ABSORPTION IN PACKED AND BUBBLE COLUMNS

Fortunato Ritorto

ECOPROGETTI SRL, C. Susa 6, 10098 Rivoli, Italy

E-mail address: aria@ecoprogettisrl.it

April 2025

ABSTRACT

The purpose of this monograph is to deal with the absorption of gases in liquids within the ecological applications, especially if mass transfer is accompanied by chemical reaction.
Both packed towers and bubble columns are considered, the former for the removal of gas-phase pollutants present in low concentrations and fixed by suitable reagents added to the scrubbing liquid, the latter for pollutants which are in the liquid phase, while reagents are in the gas phase (for instance ozone for oxidation of surfactants and dyes, or CO_2 for basic waste water neutralization) .
Theoretical formulas are followed by several numerical examples to allow designers to easily come up to the final sizing of process equipment.
For packed towers the unsteady-state operation is also dealt with, to face the case of periodical replacement and disposal of the scrubbing liquid.
Moreover, the actual possibility of solvent abatement using only water is considered.
Finally, the particular problem of CNCl desorption within the process of HCN removal, using NaClO and NaOH, is dealt with in the Appendix.

Keywords: Mass transfer with chemical reaction; Solvent absorption; Bubble columns; HCN oxidation; Ozone oxidation; Neutralization with CO_2

INTRODUCTION

Gas absorption accompanied by chemical reaction has been the subject in the past of exhaustive treatment from the theoretical point of view (excellent are the books by Danckwerts [10] and Doraiswamy-Sharma [12]), but scarce are the publications concerning the practical application of those principles, which is however very useful to support chemical engineers in the design of process equipment (such as packed and bubble columns). Often such equipment is sized through rules of thumb or perfunctory indications, based at most on practical experience gained in quite similar applications.

The main purpose of this monograph is to trace the path from theoretical formulas up to the final sizing, showing how to find the necessary data and explaining in detail the calculation procedure, through the development of several numerical examples.

In particular we will consider absorption applications in the ecological field of air and water pollution control, in which the author had the occasion of applying the aforesaid procedure (in more than one hundred installations).

Pollutant concentrations, in the ecological field, are usually rather low, which has greatly simplified the theoretical treatment and allowed to disregard accompanying phenomena of temperature rise.

We deemed it opportune, in par. 1.3, to sum up the principal methods available for the calculation of mass-transfer coefficients in columns with random packing, coming up to the most recent models [4, 5] which apply even to the fourth generation packing. The relevant expressions have been worked out in order to make them directly and easily usable for pollutant absorption in dilute aqueous solutions (such as the ones usually met in pollution control equipment).

In par. 1.1 and 1.4 we deal with the problem of solvent absorption in water, mainly to point out the ineffectiveness of certain wonder-working solutions that even nowadays some manufacturers propose.

In par. 1.1.3 we also face the problem, poorly developed in the literature, of unsteady-state operation of packed towers, which is of interest for all the factories that have no waste water treatment plant and so do not make a continuous bleed, but periodically replace (and dispose of) the scrubbing liquid.

In par. 2.5 and in the Appendix we then deal with HCN absorption, which, in case of simultaneous use of NaClO and NaOH as reagents, presents an interesting case (not yet faced in the literature) of desorption of CNCl, which is a toxic intermediate reaction product.

Bubble columns have been considered for two particular applications.

The former (in par. 3.2) is the ozone oxidation of surfactants and dyes, which are often present in the waste waters of the textile industry.

The latter (in par. 3.3) is the neutralization, with the CO_2 contained in boiler flue gases, of strongly basic waste waters, as the ones generated by cotton mercerization with NaOH.

In both cases the necessary equipment has been sized by coupling the hydrodynamics and mass-transfer equations with the chemical kinetics ones.

The problem of neutralization of basic waters has been faced in chapter 4 also with the use of an agitated tank in which a certain number of aerators are immersed, of the type commonly used for mixing and oxygenation of waste water in biological oxidation plants.

1. ABSORPTION OF POLLUTANTS IN PACKED COLUMNS WITHOUT CHEMICAL REACTION

1.1. GENERAL EXPRESSIONS

1.1.1. Steady-state conditions

The equilibrium relationship, for low concentrations of a pollutant in the liquid and gaseous phases (as it is almost always the case in the ecological field), is:

$$y = Hx \tag{1.1}$$

where y and x are respectively the concentrations of the pollutant in the gaseous phase (mg/m³) and in the liquid phase (mg/m³) and H is the Henry constant (for air/water/solvent equilibria, at 25°C and 1 atm, we have e.g. $H = 2.2 \cdot 10^{-4}$ for ethanol and $H = 6.9 \cdot 10^{-3}$ for ethyl acetate).

The mass balance of the upper part of the column, above sect. A (this balance determines the equation of the operating line), is:

$$G(y - y_o) = L(x - x_i) \tag{1.2}$$

where G and L (m³/sec/m²) are the specific flow rates (referred to the column section) of air and washing liquid (see the flowsheet of Figure 1).

Mass transfer in the differential column volume of height dz is given by:

$$-G\,dy = K_G a_e\,(y - y_e)\,dz$$

where K_G (m/sec) is the mass transfer coefficient (overall, referred to the gas phase), a_e (m²/m³) is the specific effective interfacial area and y_e is the concentration in the gas phase in equilibrium with the concentration x in the liquid mass.

By integrating the above differential equation, we get the bed height Z ($K_G a_e$ does not vary along the column because the gas and liquid flow rates remain practically unchanged).

$$Z = \frac{G}{K_G a_e} \cdot \int_{y_o}^{y_i} \frac{dy}{y - y_e} = H_{OG} \cdot N_{OG} \tag{1.3}$$

where N_{OG} (the value of the integral) is the number of transfer units and

$$H_{OG} = \frac{G}{K_G a_e}$$

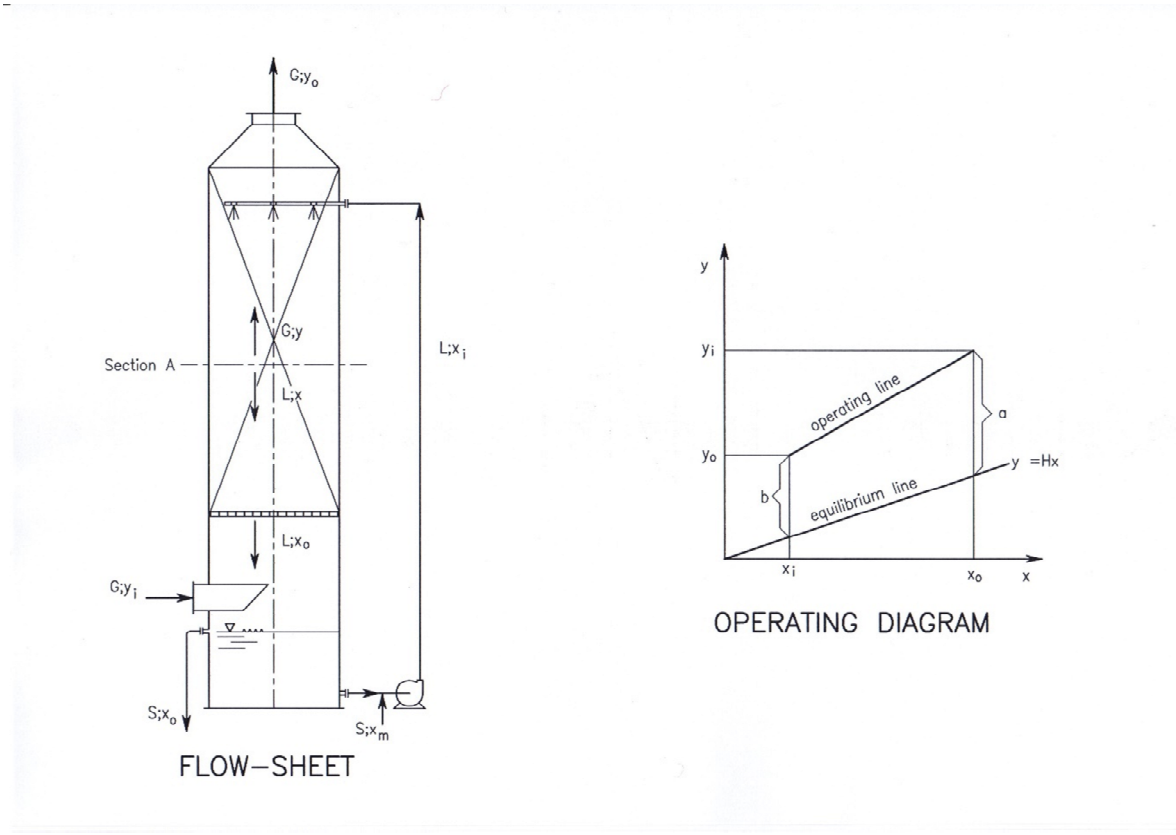

Fig. 1. Pollutant absorption in packed columns

is the height of a gas transfer unit, which can be expressed as:

$$H_{OG} = H_G + \lambda H_L = H_G + \frac{HG}{L} H_L \qquad (1.4)$$

H_G and H_L are the individual contributions to H_{OG} due respectively to the mass transfer resistance in the gas and in the liquid phase.

In the integral, the difference $y - y_e$ must be interpreted for the same x.

We then have:

$x = y_e/H$ (from (1.1))

$x = x_i + (G/L)(y - y_o)$ (from (1.2))

$y_e/H = x_i + (G/L)(y - y_o)$ (from above)

$y - y_e = (1 - HG/L)y + (HG/L)y_o - Hx_i$ (getting y_e from above)

Replacing the last expression in the integral and solving it, we get:

$$Z = H_{OG}\frac{1}{\left(1-\frac{HG}{L}\right)}\cdot \ln\frac{\left(1-\frac{HG}{L}\right)y_i + \frac{HG}{L}y_o - Hx_i}{y_o - Hx_i}$$

$$Z = H_{OG}\frac{1}{\left(1-\frac{HG}{L}\right)}\cdot \ln\frac{y_i - Hx_i - \frac{HG}{L}(y_i - y_o)}{y_o - Hx_i} \tag{1.5}$$

$$Z = H_{OG}\frac{1}{\left(1-\frac{HG}{L}\right)}\cdot \ln\frac{y_i - Hx_o}{y_o - Hx_i} \tag{1.6}$$

The last expression is obtained by taking into account the mass balance of the entire bed:

$$G(y_i - y_o) = L(x_o - x_i) \tag{1.7}$$

From this balance and from the one relating to the column bottom, namely:

$$Lx_o + Sx_m = Lx_i + Sx_o$$

where *S* is the purge and make-up flow rate, referred to the column section, it is easy to get

$$x_i = x_m + \frac{L-S}{S}\cdot\frac{G}{L}(y_i - y_o)$$

Substituting this expression to x_i in (1.5) we obtain (also introducing the parameters $r = S/L$, relative to the fraction of purged liquid, and $\eta = 1 - \frac{y_o}{y_i}$, absorption efficiency of the column):

$$Z = H_{OG}\frac{1}{\left(1-\frac{HG}{L}\right)}\cdot \ln\frac{1 - \frac{Hx_m}{y_i} - \eta\frac{HG}{Lr}}{1 - \frac{Hx_m}{y_i} - \eta\left(1 + \frac{HG}{L}\frac{1-r}{r}\right)}$$

from which

$$\eta = \left(1 - \frac{Hx_m}{y_i}\right)\cdot\frac{1 - \exp\left[\left(\frac{HG}{L} - 1\right)\frac{Z}{H_{OG}}\right]}{\left(1 + \frac{HG}{L}\frac{1-r}{r}\right) - \frac{HG}{Lr}\cdot\exp\left[\left(\frac{HG}{L} - 1\right)\frac{Z}{H_{OG}}\right]} \tag{1.8}$$

In the case of liquid not even partially recirculated, but completely discharged at the column bottom, it is obviously $r = 1$. If the make-up liquid does not contain the pollutant, then $x_m = 0$. For the efficiency calculation it is necessary to evaluate H_{OG} by (1.4) and previously H_G and H_L (which depend mainly on the type of packing material).

It is possible however to make some general considerations, valid regardless of the bed height and the packing type.

In (1.6), the numerator and denominator of the logarithm argument are respectively the segments *a* and *b* in the operating diagram of Figure 1.

Taking into account the usual values of *G* and *L* for a packed column (e.g. *G* = 1.9÷2.5 m/sec and *L* = 20 m³/h/m² = 5.556 $\cdot 10^{-3}$ m/sec), the slope of the operating line (equal to *L/G*) turns out to be greater than the slope of the equilibrium line (equal to *H*) in the case of ethanol and smaller in the case of ethyl acetate.

In the first case (being $1 - HG/L > 0$), for the reality of *Z* it must be $y_o - Hx_i > 0$ (otherwise the logarithm argument is negative; in "geometric" terms it is equivalent to saying that segment *b*, which is anyway < *a*, must be > 0).

This implies the condition $x_i < y_o/H$: if e.g. y_o = 20 mg/m³, it must be x_i < 91,000 mg/m³ (91 ppm).

In the second case ($1 - HG/L < 0$), it must be $y_i - Hx_o > 0$ (in "geometric" terms it is equivalent to saying that segment *a*, which is anyway < *b*, must be > 0).

Being for (1.7) $x_o = x_i + (G/L)\,(y_i - y_o)$, that means $y_i - Hx_i - (HG/L)\,(y_i - y_o) > 0$, that is $x_i < y_i/H - (G/L)\,(y_i - y_o)$.

Since it must still be $x_i > 0$, it follows that one cannot claim to have $y_o < [1 - L/(HG)]y_i$.

Therefore the efficiency $\eta = 1 - y_o/y_i$ has however a maximum value equal to *L*/(*HG*) (that is 32% for ethyl acetate, with G = 2.5 m/sec; it can rise to 81% if *G* is lowered to 1 m/sec) and this provided that both clean water ($x_i = x_m = 0$ and $S = L$) and a column of infinite height (!) are used for washing.

In practice, if the pollutants are substances with $H > L/G$ (that is $H > 2\div5 \cdot 10^{-3}$), possible efficiencies are certainly poor, regardless of the bed height and the packing type.

In this regard, Table 1 shows Henry constants for some of the most common solvents and pollutants [1].

The values are derived from Sander's list contained in the cited work, with free access on the Internet and including almost 5,000 substances.

The list shows a constant H^{cp} expressed in mol/m^3/Pa (it is the ratio between the concentration in the liquid phase in mol/m^3 and the partial pressure in the gas phase in Pa). Our constant *H* is obtained by multiplying H^{cp} by 2479 and inverting the result (for example for hydrogen sulphide $H^{cp} = 1.0 \cdot 10^{-3}$ mol/m^3/Pa becomes *H* = 0.40).

Table 1. Henry constant (mg/m^3_g : mg/m^3_l , at 25°C and 1 atm)

Ethyl acetate	**$6.9 \cdot 10^{-3}$**	**n-Butanol**	**$3.1 \cdot 10^{-4}$**
n-Butyl acetate	**$1.3 \cdot 10^{-2}$**	**Isobutanol**	**$4.1 \cdot 10^{-4}$**
Isobutyl acetate	**$1.8 \cdot 10^{-2}$**	**Acetone**	**$1.6 \cdot 10^{-3}$**
Ethanol	**$2.2 \cdot 10^{-4}$**	**MEK**	**$2.3 \cdot 10^{-3}$**
Propanol	**$3.1 \cdot 10^{-4}$**	**Toluene**	**0.26**
Isopropanol	**$3.1 \cdot 10^{-4}$**	**Xylene**	**0.22**
Phenol	**$1.6 \cdot 10^{-5}$**	**Formaldehyde**	**$1.3 \cdot 10^{-5}$**
Hydrochloric acid	**$2.7 \cdot 10^{-5}$**	**Ammonia**	**$6.8 \cdot 10^{-4}$**
Hydrogen sulphide	**0.40**	**Hydrocyanic acid**	**$3.4 \cdot 10^{-3}$**
Acetic acid	**$1.0 \cdot 10^{-5}$**		

1.1.2. Effective Henry constant

The classical Henry constant (H) so far considered and obtainable from literature sources (named "intrinsic" constant) is related to the substance present in the liquid in the free state. Therefore, in the case of substances that undergo for example dissociation (such as the ones of acid or basic nature), if x stands for the total concentration in the liquid, including the fraction present in the dissociated state, then H must be replaced by the modified Henry constant H^* (named "effective" constant).

This is certainly smaller than H and its value, for acid or basic substances, can be easily obtained.

We begin considering an acid substance AH that dissociates according to the classic mechanism:

$$AH \leftrightarrow A^- + H^+$$

with equilibrium constant K equal to

$$A^- \cdot H^+ / AH = K$$

The substance as a whole in solution (in mol/l) is given by

$$AH_{tot} = AH + A^-$$

and the effective Henry constant is obviously equal to

$$H^* = H \cdot AH / AH_{tot}$$

We immediately derive, from the previous expressions:

$AH_{tot} = AH + AH \cdot K / H^+$ $\quad AH / AH_{tot} = 1/(1+K/H^+)$ and finally

$$H^* = H / (1+10^{pH-pK})$$

If the acid undergoes a double dissociation (as H_2S or H_2CO_3) and therefore has two constants K_1 and K_2, the factor in brackets, which represents the virtual increase in solubility due to dissociation, becomes $(1+ 10^{pH-pK1} + 10^{2pH-pK1-pK2})$.

With a basic substance, such as ammonia, we have:

$NH_4^+ \leftrightarrow NH_3 + H^+$ $\quad NH_3 \cdot H^+ / NH_4^+ = K$ $\quad NH_{3,tot} = NH_3 + NH_4^+$ and therefore

$NH_{3,tot} = NH_3 + NH_3 \cdot H^+ / K$ $\quad NH_3 / NH_{3,tot} = 1/(1+ H^+/K)$ and finally

$$H^* = H / (1+10^{pK-pH})$$

Note that for basic substances the exponent sign of 10 changes, while K always remains the acid dissociation constant K_a ($pK = 9.25$ for ammonia at 25°C).

As a rule, the dissociation of an acid or basic substance in water causes a change in pH (the higher the dissolved amount, the greater the change). This means that the value of H^* comes out to depend on x and therefore H^* is not a true constant. In other words, the dependence of y on x is not linear and therefore none of the formulas of the previous paragraph (not only (1.8), but also (1.4)) are valid.

However, there are two exceptions.

The first is when the pH is kept constant at a preset value, thanks to the addition of a suitable reagent (so that also H^* remains constant): it is the most important case, because it is the most frequent (but we will examine it in more detail in the following paragraphs).

The second exception is when the dissociation is modest, that is when H^*/H remains between, say, 0.95 and 1, so also H^* can be considered constant as H.

For example, in the case of absorption of acid or basic substances in clean and recirculated water, this condition occurs provided that the concentration of the pollutant in the liquid is greater than a generally modest value.

To derive this value, it is sufficient to observe that for the electric neutrality it must be in the case of an acid $A^- = H^+$ and in the case of ammonia $NH_4^+ = OH^- = K_w / H^+$ (where K_w is the ionic product of water, with $pK_w = 14$ at 25°C).

In the first case we have

$$A^- \cdot H^+/AH = (A^-)^2/AH = K \qquad AH_{tot} = AH + (K \cdot AH)^{1/2} \qquad AH/AH_{tot} = 1/[1+(K/AH)^{1/2}]$$

$$H^* = H / [1+(K/AH)^{1/2}]$$

and therefore, to have $H^*/H \geq 0.95$, it must be $AH_{tot} \geq 0.95 \cdot K/(1\text{-}0.95)^2 = 380 \cdot K = 380 \cdot 10^{-pK}$.

In the second case we have

$$NH_3 \cdot H^+ / NH_4^+ = NH_3 \cdot K_w / (NH_4^+)^2 = K \qquad NH_{3,tot} = NH_3 + (NH_3 \cdot K_w / K)^{1/2}$$

$$NH_3 / NH_{3,tot} = 1/[1+(K_w/K/NH_3)^{1/2}] \qquad H^* = H / [1+(K_w/K/NH_3)^{1/2}]$$

and therefore, to have $H^*/H \geq 0.95$, it must be $NH_{3,tot} \geq 0.95 \cdot K_w/K/(1\text{-}0.95)^2 = 380 \cdot K_w/K = 380 \cdot 10^{pK\text{-}pKw}$.

In particular it must be $NH_{3,tot} \geq 380 \cdot 10^{9.25\text{-}14} = 6.76 \cdot 10^{-3}$ mol/l = 115 mg/l.

1.1.3. Unsteady-state conditions

The expressions in paragraph 1.1.1 apply to a tower in steady-state conditions.

However, they do not apply in the initial transient conditions, when, in the presence of a continuous purge immediately activated, the bottom-column volume V contains clean water (just made-up) that gradually loads with pollutant and goes towards the steady-state conditions (reached, as we shall see, in a theoretically infinite, but practically rather short time).

It is therefore interesting to evaluate the rate at which the absorption efficiency and the composition of the liquid vary in this transient phase.

It is also interesting to evaluate how the performance of a tower eventually decays when operated not with a continuous purge, but with a periodic replacement of the washing liquid. This is the typical case of factories that have no waste-water treatment plant and must therefore periodically dispose of the spent liquid and decide how often to do it.

In order to evaluate the trend of the absorption efficiency and of the concentration of pollutants in the bottom-column tank during the start-up phase (starting with clean water), the following mass balance should be drawn up in differential terms:

$$G(y_i - y_o) \cdot dt = Gy_i\eta \cdot dt = Sx_o \cdot dt + V \cdot dx_o$$

The first term represents the absorbed pollutant, which is found only partially in the purge S (and no longer completely, as in the steady-state conditions), while the rest is going to increase the concentration x_o in the bottom tank (which is also the concentration in the purge, but no longer in the liquid leaving the bed).

V is the volume of the tank (also referred to the bed section, as G, L and S).

The column bottom balance around the recirculation pump, considering for simplicity $x_m = 0$, gives $(L - S) \cdot x_o = L \cdot x_i$, or $x_i = (1 - r) \cdot x_o$.

Substituting in (1.5) this value of x_i and bearing in mind that (1.7) in unsteady-state conditions is no longer valid (it would be necessary to consider a value x'_o leaving the bed other than the value x_o in the purge and in the tank), we obtain, going on, an expression of η as a function of x_o, namely:

$$\eta = \eta_o \cdot \left[1 - H(1 - r)\frac{x_o}{y_i}\right]$$

from which

$$x_o = y_i \frac{1-\eta/\eta_0}{H(1-r)} \qquad dx_o = -\frac{y_i/\eta_0}{H(1-r)} \cdot d\eta \qquad (1.9)$$

where

$$\eta_o = \frac{1 - exp\ \left[\left(\frac{HG}{L} - 1\right)\frac{Z}{H_{OG}}\right]}{1 - \frac{HG}{L} \cdot exp\ \left[\left(\frac{HG}{L} - 1\right)\frac{Z}{H_{OG}}\right]}$$

η_o is the efficiency at the starting moment (for $t = 0$), when clean water is present in the tank ($x_o = 0$), and coincides with the value of η given by (1.8) for $r = 1$ and $x_m = 0$.

Replacing in the differential balance the values of x_o and dx_o obtained above (1.9), we get, in a few steps:

$$\left[\left(\frac{1}{\eta_o} + \frac{GH}{L} \cdot \frac{1-r}{r}\right) \cdot \eta - 1\right] \cdot dt = -\frac{V}{\eta_o r L} \cdot d\eta$$

or $$\left(\frac{\eta}{\eta_\infty} - 1\right) \cdot dt = -\frac{V}{\eta_o r L} \cdot d\eta \qquad \text{with} \qquad \eta_\infty = \frac{1}{\frac{1}{\eta_o} + \frac{GH}{L} \cdot \frac{1-r}{r}}$$

where η_∞ is the steady-state efficiency (equal to the one given by (1.8) with the relevant value of r), which is reached asymptotically in a virtually infinite (but practically very short) time.

This simple differential equation with separable variables leads immediately (with the boundary condition that for $t = 0$ we have $x_o = 0$ and $\eta = \eta_o$) to the required expression of how the efficiency varies during the transient period (the trend of x_o is then immediately obtainable through (1.9), that binds x_o to η):

$$\eta = \eta_\infty + (\eta_o - \eta_\infty) \cdot \exp(-\frac{rL\eta_o}{V\eta_\infty} \cdot t) \qquad (1.10)$$

For $t = 0$ we have $\eta = \eta_o$ and for $t = \infty$ we have $\eta = \eta_\infty$.

We come now to the case of a tower in which the liquid is completely recycled, without any bleed ($r = 0$).

From the previous expression of η_∞ we get therefore $\eta_\infty = 0$ and $\frac{r}{\eta_\infty} = \frac{GH}{L}$.

Replacing these values in (1.10) we obtain:

$$\eta = \eta_o \cdot \mathrm{e}^{-\frac{GH\eta_o}{V}t} \qquad \text{with} \qquad \eta_o = \frac{1-b}{1-\frac{HG}{L} \cdot b} \qquad \text{and} \qquad b = \exp\left[\left(\frac{HG}{L} - 1\right)\frac{Z}{H_{OG}}\right] \qquad (1.11)$$

Thus we easily obtain the value of η at the moment of start-up with clean water and the trend of η versus time t.

Once the minimum acceptable efficiency has been set, we immediately obtain the time t after which the liquid must be replaced with clean water.

From (1.9) for $r = 0$ we then obtain

$$x_o = \frac{y_i}{H}\left(1 - \frac{\eta}{\eta_o}\right)$$

that is the concentration of the pollutant in the liquid versus time, which tends asymptotically to the value $x_\infty = y_i/H$. We therefore have:

$$\frac{x_0}{x_\infty} = 1 - \frac{\eta}{\eta_0} = 1 - \mathrm{e}^{-\frac{GH\eta_0}{V}t}$$

There are two special cases:

A) The substance has a very low H value, so $HG/L \ll 1$, and besides the bed is quite high, i.e. $Z/H_{OG} > 3$.

Then we have $b \ll 1$ and therefore:

$$\eta_o = 1 \qquad\qquad \eta = \mathrm{e}^{-\frac{GH}{V}t}$$

Interestingly, η does not depend on L.

B) The substance has a rather high H value, so $HG/L \gg 1$, and besides Z/H_{OG} is not much smaller than 1. Then it turns out $b \gg 1$ and therefore:

$$\eta_o = \frac{L}{HG} \qquad\qquad \eta = \frac{L}{HG} \cdot \mathrm{e}^{-\frac{L}{V}t}$$

In this case, we find again the maximum efficiency value already identified towards the end of par. 1.1.1.

We have then $$\frac{x_0}{x_\infty} = 1 - \frac{\eta}{\eta_0} = 1 - \mathrm{e}^{-\frac{L}{V}t}$$

which shows that the time to reach certain percentages of saturation in the liquid does not depend in this case on H.

This time is also extremely short. With typical values of L = 20 m^3/h/m^2 and V = 1 m^3/m^2, it turns out that after 5 min 81% of saturation is already reached and after 15 min saturation is practically attained.

1.2. INFLUENCE OF POSSIBLE BIOLOGICAL ACTIVITY

The above formulas and conclusions are valid in the hypothesis that there is no solvent removal mechanism in the liquid phase along the column.

If through the effect of chemical reaction or biological activity (by the presence of bacterial flora on the packing material) such removal takes place, things change.

Assuming e.g. a biological activity corresponding to a chemical reaction of moderate rate, we can suppose (somewhat optimistically) that x is practically zero along the column, and therefore that y_e ($= H \cdot x$) is negligible compared to y.

The expression (1.3) then gives directly $Z = H_{OG} \cdot \ln(y_i/y_o)$.

In the presence of a (pseudo) chemical reaction, the expression (1.4) of H_{OG} becomes:

$$H_{OG} = H_G + \frac{HG}{EL} H_L$$

Given the moderate rate of the hypothesized "reaction", which certainly does not occur in the liquid film adjacent to the interface with the gas phase, it can be assumed that E (dimensionless enhancement factor for liquid-phase mass transfer due to the "reaction") is practically equal to 1.

Consequently, the value of H_{OG} remains exactly the same as the one related to absorption of purely "physical" type previously assumed.

With poorly soluble substances, for which HG/L is definitely greater than 1, H_{OG} is easily of the order of a few meters (as it will be evident from the calculations made later).

As a result, beds several meters high are necessary to have acceptable efficiencies even in the optimistic hypothesis that the column behaves not as a mere purely "physical" absorber, but as a biologically active percolator bed.

1.3. CALCULATION OF THE HEIGHT OF A TRANSFER UNIT

For the calculation of $H_{OG} = H_G + \lambda H_L$ (with $\lambda = HG/L$) H_G and H_L must be evaluated.
In the field of distillation, which is commercially much more important than absorption, the parameter *HETP* (height equivalent to a theoretical plate) is normally used. It is linked to H_{OG} by the relationship

$$HETP = H_{OG}\left(\frac{\ln\lambda}{\lambda - 1}\right)$$

For the evaluation of *HETP*, either mass transfer models (which typically lead to theoretical-empirical expressions of H_G and H_L), or rules of thumb may be used.
Between 1960 and 1980 there was a flourishing of models, which, however, led to results often in poor agreement with each other and with experimental data. This contributed to the progressive increase of distrust in the models, whose relative complication of use seemed unjustified, compared to the simplicity of the rules of thumb.
H.Z. Kister, the greatest living expert in distillation and section editor (for distillation and absorption equipment) in the last two editions (VIII of 2008 and IX of 2018) of Perry's Chemical Engineers' Handbook, thus dismisses the issue in that place (but he had already done it with the same words in his book "Distillation design" of 1992): "Due to the unreliability of even the best mass transfer model, it has been the author's experience that rules of thumb for *HETP* are more accurate and more reliable than mass transfer models".
After which, all the funds left to the designer are reduced to the formulas $HETP = 18 \cdot d$ and $HETP = 93/a$, where d (m) is the packing diameter and a (m^2/m^3) its specific surface (m^2/m^3).
The first expression is the original one, based on Pall rings (leading e.g. to *HETP* = 0.9 m for DN 50 Pall rings with $d = 0.05$ m), the second is a later Kister's extension for applicability to third or fourth generation packings (sometimes flat or saddle-shaped), for which the diameter is a parameter more difficult to define.
The above formula is valid for columns which are not too small (with a diameter greater than 0.6 m), for $0.5 < \lambda < 2$ (outside this range, *HETP* may be much greater) and for organic-hydrocarbon systems, with low surface tension. For aqueous systems the value given by the formula should be doubled, according to Kister (this may seem a coarse suggestion, but these are rules of thumb!).
For our absorption problems the above approach is inapplicable, for many reasons.

The first is that λ is normally much smaller than 0.5 and the solutions are systematically of aqueous type.

The second is that, in order to take into account the effect of a chemical reaction in the liquid phase (as it is often the case), it is necessary to have separate values of H_G and H_L, because the enhancement factor E must be applied only to H_L. Furthermore, to determine E it is necessary to evaluate the single parameter k_L (one of the constituent factors of H_L which can be obtained within the chosen model).

All this may seem an unnecessary complication, given the indeterminateness of the models, but it is the only way to appreciate the influence, for example, of the type and concentration of the reagent added to the washing liquid, as well as, more simply, of the velocity of the liquid and gas flows in the column.

However, the greatest uncertainty regarding the value calculated for the height of the packed bed (i.e. for the obtainable removal efficiency) is linked to the kinetic constants of the chemical reaction that allow the calculation of E.

These constants are difficult to find in the literature (some are reported in [2]): for instance, in the case of a mixture of organic pollutants in the fumes, which are all susceptible to chemical oxidation, the kinetic constant may be known only for some of them, so the removal efficiency, if must be expressed in terms of total residual organic carbon, remains difficult to assess.

We come now to the examination of the main models available for random packing materials (we will not consider structured packings, because they are very much used in distillation, but very little in the field of gas purification, due to the high cost and the greater tendency to foaming and clogging).

Let us first remember that there are packings of 4 successive generations. The one representative of the first generation is the Raschig ring, which produces a pressure loss that is nowadays definitely unacceptable. The main second generation packing is the Pall ring, probably (in the DN 50 version) the most used material in the last 60 years.

The ones of the third and fourth generation, of an increasingly "open" shape (often consisting of a filiform lattice), have a nominal size tendentially larger (DN 80 and even DN 100), in order to increase the free volume of the bed and therefore decrease more and more the pressure loss. The specific area a (m^2/m^3) of the packing tends to decrease as its size increases, but the surface for mass transfer between liquid and gas remains high because the

new shapes tend to favour the formation of liquid drops in free fall, whose surface adds to the one of the liquid flowing along the material.

Essentially, an excellent fourth generation packing as the LANTEC Q-PAC (DN 100) has an efficiency of the same order of magnitude as the DN 50 Pall ring, but with much lower pressure drop.

To get down in practice, with the same specific liquid flow in the column ($m^3/h/m^2$) and for the same application (in particular for systems where the liquid-phase mass transfer resistance is negligible) the DN 50 Pall ring used with a gas speed of 1.9 m/sec has the same H_{OG} (and therefore the same efficiency) as the Q-PAC used at 2.5 m/sec, but a pressure loss per meter of packing 2.2 times higher.

This means that, using the Q-PAC, for the same gas flow rate and required efficiency one can afford a column of the same height, but with a smaller diameter (of about 15%).

In addition, a recirculation pump with a flow rate 25% lower and a fan with total head (and therefore absorbed power) considerably lower are sufficient.

Correspondingly, by replacing the Pall rings with the Q-PAC in an existing tower, the treated gas flow rate can be increased by at least 30%.

The DN 50 Pall ring in polypropylene still retains its validity, because it is much easier to find and much cheaper (in Italy it costs about a quarter of the Q-PAC).

The three main models developed in the last century are the ones of Onda (1968), Bolles-Fair (1979) and Bravo-Fair (1982), all based on first and second generation packings and inapplicable to the most modern materials.

The two most significant models of the last thirty years are the one of Billet-Schultes (last version of 1999) and the one of Mackowiak (2015), both applicable to all types of packing. They are the result of research carried on essentially in Germany (Americans preferred to focus on structured packings in recent decades).

Actually, the Bravo-Fair model is valid for distillation, but practically inapplicable to absorption (the mass transfer surface is largely overestimated, at the usual gas and liquid velocities), while the Onda model gives far too high H_G values, not only with the big last generation packings, but also with the DN 50 Pall rings.

The Bolles-Fair model is only applicable to a few packings, for which the necessary parameters are provided by the authors.

In particular, apart from the Raschig rings and the first generation Berl saddles, the metal Pall rings (size 0.5" - 1" - 1.5" - 2") are the only second generation packing considered. The results are however extendable, as we will see, to plastic Pall rings, which are the ones practically used (because they are much cheaper) in ecological applications, where temperatures are generally low and conditions are often corrosive.

Also the Bolles-Fair model provides higher H_G values in comparison with the more modern and reliable Billet-Schultes and Mackowiak models. However, it can still be employed when Pall rings are used and a conservative calculation approach is preferred.

The two newer models are both valid (they give quite similar results).

The one of Billet-Schultes requires the use of several specific coefficients, typical of each particular packing and obtainable only experimentally. These coefficients are tabulated for some sixty materials, but the list (which includes also some fourth generation packing, but not the Q-PAC) was not subsequently updated.

The Mackowiak model, on the other hand, is also applicable to new products, on the basis of characteristics (essentially geometric) normally provided by manufacturers.

Billet also gives a simple formula to account for both imperfect liquid distribution at the top of the tower and column-bottom effects.

Before coming to the individual models, we list in Table 2 the values, at various temperatures, of the physical parameters of air and water (extendable to very dilute aqueous solutions) that intervene in the following formulas.

These are specific weights ρ_G and ρ_L (in kg/m³), dynamic viscosities μ_G and μ_L (in kg/m/sec) and surface tension σ_L (in kg/sec²).

As for diffusivities D_G and D_L (in m²/sec) of the various pollutants in air and water, they can be found (or calculated) on various sources (e.g. Perry). Values at other temperatures can be obtained by recalling that $D_G \propto T^{1.75}$ (T is the absolute temperature) and that $D_L \cdot \mu_L / T = const$.

We also report in Table 3 the dimensional characteristics of the DN 50 Pall rings in PP and of the following remarkable packings (always in PP) of third and fourth generation: LANTEC Q-PAC, RASCIG Super Ring n. 2 and n. 3, YAEGER (now RASCHIG) Tripack 2" and 3.5".

The nominal diameter d (m), the specific area a (m²/m³) and the void fraction ε (m³/m³) are listed.

Table 2. Physical parameters of air (*G*) and water (*L*)

Temperature (°C)	ρ_G (kg/m³)	μ_G (kg/m/sec)	ρ_L (kg/m³)	μ_L (kg/m/sec)	σ_L (kg/sec²)
10	1.247	$1.763 \cdot 10^{-5}$	999.7	$1.308 \cdot 10^{-3}$	$7.423 \cdot 10^{-2}$
20	1.205	$1.806 \cdot 10^{-5}$	998.2	$1.005 \cdot 10^{-3}$	$7.275 \cdot 10^{-2}$
25	1.185	$1.826 \cdot 10^{-5}$	997.0	$0.8937 \cdot 10^{-3}$	$7.199 \cdot 10^{-2}$
30	1.165	$1.847 \cdot 10^{-5}$	995.6	$0.8007 \cdot 10^{-3}$	$7.120 \cdot 10^{-2}$
40	1.128	$1.887 \cdot 10^{-5}$	992.2	$0.6560 \cdot 10^{-3}$	$6.960 \cdot 10^{-2}$

Table 3. Packing dimensional characteristics

	d **(m)**	***a*** **(m²/m³)**	ε **(m³/m³)**
Pall Ring DN 50	50	111.1	0.919
Q-PAC	85	98.4	0.963
Super Ring n. 2	50	100	0.96
Super Ring n. 3	75	75	0.97
Tripack 2”	50	157	0.935
Tripack 3.5”	90	125	0.95

Here are the formulas for the three practically usable models.

1) **Bolles-Fair Model** [3]

$$H_G = \psi \cdot \frac{2^{1.24}(Z/10)^{1/3}}{L^{0.6}} \cdot \sqrt{Sc_G} \qquad H_L = \phi \cdot C \cdot (Z/10)^{0.15} \cdot \sqrt{Sc_L}$$

The original expression of H_G was developed for the case of tower diameter greater than 0.6 m, ring-type packing, washing liquid of physical characteristics similar to the water ones.

In the above formulas H_G, H_L and Z (bed height) are to be expressed in feet, L (liquid specific flow rate) in lb/h/ft^2.

$Sc_G = \mu_G / (\rho_G \cdot D_G)$ and $Sc_L = \mu_L / (\rho_L \cdot D_L)$ are the Schmidt numbers in gaseous and liquid phase respectively (they contain the diffusivities, and therefore depend on the considered pollutant).

ψ (packing parameter) is equal to 140 for DN 50 metal Pall rings and is practically constant in the range of flooding ratios normally used.

We can derive $\psi = 153$ for DN 50 plastic Pall rings taking into account that, as suggested by the same authors, ψ is proportional to the ratio a / ε^3 (where a is the specific area and ε the void fraction of the packing).

C is equal to 1 for flooding ratios below 0.5 (as it is usually the case).

ϕ depends on L with an expression of the type $l \cdot L^m$ (for the rings considered by us we have $l = 0.0113$ and $m = 0.244$, with L in lb/h/ft²).

Transforming the expressions of H_G and H_L so as to merge the constants and to use S.I. units (H_G, H_L and Z in m, L in m/sec) we have

$$H_G = 2.29 \cdot 10^{-2} \cdot Z^{1/3} \cdot L^{-0.6} \cdot \sqrt{Sc_G} \qquad H_L = 7.85 \cdot 10^{-2} \cdot Z^{0.15} \cdot L^{0.244} \cdot \sqrt{Sc_L}$$

For example, with a typical value of $L = 20$ m³/h/m² $= 5.556 \cdot 10^{-3}$ m/sec, with $Z = 3$ m and with hydrogen sulphide as pollutant ($D_G = 1.72 \cdot 10^{-5}$ m²/sec, $D_L = 1.61 \cdot 10^{-9}$ m²/sec at 25°C) the following results are obtained:

$H_G = 0.705$ m $\qquad$ $H_L = 0.615$ m

2) **Billet –Schultes model** [4]

In the range of normal use (that is up to the loading point) the original formulas are as follows:

$$h_L = \left(\frac{12}{g} \cdot \frac{\mu_L}{\rho_L} \cdot a^2 \cdot L\right)^{1/3}$$

$$k_G = \frac{C_G}{2} \cdot \frac{a^{1/4}}{\sqrt{\varepsilon(\varepsilon - h_L)}} \cdot G^{3/4} \cdot D_G^{2/3} \cdot \left(\frac{\mu_G}{\rho_G}\right)^{-5/12}$$

$$k_L = \frac{C_L}{2} \cdot \left(\frac{g \cdot a \cdot \rho_L}{\mu_L}\right)^{1/6} \cdot \left(\frac{D_L}{\varepsilon}\right)^{1/2} \cdot L^{1/3}$$

$$a_e = 3\sqrt{\varepsilon} \cdot g^{0.45} \cdot {\mu_L}^{0.2} \cdot \rho_L^{0.55} \cdot \sigma_L^{-0.75} \cdot L^{0.4}$$

$$H_G = \frac{G}{k_G \cdot a_e} \qquad H_L = \frac{L}{k_L \cdot a_e}$$

where h_L (m^3/m^3) is the theoretical hold-up, k_G and k_L (m/sec) are the mass transfer coefficients in the gas phase and in the liquid phase respectively, a_e (m^2/m^3) is the effective specific surface for mass transfer, a (m^2/m^3) is the packing specific surface, ε (m^3/m^3) is its void fraction, G and L (m/sec) are the gas and liquid velocities, g is the acceleration of gravity (9.81 m/sec^2), C_G and C_L are two specific constants of the type of packing (tabulated by the authors).

For three remarkable plastic packings these constants assume the values reported in Table 4:

Table 4. Packing characteristic constants

	C_G	C_L
Pall Ring DN 50	0.368	1.239
Super Ring n. 2	0.337	1.250
Q-PAC	0.33	1.50

Actually, the two constants for Q-PAC are not reported by the authors, but have been evaluated on the basis of the values attributed to very similar packings (by shape and parameters a and ε).

For the air-water system at 25°C and for the two most interesting packings, the previous formulas are synthetically reduced, with good approximation, to:

a) Pall Ring DN 50:

$k_G = 67.33 \cdot G^{3/4} \cdot D_G^{2/3}$ $\quad$ $k_L = 21.11 \cdot L^{1/3} \cdot D_L^{1/2}$ $\quad$ $a_e = 633.2 \cdot L^{0,4}$

$H_G = 2.35 \cdot 10^{-5} \cdot G^{1/4} \cdot L^{-0,4} \cdot D_G^{-2/3}$ $\quad$ $H_L = 7.48 \cdot 10^{-5} \cdot L^{4/15} \cdot D_L^{-1/2}$

b) Q-PAC:

$k_G = 55.74 \cdot G^{3/4} \cdot D_G^{2/3}$ $\quad$ $k_L = 24.47 \cdot L^{1/3} \cdot D_L^{1/2}$ $\quad$ $a_e = 648.1 \cdot L^{0,4}$

$H_G = 2.77 \cdot 10^{-5} \cdot G^{1/4} \cdot L^{-0,4} \cdot D_G^{-2/3}$ $\quad$ $H_L = 6.31 \cdot 10^{-5} \cdot L^{4/15} \cdot D_L^{-1/2}$

For example, with a typical value of L = 20 $m^3/h/m^2$ = $5.556 \cdot 10^{-3}$ m/sec, with hydrogen sulphide as pollutant and with G = 1.9 m/sec for DN 50 Pall rings and G = 2.5 m/sec for Q-PAC, we obtain:

a) Pall Ring DN 50:

k_G = 0.0726 m/sec; k_L = 0.150 · 10^{-3} m/sec; a_e = 79.3 m²/m³; H_G = 0.330 m
H_L = 0.467 m

b) Q-PAC:
k_G = 0.0738 m/sec; k_L = 0.174 · 10^{-3} m/sec; a_e = 81.2 m²/m³; H_G = 0.417 m
H_L = 0.394 m

As for bed pressure drop, we can consider the following expression, obtained by processing and simplifying the formulas given by Billet (below the loading point):

$$\frac{\Delta p}{Z} = c_1 \cdot \rho_G \cdot G^2 \cdot exp(\, c_2 \cdot L)$$

Where for DN 50 Pall rings c_1 = 49.1 and c_2 = 38.2 and for Q-PAC c_1 = 12.7 and c_2 = 43.2 (for ρ_G, G and L the usual units apply; $\Delta p/Z$ is in Pa/m).
At 25°C, with L = 5.556 · 10^{-3} m/sec we obtain for Pall rings (with G = 1.9 m/sec) $\Delta p/Z$ = 260 Pa/m, while for Q-PAC (with G = 2.5 m/sec) $\Delta p/Z$ = 120 Pa/m.
To take into account both an imperfect distribution of the liquid at the tower top and the bottom-column effects, Billet provides the following formula, that gives the value ΔZ (m) by which it is necessary to increase the bed height obtained from the calculation (i.e. $Z = H_{OG} \cdot N_{OG}$):

$$\Delta Z = 1.5 \cdot (1 - e)/e \quad \text{with} \quad e = 1.13 \cdot m^{0.04} \cdot \left[4\pi N \left(\frac{\varepsilon}{a}\right)^2\right]^{0.1 \cdot m^{0.25}} \quad \text{and} \quad m = \frac{L \cdot \rho_L}{G \cdot \rho_G}$$

where N is the number of feed points per m² of the liquid distributor.
For instance, with a perforated pipe (i.e. ladder type) distributor (typically with 40 holes per m²), we have with Pall rings (for L = 5.556 · 10^{-3} m/sec and G = 1.9 m/sec) ΔZ = 0.45 m and with Q-PAC (G = 2.5 m/sec) ΔZ = 0.35 m.
These values do not depend, of course, on the total bed height, but have a high percentage incidence in the case of low beds.

3) **Mackowiak model** [5]

In the range of normal use (that is up to the loading point) the formulas are as follows:

$$d_T = \sqrt{\frac{\sigma_L}{(\rho_L - \rho_G)g}} \qquad h_L = 0.57 \left(\frac{a\,L^2}{g}\right)^{1/3} \qquad u_R = \frac{G}{\varepsilon - h_L} + \frac{L}{h_L}$$

$$\tau = \frac{h_L}{L}\, l \qquad l = 0.23(1-\varphi_P)^{2/3} \cdot \left(\frac{\varepsilon}{a}\right)^{1/2} \qquad a_e = \frac{6h_L}{d_T} \qquad k_L = 2 \cdot \sqrt{\frac{D_L}{\pi\,\tau}}$$

$$k_G = \frac{D_G}{d_T}\left(2 + 0.0285 \cdot \mu_G^{-2/3} \cdot \rho_G^{2/3} \cdot D_G^{-1/3} \cdot u_R \cdot d_T\right) \cdot \left(1 - \frac{h_L}{\varepsilon}\right)^6$$

$$H_G = \frac{G}{k_G \cdot a_e} \qquad H_L = \frac{L}{k_L \cdot a_e}$$

The new parameter introduced by Mackowiak is φ_P (packing form factor), which is the ratio between the perforated surface and the total packing surface (it is for instance φ_P = 0 for Raschig rings, with full wall; φ_P = 0.309 for DN 50 plastic Pall rings; φ_P = 0.5÷0.8 for the modern lattice-type packings).

φ_P can be calculated either by a geometric way, or through the experimental value of the dry-packing pressure loss (and the two values are usually in good agreement).

The Author lists φ_P (necessary only for calculating k_L) for more than 100 different packings [6], but not for Q-PAC. With the geometric method we calculated φ_P = 0.72 (with the fluid-dynamics method we got a higher value, which, conservatively, has not been taken into account).

In Table 5 we report, for Pall rings (with G = 1.9 m/sec) and for the 5 modern packings already listed above (with G = 2.5 m/sec), the values calculated with the Mackowiak model of the main parameters (k_G, k_L, a_e, H_G, H_L) and also the pressure loss (Pa/m). So it is possible to get an idea of the efficiency and energy consumption of the various materials. In all cases it is $L = 5.556 \cdot 10^{-3}$ m/sec (20 m³/h/m²) and the presence of H_2S is assumed (at 25°C). It can also be verified that the Billet-Schultes and Mackowiak models give very similar results (for Pall rings and Q-PAC).

With the operating parameters above specified (G = 2.5 m/sec, L = 20 m³/h/m²) and for H_2S removal under conditions of negligible liquid-phase mass transfer resistance (in which case H_{OG} is practically equal to H_G), LANTEC (producer of Q-PAC) gives an experimental result of H_{OG} = 0.31 m.

This means that the Billet and Mackowiak models are still, at least in this case, slightly conservative.

Table 5. Comparison between packings

	φ_P	a_e (m²/m³)	k_G (m/sec)	k_L (m/sec)	H_G (m)	H_L (m)	$\Delta p/Z$ (Pa/m)
Pall Ring DN 50	0.309	88.7	0.0636	$1.32 \cdot 10^{-4}$	0.337	0.475	260
Q-PAC	0.72	85.2	0.0783	$1.74 \cdot 10^{-4}$	0.375	0.374	120
Super Ring n. 2	0.60	85.7	0.0783	$1.55 \cdot 10^{-4}$	0.373	0.419	230
Super Ring n. 3	0.65	77.8	0.0797	$1.58 \cdot 10^{-4}$	0.403	0.452	170
Tripack 2”	0.665	99.6	0.0763	$1.72 \cdot 10^{-4}$	0.329	0.325	320
Tripack 3.5”	0.67	92.3	0.0772	$1.69 \cdot 10^{-4}$	0.351	0.357	170

1.4. NUMERICAL EXAMPLES

1.4.1. Solvent absorption

We will consider as a first example the case of 5 printing machines in the textile industry, using ethyl alcohol or ethyl acetate as a solvent. Each machine emits a maximum of 15,000 Nm^3/h of fumes at 40°C, with a solvent concentration of 800 mg/Nm^3.

For 4 machines, already existing in 1988, a removal efficiency of 50% was more than sufficient (at the time of the depurative intervention), while for the fifth, more recent, an efficiency of 95% was required.

As the calculations will show, the solution of washing with water in packed columns is applicable to ethanol, but not to acetate.

For the fifth machine, due to the high efficiency required, it is necessary to wash with disposable water (not recirculating). For the first 4, however, it is possible to recirculate the liquid, using for make-up (to compensate for the purged fraction of the recirculating liquid) the water coming out of the bottom of the column used for the fifth machine.

For reasons of size and operational flexibility, two towers, each handling 26,000 Nm^3/h of fumes, are provided for the first 4 machines (because it is practically impossible that two machines operate at the same time at their maximum emission regime).

The tower (A) for the fifth machine will have a diameter of 1.75 m, a bed height (of DN 50 Pall rings in polypropylene) of 6 m and will use clean water (24 m^3/h).

The temperature of the fumes quickly drops to about 25°C in the column (the same temperature, in practice, of the incoming water, which warms up by about 3°C).

For ethanol we have (at 25°C) $H = 2.2 \cdot 10^{-4}$; $Sc_G = 1.30$; $Sc_L = 700$.

For the calculation of H_G and H_L, the Bolles-Fair model is used for conservative purposes (considering in return the bed height as completely usable, without any allowance for end effects).

With the formulas of par. 1.3 (assuming for tower A $Z = 6$ m; $G = 1.89$ m/sec; $L = 2.77 \cdot 10^{-3}$ m/sec; $r = 1$; $x_m = 0$) we obtain $H_G = 1.62$ m and $H_L = 0.65$ m, so $H_{OG} = 1.72$ m and from (1.8) $\eta = 95.6\%$ (slightly more than required).

With the Bolles-Fair method it is necessary to proceed by trial and error to arrive at the correct sizing (because Z is needed to calculate H_G and H_L). In particular, the diameter of the

column derives from the assumption of a gas speed within the usual range, determined essentially by the need to contain pressure losses.

The bed height, rather large in this case, is determined by the opportunity to limit as much as possible the water flow rate, since this goes completely to waste (into the sewer and then to purification), also taking into account that a bed higher than 6 m would require liquid redistributors, to ensure homogeneity of the flow in the column section.

It is evident that the definition of the optimal coupling of Z and L implies an economic evaluation, to reach a good compromise between installation and operating costs.

However, we note that the "optimal" value of L can be, in the case of waste flow, much lower than the usual one in the case of recirculating liquid (for instance, here we have about 10 m³/h/m², against the usual 20 m³/h/m²).

The value of L also depends on water temperature, for its influence on the value of the Henry constant. An increase of 5°C requires, for the same efficiency, a water flow rate about 12% greater.

The two towers (B) for the first 4 machines will have a diameter of 2.5 m and a bed of 3 m. The recirculating liquid flow rate will be 100 m³/h (20.37 m³/h/m²).

Here, too, the gas quickly reaches a temperature of about 25°C.

For each of the towers we will therefore have:

$H = 2.2 \cdot 10^{-4}$; $Sc_G = 1.30$; $Sc_L = 700$; $Z = 3$ m; $G = 1.61$ m/sec; $L = 5.66 \cdot 10^{-3}$ m/sec; $r = 12/100 = 0.12$ (bleed and make-up are equal to half of the liquid discharged from tower A).

For columns B we observe that y_i is the same as tower A and that x_m (that is $x_{m,B}$) is equal to the concentration x_0 at the discharge of A (that is $x_{0,A}$). This simple balance applies:

$$G_A \cdot y_i \cdot \eta_A = L_A \cdot x_{0,A} = L_A \cdot x_{m,B} \qquad \text{so} \qquad \left(1 - \frac{H \cdot x_{m,B}}{y_i}\right) = \left(1 - \frac{H \cdot G_A}{L_A} \cdot \eta_A\right) = 0.857$$

which is the value of the first factor in (1.8).

Then, for columns B, $H_G = 0.84$ and $H_L = 0.69$ m, then $H_{OG} = 0.88$ m and finally $\eta = 57.2\%$.

If ethyl acetate is used ($H = 6.9 \cdot 10^{-3}$; $Sc_G = 1.84$; $Sc_L = 960$) instead of ethanol (all other conditions being equal), the removal efficiency would be only 20.9% for tower A (with $H_G = 1.93$ m, $H_L = 0.76$ m and $H_{OG} = 5.51$ m) and 0.08% for towers B (with $H_G = 1.00$ m, $H_L = 0.81$ m and $H_{OG} = 2.59$ m).

1.4.2. Formaldehyde absorption

As a second example, we will consider the case of a melamine impregnation line, that is a tunnel oven in which the paper impregnated with a melamine-formaldehyde resin is dried. This machine typically emits a flow rate of 40,000 Nm^3/h of fumes at 80°C with a formaldehyde concentration of up to 20 mg/Nm^3, to be reduced with an efficiency of 80÷90%.

To this purpose a packed tower can be used, preferably preceded by a quench section to lower the temperature down to 35°C (by adiabatic saturation).

Using Q-PAC as packing material, with the usual parameters G = 2.5 m/sec and L = 5.556 $\cdot 10^{-3}$ m/sec, a tower with a diameter of 2.5 m will be necessary, containing a bed 2.5 m high (the effective height is Z = 2.15 m according to Billet-Schultes, as already seen).

We will consider 4 different treatment strategies, of which only the last two are effective.

The first two envisage for scrubbing the use of simple water, recirculated by a centrifugal pump. In the first case a continuous bleed S is operated from the bottom of the tower (with $r = S/L$), in the second case no bleeding is performed for a certain time, after which the liquid is completely discharged and given for disposal.

The physico-chemical parameters of formaldehyde, at 35°C, are $H = 2.6 \cdot 10^{-5}$, $D_G = 1.92 \cdot 10^{-5}$ m^2/sec, $D_L = 2.07 \cdot 10^{-9}$ m^2/sec. Note that the H values reported in the literature, for example in [1], are the effective ones, that is, they already take into account that practically all formaldehyde is present in the liquid in the form of methylene glycol (also the value of D_L has been calculated with reference to this compound).

With the formulas of par. 1.3, using the Billet-Schultes model, we get H_G = 0.41 m and H_L = 0.35 m; therefore, by (1.4), $H_{OG} = 0.41 + 2.6 \cdot 10^{-5} \cdot 2.5 / 5.556 \cdot 10^{-3} \cdot 0.35 = 0.41$ and finally $Z/H_{OG} = 2.15/0.41 = 5.24$.

In the first case (continuous bleeding and make-up with clean water) the formula (1.8) applies with $x_m = 0$. Being $HG/L << 1$ and $Z/H_{OG} > 5$, the exponential term is practically 0 and thus the expression of η is reduced to:

$$\eta = \frac{1}{1 + \frac{HG}{L}\left(\frac{1}{r} - 1\right)}$$

From these considerations it can be deduced that, in the case of formaldehyde, if the bed is high enough, the performance does not depend on its actual height, nor on the type of packing used (because even inefficient materials would still give sufficiently high Z/H_{OG} values). Efficiencies are, however, rather low, unless significant fractions of recirculated liquid are purged (what one rarely can afford).

In fact, we immediately obtain that, to have a 90% efficiency, it is necessary to purge 10% of the recirculating liquid ($r = 0.1$), while with $r = 0.05$ efficiency already drops to 81.4%.

Note that with a tower diameter of 2.5 m the recirculated flow must be 98 m^3/h and the purged flow (with $r = 0.1$) would therefore be a high 9.8 m^3/h, with a concentration of formaldehyde of 72 mg/l.

In fact a simple balance gives $x_o = G\, y_i\, \eta / (L\, r) = 2.5 \cdot 17.73 \cdot 0.9 / (5.556 \cdot 10^{-3} \cdot 0.1) =$ 71,800 mg/m^3, where $y_i = 17.73$ mg/m^3 (corresponding to 20 mg/Nm^3).

In the second case (recirculation without bleeding) the formula (1.11) applies, which, when applied to formaldehyde, is reduced to:

$$\eta = e^{-\frac{GH}{V}t}$$

(because the exponential term b is practically 0, for the reasons already explained).

Assuming $V = 1$ m^3/m^2 (i.e. considering 1 m of liquid head in the bottom of the tower), efficiency changes from 100% at the initial moment ($\eta_0 = 99.45\%$ to be exact) to 90% after 26' and to 80% after 56', when the concentration in the bottom liquid has reached $x_o = y_i / H \cdot (1 - \eta / \eta_0) = 133{,}370$ mg/m^3 (in the formula giving η, t shall be expressed in sec if G is given in m/sec).

The unsustainability of such a frequent liquid change is evident.

The third abatement strategy is to combine the packing tower with a dedicated biological water treatment plant, fed with a flow rate $S = r\, L$ of liquid purged from the tower bottom, which, after being purified with a yield η_B, is fed back into the recirculating liquid of the tower.

Basically the concentration x_m of the liquid made up in the column is now equal to:

$$x_m = x_o\,(1-\eta_B).$$

From the overall balance $G\,(y_i - y_o) = S\,(x_o - x_m)$ we get $G\, y_i\, \eta = S\, x_m\, \eta_B\,/(1-\eta_B)$, from which

$$\frac{Hx_m}{y_i} = \frac{HG}{Lr}\frac{1-\eta_B}{\eta_B}\eta$$

Substituting this expression in the first term of (1.8) we obtain, with some algebraic steps:

$$\eta = \frac{1}{\frac{HG}{Lr\eta_B} + \frac{1-\frac{HG}{L}}{1-exp\left[\left(\frac{HG}{L}-1\right)\frac{Z}{H_{OG}}\right]}}$$

while it is $x_o = G\, y_i\, \eta\, /(L\, r\, \eta_B)$.

Again for the reasons already explained, the exponential term is practically 0, so the previous expression is reduced in our case to:

$$\eta = \frac{1}{1+\frac{HG}{L}\left(\frac{1}{r\eta_B}-1\right)}$$

The feasibility of this solution is based essentially on the great biodegradability of formaldehyde, which allows to obtain high yields η_B (of the order of 90%) with very low residence times in the oxidation tank (of the order of 3 h), which means reduced size and cost for the biological plant.

With $\eta_B = 0.9$, we in fact obtain a 90% efficiency by purging and treating in the biological plant a fraction $r = 0.11$ of the liquid flow rate recirculated in the tower, while if we are satisfied with $\eta = 0.80$ it is enough to size the biological plant for a fraction equal to 5.1% of the same flow.

The concentration x_o of formaldehyde at the biological plant inlet is 72 mg/l in the first case and 140 mg/l in the second.

Actually, the simultaneous presence in the fumes of the impregnation lines of other volatile organic compounds complicates the problem, because they are removed with very low efficiencies both in the tower (because of much higher Henry constants) and in the biological plant (because of a much lower biodegradability).

From the point of view of emissions to the atmosphere this is not particularly serious because the allowable limits for these VOCs are usually much higher, since they are not dangerous substances such as formaldehyde.

From the point of view of biological purification, their presence forces to take a small liquid flow from the first biological plant and send it to a second, smaller, but characterized by a

residence time of a few days, in order to produce a final effluent in compliance with the legal parameters.
Given the costs and the operational commitment that biological plants entail, this solution is in practice applicable when there are several melamine impregnation lines in the factory (for example 3÷5).

The fourth treatment method is to add a chemical reagent to the washing liquid, able to destroy the absorbed formaldehyde. For example, sodium hypochlorite, with concentrations corresponding to a sufficiently high redox potential (650÷700 mV), transforms formaldehyde into CO_2 and H_2O, zeroing its concentration in the recirculating liquid.
Even though the topic of absorption with chemical reaction will be dealt with extensively later, we can already note now that the Henry constant of formaldehyde is so low (that is, the substance is so soluble in water and not very volatile) that $H_{OG} = \sim H_G$ even in the absence of chemical reaction in the liquid (as already mentioned in par. 1.2, the reaction involves the E factor, which usually significantly lowers the contribution of H_L to H_{OG}).
Therefore the addition of the reagent cannot have in our case any beneficial effect on the lowering of the H_{OG} value, regardless of how fast the reaction is and therefore how high the E value is.
However, the consequence of an effective reaction, even if not particularly fast, is to zero the concentration x of the pollutant in the liquid mass along the column and thus make y_e ($= H \cdot x$) negligible compared to y. Expression (1.3) then gives directly

$$Z = H_{OG} \cdot \ln (y_i / y_o) = - \ln (1-\eta)$$

We then have

$$\eta = 1 - \exp (- Z/H_{OG})$$

With $Z/H_{OG} = 2.15/0.41 = 5.24$ a 99.5% efficiency is therefore obtained.
The reaction of formaldehyde with hypochlorite produces sodium chloride, the concentration of which cannot be allowed to increase indefinitely.
If it is not possible to operate a small continuous bleeding (of the order of 200 l/h), it is necessary to periodically replace and give for disposal (for example, once a week) the liquid contained in the tower bottom.

2. ABSORPTION OF POLLUTANTS IN PACKED COLUMNS WITH CHEMICAL REACTION

2.1. CONTROLLING RESISTANCE IN THE GAS PHASE

As already mentioned in par. 1.2, in the case of rapid and irreversible chemical reaction y_e is negligibly small compared to y along the entire column, therefore

$$N_{OG} = \int_{y_0}^{y_i} \frac{dy}{y} = \ln \frac{y_i}{y_0} = -\ln(1-\eta)$$

If η is prefixed, we so get N_{OG} and then, once we have calculated H_{OG}, we get $Z = N_{OG} \cdot H_{OG}$.
If Z is prefixed, we have $N_{OG} = Z / H_{OG}$ and then $\eta = 1 - e^{-N_{OG}}$.
H_{OG}, other than calculated, can be got from the data provided by the manufacturer of the particular packing material used. Reliable companies publish in fact H_{OG} values referring to very specific operating conditions (liquid and gas velocities, type of pollutant and reagent).
For the calculation of H_{OG} we have in this case

$$H_{OG} = H_G + \frac{H^* \cdot G}{E \cdot L} H_L$$

where H_G and H_L (m) are the individual contributions to H_{OG} due to mass transfer resistance in the gas phase and in the liquid phase respectively; H^* is the Henry constant (dimensionless) modified to take into account the presence in solution also of the substance in the dissociated state; E (dimensionless) is the enhancement factor for mass transfer in the liquid phase due to chemical reaction (it is equal to 1 in the absence of reagents or for slow reactions); G and L are the specific volumetric flows (m³/sec/m²) of gas and liquid.
As already seen, we have (for a substance of acid nature):

$$H^* = y/x = H/(1 + 10^{pH-pK})$$

where x and y are the pollutant concentrations (mg/m³), in equilibrium conditions, in the liquid and gaseous phases (x includes the fraction present in the dissociated state).
The factor in brackets, which represents the virtual increase in solubility due to dissociation, depends on pH.
If for instance we take hydrogen sulphide into account, for the first dissociation constant we have pK = 7.0 (since we are not interested in pH above 11, we can neglect the second

dissociation constant): therefore the increase factor rises geometrically above pH 8 (it is equal to 11 – 101 – 1001 for pH = 8 – 9 – 10).

Considering instead methyl mercaptan, it has pK = 10, so pH must exceed 10 to generate a high increase factor.

Returning to hydrogen sulphide, at 25°C we have $H = 0.40$. So, if for instance pH is 9, then $H^* = 0.40 / (1 + 10^{9-7}) = 0.0040$.

For the calculation of H_G and H_L the expressions already written in par. 1.3 hold.

For the following examples, in particular, we will use the Billet-Schultes model.

For H_2S at 25°C we have $D_G = 1.72 \cdot 10^{-5}$ m²/sec and $D_L = 1.61 \cdot 10^{-9}$ m²/sec.

For other possibly present pollutants, e.g. higher molecular weight odorous organic substances, D_G is equal on average to $1 \cdot 10^{-5}$ m²/sec.

We will assume that the specific gas and liquid flow rates in the tower are respectively G = 2.5 m³/sec/m² and $L = 5.556 \cdot 10^{-3}$ m³/sec/m² (corresponding to 20 m³/h/m²) and that the bed consists of Q-PAC packing for a height of 2.5 m.

As already calculated in par. 1.3, it will be $H_G = 0.417$ m, $H_L = 0.394$ m, $k_L = 0.174 \cdot 10^{-3}$ m/sec, while the useful bed height (taking into account the initial maldistribution) will be Z = 2.5 – 0.35 = 2.15 m.

To evaluate E, the Hatta number must be calculated

$$H_a = \frac{\sqrt{D_L \cdot K \cdot C_R}}{k_L}$$

where D_L is the pollutant diffusivity in the liquid phase, K is the kinetic constant of the chemical reaction, C_R is the reagent concentration, k_L the mass transfer coefficient in the liquid phase.

In the case of the reaction between H_2S and sodium hypochlorite, we have $D_L = 1.61 \cdot 10^{-9}$ m²/sec, $k_L = 1.74 \cdot 10^{-4}$ m/sec, $K = 3.2 \cdot 10^{6}$ l/mol/sec (the latter is the value reported in [2]; more recent measurements [7] suggest a value of $7 \cdot 10^{6}$ l/mol/sec, but conservatively we will continue to consider the lower value).

As for C_R, the typical used values range from 50 to 500 mg/l of NaOCl (that is from $0.672 \cdot 10^{-3}$ to $6.72 \cdot 10^{-3}$ mol/l, corresponding besides to redox potentials of the order of 600÷700 mV).

If $H_a > 2$, an irreversible reaction can be defined as fast and practically occurs entirely in the film (which is why the pollutant concentration in the liquid mass, and therefore also y_e, are practically zero).

If the reagent is present in large excess, compared to the typical pollutant concentrations at the liquid-gas interface, the reaction is also pseudo-first order. We are then in the conditions in which the simple relation $E = H_a$ applies.

These conditions exist for C_R = 500 mg/l, but not for 50 mg/l. Referring to the next paragraph for the (rather complex) analysis of the reasons, we continue the calculations with $C_R = 6.72 \cdot 10^{-3}$ mol/l.

We get $H_a = \sqrt{1.61 \cdot 10^{-9} \cdot 3.2 \cdot 10^{6} \cdot 6.72 \cdot 10^{-3}} / 1.74 \cdot 10^{-4} = 33.8$ and $E = H_a = 33.8$.

We can now calculate H_{OG}. We have

$$H_{OG} = H_G + \frac{H^* \cdot G}{E \cdot L} H_L = 0.417 + \frac{0.004 \cdot 2.5}{33.8 \cdot 5.56 \cdot 10^{-3}} \cdot 0.394 = 0.417 + 0.021 = 0.44 \text{ m}$$

The first addend (H_G) is predominant, which means that the mass transfer resistance in the liquid phase is negligible (such resistance, in fractional terms, is equal to $R_L = 1 - H_G / H_{OG}$). The mass transfer resistance in the gas phase, expressed by H_G, is obviously independent of the reagent concentration and represents the minimum H_{OG} value asymptotically attainable with the growth of C_R.

It is evident from the previous numbers that it makes no sense, in this application, to resort to hypochlorite excesses greater than 500 mg/l: the advantage in terms of H_{OG} (and therefore of efficiency) becomes irrelevant.

As for the efficiency calculation, we observe that in the 2.15 m of useful bed there is included a number of transfer units $N_{OG} = Z / H_{OG}$, that is 2.15/0.44 = 4.9 units.

The efficiency $\eta = 1 - e^{-N_{OG}}$ is therefore equal to 99.3%.

As we will see in the next paragraph, with C_R = 50 mg/l we obtain H_{OG} = 0.50 m, so the gas-phase resistance remains controlling anyway, N_{OG} = 2.15 / 0.50 = 4.3 units and efficiency becomes 98.6%, with a rather modest variation in relation to the different excess of reagent.

Always assuming that the pollutant solubility, the chemical reaction rate and the reagent excess are such as to make the mass transfer resistance in the liquid phase negligible (so that H_{OG} is practically equal to H_G), we can make some interesting considerations:

- H_G is proportional to $D_G^{-2/3}$ (according to Billet), so that, in the case of a generic pollutant with an average D_G of $1 \cdot 10^{-5}$ m²/sec, H_G increases from 0.417 m (for H_2S) to 0.60 m. Assessing H_{OG} = 0.63 m, to take into account a minimum liquid phase resistance, we have N_{OG} = 3.4 and η = 96.7%. For the sake of completeness, we point out that according to Mackowiak $H_G \propto D_G^{-0.7}$, according to Bolles-Fair $H_G \propto D_G^{-0.5}$.
- H_G is proportional to $L^{-0.4}$ (according to Billet), so the influence of the washing liquid flow rate is considerable. If for instance the flow rate is halved, H_G grows by 32%. With 10 m³/h/m², instead of 20, in the previous example we would have H_{OG} = 0.83 m instead of 0.63 m, so N_{OG} = 2.59 and η would drop from 96.7 to 92.5%. According to Mackowiak $H_G \propto L^{-0.57}$ and according to Bolles-Fair $H_G \propto L^{-0.6}$, so the influence of L (and its variations) would be even greater.
- N_{OG}, and therefore η, change little with the variation of the gas speed, because H_G depends little on G: in practice, for a given height Z, as the speed increases, what is lost in residence time is recovered in turbulence. According to Billet $H_G \propto G^{0.25}$, according to Mackowiak $H_G \propto G^{0.2}$, according to Bolles-Fair H_G does not depend on G. Therefore, according to Billet and Mackowiak, there is a slight efficiency advantage for low G values (that is, as the residence time increases).

2.2. CALCULATION OF THE ENHANCEMENT FACTOR

In order to evaluate the enhancement factor E in the case of an irreversible reaction of the second order, it is first necessary to calculate both H_a (as already seen) and E_i (enhancement factor for instantaneous reaction).

Within the framework of the film theory we have

$$E_i = 1 + \frac{D_R \cdot C_R}{z \cdot D_L \cdot A^*}$$

where D_R is the reagent diffusivity, z the number of moles of reagent reacting with a mole of pollutant, A^* the pollutant concentration (mol/l) in the liquid at the interface.

The penetration theory provides a more accurate, but very complex expression of E_i.

But if E_i turns out to be greater than 3, then we simply have

$$E_i = \sqrt{\frac{D_L}{D_R}} + \sqrt{\frac{D_R}{D_L}} \cdot \frac{C_R}{z \cdot A^*}$$

In the case that $D_L = D_R$, then the two theories give a perfectly coincident value of E_i (also for $E_i < 3$):

$$E_i = 1 + \frac{C_R}{z \cdot A^*} \tag{2.1}$$

The evaluation of diffusivities, when ionic species intervene in the reaction, is a very complex subject.

In case H^+ and OH^- ions are involved, much more mobile than the others, it is justified to consider for them a diffusivity (at room temperature) of the order of $3 \cdot 10^{-9}$ m²/sec.

If other ions are involved, Danckwerts [8] recommends that the diffusivities of all species in solution be considered equal.

As a result, for instance, for oxidations with sodium hypochlorite (which however has a diffusivity of the order of $1.6 \cdot 10^{-9}$ m²/sec) we will simply consider the expression (2.1).

Once calculated E_i (in the way we shall see), if $H_a > 2$ and $E_i > 5 \cdot H_a$, then the reaction is pseudo-first order, and we can set $E = H_a$ (because E is smaller than H_a by no more than 10%). Otherwise E can be anyway calculated (whatever the values of H_a and E_i) by means of the diagram of Van Krevelen and Hoftijzer, or by the explicit expression of Baldi and Sicardi (the best among the many that have been suggested) [9]:

$$E = 1 + (E_i - 1) \cdot \left[1 - exp\left(-\frac{\sqrt{1 + H_a^2} - 1}{E_i - 1}\right)\right] \qquad (2.2)$$

For the calculation of E_i, A^* must be evaluated.

From the obvious mass balance $k_G\, a_e\, (y - y^*) = E\, k_L\, a_e\, (x^* - x)$, or

$$\frac{G}{H_G}(y - y^*) = \frac{EL}{H^* H_L}(y^* - y_e)$$

we obtain (if $y_e = 0$):

$$y^* = R_L \cdot y \quad \text{with} \quad R_L = 1 - H_G/H_{OG} = 1/\left(1 + \frac{E}{H^*} \cdot \frac{H_G}{H_L} \cdot \frac{L}{G}\right) \quad \text{and then} \quad A^* = \frac{y^* \cdot 10^{-6}}{PM \cdot H^*} \qquad (2.3)$$

where asterisks mark the values of y and x at the interface (A is the expression of x in mol/l, being PM the pollutant molecular weight), while R_L is the fractional liquid-phase resistance. As it appears from the above expressions, R_L (and therefore y^* and A^*) depend on E, which is not yet known.

Then it is necessary to proceed by successive iterations, assuming as first attempt $E = H_a$ and then calculating in sequence R_L, y^*, A^* and E_i (with (2.1)).

If $E_i > 5\ H_a$, then $E = H_a$ was correct, otherwise E is calculated with (2.2).

With the new E value we recalculate R_L, y^*, A^*, E_i and a further E value and we go on until convergence (that is until the last value calculated for E coincides in practice with the previous one).

Theoretically for each y value we have a different E, because along the column there is the variation of C_R (which is minimum at the bottom and maximum at the top) and especially of A^* (which, like y, is maximum at the bottom and minimum at the top).

The most critical point, from the point of view of the possibility that the reaction is pseudo-first order, is the column bottom, because there E_i is minimum and therefore more unlikely $> 5\ H_a$.

However, if at the column bottom we are already in conditions of pseudo-first order reaction, then in the upper sections we will be even more so; moreover, if the excess of reagent is already substantial at the bottom, probably H_a (which depends on C_R) and E (which is equal to H_a) will increase only slightly going up along the column.

Actually it is not so much the variations of E along the bed that should attract attention, but the ones of H_{OG}.

If H_{OG} remains reasonably constant, then it is a posteriori legitimate to have taken it out of the integral (see expression (1.3)), otherwise the very method of calculating Z as a product of H_{OG} by N_{OG} appears undermined: the integral should be numerically solved by associating to each y value the corresponding H_{OG} value.

Note that even if we are not in conditions of pseudo-first order reaction in the lower trunk of the column, but the E values (although very variable along the column) are however all high enough to make H_{OG} practically equal to H_G at every point, the variability of E is not a problem and the final result (the height Z) is exactly the same that would be achieved by greatly increasing the excess of reagent in order to have a practically constant E value along the column.

On the other hand, it can happen that the excess of reagent is such as to ensure a practically constant E value along the bed, but insufficient to achieve a full control in the gas phase. In other words, it can happen that H_{OG} is reasonably constant, but remains far greater than H_G. Also in this case the simplified calculation method ($Z = H_{OG} \cdot N_{OG}$) remains valid.

It is then easy to understand that, in the presence of two H_{OG} values calculated at the two ends of the column and not too different from each other, it is allowable (given the numerous approximations already implied in the method) to consider their arithmetic mean value (or still better their logarithmic mean) and continue quietly in the usual way.

Having fixed the C_R value in the column bottom (which is the one supposedly kept constant by a proper regulation system), it is necessary to evaluate what is the corresponding C_R value at the bed top.

From a simple mass balance, assuming a removal efficiency η, we have:

$$y_i \cdot \eta \cdot G \cdot z \cdot PM_R / PM = \Delta C_R \cdot L \cdot 10^3$$

from which the concentration increase ΔC_R (in mg/l) of the reagent (with molecular weight PM_R) between column bottom and top is obtained.

To come to a numerical example, we will consider for y_i (pollutant inlet concentration) a value of 20 mg/Nm³ of H_2S (that is 18.3 mg/m³ at 25°C, with PM = 34 g/mol).

With sodium hypochlorite (PM_R = 74.45 g/mol) we have z = 4 for the transformation of H_2S into sulphate.

We will then consider η = 0.98, G = 2.5 m/sec and $L = 5.556 \cdot 10^{-3}$ m/sec, hence ΔC_R = 70.7 mg/l.

Returning then to the numerical example of par. 2.1, consider the case of an excess of hypochlorite in the column bottom equal to 50 mg/l ($C_R = 6.72 \cdot 10^{-4}$ mol/l).

We have $H_a = \sqrt{1.61 \cdot 10^{-9} \cdot 3.2 \cdot 10^{6} \cdot 6.72 \cdot 10^{-4}} / 1.74 \cdot 10^{-4} = 10.7$

To calculate E_i with (2.1) it is necessary to evaluate A^* with (2.3), where in the expression of R_L we will assume for E, as a first attempt, $E = H_a = 10.7$, obtaining:

$R_L = 1 \,/\, \left(1 + \frac{10.7}{0.004} \cdot \frac{0.417}{0.394} \cdot \frac{5.556 \cdot 10^{-3}}{2.5}\right) = 0.137$ $\qquad$ $y^* = 0.137 \cdot 18.3 = 2.51$ mg/m³

$A^* = \frac{2.51 \cdot 10^{-6}}{34 \cdot 0.004} = 1.85 \cdot 10^{-5}$ mol/l $\qquad$ $E_i = 1 + \frac{6.72 \cdot 10^{-4}}{4 \cdot 1.85 \cdot 10^{-5}} = 10.1$

H_a is definitely greater than 2, so the reaction occurs entirely in the film (and therefore $y_e = 0$), but E_i is much less than $5 \cdot H_a$ and as a result we are far from the conditions of pseudo-first order reaction.

Using then (2.2) we calculate (with $H_a = 10.7$ and $E_i = 10.1$) $E = 6.99$ and proceed to a second iteration, using this value for the calculation of R_L. We get $R_L = 0.196$, $A^* = 2.64 \cdot 10^{-5}$ mol/l and $E_i = 7.34$ and then, with (2.2), $E = 6.00$.

Finally, we arrive at a convergent E value equal to 5.43 (very different from $E = H_a = 10.7$, as it would have been in the case of a pseudo-first order reaction).

The value of H_{OG} is therefore equal to:

$$H_{OG} = H_G + \frac{H^* \cdot G}{E \cdot L} H_L = 0.417 + \frac{0.004 \cdot 2.5}{5.43 \cdot 5.56 \cdot 10^{-3}} \cdot 0.394 = 0.417 + 0.131 = 0.55 \text{ m}$$

The gas-phase resistance is prevailing, but not completely.

Now let us see what are the conditions at the top of the column (assuming an efficiency of 98%).

Here the excess of reagent is equal to 50 + 70.7 = 120.7 mg/l (that is $C_R = 1.62 \cdot 10^{-3}$ mol/l) and therefore $H_a = 16.6$. We obtain (assuming $E = H_a$) $R_L = 0.0929$ and now being $y = (1 - 0.98) \cdot 18.3 = 0.366$ mg/m³, we have $y^* = 0.0929 \cdot 0.366 = 0.034$ mg/m³, $A^* = 2.50 \cdot 10^{-7}$ mol/l, $E_i = 1621$.

E_i is largely greater than $5 \cdot H_a$, so the hypothesis of a pseudo-first order reaction (and therefore of $E = H_a$) was fully justified (on the other hand, as proof, the expression (2.2) with $E_i = 1621$ and $H_a = 16.6$ gives $E = 16.55$).

The value of H_{OG} is therefore equal to:

$$H_{OG} = 0.417 + \frac{0.004 \cdot 2.5}{16.6 \cdot 5.556 \cdot 10^{-3}} \cdot 0.394 = 0.417 + 0.043 = 0.46 \text{ m}$$

Here the resistance is almost totally in the gas phase.

However, the H_{OG} values at both ends of the bed are only slightly different, so it is justified to assume for H_{OG} the average value (0.548 + 0.460) / 2 = 0.50 m (the logarithmic mean is practically identical). Efficiency, as already calculated in the previous paragraph, is 98.6% (in satisfactory agreement with the 98% hypothesis made to calculate E at the top of the column).

With an excess in the column bottom of 500 mg/l ($C_R = 6.72 \cdot 10^{-3}$ mol/l) and therefore H_a = 33.8, we calculate immediately E_i = 261, equal to 7.7 times H_a, so the hypothesis of pseudo-first order reaction (and therefore of $E = H_a$) made in the previous paragraph was fully justified.

Given the large excess of hypochlorite, compared to what consumed along the bed, the value of H_a and therefore of E at the top of the column is only slightly higher than at the base. However, the H_{OG} value remains practically the same, because already at the base it was only very slightly higher than H_G.

2.3. CONTROLLING RESISTANCE IN BOTH PHASES

If the mass transfer resistance in the liquid phase is not negligible, many of the conclusions made at the end of par. 2.1 change significantly.

Considering e.g. methyl mercaptan, the values of the various chemical-physical parameters are not substantially different from the ones of H_2S (we have now $H = 0.152$, $D_G = 1.28 \cdot 10^{-5}$ m²/sec, $D_L = 1.26 \cdot 10^{-9}$ m²/sec, $K = 2.1 \cdot 10^6$ l/mol/sec [2], $k_L = 1.54 \cdot 10^{-4}$ m/sec).

The fundamental difference is given by the pK equal to 10 instead of 7, because this parameter affects exponentially the total solubility of the substance (including the dissociated form).

For pH less than 10 this solubility is minimal, because H^* (which is inversely proportional to the total solubility) is practically equal to H (which is quite high). For pH greater than 10, H^* becomes an increasingly smaller fraction of H (that is, the solubility increases) and the liquid-phase resistance decreases correspondingly.

If we try to calculate H_{OG} and η for pH = 9 and pH = 10.5 with the above formulas (considering $C_R = 6.72 \cdot 10^{-3}$ mol/l and assuming a pseudo-first order reaction, also because the plausible concentrations of mercaptan in the fumes are quite lower than the ones of H_2S), we get:

- for pH = 9, $H^* = 0.152 / (1 + 10^{9-10}) = 0.138$; $H_a = 27.4$; $H_G = 0.508$ m; $H_L = 0.445$ m

  $$H_{OG} = 0.508 + \frac{0.138 \cdot 2.5}{27.4 \cdot 5.556 \cdot 10^{-3}} \cdot 0.445 = 0.508 + 1.01 = 1.52 \text{ m}$$

  $N_{OG} = 2.15 / 1.52 = 1.42$ $\eta = 75.8\%$

- for pH = 10.5, $H^* = 0.152 / (1 + 10^{10.5-10}) = 0.0365$; H_a, H_G and H_L do not change

  $$H_{OG} = 0.508 + \frac{0.0365 \cdot 2.5}{27.4 \cdot 5.556 \cdot 10^{-3}} \cdot 0.445 = 0.508 + 0.267 = 0.775 \text{ m}$$

  $N_{OG} = 2.15 / 0.775 = 2.77$ $\eta = 93.7\%$

In the first case the liquid phase resistance is so high as to be controlling (and efficiency is significantly affected), in the second this resistance is considerably lower, even if not negligible (efficiency is however already good).

Even better results ($\eta = 97\%$) would be obtained at pH = 11, but at this pH the CO_2 contained in the air is also absorbed to a remarkable extent, and the consumption of NaOH rises considerably.

If the liquid phase resistance is controlling, not only does the efficiency decrease, but the column gas velocity acquires a significant influence.

If in the previous calculation at pH 9 we assume a speed of 1.5 m/sec instead of 2.5 m/sec, we get

$$H_{OG} = 0.447 + \frac{0.138 \cdot 1.5}{27.4 \cdot 5.556 \cdot 10^{-3}} \cdot 0.445 = 0.447 + 0.605 = 1.05 \text{ m}$$

N_{OG} = 2.15 / 1.05 = 2.05 η = 87.1% (instead of 75.8%).

So the longer residence time has in this case a quite beneficial effect.

But the closer we get to optimal physico-chemical conditions, the more the benefit diminishes.

In fact at pH 10.5, with G = 1.5 m/sec, we get H_{OG} = 0.447 + 0.160 = 0.607 m and η = 97.1% instead of 93.7% for G = 2.5 m/sec.

A resistance control even in the liquid phase can also arise in case of choice of a non-optimal reagent.

Let us take e.g. hydrogen peroxide as a potential alternative to sodium hypochlorite.

The usual reagent concentration (in basic environment) is 5 g/l (0.147 mol/l), while the kinetic constant K of the reaction with H_2S is 1.15 l/mol/sec [2].

The Hatta number is therefore equal to $\sqrt{1.61 \cdot 10^{-9} \cdot 1.15 \cdot 0.147}/1.74 \cdot 10^{-4} = 0.095$, which corresponds to a rather slow reaction with E = 1.

At pH 9, in the fluid-dynamics conditions already considered above, we have therefore:

$$H_{OG} = H_G + \frac{H^* \cdot G}{E \cdot L} H_L = 0.417 + \frac{0.004 \cdot 2.5}{1 \cdot 5.556 \cdot 10^{-3}} \cdot 0.394 = 0.417 + 0.709 = 1.13 \text{ m}$$

hence N_{OG} = 2.15 / 1.13 = 1.9, $\eta = 1 - e^{-N_{OG}}$ = 85.1% (against 99.3% with 0.5 g/l of NaOCl).

Actually under these conditions (H_a < 2) the reaction does not occur anymore completely in the film, so y_e can be significantly different from 0 and the value of the integral that gives N_{OG} changes accordingly: efficiency can be in practice much lower than the one calculated above.

The reaction constant with methyl mercaptan is not known, but presumably, by analogy with the case of hypochlorite, it is of the same order or smaller than with H_2S.

As a result H_a will still be much less than 1 and therefore E = 1. So, always at pH 9:

$$H_{OG} = 0.508 + \frac{0.138 \cdot 2.5}{1 \cdot 5.556 \cdot 10^{-3}} \cdot 0.445 = 0.508 + 27.6 = 28.1 \text{ m}$$

hence $N_{OG} = 2.15 / 28.1 = 0.077$ and $\eta = 7.4\%$ (against 75.8% with hypochlorite).

In this case the resistance control is completely in the liquid phase, while for H_2S it is almost equally shared between the liquid and gaseous phase.

As pH increases, for H_2S the resistance control moves progressively into the gas phase, and efficiency increases correspondingly ($\eta = 96.5\%$ at pH 9.5, $\eta = 98.8\%$ at pH 10).

However, the above consideration made for y_e always holds true: efficiencies can therefore be much lower.

For mercaptan, even at pH 10.5 the control remains firmly in the liquid phase ($H_{OG} = 0.508 + 7.31 = 7.82$ m) and efficiency remains very low (24%, against 93.7% of hypochlorite).

It is possible to dramatically increase the reaction rate, in the case of hydrogen peroxide, activating its action by means of U.V. rays, for example, but in practical applications the effect of the rays is greatly weakened by the poor transparency of recirculating liquid solutions (hardly are the fumes completely free of solid particles).

The above calculations show the importance and the influence, on the obtainable efficiencies, of the adoption of optimal operating conditions, both hydrodynamic (speed and residence time) and chemical.

In particular, it is interesting the conclusion that, if reagents and their concentrations (pH and redox potential) are chosen in each column in an appropriate manner, so that the chemical reaction with the pollutants to be removed is rapid and irreversible, two important effects are obtained:

- the equilibrium concentration of these pollutants in the gas phase is zero ($y_e = 0$)
- the mass transfer resistance in the gas phase is controlling ($H_{OG} = \sim H_G$).

Under such hypotheses the obtainable efficiency depends only on the packing type, the bed height and the liquid flow rate, while it is little influenced by the residence time of the fumes in the tower and by the specific reagents and pollutants considered (the only characteristic parameter of the involved substances is D_G, which can vary between $0.6 \cdot 10^{-5}$ and $1.8 \cdot 10^{-5}$ m²/sec and appears however with an exponent smaller than 1 in the expression of H_G).

With regard to the rate and irreversibility of the chemical reactions of major interest in the ecological field, it can generally be noted that:

- oxidation reactions are generally irreversible and can be more or less fast, but usually have a finite rate, which should be known to quantify their influence on the overall mass transfer resistance,
- acid-base reactions are typically purely ionic and practically instantaneous (with some exceptions, such as CO_2 neutralization), so the mass transfer resistance in the liquid phase is normally negligible; they are however generally reversible equilibria, so the y_e value may be not negligible in the calculation of N_{OG}.

2.4. REVERSIBLE REACTIONS

To better understand the problems that reversible reactions can pose consider e.g. H_2S removal using only caustic soda addition.

The acid neutralization reaction is practically instantaneous, so that in all the points of the liquid phase, including the film, there is a chemical equilibrium between the reacting species. The diffusion equations are therefore controlling, without the need for any expression of chemical kinetics.

If the diffusivities of H_2S and HS^- are considered equal (as it is true in first approximation), we can use in practice the equations of par. 1.1, valid for purely physical absorption of the pollutant, except that its concentration x in the liquid phase must be considered as the sum of both free (H_2S) and dissociated (HS^-) forms [10].

The latter term is essentially the H_2S that reacted with NaOH.

To this purpose it is sufficient to introduce the modified Henry constant $H^*=H/(1+10^{\,pH-pK})$, instead of the normal value H, not only in the expression (1.4) of H_{OG}, but also in the one of $y_e = H \cdot x$, which intervenes in the calculation of N_{OG} of the expression (1.3), and ultimately in the equation (1.8) that provides the column efficiency.

Strictly speaking, if the diffusivities were to be taken into account, the expression $H^* = H / (1 + \sqrt{D_{HS^-}/D_{H_2S}} \cdot 10^{\,pH-pK})$ should be considered for H^*.

In practice the fundamental difference in comparison with the case of the irreversible reaction (which is achieved by adding NaOCl as well as NaOH to the washing liquid) is that y_e is no longer zero, as assumed at the beginning of par. 2.1, but it can reach remarkable values compared to y, especially in the usual case of almost totally recirculated washing liquid: the performance is heavily affected.

Considering the same operating conditions assumed in par. 2.1 (i.e. Z = 2.15 m, G = 2.5 m/sec, $L = 5.556 \cdot 10^{-3}$ m/sec), the formula (1.8), with $x_m = 0$, gives the following values of η, as a function of pH and r (purged liquid fraction):

pH	9	9	9	10	10	10	11	11	11
r	0.005	0.05	1	0.005	0.05	1	0.005	0.05	1
η (%)	0.28	2.79	49.9	2.72	22.5	97.8	21.8	74.1	99.3

The first data processing corresponds to a configuration similar to the one examined in par. 2.1 (a 0.5% bleed is typical of recirculation scrubbing with irreversible chemical reaction): efficiency goes from 99.3% by dosing hypochlorite, with an excess of 500 ppm, to 0.28% by adding only caustic soda.
Things improve with the increase in pH and bleed, but to have acceptable yields with soda alone it is necessary to go to pH 10, in absence of recirculation, or to pH 11 with bleeding of at least 5% of the liquid.

However, with other reversible reactions achieving high yields is much less problematic.
Consider, for example, the removal of ammonia by sulphuric acid or of acetic acid and phenol by caustic soda.
The necessary parameters for the calculation are Henry constant, pK_a and diffusivities.
At 25°C we have:

- Ammonia: $H = 6.8 \cdot 10^{-4}$, $pK_a = 9.25$, $D_G = 2.52 \cdot 10^{-5}$ m^2/sec, $D_L = 2.00 \cdot 10^{-9}$ m^2/sec.
- Acetic acid: $H = 1.0 \cdot 10^{-5}$, $pK_a = 4.76$, $D_G = 1.24 \cdot 10^{-5}$ m^2/sec, $D_L = 1.24 \cdot 10^{-9}$ m^2/sec.
- Phenol: $H = 1.6 \cdot 10^{-5}$, $pK_a = 9.99$, $D_G = 8.51 \cdot 10^{-6}$ m^2/sec, $D_L = 9.74 \cdot 10^{-10}$ m^2/sec.

The formulas to be used to calculate the efficiency are (1.8) (with $x_m = 0$ and H^* instead of H) in the case of a column operated with a continuous bleed, and (1.11) (with H^* instead of H) in the case of no bleed and periodically replaced liquid.
Assuming that the *pH* of the scrubbing liquid is controlled at a value sufficiently far from pK_a (e.g., *pH* 3 for ammonia, *pH* 9 for acetic acid, *pH* 11 for phenol), effective Henry constant H^* values are obtained that are small enough to make H_{OG} practically equal to H_G, and therefore minimal (the controlling resistance is completely in the gas phase).
In particular, with the formulas of par. 1.1.2, we get respectively $H^* = 3.8 \cdot 10^{-10}$ for ammonia, $H^* = 5.8 \cdot 10^{-10}$ for acetic acid, $H^* = 1.4 \cdot 10^{-6}$ for phenol.
With the formulas of par. 1.3, considering Q-PAC packing with the usual parameters G = 2.5 m/sec and $L = 5.556 \cdot 10^{-3}$ m/sec, we obtain the following values of H_G and H_L, and then of $H_{OG} = H_G + H^* G/L \cdot H_L$:

- Ammonia: $H_G = 0.32$ m, $H_L = 0.35$ m, $H_{OG} = 0.32$ m.
- Acetic acid: $H_G = 0.52$ m, $H_L = 0.45$ m, $H_{OG} = 0.52$ m.
- Phenol: $H_G = 0.67$ m, $H_L = 0.51$ m, $H_{OG} = 0.67$ m.

With the typical parameters of DN 50 Pall rings, the H_{OG} values would have been even lower. This means that, with an effective bed height of Z = 2.15 m, the parameter Z/H_{OG} is in all cases greater than 3.2 and therefore, being also $H^*G/L << 1$, the exponential term that appears both in (1.8) and in the b expression of (1.11) is very small compared to 1 and could be disregarded without making a significant error.

This implies that efficiencies are poorly dependent on the diffusivities and the type of used packing, because H_{OG} does not appear elsewhere in the formulas.

Assuming $V = 1\ m^3/m^2$, the following results are obtained:

- For ammonia, with a continuous bleed equal to only 0.2% of the recirculated liquid an efficiency of 99.9% is achieved, while, in the absence of bleed, after 3000 h of operation an efficiency of 98.9% is still obtained (at this point attention should be paid to the concentration achieved by ammonium sulphate, rather than to the efficiency decrease).
- For acetic acid, with a continuous bleed corresponding to r = 0.002 the efficiency is 98.4%, while, in the absence of bleeding, after 3000 h of operation there is still an efficiency of 96.9%.
- For phenol, with a continuous bleed of 0.5% the efficiency is 85.6%, while, in the absence of bleeding, after 12 h and 24 h of operation the efficiency drops to 83% and 72% respectively.

2.5. OTHER EXAMPLES OF REACTIONS

2.5.1. HCN reaction with NaOH and NaClO

The removal of HCN by caustic soda and sodium hypochlorite, industrially applied, provides an interesting example of a complex reaction.

Hydrocyanic acid reacts with caustic soda and is salified to cyanide according to the following reaction:

1) $HCN + NaOH \rightarrow NaCN + H_2O$

Cyanide is then oxidized by hypochlorite according to the following mechanisms:

2) $NaCN + NaClO + H_2O \rightarrow CNCl + 2\ NaOH$

3) $CNCl + 2\ NaOH \rightarrow NaCNO + NaCl + H_2O$

There is initially the formation of cyanogen chloride, which then, in a basic environment, hydrolyzes to sodium cyanate (cyanogen chloride is as toxic as hydrocyanic acid, cyanate much less).

The overall reaction of 2) and 3) is as follows:

4) $NaCN + NaClO \rightarrow NaCNO + NaCl$

The oxidation by hypochlorite can then continue upon cyanate, with the formation of bicarbonate and nitrogen:

5) $2\ NaCNO + 3\ NaClO + H_2O \rightarrow N_2 + 2\ NaHCO_3 + 3\ NaCl$

The overall reaction, resulting from 2), 3) and 5), is as follows

6) $2\ NaCN + 5\ NaClO + H_2O \rightarrow N_2 + 2\ NaHCO_3 + 3\ NaCl$

Reaction 1) is actually an equilibrium, shifted the more to the right the higher the *pH*.

As HCN is a very weak acid ($pK = 9.2$), very high *pH* (certainly higher than *pK*) are necessary to minimize the HCN concentration in water.

To achieve the desired concentrations in the fumes (< 0.5 mg/Nm^3) using caustic soda alone would require excessively high *pH* values of the scrubbing liquid (of the order of 12), at which the CO_2 present in the fumes would also be absorbed, considerably increasing the soda consumption (often the flow containing HCN also includes combustion fumes, with a CO_2 presence much more remarkable, therefore, than the typical one in the air). In addition, the liquid purged from the scrubbing tower, if subsequently undergoes a drop in *pH*, could release the salified HCN again.

The method of calculating the removal efficiency, using only caustic soda, is however the one already shown in par. 2.4.

On the contrary, the reactions with hypochlorite are irreversible and, with the presence of a moderate excess of this reagent (that is, with a sufficiently high value of the redox potential), they are able to practically cancel the concentration of HCN and cyanide in the liquid mass.

However, the *pH* must be kept sufficiently high for two purposes:

- to hydrolyze and destroy cyanogen chloride (as toxic as HCN),
- to increase the virtual HCN solubility in water, thanks to the fact that reaction 1), although reversible, is practically instantaneous.

The rate of reaction 1), in addition to being very high, is independent of *pH*, while the rate of reactions 2), 3) and 5) has a finite value that depends on *pH*.

In particular, a high *pH* favours reaction 3), as already mentioned, but disadvantages reaction 2) and 5).

In the *pH* range between 10 and 11 the virtual HCN solubility increases by a factor equal to $(1+10^{pH-pK})$ by dissociation. For example, for pH =10.5 the increase is about 21 times.

In that field reaction 2) is still (despite the rather high *pH*) a fast one, which occurs completely in the liquid film adjacent to the liquid-gas interface in the packed bed.

This means that the concentration of free and combined HCN is practically zero in the liquid mass.

Moreover, for the combined effect of high reaction rate and high virtual solubility the mass transfer resistance in the liquid phase becomes almost zero: hence the HCN removal efficiency only depends on the diffusive phenomena in the gas phase.

In the same *pH* range reaction 3) is still quite slow, despite the high *pH*, and therefore occurs not in the film, but in the liquid mass. The completion of the reaction therefore depends on the volume occupied by the recirculating liquid. The capacity of the storage tank at the base of the column must be sufficient for a complete hydrolysis of cyanogen chloride.

At these high *pH* reaction 5) is very slow. The cyanide oxidation therefore stops practically at the cyanate stage.

Coming now to the column sizing, we remark that the chemical-physical characteristics at 25°C of HCN (which has PM=27 g/mol) are as follows: $D_G = 2.02 \cdot 10^{-5}$ m^2/sec, $D_L = 1.89 \cdot 10^{-9}$ m^2/sec, $H = 3.41 \cdot 10^{-3}$, $pK = 9.2$.

We will assume an operating pH of 10.5 and an inlet HCN concentration of 10 mg/Nm^3 (9.2 mg/m^3 at 25°C).

The bed will be 2.5 m high and consisting of Q-PAC packing. The specific flow rates will be G = 2.5 m/sec and $L = 5.556 \cdot 10^{-3}$ m/sec.

Using the Billet-Shultes model (par. 1.3) we get H_G = 0.375 m, H_L = 0.363 m, $k_L = 0.188 \cdot 10^{-3}$ m/sec, while the useful height of the bed will be $Z = 2.5 - 0.35 = 2.15$ m.

Then we have $H^* = H / (1+10^{pH-pK}) = 3.41 \cdot 10^{-3} / (1+10^{10.5-9.2}) = 1.63 \cdot 10^{-4}$.

For the kinetic constant K of reaction 2) the following expression applies [11]: $K = (310 + 583 / [OH^-])$ l/mol/sec.

Taking into account that the pK_w of water at 25°C is 14.0, at pH 10.5 we have $[OH^-] = 10^{10.5-14.0} = 3.16 \cdot 10^{-4}$ mol/l and therefore $K = 1.84 \cdot 10^6$ l/mol/sec.

Considering finally an excess of hypochlorite C_R of $6.72 \cdot 10^{-4}$ mol/l (50 mg/l), the Hatta number is equal to:

$$H_a = \frac{\sqrt{D_L \cdot K \cdot C_R}}{k_L} = (1.89 \cdot 10^{-9} \cdot 1.84 \cdot 10^6 \cdot 6.72 \cdot 10^{-4})^{1/2} / 0.188 \cdot 10^{-3} = 8.13$$

Being $H_a > 2$, the reaction is fast and occurs completely in the film. Moreover, the excess of reagent is such, compared to the concentration of the pollutant, that the reaction is also pseudo-first order, so $E = H_a$.

This is easily verified by the method of par. 2.2, calculating $R_L = 1/(1+E/H^* \cdot H_G/H_L \cdot L/G) = 1/(1+ 8.13/1.63 \cdot 10^{-4} \cdot 0.375/0.363 \cdot 5.556 \cdot 10^{-3}/2.5) = 8.66 \cdot 10^{-3}$, then $y^* = R_L \cdot y = 8.66 \cdot 10^{-3} \cdot 9.2 = 0.0797$ mg/m^3, then $A^* = y^* \cdot 10^{-6}/PM/H^* = 0.0797 \cdot 10^{-6}/27/1.63 \cdot 10^{-4} = 1.81 \cdot 10^{-5}$ mol/l and finally $E_i = 1 + C_R / z / A^* = 1 + 6.72 \cdot 10^{-4}/1/1.81 \cdot 10^{-5} = 38.1$.

Being E_i equal to about $5 \cdot H_a$, the condition for the reaction to be considered pseudo-first order is fulfilled.

We then have:

$H_{OG} = H_G + H_L \cdot H^*/E \cdot G/L = 0.375 + 0.363 \cdot 1.63 \cdot 10^{-4}/8.13 \cdot 2.5/5.556 \cdot 10^{-3} = 0.375 + 0.003 = 0.38$ m, from which it appears that the mass transfer resistance, already at the column bottom, is totally in the gas phase.

It is no use to calculate the conditions at the column top, because H_{OG} can be at least as large as H_G (0.375 m) and therefore is constant throughout the column.

Thus $N_{OG} = Z / H_{OG} = 2.15/0.38 = 5.66$ and efficiency is $\eta = 1 - e^{-N_{OG}} = 99.7\%$.

If *pH* is raised to 11, the result is practically the same (H_a = 4.58; E_i = 21.9; $E = H_a$; H_{OG} = 0.38 m; η = 99.7%).

As for CNCl hydrolysis, the reaction rate *r* (mol/l/sec) is given by:

$$r = d\,[\mathrm{CNCl}]/dt = -K\,[\mathrm{OH^-}]\,[\mathrm{CNCl}]$$

with K = 4.53 l/mol/sec.

The reaction between CNCl and NaOH takes place in homogeneous liquid phase, in particular in the recirculating liquid storage tank at the base of the column.

A specific volume V of the order of 1 m^3 per m^2 of column section $\bar{S}$ is normally provided for this tank. Let us then check what is the conversion of cyanogen chloride into cyanate that is so obtained.

We will consider this tank as an ideal reactor (perfectly agitated) from which a bleed flow S (m^3/sec per m^2 of column section $\bar{S}$) is continuously discharged. In bleed S (usually 0.5% L) the cyanogen chloride concentration C_A is therefore equal to the one in the tank.

The amount Q of CNCl generated (expressed in mol/sec) is equal to the one of HCN (PM = 27 g/mol) entering the column (assuming for simplicity and precaution that it is completely absorbed).

If this amount actually reaches the recirculation tank, it would be equal to what reacts in the tank plus what exits with the bleed.

That is:

$Q = y_i\, G\, \bar{S}\, /10^3/PM = V\, \bar{S}\, (-r)10^3 + S\, \bar{S}\, C_A\, 10^3 = V\, \bar{S}\, K\, C_A\, [\mathrm{OH^-}]10^3 + 0.005\, L\, \bar{S}\, C_A\, 10^3$

hence $C_A = 10^{-6}\, y_i\, G\, /PM\, /\, (V\, K\, [\mathrm{OH^-}] + 0.005\, L) = 10^{-6} \cdot 9.2 \cdot 2.5/27/(1 \cdot 4.53 \cdot 3.16 \cdot 10^{-4} + 0.005 \cdot 5.556 \cdot 10^{-3}) = 5.84 \cdot 10^{-4}$ mol/l, that is 35.9 mg/l, as CNCl has PM = 61,5 g/mol.

Practically there is a bleed of $0.005 \cdot L \cdot 10^3 \cdot C_A = 0.005 \cdot 5.556 \cdot 5.84 \cdot 10^{-4} = 1.62 \cdot 10^{-5}$ mol/sec/m^2 of CNCl out of $y_i\, G \cdot 10^{-3}/PM = 9.2 \cdot 2.5 \cdot 10^{-3}/27 = 8.52 \cdot 10^{-4}$ mol/sec/m^2 generated (98.1% is destroyed).

If *pH* was raised to 11, then it would be $[\mathrm{OH^-}] = 1.0 \cdot 10^{-3}$ mol/l and C_A would be equal to $1.87 \cdot 10^{-4}$ mol/l (11.5 mg/l): 99.4% of CNCl would be destroyed.

Obviously, to reduce the CNCl concentration at the discharge it is also possible to intervene in other ways, for example by increasing the specific volume V (also through a bleed storage tank separated from the column).

We said before “If this amount actually reaches the recirculation tank”, and not by chance.
The problem is that, once formed in the liquid film in the tower, the cyanogen chloride (which is gaseous at room temperature), due to the slowness of its hydrolysis reaction with caustic soda, has both all the time and favourable hydrodynamic conditions to desorb and transfer almost completely into the fumes, going out with them from the chimney, rather than proceed with the scrubbing liquid down to the recirculation tank.
The demonstration of this assertion is rather complex and has required the elaboration of a specific kinetic-diffusive model, not yet dealt with in the literature (see the Appendix).

2.5.2. HCN reaction with NaOH and H_2O_2

We have seen in the previous paragraph that the utilization of the reaction of HCN with NaClO poses a problem due to the desorption of CNCl, initially formed, before it has time to hydrolyze to cyanate.

The reaction of HCN with hydrogen peroxide, always in the presence of caustic soda, does not pose this type of problem, because the product of the oxidation reaction is directly cyanate, which is then hydrolyzed, according to the following mechanism:

1) $HCN + NaOH \rightarrow NaCN + H_2O$

2) $NaCN + H_2O_2 \rightarrow NaCNO + H_2O$

3) $NaCNO + 3\ H_2O \rightarrow NH_4OH + NaHCO_3$

However, reaction 2), unlike reaction 2) of the previous paragraph, is very slow and occurs neither in the film, nor in the liquid percolating along the bed, but only in the column bottom (provided it has there a sufficient residence time).

According to Sarla [13] reaction 2) is pseudo-first order, with a constant K (including the reagent concentration) equal to 1.28 h^{-1} at a H_2O_2 concentration of 132.3 $\cdot 10^{-3}$ mol/l (i.e. 4.5 g/l). Actually, the K constant is not independent of the H_2O_2 concentration, but neither proportional to it, so it is more appropriate to consider the hypothesis of the pseudo-first order reaction, with reference to specific operating conditions.

Reaction 3) is even slower than reaction 2) (at least 8 times), so cyanate can be considered in practice as the final reaction product.

The Hatta number of reaction 2) is equal to $(D_L \cdot K)^{1/2}/k_L = (1.89 \cdot 10^{-9} \cdot 1.28/3600)^{1/2}/1.88 \cdot 10^{-4} = 0.0044$. Being $\ll 1$, the reaction does not occur in the film.

But since $k_L \cdot a_e$ ($= 1.88 \cdot 10^{-4} \cdot 81.2 = 1527 \cdot 10^{-5}$ sec^{-1}) $\gg h_e \cdot K$ ($= 0.03 \cdot 1.28/3600 = 1.07 \cdot 10^{-5}$ sec^{-1}), the diffusion rate of hydrogen cyanide in the liquid (a_e is the effective specific area in m^2/m^3) is much greater than the reaction rate, so the latter does not occur even within the liquid contained in the bed (h_e is the hold-up in m^3/m^3; the values of D_L, k_L, a_e, h_e are the same as the ones already used in the previous paragraph).

It follows then that HCN absorption in the bed is governed by the expressions of par. 1.1 valid for the purely physical phenomenon, except that in them it is necessary to consider the effective Henry constant H^* to take into account the instantaneous reversible reaction 1) with caustic soda.

Actually it is also necessary to take into account that in the bottom tank the reaction 2) takes place, so that the x_o concentration (in the tank and in the bleed) is different from the one (which we could call x_o') at the bed exit.

In practice (1.7) is no longer valid, but should be replaced by the following mass balances (considering for simplicity $x_m = 0$):

$$(L - S)\, x_o = L\, x_i \qquad\qquad G\,(y_i - y_o) = S\, x_o + V\, K\, x_o$$

The first balance (thought around the recirculation pump) leads to $x_i = (1 - r)\, x_o$.

The second says that the absorbed pollutant is equal to what comes out with the bleed plus what reacts in the tank (of specific volume V in m, that is m^3 referred to m^2 of column section). We get then:

$$x_o = \frac{G y_i \eta}{Lr + VK} \qquad\qquad x_i = (1 - r)\frac{G y_i \eta}{Lr + VK}$$

Replacing this value of x_i in (1.5), we get, after some steps:

$$\eta = \frac{1 - exp\left[\frac{Z}{H_{OG}}\left(\frac{H^* G}{L} - 1\right)\right]}{\left(1 + \frac{H^* G}{L}\,\frac{1 - r}{r + \frac{VK}{L}}\right) - \frac{H^* G}{L}\left(1 + \frac{1 - r}{r + \frac{VK}{L}}\right) \cdot exp\left[\frac{Z}{H_{OG}}\left(\frac{H^* G}{L} - 1\right)\right]}$$

which is very similar to (1.8), except for the absence of x_m and the introduction of the VK/L factor, due to the chemical reaction with H_2O_2 (in particular, if we set $K = 0$, we have the expression of the efficiency using only caustic soda).

Proceeding to a concrete example, we will assume as usual $Z = 2.15$ m, $G = 2.5$ m/sec, $L = 5.556 \cdot 10^{-3}$ m/sec, $r = 0.005$ (typical of recirculation systems with chemical reaction).

For H_G , H_L , H_{OG} and H^* we will assume the same values and expressions as in the previous paragraph, namely (for Q-PAC packing) $H_G = 0.375$ m, $H_L = 0.363$ m, and besides:

$H^* = H / (1+10^{pH-pK}) = 3.41 \cdot 10^{-3} / (1+10^{pH-9.2})$ $\qquad\qquad$ $H_{OG} = H_G + H_L \cdot H^* G/L$

To have acceptable efficiencies, it is necessary to assume rather high values of both pH (for example 10.8, even if high pH values favour the decomposition of hydrogen peroxide) and V (for example 4 m^3/m^2, even if the tank becomes rather bulky).

This gives $H^* = 8.36 \cdot 10^{-5}$, $H_{OG} = 0.389$ m and finally $\eta = 87.1\%$, corresponding (with $y_i = 9.2$ mg/m^3) to $x_o = 2.5 \cdot 9.2 \cdot 0.871 / (5.556 \cdot 10^{-3} \cdot 0.005 + 4 \cdot 1.28/3600) = 13{,}816$ mg/m^3.

The r value is not particularly critical. With $r = 0$, η drops to 86.8%, but a minimum bleed is always necessary to dispose of reaction products and other pollutants (e.g. dust) that tend to accumulate .

As seen, in the bleed there is a concentration of 13.8 mg/l as HCN (c_o = 13.3 mg/l as CN). It is above the c_l limit allowed for waste waters, but this is a very small flow, compared to the presumable total discharge of a factory. However, if necessary, it is sufficient to direct the bleed towards a small agitated tank that guarantees a residence time of 2÷2.5 h to drop below the concentration of 1÷ 0.5 mg/l (this is obtained immediately from $K\,t = \ln\, c_o/c_l$).

Rather critical for tower performance is the *pH*. Dropping to *pH* 10.5, η decreases from 87.1% to 77.7%.

Very critical is the V value: with $V = 2$ m we would have $\eta = 77.7\%$, with $V = 1$ m (as in usual towers) $\eta = 64.6\%$.

To achieve efficiencies even higher than 90÷95% (with $V = 1$ m and $pH = 10.5$) the reactivity of hydrogen peroxide should be increased, which is virtually possible by adding the catalytic effect either of UV rays (K rises to 5.9 h^{-1}), or of a soluble copper salt (with 25 mg/l of Cu^{++} K rises to 8.3 h^{-1}), or of both (K rises to 46 h^{-1}).

But the action of UV rays is usually hindered by the lack of clearness of recirculated scrubbing liquids, while the presence of copper can give rise to annoying precipitates.

Another possible solution is the use of H_2SO_5 (Caro's acid) instead of hydrogen peroxide: with it K rises to 16 h^{-1}.

However, the reagent must be prepared on site (from highly concentrated sulphuric acid and hydrogen peroxide) and used immediately. The great danger of the two components and the remarkable heat development require the use of special plants for the preparation of the reagent, which is therefore expensive and justified only in the case of large-scale applications (such as in the mining and metallurgical industry).

3. ABSORPTION IN BUBBLE COLUMNS WITH CHEMICAL REACTION

3.1. HYDRODYNAMICS AND MASS TRANSFER

In a bubble column the gas is fed to the bottom of the column (which can also take the form of a tank), through a sparger made of perforated pipes or fine bubble diffusers, and rises upwards in the form of swarms of bubbles.

The liquid can flow cocurrent or countercurrent to the gas.

With the usual superficial gas velocities, typical of the so-called "quiescent regime", plug flow can be assumed for the gas phase (that is without appreciable back-mixing, or axial mixing), while for the liquid phase it is possible to assume a complete back-mixing (with consequent uniformity of the concentrations in the liquid phase within the entire column).

We will indicate with:

- v_G (m/sec) the superficial gas velocity, or the effective volumetric flow rate, at liquid pressure and temperature, divided by the cross-sectional area of the vessel,
- v_L (m/sec) the superficial liquid velocity, that is the volumetric flow referred to the column section, with a positive or negative sign depending on whether the two phases flow cocurrent or countercurrent,
- v_{SL} (m/sec) the relative velocity of gas and liquid, or slip velocity,
- ω the gas fractional hold-up.

By definition we have:

$$v_{SL} = \frac{v_G}{\omega} - \frac{v_L}{1-\omega} \tag{3.1}$$

while, for the air-water system, v_G / v_{SL} is provided, as a function of v_G , by Hughmark's experimental diagram [14]. There are many empirical expressions that reproduce this diagram: in the quiescent regime range ($v_G < 0.05$ m/sec) the simplest one is the following:

$$\frac{v_G}{v_{SL}} = 1.45 \cdot v_G^{0.857} \tag{3.2}$$

From (3.1) ω is obtained, as a function of v_G / v_{SL} and v_L / v_{SL}, through a second degree equation:

$$\omega = \frac{1}{2}\left(\frac{v_G}{v_{SL}} + \frac{v_L}{v_{SL}} + 1 - \sqrt{\left(\frac{v_G}{v_{SL}} + \frac{v_L}{v_{SL}} + 1\right)^2 - 4\frac{v_G}{v_{SL}}}\right) \tag{3.3}$$

Having fixed v_G and v_L (with the criteria we will see) and obtained v_{SL} from (3.2), we get from (3.3) the ω value.

Note that if v_L is zero or negligible (as it often happens), we simply have $\omega = v_G / v_{SL}$ (and the Hughmark's diagram, or the expression (3.2), give directly ω as a function of v_G).

Taking into account that a volume ω of gas and an interfacial surface a are contained by definition in a unit volume of column, both consisting of n bubbles of d_B diameter, we have

$$n = \frac{\omega}{\left(\frac{\pi}{6} d_B^3\right)} = \frac{a}{(\pi d_B)^2}$$

From this equality we derive:

$$a = \frac{6\omega}{d_B} \tag{3.4}$$

As for d_B , if the bubbles are generated by a perforated pipe, they have a d_{B0} diameter (just downstream the holes) practically independent of the hole size and the order of 4.5÷6.5 mm (according to the most authoritative literature sources). We will take a conservative 6.35 mm, that is a quarter of an inch, as suggested by Hughmark.

However, the holes shall be sized with a diameter d_0 = 3÷5 mm and a gas flow rate W (kg/sec) for each hole corresponding to Reynolds numbers of the order of 10,000÷20,000 ($N_{Re,G} = \frac{4W}{\pi d_0 \mu_G}$, where μ_G is the gas viscosity).

If instead the bubbles are generated by a fine-bubble porous diffuser, they will have a diameter d_{B0} = 1÷3 mm (we can take 2 mm as an average).

The pressure at the bottom of the column will be $P_i = P_o + h_L /10$, where P_o (atma) is the pressure at the top and h_L (m) is the effective height of the column (above the sparger).

The mean pressure in the reactor will be $P_m = P_o + h_L /20$ and the average diameter of the bubbles in the column will be

$$d_B = d_{B0} \left(\frac{P_i}{P_m}\right)^{1/3} \tag{3.5}$$

The v_G value must be < 0.05 m/sec to remain in the so-called "quiescent regime" (which allows the assumed plug flow and generates the aforesaid d_{B0} diameters). On the other hand:

- Values > 0.05 m/sec would in all likelihood generate significant and difficult to control foaming,

- If fine bubble diffusers are chosen (more efficient, but more sensitive to clogging) they can hardly be placed closer than corresponding to a v_G of the order of 0.005 m/sec,
- It is however advisable not to go below $v_G = 0.0005$ m/sec to ensure a sufficient liquid mixing (and therefore the assumed uniformity of liquid-phase concentrations).

The use of the countercurrent system tends to increase ω (therefore a) and ultimately the column efficiency. However the Hughmark's diagram applies for $v_L = 0$, for v_L up to 0.1 m/sec in the cocurrent case and for small velocities in the countercurrent case (in the absence of more specific data, v_L values not exceeding 0.05 m/sec are recommended in the latter case).

If the gas temperature is different from the liquid one (t), it will quickly reach that level. Thus a normalized specific gas flow rate v_S ($Nm^3/sec/m^2$) = $v_G \cdot P_m / (1+ t /273)$ corresponds to the selected v_G value.

Coming now to the mechanism of mass transfer between the liquid and the gas bubbles, the liquid-phase mass transfer resistance is decidedly controlling (it is not necessary to evaluate the mass transfer coefficient in the gaseous phase).

The liquid phase coefficient k_L (m/sec), to be combined with the mass transfer surface a (m^2/m^3) referred to the volume, is given in the form of a Sherwood number by the following expression by Hughmark [14], valid for bubble swarms:

$$N_{Sh} = \frac{k_L d_B}{D_A} = 2 + 0.0187 \cdot N_{Re}^{0.779} \cdot N_{Sc}^{0.546} \cdot \left(\frac{d_B \cdot g^{1/3}}{D_A^{2/3}} \right)^{0.116} \qquad (3.6)$$

where $N_{Re} = d_B \cdot v_{SL} \cdot \rho_L / \mu_L$ is the Reynolds number

$N_{Sc} = \mu_L / \rho_L / D_A$ is the Schmidt number.

In the above expressions d_B (m) is the bubble diameter, g the acceleration of gravity (9.81 m/sec^2), ρ_L (kg/m^3) the liquid density, μ_L (kg/m/sec) its viscosity, v_{SL} (m/sec) the slip velocity, D_A (m^2/sec) the liquid phase diffusivity of the transferred component.

3.2. OZONE OXIDATION OF SURFACTANTS AND DYES

3.2.1. Chemical-physical principles

For the irreversible reaction

$$B + z\,A \rightarrow \text{products}$$

(where B is the pollutant and A the ozone) a pseudo-first order kinetics can be assumed, on the basis of a B concentration c_B (kmol/m^3) substantially uniform in the film and in the liquid mass. The reason will be explained later on.

The reaction rate of A, referred to the liquid volume, is:

$$r_A = K_1 \cdot c_A \cdot c_B = K \cdot c_A \qquad (\text{kmol/sec/m}^3)$$

where c_A (kmol/m^3) is the A concentration in the liquid, K_1 (m^3/kmol/sec) is the kinetic constant of the reaction (which in effect is of the 2nd order) and $K = K_1 \cdot c_B$ (sec^{-1}) is the pseudo-first order constant.

If y is the molar (and volumetric) ozone fraction in the gas phase, the ozone concentration in the liquid, under equilibrium conditions, is

$$A^* = P \cdot y / H \qquad (\text{kmol/m}^3)$$

where P is the pressure (atma) and H is Henry constant (expressed here in atm $\cdot$ m^3/kmol).

Named A_0 the actual ozone concentration in the liquid mass, the ozone flow rate (kmol/sec) transferred from the gaseous to the liquid phase is, in the absence of chemical reaction,

$$V \cdot k_L\, a \cdot (A^* - A_0)$$

where V (m^3) is the column volume, k_L (m/sec) the mass transfer coefficient, a (m^{-1}) the transfer surface referred to the column volume.

In the presence of chemical reaction A_0 obviously tends to decrease and mass transfer increases.

If the reaction is “very slow”, A_0 retains a finite value, equal to a significant fraction of A^*.

If the reaction is “slow”, A_0 becomes negligible compared to A^*, but the concentration profile in the film remains a straight line joining the A^* and A_0 values, as in purely physical transfer. The reaction still occurs completely in the mass and to a very small extent in the film.

If the reaction is "fast", it occurs at least partially in the film: the concentration profile within the film assumes an upward concavity and the transferred flow rate becomes:

$$V \cdot E \cdot k_L\, a \cdot A^*$$

where $E = \varphi/\tanh\varphi$ is the enhancement factor for mass transfer in comparison with the purely physical mechanism (hence it is $E \geq 1$). The parameter φ is the Hatta number

$$\varphi = H_a = \sqrt{KD_A}/k_L$$

with $K = K_1 c_B$ and $c_B = c_{Bi}(1 - \eta_B)$, where D_A is the ozone diffusivity in the liquid phase (m^2/sec), K (sec^{-1}) is the pseudo-first order reaction constant, c_B is the B concentration in the liquid mass, equal to the one at the column inlet (c_{Bi}) multiplied by the complement to 1 of the B removal efficiency.

We remind in this regard that in a bubble column, in the quiescent regime, a complete mixing of the liquid phase can be assumed with consequent uniformity of the relative concentrations.

It is important to underline that, being in a bubble column the volume of the film very small compared to the one of the liquid reagent mass, A_0/A^* becomes negligible already for rather low K values, such that there is still no reaction in the film. In other words A_0/A^* becomes practically equal to 0 for K values much lower than the ones leading E to depart appreciably from 1.

Usually the practical applications of ozonization (and of oxidative reactions in general) just belong to the intermediate field between slow and fast reactions: A_0/A^* is generally very small or zero, while E is worth 1 or a little more. Note that the fraction of the total reaction that occurs in the mass is equal to about $1/\cosh\varphi$, and therefore 97% if E = 1.02, 87% if E = 1.10, 51% if E = 1.50, 29% if E = 2.0, 10% if E = 3.0, 3.7% if E = 4.0.

Now consider separately the two possible cases, the first with A_0/A^* not negligible and E = 1 and the second with A_0/A^* practically equal to 0 and $E \geq 1$.

In the first case, named G the gas flow rate (kmol/sec), Q the liquid flow rate (m^3/sec), y_i and y_o the ozone volumetric fractions in the gas entering and leaving the column respectively, A_r (kmol/m^3) the kmoles of O_3 which have reacted referred to 1 m^3 of liquid passed through the column, we have:

$$G\,(y_i - y_o) = Q\,(A_r + A_0) \qquad (3.7)$$

because the ozone absorbed by the liquid is equal to the sum of the reacted one and the one which went to saturate the liquid itself up to the A_0 concentration.

The reacted ozone, in the column volume V in which the fractional gas hold-up is ω (and the liquid one is therefore $1 - \omega$), is equal to:

$$Q\,A_r = (1-\omega)\,V\,K\,A_0 \tag{3.8}$$

because the reaction rate ($r_A = K\,A_0$, in kmol/m^3/sec) refers to the volume of the liquid only.

It is then obviously $A_r = c_{Bi}\,z\,\eta_B$

While the liquid phase concentration A_0 is constant throughout the column, the ozone volumetric fraction y within the bubbles, and therefore the equilibrium concentration A^* at the liquid-gas interface, is a function of height (because of the assumed plug flow).

In particular y varies from y_i (at the base of the column, near the sparger) to y_o (at the top, near the outlet).

In the differential volume $dV = S\,dh$, at a certain height h (S is the column section), there will be a variation dy of y due to the ozone transfer and given by:

$$dV \cdot k_L a\,(A^* - A_0) = -\,G\,dy \tag{3.9}$$

where $A^* = P\,y\,/H$.

Integration over the entire height easily leads to:

$$\frac{VP}{GH}k_L a = \int_{y_i}^{y_o} \frac{-dy}{y - \frac{A_0 H}{P}} = \ln \frac{y_i - \frac{A_0 H}{P}}{y_o - \frac{A_0 H}{P}} \tag{3.10}$$

from which we obtain:

$$y_o = f\frac{H}{P}A_0 + (1-f)y_i \qquad \text{with} \qquad f = 1 - \exp\left(-\frac{VPk_L a}{GH}\right) \tag{3.11}$$

Named $\tau = V/Q$ (sec) the liquid residence time in the column, from (3.7) and (3.8) we have:

$$\tau = \frac{A_r + A_0}{\frac{G}{V}(y_i - y_o)} = \frac{A_r}{(1-\omega)KA_0} \tag{3,12}$$

Substituting the expression of y_o given by (3.11) in (3.12), we get a second degree equation that gives A_0 as a function of y_i and A_r.

$$A_0 = \frac{1}{2}\left(\sqrt{M^2 + 4N} - M\right) \quad \text{with} \quad M = A_r\left(1 + \frac{GHf}{VPK(1-\omega)}\right) \quad N = A_r y_i \frac{Gf}{VK(1-\omega)} \tag{3.13}$$

Having found A_0, we obtain y_o with (3.11) and τ with (3.12).

The efficiency of ozone exploitation (reacted ozone referred to supplied ozone) is then:

$$\eta = \frac{QA_r}{Gy_i} = \frac{\frac{A_r}{\tau}}{y_i \frac{G}{V}} \tag{3.14}$$

Going on to the second case ($A_0 = 0$, $E \geq 1$), (3.7) becomes:

$$G(y_i - y_o) = QA_r \qquad \text{from which} \qquad \tau = \frac{A_r}{\frac{G}{V}(y_i - y_o)} \tag{3.15}$$

while (3.9) becomes:

$$dV \cdot Ek_La \cdot A^* = -G\, dy \tag{3.16}$$

from which we obtain:

$$\frac{VP}{GH} Ek_La = \int_{y_i}^{y_o} \frac{-dy}{y} = \ln \frac{y_i}{y_o} \tag{3.17}$$

$$y_o = (1-f)y_i \qquad \text{with} \qquad f = 1 - \exp\left(-\frac{VPEk_La}{GH}\right) \tag{3.18}$$

τ is obtained by replacing this value of y_o in (3.15) and η is still given by (3.14).

We have respectively:

$$\tau = \frac{A_r}{\frac{G}{V} f y_i} \qquad \text{and} \qquad \eta = f$$

If you want to have an idea of the A_0 value, which is very small, just consider that, as already mentioned, the fraction of the total reaction that takes place in the mass is equal to about $1/\cosh\varphi$. Hence:

$$(1-\omega)VKA_0 = QA_r \frac{1}{\cosh\varphi} \qquad \text{from which} \qquad A_0 = \frac{\frac{A_r}{\tau}}{(1-\omega)\, K \cosh\varphi} \tag{3.19}$$

Comparing (3.12) with (3.19), it appears that for both examined cases the same solutions can be used (the ones obtained for the first case), provided the E factor is added to k_La in the expression (3.11) of f (what in practice means to always use (3.18) for f) and provided the A_0 value given by (3.13) is divided by $\cosh\varphi$.

If the reaction is slow, then $E = 1$ and $\cosh\varphi = 1$, and the formulas of the first case are found exactly. If it is fast, then $E > 1$ and $\cosh\varphi > 1$: for f the (3.18) applies and for A_0 the (3.19) (the A_0 value is in this case very small and practically irrelevant to the accuracy with which the values of y_o , τ and η are obtained).

3.2.2. Numerical example

The value of K_1, for applications where it can be argued that ozone works as an oxidizing agent, should be at least $10^4 \div 10^5$ m^3/kmol/sec.

If A_0 / A_o^* (with $A_o^* = P_o\, y_o / H$, which is the interface concentration at the column top) is greater than $0.1 \div 0.2$, it is doubtful whether ozonization is an effective treatment.

Many organic substances can consume several moles of ozone per mole of pollutant: for surfactants z can be worth $20 \div 30$, while for dyes z is of the order of 5.

In addition, account should be taken of any other substances present in the waste water, which are not of interest to remove, but which nevertheless consume the reagent parasitically.

It should also be borne in mind that ozone tends to decompose over time, especially as temperature and pH increase (the phenomenon is remarkable for pH > 8).

Apart from K_1, which obviously depends on the temperature t (°C) according to the Arrhenius equation, but which mainly depends on the type of substance to be oxidized, the parameters that vary with t are H, D_A and μ_L. We can assume:

- $H = 90.9 \cdot \exp\,[2300\,(1/298 - 1/(273 + t))]$ (atm · m^3/kmol)
- $D_A = 2.0 \cdot 10^{-6} \cdot \exp\,[-2178/(t + 273)]$ (m^2/sec)
- $\mu_L = 3.559 \cdot 10^{-5} \cdot \exp\,[456.7/(t + 116.7)]$ (kg/m/sec)

The pollutant concentration c_{Bi} in the inlet liquid is obviously very variable, as well as the desired removal efficiency η_B, which is chosen so as to respect the value $c_B = c_{Bi}\,(1 - \eta_B)$ allowed at the final discharge.

Typical examples may be for surfactants $c_{Bi} = 3 \cdot 10^{-5}$ kmol/m^3, with $\eta_B = 0.85$ and $z = 30$, whereas for dyes $c_{Bi} = 4 \cdot 10^{-5}$ kmol/m^3, with $\eta_B = 0.95$ and $z = 5$.

For the following example we will consider a bubble column with an effective height $h_L = 4$ m, equipped with fine bubble diffusers ($d_{B0} = 0.002$ m) fed with air containing ozone ($y_i = 0.012$ is a typical value of the volumetric fraction).

The liquid temperature is 25°C, so that $H = 90.9$ atm · m^3/kmol, $D_A = 1.34 \cdot 10^{-9}$ m^2/sec, $\mu_L = 0.893 \cdot 10^{-3}$ kg/m/sec. The pressure at the column top is $P_o = 1$ atma.

The liquid flow rate Q is 0.0139 m^3/sec (corresponding to 50 m^3/h).

For the superficial gas velocity a v_G value of 0.005 m/sec has been chosen.

The calculation procedure is as follows.

The pressure near the sparger is $P_i = P_o + h_L /10 = 1.4$ atma.

The average column pressure is $P_m = P_o + h_L /20 = 1.2$ atma.

The normalized specific gas flow $v_S = v_G \cdot P_m / (1 + t /273)$ is equal to 0.00550 $Nm^3/sec/m^2$.

The ratio $G/V = v_S /h_L/22.4$ is $6.14 \cdot 10^{-5}$ kmol/sec/m^3.

The v_G /v_{SL} value given by (3.2) is 0.0155. Therefore $v_{SL} = v_G /(v_G /v_{SL}) = 0.323$ m/sec.

The average bubble diameter, given by (3.5), is 0.0021 m.

N_{Sh} , given by (3.6), is equal to 299 (with $\rho_L = 1000$ kg/m^3), hence $k_L = N_{Sh} \cdot D_A /d_B = 1.90 \cdot 10^{-4}$ m/sec.

We are now able to verify the circumstances under which the reaction is actually pseudo-first order, as hypothesized.

We will use the condition of Danckwerts [15] for this purpose, namely:

$$\varphi = \frac{\sqrt{K_1 c_B D_A}}{k_L} \leq \frac{1}{2}\left(1 + \frac{z c_B}{A^*}\right)$$

(note that in this case z is the stoichiometric coefficient of A, and not of B as usual in the literature).

It is a question of finding the maximum K_1 value for which the inequality is still satisfied.

The most critical point for verification is the column base, where y (and therefore A^*) is maximum.

In particular we have there $A^* = y_i \cdot P_i /H = 0.012 \cdot 1.4/90.9 = 1.85 \cdot 10^{-4}$ kmol/m^3.

In the case of surfactant ($c_B = 4.5 \cdot 10^{-6}$ kmol/m^3, $z = 30$) we have:

$$\sqrt{K_1 \cdot 4.5 \cdot 10^{-6} \cdot 1.34 \cdot 10^{-9}}/1.90 \cdot 10^{-4} \leq \frac{1}{2}\left(1 + \frac{30 \cdot 4.5 \cdot 10^{-6}}{1.85 \cdot 10^{-4}}\right)$$

hence the maximum K_1 value is equal to $4.5 \cdot 10^6$ m^3/kmol/sec.

In the case of dye ($c_B = 2 \cdot 10^{-6}$ kmol/m^3, $z = 5$) the maximum K_1 value is $3.8 \cdot 10^6$ m^3/kmol/sec.

In practical applications K_1 values are in the range between 10^4 and 10^8 m^3/kmol/sec, but conservatively, for design purposes, they are not normally assumed to be higher than 10^5 m^3/kmol/sec. Consequently, the hypothesis of a pseudo-first order reaction can be considered well founded and acceptable.

For high K_1 values (for example 10^8 m^3/kmol/sec) the reaction becomes in all respects of the second order, so there is a depletion of B in the film, proceeding towards the liquid-gas interface. The E value is then actually lower than the one given by the expression $\varphi/\tanh\varphi$, so the column, calculated in the pseudo-first order reaction hypothesis, would be slightly undersized.

We can now continue the calculation related to the numerical example, referring specifically to the surfactant case ($c_{Bi} = 3\cdot10^{-5}$ kmol/m^3; $\eta_B = 0.85$; $c_B = 4.5\cdot10^{-6}$ kmol/m^3; $z = 30$) and assuming conservatively $K_1 = 10^5$ m^3/kmol/sec.

It is therefore $A_r = c_{Bi}\, z\, \eta_B = 7.65\cdot10^{-4}$ kmol/m^3; $K = K_1\cdot c_B = 0.45$ sec^{-1}; $\varphi = \sqrt{KD_A}/k_L = 0.129$; $\cosh\varphi = (e^{\varphi} + e^{-\varphi})/2 = 1.008$; $E = \varphi/\tanh\varphi = \varphi\,(e^{\varphi} + e^{-\varphi})/(e^{\varphi} - e^{-\varphi}) = 1.006$.

For the ω calculation with (3.3) and the following, in the first attempt we will put $v_L = 0$, while for the following attempts (once calculated τ) it will be $v_L = -\,h_L/\tau$ (the minus sign corresponds to the choice of a countercurrent liquid flow).

With $v_L = 0$ the expression (3.3) gives $\omega = 0.0155$. So $k_La = k_L\cdot 6\,\omega/d_B = 0.00839$ sec^{-1}.

Then f is calculated with (3.18), using for P the value P_m, and A_0 with (3.13), dividing the obtained A_0 value by $\cosh\varphi$. In practice:

$$f = 1 - \exp\left(-\frac{P_m E k_L a}{H\frac{G}{V}}\right) = 1 - \exp\left(-\frac{1.2\cdot1.006\cdot0.00839}{90.9\cdot6.14\cdot10^{-5}}\right) = 0.837$$

$$M = A_r\left(1 + \frac{Hf\frac{G}{V}}{P_m K(1-\omega)}\right) = 7.65\cdot10^{-4}\left(1 + \frac{90.9\cdot0.837\cdot6.14\cdot10^{-5}}{1.2\cdot0.45\cdot(1-0.0155)}\right)$$

$$= 7.72\cdot10^{-4}$$

$$N = A_r y_i \frac{f\frac{G}{V}}{K(1-\omega)} = 7.65\cdot10^{-4}\cdot0.012\,\frac{0.837\cdot6.14\cdot10^{-5}}{0.45\cdot(1-0.0155)} = 1.06\cdot10^{-9}$$

$$A_0 = \frac{1}{2\cosh\varphi}\left(\sqrt{M^2+4N} - M\right) = 1.37\cdot10^{-6} \quad \text{kmol/m}^3$$

We then have:

$$y_o = f\frac{H}{P_m}A_0 + (1-f)y_i = 0.00204 \qquad \frac{A_0}{A_o^*} = \frac{A_0 H}{y_o P_o} = 0.0608$$

A_0/A_o^* is small enough to allow us to consider the ozonization process to be effective.

We can then calculate:

$$\tau = \frac{A_r + A_0}{\frac{G}{V}(y_i - y_o)} = 1254 \text{ sec} \qquad \eta = \frac{\frac{A_r}{\tau}}{y_i \frac{G}{V}} = 0.828$$

Finally, we get $S = \tau\, Q\, /h_L = 4.36$ m^2 for the column section and $G' = 3600 \cdot v_S \cdot S = 86.2$ Nm^3/h for the gas flow rate. The ozone flow rate, fed to the column, is then $W_A = 48/22.4 \cdot G' \cdot y_i = 2.22$ kg/h (48 g/mol being the ozone molecular weight).

For v_L we get a value of $- h_L/\tau = - 0.00319$ m/sec, which is obviously different from the zero value initially assumed. Using this new value to calculate ω, slightly different values are subsequently obtained for the various results, including a new value for τ and then for v_L. With a couple of iterations convergence is achieved ($v_L = - 0.00320$ m/sec): however the final values of the significant parameters are little different from the ones of the first attempt (in particular $\tau = 1250$ sec, $\eta = 0.831$, $S = 4.34$ m^2, $G' = 85.9$ Nm^3/h, $W_A = 2.21$ kg/h).

If, despite the use of fine bubble diffusers and an already remarkable value of h_L , a low η value (and therefore a waste of ozone) is obtained (because of a rather low kinetic constant), it may be advisable to lower v_G , in order to increase τ and thus the column section, without increasing the number of diffusers and therefore the ozone consumption.

As a guide, if $K_l = 10^6$ were taken instead of 10^5 m^3/kmol/sec, the following results would have been obtained: $\tau = 1218$ sec, $\eta = 0.853$, $S = 4.23$ m^2, $G' = 83.7$ Nm^3/h, $W_A = 2.15$ kg/h.

Considering the presence of dyes instead of surfactants (with $c_{Bi} = 4 \cdot 10^{-5}$ kmol/m^3; $\eta_B = 0.95$; $z = 5$; $K_l = 10^5$ m^3/kmol/sec), the following results would have been obtained: $\tau = 315$ sec, $\eta = 0.819$, $S = 1.10$ m^2, $G' = 21.7$ Nm^3/h, $W_A = 0.557$ kg/h.

3.3. NEUTRALIZATION OF BASIC WATERS BY FLUE GASES

3.3.1. Chemical-physical principles

Two reactions occur in parallel, when carbon dioxide is absorbed in alkaline aqueous solutions (typically of NaOH):

(1) $CO_2 + OH^- \rightarrow HCO_3^-$

(2) $CO_2 + H_2O \rightarrow HCO_3^- + H^+$

These reactions, which lead to the bicarbonate formation, have a limited rate, and are therefore the controlling steps, whatever the subsequent reactions that may further take place.

As for these, there are in particular the following equilibria, which are instantly established:

(3) $HCO_3^- \rightleftarrows H^+ + CO_3^{--}$

(4) $H^+ + OH^- \rightleftarrows H_2O$

and which involve that in a highly basic environment the overall reaction is:

(5) $CO_2 + 2OH^- \rightarrow CO_3^{--} + H_2O$

with carbonate formation, while in a weakly basic environment the reaction stops at (1) (i.e. at (2) plus (4), which leads to the same result).

If only the reaction (1) occurred, one mole of CO_2 for each mole of NaOH would be stoichiometrically necessary; if only (5), only half a mole of CO_2 per mole of NaOH would be necessary. To what extent one and/or the other of the two reactions take place, and therefore how many CO_2 moles are stoichiometrically necessary, it depends on the desired final pH.

If sulphuric acid is used for soda neutralization, as it reacts uniquely according to the reaction

$$NaOH + \frac{1}{2}H_2SO_4 \rightarrow \frac{1}{2}Na_2SO_4 + H_2O$$

the reagent consumption *c* simply corresponds to the neutralized groups OH^-, and is (as acid moles per soda mole)

$$c = \frac{1}{2}\left(1 - 10^{pH-pH_i}\right)$$

where 1/2 is the ratio between the stoichiometric coefficients of acid and soda in the reaction, *pH* is the neutralization pH, pH_i the initial pH.

It is easy to verify that, if pH is < pH_i by at least two units (e.g., with pH_i = 13, if it is pH < 11), then c =1/2 regardless of the actual pH value.

In essence, consumption is virtually identical whether the final pH is 11 or 8.

The same expression of c would be valid for the CO_2 consumption if the neutralization with this reagent occurred exclusively according to the reaction (5), whereas if it occurred exclusively according to the reaction (1) it would be enough to replace 1/2 with 1.

Actually things are complicated by the existence of the equilibrium (3) between carbonates and bicarbonates, which depends on pH.

We have in fact:

$$\frac{(CO_3^{--})}{(HCO_3^-)} = \frac{K_2}{(H^+)} = 10^{pH-pK_2}$$

where K_2 is the equilibrium constant, only dependent on temperature, and pK_2 = - $\log_{10} K_2$.

Bracket expressions are concentrations in kg-ion/m^3.

Now, every existing mole in solution of CO_3^{--} implies the initial presence of 2 NaOH moles and the consumption of 1 CO_2 mole, while each HCO_3^- mole implies the initial presence of 1 NaOH mole and the consumption of of 1 CO_2 mole.

The ratio between the CO_2 moles consumed and the NaOH moles that have reacted is therefore equal to:

$$z = \frac{(CO_3^{--}) + (HCO_3^-)}{2\,(CO_3^{--}) + (HCO_3^-)} = 1 - \frac{1}{2 + 10^{pK_2-pH}} \qquad (3.20)$$

This expression in practice goes to replace the stoichiometric coefficient 1/2 in the formula given above for c, which becomes

$$c = z\,(1 - 10^{pH-pH_i})$$

Since at 30°C pK_2 = 10.29, it is easy to check that for $pH << pK_2$ z is 1, for $pH >> pK_2$ it is 1/2 .

Moreover, for low pH (8÷8.5) and pH_i higher by at least two units, c is practically equal to 1, while it rapidly decreases (tending to 0.5) as pH increases.

The behaviour with CO_2 is therefore clearly different from the one with sulphuric acid, in which c does not substantially vary throughout the entire range of neutralization pH values of practical interest.

Named A the CO_2 and B the hydroxyl ion, the reaction rate of A (referred to the liquid volume) is, because of the reaction (2):

$r_A' = K' (c_A - A_e)$ kmol/sec/m^3

while, due to the reaction (1), it is:

$r_A'' = K'' c_B (c_A - A_e)$ kmol/sec/m^3

where c_A (kmol/m^3) is the A concentration in the liquid, A_e (kmol/m^3) is the equilibrium A concentration in the liquid (remember that these are reversible reactions), K' (sec^{-1}) is the kinetic constant of the reaction (2), K'' (m^3/kmol/sec) is the kinetic constant of the reaction (1), c_B (kmol/m^3) is the hydroxyl concentration.

The reaction (2) is clearly a first order reaction, the reaction (1) (which is actually of the second order) can be considered, for our application (and for the reason later explained) a pseudo-first order reaction, that is with B concentration c_B substantially uniform in the film and in the liquid mass.

The overall rate of reaction is therefore:

$$r_A = (K' + K'' c_B)(c_A - A_e) = K (c_A - A_e)$$

where K (sec^{-1}) is the pseudo-first order global constant.

We have already seen that, due to the instantaneous equilibrium reaction (3), we have:

$$K_2 = \frac{(H^+)(CO_3^{--})}{(HCO_3^-)}$$

Also the reaction (2) is an equilibrium, even not instantaneous, with K_1 constant given by:

$$K_1 = \frac{(H^+)(HCO_3^-)}{(CO_2)}$$

The hydroxyl concentration c_B in the liquid and the initial concentration c_{Bi} (kmol/m^3) are given by:

$$c_B = 10^{pH - pK_W} \qquad c_{Bi} = 10^{pH_i - pK_W} \tag{3.21}$$

where pK_W is the ionic product of water (13.84 at 30°C).

We will call A_e (kmol/m^3) the equilibrium CO_2 concentration in water, that is the one that would be established in conditions of perfect thermodynamic equilibrium.

We will call A_r (kmol/m^3) the kmoles of CO_2 that have reacted in the tank in question, referred to 1 m^3 of liquid passed through the vessel. They are equal to the present kmoles of CO_3^{--} and of HCO_3^-, minus the kmoles of CO_2 ($A_{r,p}$) that have already reacted in other previous tanks (if there is only one tank, obviously $A_{r,p} = 0$).

The kmoles of hydroxyls that have reacted in total ($c_{Bi} - c_B$) are instead equal to twice the present kmoles of CO_3^{--}, plus the present kmoles of HCO_3^-. Hence:

$$c_{Bi} - c_B = 10^{pH_i - pK_W} - 10^{pH - pK_W} = 2\,(CO_3^{--}) + (HCO_3^-) \qquad (3.22)$$

Getting (CO_3^{--}) from the expression of K_2 and then (HCO_3^-) from the one of K_1, bearing in mind that $(CO_2) = A_e$:

$$2\,(CO_3^{--}) + (HCO_3^-) = 2\frac{K_2}{(H^+)}(HCO_3^-) + (HCO_3^-) = \left(2\frac{K_2}{(H^+)} + 1\right)\frac{K_1}{(H^+)}A_e$$

Finally, we obtain:

$$A_e = (10^{pH_i - pK_W} - 10^{pH - pK_W})\frac{10^{pK_1 - pH}}{1 + 2 \cdot 10^{pH - pK_2}} \qquad (3.23)$$

To obtain A_r, note that:

$$A_r + A_{r,p} = (CO_3^{--}) + (HCO_3^-) = c_{Bi} - c_B - (CO_3^{--})$$

where the second equality follows from (3.22). Multiplying then K_1 by K_2, in order to eliminate (HCO_3^-), we get:

$$(CO_3^{--}) = A_e K_1 K_2 / (H^+)^2$$

From this expression and from the first equality of (3.22) we finally get:

$$A_r = (10^{pH_i - pK_W} - 10^{pH - pK_W}) - A_e \cdot 10^{2pH - pK_1 - pK_2} - A_{r,p} \qquad (3.24)$$

If y is the molar (and volumetric) CO_2 fraction in the gas phase, the CO_2 concentration in the liquid, under equilibrium conditions, is $A^* = Py/H$ (kmol/m^3), where P is the pressure (atma) and H is the Henry constant (atm · m^3/kmol).

It is important to note that there is a minimum pH achievable by carrying out the neutralization with flue gases, which is of the order of 7÷8 (the greater the initial pH of the waste water, the higher the final pH). This minimum value is easily obtained, because it depends on thermodynamic and not on kinetic reasons.

The equilibrium CO_2 concentration A_e in the liquid is directly obtainable from the expression of the equilibrium constant K_1, which depends on temperature (for example, it is $4.7 \cdot 10^{-7}$ kmol/m^3 at 30°C).

At pH around the neutrality the caustic soda initially present has reacted and has been transformed practically all into bicarbonate, so (HCO_3^-) is equal to the initial soda concentration (which we will assume equal to 0.145 kmol/m^3, corresponding, at 30°C, to $pH_i = 13$).

As a result we have $A_e = (H^+) \cdot 0.145 / 4.7 \cdot 10^{-7}$ kmol/m^3.

But the concentration A_e may at most correspond to the one of saturation $A^* = Py/H$.

When (H^+) is sufficiently high as to make $A_e = A^*$, then there can be no further solubilization, the utilization efficiency of CO_2 becomes zero and the volumetric fraction y in the gas along the vessel remains the same as the initial fraction y_i in the flue gases (which we will typically assume equal to 0.1).

At the average pressure in the vessel (P = 1.25 atma with a head of 5 m) and with a value of H = 34.5 atm · m^3/kmol at 30°C, we have $A^* = 1.25 \cdot 0.1 / 34.5 = 3.62 \cdot 10^{-3}$ kmol/m^3, which turns out to be equal to A_e for (H^+) = $1.17 \cdot 10^{-8}$ kmol/m^3, corresponding to pH = 7.93. This is therefore the theoretically achievable minimum value (as we will see, the actual one will be much closer to 9, if we want an acceptable efficiency for the utilization of the CO_2 present in the flue gases).

Named A_0 the actual CO_2 concentration in the liquid mass, it will certainly be greater than A_e, for kinetic reasons.

The CO_2 flow rate (kmol/sec) transferred from the gas to the liquid phase would be, in the absence of chemical reaction,

$$V \cdot k_L\, a \cdot (A^* - A_0)$$

where V (m^3) is the vessel volume, k_L (m/sec) the mass transfer coefficient, a (m^{-1}) the transfer surface referred to the vessel volume.

In the presence of chemical reaction A_0 tends to decrease and mass transfer increases.

As the chosen neutralization pH increases, the reaction rate increases too (because the hydroxyl concentration c_B rises and so does the value of the pseudo-first order constant K) whereas the A_e value (which depends on the pH) decreases.

Due to the higher reaction rate, A_0 also decreases (though less quickly than A_e) and for pH of the order of 10 it becomes negligible compared to A^*. However, the concentration profile in the film remains a straight line that joins the values A^* and A_0, as in the purely physical transfer. The reaction still occurs completely in the mass and to a very small extent in the film.

For pH of the order of 10.5÷11 the reaction begins to take place at least in part in the film: the concentration profile within the film assumes an upward concavity and the transferred flow rate becomes:

$$V \cdot E \cdot k_L\, a \cdot A^*$$

where $E = \varphi/\tanh\varphi$ is the enhancement factor for mass transfer in comparison with the purely physical mechanism.

It is therefore $E \geq 1$: for instance at $pH = 10.5 \div 11$ E is already of the order of 1.1÷1.2.

The parameter φ is the Hatta number

$$\varphi = H_a = \sqrt{KD_A}/k_L$$

with $K = K' + K''c_B$ and $c_B = (OH^-) = 10^{pH-pK_W}$, where D_A is the CO_2 diffusivity in the liquid phase (m^2/sec), K (sec^{-1}) is the pseudo-first order reaction constant, c_B is the B (hydroxyl) concentration in the liquid mass.

We remind in this regard that in a bubble column (or tank), in the quiescent regime, we can assume a complete mixing of the liquid phase, with consequent uniformity of the relative concentrations, and a plug flow for the gas phase.

It is important to underline that, being in a bubble column the volume of the film very small compared to the one of the liquid reagent mass, A_0/A^* becomes negligible already for rather low K values, such that there is still no reaction in the film. In other words A_0/A^* becomes practically equal to 0 for K values much lower than the ones leading E to depart appreciably from 1.

Note that the fraction of the total reaction that occurs in the mass is equal to about $1/\cosh\varphi$, and therefore 97% if $E = 1.02$, 87% if $E = 1.10$, 51% if $E = 1.50$, 29% if $E = 2.0$, 10% if $E = 3.0$, 3.7% if $E = 4.0$.

Now consider separately the two possible cases, the first with A_0/A^* not negligible and $E = 1$ (i.e. for $pH < 10$) and the second with A_0/A^* practically equal to 0 and $E \geq 1$ (i.e. for $pH > 10$).

In the first case, named G the gas flow rate (kmol/sec), Q the liquid flow rate (m^3/sec), y_i and y_o the CO_2 volumetric fractions in the gas entering and leaving the column respectively, A_r (kmol/m^3) the kmoles of CO_2 which have reacted in the tank in question, referred to 1 m^3 of liquid passed through the vessel, A_i (kmol/m^3) the CO_2 concentration in the incoming liquid, we have:

$$G(y_i - y_o) = Q(A_r + A_0 - A_i) \tag{3.25}$$

because the CO_2 absorbed by the liquid is equal to the sum of the reacted one and the one which went to saturate the liquid itself from the initial concentration A_i up to A_0.

The A_i parameter has been introduced to face the case of several tanks in series: in the first (or in the only tank) $A_i = 0$, in the following ones A_i is equal to the A_0 value of the previous tank.

The reacted CO_2, in the vessel volume V in which the fractional gas hold-up is ω (and the liquid one is therefore $1 - \omega$), is equal to:

$$Q\,A_r = (1 - \omega)\,V\,K\,(A_0 - A_e) \tag{3.26}$$

because the reaction rate $r_A = K\,(A_0 - A_e)$, in kmol/m^3/sec, refers to the volume of the liquid only.

The expressions for A_e and A_r have already been given previously with (3.23) and (3.24).

While the liquid phase concentrations A_0 and A_e are constant throughout the vessel, the CO_2 volumetric fraction y within the bubbles, and therefore the equilibrium concentration A^* at the liquid-gas interface, is a function of height (because of the assumed plug flow).

In particular y varies from y_i (at the base of the vessel, near the sparger) to y_o (at the top, near the outlet).

In the differential volume $dV = S\,dh$, at a certain height h (S is the vessel section), there will be a variation dy of y due to the CO_2 transfer and given by:

$$dV \cdot k_L a\,(A^* - A_0) = -\,G\,dy \tag{3.27}$$

where $A^* = P\,y\,/H$.

Integration over the entire height easily leads to:

$$\frac{VP}{GH} k_L a = \int_{y_i}^{y_o} \frac{-dy}{y - \frac{A_0 H}{P}} = \ln \frac{y_i - \frac{A_0 H}{P}}{y_o - \frac{A_0 H}{P}} \tag{3.28}$$

from which we obtain:

$$y_o = f\,\frac{H}{P} A_0 + (1 - f) y_i \qquad \text{with} \qquad f = 1 - \exp\left(-\frac{VPk_L a}{GH}\right) \tag{3.29}$$

Named $\tau = V\,/Q$ (sec) the liquid residence time in the vessel, from (3.25) and (3.26) we have:

$$\tau = \frac{A_r + A_0 - A_i}{\frac{G}{V}(y_i - y_o)} = \frac{A_r}{(1 - \omega) K (A_0 - A_e)} \tag{3.30}$$

Substituting the expression of y_o given by (3.29) in (3.30) we get a second degree equation that gives A_0 as a function of y_i , A_e , A_i and A_r .

$$A_0 = \tfrac{1}{2}\left(\sqrt{M^2 + 4N} - M\right) \tag{3.31}$$

with $M = A_r\left(1 + \frac{GHf}{VPK(1-\omega)}\right) - A_e - A_i$ $N = A_r\left(y_i \frac{Gf}{VK(1-\omega)} + A_e\right) - A_e A_i$

Having found A_0, we obtain y_o with (3.29) and τ with (3.30).

The exploitation efficiency of CO_2 (reacted CO_2 referred to supplied CO_2) is then equal to:

$$\eta = \frac{QA_r}{Gy_i} = \frac{\frac{A_r}{\tau}}{y_i \frac{G}{V}} \tag{3.32}$$

Going on to the second case ($A_0 = 0$, $A_i = 0$, $E \geq 1$, i.e. $pH > 10$), (3.25) becomes:

$$G(y_i - y_o) = QA_r \qquad \text{from which} \qquad \tau = \frac{A_r}{\frac{G}{V}(y_i - y_o)} \tag{3.33}$$

while (3.27) becomes:

$$dV \cdot Ek_L a \cdot A^* = -G\, dy \tag{3.34}$$

from which we obtain:

$$\frac{VP}{GH}\, Ek_L a = \int_{y_i}^{y_o} \frac{-dy}{y} = \ln \frac{y_i}{y_o} \tag{3.35}$$

$$y_o = (1-f)y_i \qquad \text{with} \qquad f = 1 - \exp\left(-\frac{VPEk_L a}{GH}\right) \tag{3.36}$$

τ is obtained by replacing this value of y_o in (3.33) and η is still given by (3.32).

We have respectively:

$$\tau = \frac{A_r}{\frac{G}{V} f y_i} \qquad \text{and} \qquad \eta = f$$

If you want to have an idea of the A_0 value, which is very small, just consider that, as already mentioned, the fraction of the total reaction that takes place in the mass is equal to about $1/\cosh\varphi$. Hence:

$$(1-\omega)VK(A_0 - A_e) = QA_r \frac{1}{\cosh\varphi} \quad \text{from which} \quad A_0 = \frac{\frac{A_r}{\tau}}{(1-\omega)\, K \cosh\varphi} + A_e \tag{3.37}$$

Comparing (3.30) with (3.37), it appears that for both examined cases the same solutions can be used (the ones obtained for the first case), provided the E factor is added to $k_L a$ in the expression (3.29) of f (what means in practice to always use (3.36) for f) and provided the value of $A_0 - A_e$ of the first case is divided by $\cosh\varphi$ to have the new $A_0 - A_e$, what means in practice to always use for A_0 the expression:

$$A_0 = \frac{1}{2\cosh\varphi}\left(\sqrt{M^2+4N} - M\right) + A_e\left(1 - \frac{1}{\cosh\varphi}\right) \qquad (3.38)$$

If $pH < 10$, then $E = 1$ and $\cosh\varphi = 1$ and the formulas of the first case are found exactly.

If $pH > 10$, then $E > 1$ and $\cosh\varphi > 1$: for f the (3.36) applies and for A_0 the (3.37) (the A_0 value is in this case very small and practically irrelevant to the accuracy with which the values of y_o , τ and η are obtained).

3.3.2. Numerical example

The parameters required for the calculation which depend on temperature (t in °C and T in °K) are K', K'', K_1 , K_2 , H, K_W, μ_L , D_A.

Below we list the relative expressions (the first 5 are the ones provided by Danckwerts in the article already mentioned). Next to each formula we give in brackets the parameter value at 30°C, which is the liquid temperature considered in the example.

- $\log_{10} K' = 329.850 - 110.541 \log_{10} T - 17{,}265.4 / T$ ($K' = 0.037$ sec^{-1})
- $\log_{10} K'' = 13.635 - 2895 / T$ ($K'' = 12{,}000$ m^3/kmol/sec)
- $pK_1 = 3404.7 / T - 14.843 + 0.03279 \cdot T$ ($pK_1 = 6.33$)
- $pK_2 = 2902.4 / T - 6.498 + 0.0238 \cdot T$ ($pK_2 = 10.29$)
- $\log_{10} H = 5.30 - 1140 / T$ ($H = 34.5$ atm·m^3/kmol)
- $pK_W = 4.367 + 2869.6 / T$ ($pK_W = 13.84$)
- $\mu_L = 3.559 \cdot 10^{-5} \cdot \exp [456.7 / (t + 116.7)]$ ($\mu_L = 0.801 \cdot 10^{-3}$ kg/m/s)
- $D_A = 5.87 \cdot 10^{-15} \cdot T / \mu_L$ ($D_A = 2.22 \cdot 10^{-9}$ m^2/sec)

The CO_2 volumetric fraction y_i in the fumes is typically 0.1 (for methane combustion fumes, cooled down to less than 40°C and therefore largely dehumidified).

We will then take an initial pH_i of the waste water equal to 13, corresponding to a caustic soda concentration equal to $10^{pH_i - pK_W} = 0.145$ kmol/m^3.

If in the waste water being neutralized there is a remarkable electrolyte concentration, CO_2 solubility is smaller than in pure water. The enhancement factor K_H for Henry constant, due to sodium bicarbonate ionic strength, can be evaluated through the expression $\log_{10} K_H = 0.09 \cdot c_{Bi}$, where c_{Bi} (kmol/m^3) is the initial caustic soda concentration. It follows that, if the initial pH_i is less than 13 (when $K_H = 1.03$), the ionic strength effect is practically negligible.

The neutralization objective is to reach a $pH = 8.7$.

For this purpose we will use a tank with a useful height $h_L = 5$ m, equipped with perforated pipe diffusers with 4 mm holes, able to generate bubbles with a diameter $d_{B0} = 6.35$ mm.

The pressure at the tank top is $P_o = 1$ atma.

The liquid flow rate Q is 0.0139 m^3/sec (50 m^3/h).

For the superficial gas velocity a value $v_G = 0.02$ m/sec has been chosen (conservative enough, in general, as regards foaming).

The calculation procedure is as follows.

The pressure near the sparger is $P_i = P_o + h_L /10 = 1.5$ atma.

The average column pressure is $P_m = P_o + h_L /20 = 1.25$ atma.

The normalized specific gas flow $v_S = v_G \cdot P_m / (1 + t /273)$ is equal to 0.0225 $Nm^3/sec/m^2$.

The ratio $G/V = v_S /h_L/22.4$ is $2.01 \cdot 10^{-4}$ kmol/sec/m^3.

The v_G /v_{SL} value given by (3.2) is 0.0507. Therefore $v_{SL} = v_G /(v_G /v_{SL}) = 0.394$ m/sec.

The average bubble diameter, given by (3.5), is 0.00675 m.

N_{Sh}, given by (3.6), is equal to 738 (with $\rho_L = 1000$ kg/m^3); hence $k_L = N_{Sh} \cdot D_A /d_B = 2.43 \cdot 10^{-4}$ m/sec.

We are now able to verify the circumstances under which the reaction is actually pseudo-first order, as hypothesized.

We will use the condition of Danckwerts [15] for this purpose, namely:

$$\varphi = \frac{\sqrt{(K' + K'' c_B) D_A}}{k_L} \leq \frac{1}{2}\left(1 + \frac{z c_B}{A^*}\right)$$

where z, given by (3.20), is the ratio between the CO_2 moles and the NaOH moles that have reacted among them (in practice it is the stoichiometric coefficient of A, and not of B as usual in the literature).

Given that $c_B = 10^{pH - pK_W}$, it is a question of finding the maximum value of the pH (which determines the values of z and c_B) for which the inequality is still satisfied.

The most critical point for verification is the tank base, where y (and therefore A^*) is maximum.

In particular we have there $A^* = y_i \cdot P_i /H = 0.1 \cdot 1.5/34.5 = 4.35 \cdot 10^{-3}$ kmol/m^3.

The maximum pH value turns out to be 10.65.

In practice the pH to which we want to bring the waste water is certainly less than 10, so the pseudo-first order reaction condition is met throughout the range of practical interest.

For values greater than 10.65 the reaction becomes in all respects of the second order, so there is a depletion of (OH^-) in the film, proceeding towards the liquid-gas interface. The E value is actually lower than the one given by the expression $\varphi/\tanh\varphi$, so the tank, calculated in the hypothesis of pseudo-first order reaction, would be slightly undersized.

We can now continue the calculation related to the numerical example.

For $pH = 8.7$, we have from (3.23) $A_e = 0.586 \cdot 10^{-3}$ kmol/m^3 and from (3.24) $A_r = 0.141$ kmol/m^3 (in this case it is $A_{r,p} = 0$).

It is then $c_B = (OH^-) = 10^{pH-pK_W} = 7.24 \cdot 10^{-6}$ kmol/m^3; $K = K' + K''c_B = 0.037 + 0.0869 = 0.124$ sec^{-1}; $\varphi = \sqrt{KD_A}/k_L = 0.0683$; $\cosh \varphi = (e^{\varphi} + e^{-\varphi})/2 = 1.0023$; $E = \varphi/\tanh \varphi = \varphi\,(e^{\varphi} + e^{-\varphi})/(e^{\varphi} - e^{-\varphi}) = 1.0016$.

For the ω calculation with (3.3) and the following, we will put for simplicity $v_L = 0$ (the v_L, influence, as already seen in par. 3.2.2, is negligible).

With $v_L = 0$ the expression (3.3) gives $\omega = v_G / v_{SL} = 0.0507$. Therefore $k_La = k_L \cdot 6\,\omega / d_B = 0.0110$ sec^{-1}.

Then f is calculated with (3.36) and A_0 with (3.38), using for P the value P_m.

We get $f = 0.861$, $M = 0.146$, $N = 1.035 \cdot 10^{-4}$, $A_0 = 7.04 \cdot 10^{-4}$ kmol/m^3 (in this case it is $A_i = 0$).

Then, from (3.29):

$$y_o = f\frac{H}{P_m}A_0 + (1-f)y_i = 0.0306$$

We then calculate:

$$\tau = \frac{A_r + A_0}{\frac{G}{V}(y_i - y_o)} = 10{,}153 \text{ sec} \qquad \eta = \frac{\frac{A_r}{\tau}}{y_i\frac{G}{V}} = 0.691$$

For v_L we get a value of $h_L/\tau = 0.00049$ m/sec, which fully justifies the fact that it was neglected.

Finally, $S = \tau\, Q / h_L = 28.2$ m^2 for the tank section and $G' = 3600 \cdot v_S \cdot S = 2287$ Nm^3/h for the gas flow rate to be fed to the diffusers.

To this purpose a rotary lobe blower can be used (with a filter panel on the suction), which has an efficiency of about 70% and a power consumption of about 55 kW.

As a guide, consider that, other data being equal:

- If a head of 4 or 6 m had been used instead of 5 m, the following terns of results would have been obtained respectively: ($\eta = 0.630$; $S = 32.2$ m^2; $G' = 2505$ Nm^3/h) and ($\eta = 0.734$; $S = 25.5$ m^2; $G' = 2151$ Nm^3/h).
- If neutralization pH of 8.1 or 8.3 or 8.5 or 9 had been assumed (instead of 8.7), the following terns of results would have been obtained respectively: ($\eta = 0.259$; $S = 76.7$ m^2; $G' = 6221$ Nm^3/h) or ($\eta = 0.463$; $S = 42.7$ m^2; $G' = 3464$ Nm^3/h) or ($\eta = 0.599$; $S = 32.8$ m^2; $G' = 2660$ Nm^3/h) or ($\eta = 0.775$; $S = 24.6$ m^2; $G' = 1993$ Nm^3/h). The low efficiencies

obtained for $pH < 8.7$ justify the choice made for the neutralization pH in the example performed.

If it is necessary to reach a neutralization pH corresponding to exceedingly low efficiencies, then it could be suitable to use two tanks in series, because in the first we would have a higher pH and therefore a better exploitation of the CO_2 contained in the pertaining fraction of fumes. The relative calculations are given below.

- If the initial pH of the waste water had been 12 or 12.5, and the desired final pH had been 8.3 in both cases, the following terns of results would have been obtained respectively: ($\eta = 0.753$; $S = 2.63$ m^2; $G' = 213$ Nm^3/h) and ($\eta = 0.688$; $S = 9.08$ m^2; $G' = 736$ Nm^3/h).

The influence of initial and final pH on CO_2 exploitation efficiency can be clearly seen from the diagrams in Figure 2.

The possibility of using two tanks in series in order to optimize the neutralization process can be expressed in two different ways.

The first is that of minimizing the total necessary volume (and therefore the gas flow rate), for the same final pH as in the case of one tank. The second is that of minimizing the final pH, for the same total volume (and therefore the same gas flow rate).

In the first case we can proceed as follows.

We choose a value pH_1 as the neutralization pH for the first of the two tanks (usually the optimal value is between 9 and 10).

Using the same data as in the example with one tank (except the pH value, that now is pH_1 instead of 8.7), we calculate the corresponding results that we will name $A_{r,1}$, $A_{0,1}$, τ_1 , η_1 , S_1 , G'_1 .

For the second tank calculations the new data are the same as for the first (even pH_i , which is still 13), except that:

- the final pH is now $pH_2 = 8.7$,
- in the expression of A_r (3.24) we must set $A_{r,p} = A_{r,1}$ instead of 0,
- in the expressions of τ (3.30), M and N we must set $A_i = A_{0,1}$ instead of 0.

So we get the results τ_2 , η_2 , S_2 , G'_2 , which allow to calculate, for the whole of the two tanks, $\tau = \tau_1 + \tau_2$, $S = S_1 + S_2$, $G' = G'_1 + G'_2$, $\eta = (\eta_1 \tau_1 + \eta_2 \tau_2) / \tau$ (for the efficiency, it is necessary to make the weighted average of the values in the two tanks).

As easy to understand, there is a pH_1 value for which τ, S and G' turn out to be minimum (and η maximum). By trial and error we obtain that, in our case, pH_1= 9.63, in correspondence of which $A_{r,1} = 0.1225$ kmol/m^3, $A_{0,1} = 0.731 \cdot 10^{-4}$ kmol/m^3, $\tau = \tau_1 + \tau_2 = 7202 + 1369 = 8571$ sec, $S = S_1 + S_2 = 20.005 + 3.805 = 23.81$ m^2, $G' = G'_1 + G'_2 = 1622 + 309 = 1931$ Nm^3/h, $\eta = (\eta_1 \tau_1 + \eta_2 \tau_2) / \tau = (0.8457 \cdot 7202 + 0.6720 \cdot 1369) / 8571 = 0.818$.

In comparison with a single tank, the overall area is 23.8 instead of 28.2 m^2 (15.6% less) and the gas flow rate is 1931 instead of 2287 Nm^3/h. Overall efficiency is 81.8% instead of 69.1%. The area of the second tank is equal to 16% of the total area.

The second case, applicable for instance to an existing single tank, when a lower exit pH is desired by adding only a partition, requires slightly more elaborate calculations.

Now too it is necessary to choose a pH_1 value at the outlet of the first tank (of the order of 9÷9.5). Using the same design data as for the single tank (except pH_1) we calculate $A_{r,1}$, $A_{0,1}$, τ_1 , η_1 , S_1 , G'_1 .

For the second tank calculations we use again $A_{r,p} = A_{r,1}$ for A_r evaluation and $A_{0,1}$ as A_i value. This time however we do not know the final pH_2 value, which must be found by trial and error so as to obtain $\tau_2 = \tau - \tau_1$ (where τ is the value relative to the single tank, the volume of which coincides obviously with the overall volume of the two compartments).

Here also there is an optimal pH_1 value, equal in this case to the one that makes pH_2 minimum, and which is determined through a double series of attempts.

We obtain $pH_1 = 9.08$ and $pH_2 = 8.12$.

In particular $\tau = \tau_1 + \tau_2 = 8602 + 1551 = 10{,}153$ sec, $S = S_1 + S_2 = 23.89 + 4.31 = 28.20$ m^2, $G' = G'_1 + G'_2 = 1938 + 349 = 2287$ Nm^3/h, $\eta = (\eta_1 \tau_1 + \eta_2 \tau_2) / \tau = (0.7896 \cdot 8602 + 0.2240 \cdot 1551) / 10{,}153 = 0.703$.

Obviously τ, S and G' are the same values already obtained for the single tank, which is now divided so that the second compartment is equal to 15.3% of the total volume.

Overall efficiency is only slightly higher (70.3% instead of 69.1%), but the final pH is remarkably lower (8.12 instead of 8.7). Note that in the second compartment efficiency is very poor: this is necessary to reach the very low final pH and is however offset by the more than satisfactory efficiency of the first compartment.

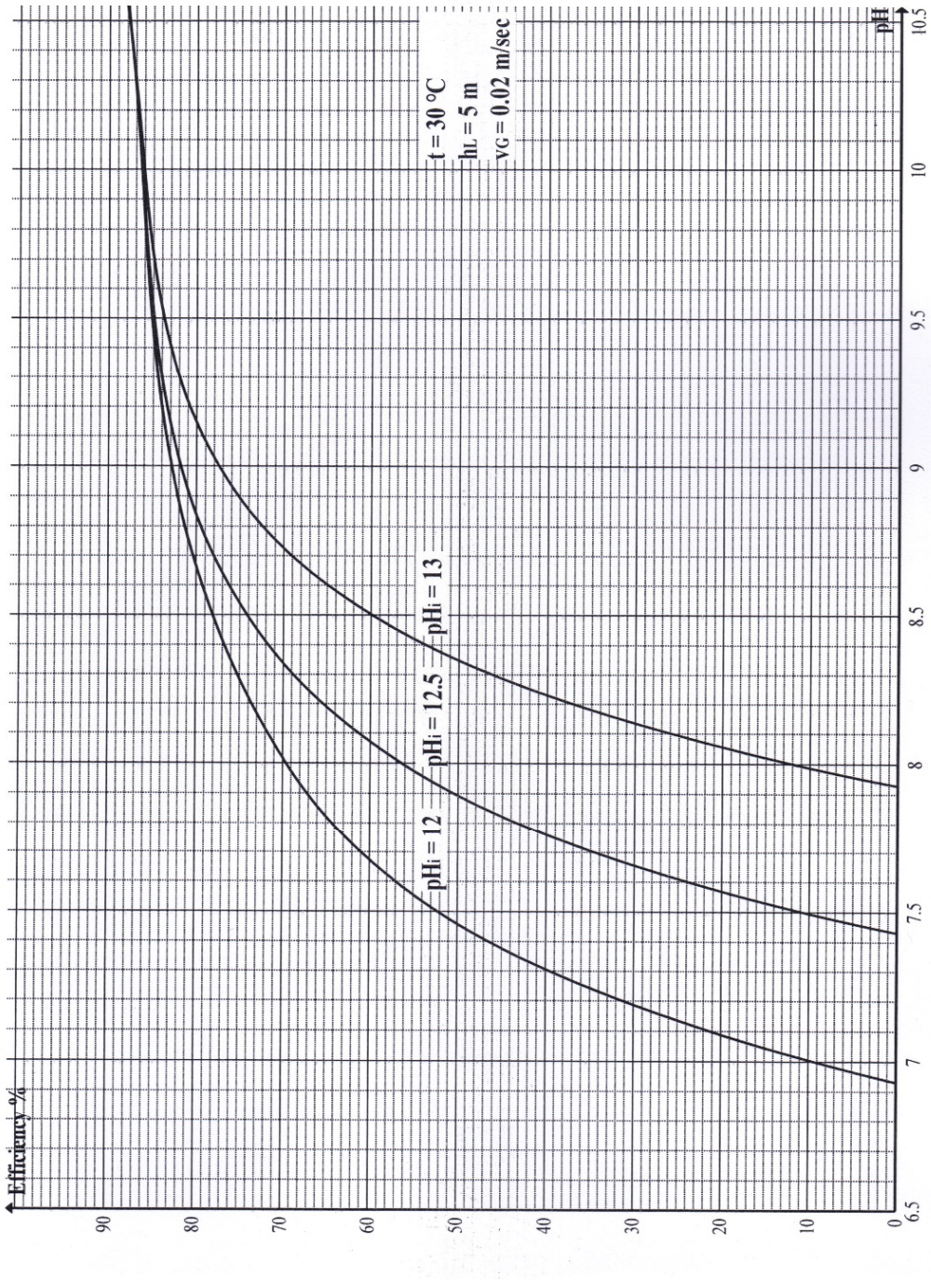

Fig. 2. CO_2 exploitation efficiency versus pH

4. ABSORPTION IN AGITATED VESSELS WITH CHEMICAL REACTION

4.1. CHEMICAL-PHYSICAL PRINCIPLES

In par. 3.3 we examined the problem of basic waters neutralization by flue gases, using a bubble vessel designed on purpose.

It is possible to carry on the same operation utilizing an existing tank, for instance the equalizing basin placed before a biological water treatment plant. This tank will typically have a bigger volume (corresponding to a liquid residence time of several hours) and a smaller useful height (for instance 2÷4 m) in comparison with the parameters generally fixed for a bubble vessel.

Flue gases dispersion into waste water can be effectively carried on, in this case, through submersible aerators, either of the turbine type, with a star-shaped impeller, or of the ejector type, fed by a centrifugal pump. On the other hand these machines are already commonly used for mixing the contents of those basins, with absorbed powers of at least 30 W/m^3.

It is sufficient to feed the aerators with flue gases instead of air, increasing if necessary their number (up to overall powers even of 200 W/m^3) in order to reach the CO_2 flow rate necessary for neutralization.

These aerators are able to produce fine bubbles and to assure a perfect mixing of the gas phase within the liquid mass, so that the CO_2 concentration in the bubbles turns out to be the same in every point of the tank.

Obviously the liquid too can be considered as perfectly mixed. Therefore the concentrations in the outgoing fluid can be assumed to be the same as the ones in the fluid within the tank, for both the gas and the liquid.

All the remarks already made in par. 3.3.1 for the neutralization in a bubble column apply unchanged to the reaction in agitated vessels, with only one fundamental difference, that is that for the gaseous phase we no longer have to assume a vertical plug flow, but a perfect mixing as for the liquid phase.

This implies that in the first case to examine, that is with A_0 / A^* not negligible and $E = 1$ (i.e. for $pH < 10$), the expressions (3.25) and (3.26) still apply, but no longer the (3.27).

In particular in (3.25) y_0 is still the volumetric fraction of CO_2 in the gas coming out from the tank, but it is also the y value inside all the bubbles dispersed in the same tank.

Moreover in (3.26) the factor (1 - ω) can be omitted, because the gas hold-up in the tanks considered here is negligible.

On the contrary, as $y = y_0$ (and therefore $A^* = Py_0 /H$) are constant all over the vessel, the expression (3.27) becomes:

$$V \cdot k_L a \cdot (A^* - A_0) = G\,(y_i - y_o) \tag{4.1}$$

which expresses in finite (and no longer differential) terms the fact that the overall CO_2 transfer from the gas to the liquid phase is equal to the variation of the CO_2 content in the gas flow rate G (kmol/sec).

From (4.1) we easily get:

$$y_o = f\frac{H}{P}A_0 + (1-f)y_i \qquad \text{with} \qquad f = \frac{1}{1+\frac{GH}{VPk_La}} \tag{4.2}$$

which is equal to (3.29), except for the different expression of f.

If $\tau = V/Q$ (sec) is the liquid residence time in the tank, the expressions (3.30) for τ, (3.31) for A_0 and (3.32) for η still apply, provided we set $\omega = 0$ and use for f the new expression (4.2).

Similarly in the second case to examine ($A_0 = 0$, $E \geq 1$, i.e. $pH > 10$) the expression (3.33) still holds, while (3.34) becomes:

$$V \cdot Ek_La \cdot A^* = G\,(y_i - y_0) \tag{4.3}$$

From which we get:

$$y_o = (1-f)y_i \qquad \text{with} \qquad f = \frac{1}{1+\frac{GH}{VPEk_La}} \tag{4.4}$$

which is equal to (3.36), except for the different expression of f.

We get τ replacing this value of y_0 in (3.33), while η is still given by (3.32).

We have respectively:

$$\tau = \frac{A_r}{\frac{G}{V}fy_i} \qquad \text{and} \qquad \eta = f = \frac{1}{1+\frac{GH}{VPEk_La}} \tag{4.5}$$

To get A_0, which is very small, we can still use the expression (3.37), setting $\omega = 0$.

Also for agitated vessels, as for bubble columns, we can say that for both cases previously examined we can use the same solution formulas (the ones obtained for the first case), provided the E factor is added to k_La in the expression (4.2) of f (which practically means to

always use (4.4) for f) and provided the value of $A_0 - A_e$ of the first case is divided by coshφ to have the new $A_0 - A_e$.

For convenience, we report below the formulas to be used in every case for agitated vessels, taking into account that the expressions for φ, E, A_e and A_r are the same already reported in par. 3.3.1.

$$f = \frac{1}{1 + \frac{GH}{VPEk_La}} \qquad M = A_r\left(1 + \frac{GHf}{VPK}\right) - A_e - A_i \qquad N = A_r\left(y_i\frac{Gf}{VK} + A_e\right) - A_eA_i$$

$$A_0 = \frac{1}{2\cosh\varphi}\left(\sqrt{M^2 + 4N} - M\right) + A_e\left(1 - \frac{1}{\cosh\varphi}\right) \qquad y_0 = f\frac{H}{P}A_0 + (1-f)y_i$$

$$\tau = \frac{A_r + A_0 - A_i}{\frac{G}{V}(y_i - y_o)} \qquad \eta = \frac{\frac{A_r}{\tau}}{y_i\frac{G}{V}} \tag{4.6}$$

4.2. HYDRODYNAMICS AND MASS TRANSFER

One of the most delicate problems is the evaluation of the mass transfer coefficient k_La and in particular of the specific area a (m^{-1}) referred to the tank volume.

The expressions reported in literature for agitated vessels do not apply in our case because they generally refer to specific powers (W/m^3) remarkably greater.

We need however the k_L value too, for the calculation of the Hatta number φ.

For this purpose we will use the following expression [16], which is the most conservative among the many that have been proposed:

$$k_L = 0.31 \left(\frac{g\rho_L}{\mu_L}\right)^{1/3} \cdot {D_A}^{2/3} \tag{4.7}$$

At 20 – 30 – 40 °C we have respectively $k_L = 0.95 \cdot 10^{-4} - 1.21 \cdot 10^{-4} - 1.51 \cdot 10^{-4}$ m/sec.

For k_La evaluation we used the data provided by the manufacturers of the aerators for oxygen transfer (which is the classic application of these machines in biological oxidation basins), converting those data and adapting them for the CO_2 case.

Diagrams are generally available that show for every aerator the atmospheric oxygen flow rate transferred in clean water as a function of liquid head and tank volume (for at least two volume values).

In dirty water oxygen transfer is generally greater, because the present substances usually tend to hinder the coalescence of air bubbles, thus increasing the transfer area.

The corrective coefficient (here for simplicity considered equal to 1) also depends on the aerator type, so the matter should be further explored by consulting the supplier.

The transferred oxygen flow rates are obtained by the manufacturers by setting conditions quite similar to the ones that apply to CO_2 absorption at pH values around 9.5, that is high enough to make A_0 negligible in comparison to A^*, but not so high as to make E appreciably greater than 1.

The transferred CO_2 flow rate is therefore $V \cdot k_La \cdot A^*$ and the efficiency, given by (4.5) with $E = 1$, is:

$$\eta = \frac{1}{1 + \frac{GH}{VPk_La}} \tag{4.8}$$

The conditions for $A_0 = 0$ and $E = 1$, in the case of oxygen transfer, are obtained adding to water suitable quantities of sodium sulphite (which reacts with oxygen) and of cobalt sulphate (which acts as a catalyst).

It is then easy, measuring the residual sulphite concentration at intervals, to determine the quantity of absorbed oxygen and so calculate $k_L'a$. Less easy is to set the above conditions: with too much sulphite and cobalt salt E turns out greater than 1 (and an exceedingly optimistic value is obtained for $k_L'a$), with insufficient quantities A_0 is not negligible and $k_L'a$ is undervalued.

However, in the right test conditions we have:

$$\bar{G} = V \cdot k_L'a \cdot A'^{*} = V \cdot k_L'a \cdot \frac{P}{H'} y_0' = G(y_i' - y_0')$$

where $\bar{G}$ is the flow rate (kmol/sec) of absorbed O_2 and $k_L'a$, A'^{*}, H', y_0', y_i' correspond to the parameters k_La , A^{*}, H, y_0 and y_i already defined for CO_2 , but referred to O_2. In particular for the air we have $y_i' = 0.209$, while H' at 20°C is worth 724 atm·m^3/kmol.

Then we get (indicating with subscript 20 the parameters referred to the test conditions, i.e. to 20 °C):

$$(k_L'a)_{20} = \frac{\bar{G}_{20} H'_{20}}{VP} \cdot \frac{1}{y_i' - \frac{\bar{G}_{20}}{G}} \tag{4.9}$$

$k_L'a$ is equal to k_La (with equal aerator and tank size), except for two factors which take into account respectively the different diffusivities of CO_2 (D_A) and O_2 (D_A') and the possibly different temperature of the operating conditions with CO_2 and of the test conditions with O_2.

We have, taking into account (4.7):

$$k_La = (k_L'a)_{20} \cdot \left(\frac{D_{A,20}}{D'_{A,20}}\right)^{2/3} \cdot \alpha_t \tag{4.10}$$

where $D_{A,20} = 1.71 \cdot 10^{-9}$ m^2/sec, $D'_{A,20} = 2.0 \cdot 10^{-9}$ m^2/sec and α_t is a factor which takes into account the variations with temperature of $k_L'a$ and k_La , linked to liquid diffusivity, viscosity and surface tension.

In practice k_La is proportional to $D_A^{2/3} \cdot \mu_L^{-1/3} \cdot \sigma_L^{-0.6}$ (surface tension σ_L affects the a value). Taking into account that $D_A \cdot \mu_L / T = const$ (where T is the absolute temperature in °K), we have:

$$\alpha_t = \left(\frac{T}{293}\right)^{2/3} \cdot \left(\frac{\mu_L}{\mu_{L,20}}\right)^{-1} \cdot \left(\frac{\sigma_L}{\sigma_{L,20}}\right)^{-0.6} \tag{4.11}$$

At 20 – 30 – 40°C we have respectively α_t = 1 – 1.302 – 1.646, in good agreement with the factor 1.024^{T-293} reported in the literature on aeration systems.

Replacing in the expression (4.8) of η the k_La value given by (4.10), coupled to (4.9), we get:

$$\eta = \frac{1}{1 + \frac{H}{H'_{20} \cdot \alpha_t}\left(y'_i \frac{G}{\bar{G}_{20}} - 1\right)\left(\frac{D'_{A,20}}{D_{A,20}}\right)^{2/3}}$$

By chance H changes with temperature according to a factor practically equal to α_t , so that η does not change with temperature.

Taking into account that $\bar{G}_{20}/(Gy'_i) = \eta'_{20}$ is the oxygenation efficiency measured in the test, we get the following simple relation between CO_2 neutralization efficiency η (around pH = 9.5) and η'_{20} :

$$\frac{\frac{1}{\eta} - 1}{\frac{1}{\eta'_{20}} - 1} = \frac{H}{H'_{20} \cdot \alpha_t} \cdot \left(\frac{D'_{A,20}}{D_{A,20}}\right)^{2/3}$$

An oxygenation efficiency of 18% (which is typically obtained at 20°C with these aerators) corresponds therefore to a neutralization efficiency of 84%, both at 20°C (H = 25.7 atm·m^3/kmol) and at 30°C (H = 34.5 atm·m^3/kmol).

As already mentioned, the $\bar{G}_{20}$ value of absorbed oxygen flow rate is made available by the manufacturers, for every aerator type and for several head values, for at least two different values of the tank volume. We will call $\bar{G}_A$ and $\bar{G}_B$ (kmol/sec) the oxygen flow rates correspondent to the tanks of area S_A and S_B (the volumes V_A and V_B will be calculated by multiplying these areas by the head h_L).

The expression (4.9) will give two different $(k'_La)_{20}$ values, which we will call $(k'_La)_A$ and $(k'_La)_B$.

In particular:

$$(k'_La)_B = \frac{\bar{G}_B \cdot H'_{20}}{V_B P\left(y'_i - \frac{\bar{G}_B}{G}\right)} \tag{4.12}$$

We can assume that $(k'_La)_{20}$ varies with the volume V of the tank proportionally to V^{Σ}.

Then we have:

$$(k_L'a)_{20} = (k_L'a)_B \cdot (V/V_B)^{\Sigma} \tag{4.13}$$

In particular it is $(k_L'a)_A = (k_L'a)_B \cdot (V_A/V_B)^{\Sigma}$

Taking into account (4.9) we have

$$\frac{(k_L'a)_B}{(k_L'a)_A} = \frac{V_A}{V_B} \cdot \frac{\bar{G}_B}{\bar{G}_A} \cdot \frac{y_i' - \frac{\bar{G}_A}{G}}{y_i' - \frac{\bar{G}_B}{G}} = (V_B/V_A)^{\Sigma}$$

from which we get the Σ value:

$$\Sigma = \frac{\ln\left(\frac{\bar{G}_B}{\bar{G}_A} \cdot \frac{y_i' - \frac{\bar{G}_A}{G}}{y_i' - \frac{\bar{G}_B}{G}}\right)}{\ln(S_B/S_A)} - 1 \tag{4.14}$$

In conclusion the k_La value to be used for neutralization calculations is given by (4.10), where α_t is given by (4.11) and $(k_L'a)_{20}$ by (4.13), in which $(k_L'a)_B$ comes from (4.12) and Σ from (4.14).

In case of presence of n equal aerators in the same tank, of volume V_V, the value of V in the formulas of chapter 4 shall be assumed to be V_V/n.

4.3. NUMERICAL EXAMPLE

4.3.1. Preliminary remarks

Unlike the case of a bubble column, the design problem for an agitated vessel has not a solution that varies with continuity.

In that case, fixed a certain liquid flow rate Q and certain values for the initial and final pH, we obtained correspondingly precise values for the tank section and the flue gases flow rate. Here, as we can accept only a whole, and not a fractional number of aerators, we must proceed differently, fixing in advance the size and the number n of the aerators and the tank volume V_V. Then we obtain, according to the desired final pH, the exact values of the treatable liquid flow and of the exploitation efficiency for the CO_2 content in the flue gases. In practice, we have to solve a verification, rather than a design problem.

To this purpose, on the basis of the liquid flow rate and of the initial pH (i.e. of the caustic soda load) we calculate the kmol/h of CO_2 (Q_c) necessary for the neutralization, assuming for simplicity a theoretical consumption of 1 CO_2 mole for every NaOH mole and a CO_2 exploitation efficiency conservatively low (for instance 70%).

At this point, as $y_i = 0.1$ is the molar (and volumetric) CO_2 fraction in the (dehumidified) flue gases, the necessary gas flow rate (Nm^3/h) turns out to be equal to $Q_c / 0.1 \cdot 22.4$ (where 22.4 $Nm^3/kmol$ is the molar volume).

After choosing the aerator model, from the manufacturer diagram that gives the aspirated flow as a function of the liquid head h_L we can determine that flow (in correspondence of an abscissa value equal to h_L (m) plus the gas pressure drop ($m.H_2O$) from the point of collection in the power station down to the neutralization basin).

Thus we get the necessary aerator number (usually rounding up to the nearest whole number).

At this point, if a tank is already available, we can check if the specific power dissipated in it is at least equal to 30 W/m^3, in order to assure a good mixing of gas and liquid. If it is too low, we can delimit with suitable partitions a portion of the tank to devote to neutralization.

On the other hand, we must also check if the necessary aerator number exceeds the one that is possible to place in the tank respecting at the same time both the distances (from the walls and between one machine and another) and the maximum specific power recommended by

the supplier. In case of violation we can resort for instance to a second tank in series to the first in order to place all the aerators, with the advantage moreover of a better overall exploitation of the CO_2 contained in the fumes, because pH in the first tank will be certainly higher than the one desired at the second tank outlet.

The calculation method in the case of two tanks is similar to the one already used at the end of par. 3.3.2. In this case Q shall be considered as known and by trial and error we find the pH_1 value (at the outlet of the first tank) leading to $\tau_1 = V_1/Q$ and then, always by trial and error, the pH_2 value leading to $\tau_2 = V_2/Q$ (the subscripts 1 and 2 refer respectively to the first and to the second tank).

Since the number of aerators is necessarily an integer, in all probability the chosen configuration (later checked with the following calculations) will allow the treatment of a liquid flow Q slightly greater than the designed one. However we point out even now that the CO_2 exploitation efficiency, and therefore the treatable liquid flow, are quite poorly affected by the tank volume (for the same number of aerators).

As for the necessary data referring to aerators, we already said how to obtain the aspirated gas flow rate G from the diagram that gives G as a function of h_L (i.e. in correspondence of the $h_L + \Delta p$ value). We emphasize the importance of this data, which must be the subject of a specific guarantee, because it is much more determinant (for the result of neutralization calculations) than the absorbed oxygen flow rates.

These last ones should be read, on the diagrams that report them as a function of the liquid head and for two different tank sizes, in correspondence of the h_L value, but both of them should be then reduced in the ratio of G_2/G_1, which are the two values of aspirated gas flow rate read in correspondence of the abscissas $h_L + \Delta p$ and h_L respectively.

A hint is then appropriate with reference to the cooling and dehumidifying system for the flue gases collected from the chimney of a factory boiler.

If cooling down to less than 40°C is not already obtained through some kind of heat recovery downstream the boiler, it is possible to bring the fraction of fumes necessary for neutralization from 180÷200°C down to ambient temperature and to a humidity content of about 3% (volumetric) thanks to a small packed tower preceded by a Venturi-shaped quench section.

The necessary water flow rate (at a temperature at least 5°C lower than the desired one for the outgoing fumes) is of the order of 5 m^3/h per 1000 Nm^3/h of dry gas and is discharged at

the tower bottom, without the possibility of recirculation. The packed bed, 2 m high, may be of polypropylene DN 50 Pall rings. Pressure drop for quench + tower (with a gas velocity in the bed of about 2 m/sec) is of the order of 1500 Pa.

The above scrubbing, in addition to eliminating SO_2 (highly corrosive) in case of oil-fired boilers, allows the use, for the same mass flow of fumes, of smaller and therefore cheaper aerators. In fact at lower temperatures the volumetric flow rate (which determines aerator sizing) is smaller.

4.3.2. Development

The values of many of the quantities required for the calculations have already been reported in par. 3.2.2.

Here too we will consider a liquid temperature of 30°C, a volumetric fraction of CO_2 in the flue gases y_i = 0.1, an initial pH in the liquid pH_i = 13 (corresponding to a caustic soda concentration of 0.145 kmol/m^3) and a liquid flow rate Q = 50 m^3/h. The NaOH load is then equal to 7.25 kmol/h.

The purpose of neutralization is to reach pH = 8.7 in an existing basin with volume V_V = 800 m^3 and a useful height h_L = 3 m (hence the average pressure in the tank is P_m =1.15 atma).

Assuming conservatively a CO_2 exploitation efficiency of 70%, we need approximatively 7.25/0.7 = 10.36 kmol/h of CO_2, contained in $10.36/0.1 \cdot 22.4 = 2320$ Nm^3/h of fumes.

Pressure drop for conveying flue gases from chimney to basin is estimated at 2000 Pa (taking into account 1500 Pa for the cooling system and 500 Pa for losses in the ducts). Therefore it is necessary to note the flow aspirated by the chosen aerator in correspondence of a value given by h_L + 0.2 = 3.2 m.H_2O.

We have chosen an aerator (of the turbine type, with a star-shaped impeller) which for such a head value gives a flow rate of 442 Nm^3/h of air (or of fumes), with a consumption of 24.3 kW. We need therefore at least 5 aerators in the basin, for a total flow of 2210 Nm^3/h and a specific power of $24.3 \cdot 10^3 \cdot 5 / 800 = 152$ W/m^3.

We point out that total absorbed power (121.5 kW) is about twice the one required in the case of the bubble tank.

With h_L = 3 m, this type of aerator is able to transfer 27.7 kg/h of O_2 in a tank of area S_A = 25 m^2 (and therefore in a volume $V_A = 25 \cdot 3 = 75$ m^3) and 22.7 kg/h in a tank of area S_B = 144 m^2 (and therefore in a volume $V_B = 144 \cdot 3 = 432$ m^3). With h_L = 3 m the aspirated air flow is equal to 448 Nm^3/h. Since the aerator, owing to the additional Δp, intakes only 442 Nm^3/h, the oxygen flow rates should be reduced in the ratio 442/448, so $\bar{G}_A = 27.7 \cdot 442/448 = 27.3$ kg/h = 27.3/3600/32 = $2.37 \cdot 10^{-4}$ kmol/sec (32 kg/kmol is oxygen molecular weight) and $\bar{G}_B = 22.7 \cdot 442/448 = 22.4$ kg/h = 22.4/3600/32 = $1.94 \cdot 10^{-4}$ kmol/sec.

The flow rate aspirated by a single aerator is G = 442/3600/22.4 = $5.48 \cdot 10^{-3}$ kmol/sec.

From (4.12) we get, using for P the value P_m= 1.15 atma:

$$(k_L'a)_B = \frac{1.94 \cdot 10^{-4} \cdot 724}{432 \cdot 1.15 \cdot (0.209 - 1.94 \cdot 10^{-4}/5.48 \cdot 10^{-3})} = 1.63 \cdot 10^{-3}\ \text{sec}^{-1}$$

From (4.14) we get:

$$\Sigma = \frac{\ln\left(\frac{1.94 \cdot 10^{-4}}{2.37 \cdot 10^{-4}} \cdot \frac{0.209 - 2.37 \cdot 10^{-4}/5.48 \cdot 10^{-3}}{0.209 - 1.94 \cdot 10^{-4}/5.48 \cdot 10^{-3}}\right)}{\ln(144/25)} - 1 = -1.14$$

Taking into account that $V = V_V/n = 800/5 = 160$ m^3, from (4.13) we have:

$$(k_L'a)_{20} = 1.63 \cdot 10^{-3} \cdot (160/432)^{-1.14} = 5.06 \cdot 10^{-3}\ \text{sec}^{-1}$$

Finally, taking into account that α_t, given by (4.11), at 30°C is worth 1.302 (as already anticipated in par. 4.2), from (4.10) we obtain:

$$k_L a = 5.06 \cdot 10^{-3} \cdot (1.71 \cdot 10^{-9}/2.0 \cdot 10^{-9})^{2/3} \cdot 1.302 = 5.93 \cdot 10^{-3}\ \text{sec}^{-1}$$

We have then $c_B = (OH^-) = 10^{pH-pK_W} = 7.24 \cdot 10^{-6}$ kmol/m^3 and $K = K' + K''c_B = 0.037 + 0.0869 = 0.124$ sec^{-1}.

The Hatta number $\varphi = \sqrt{KD_A}/k_L$ is worth $\sqrt{0.124 \cdot 2.22 \cdot 10^{-9}}/1.21 \cdot 10^{-4} = 0.137$, taking into account that k_L, given by (4.7), is worth $1.21 \cdot 10^{-4}$ at 30°C.

Then it is $E = \varphi/\tanh\varphi = 1.0063$ and $\cosh\varphi = 1.0094$.

The values of A_e, given by (3.23), and of A_r, given by (3.24), are the same as in the example of par. 3.3.2, i.e. $A_e = 0.586 \cdot 10^{-3}$ kmol/m^3 and $A_r = 0.141$ kmol/m^3.

From (4.6), using for P the value P_m and taking into account that $G/V = 5.48 \cdot 10^{-3}/160 = 0.343 \cdot 10^{-4}$ kmol/sec/m^3, we get $f = 0.853$, $M = 0.141$, $N = 8.60 \cdot 10^{-5}$, $A_0 = 6.05 \cdot 10^{-4}$ kmol/m^3, $y_0 = 0.0302$, $\tau = 59{,}220$ sec = 16.45 h, $\eta = 0.6952$.

From these results we obtain that the liquid treatable flow rate $Q = V_V / \tau$ is equal to 800/16.45 = 48.63 m^3/h, slightly smaller than the design one (50 m^3/h). Also the CO_2 exploitation efficiency ($\eta = 0.6952$) is slightly lower than the 70% value assumed to determine the necessary number of aerators. The solution found can be considered satisfactory however (if Q was actually equal to 50 m^3/h, the pH would be 8.75 instead of 8.7).

We can now check if the reaction is actually pseudo-first order, as hypothesized.

We will still use the condition of Danckwerts, as in par. 3.3.2, that is:

$$\varphi = \frac{\sqrt{(K' + K''c_B)D_A}}{k_L} \leq \frac{1}{2}\left(1 + \frac{zc_B}{A^*}\right)$$

It is a question of finding which is the maximum pH value (which determines the values of z and c_B) for which the inequality is still satisfied.

The most critical point for verification is the tank base, where $A^* = y_0\ P/H$ is maximum (because P is maximum, while y_0 is constant all over the tank). In particular we have there $A^* = 0.0302 \cdot 1.3/34.5 = 1.14 \cdot 10^{-3}$ kmol/m^3.

The maximum pH value turns out to be 10.06, smaller than the 10.65 value obtained for the bubble tank case, owing to the rather conservative k_L value given by (4.7).

In practice the pH to which we want to bring the waste water is certainly less than 10, so the pseudo-first order reaction condition is met throughout the range of practical interest.

For values greater than 10.06 the E value is actually lower than the one given by the expression $\varphi/\tanh\varphi$, so the treatable flow rate Q, calculated in the hypothesis of pseudo-first order reaction, would be slightly overestimated. In fact if E is lower, f (given by (4.4)) is smaller and τ (given by (4.5)) is greater, so $Q = V_V / \tau$ is smaller.

Going back to our example, it is interesting to point out that the tank volume (800 m^3) has a negligible influence on Q and η.

If it was 600 m^3 we would have obtained $\eta = 0.6976$ and τ = 44,262 sec = 12.29 h, so the treatable flow rate would have been 600/12.29 = 48.80 m^3/h. If it was 1500 or 3000 m^3, we would have obtained respectively $\eta = 0.6882$ with Q = 48.14 m^3/h and $\eta = 0.6785$ with Q = 47.46 m^3/h.

But if a final pH lower than 8.7 was required, then 5 aerators would have been more markedly insufficient. For instance, with V_V = 800 m^3, for pH = 8.5 we would have obtained $\eta = 0.6010$ and τ = 69,121 sec = 19.20 h, so the treatable flow rate would have been of only 41.67 m^3/h.

To evaluate the influence of the head h_L it is necessary to get from the manufacturer's diagrams a new tern of values $G, \bar{G}_A, \bar{G}_B$ in correspondence of the new h_L value.

For h_L = 2 m, instead of h_L = 3 m, the same aerator considered before gives G = 454 Nm^3/h = 5.63 $\cdot 10^{-3}$ kmol/sec, $\bar{G}_A = 1.51 \cdot 10^{-4}$ kmol/sec, $\bar{G}_B = 1.48 \cdot 10^{-4}$ kmol/sec, with a consumption of 19.7 kW (here too we made the appropriate corrections to take into account the additional Δp; S_A and S_B are always equal to 25 and 144 m^2, so now V_A = 50 m^3 and V_B = 288 m^3).

We get, always with pH = 8.7 and V_V = 800 m^3, $\eta = 0.6313$ and τ = 63,479 sec = 17.63 h, so the liquid treatable flow rate is Q = 800/17.63 = 45.37 m^3/h, with an overall absorbed power of 98.5 kW and an aspirated gas flow of 2270 Nm^3/h.

For h_L = 4 m, we have G = 394 Nm^3/h = 4.89 $\cdot 10^{-3}$ kmol/sec, $\bar{G}_A$= 2.95 $\cdot 10^{-4}$ kmol/sec, $\bar{G}_B$= 2.27 $\cdot 10^{-4}$ kmol/sec, with a consumption of 28.0 kW.

We get, with pH = 8.7 and V_V = 800 m^3, η = 0.7416 and τ = 62,213 sec = 17.28 h, so the treatable flow rate is Q = 800/17.28 = 46.29 m^3/h, with an overall absorbed power of 140 kW and an aspirated gas flow of 1970 Nm^3/h.

In the examples with h_L = 2 and 4 m we assumed the same volume (800 m^3) considered for the case of h_L = 3 m, so the area of the three tanks is different. If the same area was considered, the three volumes would have been different: however η and Q would have changed very little, since, as noted above, the volume has a negligible influence on them.

As the result, in terms of treatable flow rate with a certain number of aerators, is practically the same whichever is the h_L value, a low head configuration (2÷2.5 m) is more convenient, because it results in lower energy consumption.

Another consequence of the poor influence of the head on the liquid treatable flow rate, for the same tank area, is that the neutralization process can be carried on without any problem even in equalizing tanks with liquid level variable over time.

APPENDIX

HCN reactions in packed towers with NaOH and NaClO

In par. 2.5.1 we already listed the liquid phase reactions between HCN, NaOH and NaClO and reported the most significant kinetic constants and the relevant chemical-physical parameters related to HCN.

However, we summarize these data, adding the ones concerning CNCl.

We will indicate with A and A' (mol/l) the liquid phase concentrations of HCN and CNCl respectively, while y and y' (mg/m^3) are the respective concentrations in the gas phase.

With A^*, A'^*, y^* and y'^* we will indicate the values of the above mentioned parameters at the liquid-gas interface, while A_o and A_o' are the values in the liquid mass (and therefore at the inner end of the film).

B and C (mol/l) are the concentrations of hypochlorite and caustic soda, considered constant within the film due to the strong excess of the two reagents: this allows to consider of pseudo-first order the reactions 1), 2) and 3) of par. 2.5.1.

As already mentioned, the reaction 1) between HCN and NaOH is instantaneous, the reaction 2) between NaCN and NaClO has a constant $K_2 = 1.84 \cdot 10^6$ l/mol/sec (at pH 10.5), the reaction 3) between CNCl and NaOH has a constant $K_3 = 4.53$ l/mol/sec.

The HCN physical parameters (Henry constant and diffusivities) are (at 25°C):

$D_G = 2.02 \cdot 10^{-5}$ m^2/sec $\quad D_L = 1.89 \cdot 10^{-9}$ m^2/sec $\quad pK = 9.2 \quad H = 3.41 \cdot 10^{-3} \quad H^* = 1.63 \cdot 10^{-4}$.

The CNCl physical parameters (at 25°C) are:

$D_G' = 1.29 \cdot 10^{-5}$ m^2/sec $\quad D_L' = 1.46 \cdot 10^{-9}$ m^2/sec $\quad H' = 0.079$.

The packed bed (formed by Q-PAC) is 2.5 m high, the gas and liquid velocities are 2.5 m/sec and 20 m^3/h/m^2 respectively, with an actual hold-up of 3.0% ($h_e = 0.03$).

On the basis of the Billet-Schultes model, an effective bed height Z=2.15 m and a liquid-gas mass transfer surface $a_e = 81.2$ m^2/m^3 are obtained.

Moreover, according to the same model, the mass transfer coefficients are equal, for HCN, to $k_G = 0.082$ m/sec and $k_L = 1.88 \cdot 10^{-4}$ m/sec, while for CNCl we have $k_G' = 0.061$ m/sec and $k_L' = 1.66 \cdot 10^{-4}$ m/sec.

We have already seen in par. 2.5.1 that reaction 2), leading to the CNCl formation, is a fast reaction, with $H_a = 8.13$ (>2, so the reaction occurs completely in the film). In addition, it can be considered of pseudo-first order, so that $E = H_a$, thus obtaining $H_{OG} = 0.38$ m.

Along the column (that is, for different values of the z dimension) we have $y_e = 0$ and therefore $dy = - y \cdot dz/H_{OG}$. Hence the diagram of y versus z is given by $y = y_i \cdot \exp(-z/H_{OG})$, with $y_i = 9.2$ mg/m^3 (at the column base, for $z = 0$). The relation between y and y^* is given by $y^* = R_L \cdot y$, with $R_L = 8.66 \cdot 10^{-3}$ constant along the column.

The reaction between CNCl and NaOH is rather slow and does not occur in the film, because $H_a' = (D_L' \cdot K_3 \cdot C)^{1/2} / k_L' = (1.46 \cdot 10^{-9} \cdot 4.53 \cdot 3.16 \cdot 10^{-4})^{1/2} / 1.66 \cdot 10^{-4} = 0.0087 << 1$.

Moreover, we cannot even assume that the CNCl concentration in the liquid mass (A_o') is practically equal to 0, because to this purpose we should have:

$k_L' \cdot a_e$ $(= 1.66 \cdot 10^{-4} \cdot 81.2 = 0.013)$ $<<$ $h_e \cdot K_3 \cdot C$ $(= 0.03 \cdot 4.53 \cdot 3.16 \cdot 10^{-4} = 4.3 \cdot 10^{-5})$

a clearly not fulfilled condition.

We have pointed out that we cannot assume $A_o' = 0$ because the case of simultaneous absorption and desorption with chemical reactions treated in the literature by Pangarkar as reported in [12], and somewhat similar to ours, just makes this simplifying hypothesis, which is not acceptable in our case. On the other hand, the constancy of the B and C concentrations in the film, which occurs in our case (and not in Pangarkar's), makes easier the rigorous solution of the system of two second order differential equations that is necessary to face.

They are:

$$D_L \frac{d^2A}{dx^2} = K_2 B A \qquad \text{(A. 1)}$$

$$- D_L' \frac{d^2A'}{dx^2} = K_2 B A \qquad \text{(A. 2)}$$

because the stoichiometric coefficients of all reagents and products of reaction 2) are unit (in this Appendix x is the distance from the interface within the film).

The boundary conditions are:

- for $x = 0$ (i.e. at the liquid-gas interface):

$$A = A^* \qquad \text{(A. 3)}$$

$$D_L' \frac{dA'}{dx} = k_G' H' (A'^* - A_G') \qquad \text{(A. 4)}$$

- for $x = \delta$ (i.e. at the inner edge of the film):

$$A = 0 \qquad \text{(A. 5)}$$

$$- D_L' \frac{dA'}{dx} a_e = h_e K_3 C A_o' - L \frac{dA_o'}{dz} = (h_e K_3 C + nL) A_o' \qquad \text{(A. 6)}$$

The film thickness δ is equal to D_L/k_L : for simplicity we will use, to evaluate it, only the parameters related to HCN (it is a thickness equal to about one hundredth of a millimetre).

The condition (A.4) says that the A' flow through the interface is equal to the mass transfer in the gas phase (A_G' is the concentration y' in the gas phase expressed with units, mol/l, typical of the liquid phase).

The condition (A.6) says that the *A'* flow from the film to the liquid mass is equal to how much *A'* reacts with C in the mass itself (in the film this reaction does not occur, and in fact the equation (A.2) does not include any term for the reaction between *A'* and *C*) plus the increase in the liquid of *A'* not reacted (the minus sign is due to the fact that, with *z* increasing from the base to the top of the column, dA_o'/dz is negative). The expression of the three terms is clearer by multiplying them all by $\bar{S}\,dz$ (where $\bar{S}$ is the column section): in particular it is evident that the *A'* increase in the differential volume of height *dz* is equal to $-L\,\bar{S}\,dA_o'$.
In itself, the term dA_o'/dz is a major complication for computation, because it forces us to deal with a much more complex system of differential equations. On the other hand, it cannot be neglected, because for example it turns out a posteriori that in our case the term relative to the A_o' increase along the column is much more remarkable than the one due to the chemical reaction.
Since the diagram of A_o' versus *z* is a posteriori of exponential type, the simplest way to approach the calculation is to assume $dA_o'/dz = -n\,A_o'$, to take for *n* a conservatively high value (e.g. 2 or 3 m^{-1}) and to verify a posteriori the goodness of this assumption (as well as the actual influence of this assumption on the percentage of formed CNCl being desorbed). The *n* value that should be taken in our case is 2.2 m^{-1} (and will be justified later).
The solution of (A.1), well known and simple to obtain, using the conditions (A.3) and (A.5), is:

$$A = \frac{A^*}{\sinh\sqrt{M}} \cdot \sinh\left[\sqrt{M}\left(1 - \frac{k_L x}{D_L}\right)\right] \qquad \text{with} \qquad M = \frac{K_2 D_L B}{k_L^2} \qquad (A.7)$$

where $\sqrt{M}$ is the Hatta number.
Replacing this A value in (A.2) and integrating twice we get:

$$A' = -\frac{D_L}{D_L'}A + l_1 x + l_2$$

where l_1 and l_2 are two integration constants obtainable by imposing conditions (A.4) and (A.6). For this purpose, consider that:

$$\frac{dA'}{dx} = -\frac{D_L}{D_L'}\frac{dA}{dx} + l_1 = \frac{A^* k_L \sqrt{M}}{D_L' \sinh\sqrt{M}} \cdot \cosh\left[\sqrt{M}\left(1 - \frac{k_L x}{D_L}\right)\right] + l_1$$

Moreover, since A_o' (unknown) is the *A'* value for $x = \delta$ (where $A = 0$), we have $A_o' = l_1\delta + l_2$ and therefore:

$$A' = -\frac{D_L}{D_L'}A + l_1(x - \delta) + A_o' \qquad (A.8)$$

Then condition (A.4) gives, being $x = 0$,

$$\frac{A^* k_L \sqrt{M}}{\sinh \sqrt{M}} \cdot \cosh \sqrt{M} + D'_L l_1 = k'_G H' (A'^* - A'_G)$$

from which $l_1 = \frac{k'_G H'}{D'_L}(A'^* - A'_G) - \frac{A^* k_L \sqrt{M}}{D'_L} \coth \sqrt{M}$

While condition (A.6) gives, for $x = \delta = D_L/k_L$,

$$-\frac{A^* k_L \sqrt{M}}{\sinh \sqrt{M}} - D'_L l_1 = \frac{h_e K_3 C + nL}{a_e} A'_o$$

from which, substituting to l_1 the value found above, we obtain

$$A'_o = \frac{a_e k_L}{h_e K_3 C + nL} \left[A^* \sqrt{M} \frac{\cosh \sqrt{M} - 1}{\sinh \sqrt{M}} - \frac{k'_G H'}{k_L} (A'^* - A'_G) \right]$$

Substituting in (A.8) the found values of l_1 and A_o', we obtain the expression of A' versus x:

$$A' = -\frac{D_L}{D'_L} \frac{A^*}{\sinh \sqrt{M}} \sinh \left[\sqrt{M} \left(1 - \frac{k_L x}{D_L} \right) \right] + \frac{D_L}{D'_L} \left[A^* \sqrt{M} \coth \sqrt{M} - \frac{k'_G H'}{k_L} (A'^* - A'_G) \right]$$

$$\cdot \left(1 - \frac{k_L x}{D_L} \right) + \frac{a_e k_L}{h_e K_3 C + nL} \left[A^* \sqrt{M} \frac{\cosh \sqrt{M} - 1}{\sinh \sqrt{M}} - \frac{k'_G H'}{k_L} (A'^* - A'_G) \right] \qquad \text{(A. 9)}$$

By setting $x = 0$ in the previous expression, A' must be equal to A'^*, and therefore:

$$A'^* = \left(\frac{D_L}{D'_L} \sqrt{M} \coth \sqrt{M} - \frac{D_L}{D'_L} + \frac{a_e k_L \sqrt{M}}{h_e K_3 C + nL} \frac{\cosh \sqrt{M} - 1}{\sinh \sqrt{M}} \right) A^*$$

$$- \left(\frac{D_L k'_G H'}{D'_L k_L} + \frac{a_e k'_G H'}{h_e K_3 C + nL} \right) A'^* + \left(\frac{D_L k'_G H'}{D'_L k_L} + \frac{a_e k'_G H'}{h_e K_3 C + nL} \right) A'_G$$

By solving this linear equation, we obtain A'^* as a function of A^* and A_G'. In particular, we are interested in the value of

$$A'^* - A'_G = \frac{F A^* - A'_G}{1 + m} \qquad \text{(A. 10)}$$

with:

$$F = \frac{D_L}{D'_L} \sqrt{M} \coth \sqrt{M} - \frac{D_L}{D'_L} + \frac{a_e k_L \sqrt{M}}{h_e K_3 C + nL} \frac{\cosh \sqrt{M} - 1}{\sinh \sqrt{M}}$$

$$m = \frac{k'_G H'}{k_L} \left(\frac{D_L}{D'_L} + \frac{a_e k_L}{h_e K_3 C + nL} \right)$$

The expression (A.9) then becomes:

$$A' = \left[\frac{D_L}{D_L'}\sqrt{M}\coth\sqrt{M}\left(1-\frac{k_L x}{D_L}\right) - \frac{D_L}{D_L'}\frac{\sinh\left[\sqrt{M}\left(1-\frac{k_L x}{D_L}\right)\right]}{\sinh\sqrt{M}} + \frac{a_e k_L}{h_e K_3 C + nL}\sqrt{M}\frac{\cosh\sqrt{M}-1}{\sinh\sqrt{M}}\right]A^*$$

$$-\frac{k_G' H'}{k_L}\left[\frac{D_L}{D_L'}\left(1-\frac{k_L x}{D_L}\right) + \frac{a_e k_L}{h_e K_3 C + nL}\right]\frac{FA^* - A_G'}{1+m} \qquad (A.11)$$

The values of A^* and A_G' change along the column.

In particular for $z = 0$ (at the base) we have $y = y_i = 9.2$ mg/m^3, $y^* = R_L \cdot y = 8.66 \cdot 10^{-3} \cdot 9.2 = 0.0797$ mg/m^3, $A^* = y^* \cdot 10^{-6}/PM/H^* = 0.0797 \cdot 10^{-6}/27/1.63 \cdot 10^{-4} = 18.1 \cdot 10^{-6}$ mol/l, while $y' = 0$ and $A_G' = y' \cdot 10^{-6}/PM'/H' = 0 \cdot 10^{-6}/61.5/0.079 = 0$.

We can then proceed directly to the calculation of $A'^* - A_G'$ with (A.10) and to trace the diagram of A' versus x (at the bed bottom) by (A.11).

For the upper column sections we know $y = y_i \cdot \exp(-z/H_{OG})$ and therefore A^*, because R_L does not change along the column, but we do not know the corresponding value of y' and therefore of A_G'.

In every column section the increase in the CNCl flow is given by

$$G \cdot dy' = k_G' a_e (y'^* - y') \cdot dz$$

From (A.10) we have

$$y'^* - y' = \frac{\frac{PM' \cdot H'}{PM \cdot H^*} F y^* - y'}{1+m}$$

whereby, replacing $y^* = R_L \cdot y = R_L \cdot y_i \cdot \exp(-z/H_{OG})$, we obtain

$$\frac{dy'}{dz} = \frac{k_G' a_e}{G(1+m)}\left(\frac{PM' \cdot H'}{PM \cdot H^*} F R_L y_i e^{-z/H_{OG}} - y'\right)$$

This is a simple linear differential equation, the solution of which is:

$$y' = \frac{ab}{b - \frac{1}{H_{OG}}} e^{-z/H_{OG}} + l_3 e^{-bz}$$

where $a = \frac{PM' \cdot H'}{PM \cdot H^*} F R_L y_i$ $\qquad$ $b = \frac{k_G' a_e}{G(1+m)}$

The constant l_3 is obtained by imposing that for $z = 0$ we have $y' = 0$, from which $l_3 = -ab/(b - 1/H_{OG})$ and therefore

$$y' = \frac{ab}{\frac{1}{H_{OG}} - b}\left(e^{-bz} - e^{-z/H_{OG}}\right) \qquad (A.12)$$

Turning to numbers, we have:

$$\sqrt{M} = \frac{\sqrt{K_2 D_L B}}{k_L} = \frac{\sqrt{1.84\cdot10^6\cdot1.89\cdot10^{-9}\cdot6.72\cdot10^{-4}}}{1.88\cdot10^{-4}} = 8.131$$

$$m = \frac{k'_G H'}{k_L}\left(\frac{D_L}{D'_L} + \frac{a_e k_L}{h_e K_3 C + nL}\right) = \frac{0.061\cdot0.079}{1.88\cdot10^{-4}}\left(\frac{1.89\cdot10^{-9}}{1.46\cdot10^{-9}} + \frac{81.2\cdot1.88\cdot10^{-4}}{0.03\cdot4.53\cdot3.16\cdot10^{-4} + 2.2\cdot5.556\cdot10^{-3}}\right)$$
$$= 65.08$$

$$F = \frac{D_L}{D'_L}\sqrt{M}\coth\sqrt{M} - \frac{D_L}{D'_L} + \frac{a_e k_L\sqrt{M}}{h_e K_3 C + nL}\cdot\frac{\cosh\sqrt{M} - 1}{\sinh\sqrt{M}}$$
$$= \frac{1.89\cdot10^{-9}}{1.46\cdot10^{-9}}8.131\cdot1 - \frac{1.89\cdot10^{-9}}{1.46\cdot10^{-9}} + \frac{81.2\cdot1.88\cdot10^{-4}\cdot8.131}{0.03\cdot4.53\cdot3.16\cdot10^{-4} + 2.2\cdot5.556\cdot10^{-3}}\cdot\frac{1699.8 - 1}{1699.8}$$
$$= 19.35$$

$$a = \frac{PM'\cdot H'}{PM\cdot H^*}FR_L y_i = \frac{61.5\cdot0.079}{27\cdot1.63\cdot10^{-4}}19.35\cdot8.66\cdot10^{-3}\cdot9.2 = 1702 \ \text{mg/m}^3$$

$$b = \frac{k'_G a_e}{G(1+m)} = \frac{0.061\cdot81.2}{2.5(1+65.08)} = 0.02998 \ \text{m}^{-1}$$

Hence (with H_{OG} = 0.38 m) we finally get:

$$y' = 19{,}61\left(e^{-0.02998\cdot z} - e^{-z/0.38}\right) \ \text{mg/m}^3 \qquad (A.13)$$

which provides the diagram of *y'* versus *z*.

At the column top (*z* = 2.15 m) we have y_o' = 18.32 mg/m^3, which is the CNCl concentration emitted at the stack.

Since, always at the column top, it is $y_o = y_i \cdot \exp(-2.15/0.38)$ = 0.032 mg/m^3, we have that 9.2 - 0.032 = 9.168 mg/m^3 of HCN have been absorbed, generating 9.168·61.5/27=20.88 mg/m^3 of CNCl. Of these, therefore, 87.7% have been desorbed and the rest remain absorbed in the liquid.

Figure A1 shows the diagram of *y* and *y'* versus *z*.

For *z* > 1.72 m the *A'* flow at the interface is reversed: the *A'* generation in the film is now poor, while the concentration *y'* that has been created in the fumes is already remarkable, so there is a slight CNCl reabsorption in the liquid: from the maximum reached value (18.41 mg/m^3 for *z* = 1.72 m) *y'* drops to 18.32 mg/m^3 at the bed exit.

Through the expressions (A.7) and (A.11) we can trace the diagrams of *A* and *A'* versus *x*, within the film, for each *z* value. In practice we must first, having fixed *z* (for instance *z* = 0 at the column bottom), calculate *y* and *y'* (with (A.13)), then the corresponding values of y^*, A^*, A_G' and finally *A* and *A'*.

Figure A2 shows the diagrams for *z* = 0, *z* = 0.4 and *z* = 2.15 m.

As we can see, the *A'* diagram has a downward concavity (as it was expected, since the second derivative given by (A.2) is always negative).

The slopes for $x = 0$ and $x = \delta$ are proportional respectively to the desorbed flow into the gas and to the absorbed flow into the liquid mass. Of the latter, about 0.4% reacts globally with caustic soda along the bed and 99.6% is carried down unreacted into the column bottom, where it completes the reaction; the ratio between these two terms is given by $h_e K_3 C /(n L)$. The A_o' value is $14.0 \cdot 10^{-6}$ mol/l for $z = 0$ m, $11.2 \cdot 10^{-6}$ mol/l for $z = 0.1$ m, $6.1 \cdot 10^{-6}$ mol/l for $z = 0.4$ m and $1.87 \cdot 10^{-6}$ mol/l for $z = 2.15$ m.

From these A_o' values, calculated for different z values, it is possible to check if the assumption of $n = 2.2$ m^{-1} was correct, keeping in mind that it must be $n = \frac{dA_o'}{dz} / A_o' = d(\ln A_o')/dz$.

In essence if n is actually a constant, the diagram of $\ln A_o'$ versus z must be linear, at least in the lowest part of the bed (the first 0.4 m, say), where A_o' is rather high and therefore has a significant impact on the results.

In fact it is easy to check that the diagram of $\ln A_o'$ is practically linear, with a slope of 2.2 m^{-1} in the low part of the bed. This slope decreases progressively (even below 1 m^{-1}) in the upper part of the bed (where A_o' is small and poorly influential), which means that the actual mean n value in the entire bed is slightly less than 2.2 m^{-1}. This implies that the y_o' value calculated for $n = 2.2$ m^{-1} (i.e., $y_o' = 18.32$ mg/m^3) is slightly underestimated and therefore conservative (i.e., the CNCl desorption is at least equal to the 87.7% value we calculated). In fact, for example, for $n = 2$ m^{-1}, $y_o' = 18.43$ mg/m^3 would be obtained.

It is interesting to note that, even if n had been initially much overestimated (for example assuming $n = 5$ m^{-1}), the obtained values of A_o' and y_o' would have been significantly different from the correct values (we would have obtained $A_o' = 8.5 \cdot 10^{-6}$ mol/l instead of $14.0 \cdot 10^{-6}$ for $z = 0$ and $y_o' = 17.41$ mg/m^3 instead of 18.32), but the slope of $\ln A_o'$ versus z would have already been equal to the correct value ($n = 2.2$ m^{-1}), which allows to reach the exact results already at a second attempt, just assuming this new n value.

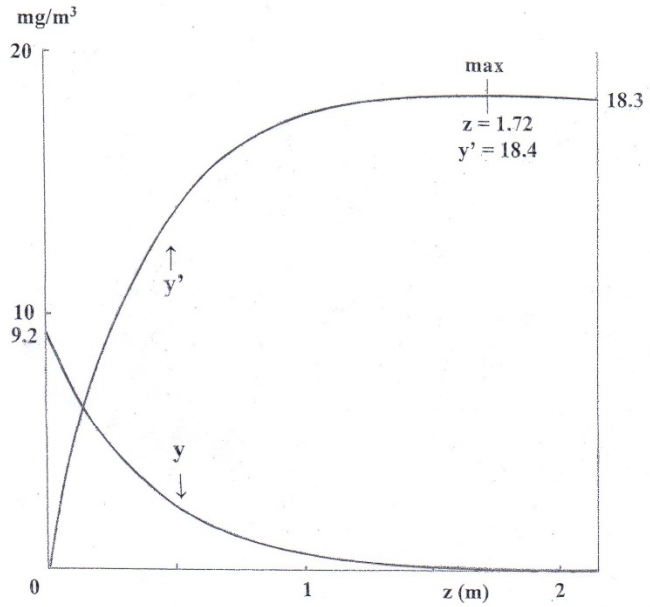

Fig. A1

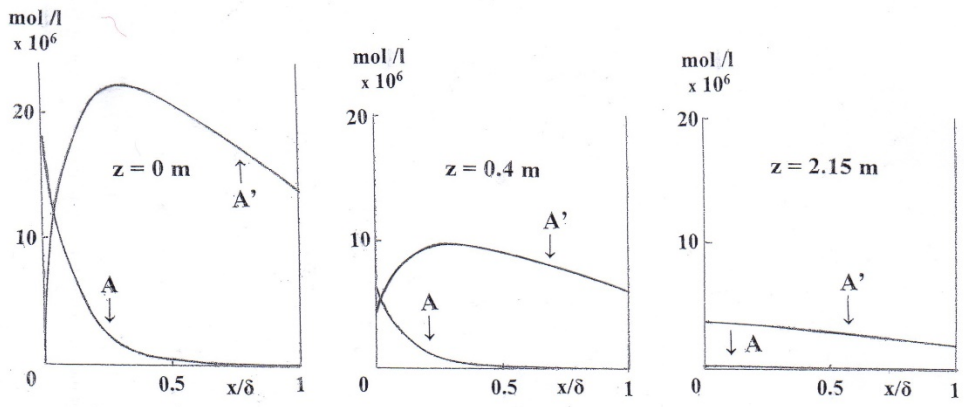

Fig. A2

Fig. A1. HCN (y) and CNCl (y') concentration profile along the column.

Fig. A2. HCN (A) and CNCl (A') concentration profile in the film at various heights.

REFERENCES

[1] Sander R. (2015) – Compilation of Henry's law constants (version 4.0) for water as solvent – Atmos. Chem. Phys., 15, p. 4399

[2] Martin G., Laffort P. (1991) – Odeurs et désodorisation dans l'environnement - Tech & Doc, Lavoisier

[3] Bolles W.L., Fair J.R. (1979) – I. Chem. E. Symp. Series – N. 56, Sect. 3.3, p. 35

[4] Billet R., Schultes M. (1999) – Trans. IChemE, Vol. 77, p. 498

[5] Mackowiack J. (2015) – Chem. Eng. Research and Design – N. 99, p. 28 – Elsevier

[6] Mackowiack J. (2010) – Fluid dynamics of packed columns – Springer

[7] Vilmain J.B., Biard P.F. et al. (2014) – Chem. Eng. Research and Design – N. 92, p. 191 – Elsevier

[8] Danckwerts P.V., Sharma M.M. (1966) – The Chemical Engineer – Oct.1966, CE258

[9] Baldi G., Sicardi S. (1975) – Chem. Eng. Science – Vol. 30, p. 623

[10] Danckwerts P.V. (1970) – Gas-liquid reactions – McGraw-Hill, p. 125-128

[11] Gerritsen C.M., Margerum D.W. (1990) – Inorg. Chem. – N. 29, p. 2757

[12] Doraiswamy L.K., Sharma M.M. (1984) – Heterogeneous reactions: analysis, examples, and reactor design – Vol. 2 – John Wiley & Sons, p. 202

[13] Sarla M. et al. (2004) – J. Hazard. Mater. B116, p. 49 – Elsevier

[14] Hughmark G.A. (1967) – Ind. Eng. Chem. Process Des, Dev. – Vol. 6, p. 218

[15] Danckwerts P.V., Sharma M.M. (1966) – The Chemical Engineer – Oct.1966, CE 247

[16] Calderbank P.H., Moo-Young M.B. (1961) – Chem. Eng. Science – Vol. 16, p. 39