Oxygen Transfer Parameter Estimation: Impact of Methodology

Pan Jiang[1] and Michael K. Stenstrom, F.ASCE[2]

Abstract: Oxygen transfer is an important part of wastewater treatment and accounts for as much as 60% of energy consumption in the activated sludge process. Prior to 1984, no standard method for quantifying oxygen transfer existed, which created problems in the design and warranties for treatment plants. The ASCE standards for the measurement of oxygen transfer in clean water and the *Standard Guidelines for In-Process Oxygen Transfer Testing* have found widespread application and have reduced design variability. The standard has allowed operators and engineers to better evaluate process operation of existing treatment plants. This paper illustrates the key concepts of the standard and shows why they are important and how they reduce the variability of oxygen transfer testing. The reasons for the standard's success are described, as are the pitfalls of earlier approaches. The paper also highlights key new areas of the revised clean water standard, including an optional correction for test water total dissolved solids concentration and applications to the loop (ditch) activated sludge process and the high-purity-oxygen activated sludge process. Finally an analysis is presented that shows how numerical treatment of the transfer data minimizes the impact of gas-side oxygen depletion. **DOI:** 10.1061/(ASCE)EE.1943-7870.0000456.

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Introduction

In 1977, under the sponsorship of the U.S. EPA, a committee organized by ASCE began the study of methods to quantify oxygen transfer rates in wastewater treatment. The Committee met as a group in Asilomar, California, in 1978 (ASCE, Municipal Environmental Research Laboratory, Univ. of Wisconsin 1979) and proposed consensus methods for establishing uniform and repeatable test conditions, estimating clean water parameters (mass transfer coefficient, or K_La, and equilibrium oxygen concentration, or C^*_∞) from reaeration data, and translating clean water rates into process conditions. The resulting methods were evaluated over the next several years by committee members, consultants, and manufacturers and refined through the collective experience of the group. The final result was the 1984 version of the ASCE standard for the measurement of oxygen transfer in clean water. The standard was subsequently improved, updated, and republished in 1991 and 2006. The standard also provides standard procedures for calculating process water rates from clean water rates, by adjusting for standard conditions such as barometric pressure, temperature, and the effects of the contaminants in the process water (α and β factors for K_La and C^*_∞, respectively). On the basis of the success of the clean water standard, the U.S. EPA and ASCE funded a new effort to develop process water testing methods, which were published by the U.S. EPA in 1989 and later adopted into a standard guideline (ASCE 1997).

Several major improvements in estimating oxygen transfer rates were incorporated into the standard. The first was the methodology of estimating K_La from non-steady-state reaeration data (Stenstrom et al. 1981). Prior to the standard, the log-deficit method, which required a priori knowledge of C^*_∞, the equilibrium oxygen concentration, was used. The equilibrium concentration differs from handbook saturation dissolved oxygen concentration because it includes the effect of hydrostatic pressure. Previously, several methods for calculating C^*_∞ from hydrostatic pressure existed, but all had pitfalls; this allowed the introduction of errors that could easily bias the overall transfer rate by ± 15 to 20% (Boyle et al. 1974). The standard uses a nonlinear regression technique, which avoids a priori methods and eliminates the possibility of bias.

A number of other improvements in testing procedures were realized, including the geometry of dissolved oxygen (DO) sampling locations, a method for adding sodium sulfite, the impact of cobalt interference in the Winkler DO measurement procedure, the impact of DO probe lag on estimates of K_La (Philichi and Stenstrom 1989), and more precise ways of defining power and its measurement.

The improved precision and reduced error associated with clean water testing created a need for improved process water testing, which led to the development of process water testing guidelines. Process water testing is not the subject of this paper, but it is worth citing several significant improvements. The most significant is off-gas testing (Redmon et al. 1983). In the 10 years following its development, off-gas testing became the method of choice for measuring oxygen transfer in subsurface aeration systems for conventional processes; it was also employed in a novel process using biological aerated filters (Stenstrom et al. 2008) and in column testing to estimate α factors (Hwang and Stenstrom 1985; Redmon 2000).

[1]Ph.D. Candidate, Civil and Environmental Engineering Dept., Univ. of California, Los Angeles, Los Angeles, CA 90095-1598.

[2]Professor, Civil and Environmental Engineering Dept., Univ. of California, Los Angeles, Los Angeles, CA 90095-1598 (corresponding author). E-mail: stenstro@seas.ucla.edu

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A second major change was the realization that α factors, which prior to 1980 had almost always been routinely specified as 0.8, were dependent not only on wastewater type, but also on aeration devices (i.e., fine pore diffusers have lower α factors than surface aerators) (Stenstrom and Gilbert 1981). Additionally α factors depend on the conditions of the activated sludge mixed liquor: processes operating with longer mean cell retention times (SRTs) have higher α factors than processes operating at low SRTs (Rosso et al. 2005).

The first goal of this paper is to describe the key concepts used in developing the clean water standard and to illustrate why they are still important. The errors introduced using previous methods, such as assumptions for C^*_∞, are quantitatively described. A second goal is to show why bubble oxygen depletion during diffused aeration does not create a bias between clean water testing and process water conditions.

ASCE Standard Model and Preexisting Models for C^*_∞

Data for the standard method in the form of DO concentration versus time, are collected from a non-steady-state reaeration test. This allows the use of a dynamic model to describe oxygen transfer rate in clean water and a best-fit parameter estimation method based on nonlinear regression.

The mathematical model for the non-steady-state test is

$$\frac{dC_L}{dt} = K_L a(C^*_\infty - C) \quad (1)$$

where C = liquid-phase oxygen concentration; C^*_∞ = equilibrium liquid-phase oxygen concentration; and $K_L a$ = overall volumetric liquid-side mass transfer coefficient.

If $K_L a$ and C^*_∞ are considered as constants through the non-steady-state testing period, and the integrated form can be used to estimate C as a function of time

$$C = C^*_\infty - (C^*_\infty - C_0)\exp(-K_L at) \quad (2)$$

where C_0 = liquid-phase oxygen concentration at $t = 0$.

To describe the transfer rate, three parameters need to be estimated: C_0, C^*_∞, and $K_L a$. Boyle et al. (1974) discussed three ways of estimating the parameters and concluded that a nonlinear method estimating all three simultaneously was best. This was a major departure from the common way of estimating $K_L a$ using the logarithmic form of Eq. (2), as

$$\ln(C^*_{st} - C) = \ln(C^*_{st} - C_0) - K_L at \quad (3)$$

where C^*_{st} is the a priori estimate of C^*_∞.

Eq. (3) can be plotted on semilog paper to estimate $K_L a$ if C^*_∞ and C_0 are known. The accuracy of the estimate for $K_L a$ depends on a good estimate for C^*_∞. The value of C_0 has less impact on $K_L a$ estimation. This log-deficit approach requires a priori knowledge of C^*_∞. There are a number of models for estimating C^*_∞, all of which involve the use of the saturation values of DO C_s (handbook values) and water depth. The value of C_s is determined from published tables as a function of barometric pressure and temperature. The choice of C^*_∞ affects the estimate of $K_L a$ in a predictable way (as subsequently shown), which means that aeration equipment suppliers prefer the method of estimating C^*_∞ that provides the highest transfer rate for their equipment. The two most common methods for predicting C^*_∞ are the surface saturation model

$$C^*_\infty = C_s \quad (4)$$

and the middepth model

$$C^*_\infty = C_s(1 + \gamma h/2P) \quad (5)$$

where C_s = DO saturation concentration at the surface; γ = weight density of water, f/L^3; P = barometric pressure, f/L^2; and h = diffuser submergence, L.

Table 1 summarizes the methods, including their impact on transfer estimation. All of these models are arbitrary to some extent, but work much better than just using surface saturation concentration as the a priori estimate of C^*_∞.

Translation of clean water transfer efficiencies into process water conditions is complicated by the oxygen depletion in the bubbles is associated with diffused aeration. In a clean water test, the transfer rate is very high in the early part of the test, but tends to zero in the later part of the test. Under process conditions, there is always transfer and always some amount of oxygen depletion in the bubbles. This difference led some investigators to speculate that the value of C^*_∞ obtained in a clean water reaeration test should be reduced for steady-state operation under process conditions to account for bubble oxygen depletion. The parameter estimation procedure is subsequently shown to produce paired estimates for $K_L a$ and C^*_∞ that are different from the "true" values and include the effects of bubble gas depletion.

Table 1. Summary of Models for a Priori C^*_{st}

Model for C^*_{st}	Equation	Comments
Surface saturation model	$C^*_{st} = C_s$	Assumes no increase due to hydrostatic pressure; good for surface aerators
Middepth model	$C^*_{st} = C_{sm} = C_{st}[P_0 + \gamma(\frac{H}{2})/P_0]$	Assumes average hydrostatic pressure equals one-half diffuser submergence
Middepth corrected model	$C^*_{st} = C_s(1 + \gamma H/2P + O_r/2O_i)$	Improvement over the middepth model$^+$
Log-mean model	$\ln C^*_{st} = \frac{1}{2}[\ln(C_s + C_s\gamma H/2P) + \ln(C_s O_r/O_i)]$	—
Bottom saturation model	$C^*_{st} = C_{sb} = C_{st}[P_0 + \gamma(H)/P_0]$	Assumes average hydrostatic pressure equals diffuser submergence; rarely provides a good fit for any aeration conditions

Note: O_i = inlet oxygen content in air by volume (20.95%); O_r = oxygen content in the air leaving the aeration tank (%); $O_r = O_i(1-E) \times 100/[(1-O_i) + O_i(1-E)]$, where E = fractional oxygen transfer efficiency H = Henry's law coefficient Y = mole fraction of oxygen in gas phase; r = weight density of water; P_0 = atmospheric pressure at the surface (psi); and 0.433 = conversion factor from feet to PSI. Source: Campbell et al. (1976).

Comparison of Methods

This section discusses the differences among the various methods and how they impact the overall estimate of transfer efficiency. Example data sets were selected from surface and diffused aeration tests operating over a range of air fluxes (air flow per unit area of tank bottom). The log-deficit method, with a priori estimates, as well as the nonlinear regression method, was used to analyze the data sets.

Fig. 1 shows the reaeration data plotted to conform to Eq. (3). The left panel represents the subsurface aeration system, and the right panel, the surface aerator. The curved lines are indicative of poor fit. For the diffused aeration system on the left, both bottom saturation and surface saturation models show curvature beginning at about 80% saturation, marked by the vertical dashed line. If the data are truncated at 80% of saturation, the error associated with incorrect values of C^*_∞ is not observable—all three regressions appear to be straight and to fit the data well. The middepth model is close to, but not equal to, the best-fit model (ASCE standard method). The right panel shows similar curvature but for middepth and bottom saturation; the surface model and the best-fit model provide similar results.

Fig. 2 shows the results of these errors on the overall mass transfer rate, called the standard oxygen transfer rate (SOTR), when specified at standard conditions. The left vertical axis shows the ratio of the transfer rate or SOTR obtained using the a priori models to that obtained using the best-fit model. In the case of the subsurface system shown on the left, a 20% bias of greater transfer (defined as positive) is obtained if a surface saturation model is used, and a 5% negative bias is obtained if the bottom saturation model is used. For the surface aerator, on the right, there is 10 to 12% negative bias when the middepth model is used and up to 22% bias when the bottom saturation model is used. The best-fit model and the most correct a priori models (middepth model for subsurface aerator, surface model for surface aerator) differ by approximately 2–5%. Bottom saturation never provides a good fit for any aeration device, at least in the experience of the writers. The best-fit model selects the correct value of C^*_∞ solely on the basis of the reaeration data, which means that there is no need to speculate about the choice of C^*_∞.

Fig. 3 illustrates the SOTRs calculated with both log-deficit method and the ASCE standard method for seven aeration systems. Four of them used subsurface aeration devices shown as Diffused A–D; the other three, Surface A–C apply to surface aerators. The results reinforce the conclusions from Figs. 1 and 2, but also show a range of saturation depths. The middepth model works well for high-efficiency diffused aeration systems, but is clearly incorrect for less efficient systems. The recent German oxygen transfer standard (DWA-M 209 2007), using a fixed value C^*_∞ equal to the middepth saturation, would clearly be in error for many of the subsurface systems. Bottom saturation is not shown because it never provides a good fit.

The extreme limits of the bias (+22% and −12%) are large by today's methods for specifying aerators. Bids are won and lost by as little as 2% differences in transfer rates. The most troublesome part of the results shown in Figs. 1–3 is the inability to detect a bias if the analysis shown in Figs. 1 and 2 is conducted to only 80% of saturation (red vertical lines at $1.61/K_La$). The curvature of the line is not obvious until the test is conducted to ≥90% ($2.3/K_La$) saturation. Therefore, it was possible to use the wrong a priori model, bias the final results, and not know that an error had been made.

To prevent this type of error, it is necessary to continue the reaeration test until the DO approaches saturation, typically greater than 96% saturation. Unfortunately, this can have an unexpected negative impact on test accuracy and precision if the log-deficit method [Eq. (3)] is used. This occurs because of error transformation. When the log-deficit method is used, the residuals are not actual errors in DO concentration, but errors in log DO concentration. Taking the logarithm of the error transforms it: small values of error are made larger, whereas large errors are reduced. Therefore, minimizing the log of the residuals does not minimize the difference in the actual residuals. All log-deficit methods minimize the log of the

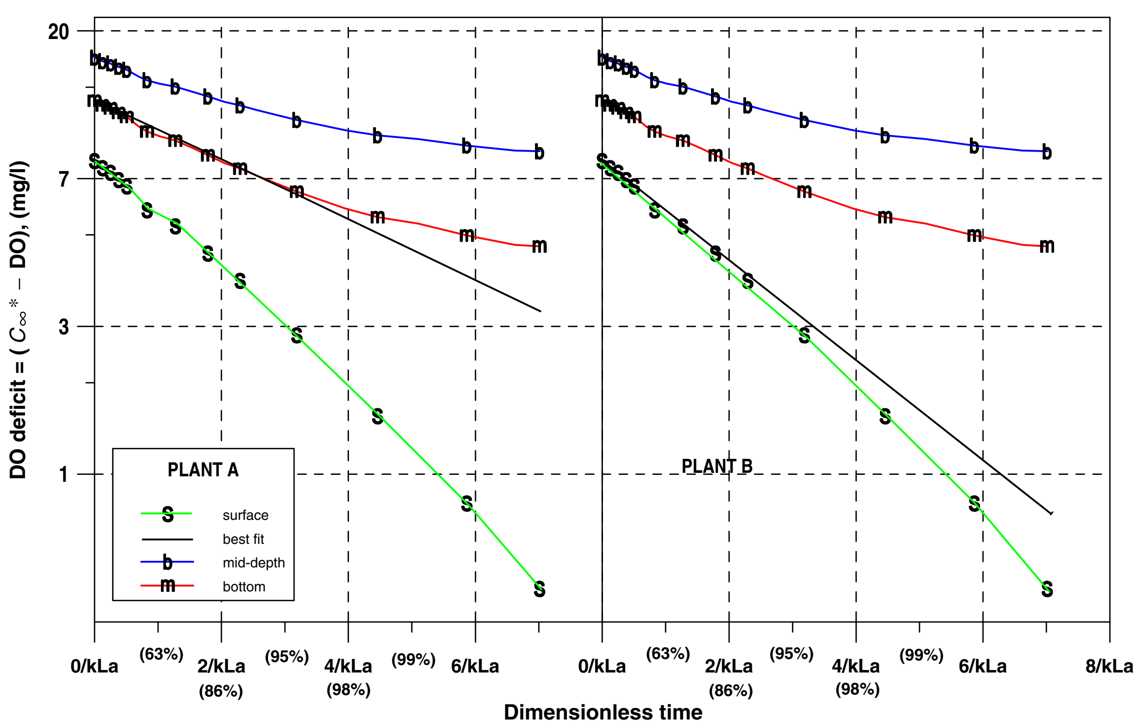

Fig. 1. Reaeration data plotted to conform to the log-deficit method of parameter estimation and the ASCE method

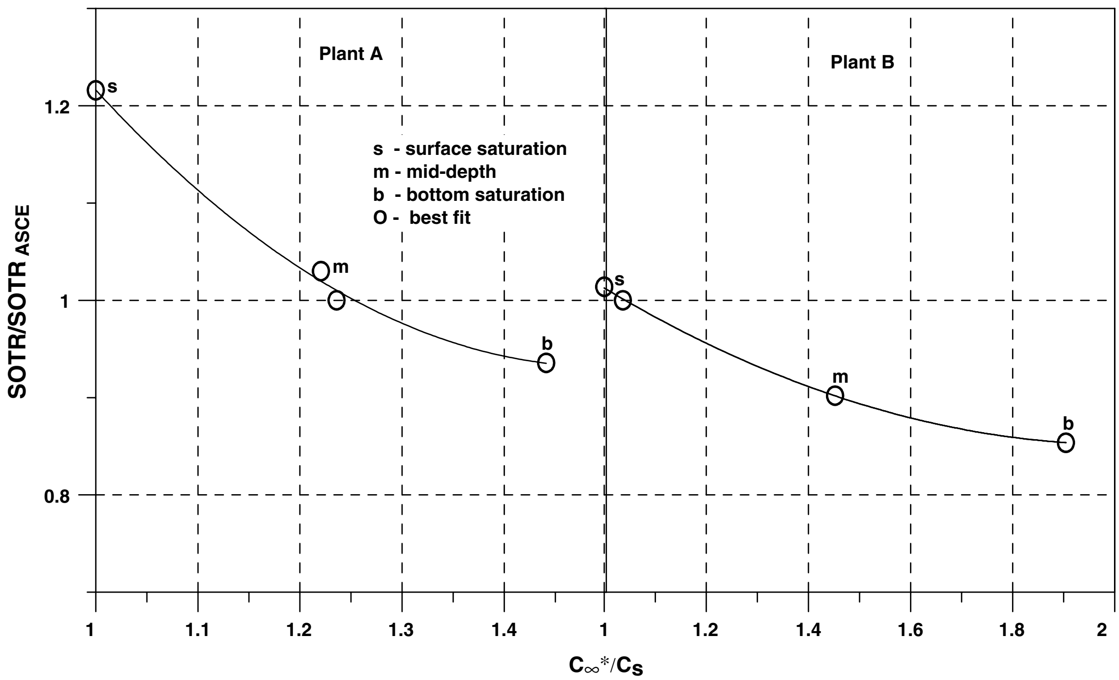

Fig. 2. Changes in predicted standard oxygen transfer rate (SOTR) as a function of equilibrium dissolved oxygen concentration

error, whereas the ASCE standard method minimizes the actual error.

A simple example is useful. Suppose the value of C^*_∞ is 10 mg/L and the error in DO measurement is ±0.1 mg/L. At 1.0 mg/L DO, the error in log-deficit method will be the difference between $\log|10-1.1|$ or $\log|10-0.9|$ and $\log|10-1.0|$, which is ±0.004. At 96% C^*_∞, near the end of a reaeration test, the error will be the difference between $\log|10-9.7|$ or $\log|10-9.5|$ and $\log|10-9.6|$, which is 0.09 or −0.12. The relative contribution of a 0.1 mg/L error in DO measurement is 24 to 31 times greater at the end than those the beginning of the test. The transformed error

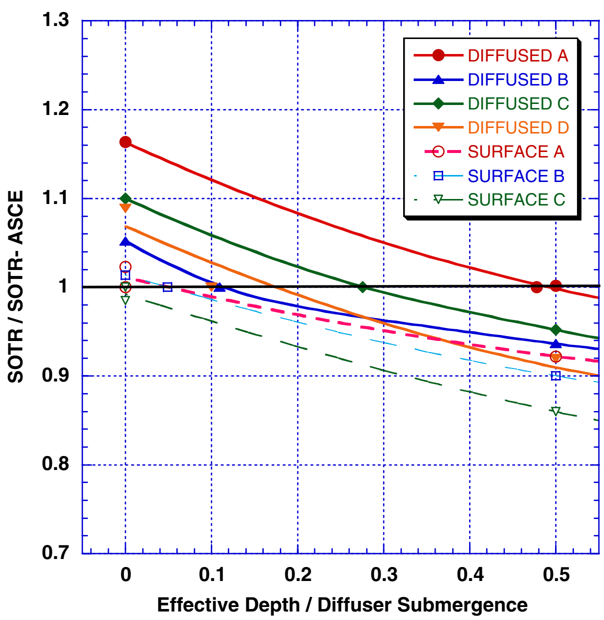

Fig. 3. Relationship between SOTRs measured with the log-deficit and ASCE methods and the depth measured

structure weighs measurements at the conclusion of the test more heavily than those the beginning. Also, if the DO measurement error is higher, it may be possible near saturation to have undefined error because of a negative deficit.

The error transformation is one possible reason for the former practice of terminating reaeration tests early (Boyle et al. 1974). The two types of errors, nonuniform residuals and bias resulting from the incorrect value of C^*_∞, require mutually exclusive modifications (continuing the test to 96% of saturation to ensure accuracy in C^*_∞ or terminating the test early to avoid transforming the error) to the data analysis methodology. The best-fit method has neither problem. The error structure is not transformed, and it is possible to conduct the test arbitrarily close to C^*_∞.

Another difference between methods is the correlation of random errors. In fitting Eq. (3) to experimental data, small, random errors in DO measurement create inversely correlated errors in the parameter estimates for K_La and C^*_∞ (an error in DO measurement is compensated by a small increase in the estimate of C^*_∞ and a small decrease in the estimate of K_La, or vice versa). Fig. 4 illustrates the contour of error associated with estimates of C^*_∞. This figure was created using data from an actual reaeration test and calculating the sum of squared error over the range of K_La and C^*_∞ values steps of 0.005/min for K_La and 0.2 mg/L for C^*_∞. The best fit occurs with $K_La = 0.045/\text{min}$ and $C^*_\infty = 9.851$ mg/L and is shown by the cross in the center. Note that overestimates of K_La are compensated by lower estimates of C^*_∞, and vice versa.

When the SOTR is calculated, the estimates of K_La and C^*_∞ are multiplied, which partially cancels the net error in SOTR. For this reason, the standard requires first that the estimates of K_La and C^*_∞, from each measuring point or be multiplied to obtain the SOTR; and second, the SOTRs from all measuring points be averaged to obtain the overall SOTR. This improvement resulting from negative correlation in the errors associated with parameters does not occur in the log-deficit procedures.

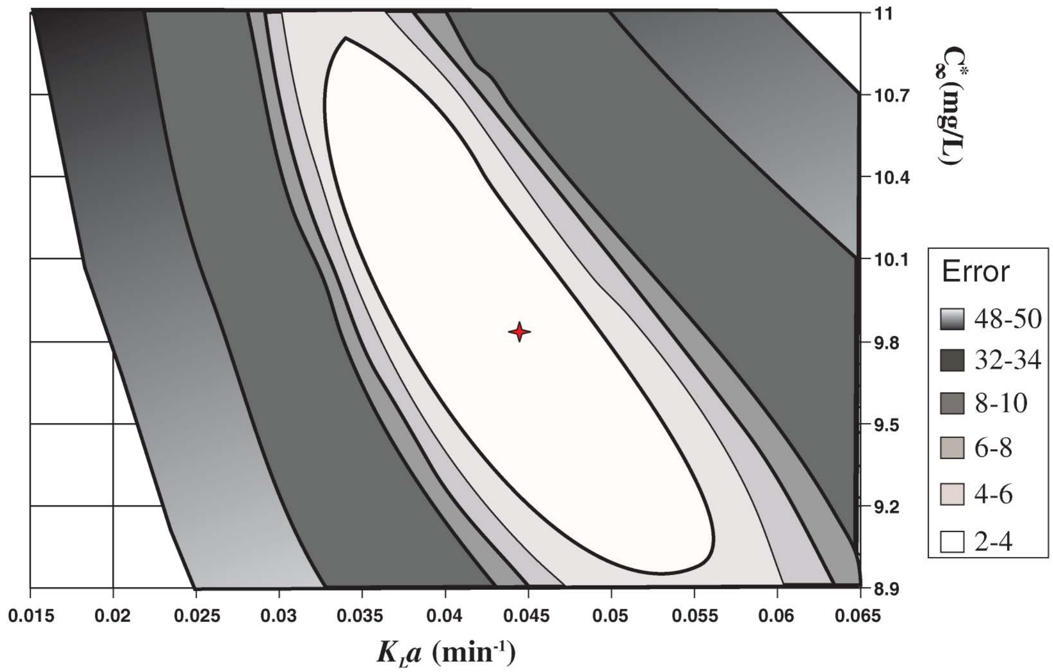

Fig. 4. Contour of the sum of squared differences with the center mark for point (0.0457, 9.851)

Gas-Phase Oxygen Depletion

A criticism of the non-steady-state reaeration test (regardless of data analysis methods) is the effect of oxygen depletion in the rising bubbles. As the bubbles rise, oxygen is absorbed by the liquid, reducing the oxygen mole fraction in the bubbles. Also, nitrogen and carbon dioxide can be stripped from the liquid, which further reduces oxygen partial pressure. The loss of oxygen is greatest in the early part of the reaeration test, when the deficit, and therefore the transfer rate, is greatest.

Fig. 5 illustrates this phenomenon for a typical reaeration test. The test was performed according to the ASCE standard, except that the off-gas from the surface of the tank was collected in a hood and analyzed for oxygen with a fuel cell oxygen analyzer (Model 320, Teledyne, City of Industry, CA).

The oxygen in the off-gas is depleted in the early part of the test and then returns to 0.2095 mole fraction at the end of the test. The effect of this deficit on parameter estimation and subsequent use of the data for steady-state design calculations was examined by Baillod (1979) and Brown and Baillod (1982). They noted that the effect of gas-side depletion on parameter estimation was to reduce the estimate of K_La and increase the estimate of C^*_∞. They formulated a conversion equation between "observed" K_La and C^*_∞ and "true"K_La and C^*_∞ by modeling oxygen transfer in a column; they concluded that the errors in observed and true K_La and C^*_∞ canceled for depths below approximately 10 m, depending on oxygen transfer rate. For this reason it was decided not to introduce the concept of true and apparent K_L a into the ASCE standard, since the effect was negligible and unnecessarily complicated the analysis.

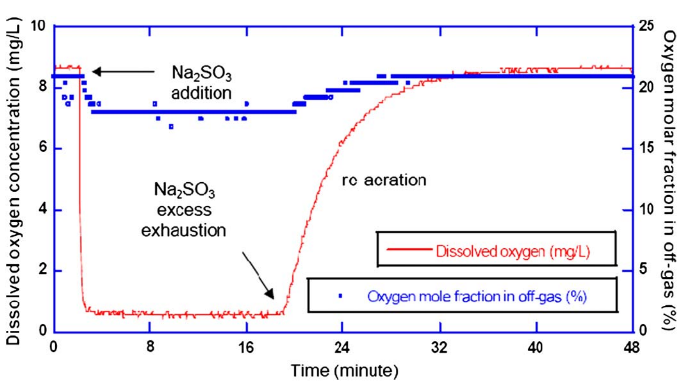

Fig. 5. Dissolved oxygen concentration and oxygen mole fraction in the off-gas during a clean water reaeration test

The writers adopted the calculation method in Brown and Baillod (1982) and expanded the database from one coarse-bubble clean water data set [e.g., low standard oxygen transfer efficiencies (SOTEs)] to several data sets, including turbines and fine pore diffusers, to cover a range of SOTEs from medium (3% SOTE/m) to high (8% SOTE/m). The results show that in all situations, the differences between products of true and apparent K_La and C^*_∞ were not significant or even measurable in most cases. For this reason, it is not necessary to adjust the value of C^*_∞ for process conditions due to gas-phase bubble depletion. In rare cases, such as fermentation systems and systems using fine pore aeration with pure oxygen, it may be necessary to compensate for gas-phase oxygen depletion.

Application of the standard to systems beyond those normally found in wastewater treatment should still be done carefully, perhaps in an evolutionary fashion. Aeration in deep reservoirs with high-purity oxygen is one area that will benefit from additional research. Advanced modeling, such as computational fluid dynamics, may be useful in these circumstances, as well in better defining aeration mechanisms (Schierholz et al. 2006; Huang et al. 2009).

Additional Improvements in the Standard

The 2006 release of the standard contains several important additions, in addition to many small improvements. The major improvements are summarized as follows:

1. The standard provides specific recommendations for loop reactors (i.e, oxidation ditches) and cites case studies showing

how the standard has been successfully applied to full-scale field clean water tests (Boyle et al. 1989).

2. The standard provides a method for estimating oxygen transfer rates for the high-purity-oxygen activated sludge (HPO-AS) process, using clean water test results in air and the gas-phase purities observed or designed for the HPO-AS process.
3. A correction factor to total dissolved solids (TDS) is also recommended but is not mandatory. The standard still requires the TDS of the tap water to be less than 2,000 mg/L, but now provides an empirical correlation to adjust the results to 1,000 mg/L TDS. This is a recommendation in the new standard and, if supported by a consensus of the users, can become mandatory in the next version of the standard.
4. The requirement for adding sodium sulfite in dissolved form has been relaxed, and it can be added as a powder in specific circumstances.
5. A pure oxygen method, which avoids deaeration using nitrogen gas or sodium sulfite, is offered as a trial method. The Committee hopes that those using the pure oxygen method can report their results to formalize the method for future releases of the standard.

Conclusions

The ASCE Oxygen Transfer Standard is more than 25 years old. Its use has eliminated many of the experimental and analysis errors previously encountered in clean water testing. The standard has created standard terms for transfer rate, such as SOTR (lb O_2/h or kg O_2/h), and efficiencies, such as SOTE (%) and standard aeration efficiency (SAE, lb O_2/hp-h or kg O_2/kW-h), and provided conversion methodology for translating to clean water into process water conditions. One of its most important contributions is the avoidance of systemic errors by eliminating the need for a priori estimates of C^*_∞. The original objections to the standard, that it was difficult to understand and that a computer was required, are no longer valid.

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