A CRITICAL REVIEW OF BASIC CRYSTALLOGRAPHY TO SALT CRYSTALLIZATION FOULING IN HEAT EXCHANGERS

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ABSTRACT

Fouling formation on heat exchanger surfaces due to crystallization of inverse solubility salts is one of the fundamental problems in process industries. Despite numerous studies carried out in recent years, comprehensive understanding of crystallization fouling mechanism remains a challenge to chemical engineers. In this review, we first focus on the basic crystallography during deposition of calcium salts, paying attention to crystal structures, crystal forms as well as nucleation and the subsequent crystal growth process. We then endeavor to relate a number of factors to fouling rate, which may be classified into 3 categories, i.e. solution composition, operating parameters and heat exchanger surface characteristics. Each aspect is discussed from crystallization viewpoint (science) and possible industrial applications (practice). Combining the basic knowledge of crystallography with the information from experimental investigations, several fouling mitigation methods have also been described which may reduce fouling. It is hoped that some of the ideas discussed here will provide possible economic and environmental benefits. Finally, we also try to throw some light on the future direction for research.

INTRODUCTION

Mineral scale formation or fouling is a process in which unwanted mineral materials, originally dissolved in process fluids, are deposited on heat transfer surfaces (Helalizadeh et al., 2000). It is a recurring problem in process plants, water heat exchangers, sea water desalination plants, household equipment and steam generation units (Kazi et al., 2010). Fouling of heat exchangers is an issue because it creates an additional barrier to the transmission of heat, increases pressure drop and promotes corrosion of tube material. These effects can rapidly reduce the heat transfer efficiency and narrow down the operating service life. Therefore, fouling has long been considered as a serious constraint in the design and operation of heat transfer equipment.

Several studies have been undertaken to determine fouling-related costs in industrialized countries (Bansal et al., 2008). A more recent investigation shows that by 2000, the cost of fouling in most industrialized countries rises to 0.25 to 0.30 percent of the gross national product (GNP) (ESDU Item 00016, 2000). For China, however, the cost on fouling is expected to be even higher due to its unique situation, where consumptions in markets are over-riding factors for production. For instance, the sugar industry in Guangxi province, which takes up more than 60% of overall sugar production in China, is suffering a severe fouling problem in heat exchangers and evaporators. The fouling rate is so rapid that the scale thickness on the heat exchanger surface can grow 0.5~1 mm per day, which leads to a dramatic drop (over 30%) in heat transfer efficiency. Fig. 1 shows the surface morphology of fouling layer obtained from heat exchanger surface. This severe problem in exchanger equipments has already blocked the normal industrial production, and the corresponding cost in fouling in total domestic industry is more than 10 billion CNY every year (Xiang and Lin, 2011).
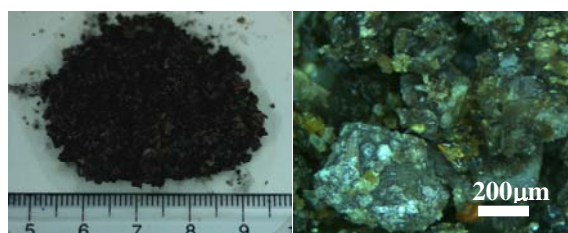

Fig. 1. Macroscopic (left) and microscopic (right) images of the deposit obtained from the heat exchanger in Liangci sugar manufacturing co. ltd.

According to Bott (1990), six categories of fouling can be classified, among which crystallization accounts for over 25% of fouling problems encountered. Crystallization fouling on the heat transfer surfaces is usually caused by the precipitation of inverse solubility salts, which are highly temperature-dependent and require a degree of super-saturation before precipitation occurs. It is widely accepted that the fouling process can be divided into two periods, i.e. induction and fouling period (Förster et al., 1999). Within the induction period, the formation of stable nuclei and the crystal growth take place at the heat transfer surface. In the succeeding fouling period an increase of fouling resistance

versus time can be measured due to the initiated formation of a compact fouling layer. The mechanism of crystallization fouling relates to many subjects, such as momentum, heat and mass transfer, chemical kinetics, materials science, etc (Helalizadeh et al., 2005). Many researchers and industrialists have been challenged by the scaling problems. They have witnessed the complexity and the difficulty in this area (Heberle et al., 2002; Bansal et al., 2005; and Müller-Steinhagen, 1993).

In this paper, we start with an overall introduction of the basic crystallography of salts fouling in heat exchangers, elaborate on a number of factors affecting fouling rate from a crystallization viewpoint, and then we list numerous effective strategies to mitigate fouling inspired from the theoretical studies. We aim at building up a general idea between crystallization investigations and industrial applications in this field. We also endeavor to generate some new interests in this field and to elaborate on some possible new directions for research.

BASIC CRYSTALLOGRAPHY OF SALT FOULING

Crystallization has been studied for many years. Therefore, an immense body of information is available in this area. It is beneficial to first briefly discuss the basic crystallography of calcium salts which are the main types of mineral scale in heat exchangers.

Crystal structure
Calcium carbonate

Calcium carbonate ($CaCO_3$), a mineral abundantly found in nature and a predominant component of hard and tenacious fouling, possesses three anhydrous polymorphs: calcite, aragonite and vaterite (Tai and Chen, 1998). The crystal structures and their corresponding information are shown in Fig. 2 (Morse et al., 2007; Kamhi, 1963).
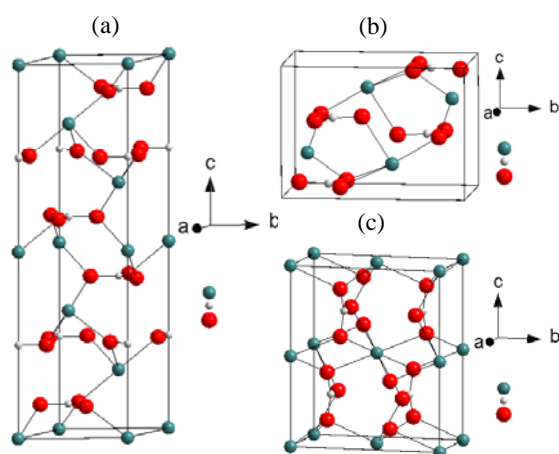

Fig. 2. Crystal structure of (a) calcite (b) aragonite and (c) vaterite. C, O and Ca atoms are represented by grey, red and dark green spheres, respectively.

It has been reported that calcite is the most thermodynamically stable form of $CaCO_3$, and vaterite is the least stable form (Wray, 1957). Calcite is usually formed at room temperature and has a hexagonal crystal form, while aragonite belongs to orthorhombic system and irreversibly changes to calcite under the condition of being

heated in dry air to around 400°C. The transformation rate increases with increasing temperature. When aragonite is in contact with water or solutions containing calcium carbonate, transformation may take place even at room temperatures. However, Wang et al. (2011) found an opposite transition phenomenon. In the presence of Zn-C composite coating surface, the morphologies of $CaCO_3$ fouling changed from calcite to aragonite. Vaterite, on the other hand, is metastable and transforms to calcite and aragonite under geological conditions, while it can also be found during high temperature precipitation of calcium carbonate (Reeder, 1990). The physical properties of the two more prevalent crystal polymorphs (i.e., calcite and aragonite) were given by Lepley (1984), but corresponding values for vaterite were not included. In order to assess the fouling propensity by carbonates, Bott (1995) tabulated the solubility and dissociation constants for calcium carbonate and for carbonic acids. Kemmer (1988) provided data showing the distribution of CO_3^{2-} related ions and CO_2 gas in solution as a function of pH.

Calcium sulfate

Calcium sulfate is one of the most commonly encountered scale forming materials. As a solid, calcium sulfate crystallizing from an aqueous solution appears in three forms: Gypsum ($CaSO_4 \cdot 2H_2O$), calcium sulfate hemihydrate ($CaSO_4 \cdot 0.5H_2O$) and anhydrites ($CaSO_4$) (Hasson and Zahavi, 1970). The crystal structures and their corresponding information are shown in Fig. 3 (Lager, 1984).
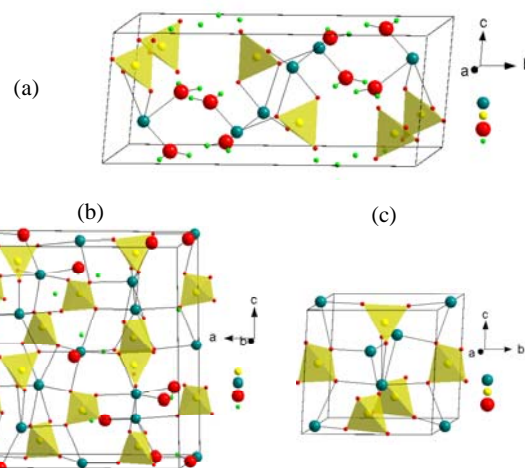

Fig. 3. Crystal structure of (a) Gypsum (b) calcium sulfate hemihydrate and (c) anhydrite. H, S, O and Ca atoms are represented by green, yellow, red and dark green spheres, respectively. The yellow polyhedra represent SO_4^{2-} group.

Gypsum is both the starting material before dehydration and the final product after rehydration and is usually precipitated in the range of 40-98°C, while anhydrite and hemihydrate are the species likely to precipitate above 98°C (Sheikholeslami and Ng, 2001). Considerable attention has been given to the various forms of calcium sulfate crystallizing from aqueous solution as

affected by temperature, pH and impurities (Austin et al., 1975; Vetter and Phillips, 1970; Nancollas et al., 1979). A large amount of solubility work has also been performed on gypsum and anhydrite, with accurate K_{sp} correlations adjusted for the appropriate temperature (Dundon and JR., 1923; Marshall and Slusher, 1968; Guan et al., 2010). Investigations indicated that the solubility of calcium sulfate was strongly affected by the presence and concentration of other ions in the system; the water quality greatly affected induction times and precipitation of calcium sulfate.

Coprecipitation of CaCO₃ and CaSO₄

During last 20th century, very little attention had been paid to the coprecipitation phenomenon (Hasson 1981, 1999). Now, with the aid of developed experimental and analytical instruments, more studies have been broadened to this area (Höfling et al., 2004). For the composite fouling of $CaCO_3$ and $CaSO_4$, some qualitative investigations indicated that $CaSO_4$ crystals tend to grow on the surface of $CaCO_3$ (Morse and Knudsen, 1977; Hasson and Karmon, 1984). The presence of $CaSO_4$ weakened the $CaCO_3$ scale, making it less tenacious and freely moving in the solution, while the coprecipitated $CaSO_4$ were found to be far more adherent than pure $CaSO_4$ deposits (Bramson et al., 1996).

Crystal form

The morphology of real crystals is determined by two factors: the internal elements, related to the periodicity and anisotropy of chemical bonds that constitutes the crystal structures (i.e. thermodynamics), and the external elements involved in the growth parameters (i.e. kinetics) (Sunagawa, 2005).

Under equilibrium conditions, the micro- and macro shape of single crystals is determined by the intrinsic crystal structures, and the ideal crystal shape is a reflection of the replication and amplification of unit cell. However, the growth morphology often varies significantly from the ideal morphology which is testified the fact that the final shape is highly sensitive to the growth conditions (Piana et al., 2005). Generally speaking, the growth rate of a crystal face is usually directly related to its surface energy if the same growth mechanism acts on each face. Faces that have high surface energies will grow quickly and tend to vanish in the final shape, while faces with low surface energies will grow slowly and determine the final shape. This theory assumes that the equilibrium morphology of a crystal is defined by its minimum surface free energy, which is also known as the Wulff's rule (1901):

$$\sum_i \gamma_i A_i = minimum \qquad (1)$$

where γ_i is the surface energy of i and A_i is the surface area of i.

Generally, the surface energy γ results from its unsaturated dangling bonds, minus the interaction of the crystal surface with the surrounding medium, such as salvation or hydration in the case of a liquid medium. Hence, the equilibrium morphology of a crystal can be tuned by changing the surface energy of the surface, and the change of the surface energy $\Delta\gamma$ with a solvent or additive

can be estimated from its molar free energy of adsorption ΔE_{ads},

$$\Delta\gamma = \frac{\Delta E_{ads}}{N_A A_{mol}} \qquad (2)$$

where N_A is the Avogadro's number and A_{mol} is the cross section per molecule.

According to Wulff's rule, if we can change the surface energy in a face-selective way, the equilibrium shape of crystals will be tuned predictably. For this, a wide variety of inorganic ions or organic additives have been employed in the morphosynthesis of calcium salts (Altay et al., 2007; Feng et al., 2000; Xie et al., 2005). Fig. 4 shows a schematic sequence of the change of the equilibrium shape of calcite crystal due to the lowering of the surface energy of the charged high-energy (001) face (Meldrum and Cölfen, 2008). Luo et al. (2008) also observed the exposed high energy (001) and (012) faces of $CaCO_3$ by using a defined solid surface template.
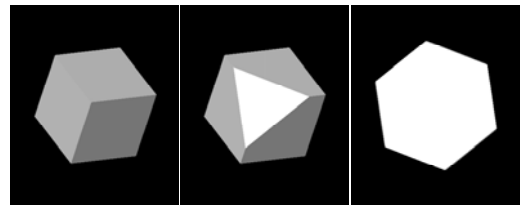

Fig. 4 Schematic show of the morphology evolution of calcite crystals from rhombus shape to a hexagonal platelet by face-selective interface energy decrease of the two {001} faces. {104} faces and {001} faces are in grey and white, respectively.

Crystallization fouling mechanism

Crystallization lies at the heart of many natural and technological processes, from the production of pharmaceuticals and nano-materials to the formation of bones and teeth, frost heave, and scale deposition (Fiona and Richard, 2009). Although crystallization is the underlying mechanism for scale formation, the process of deposition in heat exchangers is quite different from that in industrial crystallizers (Sheikholeslami, 2003). According to previous researches, crystallization fouling occurs when salts dissolved in the process fluid crystallize on a heat transfer surface. Three basic steps are necessary for crystallization to occur: attainment of supersaturation, formation of nuclei and growth of crystals at the heat exchanger surface (Mwaba et al., 2005).

Attainment of supersaturation

Supersaturation, caused by the temperature difference between heat transfer wall and the bulk, is the main driving force for soluble salts crystallizing from solution. Here, the degree of supersaturation, *S*, is often described as a ratio of the bulk concentration to the saturation concentration; and the degree of driving force, $\Delta\mu$, can be generalized by the difference of the chemical potentials between solid and liquid phases. Therefore, a generalized driving force for crystallization from solution can be expressed as a function of supersaturation (Mullin, 2001),

$$\Delta\mu = k_{B}T\ln(S+1) \tag{3}$$

where k_B is the Bolzman constant, T is the absolute temperature.

In heat transfer equipment supersaturation may be achieved by either evaporating a solution beyond the solubility limit of a dissolved salt or heating a solution containing a dissolved salt of inverse solubility to a level above its solubility temperature. Most of the frequently encountered scaling salts, for example, $CaCO_3$ and $CaSO_4$, exhibit inverse solubility characteristics. A solution of an inverted solubility salt in contact with a hot surface can attain supersaturation by the inverted solubility effect and deposit scale on the hot surface, even when undersaturation conditions prevail in the bulk of the solution. Of course, the surface must be hot enough that can trigger such an effect.

Formation of nuclei

Generally, the condition of supersaturation alone cannot be a sufficient reason for a system to start crystallization. Before crystals can develop there must exist a number of minute solid bodies in the solution, such as embryos, nuclei or seeds, which act as centers of crystallization. Nucleation may occur spontaneously or it may be induced artificially. As shown by the early experiments of Young (1911) and Berkeley (1912), nucleation can often be induced by agitation, mechanical shock, friction and extreme pressures within solutions and melts. Two modes of nucleation are distinguished (primary and secondary) together with several mechanisms. In the case of sparingly soluble salts, primary nucleation is the main mechanism. Primary nucleation can be homogeneous where the crystals are formed without the aid of foreign bodies or surfaces where other substances aid the nucleus formation (Sheikholeslami, 2003).

For homogeneous nucleation, the overall excess free energy, ΔG_{homo}, between a small solid particle of solute (assumed a sphere of radius r for simplicity) and the solute in solution, is equal to the sum of the surface excess free energy, ΔG_S, and the volume excess free energy, ΔG_V, as shown in Eq. (4):

$$\Delta G_{homo} = \Delta G_S + \Delta G_V = 4\pi r^2 \gamma + \frac{4}{3}\pi r^3 \Delta G_v \tag{4}$$

where ΔG_v is the free energy change of the transformation per unit volume and γ is the interfacial tension between the developing crystalline surface and the supersaturated solution (Gibbs, 1948).

The so-called classical theory of homogeneous nucleation utilized the concept of a clustering mechanism of reacting molecules or ions, but they do not agree on the effect of supersaturation on the size of a critical nucleus. However, most experimental investigations discovered that the true homogenous nucleation in solution systems was rarely seen since the production of an impurity-free system was virtually impossible (Teng et al., 1998; Cölfen and Mann, 2003).

For heterogeneous nucleation (Mullin, 2001), the presence of a suitable foreign body or surface can induce nucleation at a relatively low supersaturation, and the

overall Gibbs free energy change ΔG_{hetero} must be less than the corresponding free energy change in homogeneous condition, ΔG_{homo},

$$\Delta G_{hetero} = \varphi \Delta G_{homo} \tag{5}$$

where the factor φ is in the range of 0~1.

To overcome the Gibbs free energy barrier for creating a solid phase, the solution has to remain for a certain time, named delay time or induction time. Here, the induction time, τ, is considerably influenced by the level of supersaturation, state of agitation, presence of impurities and viscosity, which can be described by the following relationship,

$$\ln\tau = C_1 + C_2 \frac{\gamma^3 f(\theta)}{T^3 \cdot (\ln S)^2} \tag{6}$$

where θ is the contact angle of the crystallite on the surface, C_1 and C_2 are constants of the system. From Eq. (6) it can be seen that a long induction period is induced by a low supersaturation level, a low surface temperature and a non-wettable surface. This crystallographic knowledge is also of utmost practical importance in scale control efforts, and has been widely used in anti-fouling treatment to delay the inception of scale precipitation (Yang, 2002; Bansal et al., 2003; Katsifaras and Spanos, 1999).

The classical nucleation theory (including homogenous and heterogeneous), was stemmed from the work of Gibbs (1928), Volmer (1939), developed by Nancollas and Purdie (1964), Zettlemoyer (1969) and Söhnel and Garside (1992). The recent publication by Kashchiev (2000) is noteworthy for its in-depth analyses of the thermodynamics and kinetics of homogeneous and heterogeneous nucleation.

Crystallization fouling process

As soon as stable nuclei, i.e. particles larger than the critical size, have been formed in a supersaturated or supercooled system, they begin to grow into visible deposits. Over the past 30-40 years, efforts have been made to improve the understanding of fouling processes. A number of models have been reported for crystallization fouling by many authors (Hasson, 1962; Reitzer, 1964; Bohnet, 1987; Krause, 1993). Because of the difficulties involved in reproducible measurement of the fouling resistance and the complex nature of deposit formation, accurate and detailed mathematical modeling of fouling process is generally difficult. Kern and Seaton (1959) first described the thermal surface fouling in a heat exchanger could be expressed as a net effect of two separate processes:

fouling rate = deposition rate − removal rate (7)

In deposition process, two main steps were involved: transport of ions from the bulk to the liquid-crystal interface and integration of ions into the crystal lattice at the surface. Depending on the conditions, crystallization fouling on a heat exchanger surface can be (i) diffusion controlled (i.e. mass transfer between the fluid and heat-transfer surface), (ii) reaction controlled (i.e. crystallization reaction), or a combination of both. These mechanisms, occurring under the influence of different concentration driving forces, can be represented by Eqs. (8) and (9), respectively.

(i) $\dfrac{\mathrm{d}m}{\mathrm{d}t} = k_d A(c - c_i)$ \hfill (8)

(ii) $\dfrac{\mathrm{d}m}{\mathrm{d}t} = k_r A(c_i - c^*)^g$ \hfill (9)

where m is the mass deposited per unit area, c is the concentration of the ions in the bulk, c_i is the concentration of the ions at the solid-liquid interface, k_d is the mass transfer coefficient, k_r is the crystal growth rate constant, t is the time, g is an index, dependent on the condition of the experiment.

From a theoretical analysis, Konak (1974) showed that the index g depended on the number of types of ions taking part in the reaction. The crystal growth rate constant, k_r, depends on temperature and can be described by the Arrhenius expression (Chen, 2007),

$$k_r = k_{r0} \exp\left(-\frac{\Delta E}{RT}\right) \hfill (10)$$

where k_{r0} is the pre-exponential constant, ΔE is the activation energy, R is the gas constant and T is the absolute temperature at the solid-liquid interface.

However, the so-called 'classical' deposition rate law approach didn't take into consideration of the effects, such as nucleation or growth sites, foreign particles, in the crystallization process, which are well known to affect the fouling behaviors. Liu and Nancollas (1970), Nancollas and Reddy (1974), represented the rate of crystallization as a function of nucleation sites, n. Mullin (1960) expressed the rate of deposition as a function of the crystal surface area, $A_{crystal}$. Reitzer (1964) introduced projected area and density into describe crystallization fouling rate, which were suitable for slow scaling materials such as calcium carbonate, sodium sulfate and calcium sulfate. Taking into the consideration of sticking probability and the influence of water composition, Hasson (1981) defined an empirical parameter Ω to give a simplified form for the HTRI model.

In the removal process, the removal rate is directly proportional to the wall shear stress of the bulk flow, ς, the deposit thickness, δ, and is inversely proportional to the shear strength exerted by the fluid flow on the deposit layer, σ_f. Therefore, the rate of mass removal can be given as (Bohnet, 1987),

$$\left(\frac{\mathrm{d}m}{\mathrm{d}t}\right)_{rem} = k_{rem} \frac{\varsigma}{\sigma_f} \delta \hfill (11)$$

where k_{rem} is a proportionality constant.

Fouling is due to a combination of the deposition and removal processes, causing a growth of scale and followed by continuous increase in the fouling thermal resistance, R_f, which is shown as below (Müller-Steinhagen, 2000),

$$R_f = \frac{1}{k_f} - \frac{1}{k_0} \hfill (12)$$

where k_f and k_0 are the overall heat transfer coefficients for the fouled and the clean heat transfer surfaces, respectively.

Measuring the fouling thermal resistance can assist in extracting parameters that could be used for predicting fouling behavior in similar heat exchangers operating at similar conditions. The corresponding fouling curve derived from the fouling resistance versus time can be classified generally into three different categories, i.e. linear, falling and asymptotic, depending on different fouling processes (Fernandez-Torres et al., 2001). In crystallization fouling, linear fouling curves have been reported by many authors (Hasson, 1962; Reitzer, 1964, Ritter, 1983). While Bott and Walker (1971) observed that the fouling rate decreased with deposit formation and the linear rate changed to a falling rate. Others even reported asymptotic behavior for crystallization fouling (Watkinson and Martinez, 1975; Augustin, 1992; Bohnet, 1987; Middis, 1994).

FACTORS AFFECTING FOULING RATE

Fouling depends on various parameters such as type and composition of mineral containing in the mother liquor, heat transfer method, hydraulic and thermal conditions, as well as heat transfer surface material characteristics. These factors can be broadly classified into 3 major categories: solution composition, operating parameters and heat exchanger characteristics.

Solution composition

The composition of stock solution depends on its source, which may not be possible to change. Hence, a variation in crystallization fouling is mainly attributed to different dissolved species in solution if under the same operation conditions.

The effect of supersaturation on fouling is considered to be the utmost important single factor that determines the intensity of scaling (Sheikholeslami, 2003). It can be achieved when the solution concentration is beyond the solubility limits of its constituents. Sudmalis and Sheikholeslami (2000) pointed out that increasing the initial calcium concentration can effectively reduce the induction period for pure $CaCO_3$ thus increase the fouling rate. Kazi et al. (2010) pointed out that the deposition of $CaSO_4$ was enhanced by increasing the initial solution concentration, which was due to the increased amount of crystallization in the boundary layer and the increased total attractive force to the surface. The degree of supersaturation also has an impact on polymorph of $CaCO_3$. Hu and Deng (2004, 2005) found that higher supersaturation condition favored calcite formation, while aragonite tended to precipitate in low supersaturation condition. Spanos and Koutsoukos (1998) point out that relatively high supersaturation coupled with high pH values was suitable for the precipitation of vaterite.

The effect of pH value on fouling is not straightforward. In general, the value of pH increased, the amount of the precipitation fouling decreased and vice versa. As far as the polymorphism of $CaCO_3$ is considered, pH is seen as the most important factor with the pH range 10-12 giving rise to aragonite. At pH lower than 11 and low temperatures (~7°C) nearly pure calcite was obtained, while almost pure aragonite resulted at 58°C for a pH lower than 10 (Tai and Chen, 1998). However, $CaSO_4$ is not significantly affected by pH and tends to precipitate in various forms once the solution becomes supersaturated (Helalizadeh, 2000).

The presence of suspended particles (i.e. impurities) in the process solution can be considered analogous to the introduction of seeds in a crystallization process. The

seeding technique has been used successfully in many applications, either to make crystalline products or to have preferential crystallization on these seeds to prevent fouling of the heat transfer surfaces (Gainey et al., 1963; Rautenbach and Habbe, 1991). Bramson et al. (1995) reported that the presence of a large amount of calcium sulphate particles enhanced the overall fouling rate primarily through particulate fouling. Middis (1994) reported similar results for calcium sulfate crystallization fouling inside an electrically heated tube. Duncan et al. found that the presence of suspended sodium aluminium silicate particles augmented the crystallization fouling of sodium aluminium silicate. According to Yiantsios and Karabelas (1995), the increased deposition rate in the presence of suspended particles is a result of enhanced wall crystallization and not particulate deposition. According to Andritsos and Karabelas (1999), calcium carbonate fouling is significantly augmented in the presence of a low concentration of fine aragonite particles.

Similarly, a change of solvent or addition of a co-solvent can also lead to a change in crystal growth rates. One mechanism by which this may occur is a consequence of the effects of solvent on mass transfer of the solute via changes in solution viscosity, density and diffusivity. Another mechanism is via changes to the structure of the interface between crystal and solvent, as with some impurities. A solute-solvent system with a higher solubility is likely to produce a rougher interface and concomitantly cause faster crystal growth rates.

Operating parameters

Operating conditions have a significant effect on the deposition of salts from solution by crystallization on the heat transfer surface. Sometimes it is possible to reduce the fouling rate by controlling and adjusting the operational parameters. Hence, a series of experiments were designed to investigate the effects of operating parameters such as fluid velocity, heat flux and surface and bulk temperature on the fouling rate (Everaert and Baeyens, 2004; Zettler et al., 2005; Kukulka and Devgun, 2007).

The flow velocity has a strong effect on the fouling rate where it has direct effects on both of the deposition and removal rates through the hydrodynamic effects such as the eddies and shear stress at the surface. On the other hand, the flow velocity has indirect effects on deposit strength, the mass transfer coefficient, and the stick ability. Many investigations have been performed on scale formation during forced convective heat transfer. High velocity can sometimes reduce deposition (Hasson and Zahavi, 1970), while in other case they accelerate fouling (Hatch, 1973). According to Helalizadeh et al. (2000), at lower fluid velocities, the fouling process is clearly diffusion-controlled. With increasing flow velocity, the mechanism is changing to reaction-controlled. If the fouling process is not mass-transfer controlled, then the deposition rate should be independent of the flow velocity as long as the surface temperature remains constant.

Heat flux or thermal flux defined as the rate of heat energy transfer through a given surface, has a significant effect on the strength of deposits by influencing the number of active nucleation sites. Investigations show that deposits formed at high heat fluxes are harder to remove than that formed at lower heat fluxes (Bansal and Müller-Steinhagen, 1993). Helalizadeh et al. (2000) also showed that with increasing heat flux, the as-grown crystals became smaller and their orientation changed from perpendicular to parallel to the bubble grow direction in sub-cooled flow boiling.

Both the surface and bulk temperatures have a strong effect on the crystallization fouling rate. The inherent reason can be interpreted that the supersaturation of inverse solubility salts is temperature dependent. Since mass transfer coefficients are a linear function of temperature, fouling rates should increase similarly with surface temperature for the mass transfer controlled systems (Hasson et al., 1968). In the reaction-controlled system, temperature strongly affects fouling rate as it can significantly affect the relative rates of the diffusion and surface integration steps (Plummer and Busenberg, 1982).

Heat exchanger surface characteristics
Surface energy

Surface energy quantifies the disruption of intermolecular bonds that occurs when a surface is created, and is one of the key factors to define surface properties. Generally, the lower the surface free energy of the surface is, the weaker the adhesion of deposit on it. Low energy surfaces are more resistant to fouling and easier to clean due to weaker binding at the substratum liquid interface (Oliveira, 1997; Bohnet et al., 1992). However, Förster and others (Förster and Bohnet, 2000) negated a direct correlation between surface energy and fouling tendency with respect to induction time when the polar part of surface energy was taken into consideration.

The determination of the surface energy, γ_{23}, can be done by measuring the contact angle, θ_{12}, from liquid droplets onto these surfaces as shown in Fig. 5 (Förster and Bohnet, 1999).
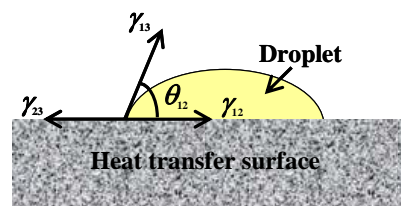

Fig. 5. Contact angle and interfacial free energies at the boundaries between three adjacent phases.

At its simplest, the theory of contact angles allows resolving the equilibrium tensions at the three-phase contact point horizontally, which leads to the well-known Young's equation (Young, 1805):

$$\gamma_{23} = \gamma_{12} + \gamma_{13} \cdot \cos\theta_{12} \qquad (10)$$

Based on Young's equation, several methods for the determination of interfacial energies have been developed in literature (Owens and Wendt, 1969; van Oss, 1994; Wu, 1982). For many industrial applications, the deployment of these methods leads to the conclusion that the only way to influence the deposition process during the induction period is to vary the energy characteristics of the heat transfer

surface, γ_{23}, resulting in a modification of γ_{12} and θ_{12} describing the thermodynamic equilibrium of crystallization. Therefore, various surface materials have been deployed to investigate the influence of surface energy on fouling. Amjad (1988) studied gypsum deposition on various metal surfaces and reported that the rate of scale formation is a function of surface area and the metallurgy of the heat exchanger. He also found that the order of the rate of deposition on different metals as: copper>brass>stainless steel. Kazi et al. (2010) studied the heat transfer fouling of different pipe materials and found out that the mineral scale deposition rates on copper, aluminum and brass were 2.13, 1.63 and 1.54 times more than that of SS 316. Yang et al. (1999) reported that the nucleation rate on a low-energy surface was lower than that on a high energy surface. They investigated copper and copper-modified, low-energy surface SAM (self-assembled mono-layer) and found less deposition on SAM surface.

Surface roughness

Surface roughness is a measure of the texture of a surface, and can be quantified by the vertical deviations of a real surface from its ideal form. Surface roughness is usually described by several parameters such as R_a (the arithmetic mean deviation) and R_z (the mean roughness depth) (Zettler et al., 2005).

The effect of surface roughness on heat transfer is well established and is widely used to improve the performance of many kinds of heating equipment (Sheriff and Gumley, 1966; Feurstein and Rampf, 1969; Taylor et al., 1992; Bohnet and Augustin, 1993). Two effects may contribute to heat transfer enhancement due to roughness: (i) an enlargement of the surface area relative to a smooth wall and (ii) an increase in near wall turbulence (Albert et al., 2011). Yoon and Lund (1994) reported that no effect of surface roughness was found in the R_a in range of 0.08 to 0.60 μm. Mcguire and Swartzel (1987) showed that surface roughness was not a factor for fouling with their surfaces having R_a values of 0.04, 0.41, 1.93 and 2.31 μm for polished stainless steel (SS), rough SS, PTFE coating and alumino-silicate coating, respectively. Herz et al. (2008) also confirmed that calcium sulfate deposition was strongly affected by the degree of surface roughness and the fouling layer on a rough surface was more, since the higher roughness caused shorter induction periods.

FOULING MITIGATION STRATEGY

Fouling mitigation strategies have long been investigated. Attempts have been made to either reduce the potential of a fluid to form deposits or to be more effective in removing of deposits (Kazi et al., 2009; Müller-Steingagen and Malayeri, 2007). Methods can be classified into two basic categories: chemical methods and physical techniques (Cho et al., 2004). Chemical methods reduce fouling by the addition of chemical additives to the fluid to be processed, while physical techniques aim to migrate fouling either through modification of heat transfer surfaces (may also be classified as material science) approach to render them less susceptible to fouling, or through pretreatment of stock solution.

Chemical methods

Many current and evolving technologies require crystallization strategies that provide control over structure, size and morphology of inorganic crystals. Additives of both organic and inorganic nature play an important role in crystallization. Additives generally exist in process solutions at very low concentration, but they are quite diverse, and those more prone to influence crystallization include high valence metallic ions, surface-active agents, polymers and antifoulants as shown in Table 1 (Puckorius, 1972).

A well-established fact in crystallization is that the presence of additives or some foreign ions and molecules, can profoundly affect nucleation (Pina et al., 1998; Orme et al., 2001; Peng et al., 2000). The parameter generally used to quantitative nucleation efficiency is the nucleation rate. Any significant change in the nucleation is usually viewed as evidence of pre-nuclear clusters or embryos reduces the rate at which they pass through the critical size barrier, and therefore retard the rate of nucleation.

Table 1. Common foulant and corresponding cleaning solvent.

Foulant	Cleaning solvent
Iron oxides	Inhibited hydrofluoric acid, hydrochloric acid, sulfamic acid, EDTA or mono-ammoniated citric acid
Calcium and magnesium scale; Oils or light greases	Inhibited hydrochloric acid, citric acid, EDTA, Sodium hydroxide, trisodium phosphate with or without detergents, water-oil emulsion
Heavy organic deposits	Chlorinated or aromatic solvents followed by a thorough rinsing
Coke/carbonac-eous deposits	Alkaline solutions of potassium permanganate or steam air decoking

One of the most effective methods to retard the unwanted deposition of inorganic or mineral salts is to choose the scale inhibitor contains carboxylic acids, sulfonic acid or phosphoric acid type functional groups (Grases et al., 1988; Grohe et al., 2006; Singh et al., 2006). Such inhibitors are primarily designed for their ability to form a sufficient number of coordinative bonds with the cations of the mineral surface. In this way, the surface energy can be significantly reduced by selective adsorption of additives and thus inhibit the growth rate.

Another most common and effective fouling control method is the use of antifoulants. Antifoulants are effective for the whole process of fouling, but they may generate an environmental problem (Yang et al., 2002). Recently, some new types of additives such as far less toxic and highly biodegradable alternatives have been developed (Ross et al., 1997; Darling and Rakshpal, 1998). Xyla et al. (1992) pointed out that these additive molecules were preferentially adsorbed at step and kink sites, blocking the active growth sites of the growing crystallites. Thus, the fouling morphology was modified in the presence of additives.

Physical techniques

Surface treatment technique

Surface treatment, a technique to obtain surface properties different from untreated stainless steel surface conditions, can significantly influence the incrustation process (Malayeri et al., 2009). Owing to the physical and geometrical properties of the modified surface, two distinctive mechanisms can be found during the deposition process: (i) reducing the work of adhesion between surface and deposit; (ii) increasing the wall shear stress. In general, minimum adhesion occurs in systems undergoing a maximum decrease in surface energy, thus poorest fouling adhesion should occur on materials with lowest surface energies. Surface geometry modifications may endeavor to increase the exerted shear forces by the fluid on the surface and change surface structure to increase hydrophobicity of the substrate.

Müller-Steinhagen and Zhao (1997) investigated a low fouling surface alloys made by ion implantation technology, and concluded that the penetration depth of ions were dependent on their energy and the mass of the atoms of the substrate material. Waterhouse and Niku-Lari (1988) applied ion sputtering on metal surface to against corrosion and wear. According to Malayeri and others (2009), the nano-modified surfaces were characterized by longer induction times, lower fouling rates and ultimately much lower asymptotic fouling resistances, resulting in the reduce of subsequent fouling rate. Al-Janabi and others (2008) applied an innovative organic/inorganic coating method to mitigate crystallization fouling on heat exchanger surface.

Physical water treatment

Physical water treatment (PWT) is an attempt to treat hard water for the purpose of preventing or mitigating fouling using a physical means, without adding chemicals to water (Cho et al., 2004). The main principle of PWT is described as bulk precipitation via heterogeneous catalysis. Various PWT methods include the use of magnetic fields, electric fields, ultrasound, vortex flows, surface charge alteration, and sudden pressure changes.

Cho et al. (2004) recently conducted a study on the mechanism of the PWT. They concluded that the main mechanism of PWT was due to bulk precipitation via heterogeneous catalysis. They said that particulates formed from bulk precipitation subsequently adhere to the heat transfer surface as a soft sludge coating. Lee et al. (2006) reported that the catalytic materials could reduce the fouling resistance by 20–38 % at a velocity range of 0.3–0.8 m/s. The scales produced on the heat transfer surface were soft and easily-removable. Tijing et al. (2010) investigated the feasibility of RF (radio frequency) electric fields in mitigating $CaCO_3$ fouling in cooling water. RF electric fields can generate between two graphite electrode plates directly in water and thus can be used to mitigate mineral fouling in a double pipe heat exchanger.

Fibre seeding techniques

Fibres can interlock at moderate concentrations to form three-dimensional structures or networks, which can alter the transport properties in liquid suspension (Kazi et al., 2002). Unlike other antifouling chemicals, wood pulp fibres not only augment heat transfer but also either inhibit the onset, reduce the magnitude, or prevent heat transfer fouling altogether. Middis et al. (1997) added pulp fibres to calcium sulfate fouling solution in a heat exchanger and observed a marked reduction in the fouling resistance. Kazi et al. (2010) extended this work to lower fibre concentration and reported no fouling for 11 days with a 0.15% bleached Kraft pine fibre in a supersaturated calcium sulfate fouling solution. They also investigated the effects of fibre concentration, fibre length, and fibre flexibility on heat transfer fouling with supersaturated calcium sulfate solutions and concluded that reducing fibre length and flexibility at the same concentration enhances fouling retardation; shorter hardwood fibres are more effective than longer softwood fibres as inhibitors; there are optimum fibre concentration for retardation and no-fouling conditions.

CONCLUSIONS

Crystallization fouling on heat exchanger surfaces in process industry is still a complicated phenomenon and the mechanism is not fully understood. Most of the models are based on semi-empirical assumptions or derived from experimental investigations.

For most of engineering designers, they pay much attention on fouling mitigation strategies, neglecting the basic information about the deposits themselves. As the starting materials crystallized from solution, it is very important to investigate the composition of the as-grown crystals, grasping the basic crystallization habits, the corresponding transformation behaviors among polymorphs and their interaction with heat transfer surfaces. With the knowledge, specific chemical additives can be introduced to control fouling by selectively adsorbing on anisotropic crystal faces depending on different deposits. On the other hand, comprehensive understanding of the surface properties is another important aspect to constitute anti-fouling strategies. Both reduction of surface energy and modification of surface topology can effectively reduce fouling. Combining the basic crystallography with advanced computer techniques, another promising area is the computer-aided technology to model fouling process at molecular level, which may make the unknown process visualized.

It would appear in the literature reviewed that the 'crystallography' tends to establish the crystal growing in a clean environment, like 'an individual tree growing in a controlled space' which is isolated from others, but the crystallization fouling is more like 'trees grown in the wild forest' with many other plants around them and wild weather conditions (un-controlled situation). This presents a major challenge in studying fouling in the way that crystallographer would. Furthermore, to what extent that the kind of crystal structure would affect heat conduction, or heat transfer in general, has not been studied fundamentally. This may be a good point to follow up in near future.

NOMENCLATURE

A_i surface area of i, m^2
C_1 constant
C_2 constant

c	concentration, kg m^{-3}
ΔE	activation energy, J mol^{-1}
ΔG	overall excess free energy, J
ΔG_S	surface excess free energy, J m^{-2}
ΔG_V	volume excess free energy, J m^{-3}
g	index in Eq. (9)
k_B	Bolzman constant, J K^{-1}mol^{-1}
k_f	overall heat transfer coefficient for the fouled heat transfer surface, W m^{-2} K^{-1}
k_0	overall heat transfer coefficient for the clean heat transfer surface, W m^{-2} K^{-1}
k_d	mass transfer coefficient, m s^{-1}
k_r	reaction constant, m^4 kg^{-1} s^{-1}
k_{r0}	pre-exponential constant, m^4 kg^{-1} s^{-1}
k_{rem}	proportionality constant for removal, m^{3}kg^{-1} s^{-1}
m	mass per unit area, kg m^{-2}
N_A	Avogadro's number, dimensionless
n	nucleation sites
r	radius, m
R	gas constant, J K^{-1}·mol^{-1}
R_f	thermal resistance, m^2 KW^{-1}
R_a	arithmetic average roughness, m
R_z	mean roughness depth, m
T	absolute temperature, K
t	time, s
n	nucleation site
S	degree of surpersaturation
ς	wall shear stress, N m^{-2}
τ	induction time, h
δ	deposit thickness, m
φ	the factor in Eq. (5)
Ω	empirical parameter
θ	contact angle, °
σ_f	shear strength, N m^{-2}
γ	surface energy, N m^{-2}
μ	chemical potential, J

Subscript

1	adhesive phase
2	substrate phase
3	surrounding phase
d	diffusion
f	fouling
r	reaction
i	interface
homo	homogeneous
hetero	heterogeneous
mol	molar
rem	removal
s	surface
v	volume

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