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Effects of Oxygen Demand on
Surface Reaeration

by

E. R. Holley, Principal Investigator
Associate Professor of Civil Engineering
University of Illinois

F. W. Sollo, Project Consultant
Principal Chemist
Illinois State Water Survey
Urbana, Illinois

Thomas Micka, Undergraduate Student
Hormoz Pazwash, Graduate Student Assistant
Department of Civil Engineering
University of Illinois

F I N A L R E P O R T

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UNIVERSITY OF ILLINOIS
WATER RESOURCES CENTER
2535 Hydrosystems Laboratory
Urbana, Illinois 61801

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ABSTRACT

EFFECTS OF OXYGEN DEMAND ON SURFACE REAERATION

An extensive literature review is presented pointing out that the transport or diffusion of dissolved oxygen in the thin region or film immediately below the water surface is the most critical region in determining the oxygen absorption rate. Literature on the effects of sodium sulfite and biochemical oxygen demand (BOD) is also reviewed.

The surface film is actually an oxygen boundary layer. This concept is supported by the definition of a boundary layer, by reaeration experiments, and by analogy with other mass and heat transfer problems. Thus, it should be expected that the film or boundary layer thickness changes with Schmidt number as well as mixing conditions and that the transport through the film can be represented by a diffusion model, as in other boundary layer problems. Temperature measurements were made to allow the calculation of the diffusion coefficient in the thermal boundary layer or film in a situation analogous to the reaeration problem. The results indicate that the diffusion coefficient is approximately equal to the molecular diffusivity even when turbulence is present.

Using the boundary layer and diffusion model, analytical solutions are presented for the vertical concentration distribution both in the turbulent film and below the film for various situations involving no oxygen demand, sulfite, or BOD. The solutions substantiate that the concentration distribution is essentially linear in the film even in the unsteady absorption problem both with no oxygen demand and with BOD. The degree of approximation involved in making certain simplifying assumptions is demonstrated. The solutions show that the oxygen demand per se of the BOD does not affect the absorption rate, but the possibility is left open for other effects, such as physical influences, to affect the absorption rate. The solutions for the effects of sulfite in increasing the absorption rate are in general agreement with available data.

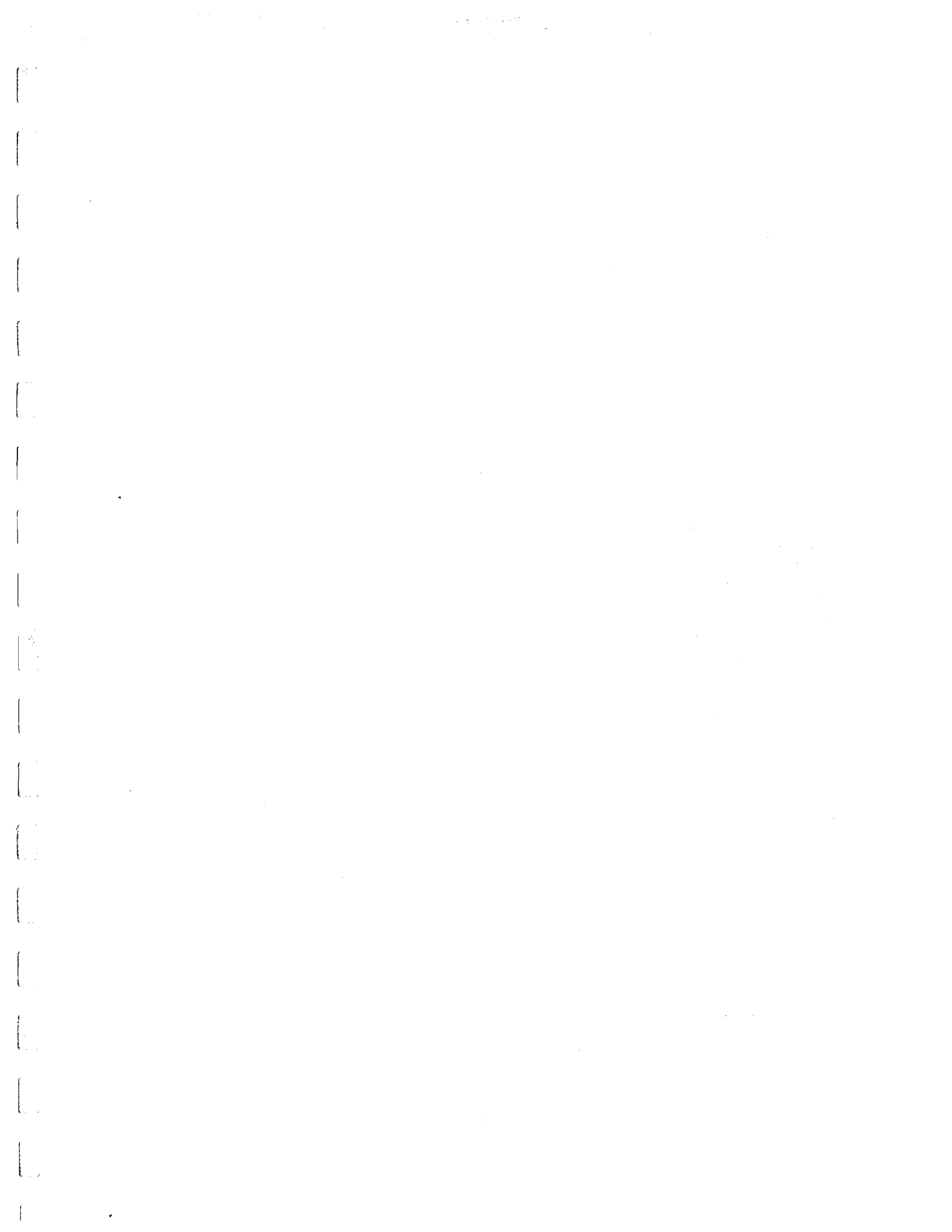
Experiments were performed at 2°C and at 20°C to evaluate the effects of BOD on reaeration rates. For both temperatures, the reaeration rates were about 1.5 times the rate for pure water. Since biological activity is almost non-existent at 2°C, the increase must have been due to the physical presence of the organisms.

Holley, E. R.

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KEYWORDS--*reaeration/*dissolved oxygen/*oxygen demand/diffusion/turbulence/water pollution



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LIST OF SYMBOLS

- A = surface area; dimensionless parameter (Eq. 4.37)
- a = A/V; amplitude of motion of oscillating grids in mixing vessel
- B = distance from water surface to mean position of top grid
- b = dimensionless parameter (Eq. 4.20)
- C = depth averaged oxygen concentration
- c = oxygen concentration
- c_s = saturation concentration
- D = depth-averaged oxygen deficit = $c_s - C$
- d = pipe diameter; local oxygen deficit as a function of y
- D* = diffusion coefficient
- f = Darcy-Weisbach friction factor
- G = mass transfer rate per unit of bottom area (Eq. 4.43)
- g = acceleration of gravity
- H = dimensionless depth = h/δ
- h = mean water depth = V/A
- K_1 = BOD rate coefficient
- K_2 = reaeration rate coefficient
- $k_2 = K_2/2.30$
- K_L = liquid film coefficient
- K_s = sulfite reaction rate (Eq. 4.18)
- L = oxygen demand
- Nu = Nusselt number
- Pr = Prandtl number
- q = rate of mass transport
- q* = dimensionless mass transport rate (Eq. 4.22)

R = depth-averaged rate of oxygen utilization per unit volume
 r = rate of oxygen utilization per unit volume; surface renewal rate (Eqs. 2.7, 2.8, and 2.9)
 S = energy slope; sulfite concentration
 Sc = Schmidt number
 T = temperature; dimensionless time = $D^* t / \delta^2$
 t = time
 U = velocity
 V = volume of water
 Y = dimensionless vertical coordinate = y / δ
 y = vertical coordinate
 α = parameter for change of absorption rate due to impurity (Eq. 2.11); thermal diffusion coefficient; dimensionless parameter = $K_L h / D^*$
 β = dimensionless parameter (Eq. 4.9)
 δ = film or boundary layer thickness
 η = dimensionless vertical coordinate = y / h
 θ = parameter for temperature dependence of K_2 (Eq. 1.3)
 κ = dimensionless parameter = $K_1 \delta^2 / D^*$
 ν = kinematic viscosity
 σ = frequency of oscillation of grids in mixing vessel
 τ = dimensionless time = $D^* t / h^2$

CHAPTER 1

INTRODUCTION

There is an increasing need for, and an increasing demand for, the reduction of stream pollution. Stream pollution takes many forms including biological wastes, chemical wastes, trash, and waste heat. In connection with biological wastes and some types of chemical wastes, dissolved oxygen is one of the resources which is needed in the process of stream self-purification. Thus, in analyzing the waste assimilation capacity of a stream, it is generally necessary to be able to predict the oxygen resources, including the rate of reaeration, i.e. the rate at which oxygen is absorbed from the atmosphere.

It is common to use either a reaeration coefficient (K_2) or a liquid film coefficient (K_L) in analyzing reaeration. The reaeration coefficient is used in an equation such as [Phelps, 1944].

$$\frac{dD}{dt} = -K_2D + R \quad 1.1$$

where D is the oxygen deficit, t is time, and R is used here as a general term to represent the rate at which oxygen is utilized per unit mass. If R is zero (no oxygen utilization), then the well-known solution for Eq. 1.1 under the initial condition of $D = D_0$ at $t = 0$ is

$$\frac{D}{D_0} = e^{-K_2t} = 10^{-k_2t} \quad 1.2$$

where $k_2 = K_2/2.30$. The value of K_2 depends, among other things, on the turbulence level in the water and on temperature. The dependence on turbulence is discussed in Chap. 2. It is commonly accepted that the temperature dependence of K_2 may be represented by the equation

$$\frac{(K_2)_{T_1}}{(K_2)_{T_2}} = \theta^{(T_1 - T_2)} \quad 1.3$$

where T is temperature in degrees centigrade and θ has a numerical value of about 1.005 to 1.030 depending on the mixing level in the water [Metzger, 1968].

In Eq. 1.1 and equations derived from it (e.g. Eq. 1.2), D is generally considered to be the average deficit at a cross section in a river and t is taken as flow time, or longitudinal distance divided by average velocity. It is probable that equations such as this, i.e. equations for the average deficit or concentration, will continue to be used in engineering work. However, in order to obtain a better understanding of the mechanisms affecting the reaeration, it is desirable to look at the details of the vertical transport of dissolved oxygen within the cross section. This latter approach is used in the majority of this report.

It is common practice to obtain empirical values of reaeration rate coefficients from laboratory and field experiments with water having no oxygen demand and to use these values for predicting reaeration in streams which have oxygen demand. The question arises concerning the possible influence of the oxygen demand on the mechanics involved in reaeration and on the value of the rate coefficients. It is the purpose of this report to investigate this question on the basis of the literature and analytical and experimental research. Two basic types of oxygen demand are considered, namely that having an extremely rapid reaction rate with oxygen (characterized, for example, by sodium sulfite) and that having an extremely slow reaction rate (characterized by biochemical oxygen demand, BOD). In addition to the oxygen demand itself, pollutants may cause other effects such as physical interference with oxygen transfer at the interface.

The work reported herein is concerned principally with surface aeration, or oxygen transfer across the natural free surface. However, much of the work is also applicable to bubble aeration and to the transfer of gases of low solubility other than oxygen.

CHAPTER 2

DISCUSSION OF SOME PREVIOUS WORK

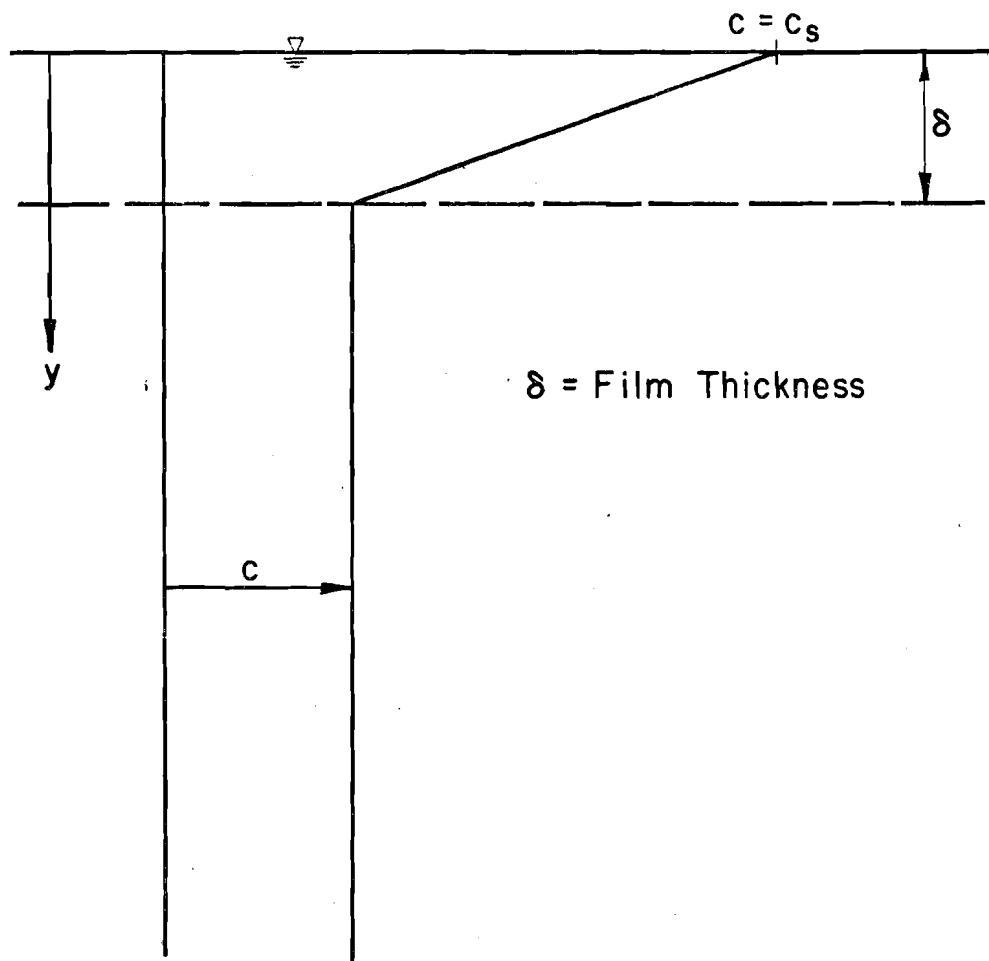
2.1) FILM THEORY

Film theory represents one of the analytical approaches that has been used to study the absorption of gases into turbulent water. This concept was presented by Whitman [1923] and by Lewis and Whitman [1924]. Since oxygen has low solubility in water, this theory states that the rate of absorption is controlled by the rate of diffusion through a water film at the free surface. The so-called "film" is not a physical film. Rather it is only a thin region in the water immediately below the free surface. For oxygen, the resistance to transfer through the gas film is negligible, so that the dissolved oxygen at the free surface is essentially in equilibrium with the atmosphere, and the concentration at the interface is the saturation concentration, c_s . This argument would seem to be reasonable in view of the work of Miyamoto [1931] who showed that the ratio between the number of oxygen molecules going into solution and the number hitting the free surface is on the order of 10^{-8} for maximum absorption rates under normal conditions. Looking at it another way, the time required for a newly created surface to become saturated is on the order of 10^{-7} sec [Pasveer, 1953]. In film theory, turbulence is assumed to keep the water well mixed below the film so that the concentration is uniform everywhere except in the film. Thus, through the thin film, a steep concentration gradient exists, and the concentration distribution is as depicted in Fig. 2.1.

Lewis and Whitman assumed that the transport through the film was solely by molecular action and therefore followed Fick's first law [Bird et al, 1960]. Assuming the concentration distribution to be linear through the film of thickness δ , Fick's law for transport through the film may be written as

$$q = AD_m^* \frac{c_s - C}{\delta} \quad 2.1$$

where q is the rate of mass transport through the area A , D_m^* is the molecular diffusivity, and C is the concentration below the film. (D^* is used to



$\delta = \text{Film Thickness}$

Fig. 2.1 Definition Sketch for Liquid Film

distinguish the diffusivity from the deficit D. Also, it may be noted that the rate of mass transport is sometimes written as dm/dt .)

Letting

$$K_L = \frac{D^*}{\delta} \quad 2.2$$

Eq. 2.1 may be written as

$$q = AK_L (c_s - C) = AK_L D \quad 2.3$$

The rate of change of the concentration C below the film is related to q by $dC/dt = q/V$, where V is the volume of water. Thus, Eq. 2.3 may also be written as

$$\frac{dC}{dt} = K_L \frac{A}{V} (c_s - C) = (K_L a) (c_s - C) \quad 2.4$$

where $a = A/V$. The quantity $(K_L a)$ is often treated as one coefficient, particularly in case of bubbling a gas through a liquid, because of the difficulty in determining the area. Comparison of Eqs. 1.1, 2.3, and 2.4 shows that

$$K_2 = K_L a = \frac{K_L}{h} \quad 2.5$$

if h is defined as a mean depth equal to V/A for surface reaeration.

Objections have been raised to at least two assumptions in Lewis and Whitman's film theory. One of these assumptions was the stagnant film at the free surface of a turbulent liquid. Various authors have observed that it was not physically reasonable to make such an assumption. Review of the paper by Lewis and Whitman [1924] does not make it clear whether they considered the film to be physically stagnant or not. In referring to the film, they used phrases such as "a layer in which motion by convection is slight compared to that in the main body" and "assuming the existence of stationary films." Thus, it seems that the essence of their model

was not a physically stagnant film, but rather it was a region in which molecular diffusion is the controlling factor in the transport process.

The second assumption which has been questioned was that of a linear gradient through the film. The linear gradient strictly corresponds only to a steady state distribution, whereas the concentration beneath the film is continually changing in many gas absorption problems. However, Dobbins [1956] has shown that the linear distribution is a reasonable assumption for oxygen absorption from bubbles. The same conclusion can be reached for most cases of natural reaeration across a free surface by investigation of the unsteady state diffusion equation. This analysis is presented later in this report (Section 4.3.1).

2.2) PENETRATION AND SURFACE RENEWAL MODELS

As an alternative to the film theory model, Higbie [1935], Danckwerts [1951], and Dobbins [1956, 1962, 1964] have presented models which are in some ways related to each other. Each of these models sought to account for the effect of mixing on the transport rate away from the free surface.

Higbie's model for the rate of gas absorption was based on the assumption that the whole body of water was stagnant for short periods of time and, during these periods, oxygen was absorbed and diffused downward solely by molecular diffusion. Then, periodically, the water was instantaneously and completely mixed. This model led to an equation which was effectively the same as Eq. 2.3 with K_L given by

$$K_L = 2 \sqrt{\frac{D_m^*}{\pi t}} \quad 2.6$$

where t' is the average time between the complete mixings. Higbie's development was summarized by Pasveer [1953]. This model is often referred to as the penetration model.

Danckwerts [1951] extended Higbie's approach by assuming that various vertical elements of the water could individually undergo complete vertical mixing with different periods between mixings. He assumed that the statistical distribution of the mixing was described by

$$f(t) = re^{-rt} \quad 2.7$$

where $f(t)$ is the proportional part of the vertical elements of water for which the elapsed time since the last mixing is between t and $t + dt$. The constant r may be interpreted as the average rate at which vertical mixing takes place. Thus, r is analogous to $1/t'$ of Eq. 2.6. Danckwerts' approach again led to Eq. 2.3 for the rate of transfer if K_L is given by

$$K_L = \sqrt{D_m^* r} \quad 2.8$$

Kishinevsky [1954] devoted almost an entire article to raising objections to Danckwerts' model. One of his primary objections concerned an assumption used in obtaining Eq. 2.7, namely that the probability that an element of water would be mixed was independent of the elapsed time since the last mixing for that element. Other detailed objections were also presented.

Dobbins [1956, 1962, 1964] used the concept of a surface film but postulated that the water in the film was periodically mixed with water from below the film. In a sense, this was a combination of film theory and Danckwerts' work. Dobbins' model is different from Danckwerts' model in that it places a limit (the film thickness) on the depth to which the dissolved gas may move by molecular diffusion. The region below the film was assumed to be uniformly mixed at all times while new surface film was continually being created and then removed. It was assumed that only molecular diffusion takes place while a given parcel of water is in the film. Dobbins also assumed that various parts of the film were mixed or "renewed" at a rate such that Eq. 2.7 described the distribution of times (or ages) since the last renewal within the film. Thus, mathematically the only difference from Danckwerts' work was the lower boundary condition used for the diffusion equation. For a film of thickness δ , he showed [1956] that these assumptions lead to

$$K_L = \sqrt{D_m^* r} \coth \sqrt{\frac{r\delta^2}{D_m^*}} \quad 2.9$$

As the surface renewal rate r approaches zero, K_L of Eq. 2.9 approaches Eq. 2.2, while for large r , Eq. 2.9 approaches Eq. 2.8.

Dobbins [1962, 1964] conducted some experiments to allow calculation of r and δ for a laboratory mixing apparatus. Absorption rates of helium and nitrogen were determined for water which was being mixed by a vertically oscillating stack of metal grids. By determining the values of K_L for the two gases and knowing values of D_m^* , it was possible to calculate values of r and δ by assuming that these two parameters depended only on the mixing condition. It was found that values of r and δ could be correlated to parameters describing the oscillation of the metal grids. As would be expected, r increased and δ decreased as the speed of oscillation (σ) of the grids was increased. However, the changes which were found for r are difficult to understand, recalling that r is effectively the average rate at which the surface film is renewed. For a σ of 18 rpm, r was calculated to be 0.171 per min, while for $\sigma = 196$ rpm, r was 3780 per min for the same amplitude of screen motion. It is true that r should increase as σ increases, but it is difficult to conceive that increasing σ by a factor of about 11 would have changed the characteristics of the mixing to such an extent that r would be increased by a factor greater than 20,000. The problem is not necessarily in the surface renewal concept per se, but rather it may be in the assumed renewal distribution (Eq. 2.7) or in the assumption that δ and r are the same for both gases. The dependence of the film thickness on Schmidt number is discussed in Chap. 3.

All of these models indicate a dependence of K_L on D_m^* . Thus, they may be incapable of representing gas transfer at extremely high mixing rates. Kishinevsky and Serebryansky [1956] have presented experimental results indicating the same values of K_L for gases with different D_m^* values under high mixing conditions. For these tests, K_L apparently was independent of D_m^* .

2.3) EMPIRICAL EQUATIONS

There have been several investigators who used either a totally empirical or a partially empirical approach in attempting to relate reaeration coefficients to mean flow parameters (e.g. Streeter and Phelps [1925], O'Connor and Dobbins [1958], Churchill et al [1962], and Krenkel and Orlob [1963]). Only one such publication is mentioned explicitly here, namely the work of Thackston and Krenkel [1969]. They considered the general dependence of reaeration on turbulent diffusion in order to obtain the hydraulic parameters to which K_2 was correlated. From both laboratory and

field data, they obtained the expression

$$k_2 = 0.000125 \left[1 + \left(\frac{U}{\sqrt{gh}} \right)^{1/2} \right] \sqrt{\frac{g S}{h}} \quad 2.10$$

where g is the gravitational acceleration, S is the energy slope, h is the mean depth, and U is the mean velocity. The Froude number U/\sqrt{gh} was included to account for changes in the surface area due to waves. They indicated that this equation gave a better overall fit to the data than the other generally used equations.

2.4) SODIUM SULFITE

Some of the past work relating to sodium sulfite and its use in aeration equipment is reviewed in this section. Some of the references cited here relate to bubble aeration.

Sodium sulfite is often used in testing and comparing aeration equipment. When an excess of dissolved, catalyzed sodium sulfite is present in water, the dissolved oxygen concentration is zero because of the rapid reaction between sodium sulfite (Na_2SO_3) and oxygen to give sodium sulfate (Na_2SO_4). Thus, it is possible to use the rate of production of sodium sulfate as a measure of the rate of oxygen absorption. It is known [Camp, 1958] that the presence of sodium sulfite in water increases the rate of oxygen absorption compared to water with no sulfite. For a constant interfacial area, the increase can be related to the steepening of the oxygen gradient at the interface due to the reaction with the oxygen. (See Section 4.2). For bubble aeration, there is the additional factor that sodium sulfite may change the bubble size, and therefore the interfacial area, for a given gas flow rate.

Fuller and Crist [1941] studied the effect of typical positive and negative catalysts (copper and mannitol) on the oxidation rate of sulfite solutions and found that the reaction is first order with respect to sulfite concentration. With addition of the negative catalyst mannitol over a 10^5 fold concentration range, a first order reaction resulted with the rate constant dependent upon the mannitol concentration. It was found that the oxidation rate was dependent on pH in some ranges.

Cooper et al [1944] studied in more detail the oxidation of aqueous sodium sulfite solution containing copper ions. In the range of sodium sulfite concentration covered (between 0.035 to almost 1 normal) the rate of oxidation was found to be a constant. Blakebrough [1967] also indicated the oxidation rate to be independent of sulfite concentration in the range from about 0.015 to 1.0 molar.

Yoshida et al [1960] found a higher absorption rate for water with catalyzed sulfite than for pure water. They interpreted this difference to be the result of smaller bubbles and thus greater interfacial area in the sulfite solution, rather than being associated with the chemical reaction. This conclusion was based on their measurement of the absorption rate for sulfite and sulfate solutions. In both cases, they stated that the bubble size was the same, and that the values of $(K_L a)$ were also the same. These conclusions are contrary to the generally accepted view that the sulfite influences the absorption rate both by changing the bubble size (in bubble aeration) and by chemical reaction with the oxygen. For example, results cited below and others given in Section 5.3 of this report indicate a higher absorption rate with sulfite than without sulfite, for a constant interfacial area.

Schultz and Gaden [1956] experimentally determined K_L values in a mixing vessel with constant interfacial area. They used 7.5 liters of sodium sulfite solution at 0.15N with cupric sulfate catalyst. For stirrer speeds from 0 to 100 rpm, they found that K_L was approximately constant at 1.2 cm/min. From 100 to 240 rpm, K_L decreased to about 0.9 cm/min. There are two strange things about their results. The first thing is that K_L for a zero stirrer speed (no turbulence) was as great as that when turbulence was present. The second strange thing is the decrease in K_L with increasing stirrer speed in the higher range. The authors did not comment on the first matter. They explained the second thing in terms of oxidation of the sulfite in a chain mechanism. They said that an intermediate product in the reaction was the rate limiting factor and that the rate of this intermediate step decreased because the higher turbulence provided a decreased exposure to the oxygen. However, it should be noted that the gradients in the explanation proposed by them would require diffusion of this intermediate product through the free surface.

O'Connor and Dobbins [1958], as a part of some other work, performed some reaeration experiments both with and without sulfite in the same vessel. They used about 2.5 liters of water at an initial sulfite concentration of 8000 ppm with a vertically oscillating lattice work to produce the mixing. Their results are presented in Fig. 2.2. They found that K_L increased with increasing turbulence. From the K_L values, it can be seen that the degree of mixing was apparently greater than that used by Schultz and Gaden, whose work was discussed above.

Camp [1958], in discussing O'Connor and Dobbins article, postulated that the rate of oxygen absorption into a sulfite solution is controlled by the rate at which the sulfite diffuses toward the free surface for the reaction with the oxygen. For the experiments of O'Connor and Dobbins, the reaeration coefficients plus the duration of the experiments show that the sulfite concentration decreased to less than half its initial value. Nevertheless, they found that the absorption rate was constant for a given turbulence.

2.5) BIOCHEMICAL OXYGEN DEMAND

When wastewaters are present, there is the possibility of many different mechanisms acting simultaneously to influence the oxygen absorption rate (e.g. surface active agents, chemicals, physical effects of suspended solids, biological utilization of oxygen, and possible changes in the saturation concentration). Thus, the problem of evaluating the influence of biological activity on oxygen absorption is rather difficult. There are at least two possible ways of approaching this problem, but neither way is entirely satisfactory. One way is to study the effects of the various mechanisms separately. The problem with this approach is that the mechanisms are no doubt not independent of each other. Thus, even if all the separate mechanisms are thoroughly understood, it might not be clear how the separate effects should be combined. The other approach is to study aeration with many or all of the types of mechanisms present simultaneously. Then through a systematic variation of various quantities, a statistical approach could be used in an effort to quantify the various effects. The problem with this approach is that an extremely large amount of data is required if reliable results are to be obtained. Most of the work reviewed in this section falls into the first approach. The analytical

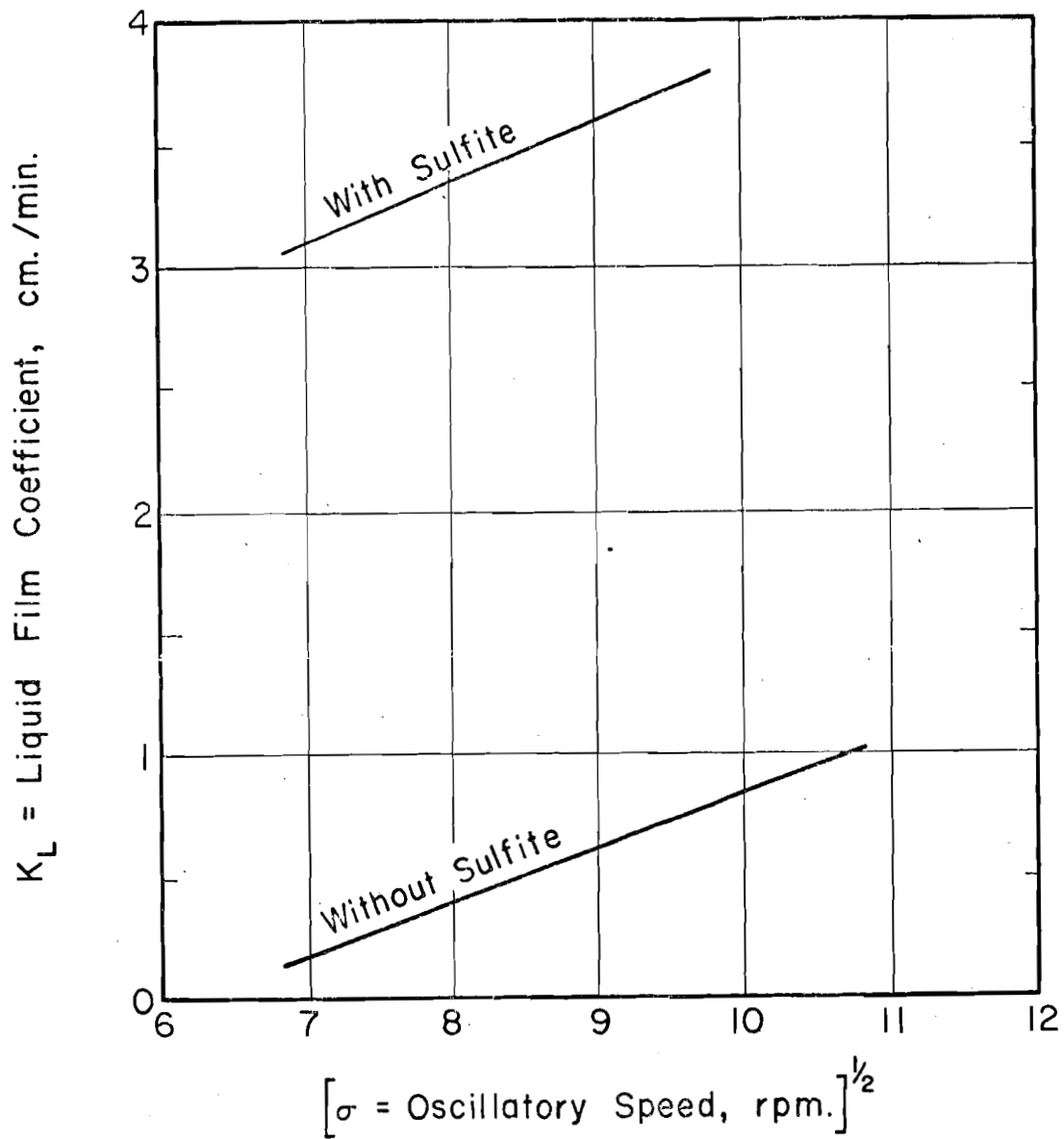


Fig. 2.2 K_L with and without Sulfite [O'Connor and Dobbins, 1958]

and experimental work reported later (Chaps. 4 and 5) also falls into the first approach, namely an attempt to study just the oxygen demand.

In evaluating the influence of some impurity or waste on aeration, a parameter α is frequently used. This parameter is defined as the ratio of the transfer coefficient with the impurity present to the coefficient for pure water:

$$\alpha = \frac{K_L a \text{ (with impurity)}}{K_L a \text{ (for pure water)}} \quad 2.11$$

In accordance with Eq. 2.5, $K_L a$ in Eq. 2.11 could be replaced by K_2 . The definition of α assumes that the appropriate value of the saturation concentration (c_s) is used when evaluating $K_L a$ or K_2 . However, it is often the case that c_s is not known or not evaluated for the water plus impurity. Then, α sometimes includes the effects of changes both in $K_L a$ and c_s .

It is generally accepted that the presence of organic materials retards the rate of oxygen absorption and causes α to be less than unity. Various values of α from almost zero to almost unity (and occasionally greater than unity) have been reported in the literature. See, for example, Kehr [1938], King [1955], Eckenfelder et al [1956]. However, apparently very little is known about how much of the change in α is due to the various factors or mechanisms present.

2.5.1) Surface Active Agents, Acids, and Other Chemicals

Some substances have a type of surface activity that make them tend to concentrate at a gas-liquid interface. Examples are protein derivatives and some microbial cells. It is known that surface active agents can cause a severe reduction in the absorption coefficient. See, for example, Holdroyd and Parker [1952] and Downing and Truesdale [1955].

Zeimenski et al [1967] studied the effect of mono- and dicarboxylic acids as well as aliphatic alcohols on the overall transfer rate. Air bubbles were used for aeration. The size of bubbles was measured by a photographic technique. It was found that the transfer coefficient $K_L a$ increased with addition of the acids or alcohols. The increase was greater at lower concentrations and was stronger for compounds of higher molecular weights. For a heptanoic acid concentration of 10 ppm, the oxygen transfer

rate increased by 180 percent. This increase in transfer rate ($K_L a$) can partly be attributed to the decrease in air bubble size caused by addition of acids. As an example, octanoic acid at a concentration of 10 ppm increased the surface area by 700 percent. However this increase in surface area is considerably lower than that of total transfer rate as a result of the added acid.

Poon and Campbell [1967] studied the effect of several dissolved chemicals on the absorption from bubbles with a constant air flow rate. The dissolved materials studied were chemicals such as inorganic salts, organic substances, carbohydrates, amino acids, protein and starch commonly found in polluted water. They covered a wide range in molecular sizes and concentrations. These chemicals produced a reduction in $K_L a$ with a stronger effect at higher concentrations. The results indicated that the concentration is not the only factor affecting the oxygen transfer rate. It was found that the large molecular substances such as peptone and nutrient broth had a strong effect on the transfer rate whereas small molecules like NaCl had very little effect.

Eckenfelder et al [1956] reported that by addition of peptone to water, the variation of oxygen transfer rate with changing concentration was rapid at low concentrations and more gradual thereafter. At 25 ppm, α was 0.5 and slowly decreased to 0.2 at 1000 ppm.

From these results, it appears that relatively large changes in α can be produced by small changes in chemical concentration for low concentrations while α is less sensitive to concentration changes at the higher concentrations. Also, substances with large molecular weight appear to have more affect than the smaller molecular weights. However, Zeimenski et al found an increase in α for the chemicals they used while Poon and Campbell found a decrease in α .

2.5.2) Suspended Solids

There are apparently some inconsistencies in the data available on the influence of suspended solids on absorption rates. Kehr [1938] noted that addition of diatomaceous earth to tap water reduced the transfer rate by about 25%. Holdroyd and Parker [1952] reported that bentonite had no effect on the transfer rate. Poon and Campbell [1967] found that suspended particles in small concentrations enhanced the transfer process.

Van der Kroon [1968] studied the effects of suspensions of clay and aluminum sulfate. His results were not at all clearly presented, but they seem to indicate a reduction in transfer rate with an increasing suspension concentration. In any case, it is not clear whether changes in the transfer rate were due to changes in the saturation concentration or changes in $K_L a$ (or both). Eckenfelder et al [1956] found that the addition of 2260 ppm of suspended solids to an activated sludge waste mixture caused α to decrease from 0.54 to 0.44. At a sludge concentration of 1000 ppm, Gaden [1955] reported a $K_L a$ value 20% of that for pure fermentation broth. In these experiments, there were no doubt influences other than just the physical presence of suspended solids.

It seems that the majority (but not all) of the data to which reference has been made indicate a decrease in the transfer coefficient due to the presence of suspended solids.

2.5.3) Biological Activity

As is well known, the presence of biological cells creates an oxygen demand in water. Hixson [1950] pointed out that the oxygen transfer process may be divided into three steps: (1) absorption of the oxygen at the interface, (2) diffusional transfer of the dissolved oxygen through the liquid, and (3) utilization of the oxygen by the cells. Others (e.g. Bennett and Kempe [1964] and Tsao [1968]) have suggested the possibility of the cells taking oxygen directly from the atmosphere.

It is not the purpose of this report to explore the many possible factors which can influence the rate at which oxygen is utilized in biological processes. Only one situation is cited here as an example, namely the case for which the oxygen utilization is proportional to the oxygen demand (L) so that R in Eq 1.1 is given by

$$R = K_1 L \quad 2.13$$

The oxygen demand then decreases in an exponential fashion (see, for example, Phelps [1944]):

$$\frac{L}{L_o} = e^{-K_1 t} \quad 2.14$$

where L_o is the ultimate oxygen demand. Since the rate of satisfaction of the

oxygen demand necessarily is equal to the rate of oxygen utilization, Eq. 2.14 implies that Eq. 1.1 may be written as

$$\frac{dD}{dt} = -K_2 D + K_1 L = -K_2 D + K_1 L_o e^{-K_1 t} \quad 2.15$$

for this case.

The oxygen utilization by cells in water where the dissolved oxygen level is extremely low has been studied by Bandyopadhyay and Humphrey [1967] and Finn [1954].

Phillips and Johnson [1961] reported aeration studies using several micro-organisms. For bubble aeration, they found an increase in the transfer coefficient with the organisms present. They suggested that the increase was due to a reduction in the size of the air bubbles.

Tsao [1968] also studied the effect of several bacterial cells on the oxygen transfer rate. The experiments were performed in a beaker at low stirrer speeds so that no bubbles were formed. He found values for α (Eq. 2.12) in the order of 1.4 when there was biological oxidation during the oxygen transfer process. As mentioned earlier, he assumed the increase to be due to the direct absorption of the cells from the atmosphere. Experiments discussed in Section 5.4 show an increase in reaeration rate in a situation where any direct uptake by the cells was not included in the measurements. The technique used by Tsao (i.e. the rate of production of gluconic acid [Tsao and Kempe, 1960]) has been criticized by Humphrey and Reilly [1965] and defended by Tsao [1969B].

Tsao [1969A] presented an interesting analysis of gas absorption including the influence of uptake by small particles in the liquid. He considered different distributions of particles next to the free surface and obtained the effect of the particles on K_L . However, the mass balance equation he used had an error in it, so the significance of his results is not clear. (The error is that the sign is wrong on the $\partial s / \partial x$ term in his Eq. 3. However, this term and therefore the error may not be too significant for small particle concentrations, but it is difficult to be sure without re-deriving his answers with the sign corrected.) In his illustration of his results, he assumed a particle concentration distribution which changed by a factor of three in a distance equal to two particle diameters. It seems that this situation might be rather difficult to achieve physically.

In any case his results could not be compared with the analytical results presented later in this report for at least three reasons: (1) He assumed the particle uptake rate to be proportional to the dissolved gas concentration while the analysis in this report assumes it to be proportional to the BOD. (2) He used a rate constant for the particles much higher (120 sec^{-1}) than considered here. (3) He assumed molecular diffusion throughout the liquid, while this report allows turbulent mixing.

In essentially all of the studies mentioned above there has been an effort to make some separation in the effects of the individual constituents of a waste. Exceptions to this, already mentioned, are Kehr [1938] and Eckenfelder et al [1956]. Kothandaraman [1969] undertook a study on samples taken from the Illinois River at Peoria. A portion of each sample was analyzed for suspended solids, dissolved solids, chemical oxygen demand (as a measure of chemical impurities) and surface active agents. A few of the samples were diluted with distilled water to obtain a wide range of concentrations. The results of the experiments indicated that the contaminants in river water alter the aeration rate to the extent of $\pm 15\%$ compared to the rate for distilled water. No consistent relationship could be established between the reaeration rate and constituent contaminants in river water.

2.5.4) Effect of Impurities on Saturation Value

In most of the investigations to which reference has been made, the effect of contaminants on the oxygen saturation value was not considered. Only in a few experiments, e.g. that by Kehr [1938], such an effect was considered.

It has been demonstrated by Isaacs and Gaudy [1968A] that there is a need for knowing the nearly exact value of saturation concentration for evaluation of total absorption rate. They demonstrated there could be a relatively large error in computed $K_L a$ values as a result of relatively small errors in the value used for the saturation concentration.

Reed and Theriault [1931] and Isaacs and Gaudy [1968B] present methods for indirectly evaluating c_s from measurements of dissolved oxygen vs. time.

CHAPTER 3

DIFFUSION AND BOUNDARY LAYER CONCEPTS

3.1) GENERAL CONCEPT

It seems that there is essentially no possibility of a stagnant film existing at the free surface of turbulent water. There is much evidence to support the presence of turbulence at the free surface, but still reference is sometimes made to supposedly stagnant films. It was essentially the recognition of turbulent mixing at the free surface that led Higbie, Danckwerts, and Dobbins to develop the models discussed in Section 2.2. The concept of surface renewal is a model to account for turbulent mixing.

Just the presence of ripples on the water surface is one indication of the presence of turbulence at the surface. Orlob [1959] and Engelund [1969] both used the free surface turbulence in a wide channel as an example of homogeneous turbulence in which to study diffusion. Holley [1970] measured the one-dimensional spectrum of turbulence at distances from 0.006 in. (0.15 mm) to 1.0 in. (25 mm) below the free surface and found the same turbulence characteristics throughout this region. Approximate calculations indicated that some of these turbulence measurements were made in the region of the oxygen surface film. It is true that Orlob's, Engelund's, and Holley's work dealt with the horizontal components of the turbulence while it is primarily the vertical component which is important in the problem of gas transport from the atmosphere. Nevertheless, due to the essential three dimensional nature of turbulence, there is no doubt that the vertical as well as the horizontal turbulence is present.

It is well recognized that many transport problems in turbulent flow can be treated by a diffusion law analogous to Fick's law for molecular diffusion [Bird et al, 1960]. Therefore, it should be possible to use a diffusion model to represent the transport of oxygen downward from the free surface in turbulent water. By analogy to Fick's law, a general transport equation for diffusion in the vertical (y) direction may be written as [Bird et al, 1960]

$$q = - AD^* \frac{\partial c}{\partial y} \quad 3.1$$

where D^* is a diffusion coefficient and c is a concentration with any turbulent fluctuations averaged out. In general, D^* may be written as $D_m^* + D_t^*$, where the subscript m refers to the molecular contribution to diffusion and the subscript t refers to the turbulent contribution, and the numerical value of D^* may be almost anything, depending on the particular mixing conditions. In the absence of turbulent mixing, D_t^* would be zero so that $D^* = D_m^*$. In other cases, D_m^* may be negligible compared to D_t^* so that it would be sufficient to say $D^* = D_t^*$.

The use of Eq. 3.1 to represent the transport away from the free surface will be referred to as a "diffusion model." Harleman and Holley [1963] and Thackston and Krenkel [1969] discussed the general significance of vertical diffusion in the reaeration problem, but neither publication gave detailed consideration to the transport immediately below the free surface.

The physical conditions in reaeration, of course, are not affected by the analytical model which is used. Thus, the assumption that the water surface is at saturation concentration is as valid for the diffusion model as for any other model. Also, the water at some distance below the surface is well enough mixed so that the oxygen concentration is essentially uniform. This condition has been empirically confirmed in reaeration experiments by withdrawing Winkler samples at the bottom, at mid-depth, and near the surface of the mixing vessel. The concentration distribution was found to be uniform. Analytical work discussed later also substantiates this condition. In view of this and the saturation concentration at the surface, the time-average concentration (c) distribution must be essentially the same as shown in Fig. 2.1, even when there is turbulence at the free-surface. That is, there is apparently a relatively small region at the surface with a steep gradient from saturation concentration at the surface to the concentration existing in the bulk of the water. A diffusion model (Eq. 3.1) can be used to represent the transport downward from the free surface in terms of this gradient immediately below the free surface.

It will be helpful to have a name by which to refer to this region of the steep gradient when turbulence is present at the surface. This region is actually an "oxygen boundary layer" and it would be reasonable to refer to it as such. This term would tend to bring to mind the analogy between oxygen boundary layers and other boundary layers, as discussed later. However, it would probably be futile to propose the use of such a name because of the widely accepted usage of the terminology "surface film". In recognition of this fact and also the fact that the diffusion model as proposed could be interpreted as a modification or substantiation of film theory to include possible effects of turbulence on diffusion below the free surface, it would probably be more appropriate to use the term "turbulent surface film". The adjective "turbulent" is used to emphasize the presence of turbulence since the term "surface film" sometimes seems to imply a stagnant film.

In a diffusion model for transport through the turbulent film, Eq. 2.3 is still valid since it just defines a coefficient K_L . Also, Eq. 2.5 still applies. Combining Eq. 2.3 and Eq. 3.1 and assuming a linear concentration distribution through the turbulent film, one can obtain the relationship

$$K_L = \frac{D_{TF}^*}{\delta} \quad 3.2$$

where D_{TF}^* is the value of D^* in the turbulent film and δ is the thickness of the turbulent film. Eq. 3.2 is of course analogous to Eq. 2.2. Eq. 2.2 may be viewed as a special case of Eq. 3.2 when $D_{TF}^* = D_m^*$. Before Eq. 3.2 could be used as a basis for predicting reaeration rates, it would be necessary to have some means of relating D_{TF}^* and δ to mean flow parameters or some other parameters which could be easily determined. At this stage, no such general correlations for D_{TF}^* and δ are known. However, some laboratory tests have been made, and they shed some light on the validity of the diffusion model and on variables that affect D_{TF}^* and δ . Also, due to past successes in correlating diffusion coefficients and boundary layer thickness with mean flow parameters, there would appear to be a reasonable chance of finding general correlations for D_{TF}^* and δ in the future.

Before describing the experimental work, it may be worthwhile to comment on the relation between the surface renewal model and the diffusion model. It is necessary that the models not be confused with the physical phenomenon which they are seeking to represent. The physical phenomenon is apparently something like this:

In turbulent water there is a random motion of the water. This random motion carries different parcels of water to the free surface at different times. If a parcel of water is below saturation concentration, then oxygen from the atmosphere moves into this parcel through molecular diffusion during the time that the parcel is at the surface.

Of course, this is an oversimplified explanation since there is no parcel of water which remains in tact even for a short exposure to the free surface. However, for this physical process, the essential difference between a diffusion model and a surface renewal model is that the surface renewal model seeks to represent this physical process by saying something about the statistical distribution of the turbulence at the surface (Eq. 2.7) while the diffusion model deals only with the average quantities, e.g. concentrations and transport rates which have averaged the effects of turbulent fluctuations (Eq. 3.1). Taylor [1921] has discussed the relation between diffusion and the statistical parameters of the turbulence for homogeneous turbulence conditions.

Recognizing the different nature of the models, it can be seen that it is not necessarily the case that one model is correct and the other incorrect. Also, the basic concepts in the models should not be confused with or equated with assumptions which might be made in applying the model. Both models seem logical in terms of what is known about the physical process. Thus, any failure of the models to give logical results probably stems from assumptions made in application, rather than from the basic concepts in the model.

3.2) Experiments on Heat Absorption

Some laboratory studies were conducted to test the validity of using a diffusion model for the downward transport from the free surface and to learn something about both the diffusion coefficient in the turbulent film and the thickness of the film. In these studies, it was desired

to determine the concentration distribution in the turbulent film. However, there is no sensor small enough to measure the steep dissolved oxygen gradients which apparently exist in the turbulent film. Since small temperature sensors are available, experiments were conducted on the diffusion of heat in a situation somewhat analogous to that for oxygen absorption. In a mixing vessel, the air over the water was heated to a temperature higher than the water temperature. The temperature difference caused heat to be absorbed by the water at the free surface and transported downward just as with oxygen in the reaeration process. The sides of the vessel were insulated to assure that transport of heat took place only in the vertical direction. Heat loss was allowed through the bottom of the tank so that a steady state temperature profile developed. Under these conditions, no heat accumulated at any point, so the rate of vertical transport was the same at all points in the vertical direction. By analogy to Eq. 3.1, it may be seen that for any two points in the vertical direction

$$\left(\alpha \frac{dT}{dy}\right)_1 = \left(\alpha \frac{dT}{dy}\right)_2 \quad 3.3$$

where α is the diffusion coefficient for heat and T is temperature. Thus, if the gradients are measured at two points and if α is known at one point, then α may be calculated at the other point.

The tank in which the temperature profiles were measured was 30 in. long by 16 in. wide by 12 in. deep. Stainless steel grids oscillated vertically to produce mixing. The six grids (flattened expanded metal, 1/2 in., No. 16) had a vertical spacing of 1 in. (See Fig 3.1.) The top grid was attached to the drive rods so that the grid could come right up to water surface without breaking the surface. The amount of mixing could be varied by changing the frequency (σ) of oscillation of the grids. The amplitude (a) was held constant at 0.85 cm. For a constant σ , the degree of mixing at the free surface could be varied by changing the distance (B) from the mean position of the top screen to the water surface. The water depth in the mixing vessel was approximately 7 in.

The maximum temperature difference in the water was less than 1°F. It is felt that there were no significant changes in fluid properties associated with this relatively small temperature difference.

Mixing Vessel
Length = 30"
Width = 16"
Water Depth = 7"

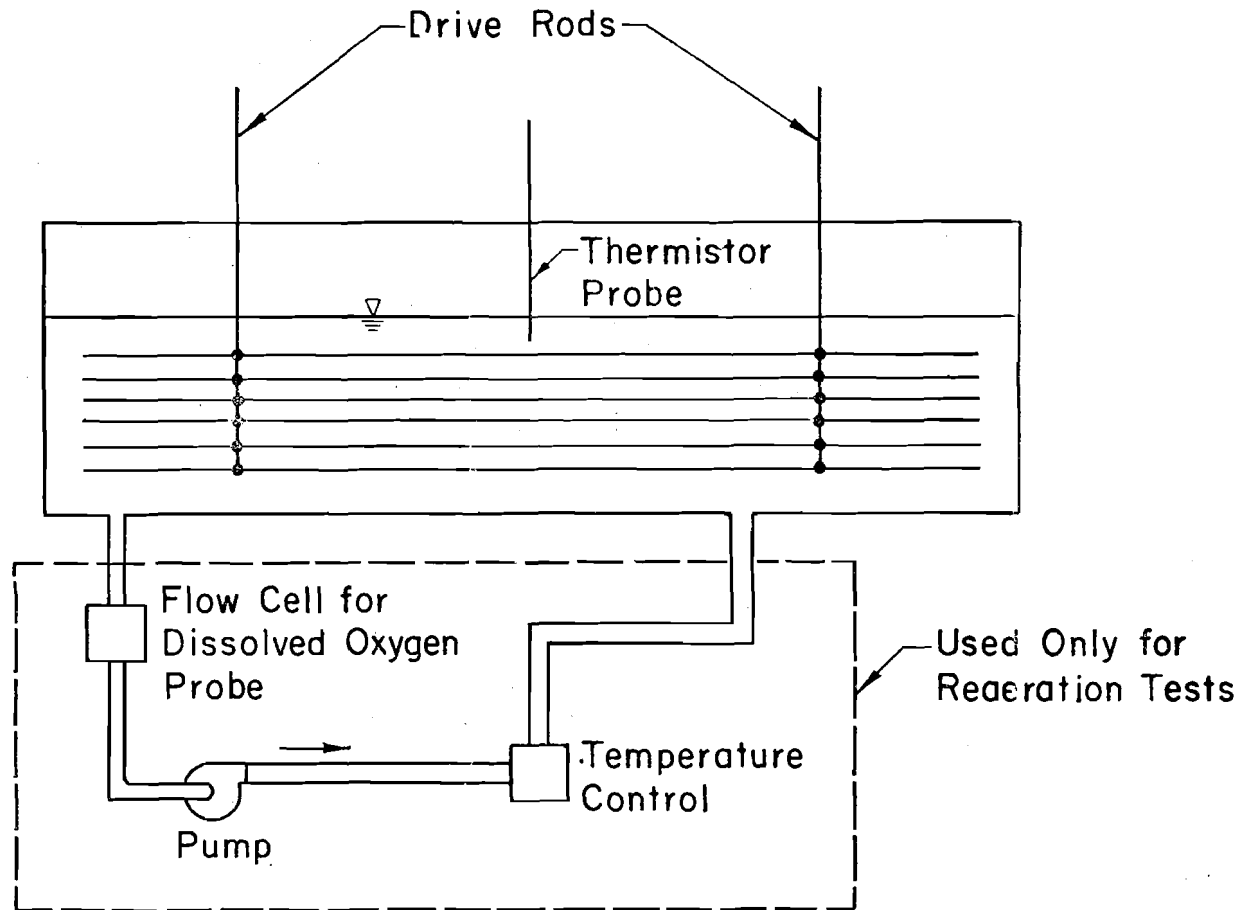


Fig. 3.1 Schematic Diagram of Mixing Vessel

For the particular grid used in these tests, the vertical diffusion coefficient in the region occupied by the grid was known from previous studies [Halaby and Taher, 1962, and Harleman et al, 1963].

The temperature sensor was a 0.014 in. (0.22 mm) diameter, glass-coated, bead thermistor (Fenwal Electronics, Framingham, Massachusetts, No. GA51L2 with a nominal resistance of 100,000 ohms at 25°C). It was mounted at the end of a 0.036 in. diameter tube. The sensor was one leg of a Wheatstone bridge. Voltage across the sensor was determined so that the thermistor's self heating would be no more than 0.01°C.

A typical temperature profile is shown in Fig. 3.2. The temperature distributions were essentially two straight lines. The thickness (δ) of the turbulent film was determined by the intersection of the two lines. From the slopes of the two lines and the known diffusion coefficient in the region occupied by the grids, it was possible to determine the diffusion coefficient of heat (α_{TF}) in the turbulent film.

Nine tests were made for different mixing conditions. The oscillatory speed (σ) was set at 100, 200, and 250 rpm and the distance from the mean position of the top screen to the water surface (B) was set at 0.9, 1.4, and 2.5 cm. In all tests, the temperature was distributed essentially as shown in Fig. 3.2. That is, there were two linear regions with a small transition. The values obtained for δ and α_{TF} are shown in Figs. 3.3 and 3.4. The data is somewhat limited and scattered, but there appear to be some conclusions that can be reached:

- (1) As the amount of mixing at the surface increased, due to either increasing the oscillatory speed or decreasing the distance between the top screen and the surface, the thickness of the turbulent film decreased and the magnitude of the diffusion coefficient increased.
- (2) For the lower degrees of mixing at the surface, the diffusion coefficient in the turbulent film was approximately equal to the molecular thermal diffusivity.
- (3) For higher degrees of mixing, the diffusion coefficient increased above the molecular value. However, even when the top screen came to the surface at the highest point in its motion ($B = 0.9$ cm), the largest diffusion coefficient in the turbulent film (at $\sigma = 250$ rpm) was still only about six times the molecular value or about 300 times less than the diffusion coefficient for mixing due to the motion of the grids. (Except for this single

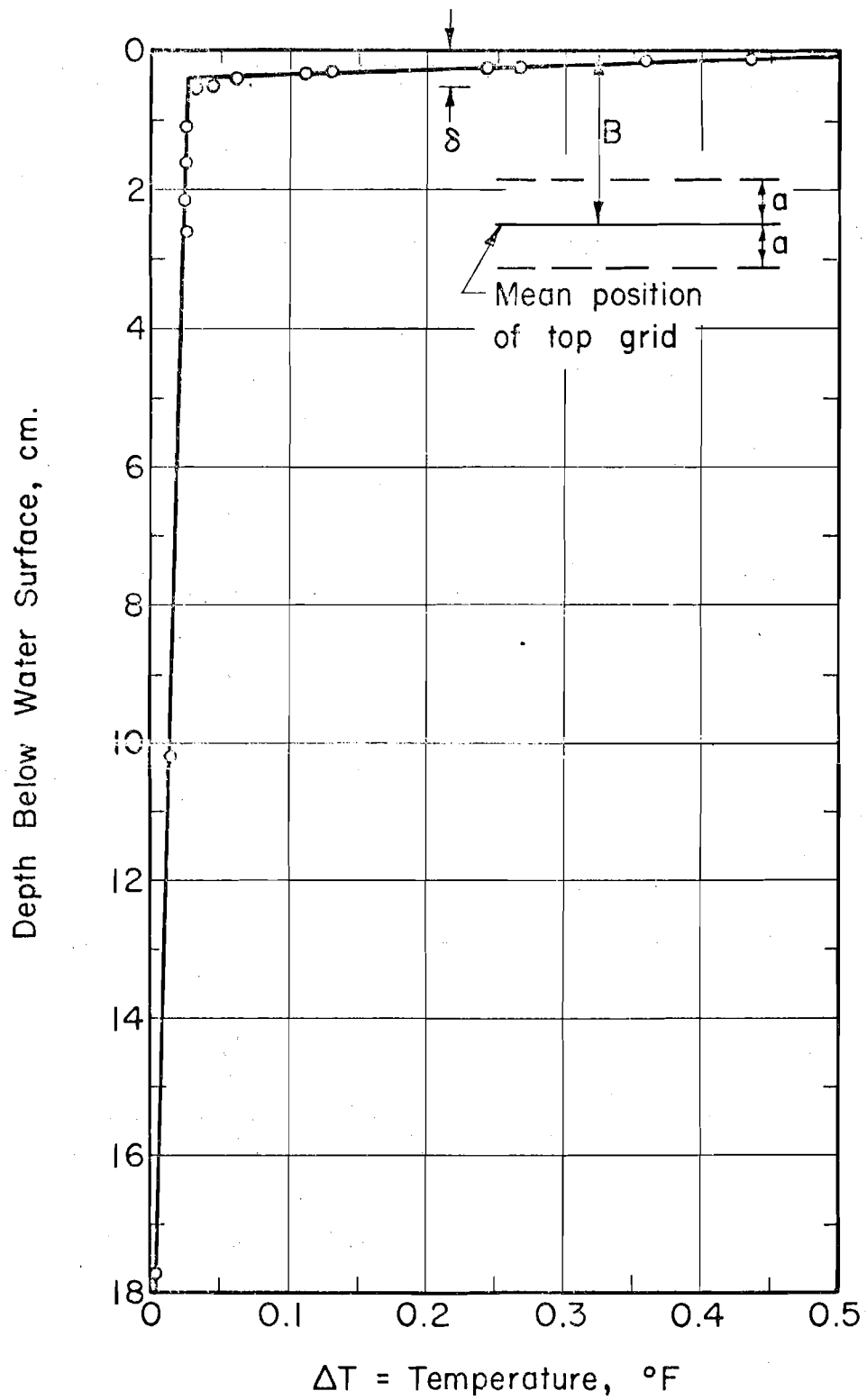


Fig. 3.2 Vertical Temperature Profile

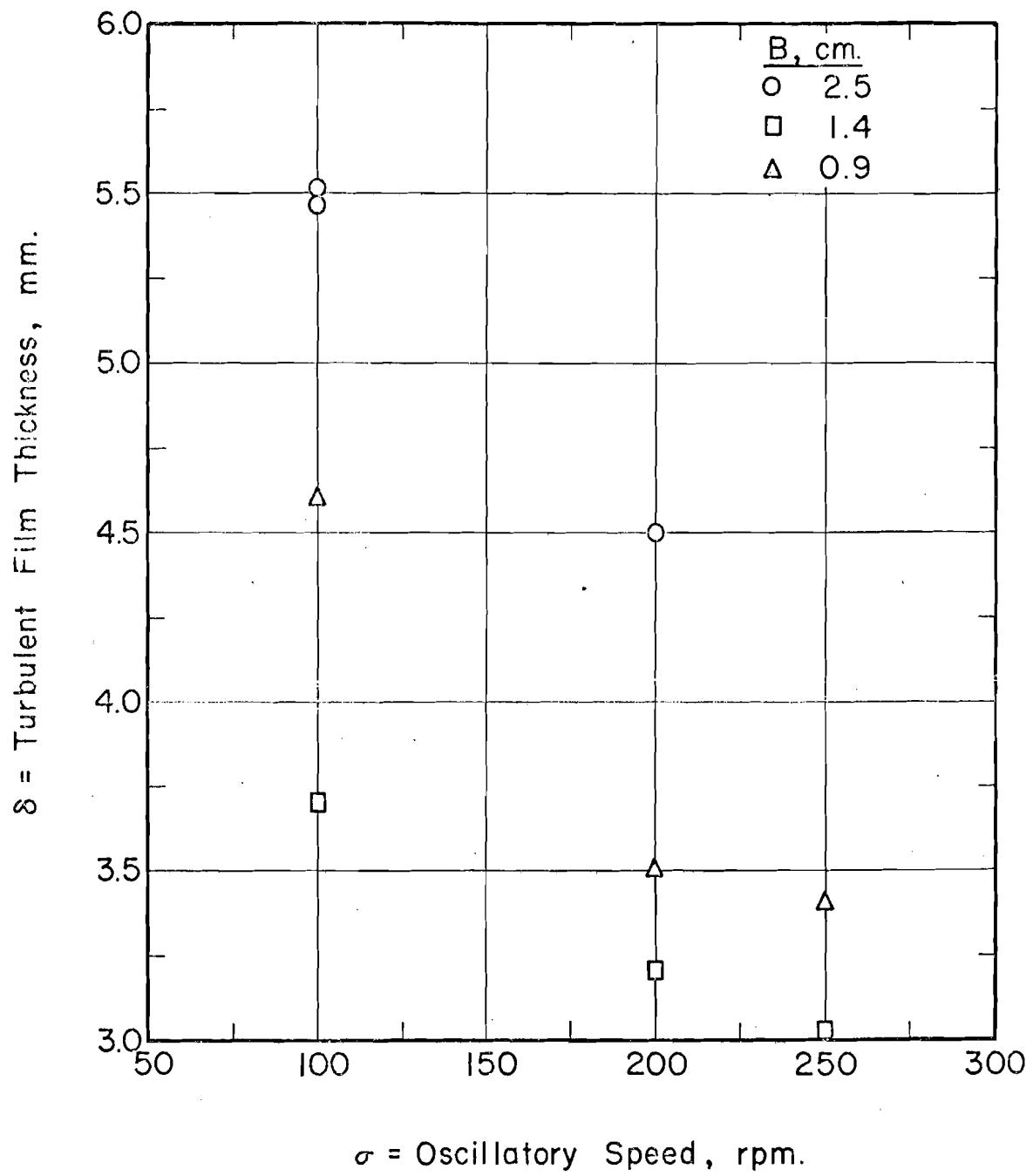


Fig. 3.3 Turbulent Film Thickness for Heat

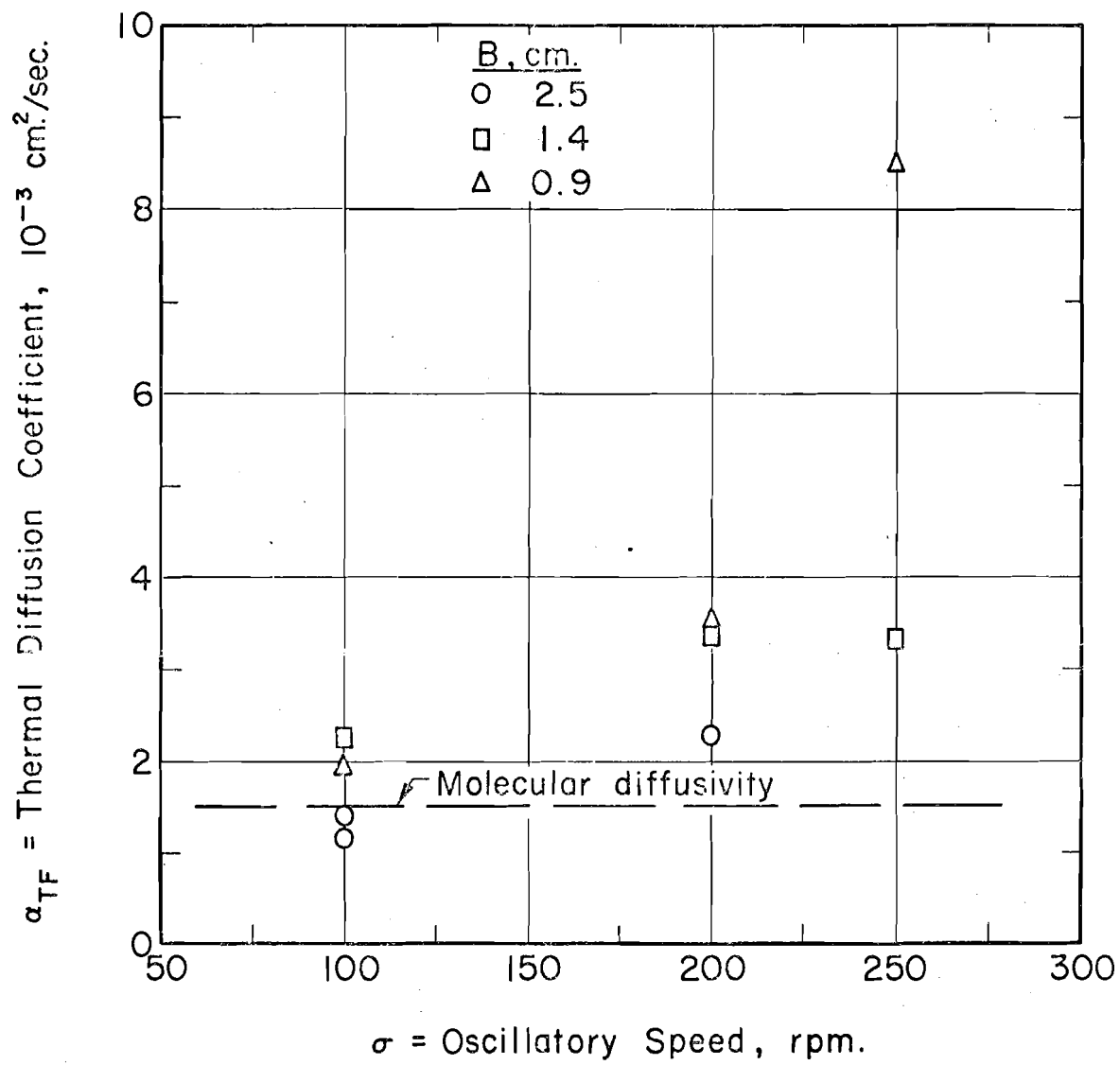


Fig. 3.4 Diffusion Coefficient in Turbulent Film

value, the next largest value of α_{TF} was about 2.3 times the molecular value.)

3.3) REAERATION EXPERIMENTS

As mentioned previously, it is not possible to measure the details of the dissolved oxygen concentration in the turbulent film. Thus, in the reaeration tests, only the total rate of oxygen absorption could be determined. Nevertheless, from the results of the tests described below, it seems possible to draw some inferences concerning the turbulent film.

The same mixing vessel described previously (Fig. 3.1) was used in the reaeration tests. Water was deaerated by circulating it through spray nozzles in a vacuum tank. During reaeration, the dissolved oxygen concentrations were determined by a Beckman membrane electrode which was placed in a flow cell through which the water from the mixing vessel was circulated. The cell was designed with a small flow section at the sensitive end of the electrode so that a velocity of 8 fps would be maintained for a flow of only 0.5 gpm. Some tests with the electrode indicated that it might be velocity sensitive up to velocities of 5 fps. The flow rate of 0.5 gpm corresponded to a detention time of about 30 minutes for the water in the mixing vessel. Since the inlet and outlet ports were in the bottom of the mixing vessel, it was felt that any mixing associated with the flow through the electrode flow cell would be negligible compared to the mixing caused by the oscillating grids.

Tests were run at 25°C for various values of σ and B. For the tap water used, the saturation concentration was determined by Winkler tests to be 8.00 mg/l. The measured concentrations were plotted in terms of deficit on semilog paper to obtain k_2 in accordance with Eq. 1.2. Knowing the depth, K_L was calculated (Eq. 2.5) and the results are shown in Fig. 3.5.

The heat diffusion tests indicated that α_{TF} was approximately equal to the molecular heat diffusivity at $\sigma = 100$ rpm and $B = 2.5$ cm. If it is assumed that the diffusion coefficient in the turbulent oxygen film was equal to the molecular oxygen diffusivity for the same values of σ and B, it is possible to calculate the film thickness for that condition (Eq. 3.2). Taking the molecular diffusivity as $0.0000241 \text{ cm}^2/\text{sec}$ at 25°C [Camp, 1958], δ for the reaeration process was calculated to be 0.27 mm. This value is approximately 20 times smaller than the δ -value for heat absorption for the same mixing conditions. (See Section 3.4 also.)

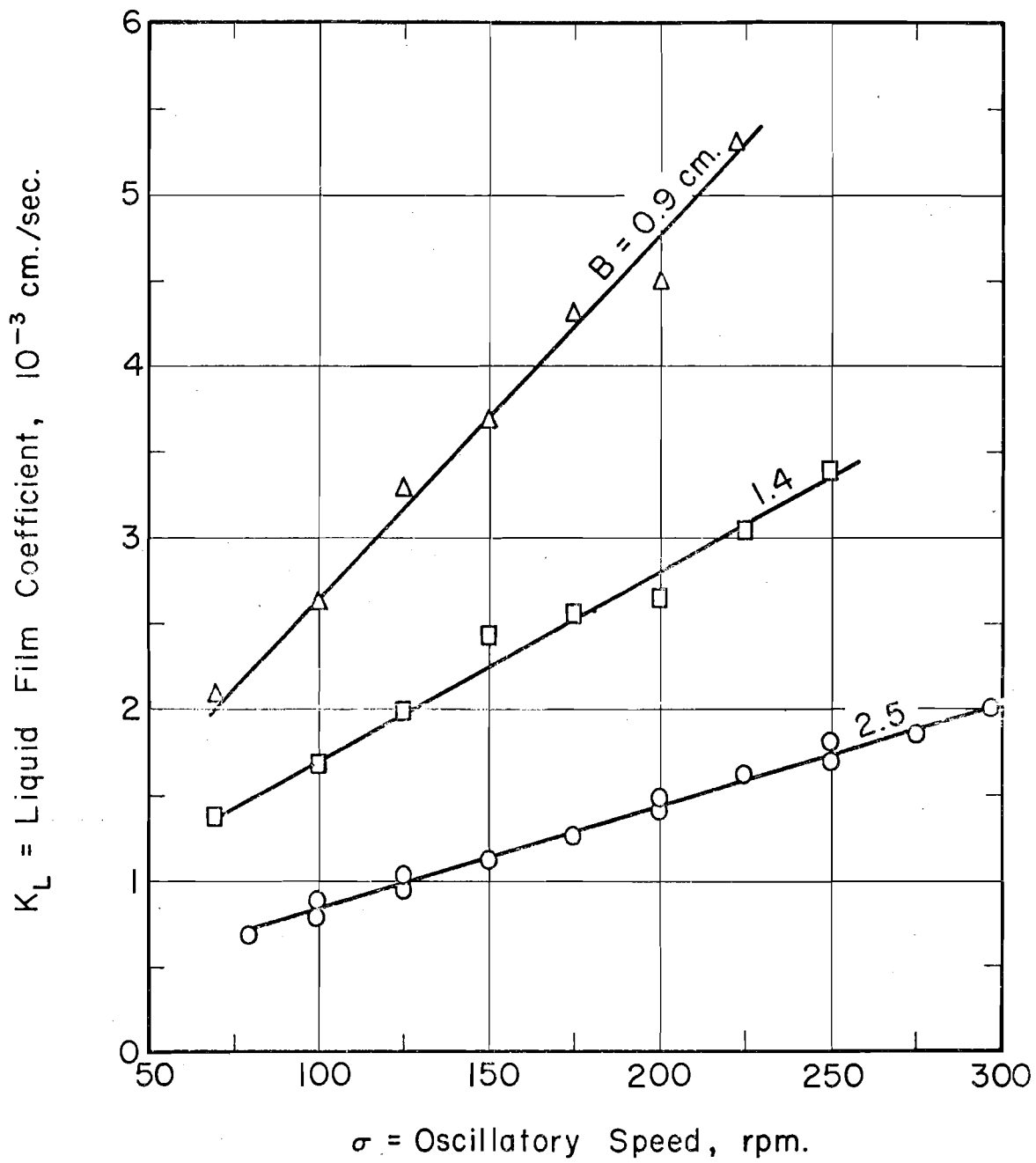


Fig. 3.5 K_L for Mixing Vessel

3.4) BOUNDARY LAYER CONCEPTS

There is a large amount of information in the literature on momentum, mass, and heat boundary layers. The analogy between transfer of momentum, mass, and heat is discussed by Bird et al [1960], Hinze [1959], and Schlichting [1960]. No attempt is made here to give a comprehensive review of related material. Rather, the purpose is to cite sufficient data to establish the fact that the thickness of mass and heat boundary layers depends respectively on the Schmidt and Prandtl numbers, as well as on mixing conditions. Since the turbulent surface film in gas absorption can also be viewed as a mass boundary layer, it should then be expected that the thickness of the turbulent surface film also varies with the Schmidt number as well as with mixing conditions. The fact that the film is indeed a boundary layer is evident just from the definition of a boundary layer [Schlichting, 1960]. However, this is further substantiated by the data of Thackston and Krenkel [1969] as represented by Eq. 2.10. Using the diffusion model and Eqs. 2.5 and 3.2 and using the Darcy-Weisbach equation (with their friction factor f) to represent the friction slope, Eq. 2.10 can be manipulated to give

$$\frac{\delta}{h} = 9850 \frac{1}{\sqrt{f} \frac{Uh}{D_{TF}^*}} \quad 3.4$$

in which δ is the thickness of the turbulent film, D_{TF}^* is the diffusion coefficient in the film, U is the average velocity and h is the average flow depth. This equation is significant in that it shows that the film thickness depends on f and Uh/D_{TF}^* in the same way that the thickness of the viscous sublayer depends on f and the Reynolds number [Schlichting, 1960]. This is an empirical verification that the turbulent surface film behaves as a boundary layer.

Data from the literature can be used to show the dependence of the thickness of mass and heat boundary layers on the Schmidt number (Sc) and the Prandtl number (Pr), where

$$Sc = \frac{\nu}{D_m} \quad 3.5$$

$$\text{Pr} = \frac{\nu}{\alpha_m} \quad 3.6$$

where D_m^* is the molecular mass diffusivity and α_m is the molecular heat diffusivity. The example which is used is that of mass and heat sublayers in established pipe flow. Some data is given in Fig. 3.6 and Table 3.1.

The points 1 through 9 (Fig. 3.6) for heat transfer were obtained by defining the edge of the sublayer as the location of the maximum of measured turbulent heat fluctuations [Schlichting, 1960]. The solid curves for heat transfer were obtained from similar curves given by Bird et al [1960] in terms of the Nusselt number, Nu. Using a diffusion model for the pipe, it can be shown that

$$\frac{\delta_p}{d} = \frac{1}{\text{Nu}} \quad 3.7$$

where δ_p is the sublayer thickness for pipe flow and d is the pipe diameter. In applying the diffusion model to the pipe, it was assumed that the concentration distribution across the pipe diameter was uniform in the central part of the pipe and had a steep gradient in the film or sublayer next to the pipe wall. Measured temperature distributions indicate that this assumed distribution is a better approximation as the Prandtl number increases [Rust and Sesonske, 1966]. By analogy, the same is probably true for mass concentration distributions as the Schmidt number increases. It was further assumed that the diffusion coefficient in the sublayer was equal to the molecular value.

Son and Hanratty [1967] summarize mass transfer data from several sources, using a dimensionless mass transfer coefficient T . Again, applying the diffusion model, it can be seen that δ_p is related to their coefficient T by

$$\frac{\delta_p}{d} = \frac{1}{\text{Re Sc } T} \sqrt{\frac{f}{8}} \quad 3.8$$

where Re is the pipe Reynolds number, and f is the Darcy-Weisbach friction factor.

It may be seen from Fig. 3.6 that as the Schmidt or Prandtl numbers increase for constant Reynolds number, the thickness of the sublayer decreases. Also, for constant Sc or Pr , the sublayer thickness decreases as the Reynolds number increases. The information in Fig. 3.6 (and much more

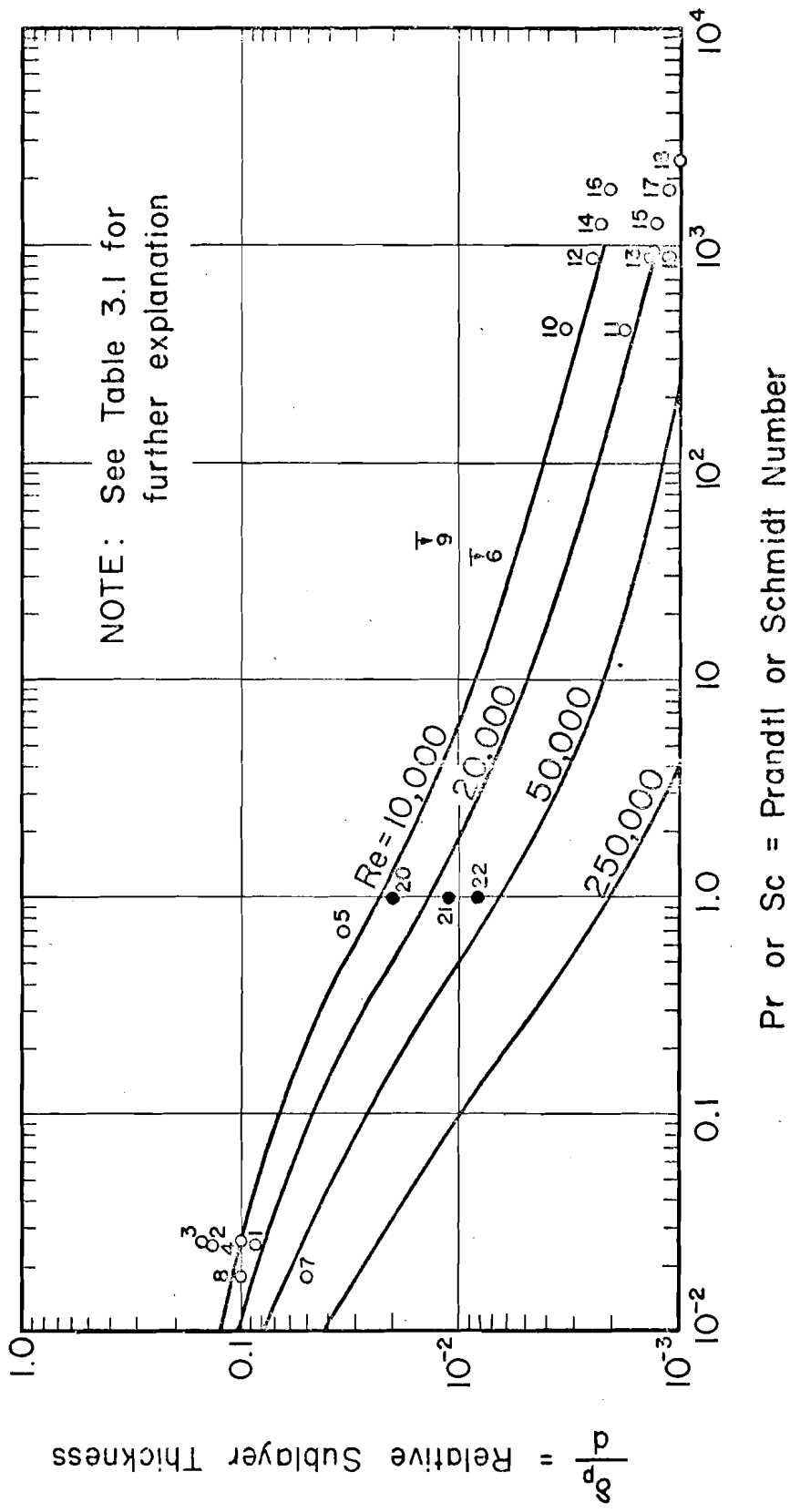


Fig. 3.6 Dependence of Heat and Mass Boundary Layer Thickness on Prandtl and Schmidt Number

Table 3.1

SUBLAYER PARAMETERS IN PIPE FLOW

Point in Fig. 3.6	Reference	Pr	Sc	δ_p/d	Re	Notes
1	Bobkov et all [1955]	0.025		0.086	70,000	a
2	"	0.025		0.134	16,000	a
3	Hochreiter & Sesonskee [1969]	0.026		0.15	26,800	a
4	"	0.026		0.1	65,200	a
5	"	0.70		0.034	22,500	a
6	"	36.		<0.009	12,600	a,b
7	Rust & Sesonskee [1966]	0.018		0.05	243,000	a
8	"	0.018		0.1	49,500	a
9	"	44.		<0.016	5800-12,600	a,b
10	Son & Hanratty [1967], Fig. 1		410	0.00323	10,000	c
11	"		410	0.00176	20,000	c
12	"		890	0.00247	10,000	c
13	"		890	0.00135	20,000	c
14	"		1230	0.00226	10,000	c
15	"		1230	0.00124	20,000	c
16	"		1785	0.00207	10,000	c
17	"		1785	0.00113	20,000	c
18	Son & Hanratty [1967], Table 1		2400	0.00103	20,000	c
19	Son & Hanratty [1967], Table 2		900	0.00131	20,000	c
20				0.0202	10,000	d
21				0.0110	20,000	d
22				0.0082	50,000	d

- a) δ_p/d obtained from location of maximum temperature fluctuations
- b) Maximum fluctuation was closer to wall than could be measured
- c) δ_p/d obtained from mass transfer coefficient (Eq. 3.8)
- d) These points are for the momentum sublayer thickness and were calculated from $\delta_p = 11.6\nu/(\text{shear velocity})$. The points are plotted at a value of unity on the abscissa since the corresponding dimensionless number would be $\nu/\nu = 1$.

similar information in the literature) clearly indicates that the thickness of the sublayer in turbulent pipe flow depends not only on Reynolds number (i.e. mixing conditions) but also on the Schmidt number or Prandtl number of the quantity being transported. Since the turbulent surface film in gas absorption problems is also a boundary layer, there appears to be adequate justification for expecting that the thickness of the turbulent film depends on Schmidt number as well as mixing conditions. This also explains why the turbulent film thickness for heat was much greater than that for oxygen in the experiments cited above in Sections 3.2 and 3.3, namely that the Prandtl number for water is much less than the Schmidt number for oxygen in water.

Figure 3.6 indicates for flow in smooth pipes that δ_p/d for the mass sublayer varies approximately as the negative one-quarter power of the Schmidt number for $400 < Sc < 2500$ for constant hydrodynamic or mixing conditions. There is not necessarily any basis for assuming that the thickness of the turbulent surface film has the same relative numerical dependence on Schmidt number. Nevertheless, if this assumption is made, there would be approximately a 25% difference in δ for helium and nitrogen, and the technique used to calculate surface renewal rates [Dobbins, 1962 and 1964] would appear to be open to serious question.

3.5) SUMMARY

In turbulent water, turbulence exists at the free surface. Thus, the concept of a stagnant film in reaeration or gas absorption is not valid. However, it is possible to represent the transport downward from the free surface in terms of a diffusion model for turbulent flow in a manner similar to other transport problems in turbulent flow. In this model, the stagnant film is replaced by an oxygen boundary layer or a "turbulent surface film". Experiments indicate that even with turbulence in the film, the diffusion coefficient in the film is approximately equal to the molecular value for low mixing rates. Further, the thickness of the film varies with the Schmidt number as well as with the mixing conditions.

CHAPTER 4

ANALYTICAL WORK

In this chapter, some analytical solutions for the one-dimensional vertical distribution of oxygen under various conditions are presented. These solutions were derived from the vertical mass balance equation for oxygen which can be written as [Bird et al, 1960]

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial y} (D^* \frac{\partial c}{\partial y}) - r \quad 4.1$$

where c is the oxygen concentration, D^* is the diffusion coefficient in the vertical (y) direction, t is time, and r is a term to represent the rate at which oxygen is utilized per unit mass. Assuming the oxygen saturation concentration (c_s) to be constant, Eq. 4.1 may be written as

$$\frac{\partial d}{\partial t} = \frac{\partial}{\partial y} (D^* \frac{\partial d}{\partial y}) + r \quad 4.2$$

where d is the oxygen deficit which is equal to $c_s - c$. A lower case letter (d) is used to indicate the deficit as a function of y as well as t . The capital letter (D) is used later for the average deficit over the depth. Eq. 4.1 and 4.2 apply most directly to water in a mixing vessel of constant depth (h) and with homogeneous mixing in horizontal planes. However, to make applications to streams, it generally is possible to interpret t as the flow time, i.e. as longitudinal distance divided by mean velocity. In such a case, it should be noted that the previously mentioned assumptions of constant depth and homogeneous mixing are still implied.

4.1) NO OXYGEN DEMAND

4.1.1) Exact Solution

With no oxygen demand, r in Eqs. 4.1 and 4.2 is zero. For convenience, the y coordinate is taken as being positive upward with $y = 0$ at the bottom of the water. Using the diffusion model discussed in Chapter 3 it is assumed that there is a turbulent surface film of thickness δ and that the rate of oxygen transport through the film is given by Eq. 2.3 with the deficit

in that equation being the deficit at the lower edge of the film so that

$$q = AK_L d(h,t) \quad 4.3$$

Because the film thickness δ is very small, it is acceptable to take $y = h$ at the bottom of the film rather than the actual water surface. The oxygen which comes through the film must be transported away by diffusion below the film so that

$$K_L d(h,t) + D \frac{\partial d(h,t)}{\partial y} = 0 \quad 4.4$$

This condition is taken as the boundary condition which the solution of Eq. 4.2 must satisfy at $y = h$. At $y = 0$, the boundary condition is

$$D \frac{\partial d(0,t)}{\partial y} = 0 \quad 4.5$$

in order for there to be no transport of oxygen out of the bottom of the water. Initially, at $t = 0$, let the distribution of d be uniform with

$$d(y,0) = D_o \quad 4.6$$

Further, assuming that the diffusion coefficient is constant in the region $0 < y < h$, standard techniques [Carslaw and Jaeger, 1959] may be used to show that the solution to Eq. 4.2 is

$$\frac{d}{D_o} = 4 \sum_{n=1}^{\infty} \exp(-\beta_n^2 \tau) \frac{\sin \beta_n \cos(\beta_n \eta)}{2\beta_n + \sin(2\beta_n)} \quad 4.7$$

where the dimensionless parameters are

$$\begin{aligned} \eta &= y/h \\ \tau &= D^* t/h^2 \end{aligned} \quad 4.8$$

and the values of β_n are the non-negative roots of

$$\beta_n \tan \beta_n = \alpha \quad 4.9$$

where

$$\alpha = K_L h / D^* \quad 4.10$$

(Note that this α is completely different from the α of Eq. 2.12.)

Eq. 4.7 may be used to calculate the deficit or concentration for a particular situation as a function of y and t by specifying values for h , D^* , and K_L . Such a computation involves the indicated summation and this can be performed numerically with very little difficulty. However, it is usually the case that all but the first term of the infinite series are negligible, as shown below. When this is the case, it is possible to simplify the solution so that it is not necessary to use numerical computations to gain some insight into the vertical distribution of oxygen.

4.1.2) Approximate Solution

The value of α is normally much less than unity. Further, on the basis of Thackston and Krenkel's equation (Eq. 2.10), α has an essentially constant value for open channel flows of clean water. This can be demonstrated as follows: (a) Assume a zero Froude number (i.e. a horizontal water surface) in Eq. 2.10. (b) Multiply Eq. 2.10 by $2.3h$ to convert k_2 to K_L . (c) Take $D^* = hu_* / 15$ [Harleman and Holley, 1963]. Recognizing that $u_* = \sqrt{ghS}$ for two dimensional flow, substitution into Eq. 4.10 gives

$$\alpha = 0.0043 \quad 4.11$$

From this value of α , β_n is approximately $n\pi$ for $n > 1$ so that $\sin \beta_n$ is approximately zero for $n > 1$. Thus, Eqs. 4.7 and 4.9 may be written respectively as

$$\frac{d}{D_0} = 4 \exp(-\beta_1^2 \tau) \frac{\sin \beta_1 \cos(\beta_1 \eta)}{2\beta_1 + \sin(2\beta_1)} \quad \text{for } \alpha \ll 1 \quad 4.12$$

and

$$\beta_1^2 = \alpha \quad 4.13$$

since $\tan\beta_1 \approx \beta_1$ for small α . After expanding the trigonometric terms in Eq. 4.12 in power series, multiplying and dividing the series, and retaining only terms of order β_1^2 , the approximate solution becomes

$$\frac{d}{D_o} = \left[1 - \frac{\beta_1^2}{2} \left(\frac{1}{3} + \eta^2 \right) \right] \exp(-\beta_1^2 \tau) \quad 4.14$$

Eq. 4.14 may now be used directly to estimate the vertical variation of deficit. For example, differentiation gives the dimensionless vertical gradient as

$$\frac{1}{D_o} \frac{\partial d}{\partial \eta} = (-\beta_1^2 \eta) \exp(-\beta_1^2 \tau) \quad 4.15$$

Also, the ratio of the deficit at the bottom of the film ($\eta = 1$) and at the bottom of the water ($\eta = 0$) at any time is

$$\frac{d(1, \tau)}{d(0, \tau)} = 1 - \frac{\beta_1^2}{2} \quad 4.16$$

For the value $\alpha = 0.0043$ cited previously, the deficit varies by only 0.2% over the depth. This indicates the difficulty of trying to measure vertical gradients of oxygen in turbulent streams.

4.1.3) Average Deficit

If Eq. 4.14 is averaged over the depth h and the average value of d is written as D , then the result may be written as

$$\frac{D}{D_o} = \left[1 - \frac{K_2 h^2}{3D^*} \right] \exp(-K_2 t) \quad 4.17$$

after substituting for β_1 from Eqs. 4.13, 4.10, and 2.5, and for τ from Eq. 4.8. The expression normally used in analyzing reaeration problems is Eq. 1.2:

$$\frac{D}{D_0} = \exp(-K_2 t) \quad 1.2$$

The difference between Eqs. 4.17 and 1.2 is the bracketed term in Eq. 4.17. This is the term which embodies the effects of having considered the deficit to be a variable with depth, and thus is an indication of the magnitude of error if the deficit is assumed to be uniform with depth. Again using $\alpha = 0.0043$, the error indicated by the bracketed term is 0.1%. Thus, this analysis verifies that no significant error is introduced in these situation by assuming the deficit to be constant over the depth.

4.2) SODIUM SULFITE

It is well known that the presence of chemicals such as catalyzed sodium sulfite can increase the rate of absorption of oxygen. This section presents some analytical considerations related to the mechanics by which the presence of sodium sulfite influences the absorption rate.

4.2.1) Finite Reaction Rate

First, assume that the reaction rate between oxygen and sulfite is extremely rapid, but finite. When an excess of sulfite is present, the oxygen concentration below the film is essentially zero and a steady state concentration can develop in the film ($\partial c / \partial t$ in Eq. 4.1 is zero). As mentioned in Section 2.4, the reaction rate between oxygen and sulfite is independent of sulfite concentration over a wide range, so r in Eq. 4.1 can be written as $r = K_s c$, where K_s is constant and given approximately as $37,000 \text{ sec}^{-1}$ [Westerterp et al, 1963]. Assuming D^* to be constant, Eq. 4.1 may be written as

$$D^* \frac{d^2 c}{dy^2} = K_s c \quad 4.18$$

Taking the boundary conditions as $c = c_s$ at $y = 0$ (free surface) and $c = 0$ at $y = \delta_s$ (bottom of film with sulfite), the solution to Eq. 4.18 is

$$\frac{c}{c_s} = \frac{\sinh b(1-y/\delta_s)}{\sinh b} \quad 4.19$$

where

$$b = \sqrt{\frac{K_s \delta_s^2}{D^*}} \quad 4.20$$

For four values of b , this solution is shown in Fig. 4.1

The absorption rate is equal to the mass flux by diffusion at the surface. Thus, the increase in absorption rate due to the sulfite must be caused by a steepening of the concentration gradient with sulfite as compared to the situation without sulfite. This steepening can take place in two ways: (1) With a linear concentration distribution, the gradient would be greater if the sulfite caused a decrease in the film thickness. (2) Without changing δ , the gradient can be increased by the sulfite's causing a curved concentration distribution. (See Fig. 4.1). Of course, a combination of decreased δ and curved concentration distribution can occur. It can be seen that for $b > 5$, the meaning of the film thickness becomes a bit obscure since the oxygen concentration goes to essentially zero for $y < \delta_s$. At this time, it does not appear to be possible to distinguish which of these two ways is associated with the increased absorption rate due to sulfite. This point is discussed further below.

The mass flux of oxygen at the surface with sulfite present is

$$q_s = -AD^* \left. \frac{dc}{dy} \right|_{y=0} = A \frac{D^* c_s}{\delta_s} \frac{b}{\tanh b} \quad 4.21$$

where A is the surface area. The corresponding mass flux with no sulfite is given by Eq. 2.1 with $C = 0$. Taking the ratio of these two quantities gives

$$q^* = \frac{\text{mass flux with sulfite}}{\text{mass flux without sulfite}} = \frac{\delta}{\delta_s} \frac{b}{\tanh b} \quad 4.22$$

where δ is the film thickness without sulfite and δ_s is with sulfite. If

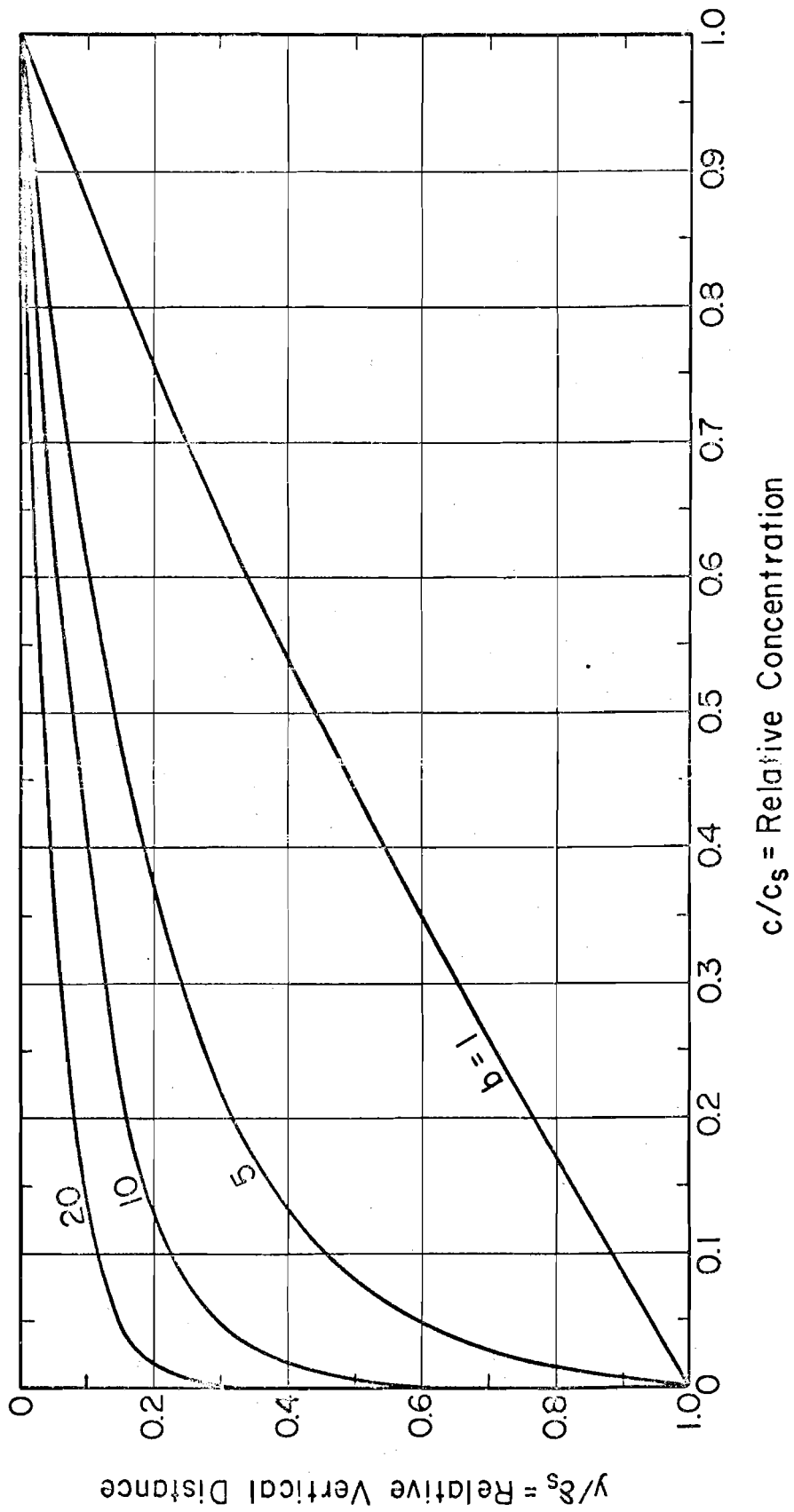


Fig. 4.1 Oxygen Distribution in Film with Sulfite

b is large enough (>2.5), $\tanh b$ will be approximately unity. Then Eqs. 4.20 and 4.22 give

$$q^* = \delta \sqrt{\frac{K_s}{D^*}} \quad 4.23$$

By measuring absorption rates to determine q^* , one of the quantities on the right-hand side of Eq. 4.23 can be calculated if the other two are known. Data in Section 5.3 (Fig. 5.3) gives q^* as approximately 18 for a 10-in. depth. Taking the previously quoted value for K_s ($37,000 \text{ sec}^{-1}$) and assuming that D^* is the molecular value ($0.00002 \text{ cm}^2/\text{sec}$) gives $\delta = 0.0004 \text{ cm}$. Using this value in Eq. 2.2 to calculate K_L without sulfite gives $K_L = 0.05 \text{ cm/sec}$, again using the molecular diffusivity. This value of K_L is equal to about 0.6 of the average measured value (Fig. 5.3). Considering the scatter in the data and the assumptions made above, this would appear to substantiate at least the order of magnitude of the values used for K_s and D^* . If the same analysis is applied to O'Connor and Dobbins data (Fig. 2.2) for $\sigma = 45 \text{ rpm}$, approximately the same agreement is found. In these examples, only the lowest degree of mixing was considered since this should come nearest to satisfying the assumption of a molecular diffusivity in the film.

Unfortunately, neither Eq. 4.21 nor 4.22 can be used to estimate the film thickness with sulfite (δ_s) because the δ_s in the denominator cancels with the δ_s in b in the numerator. Eq. 4.21 can be rewritten as

$$q_s = A c_s \sqrt{K_s D^*} \quad 4.24$$

assuming $\tanh b \approx 1$. This indicates that q_s should change relatively slowly with changing mixing conditions since K_s should be constant and D^* should change slowly on the basis on the discussion in Section 3.2. Further q_s changes only as the square root of D^* . The data of O'Connor and Dobbins indicates about a 50% increase in D^* over the range of their tests (Fig. 2.2) using Eq. 4.24 and assuming A to be constant.

Similarly, Eq. 4.23 gives some insight into the behavior of the ratio q^* . Eq 4.23 can be re-written as

$$q^* = \frac{\sqrt{D K_s^*}}{K_L}$$

4.25

which shows that as mixing increases (i.e. as K_L , the absorption coefficient without sulfite increases), the ratio q^* should decrease. This is in accordance with the data of O'Connor and Dobbins (Fig. 4.2).

The preceding analysis seems to be essentially consistent with the data available, as mentioned. However, there is one aspect of the problem which has not been considered, namely, the need for sulfite to be transported from the bulk of the water toward the free surface in order to support the oxygen-sulfite reaction. This aspect could be included in this analysis assuming a finite reaction rate, but it is somewhat simpler to do it assuming an infinite reaction rate as is done in the next section.

4.2.2) Infinite Reaction Rate

The rate of reaction between dissolved oxygen and catalyzed sodium sulfite is so rapid that it can effectively be assumed to take place instantaneously or infinitely fast. Under this assumption, it is not possible for oxygen and sulfite to both be present simultaneously at the same place in the water. Then it is somewhat easier to visualize the distributions of oxygen and sulfite. In an idealized picture, they would be as shown in Fig. 4.3 with oxygen being absorbed at the surface and diffusing downward to a plane where it reacts with the sulfite. Similarly, the sulfite diffuses upward. Since all of the reaction takes place at this one plane the distributions of both c and s are linear at steady state if the diffusion coefficients are constant. (See, for example, Bird et al [1960].) A solution can be obtained for the unsteady state diffusion of sulfite in a fashion similar to that given in Section 4.3. Such a solution indicates that the deviation from a linear profile is less than 1% of S_0 . Thus, a linear profile is assumed.

Schultz and Gaden [1956] postulated another type of distribution of sulfite in the film region based generally on the mechanics of reaction between the oxygen and the sulfite. The distribution postulated by them is not used here because it has a non-zero gradient at the free surface. Such a situation would require the diffusion of sulfite across the free surface.

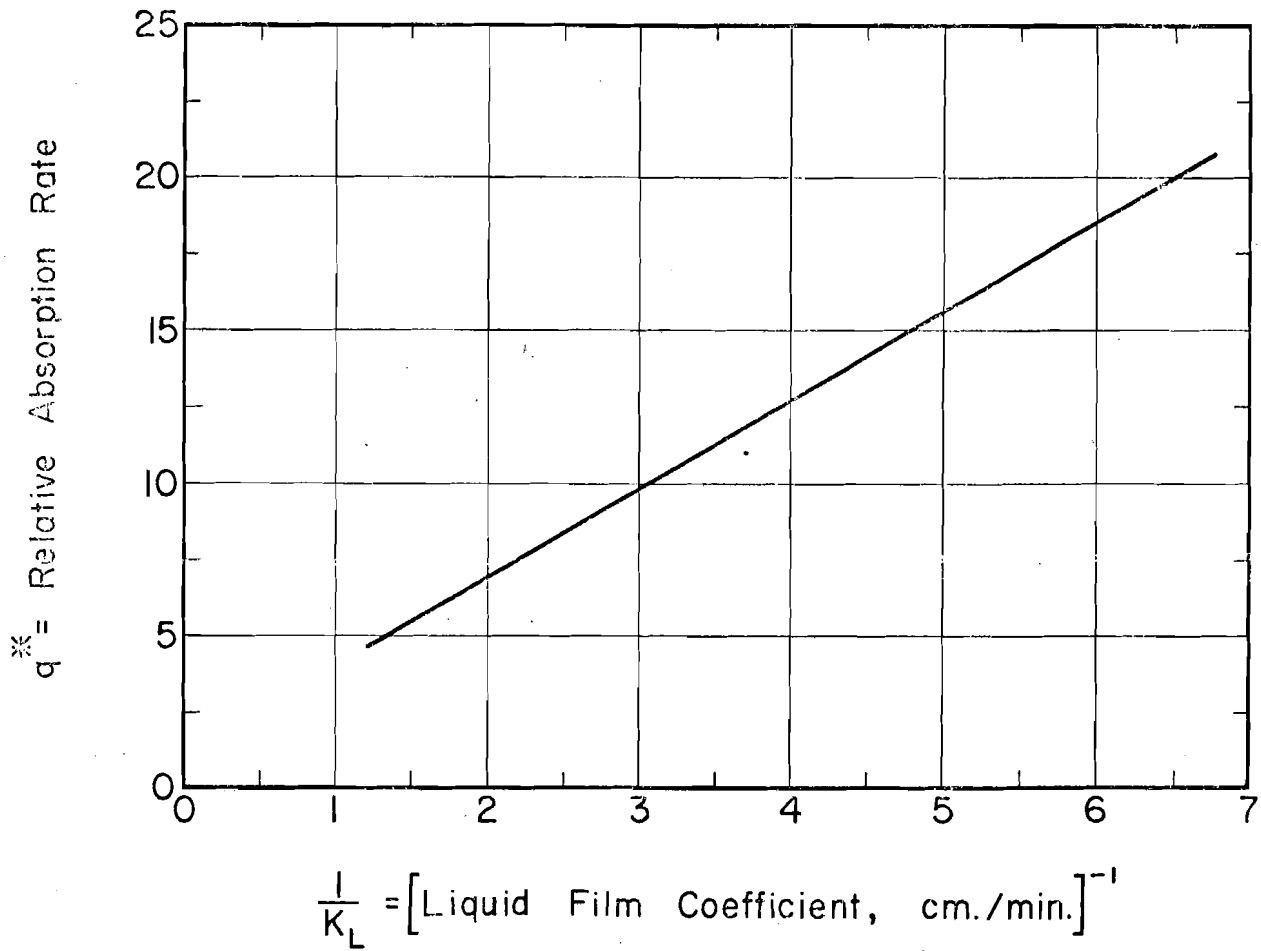


Fig. 4.2 Change in Relative Absorption Rate with K_L

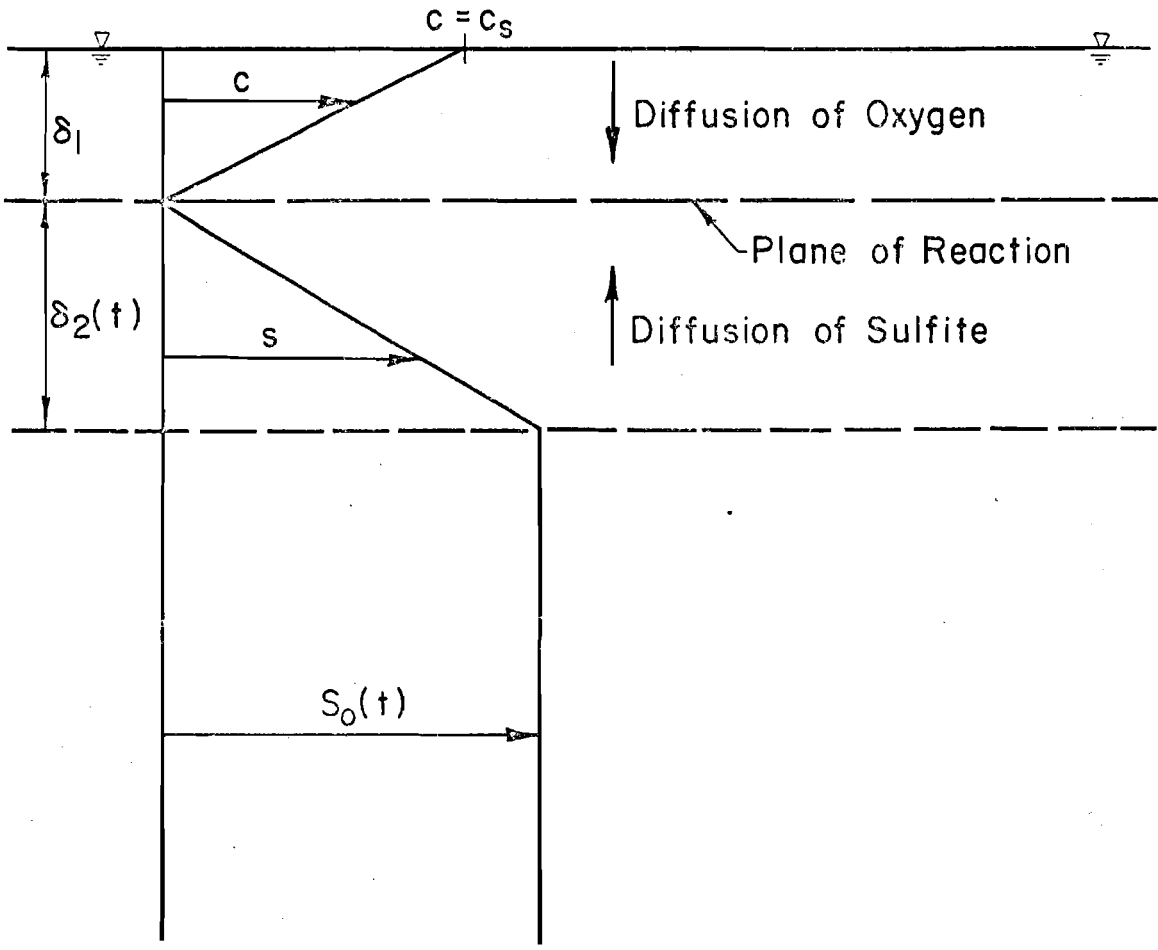


Fig. 4.3 Films with Infinite Sulfite Reaction Rate

In Chap. 5 some experimental results for the absorption of oxygen in the presence of sulfite are given. In these experiments it was observed that the sulfite concentration S_o in the water decreased linearly with time. This implies a constant absorption rate of oxygen and a constant gradient of oxygen. If the surface concentration of oxygen is constant, then δ must also be constant with time.

Using the diffusion equations, the linear distributions, and the assumed total reaction at the plane shown in Fig. 4.3, one may write

$$5D_1^* \frac{c_s}{\delta_1} = D_2^* \frac{S_o}{\delta_2} \quad 4.26$$

where the subscripts 1 and 2 refer to the regions of oxygen and sulfite diffusion and the factor 5 results from the fact that the concentrations are in mg/l and the molecular weight of sulfite is 5 times that of oxygen. Rearranging Eq. 4.26 gives

$$\frac{\delta_2}{\delta_1} = \frac{1}{5} \frac{D_2^* S_o}{D_1^* c_s} \quad 4.27$$

It is also possible to write an expression for the mass conservation of sulfite, namely that the rate of change of sulfite must equal the rate of diffusion through δ_2 :

$$\frac{dS_o}{dt} = \frac{D_2^* S_o}{h \delta_2} \quad 4.28$$

or

$$\delta_2 = \frac{D_2^* S_o}{h \frac{dS_o}{dt}} \quad 4.29$$

where h is the depth of water.

As discussed above, δ_1 was apparently constant while S_o decreased linearly with time for the experiments reported in Chap 5. From Eq. 4.29, this in turn implies a linear decrease of δ_2 with time in proportion to the decrease of S_o . It may be noted that the initial value of S_o was typically of the order of 1500 mg/l and c_s of the order of 8 mg/l. Assuming D_1^* and D_2^* to be approximately equal gives $\delta_2/\delta_1 \approx 40$ initially.

The representation of the sulfite-oxygen interaction presented in this section allows an interpretation which is in accord with available data (Fig. 2.2 and Section 5.3). However, there does not appear to be anything in the analysis to say explicitly that the rate limiting factor is the diffusion of sulfite toward the free surface. The concept of a time-varying film thickness has been applied previously [Bird, et al, 1960, p. 601, e.g.]. However, it may be noted that the data of O'Connor and Dobbins (Fig. 2.2) show that K_L with sulfite is approximately equal to K_L without sulfite plus a constant. One might ask whether there might be some other mechanism formulated which would give this type of relationship.

4.3) BIOCHEMICAL OXYGEN DEMAND

In this section, some mathematical solutions for oxygen concentrations are presented for the case of a biological oxygen demand (BOD) which has a slow reaction time. The first subsection considers the effects of the BOD on diffusion through the film and a comparison is made between the absorption rates with and without oxygen demand. The second subsection relates to the influence of bottom deposits on the oxygen distribution in the bulk of the water. As in the previous considerations, the solutions are presented in terms of a mixing vessel with the independent variable being t . For a stream, t may generally be taken as flow time.

4.3.1) Turbulent Surface Film

Consider the diffusion of oxygen through the film when there is a slow oxygen demand of concentration L present. The general situation is depicted in Fig. 4.4. On the basis of the results in Section 4.1, the oxygen concentration (c_b) in the bulk (i.e. below the film) is taken as constant over the depth h . Also, it is assumed that the oxygen demand is

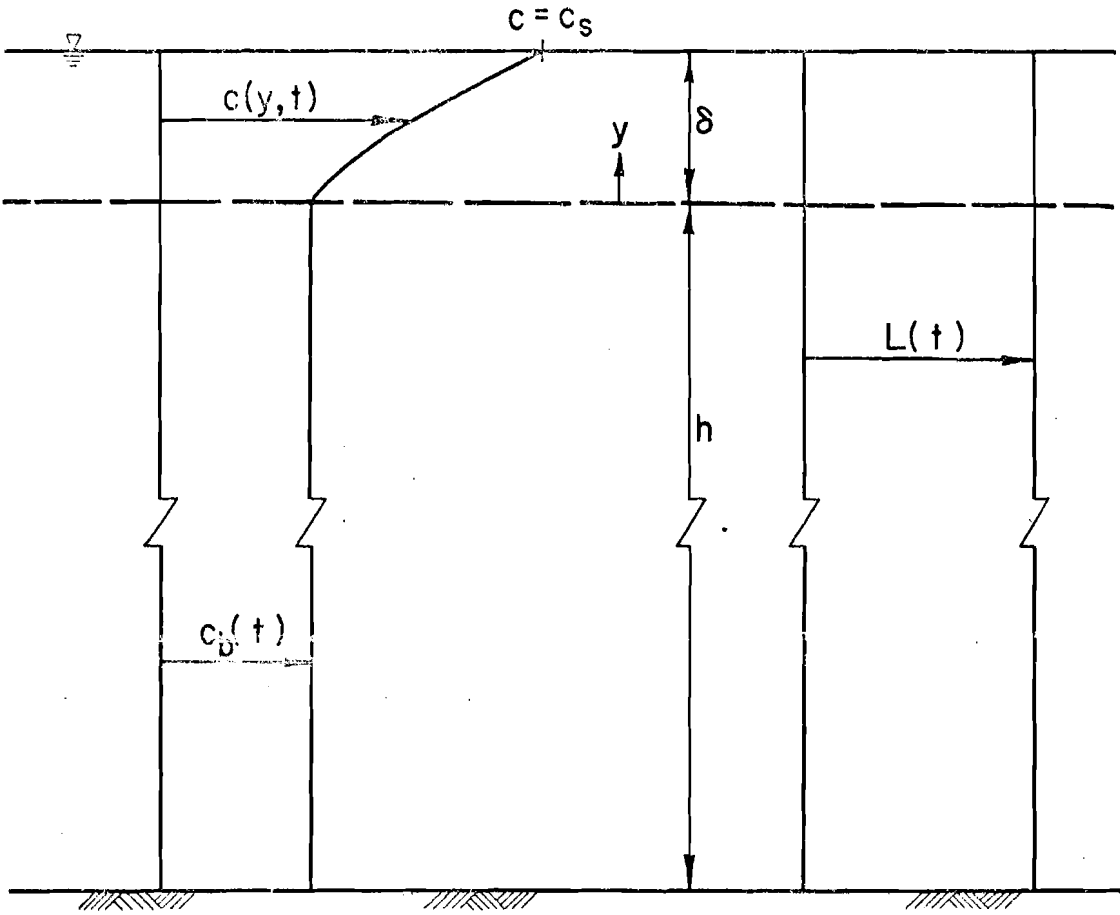


Fig. 4.4 Schematic Vertical Distributions with BOD

continuously distributed through the water rather than being associated with discrete particles. Assume that the rate of satisfaction of the oxygen demand is independent of the concentration of oxygen (c) and is given by the equation

$$\frac{dL}{dt} = -K_1 L \quad 4.30$$

If the initial oxygen demand is L_o , then the integral of Eq. 4.30 gives L at any time t as

$$\frac{L}{L_o} = e^{-K_1 t} \quad 4.31$$

Note that this implies that the oxygen concentration stays above some minimum level. Also, the assumption that dL/dt is independent of c (Eq. 4.30) states that the rate of change of L from its initial value is everywhere proportional to L . Thus, if L is initially uniformly distributed over the vertical, it will always remain uniformly distributed since dL/dt will be the same everywhere.

Further, Eq. 4.30 means that r in Eq. 4.1 equals $K_1 L$. Assuming the diffusion coefficient D^* to be constant in the film, Eq. 4.1 may be written for the film as

$$\frac{\partial c}{\partial t} = D^* \frac{\partial^2 c}{\partial y^2} - K_1 L \quad 4.32$$

The boundary and initial conditions for the turbulent surface film are taken as

$$\begin{aligned} c &= c_s \quad \text{at } y = \delta \\ c &= c_b \quad \text{at } y = 0 \\ c &= c_o \quad \text{at } t = 0 \end{aligned} \quad 4.33$$

The value of c_b in Eq. 4.33 is an unknown function of time. However, another equation may be obtained by writing an oxygen balance

for the bulk of the water, namely

$$\frac{\partial c_b}{\partial t} = \left[-\frac{D}{h} \frac{\partial c}{\partial y} \right]_{y=0+} - K_1 L \quad 4.34$$

This states that the rate of change of c_b must be given by the rate of diffusion of oxygen from the film into the bulk and the rate of utilization by the oxygen demand. As an initial condition, it is assumed that

$$c_b = c_o \quad \text{at } t = 0 \quad 4.35$$

The solution of Eq. 4.32 for the oxygen concentration in the film (using Eqs. 4.31, 4.33, 4.34, and 4.35) is

$$\frac{c}{c_s} = 1 + \frac{L_o}{c_s} e^{-\kappa T} \left[1 - \frac{\cos \sqrt{\kappa} Y - \sqrt{\kappa} H \sin(\sqrt{\kappa} Y)}{\cos \sqrt{\kappa} - \sqrt{\kappa} H \sin \sqrt{\kappa}} \right] \quad 4.36a$$

$$-2 \sum_{n=1}^{\infty} \left[1 - \frac{c_o}{c_s} + \frac{\kappa}{\kappa - A_n^2} \frac{L_o}{c_s} \right] \frac{\cos(A_n Y) - A_n H \sin(A_n Y)}{A_n^2 H \cos A_n + A_n (1+H) \sin A_n} e^{-A_n^2 T}$$

where the following dimensionless parameters have been introduced:

$$H = \frac{h}{\delta}$$

$$Y = \frac{y}{\delta}$$

$$T = \frac{D^* t}{\delta^2}$$

$$\kappa = \frac{K_1 \delta^2}{D^*}$$

4.36b

and A_n is given by the series of non-negative roots of

$$A_n \tan A_n = \frac{1}{H} \quad 4.37$$

By setting $Y = 0$ in Eq. 4.36, the solution for c_b is obtained (see Eq. 4.33):

$$\frac{c_b}{c_s} = 1 + \frac{L_o}{c_s} e^{-\kappa T} \left[1 - \frac{1}{\cos\sqrt{\kappa} - \sqrt{\kappa}H\sin\sqrt{\kappa}} \right] - 2 \sum_{n=1}^{\infty} \left[1 - \frac{c_o}{c_s} + \frac{\kappa}{\kappa - A_n^2} \frac{L_o}{c_s} \right] \frac{e^{-A_n^2 T}}{A_n^2 H \cos A_n + A_n (1+H) \sin A_n} \quad 4.38$$

Similarly, by differentiating Eq. 4.36 with respect to Y and evaluating the result at $Y = 1$, one obtains

$$\frac{1}{c_s} \left[\frac{\partial c}{\partial Y} \right]_{Y=1} = - \frac{L_o}{c_s} e^{-\kappa T} \frac{\kappa H \cos\sqrt{\kappa} + \sqrt{\kappa} \sin\sqrt{\kappa}}{\cos\sqrt{\kappa} - \sqrt{\kappa}H\sin\sqrt{\kappa}} - 2 \sum_{n=1}^{\infty} \left[1 - \frac{c_o}{c_s} + \frac{\kappa}{\kappa - A_n^2} \frac{L_o}{c_s} \right] \frac{A_n^2 H \cos A_n + A_n \sin A_n}{A_n^2 H \cos A_n + A_n (1+H) \sin A_n} e^{-A_n^2 T} \quad 4.39$$

This equation, multiplied by $c_s D^* / \delta$ gives the mass transport (absorption) rate of oxygen at the free surface.

As was done with Eq. 4.7, all of these equations could be simplified by expanding the trigonometric functions and retaining only the significant terms. However, in this case, these equations were investigated by a numerical evaluation of the various quantities.

In these equations, Y and T are dimensionless distance and time. The two parameters on which c depends are H and K , as well as the initial conditions c_o and L_o , of course. Also, it may be noted that κT equals $K_1 t$ and that H is the inverse of a dimensionless value of K_L or K_2 , i.e.

$$H = \frac{D^* h}{K_L \delta^2} = \frac{D^*}{K_2 \delta^2} \quad 4.40$$

using Eqs. 4.37, 2.2, and 2.5.

First, Eq. 4.36 will be used to represent the variation of c in the film for no oxygen demand (L_o and/or K_1 equal zero). The greatest non-linearity of the concentration distribution will occur for the fastest rate of change of c_b , the concentration in the bulk. This, in turn, corresponds to the smallest value of H . Mathematically, H can be made arbitrarily small, but physically $H = 100$ would represent an extremely small value (i.e. a depth of only 100 times the film thickness). From Eq. 3.4 it can be seen that a typical value of H for a stream might be 10,000. However, for the extreme case of $H = 100$, c is presented as a function of Y with T as a parameter in Fig. 4.5. Graphically, the lines are essentially straight. From the computations, it can be seen that the greatest deviation from a linear distribution is only 0.3%. Of course, for practical purposes, this is no deviation at all, so that it may be concluded that the gradient in the film is essentially linear even for the case of the unsteady absorption problem.

To illustrate the effects of oxygen demand, there are many possible combinations of values of K , H , L_o , and c_o . In general, the greatest effect occurs for large K and L_o . (However, if the values are too large, anaerobic conditions result.) An example of the concentration distributions in the film is shown in Fig. 4.6 for $H = 3000$, $\kappa = 0.0001$, $L_o/c_s = 5$, and $c_o/c_s = 1$. These values correspond to $K_1/K_2 = 0.3$. Again, it can be seen that the distributions are essentially linear with respect to Y .

The corresponding oxygen sag curve calculated from Eq. 4.39 is also shown in Fig. 4.6. It is possible to calculate the sag curve from the traditional equation which may be written as

$$D = D_o e^{-K_2 t} + \frac{K_1 L_o}{K_2 - K_1} (e^{-K_1 t} - e^{-K_2 t}) \quad 4.41a$$

which is the solution of Eq. 1.1 with $R = K_1 L$. In terms of the dimensionless parameters given in Eq 4.37, this may be re-written as

$$\frac{c}{c_s} = 1 + \frac{L_o}{c_s} e^{-\kappa T} \left[\frac{\kappa H}{\kappa H - 1} \right] - \left[1 - \frac{c_o}{c_s} + \frac{\kappa H}{\kappa H - 1} \frac{L_o}{c_s} \right] e^{-T/H} \quad 4.41b$$

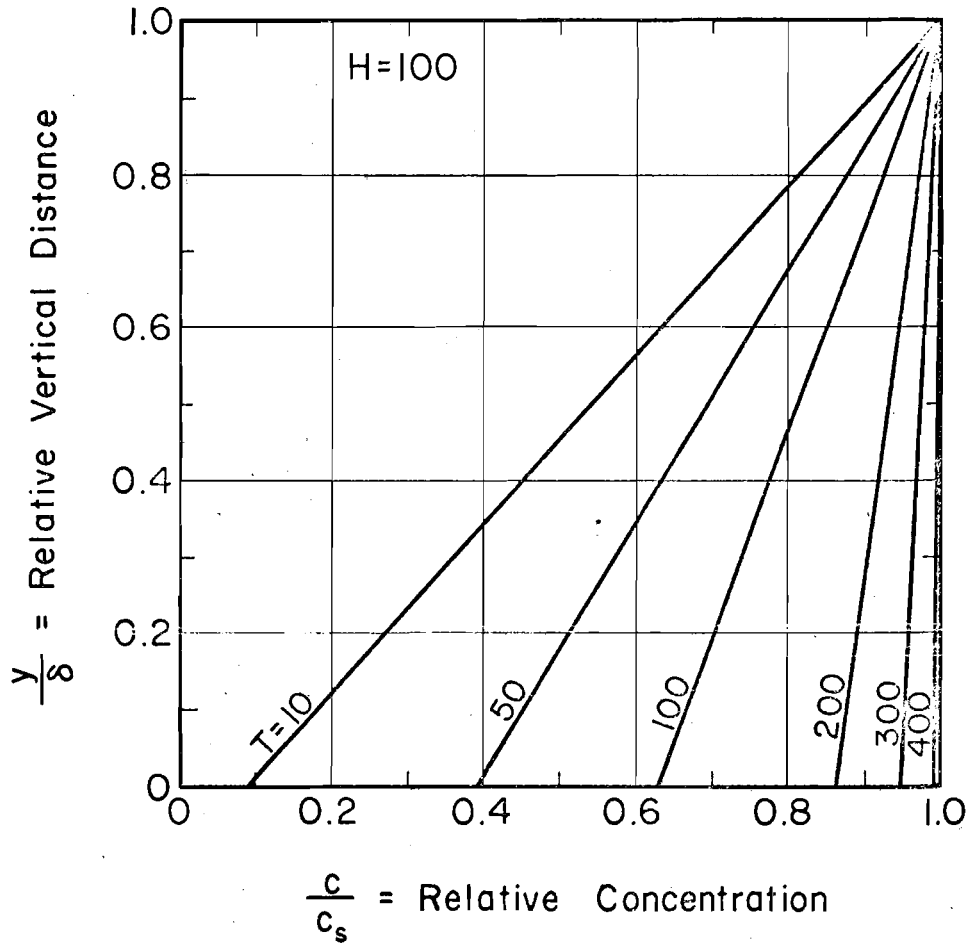


Fig. 4.5 Distribution in Film with No Oxygen Demand

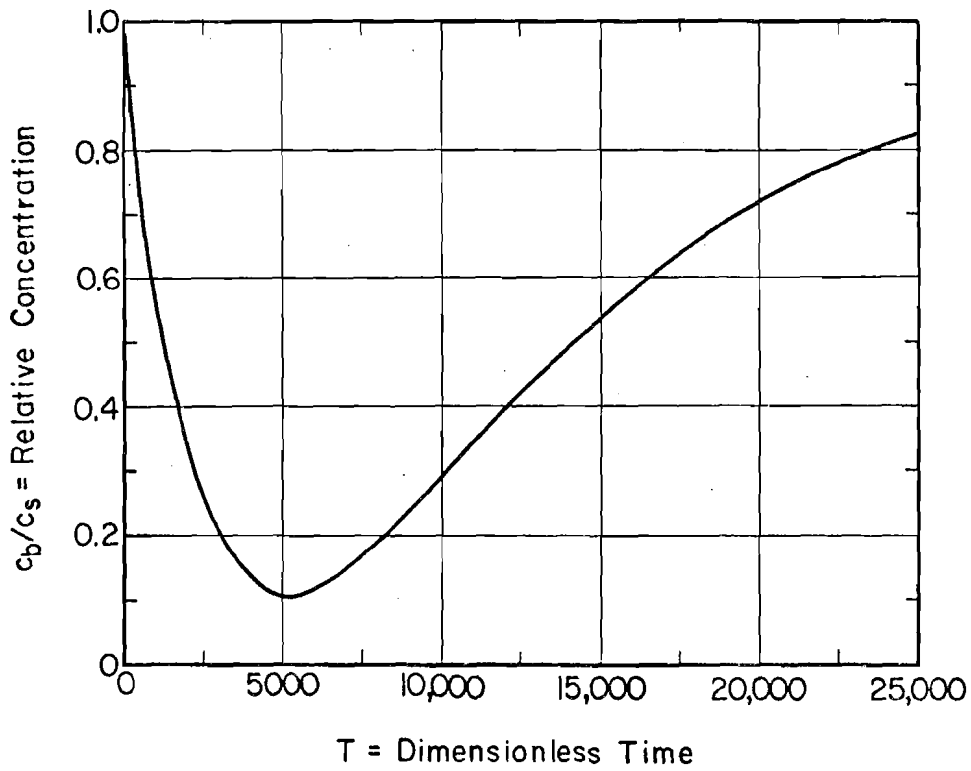
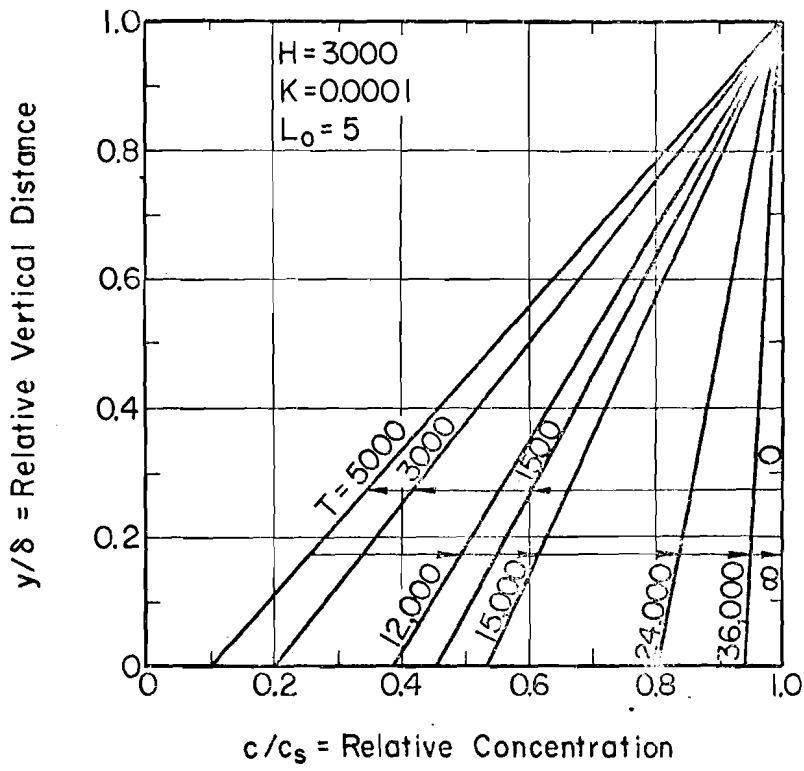


Fig. 4.6 Distribution in Film and below Film with BOD

recognizing that $K_2 \delta^2 / D^* = 1/H$ on the basis of Eqs. 2.2 and 2.5. Eq. 4.41a gives values so close to those in Fig. 4.6 that it would not be possible to see the difference in the figure. Eq. 4.41b provides an interesting comparison with Eq. 4.39 when it is recognized that $A_1^2 \approx 1/H$ from Eq. 4.38 for large H. Expansion of the sin and cos in the first bracketed term in Eq. 4.39 and retention of the terms of order κH gives the first bracketed term in Eq. 4.41b. Similarly, expansion of the first term in the infinite series in Eq. 4.39 and retention of the terms of order one give agreement with the corresponding term in Eq. 4.41b.

Only this one example is presented here, but many other cases were also investigated and these included assumptions of K_1/K_2 values up to the unrealistically high value of 1000 and L_o/c_s up to 25. In all cases, the concentration distribution in the film was essentially linear.

Recognizing that the absorption rate must be equal to the diffusion rate at the surface, and using Ficks Law and Eq. 2.3, it is possible to write K_L as

$$K_L = \frac{D^*}{\delta} \left[\frac{1}{D} \left(\frac{\partial c}{\partial Y} \right)_{Y=1} \right] \quad 4.42$$

where the derivative is to be evaluated at the surface ($Y = 1$). These calculations of the oxygen gradient in the film both with and without oxygen demand showed linear distributions of c . Thus, the bracketed term in Eq. 4.42 is the same for both cases. However, the equation also shows that the linear gradients do not necessarily mean that K_L is the same for both cases. Since the bracketed term is the same, if K_L changes with the addition of oxygen demand, the change must be due to changes in the diffusion coefficient in the film (D^*) and/or the film thickness (δ). However, changes in either of these quantities would probably not result from the oxygen demand per se but rather from the physical presence of the material possessing the oxygen demand.

Again, it should be mentioned that these equations assume the oxygen demand to be homogeneously distributed throughout the water and do not include the possibility of discrete particles taking oxygen directly from the atmosphere.

4.3.2) Bottom Deposits

This subsection considers the possible effect that biological oxygen demand due to bottom deposits might have on the oxygen concentration distribution in turbulent water. In some respects, the considerations here are parallel to those in Section 4.1.1.

In order to simplify the problem a little, it is assumed that there is no oxygen demand suspended in the water (i.e. only bottom deposits) and that the oxygen deficit is initially zero, i.e. $d = 0$ at $t = 0$ with no suspended demand. The differential equation representing the oxygen distribution is Eq. 4.1 with $r = 0$. Further, it is assumed that D^* is constant and that the transport through the film is represented by Eq. 4.3 so that the upper boundary condition at $y = h$ is again Eq. 4.4. The effect of the bottom deposits is represented in the lower boundary condition which must show a transport of oxygen at the bottom equal to the rate at which the deposits are using the oxygen. Mathematically, this may be expressed as

$$D^* \frac{\partial d}{\partial y} = -G \quad \text{at } y = 0 \quad 4.43$$

where G is the mass transfer rate per unit area (e.g. mg of oxygen per m^2 per sec). Further, assuming G is constant, the solution to Eq. 4.1 under these conditions is [Carslaw and Jaeger, 1959, p. 125]

$$\frac{d}{c_s} = \frac{Gh}{D^* c_s} \left[\frac{1}{\alpha} + (1-\eta) - 2 \sum_{n=1}^{\infty} \frac{(\alpha^2 + \beta_n^2) \cos \beta_n \eta}{\beta_n^2 (\alpha + \alpha^2 + \beta_n^2)} e^{-\beta_n^2 \tau} \right] \quad 4.44$$

where α , β_n , η , and τ are as defined previously in Eqs. 4.8, 4.9, and 4.10. It may be noticed that $G = 0$ gives d as identically zero, rather than giving Eq. 4.7. This is because the initial deficit was assumed to be zero in this section. With a zero initial deficit and no oxygen demand ($G = 0$), d will never change from zero.

Eq. 4.44 is plotted in Fig. 4.7 in terms of oxygen concentration rather than deficit for four different values of G with other parameters remaining constant and equal to the values shown on the figure. From these

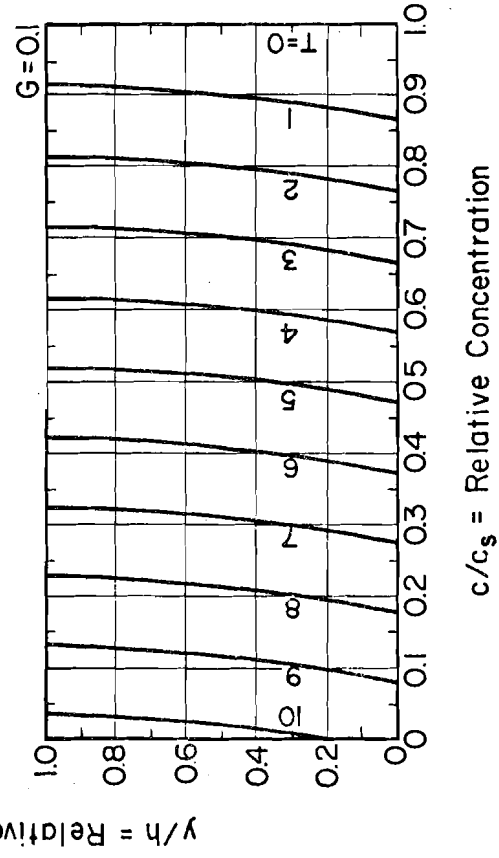
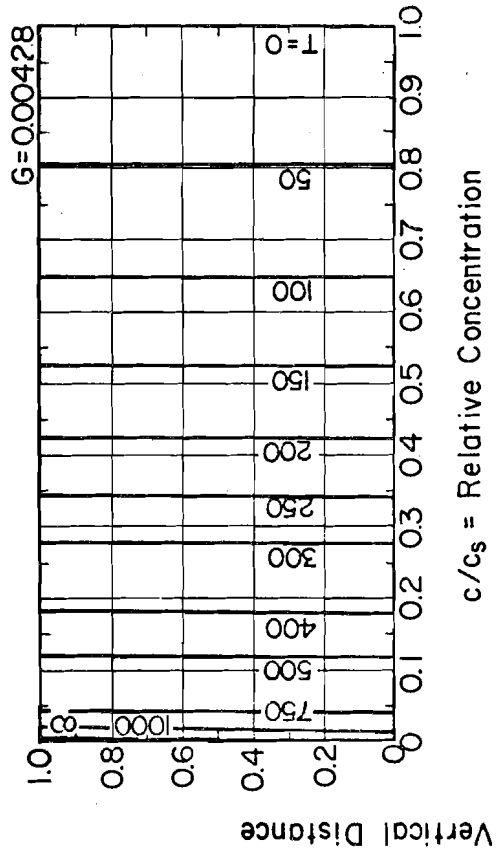
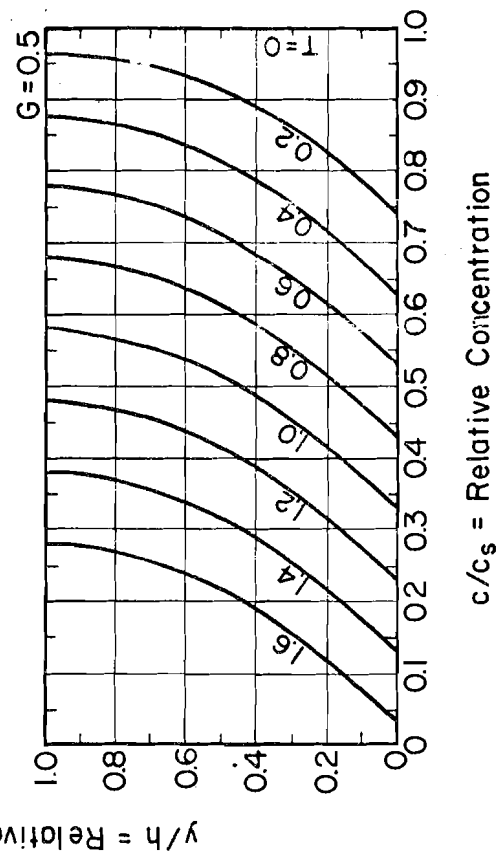
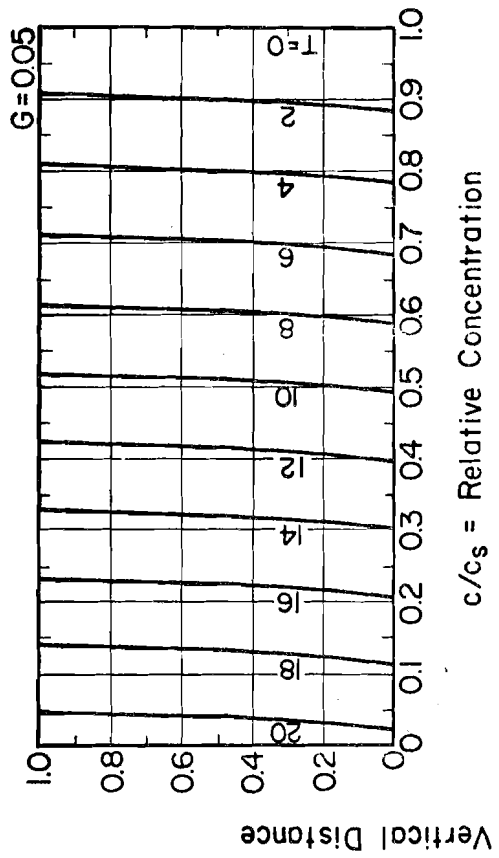


Fig. 4.7 Distributions Resulting from Bottom Deposits

examples it can be seen that when G is great enough to cause a significant vertical variation of oxygen concentration, it is also so great that the water is completely depleted of dissolved oxygen in a rather short time. In the last case, the value of G represents a more moderate oxygen demand rate, i.e. an oxygen demand rate on the order of magnitude of the reaeration rate so that no anaerobic conditions result. In this case, the vertical distribution of oxygen is essentially uniform, just as it was in Section 4.1, which considered the case with no oxygen demand.

In general, it may be noticed that as τ (or t) approaches infinity, Eq. 4.44 approaches a steady state given by

$$\frac{d}{c_s} = \frac{Gh}{D^* c_s} \left[\frac{1}{\alpha} + (1-\eta) \right] \quad 4.45$$

This expression represents an equilibrium which is achieved when the absorption rate through the surface equals the oxygen demand rate at the bottom. The maximum value that G can have and still not produce anaerobic conditions can be obtained by setting $d = c_s$ at $\eta = 0$ to give

$$G = \frac{D^* c_s}{h} \left(\frac{\alpha}{1+\alpha} \right) \quad 4.46$$

This value for G may be used in Eq. 4.45 with $\eta = 1$ to give the corresponding deficit at the bottom of the film, and therefore the change in deficit (Δd) over the depth:

$$\frac{\Delta d}{c_s} = \frac{\alpha}{1+\alpha} \quad 4.47$$

In section 4.1.2, it was shown that the value of α for streams is about 0.0043. Using this value in Eq. 4.47 gives a maximum concentration difference over the depth of about 0.4% of c_s for this maximum G which preserves aerobic conditions. This illustrates that as long as G is not so great as to produce anaerobic conditions, the oxygen concentration will be essentially uniform vertically. Of course, greater values of G may exist, but if they are great enough to cause a significant difference in concentration over the depth, there will be no oxygen distribution at all after a relatively short time.

The equation for the average deficit for this situation may be obtained from Eq. 1.1. Since Eq. 4.43 gives the mass transfer per unit of bottom area, R is equal to G/h. The solution for an initial deficit of D_0 is

$$D = \left(D_0 - \frac{G}{K_2 h}\right) e^{-K_2 t} + \frac{G}{K_2 h} \quad 4.48$$

If the initial deficit is zero, as was assumed in deriving Eq. 4.44, Eq. 4.48 may be written as

$$\frac{D}{c_s} = \frac{G}{K_2 h c_s} (1 - e^{-K_2 t}) \quad 4.49$$

From this, for t approaching infinity, the deficit is

$$\frac{D}{c_s} = \frac{G}{K_2 h c_s} \quad 4.50$$

Thus, if

$$G = K_2 h c_s, \quad 4.51$$

then $D = c_s$ as $t \rightarrow \infty$. If G is any greater than this value, then anaerobic conditions result at large times. In that case, the time at which the concentration becomes zero (i.e. $D = c_s$) can be calculated from Eq. 4.49 to be

$$t = \frac{1}{K_2} \ln \frac{1}{1 - \frac{c_s K_2 h}{G}} \quad 4.52$$

4.4) SUMMARY

In this chapter, analytical solutions and related considerations have been presented for various cases of reaeration with no oxygen demand, with sodium sulfite, and with biological oxygen demand. In each case, the

diffusion model has been assumed in deriving the solutions. Naturally, the analytical solutions are presented for highly idealized situations. Nevertheless, the solutions produce some interesting insights into the various situations.

Analytical solutions substantiate the well-known fact that the vertical distribution of oxygen is essentially uniform in flowing streams. However, bottom deposits with high BOD rates can cause significant differences of oxygen concentration in the vertical directions during the relatively short time before the water becomes anaerobic.

The analytical solutions presented for reaeration with excess sodium sulfite appear to be in general agreement with data from the literature. Apparently it is not possible to combine these solutions with measured absorption rates in order to calculate the thickness of the oxygen boundary layer or turbulent film when sulfite is present.

Analytical solutions are presented for the oxygen distribution in the turbulent film when BOD is present, assuming the BOD to be homogeneously distributed throughout the water. These solutions indicate for normal conditions that the BOD does not influence the absorption rate of oxygen by steepening the concentration gradient at the surface. However, the analytical solutions can not show whether the BOD changes the absorption rate by changing either the film thickness or the diffusion coefficient in the film.

CHAPTER 5

EXPERIMENTAL WORK

5.1) EQUIPMENT

Reaeration experiments were conducted in a mixing vessel as shown in Fig. 5.1. Mixing was created by a closed loop pumping system which circulated water through the vessels. The water was pumped in at point A and withdrawn at point B, whence it went to the pump, a coil in a constant temperature bath, a flow meter, then back to point A. The only materials in contact with the water were PVC and plexiglass plastics and stainless steel. A circulating motion was created in the vessels, but the water surface was essentially horizontal. The flow rate for all tests was 2.3 gpm. The temperature was 20°C.

The dissolved oxygen concentrations were measured with membrane electrodes (YSI Instrument Co.). The electrodes were placed at point C (Fig. 5.1) so that the sensitive end of the probe was flush with the inside wall of the mixing vessel. The probes were calibrated by the Winkler method.

5.2) NO OXYGEN DEMAND

Reaeration experiments were conducted in the mixing vessel to determine K_L in the absence of oxygen demand. These values of K_L served as a basis for determining the effects of oxygen demand in the later tests.

In these tests with no oxygen demand, the vessel was filled with tap water to the desired depth and the pump was started to circulate the water through the temperature-control bath (20°C) and to set the flow rate (2.3 gpm). Nitrogen was bubbled into the mixing vessel to lower the dissolved oxygen content. After stopping the nitrogen, the oxygen concentration was measured as a function of time using the membrane electrodes. A least-squares method was used to fit the data to Eq. 1.2 with k_2 and c_s being the free parameters determined to give the best fit of the data to the equation. The values obtained for c_s varied from 9.35 ppm to 10.09 ppm with the average being 9.78 ppm. These values all seem a bit high, but they were obtained consistently for the water used in these tests. The values obtained for k_2 were multiplied by $2.30V/A$, where V is the volume of water and A is the surface area, to obtain K_L . The volume of water in

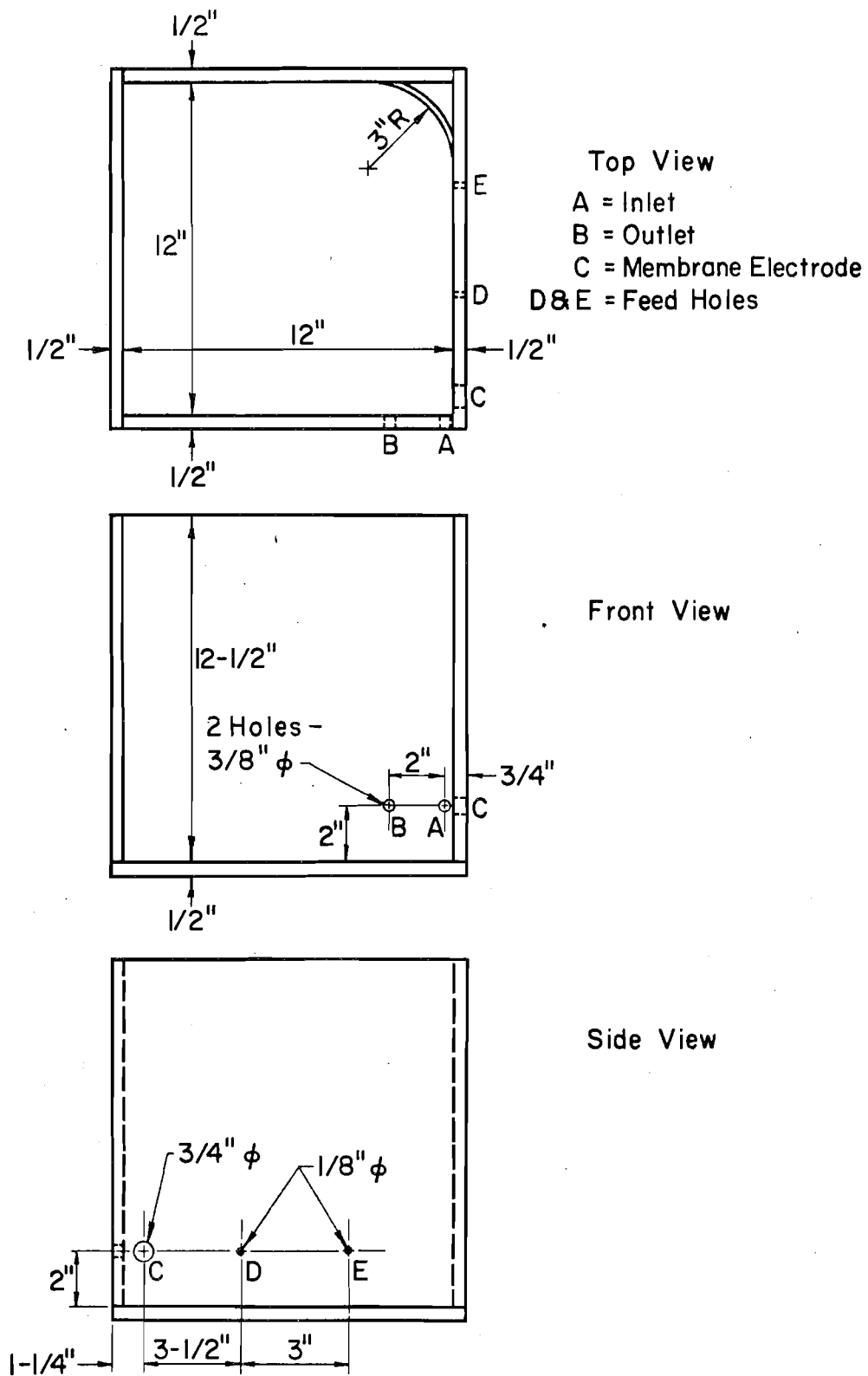


Fig. 5.1 Schematic Diagram of Mixing Vessel

the tubes, pump, flow meter, etc. (0.020 ft^3) was included in V . The K_L values are shown by the circles in Fig. 5.2. The scatter in the K_L values is approximately $\pm 10\%$. There is no apparent correlation between the scatter in the K_L values and that in the c_s values. Three experiments were also conducted using de-ionized water. For these tests, c_s was found to be 8.44 ppm. The corresponding K_L values are shown by the crosses in Fig. 5.2. It can be seen that they are consistent with the values for tap water. The line in Fig. 5.2 is drawn through the average value of K_L for each depth. There is a relatively small decrease in K_L with increasing depth. K_L at the 10-in. depth is about $2/3$ of K_L at the 4-in. depth.

5.3) REAERATION WITH SODIUM SULFITE

It was the intention in these experiments to investigate the reaeration of water containing various types of rapid oxygen demand which had different reaction rates with the dissolved oxygen. Unfortunately, the experimental program never proceeded further than tests using sodium sulfite because of the difficulties experienced in these tests.

The same mixing vessel described previously was used. De-ionized water was put into the vessel to a depth greater than that desired for the experiment, and brought to 20°C . Air was bubbled into the water to saturate it, and two or three Winkler samples were taken for determining c_s . The water level was then brought to the desired position, and sodium sulfite and catalyst were added (approximately $2000 \text{ ppm SO}_3^{=}$ and 0.15 ppm CoCl_2). At least 30 minutes were allowed to pass to give time for thorough mixing of the sulfite, then sampling was begun to determine the rate of change of sulfite to sulfate, and thus the rate of absorption of oxygen. Samples of 10 ml were withdrawn at 10 min. intervals for approximately 2 hours and titrated to determine the sulfite content. The titration technique was generally as described in Standard Methods [1965], with three modifications: (1) The samples were diluted to bring the sulfite concentration below 500 ppm before titration was begun. Water deaerated by bubbling nitrogen was used for dilution. (2) A nitrogen "blanket" was used over the sample during titration. (3) In some of the tests, an excess of iodine was added and a back titration was done.

The measured c_s values varied from 8.28 to 8.89 ppm with an average of 8.65 ppm. This average value was used in calculating K_L (Eq. 2.3).

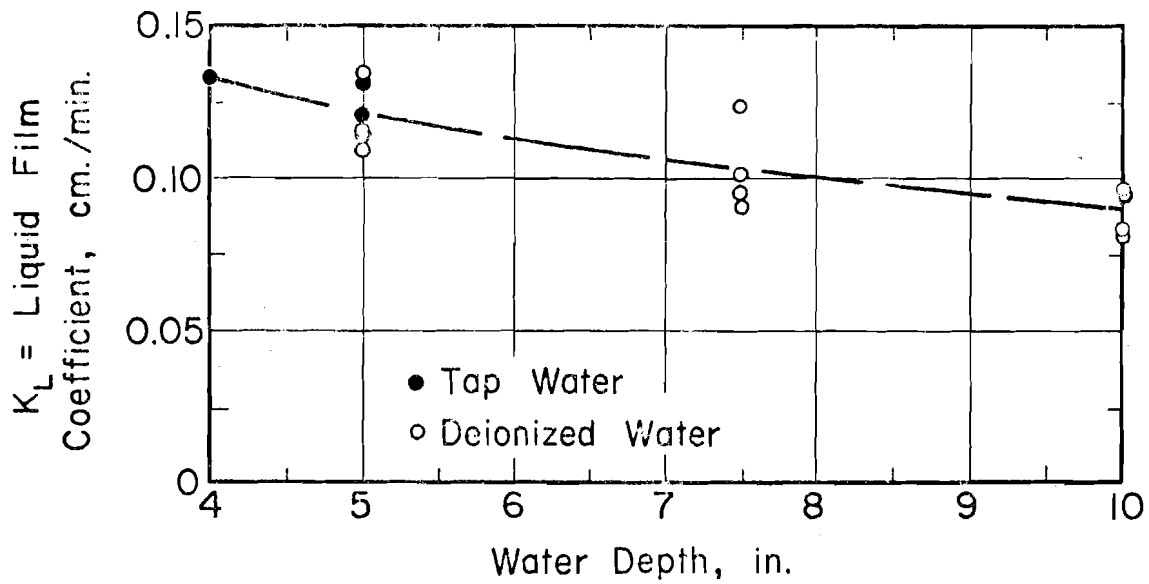


Fig. 5.2 K_L for Mixing Vessel with No Oxygen Demand.

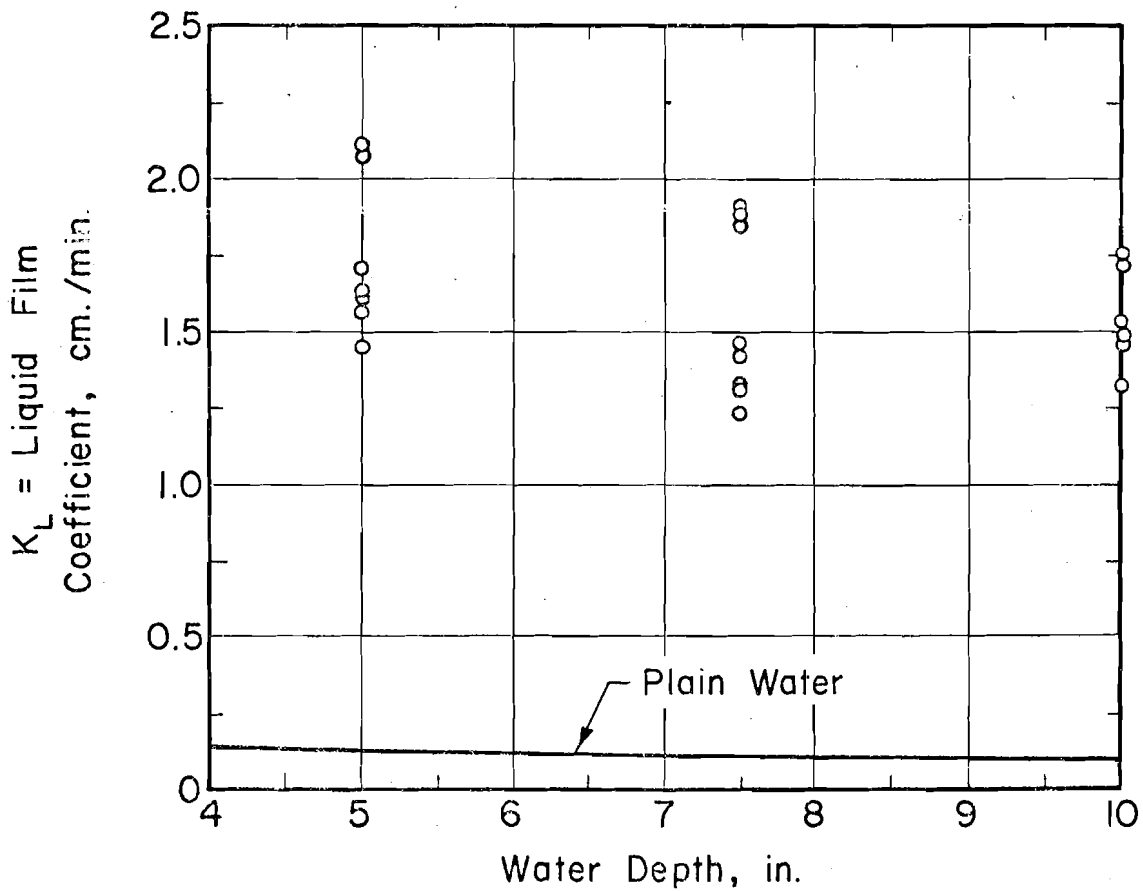


Fig 5.3 K_L with Sodium Sulfite

The K_L values for the oxygen absorption are shown in Fig. 5.3. It can be seen that the data is not very consistent. At depths of both 5 in. and 7-1/2 in., the data divides rather distinctly into two groups with one group being about 30% greater than the other. No explanation could be found for this. In particular it was observed that the separation is not correlated with the order in which the tests were done, with the person doing the tests, or with the titration technique used. Also, for these two depths, the data of oxygen absorption vs. time defined a very good straight line for all the values of K_L shown in Fig. 5.3. (A sample of the data is given in Fig. 5.4, which is discussed below.) The K_L values for the 10-in. depth also have a range of about 30%, but there is no clear separation into two groups. It may be observed though, that the rate of oxygen absorption at the 10-in. depth was slower, giving smaller changes in the volume of titrant in a certain time interval. As a result, the titrations for this depth were probably less accurate and the data of oxygen absorption vs. time showed considerably more scatter on a percentage basis than for the smaller depths.

In Section 2.4, it was pointed out that the rate of reaction between sulfite and oxygen was independent of sulfite concentration above 0.015N sulfite. Two experiments were run in which the sulfite level was allowed to go below 0.015N. The data for one of these experiments is shown in Fig. 5.4. The sharp break in the absorption rate corresponds almost exactly to 0.015N sulfite. Similar results were found in the other experiment. The slope of the line for the smaller sulfite levels gives a K_L value of 0.14cm/min, which is about the same as that for pure water. However, a check was not made to see if the dissolved oxygen concentration rose above zero in this part of the test. If it did, the rate of change of sulfite would not give the total absorption rate, of course. Another possible mechanism which could have affected the oxygen transfer rate at low sulfite concentrations would be a change in the film thickness, i.e. a downward shift in the plane of reaction in Fig. 4.3.

The lack of consistency in the data makes it rather difficult to draw any firm conclusions. Nevertheless, there are two things that can be said: (1) in these experiments, the catalyzed sulfite caused an increase in K_L by a factor of 10 to 17 relative to K_L for pure water.

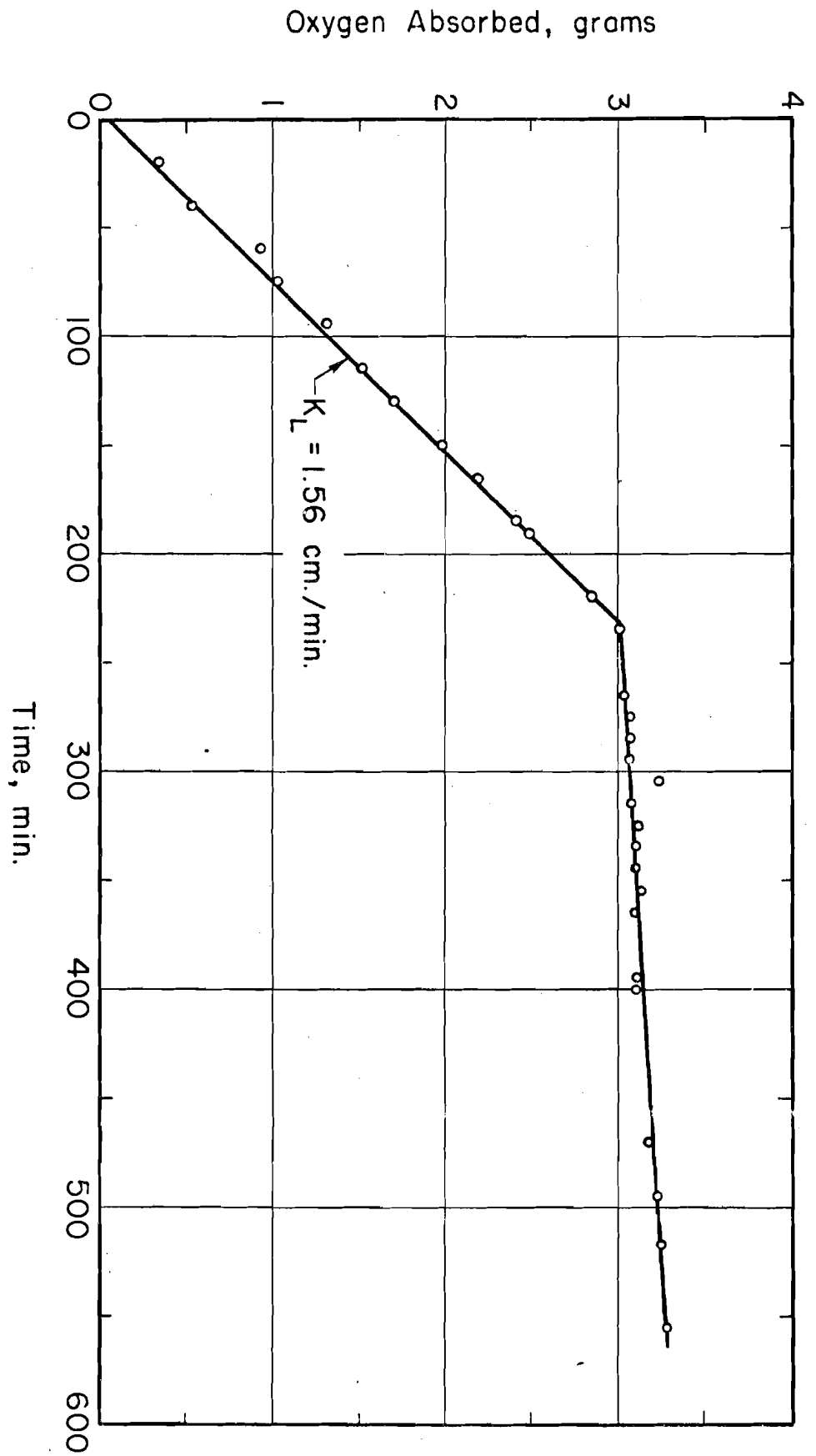


Fig. 5.4 Absorption Data with Sulfite

This is the same order of magnitude as that found by O'Connor and Dobbins (Figs. 2.2 and 4.2). (2) For sulfite concentrations below 0.015N, there is a significant drop in the absorption rate to a value approximately equal to that for pure water. This is apparently a result of the decrease in the reaction rate between sulfite and oxygen.

5.4) REAERATION WITH BIOLOGICAL OXYGEN DEMAND

The purpose of these experiments was to compare reaeration rates for water with a biological oxygen demand to the rates for pure water under similar conditions. Experiments were done to give information about the influence of both the biological and the physical properties of the micro-organisms used.

For this purpose, tests were conducted at 20°C and at 2° to 5°C. (It was the intention to work very close to 0°C, but it was necessary to work at the limit of the capacity of the cooling apparatus, and this gave slightly different temperatures on different days.) At the low temperature the rate of biological processes should be essentially zero as compared to that at 20°C, [Fair et al, 1968] so that the influence of the physical presence of the micro-organisms could be determined.

The same mixing vessel described previously was used. In addition, two other "identical" vessels and flow systems were used to allow more than one test to be made simultaneously. The three vessels were simply numbered 1, 2, 3, with No. 1 being the same one used in the other tests. It was discovered that No. 2 for some reason gave significantly different results from the other two. Thus, the results from No. 2 were treated separated, while the results from No. 1 and 3 were compared with each other and with the work reported in Section 5.2 for reaeration of pure water.

5.4.1) Tests at 20°C

Biological oxygen demand (BOD) is the oxidation of organic matter in the biological processes of micro-organisms. A culture was developed using seed mixed liquor from the Urbana-Champaign Sanitary District activated sludge plant. This mixed liquor was acclimated to acetic acid as the only carbon source. The acetic acid was added once each day with the amount being equivalent to 1000 ppm for the volume of the vessel. In the acclimation vessel, salts were initially added as follows:

<u>Salt</u>	<u>ppm</u>
NH ₄ Cl	200
MgSO ₄ ·7H ₂ O	83
FeSO ₄ ·7H ₂ O	3
MnSO ₄ ·7H ₂ O	3
CaCl ₂ ·7H ₂ O	3
KH ₂ PO ₄	22
Na ₂ HPO ₄ ·7H ₂ O	45
Na ₂ CO ₃	880

Each day after the first day, 80% of the above quantities of salts was added. At the beginning of the acclimation, the suspended solids concentration of the micro-organisms was 17,000 ppm.

For the reaeration experiments with micro-organisms, the same concentrations of nutrients salts (i.e. 80% of the values listed previously) were used in the mixing vessel. Some of the micro-organisms were transferred from the acclimation vessel to the mixing vessel, and acetic acid was fed continuously into the mixing vessel. The fed rate was adjusted by trial and error to find a value which, when maintained constant, would produce an equilibrium condition of constant dissolved oxygen concentration. The required feed rate was not measured. With constant oxygen concentration, the rate of reaeration equalled the rate of oxidation. In Eq. 1.1, dc/dt was zero and letting $R = K_1L$, K_2 was given by

$$K_2 = \frac{K_1L}{D_e} \quad 5.1$$

where D_e is the deficit corresponding to the equilibrium oxygen concentration. After maintaining this equilibrium for at least an hour and determining D_e with the membrane electrode, a floating cover was placed on the water surface to stop the reaeration. Then, a linear decrease in oxygen concentration was found and from Eq. 1.1 with $K_2 = 0$, one finds

$$K_1L = \frac{dD}{dt} \quad 5.2$$

So, it was possible to calculate K_1L from this latter procedure, and use that value in Eq. 5.1 to obtain K_2 . Obviously, this assumed that K_1L did not change when the floating cover was placed on the water surface. At the end of the test, the suspended solids concentration was measured and air was bubbled vigorously through the mixing vessel to determine the saturation concentration applicable for the water with organisms, acetic acid, and salts.

Tests were also done with only acetic acid plus salts present in various quantities to investigate any possible effect of the acid on reaeration. The range of acid concentrations used in these tests covered the possible range of concentrations resulting from the feed for the organisms. The tests with acid were conducted in vessel No. 2. The value of K_2 was determined as described in Section 5.2 for pure water. The results are presented in Section 5.4.3 below.

There were two primary experimental problems. One was that in some cases it was not possible to achieve the desired equilibrium between reaeration and oxidation rates. However, it is felt that this was to be expected due to the somewhat unpredictable behavior of micro-organisms and the trial and error approach that was being used to find the proper feed rate for the acid. The second problem was the formation of a thin film (scum) on the water surface in the tests with micro-organisms. (This film also occurred in the 2°-5°C tests discussed below.) The cause of the film could not be determined. It was physically removed at intervals of about 30 minutes (when necessary) by skimming with a fine wire screen.

5.4.2) Tests at 2°-5°C

Experiments parallel to those just described were also conducted at temperatures varying from 2° to 5°C. The only essential difference was no acetic acid was fed to the organisms during these low temperature tests. However, since some of these tests were performed by lowering the temperature of the same water used in the 20°C tests, it was possible that some acid was present. Thus, experiments were performed to check any influence of acid at the low temperatures also. Values of K_2 were determined for all tests as for pure water as described in Section 5.2, namely, removal of dissolved oxygen by bubbling nitrogen, determining D as a function of

time, and calculation of K_2 from Eq. 1.2 assuming $R = 0$ on the basis of the temperature. As mentioned previously, the film (scum) also formed during some of these tests and had to be removed by skimming.

5.4.3) Discussion of Results

The results for all the tests are summarized in Table 5.1. For reasons noted, it is felt that a few of the results were not reliable, so they were not used in further analysis discussed below.

The values of K_L for water plus acetic acid (and salts) are presented in Fig. 5.5. These tests were all conducted in vessel No. 2. Since the K_L values are within the range of reproducibility found for pure water, it was concluded that the acid and salts did not have any significant influence on the value of K_L . It may be seen that the K_L value for vessel No. 2 (20°C with no acid) was about 30% higher than the average value for vessel No. 1 at 5-in. depth as indicated in Fig. 5.2. Also, the results from vessel No. 2 seemed a bit erratic at times. For these reasons, the results from vessel No. 2 were not compared with results from the other two mixing vessels.

The results for experiments with the micro-organisms are shown in Fig. 5.6. The curve from Fig. 5.2 for pure water at 20°C is reproduced on Fig. 5.6 by the solid line. The broken line represents the solid line converted to 2°C using $\theta = 1.017$ (Eq. 1.3). This value of θ was selected to give agreement with the measurements of K_L in pure water at 2°C. As shown on the figure, the tests with micro-organisms at both 20°C and 2°C correspond to an α value (Eq. 2.12) of approximately 1.5. (The short curves were calculated to correspond to the α values indicated at the end of the curves.)

Obviously, the results are extremely limited, but they indicate essentially the same value of α at 20°C and at 2°C. Since the biological activity is essentially non-existent at 2°C, the experimental results imply that the change in K_L was apparently due to the physical presence of the micro-organisms. The mechanism by which the physical properties of the organisms affect K_L is not known.

There are two factors related to these results which should be mentioned. First, it would be expected that the film which formed on the surface would cause interference with, not enhancement of, oxygen absorption,

Table 5.1

SUMMARY OF REAERATION TESTS WITH BOD

Test No.	Chamber No.	Temp °C	Depth in.	Susp. Solids mg/l	Slugfeed Acetic Acid ml	c _s mg/l	K _L cm/min
1	1	20.0	4	0	0	8.44	0.133
2	3	20.0	5	0	0	8.44	0.121
3	1	20.0	5	0	0	8.44	0.131
6	3	20.0	5	0	0	8.44	0.147
7	1	20.0	5	0	0	8.44	0.161
13	3	1.9	4	0	0	13.08	0.096
13a	3	1.9	4	0	0	13.08	0.089
14	3	2.0	5	0	0	13.08	0.089
19	1	20.0	4.6	280	0	8.1	0.192
20	1	20.0	4.5	305	0	8.1	0.176
21	1	20.0	5	125	0	8.1	0.188
24	1	1.8	5	125	0	12.79	0.157
24a	1	1.8	5	125	0	12.79	0.140
25	1	1.8	5	170	0	12.55	0.148
4	2	20.0	5	0	0	8.11	0.163
5	2	20.0	5	0	0	8.11	0.185
8	2	20.0	5	0	0.0084	8.11	0.166
9	2	20.0	5	0	0.0504	8.13	0.166
10	2	20.0	5	0	0.101	8.13	0.165
11	2	4.8	4	0	0	11.20	0.148
12	2	4.8	4	0	0	11.20	0.150
15	2	4.8	4	0	0.0084	11.20	0.141
16	2	4.8	4	0	0.0252	11.20	0.137
17	2	4.8	4	0	0.0756	11.20	0.139
18	2	4.8	4	0	0.101	11.20	0.161
22	2	20.0	4	148	0	8.1	0.145
23	2	1.9	4	148	0	12.79	0.149
23a	2	1.9	4	148	0	12.79	0.154

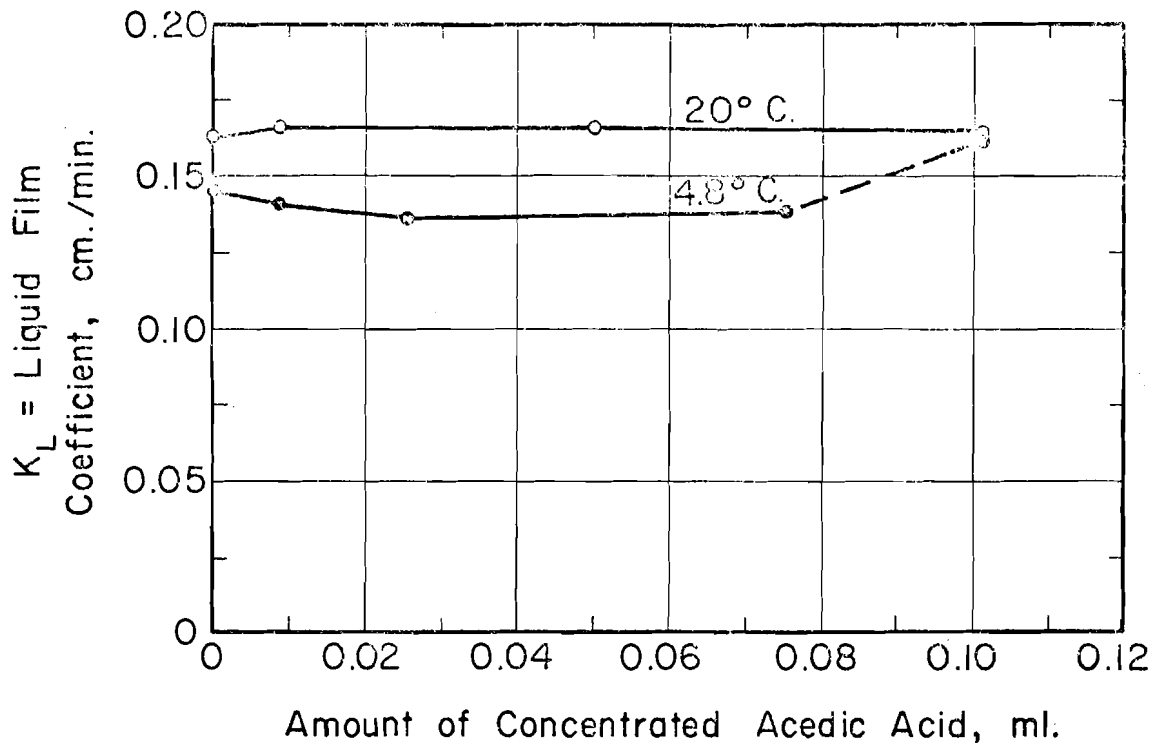


Fig. 5.5 K_L with Acetic Acid

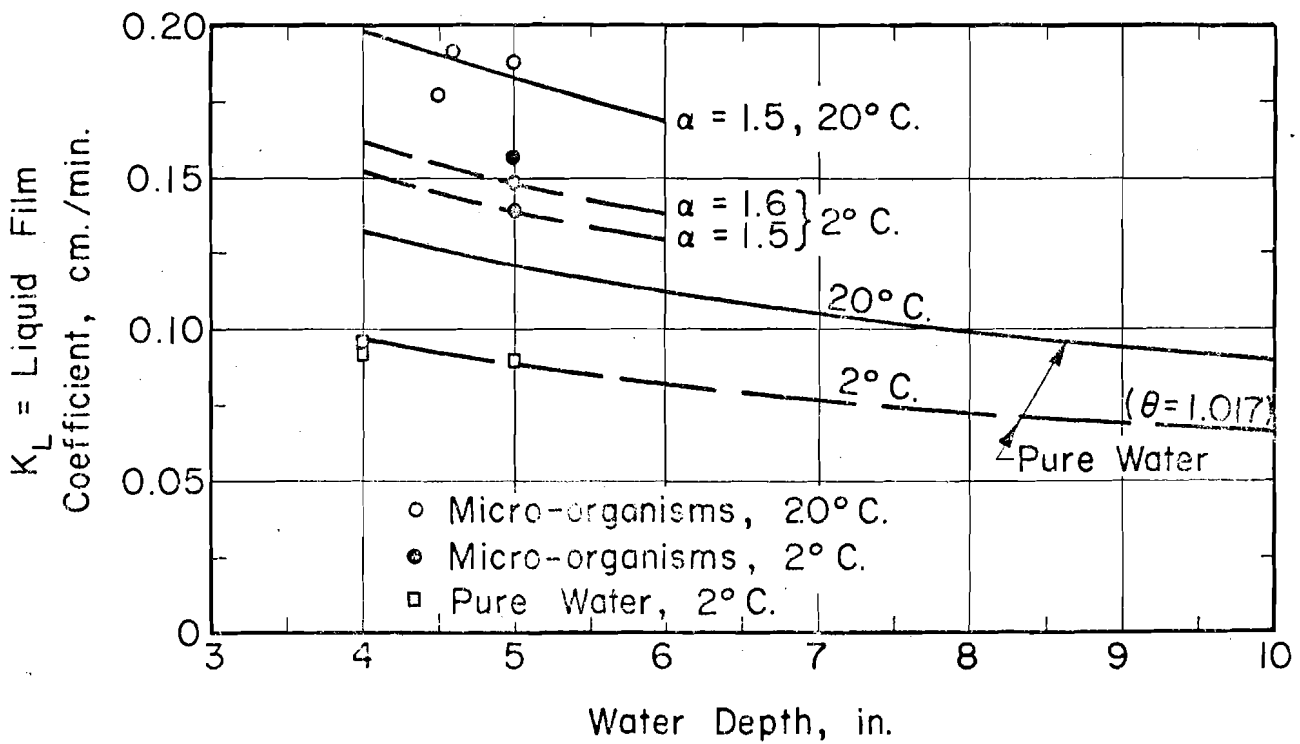


Fig. 5.6 K_L and α with BOD

if it had any effect. Thus, it does not seem that this film could account for the observed values of α . Second, the observed α values can not be explained in terms of the direct absorption of oxygen from the atmosphere by the organisms (a mechanism discussed in Section 2.5) since (a) there was essentially no biological activity in the 2°C tests, and (b) even if there were a direct absorption at 20°C, the procedures used in these experiments would not have measured the oxygen absorbed in this way. The value of K_1L was certainly not influenced by any direct absorption since there was no free surface when this value was determined (Eq. 5.2). Further, when K_2 was calculated, this value was related only to the dissolved oxygen in solution (Eq. 5.1). Thus, even if the organisms were taking oxygen directly from the atmosphere, the means used to calculate K_1L and then K_2 would not have included this absorption in the K_2 values. In any case, the combination of the 2°C and 20°C tests indicate that the primary affect of the micro-organisms was apparently physical and not biological.

5.5) SUMMARY

Reaeration experiments were conducted in a laboratory mixing vessel with plain water, with sulfite, and with BOD. The results from the sulfite experiments were extremely scattered so that it is difficult to draw any firm conclusion other than that the sulfite caused K_L to increase by a factor of about 10 to 17 as compared to plain water.

With BOD, experiments were conducted at 20°C and at 2°-5°C. At the low temperature, the biological activity was essentially zero so the effects of the physical presence of the organisms could be evaluated. For both 20°C and 2°-5°C, it was found from limited results that K_L was about 1.5 times greater than for pure water. This suggests that the increase was due to the physical presence of the organisms, but the mechanism causing this change has not been identified.

CHAPTER 6

SUMMARY AND CONCLUSIONS

Chapters 3, 4, and 5 each have a summary section at the end of the chapter. The material presented here is largely a re-statement of those previous summaries.

The concept of a physically stagnant film at the free surface of turbulent water appears not to be valid. However, the transport of oxygen through the critical region immediately below the free surface can be represented in terms of an oxygen boundary layer and diffusion model, which is similar in many respects to film theory. However, the recognition that the film concept should be replaced by an oxygen boundary layer concept points out that the boundary layer thickness should be expected to vary with both mixing conditions and Schmidt number. This boundary layer concept is supported by reaeration experiments and by analogy between oxygen absorption and other mass and heat transfer problems. Limited experiments indicate that the diffusion coefficient in the oxygen boundary layer or turbulent film is approximately equal to the molecular diffusivity for low mixing conditions.

It is possible to use analytical solutions to the vertical diffusion equation to gain some insight into the distribution of oxygen concentration to be expected under various conditions and to aid in the evaluation of the relative importance of various factors. Analytical solutions substantiate the well-known fact that the vertical distribution of oxygen is essentially uniform in flowing streams. However, bottom deposits with high BOD rates can cause significant differences of oxygen concentration in the vertical directions during the relatively short time before the water becomes anaerobic.

The analytical solutions presented for reaeration with excess sodium sulfite appear to be in general agreement with data from the literature. Apparently it is not possible to combine these solutions with measured absorption rates in order to calculate the thickness of the oxygen boundary layer or turbulent film when sulfite is present.

Analytical solutions are presented for the oxygen distribution in the turbulent film when BOD is present, assuming the BOD to be homogeneously distributed throughout the water. These solutions indicate

for normal conditions that the BOD does not influence the absorption rate of oxygen by steepening the concentration gradient at the surface. However, the analytical solutions can not show whether the BOD changes the absorption rate by changing either the film thickness or the diffusion coefficient in the film.

Reaeration experiments were conducted in a laboratory mixing vessel with plain water, with sulfite, and with BOD. The results from the sulfite experiments were extremely scattered so that it is difficult to draw any firm conclusion other than that the sulfite caused K_L to increase by a factor of about 10 to 17 as compared to plain water.

With BOD, experiments were conducted at 20°C and at 2°-5°C. At the low temperature, the biological activity was essentially zero so the effects of the physical presence of the organisms could be evaluated. For both 20°C and 2°-5°C, it was found from limited results that K_L was about 1.5 times greater than for pure water. This suggests that the increase was due to the physical presence of the organisms, but the mechanism causing this change has not been identified.

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