

# Remodelling, Optimization and Characterization of Columns for Hydrogen Chloride and Sulphur Dioxide Absorption in Exhaust Air

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**Abstract:** Hydrogen chloride and sulphur dioxide are gaseous by-products of chloridization processes that employ thionyl chloride. Absorption would be a feasible method to clean the rich gas stream. Two serial connectable absorption columns were equipped with the latest generation of packings to effect product recovery. Therefore, several tests concerning the baffle properties had to be performed. In the first experimental section, the hydraulic parameters pressure drop and hold-up were investigated. The hold up value range of the new baffles Raschig Super Ring (RSR) and Raschig Super Pak (RSP) was clearly below that of the former installed packing, Raschig Ring (RR). However, due to the low maximal flow rate, the range of stagnation and flooding could not be measured. The maximal measured pressure drop value was, for RR, only 0.3 mbar/m, which is very low compared to the measurement error. Batch experiments, where the waste gases were produced by reaction of thionyl chloride in water, showed that for the steady state determination of the separation steps it is advisable to use just one column in simplex mode with a defined gas supply by a gas cylinder. The HTU determination for RSR and a HCl/H<sub>2</sub>O system delivered a value of  $HTU_{HCl,OG} = 0.14 \pm 0.01$  m with a variation coefficient of 24.2%.

**Keywords:** Absorption · Exhaust air purification · HTU-NTU model · Hydrogen chloride · Packings

## 1. Introduction

In industry thionyl chloride is often used as a chlorination agent for the synthesis of carboxylic acid chlorides, aromatic sulfonic acid chlorides and alkyl chlorides.<sup>[1]</sup> These compounds are often assembled as intermediates for the production of active pharmaceutical substances, plant protection agents, pesticides, colorants to name but a few.<sup>[2]</sup> One of the advantages of thionyl chloride is that only gaseous by-products (HCl + SO<sub>2</sub>) are formed. This leads us to the most important part of this work.<sup>[3]</sup>

The question arises of how to treat these by-products. If the gas phase is not passed through a closed circuit, the exhaust stream has to be purified to comply with the legal emission limit values for the two compounds.

For compounds that are soluble in a liquid media, absorption is, as in this case, an appropriate process. For the treatment of a hydrogen chloride and sulphur dioxide mixture, selective absorption is recommended. Typically rich gases are exhausted, thus a product recovery would be appropriate. The chosen media for the HCl absorption is water and SO<sub>2</sub> is absorbed in a sodium hydroxide solution. Since SO<sub>2</sub> absorbs to a lesser extent (–10%) in a concentrated HCl solution (1 mol/l) than in pure water,<sup>[4]</sup> the sulphur dioxide can be absorbed in a second step. The general aim is to produce hydrochloric acid in the first column and NaSO<sub>3</sub> in the second column, both in high concentration.

For this purpose, a variety of safety documents and an extended data collection for HCl and SO<sub>2</sub> was compiled. Also, a modification of the existing installations (Section 2.1) to incorporate packings of the latest generation had to be accomplished. The second task was to overview and choose the appropriate analytical measurement methods (Section 2.2). In the third

and last part, the new packings were tested with respect to hydrodynamic and mass transfer properties (Sections 3.1 and 3.2).

## 2. Materials and Methods

### 2.1 Installation

This research was undertaken in the chemical engineering laboratories of the UAS Fribourg. The installation basically consisted of the reactor (R) and two serially connected columns, which could also be operated separately (Fig. 1). As mentioned above, HCl is expected to dissolve mostly in the first column (K1) and SO<sub>2</sub> in the second one (K2).

The reactor (Belatec) is built as a flat lid display apparatus with a volume range of 15–80 l. Columns (QVF) and tubings are mainly constructed out of glass with a nominal diameter of 225 mm (column); the tubing installation is realized in DN 25. In both columns the glass Raschig-Rings were replaced by packings of the latest generation. K1 was filled with ‘Raschig Super-Rings’ and in K2 structured packings, called ‘Raschig Super-Pak’ were used. The Table shows the specifications according to Raschig of the previously used Raschig Rings compared to the new unstructured and ordered packings.

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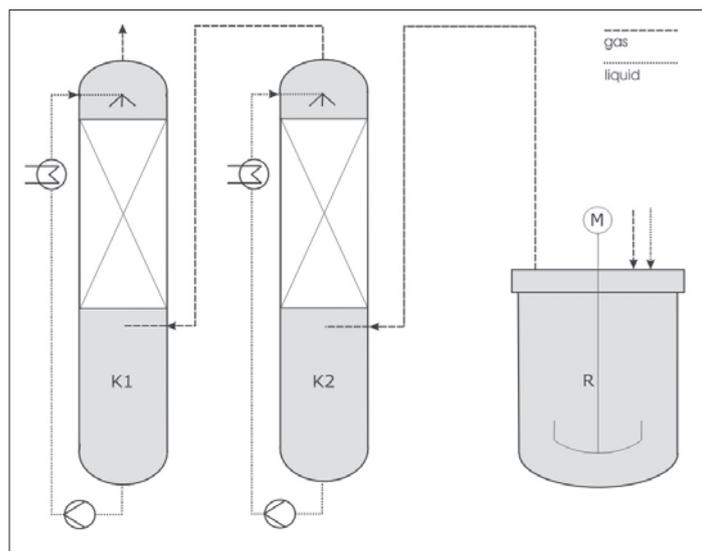


Fig. 1. Overview of installations.

Table. Comparison of packing parameters

model	material	size / (mm)	$\epsilon^a / (\text{m}^3/\text{m}^3)$	$a^b / (\text{m}^2/\text{m}^3)$	$N^c / (1/\text{m}^3)$
RR 1"	glass	25.4	0.82	195	44500
RSR # 0.6	PVDF	15.2	0.93	206	54000
RSP 250	1.4404	220	0.98	250	–

<sup>a</sup>specific packing porosity; <sup>b</sup>specific total surface area of packing; <sup>c</sup>number of rings per packing volume

## 2.2 Measurement Methods

A variety of measurements were performed during several different investigations, *e.g.* pressure drop over the columns, temperatures, flow rates and finally the inlet and outlet concentrations in gas and liquid phase.

### 2.2.1 Concentration of HCl and SO<sub>2</sub> in the Liquid Phase

As the fluids are mainly high concentrated, operations like titration, ion chromatography, as well as density, conduction or refractometric measurements can be considered for the determination of the liquid concentration. Nevertheless, one should be aware that mixtures of two or more components are often influenced by the non-measured component. Since both concentrations of the single components and concentrations of mixtures had to be measured, several measurement methods were applied.

Different titrations were tested and performed to determine the HCl and SO<sub>2</sub> concentrations. The concentration of HCl in a mixture with SO<sub>3</sub><sup>2-</sup> ions and ethanol was measured by Mohr's method<sup>[5,6]</sup> with a AgNO<sub>3</sub> solution (Titrisol® 0.1 mol/l) and K<sub>2</sub>CrO<sub>4</sub> as indicator at pH 7–10. Pretests had shown no influence of the SO<sub>3</sub><sup>2-</sup> ions as expected due to a good solubility of AgSO<sub>3</sub>.<sup>[7]</sup> HCl solutions without interfering substances were titrated with sodium

hydroxide solution (Titrisol® 0.1 mol/l) and phenolphthalein as indicator or by potentiometry.<sup>[6,8]</sup> The determination of the SO<sub>2</sub> concentration in the presence of HCl by iodometric titration at low concentrations (0.05 – 0.1 mol/l) was not possible due to SO<sub>3</sub><sup>2-</sup> decomposition in iodine-containing solutions. At sulphite concentrations higher than 1 mol/l, satisfactory measurements could be realized and the contribution from decomposition became negligible. Another difficulty is the simultaneous reaction of iodine with NaOH. So the use of an indirect method was preferred, where the remaining NaOH concentration was determined by an acid base titration and the HCl concentration by a Mohr's titration. The SO<sub>3</sub><sup>2-</sup> concentration can be calculated as in Eqn. 1:

$$c_{\text{SO}_3^{2-}} = c_{\text{NaOH,start}} - c_{\text{NaOH,end}} - c_{\text{HCl}} \quad (1)$$

Furthermore, the HCl concentration without interfering substances was analyzed by a densimeter DMA 4500 (Anton Paar, Graz, Austria) and by a DX-120 Ion Chromatograph (Dionex, Olten, Switzerland).

### 2.2.2 Concentration of HCl and SO<sub>2</sub> in the Gas Phase

For the measurement of the gas phase, preabsorption in volumes less than 100 ml

into evacuated glass balloons was realized. In analogy to the absorption in the columns, H<sub>2</sub>O was used for the HCl and NaOH for the SO<sub>2</sub> concentration measurement.

This results in close correspondence to the previously described titration methods. The technique to analyze the HCl concentration without interfering substances based on a color change is applicable for concentrations greater than 0.01 mol/l and potentiometry for concentrations greater than 0.001 mol/l. Concentrations below 0.001 mol/l should be determined by single pH-measurements (pH-Meter 744 with temperature correction, Metrohm, Zofingen, Switzerland) The above-mentioned ion chromatography is applicable for the range of concentrations between 0.001 mol/l and 0.1 mol/l.

### 2.2.3 Pressure, Temperature, Mass and Flow Rate

To avoid damage from the acidic gas components in the portable measuring instruments, the pressure drop was measured in a u-tube manometer (1 mm scaled, HTA-FR). Temperatures were determined by laboratory glass thermometers (1 °C scaled) and thermocouples (0.1 °C scaled; TFN 1293-Ex, ebros, Ingolstadt, Germany). Several weighing scales (TD5, TD1, PM 6100, AE 240, Mettler Toledo, Greifensee, Switzerland) were used to determine mass. The air- and fluid flow was measured by calibrated rotameters (M 1/160; N19.18, QVF, Mainz, Germany).

## 3. Results and Discussion

Characterization and design of absorption columns requires the determination of numerous parameters, especially to describe the properties of structured and unstructured packings. On the one hand, there are hydraulic parameters like hold-up and pressure drop that have been tested. On the other hand, the mass transfer of the two components has been investigated.

### 3.1 Hydraulics

Hydraulic experiments for hold-up and pressure drop investigations were performed on the previous filling of the column with RR and the discharged column (only relevant for pressure drop measurements), as well as on the new RSR and the RSP.

#### 3.1.1 Hold-up

Hold-up describes the volume of liquid running through the column related to the volume of baffles (structured or unstructured). This parameter has an impact on the weight and discharge volume of the column as well as on the acceleration time at commissioning and on the pressure drop of the baffles.<sup>[9,10]</sup>

The values were determined by measuring the height difference of the liquid levels of the column during operation and after stopping the pump. Subsequently, a comparison with theoretically calculated values<sup>[9]</sup> and those from the literature (Mersmann/Deiters)<sup>[11]</sup> was made. To determine the theoretical hold-up ( $H_{th}$ ), the following empirical equation for an unstructured packed column was applied:

$$H_{th} \approx 1,075 \cdot 10^{-3} \cdot \left( \frac{g'_1}{1000 \cdot d_v} \right)^{0,6} \quad (2)$$

where  $d_v$  is the volume equivalent diameter and  $g'_1$  is the trickling density. With a maximal trickling density of  $7.5 \text{ m}^3/(\text{m}^2\text{h})$ , a close correspondence of RR to the theoretical values could be observed but the stagnation- and flood range could not be reached. This was due to the fact that within the column ( $d = 225 \text{ mm}$ ) a maximal gas flow rate (empty column) of only  $0.048 \text{ m/s}$  could be realized. Nevertheless, the new baffles (RSR and RSP) showed an improved hold-up value range than that for the previous baffles (RR) and the calculated values. This can be explained by an open geometry.<sup>[12]</sup>

### 3.1.2 Pressure Drop

The pressure drop is an essential parameter of separation processes, as it influences significantly the dimensioning of fans and pumps and thus the operational costs of the plant. Apart from the experimentally determined values, the application of models like the often used Mackowiak<sup>[13,14]</sup> model is suitable for the validation of results. The height specific pressure drop of an unstructured packing for  $Re_{fi} \geq 2$  is:

$$\frac{\Delta p}{h} = c_w \cdot \frac{1-\mu}{\mu} \cdot \frac{F_g^2}{d_p \cdot K} \cdot \left( 1 - C_B \frac{a^{1/3}}{\mu} \cdot w_{fi}^{2/3} \right)^{-5} \quad (3)$$

with  $C_B$  as the model parameter for the determination of the pressure drop in a trickled packing with  $Re_{fi} \geq 2$  and  $C_B = 0.4 \text{ s}^{2/3}/\text{m}^{1/3}$ , the fiction factor  $c_w$ , the calculated particle diameter of a single piece of packing material  $d_p$  and the wall factor  $K$ .

Once more, due to the low flow rate, the range of stagnation and flooding could not be observed. The maximal measured value was in the case of RR only  $0.3 \text{ mbar/m}$ , which is very low compared to the measurement error. Hence, a comparison with the model was not undertaken.

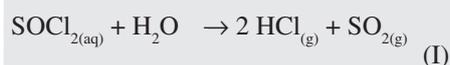
## 3.2 Mass Transfer

Information regarding the mass transfer in the thionyl chloride reaction during

batch processing and the separation step at steady state could be gained.

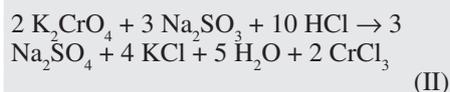
### 3.2.1 Thionyl Chloride–Water

The reactor was filled with water (25.0 kg) and ethanol (3.0 kg). Thionyl chloride (3.748 kg) was added over a period of 1 h to the reactor (R), where it reacted with the excess of water to form gaseous hydrogen chloride and sulphur dioxide.



From stoichiometry, the expected gas flow rate was  $1.40 \text{ Nm}^3/\text{h}$  HCl and  $0.69 \text{ Nm}^3/\text{h}$   $\text{SO}_2$  gas. During a first test run the gas flow rate was far below expectations. Thus in a second run, fluid samples of K1 and K2 were taken (20, 50, 80, 120 min); samples were also taken in R (0, 120 min after the reaction started).

The real sample matrix led, contrary to the pretests, to some analytical difficulties. A large pH variation of the samples caused an undefined color change of  $\text{K}_2\text{CrO}_4$  during titration. In acidic solutions the end point showed up too late ( $\text{Cr}_2\text{O}_7^{2-}$  does not precipitate with Ag ions), in alkaline solutions errors were caused by the precipitation of AgOH. Thus the pH was adjusted prior the addition of  $\text{K}_2\text{CrO}_4$ . Furthermore, a 'greenish' color in the samples of K1 complicated the detection of the end point. A reason for this behavior could be the following side reaction:



In chloride-containing solutions, chromium(III) possibly forms mixed aqua- and chlorocomplexes of various colors, depending on the applied temperature.<sup>[15]</sup>

The molar balance at the end of the experiment (Fig. 2) based on iteratively determined total masses of each run, compares favorably with the theoretically calculated amounts for reaction (I).

The total amount of HCl measured in the three runs was 40% higher than the stoichiometric yield of the thionyl chloride hydrolysis. The reason for this is on the one hand dead volume at the bottom valves, where the samples were taken, on the other hand the late detection of the end point for the HCl concentration. In the case of  $\text{SO}_2$ , the molar balance was more satisfactory, with a value of 7% above the stoichiometric yield. The most remarkable point is that 76% of the measured amount of HCl and 26% of the measured amount of  $\text{SO}_2$  is directly dissolved in the reactor. An improvement could be achieved by using a circuit sampling loop attached to the reactor, potentiometric titration for HCl and the use of a different solvent like toluene instead of ethanol. It is obvious that a steady state observation including the simultaneous measurement of HCl and  $\text{SO}_2$  was not applicable within the timeframe of this thesis. So for the steady state determination of the separation steps it was decided to use just one column in simplex mode with a defined gas supply by a gas cylinder.

### 3.2.2 Hydrogen Chloride

The physical absorption of HCl in water was performed in the column K1 with a HCl gas cylinder on the inlet air side (Fig. 3). Samples of gas and fluid were taken at the in- and outlet for the HTU determination. Additionally weight scales were provided to measure the fluid masses. Flow

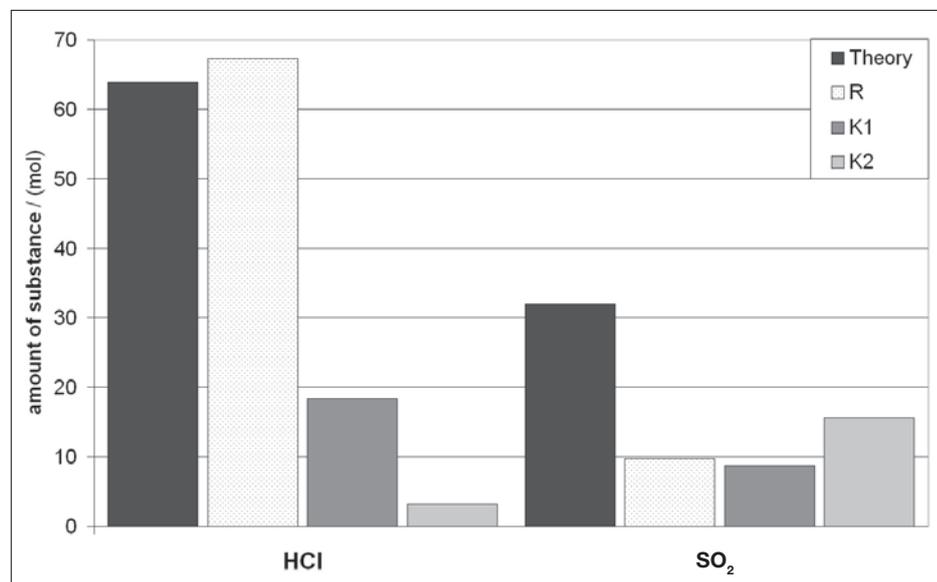


Fig. 2. Molar balance at the end of the experiment.

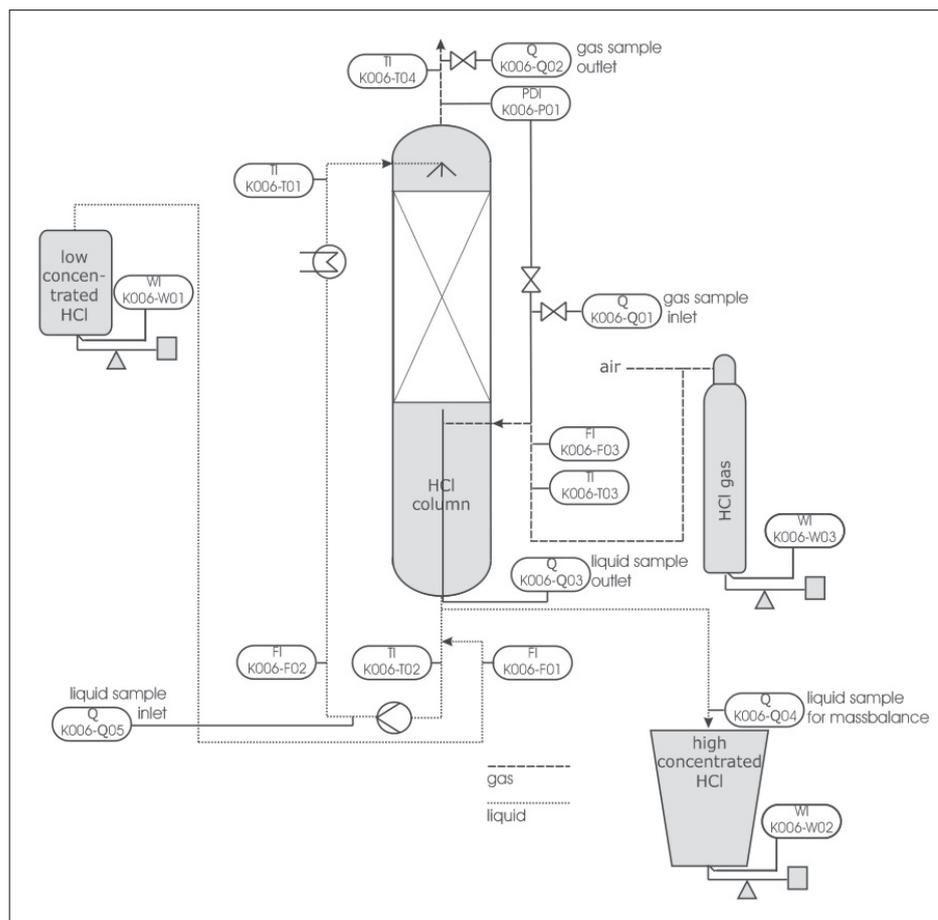


Fig. 3. Experimental R&I sheet for HTU determination.

rate and temperature were adjusted and measured during the experiments.

The height of a transfer unit (HTU) can be described by the HTU-NTU model,<sup>[16]</sup> one of the most important equations for the dimensioning of absorbers since several decades.

According to a partial balance around a gas phase volume element with constant molar flows and constant mass transfer coefficients the characteristic NTU integral (Number of Transfer Units) can be derived:

$$NTU_{i,OG} = \int_{y_{i,2}}^{y_{i,1}} \frac{dy_i}{y_i - y_{i,GG}} = \frac{\beta_{i,OG} \cdot c_g \cdot A_{Ph}}{\dot{n}_g} = \frac{\beta_{OG} \cdot A_{Ph}}{\dot{V}_g} \quad (4)$$

where  $\beta_{i,OG}$  is the overall mass transfer coefficient related to the gas phase and  $A_{Ph}$  refers to the interfacial area. For several specific applications a trivial solution of the NTU integral can be found. One of these cases is the physisorption with a linear equilibrium line. This is valid e.g. for HCl absorptions and HCl upgradings. So the NTU value becomes:

$$NTU_{i,OG} = \frac{y_{i,1} - y_{i,2}}{\Delta y_{i,1} - \Delta y_{i,2}} \ln \frac{\Delta y_{i,1}}{\Delta y_{i,2}} \quad (5)$$

The concentration difference  $\Delta y_i = y_i - y_{i,GG}$  at the gas inlet (index 1) and gas outlet (index 2) is linearly dependent on  $y_i$ , with measured values for  $y_i$  and litera-

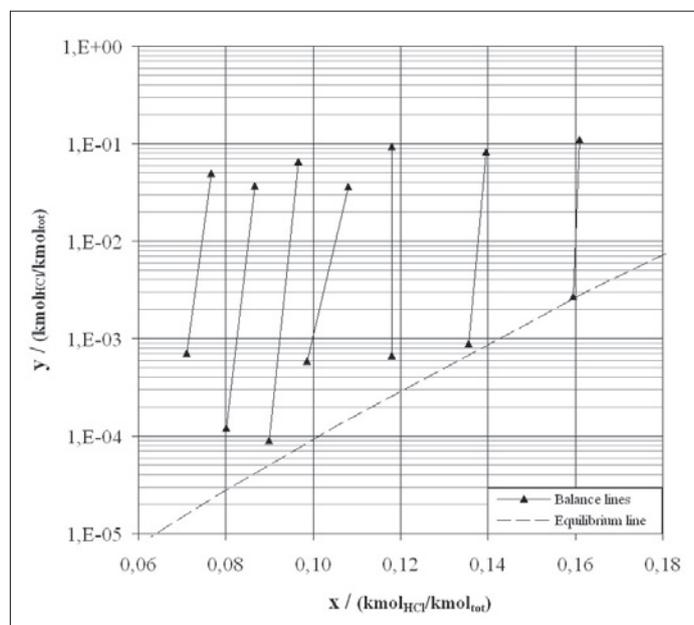


Fig. 4. Composition diagram with gas over liquid molar fraction.

ture values<sup>[17]</sup> for  $y_{i,GG}$ . The separation step height is calculated by using the known packing height of  $h = 0.815$  m and the determined NTU value.

$$HTU_{OG} = \frac{h_{\text{packing}}}{NTU_{OG}} \quad (6)$$

Finally a value of  $HTU_{HCl,OG} = 0.14 \pm 0.01$  m with a high variation coefficient of 24.2 % was determined. This value refers to RSR, a gas flow rate of 6.2–6.3 m<sup>3</sup>/h and a fluid flow rate of 0.18 m<sup>3</sup>/h. As a comparison, Raschig reported the expected values for a gas flow rate of 1–3 m<sup>3</sup>/h and a fluid flow rate of 0.18 m<sup>3</sup>/h. Due to a variation of the separation performance with a slope change of the equilibrium line respectively the HCl concentration, a value of  $HTU_{HCl,OG} = 0.12$ –0.14 m for  $x_{out} < 0.1$  mol<sub>HCl</sub>/mol<sub>tot</sub> and a value of  $HTU_{HCl,OG} = 0.14$ –0.15 m for  $x_{out} = 0.21$ –0.22 mol<sub>HCl</sub>/mol<sub>tot</sub> had been given. Taking the high variation coefficient into account, good agreement with the reported values could be found. Fig. 4 shows the composition diagram based on the corresponding gas and liquid concentrations at the inlet and outlet of each evaluated dataset.

#### 4. Conclusion

Extensive research on the properties of the substances under examination and safety instructions for the installations have been documented. Furthermore, different analysis methods were described and applied. At the newly installed baffles, hydraulic experiments such as hold-up and pressure drop tests showed behavior distinctly below the usual industrial dimensioning area. During batch test runs for

mass transfer observations it became apparent that the experiments for the HTU determination have to be done in simplex mode with a defined gas supply. The HTU experiments for RSR and a HCl/H<sub>2</sub>O system delivered a value of  $HTU_{HCl,OG} = 0.14 \pm 0.01$  m.

## 5. Perspectives

A few recommendations for further experiments will be given in the following. For chemisorptions like the absorption of SO<sub>2</sub> in NaOH, there also exists a trivial solution<sup>[15]</sup> of the NTU integral. According to the reaction of the absorbent (i) with the detergent, the detergent in the fluid phase vanishes completely and therefore  $y_{GG}$  becomes zero. So the NTU value can be written as:

$$NTU_{i,OG} = \ln \frac{y_{i,1}}{y_{i,2}} \quad (7)$$

Within the compound mixture (HCl + SO<sub>2</sub>) in the waste air stream, the SO<sub>2</sub> absorbed in the hydrochloric acid can be separated by stripping. This would have caused high investment costs and the need to rebuild the installations. Useful process designs or further detergents can be found in the literature.<sup>[6,18]</sup>

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