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OXYGEN SUPPLY LIMITATIONS IN FULL SCALE
BIOLOGICAL TREATMENT SYSTEMS

by

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Introduction

There is a diversity of opinion over the mechanisms that can control the rate of reaction in biological treatment systems. A strong case has been made for kinetic models based on the concentration of substrate as the rate controlling factor. Accordingly, many of the waste treatment designs contain variations of Michaelis Menten or Monod formulations which relate reaction rate as a function of substrate concentration.

Under certain conditions the mass transfer of substrate can control the reaction rate - so can the mass transfer of oxygen. With no mass transfer limitations, the reaction rate is dependent on cellular biochemical mechanisms.

The object of this paper is to define under what conditions the mass transfer of substrate and of oxygen are controlling and when neither is controlling. Also, it will be demonstrated that many waste treatment plants are oxygen limited, and are performing below their potentials.

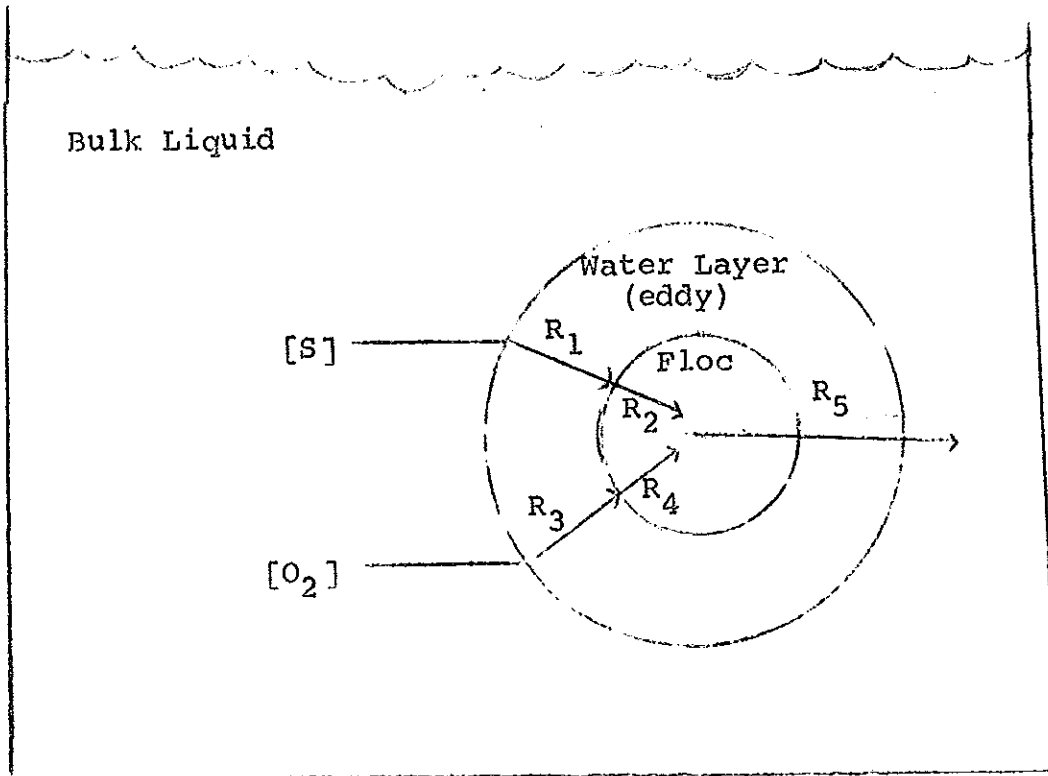


Figure I. Microscale Representation of an Aerobic Biological Reactor

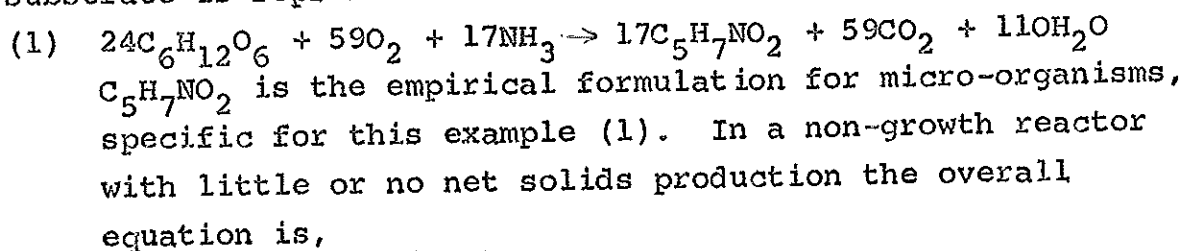
The Biological Reactor

On the micro-scale a biological waste treatment basin can be visualized as composed of biological floc particles, each surrounded by a layer or film of water (Figure 1). The thickness of the water layer is a function of the turbulence level. The floc size is a function of turbulence level, solids concentration, and solids retention time (SRT).

Both oxygen and substrate must diffuse through identical resistances - the attached water layer and the floc - to reach the reaction sites in the floc. The rate processes are defined as follows:

- R_1 - diffusion of substrate through attached water layer
- R_2 - diffusion and reaction of substrate in floc
- R_3 - diffusion of oxygen through eddy
- R_4 - diffusion and reaction of oxygen in floc
- R_5 - diffusion of products from reaction site

Biological reactors can be classified by their solids retention times. Short SRT's characterize reactors in which solids growth and yield are maximized. Long SRT's characterize reactors with little or no net solids production. The oxygen requirements of the micro-organisms for a given substrate vary considerably depending on the reactor type. For example, the overall stoichiometric equation for a growth reactor with glucose as a substrate is represented as



A comparison of the two systems and equations shows that less than half of the moles of oxygen is required by the micro-organisms to degrade a given amount of glucose in the growth reactor than that in the non-growth reactor. The latter requires much more oxygen than the former to remove an equivalent amount of glucose.

Oxygen and Substrate Mass Transfer Limitations

A biological reactor is mass transfer limited if the reaction rate can be stimulated by an increase in turbulence. Under these conditions, either oxygen or substrate may be the rate controlling reactant.

Both oxygen and substrate must diffuse through the same resistances to reach the reaction sites in the floc. The relative rates of diffusion of oxygen and substrate through the layer of attached water is measured by the diffusivity coefficient of each. For glucose and oxygen, the diffusivities in water are

$$\begin{aligned} D_{\text{glucose}} &= 0.69 \times 10^{-5} \text{ cm}^2/\text{sec} \\ D_{\text{oxygen}} &= 2.5 \times 10^{-5} \text{ cm}^2/\text{sec} \end{aligned} \quad (2)$$

The relative rate of diffusion through water for the same driving gradient is

$$(3) \quad \frac{D_{O_2}}{D_g} = \frac{2.5 \times 10^{-5}}{0.69 \times 10^{-5}} = \frac{3.6}{1}$$

An oxygen molecule will migrate through water 2.6 times as rapidly as a glucose molecule given the same concentration gradient. Assuming this ratio is valid for diffusion through the floc, the following calculations can be performed.

The stoichiometry for a growth reactor with glucose as substrate indicated that the micro-organisms require 2.5 moles of oxygen per mole of glucose. In terms of weight ratio

$$(4) \quad \frac{\text{Glucose required}}{\text{Oxygen required}} = \frac{1 \text{ mole}}{2.5 \text{ moles}} \times \frac{180 \#/\text{mole}}{32 \#/\text{mole}} = \frac{2.3}{1}$$

One pound of oxygen is needed at the reaction site to degrade 2.3 pounds of glucose; 0.4 pound oxygen per pound of glucose. In a non-growth reactor the ratio is 0.94 pounds oxygen per pound of glucose. The more of a reactant that is required by the reaction stoichiometry, the higher the bulk concentration of that reactant must be; conversely the higher the diffusivity of a reactant, the lower the necessary bulk concentration of the reactant. The relative bulk concentrations of substrate and oxygen that will result in both controlling

the reaction rate is expressed by the ratio

$$(5) \frac{c_b \text{ (substrate)}}{c_b \text{ (oxygen)}} = \frac{D_{O_2}}{D_s} \times \frac{\text{substrate required}}{\text{oxygen required}}$$

For glucose as substrate in a growth reactor:

$$(6) \frac{c_b \text{ (glucose)}}{c_b \text{ (oxygen)}} = \frac{3.6}{1} \times \frac{2.3}{1} = \frac{8.0}{1}$$

and in a nongrowth reactor:

$$(7) \frac{c_b \text{ (glucose)}}{c_b \text{ (oxygen)}} = \frac{3.6}{1} \times \frac{0.94}{1} = \frac{3.4}{1}$$

For glucose to be controlling the reaction rate, its concentration in the bulk liquid must be less than eight times that of dissolved oxygen in a growth reactor, and less than 3.4 times that of dissolved oxygen in the non-growth reactor.

For example, if a biological reactor maintains a dissolved oxygen (DO) concentration of 2.0 mg/l in the bulk liquid, the reaction will be oxygen controlled at glucose concentrations above sixteen mg/l in growth conditions and above seven mg/l in non-growth conditions.

The Effect of Turbulence on Mass Transfer

In the biological reactor, turbulence level can have a profound impact on a mass transfer controlled reaction rate. Increased turbulence promotes mass transfer of oxygen and substrate by reducing the thickness of the attached water layer on the floc and by breaking large flocs into small ones; the distances substrate and oxygen must diffuse to the reaction sites are reduced. With increased turbulence, oxygen and substrate will diffuse at greater rates and penetrate deeper into the flocs.

Turbulence results from the input of energy into the reactor. This energy is cascaded from large to progressively smaller eddies until it is lost to heat by the dissipation action of the smallest eddies (4). The smallest eddies will approximate the size of the largest flocs. Flocs larger than the smallest eddies will be reduced through shear to sizes less than these eddies (5). Therefore, the size of the attached water layer and the size of the floc is directly related to eddy size.

A mathematical description of eddy size as a function of power input and kinematic viscosity of the bulk liquid is shown in Appendix A. The enhancement of mass transfer in terms of $k_L a$, the mass transfer coefficient, as a function of power input is demonstrated in Table I.

Table I
Effect of Turbulence on Mass Transfer

	<u>Power</u> hp 1000ft ³	<u>Eddy Size*</u> Ave. Diameter in microns	<u>Increase in $k_L a$</u> Relative to 1 hp 1000ft ³
Aerated Lagoon	0.1	280	0.3
Activated Sludge	0.5	180	0.8
	1.0	160	1.0
Industrial Fermentations	2.0	134	1.4
	5.0	106	2.3
	10.0	90	3.2

*The micro-scale eddy size from Kolmogoroff $D = 2L = \left(\frac{v^3}{E} \right)$
 v = Kinematic viscosity

E = Power input per unit mass

The Biochemical Reaction

The reaction rate is controlled biochemically when mass transfer effects are eliminated; that is, when an increase in turbulence does not result in a higher rate of reaction. The micro-organisms are degrading the substrate at the maximum rate physiologically possible. This maximum rate can vary depending on the species of micro-organisms.

Micro-biologists have found that minimum dissolved oxygen levels at the surface of the cells of from 0.01 to 0.1 mg/l are required for a number of common micro-organisms to operate at the maximum rate (6). To operate at the maximum rate in the biological reactor, the cells even in the center of the floc must have 0.1 mg/l oxygen at their walls. Similarly, the critical substrate (glucose) concentration is eight times that of dissolved oxygen, i.e. 0.8 mg/l at the floc center under growth

conditions, 0.36 under non growth conditions.

If sufficient bulk concentrations of oxygen and substrate are maintained to overcome the diffusional resistances in the layer of attached water and floc plus depletion by reaction in the floc, the biological reactor will operate at the maximum rate. To determine what bulk concentrations of oxygen and substrate are necessary for the reaction to proceed at the maximum rate, consider the following example. A biological reactor designed for high biological growth contains 2000 mg/l solids, 50% viable cells; at power to volume ration of 1 HP/1000 ft³. To calculate the bulk concentration of oxygen necessary for maximum reaction rate (i.e. no mass transfer limitations, the mathematical formulation developed in Appendix B is used:

$$c_b = \frac{kr_f^2}{6D_f} + \frac{kr_f^2}{6D} \left(1 - \frac{r_f}{r_e}\right) \quad (8)$$

where c_b is the bulk concentration of oxygen, k is the reaction rate constant, r_f is the floc radius, r_e is the eddy radius, D_f and D are the diffusivity coefficients of oxygen through floc and water respectively.

$$k = 19.5 \text{ mgO}_2/\text{liter sec} \quad (\text{Appendix C})$$

$$D = 2.0 \times 10^{-5} \text{ cm}^2/\text{sec} \quad (2)$$

$$D_f = 0.5 \times 10^{-5} \text{ cm}^2/\text{sec} \quad (3)$$

$$r_e = 80 \times 10^{-4} \text{ cm} \quad (\text{Appendix C})$$

$$r_f = 22 \times 10^{-4} \text{ cm}$$

Substituting into equation 8:

$$c_b = \frac{19.5 \text{ mgO}_2/\text{liter sec} \times (22 \times 10^{-4} \text{ cm})^2}{6 \times 0.5 \times 10^{-5} \text{ cm}^2/\text{sec}} + \frac{19.5 \text{ mgO}_2/\text{liter sec} \times (22 \times 10^{-4} \text{ cm})^2}{3 \times 2.0 \times 10^{-5} \text{ cm}^2/\text{sec}} \times \left(1 - \frac{22 \times 10^{-4} \text{ cm}}{80 \times 10^{-4} \text{ cm}}\right)$$

$$c_b = 3.2 \text{ mgO}_2/\text{l} + 1.2 \text{ mgO}_2/\text{l} = 4.4 \text{ mgO}_2/\text{liter}$$

a minimum of 9.6 mg/l dissolved oxygen in the bulk liquid is required to eliminate mass transfer effects and maximize the

reaction rate in this example.

If turbulence is minimized, the size of the eddies becomes much greater than the floc sizes.

$$r_e \gg r_f, \frac{r_f}{r_e} \approx 0.$$

Equation 8 can be then transformed:

$$c_b = \frac{kr_f^2}{6D_f} + \frac{kr_f^2}{3D} \left(1 - \frac{r_f}{r_e}\right)^0 = \frac{kr_f^2}{6} \left(\frac{1}{D_f} + \frac{2}{D} \right)$$

floc resistance eddy resistance

substituting values of $D_f = 0.5 \times 10^{-5}$ and $D_e = 2 \times 10^{-5}$

$$c_b = \frac{kr_f^2}{6} (2 \times 10^5 + 1 \times 10^5)$$

$$\text{Ratio: } \frac{\text{floc resistance}}{\text{eddy resistance}} = \frac{2}{1}$$

When the layer of attached water is maximized (minimum turbulence), it comprises only one third the total resistance. The major resistance to mass transfer in the biological reactor is obviously the floc itself.

Experimental

Some experimental verification of oxygen and substrate mass transfer effects in biological reactors has been recently published by Schaezler (7), Bailod and Boyle (8), and Poon and Wang (9). Schaezler worked with a pure culture of E. coli, which did not flocculate, and had a critical DO concentration of 0.06 mg/l. He found no effect of turbulence on growth rate because the DO concentration was above minimum and there was no floc resistance to overcome.

Bailod and Boyle (8) worked with a pure, flocculent culture of Zooglea ramigera in a turbine agitated system. The reactor was maintained near DO saturation. Reaction rate was observed to be substrate limited at lower concentrations for blended cultures (smaller flocs) than for flocculated cultures (larger flocs). The blended culture was produced by placing the flocculated culture in a Waring Blender.

Poon and Wang (9) worked with parallel pure oxygen and air biological reaction systems with glucose as substrate. They reported that reaction rates were proportional to dissolved oxygen concentrations, indicating oxygen was controlling the reaction rate. In one case, the pure oxygen reactor with a DO concentration of 15 mg/l showed a rate of COD removal 65 percent greater than that of the air system held in the range of 5 to 9 mg/l.

Process Performance

Biological waste treatment basins are generally maintained at dissolved oxygen levels from 0.5 mg/l to 4 mg/l (3) (9). At these levels, if glucose is the waste, the reaction rate becomes oxygen concentration controlled at glucose concentrations above 32 mg/l (33 mg/l COD) if the reactor is held at 4 mg/l DO and maximum growth. Many of the common types of treatment plants - are operated to minimize net growth, and to maintain DO levels in the range of one mg/l. Under these conditions, glucose concentrations above 5 mg/l (5 mg/l COD) create oxygen controlled reaction rates. As shown in Table II, a number of compounds that may be found in waste streams have even lower concentration levels above which oxygen concentration controls the reaction rate in these plants.

Plants employing sludge recycle carry high solids concentrations in the reactor that promote conditions favorable for large floc formation. Power levels in these plants in the range from 0.1 to 1.0 HP/1000ft³ allow the formation of large flocs. Large flocs create mass transfer controlled reactions that require substantial bulk concentrations of oxygen to effectively penetrate the flocs. Over four mg/l oxygen was required in the design example to fully penetrate a floc 44 microns in diameter.

Table II
Maximum Substrate Concentrations Above Which
Oxygen Limits the Reaction Rate

Substrate	Chemical Formula	Molecular Weight	Diffusivity cm ² /sec x 10 ⁻⁵	Maximum Concentration* mg/l
Acetic acid	C ₂ H ₄ O ₂	60	1.24	1.9
N Butanon	C ₄ H ₁₀ O	76	0.96	1.0
Ethanol	C ₂ H ₆ O	46	1.28	0.9
Glucose	C ₆ H ₁₂ O ₆	180	0.69	3.6
Hydroquinone	C ₆ H ₆ O ₂	110	1.00	1.3
Methanol	CH ₄ O	32	1.60	1.1
Pyridine	C ₅ H ₅ N	79	0.76	1.3

*In a non-growth, mass transfer limited reactor with a DO concentration of 1.0 mg/l in the bulk liquid.

Substantially higher turbulence levels and DO concentrations in such plants will stimulate the degradation of the waste materials. Fortunately, aeration equipment can supply oxygen and turbulence simultaneously.

However, higher turbulence levels that lower floc size may cause settling problems in gravity clarification basins. If so the use of pure oxygen to provide a high DO concentration at moderate turbulence levels may be the answer. Or perhaps solids removal systems other than gravity settling should be considered.

Conclusions

1. Biological processes treating soluble wastes are likely to be rate controlled by oxygen rather than substrate.
2. The major resistance to mass transfer of oxygen to the micro-organisms in the floc is the floc itself.
3. Increased turbulence can stimulate the waste degradation rate by reducing floc size and increasing the DO level.

APPENDIX A

Mathematical Discription of Eddy Size

Energy inputs into a reactor by boundary forces (e.g. a turbine balde) create large eddies. These eddies in turn create smaller eddies, and in the process transfer the energy to them. The smallest eddies dissipate the energy through viscous effects.

If the system is in steady state and the smallest eddies are in a state of equilibrium, then its structural characteristics are only dependent on the energy input, E, and the kinematic viscosity, V. This concept is known as the Universal Equilibrium Theory, first postulated by Kolmogoroff (4).

By dimensional analysis, the size parameter that characterizes the smallest eddies in universal equilibrium is L.

$$L = \left(\frac{V^3}{E}\right)^{1/4} \quad V \left(\frac{\text{area}}{\text{time}}\right) \quad E \left(\frac{\text{power}}{\text{mass}}\right)$$

L (Length)

The size of the eddy that is the centroid of the distribution of smallest eddies has been experimentally determined to be 2L (4).

For example, the average sized eddy can be calculated for a power input of 1HP/1000 ft³ as follows:

$$E = \frac{1 \text{ HP}}{1000 \text{ ft}^3} = 550 \frac{\text{ft} \cdot \text{lb}_f}{\text{sec}} \times \frac{32 \text{ lb}_m}{\text{lb}_f} \cdot \frac{\text{ft}}{\text{sec}^2} \times \frac{454 \text{ gm}}{\text{lb}_m} \times$$

$$\frac{292 \text{ cm}^2}{\text{ft}^2} \times \frac{1 \text{ cm}^3}{\text{gm}} \times \frac{1 \text{ ft}^3}{2.29 \times 10^7 \text{ cm}^3}$$

$$E = 2.5 \times 10^2 \frac{\text{cm}^2}{\text{sec}^3}$$

$$V = 10^{-2} \frac{\text{cm}^2}{\text{sec}} \quad - \text{ water at } 20^\circ\text{C}$$

$$L = \left(\frac{V^3}{E} \right)^{1/4} = \left[\frac{\left(10^{-2} \frac{\text{cm}^2}{\text{sec}} \right)^3}{2.5 \times 10^2 \frac{\text{cm}^2}{\text{sec}^3}} \right]^{1/4} = 8 \times 10^{-3} \text{ cm}$$

L = 80 microns

2L = 160 microns

APPENDIX B

Derivation of Equation Relating Eddy Thickness and Floc Size to the Bulk Liquid Oxygen Concentration Required for Maximum Reaction Rate

Oxygen Diffusion through Eddy

(Molecular diffusion through the eddy surrounding the biological floc)

The steady state diffusion equation in spherical coordinates with no convection or reaction is

$$D \left(\frac{d^2 c}{dr^2} + \frac{2}{r} \frac{dc}{dr} \right) = 0$$

The solution is,

$$c = A + \frac{B}{r}$$

The boundary conditions are

$$D \frac{dc}{dr} = N \text{ at } r = r_f$$

$$c = c_b \text{ at } r = r_e$$

where r_f and r_e are the radius of the floc and the radius of the eddy respectively:

$N \left(\frac{\text{mass}}{\text{time} \cdot \text{area}} \right)$ is the flux of oxygen at $r = r_f$;

D is the diffusivity of oxygen in water; and c_b is the oxygen concentration in the bulk liquid at $r = r_e$.

Application of the boundary conditions yields

$$c_b - c = \frac{Nr_f^2}{D} \left[\frac{1}{r} - \frac{1}{r_e} \right]$$

setting $k = N \times \frac{\text{floc area}}{\text{floc volume}}$, and $c_f = c$ at $r = r_f$

and substituting yields,

$$\Delta c_e = c_b - c_f = \frac{kr_f^2}{3D} \left[1 - \frac{r_f}{r_e} \right]$$

where k $\left(\frac{\text{mass}}{\text{time vol}} \right)$ is the floc reaction rate, and c_f is the concentration of oxygen at the floc surface.

Oxygen Diffusion and Reaction in the Floc

The steady state equation for diffusion and reaction in a spherical shell of the floc if the reaction rate is zero order, is

$$D_f \left(\frac{d^2 c}{dr^2} + \frac{2}{r} \frac{dc}{dr} \right) = k$$

The solution is

$$c = \frac{kr^2}{6D} - \frac{A}{r} + B$$

The boundary conditions are

$$\frac{dc}{dr} = 0 \text{ at } r = 0$$

$$c = c_f \text{ at } r = r_f$$

where D_f is the diffusivity of oxygen through floc. Application of the boundary conditions yields,

$$c_f - c = \frac{k}{6D_f} (r_f^2 - r^2)$$

setting $c = c_o$ at $r = 0$, the equation becomes

$$c_f - c_o = \frac{kr_f^2}{6D_f}$$

where c_o is the oxygen concentration at the floc center.

Overall Expression

The bulk oxygen concentration required to maintain a minimum concentration at the floc center is

$$c_b = c_o + \Delta c_f + \Delta c_e$$

If c_o is small compared to Δc_f and Δc_e , the equation reduces to

$$c_b = \Delta c_f + \Delta c_e$$

substituting the previously derived expressions for Δc_f and Δc_e ,

$$c_b = \frac{kr_f^2}{6D_f} + \frac{kr_f^2}{3D} \left(1 - \frac{r_f}{r_e}\right)$$

An identical expression can be derived for substrates other than oxygen using appropriate values for the constants.

APPENDIX C

Calculation of Reaction Rate Constant K, and Floc Radius r

The reaction rate constant k is the oxygen uptake of the cells under optimal conditions, no mass transfer limitations.

Micro-organisms can reproduce in anywhere from twelve minutes to several days. For a mixed culture an average generation time of one hour will be used for this example.

At maximum growth rates, the micro-organism population follows first order kinetics:

$$\frac{db}{dt} = kb \quad \begin{array}{l} b = \text{microbial concentration} \\ t = \text{time} \end{array} \quad \begin{array}{l} k = \text{constant} \\ t = \text{time} \end{array}$$

The oxygen utilization is proportional to the microbial concentration. The constant of proportionality is a yield coefficient.

$$\frac{db}{dt} = Y \frac{dO_2}{dt} \quad \frac{dO_2}{dt} = \frac{1}{Y} \left(\frac{db}{dt}\right) = \frac{1}{Y} (kb)$$

$$k = \frac{\ln(2)}{t \ 1/2} = \frac{0.7}{1 \text{ hr}} \times \frac{\text{hr}}{3600 \text{ sec}} = 1.95 \times 10^{-4} \text{ sec}^{-1}$$

$$Y = \frac{\Delta b}{\Delta O_2} = \frac{17 \times 113}{59 \times 32} = \frac{1 \text{ gm cells}}{1000 \text{ mg } O_2} \quad (\text{see Equ. 1})$$

$$\frac{1}{b} \frac{dO_2}{dt} = \frac{k}{Y} = \frac{1.95 \times 10^{-4} \text{ sec}^{-1}}{1 \text{ gm cells} / 1000 \text{ mg } O_2} = \frac{0.195 \text{ mg } O_2}{\text{sec. gm. cells}}$$

$$1 \text{ gm cell (dry weight)} = 5 \text{ cm}^3 \text{ cells (wet)} = 5 \times 10^{-3} \text{ liter}$$

$$k = \frac{0.195 \text{ mg } O_2}{\text{sec. gm. cells}} \times \frac{\text{gm cells}}{5 \times 10^3} \times \frac{.5 \text{ liter}}{\text{liter solids}} = \frac{19.5 \text{ mg } O_2}{\text{sec liter solids}}$$

Floc Radius r

The eddy radius is $80 \times 10^{-4} \text{ cm}$. The eddy volume is

$$V_e = \frac{4}{3} \pi r_e^3 = \frac{4}{3} \pi (80 \times 10^{-4})^3 = 2.2 \times 10^{-6} \text{ cm}^3$$

The number of eddies per liter is

$$\frac{\text{eddies}}{\text{liter}} = \frac{10^3 \text{ cm}^3}{\text{liter}} \times \frac{1 \text{ eddy}}{2.2 \times 10^{-6} \text{ cm}^3} \times .5 \text{ voids } \frac{\text{sphere}}{\text{cube}} = 2.3 \times 10^8 \frac{\text{eddies}}{\text{liter}}$$

The solids concentration is 2000 mg/l. The solids density is 0.2mg/cm^3 , since solids are measured in terms of dry weight, and are approximately 80% water. The floc volume per eddy is

$$\frac{V_f}{\text{eddy}} = \frac{2000\text{mg/l} \times 1\text{cm}^3/200\text{mg}}{2.3 \times 10^8 \text{eddies/l}} = 4.4 \times 10^{-8} \text{cm}^3/\text{eddy}$$

$$r_f = \left[\frac{3V}{4\pi f} \right]^{1/3} = \left[\frac{3}{4\pi} \times 4.4 \times 10^{-8} \text{cm}^3 \right]^{1/3}$$

$$r_f = 22 \times 10^{-4} \text{cm}$$

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