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UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION
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SMR.648 - 13

SECOND AUTUMN WORKSHOP ON MATHEMATICAL ECOLOGY

(2 - 20 November 1992)

"Modeling Particle Oxidation"

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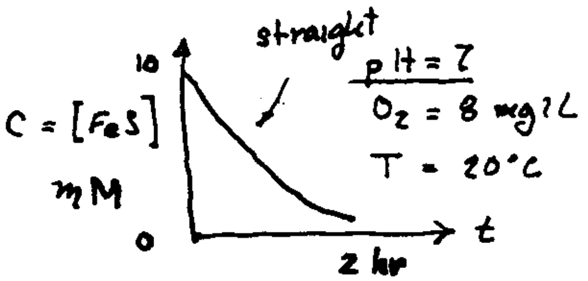
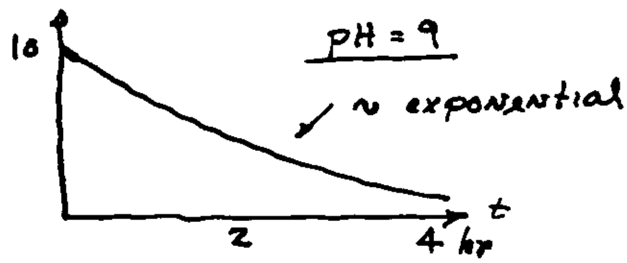
These are preliminary lecture notes, intended only for distribution to participants.

MODELING PARTICLE OXIDATION : FeS

1. DATA (Nelson, Ph.D Thesis ~ 1975)

$$\underset{\substack{\text{(PARTICLES)}\\ Fe(II)\quad S(-II)}}{FeS} + \frac{9}{4} O_2 + \frac{5}{2} H_2O \longrightarrow \underset{\substack{\text{(PARTICLES)}\\ Fe(III)}}{Fe(OH)_3} + \underset{S(II)}{H_2SO_4}$$





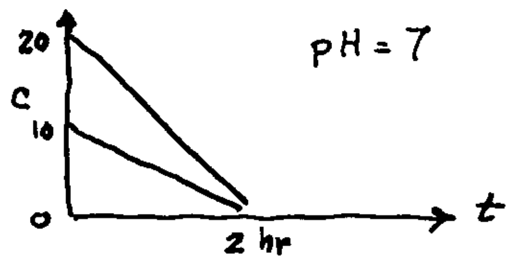
2. MODEL: $\frac{dc}{dt} = -Kc^n$ "n^{th} ORDER KINETICS"

pH = 7 $n = 0$ pH = 9 $n = 1$

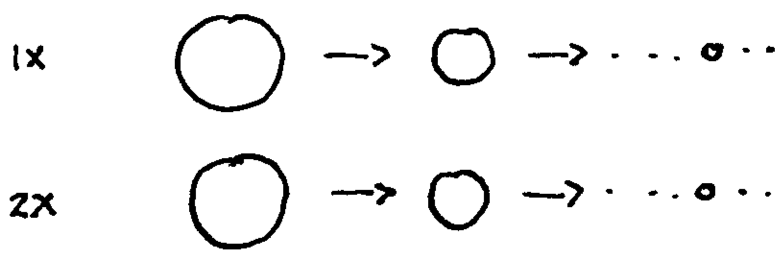
CRITICAL EXPERIMENT

WHAT IS HAPPENING?

$$\frac{dc}{dt} \neq f(c)$$



3. PARTICLE OXIDATION



PARTICLE AREA DECREASING

4. MODEL : MONODISPERSE DISTRIBUTION (ALL PARTICLES EQUAL SIZE)

a) $$C = \underset{\frac{\#\ \text{PARTICLES}}{L}}{n} \cdot \underset{\frac{\text{VOLUME}}{\text{PARTICLE}}}{V} \cdot \underset{\frac{\text{g CHEMICAL}}{\text{VOLUME}}}{\rho}$$

b) RELATIONSHIP OF V TO A.

SPHERE : $V = \frac{4}{3} \pi r^3 \qquad r \sim V^{1/3}$

$A = 4 \pi r^2 \qquad r \sim A^{1/2}$

$$\therefore \quad V \sim A^{3/2} \quad ; \quad V = \beta A^{3/2}$$

$$\therefore \quad C = n \rho \beta A^{\nu}$$

β = geometrical coef.
ν = " exponent

5. KINETICS

SUPPOSE A DECREASES AT CONSTANT RATE

$$\frac{dA}{dt} = -K \quad , \quad A = A_0 - Kt$$

$$c(t) = n \rho \beta \left(A_0 - Kt\right)^{\nu}$$

$$c(0) = n \rho \beta A_0^{\nu} \longrightarrow n \rho \beta = c(0) / A_0^{\nu}$$

FINALLY

$$c(t) = c(0) \left(1 - \frac{K}{A_0} t\right)^{\nu}$$

6. RESULTS

ESTIMATE OF K AND ν AS FUNCTION OF pH, T, O_2, I, $C(o)$

SURFACE OXIDATION

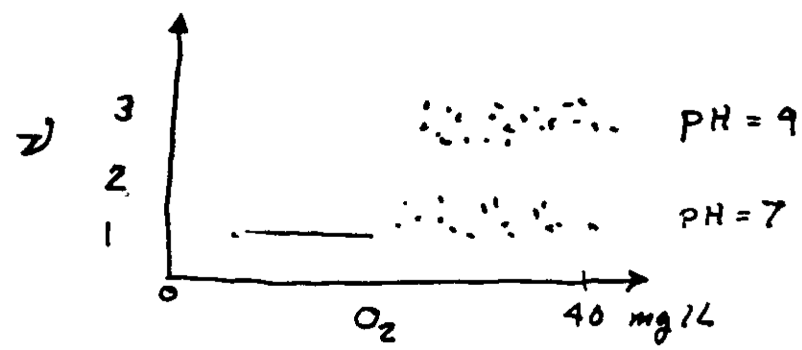
$$\equiv S-H + O_2 \xleftrightarrow{K_{eq1}} \equiv S-H \cdot O_2 \xrightarrow{K_1} Fe(OH)_3 , SO_4^=$$

$$\equiv S-H_2^+ + O_2 \xleftrightarrow{K_{eq2}} \equiv S-H_2^+ \cdot O_2 \xrightarrow{K_2} \text{"} \quad \text{"}$$

$$\equiv S-H + H^+ \xleftrightarrow{K_H} \equiv S-H_2^+$$

THIS FITS THE DATA FOR K. VERY WELL

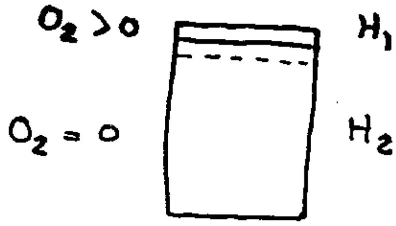
HOWEVER.



WHY DOES ν VARY AS FUNCTION OF pH?

7. PARTICLE OXIDATION IN SEDIMENTS

SIMPLE EXPERIMENT, UNIFORM SEDIMENT



H_1 INCREASING

$$\frac{d(V_1 c_1)}{dt} = -K V_1 c_1 + \frac{dH_1}{dt} A c_2$$

$$V_1 \frac{dc_1}{dt} + c_1 \frac{dV_1}{dt} = -K V_1 c_1 + \frac{dH_1}{dt} A c_2$$

$$H_1 \frac{dc_1}{dt} + c_1 \frac{dH_1}{dt} = -K H_1 c_1 + c_2 \frac{dH_1}{dt}$$

DILUTION REACTION ENTRAINMENT

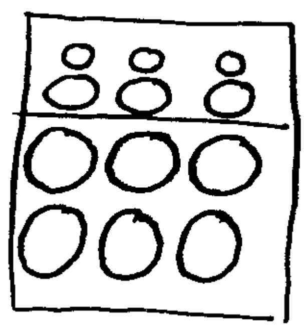
$$\frac{d(H_2 c_2)}{dt} = -\frac{dH_1}{dt} c_2$$

$$H_2 \frac{dc_2}{dt} + c_2 \frac{dH_2}{dt} = -\frac{dH_1}{dt} c_2$$

BUT $dH_2/dt = -dH_1/dt$

$$H_2 \frac{dc_2}{dt} = 0 \qquad c_2 = c_2(0) = \text{CONSTANT}$$

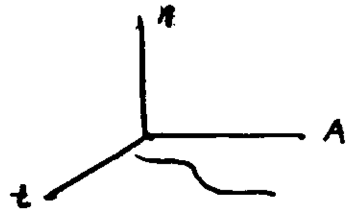
BUT WHAT is "K"



8. PARTICLE SIZE SPECTRUM

$n(A,t)$ = NUMBER OF PARTICLES IN A AND $A + dA$

PARTICLE CONSERVATION LAW



$$\frac{\partial n}{\partial t} + \frac{\partial n}{\partial A}\frac{dA}{dt} = 0$$

REACTION KINETICS $\quad \dfrac{dA}{dt} = -K$

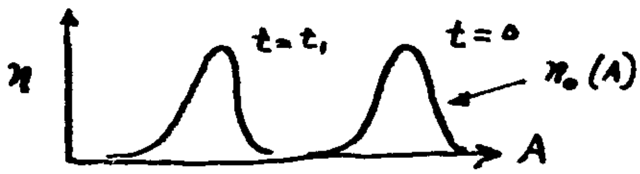
$$\frac{\partial n}{\partial t} - K\frac{\partial n}{\partial A} = 0$$

CONVECTIVE EQUATION

VELOCITY = $-K$

$$n(A,t) = n_0(A + Kt)$$

VELOCITY IN A IS REACTION



$$c(t) = \rho\beta \int_0^\infty n(A,t)\, A^{\nu}\, dA$$

BUT $\quad n(A,t) = n_0(A + Kt)$ (

$$\therefore \quad c(t) = \rho\beta \int_0^\infty n_0(A + Kt)\, A^{\nu}\, dA$$

PROBLEM: FIND ANALYTICAL RESULTS FOR REALISTIC $n_0(A)$. GAUSSIAN, LOGNORMAL, GAMMA, ... ? ...

9. SIMPLE EXPERIMENT : H_1 INCREASING

$$H_1 \frac{dc_1}{dt} + c_1 \dot{H}_1 = -K H_1 c_1 + c_2 \dot{H}_2$$

SHOULD BE :

$$H_1 \left(\frac{\partial n_1}{\partial t} - K \frac{\partial n_1}{\partial A} \right) + n_1 \dot{H}_1 = n_2 \dot{H}_1$$

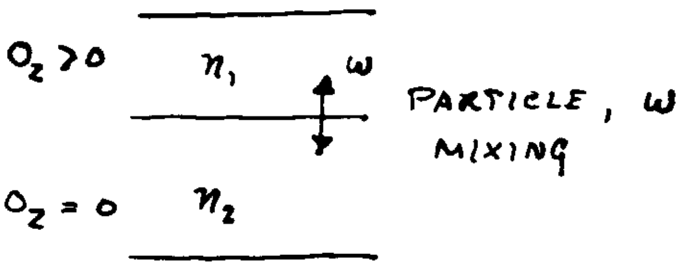
SIMPLE PROBLEM :

$$n_2(A,t) = n_0(A) \quad \text{CONSTANT}$$

$$n_1(A,0) = n_0(A) = n_0\, \delta(A - A_0)$$

$$\dot{H}_1 = \text{CONSTANT}$$

10. MORE DIFFICULT



$$H_1 \left(\frac{\partial n_1}{\partial t} - K \frac{\partial n_1}{\partial A} \right) = \omega (n_2 - n_1) H_1$$

$$H_2 \frac{\partial n_2}{\partial t} = \omega (n_1 - n_2) H_2 + S$$

$$S = n_0\, \delta(A - A_0)$$

$$n_1(A,0) = n_2(A,0) = n_0\, \delta(A - A_0)$$