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Incorporating Ferrate Oxidation into Small Drinking Water Systems

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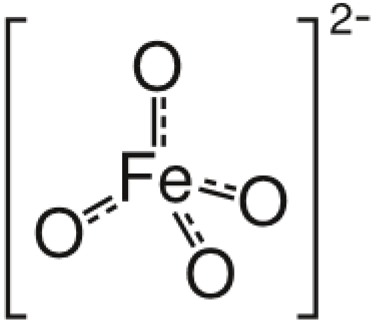
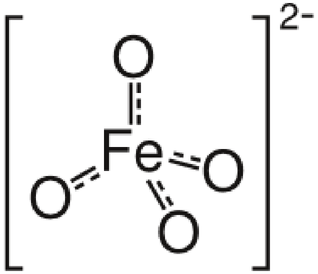




Ferrate Basics

- Decomposes in water

$$FeO_4^{-2} + \frac{5}{2}H_2O \rightarrow Fe(OH)_3 + \frac{3}{4}O_2 + 2OH^-$$

  - Forming ferric hydroxide and oxygen
- Must be produced on-site by either
  - Electrochemical method
  - Wet oxidation method

$$Fe(OH)_3 + \frac{3}{2}OCl^- + 2OH^- \rightarrow FeO_4^{-2} + \frac{3}{2}Cl^- + \frac{5}{2}H_2O$$

    - Becoming more economical
- An oxidant and disinfectant
  - Many studies showing reaction rates for a wide range of organic and inorganic solutes in water
    - e.g., Sharma et al.; Lee & von Gunten
- Won’t produce regulated DBPs
  - A good alternative for pre-Cl_2 and maybe pre-O_3

To be used in US Water Treatment

- Ferrate must:
  - Be given disinfection (CT) credit by the EPA
  - Be cost competitive
  - Not interfere with other treatments used in plant
  - Offer some advantage over existing treatment technologies; examples:
    - Better removal of trace contaminants in raw water
    - Better control of organic and inorganic disinfection byproducts
    - Less energy consumption, carbon footprint, etc.
    - Easier to use, or more reliable
    - Improve aesthetic qualities of the product water

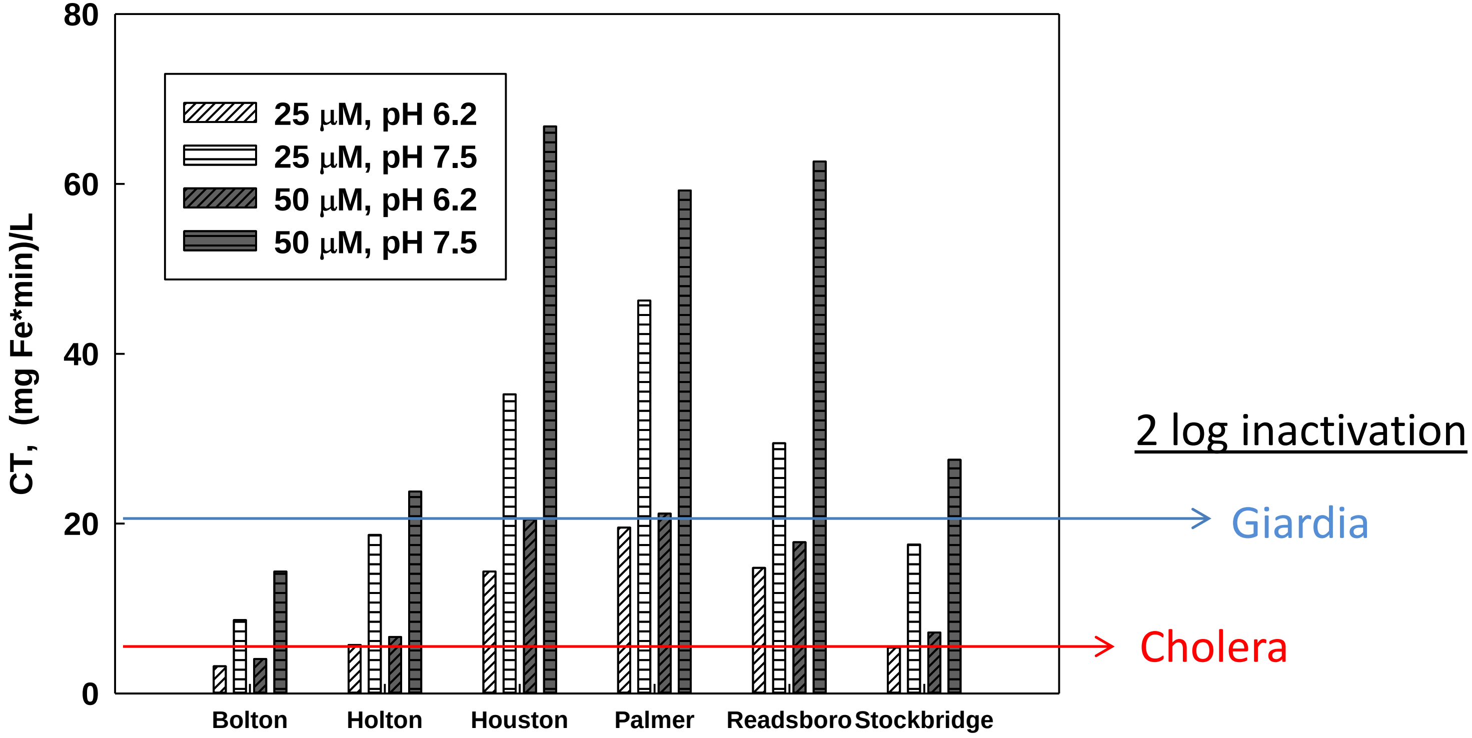
Summary of 2-log Disinfection @pH7

	M-Fe(VI)*min [(mg-Fe(VI)/L)*min]	M-Cl_2*min [(mg-Cl_2/L)*min]
E. Coli (5°C)	3×10^{-5} [1.9] †*	7.1×10^{-7} [0.05]
MS2 (5°C)	4.7×10^{-5} [2.6] ‡	2.5×10^{-6} [0.18]
Giardia (25°C)	3.8×10^{-4} [21] †	3.8×10^{-4} [27]
V. cholerae (*rugose*) (20-25°C)	6.3×10^{-5} [3.5] †	3.5×10^{-6} [0.25]

†Current EPA study; * S35150 strain

‡Hu et al. *ES&T*, 2012

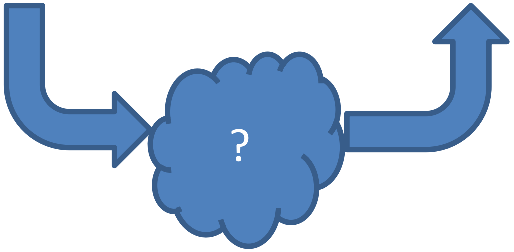
Ferrate exposure (CT product)



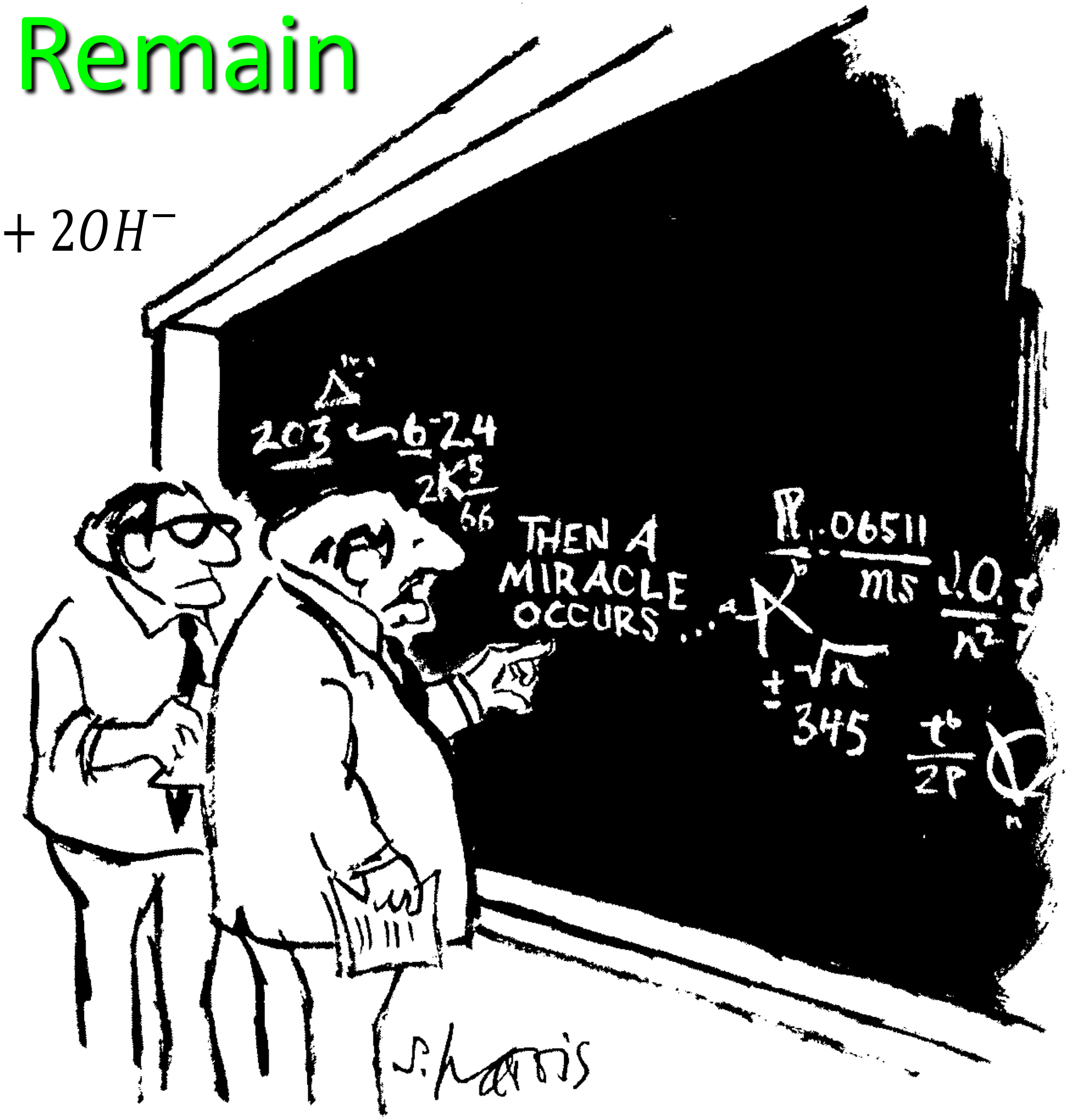
CT values at pH 6.2 are much lower than those at pH 7.5, pH had a great effect on CT values.

But Questions Remain

$$FeO_4^{-2} + \frac{5}{2}H_2O \rightarrow Fe(OH)_3 + \frac{3}{4}O_2 + 2OH^-$$

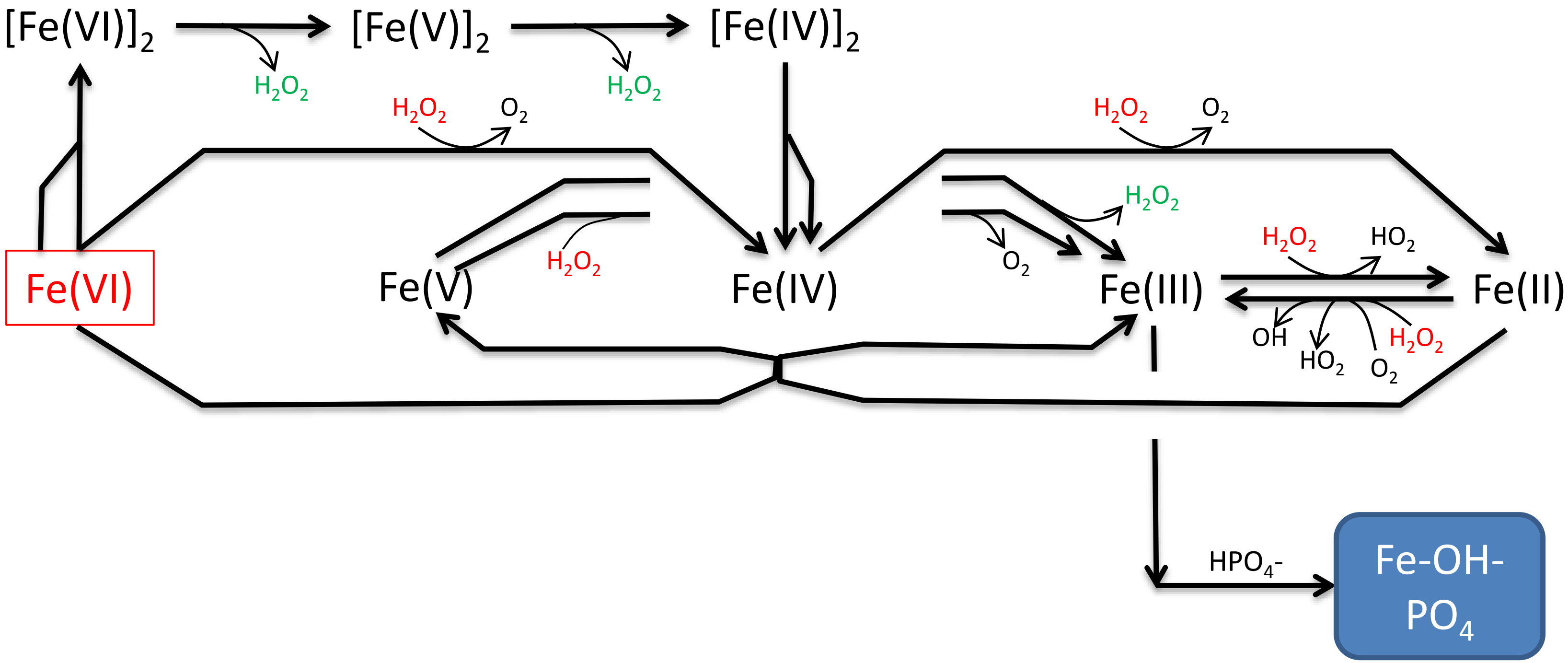


- Fe(+VI) goes to Fe(+III)
- Intermediate products and oxidation states?
  - Fe(V), Fe(IV)?
  - Are they reactive too?



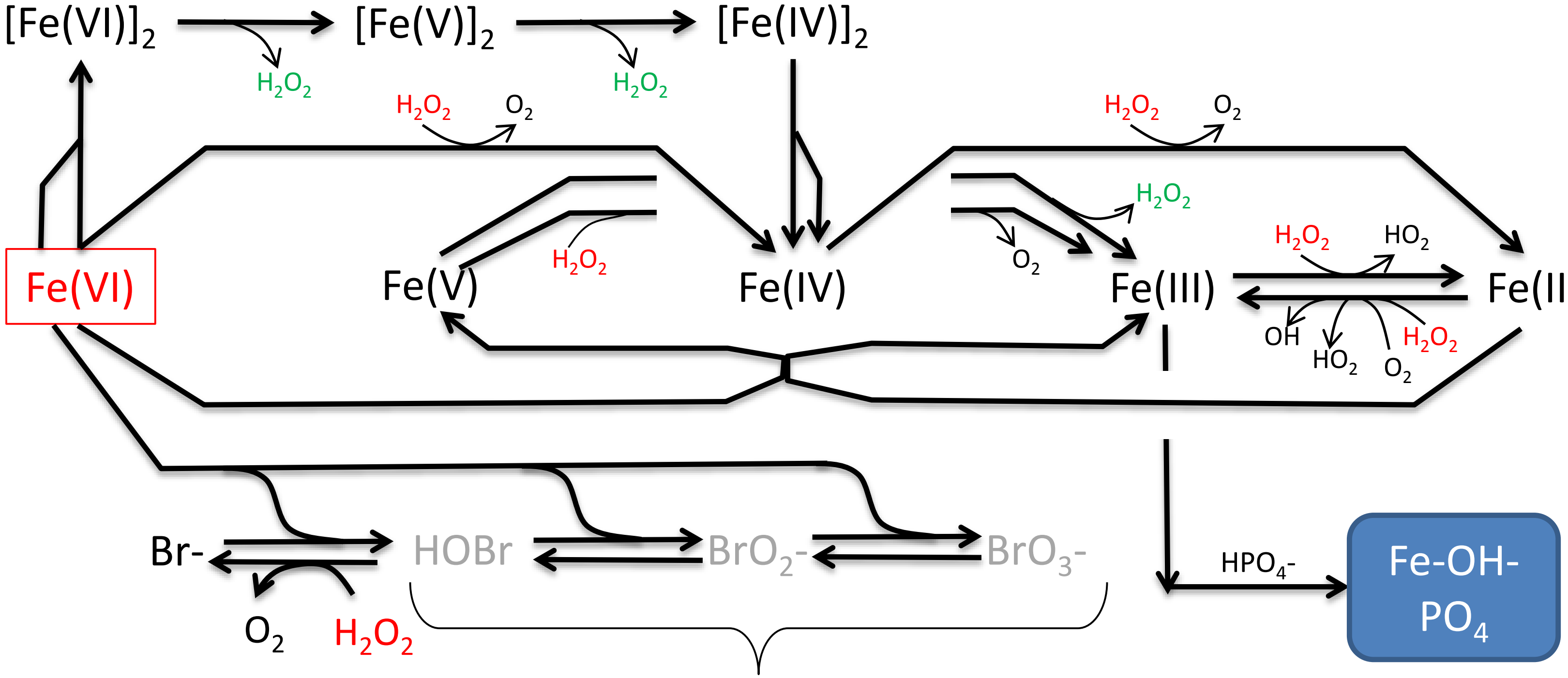
"I think you should be more explicit here in step two"

Decomposition in phosphate buffer



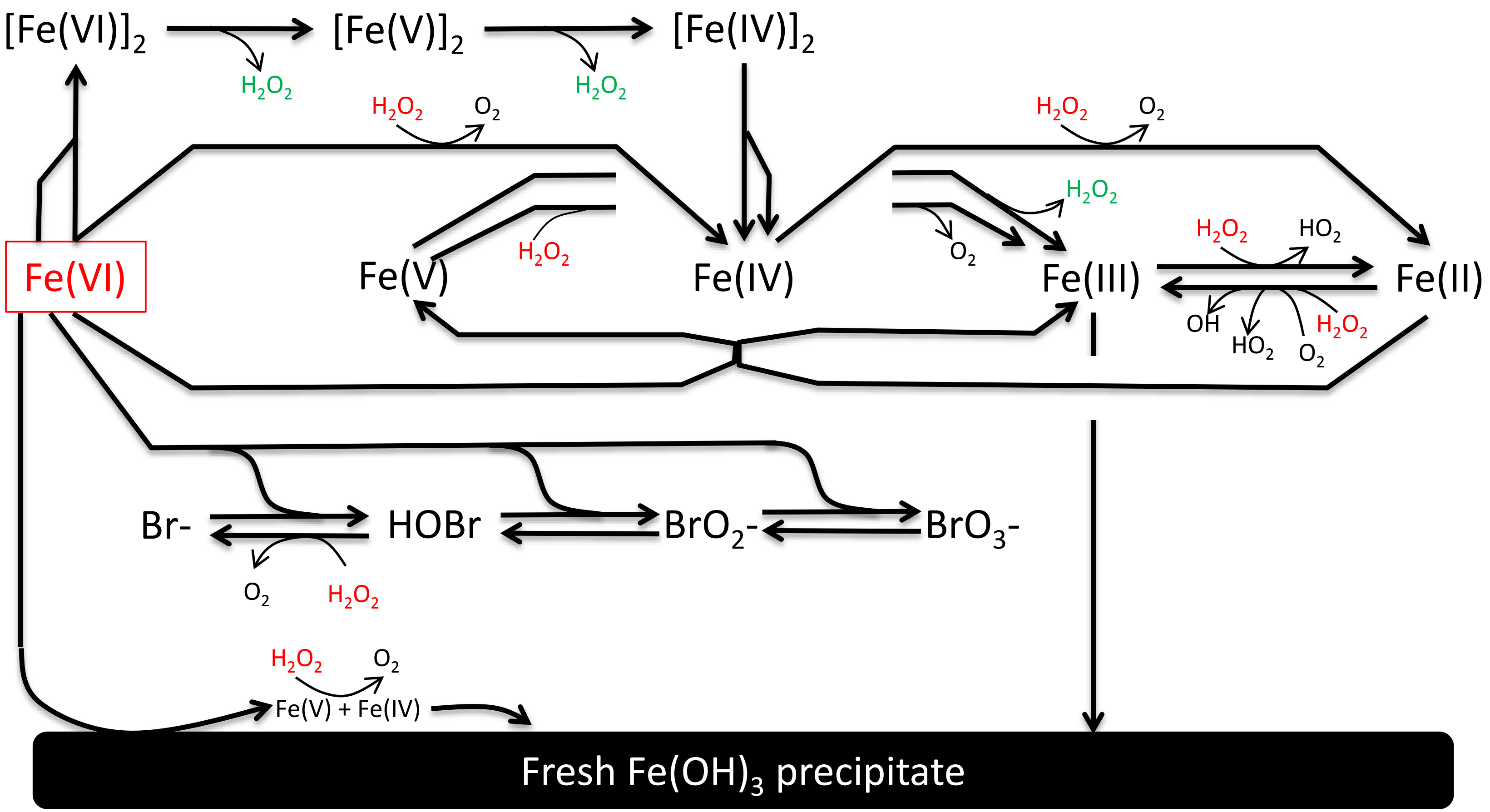
- Mechanism contributed by many groups
  - Especially those led by Bielski and von Gunten

With phosphate and bromide

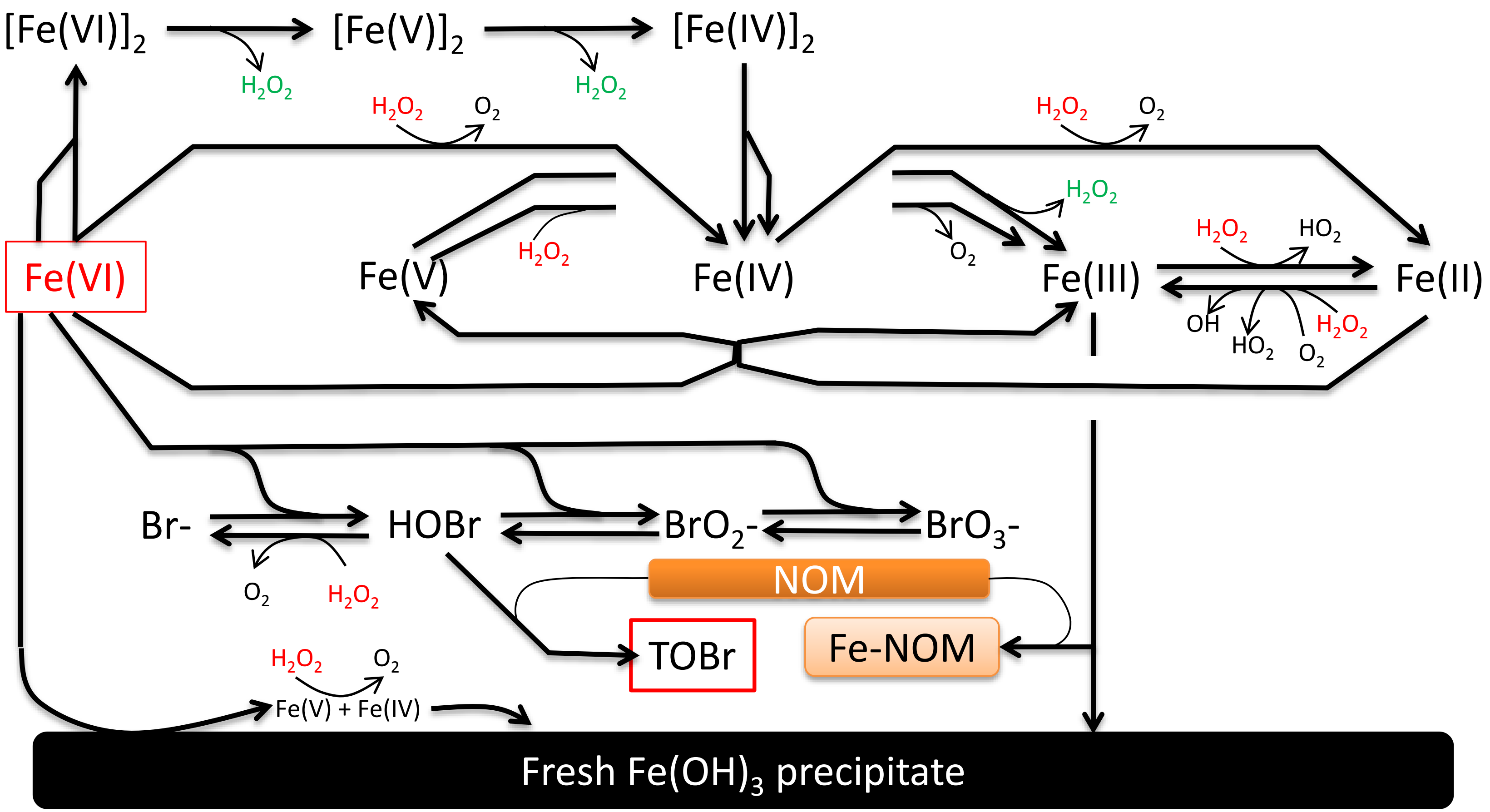


Formation is suppressed due to high H_2O_2

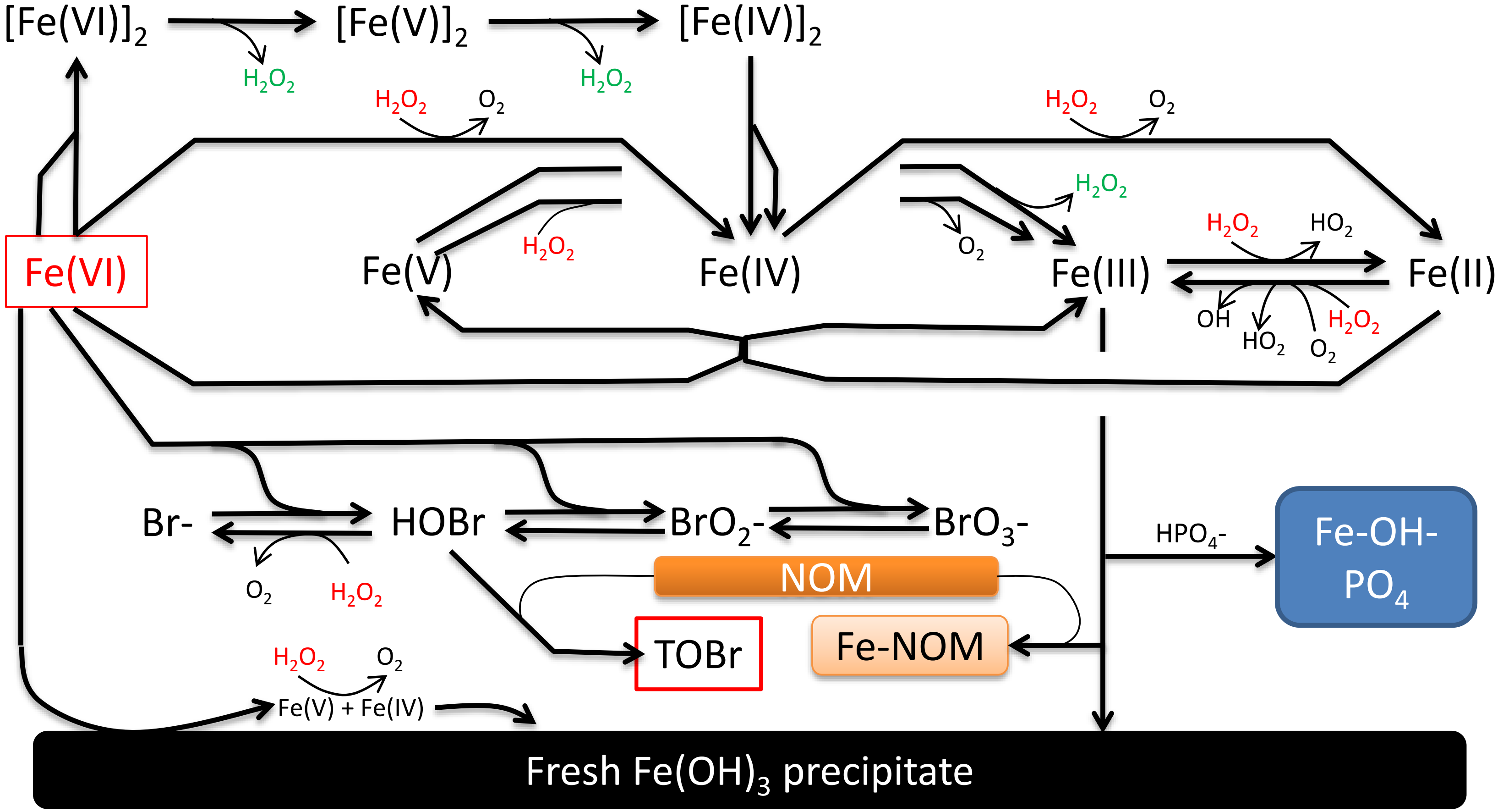
Without phosphate



Typical water with NOM



All reactions



$[Fe(VI)]_2$ $[Fe(V)]_2$ $[Fe(IV)]_2$

H_2O_2 H_2O_2

H_2O_2 O_2 H_2O_2 O_2

H_2O_2

H_2O_2 O_2 H_2O_2 HO_2

Fe(VI) Fe(V) Fe(IV) Fe(III) Fe(II)

OH HO_2 H_2O_2 O_2

Br- HOBr BrO_2- BrO_3-

O_2 H_2O_2

NOM

HPO_4-

Fe-OH-PO_4

TOBr Fe-NOM

H_2O_2 O_2

Fe(V) + Fe(IV)

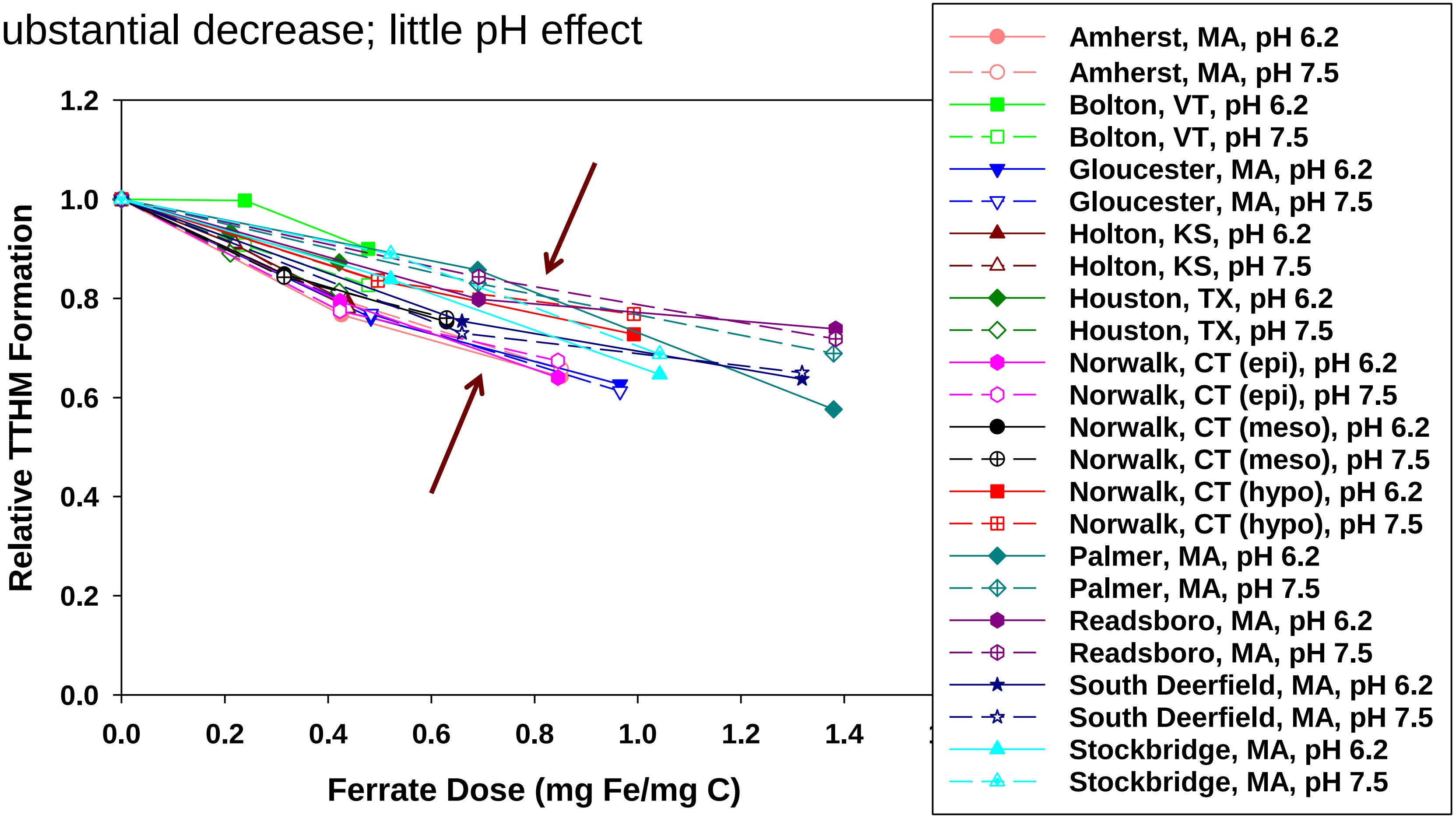
Fresh $Fe(OH)_3$ precipitate

How does Ferrate affect NOM reactivity with chlorine? DBP formation?

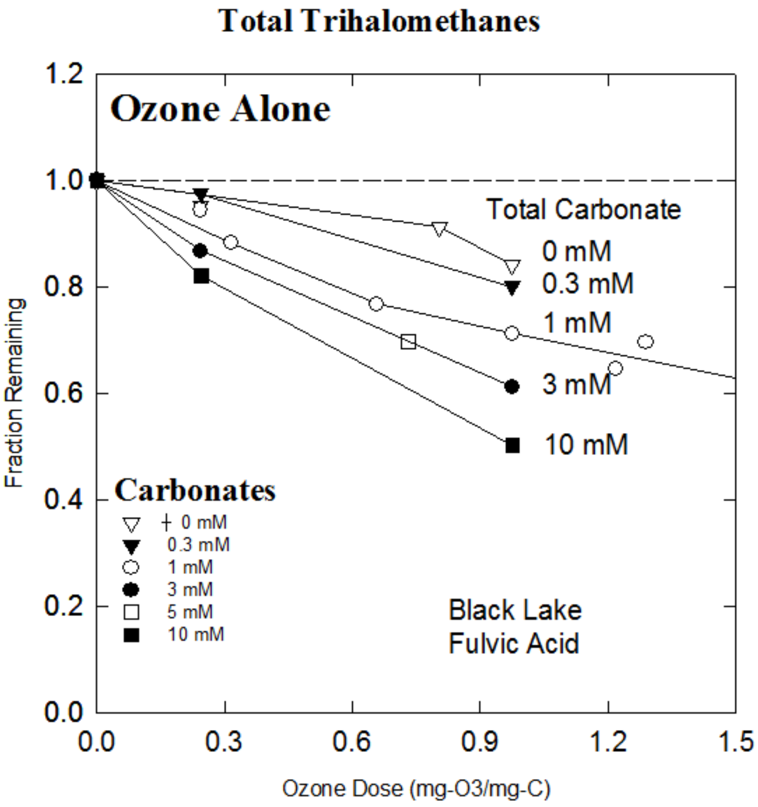
- Test Protocol
  - Treat raw water samples with ferrate
  - Allow ferrate to dissipate (<60 min)
  - Chlorinate in the lab
    - pH 7
    - Dose required for 1 mg/L residual after 72 hrs
    - 20^{o}C
  - Measure DBPs
    - Neutral Extractables (including THMs)
    - Haloacetic Acids (9 total)

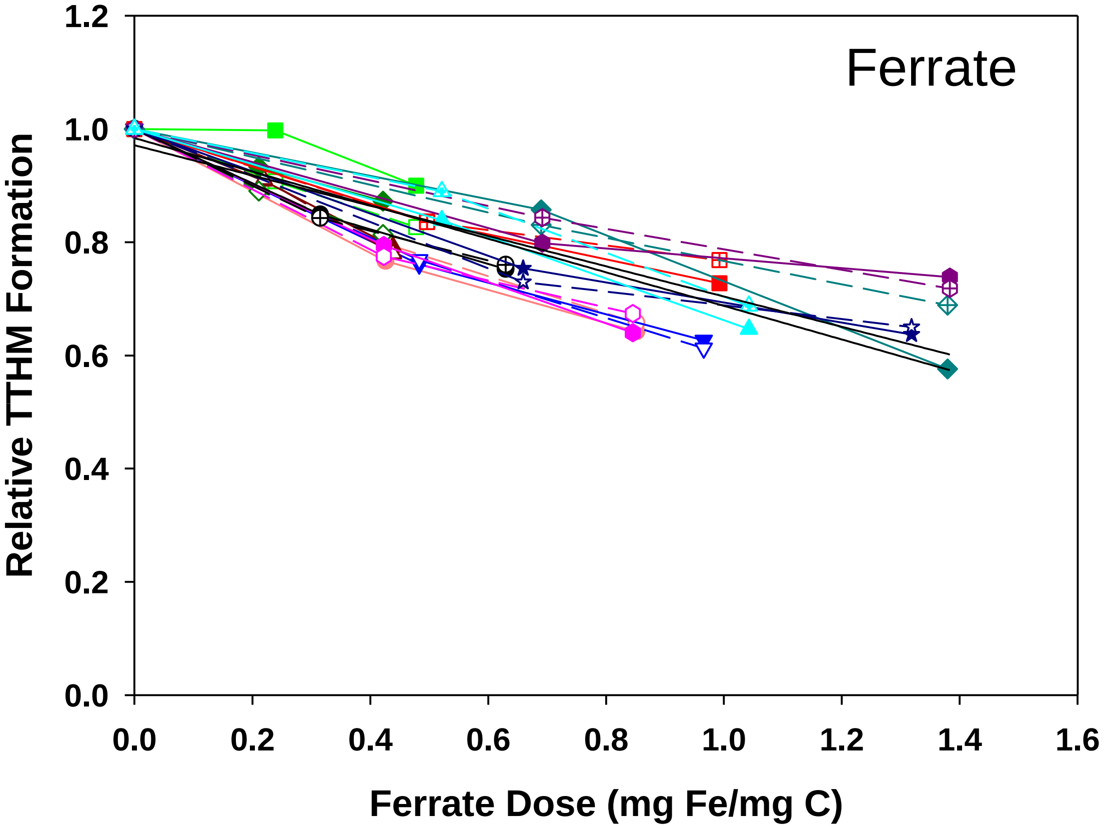
Effects of Direct Ferrate Oxidation on Trihalomethane (THM) Formation Potential

Substantial decrease; little pH effect



Comparison with ozone



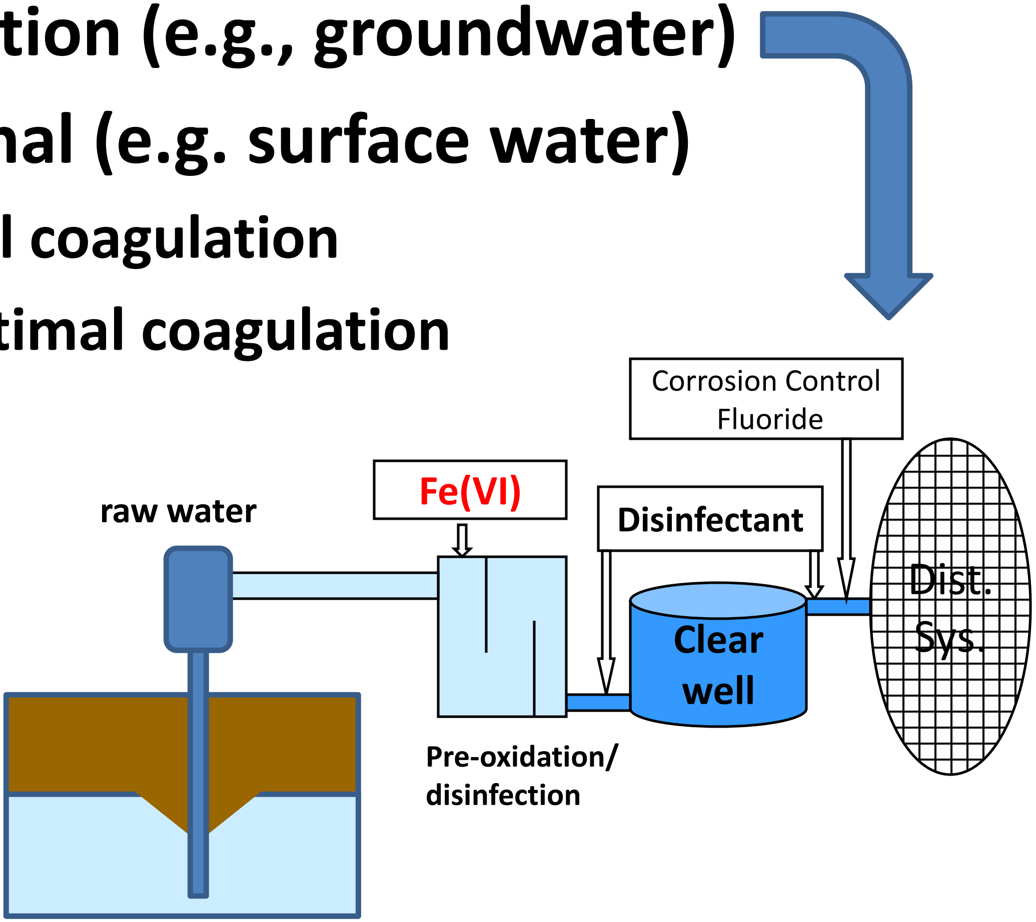


Data from: Reckhow et al., 1986

Data from: current study

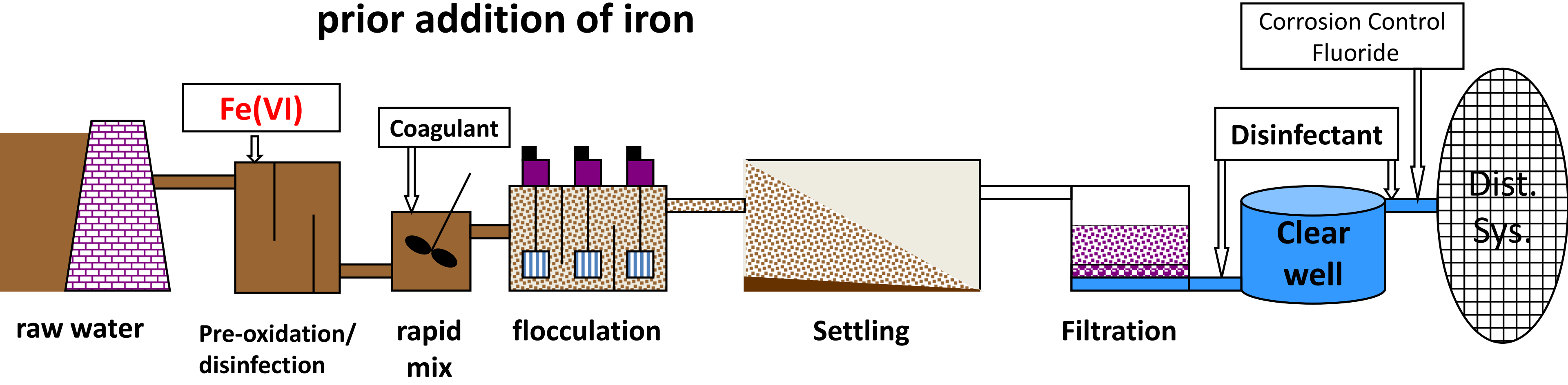
Integration into water treatment I

- **Three pre-ferrate scenarios**
  - **I: direct ferrate oxidation (e.g., groundwater)**
  - **III: part of conventional (e.g. surface water)**
    - **IIIA: ferrate & optimal coagulation**
    - **IIIB: ferrate & sub-optimal coagulation**



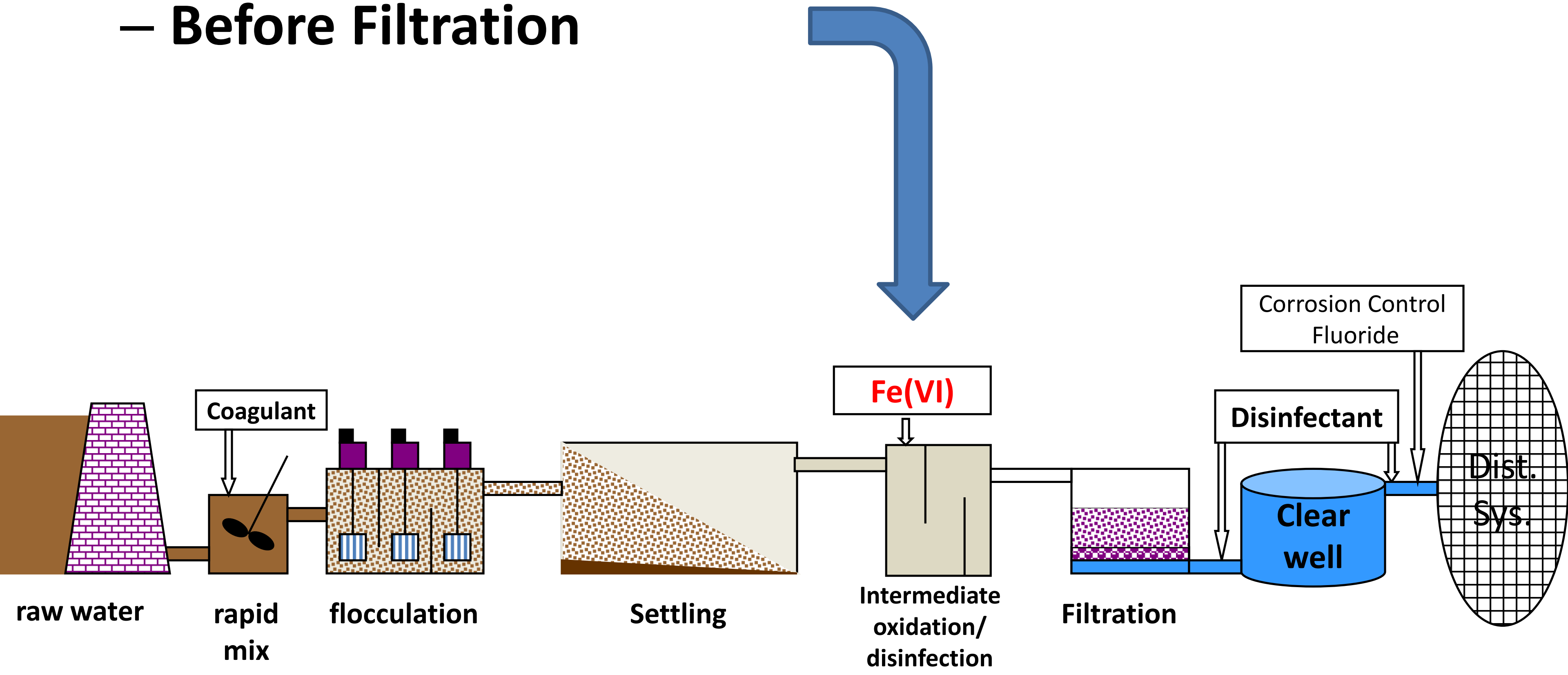
Integration into water treatment II

- **Three pre-ferrate scenarios**
  - **I: direct ferrate oxidation (e.g., groundwater)**
  - **III: part of conventional (e.g. surface water)**
    - **IIIA: ferrate & optimal coagulation**
    - **IIIB: ferrate & sub-optimal coagulation**
      - **Reduce coagulant dose to account for prior addition of iron**

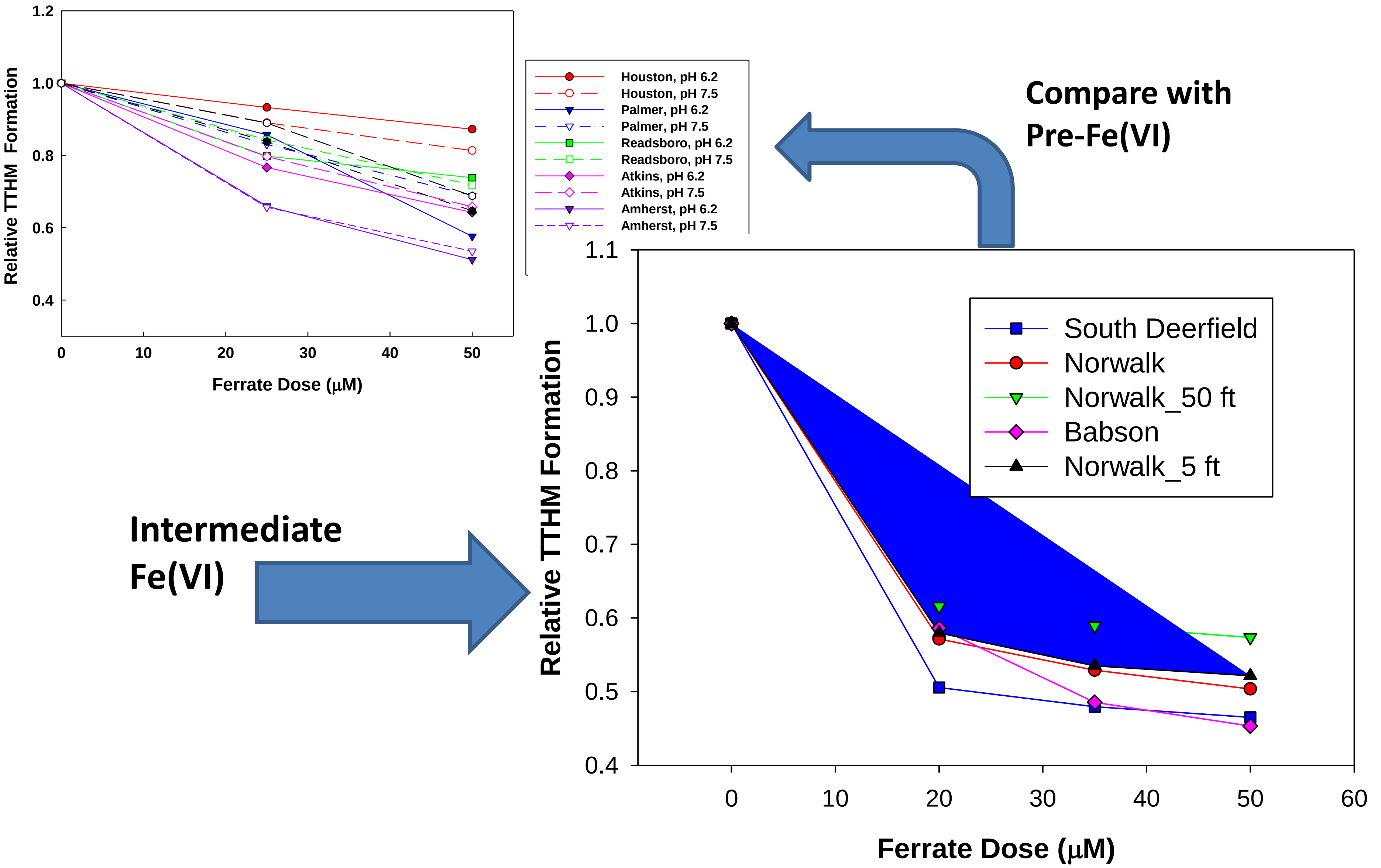


The Intermediate Ferrate Scenario

- **Point of Addition**
  - **After clarification (settling)**
  - **Before Filtration**



Intermediate Fe(VI) and THMs



Compare with Pre-Fe(VI)

Intermediate Fe(VI)

Some Conclusions I

- Ferrate decomposition is more complicated than previously recognized. Natural waters have a stabilizing effect on ferrate.
  - Some bromide oxidation occurs
  - Phosphate suppresses decomposition and oxidation of Br
- Ferrate is capable of oxidizing regulated DBP precursors with an effectiveness similar to ozone.
  - At mass doses 1-2x those for ozone
  - Bromine incorporation is less with ferrate
  - Little bromate formation.
  - Exact nature of “effective” Fe oxidant is uncertain

Some Conclusions II

- When introduced at an intermediate stage, ferrate seems to be much more effective at destroying DBP precursors than when applied as a pre-oxidant
- Early data show ferrate to be effective at inactivating many bacteria, viruses and protozoans
- Ferrate in a pre-oxidant mode does not adversely affect filtration performance (filtered water turbidities, headloss buildup and filter run length)
- Ferrate seem to be an especially interested alternative for small systems that have water quality challenges

Acknowledgments

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  - Especially: Yun Yu, Sherrie Webb-Yagodzinski, Arianne Bazilio
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The UMass Ferrate Group


Dave Reckhow


John Tobiason


Yanjun Jiang


Joe Goodwill


Josh Cunningham


Xuyen Mai

WINSSS

Water Innovation Network for Sustainable Small Systems

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Universities of Massachusetts (Amherst), Texas (Austin), Nebraska, Florida, Illinois, South Florida, and Carollo Engineers

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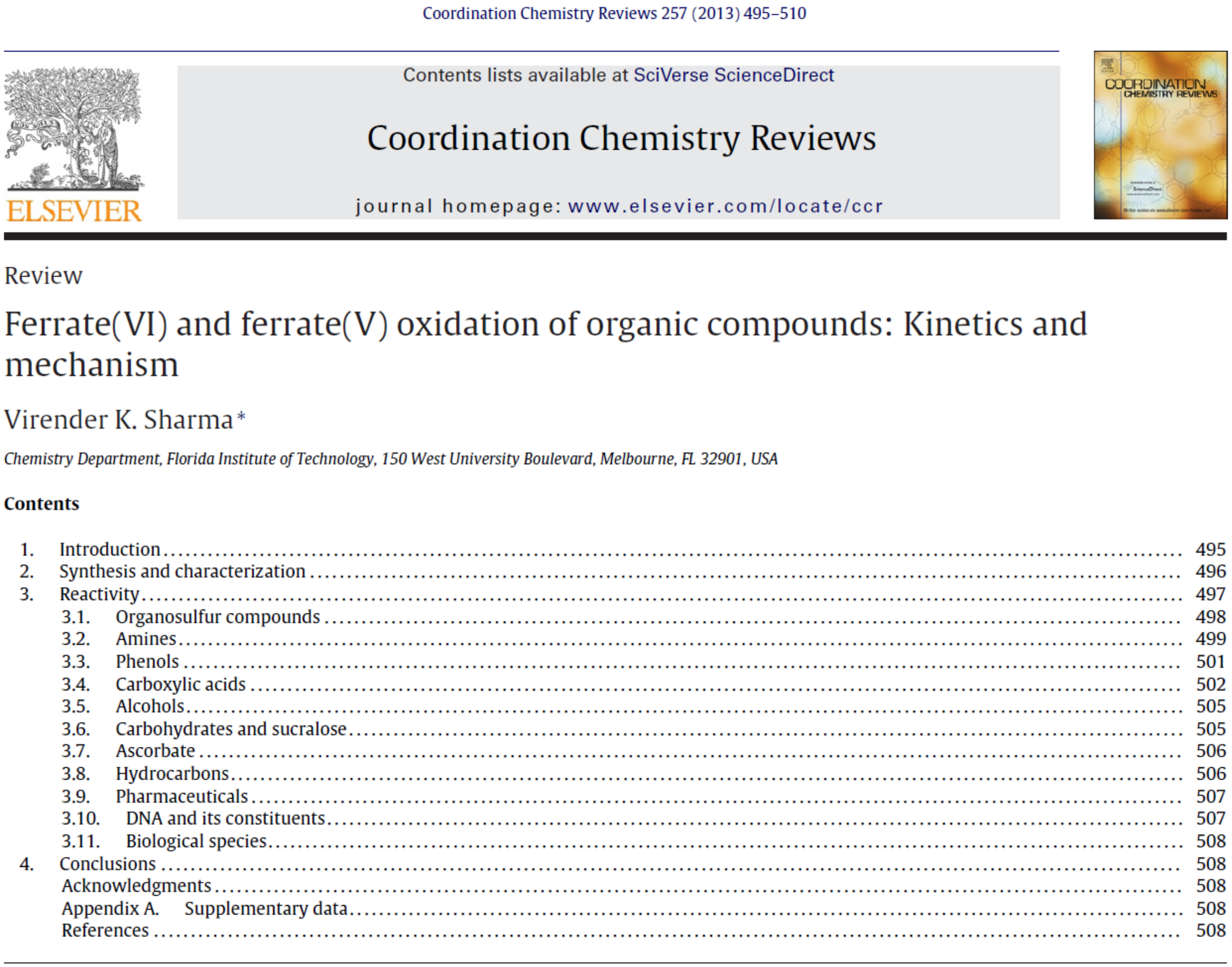
Kinetics of Ferrate with contaminants

- Prodigious literature
  - Sharma & others



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Review

Ferrate(VI) and ferrate(V) oxidation of organic compounds: Kinetics and mechanism

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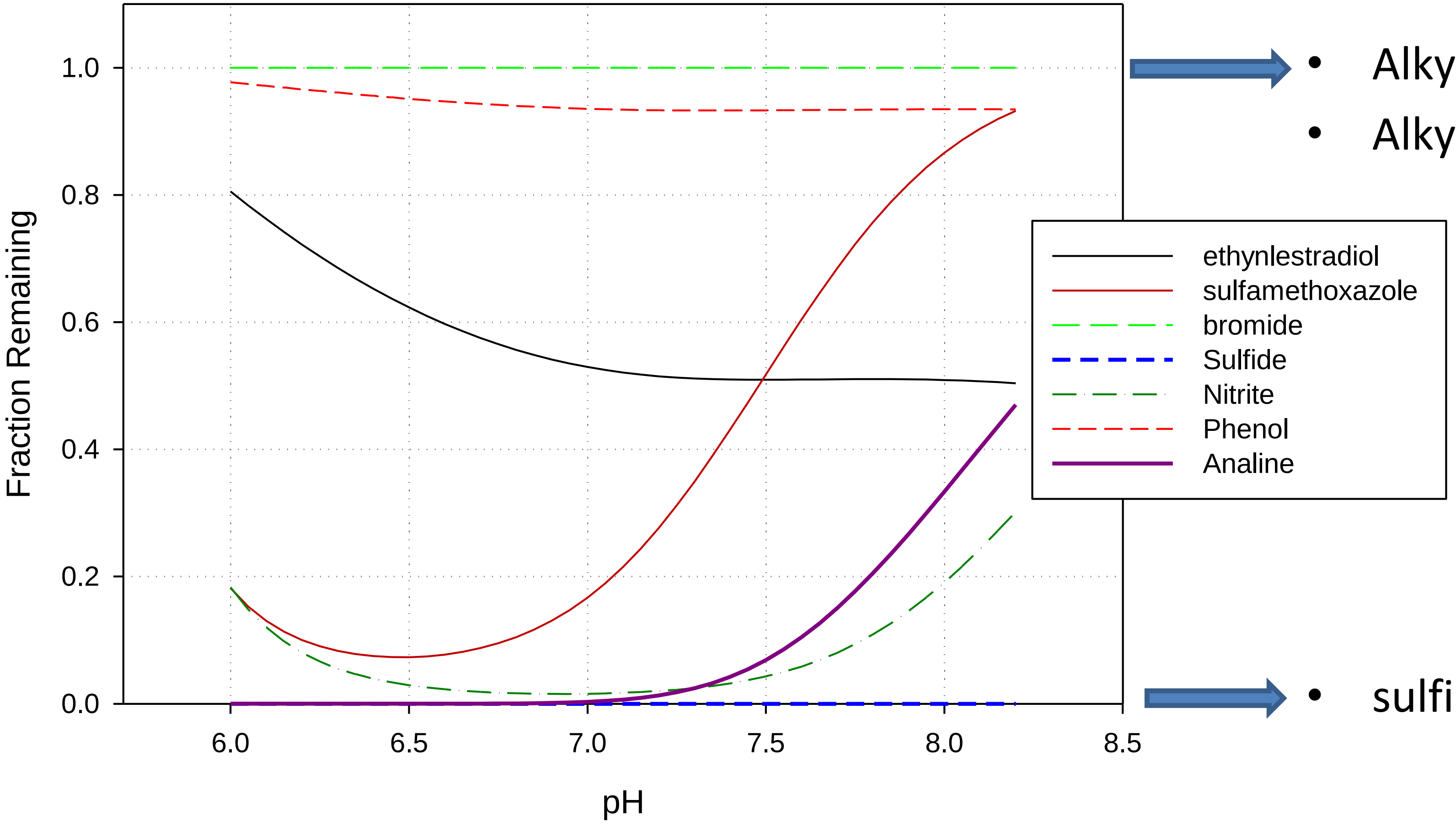
Contents

Kinetic Analysis, high dose

- 50 µM dose, Houston Water



- Alkyl alcohols
- Alkyl amines

- sulfides