MASS TRANSFER CHARACTERISTICS IN STRUCTURED PACKING FOR CO₂-EMISSION REDUCTION PROCESSES

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Acid gas treating and CO_2 capture from flue gas by absorption has gained a wide importance over the last few decades. With the implementation of more stringent environmental regulations and the awareness of the green house effect, the need for efficient removal of acid gases like CO_2 (carbon dioxide) has increased significantly. Therefore additional effort for research in this field is inevitable.

For the flue gas process the ratio of absorption solvent to gas throughput is very different compared to acid gas treating processes owing to the atmospheric pressures and the dilution effect of combustion air. Moreover, in flue gas applications pressure drop is a very important process parameter. Packing types are required that allow for low pressure drops in combination with high interfacial areas at low liquid loading per m^2.

The determination of interfacial areas in gas-liquid contactors by means of the chemical method (Danckwerts, 1970) has been very frequently applied. However, this technique is only applicable for process conditions and absorption systems that obey to the condition $2 < Ha < E_{inf}$. This condition has been derived for systems consisting of an irreversible second order reaction. Unfortunately, many of the model systems used in literature are reversible and therefore this condition possibly is not met. Versteeg et al. (1989) has demonstrated that for reversible reactions the conditions for the determination of the interfacial area by means of the chemical method are much more severe.

In the study of Raynal et al. (2004) the system used was CO_2-caustic soda in which reactions cannot be regarded as irreversible. Therefore a system check has been carried out and it is concluded that for the conditions and experimental equipment used the applicability of the results is very limited and effectively turns out to be not valid. It has been shown that observed dependency of the interfacial area on the packing height can be explained as a result of the use of the CO_2-soda system (!) and not as a characteristic of the experimental equipment.

KEYWORDS: Structured packing, Carbon dioxide, Flue gas, Gas treating
Proposed Theme: Equipment

1. INTRODUCTION

Acid gas treating has gained a wide importance over the last few decades. With the implementation of more stringent environmental regulations, the need for efficient

removal of acid gases like CO_2 (carbon dioxide), H_2S (hydrogen sulphide) has increased significantly. More specifically the capture of CO_2 has gained substantial interest as a result of the Kyoto-protocol in order to realize stabilisation of the CO_2 emission to the environment. Post-combustion removal of CO_2 from waste-gas produced by power plants with e.g. amine solutions is believed to be a very promising tool to reduce the CO_2-emissions. However, at this moment the costs of the available processes are about €.50 per tonne CO_2 removed. In order to be economically feasible these costs have to be reduced to values below about €.20 per tonne CO_2 removed. Therefore additional effort for research in this field is inevitable.

For flue gas process the ratio of absorption solvent to gas throughput is very different compared to acid gas treating processes owing to the atmospheric pressures and the dilution effect of air used as combustion agent. Moreover, in flue gas applications the pressure drop is a very important process parameter. It can be concluded that packing types are required that allow low pressure drops in combination with high interfacial areas at low liquid loading per m^2. Basically two types of packing are available: dumped and structured packing respectively. In the present study attention is focussed on structured packing as these usually have lower pressure drops compared to dumped packing.

In a previous paper by Raynal et al. (2004) results are presented on mass transfer characteristics, a/o interfacial area, for structured packing. Surprisingly, the observed interfacial areas turned out to be depending on the position in the packed column! Differences up to 50% are reported. The measuring technique used was the well-known "absorption in the chemically enhanced region". In the present study this technique is critically evaluated.

2. THEORY

In Raynal et.al (2004) the absorption rate was determined in the chemically enhanced region, as characterised by:

$$2 < Ha < E_{inf} \tag{1}$$

Strictly spoken, this boundary condition is only applicable for the combination of absorption with irreversible chemical reaction(s). In open literature there are two model systems frequently used for the determination of interfacial areas in gas-liquid contactors:

a)   the oxidation of sulphite to sulphate with air.
b)   the absorption of (diluted) CO_2 in aqueous caustic soda solutions.

One of the most important and major drawback of this so-called chemical method is that a priori information is required on the value of the liquid side mass transfer coefficient, k_l, otherwise the lower limit $Ha > 2$ cannot be estimated. A more suitable technique would be simultaneous measurements of $k_l a$ and a as proposed by Cents et al. (2005). For more details on both systems the interested reader is referred to Danckwerts (1970) and Deckwer (1985).

Raynal et al. (2004) have selected the caustic soda system for the determination of the interfacial area. Basically, two reactions occur in the aqueous caustic soda systems:

$$CO_2 + OH^- \quad <> \quad HCO_3^- \tag{2}$$

$$HCO_3^- + OH^- \quad <> \quad CO_3^{2-} \tag{3}$$
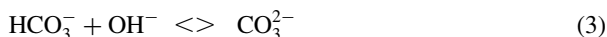
Besides these two main reactions also a third, instantaneously fast, reactions occurs:

$$H_2O + H_2O \quad <> \quad H_3O^+ + OH^- \tag{4}$$

This latter reaction can be regarded to be at equilibrium compared to the reaction rate of the two aforementioned reactions and the mass transfer rate respectively. Moreover, the reactions (2), (3) and (4) are reversible reactions and therefore the use of equation (1) is beforehand not completely justified. Versteeg et al. (1989) demonstrated that reversibility has a substantial effect on the value of E_{inf}.

Therefore the results of Raynal et al (2004) are evaluated by means of an absorption model in which all occurring reversible, parallel reactions are taken into account in the governing diffusion equations (Van Loo et al. (2005)).

2.1 ABSORPTION MODEL

The problem considered is mass transfer accompanied by reversible chemical reactions of general order with respect to both reactants and products. The description of the absorption model and the numerical treatment is illustrated for a single reversible reaction:

$$A(g) + \gamma_b B(l) \; \overset{\longleftarrow}{\longrightarrow} \; \gamma_c C(l) + \gamma_d D(l) \tag{5}$$
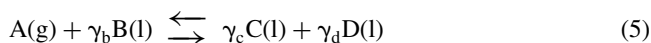
with the following overall reaction rate equation:

$$R_a = k_{R,m,n,p,q}[A]^m[B]^n[C]^p[D]^q - k_{R,r,s,t,v}[A]^r[B]^s[C]^t[D]^v \tag{6}$$

It is clear that for systems with parallel and/or consecutive reactions the number of reactions will increase.

Usually for gas-liquid systems most reactions can be expressed with sufficient accuracy with a reaction rate expression similar to (6) and therefore this expression was used in this model.

Moreover, for the caustic soda system Haubrock et al. (2005) recently demonstrated that the use of concentrations in the kinetic expression may lead to erroneous results and it is preferred to use activities and activity coefficients instead. The latter ones could be

estimated by e.g. the Pitzer approach as proposed by Haubrock et al. (2005). However, in the present study the traditional approach, concentration based equations, will be used in combination with the physical data used by Raynal et al. (2004).

The mass transfer in the gas phase is described with the stagnant film model while for the liquid phase the penetration model is used, as the penetration model is expected to be the most realistic one in describing gas-liquid absorption.

For the penetration model the balances for each species for the phenomenon mass transfer followed by a chemical reaction yields the following set of equations:

$$
\frac{\partial [A]}{\partial t} = D_a \frac{\partial^2 [A]}{\partial x^2} - R_a \ , \ \ \frac{\partial [B]}{\partial t} = D_b \frac{\partial^2 [B]}{\partial x^2} - \gamma_b R_a,
$$
$$
\frac{\partial [C]}{\partial t} = D_c \frac{\partial^2 [C]}{\partial x^2} + \gamma_c R_a \ , \ \ \frac{\partial [D]}{\partial t} = D_d \frac{\partial^2 [D]}{\partial x^2} + \gamma_d R_a
$$

$$(7), (8), (9), (10)$$

These four coupled non-linear partial differential equations must be solved numerically because an analytical solution method is not available. To be solved uniquely the four non-linear partial differential equations (7) to (10) require one initial and two boundary conditions respectively. The initial condition is given by:

$$ t = 0 \text{ and } x \geq 0, [A] = [A]_0, [B] = [B]_0, [C] = [C]_0, [D] = [D]_0 \tag{11} $$

where the concentrations $[i]_0$ satisfy $R_a = 0$ in equation (6). The boundary condition for $x = \infty$ can also be derived with the assumption of chemical equilibrium for the bulk of the liquid for a given solute loading:

$$ t > 0 \text{ and } x = \infty, [A] = [A]_0, [B] = [B]_0, [C] = [C]_0, [D] = [D]_0 \tag{12} $$

For detailed information on the calculation of the equilibrium composition according to equation (12) one is referred to Blauwhoff et al. (1985).

The second associated boundary condition is obtained by assuming that the species B, C and D are non-volatile and that the flux of component A from the gas phase is equal to the flux of component A to the liquid phase. The use of the latter assumption instead of the assuming that $[A] = [A]_i$ at $x = 0$ is convenient in view of the applicability of the model for cases where a part of the resistance against mass transfer is situated in the gas phase. This is the case in the asymptotic situation of instantaneously fast reactions:

$$
- D_a \left(\frac{\partial [A]}{\partial x} \right)_{x=0} = k_g \left([A]_{g,bulk} - [A]_{g,i} \right)
$$
$$
\left(\frac{\partial [B]}{\partial x} \right)_{x=0} = \left(\frac{\partial [C]}{\partial x} \right)_{x=0} = \left(\frac{\partial [D]}{\partial x} \right)_{x=0} = 0
$$

$$(13)$$

For more detailed information on the applied numerical method used the reader is referred to Versteeg et al. (1989).

2.2 ABSORBER MODEL

The experiments of Raynal et al. (2004) were carried out in a packed bed contactor with structured packing and the operation mode was co-current with respect to both gas and liquid phase. Gas and liquid were fed from the top of the absorber.

The absorber is simulated by a tray-to-tray procedure (Blauwhoff et al., 1985). The absorption column is considered as a series of ideally mixed (with respect to both gas and liquid phases) reactors, each corresponding to an actual tray. It must be noted that this tray-to-tray approach is applicable for both counter- and co-current operation of the column respectively. If the size of a "tray" is chosen small enough, the same approach can also be applied for packing where each "tray" in the model represents a certain length of packing.

For the present application process conditions and gas and liquid compositions are assumed to be uniform in each tray or segment. The mass transfer parameters (k_l, k_g, a, ρ) are considered to be equal for all trays of the absorber. Physical parameters like viscosity, diffusivity, equilibrium constants and partition coefficients are taken as a function of the temperature on each tray.

It is also assumed that experiments were carried out at isothermal conditions, as also stated by Raynal et al. (2004). Based on this assumption the liquid and gas temperatures are known, and liquid phase equilibrium constants, Henry coefficients, and gas and liquid phase diffusivities can be calculated. The liquid phase composition, more specifically the concentrations of unreacted CO_2 and OH-, is obtained by means of the equilibrium model.

Calculations start by taking the experimentally determined gas and liquid flows and the gas and liquid concentrations at the top of the column from Raynal et al. (2004). CO_2 gas phase concentrations at tray 1, i.e. in the gas leaving tray 1, are estimated. Subsequently, gas phase concentrations are calculated, so that the absorption driving forces are now known. The molar flux (J_{CO2}) is calculated using a micro/flux model (see section 2.1).

After the first estimation of the gas phase concentration and the subsequent molar flux calculations, tray iteration proceeds using a direct substitution method for the first iteration and a Regula-Falsi procedure for the remaining iteration steps, until the following convergence criteria is satisfied within the desired accuracy (usually < 0.01% error):

$$J_{CO2}aV_{tray} = \Phi_g^{n+1}[CO_2]_g^{n+1} - \Phi_g^n[CO_2]_g^n \tag{14}$$

The tray-to-tray procedure continues until the CO_2 specification experimentally determined by Raynal et al. (2004) is reached. An additional iterative procedure using the interval halving method is used to converge the interfacial area until the desired CO_2 specification is reached exactly at tray N. The main result from the calculation is the value of the interfacial area a (m^2/m^3).
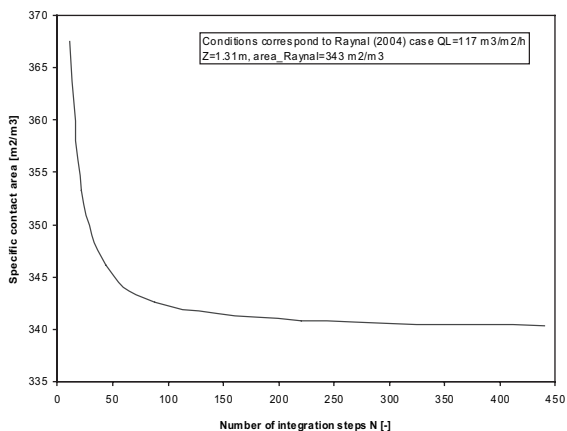
Figure 1. Minimum number of trays per section to be used in the tray-to-tray calculations.

As the experiments of Raynal et al. (2004) were carried out in a co-current packed bed contactor with structured packing, it was required to determine the minimum amount of trays (N) needed to assure that the simulations describe ideal plug flow. Therefore a number of simulations have been carried out to investigate the effect of the number (or height) of the trays on the outcome of the simulations. In Figure 1 the results of these simulations are presented.

Each section of the absorber has a height of 0.44 m. From Figure 1 it can be concluded that about 200 trays per section are required to assure that the model outcome becomes independent of the tray height. Consequently a maximum tray height of 0.0022 m would be optimal. In the re-evaluation of the data of Raynal et al. (2004) as presented in the current work a tray height of 0.005 m (88 trays) was used as a compromise between accuracy and required calculation time. From Figure 1 it can be seen that results are still accurate within 1% when N = 88 is used.

3. RESULTS

As mentioned above, one of the major drawbacks of the chemical method to determine interfacial areas in gas-liquid contactors is that beforehand the value of k_l must be know within reliable boundaries in order to fulfil the conditions stated in Equation (1). Moreover, an additional issue is the effect of reversibility of the value that can be realised for E_{inf}. Therefore simulations have been carried out for the data obtained in the study of Raynal et al. (2004) for a liquid flow rate of QL = 117 $m^3/m^2/h$. In these simulations the value of k_l has been varied between 10^{-2} $m.s^{-1}$ and 10^{-5} $m.s^{-1}$ (the range in which
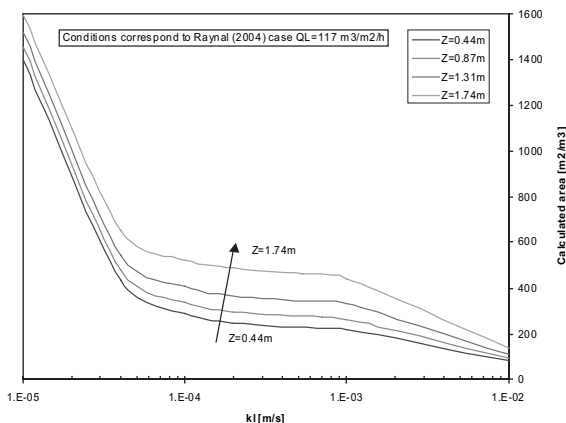
Figure 2. Relation between kl (m/s) and a (m^2/m^3) Raynal et al 2004; Q$_l$ = 117 m^3/m^2/h.

the value of k$_l$ for this type of contactors can be expected). In case the conditions of Equation (1) are fully met a range for the value of k$_l$ must be observed in which the calculated interfacial area (from the data of Raynal et al (2004)) is totally independent from k$_l$.

In Figure 2 the results of these simulations are presented.

It is obvious that no k$_l$-interval can observed were a kind of horizontal plateau occurs where the value of the interfacial area is constant! In Figure 2 it can be seen that for values $10^{-4} < k_l < 10^{-3}$ m.s^{-1} the calculated interfacial area is only slightly dependent on the value of k$_l$. It must be noted, however, that for e.g., the simulations for Z = 0.44 m the interfacial area increases about 35% if the value of k$_l$ is reduced from 10^{-3} m.s^{-1} to 10^{-4} m.s^{-1}. Moreover, with increasing packing height the simulated interfacial area increases which is in line with the findings of Raynal et al. (2004).

Overall it must be concluded that it seems that for the conditions and set-up in the study of Raynal et al. (2004) the CO$_2$-caustic soda system does not fulfil the conditions set by Equation (1).

To validate this, a so-called van Krevelen-Hoftijzer plot (Versteeg et al., 1989) has been made for the CO$_2$-caustic soda system: see Figure 3.

In this plot the enhancement factor, Ea, for the CO$_2$-soda system is calculated as function of the Ha-number. In case the conditions of Equation (1) are fulfilled the enhancement factor, Ea, should equal the value of the Ha-number. In Figure 4 the line Ea = Ha is also plotted.

As was shown by Versteeg et al. (1989) the value of the enhancement factor for complex, reversible systems, like the evaluated CO$_2$-soda system, is not only dependent
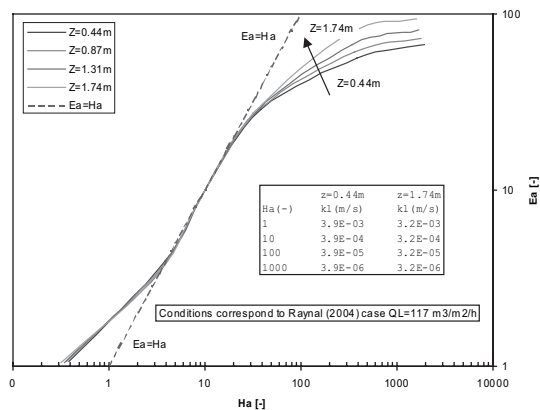
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Figure 3. Krevelen-Hoftijzer plot for the CO_2-caustic soda system.

on the Ha-number and E_{inf}, irreversible, but also on the reversibility, degree of (liquid-)conversion and partial pressure of the reactive gas. All these effects can be seen in Figure 3.

From this figure it can be concluded that only for the interval $4 < Ha < 20$ the enhancement factor calculated with the used extensive absorption model coincides with
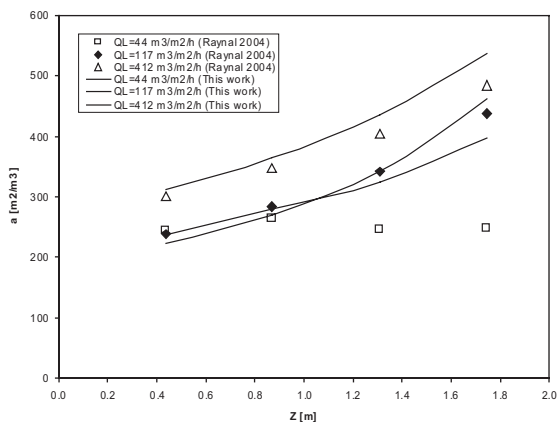

Figure 4. Comparison of the experimental and calculated relationship between the height of the packed bed z (m) and the interfacial area a (m^2/m^3).

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the line Ea = Ha. It seems justified to conclude that for the conditions and set-up used by Raynal et al. (2004) a major part of the experiments have been carried out in regions where Equation (1) is not obeyed!

In Figure 4 the reported values of the interfacial area in Raynal et al. (2004) are compared with the results of the used absorption model using the data of Raynal et al. (2004).

From Figure 4 it can be concluded that both evaluation tools result in values for the interfacial area that are dependent on the height of the packed bed. The larger the bed height, the larger the derived interfacial area is. This can easily be explained when it is noted that during the experiments the overall absorption rate of CO_2 is measured as represented by Equation (14):

$$J_{CO2}aV_{tray} = \Phi_g^2[CO_2]_g^2 - \Phi_g^1[CO_2]_g^1 \qquad (14)$$

More specifically the expression for J_{CO2} is (neglecting the effect of possible gas phase mass transfer limitations):

$$J_{CO2} = k_l E_{CO2}\big(m_{CO2}[CO_2]_g - [CO_2]_l\big) \qquad (15)$$

As shown, the value for E_{CO2} is definitely not equal to Ha. It is a (complex) function of the physical-chemical properties of the system used, the process conditions and parameters of the experiments and the investigated equipment respectively (see a/o Figure 3).

The experiments of Raynal et al. (2004) were carried out in a co-current mode (both gas and liquid flow form top to bottom respectively) which results in a continuously decreasing CO_2 gas phase concentration with the length of the packed bed column. From Figure 3 it can be concluded that with decreasing CO_2 concentration in the gas phase, especially for the higher values of Ha (e.g. above 10), the enhancement factor increases. It must be noted however, that for all simulations the calculated enhancement factors are lower than the value of Ha (!), indicating that Equation (1) is not fulfilled.

From this it is concluded that the observed dependency of the interfacial area on the packing height most likely must be attributed to the use of the CO_2-caustic soda system (!) and not as a characteristic of the experimental equipment.

Generally it must be concluded that, based on the outcome of the simulations (see Figures 2 and 3), it is not possible to reliably derive interfacial areas from the experimental data gathered in the work of Raynal et al. (2004) by means of the chemical method.

4. CONCLUSIONS

The determination of interfacial areas in gas-liquid contactors by means of the chemical method (Danckwerts, 1970) has been very frequently applied. However, this technique is only applicable for process conditions and absorption systems that obey to the condition

$2 < Ha < E_{inf}$. This condition has been derived for systems consisting of an irreversible second order reaction. Unfortunately, many of the model systems used are reversible and therefore the condition $2 < Ha < E_{inf}$ possibly is not met. It is demonstrated that for reversible reactions the conditions for the determination of the interfacial by means of the chemical method are much more severe.

In the study of Raynal et al. (2004) the system used was the CO_2-caustic soda system in which the reactions cannot be regarded as irreversible. Therefore a system check has been carried out and it is concluded that for the conditions and experimental equipment used by Raynal et al. (2004), the applicability of the CO_2-caustic soda system is limited and effectively turns out to be suited. It has been shown that observed dependency of the interfacial are on the packing height can be explained as a result of the use of the CO_2-caustic soda system (!) and not as a characteristic of the experimental equipment.

A major outcome of the present study is that it is concluded that the use of the chemical method for the determination of the interfacial area in gas-liquid contactors is a good technique but the boundary conditions of its applicability are much more limited that generally is assumed. The effect of reversibility of the occurring reactions is a very important issue and adds severe constraints to the reaction system, experimental conditions and the gas-liquid contactor respectively.

NOTATION

a	specific gas-liquid interface	$m^2\ m^{-3}$
D	diffusion coefficient	$m^2\ s^{-1}$
E	enhancement factor	–
J	mass transfer flux	$mol\ m^{-2}\ s^{-1}$
k_g	gas phase mass transfer coefficient	$m\ s^{-1}$
k_l	liquid phase mass transfer coefficient	$m\ s^{-1}$
k	reaction rate constant	–
m	partition coefficient	–
n	tray (or segment) number	–
N	total number of trays per column section	–
R	reaction rate	$mol\ m^{-3}\ s^{-1}$
R	gas constant (8.314)	$J\ mol^{-1}\ K^{-1}$
t	time	s
T	temperature	K
x	molar fraction liquid phase	–
x	position in penetration model	m
y	molar fraction gas phase	–
V_{tray}	volume of liquid on a tray or segment	m^3
α	liquid loading	$mol\ mol^{-1}$
γ	stoichiometry number	–
ρ	density	$kg\ m^{-3}$
Φ	gas flow	$mol\ (N)m^{-3}$

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SUBSCRIPTS

am	amine
back	backward reaction
eq	equilibrium
fwd	forward reaction
g	gas phase
l	liquid phase
i	component I
j	time line index
tot	total, reacted as well as unreacted

SUPERSCRIPTS

n	tray number

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