

EXPERIMENTAL STUDY ON THE ADHESION OF SINGLE CRYSTALS ON MODIFIED SURFACES IN CRYSTALLIZATION FOULING

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ABSTRACT

Since a long time it was tried to describe fouling on heat transfer surfaces by mathematical models. Most studies about fouling concentrate on the description of the thermal effects by the developing fouling resistance R_f . In general it is assumed that a homogeneous fouling layer builds up. Some fouling models include the adhesion of the uniform fouling layer. In crystallization fouling it has been observed that during a certain initial phase the fouling is formed by a non-uniform layer consisting of a population of single crystals. These single crystals are formed by inverse soluble salts such as CaCO_3 . During heterogeneous nucleation and heterogeneous growth an interface between the crystal and the heat exchanger surface occurs. The development of this interface is the reason for the adhesion of each single crystal and in total, once a uniform layer has been built up. The emerging interface is intrinsic to the heterogeneous nucleation of crystals and can be explained the thermodynamic principle of the minimum of the Gibbs free energy. In this study CaCO_3 crystals were grown heterogeneously on untreated and on modified surfaces inside a flow channel. The adhesion was measured through a micro manipulator that sheared off single crystals from the substrate that was fixed to a spring table inside a SEM.

INTRODUCTION

Fouling in general is the unwanted deposition of material on heat transfer surfaces (Epstein, 1983) (Müller-Steinhagen, 1999) and can lead to a decrease of the heat exchanger efficiency. Crystal fouling can be divided into heterogeneous nucleation, growth, adhesion, removal and aging (Bott, 1995). The fouling mass balance per unit area is equal to the difference of the deposition and the removal rate (Eq. 1). The removal rate can be described with a removal probability Γ (Förster, 2001) which is a function of the ratio of the shear force of the fluid on top of the crystals and the adhesion force F_{ad} (Chen et al., 1995).

$$\dot{m}_f = \dot{m}_d - \dot{m}_r = \dot{m}_d (1 - \Gamma(F_\tau / F_{ad})) \quad (1)$$

The shear force (Eq. 2) is proportional to the fluid flow (Hirsch et al., 1996) and the corresponding crystal surface A_{cl} .

$$F_\tau \propto \rho \cdot u^2 \cdot A_{cl} \quad (2)$$

The heat transfer changes with time due to the fouling, so that it is feasible to formulate a time dependent fouling resistance R_f (Eq. 3) (Albert et al., 2011). The fouling resistance is also proportional to the fouling mass (Eq. 4) (Mayer et al., 2010). Figure 1 shows the fouling resistance of CaCO_3 on stainless steel in an electrically heated flow channel, where at least two periods in crystal fouling are distinguishable: The induction period and the crystal growth period. The induction period refers to no significant degradation of the heat transfer.

$$R_f = \frac{1}{U_f} - \frac{1}{U_0} \quad (3)$$

$$R_f \propto \frac{m_f}{\lambda_f \rho_f} \quad (4)$$

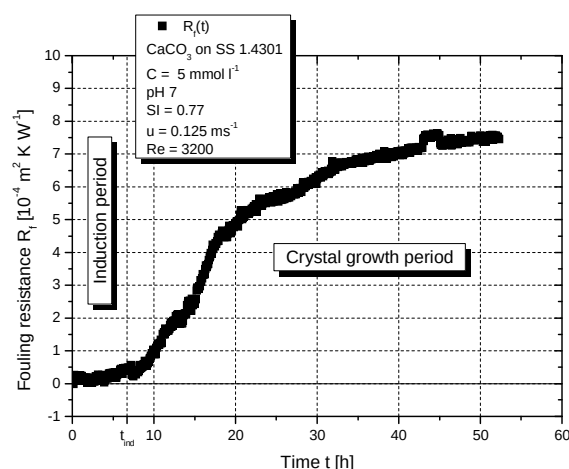


Fig. 1 Fouling resistance of CaCO_3 .

The distribution of the fouling resistance is strongly influenced by the interaction of the interface crystal/heat transfer surface and the shear stress. Understanding the adhesion at crystal fouling is crucial for a holistic mathematical model (Oliveira, 1997).

Similar to the micromanipulation method that is presented in this paper adhesion forces in bio- and food sciences have been measured through mechanical detachment of fouling matter like biofilms (Chen et al., 1998) and food deposit (Liu et al., 2003).

THEORY OF ADHESION

The process of adhesion in fouling can be described by the DLVO theory. In general the adhesion force of two bodies can consist of different mechanisms (Eq. 5) such as van der Waals force, electrostatic force, chemical bonding, hydrogen bonding, capillary forces and others (Butt et al., 2010). In general, the adhesion force is the maximum force necessary to separate two bodies in mechanical contact.

$$F_{ad} = F_{vdW} + F_{el} + F_{chem} + F_H + F_{cap} + \dots \quad (5)$$

In this study only the van der Waals forces were observed. It is commonly known that van der Waals forces are controlled by the geometry and the physical and chemical properties of the contemplated bodies. In this case the acting forces in a crystallization fouling process were approximated by an interaction of a sphere and a plate. The potential energy for these geometries can be described with a generic formula (Eq. 6) (Israelachvili, 1995) in which A_H is the Hamaker constant, R the radius of the sphere and D_0 the distance between the interacting bodies. The according van der Waals force (7) can be obtained through the derivative with respect to D_0 .

$$E = -\frac{A_H \cdot R}{6D_0} \quad (6)$$

$$F = \frac{A_H \cdot R}{6D_0^2} \quad (7)$$

According to Butt et al. (2010) the adhesion force between an inelastic sphere and a planar surface can be obtained from the radius of the sphere and the adhesive energy per surface area E_{ad} .

$$F_{ad} = -2\pi \cdot R \cdot E_{ad} \quad (8)$$

In order to specify the impact factors of the plate (metal substrate) and of the sphere (crystal) models are presented that combine surface energies and surface topography with adhesion. The so called Dupré adhesion energy (Eq. 9) delivers a relation between the surface energies of two bodies (1 and 2), respectively the interfacial energy and the adhesion energy (Butt et al., 2010).

$$E_{ad} = \gamma_1 + \gamma_2 - \gamma_{12} \quad (9)$$

The interfacial energy (Eq. 10) is the ratio of the reversible work respectively the Gibbs free energy that is needed to create an interface area at the interface of bodies 1 and 2.

$$\gamma_{12} = \left(\frac{\partial G}{\partial A} \right)_{T,p} \quad (10)$$

An approach (Eq. 11) which considered surfaces asperities with radius r in the calculation of the adhesion force was proposed by Rumpf (1974). Rabinovich et al. (2000) presented a modified Rumpf model (Eq. 12) which uses the root mean square roughness r_{rms} and the average lateral distance between asperities d for describing the influence of substrate surface. The according proportionality factor k_1 is 1.817.

$$F_{ad} = \frac{A_H}{6D_0^2} \left[\frac{R \cdot r}{R + r} + \frac{R}{(1 + r/D_0)^2} \right] \quad (11)$$

$$F_{ad} = \frac{A_H \cdot R}{6D_0^2} \left[\left(1 + \frac{32 \cdot R \cdot k_1 \cdot r_{rms}}{d^2} \right)^{-1} + \left(1 + \frac{k_1 \cdot r_{rms}}{D_0} \right)^{-2} \right] \quad (12)$$

The adhesive strength H_{ad} is defined as the adhesion force per interface area A_{cs} .

$$H_{ad} = \frac{F_{ad}}{A_{cs}} \quad (13)$$

Since Equation (1) is only valid for equal areas of adhesion A_{cs} and of fluid shear stress A_{cl} it is more likely to formulate the removal rate by regarding the ratio of the shear stress to the adhesive strength (14).

$$\dot{m}_r = \dot{m}_d \cdot \Gamma(\tau / H_{ad}) \quad (14)$$

FOULING EXPERIMENTS

The fouling samples were generated in a supersaturated solution that was pumped through a flow channel (see Figure 2) at low laminar flow ($u = 0.002 \text{ m s}^{-1}$, $Re = 43$) in order to avoid removal. The substrates ($20 \times 80 \times 2 \text{ mm}^3$) were assembled into the flow channel and heated up to 80°C electrically. In Table 1 the investigated surfaces with their particular surface modification are specified. The coatings were assembled by Fraunhofer IST and the enamel samples by Dücker. The base material was rolled stainless steel. The solution (30 L CaCO_3) was composed of Na_2CO_3 and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ to achieve a 5 mmol l^{-1} concentration respectively a saturation index of $SI = 0.77$ calculated with PHREEQC (USGS) ($SI > 0$ indicates supersaturation). The solution was kept at 25°C and aerated for 12 h with CO_2 in order to keep the solubility high. After this the pH was brought from about 5.3 to 7 with NaOH. The test duration was 10 and 20 min respectively 15 min for electropolished

DLC. Then the samples were fouled with single crystals and were dried at ambient environment.

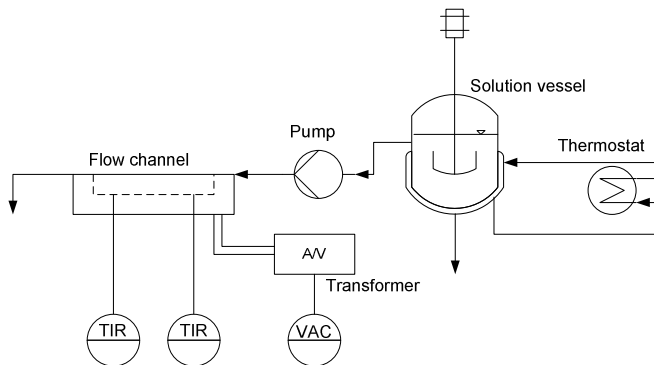


Fig. 2 Experimental setup for generating fouling samples.

Table 1. Investigated surfaces with modification; the percentage of the most frequent elements in enamel are shown in brackets.

Surface	Modification	Short term
EN 1.4301	none	SS
EN 1.4301	electro polished	SS_EP
a-C:H	coating	DLC
a-C:H	electro polished and coated	DLC_EP
a-C:H:Si:O	coating	SICON [®]
a-C:H:Si	coating	SICAN
O (0.35), Si (0.28), W (0.12), Na (0.09), B (0.02), traces of other elements	enameled	Enamel

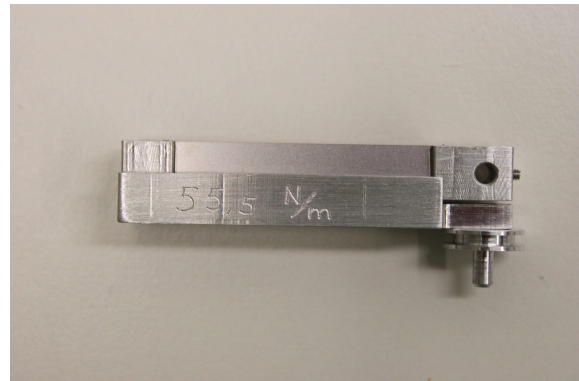
ADHESION FORCE MEASUREMENTS

The adhesion of the CaCO_3 crystals on the surfaces was measured optically inside a scanning electron microscope (SEM) (Zeiss, EVO 25). The fouled samples were fixed onto a spring table (Kleindiek Nanotechnik) with two parallel flat springs (see Figure 3). Three geometrically identical spring tables with different spring constants ($k = 45.7, 55.5$ and 79.7 N m^{-1}) were used. The crystals were sheared off with a micro manipulator (Kleindiek Nanotechnik) inside the SEM (see Figure 4). The force entry was kept orthogonal to the fixation of the flat springs. The feed force rate of the micro manipulator was steadily increased. The adhesion force was calculated by applying Hooke's law (Eq. 15) with the distance of the deflected spring table at the moment of tear-off, which was identified through image processing (ImageJ, NIH) of the SEM videos.

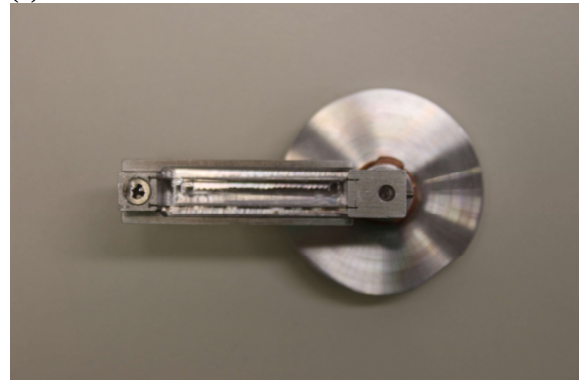
$$F_{\text{ad}} = k \cdot \Delta x \quad (15)$$

Figure 5 shows the determination of the adhesion force through the SEM video. The spring deflection of the linked spring table was measured by the difference of the length of lines $\Delta x = l_2 - l_1$ in pixels to a fixed point in the pictures from the initial picture and the last picture before tear-off. The intensity of the vacuum in the SEM needed to be

adjusted for each sample since some surfaces like enamel supercharged and accordingly high-contrast pictures were difficult to obtain. Low vacuum accounts for a lower picture sequence which made some measurements not analyzable.



(a)



(b)

Fig. 3 Spring table for use inside a SEM (length 60 mm, height 13 mm, width 14 mm); (a) lateral view, (b) top view, at right fixation of flat springs, at left sampling clamp.

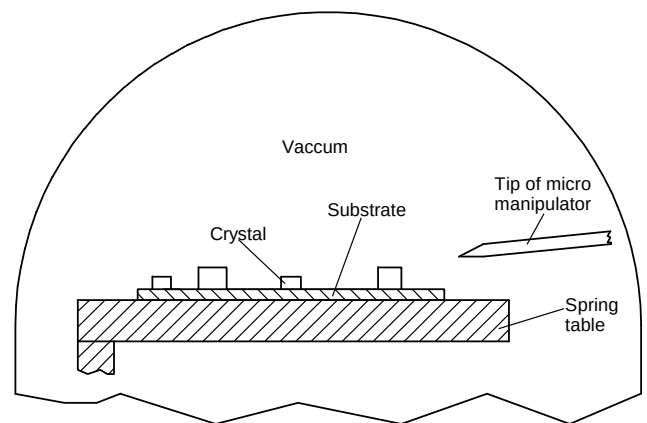


Fig. 4 Setup of the adhesion measurement technique of fouling samples inside a SEM.

The expected adhesion force should be considered at the chosen spring constant because the spring deflection must be within the frame of the chosen SEM picture with the according magnification.

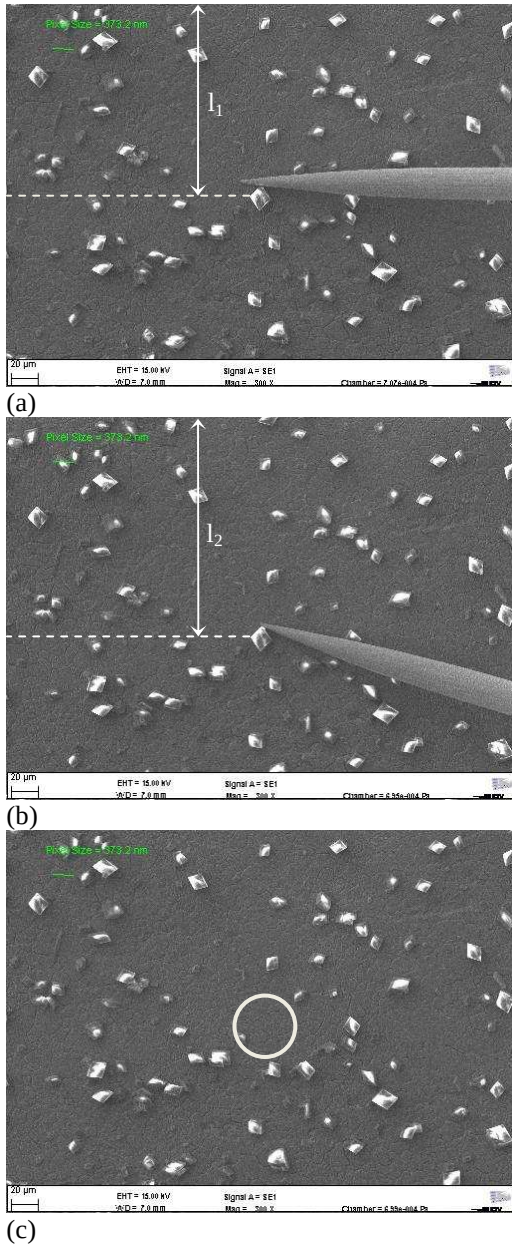


Fig. 5 Determination of the adhesion force (CaCO_3 on stainless steel) in a SEM with a micro manipulator and a spring table (spring constant = 79.7 N m^{-1}); (a) initial position, (b) deflected spring table with stressed crystal – spring deflection $\Delta x = l_2 - l_1$, (c) spring table back in initial position after tear-off of the crystal.

The interface area (Eq. 16) could not be measured exactly with this setup and it was approximated by determining half of the projected area of the single crystal in the SEM pictures with ImageJ. The surface area ratio was included because according to Geddert (2009) crystal growth starts preferred in microscopic cracks and the crystals adjust their interface to the surface topography.

$$A_{cs} \approx \frac{A_{c,SEM}}{2} + Sdr \cdot \frac{A_{c,SEM}}{2} \quad (16)$$

SUBSTRATE SURFACE CHARACTERISTICS

The surfaces of the substrates were characterized through surface topography and surface energy measurements. The surface topography was detected with an atomic force microscope (AFM, DME) and the according roughness parameters were obtained. The topography of the untreated stainless steel and the coatings DLC, SICON[®] and SICAN look very similar because the coating process with plasma assisted chemical vapor deposition (PACVD) is form-fitting. Figure 6 shows the root mean square roughness r_{rms} as well as the surface area ratio Sdr for the different surfaces. As expected the values of r_{rms} and Sdr for SS_EP, DLC_EP and Enamel are significantly lower compared to the other surfaces. The values obtained are in good agreement with those found by Förster (2001).

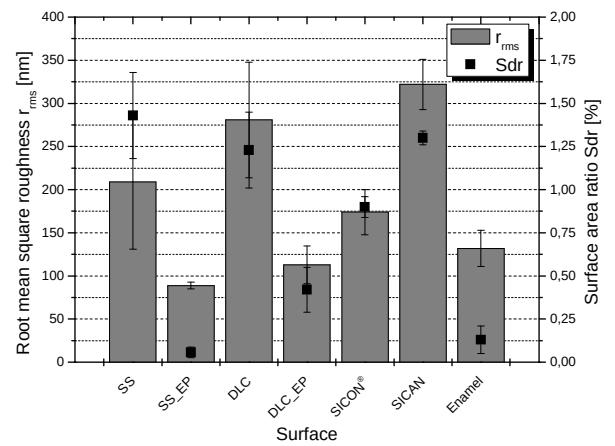


Fig. 6 Averaged root mean square roughness and surface area ratio of the surfaces.

The free surface energies were measured through drop shape analysis (DSA, Krüss GmbH). The data was plotted with the geometric mean approach by Owens et al. (1969). Figures 7 shows the detected free surface energy for the different surfaces with the according polar and disperse fractions as well as the according solid/liquid interface energy of the surfaces with water.

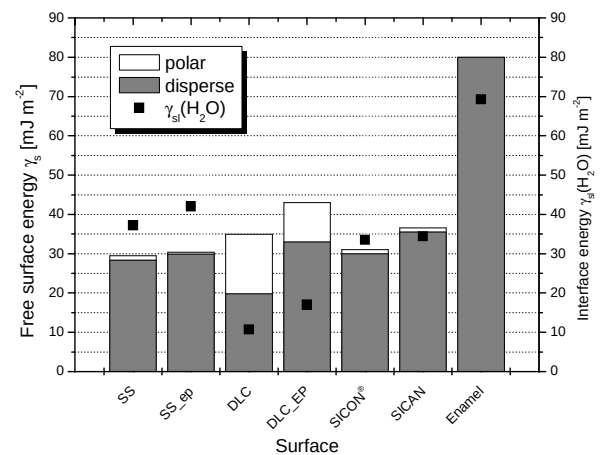


Fig. 7 Free surface energy and interface energy.

It is reasonable that the polar parts for the DLC surfaces are relatively high. The values are in good accordance with those found by Gedert (2009) and Förster (2000). For Enamel the highest total free surface energy (80 mJ m^{-2}) was measured with no polar part. The interface energy crystal/substrate was approximated with Eq. (17) (Salmang et al., 2007) where Φ is the contact angle between the solid bodies which was assumed to be 90° . According to (Santhanam et al., 1968) the free surface energy γ_c of CaCO_3 is about 140 mJ m^{-2} .

$$\gamma_{cs} \approx 2 \cdot \gamma_{sl} \cdot \cos\left(\frac{\Phi}{2}\right) \quad (17)$$

RESULTS

Figure 8 shows the averaged measured adhesion forces of the different surfaces. The obtained values of the adhesion forces were in the range of $10^{-4} - 10^{-3} \text{ N}$. The approximated adhesive strength is shown in Figure 9.

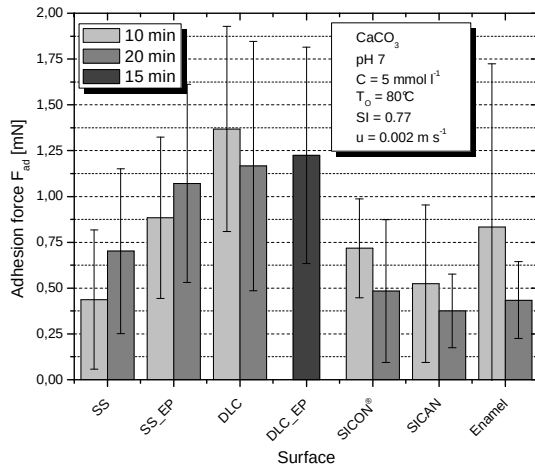


Fig. 8 Averaged adhesion forces of CaCO_3 crystals on the surfaces for different crystallization times.

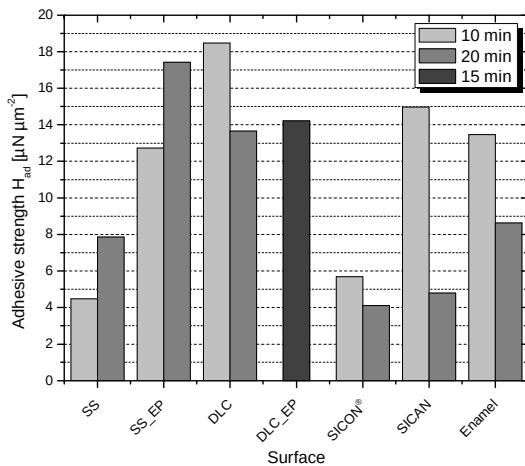


Fig. 9 Approximated adhesive strength of CaCO_3 crystals on the surfaces for different crystallization times.

The Hamaker constants were calculated with (Eq. 18) using Eq. (12). Instead of the radius R of the particles the measured characteristic length of the single crystals was taken. Figure 10 shows the averaged characteristic lengths of the CaCO_3 crystals obtained from the SEM pictures. The growth of the crystals can be identified by the time trend. According to Rabinovich et al. (2000) the minimum distance D_0 was considered to be 0.3 nm . The average distance between asperities d of the surfaces was about 25 μm determined by the AFM measurements. The Hamaker constants were calculated with (Eq. 19), combining Eqs. (8), (9), (12) and (17) by rather estimating the interface energy than regarding the adhesion force.

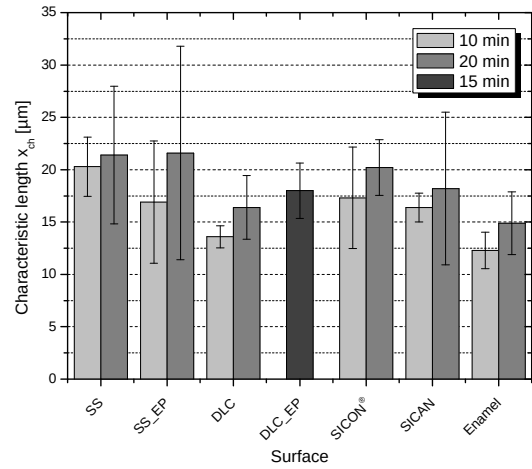


Fig. 10 Characteristic length of the CaCO_3 crystals on the surfaces for different crystallization times.

$$A_H = \frac{6 \cdot D_0^2 \cdot F_{ad}}{R} \cdot \left[\left(1 + \frac{32 \cdot R \cdot k_1 \cdot r_{rms}}{d^2} \right) + \left(1 + \frac{k_1 \cdot r_{rms}}{D_0} \right)^2 \right] \quad (18)$$

$$A_H = 12 \cdot \pi \cdot D_0^2 \cdot (\gamma_s + \gamma_c - \gamma_{cs}) \cdot \left[\left(1 + \frac{32 \cdot R \cdot k_1 \cdot r_{rms}}{d^2} \right) + \left(1 + \frac{k_1 \cdot r_{rms}}{D_0} \right)^2 \right] \quad (19)$$

The resulting Hamaker constants are shown in Figures 11 and 12. The obtained values are in the range of 10^{-17} J , considering the measured adhesion forces. By applying the free surface energies (Eq. 19) the estimated Hamaker constants are in the range of 10^{-19} J . The results are comparable to the values for metals ($4 \cdot 10^{-19} \text{ J}$) found by Israelachvili (1992) and for CaCO_3 ($2.4 \cdot 10^{-19} \text{ J}$) found by Lefèvre et al. (2009). Equation (20) shows the according value for the interaction in vacuum by applying the rule approximation with the geometric mean. The values of the Hamaker constants calculated with Eq. (19) are in good consistency (see Fig. 12).

$$A_H \approx \sqrt{A_{H,metal} \cdot A_{H,CaCO_3}} = \sqrt{4 \cdot 10^{-19} \text{ J} \cdot 2.4 \cdot 10^{-19} \text{ J}} = 3.1 \cdot 10^{-19} \text{ J} \quad (20)$$

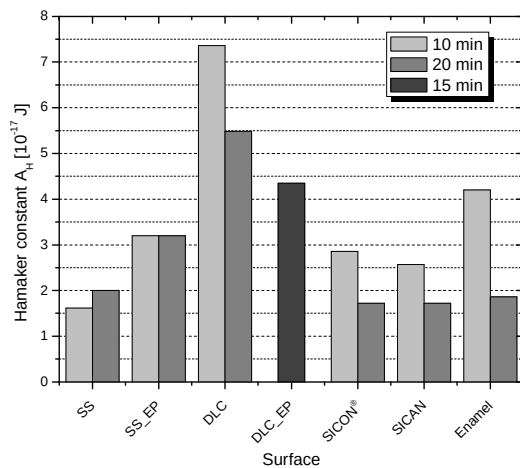


Fig. 11 Hamaker constants of CaCO₃ and the according surfaces for different crystallization times calculated with Eq. (18).

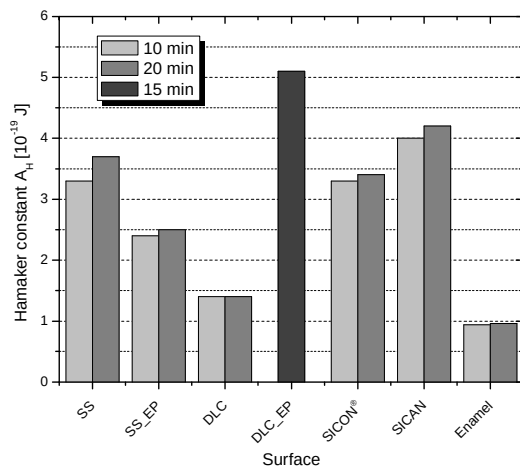


Fig. 12 Calculated Hamaker constants of CaCO₃ and the according surfaces for different crystallization times calculated with Eq. (19).

DISCUSSION

The results demonstrate the impact of modified surfaces on adhesion in crystallization fouling. According to Gedder (2009) the fouling resistance R_f is verifiable less significant on modified surfaces like SICON® and SICAN due to a reduced adhesion affinity. This is supported by the relatively low adhesion forces respectively adhesive strength on these surfaces. It can be expected that on these surfaces the fouling resistance is reduced significantly with time due to a fluid flow induced removal (Eqs. 1 and 2). The highest adhesion forces of single CaCO₃ crystals were detected on DLC and SS_EP. Since the standard deviation is high compared to the according means these measurements only show a trend of adhesive disposition concerning crystallization fouling of inverse soluble salts like CaCO₃. The adhesion of compact crystal layers on heat exchanger surfaces has to be investigated in comparison to the measurements with single crystals presented in this study. The generated fouling samples showed a fractional surface

coverage that generally occurs during the induction period at crystallization fouling, where the heat exchanger surface is usually not covered completely. It is likely that the adhesive strength is time dependent since the volume of the single crystals grows unproportional to the interface area during the fouling process. Because the contact area is depending on the substrate further studies should concentrate on the determination of this interface area and on the crystal dimensions that can be applied to the presented adhesion force models. It is likely that the adhesion in crystallization fouling differs from particle adhesion and it can be expected that the interface area can only grow until a complete coverage of the heat exchanger surface is achieved. It is even more likely that a crystal fouling layer features an interface with the substrate only at some locations formed by the initial growth of single crystals. The equivalent radius (Eq. 11) of the crystals is also needed in order to calculate the according Hamaker constants more precisely. Usually the adhesion is roughness controlled and the Dupré work of adhesion can be neglected (Butt et al., 2010). However the decreasing adhesion on SICAN, which has a relatively high surface roughness, points to an impact of the free surface energy with an increasing interface area with time. The determined Hamaker constants are about one to two scales higher than the expected dimensions of $10^{-19} - 10^{-18}$ J. The adhesion force model (Eq. 12) by Rabinovich et al. is only verified for particle-wall adhesion with r_{rms} of 0.17-10.5 nm and asperities of about 1.1 μ m which are not comparable to the surface roughness values in this study. Furthermore the adhesion force equation for plate-plate geometry needs to be taken into consideration by regarding surface topography and free surface energy. During the formation of compact crystal fouling layers the adhesion of the single crystals should interact through bridging.

CONCLUSIONS

The presented technique for the measurement of the adhesion of single crystals on different surfaces has the advantage that the resulting force on the single crystal does not interfere with other elastic forces such as the tip of the micro manipulator. Using a SEM and a micromanipulator the presented method could be applied at laboratories in industrial and academic research centers in order to validate technical requests on adhesion of comparable assembled solids such as particles and microorganisms on substrates. It is crucial to choose the appropriate spring constant for the expected adhesion forces. Considering crystallization fouling more detailed knowledge of the particular crystal dimensions/interfaces is essential for building sufficient means of the adhesive strength and the experimental Hamaker constants. The dissipation of energy during the measurement has not been considered yet. The lowest adhesion forces were detected for SICON®, SICAN and Enamel which have consequently a lower affinity to crystallization fouling.

The measured adhesion forces of single CaCO₃ crystals can be useful for detailed models of crystallization fouling (Eqs. 1- 4). Since the standard deviation of the results is high the exact identification of the heterogeneous crystal growth

rates and the according interfaces crystal/heat exchanger surface is needed. Each measurement of the adhesion of a single crystal on a heat exchanger surface must be analyzed separately. In future the exact interfaces of a crystal population on a dissimilar surface could be visualized through high resolution micro computer tomography (μ -CT). The adhesion force models considering the surface impact factors must be verified for single crystal adhesion. It could be demonstrated that the adhesion of single crystals in crystallization fouling is constrained by the surface topography and the free surface energy of the substrate and is generated at heterogeneous crystal nucleation and growth. Future work need to concentrate on the development of surfaces that inhibit the development of unwanted crystalline interfaces thermodynamically in order to prevent crystallization fouling.

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NOMENCLATURE

A	area, m^2
A_H	Hamaker constant, J
AFM	atomic force microscopy
C	concentration, mol m^{-3}
D_0	minimum distance, m
DLVO	Derjaguin, Landau, Verwey, Overbeek
DSA	drop shape analysis
d	distance between asperities, m
E	energy, J
F	force, N
G	Gibbs free enthalpy, J
H_{ad}	adhesive strength, N m^{-2}
k	spring constant, N m^{-1}
k_1	factor, dimensionless
l	distance, m
m	fouling mass, kg m^{-2}
PACVD	plasma assisted chemical vapor deposition
R	radius, m
R_f	fouling resistance, $\text{m}^2 \text{K W}^{-1}$
Re	Reynolds number, dimensionless
r	asperity, m
r_{rms}	root mean square roughness, m
Sdr	surface area ratio, dimensionless
SEM	scanning electron microscopy
SI	saturation index, dimensionless
T_o	initial surface temperature, $^{\circ}\text{C}$
U	thermal resistance, $\text{W m}^{-2} \text{K}^{-1}$
u	flow velocity, m s^{-1}
x_{ch}	characteristic length, m
Γ	removal probability, dimensionless
Φ	contact angle, dimensionless
γ	interfacial energy, J m^{-2}
λ	thermal conductivity, $\text{W m}^{-1} \text{K}^{-1}$
ρ	density, kg m^{-3}

Subscript

ad	adhesion
c	crystal
cap	capillary
chem	chemical
d	deposition
el	electrostatic
f	fouling
l	liquid
p	pressure
r	removal
s	substrate
T	temperature
vdw	Van-der-Waals
τ	shear stress
0	clean

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