

## MODELLING FOULING IN HYDRODESULFURIZATION UNIT HEAT EXCHANGERS

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### ABSTRACT

Hydrosulfurization process removes sulfur from hydrocarbon streams (e.g. Naptha, Diesel streams) to meet the environmental regulatory requirements. The process consist of a series of heat exchangers to heat a feed stream from an effluent stream.

The manuscript addresses a practical methodology of modelling the impact of fouling in the feed/effluent exchangers when both the feed and effluent streams are subject to fouling. It is common to see shell-and-tube heat exchangers in these applications with feed stream on the shell-side and the effluent stream on the tube-side. During operation, usually, only the tube-side is subject to online cleaning (water wash) and the shell-side is cleaned at the end of the cycle. A techno-economic approach is introduced to identify ‘when’ and ‘where’ to inject the wash water stream for tube-side cleaning during operation. A case study is used to illustrate the practicality of the modelling approach.

### INTRODUCTION

Crude refining mainly involves three major steps: separation, purification and conversion. Raw crude is subject to atmospheric distillation where it is separated to fluids with different boiling point ranges. These fluids require further processing before reaching the consumer needs. One process is a purification process of removing sulfur from the fluid via hydrosulfurization (HDS). The process

involves the use of hydrogen, catalyst, temperature and pressure to remove the sulfur present in a hydrocarbon stream (e.g. straight-run Naptha, Diesel streams) such that it meets the environmental regulations [1].

A typical arrangement of a HDS unit is illustrated in Figure 1. Feed stream (e.g. straight-run Naptha) is mixed with hydrogen and heated through a set of heat exchangers. The feed is further heated via the furnace before entering the reactor. Cracking and coke formation of the feed stream may occur in the furnace. The reactor consists of a catalyst which mainly performs the following reactions [2]:

1. Hydrosulfurization: removes sulfur from the feed and creates  $H_2S$ .
2. Hydrogenation: reaction of aromatics and olefins with hydrogen which saturates unsaturated  $C=C$  double bonds.
3. Reaction of hydrocarbons containing nitrogen with hydrogen and creates  $NH_3$ .

All reactions above are exothermic and the temperature of the reactor is usually controlled via the supply of a cooler recycled hydrogen stream to the reactor. The heat of the stream leaving the reactor (effluent stream) is recovered via the heat exchangers. After leaving the feed/effluent heat exchangers, the effluent stream is further cooled and enters a separation drum where the gas stream is separated from the liquid stream.

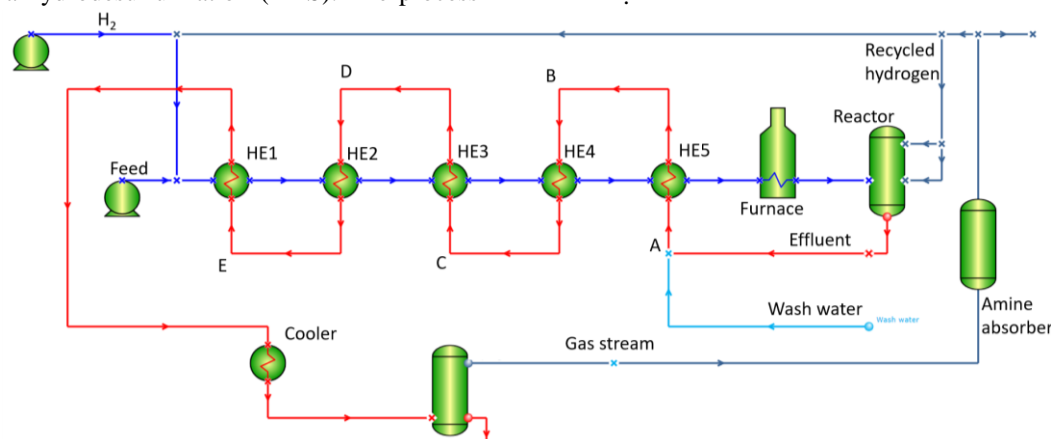


Fig. 1: Schematic of a hydrosulfurization unit. Locations A, B, C, D and E shows possible wash water injection points.

The organic chlorides maybe present in the feed streams which may form HCl when reacting with hydrogen. HCl and  $\text{H}_2\text{S}$  tends to react with  $\text{NH}_3$  creating ammonium chlorides and ammonium sulfides/bisulfides. These salts have a tendency to crystalize during operation while cooling down.

The HDS unit is likely to suffer from fouling in the feed/effluent heat exchangers [3–9], coolers [10], furnace and reactor. Common methods to minimize HDS unit fouling includes gas blanketing of feedstock tanks (to eliminate  $\text{O}_2$  [11], modifying exchanger design [11, 12], use of antifoulants [3, 13, 14], change in feed quality [15] or even nitrogen removal from hydrocarbon [16].

The focus of this manuscript is on modelling the fouling of feed/effluent exchangers. Shell-and-tube heat exchangers are commonly observed in these systems. Other heat exchanger types are also installed in some facilities which are discussed elsewhere [12, 17]. Modelling exchangers with both tube- and shell-sides fouling are discussed in literature [18] however the associated fouling mechanisms are different.

The feed stream may be subject to chemical reaction fouling (e.g. polymerization in the presence of oxygen) and the effluent stream may be subject to crystallization fouling (due to the deposition of salt). Usually the effluent stream is on the tube-side of the heat exchanger as the salt deposition can be water washed during operation and the effectiveness of water wash on removal of the salt deposits is higher on the tube-side. The shell-side is not cleaned during

operation. The feed/effluent exchanger is cleaned on both the shell-and tube-sides at the end of a cycle. An end of the cycle is determined under several factors including the drop in the efficiency of the reactor catalysts.

The sub-cycle of when to inject wash water on the tube-side and where to inject it (in the section marked A, B, C, D or E) may require optimization in practice. The question on when to inject wash water resembles a similarity to the optimization problem previously discussed in literature on when and which cleaning method to use for an exchanger fouling under a two-layer fouling model [19, 20].

In Ishiyama *et al.* [19], the thermal resistance caused by a fouled layer is described as the sum of the thermal resistance caused by a non-aged deposit (gel) and an aged deposit (coke). A less intense cleaning method (e.g. chemical cleaning) removes only the soft gel layer, while an intense cleaning method (mechanical cleaning) removes both the gel and the coke layer (Figure 2(a)). A formulation is then described on the optimum number of chemical cleaning actions required before a mechanical cleaning action is performed [19]. For the feed/effluent heat exchangers a similar formulation can be obtained. The thermal resistance in such units are the sum of the thermal resistances of the deposits formed on the tube-side and the shell-side. The optimum number of tube-side cleaning actions required (water wash) before the end of cycle where both the tube-side and the shell-side is cleaned needs to be evaluated (Figure 2(b)).

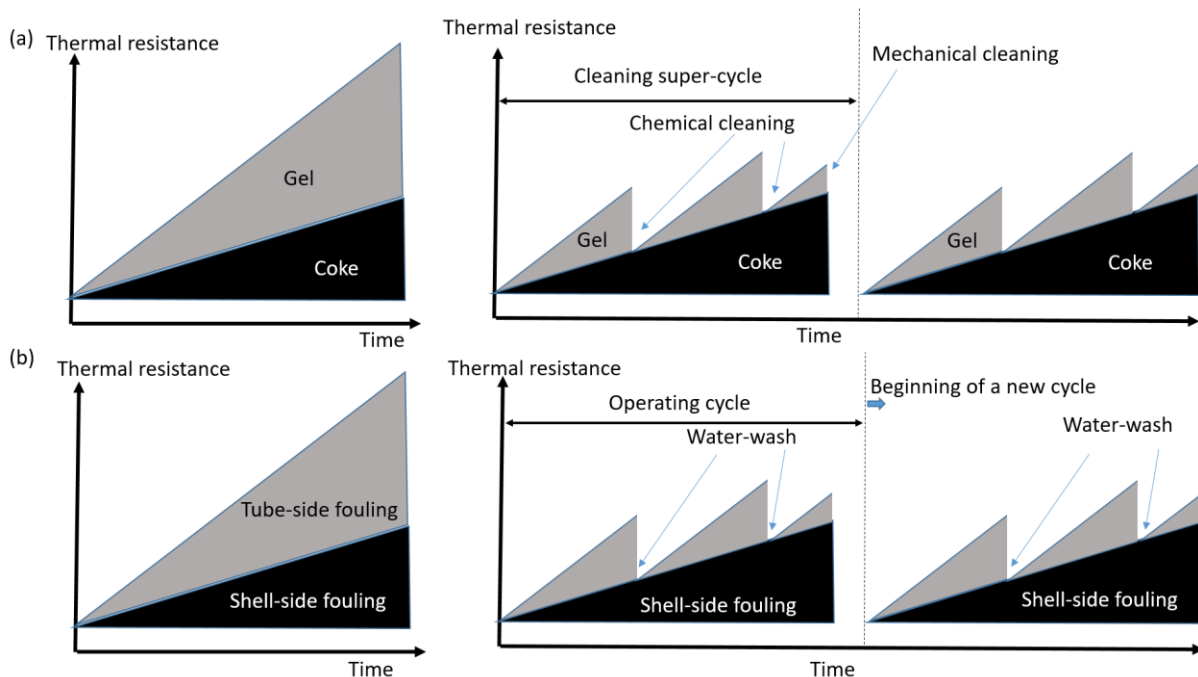


Fig. 2: Comparison of similarities between thermal resistance profile for (a) a two-layer fouling model with chemical cleaning removing the soft gel layer and the mechanical cleaning removing both the soft and hard layers; (b) feed/effluent exchanger where both the tube-side (effluent stream) and the shell-side (feed stream) are fouling.

## METHODOLOGY

### Heat exchanger network model

A commercial heat exchanger network simulator (HTRI SmartPM [21]) is used to model the feed/effluent exchangers. The feed stream consists of a two-phase naphtha stream and a non-boiling hydrogen stream. The effluent stream consists of two phase hydrocarbon stream and a mix of non-condensing gases including hydrogen, ammonia and hydrogen sulfide. A hypothetical case consisting of five exchangers in series was selected to model the network. All exchanger geometries, stream thermo-physical properties and vapour properties, stream operating conditions were entered to the software. Table 1 summarizes the stream inlet conditions to the network and Table 2 summarizes the exchanger operating conditions.

Table 1: Stream inlet conditions

	Feed stream	Effluent stream
Flow rate (kg/s)	35	35
Temperature (°C)	140	250 (at start)
Pressure (barg)	50	35

Table 2: Summary of exchanger operating condition at clean state

	Area (m <sup>2</sup> )	$U_{cl}$ (W m <sup>-2</sup> K <sup>-1</sup> )	Q (MW)
HE1	140	500	1.1
HE2	140	520	1.3
HE3	140	530	1.6
HE4	140	550	2.0
HE5	140	570	2.4

The duty heat transfer coefficient,  $U$ , of an exchanger is given by

$$\frac{1}{U} = \frac{1}{h_o} + \frac{1}{h_{od}} + \frac{d_o \ln\left(\frac{d_o}{d_i}\right)}{2k_w} + \frac{d_o}{d_i} \frac{1}{h_{id}} + \frac{d_o}{d_i} \frac{1}{h_i} \quad (1)$$

Here,  $h_o$  is the external film transfer coefficient,  $h_{od}$  is the external dirt coefficient,  $h_{id}$  is the internal dirt coefficient,  $k_w$  is the thermal conductivity of the wall,  $d_i$  is the tube internal diameter and  $d_o$  is the tube external diameter. The calculation of shell-side and tube-side heat transfer coefficients and pressure drops are based on the proprietary equation built in the software.

The external and internal dirt coefficients are evaluated via the estimation of the change in the rate of the thermal resistance and adding the change in resistance to the thermal resistance at the previous time step.

$$\frac{1}{h_{od}} = R_{f,shell} + \left( \frac{dR_f}{dt} \right)_{shell} \Delta t \quad (2)$$

$$\frac{1}{h_{id}} = R_{f,tube} + \left( \frac{dR_f}{dt} \right)_{tube} \Delta t \quad (3)$$

### Fouling model for the feed stream

In this example the feed stream is assumed to be straight-run naphtha located on the shell-side of the heat exchanger. It is also assumed that the presence of oxygen is causing a polymerization reaction with gum deposition. Such reactions were described by Taylor and Frankenfeld [22], where the immediate products of reaction of oxygen and hydrocarbons form hydroperoxides (HP). HP further reacts to form insoluble oxidized species, or in parallel reactions, to dissolved oxidized species which then convert to insolubles. Formation of gum and deposits in an oxygenated naphtha stream were experimentally investigated by Herrera *et al.* [23] which reported an apparent activation energy for the formation of hydroperoxides to be 244 kJ/mol. This corresponds to a doubling of the rate with 3-4 °C rise in temperature.

A theoretical model for the feed stream thermal fouling rate is assumed in this manuscript. This will be tested against field data in an ongoing study. The fouling model takes the form of a chemical reaction such as described in literature [24, 25]:

$$\left( \frac{dR_f}{dt} \right)_{shell} = \frac{\alpha}{h} \exp\left( \frac{-E_a}{RT_{film}} \right) \varphi \quad (4)$$

Here,  $E_a$  is the apparent activation energy for the formation of hydroperoxides.  $a$  is the deposition constant representing the feed stream chemistry and the oxygen concentration.  $h$  is the film transfer coefficient.  $T_{film}$  is the film temperature and  $R$  is the gas constant.  $\varphi$  is the probability of attachment which is modelled as

$$\varphi = \frac{2.5}{1 + \exp(0.2\tau)} \quad (5)$$

$\tau$  is the shell-side cross flow shear stress. The form of equation (4) was derived via fitting the trend in shear stress and deposition rate for fouling in hydrocarbon streams observed from field data.

### Fouling model for the effluent stream

To simplify the presentation in this manuscript, the model formulation uses a thin slab approximation, assuming the deposit thickness is much smaller than the tube internal diameter [26]. The change in the rate of thermal fouling resistance

of the effluent stream is modelled as the change in the thickness of the deposit:

$$\frac{dR_f}{dt} \approx \frac{1}{\lambda} \frac{d\delta}{dt} \quad (6)$$

Here  $\delta$  is the thickness of the foulant deposit formed on the tube-side and  $\lambda$  is the deposit thermal conductivity. The rate of change in thickness is related to the rate of mass deposition as:

$$\frac{d\delta}{dt} = \frac{1}{A_i} \frac{dV}{dt} = \frac{1}{A_i \rho} \frac{dm}{dt} \quad (7)$$

A methodology to estimate the rate of stream depositions using a thermo-dynamic approach can be compiled through solving the thermo-dynamic equations for sublimation [27–30]. The rate of deposition is presented for ammonium chloride and ammonium hydrosulfide as a function of partial pressures, total pressure and temperature.

$$\left( \frac{dm}{dt} \right)_{NH_4Cl} = f_1(P_{NH_3}, P_{HCl}, P, T) \quad (8)$$

$$\left( \frac{dm}{dt} \right)_{NH_4HS} = f_2(P_{NH_3}, P_{H_2S}, P, T) \quad (9)$$

Here,  $P$  is the system pressure and  $T$  is the system temperature.  $P_{NH_3}$ ,  $P_{H_2S}$  and  $P_{HCl}$  are the partial pressures of  $NH_3$ ,  $H_2S$  and  $HCl$ , respectively.

As an illustration, only the deposition of ammonium chloride is discussed in this article without loss of generality. The rate of deposition of  $NH_4Cl$  is quantified by adopting the methodology presented by Wu [31]:

$$\left( \frac{dm}{dt} \right)_{NH_4Cl} = \left( \frac{dm}{dt} \right)_{effluent} \times \frac{(P_{HCl} + P_{NH_3}) - \sqrt{(P_{HCl} + P_{NH_3})^2 - 4(P_{HCl}P_{NH_3} - K_1)}}{2P} \quad (10)$$

$$K_1 = \left( \frac{10^{\left( A - \frac{B}{C+T} \right)}}{2} \right)^2 \quad (11)$$

where  $A = 9.3557$ ,  $B = 3703.7$  and  $C = -41.15$ .

Figure 3 is a plot of ammonium chloride dissociation curve. The region above and below the curve denotes regions where deposition would and would not occur, respectively. It is assumed that all deposits formed will attach to the surface. The deposition rate for each exchanger is evaluated at the outlet surface temperature of the tube (or deposit) to represent the maximum deposition rate.

#### Scheduling wash water timing

For a falling rate process, the timing of ‘when’ to clean a unit is derived using cyclically averaged daily cost,  $\phi$  (e.g. for evaporators [19], exchangers with surface coating [32, 33]).  $\phi$  is defined by [19, 34]:

$$\phi = \frac{C_E \left[ \int_0^t (Q_{cl} - Q) dt' + Q_{cl} t_w \right] + C_{cl}}{t + t_w} \quad (12)$$

Here  $C_E$  is the cost of energy,  $C_{cl}$  is the cost of wash-water injection,  $Q$  is the heat duty,  $t$  is time,  $t_w$  is the period of wash-water injection.

The heat duty,  $Q$ , of an exchanger is presented via:

$$Q = (H_{feed,outlet} - H_{feed,intlet}) \times \text{mass flow rate} \quad (13)$$

Here  $H$  is the total enthalpy. Subscripts inlet and outlet represent the inlet and outlet streams respectively. Subscript ‘feed’ denotes the feed stream.

The usage of equation is extended for shells in series as:

$$\phi = \frac{C_E \left[ \int_0^t \sum_{i=1}^n (Q_{cl,i} - Q_i) dt' + \sum_{i=1}^n Q_{cl,i} t_w \right] + C_{cl}}{t + t_w} \quad (14)$$

A water wash is performed when  $\phi$  is minimum. i.e.

$$\frac{d\phi}{dt} = 0, \text{ when } \frac{d^2\phi}{dt^2} > 0 \text{ and } t + t_w < t_{cycle} \quad (15)$$

Here  $t_{cycle}$  is the length of the cycle.

As an illustration, in the case study, it is assumed that,  $t_w = 1$  day,  $t_{cycle} = 1$  year,  $C_E = 6$  US\$/GJ,  $C_{cl} = 1000$  US\$.

#### Identifying water injection point

The water injection point is determined via identifying the first heat exchanger that falls within the deposition zone. The effectiveness of the water wash is dependent on the water being at liquid state. It would be important to check how the water phase would change between the exchangers.

### CASE STUDY

A heat exchanger network illustrated in Figure 1 is modelled. The conditions of the heat exchangers at clean state is shown in Figure 3(i). The effluent stream outlet temperature is used to represent the heat exchangers at the plot which is a representation of the maximum deposition scenario (worst case).

The product of  $P_{\text{NH}_3}$  and  $P_{\text{HCl}}$  were assumed as marked by HE5 in Figure 3(i).

Fouling in the feed-effluent units decreases the furnace inlet temperature. In this case study, an operating scenario is assumed where the efficiency of the catalyst in the reactor decreases with time. The operation of the reactor is not modelled in this work, however, it is reflected via the increase in furnace outlet temperature with operation to maintain the required conversion at the reactor. The increase in furnace outlet temperature for a furnace operating at its maximum capacity would require increasing the furnace inlet temperature. This is achieved through control of the effluent temperature (in operation this

is done by controlling the cool hydrogen streams purged to the reactor).

Figure 4 shows how the effluent stream inlet temperature is varying in this case study. Two plots of the furnace inlet temperature are also plotted, reflecting the performance of no fouling and fouling (both on the tube-side and shell-side) respectively. The network heat duties associated with Figure 4 is plotted in Figure 5. When identifying the optimum cleaning timing via equations (14) and (15), the clean network duty is based on the simulation where only the feed stream (shell-side is fouling) but no effluent stream (tube-side) fouling.

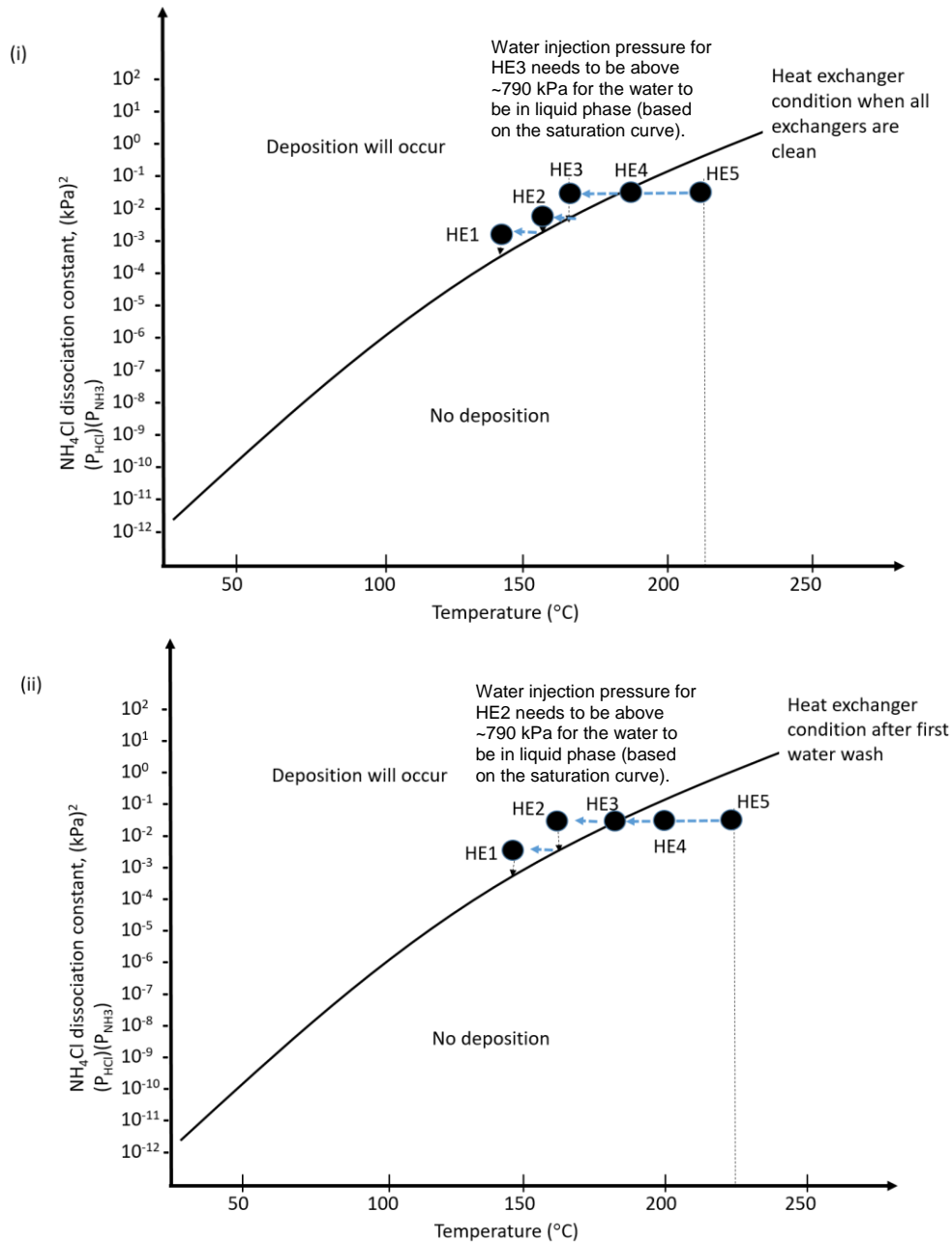


Fig. 3: Dissociation curve for ammonium chloride (based on Wu [31]). ‘HE’ denotes heat exchanger operating conditions for units HE1 to HE5 in Figure 1. (i) clean condition and (ii) after first water-wash.

The cyclically averaged daily cost of operation is plotted in Figure 6 indicating the first water wash to be economically optimum after about 2.5 months of operation. The new operating conditions of the exchangers (after the first water-wash) are now replotted in Figure 3(ii).

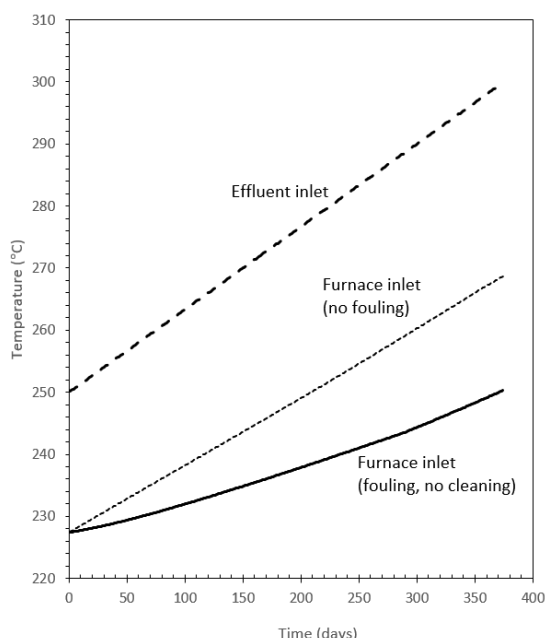


Fig. 4: Profile of effluent stream and furnace inlet stream temperatures.

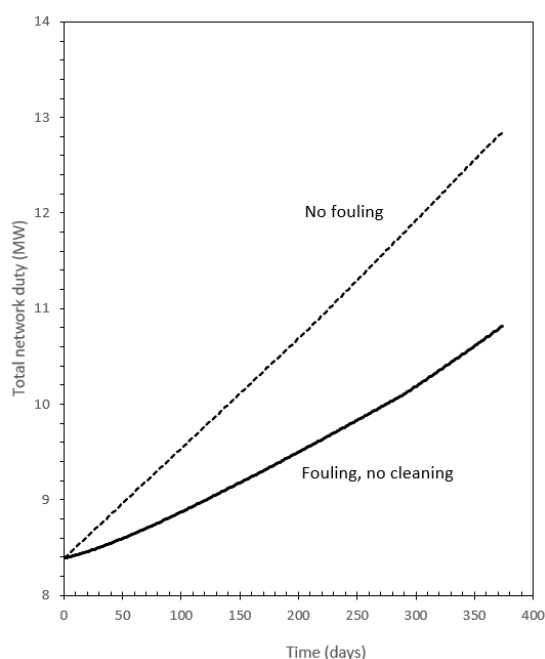


Fig. 5: Total network duty reflecting the operation in Figure 4.

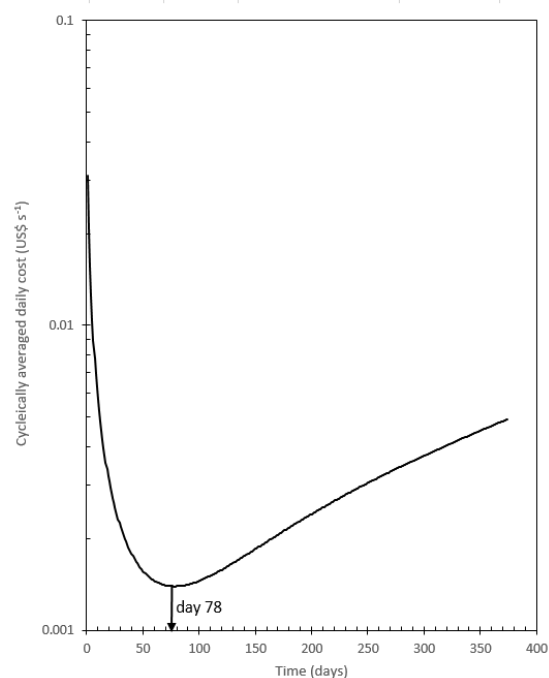


Fig. 6: Cyclically averaged daily cost indicating the optimum timing for first water wash.

The operating conditions (effluent stream surface temperature at the outlet) has shifted as the water-wash only cleans the tube-side and not the shell-side. The optimum location for wash-water injection has also shifted from location C to location D (marked in Figure 1).

Now heat exchangers HE3, HE4 and HE5 has only shell-side fouling. Repeating the calculation of daily averaged operating cost shows a minimum after another ~3.5 months of operation (Figure 7). The period for the next clean has extended as the rate and quantity of crystallization fouling reduces with operation (due to the increased effluent side surface temperature). An example fouling resistance plot is shown in Figure 8 (for HE2) where shell-side deposit remains after the water washes.

The algorithm did not recommend a third water wash as the economic benefit of waiting till the end of operational cycle. This is a result of the second water wash, where the heat exchanger location (in Figure 3(ii)) shifts further to the right and the impact of deposition of ammonium chloride on the tube-side is negligible compared to the fouling on the shell-side.

## CONCLUSIONS

- A systematic approach to model fouling in heat exchanger networks associated with hydro-desulfurization unit is introduced.
- A methodology is used to identify the optimum location for the tube-side wash water injection.
- The optimum wash water cleaning cycle is successfully generated based on maximizing plant economics, incorporating plant operational strategies.

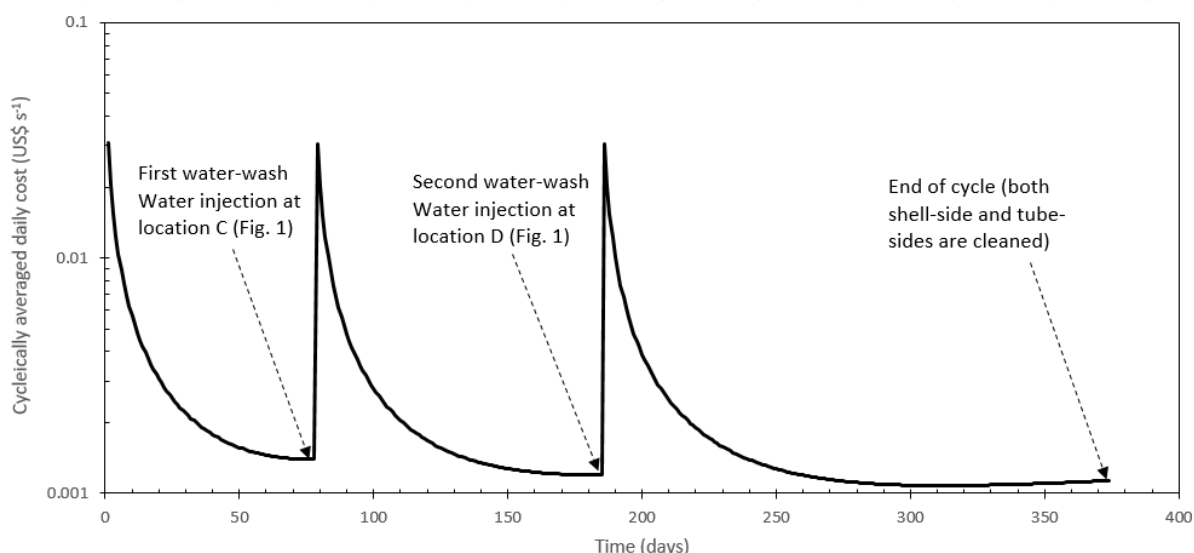


Figure 7: Summary of cyclically averaged daily cost over the operating cycle of the feed effluent exchanger.

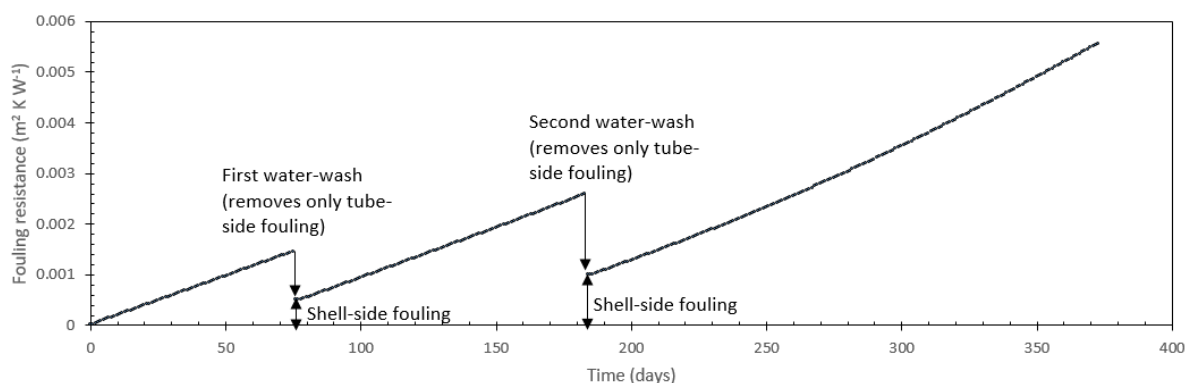


Figure 8: An example fouling resistance plot for heat exchanger, HE2.

## NOMENCLATURE

$C_E$	Energy cost, US\$ J <sup>-1</sup>
$C_{cl}$	Cost of wash water injection, US\$
$d$	tube diameter, m
$E_a$	apparent activation energy, J mol <sup>-1</sup>
$h$	film transfer coefficient, W m <sup>-2</sup> K <sup>-1</sup>
$H$	Enthalpy, J kg <sup>-1</sup>
$k_w$	wall thermal resistance, W m <sup>-1</sup> K <sup>-1</sup>
$m$	fouling deposit mass, kg
$n$	total number of heat exchangers, -
$P$	total pressure, mmHg
$P_{HCl}$	partial pressure of HCl, mmHg
$P_{H_2S}$	partial pressure of H <sub>2</sub> S, mmHg
$P_{NH_3}$	partial pressure of ammonia, mmHg
$Q$	Heat duty, MW
$R$	gas constant, J mol <sup>-1</sup> K <sup>-1</sup>
$R_f$	fouling resistance, m <sup>2</sup> K W <sup>-1</sup>
$t$	time, s
$t_{cycle}$	length of cycle, s
$t_w$	length of wash water injection, s
$T$	temperature, K
$U$	duty heat transfer coefficient, W m <sup>-2</sup> K <sup>-1</sup>
$V$	volume of deposit, m <sup>3</sup>

## Subscripts

d	dirt
feed	feed stream
film	film
i	inner
inlet	inlet stream
o	outer
outlet	outlet stream
shell	shell-side
tube	tube-side

## Symbols

$\alpha$	deposition constant, s <sup>-1</sup>
$\Delta$	difference
$\delta$	deposit thickness, m
$\phi$	cyclically averaged daily cost
$\varphi$	probability of attachment, -
$\lambda$	deposit thermal conductivity, W m <sup>-1</sup> K <sup>-1</sup>
$\rho$	density of deposit, kg m <sup>-3</sup>
$\tau$	surface shear stress, Pa

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