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1.061 / 1.61 Transport Processes in the Environment  
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## Dissolution of Gypsum and the Laminar Sub-Layer

You will use two methods to estimate the laminar sub-layer thickness in the laboratory flume. The first method is based on the observed dissolution rate of Gypsum bars, and is described below.

**Pre-Laboratory Activity:** Collected at the start of lab.

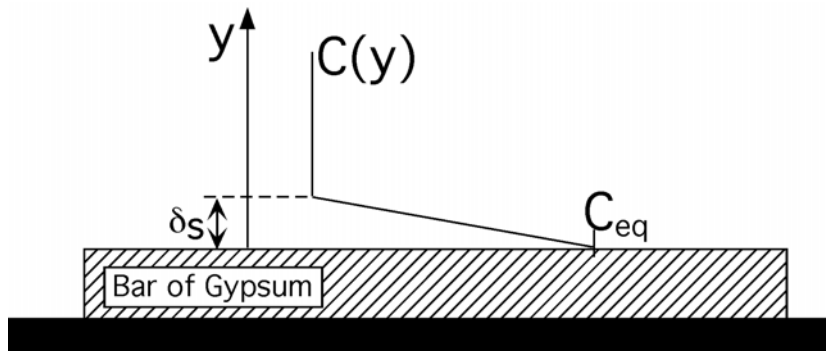
In clearly worded prose describe the following. 1) Give the thickness of the laminar sub-layer,  $\delta_s$ , in terms of mean velocity,  $U$ , and viscosity,  $\nu$ , only. 2) Give the time-scale for transport across the laminar sub-layer,  $T_\delta$ , in terms of  $U$ ,  $D_m$ , and the molecular viscosity,  $\nu$ , only. 3) Give the time-scale for transport across the full water depth,  $T_h$ , in terms of water depth  $h$  and  $U$ , only. 4) Consider the concentration profile depicted in the figure below. For what value of the product  $Uh$  (in  $\text{cm}^2\text{s}^{-1}$ ) will this profile be valid in the flume. Use  $\nu \approx 0.01 \text{ cm}^2\text{s}^{-1}$  and  $D_M \approx 10^{-5} \text{ cm}^2\text{s}^{-1}$ .

### Estimating the laminar sub-layer thickness from a boundary flux model:

To create a model for gypsum dissolution, we assume that the flux of calcium is controlled by the rate of molecular diffusion through the laminar sub-layer. Above the laminar sub-layer we assume that turbulent diffusion rapidly mixes all concentration to uniformity. Further, at the interface between the gypsum bar and the laminar sub-layer the concentration of  $\text{Ca}^{++}$  is assumed to be at equilibrium, *i.e.*  $C(y=0) = C_{\text{eq}}$ , where  $C_{\text{eq}}$  is defined below. With these assumptions we can write the transport equation that describes the dissolution of gypsum into the flume water.

$$V \frac{\partial C}{\partial t} = -D_m A_{\text{bar}} \left. \frac{\partial C}{\partial y} \right|_{y=0} = -D_m A_{\text{bar}} \frac{(C - C_{\text{eq}})}{\delta_s} \quad (1)$$

Here,  $C$  is the concentration of Calcium ions,  $\text{Ca}^{++}$ ;  $V$  is the total volume of water in the flume;  $D_m$  is the molecular diffusivity of  $\text{Ca}^{++}$  in water [ $8 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ ]; and  $A_{\text{bar}}$  is the surface area of the gypsum. The right hand side of (1) uses a finite difference approximation for the concentration gradient at the surface of the bar.



Equation (1) can be written as a first-order rate equation,

$$\frac{\partial C}{\partial t} = K(C_{\text{eq}} - C); \quad \text{where } K = \frac{D_m A_{\text{bar}}}{V \delta_s}. \quad (2)$$

If  $C = 0$  at  $t = 0$ , then (2) has the solution,

$$C = C_{\text{eq}}(1 - e^{-Kt}). \quad (3)$$

You can estimate the rate constant  $K$  by measuring the concentration of Calcium ions over time and fitting the observed  $C(t)$  to equation (3). The laminar sub-layer thickness can then be inferred from  $K$  using (2). During the early stages of the experiment the concentration of Calcium ions in the water is small compared to the equilibrium concentration, *i.e.*  $C \ll C_{\text{eq}}$ , and (2) reduces to

$$\frac{\partial C}{\partial t} = KC_{\text{eq}}, \quad (4)$$

such that  $C$  increases linearly with time. From (4)  $K$  is estimated with linear regression.

### Equilibrium Concentration:

In a very, very thin layer next to the gypsum bar,  $O(\text{nanometers})$ , we assume that the dissolved phase is in equilibrium with the solid phase. The ratio of concentrations is then given by the solubility constant,  $K_{\text{sp}}$ . At equilibrium

$$K_{\text{sp}} = \frac{[\text{Ca}^{++}][\text{SO}_4^{--}]}{[\text{CaSO}_4(\text{s})]} = 230 \frac{\text{mol}^2}{\text{m}^6} \quad (5)$$

The solid concentration is taken to be 1; and in solution  $[\text{Ca}^{++}] = [\text{SO}_4^{--}]$ ; such that the equilibrium concentration for  $\text{Ca}^{++}$  is  $\sqrt{230} \text{ mol m}^{-3} \approx 608 \text{ g m}^{-3}$ .

### Calcium Analyses

One member from each group will try to observe calcium “build up” in the water by monitoring the electrical conductivity of the water. Begin by setting up the conductivity electrode and meter at the bend in the flume. Take conductivity readings of tap water, water with 1 ppm  $\text{Ca}^{++}$ , and water with 10 ppm  $\text{Ca}^{++}$ . Next, take conductivity readings in the flume at time zero (*i.e.*, when the gypsum strips are put into the flume), 5 minutes, 10 minutes, 20 minutes, and 40 minutes.

A second member of each group should be responsible for placing the gypsum strip in the flume, **SIMULTANEOUSLY WITH THE OTHER GROUPS**. Subsequently, this member should withdraw 10 mL water samples at times 0, 5, 10, 20, and 40 minutes using the plastic pipettes and putting the samples in the acid-washed plastic bottles provided. Be sure to label the bottles.

A third member of each group will be responsible for atomic absorption (AA) measurements. Working upstairs in room 48-324, this person should familiarize her/himself with the AA sufficiently to (a) use the instrument and (b) explain its operation to the other lab group members. While water samples are being collected in 48-109, this student should use at least three samples (a blank and two standards) to examine the sensitivity of the AA as a function of  $\text{Ca}^{++}$  concentration. After the water samples have been collected, run all the samples in series with blank water in between.

After all data is collected, work as a team to estimate the rate of gypsum dissolution based on 1) the conductivity measurements and 2) the  $\text{Ca}^{++}$  measurements. Estimate the boundary layer thickness based on both estimates of  $K$ .

### **Your Lab Notebook Should Include**

- 1) A sketch of the flume indicating points of measurement and gypsum placement
- 2) A description of the sampling procedure.
- 3) A graph of calcium concentration versus time ( $C(t)$ ) with line fitted to estimate  $K$ .
- 4) A graph of conductivity vs. time with line fitted to estimate  $K$ .
- 5) Analysis to estimate  $\delta_s$  using the fitted  $K$ . Include the uncertainty in  $\delta_s$  arising from  uncertainty in your measurement of  $A_{\text{bar}}$ ,  $V$ , and  $K$ . Assume that  $D_m$  is a constant (i.e. contributes no uncertainty).
- 6) Analysis to estimate  $\delta_s$  based on  $U$ . Do the two estimates agree?
- 7) Discuss how the dissolution rate will vary with water velocity.
- 8) Estimate the time to reach equilibrium,  $T_{\text{eq}}$ .
- 9) Our analysis assumes that the flume approximates a stirred reactor, in the sense that we assume that the concentration is uniform in the water column. Use time scale analysis to show whether or not this is a good assumption.

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