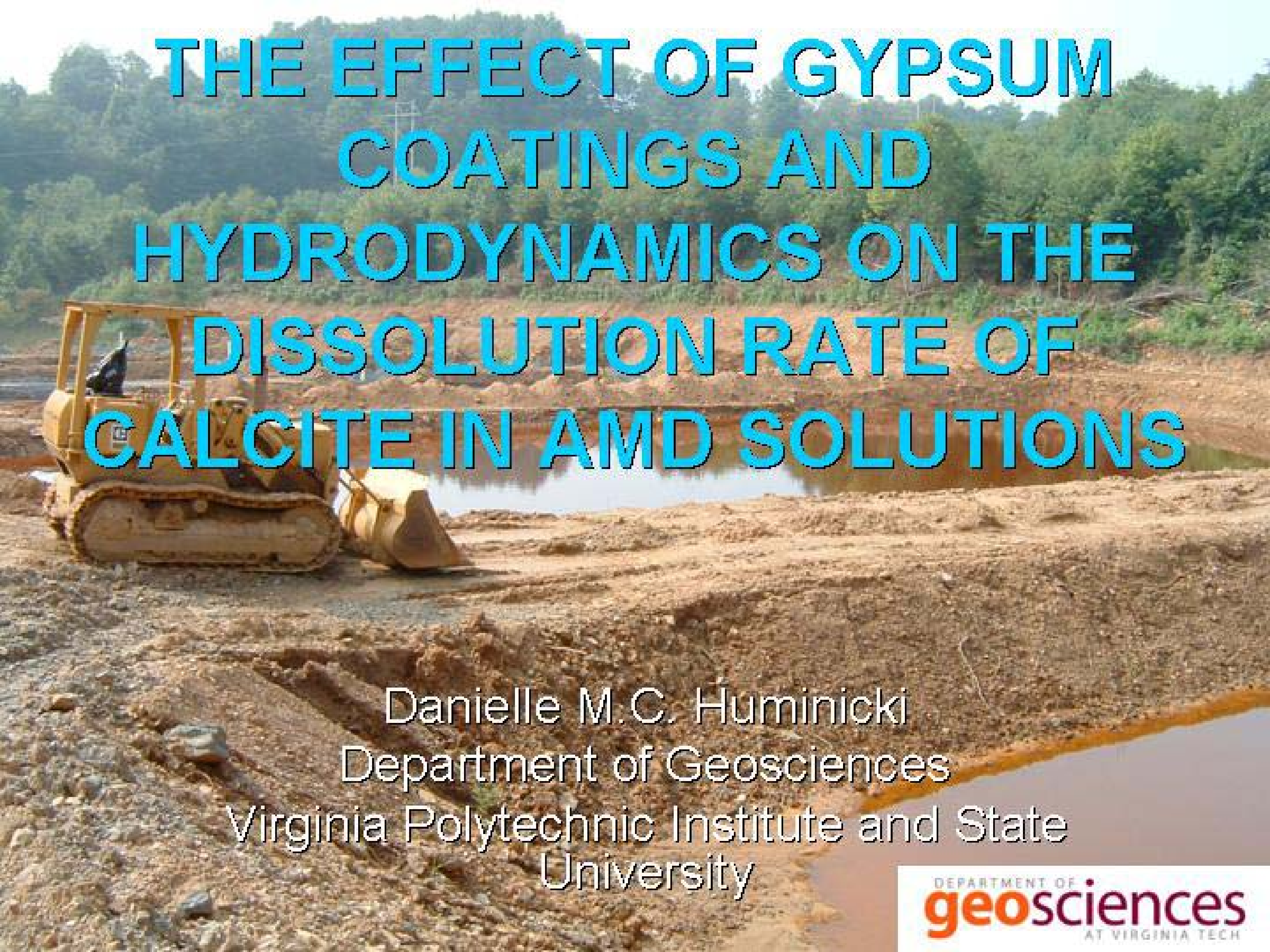


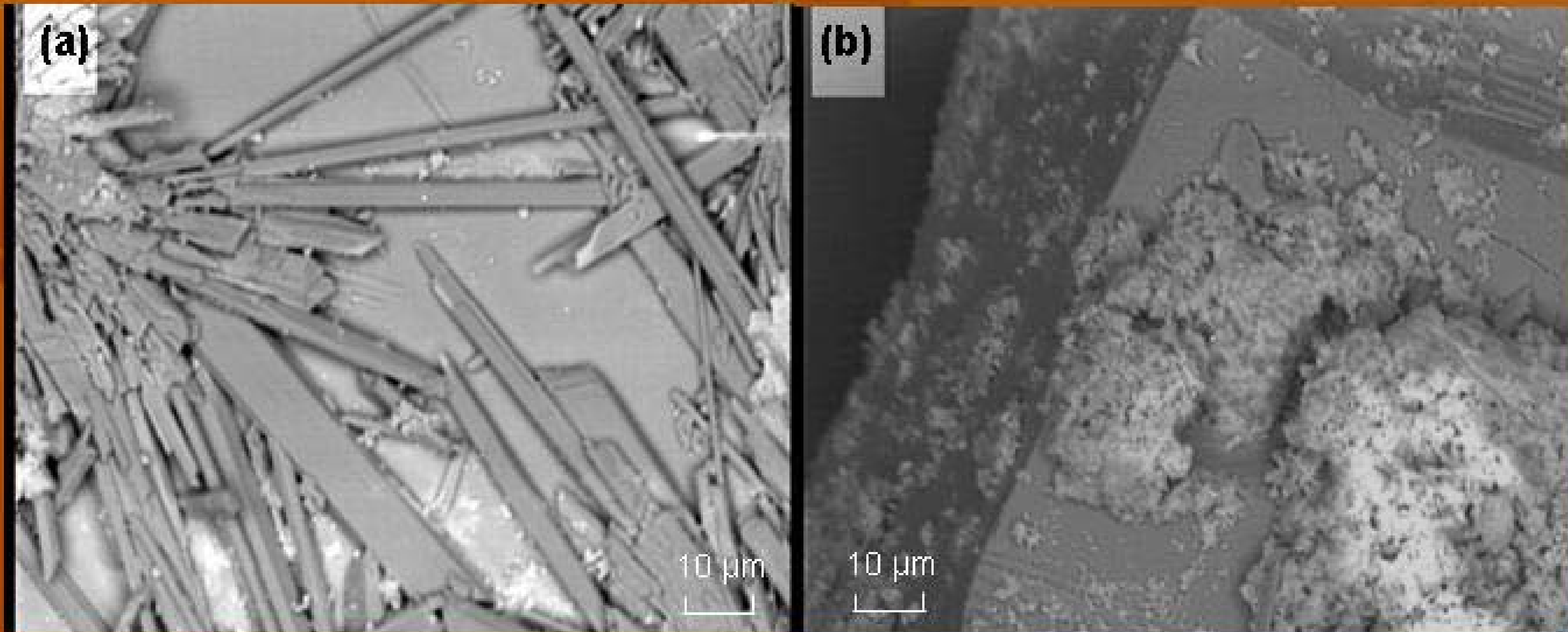
THE EFFECT OF GYPSUM COATINGS AND HYDRODYNAMICS ON THE DISSOLUTION RATE OF CALCITE IN AMD SOLUTIONS

Danielle M.C. Huminicki
Department of Geosciences
Virginia Polytechnic Institute and State University

DEPARTMENT OF geosciences AT VIRGINIA TECH

Anoxic limestone drains

Types of coatings in AMD

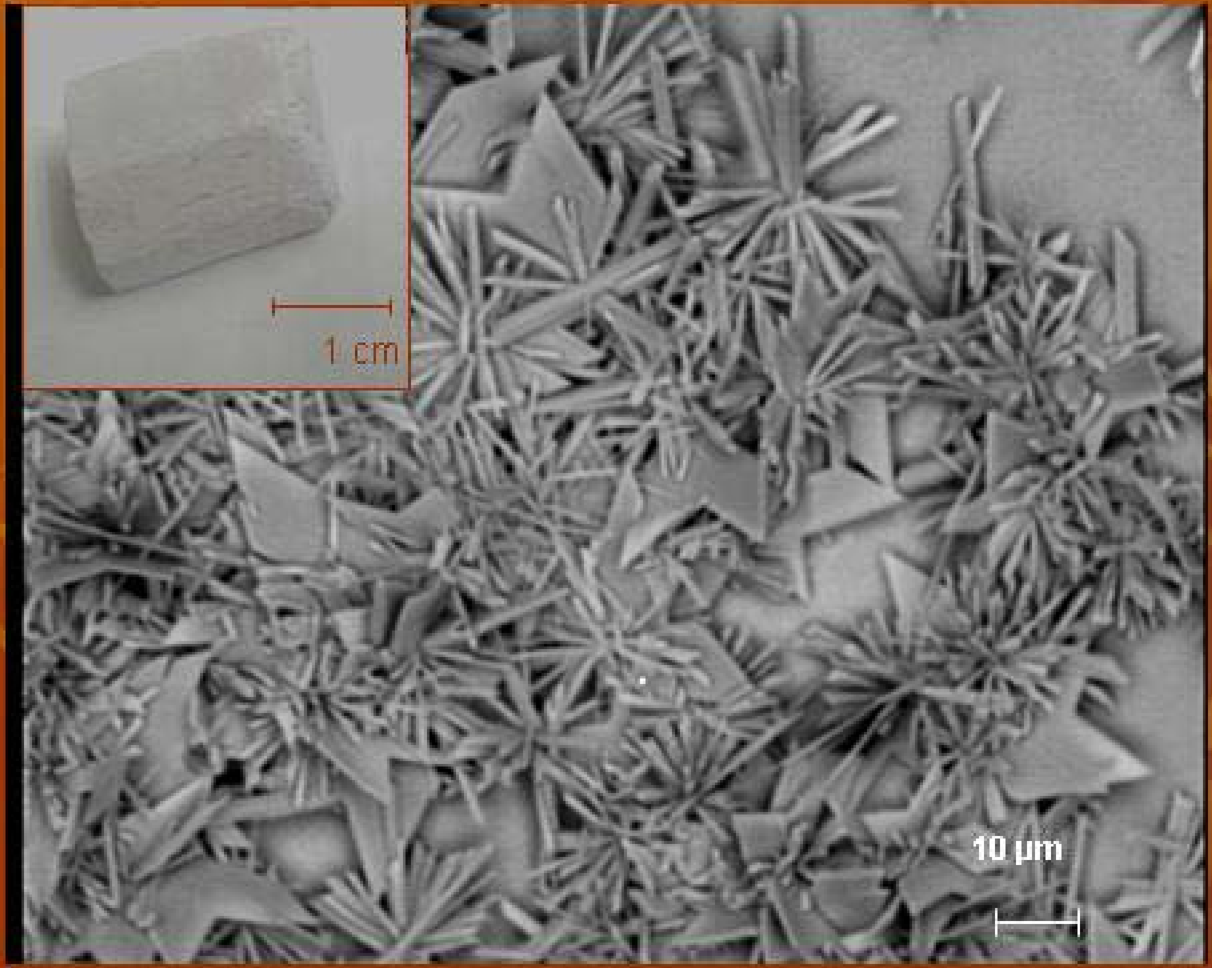


gypsum

iron and aluminum oxyhydroxides

Calcite reacted with sulfuric acid

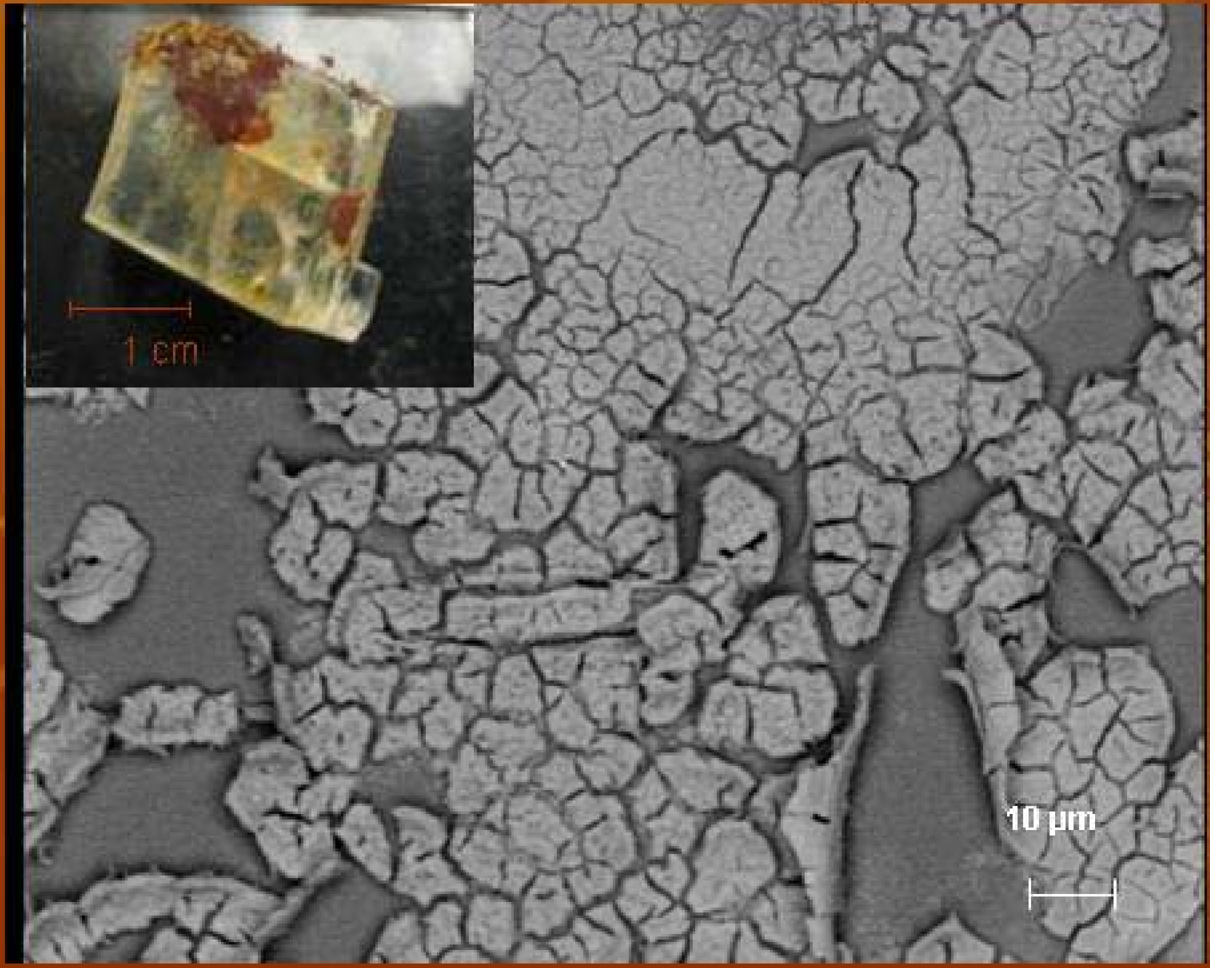
$$CaCO_3 + H_2SO_4 + 2H_2O = CaSO_4 \cdot 2H_2O + H_2CO_3$$



Calcite reacted with $FeCl_3$

$$CaCO_3 + 2H^+ = Ca^{2+} + H_2CO_3$$

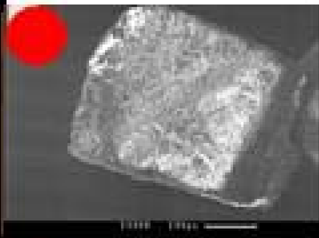
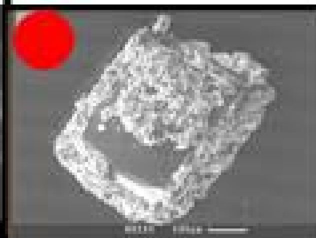
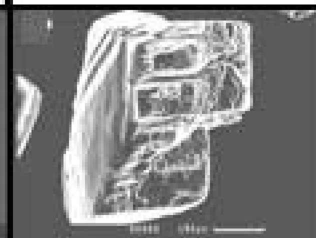
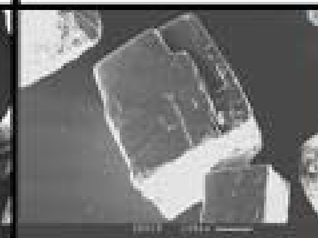
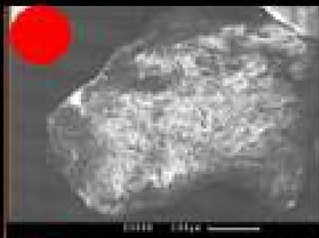
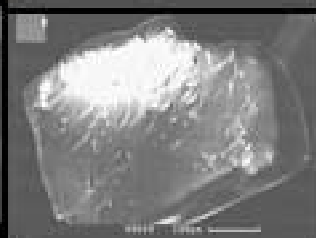
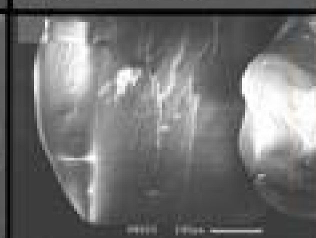
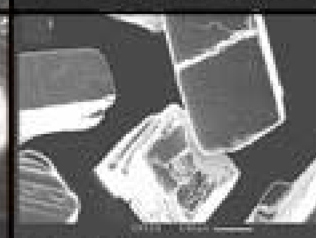
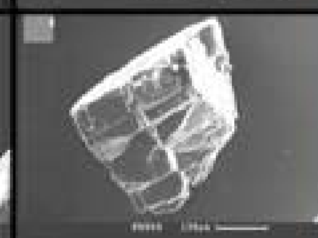
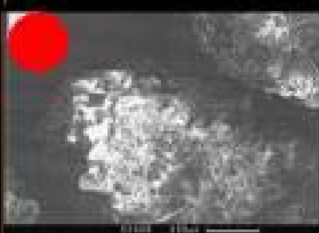
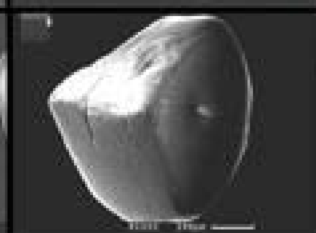
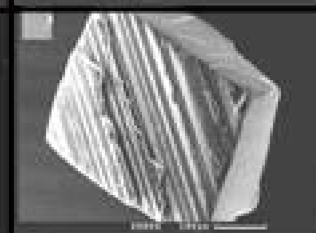
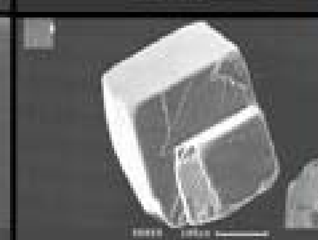
$$Fe^{3+} + 3H_2O = Fe(OH)_{3(s)} + 3H^+$$



Batch Reactor Experiments

- 20 experiments
- 0.5 gram Iceland spar calcite
- 200 mL of solution
- 0 - 1.0 M sodium sulfate solution
- pH = 1.5 to 3.5
- 1 hour
- measured pH and Ca concentration

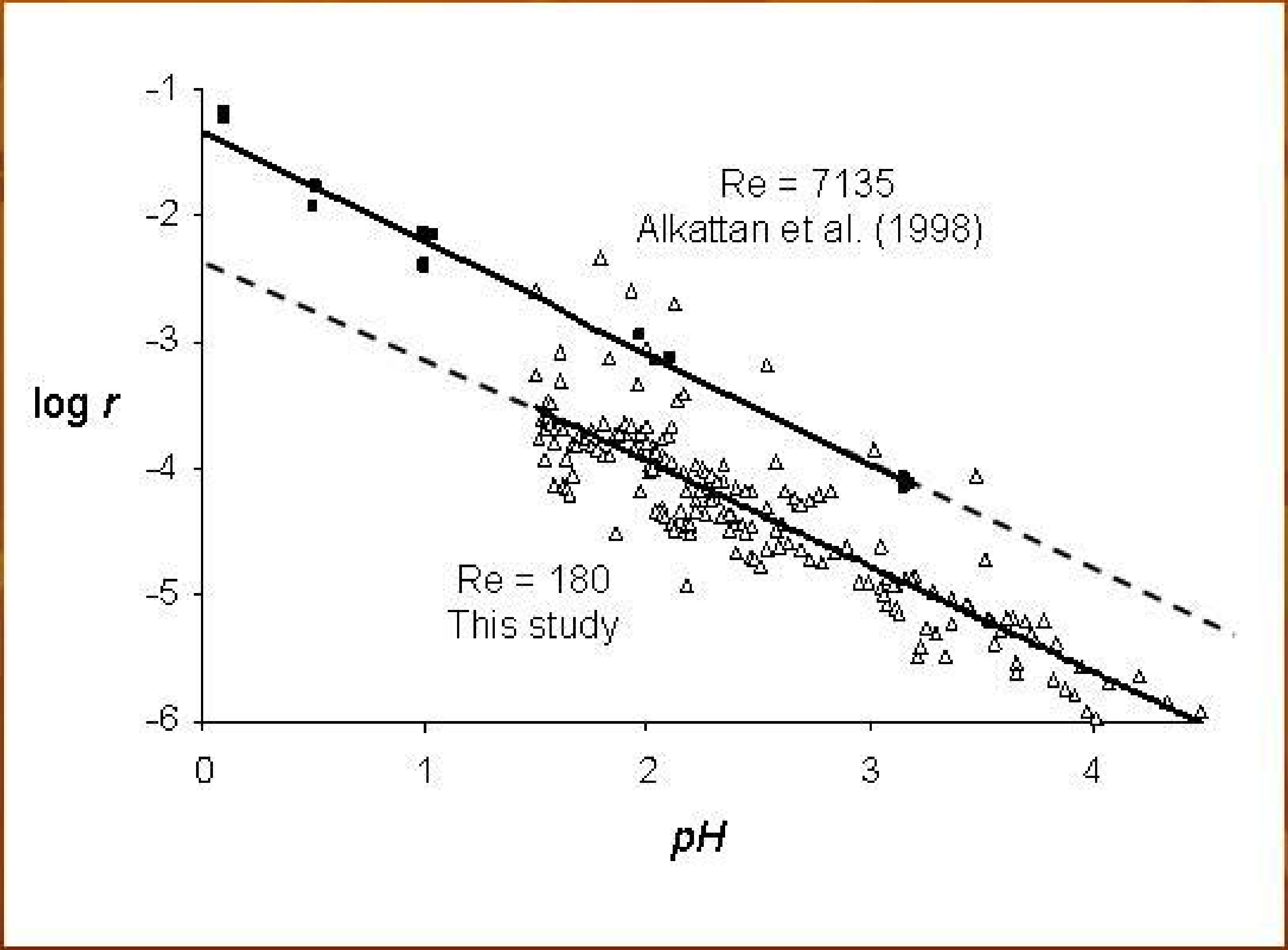
Gypsum coatings formed at low *pH* and high M_{SO4} after 1 hour

	pH				
M_{SO4}	1.5	2.0	2.5	3.0	3.5
1.0					
0.3					
0.1					
0.0					

Experiment	Rate law	log k
no sulfate	$r = ka_{H+}^{0.83}$	-2.28
sulfate no coatings	$r = ka_{H+}^{0.87}$	-1.84
coatings	$r = kt^{-0.5}$	-1.96

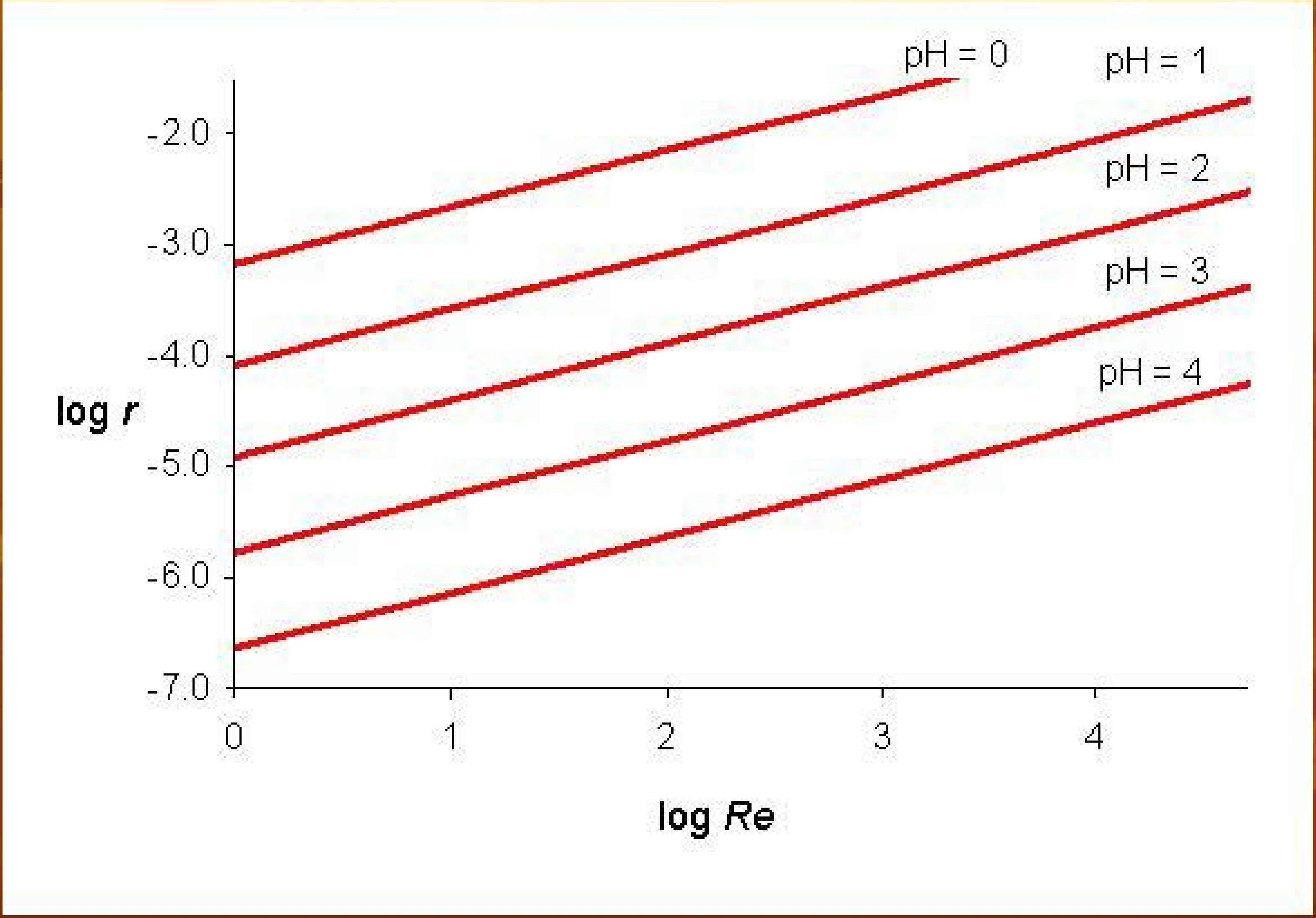
Rates as a function of *pH* & *Re*

$$\log r = -0.87pH + 0.51\log Re - 3.31$$



Rates as a function of *pH* and *Re*

$$\log r = -0.87pH + 0.51\log Re - 3.31$$



Re as a function of *q* and *D* in a packed-bed

$\log r = 0.51 \log Re - 0.87pH - 3.31$

$$Re = qD/\upsilon$$

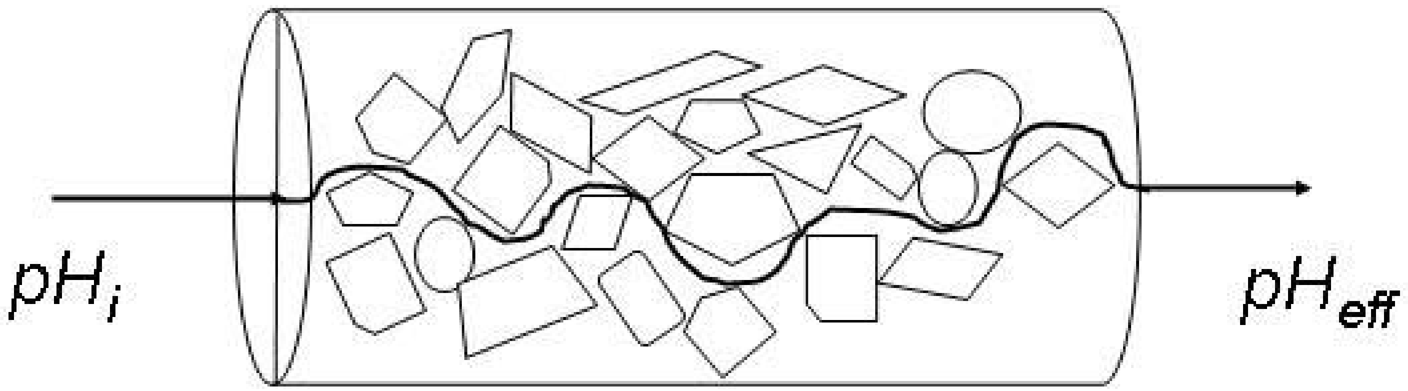
q – Darcy velocity (cm/sec)

D – pore diameter (cm)

υ – kinematic viscosity (cm^2/sec)

$\log r = 0.51 \log qD/\upsilon - 0.87pH - 3.31$

Ideal plug flow reactor



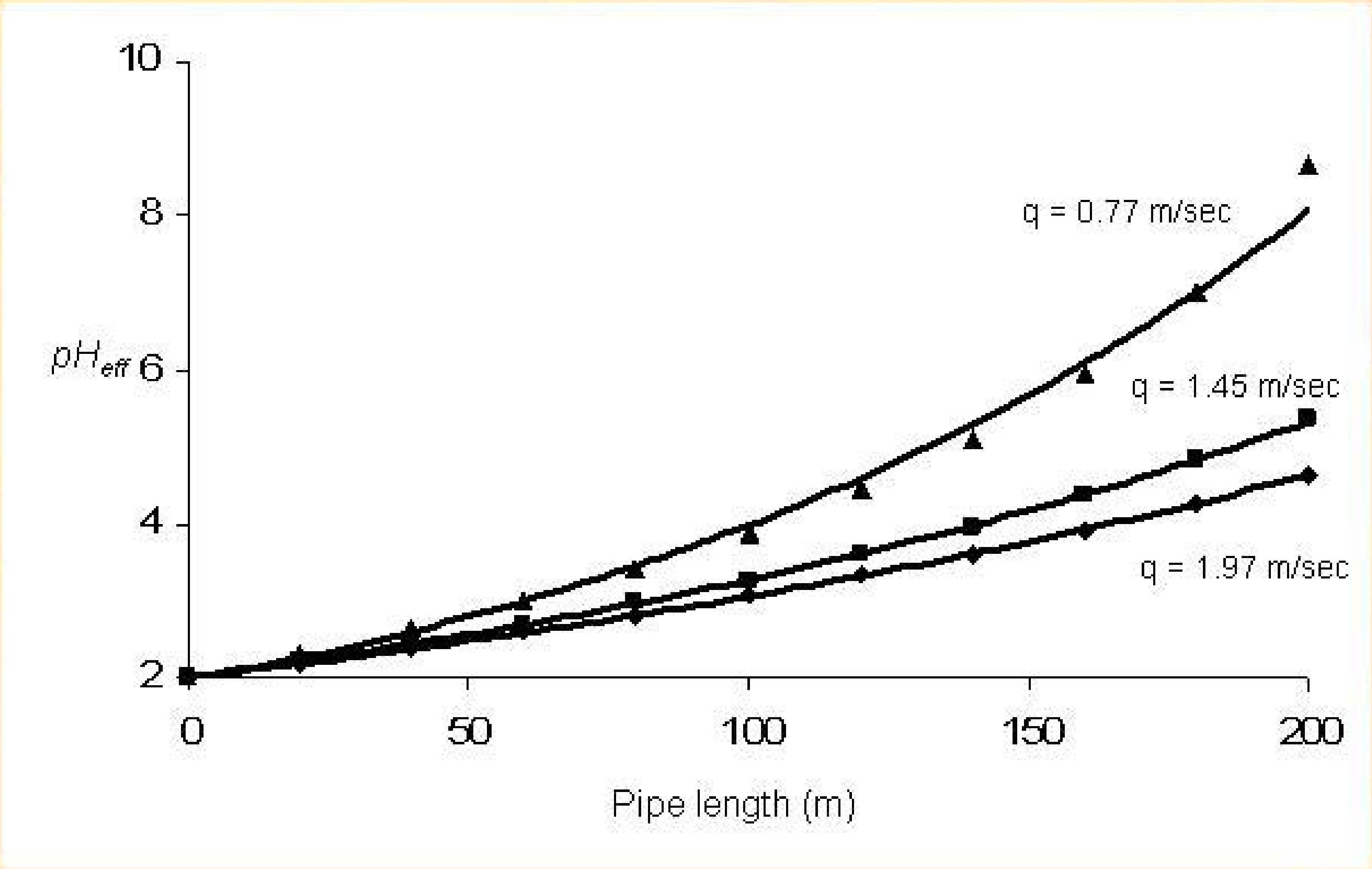
ALD = PFR

Integrated rate law	$\left(\frac{m}{m_0}\right)^{-n+1} = \frac{-kt(-n+1)}{m_0^{-n+1}} + 1$
Residence time	$t = \frac{V_P \phi}{Q}$
Mass flow rate, m^3/sec	$Q = qA_c$
Pipe volume	$V_P = A_c \times l$
k as a function of *Re*	$\log k = 0.51 \log \mathrm{Re} - 3.31$
Re as a function of *q* and *D*	$\mathrm{Re} = \frac{qD}{\upsilon}$

ALD Design

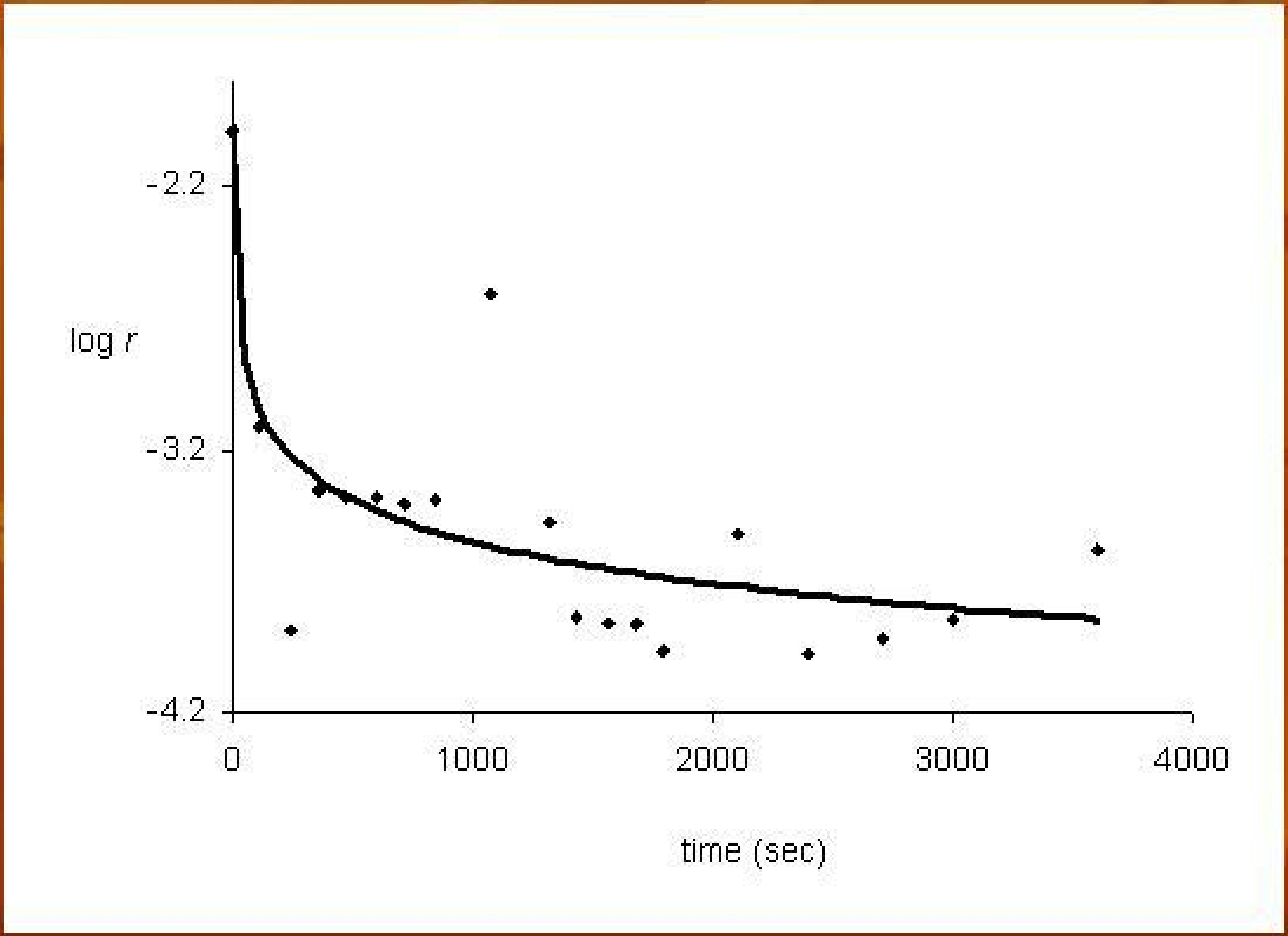
Variables	
Flow rate	Neutralization rates increase with increasing Darcy velocity
Pipe dimension	Reaction time decreases with increasing Darcy velocity and pipe length
Grain size	Rates increase with increase in grain size/pore diameter
Surface area	Rates increase with decrease in grain size

Predicted pH_{eff} as a function of flow velocity and pipe length

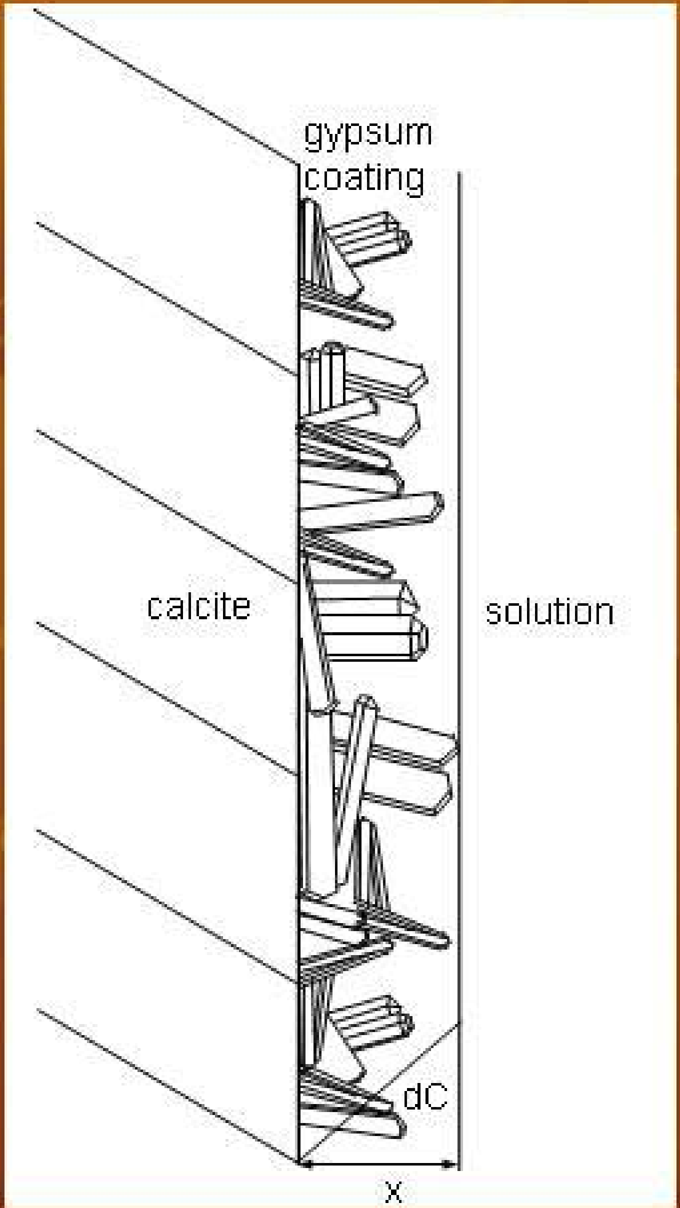


- Scale up laboratory experiments and apply results to the field using chemical engineering principles
- Use this approach to consider the trade off between the effects of important variables

Neutralization rates decrease with time as gypsum coatings form



Physical model of coatings



Fick's law of diffusion

$$J = -D\frac{dC}{x}$$

$$n_{Ca,T} = \sqrt{\frac{DC_B A_R}{f_{gyp}\phi V_M}}t^{1/2} = kt^{1/2}$$

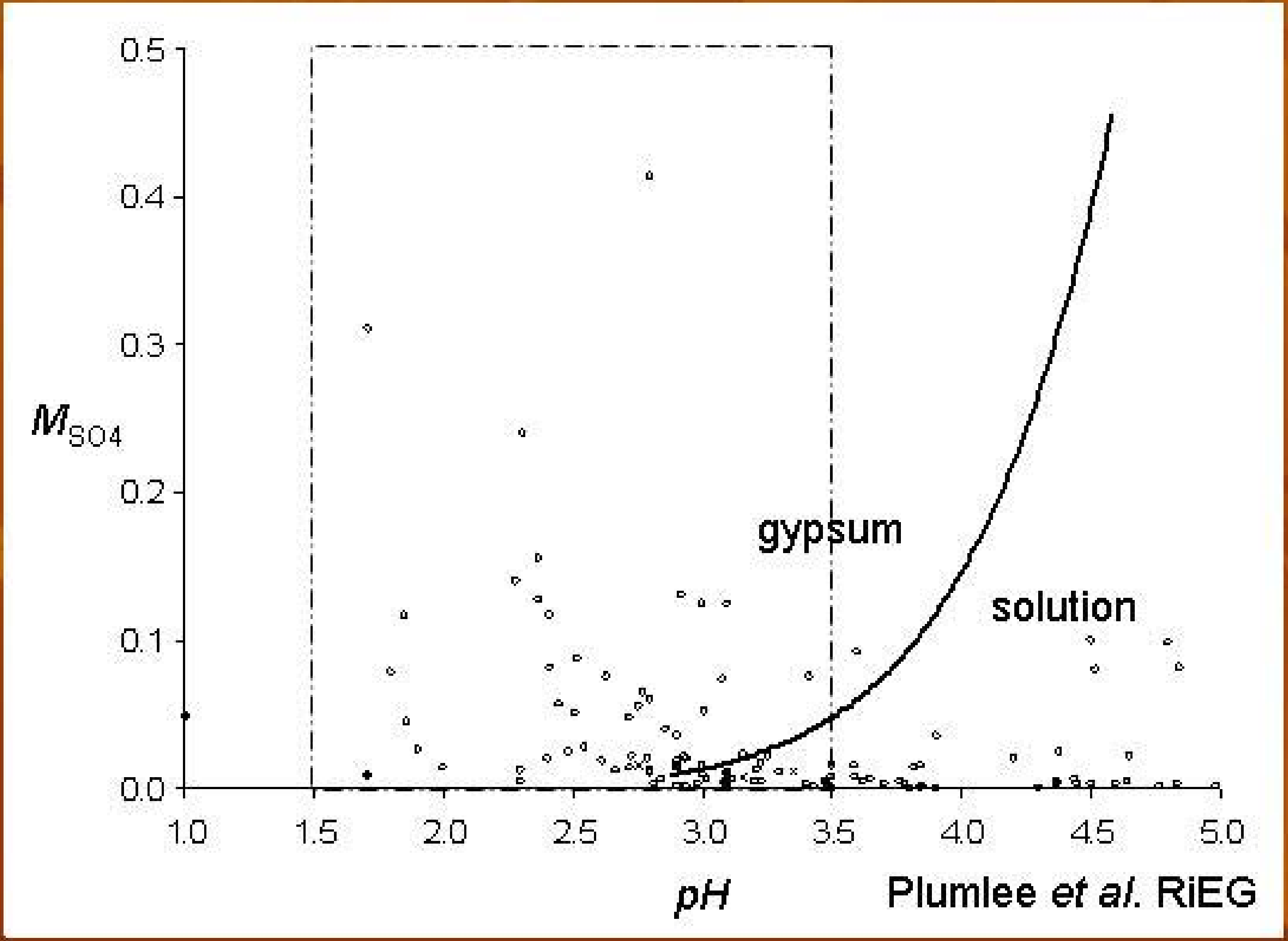
$$n_{Ca,T} = \sqrt{\frac{D C_B A_R}{f_{gyp} \phi V_M}}\, t^{1/2} = \boldsymbol{k t}^{1/2}$$

$$n_{Ca,T} = n_{Ca,L} + n_{Ca,gyp} = \boldsymbol{k t}^{1/2}$$

$$n_{Ca,L} = k t^{1/2} - n_{Ca,gyp}$$

Determine *k* empirically from the data

Equilibrium gypsum saturation as a function of M_{SO4} and pH



Suggestions for gypsum coating control

(1) Dilution of high sulfate solutions
(2) Use dolomite to neutralize AMD
(3) Poison surfaces with a surfactant

- Used laboratory experiments to determine the effect of pH, stirring and gypsum coatings on neutralization rates of calcite
- Scaled up the results using chemical engineering principles to apply them to the field and the design of optimal ALD