Geo Chemistry of Mine Drainage Treatment

TIPS

?

What we are going to cover:

TIPS

Chemistry of Acidity

- Net Acidic vs. Net Alkaline

Chemistry of Aluminum

- Aluminum Equilibrium Chemistry
- Aluminum Kinetics

Chemistry of Iron

- Iron Equilibrium Chemistry
- Iron Kinetics

Why are Acidity Measurements Important?

TIPS

1. Used to characterize water as Net Alkaline or Net Acidic for the purposes of determining an appropriate type of treatment

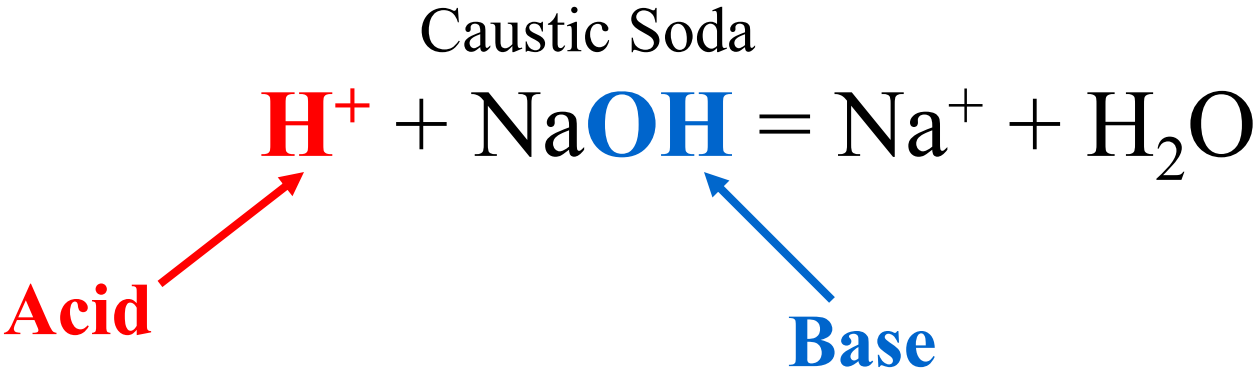
2. Used to calculate the amount of chemical reagent needed to neutralize all protons (H^+)

Chemistry of Acidity

TIPS

Q: What is Acidity?

A: It is the amount of base required to raise the pH of a raw water sample to a specific pH endpoint.



Chemistry of Acidity

TIPS

So an acidity measurement is just a measurement of **hydrogen ions**

H^+

Sources of Acidity

TIPS

- pH Acidity

$$pH = -\log [H^+]$$

- Mineral Acidity

$$Mn^{2+} + 0.5O_2 + H_2O = MnO_2(s) + 2H^+$$

$$Fe^{2+} + 0.5O_2 + 2.5H_2O = Fe(OH)_3(s) + 2H^+$$

$$Fe^{3+} + 3H_2O = Fe(OH)_3(s) + 3H^+$$

$$Al^{3+} + 3H_2O = Al(OH)_3(s) + 3H^+$$

How is Acidity Measured?

TIPS

There are two methods used to measure Acidity:

1. By a "Calculated" Acidity using dissolved metal concentrations (Filtered) and pH

2. By a laboratory or "Measured" acidity

Calculated Acidity: pH Acidity

TIPS

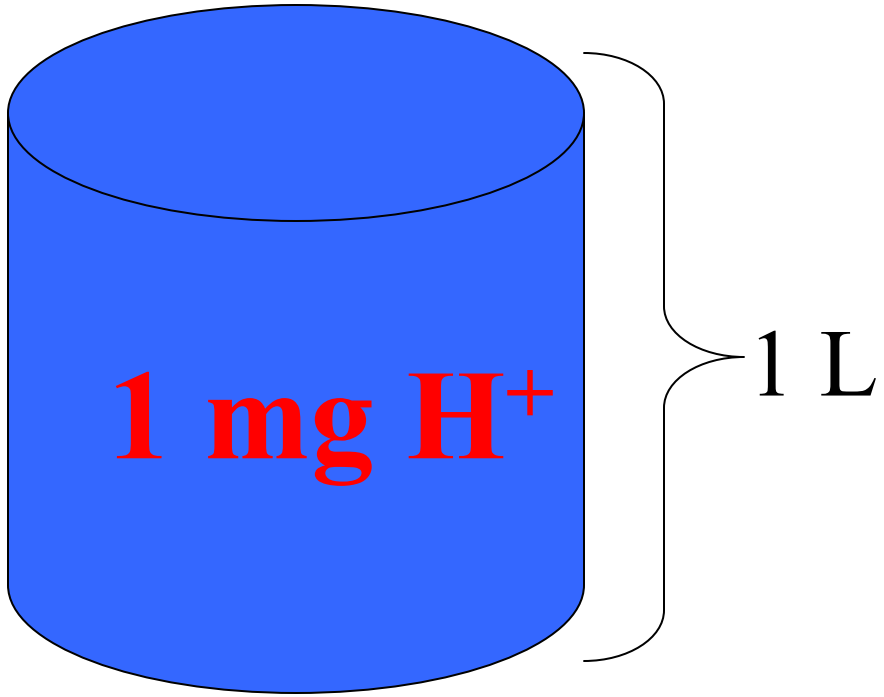
1. pH Acidity

pH = 3.0

pH = -log [H^+]

[H^+] = 10^{-pH}

[H^+] = 0.001 moles/L



$$\frac{0.001 mole H^+}{L} \times \frac{1.0 g H^+}{1.0 mole H^+} \times \frac{1 mole CaCO_3}{2 moles H^+} \times \frac{100 g CaCO_3}{1 mole CaCO_3} \times \frac{1000 mg}{1.0 g} = \frac{50 mg}{L} as CaCO_3$$

Acidity = 50 mg/L as $CaCO_3$ OR 1.0 mg of H^+/L (1.0 ppm)

Calculated Acidity: Mineral Acidity

TIPS

- If the concentration of **Dissolved** metals is known (**From Filtered Sample**), one can estimate the amount of acidity that will be produced upon hydrolysis

$$Al^{3+} + 3H_2O = Al(OH)_3(s) + 3H^+$$

If you know the concentration of this

You can calculate the concentration of this

$$\frac{1.0 mg Al^{3+}}{L} \times \frac{1 mole}{26 g} \times \frac{3 moles H^+ produced}{1 mole Al hydroloysis} \times \frac{1 mole CaCO_3}{2 moles H^+} \times \frac{100 g CaCO_3}{1 mole CaCO_3} =$$

5.5 mg/L of Acidity as $CaCO_3$

Calculated Acidity

TIPS

pH and Mineral Acidity as $CaCO_3$ =

$$50\left(\frac{2Mn^{2+}}{54.94}+\frac{2Fe^{2+}}{55.85}+\frac{3Fe^{3+}}{55.85}+\frac{3Al^{3+}}{26.98}+1000\times10^{-pH}\right)$$

Concentrations of dissolved metals must be in mg/L

Methods for Calculating Net Acidity

TIPS

Net Acidity = Calculated Acidity - Alkalinity

Net Acidity = Hot Acidity

TIPS

Summary of Acidity

- Net Acidity = Calculated Acidity - Alkalinity

- Net Acidity = Hot Acidity

Introduction to Concepts of GeoChemistry and Aluminum GeoChemistry

$Fe(OH)_2$ $Al(OH)_3$ $KFe_3(SO_4)_2(OH)_6$

OH^- Fe^{3+}

Fe^{2+} Mn^{2+}

Al^{3+} H^+

MnO_2 $Fe(OH)_3$

How Chemical Species Occur in Water

TIPS

- Simple cations and anions (K^{+}, Fe^{+2} , H^{+2})
- Multi-element cations and anions (OH^{-}, SO_4^{2-}, HCO_3^{-})
- Uncharged Species (O_2, H_2S, CO_2)
- Cation – Anion Complexes, which may have + or - charge ($AlSO_4^{+}$, $Al(OH)_4^{-}$, $FeSO_4^{o}$)
- Suspended Particles (oxides/hydroxides of ferric ion and aluminum)
  - By convention dissolved vs. suspended matter is commonly separated at 0.45 μm

Modeling Water Chemistry

TIPS

1. Equilibrium Chemistry

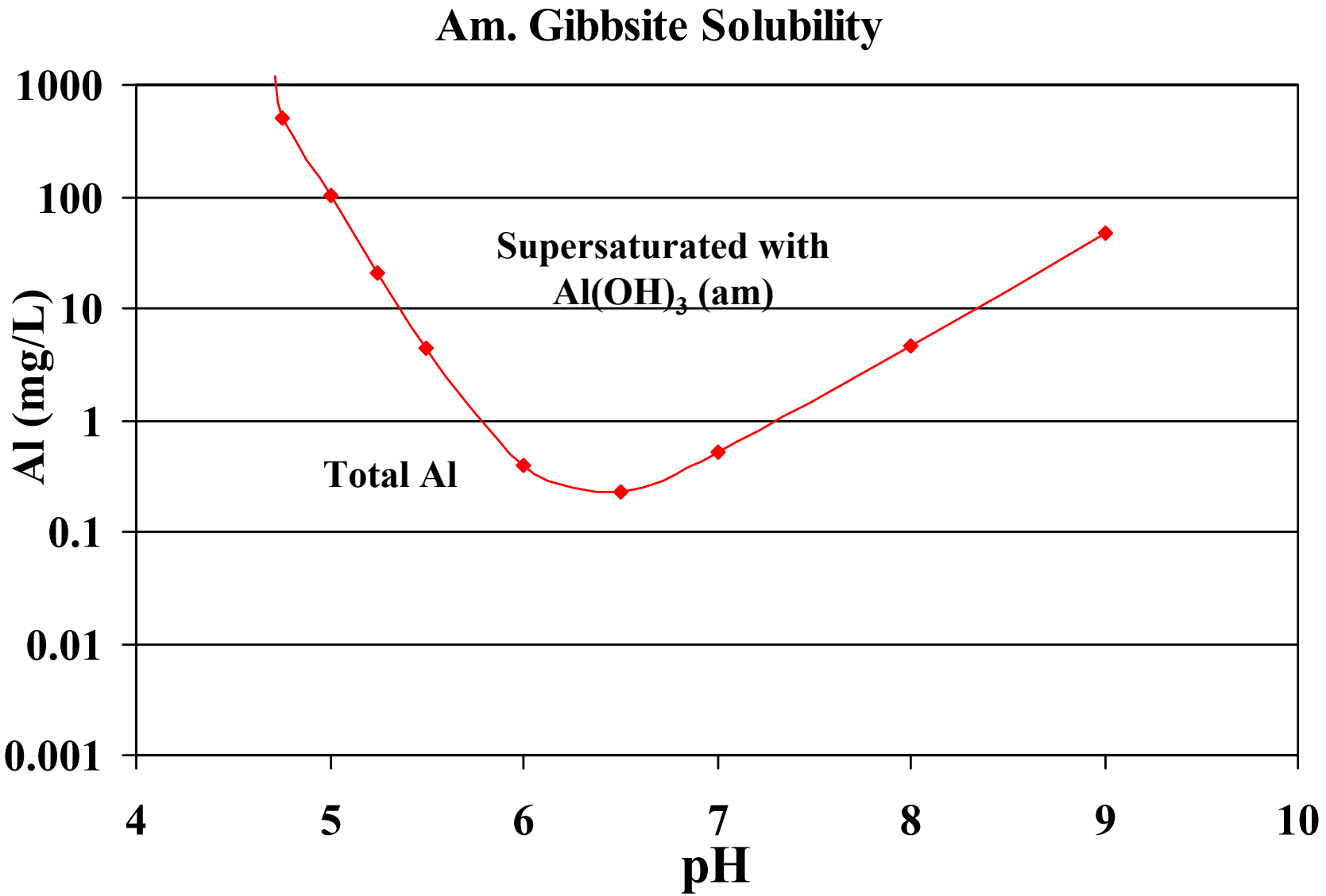
   - Chemical reactions occur because water is not in chemical equilibrium with minerals and gases
   - Allows us to predict the solubility/stability of minerals in passive treatment systems at specified pH, Eh, Temp, etc.

2. Kinetic Chemistry

   - Allows us to predict the time it will take a water to reach chemical equilibrium

Chemistry of Aluminum

TIPS



1. At what pH would one obtain maximum Al^{+3} removal?

Treatment Cost/Benefit Analysis

TIPS

pH	Al (mg/L)	% Al reduction	Fe (mg/L)	% Fe reduction	Mn (mg/L)	%Mn reduction	Mg (mg/L)	%Mg reduction	Annual Cost for a 1 gpm discharge assuming caustic soda = $.50/gal
3.01	65.3	0.00	11.2	0.00	62	0.00	130	0.00	$0
4.43	57.3	12.25	4.49	59.91	57.8	6.77	124	4.62	$70
4.93	2.54	96.11	0.317	97.17	57.4	7.42	120	7.69	$277
5.83	0.215	99.67	0.242	97.84	55.4	10.65	116	10.77	$312
7.74	0.0303	99.95	0.241	97.85	58	6.45	119	8.46	$330
8.24	0.162	99.75	0.236	97.89	53.3	14.03	118	9.23	$342
8.47	0.507	99.22	0.255	97.72	43.7	29.52	122	6.15	$382
9.48	0.454	99.30	0.214	98.09	35.4	42.90	113	13.08	$421
9.97	2.81	95.70	0.249	97.78	6.2	90.00	98.4	24.31	$509
10.41	3.44	94.73	0.229	97.96	0.543	99.12	58.3	55.15	$651

Flow Rate (gpm)	Annual Cost if Treatment pH = 7.74	Annual Cost if Treatment pH = 10.41	Difference in Annual Cost
10	$3,300	$6,510	$3,210
20	$6,600	$13,020	$6,420
30	$9,900	$19,530	$9,630

Aluminum Kinetics

TIPS

- How much time does it take for this reaction to occur?

$$Al^{3+} + 3H_2O = Al(OH)_3(s) + 3H^+$$

- 20 mg/L of Al precipitated in 100 ft due to pH increase as a result of 2 waters mixing

100 ft Down Stream from Discharge
pH 5.42
Hot Acidity = - 44 mg/L
Al = 10.3 mg/L
Sulfate = 744 mg/L

Discharge enters stream
pH = 3.3
Hot Acidity = 368 mg/L
Al = 31.88 mg/L
Sulfate = 789 mg/L

"Stream"
pH = 6.4
Hot Acidity = -31 mg/L
Al = 1.0 mg/L
Sulfate = 741 mg/L

Summary of Al Chemistry

TIPS

- The minimum solubility (concentration) of dissolved Al^{+3} occurs at pH ~ 6.5; solubility increases with increasing or decreasing pH (amphoteric)

- Precipitation of Al can occur in any treatment system creating a favorable pH condition.

- The Kinetics of Aluminum precipitation is instantaneous (relative to other mine drainage metals)

Chemistry of Iron

- Two Oxidation States
  - Ferrous Iron (Fe^{2+}) – "Reduced Iron"
  - Ferric Iron (Fe^{3+}) – "Oxidized Iron"

$$Fe^{2+} = Fe^{3+} + e^- \qquad E^0 = +0.77 \text{ volts}$$

Chemistry of Iron

Oxidation of Fe^{2+} to Fe^{3+}

TIPS

$$Fe^{2+} = Fe^{3+} + e^-$$

$$+ \quad H^+ + 0.25O_2(g) + e^- = 0.5H_2O$$

$$Fe^{2+} + H^+ + 0.25O_{2(g)} = Fe^{3+} + 0.5H_2O$$

- The equation above illustrates that 1.0 mg/L of O_2 is needed to oxidize 6.99 mg/L of Fe^{2+}

Ferric Iron (Fe^{3+})

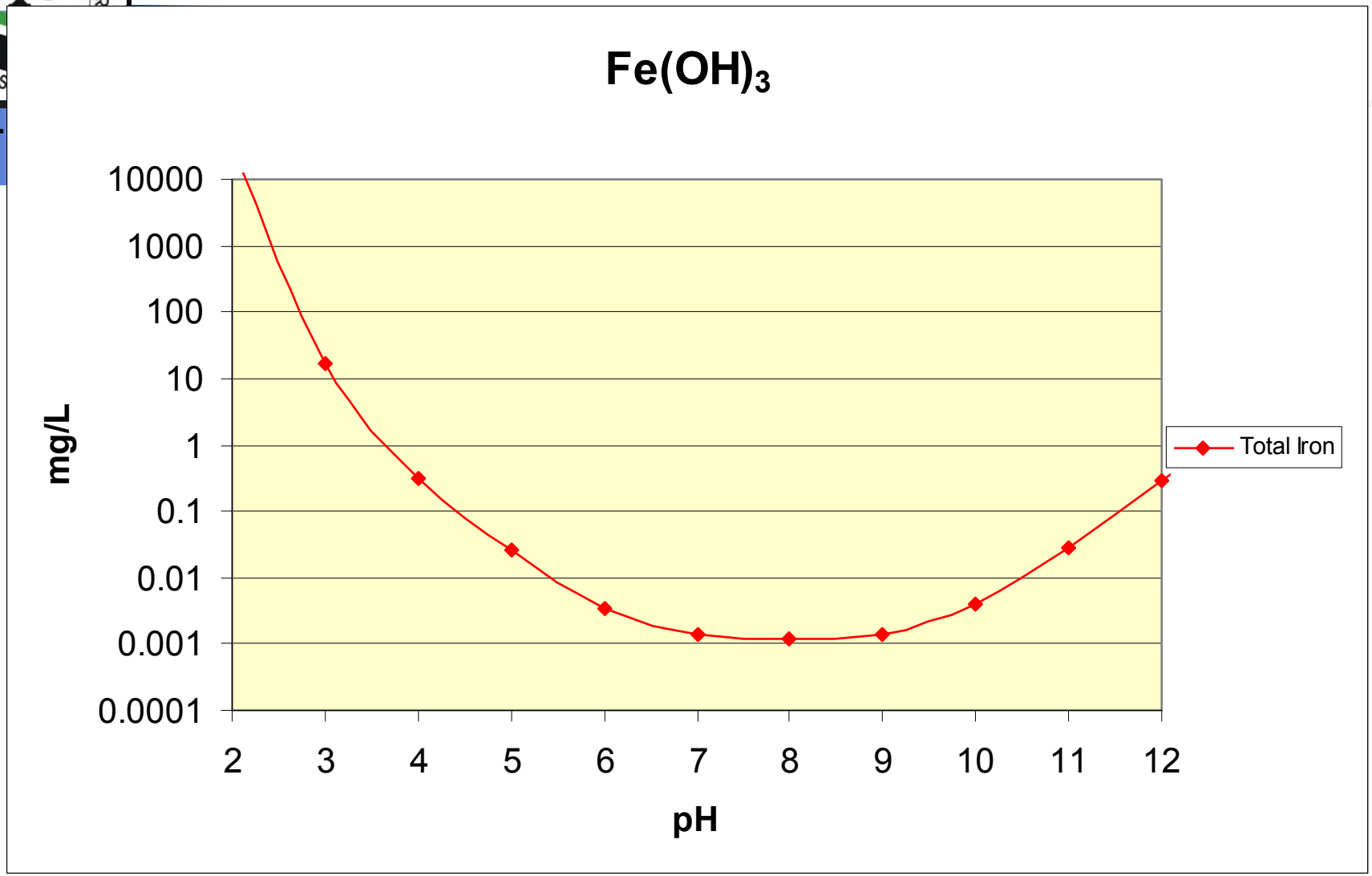
- Ferric Iron (3+ charge) occurs in the following forms:
  - Ionic Form Fe^{3+}
  - Aqueous complexes, such as, $FeSO_4^+$ and $FeOH^{2+}$

Ferric Iron Cont.

TIPS

- Solids such as:
  - Fe_2O_3 (hematite)
  - FeOOH (goethite)
  - (K,Na,H) $Fe_3(SO_4)_2$ $(OH)_6$ (Jarosite)
  - $Fe(OH)_3$ (amorphous ferric hydroxide)
  - $Fe(OH)_3$ (amorphous) or Fe_5HO_8 $4H_2O$ (Ferrihydrite)
  - $Fe_8O_8(OH)_6$ (SO_4) (variable) (Schwertmannite)

Ferric Iron Solubility Control



2. At what pH(s) would you except to find waters with the highest concentrations of Ferric Iron (High Solubility)?

Ferrous Iron (Fe^{2+})

TIPS

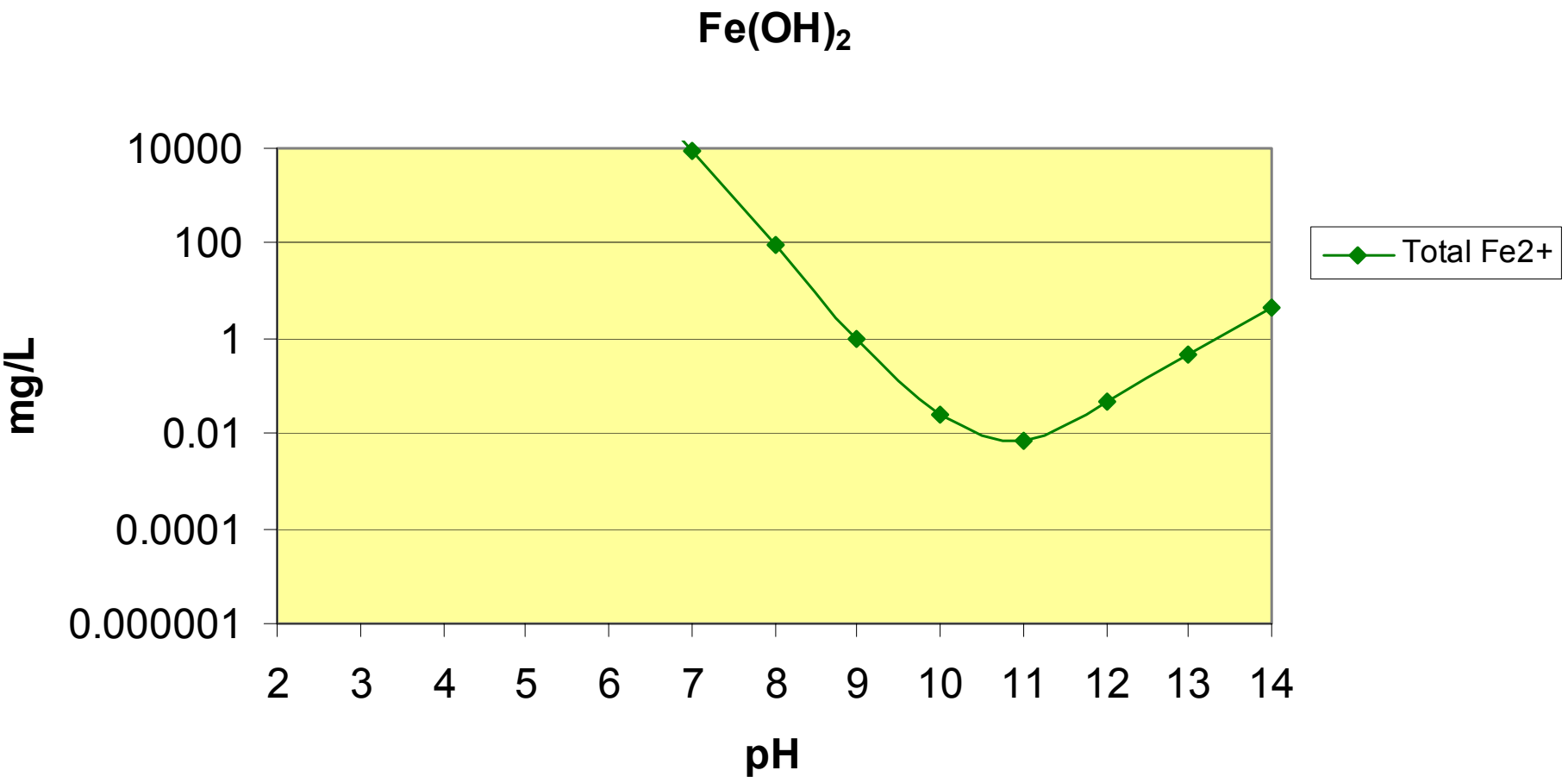
- Ferrous Iron (2+ charge) occurs in the following forms:

$Fe(OH)_2$

- Ionic Form Fe^{2+}
- Aqueous complexes, such as, $FeSO_4^0$ and $FeHCO_3^+$
- Solids such as:
  - $Fe(OH)_2$ (Ferrous Hydroxide)
  - $FeCO_3$(Siderite)
  - FeS_2 (Siderite)

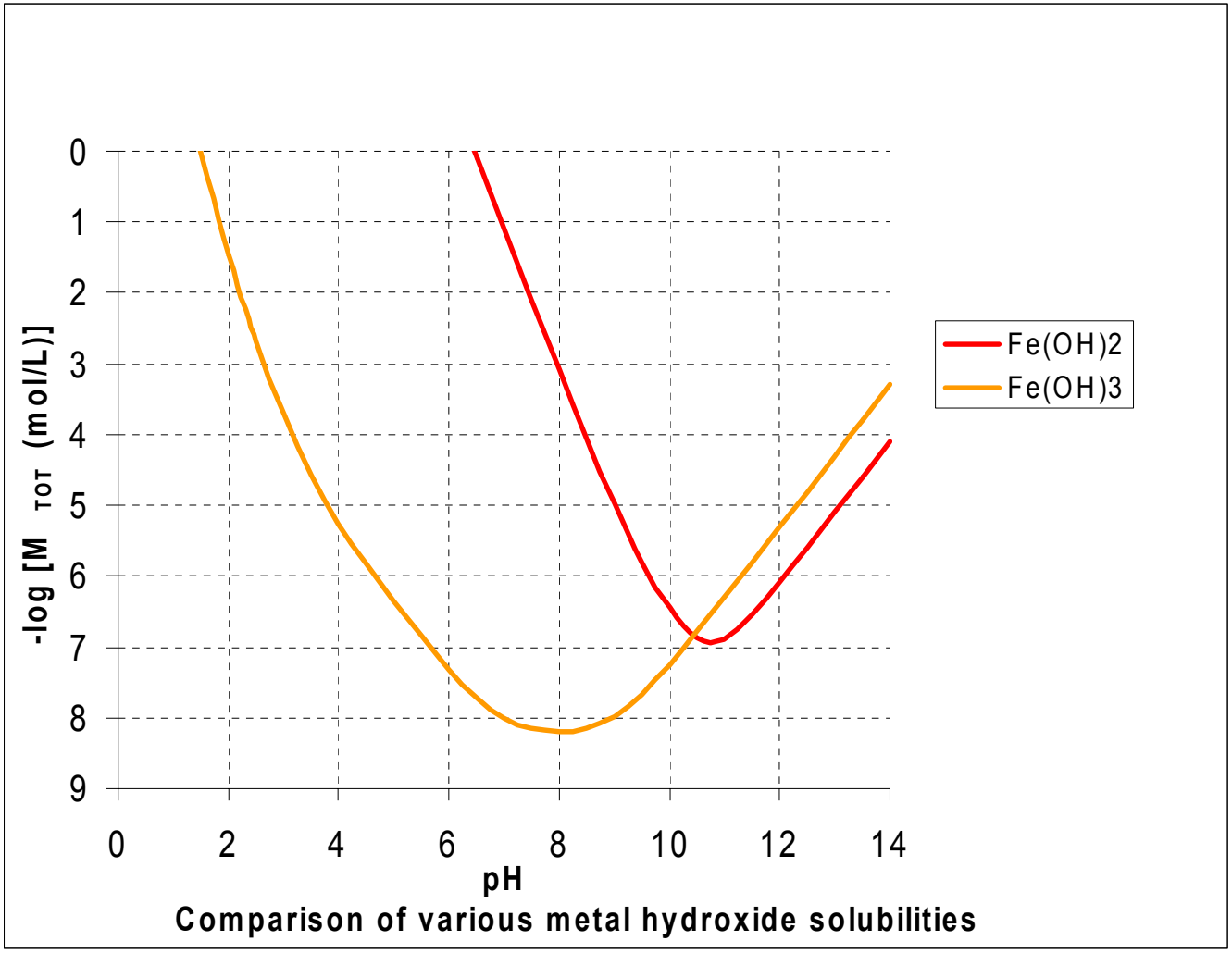
Ferrous Iron Solubility

TIPS



Ferrous Iron (Fe^{2+})

TIPS



Eh – pH Diagrams

TIPS

- Eh – pH diagrams are useful in explaining the chemistry of Iron solutions and precipitates under equilibrium conditions.

- Some Iron reactions involve both transfer of protons (H^+) and electrons (e^-), as is the case with the transformation of ferrous iron to ferrihydrite:

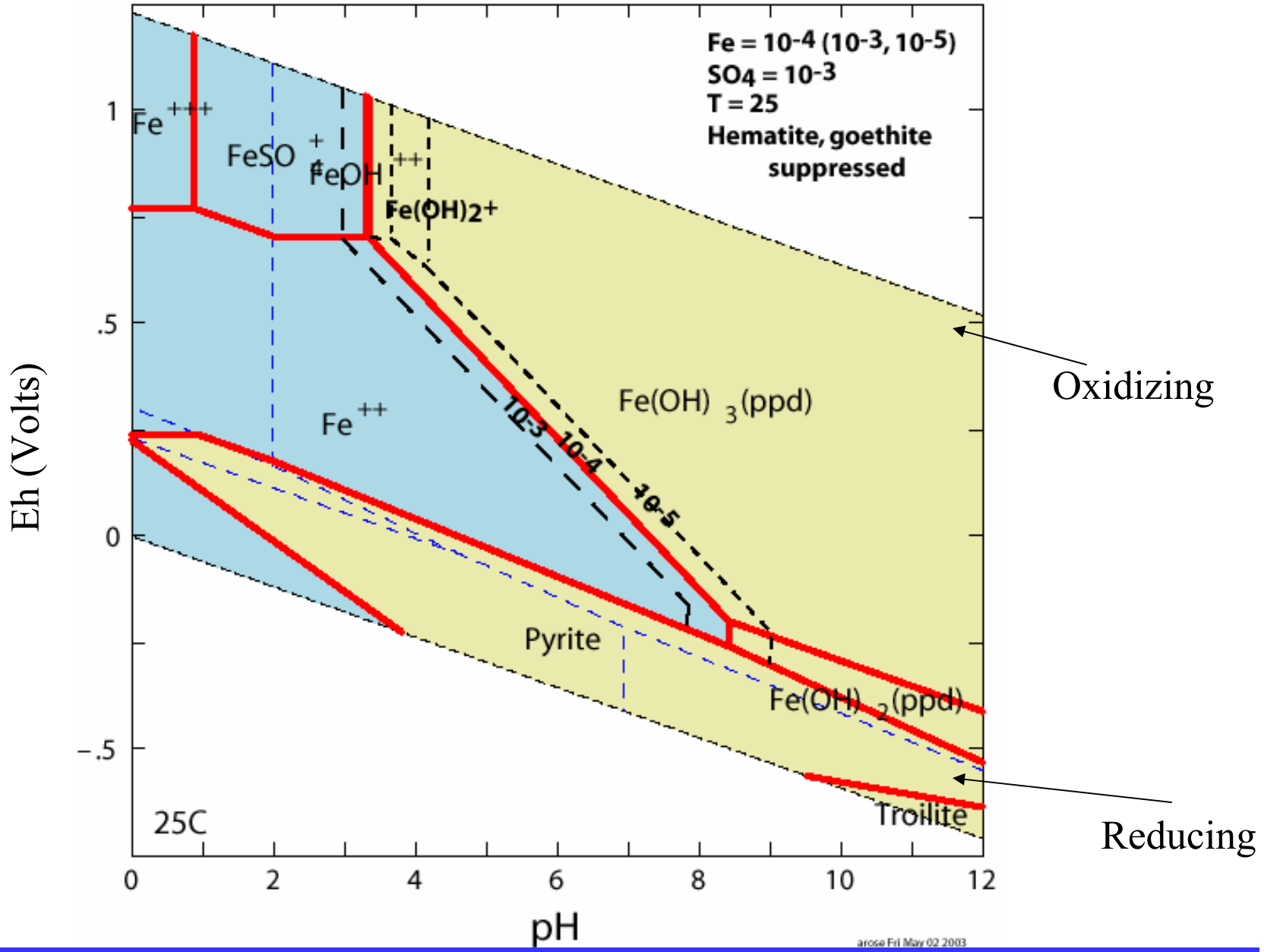
$$Fe^{2+} + 3H_2O = Fe(OH)_3\,(s) + 3\mathbf{H}^+ + e^- \qquad E^0 = +0.98 \text{ volts}$$

- Some Iron reactions are independent of pH, such as:

$$Fe^{2+} = Fe^{3+} + e^- \qquad E^0 = +0.77 \text{ volts}$$

- An Eh – pH diagram can be made by solving these equation for a set of conditions (activity, pH, etc.)

Stability Diagram for Ferrihydrite



1. Can Eh – pH diagrams be used to describe the the chemistry of Aluminum?

Iron Summary

TIPS

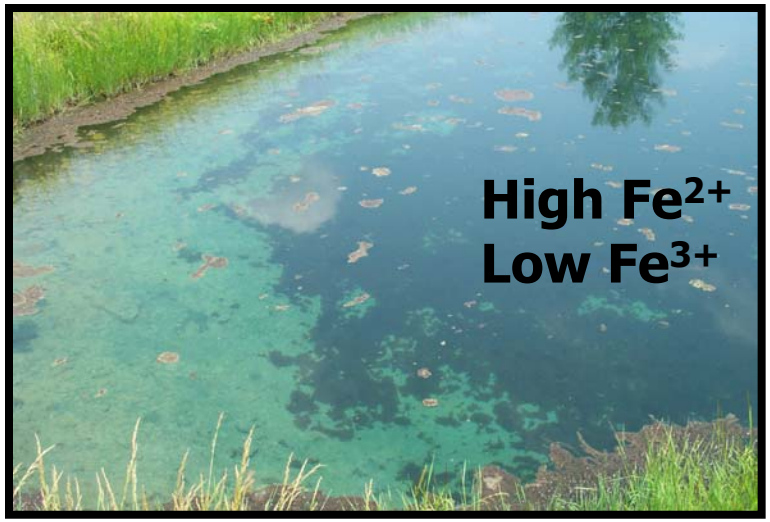
- Fe^{2+} is much more soluble than Fe^{3+}(stays dissolved in higher concentrations over a large pH range)
- The lowest solubility for Fe^{3+} is ~ pH 8.0, however, in general, water will meet iron effluent limits at pH 3.5-4.5 (assuming all of the iron in the water is ferric).
- The lowest solubility for Fe^{2+} is ~ pH 11.0, however, in general, water will meet iron effluent limits at pH 7.5-9.0.
- To passively treat for Fe^{2+}, ample oxygen must be present and pH conditions must be prime (pH>6.3)

Kinetics of Iron Oxidation

TIPS

How much time will it take for this water…

To look like this water?



How long will it take this reaction to occur?

$$Fe^{2+} + 3H_2O = Fe(OH)_3\,(s) + 3\mathbf{H}^+ + e^- \qquad E^0 = +0.98 \text{ volts}$$

TIPS

3 Oxidation Methods for Fe^{+2}

1. Biotic Oxidation
2. Abiotic Homogeneous Oxidation
3. Abiotic Heterogeneous Oxidation

1. Biotic Oxidation

TIPS

- Microbial oxidation by Thiobacillus ferrooxidans
  - Microbial oxidation is the dominate oxidation process at pH < ~ 4

$$Rate\left(\frac{mole}{L^{-}s}\right) = k_{bio} C_{bact} (Fe^{2+})(O_2)(H^{+})$$

• Where: k_{bio} = rate constant in L^3/mg-mol^2-s

  - Rate of Oxidation is dependent on:

    Amount of Fe2+ in solution

    Amount dissolved Oxygen in solution

    Amount of bacteria in solution

    pH of solution

TIPS

2. Abiotic Homogeneous Oxidation

- Homogenous oxidation is the dominate oxidation process at pH > ~ 7

$$Rate\left(\frac{mole}{L^{-}s}\right) = \frac{dFe}{dt} = \frac{-k_{abiotic}\left(Fe^{2+}\right)\left(O_2\right)}{\left(H^{+}\right)^2}$$

2. Abiotic Homogeneous Oxidation

TIPS

$$Rate\left(\frac{mole}{L^{-}s}\right) = \frac{dFe}{dt} = \frac{-k_{abiotic}\left(Fe^{2+}\right)\left(O_2\right)}{\left(H^{+}\right)^2}$$

- Oxidation Rate increases 100x's for every unit increase in pH, so increase pH any way you can including outgasing CO_2 through aeration.

3. Abiotic Heterogeneous Oxidation

TIPS

- Oxidation facilitated by suspended Fe oxides is the dominate oxidation process at pH 6-7
  - Fe oxidation at near neutral pH can be enhanced by adding or retaining the suspended Iron Hydroxide particles to allow the particles to grow larger and settle faster (due to charged Iron oxides surfaces)

$$Rate\left(\frac{mole}{L^{-}s}\right) = \frac{dFe}{dt} = \frac{-k_{abioticHetero}\left(Fe^{2+}_{dissolved}\right)\left(O_2\right)\left(Fe^{3+}_{Total}\right)}{\left(H^{+}\right)}$$

  - The oxidation rate only increases 10 fold with each unit increase in pH (unlike the 100 fold Homogeneous oxidation)

3. Abiotic Heterogeneous Oxidation

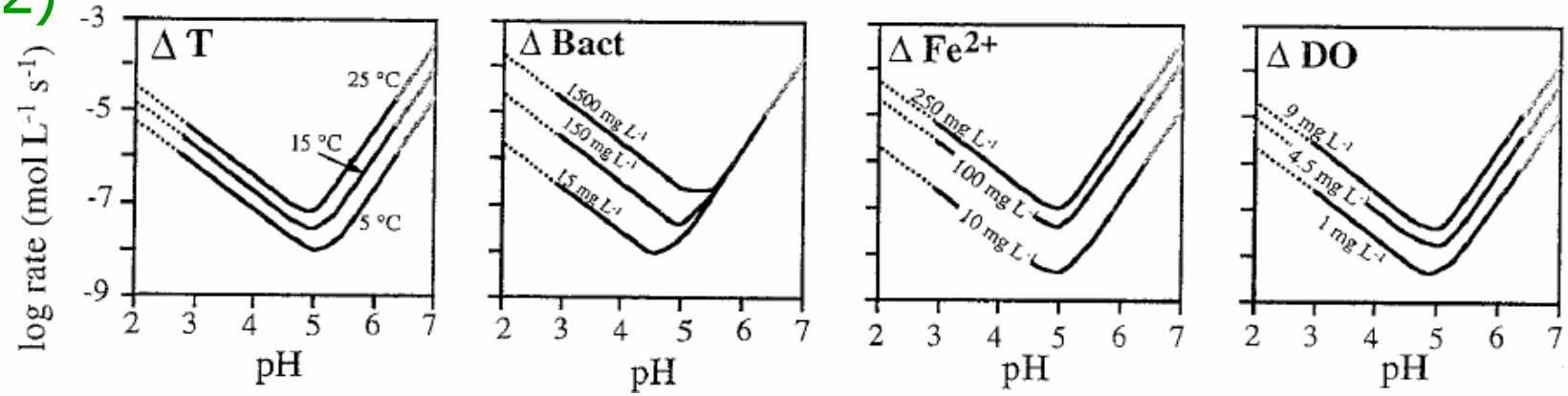
TIPS

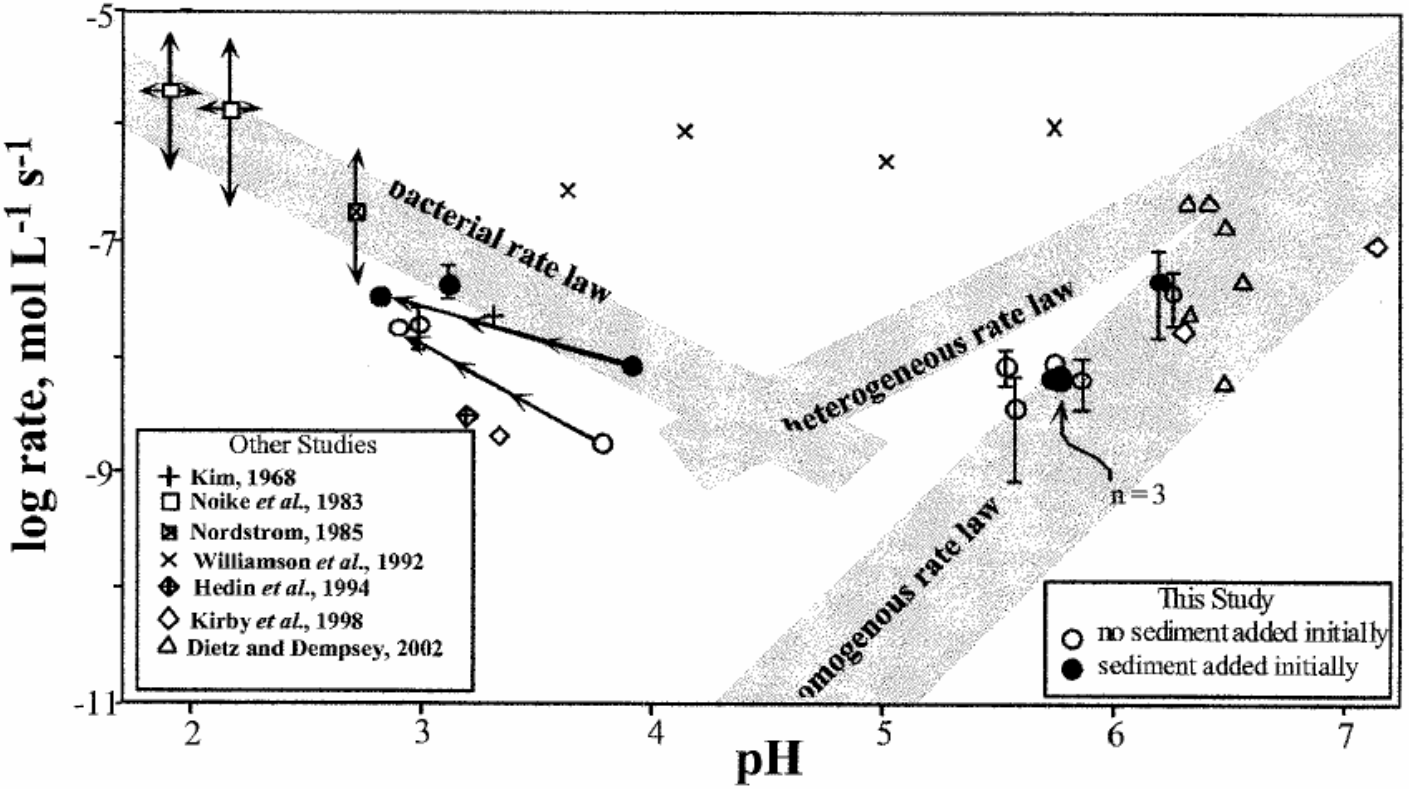
$$Rate\left(\frac{mole}{L^{-}s}\right) = \frac{dFe}{dt} = \frac{-k_{abioticHetero}\left(Fe^{2+}_{dissolved}\right)\left(O_2\right)\left(Fe^{3+}_{Total}\right)}{\left(H^{+}\right)}$$

- Fe oxidation is enhanced by adding or retaining suspended iron oxides/hydroxides

- Heterogeneous oxidation increases sludge densities from 1-3% to over 20% solids.

- Factors that affect Iron oxidation rates (from Kirby, 2002)





THE END

TIPS

AS YOU CAN CLEARLY SEE IN SLIDE 397...
GAAAAH!
"POWERPOINT" POISONING.
© 2000 United Feature Syndicate, Inc.