Activated Iron Solids (AIS) Treatment of High Iron AMD

By
Jon Dietz, Ph.D.
Environmental Engineering & Science
Iron Oxide Technologies, LLC
dietzetal@adelphia.net
www.DGengr.com

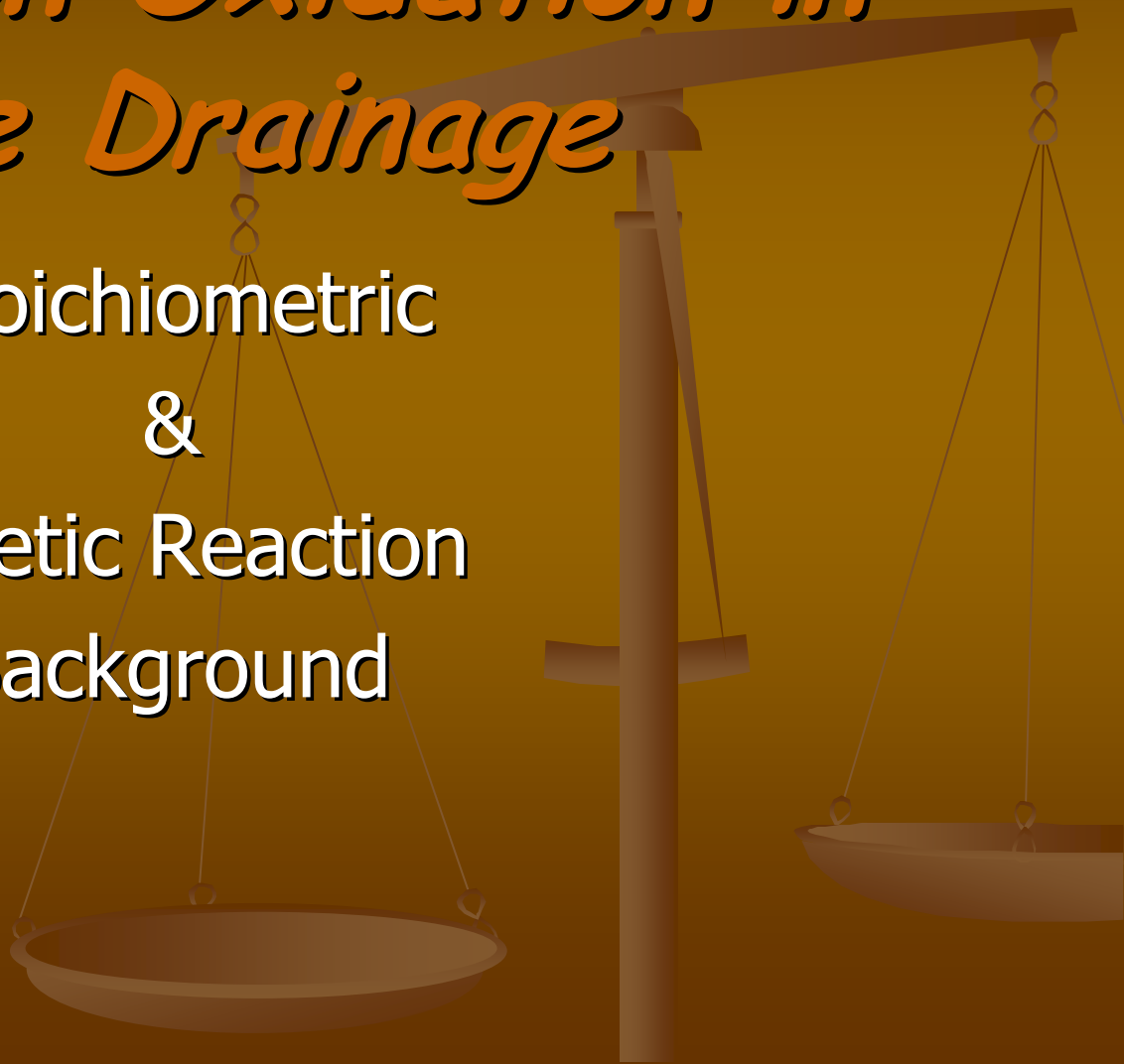
Ferrous Iron (Fe^{2+}) Oxidation Oxidation in Mine Drainage

Stoichiometric

&

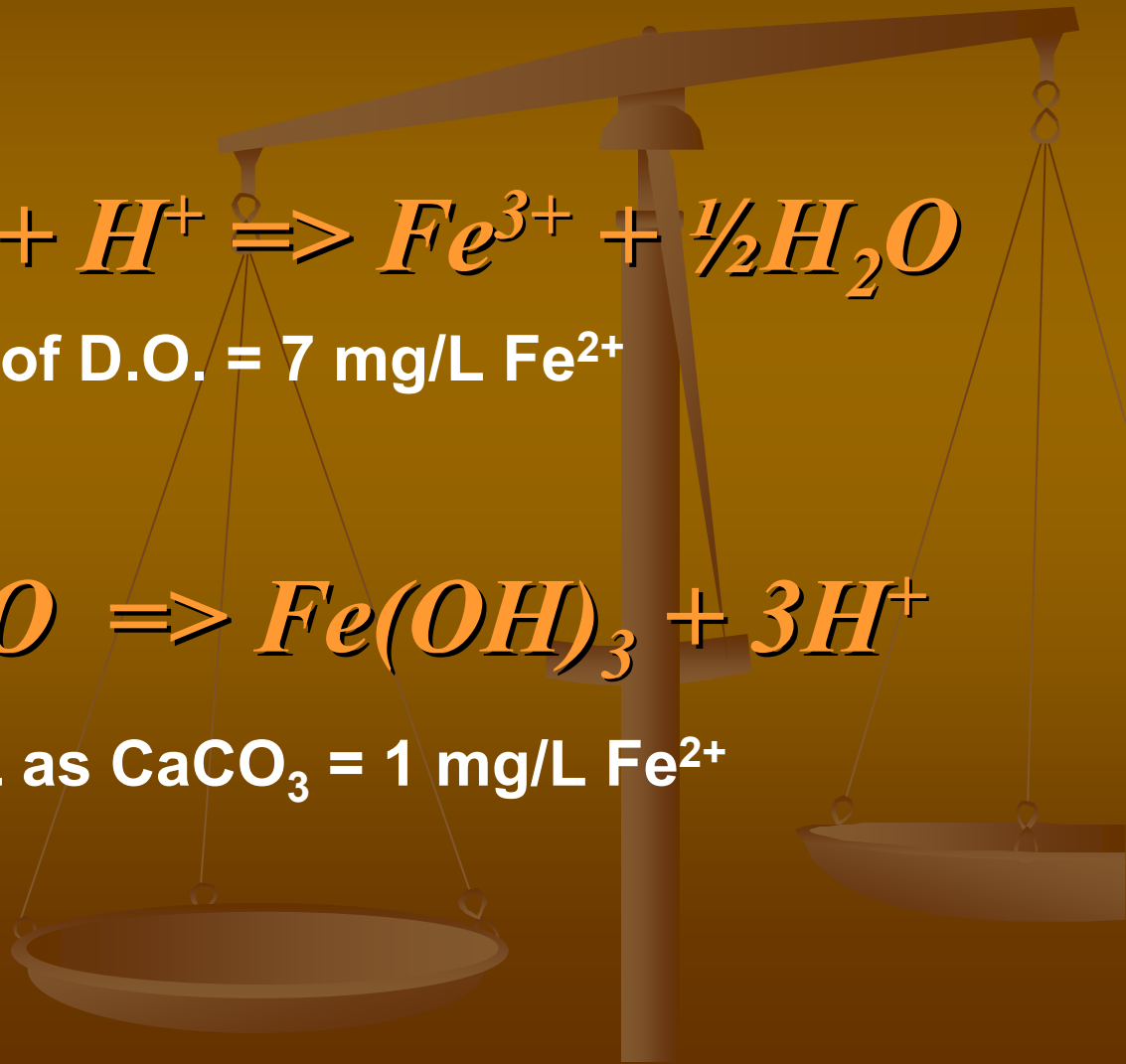
Kinetic Reaction

Background



Oxidation & Hydrolysis

(overall equations)



$$Fe^{2+} + \tfrac{1}{4}O_2 + H^+ \Rightarrow Fe^{3+} + \tfrac{1}{2}H_2O$$

1 mg/L of D.O. = 7 mg/L Fe^{2+}

$$Fe^{3+} + 3H_2O \Rightarrow Fe(OH)_3 + 3H^+$$

1.8 mg/L as $CaCO_3$ = 1 mg/L Fe^{2+}

Ferrous Iron Oxidation Processes In AMD Treatment

Homogenous Ferrous Iron Oxidation (HomOX)

(Passive & Conventional Chemical Treatment Oxidation Process)

A solution-based oxidation process whereby Ferrous Ions and hydroxide complexes (Fe^{2+}, $Fe(OH)^{+}$ & $Fe(OH)_2^{0}$) react with dissolved oxygen to form ferric iron (Fe^{3+}).

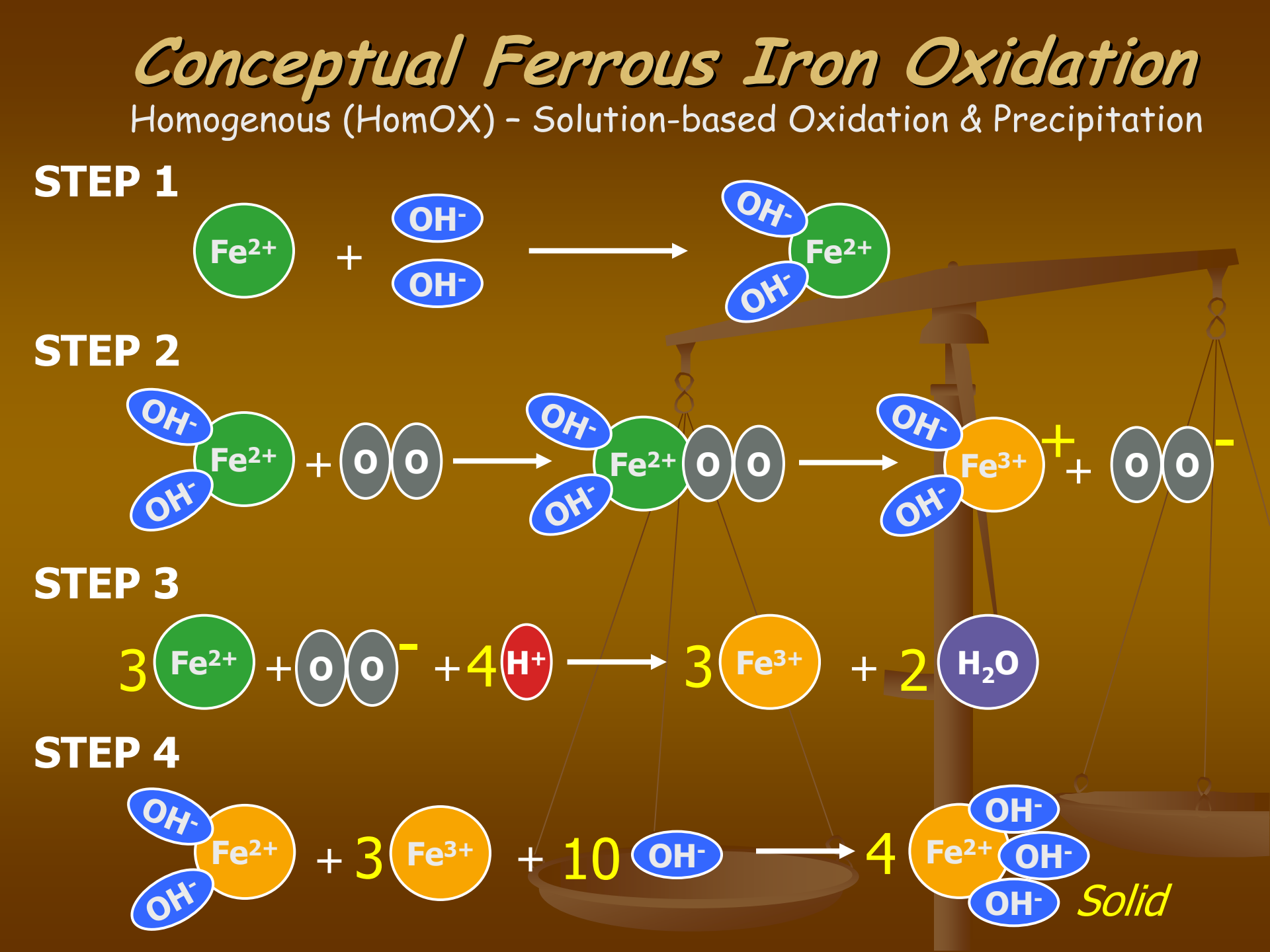
Heterogenous Ferrous Iron Oxidation (HetOX)

(AIS Treatment Oxidation Process)

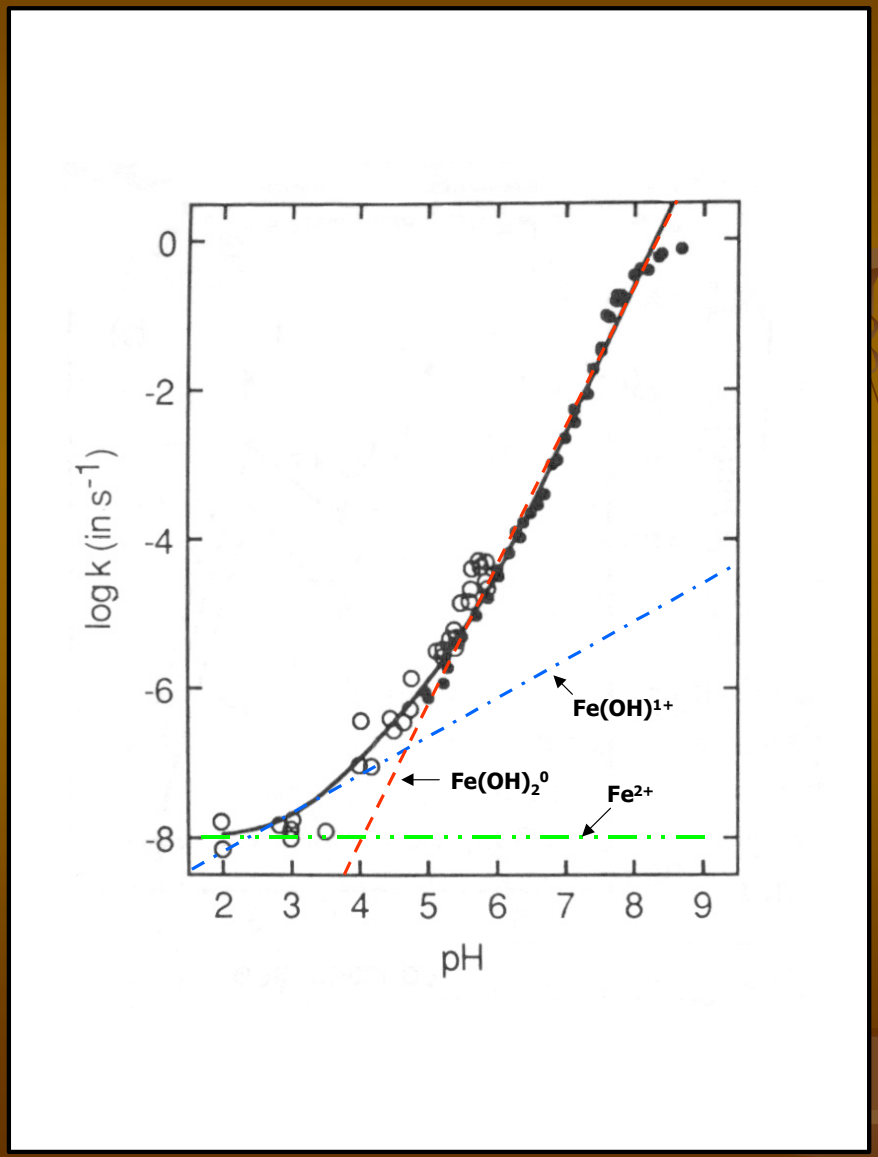
A solid/solution interface oxidation process whereby Ferrous Iron (Fe^{2+}) is sorbed to the surface of iron oxide (or other oxide surfaces) and in the presence of dissolved oxygen is catalytically oxidized to ferric iron (Fe^{3+}).

Conceptual Ferrous Iron Oxidation

Homogenous (HomOX) - Solution-based Oxidation & Precipitation



HomOX Reaction Rate Data



At $[O_2]$ = 1.26 mM and 25°C (portions of figure reproduced from Wehrli 1990). Open circles (o) are from Singer & Stumm (1970), and solid circles (•) are from Millero *et al.* (1987).

Dashed lines are estimated rates for the various dissolved Fe(II) species.

Homogeneous Ferrous Iron Oxidation Kinetic Equations

Abiotic HomOX Rate Equations:

Total Rate (M s^{-1}) =

$$-(k_{Ho,0}+(k_{Ho,1}\times K_1/\{H^+\})+k_{Ho,2}\times\beta_2/\{H^+\}^2))\times[Fe(II)_{diss}]\times[O_2]$$

At 6<pH<8

Total Rate (M s^{-1}) = $-k_{Ho,2}\times\beta_2/\{H^+\}^2\times[Fe(II)_{diss}]\times[O_2]$

or

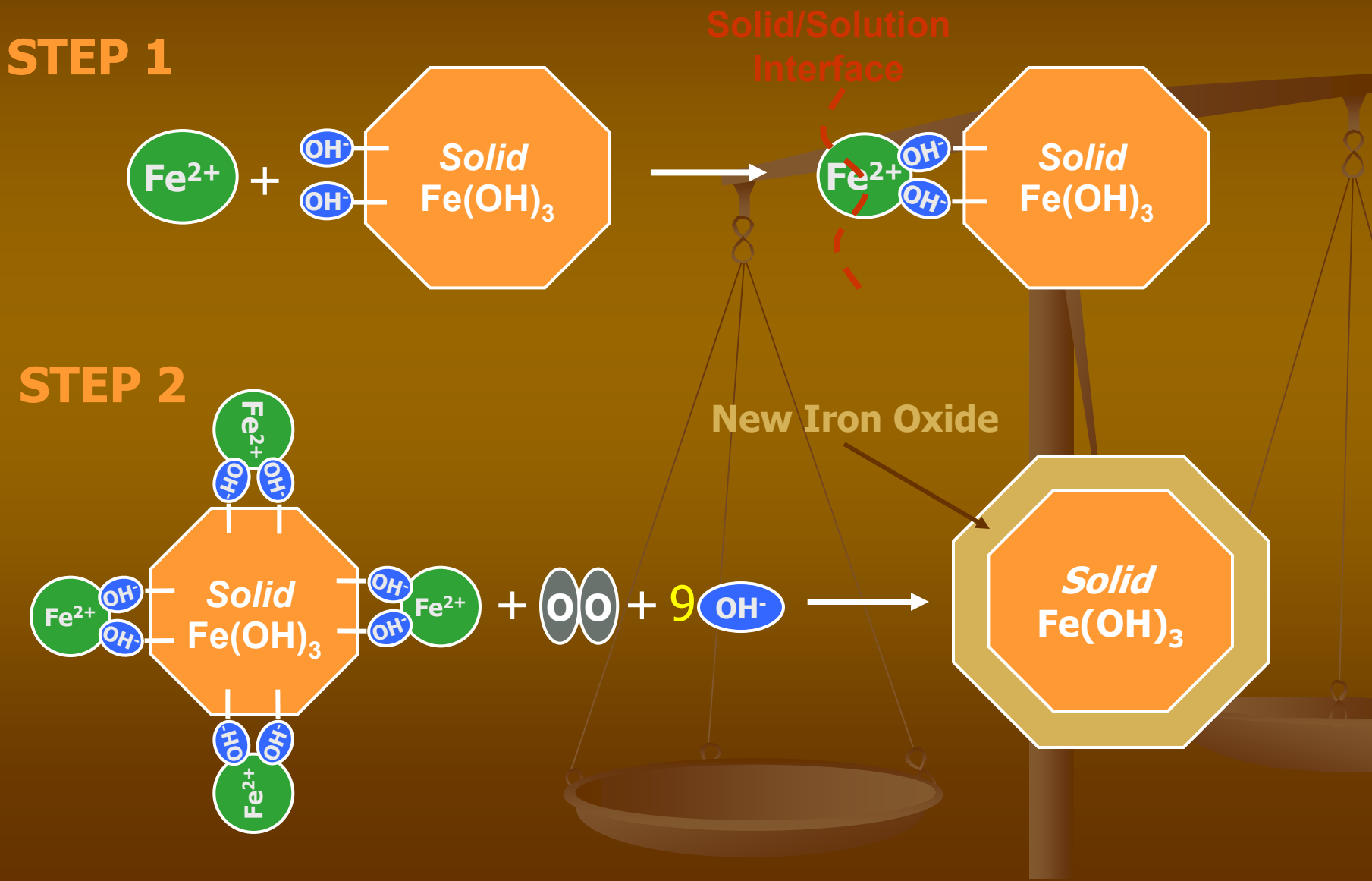
$$-d[Fe(II)_{diss}]/dt = k_H/\{H^+\}^2\times[Fe(II)_{diss}]\times[O_2]$$

(Stumm & Morgan 1996)

k_H = 2.7x10^{-14} M s^{-1} ; E_a^{app} = 237 kJ/mol at 25°C (6<pH<8)
Millero *et al.* (1987) constants as converted by Dempsey *et al.* (2001)

Conceptual Ferrous Iron Oxidation

Heterogeneous (HetOX) – Surface-based Oxidation & Precipitation



HetOX Rate Equations

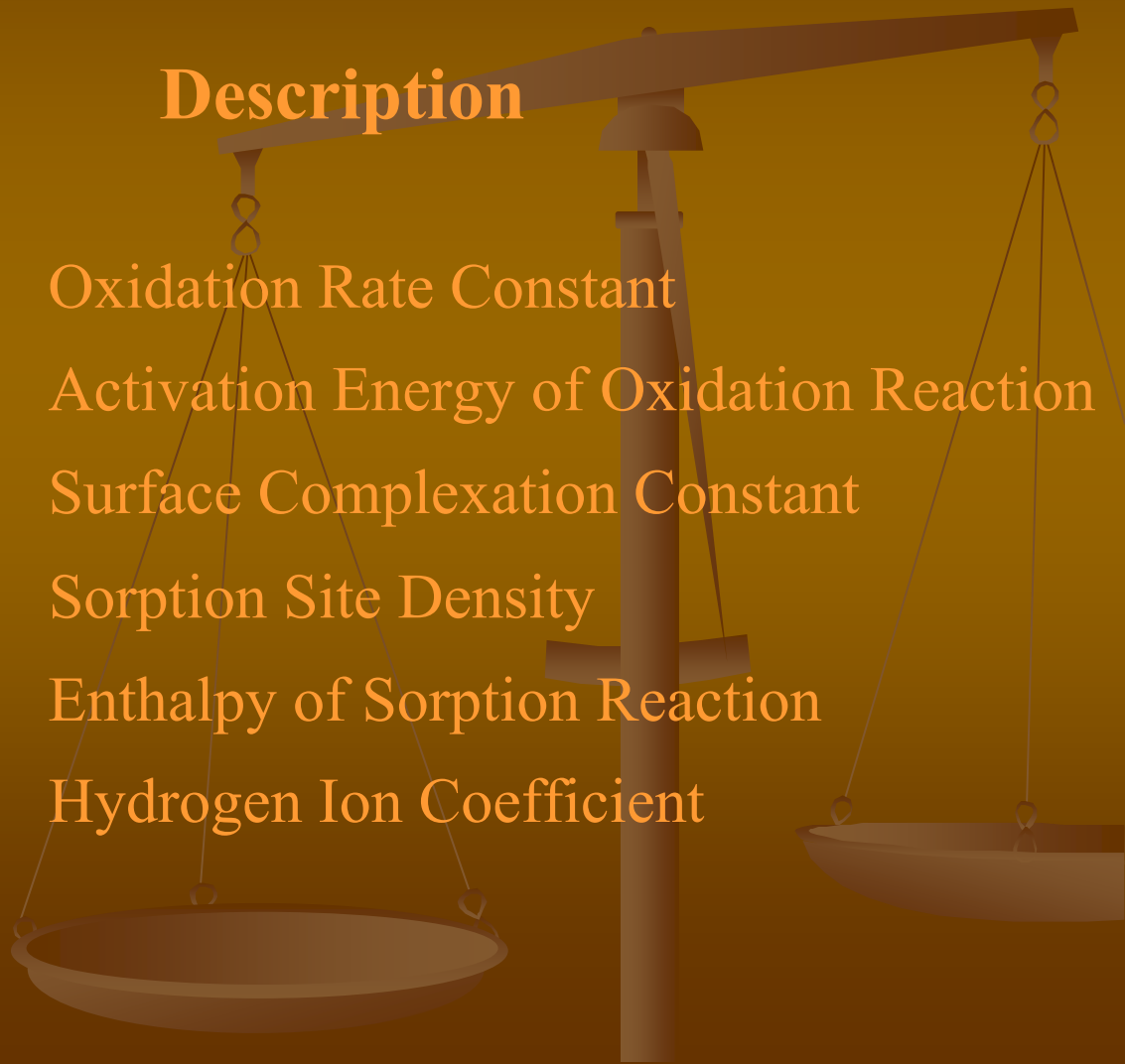
$$-\frac{\partial[Fe(II)]}{\partial t}=\left(k_{He1}\times[DO]\times\frac{[\equiv Fe(III)]\times\Gamma_x}{1+\left(\frac{\{H^+\}^x}{[Fe(II)_{diss}]\times K_x^{app}}\right)}\right)+\left(k_{He2}\times[DO]\times\frac{[\equiv Fe(III)]\times\Gamma_x}{1+\left(\frac{\{H^+\}^x}{[Fe(II)_{diss}]\times K_x^{app}}\right)}\right)$$

$$pK_{x,T2}^{app}=pK_{x,T1}^{app}-\left(\frac{\Delta H_{rxn,x}^0}{2.303\times R}\times\frac{T_2-T_1}{T_2\times T_1}\right)$$

$$pk_{Hex,T2}=pk_{Hex,T1}-\left(\frac{E_{a,x}}{2.303\times R}\times\frac{T_2-T_1}{T_2\times T_1}\right)$$

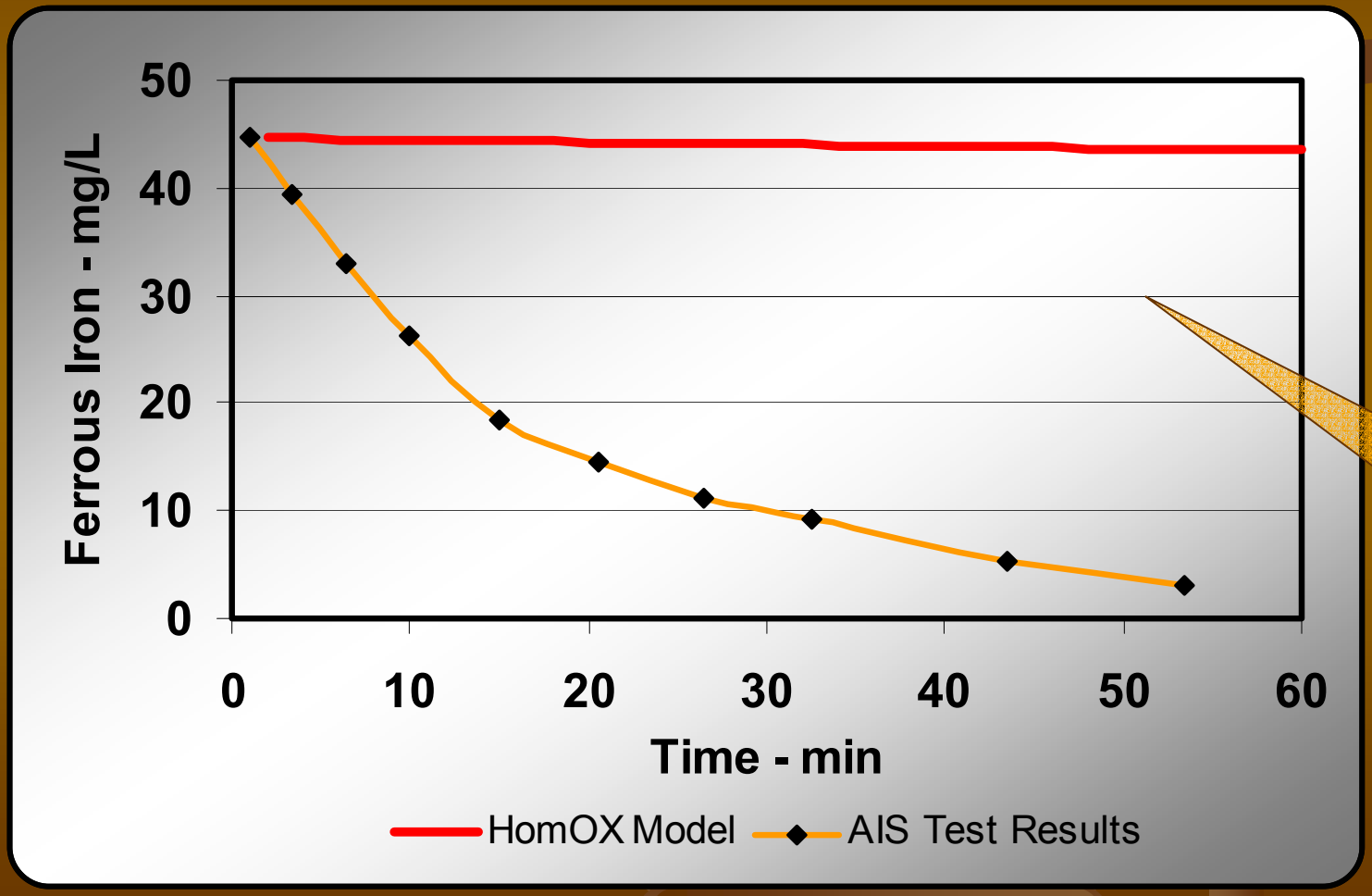
Constants in the Heterogeneous Ferrous Iron Oxidation (HetOX) Model

Model Parameter	Description
k_{Hex} ($M^{-1}s^{-1}$)	Oxidation Rate Constant
$E_{a,x}$ (kJ/mol)	Activation Energy of Oxidation Reaction
K_x^{app} (M^{x-1})	Surface Complexation Constant
Γ_x (mol/mol)	Sorption Site Density
$\Delta H^0_{rxn,x}$ (kJ/mol)	Enthalpy of Sorption Reaction
$\{H^+\}$ Coefficient (x)	Hydrogen Ion Coefficient



Homogeneous versus Heterogeneous

Test Conditions: pH=6.81, DO=9 mg/L, AIS=0.413 g/L as Fe(III), T=10.1°C

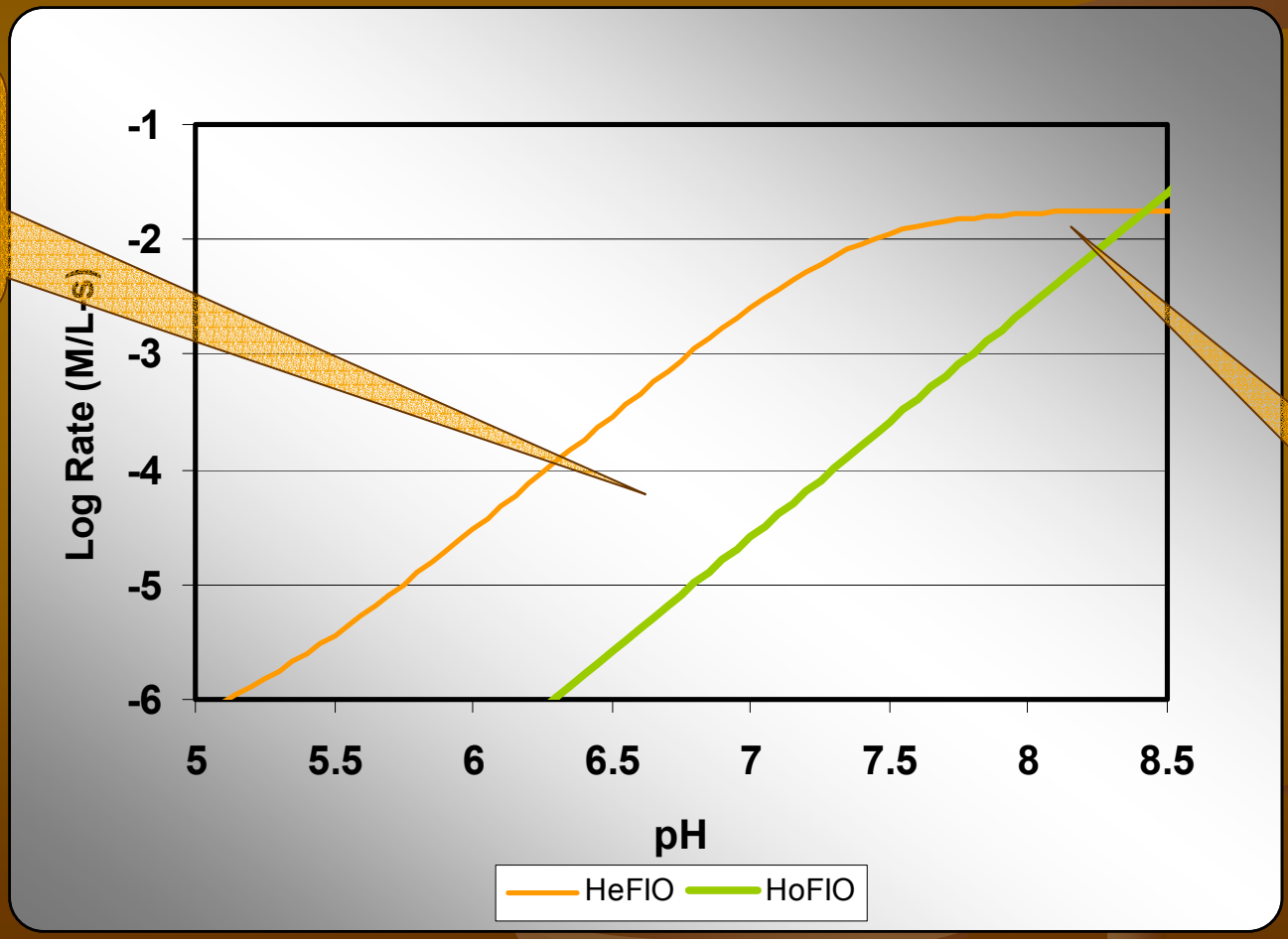


HomOX < 3% of observed decrease

Homogeneous versus Heterogeneous

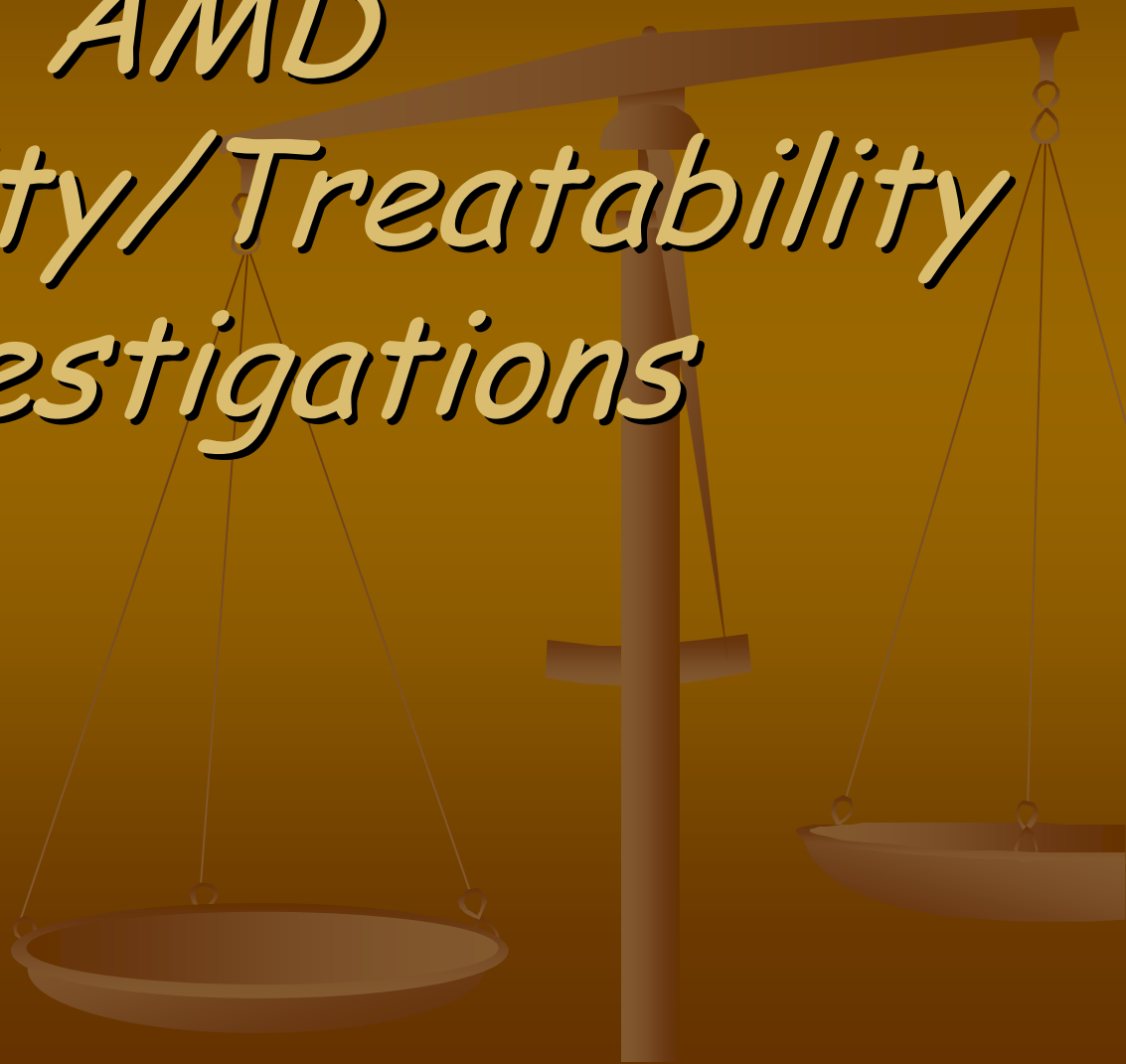
Conditions: DO=8 mg/L, AIS= 1 g/L as Fe(III), T=12°C

AIS Oxidation is 100-fold faster at acidic pH

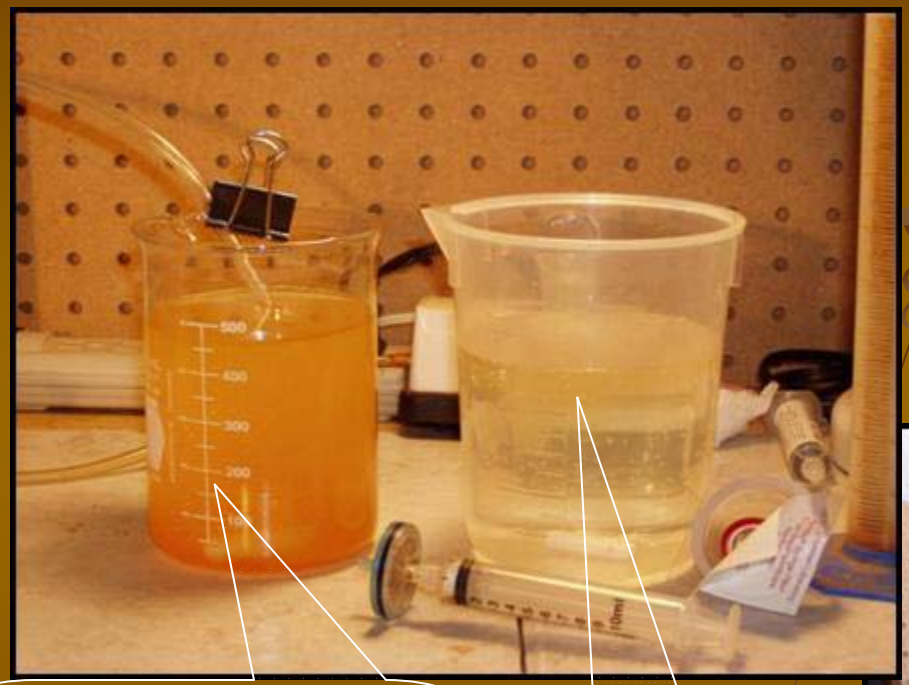


HomOX > HetOX at pH > 8

AMD Feasibility/Treatability Investigations



Bench-Scale Testing Approach



Pre-aeration Test
Aeration to 90% DO Saturation & pH increase from 6.1 to 6.9

Passive Treatment Test
Aeration to 40% DO Saturation & pH increase from 6.1 to 6.3

AIS Treatment Test
Added Iron Oxides, Aeration & Mixing provided

Small-Scale Testing Approach

AIS AMD Treatment

for removal of iron from mine drainage

(PATENT PENDING)

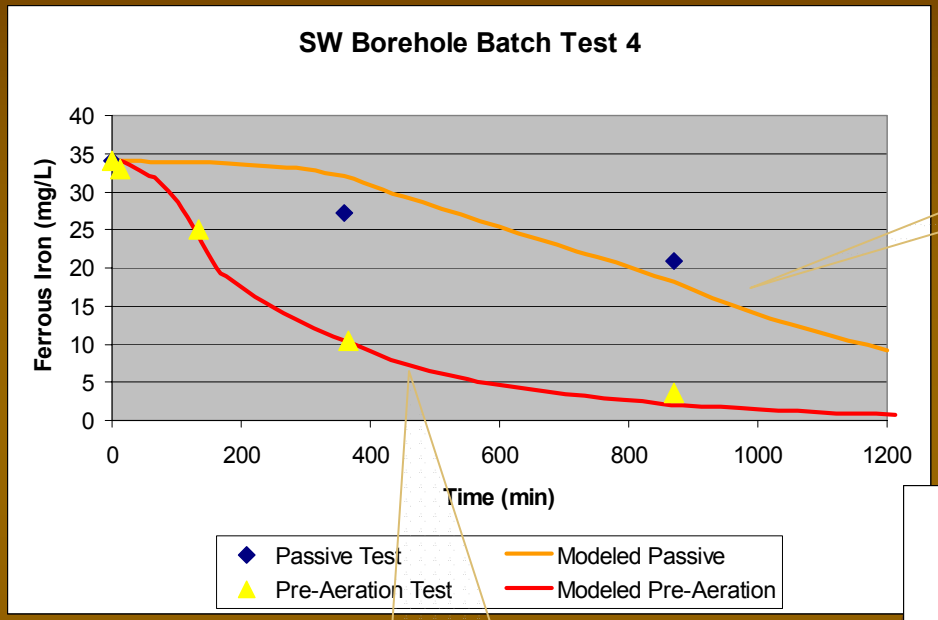
The First Full-Scale AIS AMD Treatment System

St. Vincent College AIS/SBR Demonstration Project

Summary of AIS Bench-Scale and Small-Scale Studies

- AMD Discharges - Tests have been conducted on 6 AMD discharges from across Pennsylvania
- Small-Scale (100 gal) Batch Tests - 7 tests conducted with AIS ranging from 0.02-1.35 g/L.
- Small-Scale Flow-through Tests - 7 tests conducted with steady-state AIS ranging from 0.02-1.96 g/L.
- Bench-Scale Batch Tests - 26 tests conducted with initial AIS from 0.01-2.4 g/L; pH from 5.3-6.8; temperature from 10-23°C.
- Full-Scale Demonstration – ongoing study at the Lower Saxman Run AMD discharge over the past 2 years with a 10,000 gal Sequencing Batch Reactor (SBR)

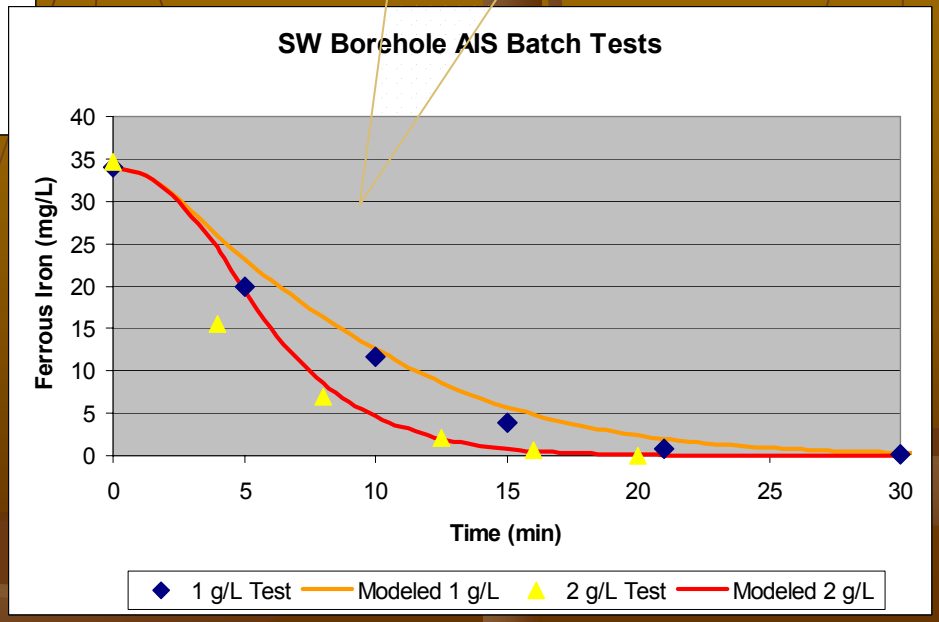
Recent Test Results & Model Simulations
Activated Iron Solids (AIS) Comparison



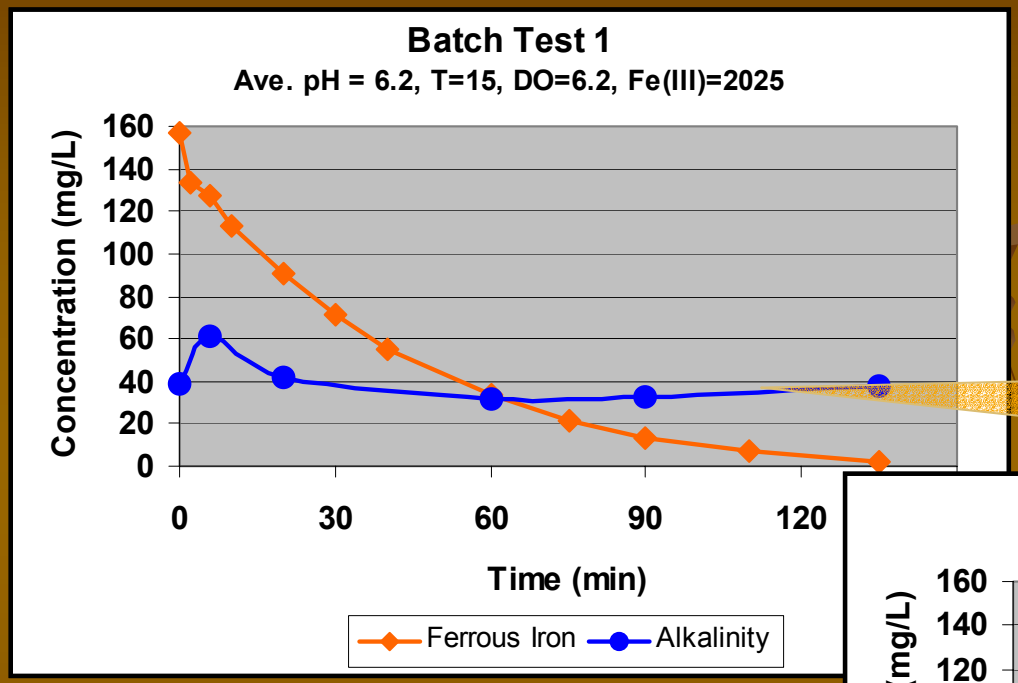
Simulates Passive Treatment Approach

AIS Treatment is between 50 & 100-fold faster

Simulates Passive Treatment Approach with Pre-aeration

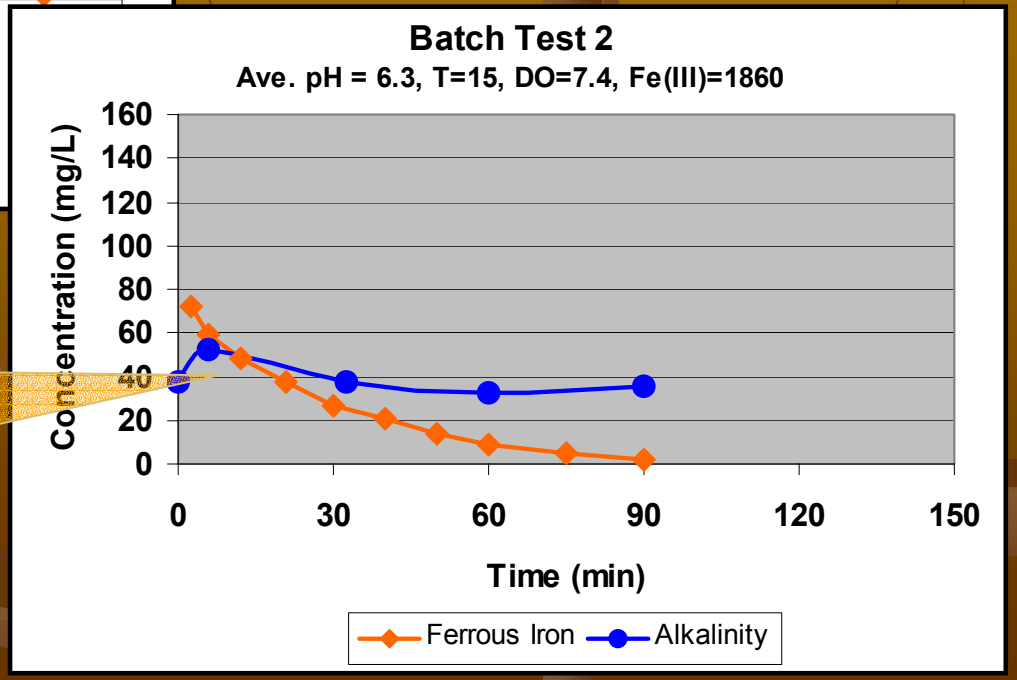


Summary of AIS Tests With Addition of Pulverized Limestone



St. Michaels AMD Discharge is net acidic by 280 mg/L & calcite solubility modeling indicates an ALD can not achieve net alkalinity

Test was with 100% of Untreated AMD and 2 times the required limestone

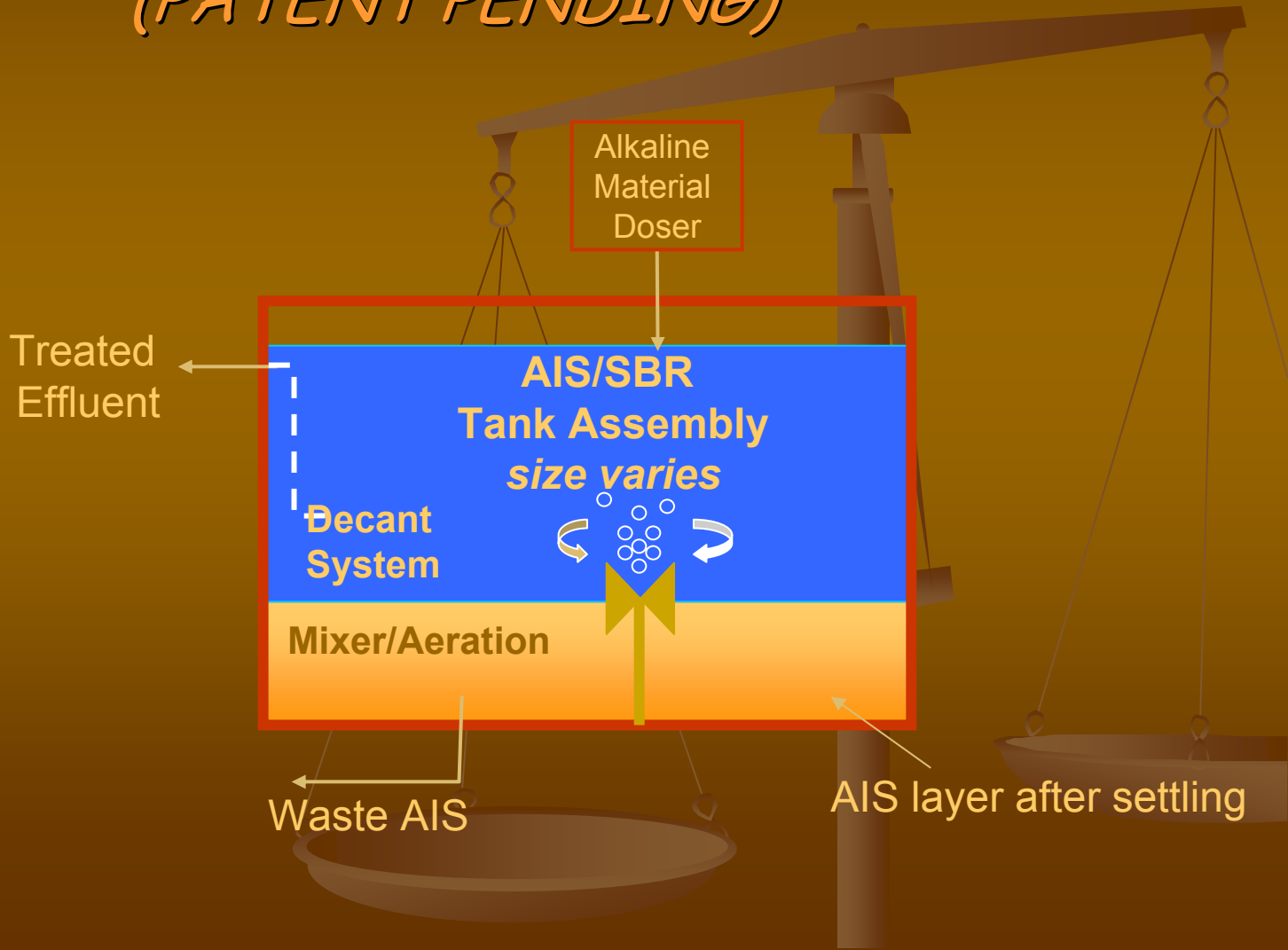


Test conducted by mixing 50% of Untreated AMD with 50% treated AMD from Batch 1 to Simulate AIS/SBR Conditions

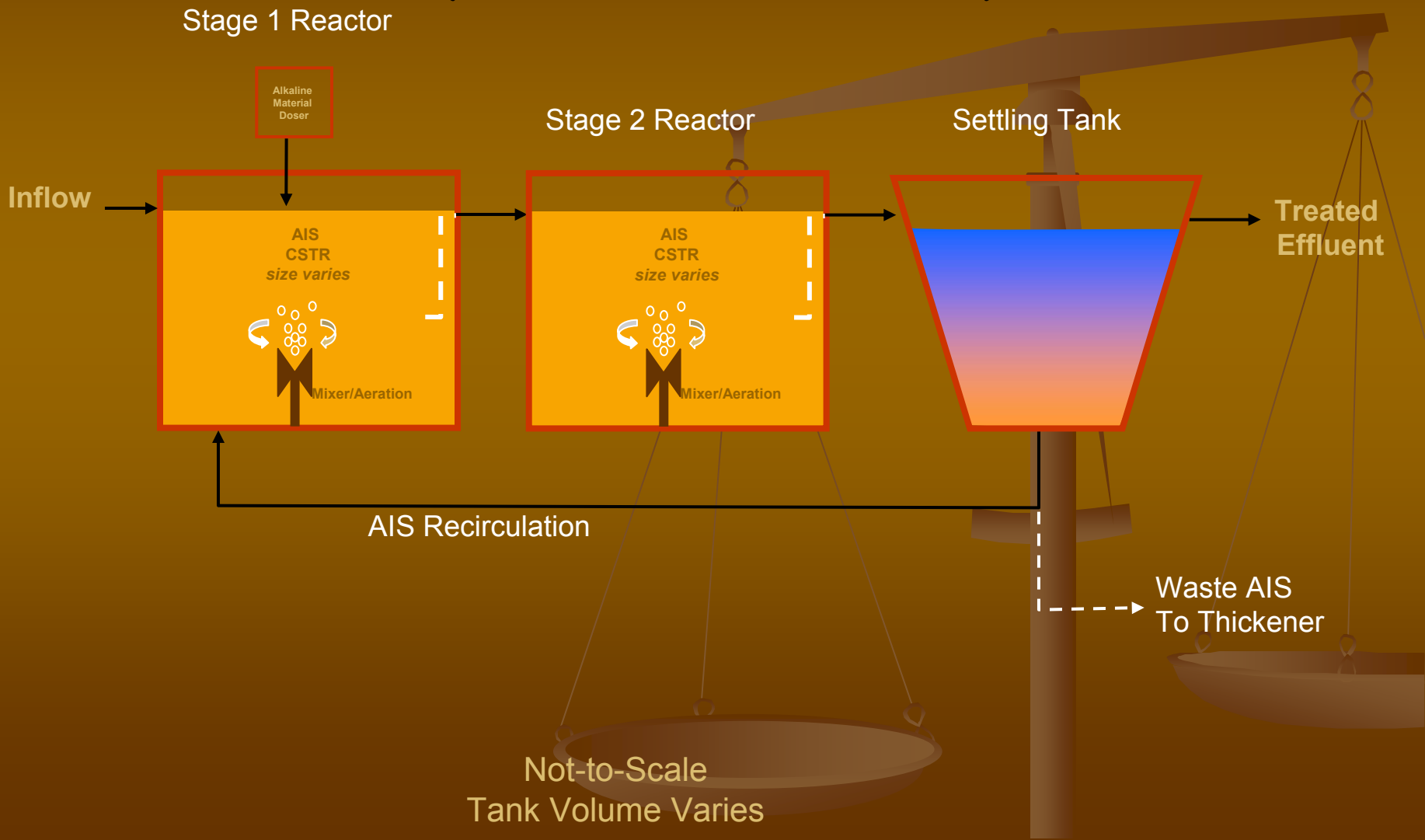
Iron Oxide Technologies, LLC

System Designs Developed to Treat Acidic Mine Drainage

Activated Iron Solids/Sequencing Batch Reactor (AIS/SBR) Treatment For Removal of Iron from Mine Drainage (PATENT PENDING)



AMD Treatment in a Two-Stage Flow-Through AIS System (PATENT PENDING)



Why Choose AIS Treatment ?

Comparison of Various AMD Treatment Technologies & Costs for the Crabtree Discharge

Characteristics: Flow = 5.5 MGD; pH = 6.1; Iron = 70 mg/L

Treatment Type	Treatment System Area[1] (acres)	Detention Time (hrs)	Effluent Total Iron (mg/L)	Capital Costs (× million)	O&M Costs (× million)[5]	25-year Project Costs (× million)
AIS Treatment	**0.5**	**2**	**< 1**	**$ 1.2**	**$ 0.115**	**$ 4.1**
Lime Treatment	5	14	< 1	$ 0.7	$ 0.350	$ 9.5
Aerobic Pond	50 (200)[2]	125 (500)[2]	< 1 (~20)[3]	$ 4.5	$ 0.100 ($ 0.180)	$ 7.0 ($9.0)
Pre-aeration /Aerobic Pond	10 (30)[4]	25 (90)[4]	<1 (~3)[3]	$ 3.0	$ 0.125	$ 6.1

1. Treatment system area includes actual treatment area/volume plus land support area (e.g., embankments, access roads, solids handling facilities and etc.);
2. Value in () is the homogeneous oxidation model required area/detention time versus the 20 GDM removal rate;
3. Value in () represents predicted cold weather effluent iron from the aerobic pond system;
4. Value in () is for critical cold weather sizing of the Aerobic Pond;
5. O&M costs have included iron solids recovery, but not disposal costs or beneficial reuse of the iron oxide solids.;

AIS Solids Analysis

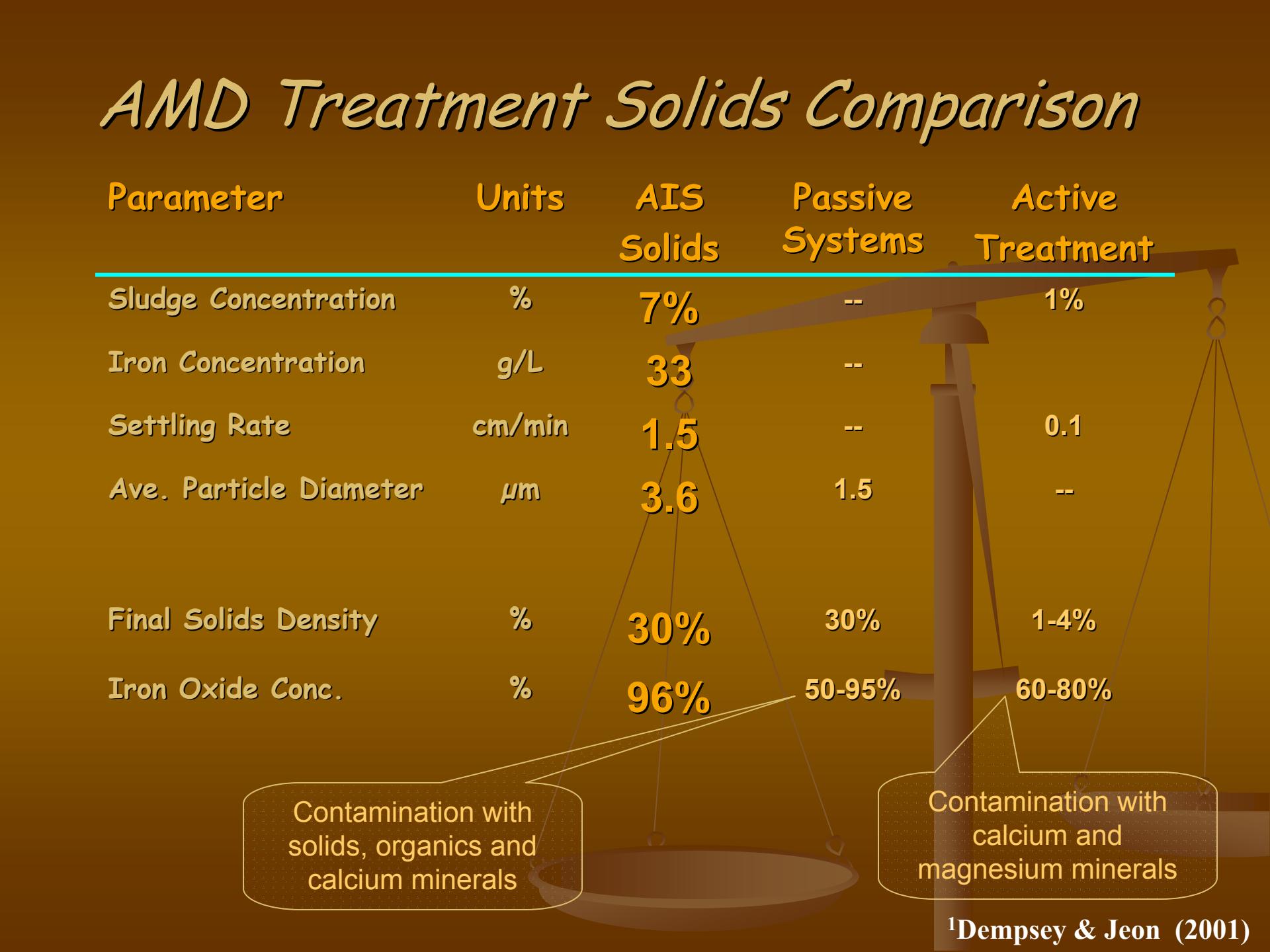
Laboratory Analysis of AIS Sample from the Saxman Run AIS/SBR Demonstration System				
	Unit	**Detection Limit**	**Result**	**% Content**
Solids Content (Wet)	%	0.01		29.7
Dry Weight Basis				
Iron	mg/kg	100	502,000	50.2
Manganese	mg/kg	100	1,150	0.115
Aluminum	mg/kg	500	1,020	0.102
Calcium	mg/kg	1,000	6,820	0.682
Magnesium	mg/kg	1,000	<1,000	0.05
Sodium	mg/kg	2,000	<2,000	0.1
Potassium	mg/kg	1,000	<1,000	0.05
Silica	mg/kg	65	5,690	0.569
Sulfate	mg/kg	123	1,710	0.171
Chloride	mg/kg	123	146	0.0146

AIS Solids Analysis

AIS Composition Based on Analytical Results	
AIS Constituent	**% Dry Weight**
Iron Oxide as $Fe(OH)_3$	96.06
Silicate as SiO_4	1.54
Calcite as $CaCO_3$	1.52
Gypsum as $CaSO_4$	0.58
Aluminum Oxide as $Al(OH)_3$	0.22
Manganese Oxide as $Mn(OH)_3$	0.20
Total	**100.11**

AMD Treatment Solids Comparison

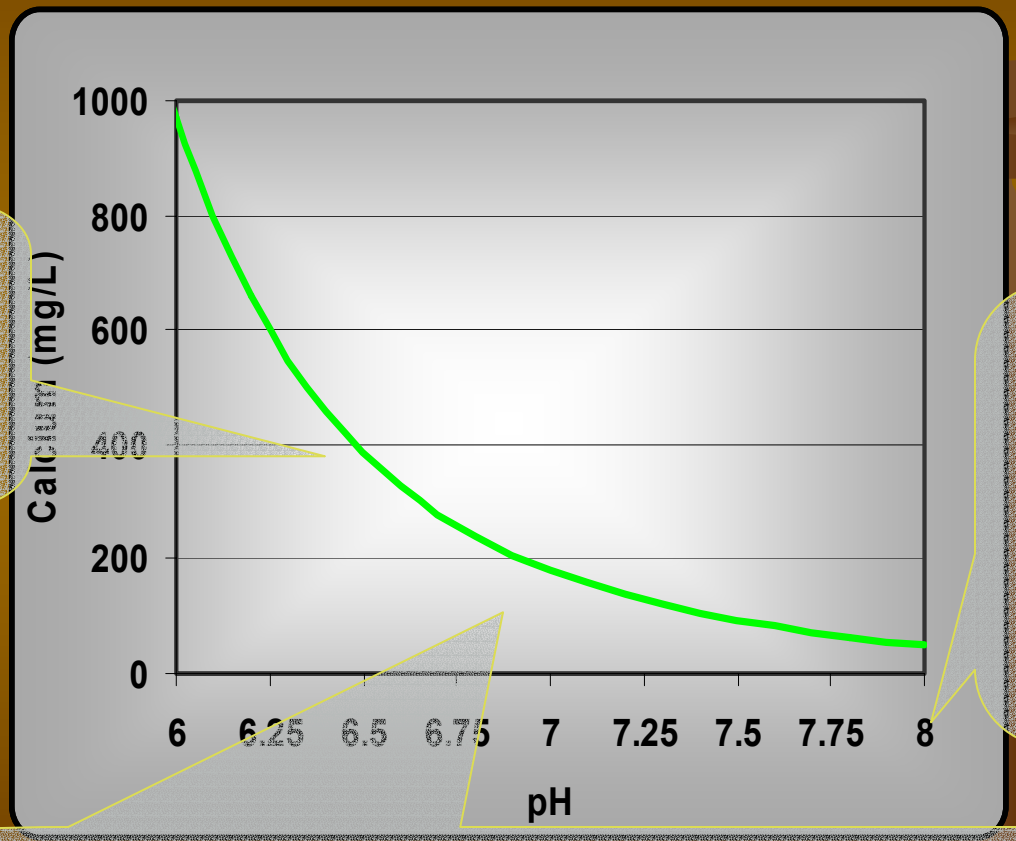
Parameter	Units	AIS Solids	Passive Systems	Active Treatment
Sludge Concentration	%	7%	--	1%
Iron Concentration	g/L	33	--	
Settling Rate	cm/min	1.5	--	0.1
Ave. Particle Diameter	µm	3.6	1.5	--
Final Solids Density	%	30%	30%	1-4%
Iron Oxide Conc.	%	96%	50-95%	60-80%



[1]Dempsey & Jeon (2001)

Calcium Solubility as a Function of pH

Acidic pH of AIS Treatment minimizes the precipitation of calcium (as calcite).



As pH increases the solubility of calcium (as calcite) decreases. This solubility is used in lime (CaO) softening of waters for industrial and drinking water use.

Calcium precipitation also contributes to sludge volumes and density issues in passive and conventional chemical treatment of AMD and can contribute 50% or more of sludge volume affecting longevity and maintenance/operation costs.

Potential Beneficial Reuse of Iron Oxides

- **Pigments** – Hedin Environmental
- **Pollution Abatement** - (Municipal, Agricultural & Industrial Wastewater Treatment, Groundwater Remediation)
  - Sorption & Precipitation (inner and outer sphere)
    - Trace Metals (Ag, Ba, Cu, Cd, Cr, Hg, Ni, Pb, Zn)
    - Trace Anions (arsenate, arsenite, chromate, phosphate, selenate, selenite)
    - Organics (pesticides, cyanides, PAHs).
  - Redox (electron transfer process)
    - Redox Buffer
    - De-halogenation (TCEs, CCl_4)
    - Organics (Cyanide, Nitrobenzenes)
    - Metals (Mn^{2+}, Cr^{6+}, U^{6+})
- **Metallurgical Use -** (e.g., powdered metals)
- **????**

Summary of AIS Treatment Advantages?

- Increased Reaction Rates decrease detention times and treatment system size.
- Lower land area and capital costs in comparison to passive treatment.
- Easier maintenance and replacement in comparison to passive treatment.
- Lower O&M costs in comparison to conventional active treatment.
- Lower solids recovery and handling costs than passive treatment and conventional chemical.
- Greater purity and less contamination than passive or conventional active treatment solids.
- Greater potential to develop beneficial reuses for iron oxide solids.

Activated Iron Solids (AIS) Treatment of AMD

Iron Oxide Technologies, LLC
dietzetal@adelphia.net
www.DGengr.com