An Application Model Of Foam Fractionators Used In Aquaculture

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Abstract

Closed cycle aquaculture production is subject to an accumulation of suspended solids (<100 mm) and dissolved organics. Of particular concern are solids in the 5 to 10 mm size, since these solids have been identified as causing mortality and poor performance due to gill infections in salmonids, and are not easily removed by conventional methods of screening. Foam fractionators have been used with some success to remove fine suspended solids and excessive nutrient concentrations. Foam from fractionator columns needs to be concentrated to prevent excessive water loss. A mathematical model is developed that can be used to predict volatile solids removal rates and fine suspended particles from a typically configured foam fractionator that uses an inverted funnel to concentrate foam. The mathematical model includes the effects of superficial gas velocity, particle diameter, bubble diameter, protein concentration, pH, gas void ratio, column liquid flow rate and foam overflow height as well as column geometric variables such as diameter and submergence depth.

Intensive aquaculture is contributing an increasing amount of the annual fish and seafood being marketed in the USA and world markets. Lack of suitable water supplies and more stringent control of waste and nutrient discharge from hatchery facilities accentuates the demand for closed system production units that can be used to produce fingerlings for growout facilities or food fish directly on an economically competitive basis.

Closed cycle aquaculture production systems are usually defined as exchanging 10% or less of the system’s water volume on a daily basis. Operating a closed-cycle system under economically competitive conditions, e.g., one pound or greater of fish per gallon of water and daily feeding rates that are 1 to 3% of the total fish biomass, presents significant engineering challenges to maintain water quality conditions that can sustain high fish productivity. Typically closed production units are subject to an accumulation of suspended solids (<100 μm) and dissolved organics (protein). Of particular concern are solids in the 5 to 10 μm size, since these solids have been identified as causing mortality and poor performance because of gill infections in salmonids (Chapman et al., 1987). Others have reported on the adverse effects of solids on fish health and gill damage (Stickney, 1979; Wicke, 1980). Particles > 100 μm are settleable (Rudolf and Belmont, 1982) and because of their size are not generally viewed as being a primary object of removal by foam fractionation.

Foam fractionation has been used with some success to remove fine suspended solids and excessive nutrients. Lomax (1976) compared fish culture systems that used a biofilter in combination with either a sedimentation tank, foam fractionation units or mechanical filters. Lomax’s opinion was that in terms of cost and effectiveness, the biofilter with fractionation was the best design combination. Lawson (1978) analyzed the effects of flow rate, geometry and aeration rates on fractionator performance, but used Triton X-100 as the water contaminant as opposed to using fish culture water which could greatly affect fractionator performance. Kown (1971) reported that increasing fractionator column diameter decreased solids removal rates. There has been considerable mathematical modelling of the fractionation process (Wilson et al., 1976; Lemlich, 1966; Sastri and Fuerstenua, 1970). Generally, the models take the form of a model presented by Dwyer (1973):

\[ C(t) = C_0 e^{-b t} \]  

(1)

where

- \( C \) = concentration of pollutant, mg/L
- \( C_0 \) = initial concentration of pollutant (t = 0), mg/L
- \( t \) = time, s
- \( b \) = closure constant, 1/s

Unfortunately, these studies are restrictive to particular applications, with none of the studies to date...
specifically using waste waters that could be consid-
ered typical of closed cycle aquaculture systems. Also,
the models have failed to separate the effects of foam
fractionator operational and/or design parameters upon
fractionator performance.

The objective of this paper is to develop a predic-
tive model of a practical foam fractionator design.

Materials and Methods

Mathematical Analysis

Chen (1991) developed a mathematical model
which described dissolved solids (C_d) and fine sus-
pended solids (C_p) removal rates as affected by both
design and operating parameters. Dissolved proteins
were identified as the primary surfactant material in the
fractionation process and the surfactant proteins con-
stituted 11% (SE = 2.5%) of the total protein levels in
the fish waste water. Without surfactant material, foam
fractionation ceases. Removal of fine solids (C_p)
cannot occur without concomitant removal of dissolved
proteins (C_d). Thus, although uncoupled equations
were presented to describe removal rates of C_d and C_p,
the processes are in fact coupled. Chen (loc cit) modellled
the foam fractionation process in two parts, disolved nutriment and suspended particle transfer to
air bubbles as they traveled from the air stone up
through the column length.

A typical fractionator design is depicted in Figure 1.
Simply stated, the model developed by Chen (loc cit)
states that the loss of solids from the liquid is equal to
the solids accumulated on the air bubbles, one being
the negative of the other:

\[
\frac{dC_d}{dt} = -R_d \\
\frac{dC_p}{dt} = R_g
\]  
(2a)

(2b)

where

\[ C_d = \text{concentration of solids in liquid, mg/L} \]
\[ R_d = \text{removal rate of solids from liquid, mg/L per sec} \]
\[ C_p = \text{concentration of solids in gas, mg/L} \]
\[ R_g = \text{removal rate of solids from gas, mg/L per sec} \]

Chen (loc cit) divided the solids removal rates into
dissolved and suspended fine solids:

\[
R_d = R_{d,d} + R_{d,p} \\
R_g = R_{g,d} + R_{g,p}
\]  
(3a)

(3b)

where

\[ R_{d,d} = \text{dissolved solids removal rate from liquid, mg/L per sec} \]
\[ R_{d,p} = \text{suspended solids removal rate from liquid, mg/L per sec} \]

\[ R_{g,d} = \text{dissolved solids removal rate from gas, mg/L per sec} \]
\[ R_{g,p} = \text{suspended solids removal rate from gas, mg/L per sec} \]

Chen (loc cit) developed mathematical expres-
sions for Equations 3a,b by assuming that gradients
over a short distance in the fractionator in the direction
of flow (z) could be neglected (high mixing rates), and
that net water flow over small increments of z was zero:

\[
R_{d,d} = \frac{d(C_d)}{dt} = -1.59 (C_d - k T_d)D^{0.5} \\
U_g/(1-E_g)U_p^{0.5}E^{0.5}
\]  
(4)

\[
R_{d,p} = \frac{d(C_p)}{dt} = -S (C_p)U_g/(P_s/B_s (1-E_p) U_g)
\]  
(5)

\[
R_{g,d} = \frac{d(T_d)}{dt} = 0.53(C_d - k T_d)D^{0.5} \\
(U_g/E_g)U_g^{0.5}E^{0.5}
\]  
(6)

\[
R_{g,p} = \frac{d(T_p)}{dt} = 0.33(S C_p U_g)/(P_s/B_s E_g U_g)
\]  
(7)

where

\[ C_d = \text{dissolved solids concentration in bulk solution, mg/L} \]
\[ C_p = \text{fine solids concentration in bulk solution, mg/L} \]
\[ T_d = \text{surface concentration of fine solids, g/m}^2 \]
\[ k = \text{adsorption coefficient, 1/m} \]
\[ T_p = \text{surface concentration of dissolved solids} \]
\[ \text{(surfactants), g/m}^2 \]
\[ D = \text{dissolved solids (surfactants) diffusion} \]
\[ \text{coefficient, m}^2/\text{s} \]
\[ U_g = \text{superficial gas velocity, m/s} \]
\[ U_p = \text{rising velocity of a single bubble, m/s} \]
\[ B_s = \text{radius of individual gas bubble, m} \]
\[ S = \text{fine suspended particle removal coefficient,} \]
\[ \text{m}^2/\text{s} \]
\[ P_s = \text{radius of suspended particles, m} \]
\[ E_g = \text{gas holdup, dimensionless} \]

Superficial gas velocity is defined as the ratio of
volumetric air flow through the fractionator column and
the cross sectional area of the column:

\[ U_g = Q/A \]  
(8)

where

\[ U_g = \text{superficial gas velocity, m/s} \]
\[ Q = \text{air flow rate through column, m}^3/\text{s} \]
\[ A = \text{cross sectional area of fractionator column, m}^2 \]

Gas holdup is the ratio of fractionator column height
without aeration to height with aeration (typical values
are around 0.1 to 0.2).

Equation 4 describes the product of the flux of
dissolved solids from the column liquid onto a bubble
surface and the flux of gas bubbles through a cross
section of the fractionator column. The constant in Equation 4 is the reduced value of several geometric terms describing area and volume, i.e., it is not an empirical constant. Equation 5 represents the area of bubbles flowing through the fractionator column and their impact with suspended fine solids during the travel through the column, with removal rates being predicted based upon the collection efficiency term, S. Chen neglects diffusion of solid particles to the bubble surface, i.e. Chen models impact only. Reay and Ratcliffe (1973) reported that for particles > 3-4 micron, bubble collection of solids is governed by impact.

Equation 7 is never used, since Chen has assumed particle loads on bubbles do not affect removal rates of particles from the bulk liquid (Equation 5). Equation 6 (the constant 0.58 is the result of the same geometric constants in Equation 4, except it is divided by three to convert a surface concentration, \( T_{D} \), to a volumetric concentration of the gas bubble) is solved for \( T_{D} \) in terms of \( C_{D} \) and then substituted back into Equation 4. The final set of equations are as follows (see Chen, loc cit, for a complete mathematical derivation):

\[
d(C_{D})/dt = -1.59(C_{D}/(D^{0.5})U_{D}) \exp(1.59 k(D^{0.5}/U_{D})^{10}/(3(E_{p}(U_{D}^{1.5})^{0.5})))/(1-E_{p}(U_{D}^{1.5})^{0.5}) \) \( (9) \)

\[
d(C_{D})/dt = -5(C_{D}/U_{D})(P)/(B^{0.5}(1-E_{p}(U_{D})) \) \( (10) \)

where

\[
H = \text{column length, m}
\]

Equations 9 and 10 can both be solved easily and have the form:

\[
C(t) = C_{0} \exp(C - bt) \) \( (11) \)

Chen (loc cit) experimentally determined the unknown coefficients in Equations 9 and 10 as:

\[
D = 1.11 \text{ E-12 m}^{2}/\text{s (standard deviation of 0.71E-12, 9 test runs)}
\]

\[
k = 1.03 \text{ E+4, } 1/\text{m}
\]

\[
S = 3.88E-3 \text{ (standard deviation of 1.20 E-3)}
\]

\[
(1/k_{b}) = \text{coefficient (units of length) relating } T_{D, a} \text{, which is the adsorption isotherm of protein on a bubble surface, and } C_{D} \text{, the bulk solution concentration of dissolved proteins; Chen (loc cit) presented the following regression of data to relate } C_{D} \text{ and } T_{D, a} \text{ for bubble surface concentrations after bubbles have travelled through a 2 meter high column filled with bulk solution: } T_{D, a} = k_{a} C_{D} \text{ where } k_{a} = 0.7 \text{ E-6 (R}^{2} \text{ of 0.84, SE of coefficient of 9.9 E-6, DOF (Degree of Freedom) of 15).}
\]

Both Equations 9 and 10 are first order. Chen (loc cit) verified that both dissolved and suspended particles behaved in a first order manner in a series of experiments operated in batch mode at various concentrations for both variables of interest.

Note that Equations 9 and 10 contain directly or indirectly most of the operating parameters involved in using a foam fractionator. These equations omit the effects of the collection process, and only model the bubble enrichment process as bubbles travel from an air diffuser up through the fractionator water column to the air/water interface. Thus, predicting actual operation of a practical foam fractionation design is still not possible.

Using Equation 10 requires a characterization of the size of the fine suspended particles contained in the bulk solution. Chen et al. (1992) analyzed solids from several waterborne systems and found that the dominant size of particles by number were 8 to 11 nanometer. This value of course could be assigned differently to the model, if the bulk solution is known to be different.

Development of an Applied Model

Modelling the removal rate of suspended particles also produces some redundancy in modelling protein removal rates, since suspended particles are in part made up of protein materials. Weeks et al. (1992) reported that suspended solids were approximately 50% protein and that the condensate enrichment resulted almost entirely from collection of volatile solids; fixed solids remained the same between fish culture water and foam condensate, although the foam condensate increased in total solids by approximately 600 mg/L from 800 mg/L to 1,500-1,600 mg/L.

Unfortunately, Equations 9 and 10 cannot be applied directly since they model production rates at the water air interface at the top of the column. Some means are generally used to concentrate the foam in order to minimize water losses. Weeks et al. (1992) presented a foam fractionation design (see Figure 2) that has been applied in commercial settings. As can be seen in the figure, an inverted 60° funnel is placed at the top of the column to concentrate the foam and to utilize the velocity of the escaping air bubbles to push the foam on through the funnel for condensate storage or disposal.

Weeks et al. (loc cit) found that only a fairly narrow range of overflow heights could be used in practical applications (placing the mouth of the funnel at the air-water interface was defined as a zero height) for the 15 cm diameter column design studied. Surprisingly, using zero overflow heights resulted in condensate that was only 60% higher in volatile solids, although production rates of foam were high, and an 8 cm overflow height resulted in a 270% increase in volatile solids concentration but very low levels of foam production (ML/mn). The ratio of solids removal rates between the zero overflow and the 8 cm height was 2.88. Clearly, this implies management options are available as to how best to operate a foam fractionator, which would depend upon what is desired to be
accomplished, e.g. minimizing effluent or maximizing solids removal.

Variables Affecting Removal Rates

Gas Holder (E_g)

Foam fractionator performance is dependent upon gas hold up, which is the fractional increase in column liquid height due to aeration. The increase is obviously related to the amount of aeration. Chen (loc cit) obtained the following relationship between E_g and U_g:

$$E_g = 4.1 \times U_g^{0.83}$$

(11)

(original regression equation was: \( \ln(E_g) = 1.41 + 0.83 \ln(U_g) \); \( r^2 = 0.98 \), SE coeff = 0.15, N = 9)

Equation 11 was used in the application model of this paper to describe E_g as a function of U_g.

Bubble Rising Velocity

Equations 9 and 10 employ the velocity associated with a single bubble rising in a column. A fractionator operates using a bubble swarm. The decreased density difference between the bubble and the surrounding fluid decreases the buoyancy force, which slows the velocity of the bubbles in the bubble swarm. Chen (loc cit) video taped rising bubbles in a column with a bulk fluid dissolved protein concentration of 120 mg/L. His data are given in Table 1. Data in Table 1 was regressed to give the following expression:

$$\ln(U_b) = -1.55 - 25.8 \times (U_g)$$

(12a)

\( r^2 = 0.97 \), SE coeff = 3.12, N = 4

Equation 12 can be more conveniently expressed by taking the exponential of both sides of the equation:

$$U_b = 0.21 \exp(-25.8 \times U_g)$$

(12b)

Shah et al. (1982) presented a simpler form to predict bubble rising velocity for bubble swarms:

$$U_b = U_g/E_g$$

(13)

Table 2 gives a comparison of the predicted bubble rising velocities using Equation 12 or 13. As can be seen from the comparison between the two model predictions in Table 2, Shah’s method (Eq. 13) predicts the opposite effect as observed from the Chen’s data and as described by the regression equation, Eq. 12. Therefore, Equation 12 will be used in the application model for this paper to predict foam fractionator performance.

A practical range exists for U_g since continued increases in U_g will eventually result in the formation of Taylor bubbles or gas slugs (thus not suited for fractionation). Reinemann and Timmons (1989) reported that gas void ratios (E_g) above 25% will begin to form slug flow in tap water. It would be expected that due to higher surface tension effects from dissolved solids in the fish culture water, the E_g value could be extended and still maintain bubbly flows.

Bubble Size

Chen (loc cit) presented data (Table 3) which can be used to predict bubble size as affected by protein concentration (PC) and superficial air velocity (U_g). Neither Equation 12 or 13 had included the effects of protein concentration.

A regression of the data given in Table 3 provides the following relationship to describe the effects of superficial gas velocity and protein concentration on bubble diameter, B_g:

$$B_d (\text{mm}) = 2.58 + 28.1 \times U_g \times \exp(-0.0098 \times (\text{PC}, \text{mg/L}))$$

(14)

(\( r^2 = 0.82 \), SE coefficients = 5.4 and 0.0013, DOF = 17)

Since equation Equation 12 predicts bubble rising velocity at a PC of 120 mg/L, Equation 14 could be used to adjust the rising velocity based upon change in bubble diameter. Roughly, the bubble rising velocity will change proportionally to the change in bubble diameter; therefore the rising velocity is proportional to the volume of the bubble (buoyancy effect) and inversely proportional to the drag area of the bubble—or \( B_d ^2 / B_g ^2 \).

Effects of pH

The pH of the bulk solution has been seen to affect the foam fractionation process (Grieves, 1972). Chen (loc cit) analyzed the effects of pH upon the equilibrium concentration of dissolved proteins on the bubble surface (Table 4) as reflected in the adsorption equilibrium coefficient, K_a. In applying the application model, pH effects can be included by using a more specific K_a value for each specific pH value in Equation 9 rather than the average K_a value as shown in Table 4. A regression of the data in Table 4 (trivial since only 3 data points) is:

$$K_a = -3.50E-5 + 1.88E-5 \times (\text{pH})$$

(15)

\( r^2 = 0.86 \), SE coeff = 6.70E-6, DOF = 1

Note that Equation 9 uses the inverse of K_a , 1/10,300 m.

Closure of the Application Model

Chen’s (loc cit) model was specifically developed to model removal rates of proteins. In fact, Chen argued that the dissolved solids removed via fractionation were exclusively proteins. Recent data pre-
sented by Weeks et al. (1992) indicated that the conden-
sate solids were a combination of dissolved pro-
teins and other solids, and could not be strictly accounted
for by proteins alone. Weeks et al. (loc cit) reported the
volatile solids removal rates, foam-condensate pro-
duction rates and condensate solids characteristics for
a variety of operating conditions and foam overflow
heights (Table 5 provides the physical characteristics
and operating conditions of the fractionator design
used, and the performance data is presented in Table
6).

An application model was developed from the data
in Tables 5 and 6 by using Equations 9 and 10 to predict
the dissolved and fine particle removal rates and then
developing a correction factor to account for the collec-
tion efficiency of the foam fractionator design (simply
the ratio of the measured to the predicted amount
of solids removed). Since Chen's models were strictly
developed for batch operation, data given by Weeks et
al. (loc cit) was expressed as removal rates per resi-
dence time of fluid in the column (volume of column
divided by water flow rate through column). The
removal rate data reported by Weeks et al. (loc cit) was
for a concentration of total suspended solids in the bulk
fluid of 10.1 mg/L. The time of residence as calculated
from the Weeks et al.'s data was substituted into
Chen's exponential equations to calculate the removal
rates per unit residence time of fluid in the foam
fractionator column.

Results and Discussion

A multiple regression was performed using the data
in Table 6 to develop correction terms to reflect the
collection efficiency associated with a concentrating
funnel placed on top of a foam fractionator column. The
measured condensate rates of removal were regressed
with the predicted data (Equations 9 and 10) using the
operating conditions of overflow height \( H_f \) and
superficial gas velocity \( U_g \) as independent variables.
The correction factors for the dissolved solids and the
suspended fine particles are referred to as \( B_G \) and \( B_p \),
respectively, and are as follows:

\[
B_G = 0.012 - 0.000076 \cdot H_f - 0.086 \cdot U_g \quad (16)
\]

\[
(\hat{R} = 0.96, \text{SE coef} = 0.00015, \text{DOF} = 51)
\]

\[
B_p = 0.19 - 0.017 \cdot H_f \quad (17)
\]

\[
(\hat{R} = 0.49, \text{SE coef} = 0.0024, \text{DOF} = 52)
\]

where \( H_f \) is distance from top of liquid to bottom edge of funnel,
cm.

Including an interaction variable of overflow height
and superficial air velocity did not improve the regres-
sion for \( B_G \) or \( B_p \). The superficial gas velocity was not
statistically significant (at the 10% level or smaller) in
the regression for \( B_p \).

Application of Models

Equations 9 and 10 can be applied to predict the
performance of a typically configured foam fraction-
ator. These results must be viewed in the context that
the collection efficiency has not been included. Thus,
the figures will show removal rates as if there was
100% collection of solids at the top of the fractionator
column, and will therefore be used only to illustrate
relative effects. The effects of bubble size (Figure 3)
can be shown by applying Equations 9 and 10 directly
(assumes bubble size is not a function of the other
operating parameters). The control of bubble size is
impractical when glass bonded diffusers are used,
since all bubbles will be within a narrow range (usually
from 2.5 to 3.5 mm diameter bubbles), even when
different diffuser types are used (Chen, loc cit). Thus,
Equations 9 and 10 can express bubble size as a
function of superficial gas velocity and the protein
concentration of the bulk fluid (Equation 14). After
making this substitution, Equations 9 and 10 are a
function of only one operational parameter, superficial
gas velocity. Effects of superficial gas velocity (where
\( B_G, B_p, U_p \) are all expressed as a function of \( U_g \)) are
shown in Figures 4-7. All results are shown as the ratio
of current concentration \( C \) to initial concentration \( C_0 \) of
either dissolved solids (Equation 9) or fine particles (Equation 10).

Actual performance of foam fractionators can be
predicted by including correction terms for collection
efficiency as developed in the preceding section. The
following is an example to demonstrate the application
of the equations presented in this paper to predict
solids removal rates for a foam fractionator where a
funnel is used to concentrate foam.

Problem Statement

Calculate the initial removal rates of volatile solids
(VS) for a fractionator that is 1.0 m in height, 10 cm in
diameter, and is operated with a 20 L/min bulk fluid flow
rate. The fractionator is as described by Figure 1 (glass
bonded diffuser with inverted funnel to trap and con-
centrate foam). The funnel is set for a 4 cm overflow
height (bottom edge of funnel is 4 cm above the water
level in the column) and the concentration of VS in the
fish tank is 300 mg/L with a total protein concentration
(PC) of 50 mg/L and a pH of 8.0. Assume the fine
suspended solids average 10 microm in diameter (con-
sidered typical). Calculate the solids removal rate from
a single fractionator column.

Solution: \( \Delta C_G = \Delta C_P + \Delta C_s \)

Assume that \( \Delta C_G \) that can be predicted based
upon the volatile solids concentration (VS) and \( \Delta C_p \)
can be predicted from the concentration of total sus-
pended solids (TSS). Foam production rates are a function of \( U_g \), \( E_p \), \( U \), \( D_r \):

\[
U_g (\text{m/s, Equ. 8}) = \frac{Q}{A} = \frac{(20 \text{ L per min})}{(0.052)(0.06/60 \text{ s})} = 0.04 \text{ m/s}
\]

\( E_p \) (dimensionless, Equ. 11) = \( 4.1 \quad (U_g)^{0.83} \)

\( U \) (m/s, Equ. 12b) = \( 0.21 \exp(-25.8 \; U) \)

\( = 0.21 \exp(-25.8 \times 0.04) \)

\( = 0.07 \text{ m/s} \)

*Assumes \( U_b \) is equal to \( U \)

\( B_d \) (mm, Equ. 14) = \( 2.58 \times 28.1(0.04) \)

\( = 0.0998 \times 50 \text{ mg/L} \)

\( k_b \) (m, Equ. 15) = \( 3.50 \times 10^5 \times 1.68 \times 10^6 \)

\( = 9.94 \times 10^5 \) or \( k = \frac{1}{k_b} = 10.06 \text{ s} \)

Other values needed to use Equations 9 and 10:

\( 1.59 \times 10^9 = 1.7 \text{ E-6}; 1.59 \times 10^9 \times 1.3 = 5.7 \text{ E-3} \)

Substituting the above values into Equation 9 (where \( C_{d,0} \) is the initial concentration of \( C_d \)):

\[
d(C_d)/dt = -C_{d,0}((1-E_d) / (U_g^{0.83})) \exp[(5.7E-3 \times 0.04) \times 0.079 \times 0.001689) \times \exp[5.7E-3 \times 0.04 \times 1.00 \times 0.28 \times 0.079 \times 0.001689)]
\]

\( = -C_{d,0}(1.73E-2)\times \exp(-1.73E-2) \)

Solving: \( C_d(t)/C_{d,0} = \exp(-1.73E-2) \)

The model has been developed to represent solids removal rates per unit residence time (time required for an amount of bulk liquid to pass through a column equal to the column volume). Calculate residence time:

\( t (s) = \frac{\text{Volume/flow rate}}{(1 \text{ m/s} \times 0.052 m^2)/(20 \text{ L/min})(0.6/60 \text{ s})}
\]

\( = 24 \text{ s} \)

Substitute \( t = 24 \text{ s} \) into exponential:

\( C_d(t=24) / C_{d,0} = \exp(-1.73 \times 24) = 0.66 \)

or removed \( C_d \) is 1.0 - 0.66 = 0.34 \( C_{d,0} \)

The removal must be corrected for collection efficiency:

\( B_d \) (Equ. 16) = \( 0.012 - 0.00076 \text{ cm} \)

\( = (0.4 \text{ m/s}) \)

\( = 0.0055 \text{ cm} \)

The dissolved volatile solids removed per retention time can now be calculated using an initial concentration of volatile solids of 300 mg/L:

\( \Delta C_d \times B_d = \frac{0.34 \times 300 \text{ mg/L}}{0.0055 \times 0.2 \text{ L/m} \text{ x} \text{ s}} \)

\( = 4.8 \text{ mg/L per retention time} \)

Now, calculate the fine solids removal rate (radius of particles is 0.000005 m and where \( C_{p,0} \) is the initial concentration of \( C_p \)):

\( d(C_p)/dt \) (Equ. 10) = \( -C_{p,0}(3.88E-3)(0.04 \text{ m/s}) \)

\( (0.000005 \text{ m})/(0.00162 \text{ m}^2)(1.028)(0.07 \text{ m/s}) \)

\( = -C_{p,0} \times (6.01E-3) \)

Solving the last differential equation:

\( C_p(t)/C_{p,0} = \exp(-6.01E-3/t) \)

\( = 0.87 \) or removed \( C_p \) is 1.0 - 0.87 = 0.13 \( C_{p,0} \)

The removal rate must be corrected for collection efficiency:

\( B_p \) (Equ. 17) = \( 0.19 - 0.017 \text{ cm} \)

\( = 0.12 \text{ cm} \)

The fine suspended solids removed per retention time can now be calculated using an initial concentration of fine solids of 10 mg/L:

\( \Delta C_p \times B_p \) = \( 0.13 \times 10 \text{ mg/L} \times 0.12 \times 20 \text{ L/min x} \text{ s} \text{ min}60 \text{ s) x 24 s} \)

\( = 1.25 \text{ mg/L per retention time} \)

If the concentration in the bulk solution remained at 300 mg/L VS and 10 mg/L TSS (steady-state condition where production rate of VS and TSS was balanced by the removal rates from the foam fractionators), then the 24 hour removal rates would be:

\( \Delta C_d \times 24 \text{ hr} = 0.19 \text{ mg/L} \times 60 \text{ min/hr} \times 60 \text{ min/hr} \times 24 \text{ hr} \)

\( = 16,400 \text{ mg/day or 16.4 g/day} \)

\( \Delta C_p \times 24 \text{ hr} = 0.052 \text{ mg/L} \times 60 \text{ min/hr} \times 24 \text{ hr/day} \)

\( = 4,500 \text{ mg/day or 4.5 g/day} \)
As a "rule of thumb" check of these predictions, Weeks et al. (1992) reported the average TVS concentrations in foam condensate from all operating conditions analyzed as 872 mg/L. Using this condensate concentration and the previously calculated ΔC_{TVD,IV}, the volume of condensate collected in a 24 hour period from one 10 cm diameter column would be estimated as:

\[
\text{Volume Condensate} = \frac{(16,400 \, \text{mg/L})}{(872 \, \text{mg/L})} = 18.8 \, \text{L}
\]

This value is consistent with the author's observations of fractionator performance over the last several years. Other observations include erratic performance from fractionator units. Lack of consistency is attributed to large to anti-surfactant properties of fish feeds, e.g. oil top dressings used on pelleted feeds. Predictions of developed equations in this paper should be used as estimates of performance.

Literature Cited


Lawson, T.B. 1978. Venturi design parameters for air injection into a foam fractionation system. PhD dissertation. The University of Maryland, College Park, MD, USA.


### Table 1. Measured single bubble rising velocity as part of a bubble swarm for various superficial air velocities in a fractionator column (protein concentration in bulk fluid of 120 mg/L; Chen, 1991)

<table>
<thead>
<tr>
<th>$\bar{U}_g$(m/s)</th>
<th>$\bar{U}$(m/s)</th>
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</thead>
<tbody>
<tr>
<td>0.0011</td>
<td>0.22</td>
</tr>
<tr>
<td>0.0093</td>
<td>0.16</td>
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<tr>
<td>0.022</td>
<td>0.11</td>
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<tr>
<td>0.038</td>
<td>0.085</td>
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</table>

### Table 2. Predicted bubble rising velocity ($U_b$) using data from Chen (1991) versus prediction given by Shah et al. (1982)

<table>
<thead>
<tr>
<th>$\bar{U}_g$(m/s)</th>
<th>$E_g$ (Equ 11)</th>
<th>$E_g$ (Equ 12)</th>
<th>Shah (Eq. 13)</th>
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<tr>
<td>0.005</td>
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### Table 3. Changes in measured bubble diameter (Bd, mm) at various superficial air velocities ($U_g$) and protein concentrations (PC) (from Chen, 1991)

<table>
<thead>
<tr>
<th>Bubble Diameter, mm</th>
<th>Protein Concentration, mg/L</th>
<th>$U_g$ (m/s)</th>
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### Table 4. Regression coefficients developed by Chen (1991) to describe the effects of pH on the protein adsorption equilibrium coefficient ($k_a$)

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<tr>
<th>pH</th>
<th>$k_a$ (m)</th>
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<td>avg</td>
<td>9.7xE-5</td>
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### Table 5. Operating and design characteristics of the foam fractionators used by Weels et al. (1992)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<td>Piper diameter</td>
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<tr>
<td>Submergence depth</td>
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<tr>
<td>Airflow rates (expressed as $U_g$ m/s)</td>
<td>33.0, 37.8, 42.5, 51.9, 65.1 L/min</td>
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<tr>
<td>Water flow rates</td>
<td>11.4, 22.7, 34.1 L/min</td>
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<tr>
<td>Overflow heights</td>
<td>0.3, 4.5, 7, 8 cm</td>
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</table>
Table 6. Effects of superficial gas velocity (U_g, m/s) and overflow height (H_o, cm) on foam fractionator performance in terms of volatile solids removal rates (VSSR, mg/min) and dissolved and fine particle removal rates per unit residence time (ΔC_{DP} and ΔC_{DFP}) (from Waksal et al., 1992; culture water characteristics:307 mg/L volatile solids, 825 mg/L fixed solids, 10 mg/L suspended solids and 0.5 mg/L total Kjeldahl nitrogen).

| Trial | Retention time (sec) | Prod rate foam (ml/min) | VSSR mg/min | ΔC_{DP} mg/L | ΔC_{DP} mg/L
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</table>

*Vol of liquid treated (volume of bulk fluid passing through column per unit residence time)

*Expressed as mg per unit retention time of bulk fluid through fractionator column.
Figure 1. Typical foam fractionator design (from Chen, loc. cit.).

Figure 2. Foam fractionator design used by Weeks et al. (1992).

Figure 3. Relative change in dissolved or fine solids concentration with time (Cd(t)/Cd(t=0) or Cp(t)/Cp(t=0)) as affected by bubble radius (effect is exactly the same) (Ug=0.03 m/s, L=1.0 m, bubble size is not a function of protein concentration or superficial gas velocity).
Figure 4. Relative change in dissolved or fine solids concentration with time \((\text{Cd}(t)/\text{Cd}(t=0))\) or \((\text{Cp}(t)/\text{Cp}(t=0))\) as affected by superficial gas velocity \((U_g, \text{m/s})\) and where bubble size is a function of superficial gas velocity and protein concentration \((\text{PC})\) \((L=1.0 \text{ m}, \text{Pr}=5 \text{ micron}, \text{PC}=0 \text{ mg/L})\).

Figure 5. Relative change in dissolved or fine solids concentration with time \((\text{Cd}(t)/\text{Cd}(t=0))\) or \((\text{Cp}(t)/\text{Cp}(t=0))\) as affected by superficial gas velocity \((U_g, \text{m/s})\) and where bubble size is a function of superficial gas velocity and protein concentration \((\text{PC})\) \((L=1.0 \text{ m}, \text{Pr}=5 \text{ micron}, \text{PC}=0 \text{ mg/L})\).
Figure 6. Relative change in dissolved or fine solids concentration with time (Cd(t)/Cd(t=0) or Cpt(t)/Cpt(t=0)) as affected by protein concentration (PC) (L=1.0 m, Pr=5 micron, Ug=0.03 m/s) where bubble size is a function of Ug and PC.

Figure 7. Relative change in dissolved or fine solids concentration with time (Cd(t)/Cd(t=0) or Cpt(t)/Cpt(t=0)) as affected by protein concentration (PC) (L=1.0 m, Pr=5 micron, Ug=0.03 m/s) where bubble size is a function of Ug and PC.
Ozone Use in Recirculating Systems: Comparisons With Other Disinfections Options

T.B. Lawson and G. Merry
Louisiana State University
Baton Rouge, Louisiana

ABSTRACT

Ozone has been widely used in the European wastewater treatment and drinking water industries since the early 1900's. For over two decades it has been used by over 80% of European aquarists. Interest in using ozone in recirculating aquaculture systems has been revived recently. Ozone has proven to be effective against a variety of fish and human pathogens at low dosages. Ozone is also effective at removing turbidity, odor, odor and organics from culture water. Water quality does not affect ozone as it does chlorine and UV irradiation. Ozone also does not combine with ammonia as chlorine does. On-site pure oxygen production will double the quantity of ozone generated as compared to air, reducing system and operating costs. Skimming towers remove residual ozone and eliminate the need for detention chambers.

Introduction

Disinfection is the reduction of infectious organisms in aquaculture systems. It differs from sterilization, which is the complete destruction of all living organisms in a system. Disinfection is usually necessary in heavily loaded systems to minimize the transmission of disease organisms and parasites, consisting of bacteria, viruses, protozoans, fungi and worms.

Disinfection is used primarily in hatcheries but is becoming more prevalent in flow-through and recirculating systems. Higher stocking densities, temporary declines in dissolved oxygen, rapid temperature and/or pH changes, and increases in ammonia, nitrite, carbon dioxide or organics cause stresses on the cultured animals, making them more susceptible to infections. Normally harmless organisms may become infectious when environmental factors cause a sudden increase in their numbers. The environment and health of the host determine whether the organisms remain latent or become infectious. Heavy infestations often occur on seemingly healthy fish despite carefully maintained and controlled environmental factors (Spotte 1970). Disinfection in large recirculating systems is expensive, but as discharge regulations tighten and recreational use of natural water increases, recirculating system aquaculture with disinfection becomes more attractive.

The need for control of infectious microorganisms in recirculating systems is clear. Because of dense stocking rates, stress factors and water reuse in recirculating systems, infections can spread rapidly. All things considered, we feel that ozone has the greatest potential for disinfection in recirculating systems. This paper discusses the various options and makes comparisons of ozone to other disinfection methods. Finally, we close our argument with conclusions and recommendations.

Disinfection Options

Basically, four disinfection options are considered feasible for recirculating aquaculture systems: heat, chlorination, ultraviolet (UV) irradiation, and ozone. For various reasons, mostly economical, other disinfection processes have not proven to be feasible. The effectiveness of a given disinfecting agent or method depends on concentration used, contact time, temperature, turbidity, particulate concentration and type of disease organism or parasite (Huguenin and Colt 1989).

Heat

Water in recirculating systems can be sterilized or disinfected with steam or by elevating the water temperature. Small steam generators are commonly used to sterilize equipment and tanks before putting in fish or after a disease incident. Steam is also used to sterilize boats, aines, nets, buckets and other equipment which are avenues for infection.

Culture water can be disinfected by elevating the temperature with a steam boiler, electric or gas-fired heater or heat exchanger. The percent kill of the microorganisms depends on the final temperature, holding time and the species of target microorganism. Since water has a high specific heat, considerable energy is required to heat to the proper disinfesting temperature. It must then be cooled prior to biological filtration or before it re-enters culture units since fish and nitrifying bacteria cannot tolerate the high temperatures required for disinfection (Wheaton 1977). A major disadvantage to using heat disinfection methods

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in recirculating systems is the energy required for heating and cooling (Dupree 1981).

**Chlorine**

Chlorine is an inexpensive and readily available chemical disinfectant, and equipment for its application is readily available (Dupree 1981). Chlorine is added as chlorine gas (Cl₂), calcium hypochlorite (Ca(ClO)₂), or sodium hypochlorite (NaClO₃). In all cases the active disinfecting agent is the hypochlorite ion (OCl⁻) or hypochlorous acid (HOCI). These exist in a pH-dependent chemical equilibrium (Piedrahita 1991):

$$\text{HOCl} \leftrightarrow \text{OCl}^- + \text{H}^+; \quad (pK_a = 7.54 \@ 25^\circ\text{C}) \quad (1)$$

Chlorine, HOCl and OCl⁻ are strong oxidizing agents. A disadvantage is that they react with a variety of organic and inorganic compounds to form hazardous by-products, such as chloramines. These compounds may be toxic to fish (Piedrahita 1987). The HOCl and OCl⁻ compounds are more toxic to fish than the free available chlorine and chloramines and must be removed from culture systems by dechlorination methods. The reported safe level of residual chlorine in aquaculture systems is 0.5 to 3 mg/L (Piedrahita 1991).

Dechlorination can be accomplished using one of several procedures available. Reducing agents like sodium thiosulfate (Na₂S₂O₃) and sodium sulfite (Na₂SO₃) and certain materials, one of which is activated carbon, are added to the system. They reduce chlorine to inactive compounds, but they do not affect chloramines (Dupree 1981). Reducing agents should be used cautiously since they may have toxic properties of their own. Piedrahita (1991) reported that reducing agents should be used in amounts no greater than 1 to 3 mg/L. A limited amount of chlorine can be destroyed with UV light, but UV light effectiveness is inhibited in systems where sodium thiosulfate is used for dechlorination (Seegert and Brooks 1978).

Aeration is often suggested as a dechlorination method; however, it is doubtful that chloramines are completely removed by aeration. Bedell (1977) reported that aeration is not effective in water high in organics. He stated that both chlorine and chloramines can best be removed with activated carbon. This may be practical for small systems, but activated carbon use has not been shown to be economical in large recirculating systems.

**Ultraviolet Light**

Ultraviolet (UV) irradiation, also referred to as UV light, is a popular disinfection method and is routinely used in hatcheries. It is effective in the control of bacteria, viruses, and other microorganisms (Dupree 1981). Its killing effect is largely a function of light wavelength. Koller (1965) and Wheaton (1977) reported the most effective light wavelength to be 2500 to 2800 Å (angstrom). The effectiveness drops rapidly on either side of the peak: 0.4 and 0.002% at 3200 and 7000 Å, respectively. Hoffman (1974) stated that 2537 Å is not dangerous to fish and is effective in killing a variety of fish pathogens. The mechanism by which microorganisms are killed is not completely understood, but it is believed that UV energy interrupts the genetic chemistry (DNA) of living cells (Moe 1989).

Ultraviolet light is measured in microwatts per square centimeter of contact area (μW/cm²). Spotts (1979) recommended a minimum dosage of 35,000 μW/cm² for disinfecting aquarium water. Dosages required to achieve 99 - 100% kill vary from 35,000 to 156,000 μW/cm², which is adequate for killing practically all disease-causing organisms which trouble aquaculture systems. Yeasts appear to be more resistant than bacteria (Pugazhenthi and Colt 1989). The lethal dose varies with age, size and species of target microorganism, water turbidity, ionic strength and water depth.

The efficiency of UV bulbs decreases with age due to degradation of the electrodes, caused by switching on and off, and because of the gradual darkening of the inner glass surfaces of bulbs. This darkening effect is called solarization. Because of solarization, the effective life of most bulbs is 6 to 12 months, after which they must be replaced (Moe 1989). Bulb efficiency is also reduced by biological slime and mineral deposits which collect on the outside.

Impurities in the water are the major limiting factor determining bulb effectiveness. Turbidity, organic material, and color absorb UV light rays and prevent exposure to target organisms. Suspended particulates shield smaller microorganisms from the light, thus further reducing its effect. UV light can only penetrate water to a depth about 50 mm (2 in). Therefore, it is recommended that water being treated should be no deeper than 25.4 mm (1 in) to ensure complete penetration (Moe 1989). Slow flow rates through UV light units are recommended for proper exposure times. Spotts (1970) recommended flow rates no greater than 3 lpm per mm of bulb (2 gpm/ft).

Three types of UV irradiation units are manufactured for aquaculture use. The suspended type is the oldest and most simple. These units are suspended about 50 to 150 mm (2 to 6 in) above the water surface, and water flows slowly beneath the lamps in a thin layer. Figure 1 illustrates this type of UV unit. Water is switched back and forth beneath the UV bulbs by
baffles, thus receiving a longer exposure to the light rays. Units of this type are subject to coating by biological slime and mineral deposits. Other types are the submerged and jacketed types. In submerged units the UV bulbs are contained inside a PVC tube, and the water flows between the tube and the bulb. The bulb operates at the same temperature as the culture water. Jacketed bulb types have a quartz sleeve over the UV bulb, and water flows on the outside of the sleeve. Most commercial UV light units available today are of this type. UV bulbs which do not contact the water (such as in jacketed and suspended bulb units) operate at their most effective temperature around 40°C (104°F). Bulb efficiency declines as the temperature declines and is only about 50% at 21°C (70°F) (Moe 1985). Thus, submerged bulb units are the least efficient type.

Disadvantages to UV light use are numerous. Since UV light leaves no residuals in the water any interruption in power will cause disruption of the disinfection process and leave the system unprotected. Even when functioning properly UV light will not affect microorganisms in pipes, pumps, culture units, etc. since they will not be exposed to the light. UV units are maintenance-intensive since the bulbs require frequent cleaning. Additionally, water impurities severely reduce UV light effectiveness. Finally, the applicability of UV light on a large scale is questionable because of the low flow rates recommended.

Ozone

Ozone (O₃) is a three atom allotrope of oxygen. The three oxygen atoms are loosely held together in an unstable bond. A single oxygen atom is quick to break away and reacts with most of the organic and inorganic molecules it comes into contact with. Hence, ozone is a powerful oxidizing agent, second only to fluorine.

Ozone has been used in the sewage treatment industry in Europe since the early 1900's. It was later used for sterilizing potable water supplies. Two decades ago it came into widespread use in the aquarium trade. In the 1970's 6 out of 10 European aquarists were using ozone (Stopka 1976). It has been slow to be adopted in the United States, however. A flurry of research expounded the use of ozone in the 1970's and early 1980's, but it was considered to be too expensive. Interest in ozone use has since been revived.

In aquaculture systems ozone is reported to provide many benefits and has distinct advantages (Wedemeyer et al. 1979; Williams et al. 1982 and Rosen 1972). Ozone use in aquaculture systems has been cautious due to its potential toxic effects on fish, invertebrates and bacteria in biofilters (MacLean et al. 1972; King and Spottet 1974). Ozone toxicity has been reviewed by Rosenthal (1980), Wedemeyer et al. (1979) and other researchers. These studies conclude that, if residual concentrations remain low, ozone can be safely used with significant advantages.

The effectiveness of ozone as a disinfecting agent is a function of dosage and contact time. Contact time is acquired by dispersing ozone throughout the culture water. Contact time and ozone concentration vary with the target microorganism and water quality. It effectively destroys bacteria, viruses, fungi, algae and protozoa (Lohr et al. 1986). Ozone kills by "burning" delicate cell membranes and actually enters the cell, destroying the cell nuclear chemistry (Moe 1986). Effects of ozone on various organisms are reviewed by Hoffman (1974), Colberg and Lingg (1976), Lohr and Gratzek (1980), Wedemeyer et al. (1976) and others.

In addition to its disinfecting properties, ozone is reported to reduce nitrates (Evans 1972; Colberg and Lingg 1978), BOD and COD (Colberg and Lingg 1978) and causes the precipitation of iron and manganese (Wheaton 1977). Ozone "breaks" long chain organic molecules into shorter chain molecules which are more easily degraded by bacteria. The gelatinous coating on tank walls and in pipes and sumps is reduced, thus lessening the chances for clogging and short-circuiting in these units. Total system solids loading is reduced with ozone. Its oxidative potential is also a disadvantage, however, in that ozone is very corrosive. All system components, such as PVC, plastics, O-rings, pumps, etc., having direct contact with ozone must be fabricated from ozone-resistant material.

Effect of pH. The decomposition of ozone is accelerated in the presence of hydroxyl ions (Weiss 1935). Therefore, rapid reduction of ozone is reported at pH 8.0 and above. Colberg and Lingg (1976) reported that, in their experience, even though the concentration of ozone was lowest at higher pH values, the oxidation capacity was greater. Ozone seems to be more effective at pH below 7.0 (Wheaton 1977).

Effect of Organic Matter. Since color, odor and turbidity can be removed by ozone, this indicates that they also have an ozone demand (Dupree 1981). Water containing high organic loads must be treated with higher dosages of ozone. As organic matter is oxidized, more free ozone becomes available. Therefore, it is wise to cut back on the ozone output a few days after installation in older systems (Moe 1895).

Effect of Salinity. Evidence supports the use of ozone in marine systems (Honn and Chavin 1976; Sutterlin et al. 1984; Moe 1895). However, since marine systems normally have higher pH values, ozone decomposition is more rapid. Ozone may have detrimental effects on seawater. It is reported to deleter what trace elements, particularly manganese (Spotte 1970) and calcium (Moe 1986). Ozone reacts with the chloride and bromide ions, forming toxic hypochlorites and hypobromites (Moe 1895).
Comparison of Methods

Ozone vs. Chlorine Disinfection

Ozone does not leave harmful residuals (Hewes and Davison 1971), as chlorine does, since it rapidly degrades to molecular oxygen (Layton 1972). The half-life of ozone is about 15 minutes (Honn et al. 1976). Ozone has twice the chemical oxidative capacity of the hypochlorite ion (Roosen 1972). Ozone does not react with ammonia like chlorine, allowing it to react much quicker. The effectiveness of chlorine on a mg/l basis is much less than that of ozone (Venosa 1972). Ozone is not as affected by pH and temperature changes as chlorine.

Ozone vs. UV Irradiation

Ozone rapidly oxidizes turbidity, organics and color-causing agents. Its efficiency is therefore not affected by these materials. Impurities in the water severely reduces the efficiency of UV light since they absorb the light rays and shield microorganisms from the killing effects of the light. Thus, ozone does not require costly pre-filtration like UV light systems to be effective (Lohr and Gratzek 1986).

Generation of Ozone

Ozone is a very unstable gas. Thus, it must be generated on-site and used immediately. It’s production is measured as mg ozons per hour. Most ozone generators used in the aquaculture industry use one of two methods to produce ozone: UV irradiation or silent electrical (corona) discharge. The UV irradiation method is less efficient than the two and is used primarily in small ozone generators used in the aquarium trade. In this method air is passed through a chamber containing a UV bulb which emits light in the 1,000 to 2,000 Å range (Gein et al. 1985). The UV light splits some of the oxygen molecules. The single oxygen atoms then attach to other O₂ molecules and form ozone (O₃). The UV approach is only applicable to small systems because of the low concentration of ozone produced (Honn et al. 1976). The feed gas must be dry since moisture decreases the amount of ozone produced and accelerates the formation of corrosive nitrous oxides. Also, air compressors must be free of residual oil since any hydrocarbons present will reduce ozone production (Honn et al. 1976).

Coronas discharge generators are capable of large-scale ozone production. A high voltage is impressed across two plates through which air or pure oxygen passes. The oxygen molecules are “excited” by the electrical charge and form ozone. The process is energy-consuming and produces heat.

Either air or pure oxygen can be used to produce ozone. The same ozone generator uses twice the power to produce ozone from air as it does to produce ozone from pure oxygen. Even though oxygen must be purchased, the cost is still usually less than ozone production using air (Wheaton 1977).

Ozone Dosage

Sufficient time must be allowed for ozone to be dispersed through the water. This brings about the required contact between the ozone and the target organism. Contact time and ozone concentration vary with the target organism and water quality.

The scientific literature indicates that ozone concentrations of 0.5 to 1.0 mg O₃/l and contact times of 1 to 2 hours are sufficient to kill most pathogens in aquaculture systems (Dunne 1981), however this varies considerably. Wedemeyer et al. (1975) reported that the minimum dosage required to control Aeromonas on fish eggs without damage to eggs or fry was 0.03 mg/l. Ozone was toxic to eggs at 0.3 mg/l. Wedemeyer et al. (1975) reported that an ozone concentration of 0.01 mg/l caused complete inactivation of enteric red mouth (ERM) bacterium in 30 seconds while 10 minutes was required to inactivate A. salmonicida. It was felt that pH and other water quality factors could have caused the differences. At the Dworekhat National Fish Hatchery in Idaho an ozone residual of 0.20 mg/l for 10 minutes achieved control over the virus infectious hematopoietic necrosis (IHNV) (Owens 1985).

Ozone treatment normally does not leave a residual in the treated water. However, for disease protection some researchers have advised that a very low residual is not harmful to fish and may prevent disease from reoccurring. Wedemeyer et al. (1979) determined that a safe permissible exposure level of ozone to fish was 0.002 mg/l. Toxicity effects vary considerably in the literature. Arthur and Mount (1975) reported that ozone was toxic to fathead minnows at 0.2-0.3 mg/l. Roseland (1974) and Honn et al. (1976) reported gill damage to rainbow trout at 0.01-0.06 mg/l. In other toxicity testing Wedemeyer et al. (1978) observed no differences between salmon exposed for three months to 0.025 mg O₃/l and the control. However, damage was observed at 0.05 mg/l. Sutterlin et al. (1984) reported that 1.82 g O₃ per kg fish with a one hour exposure time was sufficient to maintain water clarity with no ill effects on Atlantic salmon smolts. Treatment still had no affects when extended to 8 hours, but high mortalities occurred when the ozone generator was accidentally left running for 15 hours. Honn and Chavin (1976) noted no deleterious effects of 0.132 mg O₃/l in a seawater system containing nurse sharks. With so much variability being reported, the only positive method to determine ozone dosages and contact times is with on-site bench scale testing.

Precautions must be taken not to expose humans to high levels of ozone. Ozone can be detected in air by its odor, often described as "sharp" and "fresh". Humans can smell ozone in the range of 0.05 mg/l. The maximum safe concentration for an 8-hour work day is 0.1 mg/l (Owens 1985). Ozone in air can cause headaches,
nausea, and eye irritation (Moe 1989). Human exposure can be minimized by applying ozone for a few hours at night or during "off" periods when personnel will not be exposed.

**Analytical Methods**

Because of its recommended limitations, ozone is measured in very low concentrations, and is, at times, difficult to detect. Instrumentation to directly measure ozone in water is commercially available; however, it is expensive and the sensitivity is usually not great enough to measure ozone in 0.001 mg/l increments.

Several wet chemistry methods are available (APHA 1985; Owsley 1988). The DPD (N-diethyl-P-phenylenediamine) method is relatively simple but has limitations (Paulin 1967). The test must be completed within 5 minutes after taking the sample and has many interferences (Owsley 1988). A modified DPD method showed good results and increased accuracy (Wedemeyer et al. 1978).

The standard accepted procedure for measuring ozone in water is the indigo Blue method (Bader and Hoigne 1982). It is stable for up to 4 hours and has the least interferences of any of the analytical methods available.

Another method which can be used as an indicator is redox potential, which is a measure of the relative amount of the positive and negative charges on the oxidized and reduced molecules in solution. A high redox potential is necessary in culture water for optimum cell respiration. High organic loads depress the redox potential in aquaculture systems. Thus, most aquaculture waters have a low redox potential. The addition of ozone will oxidize more of the reduced molecules, thus elevating the redox potential. The higher the redox potential, the more "pure" the water.

Redox potential is reported in mv (millivolts). Healthy aquaculture systems should have a redox potential ranging from 200 to 350 mv. Levels below 200-250 mv indicate the presence of toxic, reduced compounds while levels above 400-450 mv indicate too active an oxidative environment, which can potentially damage plant and animal tissues and cells. Over-treatment with ozone can produce too high a redox potential (Moe 1989). Redox potential can be maintained at a comfortable 300-350 mv with careful ozone regulation. Commercial automatic control units are available which continuously monitor redox potential and adjust ozone output to maintain redox potential at specified levels.

**Applications**

Ozone units can be incorporated into recirculating systems in a number of schemes. The choice is left to the aquaculturist and is dependent on system design, site conditions and economics. It is generally agreed that ozonation should precede solids removal and/or biological filtration (Fig. 2). Since dissolved and suspended organic materials are rapidly oxidized by ozone, the load going to settling basins, tube settlers, or sand filters (whichever method is used for solids removal) is reduced, lessening the chance for clogging or short-circuiting in these units. Due to the decrease in solids it may be possible to decrease the size of these units, reducing the initial capital investment and operating costs.

Ozone has the effect of splitting large organic molecules into smaller biodegradable materials which are more easily removed by heterotrophic bacteria. Organic matter reduction prior to biological filtration has the effect of reducing the population of heterotrophic bacteria in the filters. Heterotrophs feed on organics and are the first to become established in biofilters. They compete for space on biofilter substrate with nitrifying bacteria. Too high a population of heterotrophs may inhibit nitrification (Paller and Lewis 1988).

The direct ozonation of water in the culture unit is the most simple method of application. In this method ozone is introduced through airstones or diffusers at the bottom of a water column. This method is most frequently used in home aquaria and small recirculating systems, however, caution must be used to guard against the potentially toxic effects of ozone residuals. Ozone can be applied as a "dose", lasting just a few hours. Continuous direct ozonation is not recommended. In lieu of direct application in culture units, ozone can be applied through a separate mixing chamber following the culture unit and preceding solids removal/biological filtration. In this technique, large doses can be applied and residuals can be removed by aeration. Aeration causes the ozone to degrade to molecular oxygen. Contact time is governed by the size of the chamber.

Some recirculating systems are designed for easy retrofit of an ozone generator. For existing systems the sidestream method of injection (Fig. 3) generally works best since it requires a minimum amount of plumbing changes. An alternate method is to combine ozone with a foam fractionator so that the benefits of both can be realized (Rosenthal 1980). The benefits of foam fractionation in aquaculture systems are well known (Wheaton et al. 1979; Lewason and Wheaton 1980), and the combination of foam fractionation and ozone can be very effective. Rosenthal (1980) reported that heavy metals were removed from culture water by foam fractionation and ozonation used in combination. Ozone changes some complex organics into more surface-active compounds which produce a more stable foam and increase the efficiency of the operation (Moe 1989).

Figure 4 illustrates a counter-flow foam fractionator with ozone injection. The water enters the foam column near the water surface and flows downward against the upward flow of air (or pure oxygen) and ozone, which is introduced through a fine bubble diffuser near the
bottom of the column. The water current is generated by a second diffuser placed in the smaller column. Foam is collected in the conical-shaped collector at the top of the column. Foamate is then collected in a container and saved for disposal. Foam units can be used individually or in multiple units, depending on system needs. They may be installed on the inside or outside of culture units, or they may be installed into a separate mixing chamber. Several models of foam fractionators incorporating ozone are commercially available.

Ozone Removal

Because of its toxicity to fish ozone must be removed from culture water in a short period of time. It can be removed by allowing culture water to be held in an aeration chamber for a period of time. However, this may not be practical in some systems due to the size of chamber required. Carbon filters are also very effective for removing ozone (Owesley 1985). However, for reasons previously discussed, carbon adsorption is not normally economical in large recirculating systems.

A faster, more economical method for ozone removal is to strip it from solution using a stripping tower (Owesley 1981). Complete removal occurs in properly designed units. Figure 5 illustrates a stripping tower. Tower packing material consists of plastic modules or other rigid, nonbiodegradable material which has a high surface area. Ozone laden culture water enters the top of the tower. Air enters at the bottom of the column and flows upward through the packing material. Ozone is "stripped" from the water by the counter-current action of the process. "Clean" culture water collects in the bottom of the tower and is returned to the culture unit. If desired, the unit can be covered and the ozone offgas vented to the outside. A word of caution is in order here: the designer should be aware the amount of ozone in the air at the bottom of the tower is below level of the air inlet so that water does not back up into the air compressor when power is off.

Conclusions and Recommendations

Ozone is a viable method for disinfecting and removing organics from culture water. It has also been proven an effective disinfectant. Need to fluorine, it is the most powerful oxidizing agent known.

Ozone has been successfully used in Europe for many years. It reacts twice as fast as chlorine and is not as restrictive in water quality requirements as is chlorine and UV irradiation. Ozone does not react with ammonia like chlorine and leaves no harmful residuals in the water.

Ozone must be generated on-site since it is an unstable gas. Production is doubled using pure oxygen instead of air.

Ozone is highly corrosive. All materials which directly contact ozone must be ozone-resistant.

The concentration of ozone can be determined using a variety of analytical methods. The most common is the Blue Indigo method. Another method showing potential is redox potential.

Caution should be exercised when using ozone. Residuals in culture units should not exceed 0.002 mg Cyl. Ozone in air should not exceed 0.1 mgfL for an 8-hour shift to protect humans who may be exposed. Ozoneation should be done at off-hours when employees are not normally present.

Potentially, the most promising method of ozone injection is in combination with foam fractionation.

Stripping towers remove residual ozone and eliminate the need for costly detention chambers.

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Figure 1. A suspended bulb UV irradiation unit.

Figure 2. Sequence of treatment processes in a semi-closed recirculating system loop.

Figure 3. Ozone injected as a side stream.
Figure 4. Ozone used in combination with a counter-current foam fractionator.

Figure 5. A packed tower used for ozone stripping.
Design Procedure for Hooded Surface Oxygen Absorption Systems

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Abstract

A design procedure addressing effluent total dissolved gas pressure limits along with standard performance indicators such as oxygen absorption efficiency (kg absorbed/kg applied), and transfer efficiency (kg/kWh), is presented for surface agitation equipment operating in an oxygen-enriched atmosphere. Application of this reactor type in closed culture systems is attractive given its insensitivity to biological fouling and ability to operate without the need for a significant hydraulic gradient. Performance algorithms were developed through application of chemical reactor theory, Henry’s Law and the Ideal Gas Law. In the analysis, gas and liquid phases were treated as being homogeneous. The design steps presented are unique in that required mass transfer coefficients ($K_a$), operating pressures (CP), and oxygen feed rates (G/L) are calculated for target changes in both dissolved oxygen and nitrogen without the use of iterative numerical procedures. A second calculation sequence establishes the sensitivity of system performance to changes in G/L when CP and $K_a$ are known.

Introduction

Successful operation of closed or semi-closed culture systems requires regulation of dissolved gas levels within acceptable limits. Regulation generally demands oxygen (DO) supplementation at rates that can approach the mass rate addition of feed per day, i.e., 1 kg O$_2$/kg feed (Colt et al. 1991). Oxygen supplementation is frequently achieved by exposing culture water to oxygen-enriched gas within equipment designed to provide large gas-liquid interfacial areas as well as intensive mixing (Colt and Watten 1988; Boyd and Watten 1989). Equipment of this type has the unique ability to economically saturate or supersaturate water with DO, while concurrently stripping dissolved nitrogen (Watten and Beck 1985; Watten et al. 1991). Supersaturation with DO can increase allowable fish loading (kg/m3) or rearing densities (kg/m2) several fold (Collins et al. 1984; Gowan 1987; Colt et al. 1991). These increases, in turn, can lower production costs by minimizing required rearing vessel volumes, reducing the energy used to circulate water among system components, and by decreasing the size of treatment units that are sensitive to hydraulic loading (e.g., clarifiers and biological filters). Supersaturation with DO, however, may result in gas bubble trauma or, in extreme cases, oxygen toxicity. The latter results from the oxidation of cellular components and leads to respiratory failure (Gossett et al. 1984; Colt et al. 1991). Oxygen toxicity can be avoided by keeping the tension of DO below 300 mm Hg (Table 1). The pathology of gas bubble trauma includes the formation of gas emboli and hemostasis, which act together to reduce fish growth and increase mortality (Bouch 1980; Weltkamp and Katz 1980; Kruse 1991). Gas bubble trauma is caused by exposure to a total dissolved gas pressure that exceeds the sum of hydrostatic pressure and local barometric pressure—i.e., when $\Delta P > 0$ where

$$\Delta P = (\Sigma F_i C_i) - BP - HP + VP \quad (1)$$

The net change in $\Delta P$ across an oxygen absorber will be fixed by the relative rate of dissolved nitrogen (DN) desorption as indicated by the $\Delta DO$ stripping ratio (Watten et al. 1991):

$$\Delta DO = (\Delta DO)_{AB} / (\Delta DN)_{AB} \quad (2)$$

Stripping ratios greater than 2.2 provide a net reduction in dissolved gas pressure whereas ratios less than 2.2 result in an increase. Therefore excessive $\Delta P$ can be avoided by designing equipment that provides the required nitrogen as well as oxygen transfer rates. A design procedure that addresses total gas pressure limits along with standard performance indicators (AE, TE, and transfer costs) is presented in this paper for hooded surface oxygen absorption equipment. Application of this reactor type in closed culture systems is attractive given its insensitivity to biological fouling and ability to operate without the need for a significant hydraulic gradient. The design procedure is unique in that operating conditions are identified for target changes in dissolved gases directly without the need for the iterative numerical procedures described by Watten et al. (1990).

Principles of Operation

Major components of an enclosed surface oxygenation system are shown in Figure 1 (Watten et al. 1990). The rate of gas absorption or desorption achieved will be governed by the product of the effective mass transfer coefficient, $K_a$, and the prevailing dissolved gas deficit (Lewis and Whitman 1924):

$$\frac{dG}{dt} = (K_a)_{AB} (C_1 - O)_{AB} \quad (3)$$

The coefficient $K_a$ reflects operating conditions within the enclosure. Important conditions include
characteristics of the liquid, turbulence, and the extent of the gas-liquid interfacial area present:

\[
(K_{L}a)_{LT} = \frac{D_A}{\Delta V}
\]  

(4)

Turbulence and interfacial area in turn are related to reactor geometry, agitation type, and power input. Figure 1 shows mixing by a rotating propeller. Surface agitation can also be provided by rotating turbines, paddles or by jetting water (Pettit 1981; Meade et al. 1991). The effective \( K_{L}a \) for a specific agitation type can be varied by changing the extent of agitation or spray head submergence (Watten et al. 1990; Meade et al. 1991).

The \( K_{L}a \) value for a system is typically identified through analysis of steady-state oxygen transfer data given the difficulty of measuring the variables \( D, A, \) or \( \Delta \) independently (Equation 4). In the case of the surface oxygenation system, \( K_{L}a \) is obtained from the following expression assuming both gas and liquid phases are homogeneous, i.e. the system is operating as a mixed-flow reactor (Watten et al. 1990):

\[
(K_{L}a)_{OL,LT} = \frac{(GTR)_{OL}}{(C^* - C_{agg})_{OL,AB}V 10^{-5}}
\]  

(5)

Once established, \((K_{L}a)_{OL}\) values can be corrected for the effects of non-standard liquid characteristics such as temperature, surfactants, or dissolved gas species \( N_2 \) using the following expression (Tsiouplou et al. 1985; Stenstrom and Gilbert 1981; APHA 1985):

\[
(K_{L}a)_{OL} = (K_{L}a)_{OL,20} \times 1.024^{T-20} \times C_i
\]  

(6)

In addition to the enhancement of \( K_{L}a \), gas transfer rates within the enclosed surface oxygenation system are accelerated by elevating dissolved gas deficits (\( C^* - C_i \)) through enrichment of the gas phase with commercial oxygen. Following Henry’s Law, the change in mole fraction \((C_i)\) of oxygen in the gas phase increases the saturation concentration \((C)\) of DO and decreases the \( C^* \) of DN (Cot 1984):

\[
C'_i = C_i/(K_{L}a)_{OL} 1000 [CP - VP] 760
\]  

(7)

This operating characteristic, common to oxygen contact equipment, allows for an efficient DO above air saturation concentrations. The decrease in \( C^*_i \) also enables DN to be stripped, thereby controlling total dissolved gas pressures. Nitrogen stripped from solution enters the gas phase then is purged from the enclosure by venting off-gas. Positive enclosure gauge pressures allow for passive off-gas venting. Negative gauge pressures require energy to remove off-gas either through application of a vacuum pump or water jet exhauster (Fig. 1).

Design factors affecting the rate of oxygen addition and nitrogen desorption include the oxygen feed rate \((G/L)\), enclosure pressure \((CP)\), \( K_{L}a \), water residence time \((V/Q_i * 0.06)\), and influent DO and DN concentrations. Carbon dioxide \((DC)\) stripping over typical \( G/L \) rate \((< 5\%)\) is negligible. Therefore the effect of \( DC \) on system performance can be ignored (Watten et al. 1991). Application of reactor theory provides a means of correlating important design conditions with system performance. For example, effluent DO or DN can be predicted under steady-state conditions by treating gas transfer as a first order reaction with respect to the dissolved gas deficit (Equation 3), and by using the general conversion model for a mixed flow reactor (Levenspiel 1979):

\[
\frac{(C^* - C_{agg})_{AB}}{C^* - C_{agg}} = \frac{1}{1 + (K_{L}a)_{OL} / (V/Q_i * 0.06)}
\]  

(8)

Alternatively, the residence time \((V/Q_i * 0.06)\) required to achieve a desired change in the dissolved gas deficit can be obtained from:

\[
\frac{AV/Q_i * 0.06}{1} = \frac{(C^* - C_{agg})_{AB}}{(K_{L}a)_{OL} V 10^{-5}}
\]  

(9)

The \((C^*)_{AB}\) used in Equations 8 and 9 represents the saturation concentration for a specific gas species within the enclosure. These concentrations will vary with enclosure pressure \((CP)\) and gas composition \((g)\) (Equation 7). Therefore, when designing equipment to satisfy selected changes in both DO and DN, it is necessary to find the combination of \( CP \) and \( g \) that meets the \((C^*)_{AB}\) requirements simultaneously (Fig. 2) and then solve for the appropriate \( G/L \). Application of Equation 8 reveals the fraction of the dissolved gas deficit remaining after treatment will decrease exponentially with increases in \( (K_{L}a)_{OL} \) or \((V/Q_i * 0.06)\) (Fig. 3). It is also apparent that increasing the product \((K_{L}a)_{OL} / (V/Q_i * 0.06)\) beyond 3 or 4 does little to improve the extent of gas transfer (Fig. 3).

Along with an analysis of gas transfer rates, performance of oxygen contact equipment is often assessed in terms of oxygen absorption efficiency, the ratio of mass of oxygen absorbed to mass oxygen applied \((AE\%)\), and transfer efficiency, the ratio of mass oxygen absorbed to energy input \((TE, \text{k}g \text{O}_2/\text{kWh})\). Elevating \( G/L \) generally increases at a diminishing rate \( \Delta \text{DO}, \Delta \text{DN}, \) and \( TE \) but reduces \( AE \) (Fig. 4). Use of a sub-atmospheric enclosure pressure \((CP)\) will enhance nitrogen desorption while decreasing both \( AE \) and \( TE \) (Fig. 4). Thus both oxygen and power requirements increase as the required nitrogen desorption rates increase. The performance of the mixer or surface agitation employed can be characterized by calculating standard aeration efficiency \((SAE)\) (Boyd and Watten 1989):

\[
SAE = \frac{[(K_{L}a, C^*_{OL,CP}) V 10^{-3}]}{PW_{water}}
\]  

(10)
Here the \( C^*_{O2} \) used represents the standard air saturation concentration at 20°C and one atmosphere of pressure. Typical SAE values for propeller and paddle wheel type agitators range between 1.15 and 2.25 kg O2/kW-h (Boyd and Watten 1969).

Design Procedures

The design of an enclosed surface agitation system must include a value for \((K_{a})^{20}_s\) that corresponds to the selected agitator type. Enclosure pressure and the oxygen feed rate must also be identified. A required agitation of DO and DN can be achieved using a number of different combinations of these variables. Therefore, the engineer's task is to identify the site specific combination that minimizes operating costs as well as the risk of system failure. This is accomplished with the design procedure developed here (Fig. 5, Procedure 1) by establishing oxygen and nitrogen stripping rates, selecting \((K_{a})^{20}_s\) value and then calculating the required CP, G/L, and resultant performance indicators. The calculation procedure is then repeated using alternate values of \((K_{a})^{20}_s\), and the results plotted as in Figure 6. Establishing performance indicators such as TE or transfer costs will require a previously identified correlation among agitator cost, power requirements, and \((K_{a})^{20}_s\).

A second design procedure (Fig. 5, Procedure 2) was developed to establish the sensitivity of a given systems performance to changes in G/L when CP is known. This second procedure also provides a means of checking values of CP and G/L calculated for selected \((\Delta DO)_{AB}\) values using Design Procedure 1. For Design Procedure 2, CP and \((K_{a})^{20}_s\) are identified for the system being modeled. An initial selection of the mole fraction in DO and DN of the air phase was made allowing resultant changes in DO and DN to be calculated along with the required G/L. The procedure is then repeated by using increasing or decreasing values of \(C^*_{O2}\) and the results are plotted as in Figure 7. Selection of a low value of \(C^*_{O2}\) will result in relatively high AE, and relatively small values of \((\Delta DO)_{AB}\) and \((\Delta DN)_{AB}\), G/L and TE (Fig. 7).

Performance algorithms used in both Design Procedures 1 and 2 were developed by applying a materials balance on the gas and liquid phases of the system along with the Ideal Gas Law and Equations 5-8. In the analysis both gas and liquid phases of the system were treated as being homogeneous. Further, the effect of DC on system performance was ignored (Watten et al. 1991) as was the effect of other gases present in trace concentrations. Performance predictions agree with those established by using the computer simulation program of Watten et al. (1990) previously verified by 114 observed versus model predicted effluent DO and DN comparisons. Several calculation steps are identical to those used in the packed column design protocol described previously (Watten 1990). Steps that are common to both reactor types are included here for the readers convenience.

Design Procedure 1

Step 1-1. Select target changes in DO and DN on the basis of a desired oxygen drop across the rearing vessel, expected rearing unit hydraulics, and criteria for individual and total dissolved gas pressures (Table 1). Calculate the required change in DO (mg/l) as follows:

\[
(\Delta DO)_{AB} = ECOC + (DO_{out})_{RV} - (DO_{in})_{AB}
\]  

(11)

If plug-flow rearing units are used, the required \((\Delta DN)_{AB}\) is based on the \(\Delta P\) of water being treated, and a selected value of \(\Delta P\) for the water entering the head end of the rearing vessel — i.e.,

\[
(\Delta DN)_{AB} = \frac{(\Delta DO)_{FCO2} \Delta P_{in} - (\Delta DO)_{FCO2} \Delta P_{out}}{\Delta P_{in}}
\]  

(12)

Alternatively, if mixed-flow rearing units are employed, \((\Delta DN)_{AB}\) can be based on the DN concentration in the supply water and a target \(\Delta P\) and DO concentration in the rearing unit effluent:

\[
(\Delta DN)_{AB} = \frac{(BP + (\Delta P_{out})_{RV} - (DO_{out})_{RV} (FCO2) + VP)}{\Delta P_{in}} - (DN_{in})_{AB}
\]  

(13)

If DO concentrations must be increased without a change in \(\Delta P\), the required \(\Delta DN\) is then simply the product of \(\Delta DO\) and the critical stripping ratio:

\[
(\Delta DN)_{AB} = (\Delta DO)_{AB} (FCO2)\n\]  

(14)

The calculation procedure requires that the calculated \((\Delta DN)_{AB}\) value is positive and that the corresponding \((\Delta DN)_{AB}\) value is negative. Further, the required change in DN must be less than the influent DN concentration.

Step 1-2. Calculate the required dissolved oxygen and nitrogen transfer rates using \((\Delta DO)_{AB}\), \((\Delta DN)_{AB}\), and the system water flow rate:

\[
(\Delta GTR)_{CO2} = (\Delta DO)_{AB} QL \times 10^{-3}
\]  

(15)

\[
(\Delta GTR)_{N2} = (\Delta DN)_{AB} QL \times 10^{-3}
\]  

(16)

Step 1-3. Using a selected value of \((K_{a})^{20}_s\) and \((\Delta GTR)_{CO2}\) and \((\Delta GTR)_{N2}\) values from Step 1-2, solve for the required saturation concentrations of DO and DN within the enclosure:

\[
C^*_{O2} = \frac{(\Delta GTR)_{CO2}}{(K_{a})^{20}_s \times 1.024 \times 10^{-3} \times V \times 10^{-3}} + (DO_{out})_{AB}
\]  

(17)
\[ C'_{N_2} = \left( \frac{(\text{GTR})_{N_2}}{(K_{s1})_{N_2} \cdot \text{G}_2 = 1.024 \text{ T}^{-2} \text{ V}^{-1}} \right) + (\text{DN}_{\text{out}})_{AB} \]  

(18)

Selecting a relatively high value of \((K_{s1})_{N_2}\) will result in a relatively low CP and G/L and a relatively high required power input.

Step 1-4. Using Henry's Law, calculate gas phase partial pressures with respect to both \(O_2\) and \(N_2\) that correspond to the saturation concentrations established in Step 1-3. The partial pressure ratios are defined here as:

\[ P_{O_2} = \frac{(C')_{O_2} \cdot \beta_{O_2} \cdot K_{O_2} \cdot 1000)_{AB}}{1} \]  

(19)

\[ P_{N_2} = \frac{(C')_{N_2} \cdot \beta_{N_2} \cdot K_{N_2} \cdot 1000)_{AB}}{1} \]  

(20)

The product of \(\beta_{O_2} \text{K}_{O_2} \text{K}_{N_2}\) is given in Table 2 as a function of temperature and pressure.

Step 1-5. The required absolute pressure within the enclosure can now be calculated by using \(P_{O_2}, P_{N_2}\), and a water vapor pressure (VP) value from Table 2:

\[ \text{CP} = 760 \left( P_{O_2} + P_{N_2} \right) + \text{VP} \]  

(21)

Step 1-6. Calculate the gas phase mole fraction \(X_2\) of both oxygen and nitrogen, using CP and the \(C'\) values from Step 1-3:

\[ X_2 = \frac{(C')_{O_2} \cdot \beta_{O_2} \cdot K_{O_2} \cdot 1000)_{AB}}{1} \]  

(22)

\[ X_2 = 1 - X_2 \]  

(23)

Step 1-7. Establish the required molar flow rate of oxygen to the enclosure:

\[ (\text{QM})_{O_2} = X_2 \left( \frac{(\text{N})_{O_2}}{\text{N}_2} \right) \]  

(24)

\[ \text{QM} = \left( [F_0] \right) \left( \frac{(\text{N})_{O_2}}{\text{N}_2} \right) \]  

(25)

Step 1-8. Convert the molar flow rate of oxygen to a standard volumetric flow rate (21.1°C and 760 mm Hg) using the Ideal Gas Law:

\[ QV = 0.0821 \text{ QM} \times 21.1 \text{ (273.15 + 21.1)} \]  

(26)

Step 1-9. Calculate the effective gas-liquid ratio (G/L) as follows:

\[ G/L = \frac{QV/QL}{150} \]  

(27)

Step 1-10. Standard performance indicators can now be established, including AE and TE:

\[ \text{AE} = \frac{(\text{ADO})_{\text{AB}} \cdot \text{QL} \cdot 100}{(\text{MW})_{O_2} \cdot \text{QM}} \]  

(28)

\[ \text{TE} = \frac{(\text{ADO})_{\text{AB}} \cdot \text{QL} \cdot (6 \times 10^{-5})}{\text{PW}} \]  

(29)

Total energy input (PW) represents the sum of the power required to operate the agitator \(\text{PW}_{\text{Agitaor}}\) to pump water through the enclosure \(\text{PW}_{\text{pump}}\) and to extract off-gas \(\text{PW}_{\text{compressor}}\) when the enclosure pressure is less than the local atmospheric pressure. Neglecting the effect of friction in the water supply line and assuming the combined pump and motor efficiency is 0.7, \(\text{PW}_{\text{pump}}\) can be estimated by using the following equations:

\[ \text{PW}_{\text{pump}} = \frac{[\text{H} \times \text{G}(\text{QL} \times 60,000)]}{0.7} \]  

(30)

\[ \text{H} = (\text{CP} - \text{BP} \cdot 0.0136) + Z \]  

The specific mass of water \(\text{G}\) required is given in Table 2. An estimate of the energy required to extract off-gas can be obtained from the adiabatic compression formula described by Yunt (1979):

\[ \text{PW}_{\text{compressor}} = \frac{\text{QRT}}{\text{N}} \left( \frac{[P]}{[P_i]} - 1 \right) \]  

(31)

The mass flow rate \(Q\) of off-gas required above is related to the composition and molar flow rate of the off-gas as follows:

\[ Q = \frac{(\text{N}) \cdot \text{G}(\text{QL} \times 60,000)}{(\text{M})_{O_2} \times 0.032)}\)  

(32)

The molar flow rate of off-gas, \(O_2\), is obtained from the required nitrogen desorption rate, water flow rate, and \(\chi_{O_2}\) by using the expression:

\[ QN = \frac{1}{\chi_{O_2}} \]  

(33)

At this time total, variable, and fixed costs should be calculated using local power and commercial oxygen costs along with calculated values of AE and TE.

Design Procedure 2

Step 2-1. Identify \((K_{s1})_{N_2}\) for the selected surface agitation system.

Step 2-2. Select a gas phase \(\chi_{O_2}\) value (0.25 to 0.8) and calculate the corresponding value of \(\chi_{N_2}\) - i.e.,

\[ \chi_{N_2} = 1 - \chi_{O_2} \]  

(34)

Step 2-3. Given \(\chi_{O_2}\) and \(\chi_{N_2}\), calculate the resultant saturation concentrations of DO and DN within the enclosure by using Henry's Law, the selected CP (absolute), and solubility coefficients presented in Table 2.
Step 2-4. Calculate the absorber effluent DO and DN using \((C')_{AB}\) values from Step 2-3, \((K_a e)_{AB}\) values from Step 2-1, and the following expression:

\[
(C')_{AB} = \frac{1000 \text{ } K_a \text{ } X_1 \text{ } (CP - VP)}{760}
\]  

(35)

Step 2-5. Given influent and effluent DO and DN, calculate \((\text{ADO})_{AB}\) and \((\text{ADN})_{AB}\), and then solve for the required molar flow rate of oxygen \((\text{QM})_{02}\) into the enclosure as in Step 1-7.

Step 2-6. Convert the molar flow rate of oxygen to a standard volumetric flow rate as in Step 1-8.

Step 2-7. Calculate the effective gas-liquid ratio as in Step 1-9.

Step 2-8. Calculate the standard performance indicators as in Step 1-10.

Step 2-9. Establish a \(AP\) value for the contactors effluent using Equation (1) to ensure that total dissolved gas pressures are acceptable (Table 1).

Step 2-10. If desired, select a new value of \(X_{CO2}\) and repeat the design calculations starting at Step 2-2.

Literature Cited


Table 1. Dissolved gas criteria for intensive culture conditions (Colt et al. 1991).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cold water (12°C)</th>
<th>Warm water (25°C)</th>
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<tbody>
<tr>
<td>DC (low)</td>
<td>5-6 mg/l</td>
<td>3-4 mg/l</td>
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<tr>
<td>DC (high)</td>
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<td>300 mm Hg</td>
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<tr>
<td>ΔP (all life stages)</td>
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<tr>
<td>ΔP (specific life stages)</td>
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</tr>
<tr>
<td>eggs</td>
<td>45 mm Hg</td>
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<td>sac. try</td>
<td>35 mm Hg</td>
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<td>early juveniles</td>
<td>10 mm Hg</td>
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</tr>
<tr>
<td>advanced juveniles</td>
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</table>

*Unknown.*

Table 2. Water vapor pressure and dissolved oxygen and nitrogen solubility parameters as a function of water temperature (Colt 1984). T = water temperature, °C; γ = specific mass of water, kN/m²; VP = water vapor pressure, mm Hg; β = Bunsen's coefficient, liter gas/l water at 760 mm Hg pressure; βK<1000 = gas solubility, mg/l at a partial pressure of 760 mm Hg; F = gas tension per mg/l, mm Hg.

<table>
<thead>
<tr>
<th>T</th>
<th>VP</th>
<th>β</th>
<th>βK1000</th>
<th>F</th>
<th>β</th>
<th>βK1000</th>
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<td>A</td>
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<td>Gas-liquid interfacial area ( \text{(m}^2 \text{)} )</td>
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<td>Total hydraulic head ( \text{(m H}_2\text{O)} )</td>
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<tr>
<td>K</td>
<td></td>
<td>Ratio of molecular weight to volume for a gas ( \text{(mg/ml)} )</td>
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<td>K_a</td>
<td></td>
<td>Overall mass transfer coefficient ( \text{(h}^{-1} \text{)} )</td>
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<tr>
<td>MW</td>
<td></td>
<td>Molecular weight ( \text{(mg/mole)} )</td>
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<tr>
<td>N</td>
<td></td>
<td>((k-1)/k) (dimensionless)</td>
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<td>P</td>
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<td>Partial pressure ratio, ((C_{\text{eq}}/K)\times1000) (dimensionless)</td>
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<td>P_i</td>
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<td>Absolute compressor inlet pressure ( \text{(kPa)} )</td>
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<td>P_o</td>
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<td>Absolute compressor outlet pressure ( \text{(kPa)} )</td>
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<td>PW</td>
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<td>Total power input ( \text{(kW)} )</td>
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<tr>
<td>PW_e</td>
<td></td>
<td>Power used to exhaust off-gas ( \text{(kW)} )</td>
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<tr>
<td>PW_a</td>
<td></td>
<td>Power used to agitate water ( \text{(kW)} )</td>
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<tr>
<td>PW_p</td>
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<td>Power used in pumping water ( \text{(kW)} )</td>
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<td>Q</td>
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<td>Mass flow rate of off-gas ( \text{(kg/s)} )</td>
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<td>QL</td>
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<td>System water flow rate ( \text{(l/min)} )</td>
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<td>QM</td>
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<td>Molar flow rate of oxygen ( \text{(moles/min)} )</td>
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<td>QN</td>
<td></td>
<td>Molar flow rate of off-gas ( \text{(moles/s)} )</td>
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<td>QV</td>
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<td>Volumetric flow rate of oxygen ( \text{(l/min \text{O}}_2 \text{)} )</td>
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<tr>
<td>R</td>
<td></td>
<td>21.1°C and 760 mm Hg</td>
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<tr>
<td>SAE</td>
<td></td>
<td>Standard aeration efficiency ( \text{(kg O}_2/\text{kWh)} )</td>
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<tr>
<td>t</td>
<td></td>
<td>Time ( \text{(h)} )</td>
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<tr>
<td>T</td>
<td></td>
<td>Water temperature ( \text{(°C)} )</td>
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<tr>
<td>T_i</td>
<td></td>
<td>Absolute temperature of gas at compressor inlet ( \text{(°K)} )</td>
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<tr>
<td>TE</td>
<td></td>
<td>Oxygen transfer efficiency ( \text{(kg/kWh)} )</td>
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<tr>
<td>V</td>
<td></td>
<td>Volume of liquid in contactor ( \text{(m}^3 \text{)} )</td>
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<tr>
<td>VP</td>
<td></td>
<td>Vapor pressure of water ( \text{(mm Hg)} )</td>
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<tr>
<td>X</td>
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<td>Mole fraction in gas phase (dimensionless)</td>
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<td>Z</td>
<td></td>
<td>Head loss across the contactor ( \text{(m)} )</td>
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<tr>
<td>α</td>
<td></td>
<td>((K_{\text{eq}}/K_{\text{eq,eq}})) (dimensionless)</td>
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<td></td>
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<tr>
<td>β</td>
<td></td>
<td>Bunsen coefficient ( \text{litres gas/litres water at 760 mm Hg absolute pressure} )</td>
<td></td>
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<tr>
<td>γ</td>
<td></td>
<td>Specific mass of water ( \text{(kN/m}^3 \text{)} )</td>
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<tr>
<td>ΔL</td>
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<td>Liquid film thickness ( \text{(m)} )</td>
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<tr>
<td>ΔP</td>
<td></td>
<td>Uncompensated differential dissolved gas pressure ( \text{(mm Hg)} )</td>
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<tr>
<td>ΔDO</td>
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<td>Change in DO concentration ( \text{(mg/l)} )</td>
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<tr>
<td>ΔDOON</td>
<td></td>
<td>Stripping ratio, ( \text{DO}<em>{\text{in}}/\text{DO}</em>{\text{out}} ) (dimensionless)</td>
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<td>ΔDN</td>
<td></td>
<td>Change in DN concentration ( \text{(mg/l)} )</td>
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<tr>
<td>ΔN</td>
<td></td>
<td>Change in DN concentration ( \text{(mg/l)} ) (dimensionless)</td>
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Figure 1. Major components of an enclosed propeller type surface agitator designed for contacting oxygen with water at subatmosphere pressure.

Figure 2. Combinations of gas composition ($x_g$) and enclosure pressure (CP) that provide dissolved oxygen (DO) and dissolved nitrogen (DN) saturation concentrations of 14.4 and 15.3 mg/l, respectively (T=15°C). The design point marked represents the combination $x_g$ and CP that provides the required DO and DN saturation concentrations simultaneously.

Figure 3. Dissolved gas deficit remaining after treatment ($C - C_{O2,AB}$) versus $K_{La}$ (V/Q 0.06) at three temperatures.
Figure 4. Effect of enclosure pressure and oxygen feed rates on the performance of an enclosed surface oxygenation system (T = 18°C; Q_s = 190 l/min; (K_{L}a)_{20} = 100 l/m²; V = 0.086 m³; DO_{in} = 8.0 mg/l; DN_{in} = 16.36 mg/l).

Design Procedure - 1

1. Establish Required Rates of O_2 Addition and H_2 Desorption
2. Select a value for (K_{L}a)_{20}
3. Calculate the Required System Pressure and O_2 Feed Rate
4. Summarize Performance
5. Is Performance Acceptable?
   - YES: End
   - NO: Go back to step 3

Design Procedure - 2

1. Identify System Pressure and (K_{L}a)_{20}
2. Select Composition of Gas within the Container
3. Calculate Gas Transfer Rates and Derive for the Required Oxygen Feed Rate
4. Summarize Performance
5. Is Performance Acceptable?
   - YES: End
   - NO: Go back to step 3

Figure 5. Computation sequence for design procedure 1 and 2.
Figure 6. Effect of selected \((K_a)_{20}\) values on transfer costs, oxygen absorption efficiency (AE), and transfer efficiency (TE) when operating with an effluent DO and DN of 16.0 mg/l and 14.6 mg/l, respectively (T = 15°C; barometric pressure = 760 mm Hg; DO\(_{20}\) = 5 mg/l; DN\(_{20}\) = 18.6 mg/l; V = 2.5 m\(^3\); Q\(_L\) = 1000 l/min; power cost = $0.09/kWh; oxygen cost = $0.1855/kg).

Figure 7. Effect of selected oxygen mole fraction values (y\(_{20}\)) on effluent dissolved oxygen (DO), effluent dissolved nitrogen (DN), oxygen absorption efficiency (AE), transfer efficiency (TE) and the required gas-liquid ratio (G/L) (T = 15°C; enclosure pressure = 760 mm Hg; \((K_a)_{20}\) = 50 l/h; power applied = .125 kW; Q\(_L\) = 189 l/min; V = 0.8 m\(^3\); DO\(_{20}\) = 9 mg/l; DN\(_{20}\) = 17.9 mg/l).
Carbon Dioxide Removal for Intensive Aquaculture

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Abstract

The management of carbon dioxide in intensive aquaculture tends to be ignored and may be achieved more as an incidental outcome of other management activities than as a deliberate objective. Carbon dioxide dissolved into the water tends to depress the pH, and as the intensity of culture operations increases, so does the magnitude of the pH drop caused by the carbon dioxide produced by the fish.

Carbon dioxide exists in solution as part of a chemical equilibrium system, the carbonate system, and this makes the analysis and study of removal mechanisms more difficult than for other gases such as oxygen or nitrogen. Estimates of the amount of carbon dioxide that must be removed to achieve a given pH or carbon dioxide concentration must take into account considerations of water chemistry as well as gas exchange. In addition, carbon dioxide constitutes a very small proportion of a normal atmosphere (~0.03%) and this presents special difficulties in designing carbon dioxide removal techniques for aquaculture.

Procedures are recommended for carbon dioxide removal and are based on studies carried out with a packed column aerator. The test column was 3.0 m high, 0.2 m in diameter, was fitted with 1.58 cm Pall® rings, and was used with a countercflow of air. The column was open to the atmosphere at the top which prevented pressurization. Tests were carried out at hydraulic loading rates comparable to those recommended for oxygen addition. Gas (air) flow rates were varied over a broad range and a minimum gas to liquid (volume to volume) flow rate ratio of 5.0 was found to be suitable for carbon dioxide removal. The columns need not be deeper than approximately 1.5 m. Removal of carbon dioxide under these conditions caused a reduction in CO₂ concentration of over 90% of the incoming value. The alkalinity of the water (and the total carbonate concentration), the depth of the column, the G/L ratio and the initial carbon dioxide concentration were found to affect the efficiency of removal.

Introduction and Background

The removal of carbon dioxide from culture water in intensive aquaculture systems has not been given much attention in the commercial or scientific communities. For the most part, whatever carbon dioxide control is exerted in intensive aquaculture systems takes place as an incidental result of management actions designed for other purposes, such as aeration. As a result, there is a dearth of published information on CO₂ removal and control in intensive systems. The design guidelines presented here are based on laboratory experiments carried out with a 3.0 m tall, 0.2 m diameter laboratory column filled with 1.58 cm Pall® rings, and on very limited field application of various types of packed columns. A packed column was selected as the degassing method because it facilitated the quantification of the carbon dioxide removal rates, the study of the effect of water quality and operational parameters on the rates of removal, and analysis of the effects of chemical reactions and gas exchange rates on the overall rate of carbon dioxide removal from culture water. In addition, packed columns have been extensively studied and are widely used in aquaculture for both oxygenation and degassing. An initial consideration in the work was to determine if carbon dioxide removal was compatible with aeration (oxygen addition) as simultaneous operations in a packed column.

The operation of PCA's has been well described (e.g., Hackney and Colt 1982, Nimshalchandran et al. 1986, Wattan and Boyd 1986; Wattan and Boyd 1990; Wattan 1990) for gases such as nitrogen (N₂) and oxygen (O₂). Traditionally, CO₂ transfer has been approximated following an approach similar to that used for nitrogen gas, where mass transfer rates are assumed to be proportional to molecular diameter or molecular diffusivity of the gases (Colt and Bouck 1984; Wattan 1990). In addition, CO₂ removal has been estimated by assuming the equilibrium reaction between CO₂ and H₂CO₃ (carbonic acid) to be instantaneous (Colt and Bouck 1984; Howe 1986). These studies have noted that the actual transfer may be slower due to kinetic effects.

In a packed column, the gas exchange rate is limited by transfer at the gas-liquid interface and can be modeled using the Whitman two-film model (Hackney and Colt 1982). Hackney and Colt (1982) adopted the two-film model to PCA's by noting that within a certain range (flow rates less than that which caused flooding)
the transfer of oxygen was independent of flow rate, but
depended on column depth and on an overall mass
transfer coefficient. A simplified form of the equation is:

\[ \ln(\frac{C_i - C_o}{C_i - C_{sat}}) = KZ \]  
(1)

where

- \(C_i\) = saturation concentration (g.m\(^{-3}\))
- \(C_o\) = influent concentration (g.m\(^{-3}\))
- \(C_{sat}\) = effluent concentration (g.m\(^{-3}\))
- \(Z\) = overall PCA mass transfer coefficient (m\(^{-1}\))
- \(N\) = column height (m)

The value of \(K\) has been found to vary with
temperature and with water quality, but measured
values are normally standardized to 20° C and clean
water (Cott and Bouck 1984; Boyd and Watten 1989;
Watten 1990):

\[ K(20)_{\alpha} = K(T)_{\alpha} \times 1.024^{\frac{T-20}{10}} / \alpha \]  
(2)

where

- \(K(20)_{\alpha}\) = overall clean water PCA mass
  transfer coefficient at 20° C (m\(^{-1}\))
- \(K(T)_{\alpha}\) = overall mass transfer coefficient as
  measured in the field (m\(^{-1}\))
- \(T\) = water temperature during
  determination of \(K(T)_{\alpha}\) (° C)
- \(\alpha\) = ratio between the gas transfer
  coefficient in field water and in clean
  water

The value of \(K\) can be estimated from Equation (1)
using measurements of influent and effluent
concentrations to a column and information on
saturation concentration inside the column. Typical \(K\)
values for oxygen have been estimated (e.g. Hackett
and Cott 1982; Watten 1990) for various packing
media types and sizes. An alternate method for
estimating the transfer coefficient may be adapted
from the procedure suggested by ASCE (1984). In this
procedure, a non-linear regression method is used to
estimate the gas transfer coefficient and the saturation
concentration (Grace and Piedrahita 1989). The
saturation concentration obtained with the non-linear
method constitutes an "effective" value for the mass
transfer model, but does not necessarily represent the
saturation concentration at a specific point in the column.

The mass transfer coefficient generally is
considered to be constant under operating conditions
in which gas flows and liquid flows are less than those
which cause flooding for a specific gas transfer system.
In addition, reduced gas transfer may be caused by G/
L ratios so low that the gas composition inside the
column is significantly altered resulting in changes in the
saturation concentration. For gases other than oxygen, the overall transfer coefficient is usually considered to be proportional to the molecular diffusivity
or molecular diameter of the species transferred (Tsirovouli et al. 1985; Cott and Bouck 1984; Watten
1990). Based on molecular diffusivities, the mass
transfer rate coefficient for carbon dioxide should be
0.78, with a possible range between 0.65 and 0.98
associated with the uncertainties in the estimates of
molecular diffusivities available (Perry et al. 1984),
whereas based on molecular diameter, the ratio should
be approximately 0.91 (Weast and Astle 1980). These
values contrast with those recommended in the literature,
of 1.00 (Speece and Humenick 1973; Cott and Bouck
1984). Other effects such as chemical reactions may
produce an apparent transfer coefficient which differs
from the true mass transfer coefficient. While the true
mass transfer coefficient may be difficult to determine,
the apparent transfer coefficient can be approximated
with a linear or non-linear regression of sample data
using Equation 1.

The Need for Carbon Dioxide Removal

Carbon dioxide is a waste product of metabolism,
and under certain conditions in intensive aquaculture
operations may be the factor limiting fish density. If
dissolved oxygen is eliminated as a possible water
quality limiting factor by the use of pure oxygen injection,
then unionized ammonia and carbon dioxide concentration
may become the limiting factors. Simplified mass balances may be carried out to illustrate
these situations. Dissolved oxygen consumption, total
ammonia nitrogen and carbon dioxide production rates
may be expressed as functions of feed in a tank as 0.2,
0.03 or 0.28 kg/kg of feed respectively (Cott 1986).
If pure oxygen is used and dissolved oxygen concentration
is maintained at safe levels, and if no carbon dioxide is
removed in the process of oxygen injection, then a
mass balance on carbon dioxide and unionized
ammonia can be carried out as illustrated in Figure 1 for
fish being fed at 2 % body weight per day, and for an
alkalinity of 4 meq/L. In Figure 1, the unionized ammonia
and carbon dioxide concentrations are allowed to rise
without treatment as the fish loading increases. As a
result, carbon dioxide depresses pH and unionized
ammonia concentration is kept below 0.010 mg-N/L
considered as a "safe" level (Cott 1987) for fish loading
rates over 15 kg/Lmin. Carbon dioxide, on the other
hand, rises over the recommended "safe" level of 30
mg/L as the fish loading rate exceeds approximately
3.7 kg/L/min, which would become the calculated
maximum loading rate in the system. Similar calculations
can be made if the carbon dioxide concentration in the
culture system is controlled and not allowed to exceed
30 mg/L. The resulting unionized ammonia
concentration reaches a level of 0.010 mg-N/L at a
loading rate of approximately 11.5 kg/L/min, an increase
of over 200 % over the original allowable loading rate
of 3.7 kg/L/min (Figure 2).

A related factor that can become limiting is the pHy
value. As carbon dioxide is added to the water, the pH
is depressed. The magnitude of the drop depends
primarily on the alkalinity of the water. The pH value
for the same conditions as in Figure 2 is shown in Figure
3, for cases in which the CO\(_2\) concentration is controlled
at 30 mg/L. At an alkalinity of 4.0, pH reaches a value of 8.5 to approximately the same fish loading rate as the 30 mg/L CO₂ concentration is reached. For lower alkalinities, the pH values drop rapidly (Figure 3), reaching values that may be considered stressful to fish at fish loading rates that are likely to be lower than for carbon dioxide or unionized ammonia concentration. For example, unionized ammonia concentration for a system in which carbon dioxide concentration is not allowed to rise above 30 mg/L is shown for three alkalinity values (Figure 4). At the low alkalinities, unionized ammonia nitrogen remains low for the range of fish loading rates considered.

The sensitivity of nitrifier bacteria to pH is an additional reason for controlling pH and carbon dioxide concentration in systems with biological filters. Nitrifier bacteria have been shown to have a narrow pH range for optimum activity (e.g. approximately 7.0 to 8.0 for nitrosomonas and 7.5 to 8.5 for nitrobacter (Grady and Lim 1980)). The decline in nitrification activity also has been shown to be very sensitive to pH outside the optimum ranges mentioned, with decreases as high as 50% over less than 0.5 pH units (Grady and Lim 1980). It is clear then, that controlling carbon dioxide concentration can result in increased loading rates under certain conditions. The increased loading rates achievable with carbon dioxide control will depend on the particular situation and specifically on the rates of CO₂ and ammonia production by the fish and on the "safe" levels for these parameters. Additional factors affecting the loading rates and how they are affected by carbon metabolite production, are parameters such as alkalinity and temperature, that determine how the carbon dioxide produced by the fish affects pH.

Carbon Dioxide Removal

Unlike other important dissolved gases (N₂, O₂), carbon dioxide exists in solution as part of a chemical equilibrium system. As CO₂ is stripped from solution, a shift in the carbonate carbon equilibrium occurs. The carbonate carbon equilibrium is described by a pH dependent set of relationships between carbon dioxide, carbonates (CO₃⁻), bicarbonates (HCO₃⁻), and carbonates (CO₂)(Stumm and Morgan 1981, Snerlurk and Jenkins 1980).

\[ \text{CO}_3^- \rightarrow \text{CO}_2 \text{CO}_3^- \]  
(3)

\[ \text{CO}_2 + \text{H}_2 \rightarrow \text{H}_2 \text{CO}_3^- \]  
(4)

\[ \text{H}_2 \text{CO}_3^- \rightarrow \text{H}^+ + \text{HCO}_3^- \]  
(5)

\[ \text{HCO}_3^- \rightarrow \text{H}^+ + \text{CO}_2 \text{O}^- \]  
(6)

Total carbonate carbon (CO₃⁻CO₂) is defined as the sum of aqueous carbon dioxide, carbonic acid, bicarbonate and carbonate concentrations:

\[ \text{CO}_2 + [\text{H}_2 \text{CO}_3^-] + [\text{HCO}_3^-] + [\text{CO}_3^-] \]  
(7)

where:

\[ [\text{H}_2 \text{CO}_3^-] = [\text{H}_2 \text{CO}_3^-] + [\text{CO}_2 \text{CO}_3^-] \]  
(8)

and the square brackets denote molar concentration. An additional term that is often used in calculations involving the carbonate system is alkalinity (ALK), which may be defined in a simplified way as:

\[ \text{ALK} = [\text{H}_2 \text{CO}_3^-] + 2[\text{CO}_2 \text{O}^-] + [\text{OH}^-] \cdot [\text{H}^+] \]  
(9)

and has units of equivalent per liter (eq/L, or more commonly meq/L) (Stumm and Morgan 1981, Snerlurk and Jenkins 1980). Alkalinity is easily measured and is often used to estimate total carbonate carbon concentration and the concentration of the various species of the carbonate system. The concentration of each species is dependent on the total carbonate carbon (or alkalinity) and a pH dependent "ionization" fraction indicating the proportion of the total carbon that is present in each form. As an example, the concentration of carbon dioxide (in mg/L) as a function of pH and alkalinity of the water is shown in Figure 5 for 25°C. From this figure, one can see that for a given pH, the concentration of carbon dioxide present is strongly dependent on alkalinity, and will be higher as the alkalinity increases. Conversely, a given concentration of carbon dioxide may be present in solution at different pH values, depending on the alkalinity of the water. In addition, the pH change associated with a given carbon dioxide concentration change depends on the initial conditions (alkalinity, pH and CO₂ concentration) and on the magnitude of the concentration change. If the alkalinity is relatively high, pH may be within biologically acceptable levels, but CO₂ may be present at concentrations that can affect oxygen transfer to the blood (Spotts 1979) (see Figure 5).

Temperature is an additional factor affecting the relationship between carbon dioxide and pH. Figure 6 compares the values at 25°C. Use of Figure 5 to estimate the carbon dioxide concentration at a temperature of 15°C for example, would result in an underestimation of CO₂ concentration of approximately 18%. For approximate calculations, the CO₂ values obtained from Figure 5 can be increased by 1.8% for each degree below 25°C, and decreased by 1.8% for each degree over 25°C.

When carbon dioxide is removed from solution, the total carbonate carbon is reduced by an amount equal to the carbon removed as CO₂. The removal of CO₂, however, causes a pH shift and the ionization fractions change. The result is that the amount of CO₂ transferred is not equal to the change in CO₂ concentration. For a packed column, or a segment of one:

\[ \Delta [\text{CO}_2] = \text{CO}_2 \text{CO}_2^- \cdot \text{O}^- \cdot \text{O}^- \cdot \text{O}^- \]  
(10)

\[ \text{CO}_2 \text{removed} = \text{CO}_2 \text{CO}_2^- \cdot \text{O}^- \cdot \text{O}^- \cdot \text{O}^- \]  
(11)
where:

\[ \Delta [CO_2] = \text{change in CO}_2 \text{ concentration} \]

\[ C_{CO_2} = \text{initial total carbonate carbon} \]

\[ C_{CO_3} = \text{final total carbonate carbon} \]

\[ e_{CO_2} = \text{initial CO}_2 \text{ ionization fraction} \]

\[ e_{CO_3} = \text{final CO}_3 \text{ ionization fraction} \]

The magnitude of the pH change for a given carbon dioxide addition or removal will depend on the alkalinity of the water. In general, the higher the alkalinity, the less pronounced the pH change is for a given addition or removal of CO\(_2\).

**Design Guidelines**

As has been mentioned, the design guidelines presented here are based on experiments carried out in a 3 m tall, 0.2 m diameter column filled with 1.59 cm Perl rings (Figure 6). To facilitate extrapolation of the data to other packed column designs and packing media, an attempt was made to relate the CO\(_2\) transfer properties to dissolved oxygen transfer characteristics that may be readily available or easily obtained experimentally. All oxygen transfer rate coefficients were obtained using the non-linear approximation method based on recommendations developed by ASCE (1984), whereas carbon dioxide transfer rate coefficient calculations were based on mass balances for column sections between ports where samples were obtained. Details of the experimental set up and calculation procedures are available elsewhere (Grace and Pedrazhite, 1989; Grace, 1991).

Data analysis for oxygen runs included determination of the overall transfer coefficient and a mass balance between gas and liquid phases for each column segment between sample ports. A spreadsheet was developed to perform the mass balance and calculate the following information at each sample port (i.e. specific column depth Z): gas mole fraction, oxygen saturation concentration, K for the column segment and K from the top of the column to depth Z.

Data analysis for CO\(_2\) included the calculation of CO\(_2\) from measurements of pH and alkalinity and mass balance calculations to estimate the CO\(_2\) content of the gas phase inside the column based on the measured CO\(_3\) concentrations at the sampling ports. The mass balance spreadsheet was used to calculate the same parameters as in the O\(_2\) mass balance including the gas transfer coefficients.

Twenty three oxygen runs and 54 carbon dioxide runs were performed with various G/L ratios and liquid flow rates. Oxygen runs provided useful results which described the performance of the laboratory PCA and could be used as a reference for the carbon dioxide runs. The oxygen runs also allowed comparison with previously published PCA studies (e.g. Hackney and Colt 1982). Oxygen transfer was measured in the PCA for liquid flow rates between 18.9 and 86.2 L/min (hydraulic loading rates of 39.7 to 139.3 m\(^3\) m\(^{-2}\) h\(^{-1}\)) and G/L ratios of 0.16 to 8.19. Average mass transfer coefficients, as determined by the non-linear regression method, and corrected to 20°C (K\(_C\)) ranged from 1.86 to 2.31 m\(^2\). The lower values were obtained for G/L ratios less than 1.0, and are probably distorted values due to changes in the dissolved oxygen saturation concentrations in the column caused by the low G/L ratio (Hackney and Colt 1982). Differences in the transfer coefficients also were caused by media packing and by temperature. The limited oxygen data generated in this study suggests that a value of 1.007 as opposed to the 1.024 used in Equation 2 would provide a more accurate description of gas transfer coefficient changes as affected by temperature in the column used.

Removal of carbon dioxide was investigated for G/L ratios between 0.14 and 17.9 and for alkalinities between 0.36 and 5.93 meq/L. The calculated mass transfer coefficients ranged from 0 to 2.09 m\(^{-1}\) for the top 1.07 m section of the column, 0.11 to 1.85 m\(^{-1}\) for the top 1.54 m, and from 0.17 to 1.32 m\(^{-1}\) for the full column depth. The wide range of transfer coefficients calculated suggests that there were factors that were not properly accounted for in the calculations of mass transfer coefficients for CO\(_2\) in the column. The CO\(_2\) percent removal at a given depth in the column was found to be affected primarily by G/L ratio (Figures 7 and 8). It was also affected by alkalinity and by temperature. The G/L ratio significantly affected the carbon dioxide stripping capability of the laboratory PCA, particularly for G/L ratios less than 5.0 (Figures 7 and 8). The decrease in efficiency of transfer at the low G/L ratios was due to the increase in CO\(_2\) in the gas phase, and the resulting change in saturation concentration. As an example, at an alkalinity of 0.50 and a G/L ratio of 0.52, the influent carbon dioxide mole fraction was measured as 0.00041 (saturation concentration = 0.69 mg/L) and the effluent mole fraction was calculated as 0.0187 (saturation concentration = 31.5 mg/L) based on a mass balance for the PCA. The influence of G/L ratios above 5.0 was greatly reduced but still noticeable. Again, as an example, for an alkalinity of 0.50 meq/L, the CO\(_2\) mole fraction in the gas phase increased from 0.00040 at the base of the column to 0.00023 and 0.00012 (corresponding to CO\(_2\) saturation concentrations of 3.1 and 0.08 mg/L) for G/L ratios of 7.6 and 17.1 respectively. The effect of alkalinity was minor when compared to that of G/L ratios (Figures 7 and 8), but resulted in noticeable differences in CO\(_2\) removal efficiencies for the column. The efficiency of carbon dioxide removal decreased as the alkalinity increased (Figure 9), and although the decrease is not very high, it represents important differences that must be kept in mind during the design process. At the highest alkalinities tested (4.7 and 8.9 meq/L), the efficiency of removal remains below 90% even at the end of three meter column, while it exceeds 90% by the 1.5 m depth for the lower alkalinity waters (0.5 and 2.1 meq/L) (Figure 9). The decline apparently is due to the increased reservoir of carbonate carbon present at higher alkalinities. While the actual rate of
mass transfer may not be affected by the carbon present other than CO₂ (due to the relative speed of the hydroxylation reactions when compared to the rate of mass transfer or the residence time in the column), the efficiency of removal is affected since some of the carbon present as rate compares to bicarbonate react and form CO₂ after the water exits the column. The carbon present as bicarbonate or carbonate does not have enough time to react within the column and readjust to the new pH created by the CO₂ removal and result in bicarbonate removal from the column. Achievement of chemical equilibrium takes place after the water has exited the column, and some CO₂ is produced from reactions of the carbonate system. As a result, alkalinity increases and the reservoir of total carbonate carbon is greater for a given carbon dioxide concentration, the efficiency of carbon dioxide removal decreases, if this efficiency is estimated based on the change in CO₂ concentration between the influent and effluent streams for the column (Figure 9).

Calculation of mass transfer coefficients was based on mass balances and on the application of Equation 1. Estimates of saturation concentration in the column are needed in addition to measurements of carbon dioxide concentration to be able to calculate the gas transfer coefficient. In addition, information is needed on the rate of the chemical reactions affecting carbon dioxide in solution, and on how the rate compares to the mass transfer rate and to the flow rate through the system. As indicated above and elsewhere (Grace 1991), evidence from the column suggests that the rate of chemical hydroxylation of carbon dioxide is slow relative to the rate of flow through the column and to the rate of mass transfer. Under that set of conditions, mass transfer rates may be estimated from Equation 1 using carbon dioxide concentrations and assuming that no chemical reaction takes place inside the column.

The gas transfer coefficients obtained for CO₂ using the methods described above were observed to change primarily with G/L ratio, with column depth and with alkalinity of the water (Grace and Piedrahita 1989; Grace 1991). The values declined rapidly for G/L ratios below approximately five. They also tended to stay approximately constant for the top 1.8 m of the column, but decreased for the bottom column segments. The calculated coefficients also decreased as alkalinity increased. Calculations were carried out with an implicit assumption of plug flow for the gas phase being used in the mass balances. The calculated values of gas transfer coefficient were expected to remain constant for the hydraulic loading rate used. Variations obtained in the calculated results are thought to be due primarily to gas flow characteristics that are not accounted for with the assumption of plug flow used for the mass balances and the calculation of gas transfer rates.

Saturation concentrations, in turn, depend on the mole fraction of the gas in the column. For relatively high G/L ratios, the mole fraction of the gases does not change significantly inside the column, hence saturation concentration stays approximately constant throughout the column and a single value may be used for calculating the gas transfer coefficient at any point in the column. This is the case for oxygen transfer in aeration columns at G/L ratios over approximately 1 (Hiscovey and Colt 1982). For carbon dioxide, on the other hand, the mole fraction in a normal atmosphere is low (≈ 0.03%) and the amount removed from solution is sufficient to cause a significant change in the saturation concentration through the column. Not being able to account for the changing saturation concentration at different points in the column makes the calculation of the gas transfer coefficient uncertain. The change in saturation concentration is noticeable for all G/L ratios tested, but the difficulty is especially noticeable for G/L ratios less than approximately five and the saturation changes become larger.

Predicting how the saturation concentration changes in the column requires detailed knowledge of the gas flow properties in the column, i.e., whether it is plug or mixed flow, or some intermediate model. If the changes in saturation concentration can be predicted, then accurate estimates of gas transfer rate coefficients can be made, and the rate coefficients should be independent of alkalinity and G/L ratio, and should be constant for hydraulic loading rates that are below the critical flooding value. With accurate estimates of the gas transfer coefficient for carbon dioxide, CO₂ concentrations can be estimated given values of G/L ratio, column depth, CO₂ content in air being injected into the column, and incoming water pH and alkalinity (or CO₂ concentration) values. The procedure follows a iterative process to arrive at CO₂ concentrations that are consistent with changes in CO₂ content in the gas phase. Uncertainties in the estimation of the CO₂ gas transfer coefficient for packed columns, and the need to use a complex iterative calculation procedure make the process impractical for design purposes at the present time. At the present time, a more practical approach is to base estimates of carbon dioxide removal in packed columns on information such as that presented in Figures 7 and 8. The iterative procedure will become more useful and reliable as more information becomes available and as procedures are developed to relate the oxygen and carbon dioxide transfer coefficients, and to predict gas flow conditions inside the packed column.

Summary

In implementing a carbon dioxide removal scheme, it is important to realize that the flow and operational requirements are quite different from those for oxygen addition through aeration with atmospheric air or from pure oxygen injection. As has already been mentioned, even if a PCA is used for oxygen injection or aeration, the G/L requirements for carbon dioxide removal are
one to two orders of magnitude greater than for aeration or oxygen injection. In addition, the flow rates required for the two operations can be very different depending on efficiencies and on operational requirements. Figure 10 is an example of the ratio between the flow rate required for carbon dioxide control and for oxygen injection when pure oxygen is used (calculation details are given in the figure legend). In this example, the flow requirement for oxygen addition is greater than for carbon dioxide only at fish stocking rates of less than about 5 fish/L/min. At higher stocking rates, the flow required to control carbon dioxide concentration and maintain it at 30 mg/L is higher than for oxygen injection.

Carbon dioxide stripping appears to have been affected significantly by changing gas composition inside the packed column. As CO₂ transfers out of solution into the countercurrent gas flow, the partial pressure of CO₂ in the gas phase increases and the saturation concentration decreases, reducing the driving force for gas transfer. The lower the G/L ratio the greater the effect on the total gas composition. For the lowest G/L ratios the effluent gas had a CO₂ partial pressure and saturation concentration approximately equivalent to the influent dissolved concentration (e.g., mole fraction of 0.035 in the gas leaving the column and corresponding saturation concentration of 53 mg CO₂/L for an influent concentration of 74 mg CO₂/L). For the high G/L ratios such as 17.2, effluent partial pressure of CO₂ corresponded to a saturation concentration of 2.07 mg/L (influent and effluent CO₂ concentrations of 30.0 and 2.19 mg/L respectively).

The importance of describing CO₂ transfer will increase as fish densities in culture systems are increased. Carbon dioxide is a very soluble gas and it is relatively simple to remove from solution. System designers must be aware, however, that conventional equations for packed column aerators overestimate the amount of CO₂ removed. The result will be a higher CO₂ concentration in the culture system than predicted.

Packed columns used for pure oxygen may not offer sufficient opportunity for CO₂ to be removed. At the low G/L ratios characteristic of pure oxygen or of aeration systems (usually below G/L = 1.0), very little CO₂ is transferred as the test results indicate. A G/L ratio greater than 5.0 is recommended to remove CO₂ in a PCA, and the higher the alkalinity, the higher the G/L ratio needs to be. Until the gas flow characteristics in the column can be described better, column design may be carried out using guidelines as shown in Figures 7, 8 and 9, where over 90% of the influent carbon dioxide is removed in a column that is less than 1.5 m deep as long as the G/L ratio is above approximately 5 and the alkalinity is low (2.1 meq/L or lower in the experimental trials). The efficiency or removal is noticeably lower for higher alkalinites. In all cases, an increase in removal efficiency of approximately 10% is achieved by increasing the column depth from 1.0 to 1.5 m, while the increase obtained by increasing the column depth to 3.0 m is less than 5%, and shallow columns (depth less than 1.5 m) are recommended for carbon dioxide removal. Further work to characterize gas flow rates should make possible the use of more accurate design procedures such as those used for oxygen injection systems in packed columns.

Acknowledgement

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Literature Cited


![Graph](image1)

Figure 1. Carbon dioxide and unionized ammonia concentrations as functions of fish loading rate. Influent water supply is at 25°C, pH of 7.5 and free of total ammonia nitrogen. Additional assumptions and conditions for the calculation are stated in the text.

![Graph](image2)

Figure 2. Carbon dioxide and unionized ammonia concentrations as functions of fish loading rate when the CO₂ concentration is controlled and maintained at 30 mg/L. Influent water and other assumptions as in Figure 1.
Figure 3. Effluent pH resulting from CO₂ production by fish. The calculations are repeated for alkalinity values of 0.25, 1.0 and 4.0 meq/L. Other assumptions and conditions for the calculations are as in Figure 2, where CO₂ is not allowed to rise over 30 mg/L.

Figure 4. Unionized ammonia nitrogen concentration for fish stocked in three different waters. In all cases the carbon dioxide concentration is not allowed to rise over 30 mg/L. Assumptions and conditions are as for the previous figures.

Figure 5. Carbon dioxide concentration as a function of pH and alkalinity for fresh water at 25°C. The lines correspond to alkalinities of 0.25, 0.50, 1.0, 2.0, 4.0 and 6.0 meq/L, with increasing alkalinities as indicated in the graph.
Figure 6. Packed column installation used for aeration and degassing tests.

Figure 7. Carbon dioxide removal efficiency at different depths in the column, for G/L ratios between 0.5 and 17. Water alkalinity for these runs is 0.5 meq/L.
Figure 8. Carbon dioxide removal efficiency at different depths in the column, for G/L ratios between 0.5 and 17. Water alkalinity for these runs is 5.9 meq/L.

Figure 9. Maximum carbon dioxide removal efficiency obtained for different alkalinites. Removal efficiency was estimated from measured CO₂ concentrations.

Figure 10. Ratio between the flow required for carbon dioxide control and for oxygen injection. Return oxygen concentration from the oxygen injection system is 700% of saturation; dissolved oxygen concentration in the culture tank is maintained at 150% of saturation; carbon dioxide is not allowed to rise above 30 mg/L; and the removal efficiency of the CO₂ removal process is 90%. Influent water and other assumptions are as for Figure 1.
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