The effect of gypsum coatings and hydrodynamic factors on ALD performance

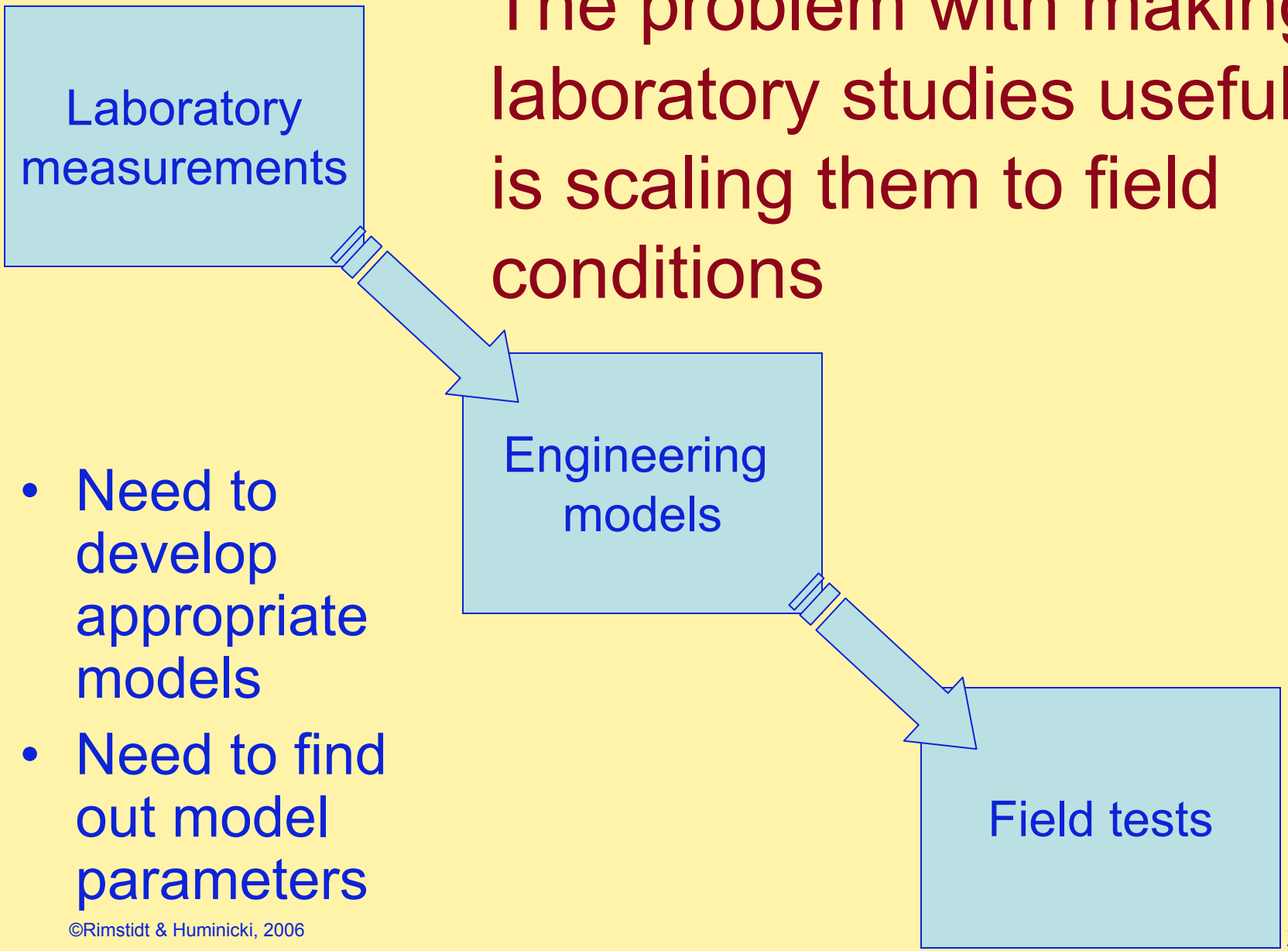
J. Donald Rimstidt

Danielle M.C. Huminicki

Department of Geosciences
Virginia Tech
Blacksburg VA 24061

DEPARTMENT OF geosciences AT VIRGINIA TECH

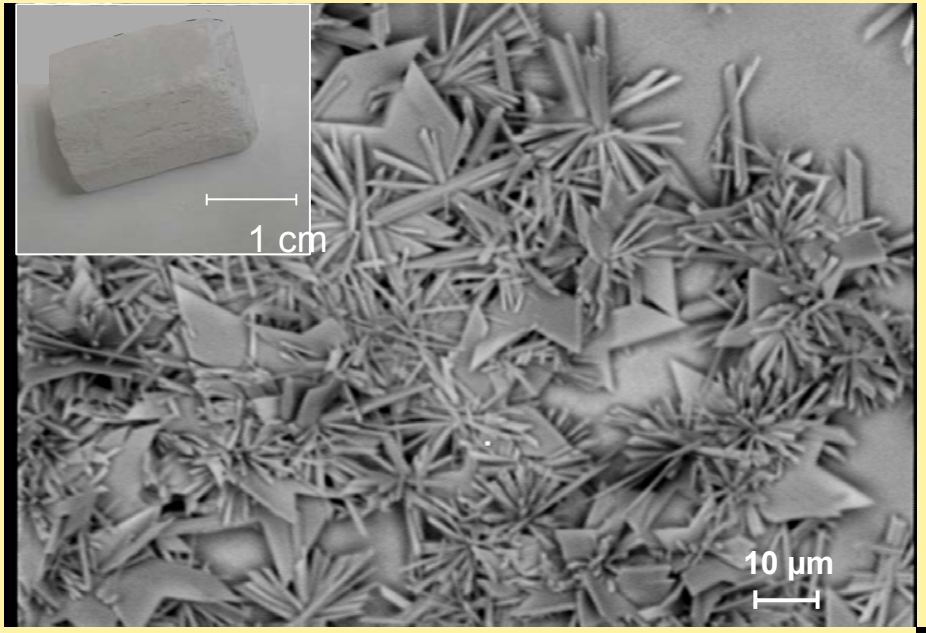
The problem with making laboratory studies useful is scaling them to field conditions



- Need to develop appropriate models
- Need to find out model parameters

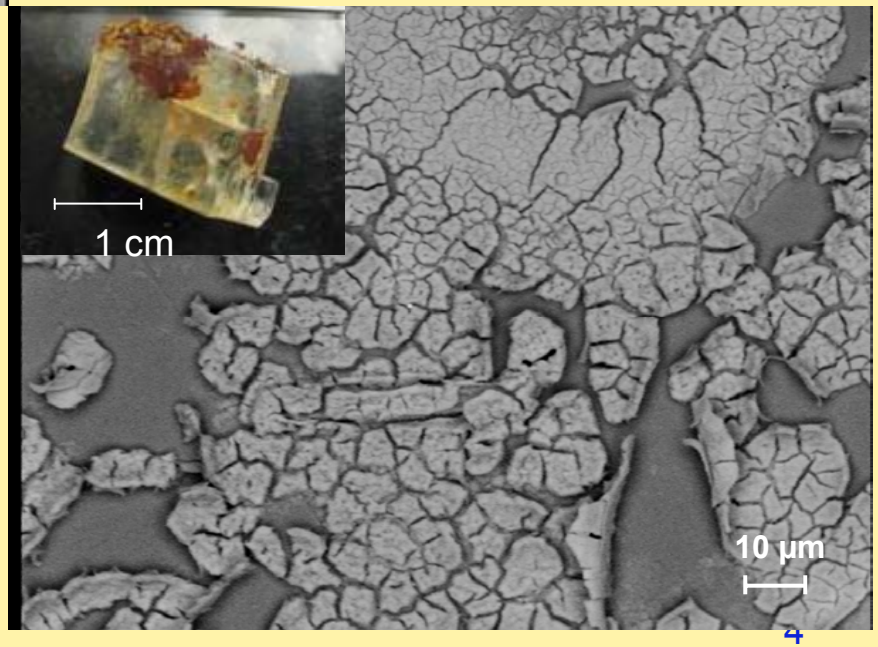
In this talk I will show how geochemical engineering principles can be used to evaluate the effect of:

- Gypsum coatings on ALD performance
- Hydrodynamics on ALD performance

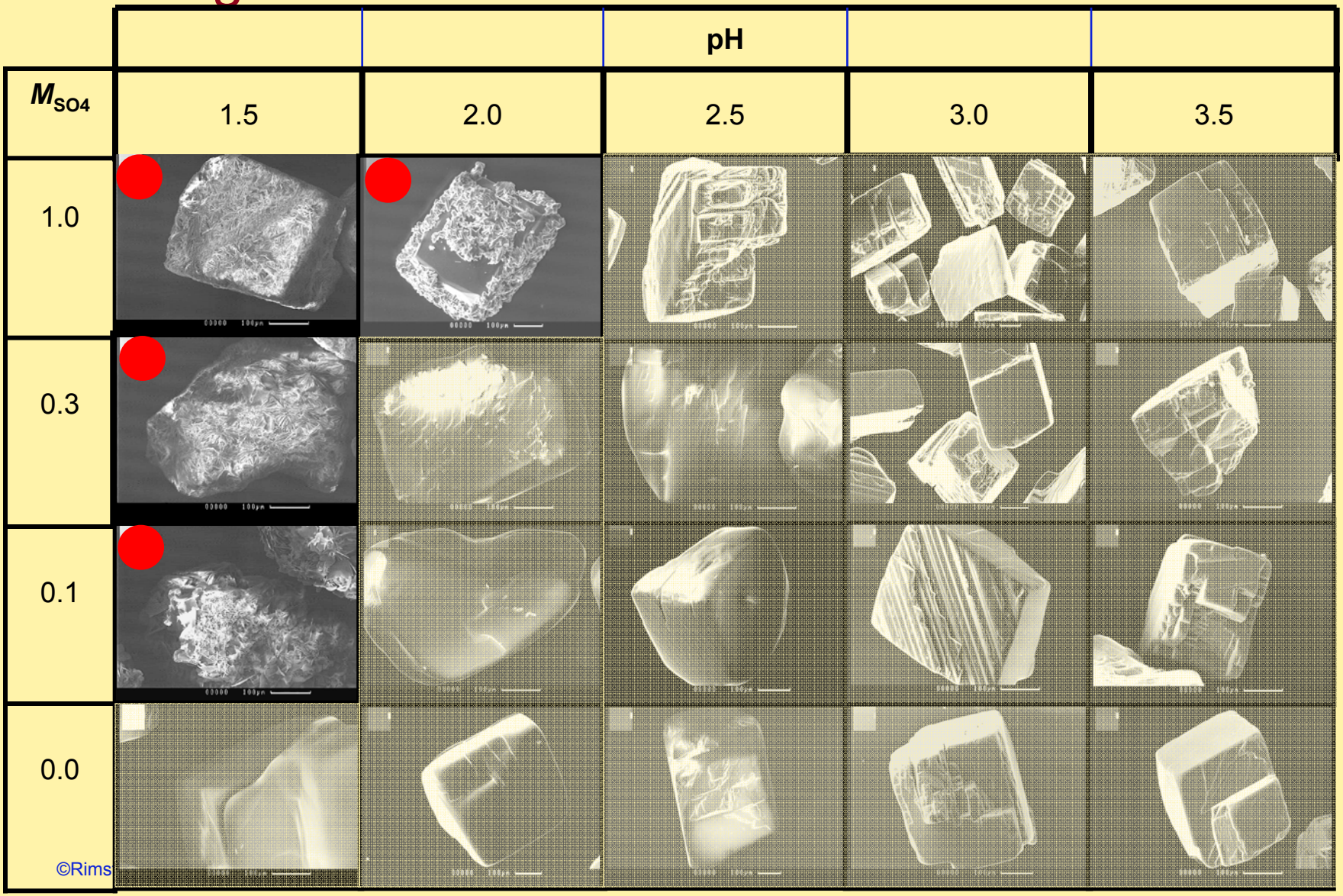


Gypsum coatings are strongly adherent so they are difficult to remove

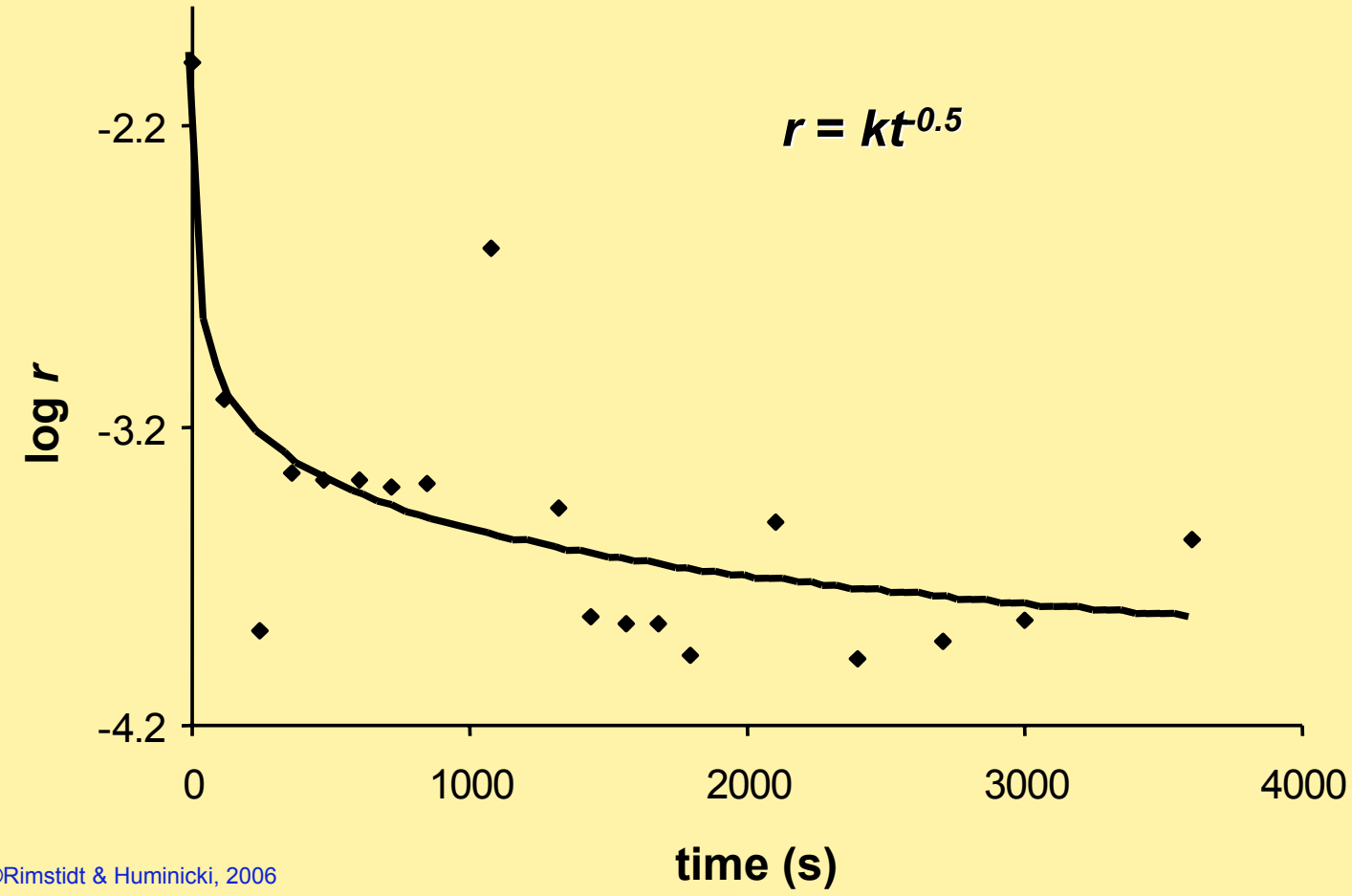
HFO coatings are not so they can be removed by flushing

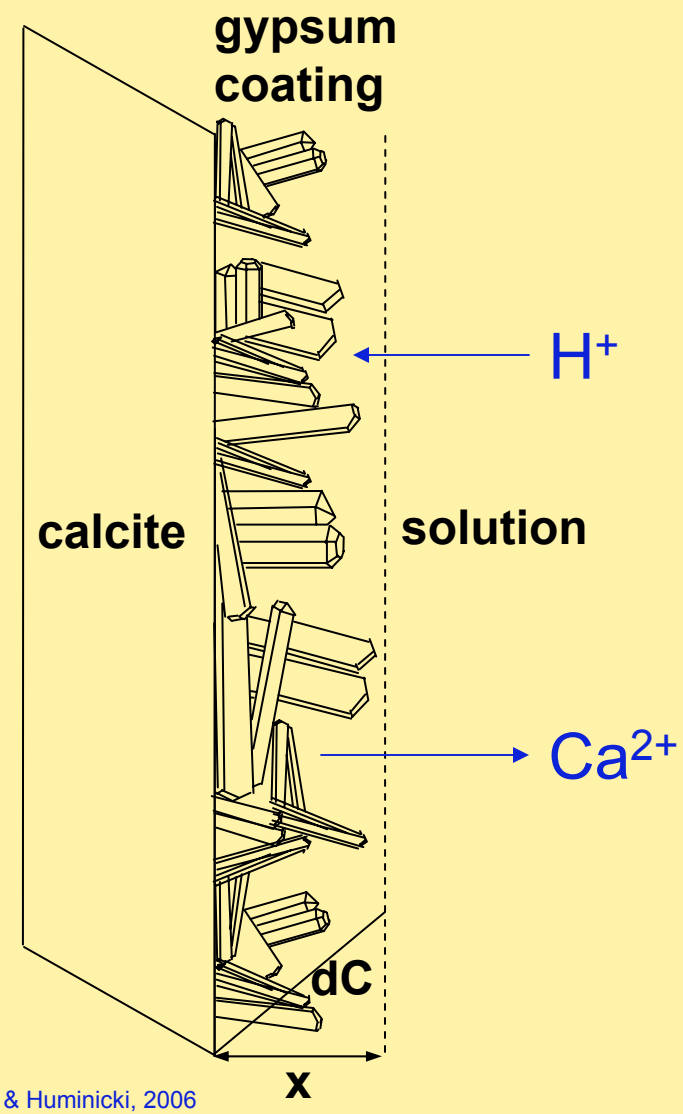


Gypsum coatings form at low pH and high sulfate concentrations



The gypsum coatings cause the calcite dissolution rate to decline over time





The rate declines because the gypsum coating acts as a barrier to hydrogen ion transport to the calcite surface

Fick's law of diffusion

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

Integrating Fick's first law using the appropriate boundary conditions gives us the number of moles of calcium released from the dissolving calcite as a function of time

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

The gypsum layer builds up as a function of $t^{1/2}$ so the rate declines as a function of $t^{1/2}$

The Ca is distributed between solution and the precipitating gypsum

$$n_{Ca,T} = n_{Ca,sol} + n_{Ca,gyp} = kt^{1/2}$$

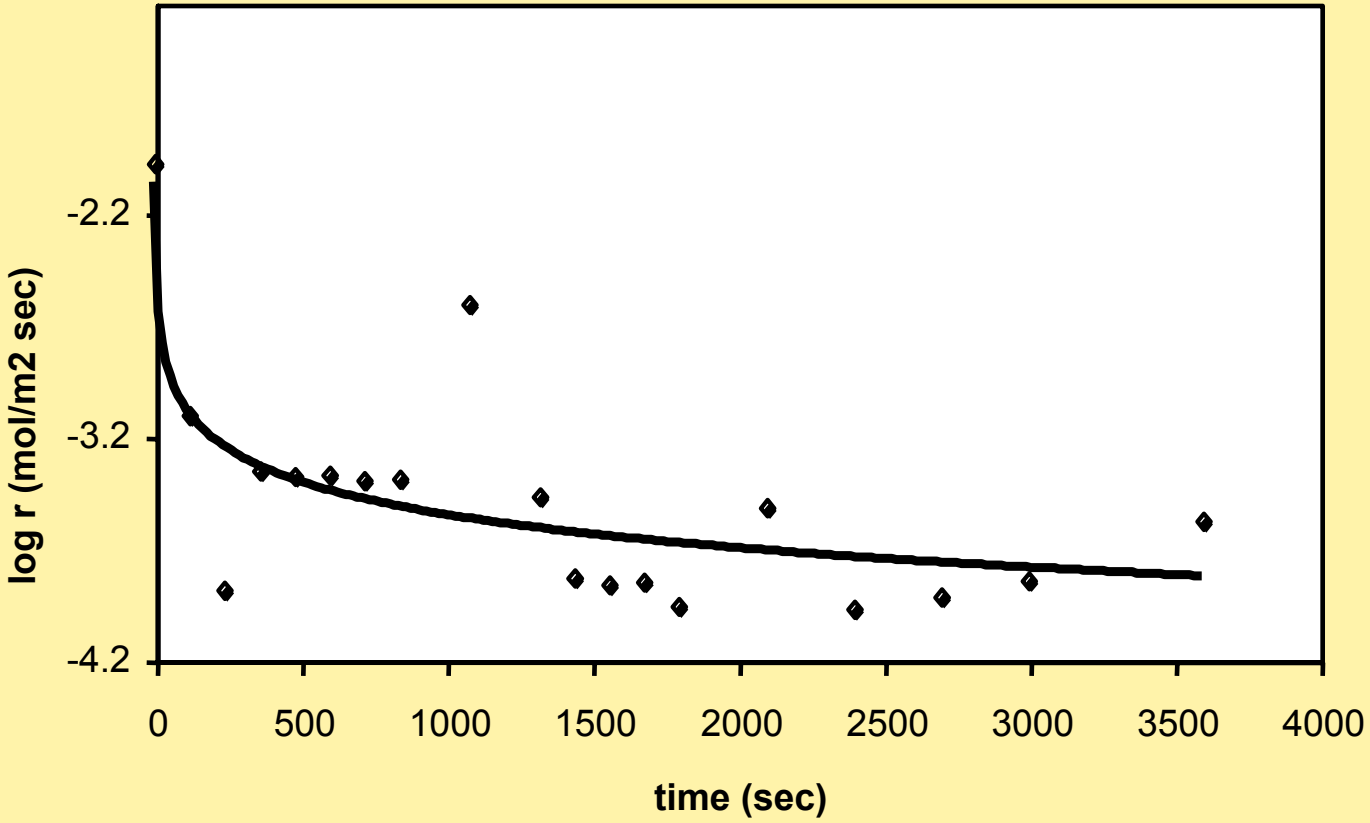
$$n_{Ca,sol} = kt^{1/2} - n_{Ca,gyp}$$

Determine *k* empirically from the data and then find *D* from *k*:

$$k = \sqrt{\frac{DC_B A_R}{f_{gyp}\phi V_M}}$$

H^+ diffusion coefficient in gypsum coating = 5.2×10^{-14} m^2/s
H^+ diffusion coefficient in seawater = 9.31×10^{-8} m^2/s

We tested the model by predicting the results of our experiments



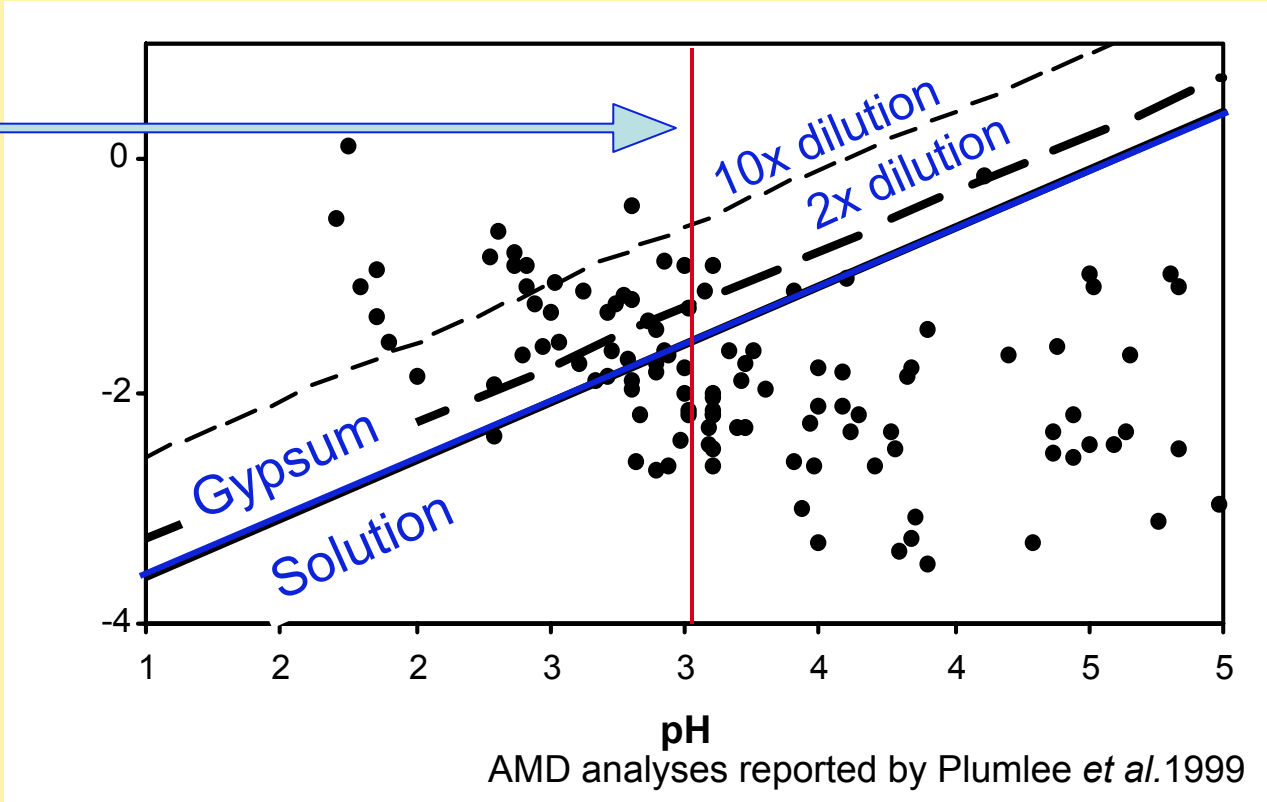
Gypsum coatings can be controlled by lowering the $(a_{Ca})(a_{SO4})$ activity product

- Sulfate activity can be lowered by diluting the solutions with water from non-AMD sources
- Calcium activity can be lowered by using dolomite to neutralize the acidity

Neutralization of AMD by calcite releases 1 mole of Ca per 2 moles of H^+ consumed so we can estimate the ($a_{Ca}a_{SO}$) activity product from pH and m_{SO4}

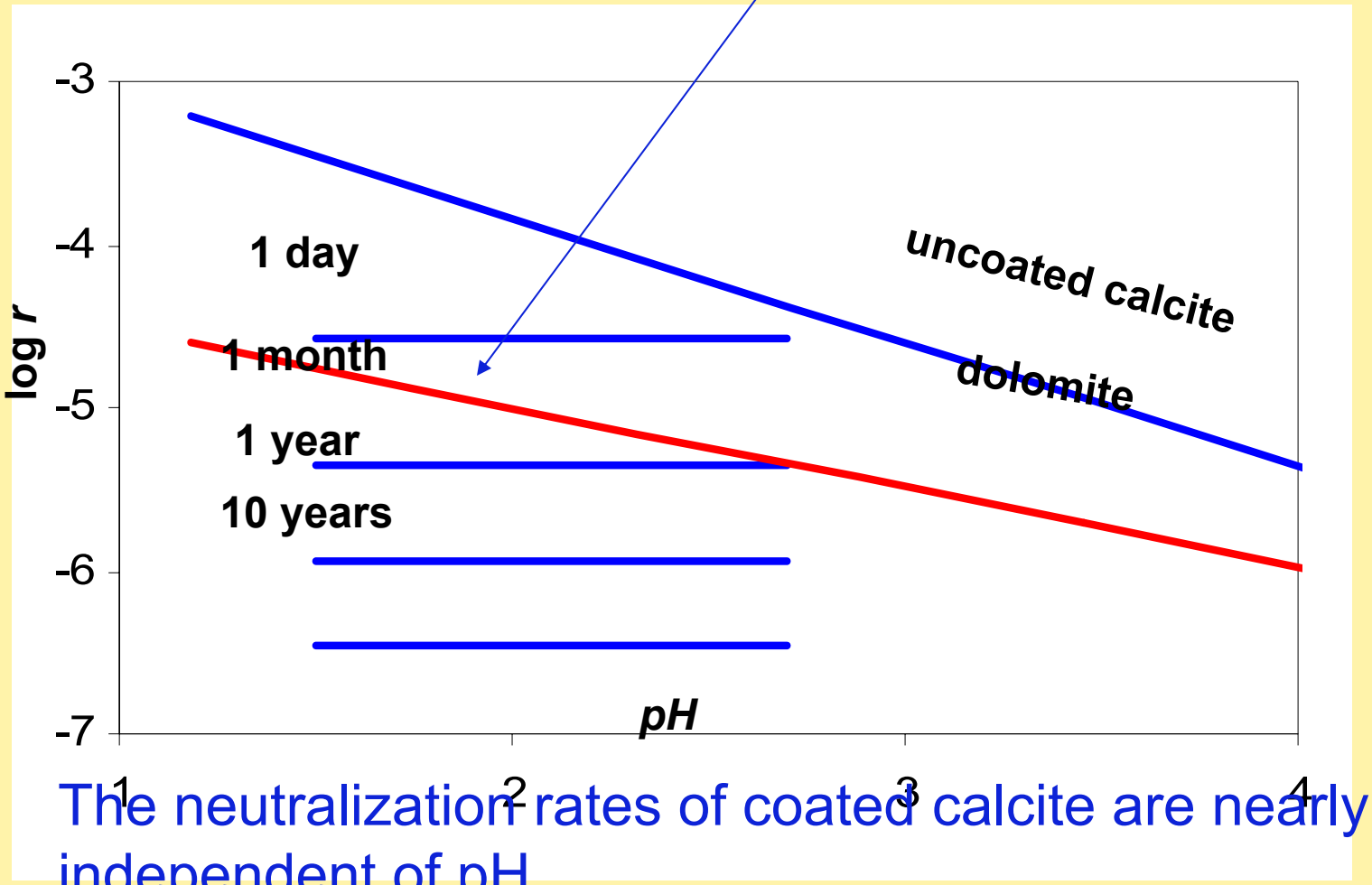
Diluting the solution can avoid gypsum formation in some cases

Gypsum mostly forms at pH<3



AMD analyses reported by Plumlee *et al.*1999

Rate of neutralization by dolomite is greater than calcite with gypsum coatings after ~1 month of reaction

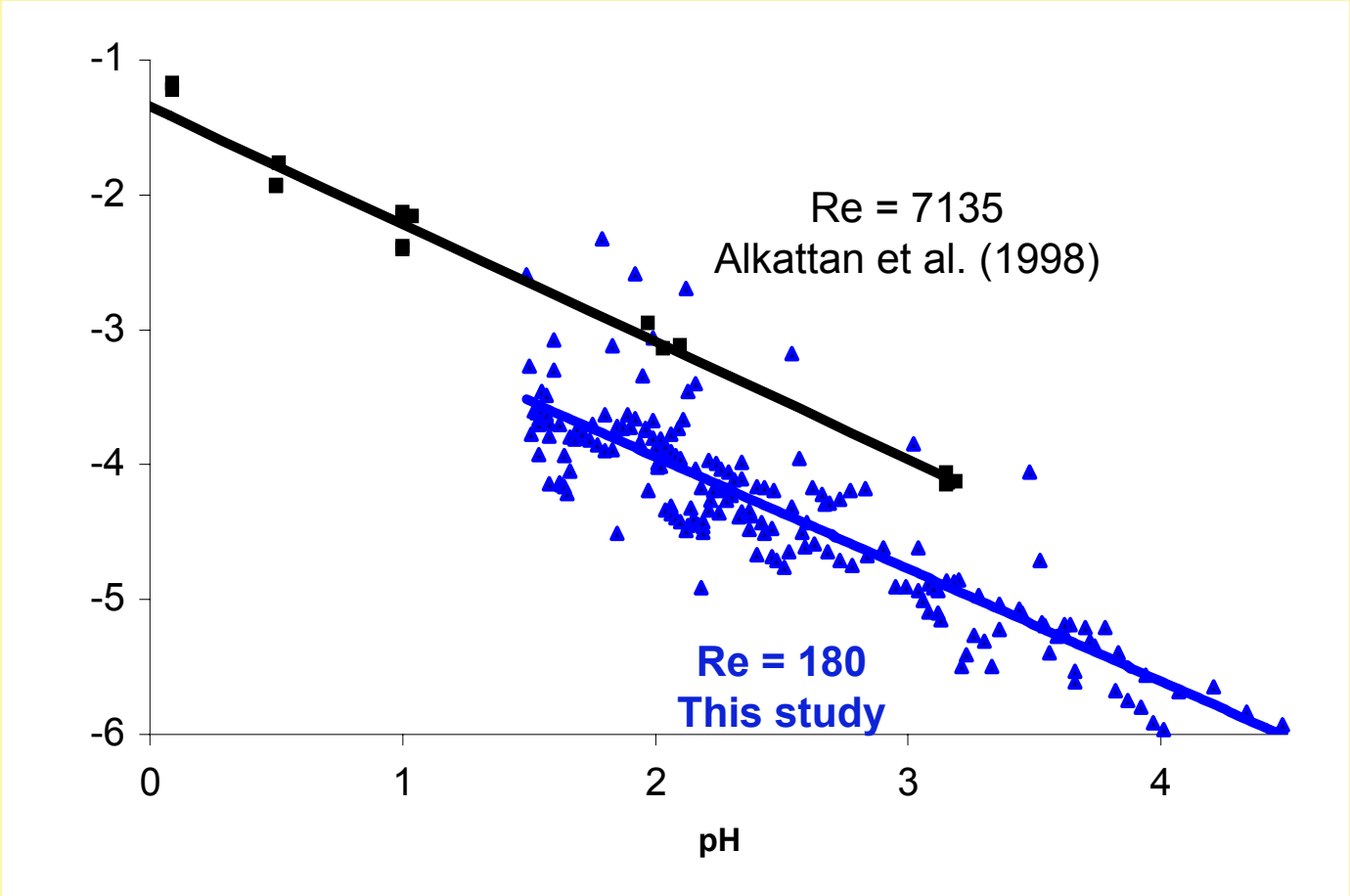


The neutralization rates of coated calcite are nearly independent of pH

Most of our experiments showed no gypsum coating development and the rates were controlled by pH

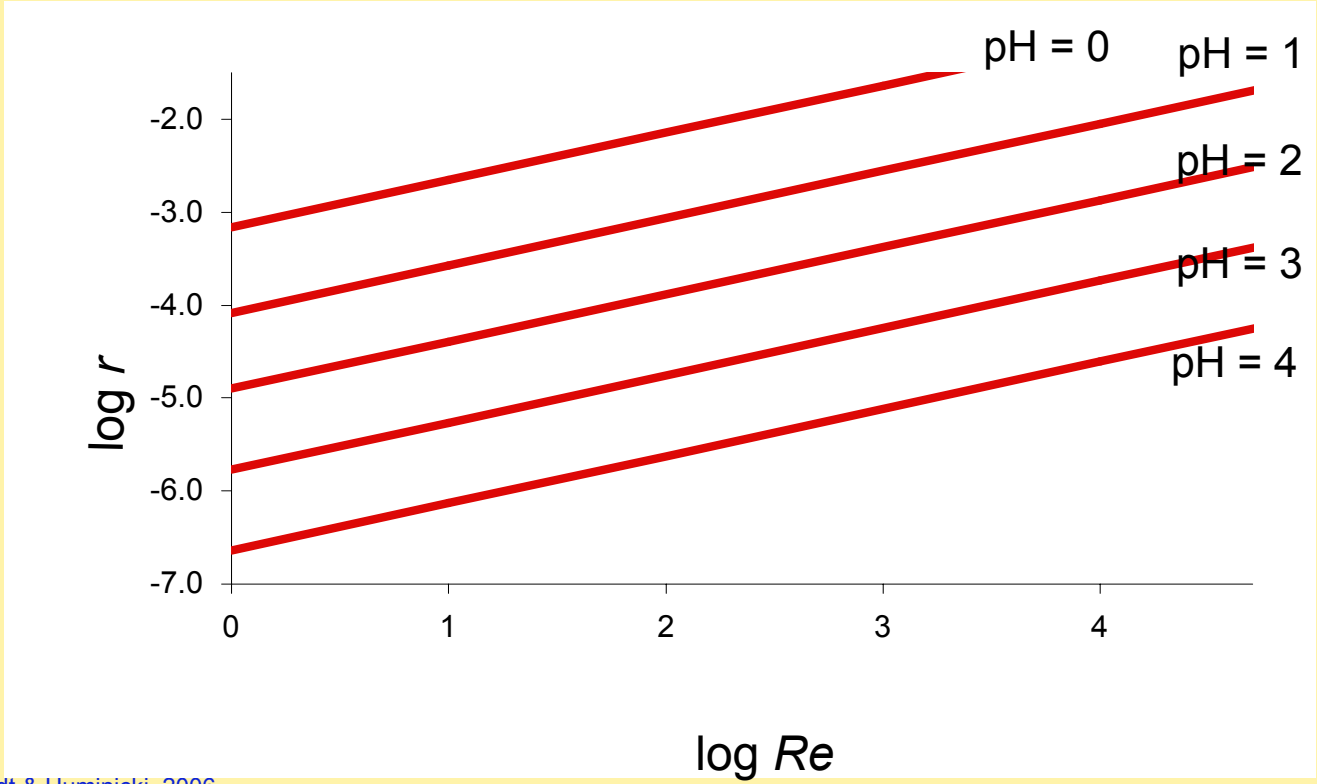
Experiment	Rate law	log *k*
no sulfate	$r = k a_{H+}^{0.83}$	-2.28
sulfate no coatings	$r = k a_{H+}^{0.87}$	-1.84
coatings	$r = k t^{-0.5}$	-1.96

Calcite dissolution rates are also controlled by Reynolds number



We fit calcite dissolution rates as a function of pH and Re

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



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

log *r* = 0.51 log *Re* – 0.87*pH* – 3.31

$$Re = qD/\upsilon$$

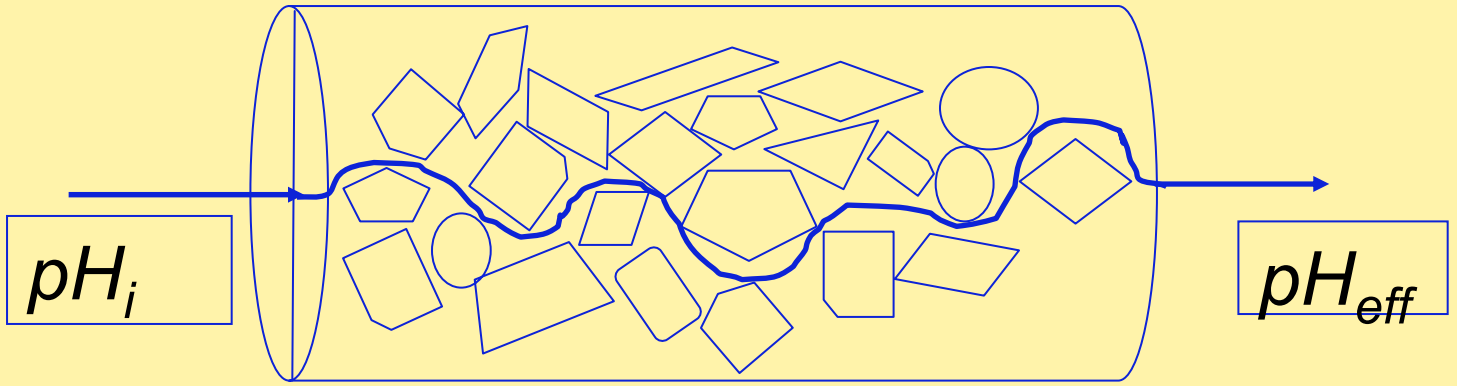
q – Darcy velocity (cm/sec)

D – pore diameter (cm)

υ – kinematic viscosity (cm^2/sec)

log *r* = 0.51 log qD/υ – 0.87*pH* – 3.31

We can model ALDs as ideal plug flow reactors

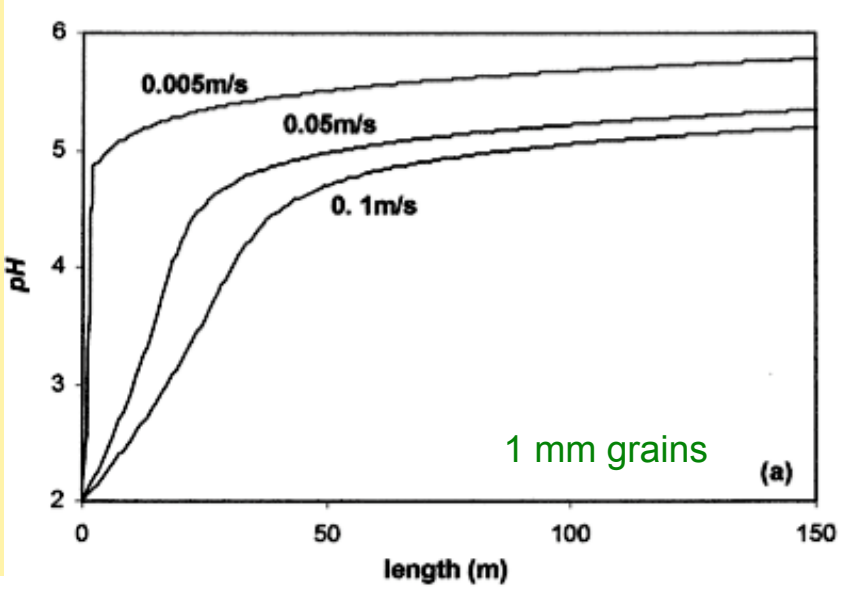


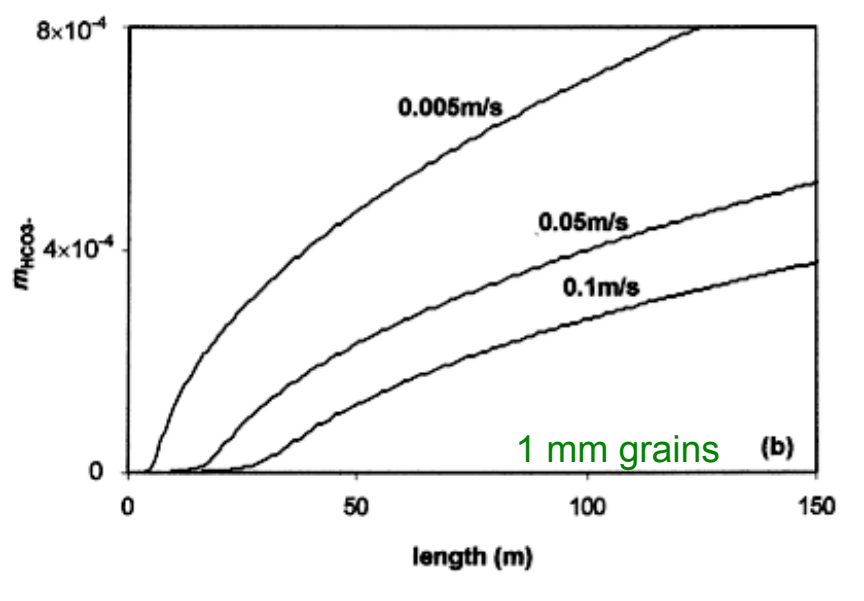
ALD = PFR

Governing equations

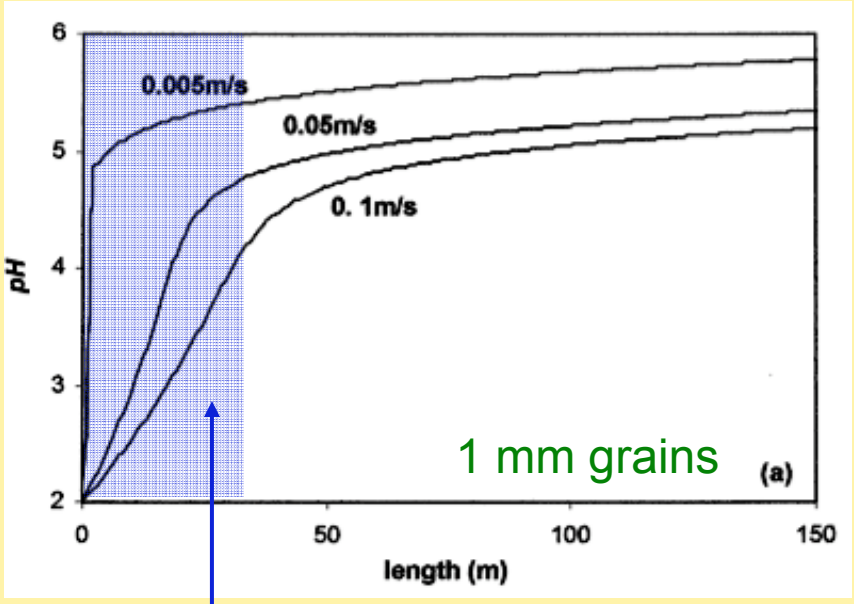
Integrated rate law	$\left(\frac{m}{m_0}\right)^{-n+1} = \frac{-kt(-n+1)}{m_0^{-n+1}} + 1$
Residence time	$t = \frac{V_P \phi}{Q}$
Mass flow rate, m^3/sec	$Q = qA_c$
Reactor volume	$V_P = (A_c)(l)$
k = f(Re)	$\log k = 0.51 \log \mathrm{Re} - 3.31$
Re = f(q, D)	$\mathrm{Re} = \frac{qD}{\upsilon}$

Low Darcy velocity leads to long contact times resulting in neutralization over a shorter reactor length





Low Darcy velocity means low through-put so larger installations are required

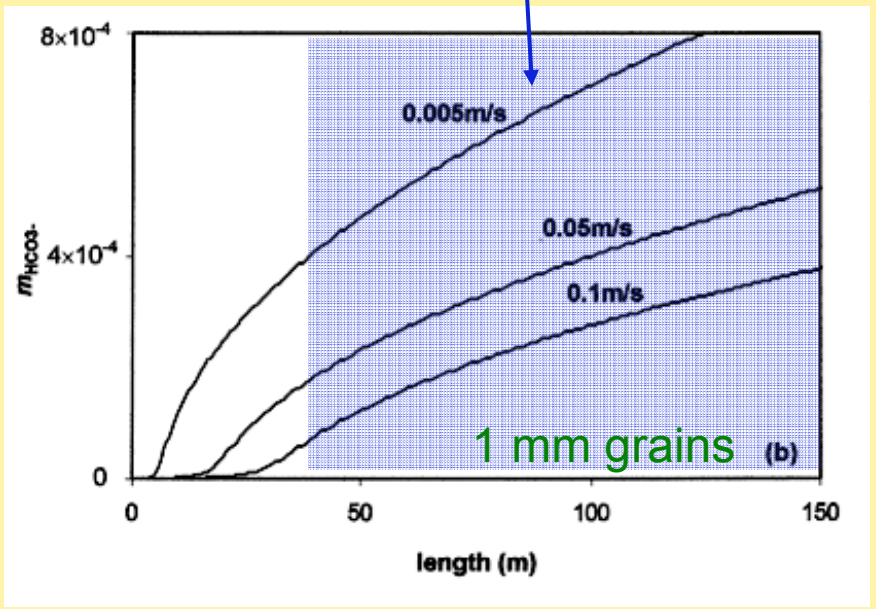


H^+ neutralization

H_2CO_3 is converted to alkalinity by the reaction:

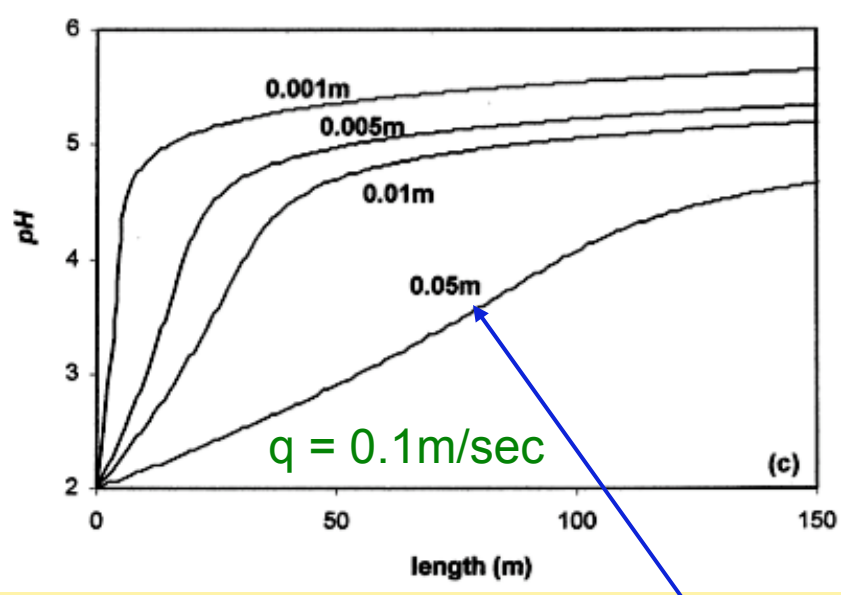
$H_2CO_3 + CaCO_3 = Ca^{2+} + 2HCO_3^-$

Alkalinity generation



H^+ is neutralized by the reaction:

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



Small grains have large surface areas so they neutralize acid more rapidly

Grain size

Small grains have small pores that clog more easily