Structure and Reactivity of Nano-Particles Containing Zero-Valent Iron: Bridging the Gap Between Ex Situ Properties and In Situ Performance

Paul Tratnyek
Department of Environmental and Biomolecular Systems
OGI School of Science & Engineering
Oregon Health & Science University

http://www.ebs.ogi.edu/tratnyek/
http://cgr.ese.ogi.edu/iron/

THE REACTION SPECIFICITY OF NANOPARTICLES IN SOLUTION

Application to the Reaction of Nanoparticulate Iron and Iron-Bimetallic Compounds with Chlorinated Hydrocarbons and Oxyanions

- Synthesis and characterization of Fe and Fe-Oxide nanoparticles
- Measurements solution and gas reactivity with Fe nanoparticles
- Vacuum based studies of supported Fe nanoparticles
- Models of particle structure and effects of structure on reactivity

Pacific Northwest National Laboratory: D. Baer, J. Amonette, J. Linehan , K. Pecher, B. Kay, Z. Dohnalek, M. Dupuis, E. Bylaska, A. El-Azab, others

Oregon Health & Science University: P. Tratnyek, J. Nurmi, V. Sarathy

University of Minnesota: L. Penn and M. Driessen

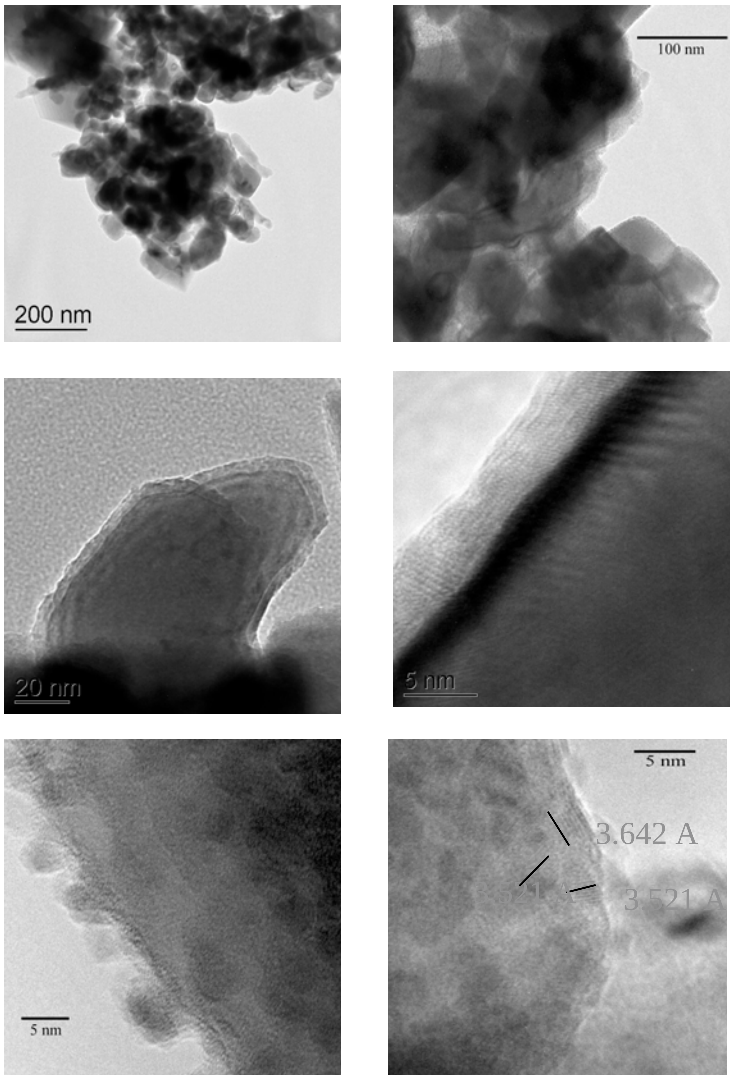
Iron and Iron Oxides Studied

Name	Source	Method	Particle Size (dia.)	BET Surface Area	Major Phase	Minor Phase
Fe^{H2}	Toda Americas, Inc.	High temp. reduction of oxides with H_2	70 nm	29 m^2/g	α-Fe^0	Magnetite
Fe^{BH}	W.-X. Zhang, Lehigh Univ.	Precip. w/ $NaBH_4$	10-100 nm	33.5 m^2/g	Fe^0	Goethite, Wustite
Fe^{EL}	Fisher Scientific	Electrolytic	150 µm	0.1-1 m^2/g	99% Fe^0	
Fe_3O_4	PNNL	Precip from $FeSO_4$ w/ KOH	30-100 nm	4-24 m^2/g	Fe_3O_4	
Fe_2O_3	Nanotek, Corp.	Physical Vapor Synthesis (PVS)	23 nm	50 m^2/g	γ-Fe_2O_3	

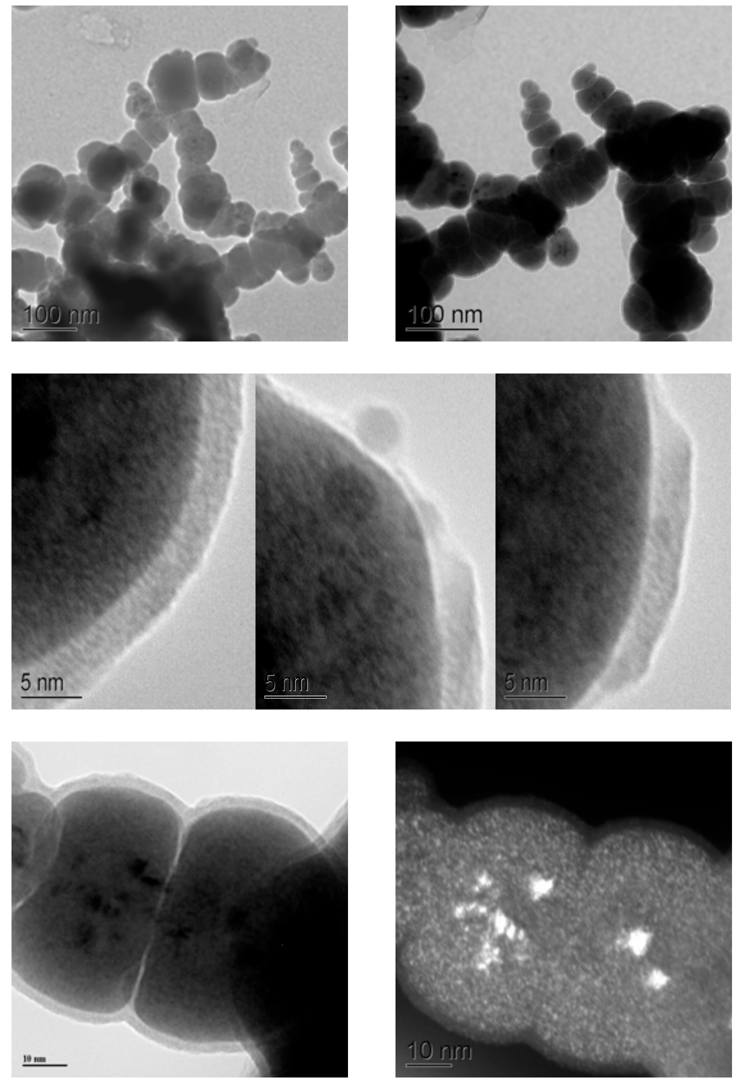
Nurmi et al. (2005) ES&T 39: 1221-1230.

Structure from TEM

Fe^{H2} (Toda)

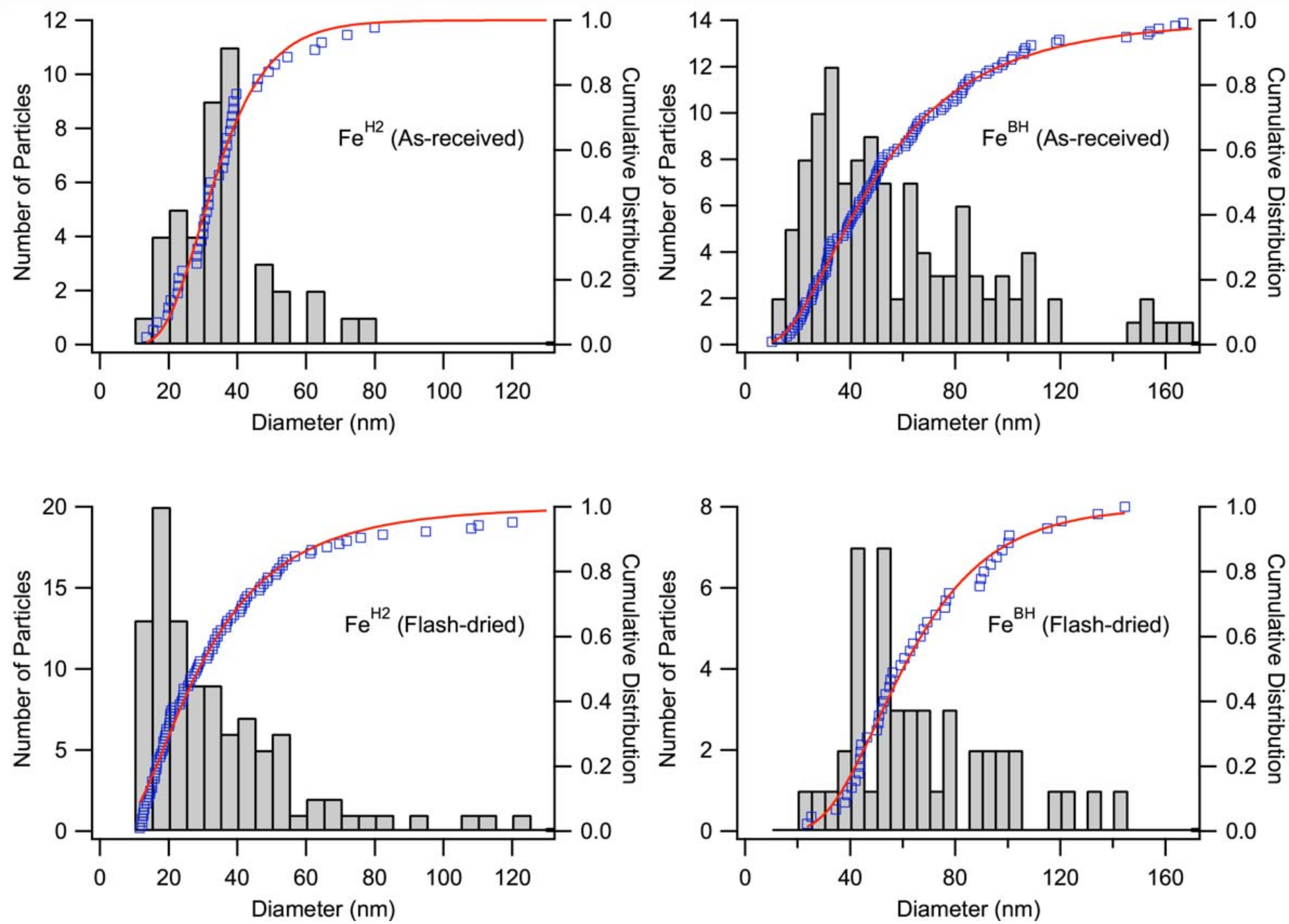


Fe^{BH} (Zhang)



Nurmi et al. (2005) ES&T 39: 1221-1230.

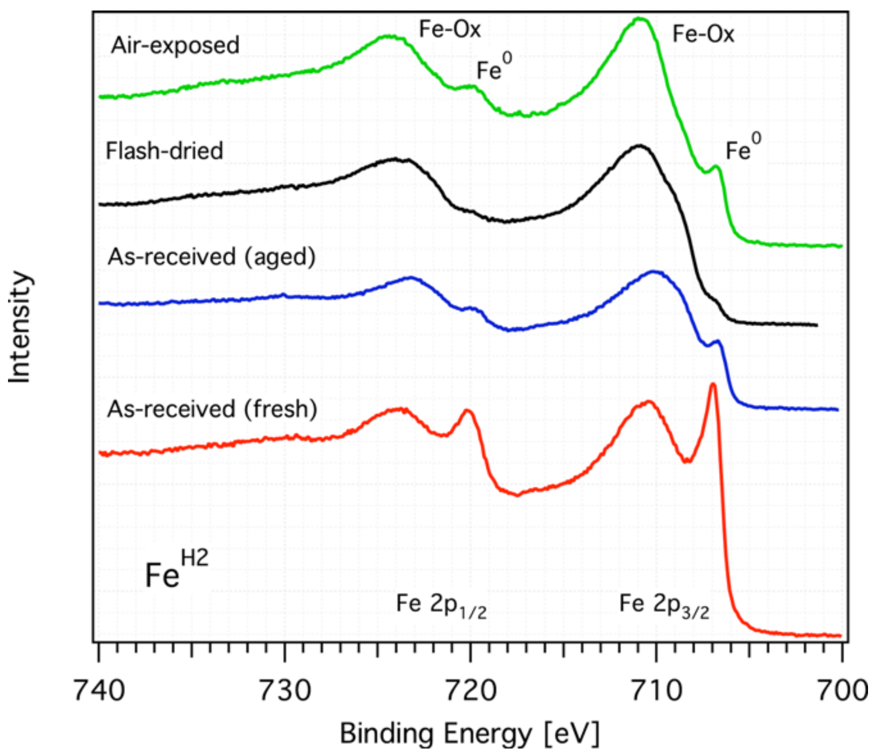
Particle Size from TEM



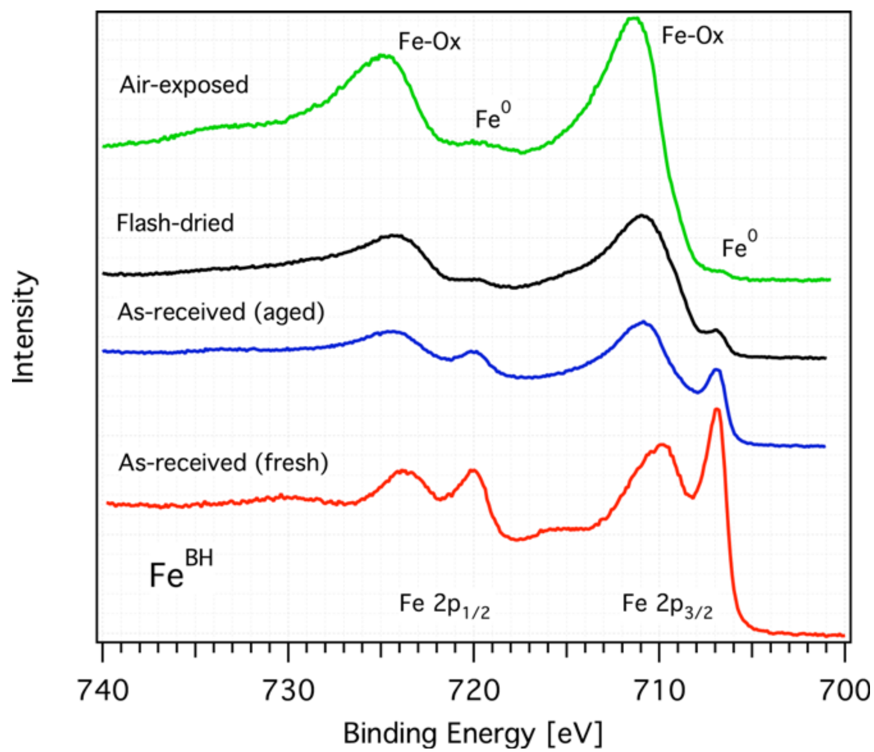
Nurmi et al. (2005) ES&T 39: 1221-1230.

Composition from XPS

Fe^{H2} (Toda)



Fe^{BH} (Zhang)



Nurmi et al. (2005) ES&T 39: 1221-1230.

Summary of Structure/Composition

Name	Sample History	Mean Particle Size from TEM (nm)	Shell Thickness (nm)	TEM Structure	XRD (Grain Size nm)	XPS	STXM
Fe^{H2}	As-received	~38 Fe^0 ≥60 nm oxide plates	Fe-Oxide ~3.4	“large”plates (oxide) and smaller Fe^0 irregularly shaped particles with crystalline oxide shell	Fe^0 (~30) oxide (~60)	Fe^0+Fe^{+3}	Fe^0 + oxide
Fe^{H2}	Flash-dried	~44 Fe^0		As above with more large plates		Less Fe^0	
Fe^{BH}	As-received	~59 (20-100)	~2.3	Three levels of structure: i) small crystallites (<1.5 nm), ii) 20-100 nm spherical aggregates with an amorphous coating, and iii) chains of 20-100 nm particles	Mostly Fe^0 (<1.5)	Fe^0+Fe^{+3} + B and Na	Mostly Fe^0
Fe^{BH}	Flash-dried	~67 (20-100)	~3.2	As above with thicker coating		Less Fe^0 +B and Na	

Nurmi et al. (2005) ES&T 39: 1221-1230.

Solution Chemistry—Methods

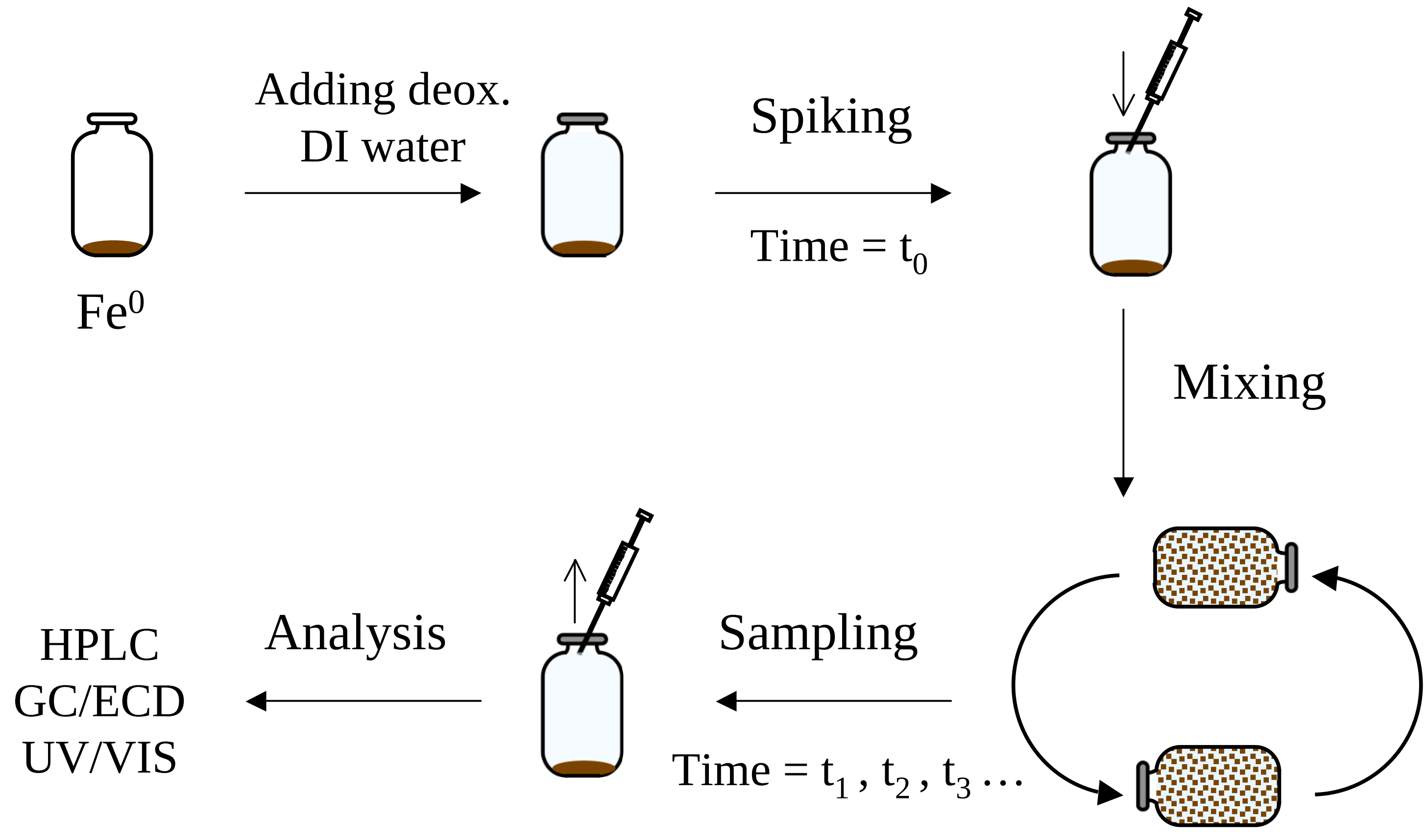
Electrochemical Cell

- Flash drying
- Packed powder electrode
    - Fabrication
    - Validation
- Data presentation
- Electrochemical model

Batch Reactor

- Flash drying
- Pre-exposure period
- Buffer selection
- Ox/Fe ratio
- Mixing rate
- Kinetic model

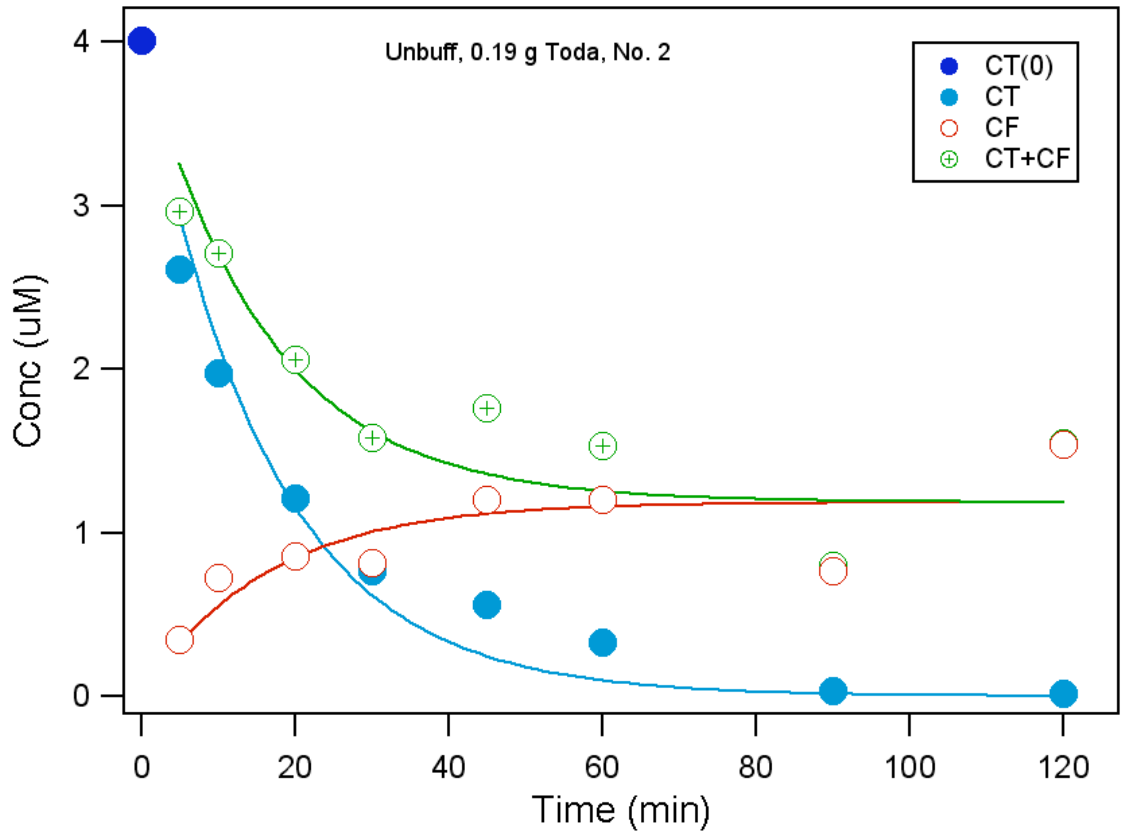
Protocol for Batch Experiments



- Flash drying
- Pre-exposure period
- Buffer selection
- Ox/Fe ratio
- Mixing rate
- Kinetic model

Batch Experiments with CCl_4

CCl_4 (CT) + Fe(0) → $CHCl_3$ (CF) + Unk + Cl^- + Fe(II)



1. pH:
   - 7.3, 8.4, 9.0
2. Buffers:
   - Borate
   - EPPS
3. Type:
   - Fisher Electrolytic
   - Nano (Zhang, Toda)
4. Pretreatment:
   - Flash drying

Nurmi et al. (2005) ES&T 39: 1221-1230. Sarathy and Tratnyek (in prep.)

k_{sa} vs. k_m plots

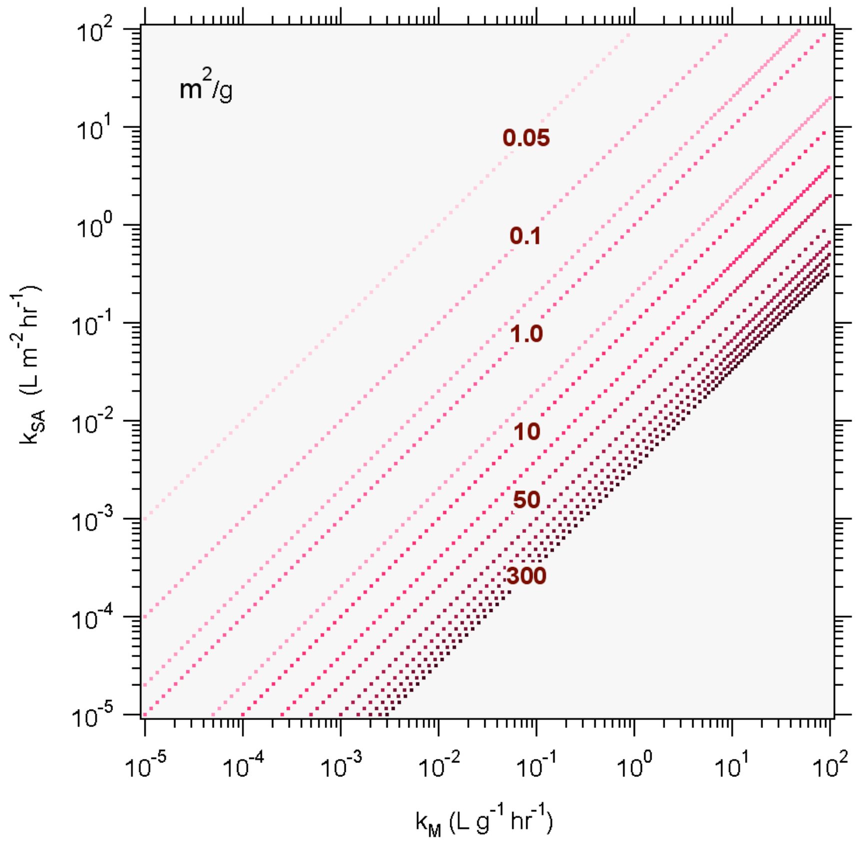
From:

$$k_M = k_{SA}\, a_s$$

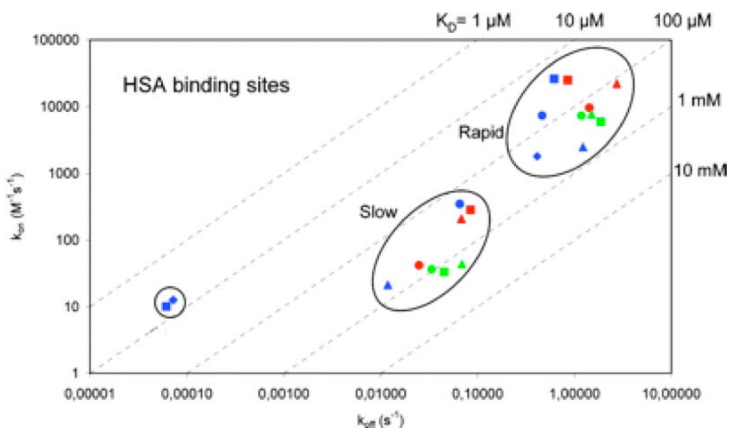
It follows that:

$$\log k_{SA} = \log k_M - \log a_s$$

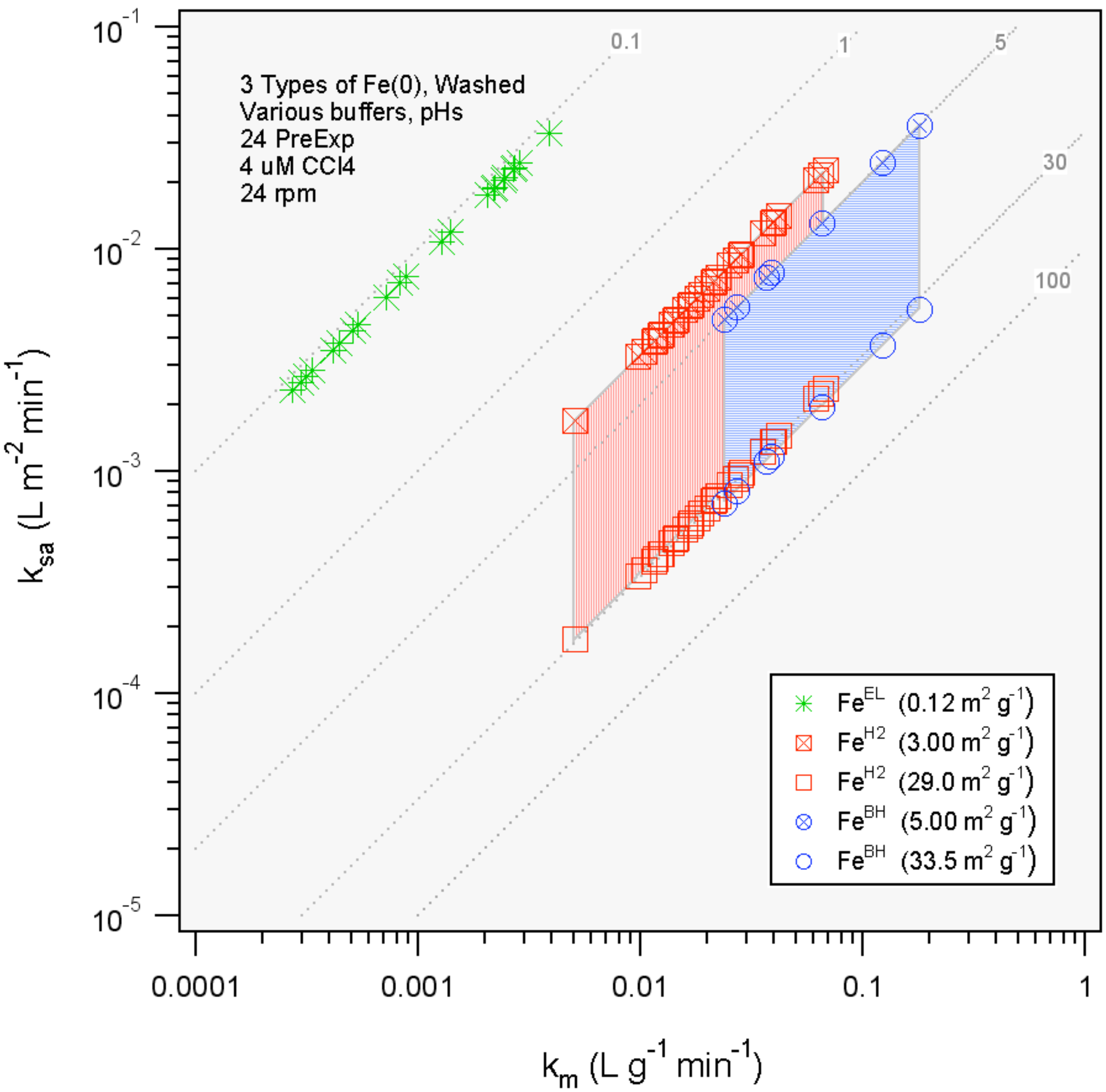
Plotting log k_{SA} vs. log k_M gives contours of constant a_s.



Cimitan et al. (2005) J. Med. Chem. ASAP



Effect of Surface Area—Our Data Only



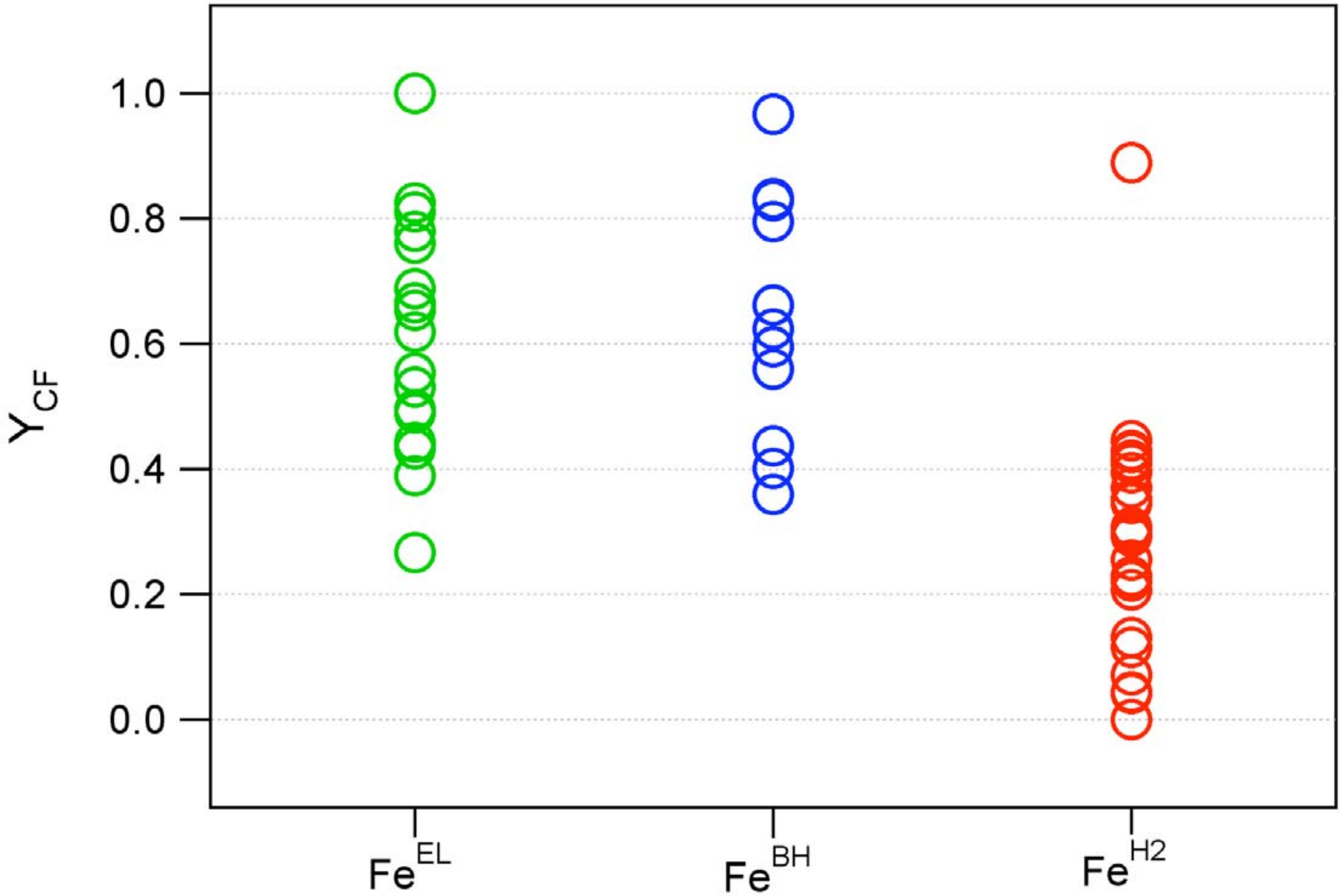
- k_M (Nano > Micro)
- k_M (Fe^{BH} ? Fe^{H2})
- a_s (TEM < BET)
- k_{SA} (Nano ≈ Micro)
- k_{SA} (Nano < Micro)

… Uncertainties in a_s are important

… No “intrinsic” nano-size effect

Nurmi et al. (2005) ES&T 39: 1221-1230

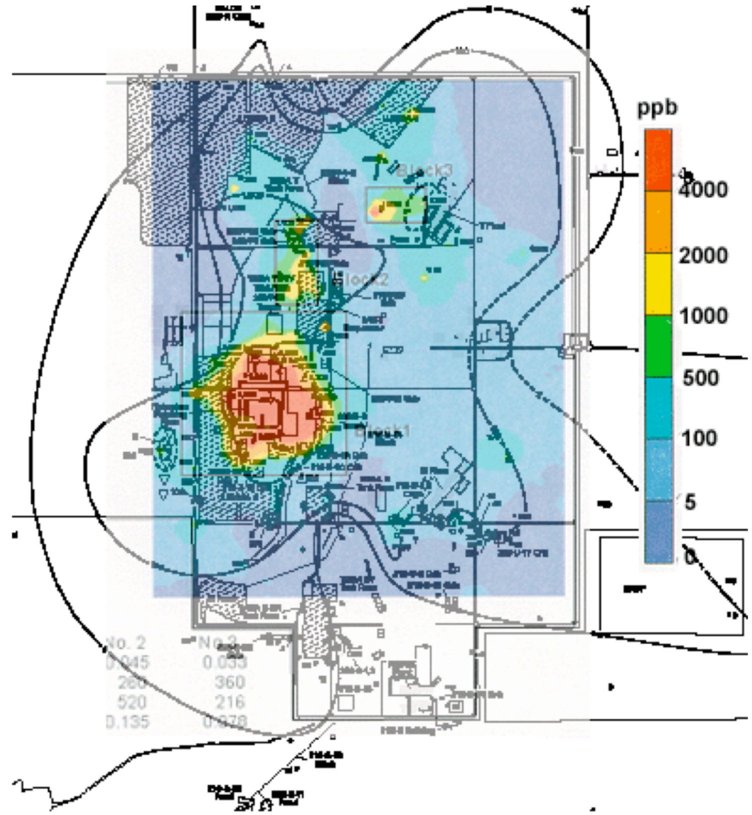
Chloroform Yield



Nurmi et al. (2005) ES&T 39: 1221-1230. Sarathy et al. (in prep.)

Application to Site Remediation

- 200 W Area of Hanford
  - 750,000 kg spilled
  - Vadose and GW zones
  - 11 km^2 plume
  - up to 7000 ug/L
- ITRD TAG since 1999
  - Completed PITT
  - Reviewed Natural Attenuation
  - Modeled Reactive-Transport
  - Reviewed Treatment Options
- Status
  - Active intervention probably needed soon
  - “Critical” Need for Remediation Technology (TIP No. 0006)



Summary and Credits

Summary:

- Nano Fe^0 has a shell of Fe_3O_4, other oxides, and impurities.
- Specific surface area is an important and challenging property.
- Nano Fe^0 gives greater k_m, but not necessarily greater k_{SA}.
- Some nano Fe^0 gives more favorable products (low Y_{CF}).
- Low Y_{CF} and injectability offer prospects for remediation.

Funding:

- DOE Office of Science, Nanoscale Science, Engineering, and Technology Program (DE-AC05-76RLO 1830)
- DOE Office of Science, Environmental Management Sciences Program (DE-FG07-02ER63485)
- SERDP and ESTCP

Acknowledgements

1. Tratnyek Group

   Vaish Sarathy, Jim Nurmi, Joel Bandstra (PSU)

   Bumhan Bae (Kyungwon Univ.)

2. Pacific Northwest National Laboratory

   Don Baer, J. Amonette, E. Bylaska,

   Z. Dohnalek, M. Dupuis, A. El-Azab,

   B. Kay, J. Linehan , K. Pecher, J. Rustad

3. Other Collaborators

   R. Lee Penn and M. Driessen (U. Minnesota),

   Y. Qiang and J. Antony (U. Idaho),

   Rick Johnson (OHSU)

4. Samples

   K. Okinaka and Andy Jazdanian (Toda Kogyo Corp.)

   W.-X. Zhang (Lehigh U.)

   Clint Bickmore (OnMaterials, LLC)

   D. Vance (Arcadis), and others