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Crystallization fouling of $CaCO_3$ – Analysis of experimental thermal resistance and its uncertainty

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ABSTRACT

Crystallization fouling occurs when dissolved salts precipitate from an aqueous solution. In the case of inversely soluble salts, like calcium carbonate ($CaCO_3$), this may lead to crystal growth on heated walls. Crystallization may also take place in the bulk solution either via homogeneous nucleation or heterogeneous nucleation on suspended material.

In this paper, surface crystallization of $CaCO_3$ and crystallization in the bulk fluid and its effect on the fouling rate on a heated wall are studied. The fouling experiments are done in a laboratory scale set-up of a flat plate heat exchanger. Accuracy of the results is analyzed by uncertainty analysis. SEM and XRD are used to determine the morphology and the composition of the deposited material.

The uncertainty analysis shows that the bias and precision uncertainties in the measured wall temperature are the largest source of uncertainty in the experiments. The total uncertainty in the fouling resistance in the studied case was found to be ±13.5% at the 95% confidence level, which is considered to be acceptable.

Surface crystallization rate is found to be controlled by the wall temperature indicating that the surface integration dominates the fouling process. The flow velocity affects the fouling rate especially at high wall temperature by decreasing the fouling rate with increasing flow velocity. Crystallization to the bulk fluid is found to enhance significantly the fouling rate on the surface when compared to a case in which fouling is due to crystal growth on the surface.

1. Introduction

Fouling, which is often described as the deposition of unwanted material on a heat transfer surface, diminishes the heat transfer and increases the pressure drop of the process units such as heat exchangers. Due to fouling, operation and maintenance costs are increasing significantly. In addition, heat transfer equipment are often oversized for required duty because of the expected fouling. Therefore, fouling is a major challenge in design and operation of heat exchangers. By decreasing the fouling of heat exchangers, harmful environmental and economic effects can be reduced.

One detrimental fouling mechanism in a wide range of industrial applications is crystallization fouling. Crystallization fouling is caused by dissolved salts which precipitate out of the solution due to supersaturation. Calcium carbonate is a common salt causing crystallization fouling especially in cooling water systems, desalination processes, and in drinking water systems. [1,2] Calcium carbonate has inverse solubility which means that supersaturated conditions may be achieved either by heating the solution above the limit temperature in which the supersaturation occurs or by increasing the concentration by evaporating the solution above the solubility limit. Crystallization fouling of calcium carbonate may also be caused by increase in pH, which decreases the solubility of calcium carbonate. In heat exchangers, heated surfaces are therefore easily exposed to the crystallization fouling.

Crystallization fouling is a complex phenomenon which is affected by hydrodynamic and thermal conditions of the system, but also related to chemical kinetics, thermodynamics and material properties [3]. Fouling behavior of the same salt may therefore vary in different systems and operation conditions which make it essential to understand the fouling behavior of the process in question in order to reduce fouling in it.

Mechanism of crystallization fouling is usually defined to include two main steps: transport of ions from the bulk fluid to the vicinity of the surface, and attachment of the depositing material to the surface [3]. The mass transport step is attributed to the molecular diffusion of ions through the laminar boundary layer at the surface. The driving force for the diffusion is the concentration difference between the bulk fluid (C_b) and the interfacial

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Nomenclature

B	bias uncertainty
C	concentration (kg/m^3)
Dh	hydraulic diameter (m)
E_a	activation energy (J/mol)
k_r	reaction rate constant (m^4/kg s)
k_0	pre-exponential factor (m^4/kg s)
m_d	mass deposition rate (kg/m^2 s)
n	order of reaction
P	precision uncertainty
q	heat flux (W/m^2)
R	gas constant (J/mol K)
R_f	fouling resistance (m^2 K/W)
T	temperature (K)
t	time (s)
$\hat{U}_i$	total uncertainty in parameter i
U	total heat transfer coefficient between the heated surface and bulk fluid (W/m^2 K)
v	flow velocity (m/s)

Greek letters

β	mass transfer coefficient (m/s)

Subscript/superscript

b	bulk
i	interphase
sat	saturation
t	at the certain time t
w	wall/surface
0	initial

Acronyms

SEE	Standard Error of Estimate
SEM	Scanning Electron Microscopy
XRD	X-ray Diffraction

concentration at the surface (C_i). Mass transport of the ions to the vicinity of the surface can be described as [4,5]:

$$m_d = \beta(C_b - C_i) \tag{1}$$

The attachment step is described by the strongly temperature dependent surface integration of ions into the crystal lattice which has often found to follow Arrhenius type rate equation driven by the nth potential of the concentration difference between the saturation concentration (C_{sat}) and the interfacial concentration (C_i) [2,4–6]:

$$m_d = k_r(C_i - C_{sat})^n \tag{2}$$

$$k_r = k_0 e^{-E_a/RT} \tag{3}$$

In the case of heat exchanger with a constant heat flux, the surface temperature (T_s) at the fouling layer-liquid interphase is depending on the local heat flux and the fluid side heat transfer coefficient. Schematic of the concentration and temperature profiles in the studied system are given in Fig. 1. [7]

Crystallization fouling of calcium carbonate in forced convection systems can be controlled by mass transfer, surface integration, or both [8]. Mass transfer of the ions is a prerequisite for crystallization fouling. Mass transfer may control the fouling process particularly when crystallization fouling takes place on a heat exchanger surface and a laminar boundary layer occurs. In the regions further from the surface mass transfer is enhanced due to turbulence and the rate controlling step may be surface attachment. [2]

Wall temperature has a clear effect on crystallization fouling of inversely soluble salts. An increase in the wall temperature increases also supersaturation, which enhances the fouling rate both in mass transfer and surface integration controlled fouling. In addition, mass transfer coefficients are linear functions of temperature, which also increases the mass transfer with higher wall temperatures. [3,7] The effect of the wall temperature is though greater with the crystallization fouling process controlled by the surface integration [9]. Flow velocity instead has a complicated role on fouling: On the other hand, an increase in the flow velocity enhances mass transfer resulting from the increased turbulence and further ions transport which promotes deposition. [10] But again, increased shear at the interphase reduces the probability of the adhesion of the depositing material reaching the solution-fouling layer interphase. Therefore, an increase in the flow velocity may either increase the fouling rate (mass transfer controls) or decrease it if the interfacial shear has the greater effect (surface integration controls). [2,11–13]

Hasson et al. [7] found that $CaCO_3$ deposition in turbulent, constant heat flux conditions at annular test section, with unfiltered, supersaturated tap water is controlled by the diffusion mechanism which is seen as an increased fouling rate with an increasing Reynolds number at the constant surface temperature. Instead, Augustin and Bohnet [14] have defined crystallization fouling of $CaCO_3$ in an annular duct to be controlled by the surface integration. Helalizadeh et al. [3] found out that at low flow velocities of the mixed $CaCO_3$–$CaSO_4$ solution the fouling process in the annular duct is diffusion controlled, but increasing the flow velocity changes the mechanism to the surface integration controlled. Also Fahimia et al. [13] have proposed that the crystallization fouling process is controlled by the mass transfer at low flow velocities, but with increasing velocities the surface integration controls the fouling process. This conclusion was also proposed by Najibi et al. [9] for crystallization fouling of calcium carbonate in convective, single-phase heat transfer conditions. Instead, Mwaba et al. [6,15] proposed crystallization fouling of $CaSO_4$ in a rectangular flow channel to be controlled by the surface integration. This founding was in agreement with the studies of Bansal and Müller-Steinhagen [16] who found out that crystallization fouling of $CaSO_4$ in a plate heat exchanger is surface integration controlled. Therefore, controlling fouling mechanism varies depending on the studied system.

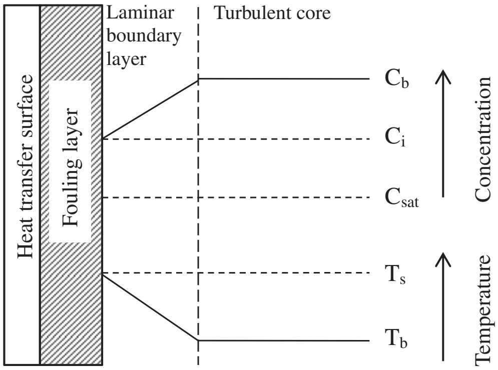

Fig. 1. Schematic of the concentration and temperature profiles at the heat transfer surface [7].