1. Introduction

Heat exchange is typically used as a unit operation for many processes and products in various industries, such as food, textile, petroleum, chemical and pharmaceutical (Müller-Steinhagen et al. 1993; Bohnet 1987). Hereby, liquids are applied as heat carriers or product streams which often contain certain amounts of suspended, dissolved or particulate materials of diverse species (Zhao and Chen 2013). Heat exchanger surfaces often provide advantageous conditions for these materials to adhere and form stable deposits, which in general is referred to as fouling (Zettler and Müller-Steinhagen 2005). Typically, these fouling deposits possess inferior thermal conductivity which can impair the heat exchanger efficiency significantly (Müller-Steinhagen and Zettler 2011). Additionally, these deposits can narrow the cross sectional area and as a consequence can lead to conditions ranging from pressure-loss augmentation to partial or total blockage, which in worst cases results in process shutdown (Bohnet 1987).

Since 1945 (Somerscales 1990), there has been scientific research on mitigating fouling. However, it is not entirely understood how biological, physical and chemical processes lead to the deposit formation, for which more detailed information is required (Bohnet 1987; Zhao and Chen 2013).

Modern anti-fouling strategies have focused on increasing the duration of the induction period. This is often done by decreasing the adhesive propensities of the interacting constituents (Förster et al. 2000). Modifying the surface free energy (SFE) parameters of heat exchanger surfaces is one way to successfully mitigate fouling and adhesive propensities (Augustin et al. 1999; Müller-Steinhagen et al. 2005; Al-Janabi and Malayeri 2015). Hereby, applying diamond-like carbon (DLC) coatings to heat exchanger surfaces proved to be beneficial in various fouling experiments (Augustin et al. 2005; Rosmaninho and Melo 2007). The SFE property of DLC coatings can be modified by doping of various elements in the PACVD (Plasma assisted chemical vapor deposition) process to obtain the desired SFE condition (Grischke et al. 1995).

Heat exchanger surfaces are often subjected to frequent and severe chemical and thermal cleaning treatments as a direct cause of fouling occurrence. Geddert et al. (2011) showed how diverse cleaning treatments can alter SFE parameters of DLC surfaces. For this reason, it was investigated to which extent SFE properties of modified heat exchanger surfaces can alter, when subjected to typical cleaning treatments. In relation to these findings, it was tested if a conditioning procedure can set a constant state of SFE properties and withstand further cleaning or thermal treatments.

A new approach is introduced, including conditioning for fouling determination. Here, it is investigated how the fouling development of a new modified heat exchanger surface performs, compared to that after conditioning and after consecutive fouling experiments. The intent is to correlate definite SFE parameters to fouling propensities. Additionally, surface characterization tests were performed before and after each treatment to examine the stability of the modified surfaces. The crystallization fouling experiments were performed in a plate type heat exchanger with electrical heating. Calcium sulfate was applied as a model contaminant for fouling determination provided as dissolved ions at supersaturated condition in the liquid solution..

In the end, molecular interactions will be considered to assess the adhesion propensities. It is referred to a plat-sphere model to evaluate the interactions between solid crystals and DLC surfaces immersed in water. Here, it is discussed how the molecular interaction of the key constituents contribute to adhesion propensities. Special attention is given to polar interaction energies, since in polar media such as water, these are often key factors determining adhesion (van Oss 2008a). The energetic contemplation from classical nucleation theory is evaluated for homogeneous nucleation in order to determine the dimension of critical radii for crystal particle formation. Therefore, the SFE of a $CaSO_4$-$2H_2O$ was evaluated by contact angle measurement and compared to literature data. Herewith, it could be assessed how the modification of SFE parameter influenced the work of adhesion by applying the model Hamaker (1937). Afterwards, the relevant distances between particle and wall are considered and the dominating forces determined. Recently, Al-Janabi and Malayeri (2015) developed a new fouling criterion considering SFE parameters as most dominant for fouling mitigation. This criterion is assessed by evaluating two different crystal data to the investigated fouling procedure. A summarized conclusion is presented, stating how molecular interaction can lead to repulsive particle-wall interactions between crystal particles and modified heat exchanger surfaces in the given case of $CaSO_4$ fouling.

2. Fouling on heat exchanger surfaces

In general the term fouling refers to the accumulation of unwanted deposits on heat exchanger surfaces (Bott 1995). The various materials depositing on the surface may be of inorganic or organic character. Deposits of inorganic character could be particles of dust and grit, waterborne mud and silts, calcium and magnesium salts or iron oxide. Organic deposits could be biological substances (e.g. bacteria, fungi and algae), oils, waxes and greases, heavy organic deposits (e.g. polymers), tars or carbon. Often depositing materials originate from liquids or gases used as heat carriers, but may also be chemically generated involving the wall or heat transfer equipment. (Bott 1995; *VDI-Wärmeatlas* 2013, C4)

It is crucial to identify the deposited material before addressing the fouling issue. A classification in crystallization, particulate, chemical reaction, corrosion and bio-fouling is appropriate to distinguish by source and mechanism (Bott 1995; Epstein 1983b; Palen 1986). Identifying the mechanism of fouling enables appropriate countermeasure strategies. Often though, fouling occurs in combinations of various mechanisms, such as in milk processing in the dairy industry. Here, Boxler et al. (2014) report fouling to occur in a combination of particulate milk proteins and dissolved calcium-minerals. Additionally, fouling may occur by a single mechanism although influenced by various fouling components, such as mixed salt crystallization (Helalizadeh et al. 2000). Therefore, a lot of research has been done on the fundamental understanding of the fouling process, aiming at possible counteractions to successfully avoid fouling.

Numerous industrial fields, e.g. food, chemical, oil or electrical generation, rely on heat exchanger apparatus and predictions indicate their demand to grow in the future (Garrett-Price et al. 1985). More than 90% of heat exchanger processes are prone to fouling (Müller-Steinhagen et al. 1993; Garrett-Price et al. 1985; Melo et al. 1988). The fouling layer covering the heat exchanger surface causes an additional thermal resistance, hence decreasing the thermal efficiency of the apparatus. The conductivities of stable fouling layers are often low compared to stainless steel (e.g. $\lambda(CaSO_4) = 0.6 - 2.3\ Wm^{-1}K^{-1}$) (*VDI-Wärmeatlas* 2013, C4). This causes a reduction of thermal efficiency even at small layer thicknesses. In convective heat exchangers, fouling narrows the cross sectional flow area resulting in increased pressure-drops, thus increasing electrical energy demand (Bott 1995).

Another factor raising operating costs is the need for cleaning and maintenance. Cleaning is crucial to avoid possible product contamination and process shutdown as well as maintain process efficiency and product quality. Thus, industries require additional investments for detergents, cleaning equipment and operating costs. The cleaning process causes loss of production time, or alternatively, in cases of redundant operating mode of two identical heat exchangers, raises investment costs (Bott 1995). Oversizing the heat exchanger surface in the anticipation of fouling increases investment costs for the heat exchanger (Melo et al. 1988). Further, additional heat transfer area may lead to unfavorable partial load processing. Emergency shutdown of plants as a direct result from fouling can be particularly expensive. Costs directly related to fouling occurrences are estimated to be 0.15 - 0.25% of the GDP of an industrialized country (Melo et al. 1988; Garrett-Price et al. 1985; Müller-Steinhagen et al. 1993).

According to Epstein (1983b) the general mechanism of fouling is classified in five consecutive steps:

- **Initiation**

The initiation phase is a time period lasting from the beginning of a process or experiment until there is noticeable fouling on the heat transfer surface. In this period the fouling-causing components are brought into contact with the heat transfer surface. Appreciable changes in heat transfer and pressure drop cannot be observed. However, the conditions of the surface can change, e.g. through nucleation in crystallization fouling or immobilization of microorganism in bio-fouling. The range of this period depends on many factors such as operational parameters and heat exchanger design. Decisive operating parameters can be bulk and wall temperature, heat flux, flow velocity, Reynolds number and concentration of the fouling causing component. Aspects of design include energetic and topographic surface properties.

- **Transport**

The fouling components must be transported from high concentration regions of the bulk flow to the lower concentration near the wall. The fouling causing components can be particles, ions, oxygen or crucial reactants. For fouling causing deposits such as sub-micrometer particles, ions or molecules the transport is of a diffusive nature. At relatively low fluid velocities in horizontal tubes and relatively large and dense particles, gravity may control the core deposition process.

- **Attachment**

The fouling layer material adheres to the heat exchanger surface, or assembles into already attached material and reacts with neighboring elements. The process of attachment combines adherence and layer growth. If a chemical reaction occurs, it has to be distinguished from reaction- or diffusion-controlled attachment. If no reaction occurs the velocity of diffusion or sedimentation transport becomes the key factor of the attachment rate.

- **Removal**

In the presence of fluid flow and depending upon the build-up of the fouling layer´s shear resistance, a wear-off, erosion or dissolution may occur. Here, induction and growth phase often originate from the superimposed effect of adhesive forces facing the applied fluidic stress.

- **Aging**

Immediately after deposition of a fouling layer, changes of its physical and chemical properties such as shear resistance, density, conductivity, porosity or elemental composition may occur, which in general is referred to as aging. Aging can be morphological and/or chemical. Morphology predicates the change in crystal structure and may be thermally activated. A chemical reaction can vary the composition of the deposit. The scope of this variation strongly depends on the depositing material as well as on the process conditions.

The following discussion is limited to crystallization fouling of calcium sulfate ($CaSO_4$). This substance acts as a model system to investigate the fouling behavior of different substrates. Two major reasons led to chose for $CaSO_4$ as model contaminant. First, calcium sulfate and its hydrates are well explored and documented (Gmelin, 1961), as well as explored in many research studies concerning fouling behavior (Al-Janabi, 2015). Second, its´ solubility equilibrium is strongly temperature dependant while minor affected by pH. Additionally, it is possible to realize great supersaturation in the solution (Gmelin, 1961).

2.1. Crystallization fouling

In a survey by Müller-Steinhagen et al. (1993) on the occurrence of different fouling species at 1,000 New Zealand enterprises, crystallization fouling was identified as the second most frequent fouling mechanism with an incidence of 24.5%. The predominant crystals depositing in water coolers are $CaSO_4$ and $CaCO_3$ (Epstein 1983b).

Crystallization is a transformation process of one or more materials, from the amorphous-solid, liquid or gaseous state into a crystal state (Mersmann et al. 2005). Supersaturation is the driving force to convert the dissolved material to a crystalline state. It may be established by either reduction of the solvent, e.g. evaporation, or varying the solution equilibrium by shifting the driving temperature and/or the pH-value (Augustin 1993). Whenever a liquid system supersaturates it strives for thermodynamic equilibrium by establishing a solid crystal phase, which is referred to as nucleation (Fu et al. 2012). For inverse soluble salts like $CaSO_4$ and $CaCO_3$ supersaturation is established via heating of the solution, whereas for cooling crystallization a temperature reduction is required (Mullin 2001). The entire process of crystallization may be divided into two major subjects, nucleation and crystal growth.

2.1.1 Nucleation

To initiate crystallization, the condition of supersaturation alone is insufficient to cause a system to crystallize. In the solution a number of minute solid bodies, embryos, seeds or nuclei must exist in order to act as centers of crystallization. The nucleation may be caused either by a spontaneous process, or, e.g. in the presence of foreign particles, may be induced artificially. Mullin (2001) describes two types of nucleation: primary and secondary. Primary nucleation occurs in systems without prior crystalline matter. Secondary nucleation occurs in the vicinity of pre-existing crystals in the supersaturated system. Further, primary nucleation is distinguished in homogenous (spontaneous) nucleation, independent from foreign particles caused by nuclei in the solution and heterogeneous nucleation caused by foreign particles, such as a solid substrate. (Mullin 2001; Matz 1970)

The formation of a stable nucleus is quite difficult, since the constituent molecules/ions need to coagulate, resist the tendency to re-dissolve and become oriented in a crystal lattice at the same time. Therefore, Mullin (2001) discusses a gradual cluster build-up of the various molecules which form a stable nucleus beyond a critical cluster size. For this matter Mullin referred to a similar behavior observed in biological growth processes.

The classical theory of nucleation is based on the matter of vapor condensation to a liquid surface, which may be extended to crystallization from melts and solutions (Gibbs et al. 1928; Volmer 1939; Becker and Döring 1935; Mullin 2001; Nielsen and Söhnel 1971). An energetic approach to describe the nucleation is the consideration of a critical spherical nucleus with a critical radius $r_{crit.}$. To form a stable primary homogeneous nucleus the critical excess free energy $\Delta G_{crit.}$ needs to be invested to induce the phase change. Mullin (2001) defined the total excess free energy ΔG, between a small particle of solute and its surrounding medium to be equal to the sum of ΔG_S and ΔG_V. Here, ΔG_S is the excess free energy between the surface of the particle and the bulk of the particle and needs to be invested to create a new interface. The volume excess free energy ΔG_V, is the excess free energy between a very large particle ($r = \infty$) and the solute in solution and is set free to realize the phase change, see Fig. 2.1 and Eq. 2.1.1-1. (Mullin 2001)

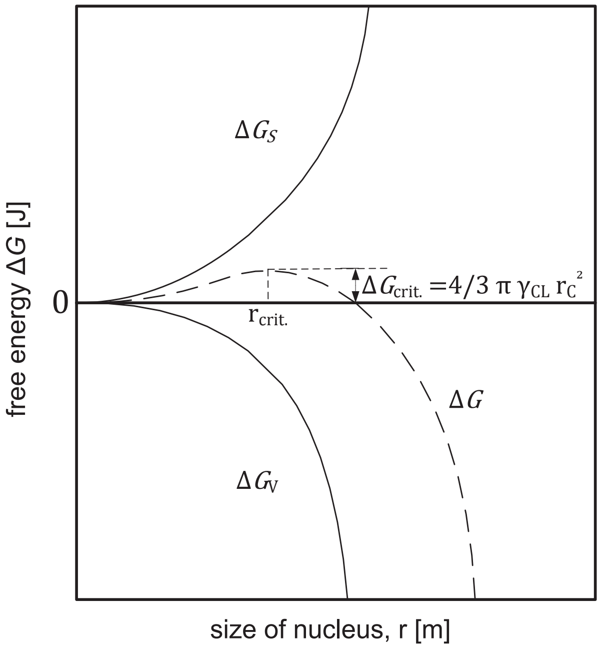

Fig. 2.1 Gibbs free energy over nucleus size (Mullin 2001)

$$\Delta G = \Delta G_V + \Delta G_S = -\frac{4}{3}\pi r^3 \frac{\Delta\mu_{CL}}{\upsilon} + 4\pi r^2 \gamma_{CL} \qquad (2.2.1\text{-}1)$$

Here, $\frac{\Delta\mu_{CL}}{\upsilon}$ describes the free energy change per unit volume over the change of the chemical potential $\Delta\mu_{CL}$ between nucleus and bulk over the molecular volume ($\upsilon = \frac{M}{\varrho N_A}$ [m^3]), and γ_{CL} is the interfacial energy between nucleus and fluid bulk phase. Considering Fig. 2.1 ΔG passes through a maximum, which may be identified by setting $d\Delta G/dr = 0$, resulting in the critical radius for a spherical nucleus. (Mullin 2001; Uhlmann and Chalmers 1965; Fu et al. 2012; Nielsen and Söhnel 1971)

$$\frac{d\Delta G}{dr} = 8\pi r\,\gamma_{CL} - 4\pi r^2 \frac{\Delta\mu_{CL}}{\upsilon} = 0; \qquad r_{crit.} = \frac{2\,\gamma_{CL}\,\upsilon}{\Delta\mu_{CL}} \qquad (2.1.1\text{-}2)$$

Inserting $r_{crit.}$ in Eq. 2.1.1-1 results in the critical excess free energy, see Eq. 2.1.1-3:

$$\Delta G_{crit.,hom.} = \frac{16}{3}\frac{\pi\,{\gamma_{CL}}^3\,\upsilon^2}{{\Delta\mu_{CL}}^2} = \frac{4}{3}\,\pi\,\gamma_{CL}\,{r_{crit.}}^2 \qquad (2.1.1\text{-}3)$$

The process of building a stable crystalline lattice results in a reduction of the Gibbs´ free energy for the newly formed particle in order to obtain thermodynamic equilibrium (Fu et al. 2012). Establishing a stable crystalline lattice in a supersaturated system depends on its size; particles $r < r_{crit.}$ may dissolve since this is the only possibility for particles to reduce their free energy. Therefore, $r_{crit.}$ is the minimum size of a stable nucleus and consequently particles with $r \geq r_{crit.}$ will start to grow. (Uhlmann and Chalmers 1965; Matz 1970; Fu et al. 2012)

The rate of homogeneous nucleation per time and volume may be expressed via an Arrhenius reaction velocity equation Fu et al. (2012):

$$J_{hom.} = C_1\,exp\left(\frac{-\Delta G}{k_B T}\right), \text{ with } C_1 = \left(\frac{4\pi}{3\upsilon}\right)^{\frac{1}{3}} \left(\frac{\gamma_{CL}}{k_B T}\right)^{\frac{1}{2}} D\,c_e N_A \qquad (2.1.1\text{-}4)$$

where k_B is the Boltzmann constant (1.3805·10^{-23} J K^{-1}), T is the bulk temperature and C_1 is a kinetic pre-exponential factor [m^{-3} s^{-1}], D the diffusion coefficient [m^2 s^{-1}] and N_A is Avogadro´s constant. Introducing the term c^* as the ratio of bulk solution concentration c_b to that at equilibrium state c_e, results according to (Fu et al. 2012) in:

$$J_{hom.} = C_1\,exp\left[-\frac{16\pi}{3}\,\frac{{\gamma_{CL}}^3\upsilon^2}{{k_B}^3 T^3 ln^2 c^*}\right] \qquad (2.1.1\text{-}5)$$