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# Towards Tailored Column Packings for Emission Reduction of Marine Ships

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### Abstract

With January 1st, 2020 marine ships are subject to stricter sulfur dioxide emission legislation. To reach the emission reduction goals, packed absorption columns are frequently employed for flue-gas treatment on board the ship. However, currently available column packings do not properly match the key demands for this application. The *HiPaSEED* project aims to provide a new packing specifically tailored towards flue-gas desulfurization on marine ships.

In the wake of preliminary studies, an existing pilot plant for the characterization of column packing hydraulics was made fit for mass-transfer measurements. Hydraulic characterization of the column packing Raschig RSP 250Y was performed and results are in good agreement with literature data. Furthermore, first mass transfer measurements using a CO<sub>2</sub>-NaOH test system were performed. It is indicated that the number of transfer units  $NTU_{0G}$  decreases with increasing gas load.

In the future, these findings will be used to derive a new geometric structure for a high-performance packing for an application in flue-gas desulfurization on marine ships.

# Introduction

Starting January 1st, 2020, SO<sub>x</sub> emissions from marine ship engines are subject to stricter abatement regulations. For ships operating outside of designated emission control areas (ECAs) the limit for SO<sub>x</sub> emissions in the off-gas was lowered to 0.50% (mass by mass). To adhere with these regulations, ships must use fuel oils which meet the specified emission limits, such as liquid natural gas (LNG) or ultra-low sulfur oil blends. Alternatively, the use of exhaust gas cleaning systems in the form of packed absorption columns is frequently employed as the same level of emission reduction is achieved. [1]

Available column packings do not properly match the key demands of exhaust gas cleaning systems on marine ships: high hydraulic capacities while simultaneously being spacesaving and highly efficient for mass transfer. Conversely, the emerging and strongly increasing market for flue gas desulfurization systems on marine ships demands large volumes of such packings.

The main goal of the HiPaSEED (*High Performance Packings for Seawater Desulfurization on Marine Ships*) project is the development of an innovative metal column packing specifically tailored towards the requirements of fluegas desulfurization of marine ship exhaust gases. The basis for column packing conception and optimizations within the HiPaSEED project lies in a strong understanding of the absorption system SO<sub>2</sub>/seawater. Afterwards, the main mass-transfer resistance will be evaluated through masstransfer experiments and described through relevant model equations. Based on these learnings, high void-fraction packing structures will be geometrically defined and characterized through CFD simulations coupled with masstransfer modeling. The structures with the most promising predicted performance will be manufactured as prototypes, and their hydraulic and mass-transfer performance will be validated experimentally. Finally, the optimum geometrical structure will be defined, considering economically feasible methods for production. As a result, a new product – a specifically tailored high-performance packing for flue-gas desulfurization systems on marine ships – will be available for market introduction.

State-of-the-art development of tower packings is still of mostly empirical nature and packings are usually developed independently of their application. Commonly, new packings are developed based on experience with the performance of existing products and how those have been successfully improved in the past. In this proposed project, the basis for development is the insight and understanding of the specific absorption system coupled with the specific requirements on marine ships which forms the basis of system modelling and simulation. Based on this sound theoretical understanding, geometrical shapes of a new packing will be derived. In case this approach is successful, it would be a radical breakthrough in the development of tower packings.

# Hydraulic characterization of column packings

To describe the hydraulic performance of column packings, the pressure drop  $\Delta p$  and the liquid hold-up  $h_L$  are measured as functions of irrigation density *B* and F-Factor *F*.

Irrigation density is a measure for the specific liquid load during column operation and is defined as the ratio of liquid volume flow  $\dot{V}_{L}$  and column cross-section *A*:

$$B = \frac{\dot{V}_L}{A}$$

The specific gas load is expressed with the help of the F-Factor F, which is a measure for the kinetic energy of the inflowing gas:

$$F = \frac{\dot{V}_G}{A} \sqrt{\rho_G}$$

The liquid hold-up  $h_L$  is defined as the ratio between liquid volume  $V_L$  inside the packing and the overall packing volume  $V_P$ :

$$h_L = \frac{V_L}{V_P}$$

For flue-gas desulfurization on marine ships operators usually desire high liquid hold-ups during operation as it is generally believed that higher liquid hold-ups are beneficial for absorption systems with relatively slow kinetics.

For a given irrigation density, an increase in the F-factor leads to an increased pressure drop over the column packing. At the *loading point*, the gas flow is high enough to start impeding liquid flow. After passing the loading point, pressure drop rises more steeply until the *flooding point* is reached, where all liquid flow is restricted, and the column packing fills with liquid. Absorption columns are usually operated between loading and flooding point.

#### Mass-Transfer Modeling

When modelling mass-transfer properties of absorption columns, the two-film model of mass-transfer is frequently employed. The two-film model is based on the concept that the interfacial area between gas and liquid phase exists in the form of a rigid film. It is further supposed that the entirety of the mass-transfer resistance is localized in small boundary layers  $\delta_G$  and  $\delta_L$  around the interfacial area and that there is no convective mass transfer in the boundary layers. The interfacial area itself has no mass-transfer resistance, for it is

assumed to be of infinitesimal nature. The situation is



illustrated in fig. Figure 1 below.

Figure 1: Concentration gradients and boundary layers around the interfacial area according to two-film theory.

For stationary conditions, the molar flux density of component *i* being transferred is proportional to the concentration gradients in the respective boundary layer:

$$J_{i,G} = \frac{1}{RT} \beta_{i,G} (p_{i,G} - p_i^*)$$

$$J_{i,L} = \beta_{i,L} \big( c_i^* - c_{i,L} \big)$$

Assuming equilibrium conditions at the interface, a relation between interfacial partial pressure in the gas phase and the interfacial concentration in the liquid phase can be specified (*Henry's Law*):

$$p_i^* = H_i c_i^*$$

Equating  $J_{i,G}$  and  $J_{i,L}$  and subsequently eliminating  $p_i^*$  and  $c_i^*$  leads to an expression containing the overall gas-side mass transfer coefficient  $\beta_{i,OG}$ , resulting in

$$J = \frac{1}{\frac{1}{\beta_{i,G} + \frac{H_i}{RT} \frac{1}{\beta_{i,L}}}} \frac{(p_{i,G} - p_i^*)}{RT} = \beta_{i,OG} \frac{(p_{i,G} - H_i c_{i,L})}{RT}$$

By analogy, an expression for the overall liquid-side mass transfer coefficient  $\beta_{i,oL}$  can be derived.

For determining the volumetric overall mass transfer coefficient  $\beta_{i,OG}a_{eff}$ , the HTU/NTU model is used wherein the height of the column packing is written as the product of the height of a transfer unit (HTU) and the number of transfer units (NTU):

$$H = HTU_{i,OG} \cdot NTU_{i,OG}$$

In the case of a chemical reaction taking place directly in the interfacial area the number of transfer units can be expressed as

$$NTU_{i,OG} = \ln\left(\frac{c_{i,in}}{c_{i,out}}\right)$$

Finally, the volumetric overall mass transfer coefficient may be calculated using

$$\beta_{i,OG}a_{eff} = \frac{u_G}{HTU_{i,OG}} = \frac{u_G}{H} \cdot NTU_{i,OG}$$

By using specific gas-liquid pairings for absorption or desorption experiments, it is possible to evaluate the effective interfacial area  $a_{eff}$  of column packings as well as their gas and liquid side mass transfer coefficients. For this approach to work, the overall mass transfer resistance of the test system must be entirely localized within either the liquid or gas phase. Lists of suitable test systems can be found in [3] and [4]. Examples include absorption of CO<sub>2</sub> into NaOH, absorption of SO<sub>2</sub> into NaOH or desorption of CO<sub>2</sub> from H<sub>2</sub>O. The methodology is relatively new and is subject to ongoing standardization efforts. [2]

#### **Materials and Methods**

The absorption column pilot plant at the Chair for Process Technology and Industrial Environmental Protection at Montanuniversität Leoben is suitable for the hydraulic characterization of column packings via an experimental assessment of dry and irrigated pressure drops. The relatively large size of the plant allows for the testing of column packings under realistic conditions, thereby ensuring a proper subsequent scale-up. The pilot plant (fig. **Error! Reference source not found.**) consists of two columns manufactured from polypropylene. During operation ambient air is taken in and saturated with water in the first column (d = 600 mm). The saturated air is



Figure 2: Schematic of the absorption column pilot plant. Left: Saturation column, Right: Measurement Column.

subsequently introduced into the second column (d = 450 mm), where the actual hydraulic characterization and mass-transfer measurements take place over a packing height of up to 2000 mm. Experiments can be conducted in both closed-loop and open-loop configurations and a total of up to 5000 liters of washing liquid may be prepared and stored in basins. Since the plant is operated under negative pressure this allows for the use of potentially hazardous gases such as SO<sub>2</sub> or NH<sub>3</sub> in mass-transfer measurements.

For the preliminary studies presented within this work the test system  $CO_2$ -NaOH was selected. The sodium hydroxide solution had a concentration of 1 mol/L and  $CO_2$  input concentration ranged from about 370 ppm (atmospheric  $CO_2$ ) to 6000 ppm (added from gas cylinders to the ambient air introduced into the system).

# **Preliminary Results**

Fig. 3 illustrates the results of the hydraulic characterization of the Raschig RSP 250Y column packing. Irrigation densities varied between B = 0 (dry pressure drop) to  $B = 60 \text{ m}^3/(\text{m}^2\text{h})$  and the F-Factor was slowly increased for a given irrigation density. Each test run was completed upon reaching the flooding point.



Figure 3: F-Factor dependent pressure drop over column packing Raschig RSP 250Y for different irrigation densities.



Figure 4: Measured F-Factor dependency of  $NTU_{i,OG}$  values of column packing Raschig RSP 250Y for different irrigation densities between 10 and 50 m<sup>3</sup>/(m<sup>2</sup>s). Test system: CO<sub>2</sub>-NaOH.

Fig. 4 shows the results from the mass transfer measurements using the CO<sub>2</sub>-NaOH test system. The NTU value decreases with an increasing F-Factor. Although a clear trend can be seen using the entirety of the recorded data, individual measurement results scatter rather strongly so that no clear trend for individual irrigation densities can be observed from the available measurement results.

## **Conclusion and Outlook**

The preliminary results presented show a good conformity between pressure drop measurements obtained on the pilot plant and literature data. [5]

Mass transfer measurements with the test system CO<sub>2</sub>-NaOH suggest that the number of transfer units  $NTU_{OG}$  decreases with increasing gas load, expressed as F-factor. The influence of irrigation density on mass transfer could not yet be resolved with the generated data, although literature suggests that increases in irrigation density should strongly correlate with increased  $NTU_{OG}$  values. [5]

Future measurements coupled with an increased understanding of the absorption system SO<sub>x</sub>/seawater will be used for providing an innovative packing specifically tailored towards an application in flue-gas desulfurization on marine ships.

Symbol	Definition	SI Unit
Α	column cross-section	m²
a <sub>eff</sub>	effective interfacial area	m²/m³
B	irrigation density	m³/(m²h)
С	concentration	mol/m³
d	column diameter	mm
D	molecular diffusivity	m²/s
HTU	height of transfer unit	m
F	F-Factor	√Pa
h	hold-up	m³/m³
Н	Henry's Law constant	m³Pa/mol
J	molar flux density of component <i>i</i> being transferred	mol/(m²s)
NTU	number of transfer units	1
Р	(partial) pressure	Pa
R	ideal gas constant	J/(molK)
Т	temperature	К
$u_G$	gas velocity	m/s
V	volume	m³
<i>V</i>	volume flow	m³/s
ß	mass-transfer coefficient	m/s
δ	boundary layer thickness	m
ρ	density	kg/m³
Subscript		
G	gas	
i	component i	
in	column input	
out	column output	
L	liquid	
0	overall	
Р	packing	
tot	total	
Superscript		
*	interface	

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## References

 International Maritime Organization. (2020, March 3). Sulphur 2020 – cutting sulphur oxide emissions. [Online]. Available:

http://www.imo.org/en/mediacentre/hottopics/pages/sulph ur-2020.aspx

- [2] Messung und Auswertung von Fluiddynamik und Stofftransport in gepackten Kolonnen, VDI 2761-2, 2018.
- [3] A. Hoffmann et al., "Standardization of Mass Transfer Measurements: A Basis for the Description of Absorption Processes", *Trans IChemE*, Part A, Jan. 2007. doi:10.1205/cherd06134

- [4] L.Hegely et al., "Absorption methods for the determination of mass transfer parameters of packing internals: A literature review," *AIChE Journal*, Vol 63, No. 8, Aug. 2017. doi:10.1002/aic.15737
- [5] L. Valenz et al., "Comprehensive Study of Hydraulic and Mass-Transfer Characteristics Determination under Absorption Conditions Performed on Structured Packings Raschig Super-Pak," *Chem. Eng. Trans.*, Vol 69, 2018. doi:10.3303/CET1869031