



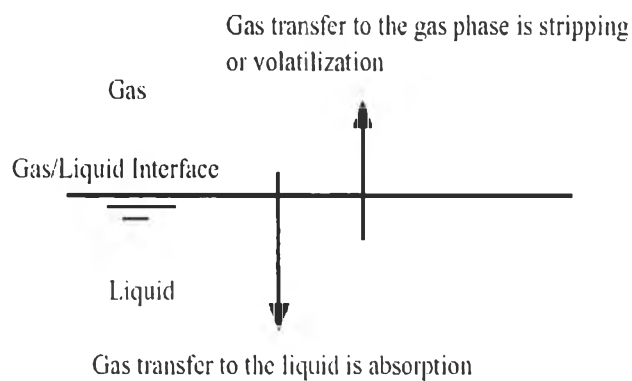
## CHAPTER 2

### BACKGROUND AND LITERATURE REVIEW

#### 2.1 Theoretical Background

##### 2.1.1 Gas Transfer

Gas transfer is an important process used in water and wastewater treatment. It is also very important when analyzing the impact of pollutants on the environment, such as discharging partially treated wastewaters to the stream (Stenstrom, 2001).



**Figure 2.1** Gas transfer (Stenstrom, 2001)

A subtle distinction

Volatilization - Stripping due to natural phenomenon.

Stripping - Stripping due to a mechanical device - aeration.

## 2.1.2 Oxygen Transfer

The most common application of oxygen transfer is in the biological treatment of wastewater. Because of the low solubility of oxygen and the consequent low rate of oxygen transfer, sufficient oxygen to meet the requirements of aerobic waste treatment does not enter water through normal surface air-water interfaces. To transfer the large quantities of oxygen that are needed, additional interfaces must be formed. Either air or oxygen can be introduced into the liquid, or the liquid in the form of droplets can be exposed to the atmosphere. (Metcalf and Eddy, 2003)

Oxygen transfer is important in many environmental systems. Oxygen transfer is controlled by the partial pressure of oxygen in the atmosphere (0.21 atm) and the corresponding equilibrium concentration in water (approximately 10 mg/L). According to Henry's Law, the equilibrium concentration of oxygen in water is proportional to the partial pressure of oxygen in the atmosphere (Gas Transfer, 2002).

### 2.1.2.1 Evaluation of Oxygen Transfer Coefficient

For a given volume of water being aerated, aeration device are evaluated on the basis of the quantity of oxygen transferred per unit of air introduced to the water for equivalent conditions (temperature and chemical of the water, depth at which the air is introduced, etc.). The evaluation of the oxygen transfer coefficient in clean water and wastewater is considered in the following discussion (Metcalf and Eddy, 2003).

*Oxygen transfer in clean water:* The accepted procedure for determining the overall oxygen transfer coefficient ( $K_L a$ ) in clean water, as detailed in ASCE (1993), should be outlined as follows in the methodology, chapter 3. The accepted test method involves the removal of dissolved oxygen (DO) from a known volume of water by addition of sodium sulfite followed by reoxygenation to near the saturation level. The

DO of the water volume is monitored during the reaeration period by measuring DO concentrations at several different points selected to best represent the contents of tank (Metcalf and Eddy, 2003). The minimum number of points, their distribution, and range of DO measurements made at each determination point are specified in the methodology, chapter 3.

The oxygen transfer rate can be estimated by determining the volumetric oxygen transfer coefficient ( $K_La$ ) and equilibrium oxygen concentration from a nonsteady state reaeration test. The volumetric mass transfer coefficient and equilibrium dissolved oxygen (DO) concentration are usually estimated by fitting the concentration versus time data to the two-film model, as follows:

$$\frac{dDO}{dt} = K_La(DO_s^* - DO) \quad (2.1)$$

where:

- DO = DO concentration, in milligrams per liter;  
 $DO_s^*$  = saturation DO concentration, in milligrams per liter, at equilibrium;  
 $K_La$  = volumetric oxygen transfer coefficient,  $t^{-1}$ ; and  
 t = time

The equation for oxygen transfer and parameter estimation techniques used in this research is the exponential method. This exponential equation integrated form of the previous equation is

$$DO = DO_s^* - (DO_s^* - DO_0)e^{(-K_La t)} \quad (2.2)$$

where:

- $DO_0$  = DO concentration at  $t = 0$  (Stenstrom *et al.*, 1981).

The exponential method was selected in this research because the sum of square errors of this method is less and the residuals (the different

between the expected and measured value) are more uniform than other methods. Truncation of data when DO approaches  $DO_s^*$  is not required. The other reasons are  $DO_s^*$  can be estimated from the data, which means no error is introduced and the precision of the estimates for  $DO_s^*$  and  $K_La$  is much greater than the other methods (Stenstrom *et al.*, 1981).

The standard oxygen transfer rate (SOTR) were determined by correcting the values of  $K_La$ , and  $C_\infty^*$  estimated for each determination point to standard conditions by:

$$K_La_{20} = K_La \theta^{(20-T)} \quad (2.3)$$

$$C_{\infty,20}^* = C_\infty^* (1/(\tau\Omega)) \quad (2.4)$$

where:

- $K_La$  = determination point value of apparent mass transfer coefficient estimated according to Section 3.3.2;
- $K_La_{20}$  = determination point value of  $K_La$  corrected to 20°C;
- $\theta$  = empirical temperature correction factor (1.024), defined by Equation 2;
- $C_\infty^*$  = determination point value of steady-state DO saturation concentration estimated according to Section 3.3.2;
- $C_{\infty,20}^*$  = determination point value of steady-state DO saturation concentration corrected to 20°C and a standard barometric pressure of 1.00 atm (101kPa);
- $\tau$  = temperature correction factor; =  $C_{st}^* / C_{s20}^*$ ;
- $C_{st}^*$  = tabular value of dissolved oxygen surface saturation concentration, mg/L, at the test temperature, a standard total pressure of 1.00 atm and 100% relative humidity;
- $C_{s,20}^*$  = tabular value of dissolved oxygen surface saturation concentration, mg/L, at 20°C, a standard total pressure of 1.00 atm and 100% relative humidity;

- $\Omega$  = pressure correction factor; =  $P_b/P_s$  for tanks under 20 ft (6.1 m) (for deeper tanks or elevation changes greater than 2,000 ft (610 m));
- $P_b$  = barometer pressure at test site during test,  $fL^{-2}$ ;
- $P_s$  = standard barometric pressure of 1.00 atm (101kPa),  $fL^{-2}$ ;  
and
- $T$  = water temperature during test, °C.

The average value of SOTR were calculated by averaging the values at each of n determination points by

$$SOTR = \frac{\sum_{i=1}^n K_L a_{20i} C_{a20i}^* V}{n} \quad (2.5)$$

$$= \frac{\sum_{i=1}^n SOTR_i}{n} \quad (2.6)$$

where:

$$SOTR = K_L a_{20i} C_{\infty 20i}^* V$$

$V$  = liquid volume of water in the test tank with aerator tuned off, liters; and

$SOTR$  = standard oxygen transfer rate, Kg/hr.

The individual values of  $K_L a_{20i}$ ,  $C_{\infty 20i}^*$ , the tank average values of  $\bar{K}_L a_{20}$ ,  $\bar{C}_{\infty 20}^*$ , actual test temperature, and unaerated liquid volume were reported along with SOTR.

$$\bar{C}_{20}^* = \frac{\sum_{i=1}^n C_{20i}^*}{n} \quad (2.7)$$

$$\bar{K}_L a_{20} = \frac{SOTR}{\bar{C}_{20}^*} \quad (2.8)$$

Frequently the standard aeration efficiency (SAE), or rate of oxygen transfer per unit power input, is computed from:

$$\text{SAE} = \text{SOTR/Power Input} \quad (2.9)$$

where: power are expressed by using amp meter and volt meter (ASCE, 1993).

### 2.1.2.2 Effect of Temperature on Oxygen Transfer Rate

Aeration, mass transfer coefficients are influenced by temperature due to the effect on the diffusivity and viscosity.

$$K_L a = K_L a_{20} \cdot \theta^{T-20} \quad (2.10)$$

Reported values of  $\theta$  range from 1.012 to 1.04. The most reliable estimates are 1.020 for diffused aeration and 1.028 for surface aeration. In this study, ASCE standard uses 1.024 and this value must be used when doing a standard test (Stenstrom, 2001).

### 2.1.3 Aeration System

There are several types of aeration system used for wastewater treatment. The systems used depend on the function to be performed, type and geometry of the reactor, and cost to install and operate the system (Metcalf and Eddy, 2003). This research focused on surface aerator, which was performed in the experiments.

#### 2.1.3.1 Mechanical Aerators

Mechanical aerators are commonly divided into two groups based on major design and operating features: aerators with a vertical axis and aerators with a horizontal axis. Both groups are further subdivided into surface and submerged aerators. In surface

aerators, oxygen is entrained from the atmosphere; in submerged aerators, oxygen is entrained from the atmosphere and, for some types, from air or pure oxygen introduced in the tank bottom (Metcalf and Eddy, 2003). This research focuses only surface mechanical aerators with vertical axis.

### 2.1.3.2 Surface Mechanical Aerators with Vertical Axis

Surface mechanical aerators with a vertical axis are designed to induce either updraft or downdraft flows through a pumping action. Surface aerators consist of submerged impellers that are attached to motors mounted on floats or on fixed structures. The impellers are fabricated from steel, cast iron, noncorrosive alloys, and fiberglass-reinforced plastic and are used to agitate the wastewater vigorously, entraining air in the wastewater and causing a rapid change in the air-water interface to facilitate solution of the air. Surface aerators may be classified according to the type of impeller used: centrifugal, radial-axial, or axial; or the speed of rotation of the impeller: low and high speed. High-speed aerator (speed 300-1200 RPMs) (Qasim, 1986) is used in this research. The impeller is coupled directly to the rotating element of the electric motor. High-speed aerators are almost always mounted on floats or on fixed structures. Surface aerators may be obtained in sizes from 0.75 to 100 kW (1 to 50 hp) (Metcalf and Eddy, 2003).

In surface aerator, oxygen is transferred to water droplets from the atmosphere and from the air bubbles to the bulk solution (Stenstrom, 2001).

$$N = N_{of} \beta \left( \frac{DO_s - DO}{9.07} \right) \alpha 1.024^{(T-20)} \quad (2.11)$$

where:

$N$	=	transfer rate, lbs O <sub>2</sub> /hr/aeration unit
$N_0$	=	transfer rate for standard conditions, 20°C, zero DO (lbs O <sub>2</sub> /HP-hr)
$DO_s$	=	saturation value of dissolved oxygen (9.07 at 20°C, in pure water)
$\beta$	=	ratio of oxygen saturation in process water to tap water
$\alpha$	=	alpha factor – corrects for contaminants that affect transfer

#### 2.1.4 Surface Active Agent

Surfactants (contraction of the term surface active agents), are substances that tend not only to accumulate at surfaces, but modify the interfacial properties of the surfaces, in which they are present. More generally, they are active at interfaces that can be between liquid-solid, liquid-liquid, or liquid-gas pairs of phases. Surfactants are amphiphilic molecules having two major components, a hydrophilic, or water soluble, head group, and a hydrophobic, or water insoluble, tail group. The hydrophobic group is usually a long-chain hydrocarbon; the hydrophilic group is an ionic or highly polar group. Depending on the nature of hydrophilic group, surfactants are classified as: anionic, cationic, zwitterionic, and nonionic surfactants (Rosen, 1988).

In this research, sodium n-dodecyl sulfate was used as a surfactant. This type of surfactant is alkyl sulfates, also called alcohol sulfates, which is anionic surfactant. It is formed by making the sulfuric acid esters of linear alcohols. They tend to be sensitive to water hardness. The properties of the alkyl sulfates vary with the alkyl chain length distribution. Mostly, this type is a ingredient for making soaps and detergent.



#### 2.1.4.1 Effect of Surface Active Agent on Oxygen Transfer Rate

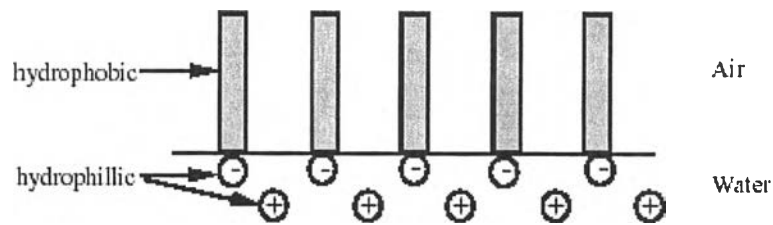
Stenstrom (2001) summarized mechanism of adsorption that when many organic compounds present in sewage water are surface active agent. These compounds are called surfactants, they tend to adsorb or accumulate at the liquid-solid or liquid-gas interface. Surfactants have polar and non-polar parts of the molecule. The simplest has a polar end, often charged, and a non-polar end, such as a hydrocarbon. The most common surfactant is soap and detergent, which was originally manufactured by mixing animal fat and lye (sodium hydroxide). The result is a surfactant with a negatively charged end (the sodium is released to solution as the balancing cation). Hydrogen bonding among water molecules will gradually force the surfactant's non-polar end to the surface. This happens because the polar ends of the water molecules attract each other, and squeeze the surfactant out of the way. The result is the surfactant at the interface (e.g., the air bubble surrounded by water) with the polar or charge end in the water and the non-polar end protruding into the bubble. The net effect is to reduce oxygen transfer in the area around the bubble by reducing molecular diffusion of oxygen.

The time required for adsorption varies with the surfactant type. Small surfactants molecule such as acetic acid adsorb quickly. The time to reach equilibrium depends upon many different properties, but is inversely proportional the molecular weight of the surfactant.

Basically there are four effects of surface active agents (SAA) on gas transfer:

1. The adsorbed film, which may partially or totally cover the water surface and thus act as an insulating membrane separating the gas and

the aqueous phase. Oil sheen is an example. This effect increases resistance to gas transfer.

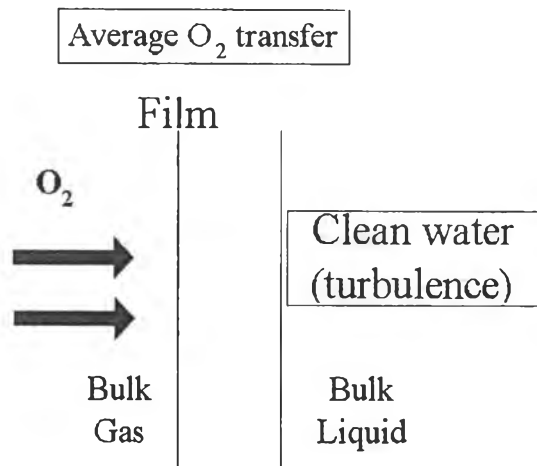


**Figure 2.2** Absorbed film between Water and Air surface (Stenstrom, 2001).

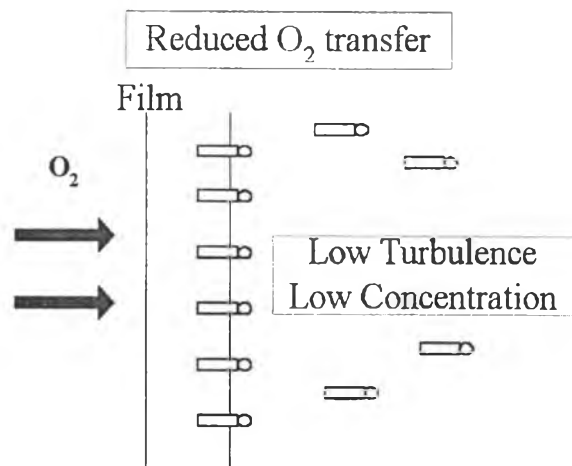
2. Water in a pure state generally consists of aggregates of 4 to 8 molecules of water that are in a state of dynamic equilibrium. When SAA molecules are introduced to the pure water, they tend to affect the water structure by stabilizing the more ordered arrangements. The SAA molecules anchored to the water surface with their hydrophilic ends will act like magnet heads that immobilize several layers of crystalline water structures and attract a blanket of counter ions. This surface hydration layer, may extend several thousand angstroms into the aqueous phase, which eliminates random surface motion (i.e., encourages surface stagnation).
3. Surface active agents can influence bubble dynamics. During the bubble rise the SAA film adsorbed on the bubble wall will be driven to the far end of the bubble where it condenses, forming a solid cap. As a result a surface force will be set in the direction of the front end of the bubble, opposing the liquid drag forces which may cause retardation in the velocity of bubble rise.

4. Diffusers produce smaller bubbles in the presence of surfactants. Larger bubbles with  $Re > 800$  undergo fragmentation in the presence of SAA. The smaller bubbles have greater surface area per unit volume of gas supplied, which increases gas transfer rate (Stenstrom, 2001).

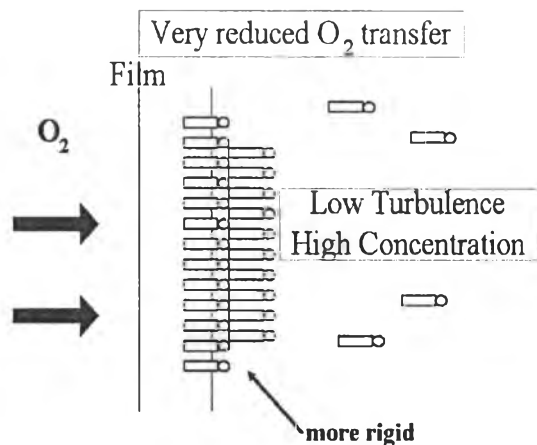
The following four figures showed the effect of surfactant when it was presented in the water. Figure 2.3 is the general oxygen transfer with turbulent condition. The oxygen can transfer without any obstruction. Figure 2.4 shows the effect when low surfactant concentration presented with low turbulence condition. The surfactant molecules adsorb at the gas-liquid interface film causes the oxygen transfer is reduced. Figure 2.5 is similar to the previous but the higher surfactant concentration is presented. More surfactant molecule adsorbs at the gas-liquid interface film and increases the resistance to oxygen transfer. As a result, oxygen transfer is reduced. High turbulence can reduce this effect. Turbulent condition reduces the surfactant molecule at the gas-liquid interface film resulting in increasing the oxygen transfer as shown in Figure 2.6.



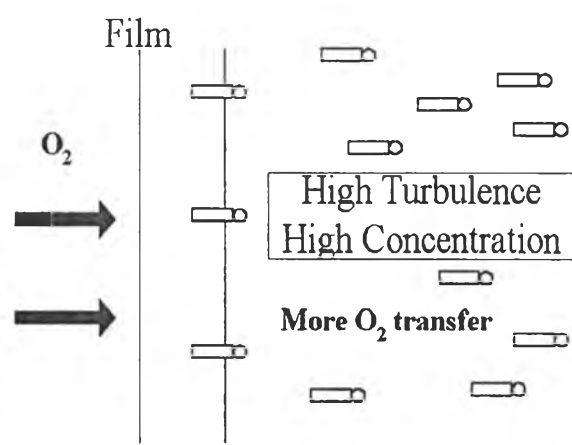
**Figure 2.3** Oxygen Transfer in Clean Water



**Figure 2.4** Oxygen Transfer in Low SAA Concentration and Low Turbulence



**Figure 2.5** Oxygen Transfer in High SAA Concentration and Low Turbulence

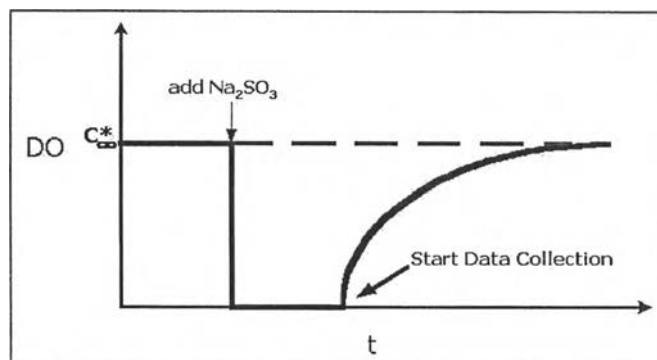


**Figure 2.6** Oxygen Transfer in Low SAA Concentration and Low Turbulence

### 2.1.5 Deoxygenation

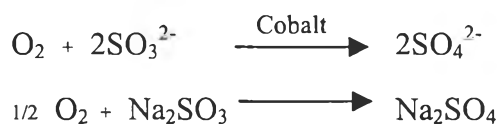
This test is the basis for clean water testing which is used for most performance testing of aeration equipment. The test is performed and the data are analyzed based upon one of the previously described equations. To perform the test, one usually supplies a deoxygenating chemical to remove the oxygen. Aeration is provided and the rates of transfer are calculated from the rate at which the water can be reoxygenated. The graph below shows

the DO concentration during a test. The sulfite is rapidly added and the DO plunges quite rapidly to zero or near zero. After some period, the DO returns and the concentration gradually increases to the equilibrium value.



**Figure 2.7** DO concentration during the test

To perform a nonsteady-state reaeration test, one adds sodium sulfite to deaerate or strip the water of DO, as follows:



The reaction is very fast and is catalyzed by cobalt ion. Cobalt is usually added as Cobalt-Chloride. The reaction is so rapid that measurable DO and sulfite can not be presented at the same time.

Sulfite is usually added by first dissolving the sulfite in water and then pouring the water into the reactor. This avoids clumps of sulfite that dissolve too slowly. A saturated sulfite solution contains 2.23 lb/gal at 20°C and 3.00 lb/gal at 30°C. Add 7.88 mg/L sulfite per 1 mg/L DO plus some excess to insure that all the DO is removed. For low rate aeration systems, usually only 25% extra is added. For very large systems, as much as 100% excess is added (Stenstrom, 2001).

## 2.1.6 Calculation Power Input

### 2.1.6.1 Energy Dissipation in Mixing

The power input per unit volume of liquid can be used as a rough measure of mixing effectiveness, based on the reasoning that more input power creates greater turbulence, and greater turbulence leads to better mixing. The study of the establishment and effect of velocity gradients in coagulation tanks of various types and developed the following equations that can be used for the design and operation of mixing systems (Metcalf and Eddy, 1997).

$$G = \sqrt{\frac{P}{\mu V}} \quad (2.12)$$

where:

- G = mean velocity gradient, 1/s
- P = power requirement, ft · lb/s (W)
- $\mu$  = dynamic viscosity, lb · s/ft<sup>2</sup> (N · s/m<sup>2</sup>)
- V = volume, ft<sup>3</sup> (m<sup>3</sup>)

### 2.1.6.2 Power Requirement for Mixing

The power requirement for mixing using propeller was described in this research. Using propeller for mixing in wastewater processes usually occurs in the regime of turbulent flow in which inertial force predominate. As a general rule, the higher the velocity and the greater the turbulence, the more efficient the mixing. On the basis of inertial and viscous force, the mathematical relationships have been developed for power requirements for turbulent conditions as follow (Metcalf and Eddy, 1997):

$$\text{Turbulent: } P = k\rho n^3 D^5 \quad (2.13)$$

where:

- $P$  = power requirement, ft-lb/s (W)  
 $k$  = constant [0.32 ,ratio for propeller, 3 blades, (Metcalf and Eddy, 2003.)]  
 $\rho$  = mass density of fluid, slug/ft<sup>3</sup> (kg/m<sup>3</sup>)  
 $D$  = diameter of impeller, ft (m)  
 $n$  = revolutions per second, rev/s

For turbulent range, it is assumed that vortex conditions have been eliminated by four baffles at the tank wall, each 10 percent of the tank diameter (Metcalf and Eddy, 2003). The Reynolds number is given by

$$N_R = \frac{D^2 n \rho}{\mu} \quad (2.14)$$

where:

- $D$  = diameter of impeller, ft (m)  
 $n$  = revolutions per second, rev/s  
 $\rho$  = mass density of fluid, slug/ft<sup>3</sup> (kg/m<sup>3</sup>)  
 $\mu$  = dynamic viscosity, lb · s/ft<sup>2</sup> (N · s/m<sup>2</sup>)

Vortexing, or mass swirling of the liquid, must be restricted with all types of impellers. Vortexing causes a reduction in the difference between the fluid velocity and the impeller velocity and thereby decreases the effectiveness of mixing. The usual method in circular tanks is to install four or more vertical baffles extending approximately one-tenth the diameter out from the wall. These effectively break up the mass rotary motion and promote vertical

mixing. Concrete mixing tanks may be square and the baffles may be omitted (Metcalf and Eddy, 1997).

## 2.2 Literature Review

Oxygen transfer rates decrease in the presence of surface active agents (surfactants). Surfactants tend to 1) stabilize the interface, making the gas/liquid interface more rigid; 2) decrease surface renewal; 3) increase interfacial viscosity. When surfactant concentration increases, the time of bubble formation and bubble volume decreases. The adsorption of the surfactants onto the gas/liquid interface decreases the available surface area for molecular diffusion, and forms a hydration layer at the surface, resulting in higher surface viscosity and increased thickness of the surface layer, which increases resistance to oxygen transfer (Masutani *et al.*, 1991).

Stenstrom (1978) noted that the equations for oxygen transfer and parameter estimation techniques used today include the differential technique, the log deficit method, and the exponential method. The overall analysis of three methods for parameter estimation suggests that the exponential method is the most suitable for estimating the oxygen transfer. As a result, the exponential and differential technique tend to produce estimates which have larger residuals in the early states of the nonsteady state test, while the log deficit method produces estimates which have larger residues toward the end of the test. The log deficit technique needs data truncation while the other two methods do not require it. The differential technique is the easiest to perform but suffers from large variability in the data, due to the magnifying effects of the differentiation. Therefore, the exponential method of parameter estimation provides the most precise estimates of  $K_L a$  and  $DO_s^*$ .

Stenstrom *et al.* (1981) found that the most common procedure for estimating the oxygen transfer rate of an aeration system is to estimate the clean water rate and then translate that rate to field conditions with alpha, beta, and theta correction factors. Estimates of the clean water transfer rate are usually made by determining the volumetric oxygen transfer coefficient and equilibrium oxygen



concentration from a nonsteady state reaeration test. They demonstrated the use of the exponential parameter estimation technique using two nonlinear programming techniques, the complex method and the linearization technique. Both techniques can accommodate an adequate number of observations. These eliminate the need for estimating  $C_s^*$  from handbook or depth/correction methods, and also eliminate the data truncation when the DO concentration approaches saturation.

Brown and Stenstrom (1981) showed the pitfalls of experiment to perform parameter estimates. The precise estimation of reaeration coefficients from unsteady-state oxygen transfer data is very important. An unambiguous estimation technique and an adequate set of observed values of concentration versus time are required. Many tests performed over a wide temperature range are required to verify a temperature.

Masutani and Stenstrom (1991) noted the correlation of the volumetric mass transfer coefficient ( $K_{La}$ ) and the liquid film coefficient ( $K_L$ ) with dynamic surface tension (DST) in the presence of a surface active agent. When the surfactant concentration increased, the time of bubble formation and bubble volume decreased. The larger decrease in  $K_{La}$  occurs with higher surfactant concentrations. Repeated unsteady state surfactant aeration testing indicated  $K_{La}$  increased as the number of experiments on the sample solution increased. An antifoam agent decreased  $K_{La}$  value. As a result,  $K_{La}$  can be estimated from aeration parameters, surfactant concentration, and the DST value.

Oxygen transfer rates of water containing surface active agents are reduced compared to clean water condition. In oxygen transfer tests with surfactants, the type of surfactant influences the oxygen transfer rate to a higher extent than by their concentration (Wagner *et al.*, 1996).