

DEVELOPMENT OF A CONCEPTUAL MODEL OF CRYSTALLIZATION IN A HEAT EXCHANGER

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ABSTRACT

We evaluated crystallization fouling using various sized devices; the plant, bench scale and laboratory scale. These are focused on establishing factors, such as temperature, liquid velocity and surface roughness. The fouling rate is defined as the difference between the deposition rate and the removal rate of the fouling. Kern and Seaton expressed each rate as follows: the rate of transport and deposition are constant with time, the rate of deposition varies with concentration and mass flow rate, the removal rate varies directly with the shear stress and the deposit thickness. Reitzer said that the deposition rate of crystallization fouling is dependent on supersaturation. We created a combined Kern-Seaton-Reitzer model for the calculation of our crystallization fouling rate. However, the parameter of the plant and test unit did not agree with each other, perhaps because of scaling up problem. We focused on a shear rate, and constructed a new apparatus that evaluates crystallization fouling.

We used some organic systems for the experiment. The dissolved process liquid is cooled, and the crystalline nucleus is generated. The fouling factor is calculated based on the temperature obtained from the experiment. We observed the relation between the fouling factor and the shear rate, the fouling factor and the supersaturation (the temperature and the concentration of the process liquid). We set about restructuring the fouling model based on our study, and this result is reported in this talk.

INTRODUCTION

Obstructions caused by the fouling of equipment and pipes not only cause energy and quality losses, but also maintenance issues. To achieve a super-stable operation of the plant, we need technology that will eliminate existing problems and enable us to anticipate and prevent future problems when developing new processes.

Some products in our corporation have crystallization systems, for example, a forced-circulation crystallizer. A forced-circulation crystallizer occasionally has problems – the fouling behavior in its heat exchanger, because the crystals grow up on the pipe of the cooling heat exchanger. Accordingly, we originally developed a fouling simulator, which explicated the relation between the fouling rate and the operating condition of the plant.

EXPERIMENTAL METHOD

1. Bench-size simulator

We developed a fouling simulator having a one-tube heat-exchanger unit with an inner diameter of 10.3mm and a length of 1000mm. Figure 1 shows a schematic illustration of this system. This system also featured a slurry tank and a recovery heater. In this system, the linear velocity range we used was from 1.2 to 2.8ms⁻¹ at the heat-exchanger, equal to a shear rate range of 120 to 270s⁻¹.

An organic solvent sample was prepared within the slurry tank. The slurry was then sent to the heat-exchanger removing the sample's heat duty. The crystals that were formed adhered to the inner wall of the one-tube heat-exchanger. This resulted in thermal resistance distributed unevenly along the length of the heat-exchanger. During the experiment, we recorded the temperature of the slurry and coolant at the inlet and outlet of the heat-exchanger using platinum resistance thermometers, flow rate was measured using a Coriolis-type flow meter. Thereby we were able to estimate the fouling rate relative to the variation of heat duty and overall heat transfer coefficient. The fouling rate was found to depend on the liner velocity and heat duty. After cooling, the slurry to the pre-set temperature at the recovery heater and returned to the slurry tank.

2. Lab-size simulator

Figure 2 shows a schematic illustration of this system. We developed the fouling simulator utilizing a concentric cylinder system – this consisted of a cooling jacket surrounding an inner cylindrical chamber. Within this chamber we placed a temperature controllable spindle, the gap between chamber and spindle being approximately 1.1 mm. The temperature in cooling jacket and spindle was controlled by coolant water. Said coolant temperature was controlled by refrigerated/heating circulators (JULABO, F25-ME), and piped into the chamber and the spindle. When the spindle was rotated the system enabled a well-defined shear rate range; the rate was used from 0 to 186s⁻¹.

An organic solvent sample, with established temperature over solubility point, was introduced to the aforementioned inner chamber. During the experiment, we recorded the temperature of both the sample and the coolant within the chamber and the spindle, using platinum resistance thermometers and a data logger. As the sample temperature declined, crystal was generated at a

supersaturation point. This crystal adheres to both the outer wall of the inner cylindrical chamber and the spindle. This result in thermal resistance inconstantly distributed within the chamber. The supersaturation point depended upon the shear velocity and the cooling rate; slower shear rate becomes larger supersaturation point.

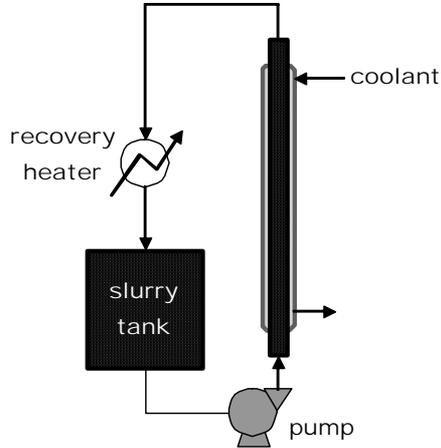


Figure 1 A schematic illustration of the experimental system – Bench-size simulator. The slurry at the slurry tank sent to heat-exchanger, after that returned to the slurry tank. The coolant and the slurry temperature monitored using platinum resistance thermometers, and flow rate monitored via a Coriolis-type flow meter.

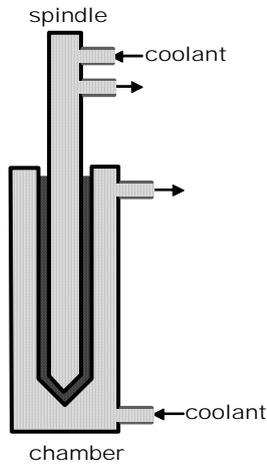


Figure 2 A schematic illustration of the experimental system – Lab-size simulator. The gap is filled with the sample slurry, and the spindle rotates at a constant rate during cooling. The coolant and the slurry temperature monitored using platinum resistance thermometers, and flow rate monitored via a flow meter.

APPROACH IN NUMERICAL ANALYSIS RESULTS

1. Bench-size simulator

Due to the supersaturation in the heat exchanger, fouling occurs on the tube wall because this surface is cooler due to heat transfer to the coolant outside the wall. Fouling rate can be considered as the net effect to two opposing factors: deposition on the tube wall, and removal

due to shear rate on the fouling surface. Mathematically, it can be written as:

$$\frac{dx_f}{dt} = m_d - m_r, \quad (1)$$

where x_f is fouling thickness [m]. The deposition rate depends on supersaturation, as reported by Reitzer [1]:

$$m_d = k_0(\Delta C)^{n_0} = k_1 \left(\frac{Q/A}{hi} \right)^{n_1}, \quad (2)$$

where ΔC is supersaturation [mass fraction], Q is heat duty, A is heat transfer area[m²], hi is heat transfer coefficient, k_0 , k_1 , n_0 , and n_1 are parameters. And formation and removal rate can be estimated, as reported by Kern and Shearon [2]:

$$\frac{dx_f}{dt} = k_0 CW - k_2 \tau x_f, \quad (3)$$

where C is liquid concentration, W is constant weight flow, τ is shear rate, k_0 and k_2 are parameters. Especially removal term can be written as:

$$m_r = k_2 \tau x_f. \quad (4)$$

We combined equation (1), (2) and (4) into next equation:

$$\frac{dx_f}{dt} = k_1 \left(\frac{Q/A}{hi} \right)^{n_1} - k_2 \tau x_f. \quad (5)$$

At our bench-size simulator, x_f is the mean value calculated using thermal conductivity λ [W/m K]. So we simulated fouling resistance R_f [m² K/W] that can be calculated directly. For cylindrical tube (outside area standard), overall heat transfer coefficient can be written as;

$$\frac{1}{U_0} = \frac{r_o}{hir_{xf}} + \frac{r_o}{\lambda} \ln \left(\frac{r_i}{r_i - x_f} \right) + \frac{1}{h_o} \quad (6)$$

It means R_f for tube (cylinder shape) can be written as:

$$R_f = \frac{r_o}{\lambda} \ln \left(\frac{r_i}{r_i - x_f} \right), \quad (7)$$

where r_i is inside radius of tube [m], r_o is outside radius of tube [m]. And removal term for R_f depends on fouling squared of velocity and fouling thickness, as reported by Bohnet [3]. We reconstructed equation (5):

$$\frac{dR_f}{dt} = k_1' \left(\frac{Q/A}{hi} \right)^{n_1} - k_2' u^2 x_f^2, \quad (8)$$

2. Lab-size simulator

In order to construct the equation for lab-size simulator using the parameter similar to a bench, we modified equation (1), (2) and (4) into a equation,

$$\frac{dx_f}{dt} = m_d - m_r = k_1(\Delta C)^{n_1} - k_2 \tau x_f^{n_2}. \quad (9)$$

Here, shear rate τ is defined by equation (10),

$$\tau = \frac{2\omega R_b^2}{(R_c^2 - R_b^2)} \quad (10)$$

where R_c is inside radius of chamber [m], R_b is outside radius of spindle [m], ω is angular velocity [s⁻¹].

Here, we need to calculate the fouling thickness and solute concentration in solution as;

$$x_{f,t+\Delta t} = x_{f,t} + \frac{dx_f}{dt} \Delta t \quad (11)$$

$$m_{solv} C_{t+\Delta t} = m_{solv} C_t + k_1 (\Delta C)^{n_1} \rho_f A \Delta t \quad (12)$$

Heat transfer equation for a concentric cylinder viscometer can be described, as reported by Inasawa et.al. [4]. We modified these equations into new our system. Given the initial slurry temperature and the spindle and coolant temperature profiles, the slurry temperature can be calculated based on energy balance,

$$\frac{dT_{sl}}{dt} = \frac{U_{sp-sl} A'}{\rho_{sl} V_{sl} C_{p-sl}} (T_{sp} - T_{sl}) - (1 - \beta) \frac{U_{sl-cl} A}{\rho_{sl} V_{sl} C_{p-sl}} (T_{sl} - T_{cl}) + \frac{k_1 (\Delta C)^{n_1} \rho_f A \Delta H_{cry}}{\rho_{sl} V_{sl} C_{p-sl}} \quad (13)$$

$$\beta = 1 - \frac{U_{sl-cl}}{U_{0-sl-cl}}, \quad (14)$$

where ΔH the enthalpy of crystallization [J/mol], k_1 and n_1 are parameters.

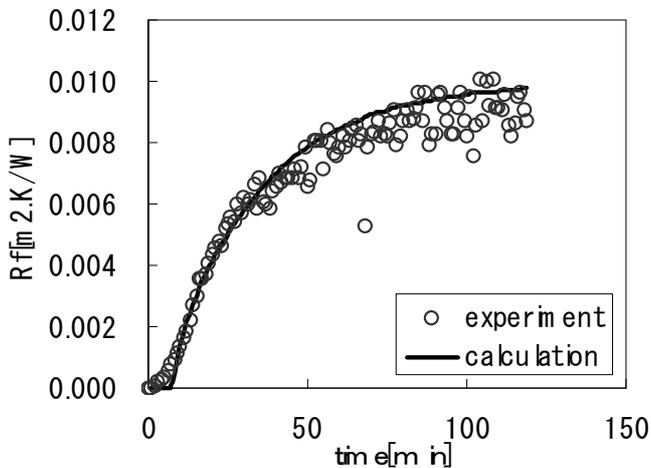


Figure 3 Optimum fit of the model to the R_f data at 1.6m/s. Due to prolong cooling time, R_f increases immediately, and gradually reached its peak.

RESULT AND DISCUSSION

1. Bench-size simulator

By measuring the increase of cooling water temperature and coolant flow rate, the effective value of overall heat transfer coefficient during the experiment can be calculated,

$$Q = C_{p-cl} w_{cl} (T_{cl-out} - T_{cl-in}), \quad (15)$$

$$U = \frac{Q}{A \Delta T_{ln}}, \quad (16)$$

where w is flow rate[kg/h], ΔT_{ln} is log-mean temperature difference[K].

The fouling resistance R_f can be obtained from

$$R_f = \frac{1}{U} - \frac{1}{U_0}, \quad (17)$$

where U_0 is initial overall heat transfer coefficient [W/m² K].

Using the measured R_f , the parameter set (k'_1 , k'_2 and n'_1) in equation(8) can be determined through curve fitting for equation(8), and good agreement was obtained as shown in Figure 3. Such good correspondences using fixed parameter set (k'_1 , k'_2 and n'_1) were seen, when the process velocity was used from 1.6 to 2.8m/s, and process temperature was fixed. These velocity means process flow was turbulent.

$$\frac{dR_f}{dt} = 0.015 \left(\frac{Q/A}{hi} \right)^4 - 8u^2 x_f^2, \quad (18)$$

2. Lab-size simulator

By measuring the increase of cooling water temperature as well as the slurry temperature, the effective value of overall heat transfer coefficient during the experiment can be calculated,

$$Q_{sl-cl} = \rho_{cl} F_{cl} C_{p-cl} (T_{cl-out} - T_{cl-in}), \quad (19)$$

$$U_{sl-cl} = \frac{Q}{A(T_{sl} - T_{cl})}. \quad (20)$$

The fouling resistance R_f can be obtained from equation (17). By varying the supersaturation and shear rate, the effect on the value of R_f can be studied.

Using the measured x_f , the parameter set (k_1 , k_2 , n_1 and n_2) in equation (9) can be determined through curve fitting for equation (9), and passable agreement was obtained as shown in Figure 4 and5.

$$\frac{dx_f}{dt} = 5 \times 10^{-5} (\Delta C)^4 - 3 \times 10^{-6} \tau x_f^2 \quad (21)$$

In the previous paper [4], the model of the lab simulator differed from the bench. In this paper, we applied the similar equation to the bench and the lab simulator. As a result, we found the parameter set at these equations in an organic sample. That means mathematical model with such obtained parameter set can explain fouling behavior with each parameter for experimental datum. If we add experiments and build up a store of a parameter set, we will find interrelation of each parameter. And this lab simulator will be index of scale-up.

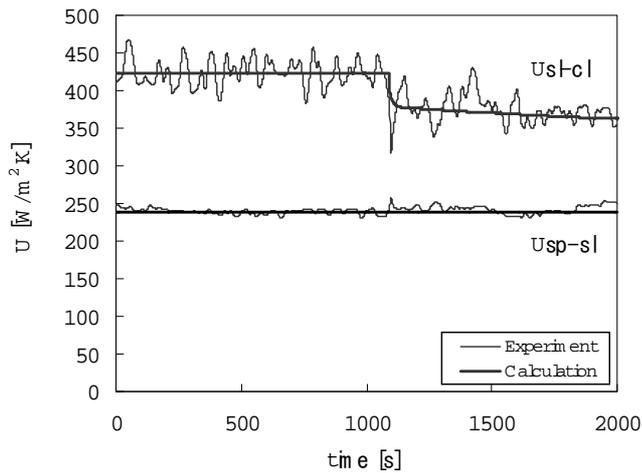


Figure 4 Optimum fit of the model to the U_{sl-cl} and U_{sp-sl} data under shear rate $46.5s^{-1}$. The thin lines are experimental datum, and the thick lines are calculated datum using our fouling model. The drop at about 1091s, corresponds to the onset of crystallization.

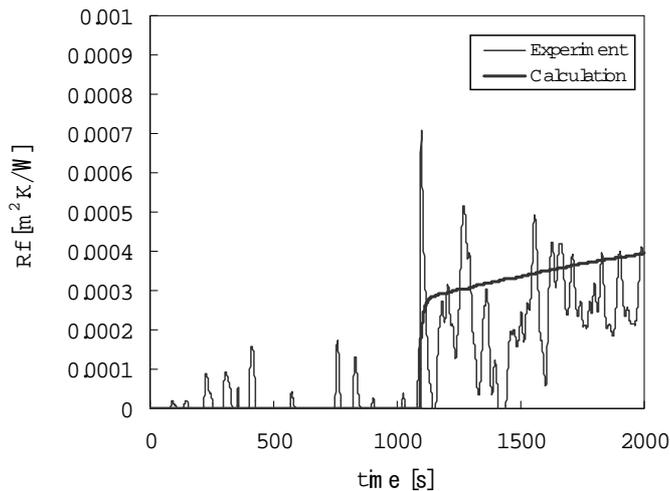


Figure 5 Optimum fit of the model to the R_f data under the identical condition with Figure 4. The thin line is experimental data, and the thick line is calculated data using our fouling model. The increase at about 1091s, corresponds to the onset of crystallization.

CONCLUSION

1. A modified model can explain fouling behavior at Bench-size simulator with fixed parameter set, when process is fixed and process flow is turbulent.
2. A mathematical model can explain fouling behavior at Lab-size simulator, with each parameter for experimental datum.
3. The above mentioned, we expect Lab-size simulator can be applied in scale-up.

NOMENCLATURE

Q	heat duty	W
A	heat transfer area	m^2
C	liquid concentration	—
ΔC	supersaturation	mass fraction
H_i	heat transfer coefficient	$W/m^2 K$
ΔH	the enthalpy of crystallization	J/mol
R_b	outside radius of spindle	M
R_c	inside radius of chamber	M
R_f	fouling resistance	$m^2 K/W$
r_i	inside radius of tube	m
r_o	outside radius of tube	m
ΔT_{ln}	log-mean temperature difference	K
U	overall heat transfer coefficient	$W/m^2 K$
U_0	initial overall heat transfer coefficient	$W/m^2 K$
w	flow rate	kg/h
W	constant weight flow	
x_f	fouling thickness	m
τ	shear rate	s^{-1}
λ	thermal conductivity	$W/m K$
ω	angular velocity	s^{-1}
k_0	parameter	
k_1	parameter	
k_2	parameter	
n_0	parameter	
n_1	parameter	

Subscript

sl	solution
sp	spindle
cl	coolant water

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