Fourth Annual Conference on Carbon Capture & Sequestration

Developing Potential Paths Forward Based on the Knowledge, Science and Experience to Date

Advanced Conversion/Capture Concepts

Accelerated cation release during non-steady state dissolution of Mg-silicates:

Implications for mine tailings and sequestration of CO_2

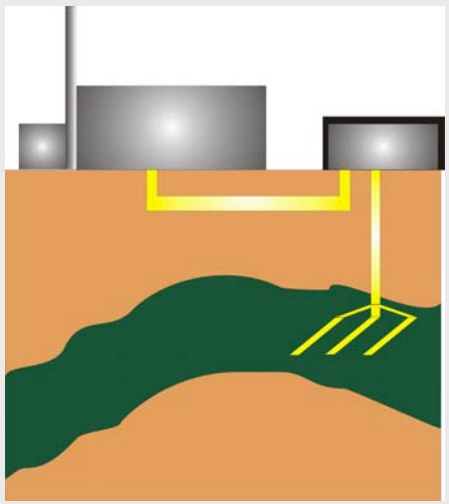
James Thom & Greg Dipple

May 2-5, 2005, Hilton Alexandria Mark Center, Alexandria Virginia

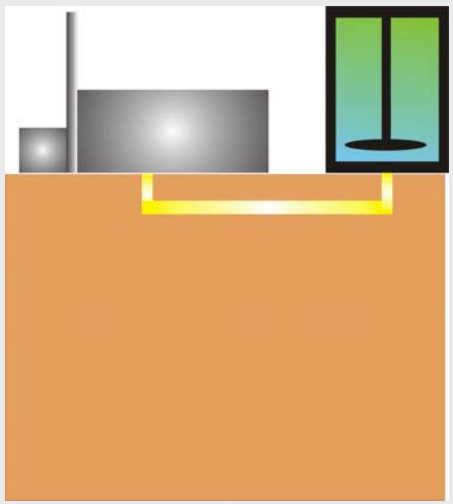
Mineral Sequestration

- Fixation of carbon dioxide in carbonate minerals brought via dissolution of silicate minerals

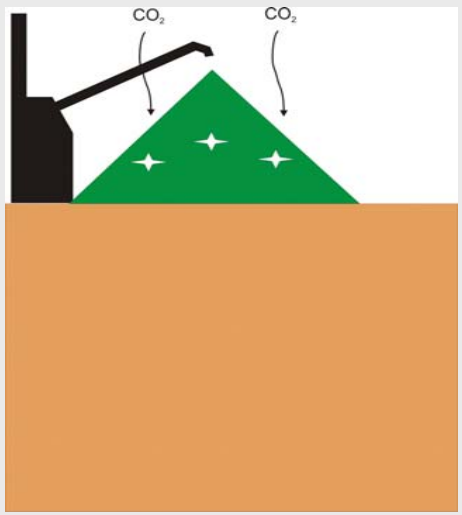
$$Mg_3Si_2O_5(OH)_4 + 3CO_2 = 3MgCO_3 + 2SiO_2 + 2H_2O$$



Ultramafic Aquifers



Industrial Reactors

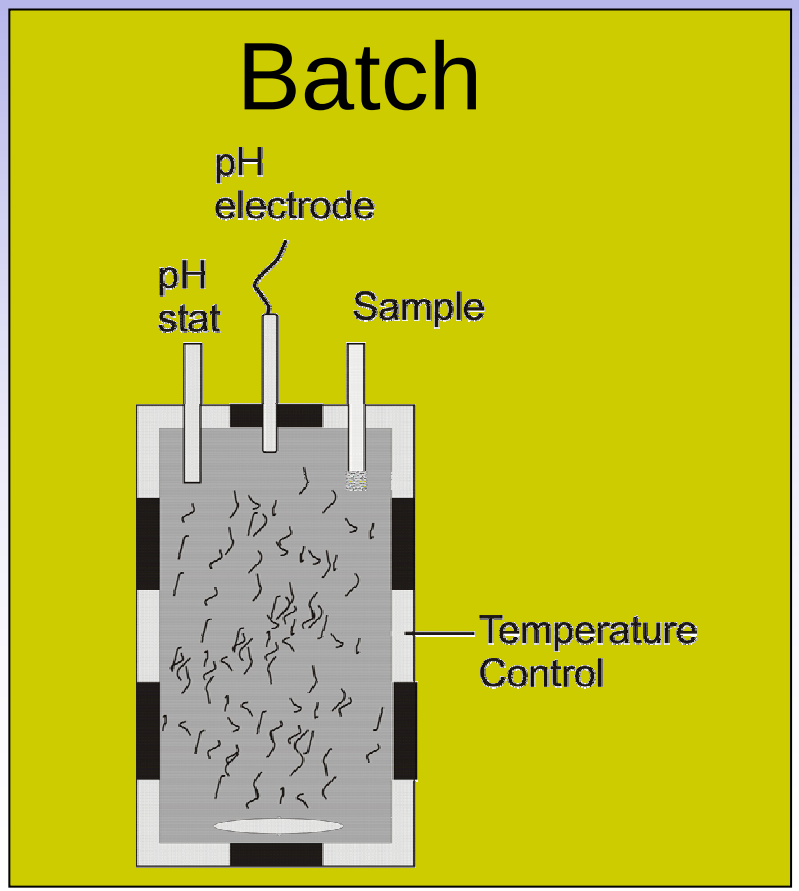


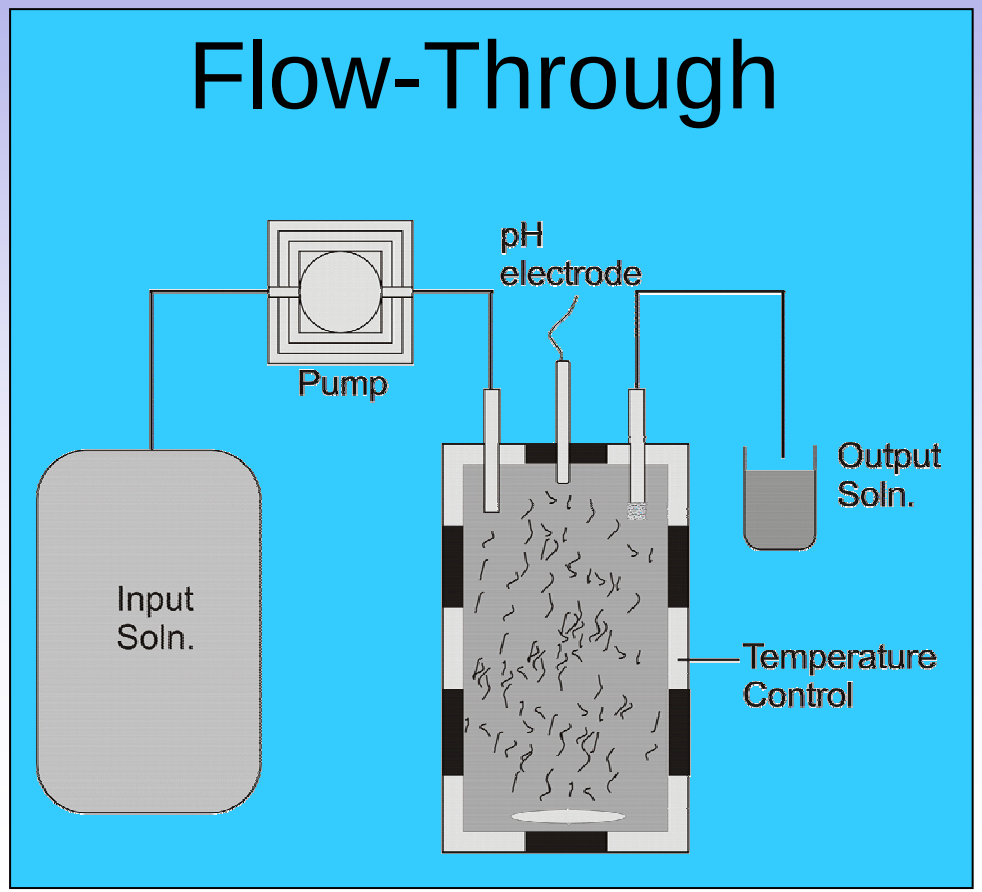
Mine Tailings

Greenhouse Gas Fixation within Mine Tailings

Magnesium Flux

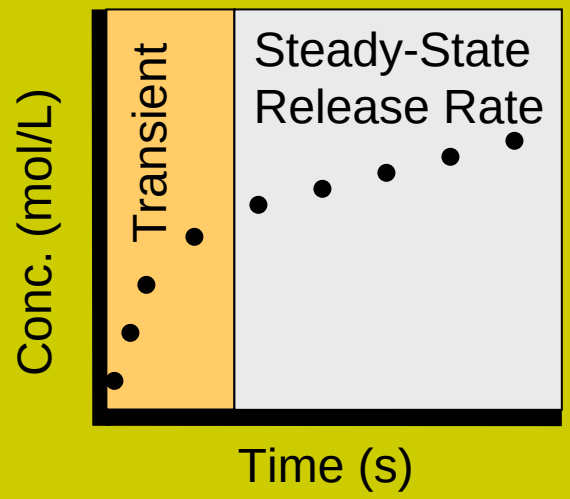
- Rate dictated by cation (Mg) flux: commonly adopted rate laws are derived from laboratory bench top experiments





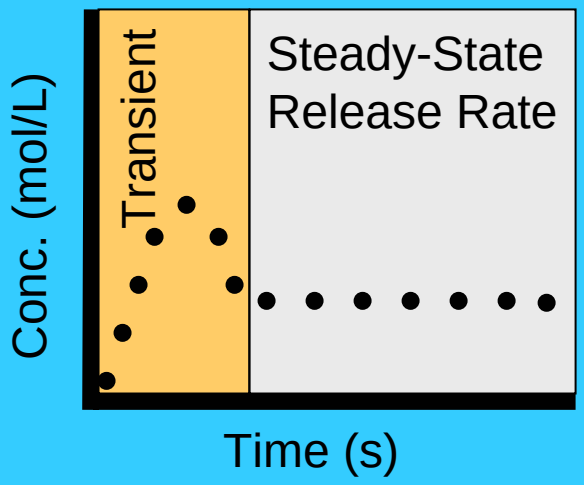
Typical Data

Batch



$$F_C = \frac{\partial C_{out}}{\partial t} = R$$

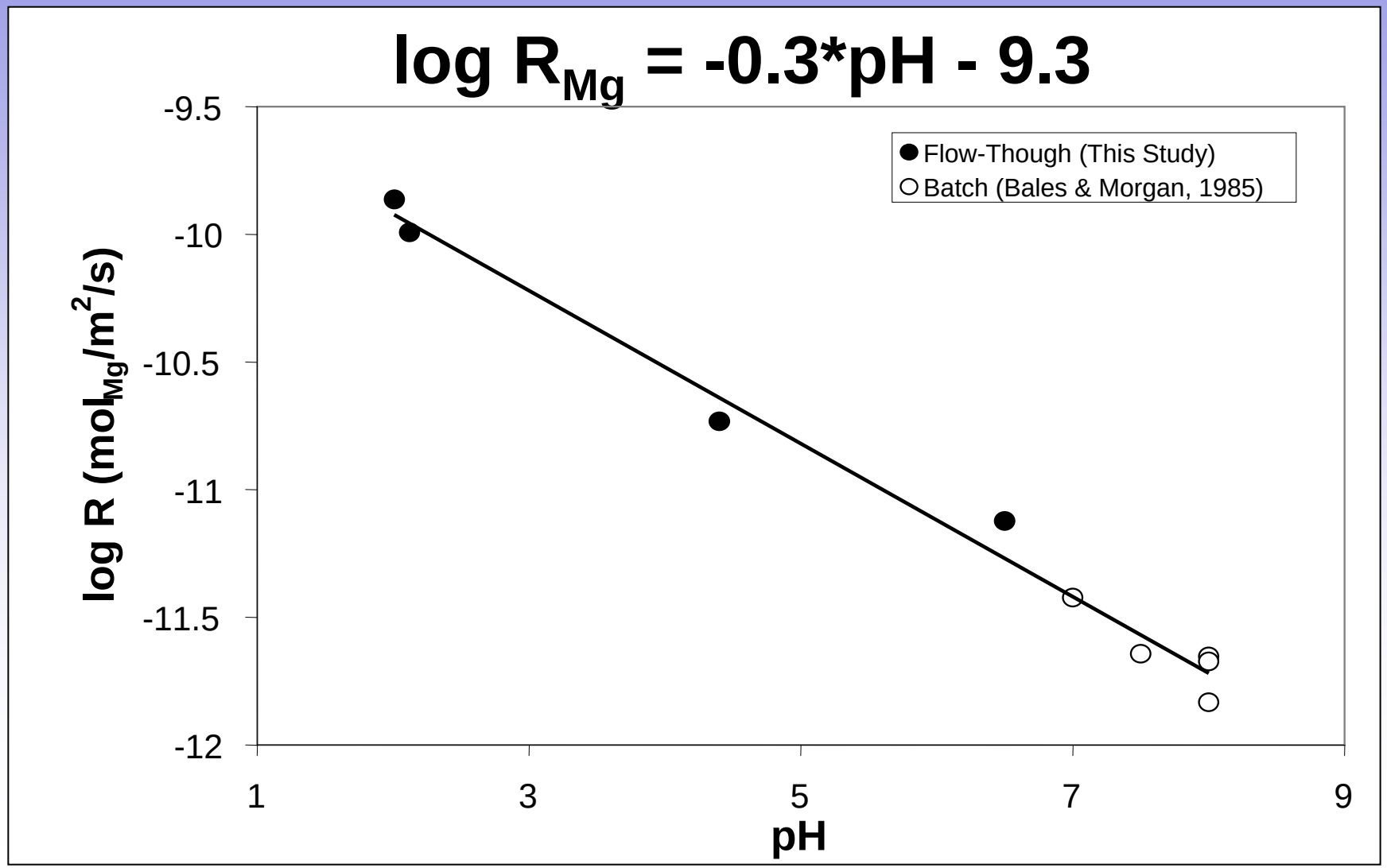
Flow-Through



$$F_C = \frac{\partial C_{out}}{\partial t} = R + \frac{C_{in}}{\tau} - \frac{C_{out}}{\tau}$$

Early stage transient dissolution explained as a sample preparation artifact

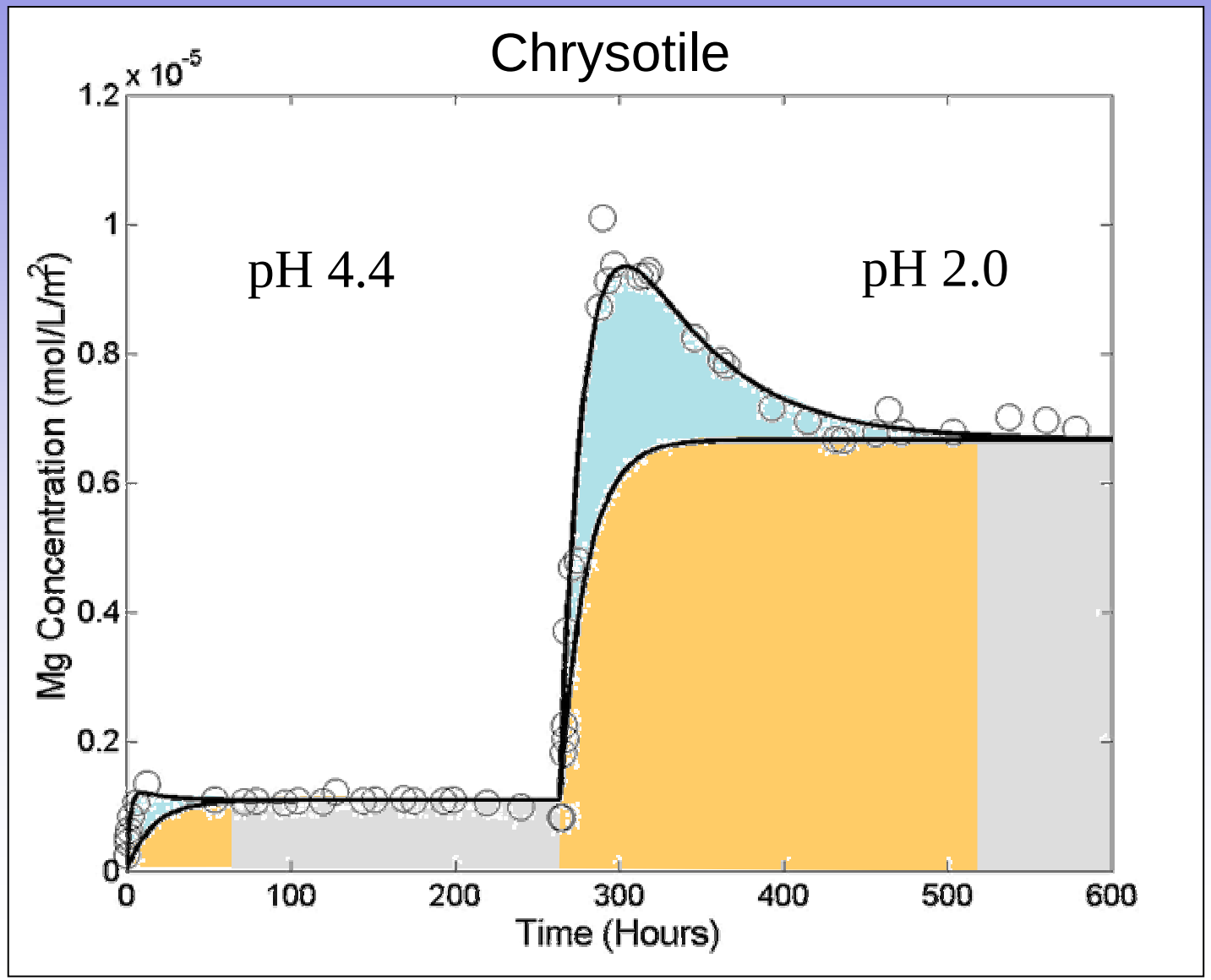
Chrysotile Steady-State Mg-Flux



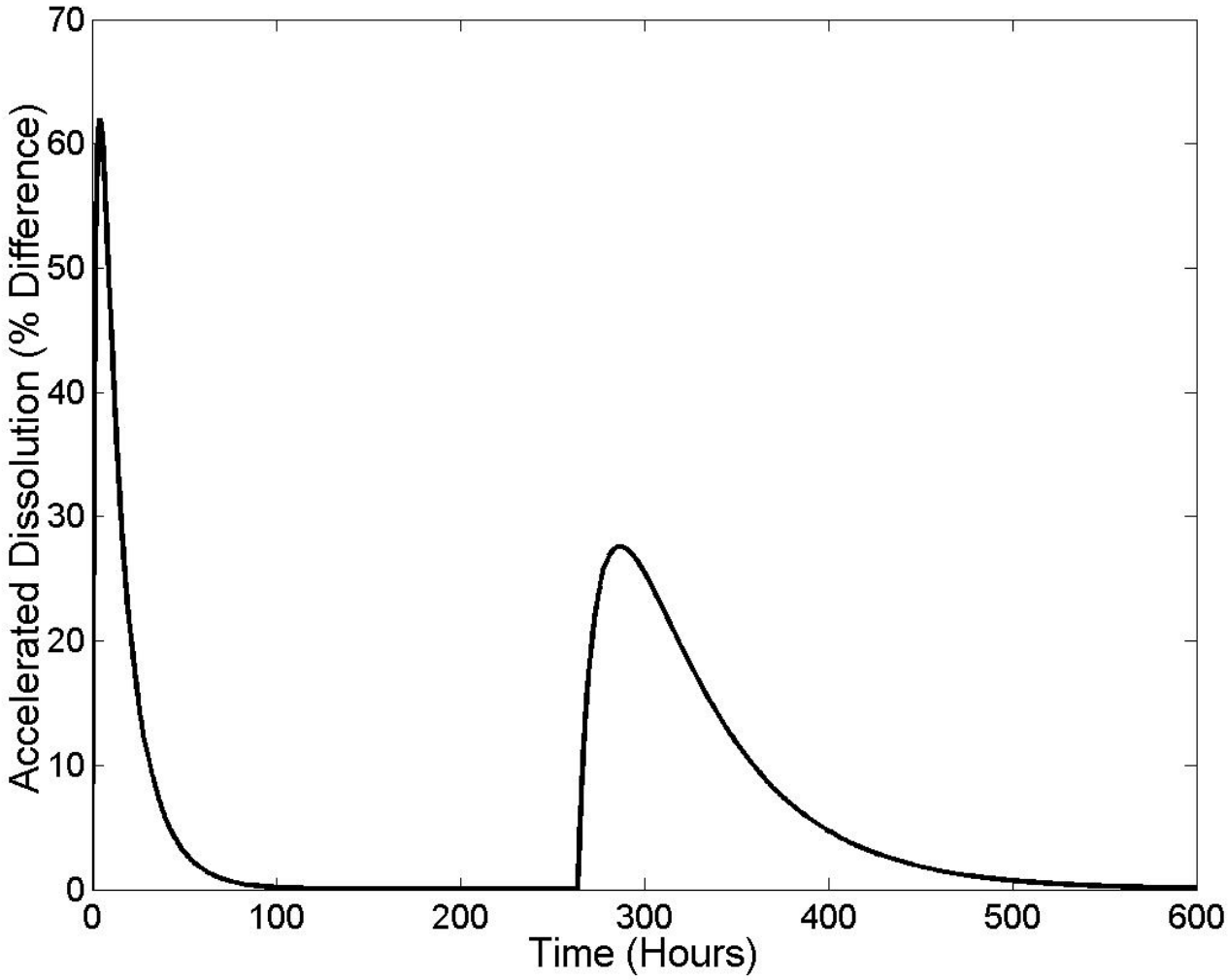
Non-Steady-State Rate Laws

- Samson & Eggleston (1998, 2000) proposed that transient dissolution reflects inherent surface process, not preparation artifacts.
- Transient dissolution is inherent property that is predictable, reproducible and can ***accelerate cation release.***
- Transients may result from changes in:
  - solution composition
  - pH
  - Temperature
  - And other external forcings

pH-Jump Experiment



Accelerated Dissolution



Equals ~45 Extra Hours

Modeled Dissolution Responses

Zeroth Order Reaction + First Order Transient
Single Pass Flow Thorugh

$$F_C = \frac{\partial C_{out}}{\partial t} = R + k_{C_{ex}} C_{ex,o} e^{-k_{C_{ex}} t} + \frac{C_{in}}{\tau} - \frac{C_{out}}{\tau}$$

Integrating the Differential Equation*

$$C_{out} = \tau R(1 - e^{-t/\tau})$$

$$C_{out} = \frac{k_{C_{ex}} C_{ex,o} \tau}{1 - k_{C_{ex}} \tau} \left[e^{-k_{C_{ex}} t} - e^{-t/\tau} \right]$$

Steady-State*

$$C_{out} = \tau R$$

pH-Jump Experiment

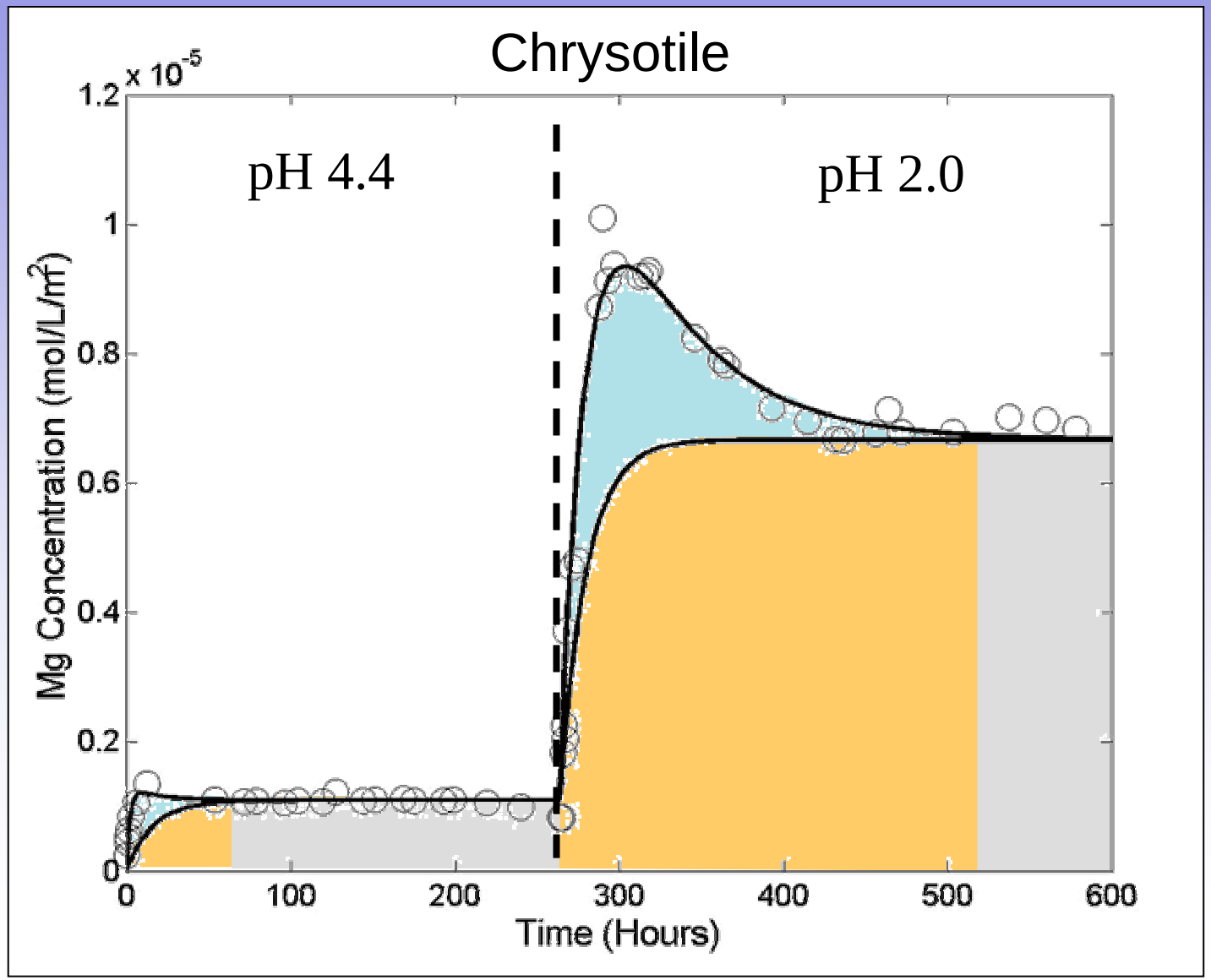
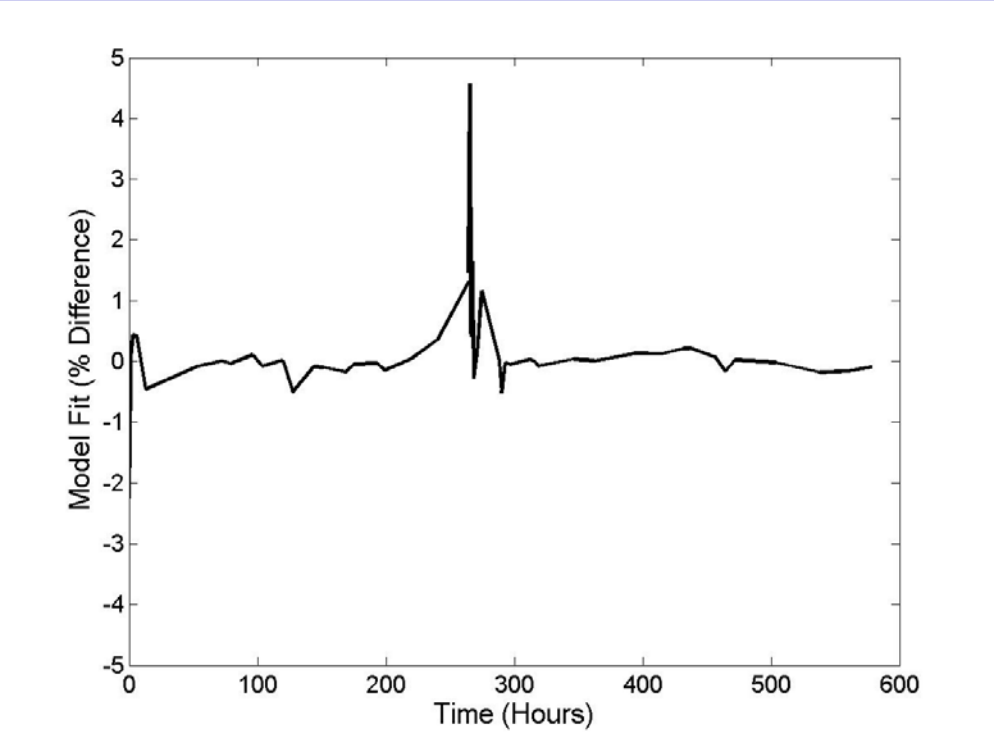
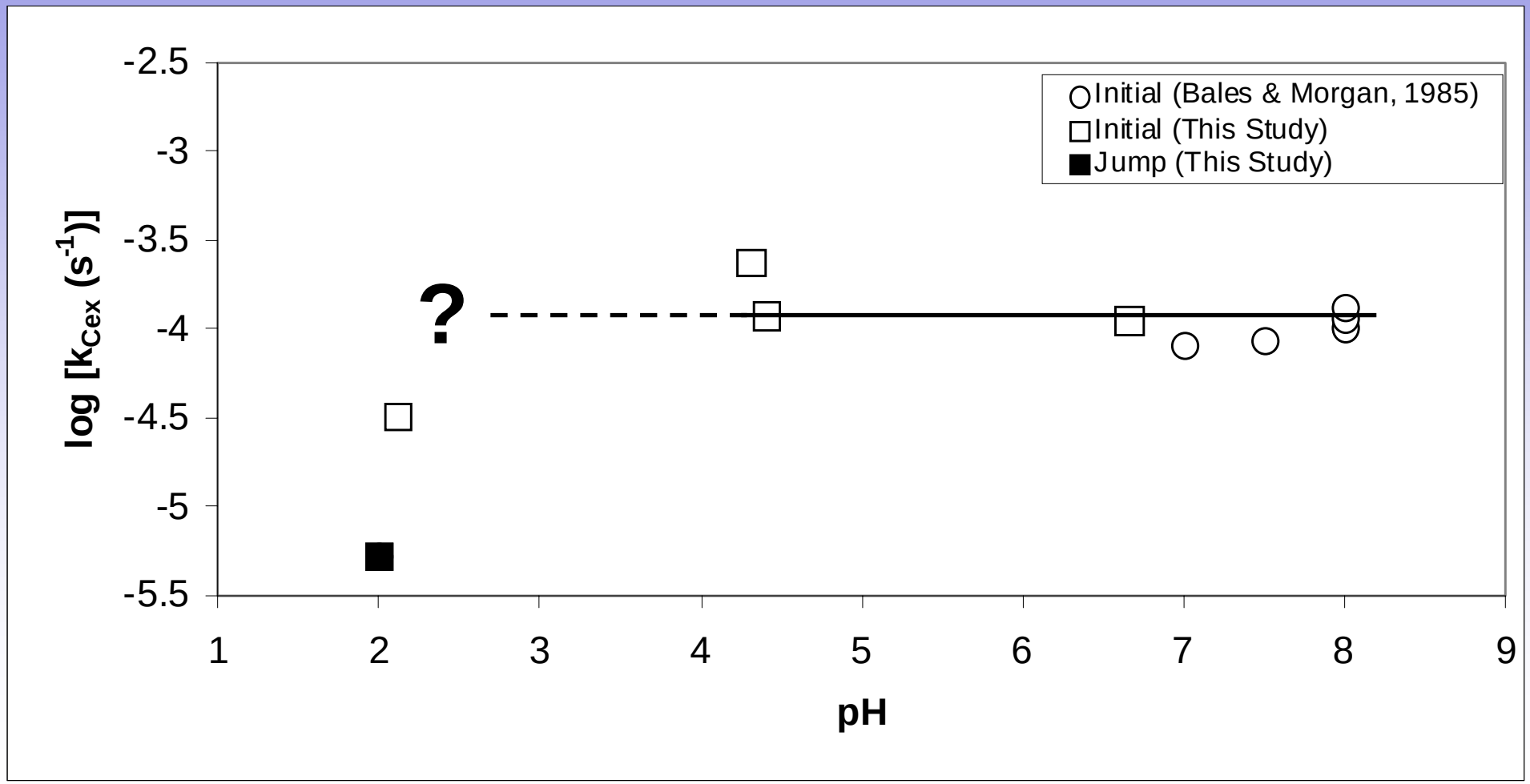


Table of Fit Coefficients

Steady-State pH	$[C_{ex}]_o$ $(mol \cdot m^{-2})$	k_{Cex} (s^{-1})	R $(mol \cdot m^{-2} \cdot s^{-1})$
4.4	-5.93	-3.93	-10.73
2.0	-4.73	-5.28	-9.94



First-Order Transient Rate Constants



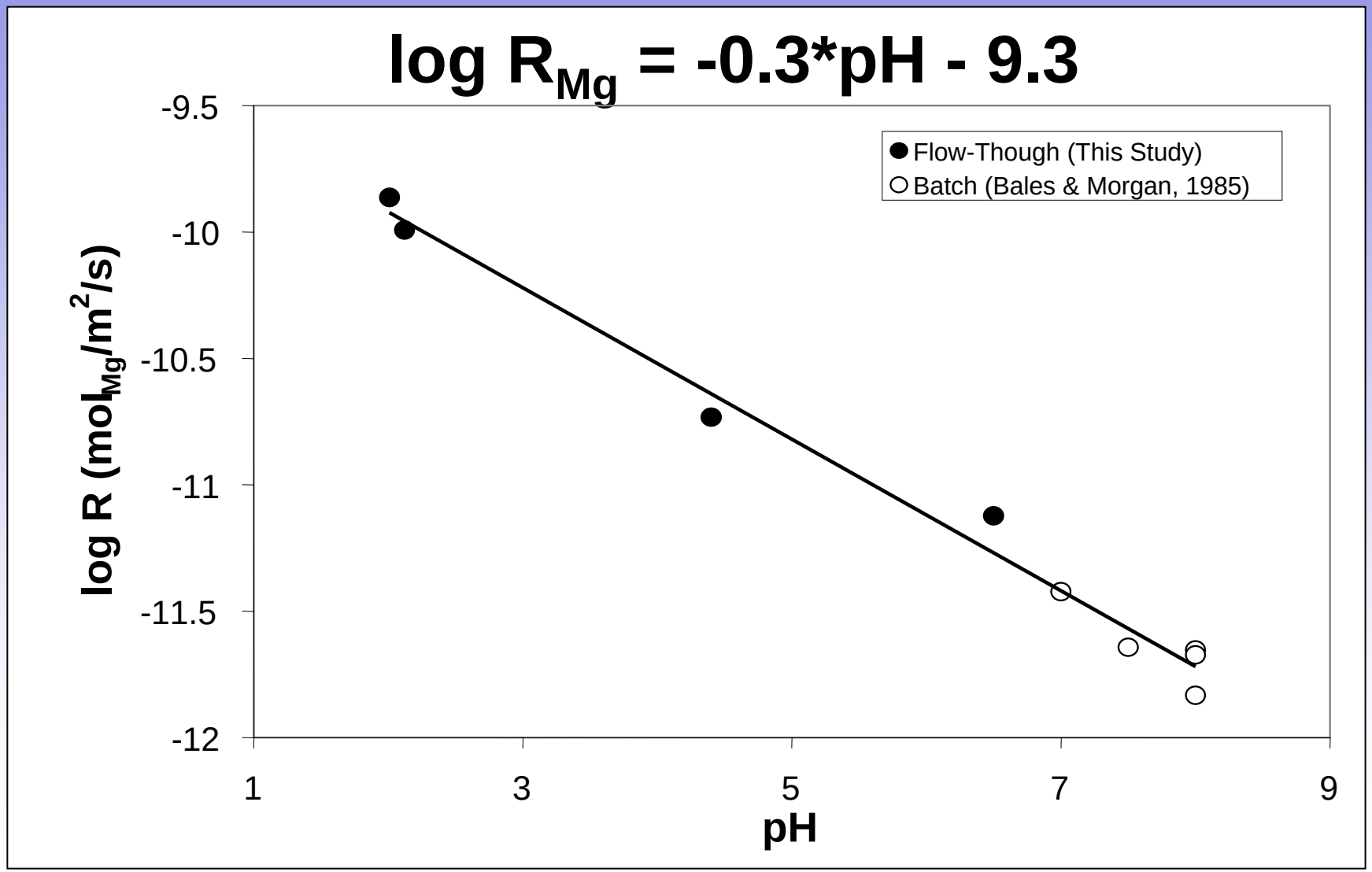
Conclusions

- The steady-state Mg flux for chrysotile is:

$$\mathbf{\log R(mol_{Mg}/m^2/s) = -0.3*pH - 9.3}$$

- Transient surface effects are reproducible and predictable and accelerate cation release
- pH cycling can increase cation release rates over steady-state conditions.
- We are building a new rate law for the transient-non-steady-state dissolution phenomena, initial results encouraging

Chrysotile Steady-State Mg-Flux



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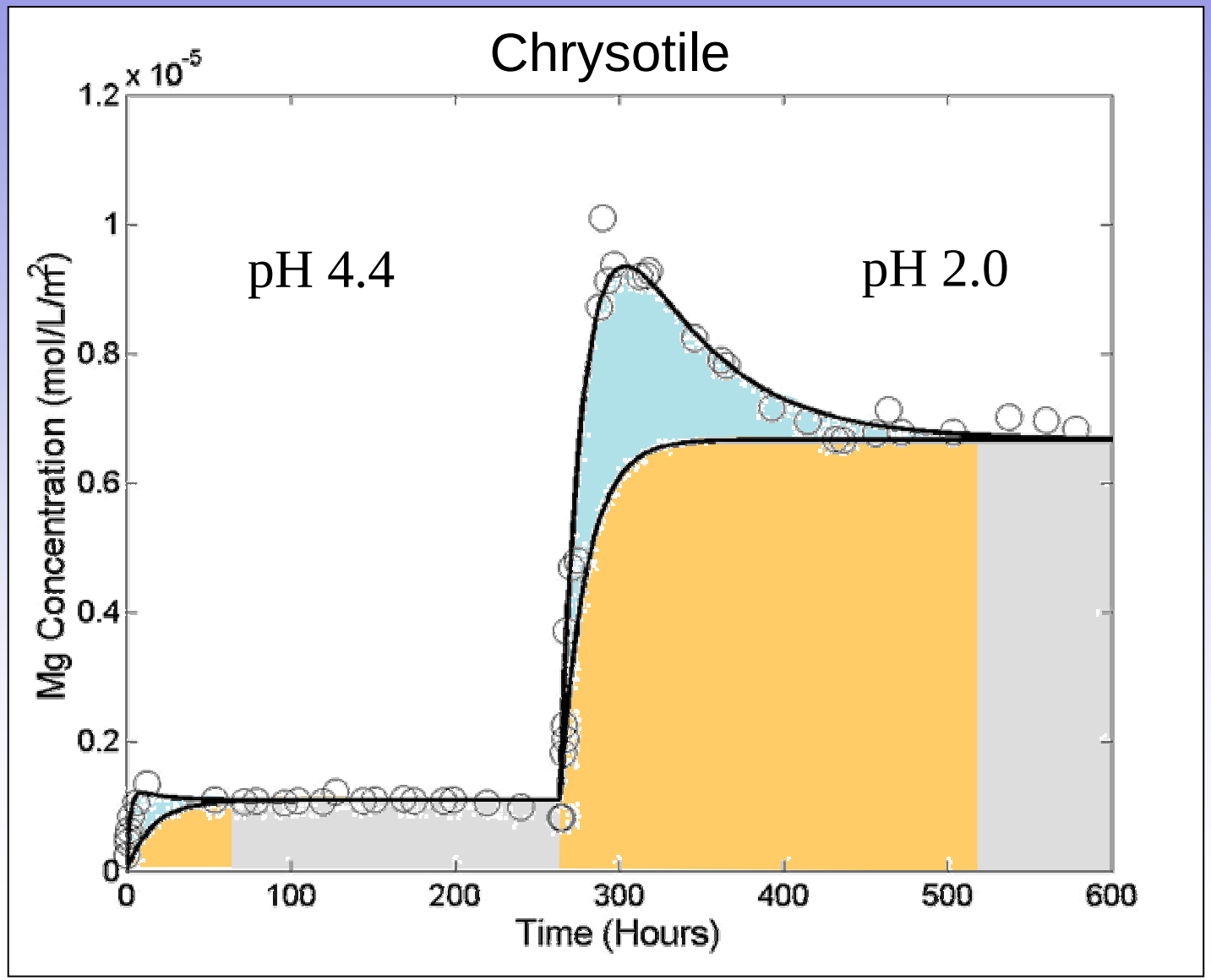

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