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Volker Höfling*

Wolfgang Augustin †

Matthias Bohnet‡

*Technical University of Braunschweig

†Technical University of Braunschweig

‡Technical University of Braunschweig

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CRYSTALLIZATION FOULING OF THE AQUEOUS TWO-COMPONENT SYSTEM CaSO₄/CaCO₃

Volker Höfling, Wolfgang Augustin and Matthias Bohnet

Institute of Chemical and Thermal Process Engineering, Technical University of Braunschweig
Langer Kamp 7, D-38106 Braunschweig, Germany
T:+49 531 3912781 F:+49 531 3912792 ictv@tu-bs.de

ABSTRACT

Solutions, which cause fouling problems, consist mostly of more than one single component. Up to now only few studies concerning the fouling phenomena in such multicomponent systems exist. Therefore batch and continuous experiments with the aqueous two-component system CaSO₄/CaCO₃ were carried out, investigating especially the influence of pH-value on the fouling behaviour. As measure for the crystalline deposit the fouling resistance R_f was used:

$$R_f = \frac{1}{k_f} - \frac{1}{k_0} \quad (1)$$

The composition of the obtained fouling layers were analysed by x-ray diffraction and scanning electron microscopy (SEM). Further the strength of the crystalline deposits were determined in abrasion experiments. The measured abrasion was correlated with crushing strength values.

In the fouling experiments a strong effect of the pH-value on crystallization fouling was observed. Lowest fouling tendency was seen for experiments at pH 7.0. At different pH-values the crystalline layers showed big differences in their macroscopic as well as in their microscopic structure. As it could be seen with the SEM the crystals differed in their size but also in their shape. Below pH 6.0 only calcium sulphate was detected by x-ray diffraction, which agrees with the saturation theory. At higher pH values besides calcium sulphate also calcium carbonate was found in different modifications. The different layer composition leads to different strength of the layers. Highest strength values in the crystalline upper and middle layer were measured for crystalline scales grown at pH 7.0, followed by layers at pH 6.5.

At the moment it is difficult to correlate the fouling behaviour clearly to the different experimental conditions.

INTRODUCTION

In the past remarkable research work was performed to investigate the fouling process for systems with one single salt, mainly the so called hard salts calcium sulphate and calcium carbonate. But in practice salt solutions consist mostly of more than one single component. Up to now only few studies investigating the fouling process in multicomponent systems exist.

Helalizadeh et al. (2000) investigated mixed salt crystallisation fouling of CaSO₄/CaCO₃ on heat transfer surfaces during convective heat transfer and subcooled flow boiling in a bulk temperature range between 60°C and 90°C determining effects of flow velocity, surface temperature, bulk temperature and solution concentration.

Chong and Sheikoleslami (2001) studied effects of CaSO₄ on CaCO₃ precipitation at temperatures between 60°C and 80°C. They found that even small amounts of sulphate affects the thermodynamics, kinetics and the scale structure of calcium carbonate, so that the data for the pure salts cannot be applied. For this reason it is important to gain experimental data for the fouling behaviour of multicomponent systems.

The driving force for crystallization processes is the supersaturation. The grade of saturation is expressed by the saturation index, which is defined as the difference between the actual pH value and the saturation pH value pH_s (Langelier, 1946):

$$S = pH - pH_s \quad (2)$$

As it is known the saturation index for CaCO₃ depends strongly on the pH-value, meanwhile for CaSO₄ between pH 4 and pH 10 the saturation index is almost constant (Fig. 1).

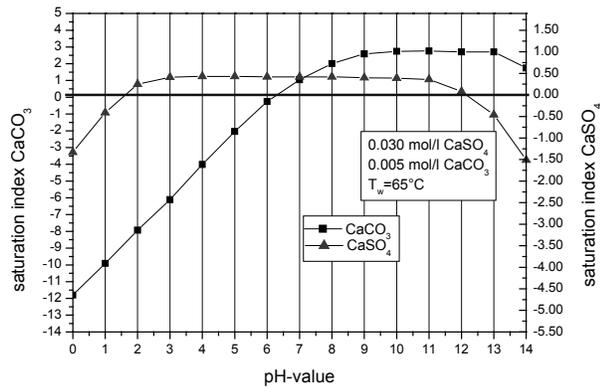


Fig. 1 Saturation index for CaSO₄ and CaCO₃

The effect of pH-value on the fouling behaviour of pure CaCO₃ was investigated by Augustin and Bohnet (1995). They found a big influence on the scaling tendency of this parameter.

The focus of the present study is to determine the influence of the pH-value on the fouling behaviour in the aqueous two-component system consisting of CaSO₄/CaCO₃. Therefore fouling experiments at different pH values were carried out and the obtained scales were investigated by scanning electron microscopy and x-ray diffraction. To determine the strength of the layers abrasion experiments have been performed.

EXPERIMENTS

Batch-Experiments

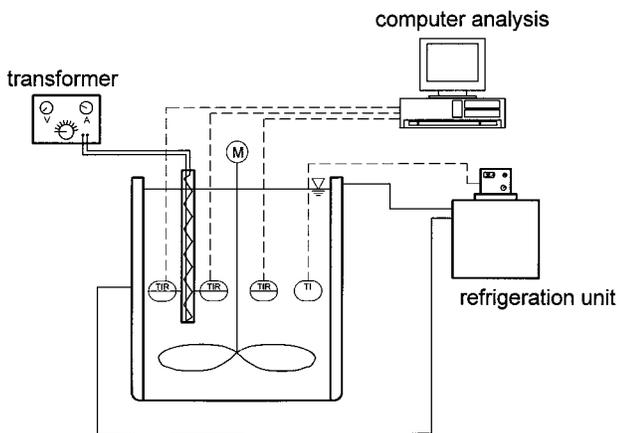


Fig. 2 Laboratory test rig

For the investigation of the influence of the pH-value in a first step batch experiments with a laboratory test rig shown in Fig. 2 were carried out.

The main component of the test unit is a double-walled vessel with a volume of 2.8 litres which is filled with the aqueous salt solution of CaSO₄ and CaCO₃. A low stirring propeller-mixer rotating with a circumferential velocity of 0.5 m/s helps to avoid temperature and concentration gradients. The crystallisation process takes place at a cylindrical heating element which is shown in Fig. 3.

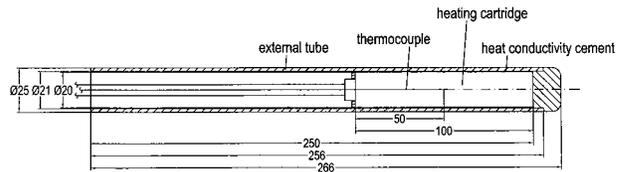


Fig. 3 Heating element

It consists of a commercial heating cartridge at which two thermocouples are fixed. The heating cartridge is put into an external tube of stainless steel (1.4571). The space between heating cartridge and external tube is filled with heat conductivity cement. The temperatures of the thermocouples are recorded online by computer analysis. The fluid temperature can be held constant with a refrigeration unit over the double-wall.

Within the scope of this study two different test-series were carried out. The concentrations in the first series were 0.03 mol/l CaSO₄ and 0.005 mol/l CaCO₃. The experiments were done with different starting pH-values between pH 4.0 and pH 7.0. In a second test series the experiments were done with a lower calcium carbonate concentration of 0.001 mol/l. The calcium sulphate concentration was kept on 0.03 mol/l. Here the starting pH-value was varied between pH 4.0 and 9.0.

The test solutions were prepared with the salts CaCl₂, Na₂CO₃ and Na₂SO₄ in deionised but with CO₂ saturated water. All salts were of analytical grade. To maintain CO₂ saturation a CO₂ layer was put above the solution.

The experiments were run in batch operation. The fluid temperature was constant at 42 °C and the heat flux 34 kW/m² during the whole test time. The pH-value was fixed at the beginning of each experiment by adding NaOH or HCL respectively. Due to the crystalline layer formation the concentrations of the salts decreased, which lead to changes of the saturation conditions during the experiments.

Continuous experiments

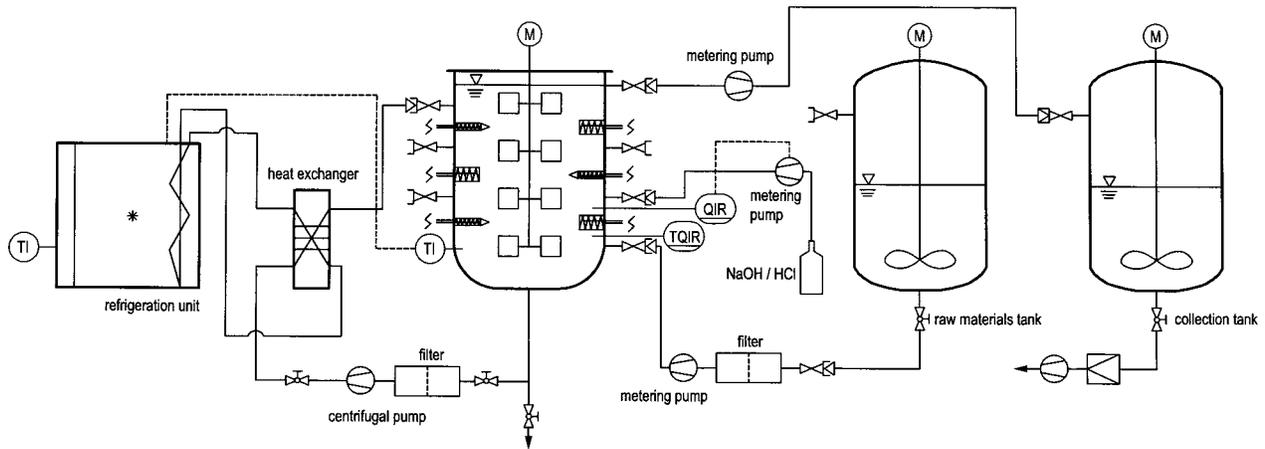


Fig. 4: Continuous test rig

To verify tendencies observed in the batch experiments for constant solution conditions continuous experiments at different pH-values were carried out. Therefore the in Fig. 4 displayed test rig has been built. The test rig consists of three units: an experimental vessel, a cooling unit and a dosage unit.

The experimental vessel has a volume of 30 litres. Up to six heating elements both cylindrical and rectangular can be built in. A stirrer with disk mixers at four different levels moves the solution with a circumferential velocity of 0.26 m/s, which leads to a flow against the plates of approximately 0.03 m/s. The fluid temperature in the vessel is held constant at 42°C over a cooling loop with a heat exchanger. The dosage systems allows to keep the salt concentration in the vessel constant.

From a raw materials tank fresh salt solution is pumped continuously into the experimental vessel and the same amount is pumped out of the experimental vessel into a collection tank. After emptying the raw materials tank, the salt concentration in the collection tank is analysed by titration. The calcium and sulphate concentration is determined with a calcium sensitive electrode and Ethylene-Diamine-Tetra-acetic Acid (EDTA) as titrant and carbonate concentration is measured with an pH-electrode and HCl. After adding the missing salts, raw materials tank and collection tank are changed. The pH- value is kept the whole test time constant by adding HCL or NaOH.

For handling reasons the calcium sulphate concentration was lowered to 0.0275 mol/l CaSO_4 in comparison to the batch experiments. The calcium carbonate concentration was in all experiments constant at 0.005 mol/l CaCO_3 . The solutions were prepared as described before. The heat flux

of each heating element was 18.5 kW/m² over the whole test time.

Determination of the Layer Strength

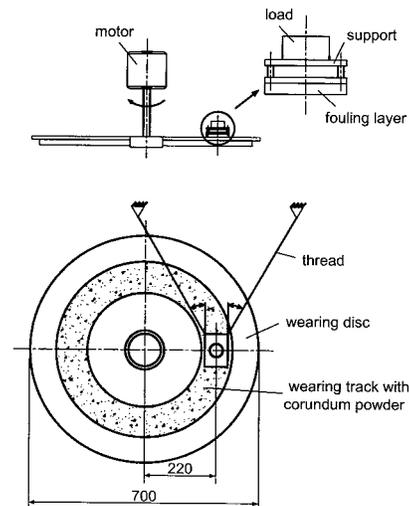


Fig. 5 Wearing disc

A direct measurement of the strength of a layer formed on a heat transfer surface is difficult. The layers are thin and the strength is not distributed homogeneously over the whole sample. Therefore a wearing disc, shown in Fig. 5, is used for the strength measurements (Bohnet et. al., 1999). The fouling layer is pressed with a definite force of 1.5 mN/mm² against a rotating disc, which is strewed with corundum powder.

After a given number of turns the abrasion is determined by measuring the layer thickness. The abraded thickness is not

an absolute strength parameter, because it depends on the wearing parameters e.g. press force, number of turns etc. A calibration with a strength value is therefore necessary. In order to correlate the measured abrasion with a strength value of an independent test method crushing strength experiments according to DIN 18136 with gypsum blocks were done. The gypsum blocks had different strength properties, which were adjusted by varying the water and gypsum ratio. With blocks of the same consistence also abrasion experiments were performed and the results of both experiments were correlated (Fig. 6).

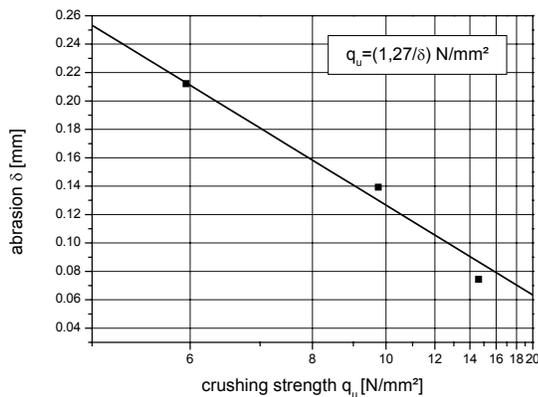


Fig. 6 Correlation between abrasion and crushing strength

With the found correlation

$$q_u = \frac{1.27}{\delta} \left[\frac{N}{mm^2} \right] \quad (3)$$

it is possible to convert the measured abrasion into strength values.

Determination of Crystal Structure and Modification

The fouling conditions have a big effect on the crystalline structure of the formed fouling layers, but also on the modifications of the crystallized salts.

Calcium sulfate exists in the modifications hemihydrate, dihydrate and anhydrate. In fouling experiments mostly calcium sulfate dihydrate is observed. Also calcium carbonate can be found in three different forms, named aragonite, calcite and vaterite. At ambient conditions generally calcite is the most stable, vaterite the most unstable modification. In contrast to calcium sulfate sometimes all three modifications can be detected at the same time.

Besides a different structure the modifications have also differences in their physical properties. This is among other things important for the strength of the fouling layer. Therefore the obtained fouling layers were analyzed with x-ray diffraction and SEM.

The x-ray diffraction investigations were carried out with a Seifert XRD 300 PTS with goniometer MZ4. The scanning electron microscopy was done with a Zeiss DSM-950.

RESULTS

Influence of pH-value in Batch-Experiments

The experiment with a starting pH-value of pH 4.0 showed the strongest incrustation of the heating element, which can be seen in Fig. 7.

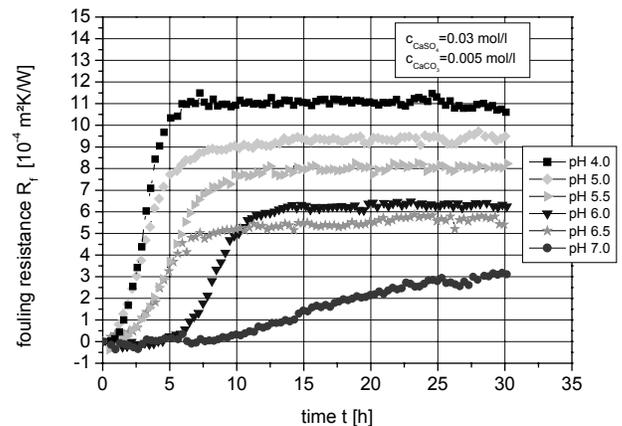


Fig. 7 Fouling resistance R_f for different pH-values in the system 0.03 mol/l CaSO_4 /0.005 mol/l CaCO_3

With increasing pH values less fouling tendency is observed. This is valid for the end value, which is the value of the fouling resistance at the end of the experiment due to the loss of supersaturation of the solution, as well as for the increase of the fouling resistance at the beginning of the experiment in the growth phase. Determining the slope of each curve in this period there is found a linear relation between the increase of the fouling resistance and the pH-value in the investigated pH-range. The initial rise of the fouling curve for each experiment is shown in Fig. 8.

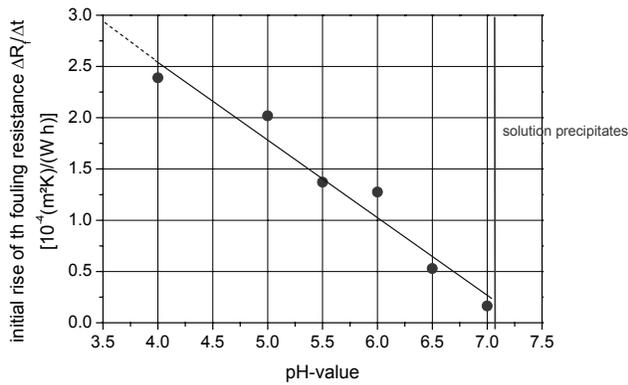


Fig. 8 Rise of the fouling resistance for different pH-values phase in the initial growth phase

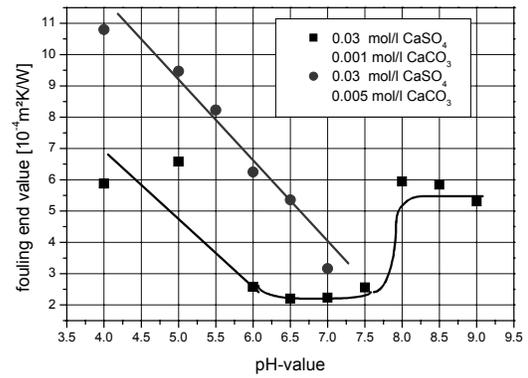


Fig. 10 End value of the fouling resistance for different pH-values

In the system 0.03 mol/l CaSO₄ and 0.001 mol/l CaCO₃ for the experiments at pH 4.0 and 5.0 strong fouling was observed. The formation of only thin layers occurred with pH-values between pH 6.0 and 7.5 and again a relatively high value for the fouling resistance was obtained for experiments between pH 8.0 and pH 9.0. The results of all experiments are demonstrated in Fig. 9.

There can be seen differences in the macrostructure of the crystalline fouling layers at different pH-values. In Fig. 11 photos of encrusted heating elements are demonstrated.

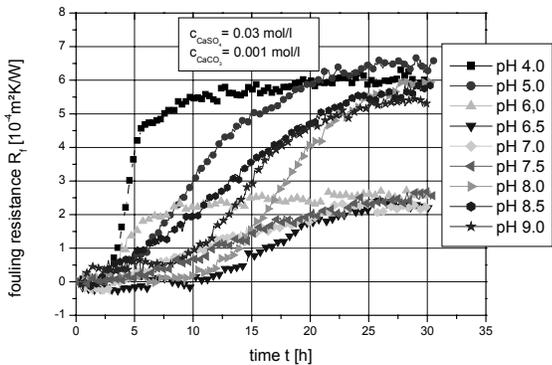


Fig. 9 Fouling resistance R_f for different pH-values in the system 0.03 mol/l CaSO₄/0.001 mol/l CaCO₃ value

Comparing the two test series respective their end values (Fig. 10), it can be noted that the higher carbonate concentration leads to higher end values at the same pH-value. For the test series with 0.03 mol/l CaSO₄ and 0.005 mol/l CaCO₃ a linear relationship between fouling end value and pH-value was determined.

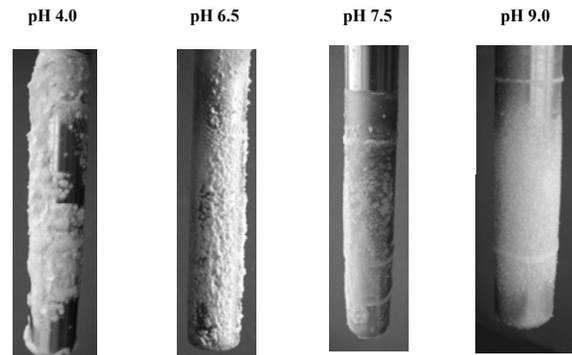


Fig. 11 Encrusted heating elements at different pH-values (0.03 mol/l CaSO₄/ 0.001 mol/l CaCO₃)

At pH 4.0 a flaky, weak and coarse crystalline layer was formed. With a pH-value of 6.5 the layer was still weak and flaky, but the crystals were a little bit finer. At pH 7.5 a different appearance of the crystalline layer is noted. At this pH-value the crystals have a fine shape and the layer is adhesive attached to the surface of the heating element. The layer at pH 9.0 is dense and fine crystalline and shows a strong adhesion on the metal surface.

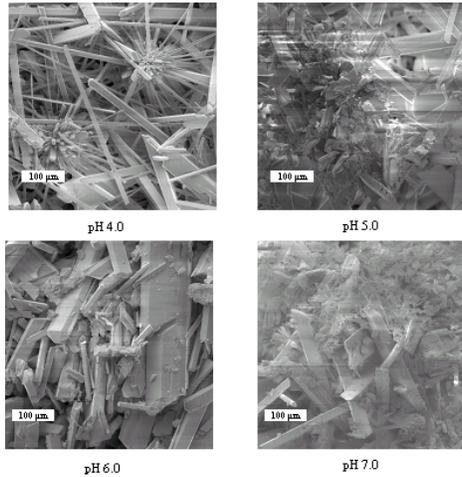


Fig. 12 SEM photos of test series 0.03 mol/l CaSO_4 /0.005 mol/l CaCO_3

With the SEM only long needle shaped crystals were observed for the layers of the first test series (0.03 mol/l CaSO_4 /0.005 mol/l CaCO_3) at pH 4.0, pH 5.0 and pH 6.0 (Fig. 12). X-ray diffraction proved, that at pH 4.0 and pH 5.0 only calcium sulphate dihydrate was formed. In the layer of pH 6.0 also small amounts of aragonite were detected. The SEM photo of the layer grown at pH 7.0 shows besides calcium sulphate needles also small spherulitic structures, which are aragonite. The results of the x-ray diffraction investigations can be seen in Tab. 1.

Tab. 1: Results of x-ray diffraction investigations of the experiments test series 0.03 mol/l CaSO_4 /0.005 mol/l CaCO_3

pH-value	crystal modification
4.0	calcium sulphate dihydrate
5.0	calcium sulphate dihydrate
6.0	calcium sulphate dihydrate, aragonite
7.0	calcium sulphate dihydrate, aragonite

For the second test series (0.03 mol/l CaSO_4 /0.001 mol/l CaCO_3) at pH 4.0 only calcium sulphate dihydrate was observed. At pH 7.0 and 7.5 besides calcium sulphate dihydrate aragonite was detected. At pH 7.0 also small amounts of calcite were found by x-ray-diffraction. At pH 9.0 the third modification of calcium carbonate, the so called vaterite was observed besides calcium sulphate dihydrate. The scanning SEM photos as well as the results of the x-ray diffraction investigations are displayed in Fig. 13 and Tab. 2.

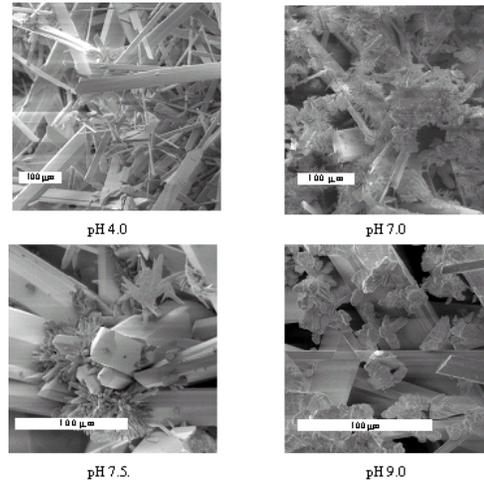


Fig. 13 SEM photos of test series 0.03 mol/l CaSO_4 /0.001 mol/l CaCO_3

Tab. 2: Results of x-ray diffraction investigations of the experiments test series 0.03 mol/l CaSO_4 /0.001 mol/l CaCO_3

pH-value	crystal modification
4.0	calcium sulphate dihydrate
7.0	calcium sulphate dihydrate, aragonite, calcite
7.5	calcium sulphate dihydrate, aragonite
9.0	calcium sulphate dihydrate, vaterite

Influence of pH-value in Continuous Experiments

The continuous experiments showed also a strong dependency of the pH-value.

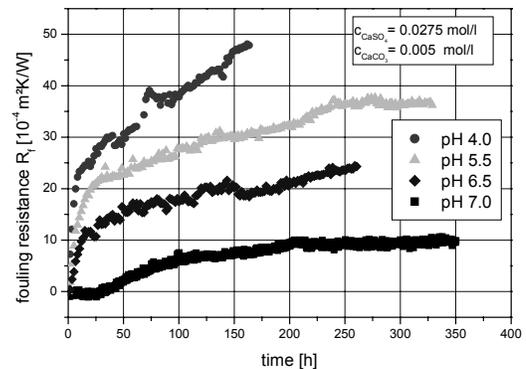


Fig. 14 Fouling resistance R_f for different pH-values

As seen in Fig. 14 there was noted a decrease in fouling tendency with increasing pH-value. Although the salt concentration was constant over the whole test time, an asymptotic fouling curve was obtained for some experiments. As expressed by the different values of R_f at the end of the experiments the thickness of the crystalline layers varied with the different pH-values.

Strength of the Crystalline Layers

As described before the strength of the layers obtained in the continuous experiments was measured by abrasion experiments. The determined strength values are displayed in Fig. 15 in dependency of the layer thickness. The layer thickness is measured from the crystalline upper layer ($x_f = 0$ mm) to the layer next to the heat transfer surface.

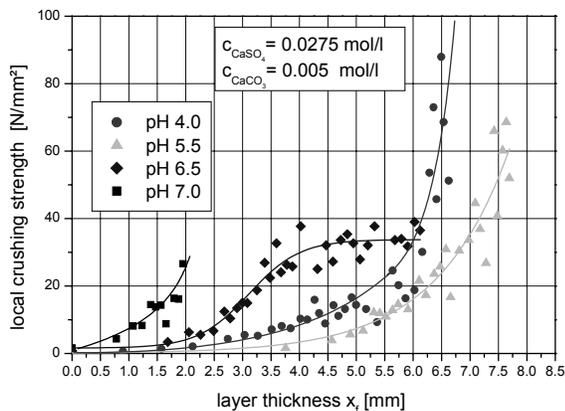


Fig. 15 Local strength in dependency of the layer thickness measured from the crystalline upper layer ($x_f = 0$ mm)

In Fig. 15 can be seen that the layers of the experiments at pH 6.5 and pH 7.0 have a relatively high strength compared to the strength of the experiments at pH 4.0 and pH 5.5 in the upper and middle crystalline layer. Near the heat exchanging surface the situation is different. Here very high strength values were measured for the layers emerged from the experiments at pH 4.0 and pH 5.5.

A reason for the different strength behaviour may be found in the different crystalline structure of the layers. As shown in Fig. 16 completely different layer structures and crystal sizes were obtained at the different experimental conditions.

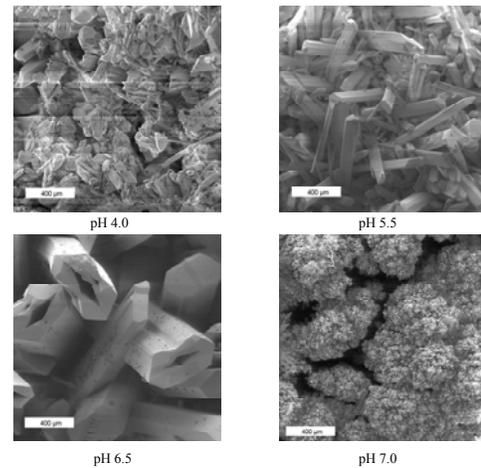


Fig. 16 Scanning electron microscope photos of the continuous experiments (0.0275 mol/l CaSO_4 /0.005 mol/l CaCO_3)

As x-ray diffraction showed also the crystalline composition of the layers varies with the different pH-values. The results are given in Tab. 3.

Tab. 3: Results of x-ray diffraction investigations of the continuous experiments (0.0275 mol/l CaSO_4 /0.005 mol/l CaCO_3)

pH-value	crystal modification
4.0	calcium sulphate dihydrate, calcium sulphate hemihydrate
5.5	calcium sulphate dihydrate, calcium sulphate hemihydrate
6.5	calcium sulphate dihydrate, aragonite
7.0	calcium sulphate dihydrate, aragonite

DISCUSSION

The experiments carried out showed a strong influence of the pH-value on the fouling behaviour of the aqueous two-component system $\text{CaSO}_4/\text{CaCO}_3$. Strongest fouling behaviour was observed for all test series at pH 4.0, lowest fouling tendency at pH 7.0. This results cannot be explained yet. According to the saturation theory for the single components, saturation of calcium carbonate increases with higher pH-values. Saturation of calcium sulphate is almost constant in the investigated pH-range. Therefore stronger scaling should take place at higher pH-values, as seen at pH values between pH 8.0 and pH 9.0.

With X-ray diffraction only modifications of calcium sulphate were detected in scales of experiments at pH-values below pH 6.0. This corresponds with the saturation behaviour of the salts, as at these pH-values all investigated solutions were undersaturated respective calcium carbonate and supersaturated respective calcium sulphate.

Remarkable differences in crystal size could be observed by scanning electron microscopy. It was seen that the thickness of the calcium sulphate needles diminished with lower pH-values. The effect reported by Sudmalis and Sheikholeslami (2000) for precipitation experiments, that coprecipitation of CaCO_3 and CaSO_4 reduces the crystal size of both salts could not be observed in the fouling experiments carried out.

The highest strength values in the crystalline upper and middle layer were measured for the crystalline layer grown at pH 7.0, followed by the layer formed at pH 6.5. The high strength of these layers can be explained by the presence of the calcium carbonate modification aragonite in these layers. Bramson et. al. (1995) and Helalizadeh et. al. (2000) observed in their studies, that calcium carbonate enhances the strength of calcium sulphate scale layers. The strong increase of strength in the bottom layer at pH 4.0 and pH 5.5 may be due to crystalline transformation processes. In these experiments besides the crystal modification calcium sulphate dihydrate also hemihydrate was detected.

CONCLUSIONS

The influence of pH-value on the fouling behaviour of the aqueous two-component system $\text{CaSO}_4/\text{CaCO}_3$ was investigated in batch experiments as well as in continuous experiments with solutions of different salt concentrations. A strong effect of pH-value was noted in all test series. Strongest fouling tendency was observed for experiments at pH 4.0. Few incrustation took place at pH 7.0. Up to now it is difficult to correlate the fouling curves clearly to the different experimental conditions, as the fouling behaviour does not correspond with the saturation theory for the single components.

The obtained crystals layers showed differences in their macroscopic and microscopic structure. Below pH 6.0 only calcium sulphate was detected by x-ray diffraction, which agrees with the saturation theory. At higher pH values besides calcium sulphate also calcium carbonate was found in different modifications.

Strength measurements showed highest strength values in the crystalline upper and middle layer for scales formed at pH 7.0, followed by crystalline layers grown at pH 6.5.

Future research should try to find an explanation for the fouling behaviour observed. Therefore a better under-

standing of the crystallization process in multicomponent systems is necessary.

ACKNOWLEDGEMENT

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NOMENCLATURE

c	concentration, mol/l
k_f	heat transfer coefficient of encrusted surface, $\text{W/m}^2\text{K}$
k_0	heat transfer coefficient of clean surface, $\text{W/m}^2\text{K}$
q_u	crushing strength, N/m^2
R_f	fouling resistance, $\text{m}^2\text{K/W}$
S	saturation index
T_w	wall temperature, $^\circ\text{C}$
t	time, h
x_f	thickness of the fouling layer, m
δ	abrasion, m

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