KINETICS AND QUANTITY OF CRYSTALLIZATION FOULING ON POLYMER SURFACES: IMPACT OF SURFACE CHARACTERISTICS AND PROCESS CONDITIONS

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ABSTRACT

Kinetics and quantity of crystallization fouling on different polymeric surfaces are studied for the model salts of $CaSO_4$ and $CaCO_3$ and compared with those on stainless steel. The promising low scaling affinity of the polymers is attributed to their different surface properties compared to stainless steel. The crystallization kinetics and quantity are also affected by the degree of supersaturation due to higher local temperatures and concentrations. The results can be utilized in thermal desalination plants.

INTRODUCTION

Fouling is the deposition of unwanted particles, precipitates or scales on heat transfer surfaces. This results in operational problems caused by heat transfer loss, pressure drop increase or flow maldistribution. Fouling-related costs are due to heat exchanger oversizing, energy losses and increased maintenance costs (Steinhagen et al., 1993). To reduce economic losses and downtimes of fouled heat exchangers i.e. using appropriate cleaning and maintenance approach, a detailed knowledge of any occurring fouling mechanism is essential. The present work is focused on crystallization as dominant fouling mechanism in desalination plants.

Several studies related to crystallization fouling kinetics on metallic surfaces and its modifications as well on some polymers are available in literature (Förster et al., 1999; Bohnet, 2003; Kazi et al., 2010). However, special polymeric materials suitable as heat transfer surfaces in corrosive environments require investigations in respect to their fouling affinity.

The choice of polymeric materials and surface modifications are profoundly connected to the scaling adhesion properties. An investigation of mineral scaling is given for different surfaces with varying surface free energy and composition. Besides salt species and concentration the influence of wall temperature is also studied at thermal seawater desalination conditions.

EXPERIMENTAL
Surface Characterization

For a detailed understanding of the processes taking place at the surface-crystal interface the characterization of surface topology and surface free energy and its components is essential. Roughness profiles and extracted roughness parameters are quantified with a tactile scanning method according to DIN EN ISO 4287. The mean arithmetic roughness R_a (eq. 1) is used for a topological characterization.

$$R_a = \frac{1}{l} \int_0^l |z(x)| dx \qquad (1)$$

Here l is a single measuring length and $z(x)$ the ordinate.

The surface free energy identification is performed using the method of static contact angle measurement. The static contact angle θ at the triple point of the participating phases results from the thermodynamic equilibrium at the interfaces of solid, liquid and surrounding gas-phase (eq. 2) (Young, 1805; Zisman, 1963).

$$\cos\theta = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}} \qquad (2)$$

Here, the surface free energy of the liquid γ_{LG} can be measured by the pendant drop method. The surface free energy of the solid γ_{SG} can only be calculated with a substitution of the interfacial energy between the solid and liquid phase γ_{SL}. For polymer surfaces two potential models can be used for this substitution. Besides the OWRK-model developed by Owens and Wendt (1969), Rabel (1971) and Kaelble (1970), the method developed by Wu (1971) is applicable and used in the present work (see eq. 3). A comparison of both models can be found in a previous work (Dreiser and Bart, 2012a).

$$(1+\cos\theta)\cdot\gamma_{LG} = 4\cdot\left(\frac{\gamma_{SG}^p\cdot\gamma_{LG}^p}{\gamma_{SG}^p+\gamma_{LG}^p} + \frac{\gamma_{SG}^d\cdot\gamma_{LG}^d}{\gamma_{SG}^d+\gamma_{LG}^d}\right) \qquad (3)$$

Contact angle measurements with a minimum of two liquids with known polar and disperse parts are necessary to solve the set of equations. These measurements are carried out with an OCA 15 EC setup (Dataphysics) and results are given by Dreiser and Bart (2012b).

Screening Apparatus

For a basic analysis of kinetics and quantity of fouling deposition on different surfaces, a screening apparatus was operated at various conditions. Fig. 1 shows the scheme of the setup.
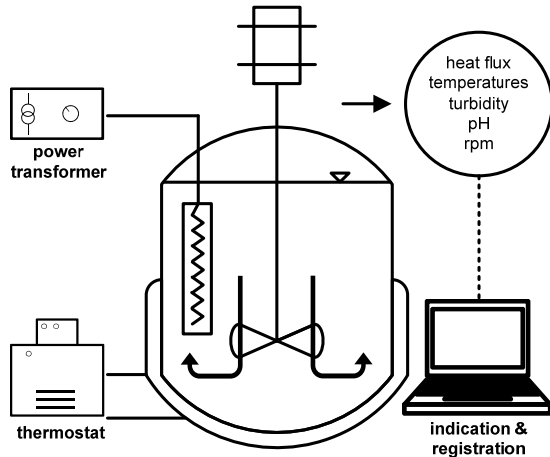

Fig. 1 Schematic setup of the screening apparatus.

Experiments are carried out in a temperature controlled reactor with an initial bulk temperature T_b and bulk concentration c_0. Different surfaces are studied on a heating block (includes 2 cartridges), which allows a defined heat flux adjustment for plane surface materials with a heat transfer area of $A = 24$ cm^2.

An accurate energy balance due to the transient registration of all temperatures of interest (wall temperature of heat transfer surface and bulk temperature, Pt100 resistor-type thermometers) as well as the inserted heat flux is guaranteed. Additionally turbidity, pH value and rotor speed are monitored. The energy balance enables the calculation of the transient overall heat transfer coefficient for the scaled surface U_f. The initial wall temperature is set with a fixed heat flux density. During the process of crystallization fouling of inverse soluble salts on the heat transfer surface the wall temperature changes over time. The fouling resistance R_f is then calculated according to eq. 4 referring to the initial overall heat transfer coefficient U_0.

$$R_f = \frac{1}{U_f} - \frac{1}{U_0} \qquad (4)$$

After each experiment, the mass of the fouling deposit is additionally determined.

Materials and Preparation

Besides stainless steel (1.4571), a standard material in apparatus design, the thermoplastic polymers polyether-etherketone (PEEK) and polysulfone (PSU) are studied in different modifications obtained from Victrex Europa GmbH (PEEK) and Dr. D. Müller GmbH (PSU). These polymers were found to be durable at desalination

conditions (Christmann et al., 2012; Dreiser and Bart, 2012c).

Prior to contact angle measurements, the surfaces of the test materials are cleaned with water and dried with pressurized air. Also for fouling experiments both the test surfaces and the reactor are cleaned before each run. The calcium sulfate solution is oversaturated by dissolving stoichiometric amounts of calcium nitrate teatrahydrate and sodium sulfate before merging. An analogous procedure is carried out for the preparation of an oversaturated calcium carbonate solution by dissolving and merging solutions of calcium chloride-dihydrate and sodium bicarbonate. The final solution is filtered to prevent an impact of seed crystals and other particles.

RESULTS AND DISCUSSION
Kinetics and Quantity

Metallic surfaces show strong interactions with scaling compounds, which usually results in very thick deposit layers. Some polymers, however, feature adhesion properties, which reduce the deposition of certain crystals. Fig. 2 compares the fouling resistance over time for a stainless steel surface and a polymeric surface.
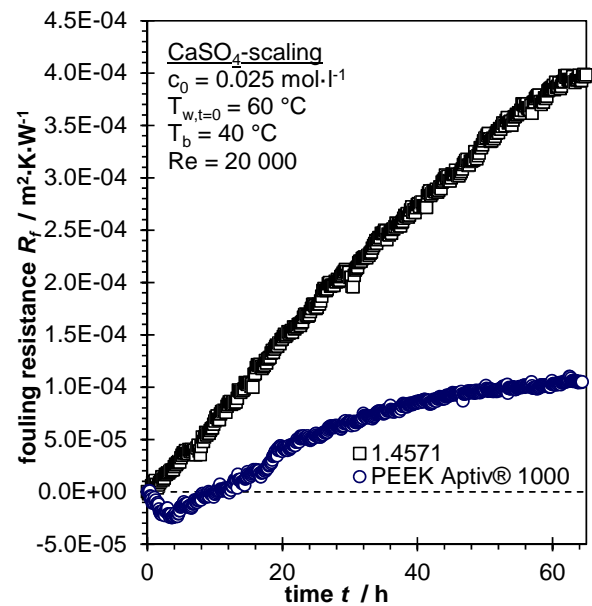

Fig. 2 Fouling characteristics of CaSO$_4$-scaling for a stainless steel (1.4571) and a PEEK surface.

The polymer (PEEK Aptiv® 1000) shows some major advantages with respect to its fouling kinetics and quantity compared to the steel surface. With regard to the kinetics, the polymer surface manifests a pseudo induction period of about 10 hours, where the fouling resistance possesses negative values. This inverse effect can be explained by the temporary increase of local turbulence and heat transfer coefficient due to a disturbance of the laminar boundary layer by nucleating crystals on the comparatively smooth polymer surface (R_a = 0.028 µm). Heat transfer enhancement due to crystallization fouling is well known and has been discussed in detail by Albert et al. (2009). However, the profile of the polymer fouling curve appears

to be of asymptotic character and reaches almost a steady maximum value. The fouling kinetics on the steel surface, in contrast, is approximately linear with a positive correlation and a significantly higher final value at the end of the experiment. No induction period is observed since the steel surface is rougher (R_a = 0.121 µm) than the polymeric one, which enhances the nucleation process.

The advantages of polymeric heat transfer surfaces regarding their scaling affinity are promising for the design of polymer film heat exchangers for corrosive environments such as seawater desalination plants (Dreiser et al., 2013). However, for further surface and process optimization plus design criteria the study of polymer modifications and various operating conditions is essential.

Surface Properties

The influence of surface properties on scaling is exemplarily presented for the model salt of calcium sulfate and different PEEK surfaces. Table 1 shows the surface free energy, polarity and mean arithmetic roughness of three studied PEEK polymers.

Table 1. Surface properties of different PEEK modifications.

PEEK Aptiv®	γ_{SG} , mN·m^{-1}	$\Psi_p = \gamma_{SG}^p / \gamma_{SG}$, -	R_a , µm
1000	33.2	0.59	0.028
2000	30.4	0.43	0.502
1103	40.6	0.48	0.842

The corresponding transient values of the fouling resistance for the same conditions of calcium sulfate scaling are given in Fig. 3 for the different PEEK polymers.
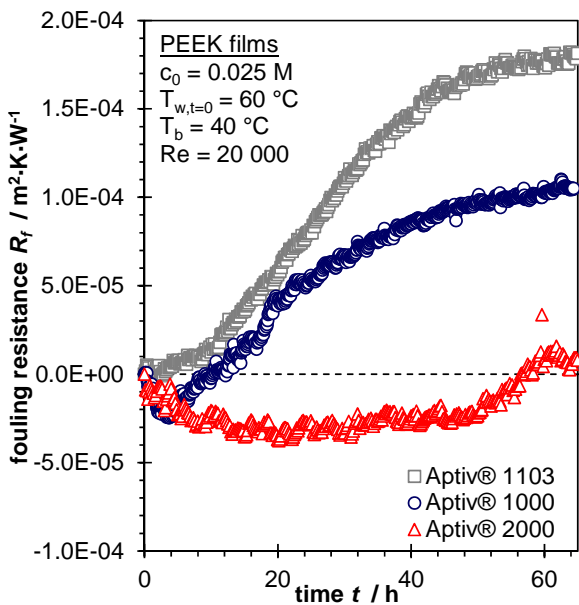

Fig. 3 Transient fouling resistance for different PEEK modifications (CaSO$_4$-scaling).

All PEEK surfaces feature a significantly smaller scaling affinity and final fouling resistances compared to

stainless steel. However, some general deviations in kinetics and quantity of deposition can be observed. The Aptiv® 2000 polymer with the lowest scaling deposition also has the lowest surface free energy. The Aptiv® 1103 polymer (includes 30 % mineral filler) with the highest surface free energy also shows the strongest interaction with the deposit.

Taking the relevant fouling results (Table 2) into account it is obvious that an overlap of topological and energetic effects complicates a simple interpretation.

Table 2. Relevant fouling results of different PEEK modifications.

PEEK Aptiv®	m_d , g·m^{-2}	$t_{ind.}$, h	R_f^* , 10^{-4}·m^2·K·W^{-1}
1000	91.0	10.3	1.1
2000	4.2	56.5	0.1
1103	70.8	2.8	1.8

Evaluating the mass of the deposit at the end of an experiment, it should be mentioned that the covered area is also important for a relationship with other parameters ($t_{ind,}$ R_f^*). Considering a surface free energy of the CaSO$_4$-deposit of γ_{CG} = 47.88 mN·m^{-1} (Förster et al., 1999) an interfacial energy difference to the heat transfer surface is defined as:

$$\Delta\gamma_{CS} = \gamma_{CG} - \gamma_{SG} \qquad (5)$$

Fig. 4 represents the tendency of relative heat transfer coefficient, which corresponds to the asymptotic fouling resistance of Fig. 3, as a function of the calculated interfacial energy difference between the polymer surfaces and the gypsum deposit.
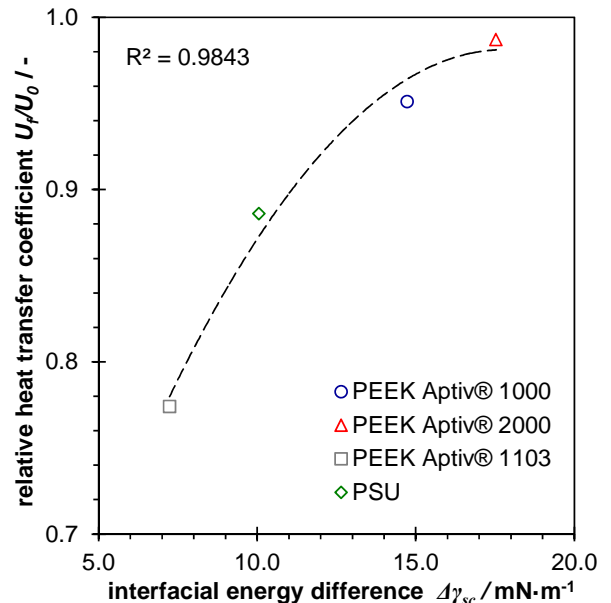

Fig. 4 Relative heat transfer coefficient vs. interfacial energy difference for polymeric surfaces (68 h of CaSO$_4$-scaling).

A lower interfacial energy difference results in stronger interactions, which implicates both a shorter induction period and a higher amount of final scaling deposit. To mitigate scaling high interfacial differences should be achieved in heat transfer surface design. Low adhesion at the solid-crystal-interface also simplifies heat exchanger cleaning.

For an isolated consideration of interfacial energy and its components, surfaces of the same composition and approximately same surface roughness need to be compared in future investigations. Preliminary results show that a plasma treatment of some PEEK surfaces can enhance the time of induction significantly due to changes of the surface free energy (surface topology remains nearly unaffected).

Process Conditions

Varying operating conditions influence both the heat transfer performance and the scaling kinetics in heat exchangers. The study of the impact of process conditions on scaling supports an efficient design of heat exchangers. The deposition is mainly driven by the supersaturation as a result of higher temperature or concentration of the salt species. By varying these parameters, general conclusions of the scaling kinetics gain the knowledge of the crystal-surface interaction. Due to the low adhesion of gypsum scales on polymer surfaces, calcium carbonate was selected as model salt. Fig. 5 represents the $CaCO_3$-scaling kinetics as a function of initial wall temperatures.
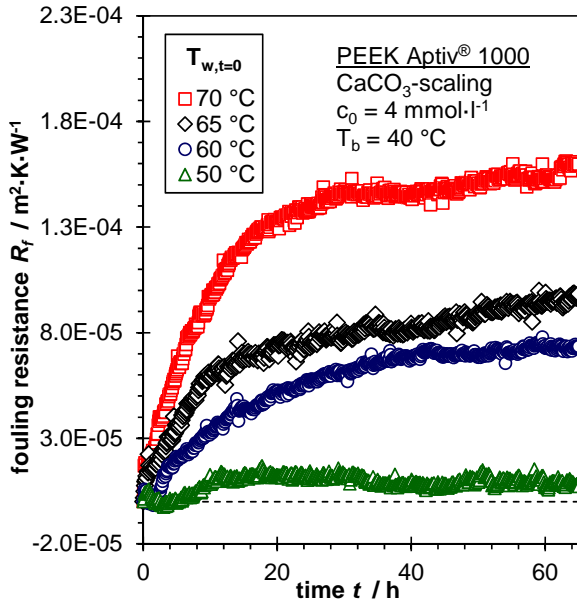

Fig. 5 Fouling resistance versus time for PEEK Aptiv[®] 1000 surface as a function of initial wall temperature ($CaCO_3$-scaling).

As expected, the fouling quantity increases with the wall temperature due to higher local supersaturation. The exponential relation between fouling quantity and initial wall temperature (also reported by Dreiser et al., 2013) influences the nucleation process, resulting in varying induction periods. The effect of the heat transfer reduction affects the design and cleaning of multi-effect-distillers, where single stages are operated at different temperatures. In thermal seawater desalination the salt concentration of the brine is also changing during the process. The quantitative impact of the $CaCO_3$-concentration on scaling quantity is presented in Table 3.

Table 3. Impact of concentration on $CaCO_3$-scaling on PEEK Aptiv[®] film ($T_{w,t=0}$ = 60 °C, T_b = 40 °C).

c_0, mmol·l^{-1}	m_d, g·m^{-2}	R_f^*, 10^{-5}·m^2·K·W^{-1}
3.0	2.9	1.2
3.5	7.2	4.1
4.0	24.6	7.2

The effects of supersaturation caused by both, high initial concentration or high initial wall temperature impact the scaling behavior significantly. The correlations obtained for model salts claim further validation with complex salt mixtures (artificial seawater) relevant for thermal desalination.

CONCLUSIONS

The investigations of mineral scaling on polymeric heat transfer surfaces lead to following conclusions:

1. The studied polymeric surfaces feature major advantages in kinetics and quantity of scale deposition, which also depend on the interfacial energy difference to the scaling deposit.
2. Quantified impacts of surface properties on scaling can be applied in surface optimization (plasma treatment etc.) and development of novel surfaces for polymer film heat exchangers.
3. Scaling due to unfavorable process conditions of polymer based desalination plants should be reconsidered for an overall optimized operation (pressure and temperature of each stage, counter-current flow or parallel feed of seawater).
4. For validation of the findings with single model salts further studies with complex salt mixtures (seawater) are requested.

NOMENCLATURE

A heat transfer surface, m^2
c_0 initial concentration, mol·l^{-1}
m_d mass of deposit, g·m^{-2}
U overall heat transfer coefficient, W·m^{-2}·K^{-1}
$t_{ind.}$ time of induction period, h
T_b bulk temperature, °C

$T_{w,t=0}$ initial wall temperature, °C
R_a mean arithmetic roughness, μm
Re Reynolds number of stirred vessel, -
R_f fouling resistance, $m^2 \cdot K \cdot W^{-1}$
R_f^* asymptotic fouling resistance, $m^2 \cdot K \cdot W^{-1}$

Greek letters

$\Delta\gamma_{ij}$ interfacial energy difference between the phases i and j, $mN \cdot m^{-1}$
γ_{ij} interfacial energy between the phases i and j, $mN \cdot m^{-1}$
θ static contact angle, °
ψ_p polarity of surface, -

Subscripts and Indizes

0 initial value
d disperse part
f fouled surface
C crystal phase
G gas phase
L liquid phase
p polar part
S solid phase

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