INVESTIGATIONS OF CRYSTALLIZATION FOULING IN COLUMNS

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ABSTRACT

Fouling represents one of the main causes of malfunctions in distillation columns. However, there is a lack of a standardized methodology for the measurement of fouling in columns. Within the scope of the joint project SAMARA, investigations for the development of a standardized method for the measurement of fouling in columns will be performed. For this purpose, a smaller screening test rig and a larger standard test rig for the investigation of crystallization fouling in columns are developed. Both test rigs are to be operated with the fluid system saturated sodium chloride water solution and air. The increasing pressure drop due to fouling is related to the amount of crystalized salt to obtain the fouling progress independent of the various mass transfer rates of the internals. These studies can be used to gain insight into the fouling tolerance of various internals, as well as the scalability of fouling.

INTRODUCTION

The formation or deposition of solids on solid surfaces, which are in contact with fluids, is generally known as fouling. Causing technical impairment of components and test rig, such as in columns, fouling is an undesirable process in process engineering.

A rough classification of the economic impact caused by fouling in industry is possible according to Steinhagen [1]. From surveys about fouling in heat exchangers, the economic damage in New Zealand is estimated to be 0.1 to 0.17 % of the annual gross national product. For industrialized countries, Steinhagen assume an economic damage of 0.2 to 0.34 % of the corresponding gross national product. For Germany, this would represent an economic damage caused by fouling of 6.9 to 11.7 billion € in 2020.

Significant contributions to the economic damage caused by fouling are, among others, the oversizing of equipment or the increased use of energy to compensate for a reduced performance caused by fouling. Furthermore, costs are incurred for the acquisition, installation and operation of cleaning equipment for the fouled test rig. Last but not least, there is an economic impact due to the loss of production caused by the reduced availability of the equipment as a result of the cleaning process.
A compilation and analysis of 900 malfunctions in columns in industry was carried out by Kister [2] for the period from 1952 to 2002. In 121 cases, fouling was the reason for the malfunctions in the columns. This corresponds to a rate of about 13 % of the malfunctions and thus represents the most frequent reason for malfunctions in columns. Over the period, the incidents due to fouling increased over the years, so that this will continue to be a major challenge for plant operators in the future.

Despite the technical and economic relevance of fouling in columns, the systematic study of fouling in columns is limited to the work of Chen, Heberle, Großerichter and Zhou [3, 4, 5, 6]. The results of these works sometimes vary significantly from each other. Among other things, this may be due to the different research focus of the studies. Furthermore, no studies have yet been published on the reproducibility of these results.

In addition to the few studies on fouling in columns, another issue is the lack of a standardized and referenceable method for evaluating separating and non-separating internals regarding their sensitivity to fouling. On the one hand, this represents an obstacle to innovation for the manufacturers of column internals, such as trays, random and structured packings, for the development and testing of more fouling-tolerant solutions. On the other hand, operators of columns in fouling-sensitive processes have no basis for actions to reduce fouling.

Within the scope of the joint project SAMARA ("Development of a standardized methodology for the design and evaluation of test rig and equipment in fouling-sensitive separation processes"), the aim is to develop, set up, operate and qualify standard test rig for the quantitative evaluation of the fouling potential of components and systems under defined and reproducible conditions. Furthermore, a uniform procedure for the operation of the equipment is to be defined. The experimentally determined raw data are to be condensed into characteristic key values. Due to the technical relevance for gas/liquid separation operations in rectification and absorption columns, the standard

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test rigs are to be developed for the investigations of column internals and for evaporator tubes.

For this reason, a smaller screening test rig and a larger standard test rig for the investigations of crystallization fouling in columns are to be set up at the Institute of Plant and Process Technology at the Technical University of Munich (TUM) as part of the joint project SAMARA. With the help of these investigations, insights regarding the fouling tolerance of different internals under different operating conditions, as well as insights about the scalability of fouling can be gained.

SELECTION OF THE FLUID SYSTEM

The selection of the fluid system for the investigations of fouling in columns is of essential importance, since the fluid system determines the mechanism of fouling. The fouling mechanism is relevant for the applicability of the results from the experimental studies to the industrial processes.

For the published malfunctions in the period 1952 - 2002 due to fouling in columns, Kister [2] also gives the causing fouling mechanism. The frequencies of the causing fouling mechanisms are shown in Figure 1. Coking and fouling due to scale and corrosion products are the most frequent causes of malfunctions. Crystallization fouling is also of industrial significance with a rate of 14 %. Particle fouling and polymerization in columns are of minor importance. For almost one third of the malfunctions due to fouling, the cause is not given in Kister.

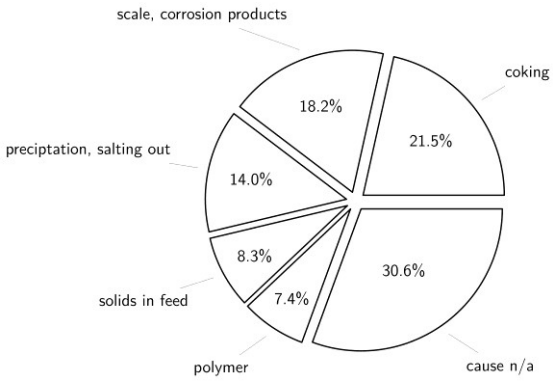

Fig. 1 Number of published fouling incidents in columns in the period 1952 - 2002 according to Kister [2].

Among the three industrially significant fouling mechanisms of coking, fouling due to scale and corrosion products and crystallization fouling, the crystallization fouling is the most suitable mechanism for the investigations within the SAMARA joint project. The fouling mechanism of coking is mainly causing problems in the petrochemical industry. However, these chemical systems are not handleable for the investigations in a pilot plant. The fouling mechanism of scaling is generally suitable for investigations. In Heberle [4], for example, investigations on scaling using the fluid system of a $Ca(OH)_2$-water solution and air enriched with CO_2 is described. The column can be cleaned of fouling by using an HCl-water solution, thus allowing the internals to be reused in further experiments.

However, the mechanism of crystallization fouling is best for the investigations of fouling in columns. The equipment and material requirements for crystallization fouling are less than for a reactive system. In contrast to scaling, the concentration of the reactants has not to be determined for crystallization fouling, because here the fouling is forced by the supersaturation of a saturated salt solution. This reduces the number of influencing parameters for the investigations.

In principle, several salts are suitable for the investigations of crystallization fouling. However, the use of sodium chloride offers some advantages. Figure 2 shows the solubility in water of selected salts versus the temperature. Sodium chloride, unlike the other salts, shows an approximately constant solubility in water over a wide temperature range. This property is important for the studies since crystallization fouling is forced by the supersaturation of the solution, which requires the evaporation of the solvent. Because of the heat of evaporation, a temperature profile is formed in the column. Due to the approximately constant solubility of NaCl in water, supersaturations of the solution based on the temperature profile that forms in the column can be almost excluded. Furthermore, NaCl is not hazardous to health and is easy to obtain. Also, cleaning of the column is unproblematic after the experiments since the salt is readily soluble in water. However, the highly corrosive effect of the NaCl water solution restricts the materials of the internals and components in contact with the fluid to glass, non-corrosive stainless steel and plastics.

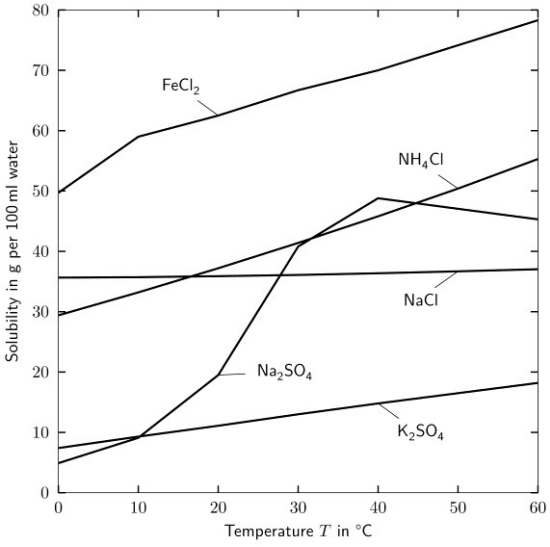

Fig. 2 Solubility of selected salts in water versus the temperature.

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CONCEPT OF MEASUREMENT

The aim of the SAMARA joint project is to develop a standardized method for the evaluation of column internals, such as trays, random packings or structured packings, regarding their tolerance to fouling. However, due to the different separation efficiencies of the internals, a direct comparison of the fouling tolerance of various internals is difficult. Therefore, the investigations of crystallization fouling on column internals are performed independently of the mass transfer rates of the internals, so that a comparison of the fouling tolerance from different column internals is possible.

For the investigations, the measurement concept according to Großerichter [7] is used, which is presented in the following. The progress of fouling is monitored by the increase in pressure drop in the column. As a result of the deposits on the column internals, the free area for the gas flow in the column is reduced. Thus, the pressure drop over the column internals increases. Above a certain pressure drop increase, the operation of the column is no longer practical, and the internals fail due to fouling. The pressure drop increase is detected by measuring the differential pressure over the column internals.

In order to obtain the fouling progress independent of the separation efficiency of the column internals, the amount of precipitated solids is set as the index of fouling resistance. Since the investigations involve a saturated solution, the amount of solid precipitated is proportional to the amount of evaporated water. The amount of evaporated water is determined by measuring the relative humidity of the gas stream at the inlet and outlet of the column.

Using this measurement concept, the increase in relative pressure drop can be plotted versus the amount of solids precipitated. Column internals with a high tolerance to fouling are characterized by a high amount of precipitated solids. Column internals with a low tolerance to fouling reach the limit for failure of the internals already after a small amount of precipitated solids.

Comparing this concept of fouling measurement on column internals with the usual methods of fouling measurement in heat exchangers, the increase in pressure drop in the column would correspond to the increase in the thermal fouling resistance R_f. The increase of the thermal fouling resistance in the heat exchanger directly causes a reduction of the transferred heat flux. By contrast, the increase of the pressure drop in the column does not directly cause a reduction of the mass transfer rate. However, an increased pressure drop can lead to a reduced capacity, maldistribution and entrainment. This has the consequence that the mass transfer in the column is mostly decreased.

The amount of salt precipitated acts as an index of fouling resistance in the concept outlined previously, in order to compare the column internals with different separation efficiencies. The measurement of fouling in heat exchangers is therefore usually carried out at constant fluid temperature or heat flux and then relates the increase of the thermal fouling resistance to the operating time.

DESIGN AND OPERATION OF THE SCREENING TEST RIG

Within the scope of the project, a small screening test rig is developed, set up and operated at the TUM. The test rig is to be used to investigate a large number of different internals with regard to their tolerance of fouling. The screening test rig focuses on the qualitative investigation of fouling on column internals. The investigations are intended to provide indications of the initial points of fouling and to reveal differences between the various designs of column internals. Furthermore, the screening test rig is used as a basis for decision-making regarding the more elaborate investigations in the larger standard test rig.

Figure 3 shows a photo and the flowsheet of the screening test rig, which is operating at ambient temperature and pressure. The saturated sodium chloride solution is provided by the stirred tank T1, which is pumped to the head of the column C1 by the pump P1. The pump P1 supplies a variable volume flow of 37 to 137 l/h. Before the solution feeds into the column, the flow rate and temperature of the solution is recorded. In the column, trays with few holes or single valves can be screened, as well as single to a very few random packings elements. The investigation of single structured packing plates and small structured packing sections is also possible. For this purpose, the middle part of the column glass can be replaced, so that investigations in a DN50 and a DN100 column are possible. The sodium chloride solution is then returned to tank T1.

The gas flow is provided by blower B1 and passes through the column in countercurrent. The blower provides a variable volume flow of up to 120 m³/h. Before the gas flow enters the column, the volume flow, pressure, humidity and temperature of the air are measured. Due to the evaporation of the water in the column, the sodium chloride solution supersaturates and the salt partially crystallizes. Part of the crystallized salt is precipitated on the column internals, while the rest returns with the solution to the feed tank. At the head of the column, the temperature and humidity of the gas stream are measured again before the gas flow exits back into the atmosphere.

The rotameters currently installed in the test rig allow liquid loads of 19 to 70 $m^3/(m^2\ h)$ and gas loads of 0.5 to 4.6 $Pa^{0.5}$ for the investigations in the DN50 column. In the DN100 column, liquid loads of 5 to 17 $m^3/(m^2\ h)$ and gas loads of 0.1 to 1.2 $Pa^{0.5}$ can be realized.

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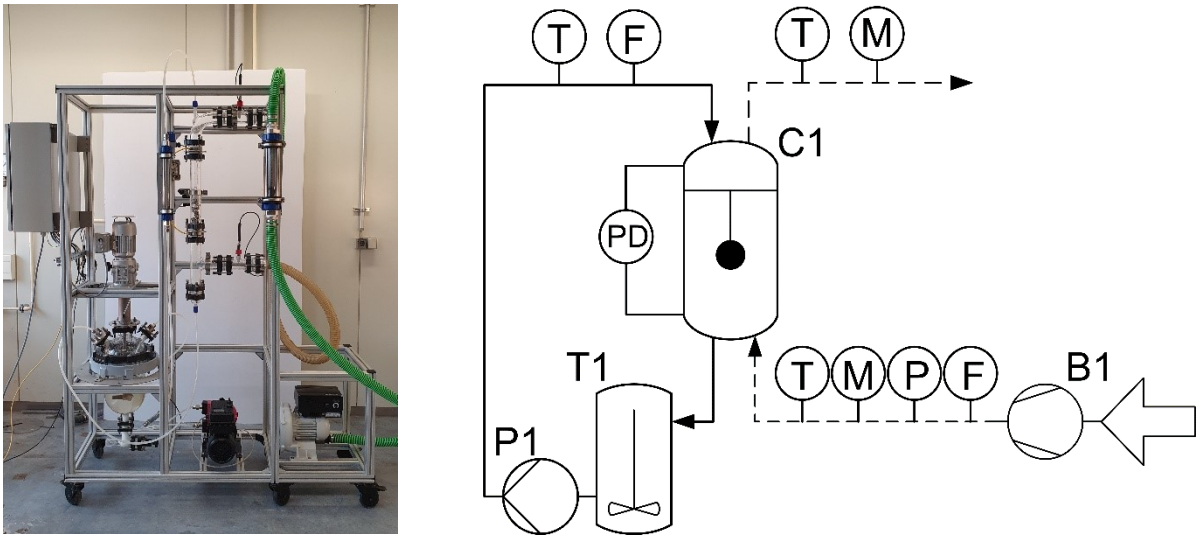

Fig. 3: Photo and flow diagram of the screening apparatus in the configuration of a DN50 column.

A camera is installed at the column for optical detection of the fouling in order to gain insights regarding the initial points and the mechanisms of the fouling. Furthermore, the column internals can be characterized by the implemented instrumentation with regard to their fouling tolerance according to the presented concept of measurement.

PRELIMINARY EXPERIMENTS OF THE SCREENING TEST RIG

In preliminary investigations, the fouling process of metal Pall-Rings 25 was followed visually at a liquid load B of 20 m³/(m² h) and a gas load F of 1 $Pa^{0.5}$. Figure 4 shows photos of the Pall-Rings at the beginning, after 1 h of operation and after 5 h of operation. Already after 1 h of operation, deposits can be seen on the edges of the packing elements. The salt crystals grow with increasing operating time. The surface of the packing elements remains largely without deposits even after 5 h of operation. These observations are in agreement with the observations made by Großerichter [7], who also considers the edges of a random packing element as the fouling prone areas.

According to Großerichter, the flow resistance of the liquid and the flow of the gas around the edges of a random packing element lead to the formation of an area at the edges where the liquid is at rest. This stationary liquid is in intense contact with the gas flow, so there is a high mass transfer between gas and liquid. As a result, the stationary liquid becomes locally supersaturated and the salt crystallizes on the packing.

On the surfaces, the packing is usually continuously overflowed by the liquid. Due to the constant movement of the liquid, hardly any local supersaturation occurs. Formed salt crystals can also only adhere to the surface very poorly, as the flow immediately takes them away again.

In further investigations, the fouling behavior of the Pall-Rings at different operating points was observed. Figure 5 shows the metal Pall-Rings after 5 h of operation at the operating points:

(1) B = 20 m³/(m² h); F = 1 $Pa^{0.5}$,
(2) B = 20 m³/(m² h); F = 2 $Pa^{0.5}$ and
(3) B = 30 m³/(m² h); F = 2 $Pa^{0.5}$.

At all operating points, as in the previous investigations, it can be seen that the fouling mainly forms at the edges of the packing.

The amount of deposits at operating point (1) is visually intermediate between the other two operating points. Operating point (2) shows visually the most fouling. Compared to the other operating points, this operating point is characterized by a high gas load combined with a low liquid load. Due to the disproportionately high gas flow, the salt crystals in stationary liquids strongly crystallize at the edges of the packing. This leads to the formation of a large number of deposits on the random packing elements.

Operating point (3) visually shows the least amount of deposits. This operating point is characterized by a high liquid load. The increased flow makes it more difficult for salt crystals to deposit on the packing. Furthermore, larger crystals already deposited are carried along by the flow and thus removed from the random packing surface.

The first investigations with the screening test rig show that fouling on random packings can be enforced and visually monitored within a reasonable time. The edges of the random packing are identified as especially prone to fouling and the initial points of the fouling. This is in agreement with the results of Großerichter [7]. Furthermore, the amount of fouling can be influenced by the selected operating point.

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Fig. 4 Fouling on metal Pall-Rings 25 after 0 h, 1 h and 5 h of operation at a liquid load of $B = 20$ m³/(m² h) and gas load of $F = 1$ Pa$^{0.5}$.

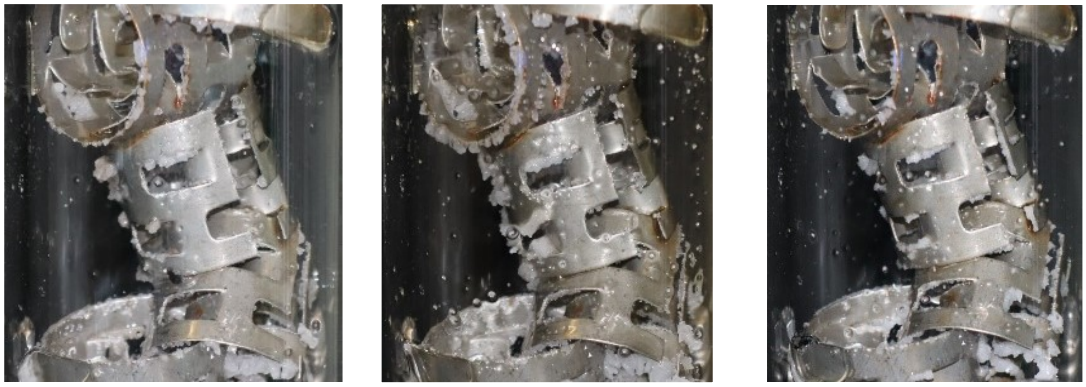

Fig. 5 Fouling on metal Pall-Rings 25 after 5 h of operation at $B = 20$ m³/(m² h) / $F = 1$ Pa$^{0.5}$ (left), $B = 20$ m³/(m² h) / $F = 2$ Pa$^{0.5}$ (center) and $B = 30$ m³/(m² h) / $F = 2$ Pa$^{0.5}$ (right).

CONCEPT OF THE STANDARD TEST RIG

The design, construction and operation of the standard test rig is a central element of the SAMARA joint project. The focus is on the quantitative investigation of the fouling tolerance of various column internals. Combined with the investigations from the screening test rig, insights about the scalability of fouling can be gained. Furthermore, the investigations from the standard test rig will be used to establish principles for the transferability of the results to industrial processes. Last but not least, the investigations performed in the standard test rig will be used as a basis for the development of the standardized procedure for evaluating the fouling tolerance of column internals.

Figure 6 shows the flow diagram of the standard test rig. Here, the circuit of the saturated sodium chloride solution is shown in red, and a rinsing circuit is shown in blue. The saturated sodium chloride solution is provided by tank T1, which is tempered to a temperature of 25°C using the heating jacket H1. The pump P1 feeds the solution either into column C1, which has a diameter of 300 mm, or into column C2, which has a diameter of 150 mm. Column C1 is mainly used for the investigation of trays, column C2 is mainly used for the investigation of random and structured packings.

The blower B1 provides the gas flow, which is humidified in column C3. In this way, it is possible to achieve almost similar test conditions in summer and winter, despite the different weather conditions resulting in varying air humidity. The pre-humidified gas stream is then fed either into column C1 or into column C2.

The progress of fouling is monitored by the differential pressure transducer PD. The transducer can determine the differential pressure at five equidistant levels to the sump of the column by the successive opening and closing of the magnetic valves at the columns. The further measuring technique is used to determine the amount of salt precipitated and to determine the operating conditions. Furthermore, with the use of a suitable control and regulation program, a largely automated operation of the plant is possible.

The deposits in the columns can be subsequently rinsed out via the rinsing circuit using deionized water. The well-designed arrangement of the saturated sodium chloride solution circuit and the rinsing circuit makes it possible to rinse one column and prepare it for the next investigation while experiments are carried out in the other column. The plant is currently under construction and is expected to go into operation in the third quarter of 2022.

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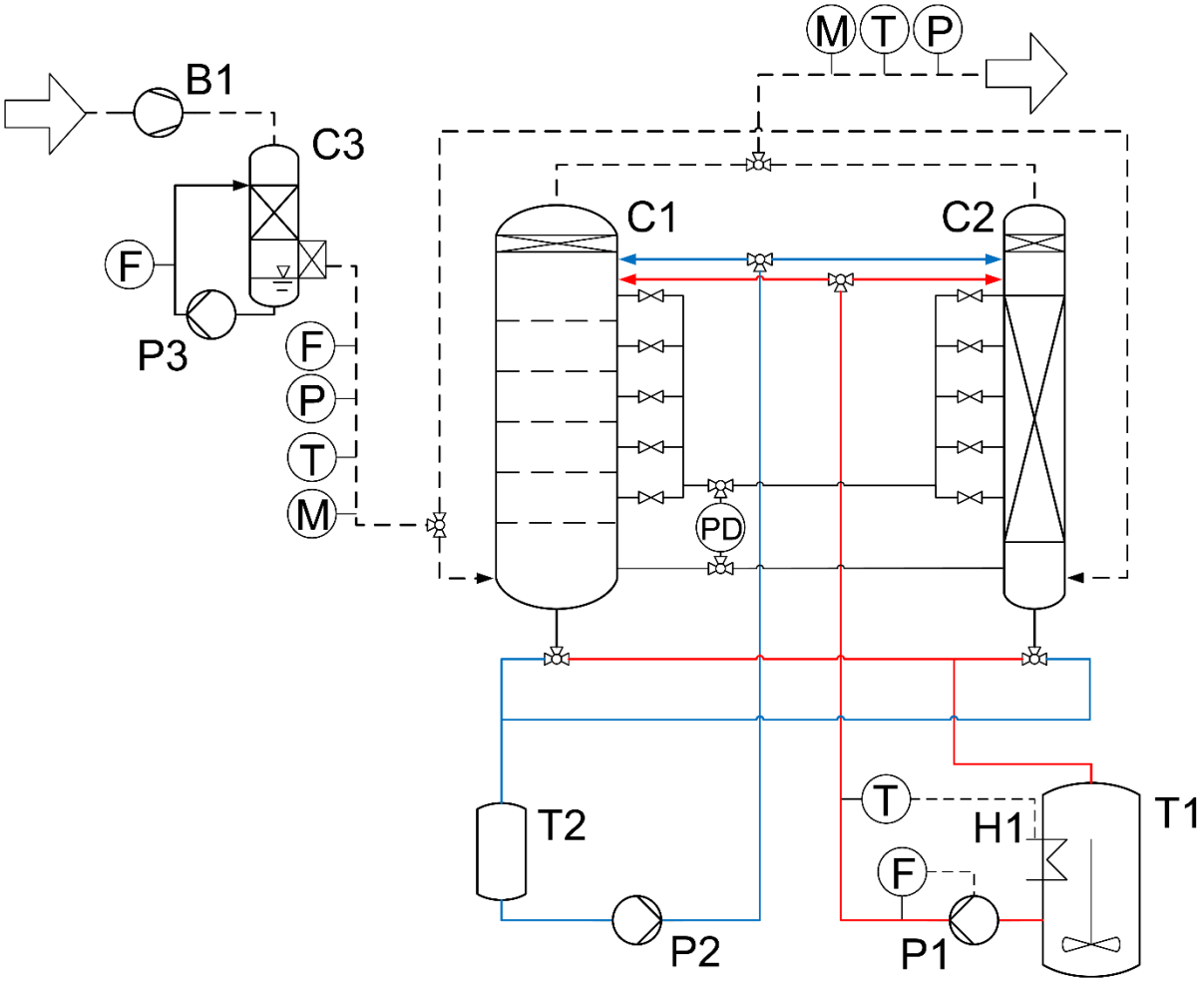

Fig. 6 Concept of the standard apparatus with circuit of the saturated NaCl water solution (red) and the rinsing circuit (blue).

CONCLUSION

The objective of the joint project SAMARA is the development of a standardized method for the evaluation of test rig and equipment in fouling-sensitive separation processes. For this purpose, crystallization fouling on column internals is being investigated at TUM. The choice of the fluid system is essential for the investigations, since this determines the fouling mechanism. For the investigations at TUM, the fluid system consisting of a saturated sodium chloride solution and air was found to be the most suitable. The measurement concept is to obtain the fouling progress independently of the different separation efficiencies of the column internals. For this purpose, the pressure drop over the column internals is compared with the precipitated amount of solids.

For the investigation of crystallization fouling, a smaller screening test rig and a larger standard test rig are developed, set up and operated at the TUM. The screening test rig is mainly used for the qualitative determination of the fouling and the investigations intended to provide indications of the initial points of fouling.

The first preliminary investigations with the test rig were already performed. The fouling can be forced and visually observed within a reasonable time using the screening test rig. The first results with metal Pall-Rings 25 show that the edges of the random packing are especially prone to fouling and are the initial points of the fouling. Furthermore, the amount of fouling shows a dependence on the selected operating point.

The standard test rig is designed for the quantitative measurement of fouling on column internals and is currently under construction.

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NOMENCLATURE

R_f thermal fouling resistance, $(m^2K)/W$
B liquid load, $m^3/(m^2\,h)$
F gas load, $Pa^{0.5}$

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