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

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DOE BES/EMSP Project

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

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

University of Minnesota: L. Penn and M. Driessen

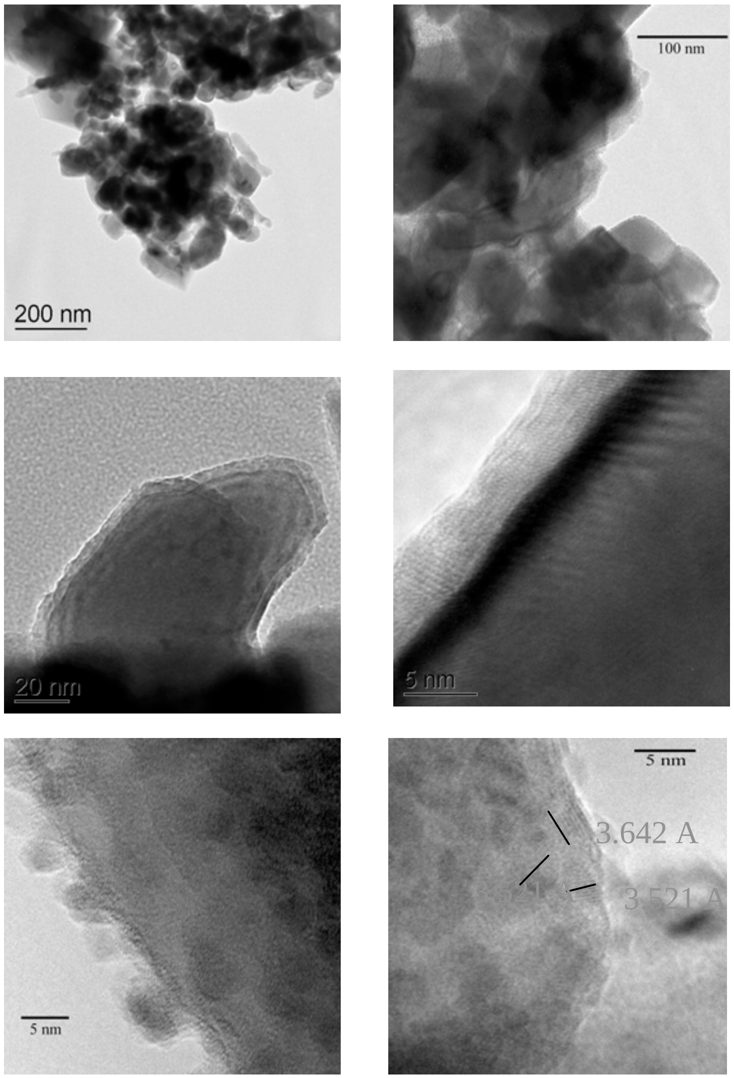
Iron and Iron Oxides Studied

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	

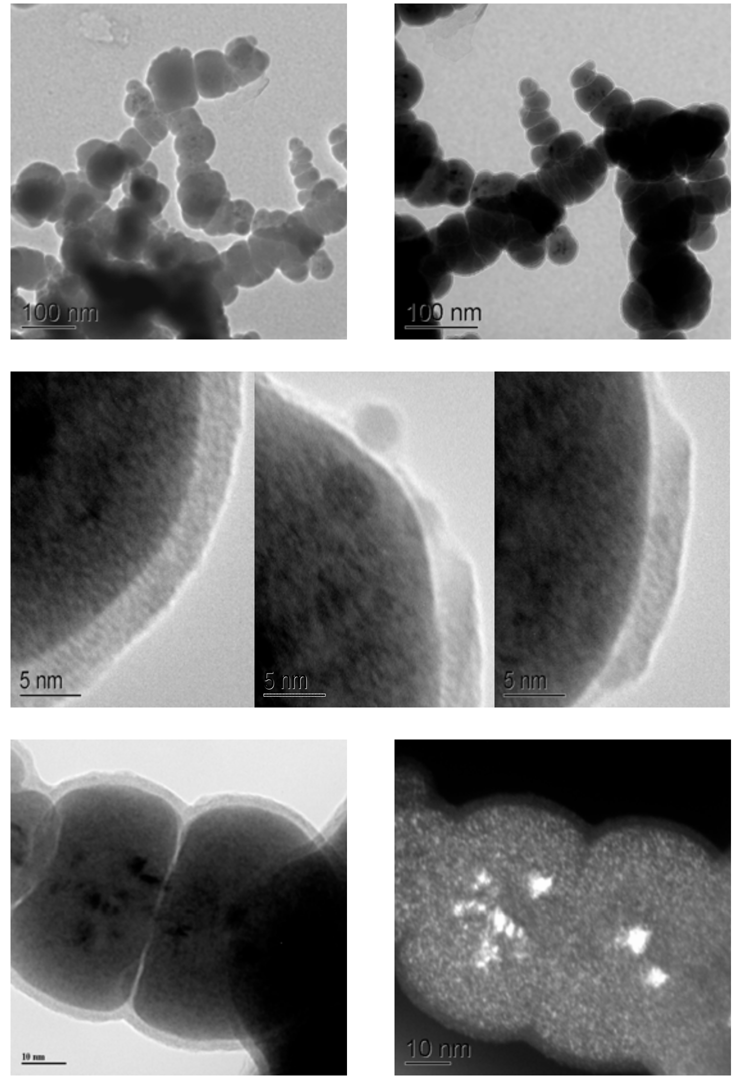
Nurmi et al. (2005) ES&T 39: 1221-1230.

Structure from TEM

Fe^{H2} (Toda)

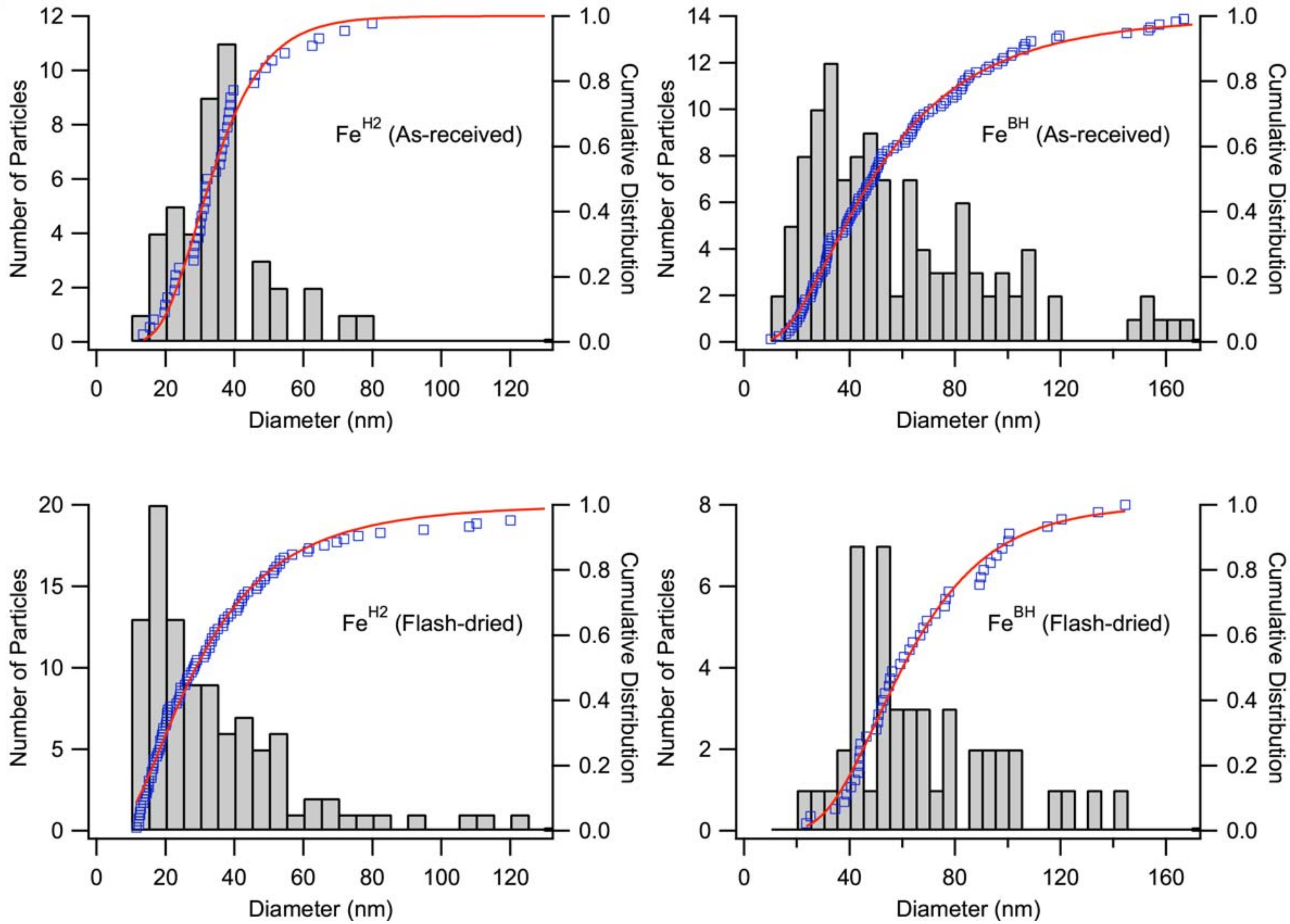


Fe^{BH} (Zhang)



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

Particle Size from TEM



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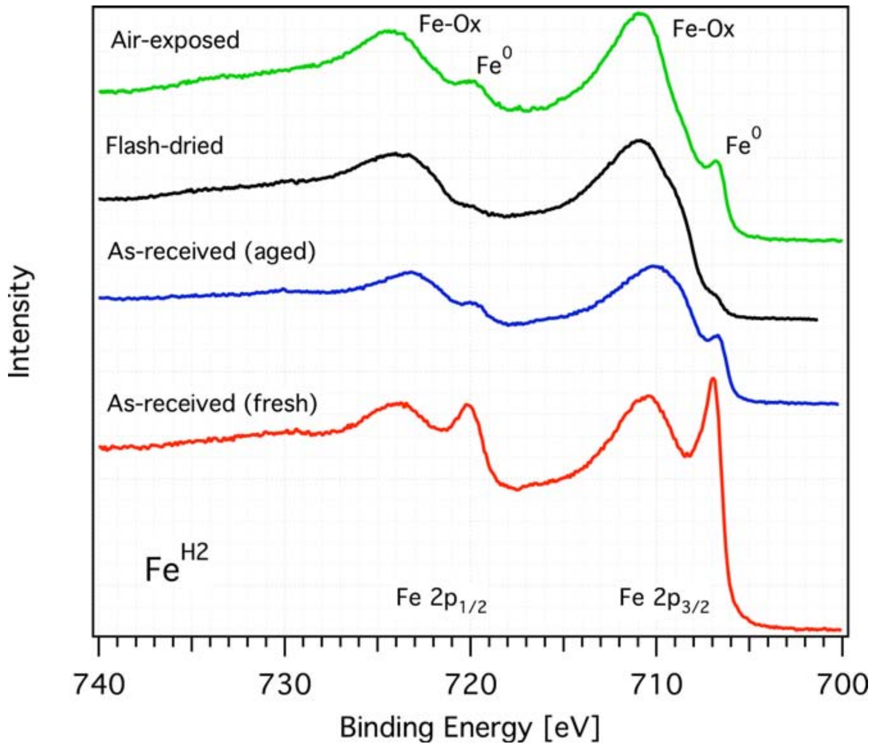
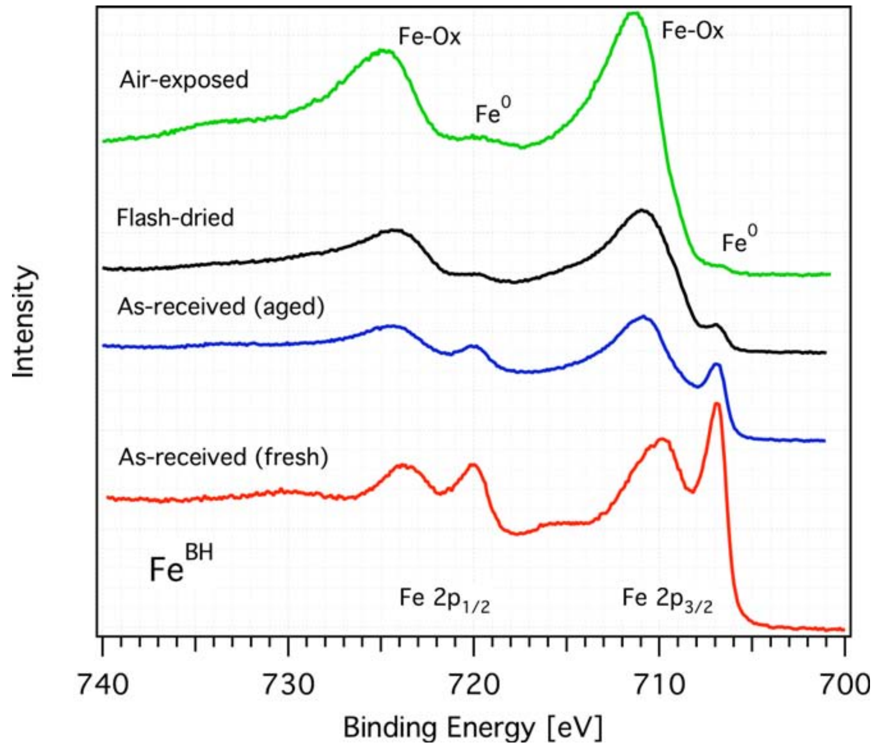
Composition from XPS

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	

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Solution Chemistry—Methods

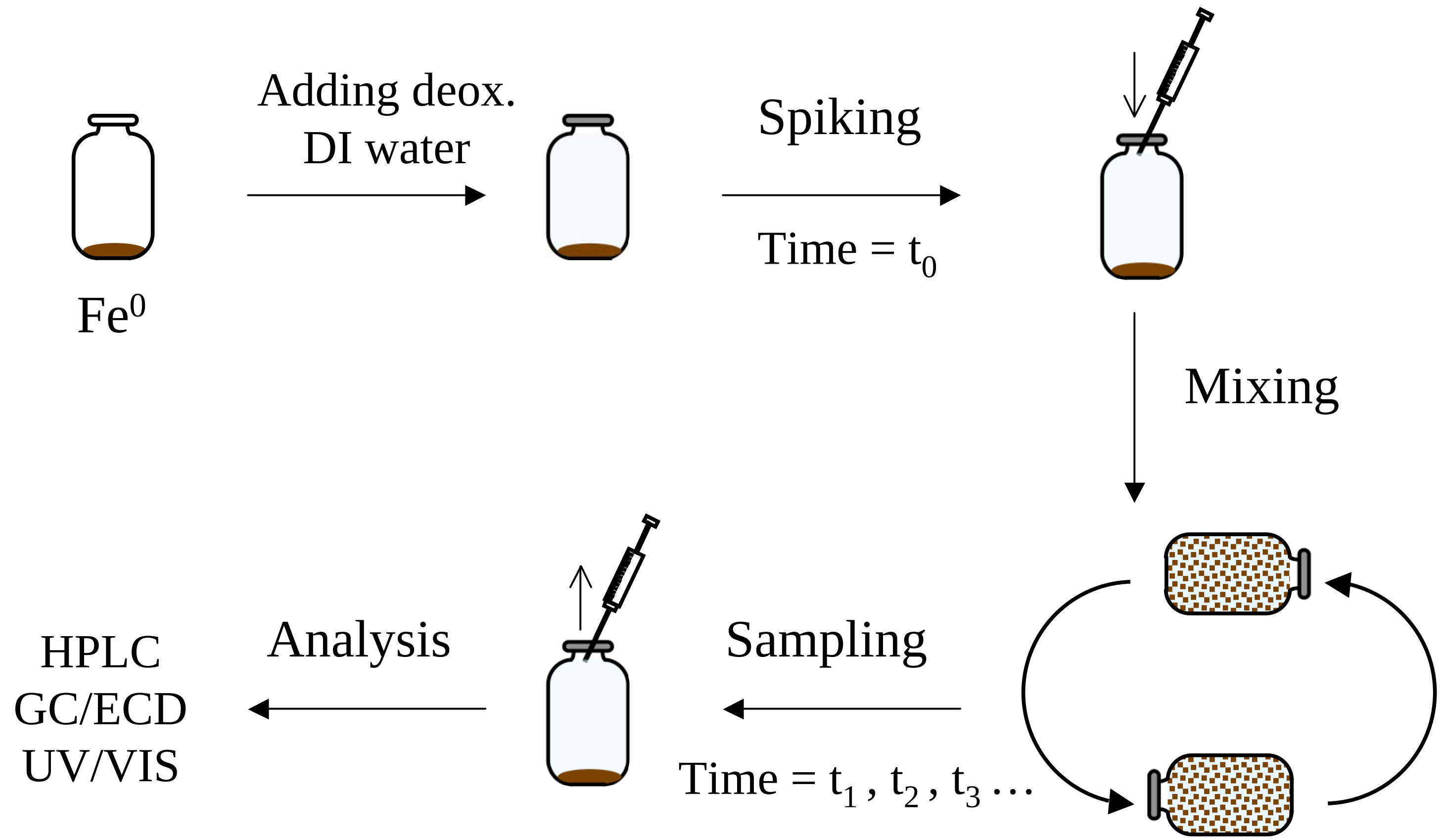
Electrochemical Cell

- 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

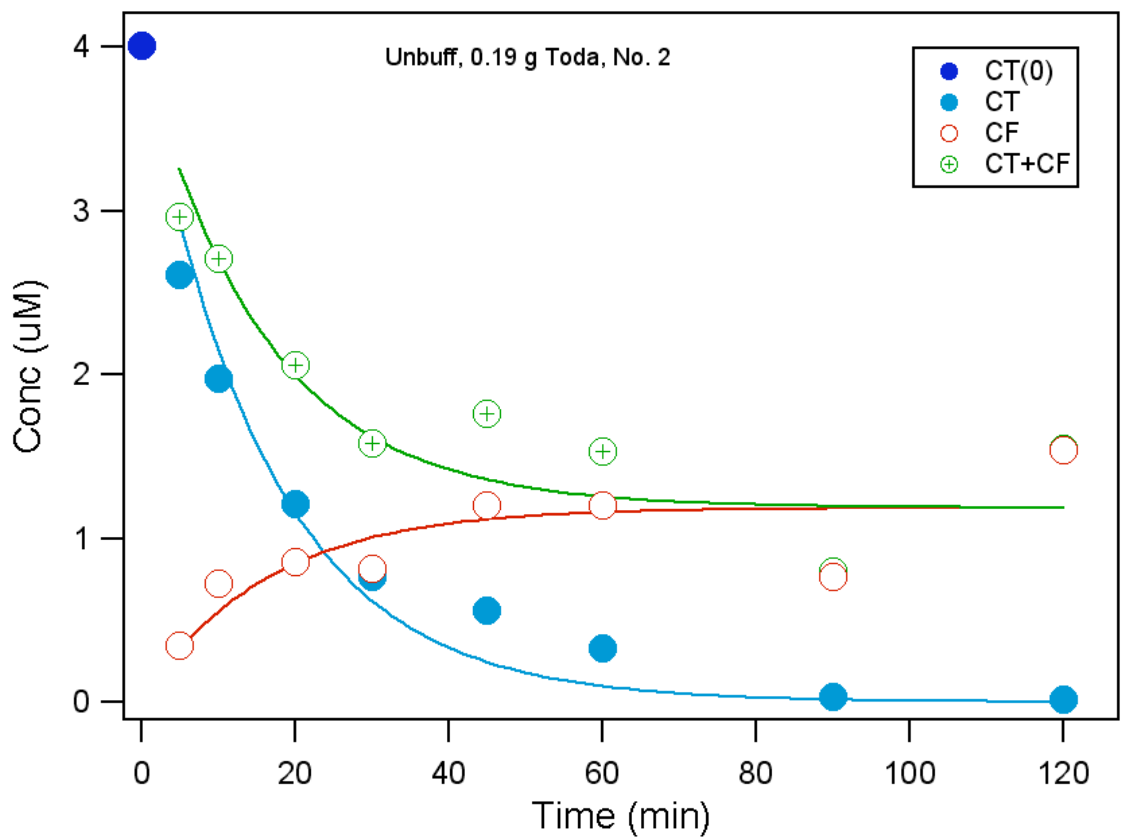
- Buffer selection
- Ox/Fe ratio

- Mixing rate
- Kinetic model

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

Batch Experiments with CCl_4

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



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

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k_{sa} vs. k_m plots

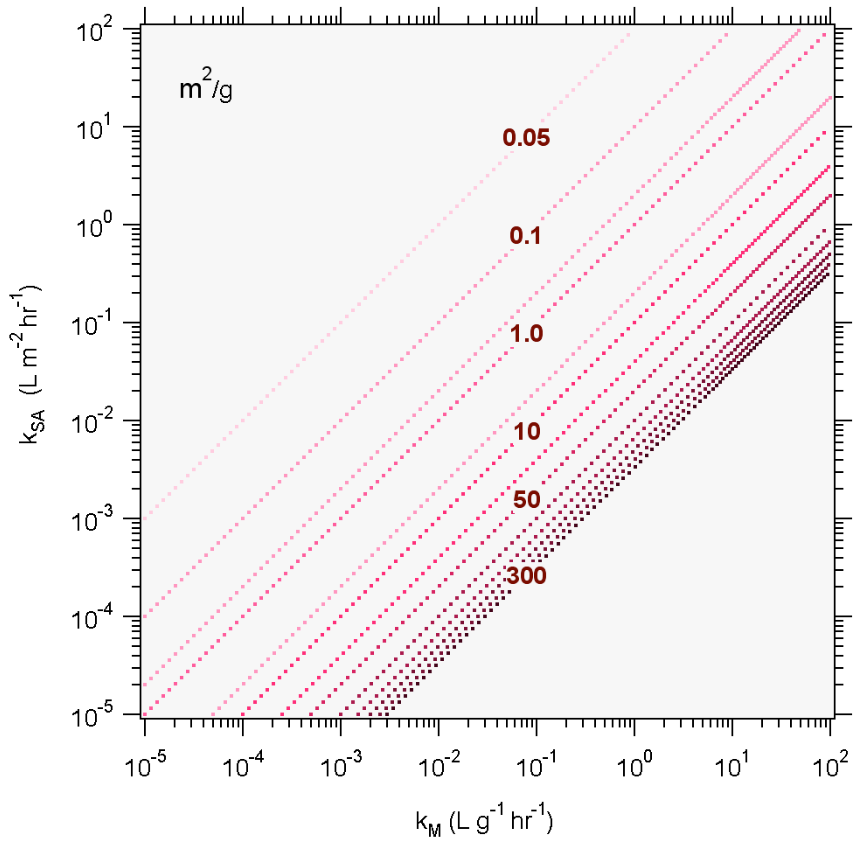
From:

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

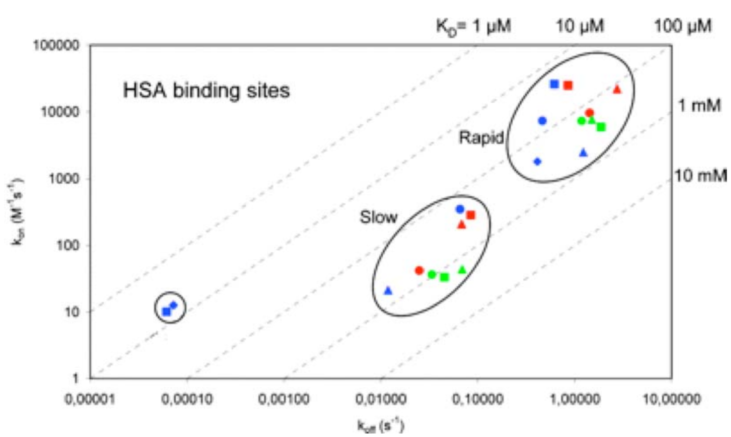
It follows that:

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

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



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



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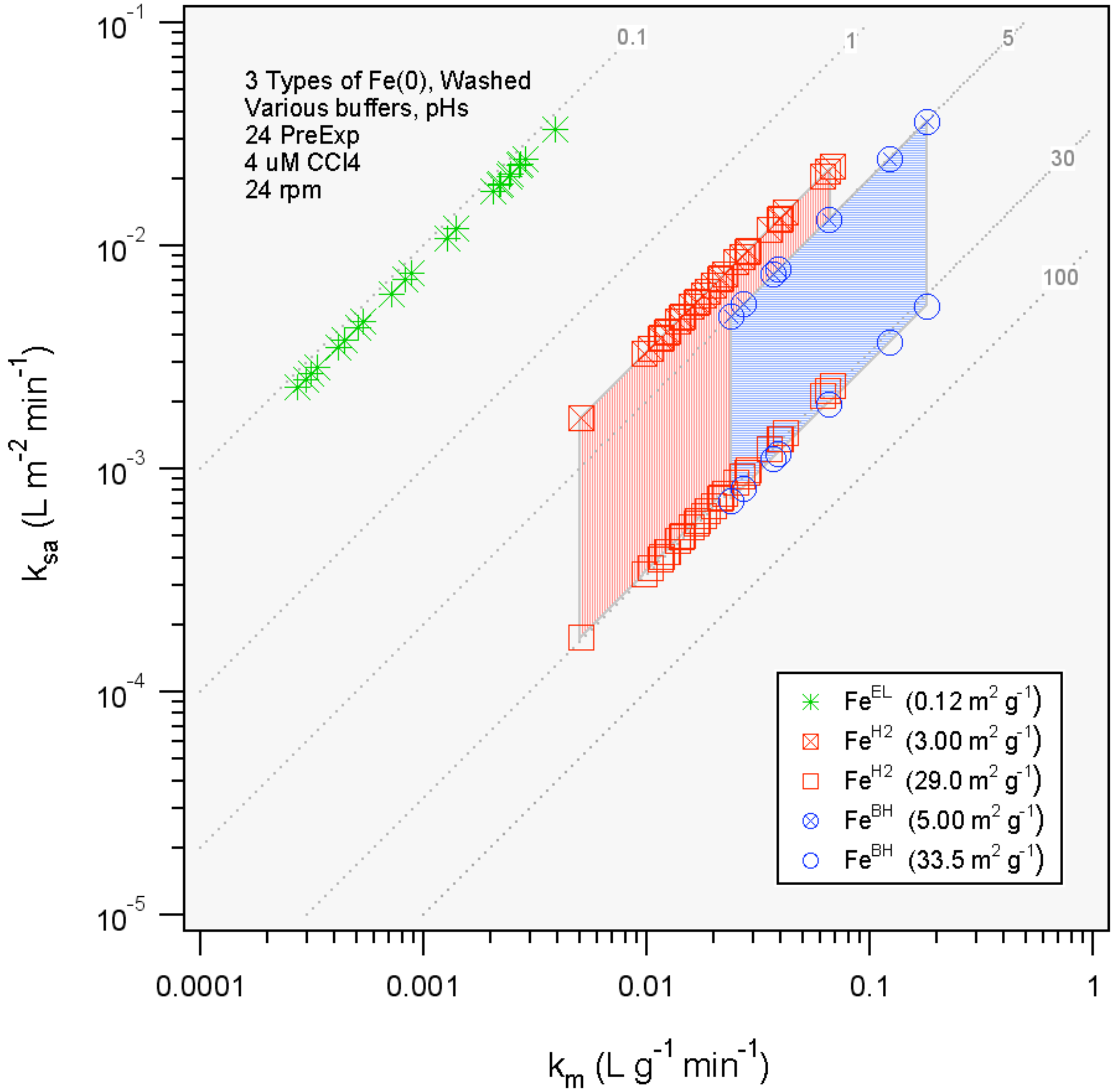
Effect of Surface Area—Our Data Only



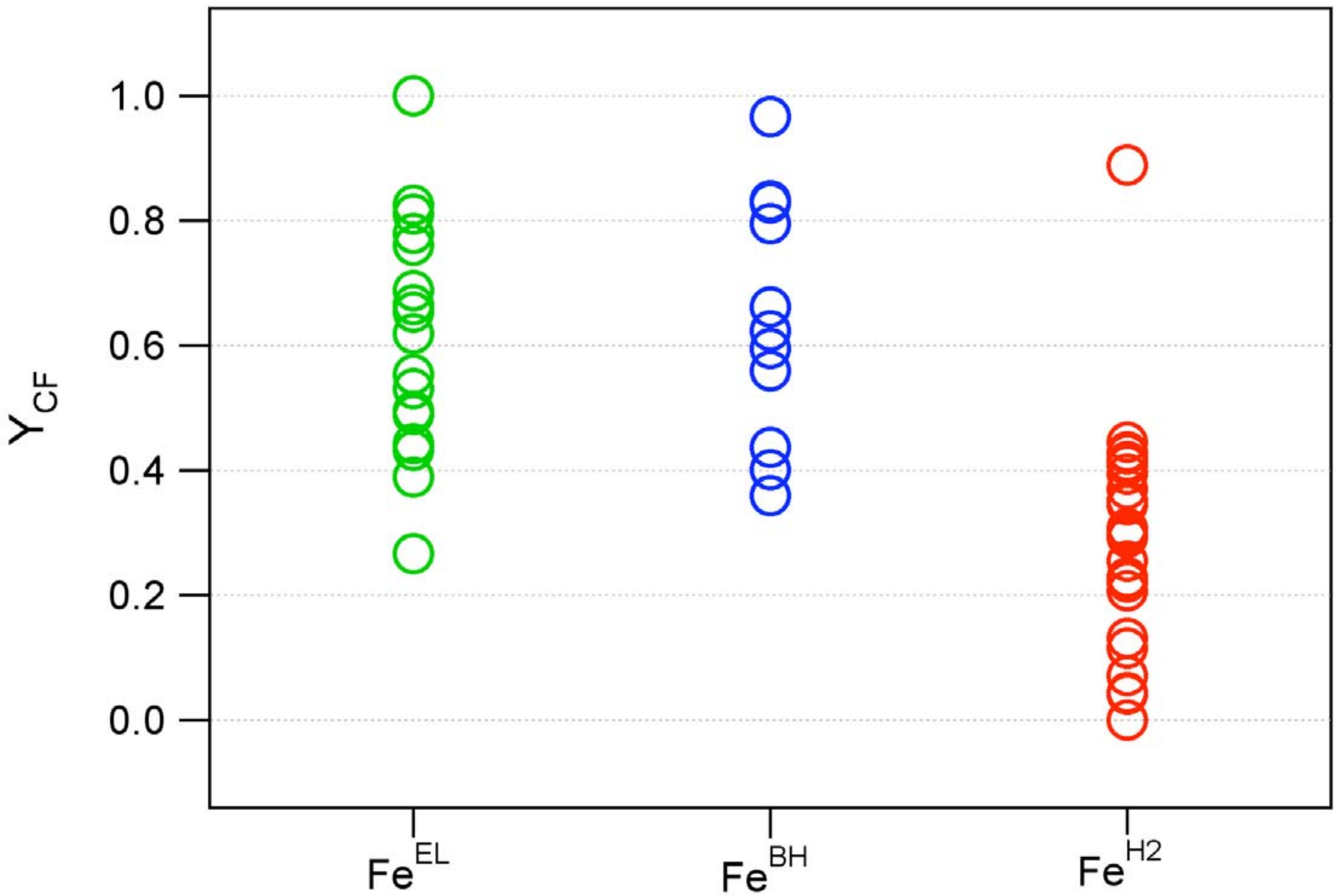
- k_M (Nano > Micro)
- k_M (Fe^{BH} ? Fe^{H2})
- a_s (TEM < BET)
- k_{SA} (Nano ≈ Micro)
- k_{SA} (Nano < Micro)

… Uncertainties in a_s are important

… No “intrinsic” nano-size effect

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

Chloroform Yield



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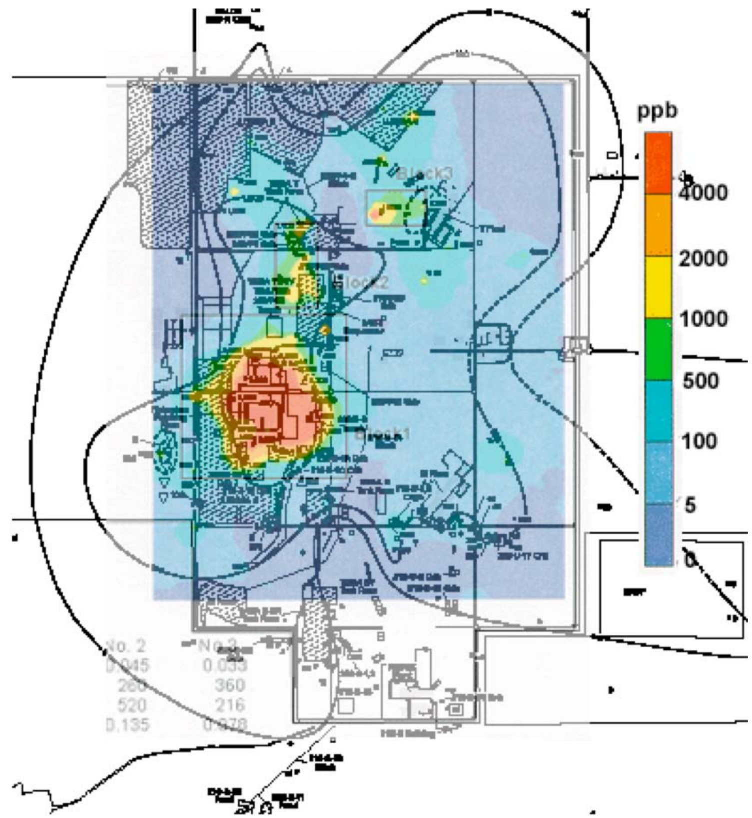
Application to Site Remediation

- 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)



DOE Various Sources

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.

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