MASS TRANSFER FROM SMOOTH ALABASTER SURFACES IN TURBULENT FLOWS

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Abstract. The mass transfer velocity for alabaster plates in smooth-wall turbulent flow is found to vary with the friction velocity according to an analytic solution of the advective diffusion equation. Deployment of alabaster plates on the sea floor can perhaps be used to estimate the viscous stress, and transfer velocities for other species.

Introduction

Fluxes of chemical species across the sediment-water interface in the world's oceans play an important role in many of the dominant geochemical cycles. In addition, it is often necessary to estimate the flux of a given species to determine its source strength in the sediment or in the overlying water. For both these reasons it is essential to develop techniques to estimate sediment-water fluxes. Presented here are laboratory measurements of the effect of bottom stress on the dissolution rate of a smooth alabaster plate. The results suggest that deployment of alabaster plates in the field can yield reliable estimates of transfer velocities for other chemical species through the boundary layer overlying the sediment-water interface.

Santschi et al. [1983] used three different techniques based on the release or absorption of soluble species, including the dissolution of alabaster ($CaSO_4 \cdot 2H_2O$), to estimate transfer velocities. The alabaster technique is simple to employ, and has the virtue that the dissolution is controlled almost entirely by transport through the aqueous boundary layer, so the method will give a straightforward estimate of the transfer velocity [Berner and Morse, 1974; Boudreau and Guinasso, 1982]. Transfer velocities for other species can then be inferred with fair confidence if the molecular diffusivities are known.

The technique is complementary to techniques based on measurements of currents, bottom stress, or turbulence, and in principle is more direct; whether it yields more reliable estimates in practice remains to be seen. It is clear though, that the various techniques should be compared. Use of the alabaster technique can then move in two directions: estimates of fluxes based on fluid dynamic measurements can be made with more confidence; and alabaster deployments may be used to estimate the average viscous stress at the bottom.

We describe here experiments in which alabaster dissolution and bottom stress were measured together in a flume, and show that the transfer velocity is very simply related to the mean stress by a model relatively free of assumptions.

Theory

Consider the surface of a soluble solid over which water is flowing. Let x be the downstream coordinate, y the cross-stream coordinate, and z the distance from the surface. Let us assume that dissolution is limited by diffusion into the water rather than by the kinetics of the change from solid phase to dissolved phase. That is, the concentration $C(x,y,z,t)$ of the dissolved species at the solid-water interface is virtually in equilibrium with the solid:

$$C(x,y,z,t) = C_S \qquad (1)$$

where C_S is the saturation concentration of the chemical species in the presence of the solid.

In dissolution experiments the concentration in the bulk of the fluid varies by less than one percent except in a diffusive region within a mm of the surface. Let C_W be the time-averaged concentration at some reference point in the system. Then the mass transfer velocity may be defined in terms of the time-average mass flux into the fluid at the interface $F(x,y)$ according to:

$$K(x,y) \equiv \frac{F(x,y)}{C_S - C_W} \qquad (2)$$

It will be possible to define useful averages over times long compared with the time scale of fluctuations of the input variables, but short compared with any trends, for example, in C_W due to build-up, or in C_S due to temperature changes.

Let $\langle K \rangle$ be the spatially averaged mass transfer velocity for a surface of finite area, such as a small plate, and let $\langle F \rangle$ be the spatially averaged mass flux. Then (2) may be integrated over the surface to give:

$$\langle K \rangle = \frac{\langle F \rangle}{C_S - C_W} \qquad (3)$$

where the integrals are over the surface area exposed to the fluid. The "film thickness", Z, used by some authors may be defined in terms of $\langle K \rangle$ as:

$$Z \equiv \frac{D}{\langle K \rangle} \equiv \frac{D(C_S - C_W)}{\langle F \rangle} \qquad (4)$$

where D is the molecular diffusivity of the species.

<K> for a Smooth Flat Plate

Short plate limit. Consider a small, smooth, soluble plate mounted flush with the bottom of a flume. The characteristics of the flow over the plate are independent of horizontal position, and depend only on the height, z, above the plate. The flow in such a system is usually turbulent, e.g., the Reynolds number for a flow speed of 10 cm/s and a depth of 10 cm is around 10^4. Nevertheless, it proves useful to consider the laminar case because the dissolution rate for a short plate is not sensitive to whether the flow is turbulent or not.

Knudsen and Katz [1958] present an analytic solution to the advective diffusion equation giving <K> for laminar flow over a plate of length L if effects at the side edges are neglected. The flow field in this situation is simply given by:

$$u(z) = (u_*^2/v)z \qquad (5)$$

where v is the kinematic viscosity of water, $u(z)$ is the mean downstream velocity and u_*, the friction velocity, is related to the bottom stress τ, by:

$$\tau = \rho_w u_*^2 \qquad (6)$$

where ρ_w is the water density. The concentration is constrained to be C_s at the plate and C_w at the leading edge and at large z. The expression for <K> is then

$$<K> = (0.81)\ Sc^{-2/3}\ (v/L)^{1/3}\ u_*^{2/3} \qquad (7)$$

where the Schmidt number, Sc, is defined as:

$$Sc = v/D \qquad (8)$$

This expression may be cast in non-dimensional form as:

$$<K_+> = (0.81)\ (L_+)^{-1/3}\ (Sc)^{-2/3} \qquad (9)$$

where $<K_+>=<K>/u_*$ is the dimensionless transfer velocity, or Dalton number, and $L_+=Lu_*/v$ is the dimensionless plate length.

Son and Hanratty [1967] have shown from the dissolution of benzoic acid in pipe flow that, even though the flow may be turbulent, (9) predicts mass transfer velocities within 5% or so for L_+ less than 600. The reason is that (5) also holds in the mean for smooth-wall turbulent flows within the viscous sublayer, i.e. for $z_+ \le 5$, where $z_+= zu_*/v$. Thus it appears that for L_+ small enough that the concentration field does not penetrate beyond the viscous sublayer within the region over the plate, (9) holds to an excellent approximation even for turbulent flow.

Long plate limit. If $L_+ >> 10^3$ (but small enough that the concentration has not built up in the bulk fluid), $<K_+>$ approaches the value it would have for a plate of infinite length. For laminar flow $<K_+>$ decreases with $L_+^{-1/3}$ as L_+ increases because the high concentration layer through which molecules must diffuse becomes increasingly thicker downstream. For turbulent flow, on the other hand, advection dominates diffusion at some height above the surface so that the thickness of the high concentration boundary layer approaches a finite limit downstream, and the local vertical flux becomes independent of the downstream position. For very large L_+, the region near the leading edge in which the flux is relatively large is unimportant, and $<K_+>$ becomes approximately independent of L_+.

Several experiments performed to measure $<K_+>$ in this limit for turbulent flow were reviewed by Kader and Yaglom, [1972], who proposed as a best estimate:

$$<K_+> = 0.078\ Sc^{-2/3} \qquad for\ L_+ \to \infty \qquad (10)$$

or, if we dimensionalize:

$$<K> = 0.078\ Sc^{-2/3}\ u_* \qquad for\ L_+ \to \infty \qquad (11)$$

Because the flux in the region near the leading edge is enhanced, (11) is a lower limit for <K> for finite length plates. Given that turbulent flow must be more efficient at chemical transport than molecular diffusion at any given u_*, (7) is also a lower limit for $<K_+>$ for all flows. Figure 1 plots (7) and (11) for Sc = 980 and L = 10 cm, appropriate for our alabaster plates at 25°C. The greater of the two curves at any u_* may be taken as a theoretical lower limit for <K> for these values of L and Sc.

The Experiment

The 6 m x 30 cm flume at the University of South Florida was used, with a water depth of 10 cm. Alabaster plates, 10 cm x 10 cm x .65 cm, were mounted flush with a false bottom 4 m downstream from the entry section, where the turbulent velocity profiles were fully developed. The sides and the bottoms of the plates were coated with polyurethane to prevent dissolution from areas other than the top surface. The alabaster, which had been mined near Pisa, Italy, is white when 99% pure, and becomes obviously discolored with greater impurity than this. Only white material was used for the experiments.

Friction velocity (u_*) was measured with a flush-mounted hot-film probe adjacent to the alabaster plates. These stress probes, based on heat transfer, are a standard tool in fluid dynamical studies, with well established theoretical [e.g., Bellhouse and Schultz,1966] and experimental [e.g., Kreplin and Eckelmann, 1979] performance records, and have been shown to work reliably in benthic boundary layers [Gust and Weatherly, 1985; Palmer and Gust, 1985]. The theory of operation for the probes is analogous to the argument leading to (9) with temperature replacing concentration, and the Prandtl number replacing the Schmidt number. The probes used were epoxy-encapsulated nickel grids, 3 mm on a side, with a resistance of approximately 50 ohms at 20°C and a 3 dB frequency response of better than 20 Hz [Gust and Southard, 1983]. They were run in constant-temperature mode with an overheat ratio of 1.05 with TSI 1050 and DISA 55M hot-film anemometers. The output was recorded on a digital cassette recorder with 12 bit resolution in the 0-5 V range, at 32 Hz sampling frequency. The sensor was calibrated prior to the runs by comparison with a probe previously calibrated in the flume using the energy-gradient method described by Gust and Southard (1983), ensuring error bars for u_* of less than 5%.

The alabaster plate was weighed dry, and mounted in the flume. Water, which had been distilled and deionized prior to the experiment, was then circu-

TABLE 1. Data from the flume experiments

u_* cm/s	T °C	Sc	Δt 10^4 s	ΔM g	Cw-Cs ppm	$\langle K \rangle$ 10^{-4} cm/s	$\langle K' \rangle$ 10^{-4} cm/s
0.17	24.0	1026	5.76	3.05	600	2.05	2.12
0.27	24.0	1026	6.01	4.01	600	2.58	2.67
0.30	24.0	1026	5.81	4.37	600	2.92	3.02
0.48	26.0	940	4.58	5.06	600	4.28	4.17
0.62	28.0	861	3.29	5.18	600	6.12	5.63
0.81	29.5	816	4.28	8.94	595	8.17	7.21
0.57	29.0	824	4.02	6.10	592	5.96	5.33
0.17	29.0	824	4.53	2.77	588	2.47	2.21
0.48	26.5	920	6.10	7.61	585	4.96	4.76
0.85	27.0	899	3.55	6.97	582	7.85	7.43
0.25	30.0	798	8.65	7.23	569	3.36	2.92
0.43	30.5	781	8.64	10.58	577	4.89	4.20
0.68	30.5	781	6.02	7.18	574	7.06	6.06
0.26	31.0	764	8.59	10.43	553	4.16	3.57
0.42	31.0	764	7.15	18.80	561	5.97	5.13
0.70	31.0	764	7.78	8.69	557	9.98	8.57

lated through the flume for several hours while the surface velocity, water temperature, and stress probe output were periodically measured. After a run, the alabaster plate was allowed to dry at room temperature and was reweighed, giving the weight loss for the run. The data for sixteen runs conducted in the summer of 1984 are listed in Table 1.

Results

The average flux of Ca^{++} for a run can be calculated from the mass loss of the alabaster plate via the equation:

$$\langle F \rangle = (0.2328/L^2)\ \Delta M/\Delta t \tag{12}$$

where 0.2328 is the weight fraction of Ca^{++} in alabaster, L is the length of the plate, ΔM is the mass loss, and Δt is the duration of the run. The uncertainty in $\langle F \rangle$ is approximately 5%, mostly due to uncertainty in ΔM. $\langle K \rangle$ may be calculated from $\langle F \rangle$ using (2), where C_S has been determined with 1% accuracy by previous workers [Christoffersen and Christoffersen, 1976; Marshall and Slusher, 1966], and C_w is determined by atomic absorption analysis of water samples taken during the run. The value of C_S at 25°C is 608 ppm, while C_w was much lower during the experiment, ranging from 10 ppm in water newly added to the flume, to a maximum of 55 ppm. The uncertainty in $\langle K \rangle$ due to the uncertainties in $\langle F \rangle$, C_S, and C_w is less than 10%.

The temperature of the water for the various runs ranged from 23°C to 32°C due to cycling of the room air conditioning system and a partial failure of the water heat-exchanger system. There is expected to be a variation of $\langle K \rangle$ with temperature through the temperature dependence of ν and Sc, appearing in (7) and (11). The data for $\langle K \rangle$ were normalized to 25°C, to obtain a new transfer velocity, $\langle K' \rangle$, by assuming that $\langle K \rangle$ varies as $Sc^{-2/3}$. This correction increases the variance between the data and the model in Figure 1, but only by 10%, an insignificant amount. The diffusivity, D, was calculated for the Ca^{++} and SO_4^{--} ion pair using the equation [see Lerman, 1979]:

$$D = \frac{[Ca^{++}] + [SO_4^-]}{\dfrac{[Ca^{++}]}{D(SO_4^-)} + \dfrac{[SO_4^-]}{D(Ca^{++})}} \tag{13}$$

where square brackets are used for concentrations, and where the diffusivities for the Ca^{++} and SO_4^{--} ions, $D(Ca^{++})$ and $D(SO_4^{--})$, are from Li and Gregory [1974]. Figure 1 presents the results for $\langle K' \rangle$ versus u_*, as well as the short plate limit (7) for L=10 cm and the long plate limit (11), for 25°C. The data lie in the short plate limit, or in the intermediate region between the two limits. Friction velocities greater than 2 cm/s are required for a 10 cm plate to be in the long plate limit. The data points tend to lie under the short plate limit at $u_* < 0.4$ cm/s, and perhaps a bit above it at $u_* > 0.7$ cm/s. Although these deviations could be due to experimental errors, they could also suggest either that $\langle K' \rangle$ varies more strongly than with the 2/3 power of u_* of the short plate limit, or that we have underestimated the Schmidt number, and the curve rises away from the short plate limit as the intermediate region between the two limiting curves is approached. In general, the fit of the data to the short plate limit is impressive; it shows that (7), arrived at analytically using a laminar velocity profile very near the surface of the alabaster, describes mass transfer well for a turbulent system with a smooth bottom, friction velocities less than 1 cm/s or so, and a plate length of less than 10 cm.

Discussion

These results will ultimately be of great use in oceanic applications, since u_* for the benthic boundary layer is seldom much greater than 1 cm/s. Mass loss from alabaster plates at marine sites will yield estimates of the friction velocity associated with the viscous bottom stress, averaged over the duration of a deployment. It is an advantage for estimating chemical fluxes that alabaster dissolution will not be affected by that part of the bottom stress due to pressure imbalances around roughness elements. The transfer velocity for other species at the sediment-water interface could be estimated from (7) or (11), using u_* from an alabaster deployment, although more work must be done to determine the appropriate length, L, to use for species distributed over the ocean floor.

We also recognize that more flume experiments are necessary to test the temperature dependencies
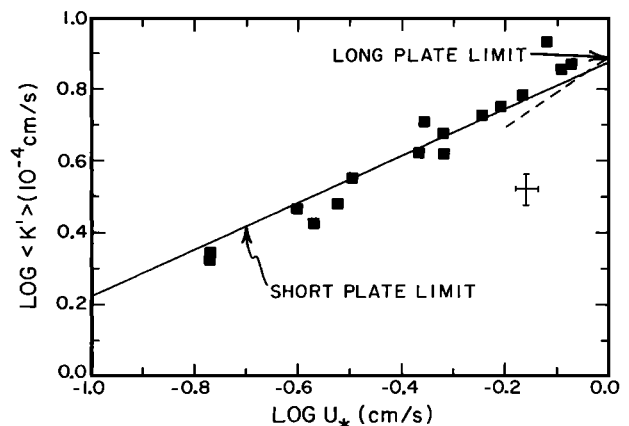

Fig. 1. Mass transfer velocity, adjusted to 25°C, versus friction velocity, u_*, for the flume experiment. The short plate limit (7) and the long plate limit (11), for L = 10 cm, are also plotted.

implied by the model. It will also be necessary to perform side-by-side field deployments of alabaster plates and stress probes to develop alabaster plates into a reliable field tool.

Conclusion

The dissolution of a smooth alabaster plate exposed to smooth-wall turbulent boundary layer flow in a laboratory flume behaves as expected from theory and from similar experiments in pipe flows. In particular, the short plate limit, derived using the advection-diffusion equation for laminar flow, applies for a 10 cm square alabaster plate at friction velocities up to 1 cm/s, and Reynolds number up to 20,000. The alabaster technique promises to be an inexpensive means of estimating bottom viscous stress, and with further work it may be possible to confidently infer transfer velocities for other species from alabaster deployments.

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