

CONTRACT MELiSSA PRF 130820.

**MODELING OF PHYSICAL LIMITATIONS IN
PHOTOBIOREACTORS.**

STUDY OF THE PHYSICAL STAGE FOR THE CO₂ MASS
TRANSFER IN COMPLEX MEDIA OF PHOTOBIOREACTORS
AT HIGH pH

TECHNICAL NOTE 19.4.
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MODELING OF PHYSICAL LIMITATIONS IN PHOTOBIOREACTORS.

TN.19.4; Study of the physical stage for the CO₂ mass transfer in complex media of photobioreactors at high pH.

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INTRODUCTION.

When microorganisms such as the cyanobacterium *Spirulina platensis* are cultivated in photobioreactors, it may occur two main physical limitations on growth kinetics:

- the limitation by the available radiant light energy inside the reactor which has been investigated in technical notes TN 19.1 - TN 19.3.

- the limitation by the CO₂ transfer rate and by the disponibility in the carbon source inside the reactor (i.e. the bicarbonate ion HCO₃⁻ for most of the cyanobacteria). In this last case, dynamic and steady-state physical and biological phenomena are strongly intricated.

At high pH values ($8 < \text{pH} < 10$), the total dissolved carbon (CO₂ + HCO₃⁻ + CO₃²⁻) is essentially composed by bicarbonate HCO₃⁻ and carbonate CO₃²⁻ ions. For example, at pH 9.5, the concentration in carbonate and bicarbonate ions is about 2000 fold higher than the CO₂ concentration. This is an important particularity compared to the classical approach for the oxygen transfer rate analysis, because this creates an important buffer reserve in total dissolved carbon in photobioreactor culture media. Then, this entails that the well-known hypothesis of non-accumulation of dissolved gases in the medium is no longer satisfied and the mass balance equations must be written in the general case, with accumulation term in the liquid medium. This leads to solve nonstationnary differential equations which may be simplified to algebraic equations in pseudo steady-state following the operating conditions.

Additionally, the cyanobacteria are known to concentrate the intracellular bicarbonate if the extracellular concentration is low. This concentration proceeds against the HCO₃⁻ concentration gradient but enables to maintain the activity of the Rubisco at a high level. Nevertheless, this active transport consumes a part of the produced ATP and then the energetic yield of photosynthesis decreases, giving lower growth rates (LEHMAN, 1978; MILLER and COLMAN, 1980; COLEMAN and COLMAN, 1981; MILLER *et al.*, 1984).

The study of the limitation by the carbon source and its modeling inside photobioreactors then appears as a complex problem since informations must be obtained at three levels:

- the study of the dynamic CO₂ gas-liquid transfer with eventually the limitation by the CO₂ transfer rate;

- the study of chemical equilibria in complex media with high ionic strenght in order to calculate the CO₂-HCO₃⁻-CO₃²⁻ concentrations in the culture medium;

- the study of HCO₃⁻ limiting concentrations on the physiology and the metabolism of *S. platensis* in order to postulate kinetic law.

Moreover, the general modeling of these coupled phenomena requires the mass balance on O₂ and CO₂ in the gas phase to be performed to complete the previous informations.

Two main cases may then be examined for the CO₂ transfer:

1- Nonstationary transfer rate:

In this case, it exists a positive or negative accumulation of total dissolved carbon in the liquid phase. The CO₂ dissolved concentration is far to the thermodynamic equilibrium and the microorganisms never can be in limiting conditions by the CO₂ transfer rate. However, if the bicarbonate concentration is low, a biological mineral limitation by the carbon source may appears.

2- Pseudo steady-state transfer rate:

In this case, if the microorganisms are not limited by the CO₂ transfer rate, this means that the CO₂ dissolved concentration is close to the thermodynamic equilibrium $C_{CO_2}^*$ and the molar volumetric rate of CO₂ uptake is $r_{CO_2} = K_L a (C_{CO_2}^* - C_{CO_2})$ with a dissolved carbon dioxide concentration fixed by the microorganisms and equal to $C_{CO_2} = C_{CO_2}^* - \frac{r_{CO_2}}{K_L a}$ (if the gas phase is assumed perfectly mixed). Then the CO₂ transfer rate is purely diffusional. This case is commonly encountered when the pH of the medium is controled at a given level by supplying the medium with CO₂. Another important case is the appearance of a mineral limitation by the bicarbonate concentration.

It may be also possible that the microorganisms are limited by the physical CO₂ transfer rate. So, the growth rate is fixed by the technological characteristics of the apparatus and the molar volumetric rate of CO₂ uptake is equal to $r_{CO_2} = K_L a C_{CO_2}^*$.

The work described in this technical note concerns only the physical stage for the CO₂ transfer in photobioreactors, i.e. the establishment of general mass balances on the gas and liquid phases and their simplification in comparison with experimental results obtained on CO₂ absorption and desorption experiments in photobioreactors. Then, in a first part, the methods used and the experimental results obtained are described and discussed. In a second part, the mathematical modeling of observed phenomena is presented with different levels of complexity.

1- EXPERIMENTAL DETERMINATION OF BICARBONATE CONCENTRATION.

Two different methods have been used to determine the bicarbonate concentration in the liquid phase ($C_{HCO_3^-}$) of the reactor:

- a classical acid/base titration for HCO₃⁻ concentrations higher than 5 · 10⁻³ mole/l in total dissolved carbon. This value corresponds to the lower concentration which may be determined without a perturbation of the assay by atmospheric CO₂ absorption. For such a method, an accuracy of 5 to 10% following the carbon concentration is generally considered.

- a Gas Phase Chromatography method (GPC) with a high sensitivity, allowing to determine down to 10⁻⁶ mole/l in total dissolved carbon. This method is particularly convenient for low bicarbonate concentrations because no dilution of the sample is necessary.

GPC technique for bicarbonate determination (Marty *et al.*, 1995):

The bicarbonate and carbonate ions of the sample are stripped in CO₂ gas by concentrated HCl addition (final pH of the sample must be lower than 3). A sample is taken from gas phase and injected in a chromatograph DELSI DI 700. The different components of the gas phase are separated by two helicoidal columns feeded with Porapak Q (2 m length and 1/8 inch diameter). The detector is a catharometer at the temperature of 100°C and the gas vector is hydrogen at a pressure of 1 bar.

The chromatograph response (CO₂ peak area) has been preliminary calibrated in order to obtain the molar fraction of CO₂ in the gas phase y_{CO_2} . The total dissolved carbon concentration $C_T = C_{CO_2} + C_{HCO_3^-} + C_{CO_3^{2-}}$ may then be calculated as follows (the solubility of CO₂ in dilute HCl solutions is very closed to the solubility of CO₂ in water) by:

$$p_{CO_2} = y_{CO_2} P_T, \text{ CO}_2 \text{ partial pressure}$$

$$C_T = \frac{p_{CO_2} (H V_G + R T V_L)}{V_L R T H}$$

where H is the Henry's constant for CO₂ (H_{20°C} = 25.78 l.atm/mole), and V_L, V_G are respectively the liquid and gas phase volume.

The respective concentrations of CO₂, bicarbonate and carbonate ions are then obtained at the considered initial pH of the medium by the equilibrium constants as it will be discussed latter in this TN.

The accuracy of the method has been obtained by statistical analysis with a confidence interval of 95% including sampling and calibration errors. An accuracy of 10% has been found for the total carbon concentration determination in the range 10⁻⁶-10⁻³ mole/l.

2- EXPERIMENTAL DETERMINATION OF O₂ AND CO₂ IN THE GAS PHASE.

The molar fractions of O₂ and CO₂ in the gas phase have been determined with differential gas analyzers (paramagnetic analyzer for O₂ and infra-red analyser for CO₂) for each species. The accuracy of this measure is about 5% on Δy_{O_2} and Δy_{CO_2} respectively.

3- CO₂ EXPERIMENTS IN PHOTOBIOREACTORS.

The general scheme of the pilot plant used for these experiments (reactor, gas circulation,...) has been described by CORNET (1992). The medium used was the medium described by ZARROUK (1966) with different amounts of total dissolved carbon C_T for absorption or desorption experiments. The reactional volume has been taken equal to 4 l for all the experiments.

3.1- Experimental conditions.

-Desorption experiment.

The carbonate-bicarbonate buffer was taken to NaHCO₃ = 10.5 g/l (0.128 mole/l) and Na₂CO₃ = 7.6 g/l (0.072 mole/l) giving a pH of 9.5 and corresponding to the basic medium for *Spirulina* culture (CORNET, 1992). The CO₂ molar fraction in the incoming gas flow of the reactor was chosen to 350 ppm.

Two different rotation speeds have been used in order to study the influence of volumetric transfer coefficient K_La on the dynamic mass transfer changes in the reactor. A speed of 300 rpm was used at the beginning of the experiment and 1000 rpm after a time course of 143 hours.

The pH was controlled to 9.5±0.01 by H₂SO₄ addition and the temperature was controlled to 36±0.1°C.

These experimental conditions correspond to an oversaturation of the liquid phase, resulting in a desorption of CO₂ from the medium.

- Absorption experiment.

A basic medium for *Spirulina* culture (CORNET, 1992) free of carbonate-bicarbonate buffer has been used. The CO₂ molar fraction in the incoming gas flow of the reactor was chosen to 4000 ppm (because of the apparatus constraints; nevertheless it must be noticed that the maximum value for a man on 40 days is 5000 ppm).

Three different rotation speeds have been used in order to study the influence of volumetric transfer coefficient K_La on the dynamic mass transfer changes in the reactor. A speed of 150 rpm was used at the beginning of the experiment, then 300 rpm after a time course of 166 hours, and 600 rpm after a time course of 260 hours.

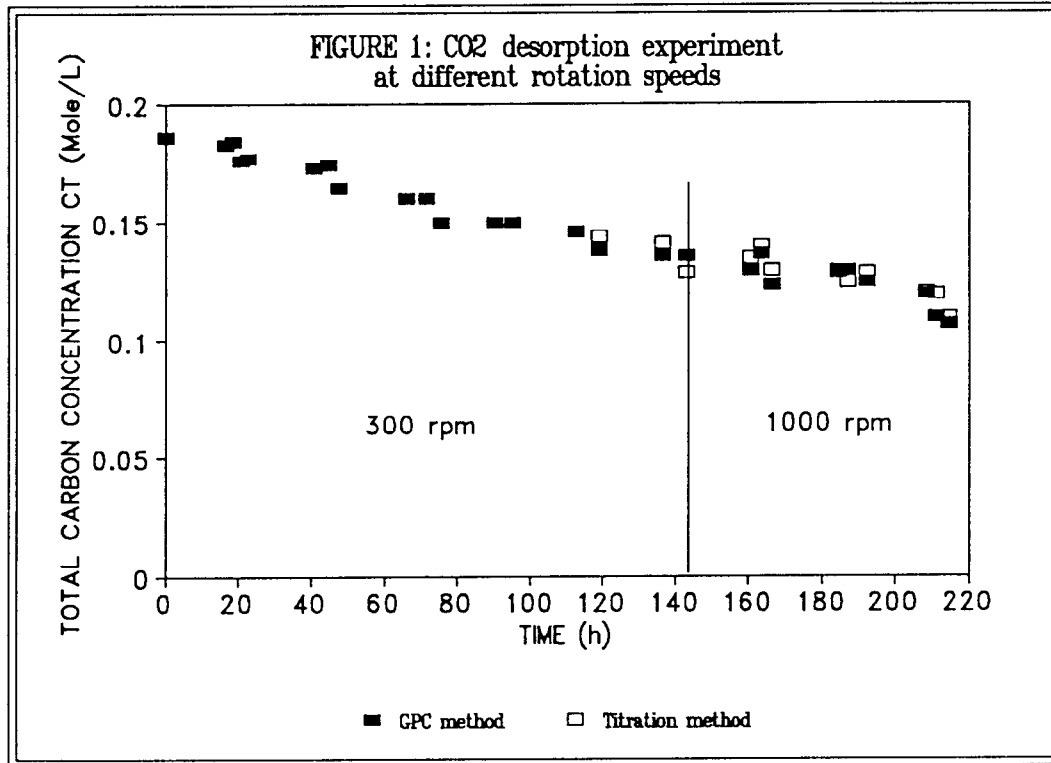
The pH was controlled to 9.5±0.01 by NaOH addition and the temperature was controlled to 36±0.1°C.

These experimental conditions correspond to an undersaturation of the liquid phase, resulting in an absorption of CO₂ in the medium.

3.2- Results and discussion.

- Desorption experiment.

The experimental results dealing with the time course of total carbon C_T measured in the liquid phase from both GPC and titration methods are shown in Figure 1.



From experimental results, the Recovery Percentage of Carbon (PRC) may be calculated from each successive set of data as follows:

$$\text{PRC} = \frac{\sum_{i=1}^N \frac{(\Delta y_{\text{CO}_2}^{i-1} + \Delta y_{\text{CO}_2}^i) G (t_i - t_{i-1})}{2 (C_T^{i-1} - C_T^i) V_L}}{N}$$

where N is the total number of data, Δy_{CO_2} the differential molar fraction between the incoming and outgoing flows of the reactor, C_T the total carbon concentration in the liquid phase, G the total molar flow rate and V_L the liquid volume of the reactor. This experiment gives the following result:

$$\text{PRC} = 100\% \pm 10\%$$

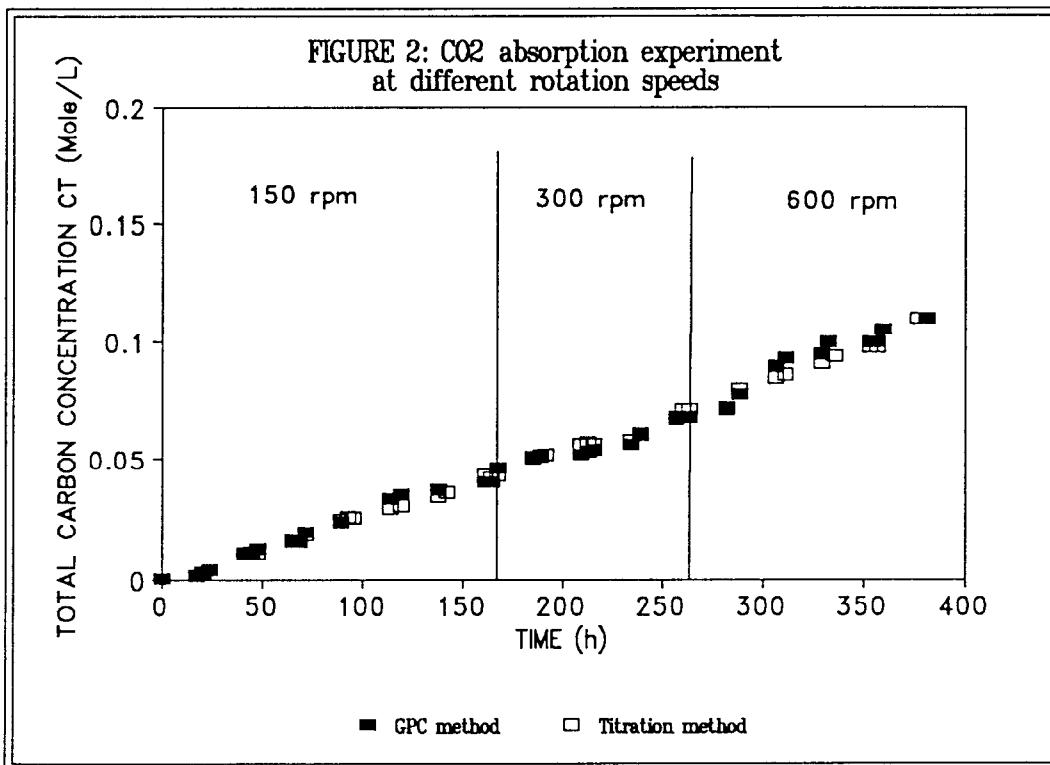
that is a good result in regard to the accuracy of the measurement of C_T and Δy_{CO_2} (Marty *et al.*, 1995).

Moreover, Figure 1 shows that total carbon concentration decreases in the liquid medium as expected in regard to the initial experimental conditions ($C_T^i = 0.186$ mole/l and $y_{CO_2}^E = 350$ ppm).

Nevertheless, the increase of the volumetric transfer coefficient $K_L a$ after a time course of 143 hours (line in Figure 1) does not significantly affect the rate of total carbon desorption.

- Absorption experiment.

The experimental results dealing with the time course of total carbon C_T measured in the liquid phase from both GPC and titration methods are shown in Figure 2.



From experimental results, the Recovery Percentage of Carbon (PRC) may be calculated from each successive set of data as follows:

$$PRC = \frac{\sum_{i=1}^N \frac{(C_T^i - C_T^{i-1}) V_L}{(\Delta y_{CO_2}^{i-1} + \Delta y_{CO_2}^i) G (t_i - t_{i-1})}}{2N}$$

which gives for this experiment:

$$\text{PRC} = 100\% \pm 10\%$$

Moreover, Figure 2 shows that total carbon concentration increases in the liquid medium as expected in regard to the initial experimental conditions ($C_T^i \approx 0$ and $y_{\text{CO}_2}^E = 4000$ ppm) and that the two measurement methods are in good agreement.

The increase of the volumetric transfer coefficient $K_L a$ after a time course of 166 hours, then 260 hours (lines in Figure 2) does not significantly affect the rate of total carbon absorption. This results in the fact that the thermodynamic equilibrium is probably reached between the gas and liquid phases in the outgoing flow of the reactor. In this last case (as in the desorption experiment), the evolution of the total carbon concentration in the reactor is only related to the molar flow rate of CO₂ in the incoming flow of the reactor. It must be pointed out that this last hypothesis should not apply in the first part of the experiment (rotation speed of 150 rpm) because the theoretical response in this part is exponential giving a low value of the CO₂ volumetric mass transfer coefficient (see hereafter).

4- MODELING DYNAMIC CO₂ GAS-LIQUID MASS TRANSFER IN COMPLEX AND HIGH pH MEDIA OF PHOTOBIOREACTORS.

4.1- Gas-liquid equilibria - CO₂ solubility.

With a reference state at infinite dilution and disymetric convention (which is the most commonly encountered reference state for electrolyte solutions), the gas-liquid equilibria for CO₂ is written as follows:

$$y_{\text{CO}_2} P \phi_{\text{CO}_2} = H \gamma_{\text{CO}_2}^m m_{\text{CO}_2} \quad (1)$$

where y_{CO_2} is the CO₂ molar fraction, ϕ_i the fugacity coefficient, H the Henry's constant for CO₂, γ_1^m the activity coefficient in molality scale and m_{CO_2} the CO₂ molality. For biological applications, with restricted range of pressure and temperature variation, the fugacity coefficient may be taken equal to unity. Moreover, the activity coefficients in molality or molarity scales, respectively γ_1^m and γ_1^c are often very close for current applications in photobioreactors (so hereafter, the superscript "m" or "c" will be omitted for convenience). Then equation (1) becomes:

$$y_{\text{CO}_2} P = p_{\text{CO}_2} = H \gamma_{\text{CO}_2} C_{\text{CO}_2} \quad (2)$$

If the medium may be assumed as a dilute solution, $\gamma_{\text{CO}_2} = 1$, so:

$$y_{\text{CO}_2} P = H C_{\text{CO}_2} \quad (3)$$

At the opposite, if the electrolyte or biological molecule concentrations are important (e.g. for electrolyte solution, a ionic strength greater than 0.1 which is the upper limit of validity for the Debye and Hückel law), the CO₂ solubility may be calculated from the assessment of γ_{CO_2} with the data of EDWARDS *et al.* (1978) or from the correction of the Henry's constant $H' = H\gamma_{\text{CO}_2}$ at infinite dilution by a Sechenov model with the data of SCHUMPE (1993).

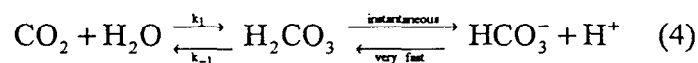
It must be noted that for CO₂ absorption or CO₂ desorption experiments in which the total carbon concentration, and consequently the ionic strength, vary with time, the CO₂ solubility is not a constant and it is time dependent.

4.2- Liquid phase equilibria and reactional scheme.

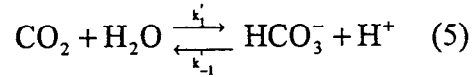
The reactions of CO₂ in aqueous media is well known and discussed in the literature (DANCKWERT, 1970; SHERWOOD *et al.*, 1975; EDWARDS *et al.*, 1978). At high pH, greater than 7, the dissolved CO₂ reacts with water to give the bicarbonate ion HCO₃⁻ and then the carbonate ion CO₃²⁻. The establishment of a reactional scheme for these species, that is a prerequisite step in writing mass balance equations, is based on the study of CO₂-HCO₃⁻-CO₃²⁻ equilibria in liquid phase. The total reactional scheme displays a relative complexity, but some simplifications may be accepted for the considered field of investigation.

Additionally, this still raises the problem of nonideal mixtures because the equilibrium constants are rigorously defined in activities $a_i = \gamma_i C_i$. In the following, this general formulation will be adopted because in many practical cases, the culture media in photobioreactors are not ideal. For example, with a gas phase at 5% CO₂ supplying a reactor at a pH of 9.5, one reaches at the equilibrium, a total carbon concentration in the liquid phase of about 2.5 moles/l, which leads to a ionic strength up to 2 moles/l. Nevertheless, it must be kept in mind that for ideal dilute solutions, the activity coefficients approach 1 and the molar concentration must be directly considered, and finally, that the mass balances must be written in term of concentrations.

The dissolved CO₂ exists under 2 different species: the aqueous CO₂ and the carbonic acid H₂CO₃ coming from the reaction of CO₂ with water. Nevertheless, less than 0.5% of the dissolved CO₂ exists under the form H₂CO₃. So the reaction of CO₂ in water is often written as follows:



Rigorously, it should be written a mass balance on the carbonic acid H₂CO₃, but many authors consider that the equilibrium between H₂CO₃ and HCO₃⁻ is instantaneous, so equation (4) becomes:

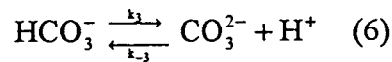


with an equilibrium constant defined from the activities of each species a_i by:

$$K_1 = \frac{a_{\text{HCO}_3^-} a_{\text{H}^+}}{a_{\text{CO}_2} a_{\text{H}_2\text{O}}} = \frac{k_1'}{k_{-1}'}$$

As the H₂CO₃ dissociation is instantaneous, the value of k₁' is taken equal as k₁, then k₋₁' is given by k₁'/K₁.

The second chemical equilibrium involves bicarbonate and carbonate ions and may be written in the form:

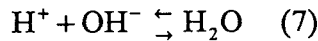


with the equilibrium constant:

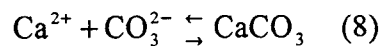
$$K_3 = \frac{a_{\text{CO}_3^{2-}} a_{\text{H}^+}}{a_{\text{HCO}_3^-}} = \frac{k_3}{k_{-3}}$$

This reaction is often considered as instantaneous (DANCKWERT, 1970), so it is not necessary to write a nonstationary mass balance on the carbonate ion CO₃²⁻. It will be considered always at the thermodynamic equilibrium with an algebraic relation.

An additional instantaneous equilibrium must be considered to complete the reactional scheme which is the water dissociation equilibrium of ionic product K_e:



It must be noticed that this reactional scheme does not take into account a possible precipitation of CaCO₃. If the medium does not contain complexants of Ca²⁺ such as EDTA or other, it must be added the following equilibrium for calcium carbonate formation:



with a solubility product:

$$K_s = a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}}$$

The values of the equilibrium constants of the model are available in the literature, specially in the paper of EDWARDS *et al.* (1978). These values are required in order to simplify the differential balances written on the gas and liquid phases.

$$\ln K_1 = \frac{-12092.1}{T} - 36.7816 \ln T + 235.482 \quad (9)$$

$$\ln K_3 = \frac{-12431.7}{T} - 35.4819 \ln T + 220.067 \quad (10)$$

$$\ln K_e = \frac{-13445.9}{T} - 22.4773 \ln T + 140.932 \quad (11)$$

4.3- Dynamical CO₂ mass transfer at thermodynamic nonequilibrium.

The general macroscopic nonstationary mass transfer equations on each species involved in the reactor, without any hypothesis on the instantaneity of equilibria nor on the kind of process, and written from the reactional scheme presented above, lead to the following system:

$$(12) \quad \begin{cases} \frac{dC_{\text{CO}_2}}{dt} = aN_{\text{CO}_2} + D(C_{\text{CO}_2}^E - C_{\text{CO}_2}^S) - k_1' C_{\text{CO}_2} + k_{-1}' C_{\text{HCO}_3^-} C_{\text{H}^+} \\ \frac{dC_{\text{HCO}_3^-}}{dt} = D(C_{\text{HCO}_3^-}^E - C_{\text{HCO}_3^-}^S) + k_1' C_{\text{CO}_2} + k_{-3} C_{\text{CO}_3^{2-}} C_{\text{H}^+} - k_{-1}' C_{\text{HCO}_3^-} C_{\text{H}^+} - k_3 C_{\text{HCO}_3^-} \\ \frac{dC_{\text{CO}_3^{2-}}}{dt} = D(C_{\text{CO}_3^{2-}}^E - C_{\text{CO}_3^{2-}}^S) + k_3 C_{\text{HCO}_3^-} - k_{-3} C_{\text{CO}_3^{2-}} C_{\text{H}^+} \end{cases}$$

With a , the exchange area by unit of reactor volume, N_{CO_2} the mass transfer flux between phases and D the dilution rate of the reactor. This differential system requires the knowledge of several rate constants to be solved. Moreover, the effect of ionic strength on these rate constants is important and have to be taken into account.

The transfer model has to be completed with a mass balance equation on CO₂ in gas phase, that is written:

$$\frac{PV_G}{RT} \cdot \frac{dy_{\text{CO}_2}}{dt} = -aV_L N_{\text{CO}_2} + y_{\text{CO}_2}^E G^E - y_{\text{CO}_2}^S G^S \quad (13)$$

where y_{CO_2} is the molar fraction of CO₂ in the gas phase and G the molar flow rate. In equation (13), because the accumulation term is generally close to zero, the pseudo steady-state hypothesis is often assumed, leading to:

$$aN_{\text{CO}_2} = \frac{1}{V_L} (y_{\text{CO}_2}^E G^E - y_{\text{CO}_2}^S G^S) \quad (14)$$

The complex problem presented by equations (12-14) may be oversimplified in regard to the experiments performed and to the objectives defined in this TN. Considering the instantaneity of equilibria (5) and (6) as it has been discussed in the establishment of the reactional scheme, and applying the system of equations (12) to a batch experiment of CO₂ absorption or desorption ($D = 0$), one obtains the following algebraic-differential system:

$$(15) \quad \begin{cases} \frac{dC_{\text{CO}_2}}{dt} = \frac{1}{K} a N_{\text{CO}_2} \\ C_{\text{HCO}_3^-} = \frac{1}{\gamma_{\text{HCO}_3^-}} \left[\frac{K_1 a_{\text{CO}_2} a_{\text{H}_2\text{O}}}{a_{\text{H}^+}} \right] \\ C_{\text{CO}_3^{2-}} = \frac{1}{\gamma_{\text{CO}_3^{2-}}} \left[\frac{K_3 a_{\text{HCO}_3^-}}{a_{\text{H}^+}} \right] \end{cases}$$

in which the constant K , equal to $(1 + \frac{K_1}{C_{\text{H}^+}} + \frac{K_1 K_3}{C_{\text{H}^+}^2})$, depending of the pH in the medium, enables to relate the CO₂ concentration to the total carbon concentration C_T by:

$$C_T = K C_{\text{CO}_2} \quad (16)$$

and $C_T = C_{\text{CO}_2} + C_{\text{HCO}_3^-} + C_{\text{CO}_3^{2-}}$

The system of equations (15) with equation (14) may be solved from the knowledge only of the equilibrium constants K_1 , K_3 and from the knowledge of the activity coefficients for each species involved in the process if the medium is nonideal. This leads to the time course of the species CO₂, HCO₃⁻ and CO₃²⁻ in the liquid phase of the reactor, as even so the CO₂ in the gas phase during absorption or desorption experiments.

4.3.1- Simplified approach for the CO₂ mass transfer study. The total carbon mass balance equation.

In the first approach presented in this TN, the calculation of activity coefficients which is a complex problem will be eluded by working with the pseudo species C_T (total carbon concentration = $C_{\text{CO}_2} + C_{\text{HCO}_3^-} + C_{\text{CO}_3^{2-}}$). Thus no hypothesis is necessary for activity

coefficients calculation because only one species exists in the liquid phase. It is important to note that this method does not reduce the level of generality of the mass transfer model but makes only the calculation of C_{HCO₃⁻} and C_{CO₃²⁻} impossible except with dilute solution approximation. In this case, the system of equations (15) becomes:

$$\frac{dC_T}{dt} = a N_{CO_2} \quad (17)$$

and the equation (14) on the gas phase always applies:

$$aN_{CO_2} = \frac{1}{V_L} (y_{CO_2}^E G^E - y_{CO_2}^S G^S) \quad (14)$$

In this equation, the molar flow rate in the outgoing flow of the reactor G^S may be obtained by writing a mass balance on the inert gas N₂ in the reactor:

$$G^S = G^E \frac{1 - y_{CO_2}^E}{1 - y_{CO_2}^S} \quad (18)$$

but, in regard to the low values of CO₂ molar fractions in the gas phase, the assumption of a constant molar flow rate G^S = G^E is often made.

In order to solve equations (14) and (17-18), the expression of the CO₂ mass transfer flux term aN_{CO₂} have to be established versus the CO₂ molar fraction in the gas phase y_{CO₂}. This entails to postulate a hydrodynamic model for the gas phase flowing in the reactor.

- The gas phase is considered as perfectly mixed:

So, the CO₂ molar fraction is the same in the gas phase of the reactor and equal to y_{CO₂}^S. The term of mass transfer flux is then written:

$$aN_{CO_2} = K_L a \left(\frac{y_{CO_2}^S P}{H} - \frac{C_T}{K} \right) \quad (19)$$

In this case, the equations (14), (17-18) and (19) present analytical solutions (if H is considered independent of time). For example, if the molar flow rate G is taken as a constant, one obtains:

$$C_T = y_{CO_2}^E \frac{PK}{H} [1 - e^{-\beta K_L a t}] + C_T^0 e^{-\beta K_L a t} \quad (20)$$

$$\text{with } \beta = \frac{1}{K} \left[\frac{1}{\frac{K_L a P V_L}{HG} + 1} \right]$$

$$y_{\text{CO}_2}^s = y_{\text{CO}_2}^E \left[1 - \frac{1}{1 + \frac{HG}{K_L a P V_L}} e^{-\beta K_L a t} \right] + C_T^0 \frac{H}{K P} \frac{1}{1 + \frac{HG}{K_L a P V_L}} e^{-\beta K_L a t} \quad (21)$$

These solutions may be linearized in order to determine the volumetric coefficient of transfert $K_L a$ from experimental data on C_T and $y_{\text{CO}_2}^s$.

- The gas phase is considered in plug flow:

So the CO₂ molar fraction is only homogeneous on a cross section of the reactor (in a bubble at a given point of space). In this case, a microscopic mass balance on one bubble integrated over all the bubbles along the gas phase of the reactor leads to:

$$aN_{\text{CO}_2} = K_L a \frac{\left(\frac{y_{\text{CO}_2}^E P}{H} - \frac{C_T}{K} \right) - \left(\frac{y_{\text{CO}_2}^s P}{H} - \frac{C_T}{K} \right)}{\ln \left[\frac{\left(\frac{y_{\text{CO}_2}^E P}{H} - \frac{C_T}{K} \right)}{\left(\frac{y_{\text{CO}_2}^s P}{H} - \frac{C_T}{K} \right)} \right]}$$

(22)

Thus, the system of equations (14), (17-18) and (22) must be numerically integrated for simulations or identifications of $K_L a$ values. It is important to note that in the case of small differences for the input/output CO₂ molar fractions (i.e. $\Delta y_{\text{CO}_2} \rightarrow 0$), equation (22) approaches equation (19) and gives the same results for the volumetric mass transfer coefficient $K_L a$.

Independently of any hypothesis on the hydrodynamic of the gas phase in the reactor, a new simplification may appears in several processing cases of transfer. It has been experimentally observed in most operating conditions (at sufficiently high $K_L a$ values) that the CO₂ molar fraction in the outgoing gas flow of the reactor $y_{\text{CO}_2}^s$ was always near to the

thermodynamic equilibrium with the CO₂ concentration in the liquid phase. Then, the rate of transfer becomes independent of the CO₂ volumetric mass transfer coefficient $K_L a$ because the CO₂ molar fraction $y_{\text{CO}_2}^s$ is directly obtained by:

$$y_{\text{CO}_2}^s \approx y_{\text{CO}_2}^* = \frac{HC_T}{KP} \quad (23)$$

and reporting in equations (14) and (17), this gives a sole differential equation for the C_T time course (with a constant molar flow rate G):

$$\frac{dC_T}{dt} = \frac{G}{V_L} \left(y_{\text{CO}_2}^E - \frac{HC_T}{KP} \right) \quad (24)$$

This equation provides the following solution for C_T :

$$C_T = \frac{KP}{H} y_{\text{CO}_2}^E \left[1 - \exp\left(-\frac{HG}{KV_L P} t\right) \right] + C_T^0 \exp\left(-\frac{HG}{KV_L P} t\right) \quad (25)$$

which is indeed independent of $K_L a$. The time constant in equation (25) depends only of the aeration conditions (from the ratio G/V_L) and of the pH (by the constant K). For example, the thermodynamic equilibrium is 150 fold longer to reach at pH 10 than at pH 8. This time ranges between some days and several months depending of the ratio G/V_L (0.02 v.v.m. to 2 v.v.m.).

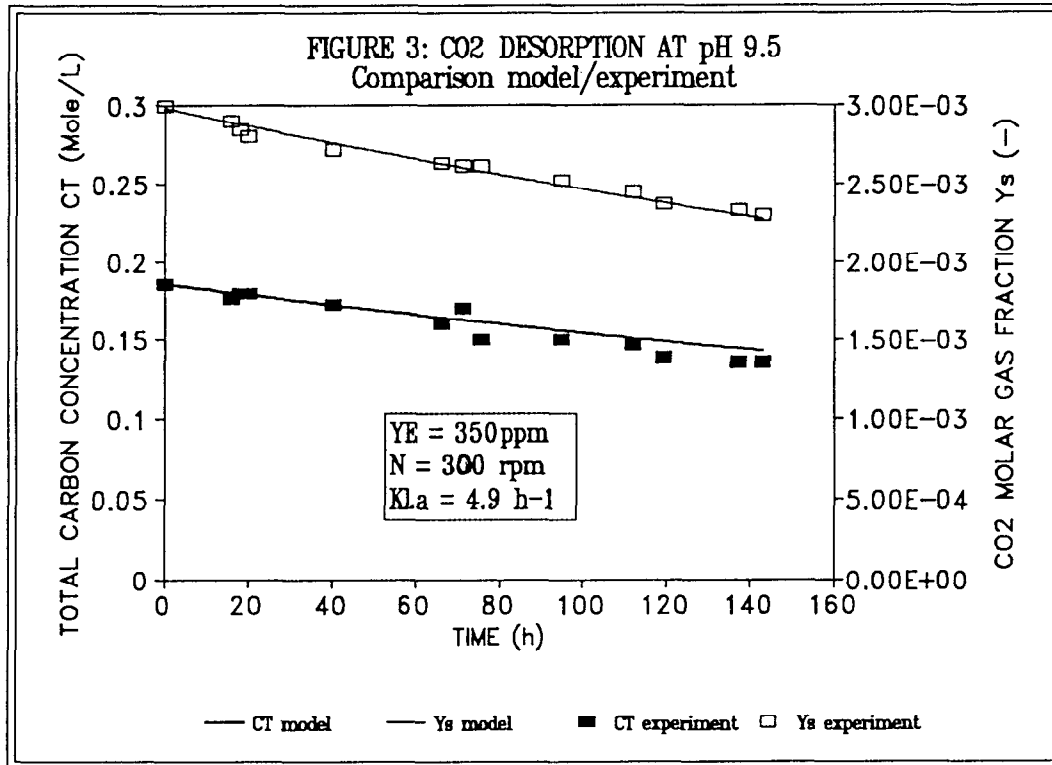
If the observation described by equation (23) is no longer satisfied, this entails that the volumetric mass transfer coefficient $K_L a$ has a low value, and in this case it may appears a enhancement of physical transfer rate by chemical reaction of CO₂ with OH⁻ at high pH.

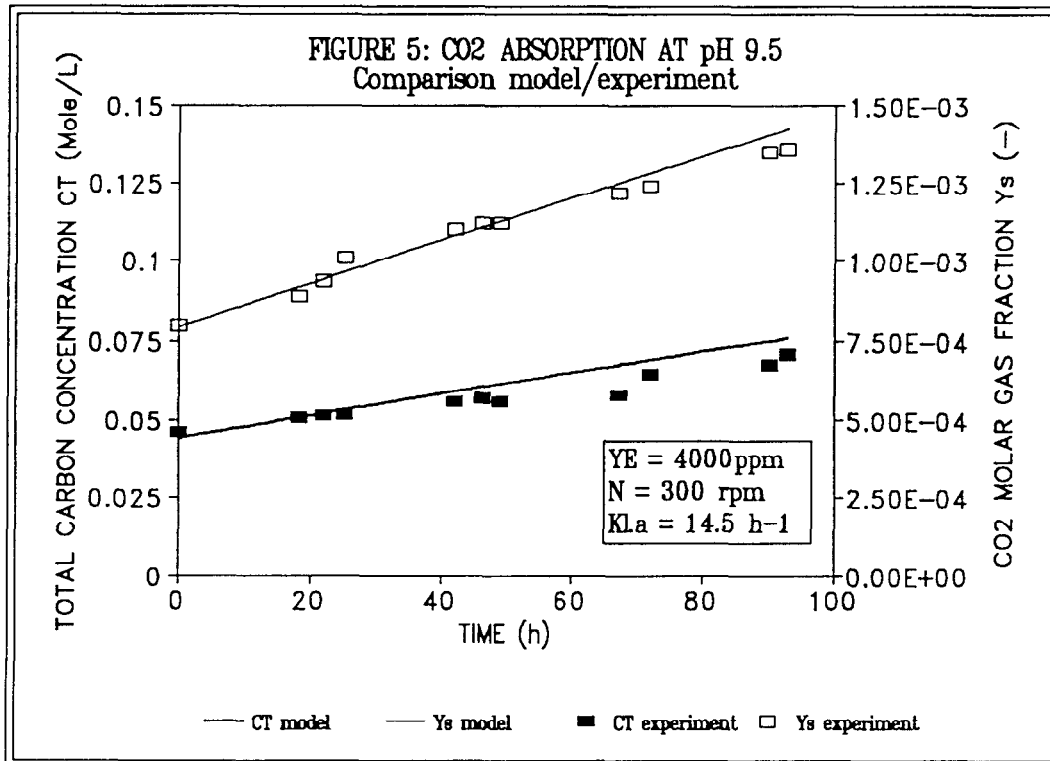
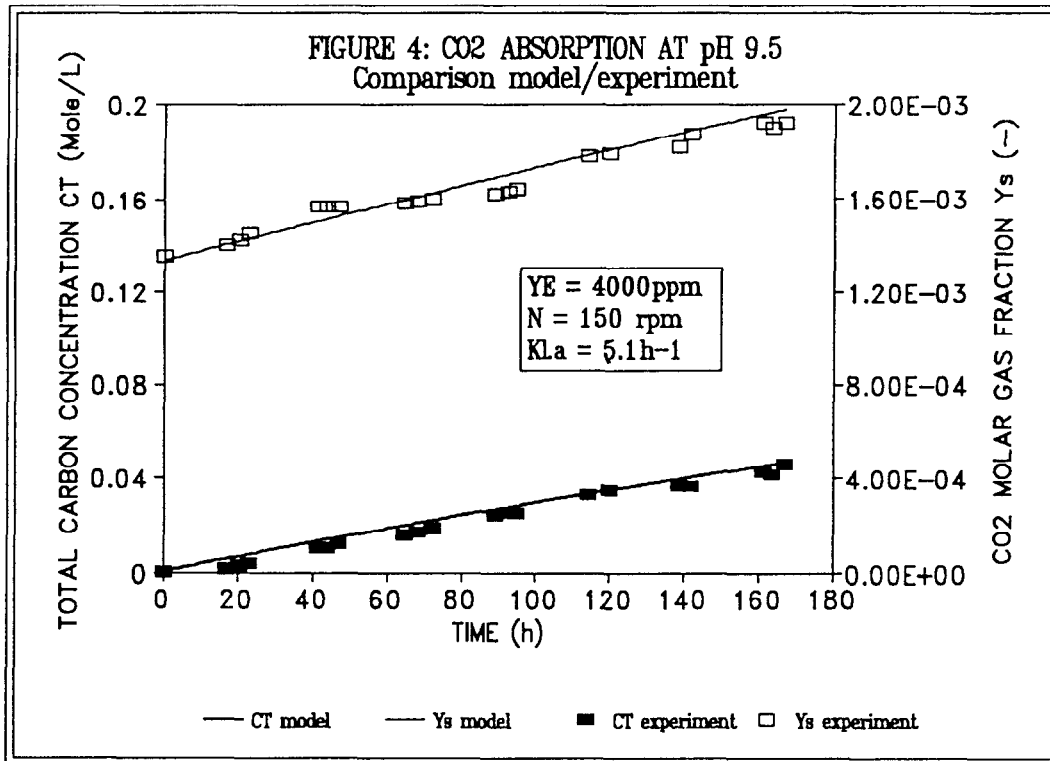
4.3.2- Results of CO₂ absorption and desorption experiments. Determination of $K_L a$ values.

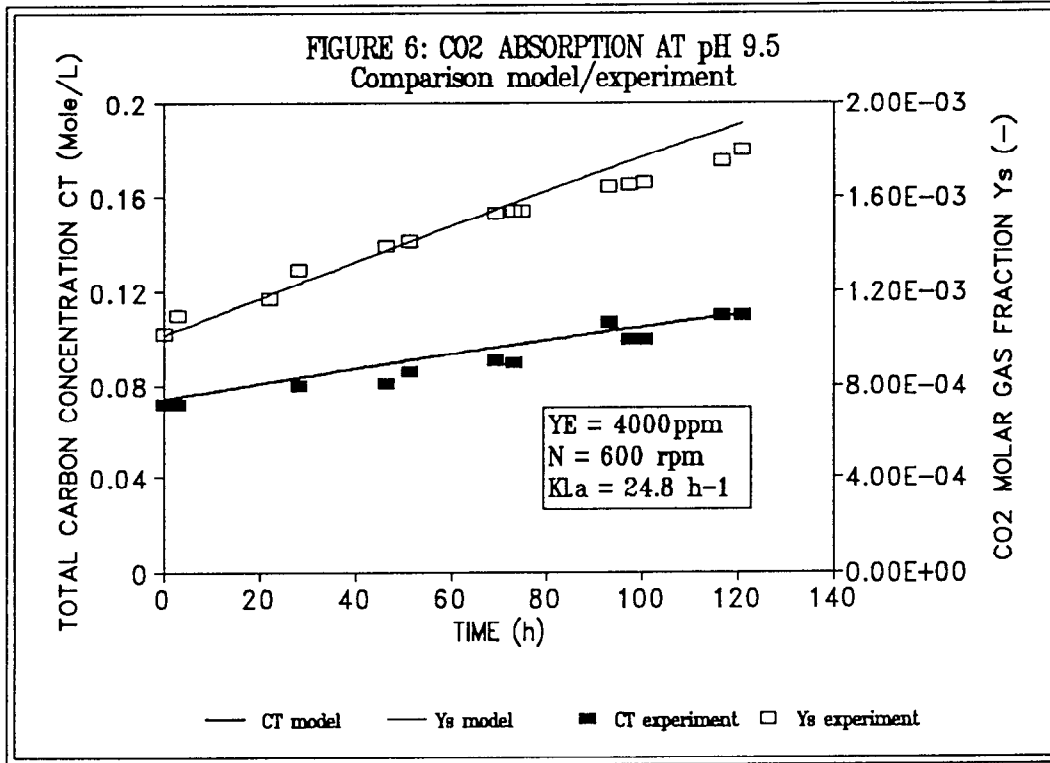
For the CO₂ absorption and desorption experiments at pH 9.5 and 36°C described in the first part of this TN, and for each rotation speed (i.e. 300 and 1000 rpm for desorption experiments; 150, 300 and 600 rpm for absorption experiments), the $K_L a$ values have been determined using the complete model given by equations (14), (17-18) and (22) from a Gauss Newton algorithm for identification procedure.

The effect of ionic strength on the CO₂ solubility in the medium has been taken into account by the predictive model of SCHUMPE (1993). It must be pointed out that we have used equation (22) that involves the hypothesis of plug flow for the gas phase in the reactor. This hypothesis has been indeed verified by independent experiments and moreover this leads to better simulations than the perfectly mixed model.

The simulations obtained from this model in absorption and desorption experiments are given in Figures 3-6 for different rotation speeds and compared to experimental results. In all cases, these figures show a good adequation between the model and experimental data. Nevertheless, special attention have to be paid that the use of perfectly mixed model for the gas phase (equation 19) provides simulations of poor quality with identified $K_L a$ values varying in a factor of 3 compared to the values obtained with the plug flow model.







The identified values for CO₂ volumetric mass transfer coefficients $K_L a$ versus the different rotation speeds are given in Table 1 (the standard deviations have been calculated from a 95% confidence interval).

These values may be compared with calculations of O₂ $K_L a$ on the reactor from the correlation proposed by CORNET (1992) and assuming the current correction for CO₂ $K_L a$ values (ROYCE and THORNHILL, 1991):

$$K_L^{CO_2} a = K_L^{O_2} a \left[\frac{D_{CO_2}}{D_{O_2}} \right]^{2/3} \quad (26)$$

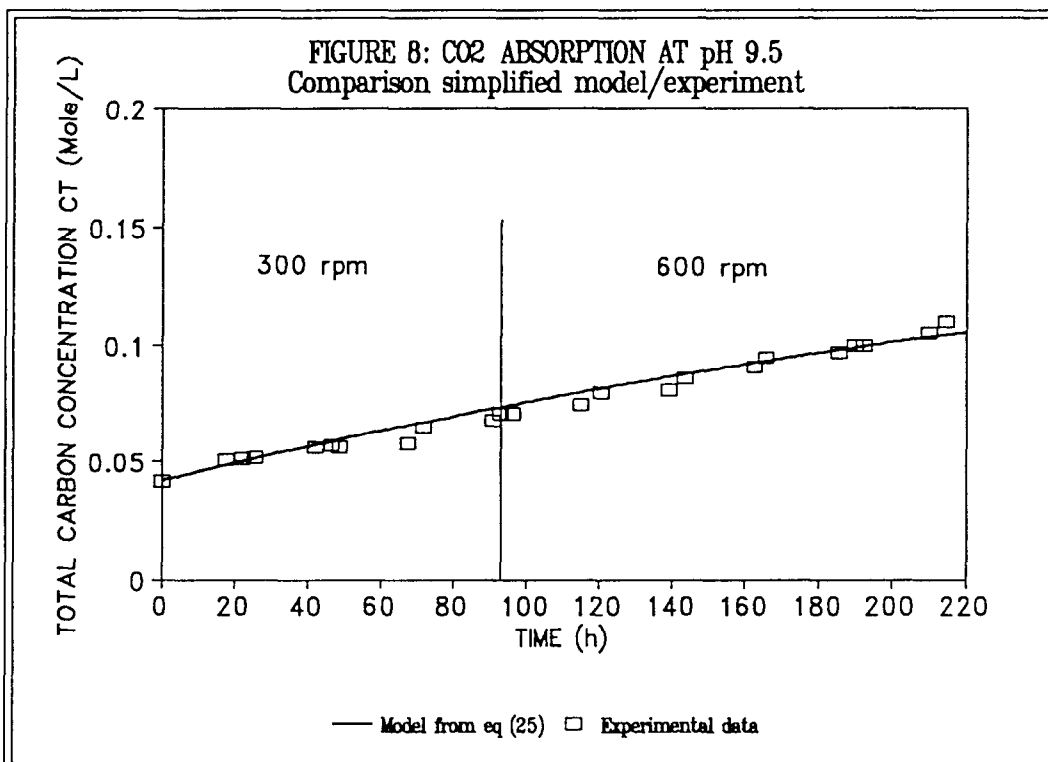
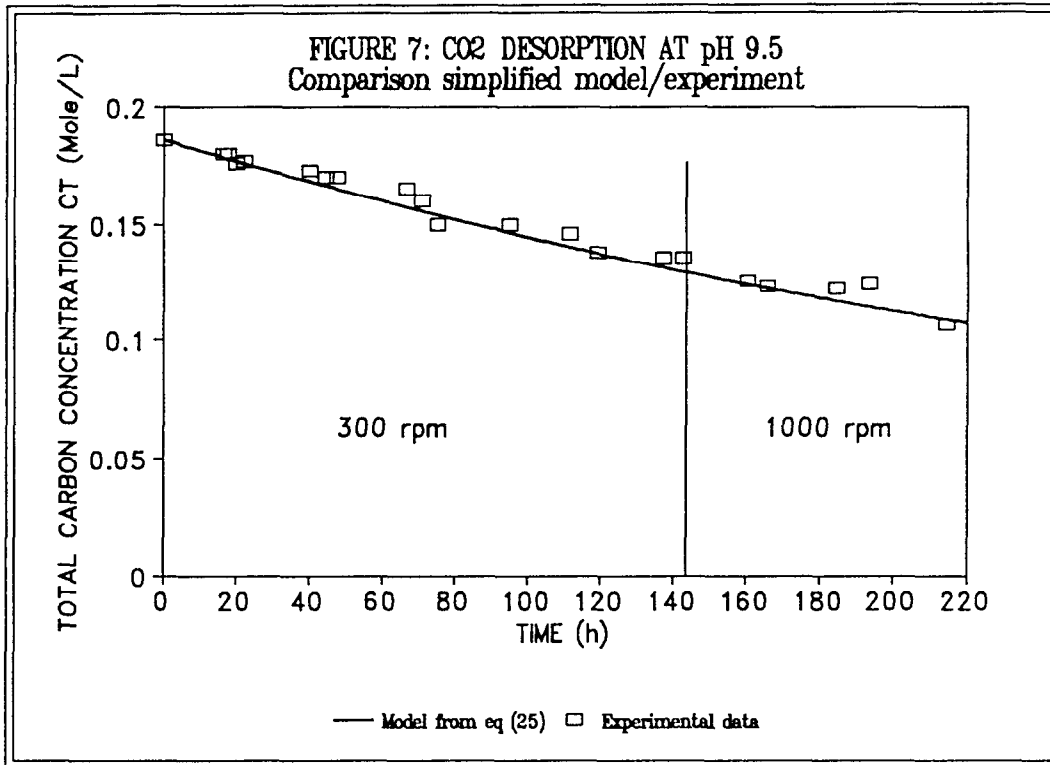
where D_i is the diffusion coefficient of species i in the liquid phase of the reactor.

Rotation speed N (rpm)	K _L a values calculated from correlation (h ⁻¹)	K _L a values identified from experimental results (h ⁻¹)
150	2.1 ± 0.5	5.1 ± 0.3
300	7 ± 2	14.5 ± 0.8 (a) - 4.9 ± 0.3 (d)
600	26 ± 5	25 ± 1

Table 1: Comparison between identified experimental values of K_La and K_La values calculated from the correlation of CORNET (1992) and from equation (26), for different rotation speeds. (a) = absorption experiment. (b) = desorption experiment.

It appears that values determined from the CO₂ experiments presented in this TN are higher than the correlation values, except at high rotation speed (600 rpm, the K_La value at 1000 rpm has not been determined because too few experimental data were available). This increase of CO₂ K_La for low rotation speeds may result in the enhancement of CO₂ transfer flux by chemical reaction, but this must be verified by further experiments at a pH where no enhancement is possible (pH lower than 7). In the same way, the difference observed in the K_La value at 300 rpm between the CO₂ desorption experiment and CO₂ absorption experiment could imply the same phenomenon of enhancement by reaction or a more complex problem not still identified. This problem is currently under investigation at the laboratory.

Figures 7 and 8 present comparisons between experimental data and the simplified model for total carbon C_T given by equation (25). This comparison has been made only for rotation speeds equal to 300 rpm or higher because, as previously discussed this model applies only if K_La value was sufficiently high. It appears that equation (25) provides good results for the C_T time course simulation in this domain of rotation speed. At the opposite, this simplified model for C_T does not apply for lower speeds as, for example, 150 rpm. Moreover, this model never gives acceptable results on the CO₂ molar fraction in gas phase and does not provide K_La values because it is independent of this parameter.



4.3.3- Calculation of the bicarbonate and carbonate concentrations in the liquid phase:

All the conclusions presented in this TN from the simplified approach of paragraph 4.3.1 using the total carbon mass balance equation remain valid if the complete system of equations (15) was used.

In this case, we have only to determine the species CO₂, HCO₃⁻ and CO₃²⁻ from the knowledge of total carbon concentration C_T. As previously discussed, it is easily done if the medium is considered as a dilute solution. So, the activity coefficients tend to 1 leading to:

$$\begin{cases} C_{\text{CO}_2} = \frac{C_T}{K} & (16) \\ C_{\text{HCO}_3^-} = \frac{K_1 C_{\text{CO}_2}}{10^{-\text{pH}}} \\ C_{\text{CO}_3^{2-}} = \frac{K_3 C_{\text{HCO}_3^-}}{10^{-\text{pH}}} \end{cases}$$

At the opposite, if the medium is not considered as ideal, that is generally the case, the proportions of CO₂-HCO₃⁻-CO₃²⁻ are different, and the calculation of activity coefficients is necessary in order to satisfy the system of equations (15). These activity coefficients γ_i may be calculated using a PITZER model modified by EDWARDS *et al.* (1978) or using a ULPDHS model developed in our laboratory (ACHARD, 1992).

This approach is actually under investigation, because it must be kept in mind that most of cyanobacteria uses HCO₃⁻ as a carbon source and in order to modelize the coupling between CO₂ transfer and HCO₃⁻ consumption by microorganisms, a good accuracy on the HCO₃⁻ concentration prediction is necessary.

CONCLUSION.

The study of CO₂ mass transfer at high pH in complex media of photobioreactors appears as a complicated unsteady-state problem which must be studied and modelized as a prerequisite step to the study of the coupling between nonstationary CO₂ mass transfer, linked to bicarbonate production by reaction and HCO₃⁻ consumption by photosynthetic microorganisms.

This requires to establish detailed knowledge models including the hydrodynamics of gas and liquid phases into the reactor in order to have good simulations of experimental results and to have accurate CO₂ K_La values which may vary in a factor of 3 if unsatisfactory hypotheses are made on the mass transfer (hydrodynamics, kinetics, equilibria and enhancement).

The results obtained have shown that the time constant for CO₂ transfer in media at elevated pH was very high, depending mainly of the pH value of the medium and of the ratio G/V_L , i.e. of the aeration conditions inside the reactor.

The CO₂ $K_L a$ values obtained show that for pH higher than 9 and low rotation speeds, a phenomenon of transfer enhancement by chemical reaction may appears. This point is actually under investigation as even so the problem of activity coefficients calculation in electrolyte solutions.

This should lead to establish a robust knowledge model as a preliminary step in studying the very complex problem of photosynthetic microorganisms limitation by the carbon source in photobioreactors.

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NOTATIONS

a	Exchange area by unit volume (m ⁻¹)
a _i	activity of species i (mole.kg ⁻¹ or dimensionless)
C _i	Concentration of species i (mole.m ⁻³)
D	Dilution rate (h ⁻¹)
D _i	Diffusion coefficient of species i in the liquid phase (m ² .s ⁻¹)
G	Molar flow rate (mole.h ⁻¹)
H	Henry's constant (m ³ .Pa ⁻¹ .mole ⁻¹)
K _i	Equilibrium constant (dimensionless)
K _e	Ionic product for water (dimensionless)
K _s	Solubility product for CaCO ₃ (dimensionless)
K _L a	Volumetric coefficient of transfer (h ⁻¹)
k _i	Kinetic rate constant for reaction i (depend of the kinetic order reaction)
m _i	Molality of species i (mole.kg ⁻¹)
N _i	Gas-liquid mass flux for the species i (mole.m ⁻² .h ⁻¹)
P, P _T	Total pressure in the reactor (Pa)
p _i	Partial pressure of species i (Pa)
R	Ideal gas constant (J.mole ⁻¹ .K ⁻¹)
r _i	Volumetric reaction rate for species i (mole.m ⁻³ .h ⁻¹)
T	Temperature (K)
t	Time (h)
V	Volume (m ³)
y _i	Molar gas fraction of species i (dimensionless)

Subscripts:

G	Relative to the gas phase
L	Relative to the liquid phase

Superscripts:

E	Relative to the incoming flow of the reactor
S	Relative to the outgoing flow of the reactor
0	Relative to initial conditions
*	Relative to gas-liquid equilibrium

Greek letters:

γ _i	Activity coefficient (m ³ .mole ⁻¹ or dimensionless)
φ _i	Fugacity coefficient (dimensionless)

APPENDIX**ABSTRACT of TN 19.4****INTRODUCTION.**

When microorganisms such as the cyanobacterium *Spirulina platensis* are cultivated in photobioreactors (PBR), it may occur two main physical limitations on growth kinetics:

- the limitation by the available radiant light energy inside the reactor which has been investigated in technical notes TN 19.1- TN 19.3. This situation is always encountered in the MELiSSA loop.

- the limitation by the CO₂ transfer rate and by the disponibility in the carbon source inside the reactor (i.e. the bicarbonate ion HCO₃⁻ for most of the cyanobacteria). In this last case, dynamic and steady-state physical and biological phenomena are strongly intricated. This situation may be encountered in the MELiSSA loop, specially during transient phases.

At high pH values ($8 < \text{pH} < 10$), the total dissolved carbon (CO₂ + HCO₃⁻ + CO₃²⁻) is essentially composed by bicarbonate HCO₃⁻ and carbonate CO₃²⁻ ions. For example, at pH 9.5, the concentration in carbonate and bicarbonate ions is about 2000 fold higher than the CO₂ concentration. This is an important particularity compared to the classical approach for the oxygen transfer rate analysis, because this creates an important buffer reserve in total dissolved carbon in PBR culture media. Then, this entails that the well-known hypothesis of non-accumulation of dissolved gases in the medium is no longer satisfied and the mass balance equations must be written in the general case, with an accumulation term in the liquid medium. This leads to solve nonstationary differential equations which may be simplified to algebraic equations in pseudo steady-state following the operating conditions.

Additionally, the cyanobacteria are known to concentrate the intracellular bicarbonate if the extracellular concentration is low. This concentration proceeds against the HCO₃⁻ concentration gradient but enables to maintain the activity of the Rubisco at a high level. Nevertheless, this active transport consumes a part of the produced ATP and then the energetic yield of photosynthesis decreases, giving lower growth rates.

The study of the limitation by the carbon source and its modelling inside PBR then appears as a complex problem since informations must be obtained at three levels:

- the study of the dynamic CO₂ gas-liquid transfer with eventually the limitation by the CO₂ transfer rate;
- the study of chemical equilibria in complex media with high ionic strength in order to calculate the CO₂-HCO₃⁻-CO₃²⁻ concentrations in the culture medium;
- the study of HCO₃⁻ limiting concentrations on the physiology and the metabolism of *S. platensis* in order to postulate kinetic law.

Moreover, the general modeling of these coupled phenomena requires the mass balance on O₂ and CO₂ in the gas phase to be performed to complete the previous informations.

Two main cases may then be examined for the CO₂ transfer:

1- Nonstationary transfer rate:

In this case, it exists a positive or negative accumulation of total dissolved carbon in the liquid phase. The CO₂ dissolved concentration is far to the thermodynamic equilibrium and the microorganisms can never be in limiting conditions by the CO₂ transfer rate. However, if the

bicarbonate concentration is low, a biological mineral limitation by the carbon source may appear.

2- Pseudo steady-state transfer rate:

In this case, if the microorganisms are not limited by the CO₂ transfer rate, this means that the CO₂ dissolved concentration is close to the thermodynamic equilibrium $C_{CO_2}^*$ and the molar volumetric rate of CO₂ uptake is $r_{CO_2} = r_{HCO_3^-} = k_L a (C_{CO_2}^* - C_{CO_2})$ with a dissolved carbon dioxide concentration fixed by the microorganisms and equal to $C_{CO_2} = C_{CO_2}^* - \frac{r_{CO_2}}{k_L a}$ (if the gas phase of the reactor is assumed as perfectly mixed). Thus the CO₂ transfer rate is purely diffusional. This case is commonly encountered when the pH of the medium is controlled at a given level by supplying the medium with CO₂. These phenomena do not exclude the appearance of a mineral limitation by the bicarbonate concentration.

It may be also possible that the microorganisms are limited by the physical CO₂ transfer rate. So, the growth rate is fixed by the technological characteristics of the apparatus and the molar volumetric rate of CO₂ uptake is equal to $r_{CO_2} = r_{HCO_3^-} = k_L a C_{CO_2}^*$.

The work described in the technical note 19.4 concerns the physical stage for the CO₂ transfer in PBR, i.e. the establishment of general mass balances on the gas and liquid phases and their simplification in comparison with results obtained on CO₂ absorption and desorption experiments in PBR.

EXPERIMENTAL PART.

A new experimental method using GPC technique has been developed for the assessment of the bicarbonate (HCO₃⁻) concentration in the reactor medium. It enables to measure 10⁻⁶ mole HCO₃⁻/l with an accuracy of ±10%. For high bicarbonate concentrations, this method was compared with the classical acid-base titration.

The CO₂ in gas phase has been determined with an infrared gas analyzer allowing to measure a molar differential fraction of CO₂ with only ±5% error.

These experimental determinations on gas and liquid phases of the reactor enable to perform CO₂ absorption and desorption experiments and to record the time course of the main variables involved in the process, i.e. the CO₂ molar fraction in gas phase and the CO₂-HCO₃⁻-CO₃²⁻ concentrations in the liquid phase. Different absorption/desorption experiments have been performed at constant pH = 9.5 and constant temperature = 36°C, with different rotation speeds of the stirrer in the 7 l-reactor already used for kinetic experiments. For all the experiments, the percentage of total carbon recovery (PRC) was always satisfactory and close to 100% ± 10%, which indicates that the main species studied on the process have been identified and correctly measured.

MODELING CO₂ MASS TRANSFER AT HIGH pH IN COMPLEX MEDIA OF PBR.

Modeling CO₂ mass transfer at high pH in PBR appears as a complex problem which requires to investigate and solve the following problems:

- the CO₂ gas-liquid equilibrium in complex electrolytic media;
- the reactional scheme of CO₂ in aqueous solutions (kinetic approach or thermodynamic equilibrium approach?);

- the formulation of conservative laws for gas and liquid phases following the previous hypothesis and the pseudo steady-state hypothesis;
- the choice of a hydrodynamic flow model for gas and liquid phases into the reactor;
- the calculation of activity coefficients in nonideal electrolytes mixtures.

In the proposed model, the reactional scheme adopted shows that it is possible to consider the CO₂-HCO₃⁻ and HCO₃⁻-CO₃²⁻ thermodynamic equilibria always satisfied in the liquid phase. The liquid phase can then be described by only one differential equation and 2 algebraic equations instead of 3 differential equations (CO₂-HCO₃⁻-CO₃²⁻). Moreover, a simplified approach has been used in this work in order to elude the complex problem of activity coefficients calculation still under investigation, without reducing the level of generality of the mass transfer model. For this, we introduced a pseudo-species total carbon C_T (C_T = CO₂ + HCO₃⁻ + CO₃²⁻), so that no hypothesis is necessary for activity coefficients calculation because only one species exists in the liquid phase.

The retained model does not assume further simplification because the CO₂ mass transfer has shown a high sensitivity to simplifications (at the opposite of O₂ transfer), especially on the gas phase.

The proposed model takes also into account the CO₂ solubility in nonideal media and uses the plug flow hypothesis for the gas phase. This feature appears as a very important fact of the model and has been independently verified. This model presents one degree of freedom that is the CO₂ volumetric mass transfer coefficient K_La which has to be identified from experimental data on the CO₂ molar fraction in the outgoing gas flow of the reactor and on the total dissolved carbon concentration in the liquid phase of the reactor.

The simulations obtained with this model agree closely with the experimental results for CO₂ absorption or CO₂ desorption experiments, for all the rotation speeds tested. The K_La values obtained compared for absorption/desorption experiments and from a correlation already established on the reactor with O₂ transfer should indicate an enhancement of the physical transfer by chemical reaction. This fact will be verified by further investigations.

Furthermore, it must be noticed that the results obtained on the liquid phase of the reactor have shown that in most cases of transfer (K_La sufficiently high, i.e. rotation speeds higher than 300 rpm), it was possible to assume a thermodynamic equilibrium for CO₂ between the liquid phase and the gas phase in the outgoing flow of the reactor. In this case the model simplifies and presents simple analytical solution for C_T, which is independent of K_La. It is then easily established that the time constant for CO₂ transfer rate depends only of pH and aeration flow rate of the reactor.

In future work, it will be necessary to establish a methodology in calculating the activity coefficients in order to distinguish between CO₂, HCO₃⁻ and CO₃²⁻ species in the liquid phase of the reactor. It must then be kept in mind that most of cyanobacteria uses HCO₃⁻ as a carbon source and in order to modelize the coupling between CO₂ transfer and HCO₃⁻ consumption by microorganisms, a good accuracy on the HCO₃⁻ concentration prediction is required.

CONCLUSION.

The study of CO₂ mass transfer at high pH in complex media of PBR appears as a complicated unsteady-state problem which must be studied and modelized as a prerequisite step to the study of coupling between nonstationary CO₂ mass transfer, linked to bicarbonate production by reaction and bicarbonate consumption by photosynthetic microorganisms.

This requires to establish detailed knowledge models including the hydrodynamics of gas and liquid phases into the reactor in order to have good simulations of experimental results and to have accurate CO₂ K_La values which may vary in a factor of 3 if unsatisfactory hypotheses are made on the mass transfer.

The results obtained have shown that the time constant for CO₂ transfer in media at elevated pH was very high, depending mainly of the pH value of the medium and of the aeration conditions inside the reactor.

The CO₂ K_La values obtained show that for pH higher than 9 and low rotation speeds, a phenomenon of transfer enhancement by chemical reaction may appear. This point is actually under investigation as even so the problem of activity coefficients calculation in electrolyte solutions.

This should lead to establish a robust knowledge model as a preliminary step in studying the very complex problem of photosynthetic microorganisms limitation by the carbon source in PBR.