Published online www.heatexchanger-fouling.com

MINIMIZATION OF CaSO₄ DEPOSITION THROUGH SURFACE MODIFICATION

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ABSTRACT

Among the various fouling mitigation strategies, surface modification is gaining increased attention due to its environmental compatibility i.e. reduced consumption of potentially harmful fouling inhibitors. One approach is to decrease the surface energy which could give rise to lower adhesive strength of deposited crystals on surfaces. The present work aims at investigating the influence of various novel coatings on the interaction energies between CaSO₄ deposits and modified surfaces. Investigated coatings are i) solvent based, ii) water based, and iii) electroless Ni-P-BN. A systematic set of fouling runs has been conducted under similar operating conditions for all coatings. The experimental results show that the deposition process is strongly affected by altering the surface properties, particularly the electron donor component. Furthermore, the contribution of the Lifshitz-van der Waals energy to the total interaction energy is marginal in comparison to that of the Lewis acid-base energy under the range of operating conditions in this study. Overall, in terms of reduced stickiness of deposits onto the surface, the solvent based coatings performed best.

INTRODUCTION

Fouling of heat transfer surfaces is a chronic problem in many industrial heat exchangers. The associated reduction in heat transfer performance and the higher pumping power often requires shut-down and off-line cleaning. Deposition processes are affected by many parameters, one of which being the surface energy of the substrate material. It has been reported that modified surfaces with reduced surface energy experience less fouling adhesion than the untreated surfaces (Müller-Steinhagen and Zhao, 1997). Therefore, the development of surfaces with low surface energy has attracted increased attention. For this purpose, numerous technologies are available that can be classified as 1) external coatings to the substrate including PTFE, fortified Ni-P-PTFE, silica coatings or nano-coating and 2) embedded coatings such as ion implantation and sputtering. There are now a large number of studies that examined various aspects of these low energy surfaces under different heat transfer modes and for different fouling materials.

Müller-Steinhagen and Zhao (1997) showed that the application of SiF_3^+ implanted surfaces during pool boiling of $CaSO_4$ solutions increases the asymptotic heat transfer coefficient by approximately 77% and 100% in comparison to a bare stainless steel surface. Gao et al. (2006) also investigated carbon steel tubes coated with an implanted layer of nickel and other unspecified metal elements, and other uncoated substrates such as brass, carbon steel and stainless steel. Their results show that for the coated carbon steel tubes the induction period is about twice as long as for the other investigated substrates. For convective heat transfer, similar deposition reduction efficiency has been reported for numerous modified surfaces by Förster and Bohnet (1999) and Zettler et al. (2005).

Despite the tangible experimental progress, there is still no generally valid correlation to predict the effects of dispersive, polar and electron donor surface energy components, and the fouling behaviour (Zettler et al., 2005, Geddert et al., 2007). Experimental results reported to-date do not provide a consistent picture (Wu and Nancollas, 1998; Visser, 2001; Rosmaninho and Melo, 2006). For instance, Visser (2001) showed that increased electron donor component will reduce the deposition of calcium phosphate. There are also several investigations that show opposite results (Wu et al., 1997; Rosmaninho and Melo, 2006).

The present study investigates the effect of interfacial interaction energies on the fouling behaviour of different modified surfaces. Stainless steel substrates are modified by applying i) solvent based nano-coatings, ii) water based nano-coatings, and iii) electroless NI-P-BN coating. Fouling experiments are carried out with calcium sulphate as a foulant during convective heat transfer and constant bulk temperature and concentration. Examination of surface characteristics in terms of surface roughness and the various surface energy components are performed to determine the most influential surface parameters for the investigated coatings.

2. CATEGORIZATION OF INTERMOLECULAR INTERACTION ENERGIES

Adhesion processes are complicated by the fact that they are determined by a combination of forces. When a particle is in contact with a solid surface, several energies are responsible for the strength of adhesion, such as chemical and electrostatic interactions, mechanical interlocking, and diffusion. Based on the DLVO theory (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948), the intermolecular interaction energies between two bodies mainly consist of:

1. The Lifshitz - van der Waals energy (E_{132}^{LW}) , which depends on the geometry and physical/chemical properties of the interacting bodies. The most common interacting geometries for fouling can be approximated as spherical-plate type yielding:

$$\Delta E_{132}^{LW} = -\frac{4\pi H_o^2 R}{H} \left(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_3^{LW}} \right) \left(\sqrt{\gamma_2^{LW}} - \sqrt{\gamma_3^{LW}} \right)$$
(1)

The van der Waals interaction potential is insensitive to variations in electrolyte concentration and pH (Israelachvili, 1991).

2. Electrostatic double layer energy (E_{132}^{EL}): when a solid surface is immersed in a liquid medium, it shows a tendency to establish an electrical charge either by ionization or dissociation of the surface or by adsorption of ions from the solution (Oliveira, 1997). This creates an ionic cloud extending into the solution, which is called the electric double layer. Interactions between these ionic clouds lead to the generation of long-range electrostatic interactions that can be repulsive or attractive, depending on whether interactive surfaces have like or opposite charge, respectively.

$$\Delta E_{132}^{EL} = \pi \varepsilon R \left(\zeta_1^2 + \zeta_2^2 \right) \left[\frac{2\zeta_1 \zeta_2}{\zeta_1^2 + \zeta_2^2} \ln \frac{1 + \exp(-\lambda_D H)}{1 - \exp(-\lambda_D H)} + \right]$$
(2)
$$\ln \{1 - \exp(-2\lambda_D H)\}$$

Later on Van Oss (1994) extended the DLVO theory to include:

3. Lewis acid-base interaction energy (E_{132}^{AB}) : when a solid that has electron donor and electron acceptor capacities is immersed in water (which has strong electron donor and electron acceptor capacity) a strong acid-base attraction will occur (van Oss et al., 1986). Accordingly, the Lewis acid/base interaction energy has a polar character and can be either attractive or repulsive (van Oss, 1994). It is predicted by

$$\Delta E_{132}^{AB} = 2\pi R\lambda \Delta E_{132 (H_o)}^{AB} \exp\left(\frac{H_o - H}{\lambda}\right)$$
(3)

$$\Delta E_{132(H_o)}^{AB} = 2 \begin{pmatrix} \sqrt{\gamma_2^+ \gamma_3^-} + \sqrt{\gamma_1^+ \gamma_3^-} - \sqrt{\gamma_3^+ \gamma_3^-} + \\ \sqrt{\gamma_2^- \gamma_3^+} + \sqrt{\gamma_1^- \gamma_3^+} - \sqrt{\gamma_3^+ \gamma_3^-} - \\ \sqrt{\gamma_1^+ \gamma_2^-} - \sqrt{\gamma_1^- \gamma_2^+} \end{pmatrix}$$
(4)

where λ is the correlation length pertaining to water molecules. For pure water, the value of λ is about 0.2 nm (Oliveira, 1997).

4. Brownian motion (E^{Br}) will bring particles into contact with the surface in question. Adhesion occurs only if the flow of the liquid is not able to provide a shear force strong enough to overcome the attractive forces between the particulate matter and the solid surface. Particles adhering to a surface have two instead of three degrees of freedom as the one perpendicular to the surface is blocked by bonding. Since Brownian motion comprises (1/2 KT_b) per degree of freedom, the corresponding free energy term of a particle adhering to a surface equals 1kT_b.

Thus, the total interaction energy ΔE_{132}^{TOT} between a deposit and a solid surface can be written as the sum of the respective interaction energies (van Oss, 1994; Oliveira, 1997):

$$\Delta E_{132}^{TOT} = \Delta E_{132}^{LW} + \Delta E_{132}^{EL} + \Delta E_{132}^{AB} + \Delta E^{Br}$$
(5)

The electrostatic double layer energy and the Brownian motion do not involve surface energy terms. Furthermore, the electrostatic double layer energy can be considered constant as bulk concentration and pH value were kept constant during the experiments. This assumption is consistent with the results presented by Visser (2001), who assumed that the contribution of electrostatic forces in water is negligible.

Therefore it is plausible to analyze the experimental results based on only the effects of the Lifshitz-van der Waals and Lewis acid-base energies.

$$\Delta E_{132}^{TOT} = \Delta E_{132}^{LW} + \Delta E_{132}^{AB}$$
(6)

By assuming H to be equal to H_o (Wang et al., 2005) ΔE_{132}^{TOT} can be expressed as

$$\frac{\Delta E_{132}^{TOT}}{C} = H_o \left\{ 2 \left(\sqrt{\gamma_2^{LW} \gamma_3^{LW}} + \sqrt{\gamma_1^{LW} \gamma_3^{LW}} - \sqrt{\gamma_1^{LW} \gamma_2^{LW}} - \gamma_3^{LW} \right) \right\} + 2\lambda \left(\sqrt{\gamma_2^* \gamma_3^-} + \sqrt{\gamma_1^+ \gamma_3^-} - \sqrt{\gamma_3^* \gamma_3^-} + \sqrt{\gamma_2^- \gamma_3^+} + \sqrt{\gamma_1^- \gamma_3^+} - \sqrt{\gamma_3^+ \gamma_3^-} - \sqrt{\gamma_1^+ \gamma_2^-} - \sqrt{\gamma_1^- \gamma_2^+} \right)$$
(7)

where $C = 2\pi R$ depends only on the crystal radius and may be considered as a constant value for the present investigation.

3. MATERIAL AND METHODS

3.1 Heat transfer substrates

The heat transfer substrates used in this investigation were all of basic stainless steel of AISI 304 BA (50×59) mm and a wall thickness of 0.3 mm. Different chemicals are coated onto these substrates:

- Solvent based coatings (SB1 SB4): These coatings are prepared by directly dispersing a mixture of various materials (hexagonal boron nitride (BN), aluminum silicate as filler, fluorinated polyethylene wax) in the butylacetate diluted binder (Silicone polyester resin) solution. The main difference between the different SB coatings is the percentage of wax in the coating composites.
- *Water based coating (WB)* is produced by directly dispersing the components (hexagonal boron nitride (BN), titanium oxide (TiO₂) as filler, fluorinated polyethylene wax) in the water.
- *Electroless Nickel-P-BN coating* is supplied by NovoPlan GmbH, Aalen, Germany. The Ni-P-BN coating consists of two layers. The first layer is a 40 μ m of NiP with 7 9% P and the second layer on top of the Ni-P is 10 μ m CNB (NiP with 12-15% boron nitride).

3.2 Contact angle and surface energy determination

The contact angle is an indicator for surface hydrophobicity i.e. a large contact angle corresponds to a hydrophobic surface and vice versa. In this study Drop Shape Analysis (DSA) is utilized to determine the contact angles of the modified surfaces. Prior to the measurements, specimens are ultrasonically cleaned with acetone and subsequently distilled water to remove any contamination from the surfaces. After that, a droplet of a test liquid is placed on the surface under controlled room temperature. The drop image is then recorded with a video camera and the contact angel determined by DSA.

Through contact angle measurements of at least three liquids, i.e. distilled water, diiodomethane and ethylene glycol with known surface tension components at room temperature $(\gamma_3^{LW}, \gamma_3^+ \text{ and } \gamma_3^-)$ as given in Table 1 (consistent with previous results of Good, 1992 and van Oss et al., 1988), and by using the Lewis acid-base approach (Equation 8) it is then possible to determine the surface energy components $(\gamma_2^{LW}, \gamma_2^+ \text{ and } \gamma_2^-)$ of the specimens. The Lewis acid-base approach provides detailed information about the modified surfaces such as interactive forces and the electron donor component:

$$\gamma_3 \cdot (1 + \cos\theta) = 2(\sqrt{\gamma_2^{LW} \cdot \gamma_3^{LW}} + \sqrt{\gamma_2^+ \cdot \gamma_3^-} + \sqrt{\gamma_2^- \cdot \gamma_3^+})$$
(8)

The summary of surface analyses of the various coatings is listed in Table 2, indicating that:

- i. the SB and WB coatings reduce the Lifshitz-van der Waals component (γ_2^{LW}) by 20-46% in comparison to the untreated stainless steel surface. In contrast, a significant increase of approximately 30% has been observed for the Nickel-NI-P-BN coatings.
- ii. the SB and WB coatings enlarge the contact angle significantly with respect to the stainless steel surface, with virtually minor change for the Ni-P-BN coatings,
- iii. the electron donor component (γ_2) is the most distinguishable parameter among the various components of the surface energy.

Liquids	Surface tension components, mNm ⁻¹						
	γ_3^{LW}	γ_3^+	γ_3^-	γ_3			
Water	21.8	25.5	25.5	72.8			
Ethylene glycol	29.0	1.92	47.0	48.0			
Diiodomethane	50.8	0	0	50.8			

Table 1. Surface tension of test liquids.

Table 2. Surface energy properties of the modified and original surfaces.

Surface	Х,	θ,	Surface energy, mNm ⁻¹				
	μm	degree	γ_2^{LW}	γ_2^{AB}	γ_2^+	γ_2^-	
SB1	40	85.2	23.73	0.58	0.01	8.59	
SB2	55	92.9	18.57	0.23	0.001	13.85	
SB3	55	87.4	27.36	0	0	9.26	
SB4	25	86.5	24.3	1.27	0.05	8.17	
WB	55	89.1	27.75	2.39	0.1	14.65	
Ni-P-	50	62	45.55	6.74	0.45	25.3	
BN							
S.S	-	79.5	35.11	0.68	0.03	3.46	

4. EXPERIMENTAL SET-UP AND PROCEDURE

4.1 Experimental test rig

Details of the test rig have been reported by Al-Janabi et al. (2009) and are only briefly described, here. Experiments are performed in a closed loop set-up which consists of two identical test sections operated in parallel. By using a centrifugal pump the solution is pumped from a 47 litres stainless steel tank through a 12 μ m filter to remove any broken crystals and other impurities from the solution which otherwise might act as additional nucleation sites. A computer-controlled data acquisition system is used to record and process all experimental data such as the flow rate, bulk temperature, heat flux, cooling water temperature and surface temperature. Calcium sulphate solution is the working fluid which maintained at constant conditions for all fouling runs of the present investigation. It is prepared by mixing an aqueous calcium nitrate tetrahydrate $(Ca(NO_3)_2 \cdot 4H_2O)$ solution with an aqueous sodium sulphate (Na_2SO_4) solution.

4.2 Clean and fouling heat transfer coefficients

Each individual specimen is first cleaned with toluene remove any contaminations and then mounted to immediately into the test rig. The experiments are started with distilled water until steady-state conditions are reached. During this period, the CaSO₄ solution is separately prepared and heated up to the desired bulk temperature of 40°C. If the surface temperature of specimens and the remaining test conditions are stable for more than 2 hours, then the distilled water is drained and replaced by the test solution. Afterwards the power supply to the test sample is adjusted to the desired value and the data collection started. During the experiments the Ca²⁺ ion concentration is determined by EDTA titration every 2-3 hours and adjusted to a constant value of 4 g/liter by manually adding equimolar calcium nitrate tetrahydrate and sodium sulphate. As soon as the surface temperature of a specimen exceeded the respective value of a clean surface by 25 %, the electrical heating will automatically be switched off. Once the test is finished, all heating lamps are immediately turned off and the control program runs the test rig down automatically and stores all measured data in an output file.

5. RESULTS AND DISCUSSION

5.1 Effect of the interfacial energies on fouling mechanism

The precipitation process depends mainly on parameters such as foulant physicochemical properties, operating conditions and surface characteristics. The foulant physicochemical properties and operating parameters, i.e. supersaturation ratio, bulk temperature, and flow velocity are kept constant for all experiments. Accordingly, it can be assumed that the different observed fouling trends for the various coatings are only a function of the surface properties.

The variation of fouling resistance with time for all modified surfaces (SB, WB, and Ni-P-BN) and for the untreated stainless steel surface is illustrated in Figure 1. A significant reduction in fouling resistance has generally been observed for SB, WB, and Ni-P-BN coated surfaces in comparison to that of the untreated surface. Initially SB and WB coated surfaces behave like the untreated surface, while the Ni-P-BN surface remains free of any deposit during the first five hours.

The important point here, however, is not only the quantitative results but also the qualitative information that is depicted in Figure 1. For the SB coated surface the deposits tended to spall-off the surface after a short period of time, followed by a second deposition process but with a lower fouling rate. The fouling behaviour of Ni-P-BN differs somewhat from that of the SB coating, as a prolonged induction time was observed. Such behaviour has not been observed for the WB coated surface. As a result, for the SB coated surface the final fouling resistance which

reached in this run is much lower than that of WB and untreated surfaces. It is an approximately $2.36 \times 10^{-4} \text{ m}^2 \text{K/W}$ in comparison to $7.6 \times 10^{-4} \text{ m}^2 \text{K/W}$ for WB and untreated surfaces.



Fig. 1 Fouling resistances as a function of time for modified and original surfaces.

The fouling rate is another value that is frequently used to analyse fouling processes. It is taken as the slope of the curve where the fouling resistance increases progressively. Figure 2 demonstrates that SB and Ni-P-BN coated surfaces reduce the initial fouling rate significantly in comparison to the stainless steel surface. Particularly, the SB2 and the Ni-P-BN coated surfaces have an initial fouling rate which is up to 70% lower than that of the stainless steel surface.



Fig. 2 Fouling rate for the different investigated surfaces.

As the physicochemical properties and the operating conditions are kept constant for all fouling runs, the only remaining parameters influencing the deposition process are the interfacial surface energies between the deposits and the modified surfaces. As plotted in Figure 3, the SB and WB coated surfaces reduce the Lifshitz-van der Waals component (γ_2^{LW}) by 20-46 % in comparison to the stainless steel surface. Such reduction causes the Lifshitz-

van der Waals energy (ΔE_{132}^{LW}) to be less attractive than in the case of the stainless steel surface. However, the Ni-P-BN coating increases the ΔE_{132}^{LW} attractive energy while its fouling rate is even lower than that for the other surfaces (SB, WB and stainless steel). This indicates that ΔE_{132}^{LW} is inadequate to interpret the adhesion process.



Fig. 3 Total Lifshitz-van der Waals energy as a function of the Lifshitz-van der Waals energy γ_2^{LW} of the different investigated surfaces.



Fig. 4 Lewis acid-base energy as a function of the electron donor component of the modified surfaces.

To characterise the deposition process based on surface properties, the other interfacial energies such as the Lewis acid-base energy seem to be more relevant. This is because all coatings display a systematic increase in the electron donor component of the surface energy, which in turns corresponds to increased Lewis acid-base energy. Under such circumstances, the surfaces are rather more repulsive than attractive as shown in Figure 4. On the other hand, the total interaction energy depends on the variation of ΔE_{132}^{LW} and ΔE_{132}^{AB} energies (see Equation (7)). The calculated results for individual terms in equation (7) are

plotted in Figure 5. Obviously, the contribution of ΔE_{132}^{AB} to the total interaction energy seems to be dominant. In particular, the influence of ΔE_{132}^{LW} for the various coatings on the total interaction energy is marginal, leaving ΔE_{132}^{AB} (electron donor component) to be the most dominant term.

Based on these results, it can be concluded that an increase in the electron donor component causes ΔE_{132}^{TOT} to increase, which in turn promotes the repulsive interaction energy between the surface and the deposits. This means that lower fouling rates are expected for surfaces having higher electron donor components, as clearly demonstrated in Figure 6. These findings are consistent with those of Visser (2001) who found that an important parameter to reduce calcium phosphate fouling is to increase the electron donor component of the surface energy.



Fig. 5 Influence of Lifshitz-van der Waals and Lewis acidbase energies on the total interaction energy.



Fig. 6 Fouling rate as a function of the total interaction energy for different modified surfaces.

There are, however, several investigations which reported an opposite trend as the above results, i.e. that the deposition rate of calcium phosphate is increased with increasing γ_2^- (Wu et al., 1997; Wu and Nancollas, 1998; Rosmaninho and Melo, 2006). Wu and Nancollas (1998) reported that the effect of the interaction energies between titanium oxide coated surfaces (Anatase and Rutile) and calcium phosphate deposits is due to the high value of the Lewis acid-base and the electrostatic energy. This finding is somehow arguable, since i) the contribution of the electrostatic energy in most cases (especially in aqueous solutions) can be considered as a repulsive interaction energy (Oliveira, 1997) or can be neglected (Visser, 2001), and ii) it was ambiguous how much the contribution of the Lifshitz-van der Waals energy of these coatings to the total interaction energies was. In addition, the observed fouling process of calcium phosphate may not have been a pure crystallization process. This is because the presence of suspended calcium phosphate particles may lead to additional particulate fouling.

For the WB coated surface, in spite of having a higher electron donor component (14.65 mN/m), the fouling rate was found to be higher than the expected trend (see Fig. 6). The weak abrasion resistance of the WB coating which is only about 0.1 fold that of that on the SB based coating may account for this befaviour. Furthermore it was observed that parts of the coating layer flaked off the surface, once the crystals started to deposit. As a consequence, the damaged surface provides additional nucleation sites which result in increased fouling rates. Figure 7 presents a picture of the WB coated surface which was taken after terminating the experiment. The surface has been cleaned with a dilute solution of HCL and then rinsed with distilled water. Although is not clearly visible due to the weak colour contrast of the coating, some spots are indicated by arrows which represent places where the flaking-off has taken place. Similar behaviour is also observed for Ni-P-BN which produced the lowest fouling rate. The adhesion of the coating layer to the substrate is weak which resulted in erosion and oxidization of the substrate stainless steel as depicted in Figure 8. It is not clear why corrosion did not occur on the flaked-off WB surface while it was observed on the flaked-off Ni-P-BN coated surface (Fig. 8). It may be speculated that an electron charge difference may exist between the stainless steel substrate and Ni-P-BN coating which contains significant amounts of Nickel, Boron-Nitride and Phosphor. This hypothesis is supported by the fact that corrosion happened mostly at the interfaces between damaged and undamaged surface coating. It should be pointed out that no sign of corrosion has been observed for untreated stainless steel substrates under similar fouling conditions.



Fig. 7 Water based coated surface after fouling test.

Figure 9 illustrates how the induction time varies with the electron donor component. It can be seen that i) only a marginal variation in induction time occurs if the electron donor component changed only slightly e.g., for SB coatings, and ii) for a significant change of the electron donor components, longer induction times are linked to higher values of γ_2^- . One exception in this Figure is the WB coated surface which shows a shorter induction time while having a higher electron donor component. This relates, as mentioned before, to the flaking-off of the coating layer during the fouling process.



Fig. 8 Ni-P-BN coated surface after fouling test.



Fig. 9 Induction time as a function of electron donor component for modified and original surfaces.

5.2 Characterization of deposits

The analysis of the fouling layer with respect to deposit shape, size and crystal structure is of great interest. Hence, great care has been taken to avoid any damage to the deposit structure. The deposit morphology is determined using a SEM (MIRA-II LMH-IB, with a magnification range between 4 and 1,000,000 times). Figure 10 presents some typical SEM pictures of the SB2, SB3, WB, and Ni-P-BN coated surfaces for a salt concentration of 4 g/liter and a heat flux of 100 kW/m².

Obviously, the structure of deposit is significantly influenced by the type of coating on which the precipitation run has been conducted. The differences, in terms of size and orientation, are distinguishably noticeable. In particular, larger, thicker and horizontally orientated crystals are the main characteristics of the WB coated surface (Figure 10c), while smaller, longer and randomly orientated crystals are typical for SB2, SB3 and Ni-P-BN coated surfaces (Figs

10a, 10b and 10d). In general, the crystals on WB coated surface are harder, and more adherent than those on SB2, SB3 coated surfaces.



Fig. 10 CaSO₄ deposit morphology for SB2, SB3, WB, and electroless Ni-P-BN coated surfaces (SEM pictures 22.36 μm x 22.36 μm)

6. CONCLUSIONS

In this study AISA 304 BA stainless steel surfaces have been modified by different types of coatings (solvent/water based coatings and electroless Ni-P-BN coating). The experimental results show that

- 1. SB (solvent based) nano-coatings reduce the Lifshitzvan der Waals surface energy significantly while no such effect was observed for the Ni-P-BN coating. All coatings cause the electron donor component to increase and consequently increase the Lewis acid-base energy. It can, therefore, be concluded that the contribution of the Lewis acid-base energy to the total interaction energy between calcium sulphate deposits and the modified surfaces exceeds the contribution of the Lifshitz-van der Waals energy which is considered marginal. Surfaces having higher electron donor component produce a higher repulsive energy which causes the adhesion force between the surface and deposits to decrease.
- 2. The WB (water based) coating was unstable to abrasion; the coating layer flaked off the surface during the fouling run. For the Ni-P-BN coatings as well, some corrosion spots have been observed. This prevented further investigation of this coating, despite its higher induction time and low fouling rate.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support of the MEDESOL Project (European project, Contract no. 036986). The first author is also grateful to DAAD,

"German Academic Exchange Service" for a PhD research studentship.

Nomenclature

- Concentration, g/L с
- Distance between a particle and a heat surface, nm Η
- Ho Minimum equilibrium distance between a particle and a heat transfer surface, nm
- k Boltzmann constant, J/K
- ġ Heat flux, W/m^2
- R Particle radius, nm
- Fouling resistance, m² K W⁻¹ R_{f}
- Т Temperature, °C
- Velocity, m/s v
- Х coating layer thickness, mm
- ΔE_{132}^{TOT} Total interaction energy, mN
- ΔE_{132}^{LW} Lifshitz-van der Waals interaction energy, mN
- ΔE_{132}^{AB} Lewis acid-base interaction energy, mN
- ΔE_{132}^{EL} Electrostatic double layer interaction energy, mN
- ΛE^{Br} Brownian motion energy, mN

Greek symbols

- γ^{AB} Lewis acid/base surface energy, mNm⁻¹
- $\stackrel{\prime}{\gamma}^{LW}$ Lifshitz-van der Waals surface energy, mNm⁻¹
- Deposit surface energy, mNm⁻¹ γ_1
- Solid surface energy, mNm⁻¹ γ_2
- Water surface tension, mNm⁻¹ γ3
- Electron donor component of surface energy, mNm⁻¹ γ^{-}
- γ^+ Electron acceptor component of surface energy, mNm⁻¹
- θ Contact angle, degree
- Electrical permittivity of the solution, CV⁻¹m⁻¹ З
- $\lambda_{\rm D}$ Debye length, nm
- λ correlation length pertaining to water molecules, nm
- Zeta potential of the particular, mV ζ1
- Zeta potential of the surface, mV ζ2

Subscript

- b bulk
- surface s

Abbreviations

- Boron Nitride BN
- DSA Drop Shape Analysis
- Ethylene-Diamine-Tetra-Acetic Acid **EDTA**
- PTFE Polytetrafluoro Ethylene
- SB Solvent based coated surface
- SEM Scanning Electron Microscope
- S.S stainless steel
- WB Water based coated surface

REFERENCES

Al-Janabi, A., Malayeri, R.M., and Müller-Steinhagen, H., 2009, Experimental investigation of crystallization fouling of grooved stainless steel surfaces during convective heat transfer. *Heat Transfer Engineering*, Vol. (30), pp. 832-839.

Derjaguin, B. V., and Landau, L., 1941, Acta Physicochem, URSS, Vol. 14, pp. 633-662.

Förster, M., and Bohnet, M., 1999, Influence of the interfacial free energy crystal/heat transfer surface on the induction period during fouling, *International Journal of Thermal Science*, Vol. 38, pp. 944-954.

Gao, M., Sun, F., Shi, Z., Lei, S., and Niu, Z., 2006, Experimental research and theoretical analysis of antifouling characteristics on the surface of Ni-based implanted tube, *International Communications in Heat and Mass Transfer*, Vol. 33, pp. 1115-1121.

Geddert, T., Kipp, S., Augustin, W., and Scholl, S., 2007, Influence of different surface materials on nucleation and crystal growth in heat exchangers, *proceeding*, *7th International Heat Exchanger Fouling and Cleaning*, Tomar, Portugal.

Good, R. J., 1992, Contact angle, wetting and adhesion, a critical review, *Journal of Adhesion Science Technology*, Vol. 6, pp. 1269-1302.

Israelachvili, J. N., 1991, *Intermolecular and Surface Forces*, 2nd adition, California, USA.

Müller-Steinhagen, H., and Zhao, Q., 1997, Investigation of low fouling surface alloys made by ion implantation technology, *Chemical Engineering Science*, Vol. 52, pp. 3321-3332.

Müller-Steinhagen, H., Zhao, Q., and Reiss, M., 1997, Ion implantation-a new method of preparing low fouling metal surfaces, *Engineering Foundation Conference on Understanding Heat Exchanger Fouling and Its Mitigation*, Lucca, Italy.

Oliveira, R., 1997, Understanding adhesion: a means for preventing fouling, *Experimental Thermal and Fluid Science*, Vol. 14, pp. 316-322.

Rosmaninho, R., Roch, F., Rizzo, G., Müller-Steinhagen, H., and Melo, L. F., 2007, Calcium phosphate fouling on TiN-coated stainless steel surfaces: role of ions and particles, *Chemical Engineering Science*, Vol. 62, pp. 3821-3831.

Rosmaninho, R., and Melo, L. F., 2006, Calcium phosphate deposition from simulated milk ultrafiltrate on different stainless steel-based surfaces, *International Dairy Journal*, Vol. 16, pp. 81–87.

van Oss, C. J., 1994, *Interfacial forces in aqueous media*, Marcel Dekker, New York.

van Oss, C. J., Good, R. J., and Chaundhury, M. K., 1986, The role of van der Waals forces and hydrogen bonds in 'hydrophobic interactions' between biopolymers and low energy surfaces, *Journal of Colloid Interface Science*, Vol. 111, pp. 378-390.

van Oss, C. J., Good, R. J., Chaundhury, M. K., 1988, Additive and non additive surface-tension components and the interpretation of contact angles, *Langmuir* 4, pp. 884-891.

Verwey, E. J. W., and Overbeek, J. Th. G., 1948, *Theory of the stability of lyophobic colloids*.

Visser, H., 2001, Improvement of construction materials used in the food industry to lengthen processing

time-a new European project (MODSTEEL), *Proceeding*, 4th International Conference on Heat Exchanger Fouling and Fundamental Approaches and Technical Solutions, Davos, Switzerland 3-10.

Wang, C., Zhao, O., and Liu, Y. L., 2005, Bacterial adhesion mechanism by thermodynamic approach. Proceedings of International Federation for Medical and Biological Engineering - 3^{rd} European Medical & Biological Engineering Conference, 11, 1508.

Wu, W. and Nancollas, G. H., 1998, Kinetics of heterogeneous nucleation of calcium phosphate on anatase and rutile surfaces, *Journal of Colloids and Interface Scienc*, Vol. 199, pp. 206-211.

Wu, W., Zuang, H., and Nancollas, G. H., 1997, Heterogeneous nucleation of calcium phosphate on solid surfaces in aqueous solution, *Journal of Biomedical Materials Research*, Vol. 35, pp. 93–97.

Zettler, H., Weiß, M., Zhao, Q., and Müller-Steinhagen, H., 2005, Influence of surface properties and characteristics on fouling in plate heat exchangers, *Heat Transfer Engineering*, Vol. 26, pp. 3-17.