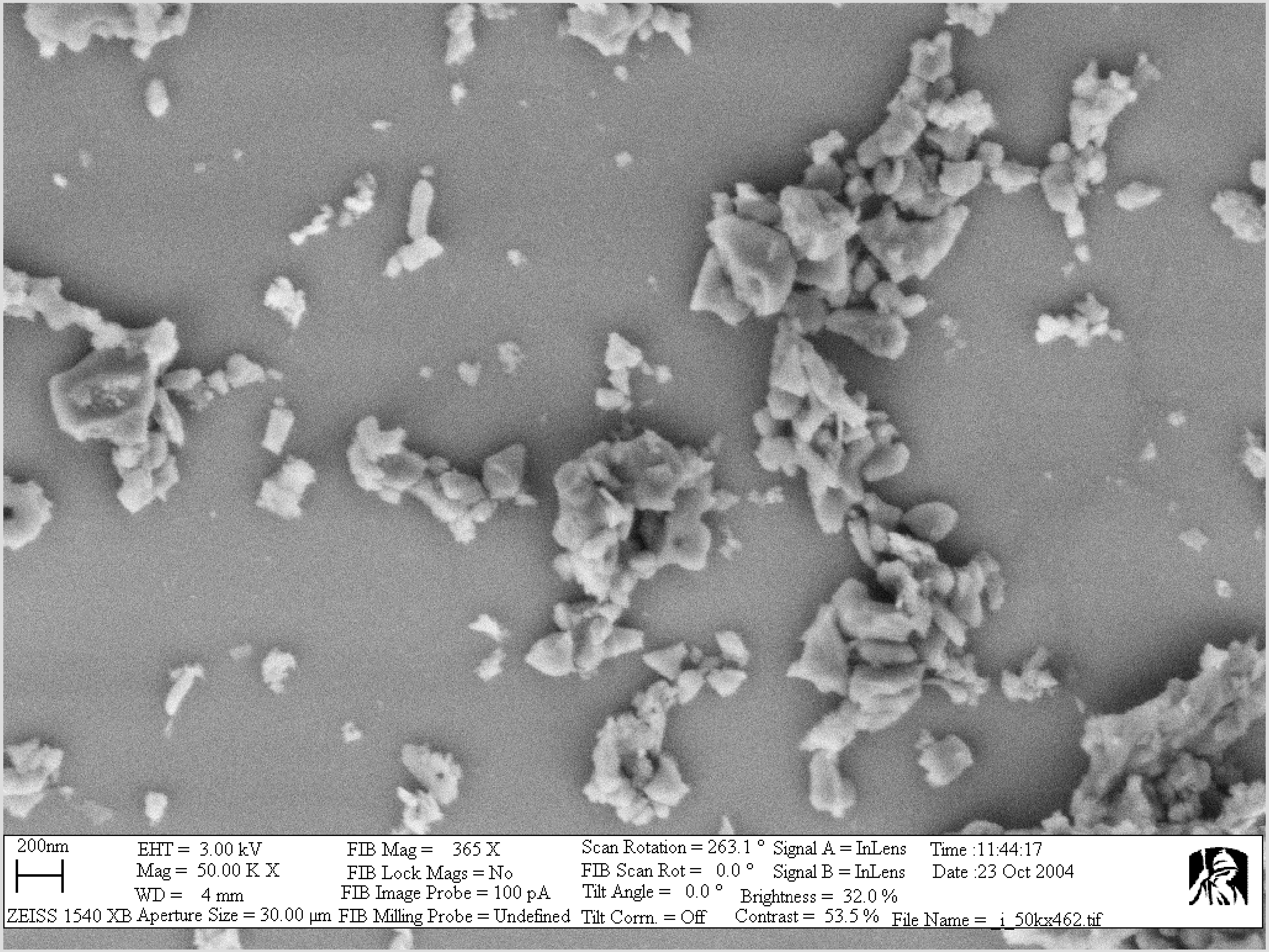
Competitor 100K



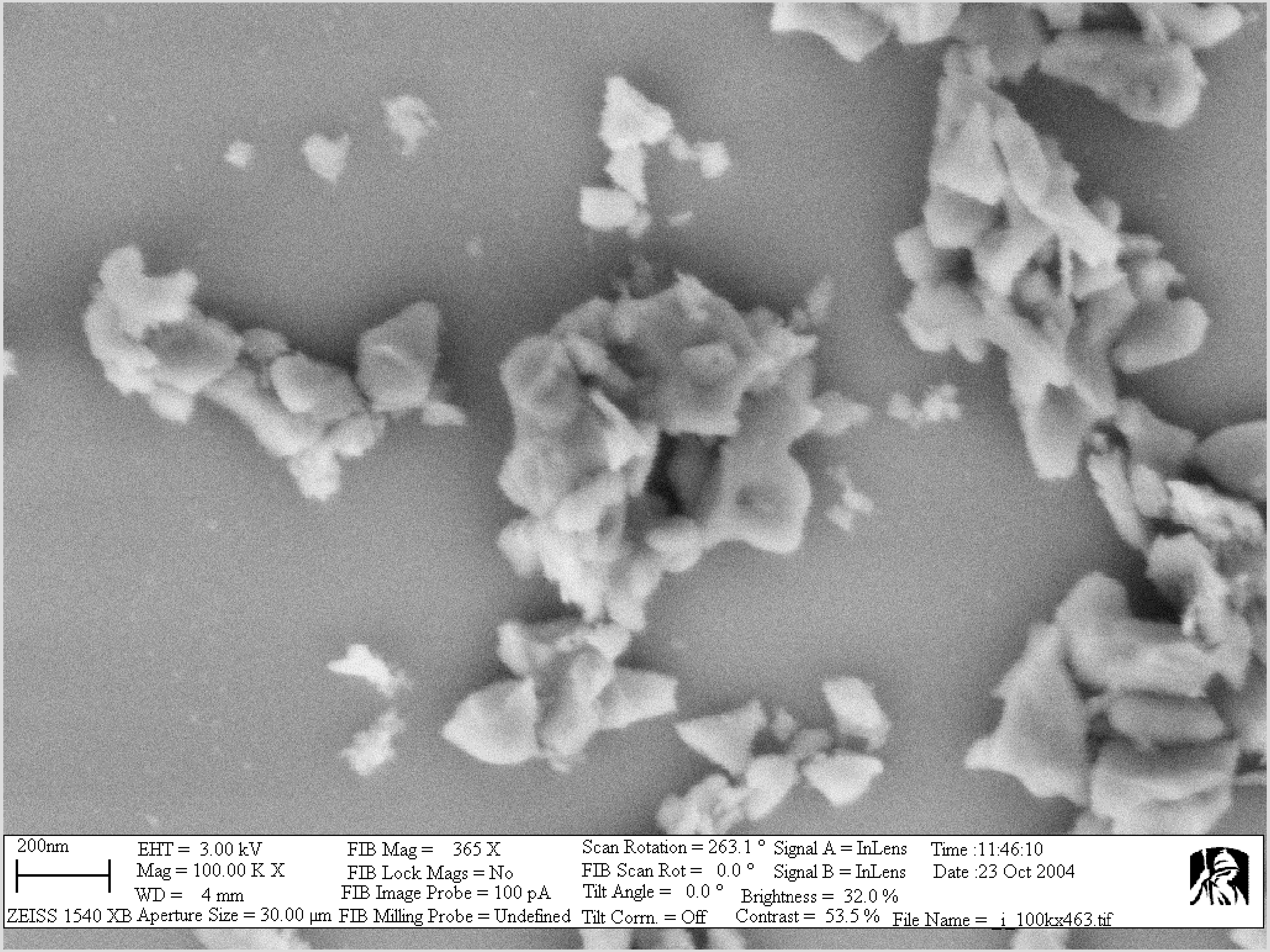
OnMaterials



OnMaterials 50kx



OnMaterials 100kx



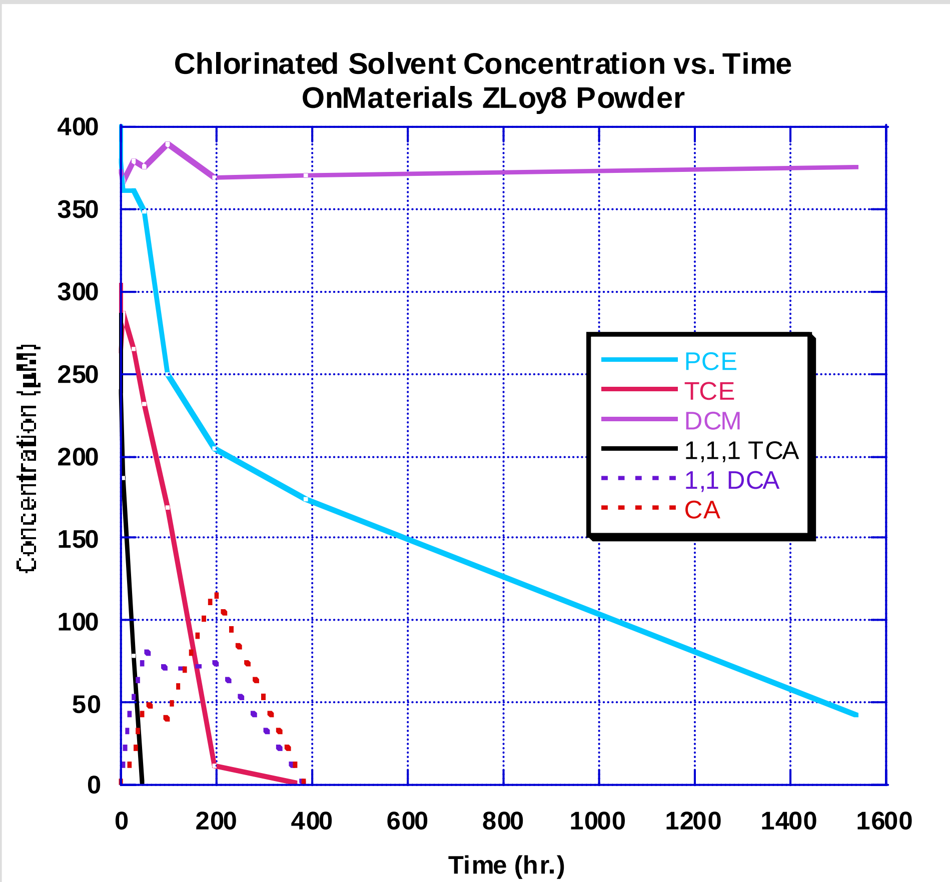
Reactivity

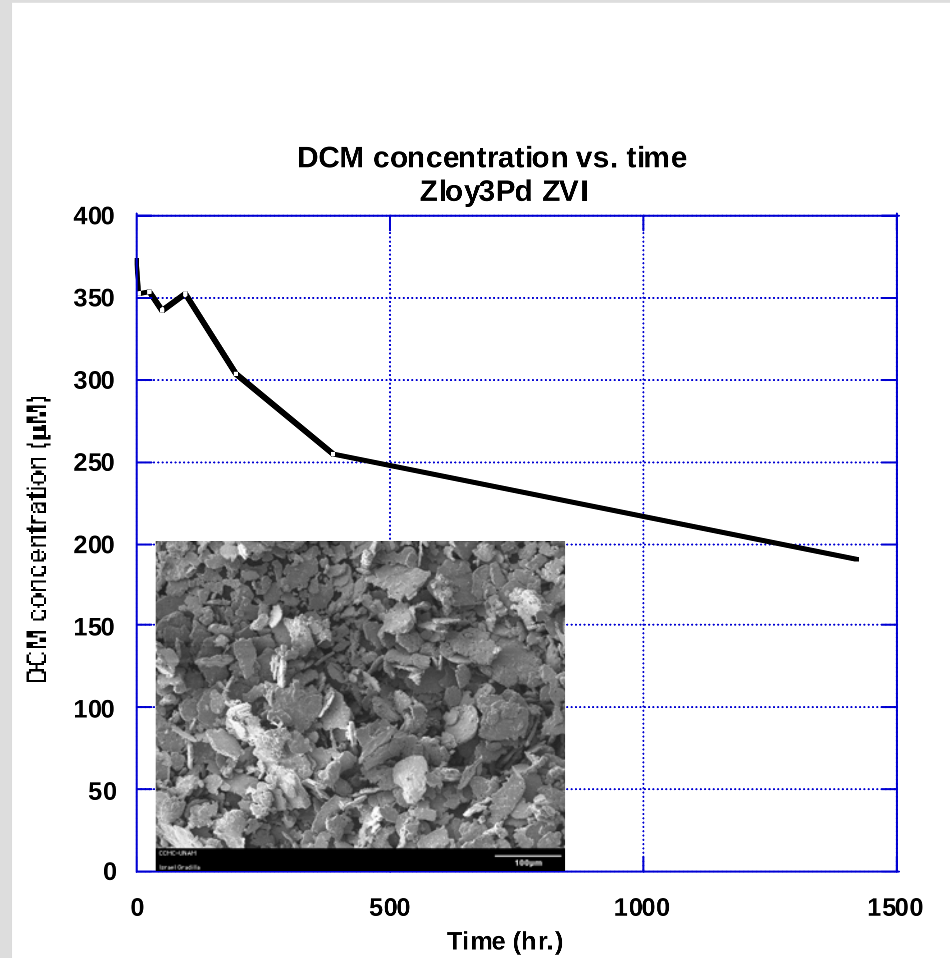
- Reactivity
  - neat
  - bimetallic
  - carbon balance
    - signature
  - normalize to surface area

    Kinetics of Halogenated Organic Compound Degradation by Iron Metal
    Timothy Johnson, Michelle Scherer, and Paul Tratnyek
    Environ. Sci. Technol. 1996, 30,2634-2640
- Lifetime
  - efficacy

    aka reactive capacity
  - reduction of water

OnMaterials Bench Testing

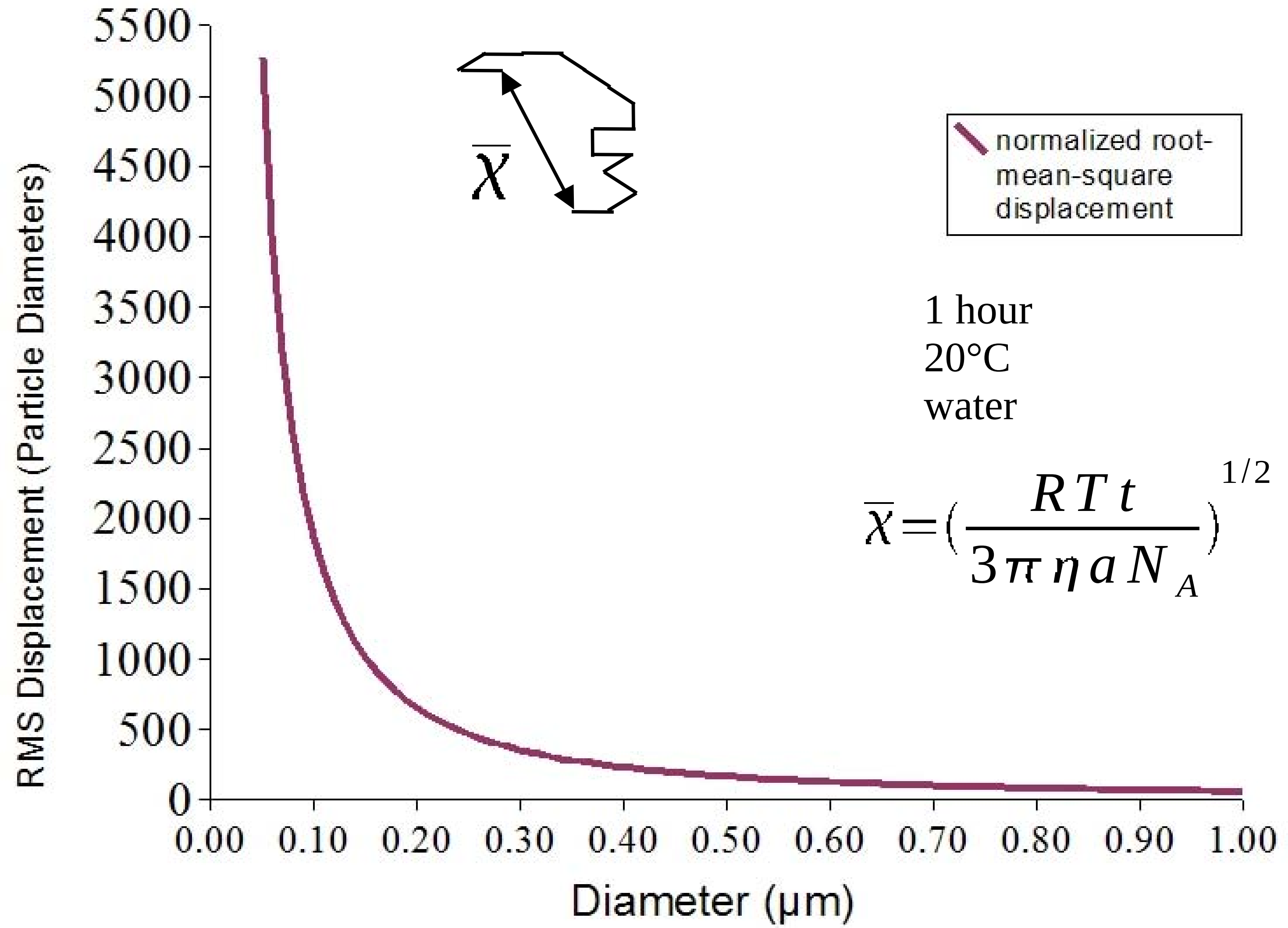




Injectability

- Colloid Concepts
  - Brownian Motion
    - thermal kinetic energy
    - effect of particle size
  - Colloidal stability
    - flocculation
      - diffuse double layer
        - isoelectric point (zero point of charge)
        - double layer overlap
        - heteropolar attraction
      - steric stabilization
    - effect of ionic concentration
      - compresses double layer
      - increase in ionic concentration decreases colloidal stability
    - magnetic field

Brownian Motion



$$\overline{\chi} = \left(\frac{R\,T\,t}{3\pi\,\eta\,a\,N_A} \right)^{1/2}$$

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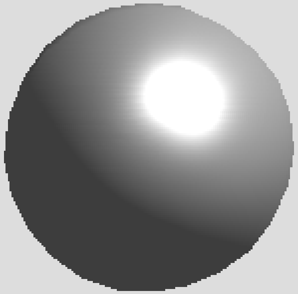
Surface Chemistry



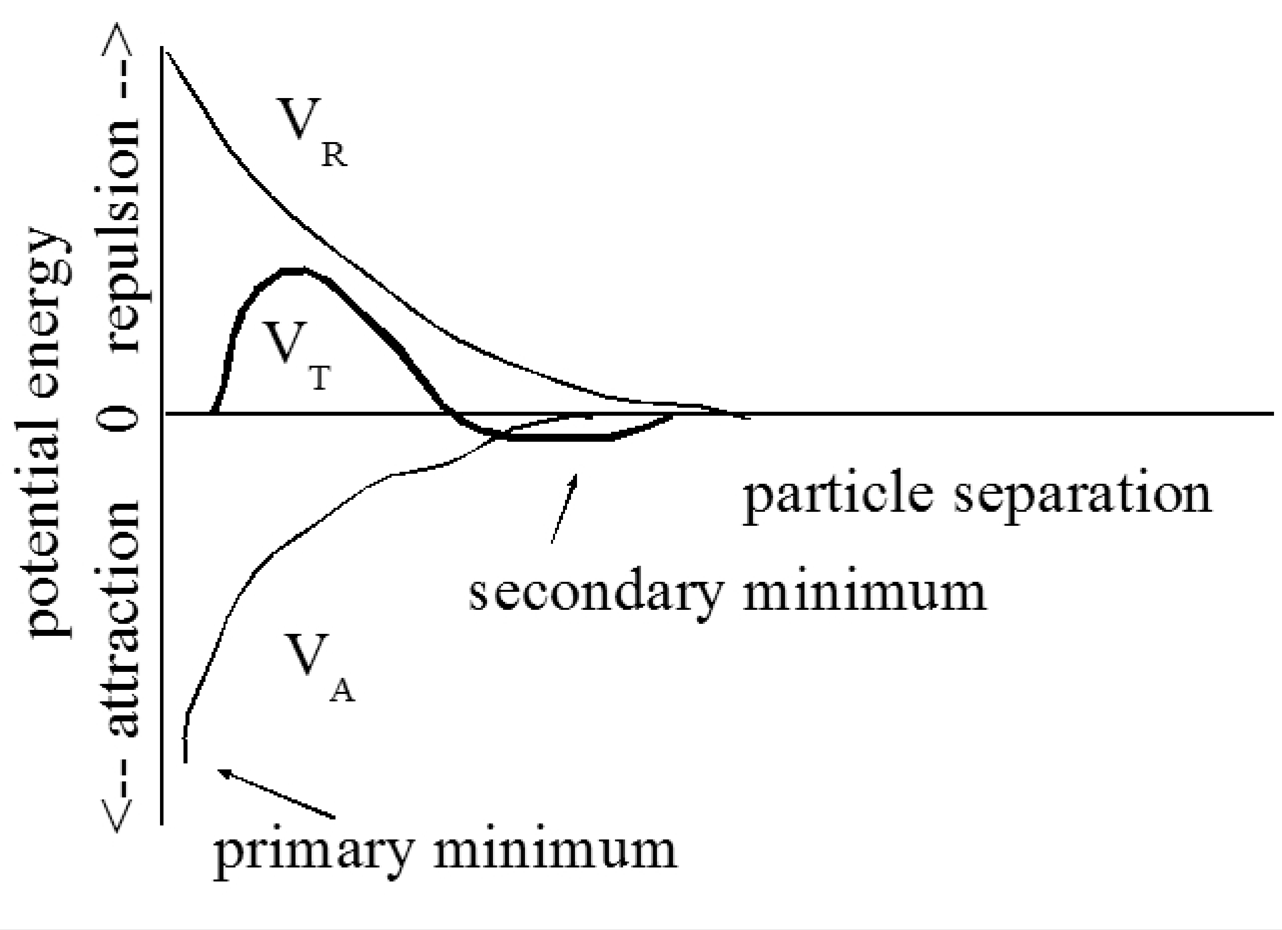
$$PZC = \frac{pK_1 + pK_2}{2}$$

Electrostatic forces

- M + OH_2 <==> MOH + H_2 (K_1)
- MOH(surface) <==> MO^-(surface) + H^+(solution) (K_2)
- the surface chemistry of zvi in water is complicated by the fact the water is a reactive medium

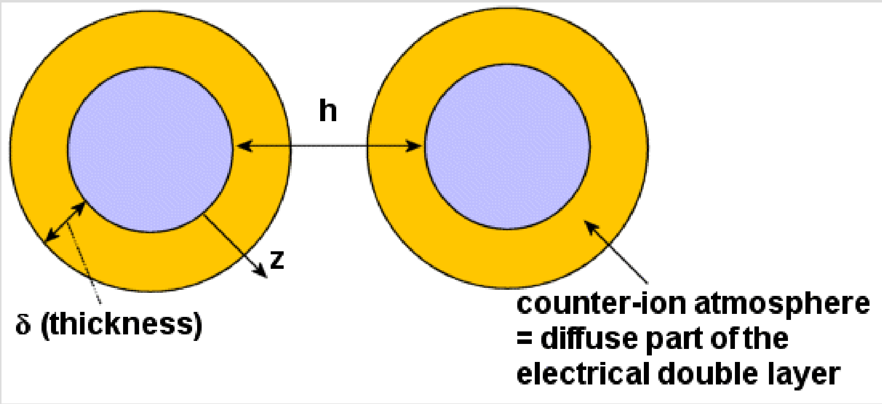
- deviations from the iso-electric point (PZC)
    - increase the attraction of either
        - hydroxyl ions or
        - hydronium ions
- this has the effect of increasing the diffuse double layer

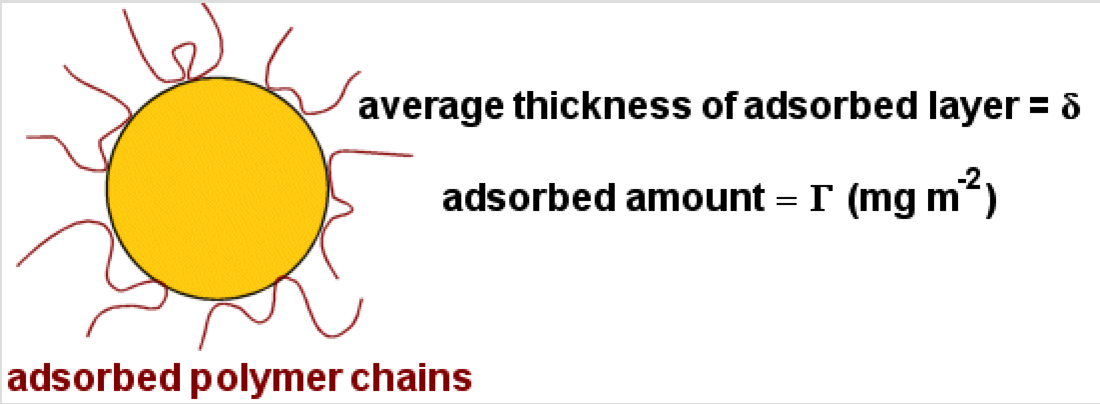
DLVO Theory



potential energy
<-- attraction 0 repulsion -->
V_R
V_T
V_A
particle separation
secondary minimum
primary minimum

Diffuse Double Layer





from Prof. Brian Vincent @
Univ of Bristol

- van der Waals interactions
- double layer thickness
  - typical thickness 1 to 10 nm
  - function of
    - ionic concentration
    - ionic charge
- steric stabilization
  - polyelectrolyte
  - surfactant
  - effect on reactivity
  - pH sensitive

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Gold on Kaolin

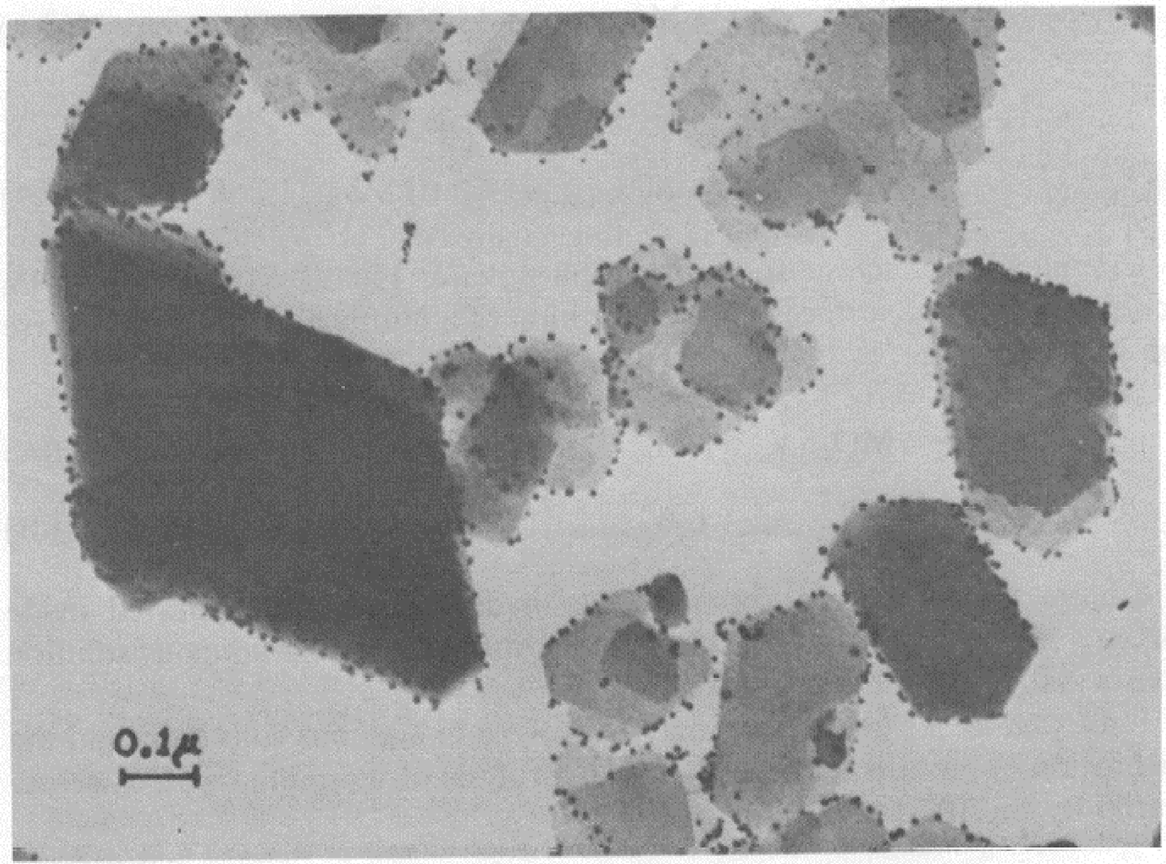

Fig. 10.4 A negatively charged gold colloid is adsorbed on the edges of kaolin in an acidified suspension. (From H. van Olphen, *An Introduction to Clay Colloid Chemistry*, Wiley-Interscience, New York, 1977.)

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Site Modeling

- Rectangular Site
  - 100 ft by 30 ft with a 20 ft screened interval
  - 30% pore volume
  - 500 µM TCE (66 PPM or ~ 50 lbs)
  - 500 µM TCM – chloroform (60 PPM or ~45 lbs)

- How much iron do you use?
  - efficacy
  - mobility
  - reactivity

Injectability Parameters

- Advantages
  - small particle size
  - discrete particles
  - low density
  - active “neat” surface
    - minimal hydroxide, oxide, etc.
  - bimetallic particles
    - change pathways
- Disadvantages
  - large particle size
  - aggregated particles
  - high density