

Rate-based Column Design – The Need to Know

Michael Haas^a, Richard Behrens^a, Friedemann Gaitzsch^a

^a BASF SE, Fluid Separations RCP/MF, Carl-Bosch-Strasse 38, 67056 Ludwigshafen am Rhein, Germany
michael.b.haas@basf.com; richard.behrens@basf.com; friedemann.gaitzsch@basf.com

Abstract. The wide use of rate-based simulation for absorption and desorption column design at BASF was presented. The required availability of mass transfer correlations and packing parameters for random and structured packing as well as trays was discussed. To keep an overview on the correlations, a database was established. An additional database for all available experimental mass transfer measurement data was setup to derive packing parameters and validate, adjust and develop mass transfer correlations. The model development of two exemplary reactive absorption examples was presented. Here, not only accurate mass transfer correlations are crucial but also absorption data of the industrially-relevant system are necessary for an accurate process simulation. The first example, phosgene in caustic soda, was developed using experimental data. The second example, nitrogen oxides (NO_x) in caustic soda, was developed using operational data from a production-scale scrubbing unit.

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Introduction

Many processes in the chemical industry involve physical or reactive absorption and desorption steps. At BASF, these unit operations are serviced by the global gas scrubbing center of expertise, located in Ludwigshafen (Germany), Houston (USA) and Shanghai (China). Additional process steps like direct cooling, quenching and gas saturation are also covered. All these processes are, to a certain extent, heat and mass transfer limited. Typically, columns, equipped with packing (random or structured), trays, or combination of thereof, are used. For column design, as well as retrofitting or debottlenecking of existing equipment, deep knowledge on separation efficiency under mass transfer limited conditions and column fluid dynamics is required.

To model these rate-limited processes, rigorous heat and mass transfer simulations have been widely used for almost two decades at BASF. At the same time weak points of the existing rate-based modelling have been discovered and questions on its fundamentals have appeared. Moreover, column designers have been progressively less involved with implementing model equations, while using process flowsheet simulation software without know-how on the accuracy and limitations of the underlying mass transfer correlations. In order to ensure successful use of rate-based column design, continuous further development of the models and education of end users is necessary. Additionally, keeping up with recent development on latest mass transfer internals and mass transfer correlations is a time-consuming effort.

Rate-based simulation

Rate-based column design for absorption and desorption processes is well established in the gas scrubbing center of expertise at BASF. This method is proven in daily work on a wide variety of real processes and considerable experience has been gathered. In-house as well as commercial process flowsheet simulation software are used. Clear preference on internal programs can be found as better control and fast implementation of methods, tools and parameters is possible. Tailor-made optimization tools, fast integration of plant data into rate-based simulations and new options for deeper process understanding are developed. Ideas on integration of mass transfer measurement data into in-house flowsheet simulation software exist.

Multiple inputs like phase equilibria, physical property data and reaction equilibria, as well as reaction kinetics, are required for any flowsheet simulation. Such input data are independently needed for all process flowsheet simulation software. In case of rate-based simulation of mass transfer columns, additional information is essential. This approach considers specific velocities, volumes and effective interfacial areas, and consequently column dimensions are an integral part of the model. Additional simulation parameters like discretization of the mass transfer zone, film discretization and film thickness averaging need to be known. Therefore, when building the flowsheet, a first pre-selection on equipment size and type of column internal is required. For each intended mass transfer internal at least one mass transfer correlation must be implemented, and a corresponding packing specific data set, called packing

parameters, must be available. It has to be emphasized that for a given mass transfer correlation, specific packing parameters are required for each packing type, size, and material of construction. Consequently, not all packing types, sizes and materials of construction can be used in combination with all mass transfer correlations.

Within BASF, mass transfer correlations from different sources have been implemented. Many correlations are published in the literature and overview articles can be found [1]. Additionally, own correlations have been developed, and combination of different correlations, as well as adapted correlations, are used. As expected, different mass transfer correlations lead to differing results and even inconsistent trends in some systems. Thus, scope of application, range of validity and accuracy of the correlations must be known. To keep an overview on the different mass transfer correlations available and the existing packing parameters, an in-house database was established in 2002 and is continuously updated. Up to date, 23 different mass transfer correlations have been implemented in the database and the internal process flowsheet simulation software. For over 50 different mass transfer internals, more than 300 sets of packing parameters are available. An overview on the content of the in-house mass transfer correlation database is given in Table 1.

Table 1.

Content of the in-house mass transfer correlation database.

mass transfer internal type	share on implemented internal type	share on implemented packing parameters
random packing	66%	74%
metal sheet structured packing	26%	20%
wire gauze structured packing	2%	3%
trays	6%	3%

For example, a Pall-Ring 50 metal packing can be currently calculated using 7 different mass transfer correlations, whereas for other packings only one or even no mass transfer correlation and packing parameters are available. Thus, one has to either cross check multiple correlations or trust the only existing one. As there is constant development on the mass transfer internals, a continuous need for new packing parameters is evident. Proven mass transfer correlations have to be reevaluated. For both topics, reliable mass transfer data are required. This also enhances knowledge about applicability and quality of mass transfer correlations.

Nevertheless, safety margins are still required as unknown uncertainties must be covered. For each individual rate-based design validity of boundary conditions, physical property data, reaction network, equilibria and kinetics must be checked. Extreme hydraulic conditions (e.g. low gas load, high liquid load), untypical geometrical ratios (packed height/column diameter), fouling, aerosol formation and many other factors may influence the design, even though the used mass transfer correlation is rated to be best-in-class.

Data from mass transfer measurements

Mass transfer measurement data can be used to carry out a fundamental comparison among separation efficiency of column internals directly based on experimental data. But with regard to rate-based column simulation, mass transfer measurements are also very valuable for enhancing knowledge about the applicability and quality of mass transfer correlations. For instance, data from mass transfer measurements can be used to validate existing mass transfer models (e.g. from the literature), to adapt the parameters of existing mass transfer models to an individual selection of measurement data or to develop new model approaches. In everyday work, measurement data are especially valuable for situationally checking the model calculation for the boundary conditions relevant to the current application (e.g. gas load, liquid load, gas- or liquid-side mass transfer limitation).

In order to fully describe the mass transfer characteristics of column internals, the gas-side volumetric mass transfer coefficient $k_G \cdot a_{eff}$, the liquid-side volumetric mass transfer coefficient $k_L \cdot a_{eff}$, and the effective interfacial area a_{eff} must be determined experimentally for each nominal size of each type of internal.

This is done with suitable test systems. Generally, air is used as the carrier gas and water as the carrier liquid. The experiments are usually conducted at ambient pressure and ambient temperature. The transfer component is selected in such a way that the mass transfer is limited so that the above-mentioned mass transfer quantities can be determined. In order to be able to experimentally determine all of the three mass transfer quantities mentioned above, measuring campaigns with three different test systems are required. In the mass transfer measurements, the load parameters gas load and liquid load are varied over a wide range of the fluid dynamic load range. Complete characterization by mass

transfer measurements therefore involves a large amount of work. Therefore, it is not economically feasible for a chemical company like BASF to completely measure all relevant internals itself. Hence, mass transfer measurement data from various sources, e.g. literature, internals manufacturers, institutions like Separations Research Program at the University of Texas at Austin (SRP) and own inhouse-measurements are used.

To achieve comparability among mass transfer measurements from different institutions, it is important that the measurements are carried out in a uniform manner. There have already been several proposals and reviews on this topic in the literature, for example [2-4]. With the same aim, the VDI guideline 2761 [5] was finally developed – among others, with the participation of BASF. An important aspect of this guideline is that the mass transfer measurements should be documented as transparently and thoroughly as possible with regard to the design of the test set-up, the test system used, the operating conditions, the measurement techniques used, etc., in order to provide a high value of information.

However, there are various challenges when using measurement data from different sources. Depending on the source, the measurement data are available in different formats with varying extent of details. Measurement data from the literature typically have the lowest amount details, because they are often limited to graphically representing a mass transfer efficiency variable as a function of a load variable. In the favorable case, there is still information about the test facility and the execution of the tests in the prose text. In the case of measurement data from external institutions (e.g. universities, industrial consortia), the measurement data are usually available to the full extent. The data is often available digitally in a table format. However, the structure of these tables and also the units of the variables differ greatly from source to source and even from measurement campaign to measurement campaign. However, background information is often missing, such as detailed information on the design of the test facility (e.g. type and drip point density of the liquid distributor). The own measurement data have the largest data extent and offer the greatest transparency.

Since mass transfer measurement data are not available in an uniform scope and format, they cannot be processed automatically, but must be processed manually, which involves a large amount of work.

Due to different data formats, units and extent of details, it is therefore not possible with reasonable effort to compare the model with the measured data, to obtain an overview of the mass transfer data, to automatically analyze or evaluate a large number of measuring points. Fast access to the mass transfer data, and thus efficient work with the data, can be made possible by combining all measurement data in a digital database with uniform data records (Fig. 1, right side).

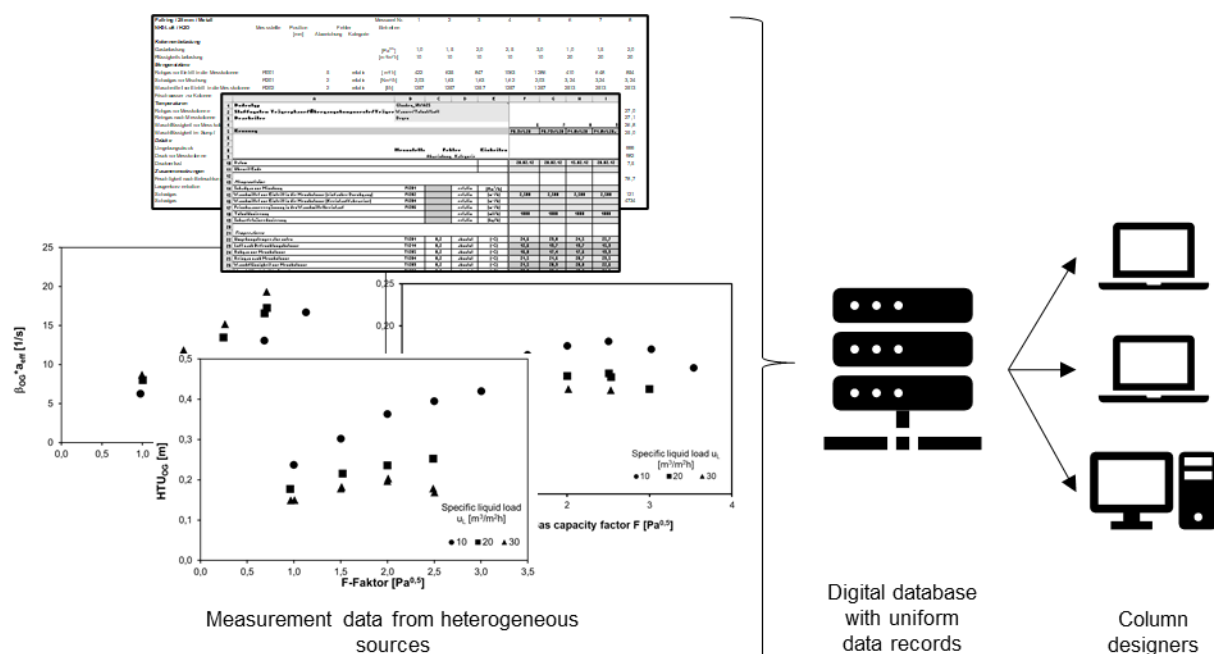


Fig. 1 Transfer of mass transfer measurement data of different formats into a digital database

At BASF, such a digital database for mass transfer measurement data has been established. The basic principle for the design of the database is that no data available in the original sources should be lost. Consequently, the database must be able to cover all possible data extents. This means, in particular, that the database is not limited to results of the test evaluation, but it is also able to store all underlying measured quantities and background information about the test facility, if they are available. This allows for the most flexible use of the data possible in the future. As efficient as working with the database will be in the future, filling the database is time-consuming in the initial phase.

Currently, the database contains approx. 500 measurement series with a total of approx. 2500 measurement points of random packings, structured packings and column trays. A browser-based app is available for accessing the database, which enables the search and selection of measurement series using data filters, the visualization of measurement data and the comparison of measurement data with mass transfer correlation results.

For the future, a higher degree of integration between this measurement database and the BASF in-house process simulation environment, as well as other data processing and calculation tools, is conceivable. With the achievement of a significantly higher number of measurement series, it might be possible to automatically analyze data, to reliably estimate missing data or to identify systematic deviations between different sources using large numbers of measurement data from these sources.

Coupled mass transfer and kinetically limited reactions

With the use of the aforementioned mass transfer database, the quality of existing mass transfer correlations can be assessed. When identifying a possible improvement of the description of the mass transfer of certain packing types, we either chose other mass transfer correlations and/or parametrize the mass transfer correlation with new packing parameters. The mass transfer correlations are then used to describe real absorption processes and to design absorption columns. Provided that the mass transfer correlation is applied within its intended range (e.g. gas and liquid load, viscosity, ...), and that all other relevant physical properties are described well, we are confident to describe the absorption process predictively [6]. Hence, no absorption experiment with the real system is necessary. This predictive description, however, is only possible in non-reactive absorption systems (i.e. sole physical absorption) or in absorption systems with instantaneous chemical reactions in the liquid phase.

For systems with kinetically limited reactions, it is crucial to conduct an absorption experiment with the real absorption system or to retrospectively validate the reactive absorption model with plant data. Such requirement is due to the fact that reaction kinetic data of the reactive gas component are difficult to measure. Most reaction kinetic data found in the literature are derived from absorption measurements itself. When evaluating such absorption measurements, a mass transfer rate of the reactive gas component must be assumed. Under- or overestimating the mass transfer rate, however, leads to an over- or underestimation of the reaction kinetics, respectively.

An absorption experiment of the real system is conducted in a laboratory column. The inlet and outlet concentrations of the experiments, together with the packing height, are converted to the height of a transfer unit (HTU). The experiment is then simulated with a rigorous rate-based model. Input data for the model are – among other things – a suitable mass transfer correlation for the packing of the laboratory column and a reaction kinetic model (despite acknowledging that the reaction kinetic model found in the literature might not be accurate). The simulation results are then converted to HTU as well and compared with the experimental data. In the following, one example of this procedure for an industrially-relevant system is presented.

Fig. 2 shows the comparison of experimental and simulated HTU of phosgene absorption experiments in caustic soda. The experiments were first evaluated with a mass transfer correlation of Billet and Schultes [7] (left-hand side). From Fig. 2, it is apparent that the overall rate of absorption of the experiment was underestimated with the liquid phase reaction kinetic found in literature (filled symbols). In the former model development, it was then decided to increase the reaction rate so that the absorption experiments were described better (open symbols). However, it was known that the Billet and Schultes mass transfer correlation depicts the effective interfacial area of the packing of the laboratory column conservatively (i.e. low effective interfacial area). Hence, as the resulting mass transfer rate might be modeled too low, it was anticipated that the reaction rate might be modeled too high. So, it was feared that using this adjusted reaction rate with other packing types, which might be described less conservatively (i.e. high mass transfer rate), could lead to an underestimation of the column height. Consequently, to eliminate this uncertainty, all phosgene absorption processes were designed with the packing type used in the phosgene absorption experiment.

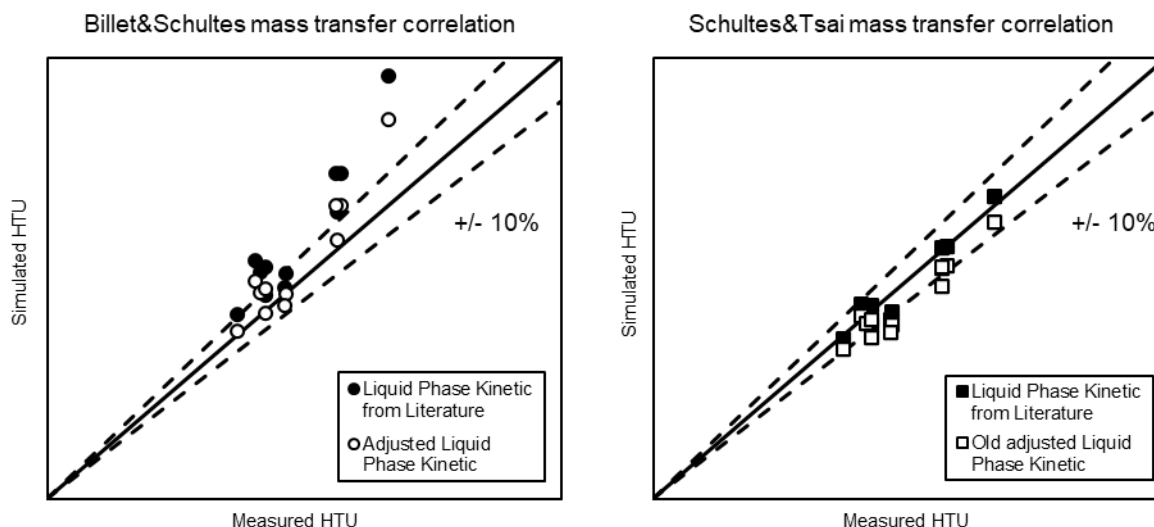


Fig. 2 Evaluation of phosgene absorption experiments in caustic soda using two different mass transfer correlation and an adjustable liquid phase kinetic taken from literature. Simulation and measured experimental results expressed here in HTU = height of a transfer unit.

Recently, meaningful experimental data of the effective interfacial area of the packing type used in the phosgene absorption experiment were found. This data was used to parametrize a mass transfer correlation, which is a combination of Billet and Schultes [7] and Tsai et. al [8] (correlation named here Schultes and Tsai). Here, the product of the effective interfacial area and the mass transfer coefficients are described by the Billet and Schultes model, and the effective interfacial area alone is described by the Tsai model. Thus, the phosgene absorption experiments in caustic soda were revisited and reevaluated with the Schultes and Tsai mass transfer correlation – see Fig. 2, right-hand side. The old, increased reaction rate now overestimated the overall absorption (open symbols). It was therefore decided to decrease the reaction rate again (filled symbols). Surprisingly, the absorption experiments were fitted best with the original reaction rate found in the literature. As the new model is now based on a mass transfer correlation, which we assume is better suited for the description of reactive absorption and which describes the mass transfer rate less conservatively (i.e. high mass transfer rate), we are now more confident in designing phosgene processes with different packing types.

Coupled mass transfer and gas phase reaction

In the previous section, the development of a rate-based model using experimental data was shown. In this section, the improvement of a rate-based model using operational data from a production-scale scrubbing unit is shown. As an example, the reactive absorption of nitrogen oxides (NO_x) in caustic soda is presented. Besides air, water and sodium hydroxide, the simulation model comprises all of the relevant nitrogen oxides (NO, NO₂, N₂O₃, N₂O₄) and nitrogen oxide acids (HNO₂, HNO₃) in the gas phase as well as their corresponding reaction products in the scrubbing liquid. All of the nitrogen compounds are interconnected in a complex reaction system which is modelled with multiple reactions in the gas phase and in the liquid phase. Some of the gas and liquid phase reactions are kinetically controlled. The reaction kinetic data were taken from the literature. The model was then used to simulate a production-scale scrubbing unit. However, even though a mass transfer correlation was used, which describes the mass transfer of the used packing best, it was not possible to achieve satisfying simulation results. The most uncertain parameters were then chosen for fitting them to operational data to obtain better simulation results. The most uncertain parameters were identified in two kinetically limited gas phase reactions.

The operational data of the production plant were retrieved from the plant information management system (PIMS) and combined with data from several online gas analyzers which had been additionally installed for several months in the plant. This way, it was possible to gain operational data sets of 69 steady states with different composition of the feed gas stream. These data sets were imported into the process simulation software containing the rate-based model for adjusting the chosen kinetic parameters by reducing the residual sum of squares between experimental data and simulation results. Fig. 3 shows the quality of this parameter adjustment on the basis of the concentration of the

apparent components NO, NO₂ and NO_x in the gas outlet stream of the scrubbing unit. It is shown that, after fitting the chosen kinetic parameters, the simulation model can be successfully used for predicting the NO_x outlet concentration of operation states of this as well as similar plants with good accuracy. However, the model shows bad accuracy regarding the NO concentration. But this is of minor importance as NO concentration is low in this kind of process and only NO_x concentration is relevant for the emission limit.

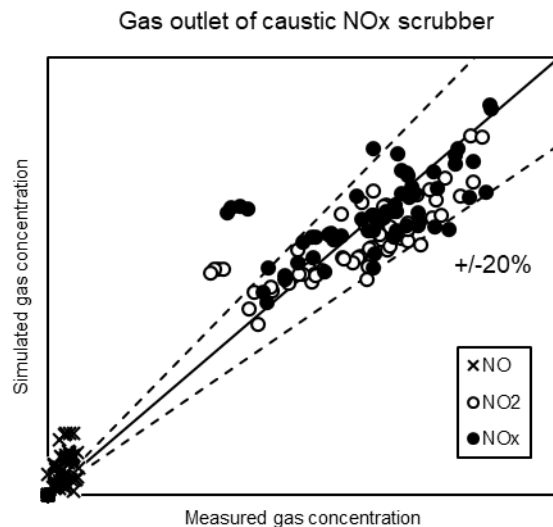


Fig. 3 Comparison of rate-based simulation results for reactive absorption of nitrogen oxides with operational data from a production-scale scrubbing unit after adjusting reaction kinetic data.

Conclusion

It is shown that rate-based simulation of heat and mass transfer limited processes like absorption and desorption does not only require an extensive set of correlations and parameters for the process flowsheet simulation software, but also comprehensive know-how and additional data. Established tools and gained knowledge has to be continuously updated to train young professionals and to keep up with new developments on mass transfer internals market. From our perspective digital databases for mass transfer measurement data and correlations are the only solution to fulfill these requirements. Coupled mass transfer and kinetically limited reactions add complexity, which particularly demands expert knowledge and experience.

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