

*Refereed Proceedings*

*Heat Exchanger Fouling and Cleaning:*

*Fundamentals and Applications*

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Engineering Conferences International

Year 2003

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## MEASUREMENT AND MODELING FOR THE MITIGATION OF ORGANIC CRYSTALLIZATION FOULING

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### ABSTRACT

One of the aromatic compound plants in Mitsubishi Chemical Corporation has a heavy crystallization fouling problem. In order to solve this problem, using a low power gamma ray sensor, we found the location of heaviest fouling and measured the fouling growth rate. We also made a crystallization fouling laboratory test unit (simulator) to study the effects of some factors, such as temperature, liquid velocity, surface roughness and liquid composition. Fouling rates of the industrial plant cooler and the laboratory fouling test unit were modeled using a combination of Kern-Seaton and Reitzer models. However, the parameters of the plant and test unit did not agree with each other, perhaps because of scale up problems. We also measured the melting process (removal) of the fouling with the test unit. The heat flux necessary to melt the foulant was measured and used for the actual plant melting system. In the industrial plant, a steam trace melting system was installed at the position of heaviest fouling, and the plant now runs better than before.

### INTRODUCTION

For the bulk chemicals industry, it is very important to operate plants steadily without shut-downs or decreases in production due to operating problems. In Mitsubishi Chemical Corporation, for such problems the loss is over one hundred million US dollars per year. Among these problems, fouling, plugging, corrosion and product quality issues account for over 25%. In order to eliminate or mitigate these problems, we started developing a technology for their prediction and prevention in 1999. We call this technology "Super Stable Operation Technology (SSOT)". The first target was technology for combatting fouling and plugging.

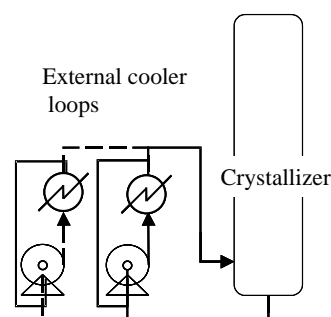


Figure 1. Flow diagram of the crystallizer of the aromatic compound plant.

Here, we report a study of the crystallization fouling problem of an aromatic compound plant. The plant has crystallizers with external circulation coolers (shown in Figure 1). The coolers are shell and tube type, and the process fluid is on the tube side. The external cooler loops of one of the crystallizers had heavy fouling even though the coolers were cleaned alternately every four hours. As a result, the plant had to be shut down and cleaned periodically. This production loss was so large that an immediate solution was required.

To detect the location and growth rate of the fouling, we developed a gamma ray sensor, and to evaluate the effects of the operating conditions, we constructed a laboratory fouling test unit. Both fouling growth rates of the plant and the laboratory test unit were measured, modeled by combination of Kern-Seaton and Reitzer's models [1,2] and compared with each other. One of the mitigation methods was applied to the full-scale plant.

### RESULTS AND DISCUSSION

#### Fouling rate measurement of the cooler loops

Usually, fouling rates of heat exchangers are measured by differences of pressure or temperature between inlet and outlet streams. However, it was not enough for us only to measure the overall fouling rate because we wanted to identify the location of heaviest fouling and measure its fouling rate by non-destructive methods.

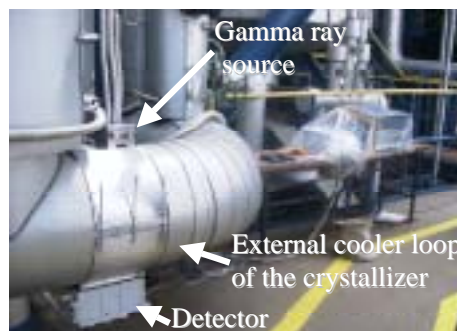
Gamma ray radiation sensors are commonly used for such measurements. (We also tried to use a supersonic wave sensor to detect the fouling rate, and are currently analyzing the data [3].) However, there were two problems. One was that the densities of the slurry (process fluid) and the deposit in the cooler loops were almost the same. (The slurry: 1,050 (kg/m<sup>3</sup>), the deposit: 1,100 (kg/m<sup>3</sup>)) The other was that normal gamma ray sensors were not convenient to use because of radiation restriction regulations in Japan. Then, a low output gamma ray sensor made by Earthnix Inc. [4] was adopted. The output of the gamma ray was small enough to allow use without government permission. To increase the sensitivity, we developed a signal integration system, which enabled us to change the integration time from 1 to 3,600 seconds.

Specifications of the gamma ray sensor are shown in Table 1.

**Table 1. Low output gamma ray sensor specifications**

Maker:	Earthnix Inc.
Detection system:	Scintillation detector
Measurement range:	0 – 3,000 kg/m <sup>3</sup>
Integration time variable range:	1-3,600 sec
Statistical error(2 sigma):	5 – 10 kg/m <sup>3</sup>
Long time drift:	smaller than 1 kg/m <sup>3</sup>
Temperature dependence:	0.1 – 1 kg/m <sup>3</sup> °C
Output of gamma ray:	3.7 MBq
Kind of source:	Cobalt

We measured the fouling thickness and fouling rate of the external cooler loop pipes (outer diameter: 508 mm, material: type 304 stainless steel) of the crystallizer. Despite the 40 mm thickness heat insulation of calcium silicate and galvanized sheet iron of 0.3 mm thickness covering the pipes, the fouling thickness in the pipes could be measured easily just by installing the sensor outside. Usually, the integration time of the gamma ray densitometer is about tens of seconds for the usual non-destructive measurements. However in this case, as there was little difference in density, we set the integration time



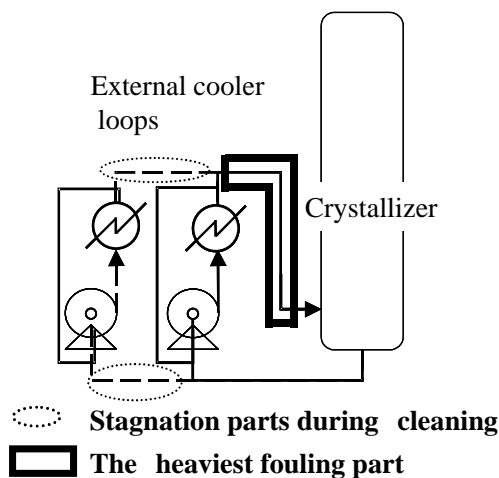
**Figure 2. Measurement of fouling thickness in the pipe by the gamma ray sensor.**

to 60 min to raise the sensitivity of the measurement.

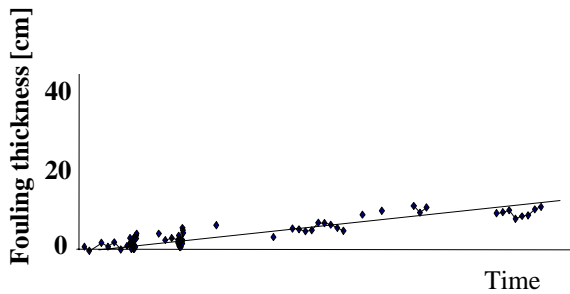
A schematic diagram of the measurement is shown in Figure 2. The upper part of the pipe is the source of gamma ray and the lower part is the detector.

As shown in Figure 1, there were two coolers and both coolers were cleaned alternately every four hours. Therefore, it was difficult to consider how the cooler tubes had become fouled so heavily. After measurement at many locations in the loop for several months, the heaviest fouled part (shown in Figure 3) was located in the section of pipe near the crystallizer which had no periodical cleaning.

The signal strength of the sensor changed according to the density between the source and detector. The density of the liquid and fouling deposit were measured as a function of temperature by experiment in advance, and fouling thickness was estimated by the deviation from a non-fouled value measured just after regular maintenance.



**Figure 3. The heaviest fouled part of the cooler loops.**

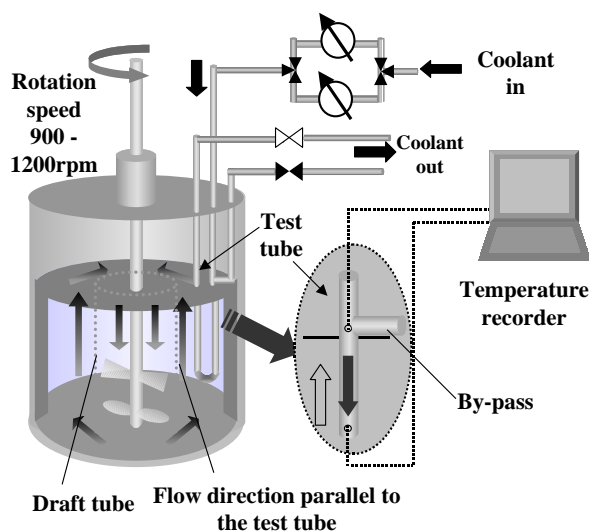


**Figure 4. Growth of the fouling thickness of the heaviest fouling part.**

The fouling growth of the heaviest fouled section is shown in Figure 4. The fouling thickness became about 100 mm in the 508 mm diameter pipe in several months. This fouling thickness corresponded well with the value estimated from the performance curve of the pump and the pressure changes in the loop.

#### Laboratory fouling test unit and test procedure

The design of the laboratory test unit is shown in Figure 5. The vessel has a test tube inserted in it, whose temperature can be controlled by coolant. The vessel has a draft inner tube around the agitator, which makes the flow direction parallel to the test tube length. The deposit forms on the outside of the tube. The fouling rate of crystallization is measured via the coolant temperature differences in the test tube. The temperature difference becomes smaller when the tube is fouled. The flow



**Figure 5. Crystallization fouling test unit.**

#### Table 2. Specifications of the fouling simulator

<b>Volume of the vessel:</b>	1.6 liter
<b>Size of the test tube:</b>	Outer diameter 4 mm, Inner diameter 2 mm, length 80 mm
<b>Material of the test tube:</b>	Stainless steel 304
<b>Flow velocity range:</b>	0 – 0.5 m/s
<b>Size of the draft inner tube:</b>	Diameter 60 mm, Height 130 mm

velocity and its directions were measured in advance by a video camera flow analysis with small float particles. The temperature in the vessel is maintained by an oil circulation jacket outside the vessel.

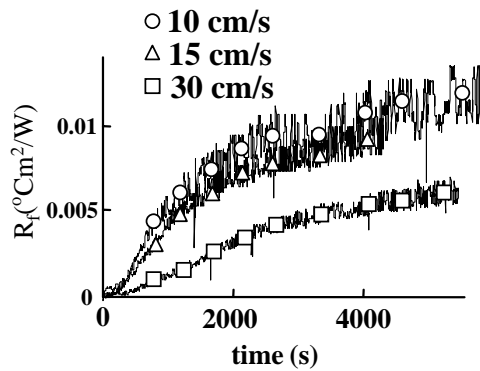
By using the laboratory test unit, the influences of temperature, liquid velocity, surface roughness, and concentrations of the components in the liquid on the crystallization fouling rate can be tested. It is also possible to investigate the dissolution process of the fouling deposit. Specifications of the apparatus are shown in Table 2.

Aromatic compound mother liquid was supplied to the tank under a nitrogen atmosphere. The liquid was heated and kept at 60°C. First, the test tube coolant was circulated using a by-pass line. The coolant was kept at 41°C and the flow rate was 10 ml/min. After changing the coolant flow into the inserted test tube line, the temperatures of the coolant in the test tube were recorded by a computer. During the experiment, mother liquid temperature and inlet temperature of the coolant were stable. Unless otherwise stated in the figures, linear flow velocity of the liquid is 30 cm/s, water concentration is 2,000 wtppm and aromatic compound concentration is 20 wt% in the experiments.

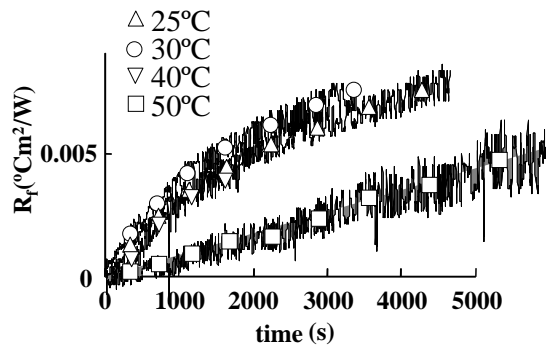
#### Experimental results

Figure 6 shows the results of fouling resistance of the test tube when changing flow velocity of the liquid by changing the rotation speed of the agitator. When the velocity of the liquid is increased from 15 cm/s to 30 cm/s, the fouling resistance is reduced by about 50%. The flow velocity of the liquid definitely has a major influence on fouling deposit formation. These results are explainable by the heat transfer coefficient changes, as shown in the calculation section below.

Figure 7 shows the results of the fouling resistance of the test tube when changing the inlet temperature of the



**Figure 6.** The influence of linear flow velocity of the liquid on the fouling resistance. Solid lines are raw data, and the symbols represent their average values. (30 cm/s: water concentration 3,000 wtppm, the others : 2,000 wtppm).



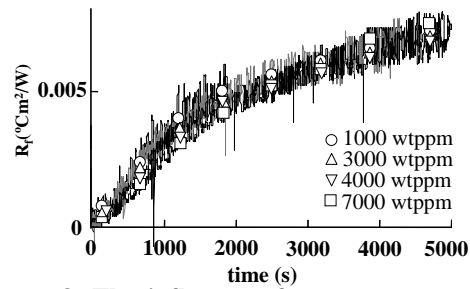
**Figure 7.** The influence of the coolant temperature in the test tube on the fouling resistance. Solid lines are raw data, and the symbols represent their average values.

coolant. The fouling resistance decreases markedly when the coolant temperature was raised to 50°C.

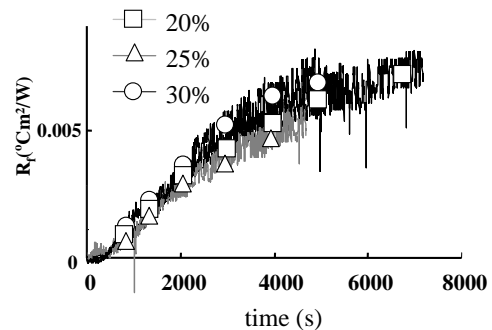
Figures 8 and 9 show the effects of water and aromatic compound concentrations in the liquid. They had no effect on the fouling resistances in the concentration range studied.

In addition, the surface roughness effect was tested with a test tube treated by electrochemical polish. However, no effect was seen in our apparatus.

The melting process of the foulant was also measured with the simulator. The heat flux necessary to melt the foulant was measured and used for the actual plant melting system. In the plant, 0.3 MPag steam traces, which could supply a heat flux a few times higher than the measured amount, were installed at the heaviest fouling part to melt the deposit. After installing the tracing, the



**Figure 8.** The influence of water concentration in the liquid on the fouling resistance. Solid lines are raw data, and the symbols represent their average values.



**Figure 9.** The influence of aromatic compound concentration in the liquid on the fouling resistance. Solid lines are raw data, and the symbols represent their average values.

duration of continuous plant operation became twice as long as pre-installation.

#### Approach to numerical analysis

The fouling rate is defined as the difference between the deposition rate and the removal rate of the fouling (equation (1)).

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

Kern and Seaton [1] expressed each rate for a simple type of dirt fouling as follows. Assuming that the rate of transport and deposition are constant with time, the rate of deposition can be expressed by equation (2). Assuming that the removal rate varies directly as the shear stress and the deposit thickness, it is expressed by equation (3).

$$m_d = K_1 c' W \quad (2)$$

$$m_r = K_2 \tau x_f \tag{3}$$

The formation (deposition) rate of crystallization fouling is expressed by Reitzer [2]. In his model, the formation rate is dependent on supersaturation, and the formation rate is written as equation (4).

$$m_d = k_1 \left[ \frac{\left( \frac{q}{A} \right)}{h_i} \right]^n \tag{4}$$

Combining the formation rate of the Reitzer model and the removal rate of the Kern-Seaton model, we created a combined Kern-Seaton-Reitzer model for the calculation of our crystallization fouling rate. (equation (5))

$$\frac{dx_f}{dt} = k_1 \left[ \frac{\left( \frac{q}{A} \right)}{h_i} \right]^n - K_2 \tau x_f \tag{5}$$

**Calculation of fouling resistance of the external cooler loop of the industrial plant**

The procedure of the cooler fouling resistance calculation is as follows.

- 1) Deposit growth rate in the cooler loops is measured by the gamma ray sensor.
- 2) From the performance curve of the cooler loop pump, the flow rate can be calculated using measured fouling positions and growth rates.
- 3) The fouled parts, which are cleaned every four hours, have no fouling after the cleaning sequences. Using the calculated flow rate,  $dx_f/dt$  in the cooler tubes is estimated by the Kern-Seaton-Reitzer model. Then equation (5) is integrated into the fouling thickness of the cooler tubes ( $x_f$ ). The fouling resistance can be obtained with the deposit thermal conductivity estimated from similar organic compound. To estimate the heat transfer coefficients, we used the Hausen equation [5] for the inside tube wall and the correlation introduced by HTFS [6] for the outside tube wall. Shear stress  $\tau$  is calculated by the common equation using friction factor (this is also described in reference [1]). The linear flow velocity of the fluid in the cooler tubes is about 2 m/s or less. The heat transfer area of the heat exchanger is about 300 m<sup>2</sup>.

**Table 3. Fitted parameters.**

	$k_1$	$n$	$K_2$
The plant cooler	1E-9	1.9	7E1
Fouling simulator	2E-8	1.9	-

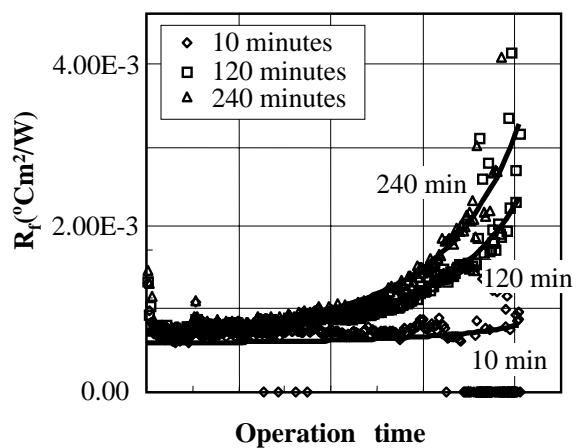
Unit:  $k_1$  [m/s(°C)<sup>n</sup>],  $K_2$  [ms/kg]

4) Using  $k_1$ ,  $K_2$  and  $n$  as fitting parameters, the calculated fouling resistance trend curve of the cooler is fitted to the actual plant fouling resistance.

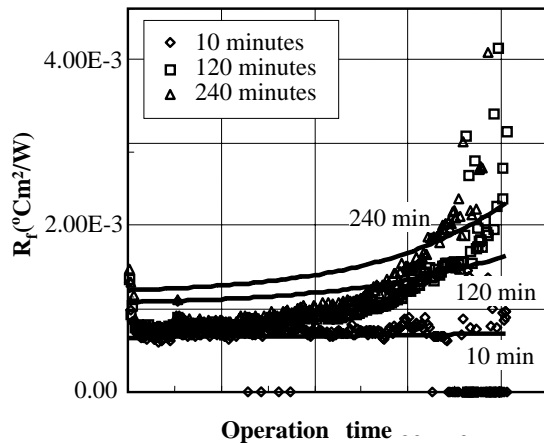
5) The fitting calculations are done for 10, 120 and 240 minutes after every cleaning sequences. The fitting values of the parameters are listed in Table 3.

The results of the calculations using the combined model are shown in the Figure 10. Even though the cooler was cleaned alternately every four hours and had no fouling in the cooler, the fouling deposit grew in the pipe near the crystallizer (the heaviest fouled part shown in Figure 3), and the flow rate of the fluid in the external cooler loop decreased. To maintain production, the heat flux of the cooler had to be constant. As the flow rate decreased, both shear stress and U value decreased. This led to heavier fouling in the cooler and the fouling resistance increased more and more rapidly.

In Figure 11, the fitting results by the original Kern-Seaton model, i.e. without the Reitzer term, are shown. In the case of the Kern-Seaton model, it is impossible to fit the fouling resistance curve of the plant cooler.



**Figure 10. Calculation results of the plant cooler fouling resistance by the Kern-Seaton-Reitzer model.** Solid lines are calculation results and the symbols are the plant data.

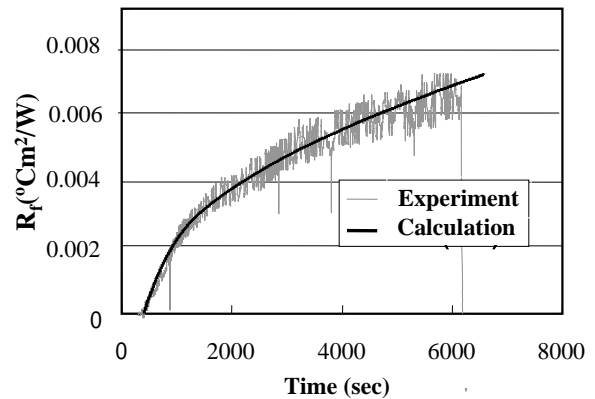


**Figure 11. Calculation results by Kern-Seaton model.** Solid lines are calculation results and the symbols are the plant data.

#### Calculation of fouling resistance of the laboratory fouling test unit

For the fouling test unit, we used the Reitzer model for fouling resistance calculation, because the flow velocity (30 cm/s) was small enough to omit removal rate considering from plant  $K_2$  value. (In the test unit calculation, although we tried to change  $K_2$  value ten times, calculation curves are almost same, because the shear stress is proportional to the square of flow velocity and the flow velocity 30cm/s makes the removal term rather small.) We adopted the same value as the plant for  $n$  because this value of the same crystallization might be independent of the equipment. The heat transfer coefficient inside the tube wall was calculated by Sieder and Tate's equation [7].  $k_i$  and the heat transfer coefficient outside the tube were fitting parameters. [In the case of the laboratory fouling test unit, the mother liquid is outside the tube and coolant is in the tube. We used  $h_o$  (outside heat transfer coefficient) instead of  $h_i$  (inside heat transfer coefficient) in the calculations.] Outside heat transfer coefficients are changed depending on the linear flow velocity of the liquid. One of the calculation results is shown in Figure 12, using the parameters listed in Table 3 and in the figure caption. In the case of the laboratory fouling simulator, fouling growth becomes smaller with time because heat flux decreases with fouling growth.

The fouling process which has crystal growth on the surface, such as aromatic compound crystallization fouling, can be expressed well by the Kern-Seaton-Reitzer model.



**Figure 12. A calculation example of a fouling simulator result.** Experimental data: figure 8, water concentration 7,000 wtppm. Calculation parameters are listed in Table 3, and outside heat transfer coefficient is  $1,400 \text{ J}^\circ\text{Cm}^2\text{s}$ .

However, the  $k_f$  values are much different between the 1.6 liter laboratory fouling test unit and the actual plant cooler. The factor of 7 difference in the liquid linear flow velocity ( the plant: 2 m/s, the test unit: 0.3 m/s) is thought to contribute to the discrepancy.

#### CONCLUSIONS

- Fouling thickness and its growth rate of the industrial plant were successfully measured by the low power gamma ray sensor with a long time integration system.
- A laboratory crystallization fouling test unit was constructed, with which we tested the effects of coolant temperature, linear flow velocity, surface roughness and concentrations of water and aromatic compound. Only coolant temperature and linear flow velocity affected the fouling rate significantly.
- Using the Kern-Seaton-Reitzer model, the trend of the fouling resistance can be expressed well. But deposition rate constant  $k_f$  values are very different between the plant and the laboratory tests.

#### ACKNOWLEDGEMENT

The authors would like to thank Professor A. P. Watkinson (The University of British Columbia) for his helpful suggestions, and Mr. T. Tsutsui for his experiment operation.

**NOMENCLATURE**

$A$  : heat transfer area [ $\text{m}^2$ ]  
 $c'$  : dirt concentration [-]  
 $h_i$  : heat transfer coefficient, inside tubes [ $\text{W}/\text{m}^2/^\circ\text{C}$ ]  
 $h_o$  : heat transfer coefficient, outside tubes [ $\text{W}/\text{m}^2/^\circ\text{C}$ ]  
 $K_1, K_2, k_f$ : constants  
 $m_d$  : formation rate  
 $m_r$  : removal rate  
 $n$  : constant exponent  
 $q$  : heat flow per unit time [W]  
 $R_f$  : fouling resistance [ $^\circ\text{Cm}^2/\text{W}$ ]  
 $t$  : time [s]  
 $W$  : constant mass flow rate of fluid [kg/s]  
 $x_f$  : fouling thickness [m]  
 $\tau$  : wall shear stress [ $\text{kg}/\text{s}^2/\text{m}$ ]

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