

STANDARDISATION OF MASS TRANSFER MEASUREMENTS – A BASIS FOR THE DESCRIPTION OF ABSORPTION PROCESSES

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Inaccurate mass transfer measurements lead to the wrong design of process equipment, since the precision of computer aided design tools depends on the accuracy of the model parameters. While standardisation has taken place for distillation systems, the quality of absorption data varies significantly and the compatibility of data from different sources is limited. Therefore, a standardised procedure to determine mass transfer parameters is presented that includes guidelines for the choice of system, the experimental setup and procedure as well as the processing of experimental data to derive reliable values for the interfacial area and the mass transfer coefficients in the gas and liquid phase. The procedure has been tested with classic and the modern random packing types and a comparison of the experimental results with the existing correlation of Billet & Schultes is presented.

KEYWORDS: absorption, column internals, interfacial area, mass transfer coefficients

INTRODUCTION

Absorption is widely used to remove minor components from process gas streams in the chemical and petrochemical industry. To allow for a selective removal of individual components and increase the capacity of the absorbent, the physical process is often accompanied by chemical reaction, resulting in complex mass transfer phenomena that have to be considered in process design. Extensive scientific work has been done to develop suitable models for absorption processes, leading to state-of-the-art tools that consider the enhancement of multi-component mass transfer by reaction in both phases as well as the complex thermodynamic behaviour of electrolyte systems [1]. But even this complexity can only lead to a column design that is as precise as the accuracy of the model parameters.

Contrary to distillation – where standardised methods to determine the separation efficiency of column internals are long established [2] – numerous systems and methods are used to evaluate the mass transfer phenomena in absorption processes (see Table 1).

This variety hampers the comparison of data from different sources considerably and calls for a standardised experimental approach to provide reliable model parameter for absorption processes. Since the predominant mass transfer resistance might lie in

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Table 1. Aqueous systems used to determine mass transfer parameters in absorption columns

Vapour	Liquid	Method	Dependency on	Literature
O ₂ -Air	H ₂ O	physical Absorption	β_V	[3] Puranik & Vogelpohl, 1974
CO ₂	H ₂ O	physical Absorption	β_L	a_{eff} [4] Shi & Mersmann, 1985
CO ₂ -Air	H ₂ O	physical Absorption	β_V	a_{eff} [5] Billet, 1995
CO ₂ -Air	NaOH-H ₂ O	chemical Absorption	β_V	a_{eff} [6] Weimer & Schaber, 1996
Air	CO ₂ -H ₂ O	physical Stripping	β_L	a_{eff} [7] Kolev & Nakov 1994
NH ₃	H ₂ O	physical Absorption	β_L	a_{eff} [8] Schultes, 1990
NH ₃ -Air	H ₂ O	physical Absorption	β_L	a_{eff} [5] Billet, 1995
NH ₃ -Air	H ₂ SO ₄ -H ₂ O	chemical Absorption	β_V	a_{eff} [9] Nakov und Kolev, 1994
SO ₂ -Air	H ₂ O	physical Absorption	β_V	a_{eff} [5] Billet, 1995
SO ₂ -Air	NaOH-H ₂ O	chemical Absorption	β_V	a_{eff} [5] Billet, 1995

either phase, and a complete wetting of the packing surface is not guaranteed in aqueous systems, suitable correlations have to be utilised to describe the mass transfer coefficients in the vapour (β_V) and liquid phase (β_L) as well as the effective interfacial area inside the column (α_{eff}). Further difficulties arise from the fact that the results strongly depend on the quality of the experimental setup (e.g.: gas- and liquid distribution, wall influence, evaporation effects) as well as the accuracy of the analytical equipment and procedure.

Existing correlations often date back several decades and have originally been developed for older packing elements. Modern high performance packings like the IMTP or Raschig-Super-Ring exhibit a large open structure that does not only provide high capacity at low pressure drop, but also goes along with a modified flow behaviour that enables high mass transfer rates [10]. Therefore, it is doubtful if old correlations are capable to reflect the flow behaviour of these modern packings and an experimental proof is required. There may also be uncertainty as to which extend existing correlations display the influence of physical properties. Kolev [11] compared different approaches to describe the influence of the liquid viscosity on the mass transfer coefficient in the liquid phase and attained contradictory results.

The above mentioned facts necessitate the definition of standardised methods to determine mass transfer model parameter for absorption processes. This need is emphasised by the fact, that the choice of mass transfer correlation has a significant influence on the determination of the column height [12]. The presented procedures should close the existing gap and act as a guideline for the chemical industry, research institutes, universities and packing manufacturers. Thus, future measurements should become more transparent and easier to evaluate.

ABSORPTION SYSTEM

One of the major issues in planning mass transfer measurements is the selection of a suitable test system. While standard systems have been published for distillation columns [2], no recommendation exists for absorption processes. However, the use of reactive absorption enables the separate determination of the mass transfer coefficients and the interfacial area [13], which is not possible with distillation systems. Since the mass transfer is influenced by chemical reaction, system conditions can be chosen to decouple the different phenomena and derive distinct values of β_V , β_L and α_{eff} .

An Enhancement Factor E can be used to describe the influence of a chemical reaction in the liquid phase.

$$\dot{N}_A = \beta_V \cdot \alpha_{eff} \cdot V_C \cdot (c_{A,V} - c_{A,V}^*) = E \cdot \beta_L \cdot \alpha_{eff} \cdot V_C \cdot (c_{A,L} - c_{A,L}^*) \quad (1)$$

For fast reactions of pseudo-first order, the following assumptions can be made:

- Concentration of A in the liquid phase is negligible: $c_{A,L} = 0$
- Enhancement Factor equals Hatta-Number for $Ha > 3$: $E = Ha$

If the mass transfer resistance lies entirely in the liquid phase, the definition of the Hatta-Number leads to an expression for the mass transfer that only depends on the effective interfacial area a_{eff} .

$$\dot{N}_A = Ha \cdot \beta_L \cdot a_{eff} \cdot V_C \cdot c_{A,L}^* = a_{eff} \cdot V_C \cdot c_{A,L}^* \cdot \sqrt{k_1 \cdot D_{A,L}} \quad (2)$$

Systems that exhibit this kind of reaction can therefore be used to determine the effective interfacial area directly [13]. However, these conditions are difficult to meet over the whole column height, and a more complex evaluation of experimental data is proposed that also takes the effect of the vapour phase mass transfer coefficient into account. This allows the use of CO₂ absorption in aqueous NaOH solution that allows low CO₂ concentrations, but also depends on the mass transfer coefficient in the vapour phase [6].

Systems that provide an instantaneous chemical reaction in the liquid phase guarantee that the concentration at the interface is equal zero. They can therefore be used to determine the volumetric mass transfer coefficient in the vapour phase.

$$\dot{N}_A = \beta_V \cdot a_{eff} \cdot V_C \cdot c_{A,V} \quad (3)$$

The absorption of SO₂ in aqueous NaOH solutions is such kind of system [5]. It can be used together with the above mentioned CO₂ absorption in aqueous NaOH to determine both: the effective interfacial area a_{eff} , and the mass transfer coefficient in the vapour phase β_V .

Once the dependency of these two parameters on the gas- and liquid load is known, physical absorption systems can be used to determine the mass transfer coefficient in the liquid phase β_L . The absorption of NH₃ in water has been used for this study, but the stripping of CO₂ from water can be used as an alternative.

A physical property database has been established for these systems and procedures have been developed to describe these properties in the relevant range of $\vartheta = 10\text{--}35^\circ\text{C}$ at ambient pressure with high accuracy.

EXPERIMENTAL SETUP

An extensive analysis of literature on procedures to determine mass transfer coefficients and interfacial area in absorption columns revealed the following special requirements for the experimental setup.

Considering these requests and measures for implementation leads to the experimental setup shown in Figure 1. Before entering the test column (1), the carrier gas is saturated with absorbent in the pre-saturator (2). The saturation level should be adequate to avoid both, the evaporation of absorbent in the test columns as well as condensation effects in the gas inlet. Sufficient mixing of the transferred component and the carrier gas has to be ensured (3) before feeding the raw gas to the test column. The packing

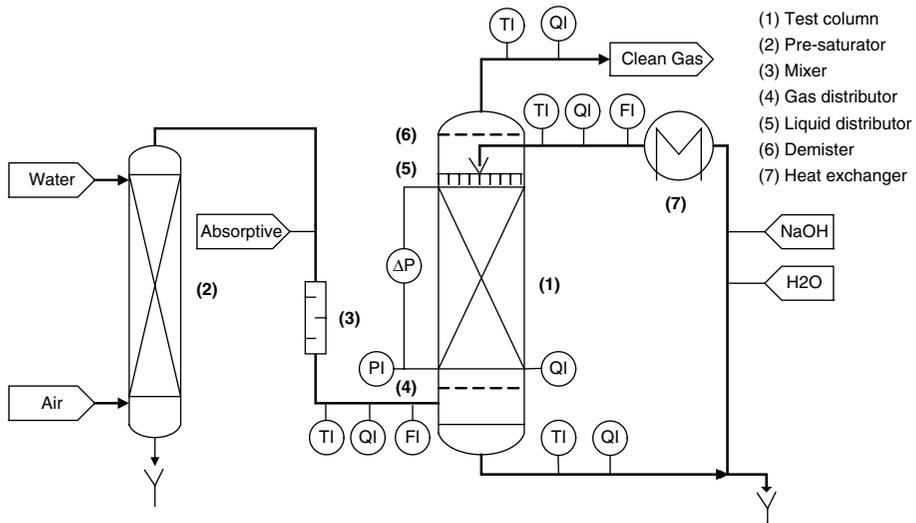


Figure 1. Ideal experimental setup for mass transfer experiments in absorption processes

height inside the test column should be variable to allow an adjustment according to the experimental conditions; but for comparison and correct data processing one height should be used for the different test systems. A gas (4) and a liquid distributor (5) guarantee a homogeneous initial distribution of both phases while a demister (6) at the top of the test column prevents a falsification of experimental results by entrainment. The temperature of the liquid feed is adjusted by a heat exchanger (7). The measurement of temperature, flow, and composition in the inlet and outlet streams allows for a balance of the test column to detect any malfunction or analytical errors.

DATA PROCESSING

Using the above mentioned absorption systems, the HTU-NTU concept can be used to determine volumetric overall mass transfer coefficients.

$$\beta_{OV} \cdot a_{eff} = \frac{\dot{G} \cdot \bar{M}_V}{HTU_{OV} \cdot \rho_V \cdot A_C} = \frac{NTU_{OV} \cdot \dot{G} \cdot \bar{M}_V}{H_C \cdot \rho_V \cdot A_C} \quad (3)$$

with:

$$NTU_{OV} = \int_{y^{in}}^{y^{out}} \frac{1}{\frac{H(T,x)}{P} \cdot x - y} dy \quad (4)$$

The following steps have to be applied to decouple the different mass transfer phenomena and derive distinct values for the three different parameters. This can only be done if the experiments with the three different absorption systems have been carried out at identical loading conditions.

1. The volumetric mass transfer coefficient for the vapour phase can be determined using the SO₂ system.

$$\langle \beta_V \cdot a_{eff} \rangle^{SO_2} = \langle \beta_{OV} \cdot a_{eff} \rangle^{SO_2} \quad (5)$$

2. The interfacial area can be calculated by using the overall mass transfer coefficient of the SO₂ and the CO₂ system.

$$\frac{1}{a_{eff}} = \left(\frac{1}{\langle \beta_{OV} \cdot a_{eff} \rangle^{CO_2}} - \frac{1}{\langle \beta_V \cdot a_{eff} \rangle^{SO_2}} \cdot \left(\frac{D_{V,SO_2}}{D_{V,CO_2}} \right)^{2/3} \right) \times \frac{P}{H_{CO_2}} \cdot \sqrt{k_{OH^-} \cdot D_{CO_2,L} \cdot c_{OH^-,L}} \quad (6)$$

3. The mass transfer coefficient in the vapour phase can be calculated according to equation (5)
4. The mass transfer coefficient in the liquid phase is determined from the experimental results of the NH₃ system. If the stripping of CO₂ from water is used as a test system, the same equation can be applied with using the corresponding experimental results and system data.

$$\frac{1}{\beta_L} = \left(\frac{a_{eff}}{\langle \beta_{OV} \cdot a_{eff} \rangle^{NH_3}} - \frac{1}{\langle \beta_V \rangle^{SO_2}} \cdot \left(\frac{D_{V,SO_2}}{D_{V,NH_3}} \right)^{2/3} \right) \cdot \frac{P}{H_{NH_3}} \quad (7)$$

The calculated model parameters can now be compared with existing mass transfer correlation or used to develop new correlations.

EXPERIMENTAL RESULTS

Different types of packings have been characterised experimentally and compared with the commonly used mass transfer correlations. The experiments have been performed for different liquid loads in the industrial relevant range and gas loads up to the flooding point. It has to be emphasized that experimental data has been obtained with and without applying the standardised techniques described above. Figure 2 shows how the selection of a particular mass transfer correlation affects the design of an industrial absorption column. The deviation of the column height determined by using the different

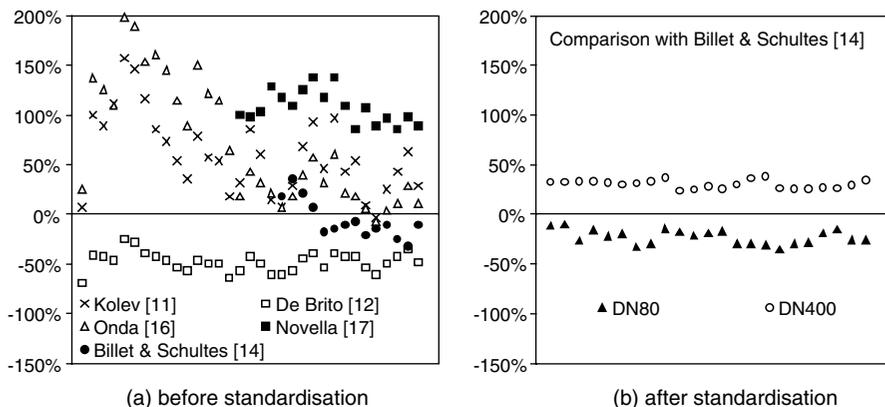


Figure 2. Comparison of experimental data with different mass transfer correlations

mass transfer correlation and by using experimentally determined HTU values is displayed for different process conditions. Figure 2a is based on experimental data obtained before standardisation but measured with “good/standard” laboratory practise, while Figure 2b incorporates results from recent experimental work following the procedures described above. In both cases the $\text{CO}_2\text{-Air}/\text{NaOH-Water}$ and $\text{NH}_3\text{-Air}/\text{Water}$ systems are used.

Comparing non standardised experiments with existing mass transfer correlations does not give clear results. While most correlations lead to a non economical overdesign that can reach values up to 200% more than required, the correlation of De Brito [15] causes an insufficient column design with separation efficiencies around 50% lower than required. The correlation of Billet & Schultes [14] clearly shows the best agreement with the experimentally determined column values but exhibits a non uniform variation between overdesign and column failure which can scatter in the $\pm 50\%$ range.

The standardisation of mass transfer measurements effects a clear improvement in the quality of the experimental data. A comparison of column heights based on experiments in two different columns and the correlation of Billet & Schultes [14], which has been chosen for its relatively good agreements with preliminary experiments, is shown in Figure 2b. It can be seen that there is still a significant deviation between experiments and theoretical results, but the non uniform variation is now prevented. The experiments clearly show the influence of the column diameter. Since the smaller column with only 80 mm diameter does not fully meet the condition of “minimised wall effects”, listed in Table 2, their detrimental influence leads to higher HTU values and thus resulting in an increased column height. The experimental results obtained in the 400 mm column should not be influenced by wall effects and therefore give lower – and more realistic – HTU

Table 2. Requirements for the experimental setup

Requirements	Reason	Implementation
Isothermal experiments	Avoidance of temperature influences on system properties	<ul style="list-style-type: none"> • Experiments at room temperature • Heating jacket • Tempering of feed streams
Minimised wall effects	Reliable data for industrial applications	<ul style="list-style-type: none"> • $d_C \geq 200$ mm for structured packings • $d_C / d_P \geq 10$ for dumped packings
Avoidance of evaporation effects	Single component mass transfer	<ul style="list-style-type: none"> • Pre-saturation of the gas-flow
Homogeneous initial gas and liquid distribution	Avoiding maldistribution and inlet effects	<ul style="list-style-type: none"> • Installation of suitable gas and liquid distributors (100–200 dripp points/m²)
Consideration of absorption in the sump of the column	Contact of gas and liquid below the packing	<ul style="list-style-type: none"> • Measurement of sump compositions and directly below the packing
Measurable clean gas composition	Ensuring mass transfer over the complete column height	<ul style="list-style-type: none"> • Adjusting the packing height • Sufficient initial raw gas composition
Packing height and way of column filling	Avoiding dominant maldistribution and undefined packing structure	<ul style="list-style-type: none"> • use of one uniform packing height for comparison with different test systems • homogeneous packing of column (test with dry pressure drop)

values which then lead to a lower column height. The deviation from the correlation is now showing an almost constant value of +30% with a scatter of only $\pm 5\%$.

SUMMARY AND CONCLUSIONS

It has to be concluded that the experimental procedure has a significant influence on the quality of the mass transfer results. To avoid a non economical overdesign or even a failure of the equipment, a procedure to determine mass transfer parameters has been developed and tested that should enhance the quality of the results. The recommended approach proposes experiments with three different aqueous systems in a standardised setup. A suitable procedure is recommended to calculate the effective interfacial area as

well as the vapour and liquid mass transfer coefficient from the experiment. The whole concept includes a database for all physical properties in the relevant range.

To allow an evaluation of new mass transfer correlations, the following specifications should at least be published together with the correlation itself.

- Information on the test system and its physical properties
- Detailed information on the experimental equipment as column diameter, packing height, and geometrical properties of the investigated packing
- Experimental procedure including the exact number of data points and the range of loading conditions
- Sufficient information on the processing of experimental data
- Area of validity for the correlation in terms of physical properties and loading conditions

This procedure will enhance the compatibility of future experimental work and allow for reliable mass transfer parameters in absorption processes. However, this work cannot be done by one single institution. This holds in particular if the influence of physical properties on the different model parameters should be investigated in more detail.

NOMENCLATURE

VARIABLES

a	Surface area per volume	m^2/m^3
A	Area	m^2
c	Concentration	kmol/m^3
d	Diameter	m
D	Diffusion coefficient	m^2/s
E	Enhancement Factor	–
F	Gas load	$\text{Pa}^{0.5}$
G	Molar gas flow	kmol/s
H	Henry coefficient	Pa
Ha	Hatta-Number	–
HTU	Height of Transfer Unit	m
k	1 st order reaction rate constant	s^{-1}
M	Molar mass	kmol/kg
N	Molar flow	kmol/s
NTU	Number of Transfer Unit	–
p	pressure	Pa
u_L	Liquid load	$\text{m}^3/\text{m}^2\text{h}$
V	Volume	m^3
x	Liquid phase mole fraction	–
y	Vapour phase mole fraction	–
β	Mass transfer coefficient	m/s
ϑ	Temperature	$^\circ\text{C}$
$\rho\tau$	Density	kg/m^3

SUB- AND SUPERSCRIPTS

<i>A</i>	Component A
<i>C</i>	Column
<i>cor</i>	corelated
<i>eff</i>	Effective
<i>exp</i>	Experimental
<i>L</i>	Liquid phase
<i>max</i>	Maximum value
<i>OL</i>	Overall liquid
<i>OV</i>	Overall vapour
<i>P</i>	Packing
<i>V</i>	Vapour phase

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