Investigation of Initial Fouling Rates of Calcium Sulfate Solutions under Non-Boiling Conditions (Work-in-Progress)

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ABSTRACT

This study initiates an experimental investigation of how process variables such as temperature and velocity affect the initial precipitation fouling rate of the inverse solubility salt, calcium sulfate, under sensible heating conditions. The effect of fluid velocity and temperature on the delay time is also being measured.

Introduction

Motivation for this work stems from the development of a mathematical model for the initial fouling rate in chemical-reaction, particulate and precipitation fouling (Epstein, 1994). In this study, the model will be tested using experimental data for calcium sulfate scaling under non-boiling conditions. According to the model, the attachment of the fouling deposit to the heat transfer surface is treated as a rate process in series with mass transfer under turbulent flow conditions. As shown in the model development, for a given solution and a fixed surface temperature, the attachment or surface integration coefficient (which is assumed to bear the Arrhenius relationship to the surface temperature and to be proportional to the fluid residence time near the surface) is inversely proportional to the square of the friction velocity, and the mass transfer coefficient is directly proportional to this velocity. Therefore, there is a maximum initial fouling rate at a given surface temperature for a range of fluid velocities, demonstrating a shift from mass transfer to attachment control. The model also predicts that this maximum rate (and its bracketing rates) and the fluid velocity at which it occurs both increase as the surface temperature is increased.

Experimental

The apparatus consists of a flow loop in which the calcium sulfate in filtered aqueous solution is continuously recirculated from a holding tank through the heated test section (d_i = 9.017 mm), a series of double pipe coolers and back to the holding tank. The test section itself is a 1.83 m long 304L stainless steel tube with an outside diameter of 9.525 mm, a wall thickness of 0.254 mm and a heated length of 0.771 m, which is subjected to electrical resistance heating at a constant and uniform heat flux. Bulk inlet and outlet temperatures were measured by thermocouples. The bulk inlet temperature was maintained at 55˚C, while clean tube surface temperatures were varied from 80 to 101˚C, as measured by ten thermocouples spaced longitudinally on the outside of the vertical tube. The rate of rise in surface temperature gives a measure of the local fouling resistance at that temperature. This Tube Fouling Unit (TFU) (Wilson and Watkinson, 1996; Rose et al., 2000) is configured such that test sections are used only once, and then sectioned to allow in situ deposit examination and further analysis of the nature of the deposit material, either by optical microscopy, scanning electron microscopy, elemental analysis or deposit coverage studies.

Due to the longitudinal temperature gradient at the surface of the tube, it was the highest temperature thermocouples that exhibited the highest rates of fouling, and thus limited the duration of an experiment. Because clean surface temperatures were as high as 101˚C, it was necessary to maintain some over-pressure on the test section to prevent the onset of boiling as the surface temperature rose due to fouling. Because of the high temperature restriction, most of the data from the low temperature regions of the tube gave barely measurable initial fouling rates, so they were neglected in the data analysis. Reynolds numbers based on local fluid properties were varied from 7000 to 21000 to provide adequate data for a complete study of the velocity effect on initial fouling rates.

Batches of calcium sulfate solution were prepared in saturated solutions (2100 ppm) from its powder. After ensuring the saturated condition by using EDTA titration, the solution was added to the holding tank. Prior to the addition of heat to the test section, the solution was circulated for one hour to ensure a thoroughly well mixed chemical system. The power to the test section was then applied to achieve the operating conditions required. Heating up the test section to steady state took approximately 30 minutes.

Results

Fouling in this system was thus far measured only thermally, although mass deposition and pressure drop measurements could also be made. The local heat transfer coefficient at a given thermocouple location along the length of the test section was determined from the following equation, where $\dot{Q}$ was evaluated from the voltage and current applied to the test section, T_b from the bulk inlet and outlet fluid temperatures and T_w calculated from the measured thermocouple temperature (T_o) :

$$U = \frac{\dot{Q}}{(T_w - T_b)} \qquad (1)$$

The fouling resistance R_f was determined from

$$R_f = U^{-1} - U_C^{-1} \qquad (2)$$

and the initial fouling rate from

$$\dot{R}_{fo} = dR_f / dt \big|_{t=0} = d\left(U^{-1}\right)/dt \qquad (3)$$

assuming that the convective heat transfer coefficient does not change with respect to time or with surface roughness effects. The flow rate and hence velocity of the fluid through the TFU was measured using a calibrated rotameter. The reported bulk velocity is the time averaged value over the duration of the experiment at any given level.

For each experiment, the thermal fouling results were measured from up to 10 thermocouples located at various axial positions, but fouling was observed only at the top thermocouples. For most of the experiments, the top thermocouples showed a linear increase in wall temperature with time after a delay time (t_d). This made the analysis for the initial fouling rate straightforward. In the region where the temperature is first increasing at a constant rate, the corresponding plot of reciprocal heat transfer coefficient versus time is linearly regressed and from equation (3) the slope is equal to the initial fouling rate.
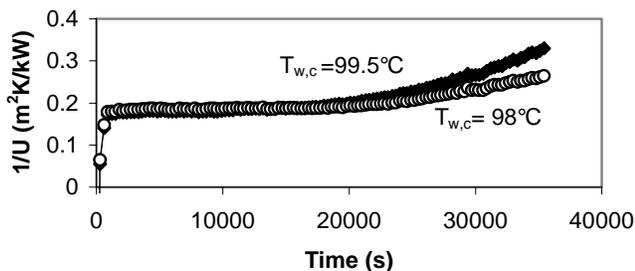
Figure 1. Reciprocal heat transfer coefficient for TFU 510 (V = 0.62 m/s)

Figure 1 shows a plot of reciprocal heat transfer coefficient versus time (Run 510) for temperatures $T_{w,c} = 99.5$ °C and $T_{w,c} = 98$ °C. Figure 2 shows a fouling Arrhenius plot $(\ln \dot{R}_{fo} = \ln A - \Delta E_f / RT_{w,c})$ for a given experiment, where individual thermocouple results were utilized to determine the surface temperature at a velocity of 0.62 m/s. The fouling activation energy ΔE_f
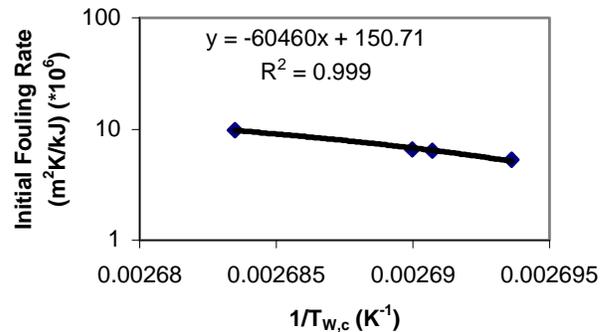
Figure 2. Arrhenius plot for TFU 510 (V=0.62 m/s)

for this experiment was determined as 503 kJ/mol, a value which characterizes the entire fouling process at the given velocity and not just the attachment process as described by the attachment-kinetics activation energy in the model.

The results for all runs performed to date are presented in Table 1. A kinetic compensation effect is evident where both the fouling activation energy, ΔE_f, and the pre-exponential term, A, increase very strongly with velocity. At a velocity of 0.62 m/s, for example, the fitted rate is a product of one term of magnitude 10^{+65} (A), and another of magnitude 10^{-71} ($e^{-\Delta E_f / RT_{w,c}}$).

Therefore, the fouling activation energy values of Table 1 are considered unreasonable. A moderate increase in ΔE_f with mass flux is expected from the mathematical model. For small fluid velocities (mass transfer control) the fouling activation energy will approach a low value, while for high fluid velocities (surface attachment control) the fouling activation energy will approach the purely attachment-kinetics activation energy (Rose et al., 2000).

To date, only a narrow range of temperature has been covered. The surface temperature range of 97-101°C includes the critical value of 98°C where gypsum is transformed into hemi-hydrate, as discussed by Mwaba et al. (2001). To obtain reasonable results for the fouling activation energy, more experiments should be carried out over a wide range of temperatures below 98°C.

From Table 1 it is however possible to use the Arrhenius expression to determine $\dot{R}_{fo}$ at a given value

of $T_{w,c}$ for each experiment and hence to tentatively isolate the effect of velocity on initial fouling rate. Thus
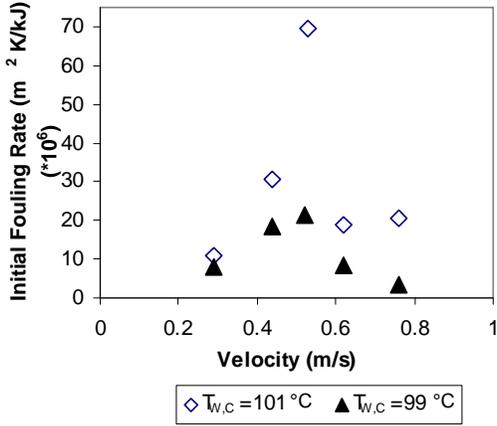

Figure 3. Effect of velocity on initial fouling rate for calcium sulfate solution
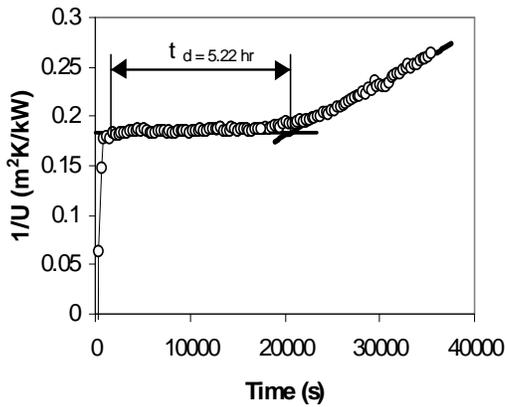

Figure 4. Delay time for $T_{w,c}$ = 98 $^\bullet$C (Run 510)

Figure 3 shows two sets of results at surface temperatures where the initial fouling rate is strongly dependent upon the velocity. In both cases we can see the presence of a maximum deposition rate at a critical velocity as predicted by the previously discussed model. The two plots indicate how strong a dependence the fouling rate has on surface temperature, with appreciable differences observed for only a 2°C temperature change.
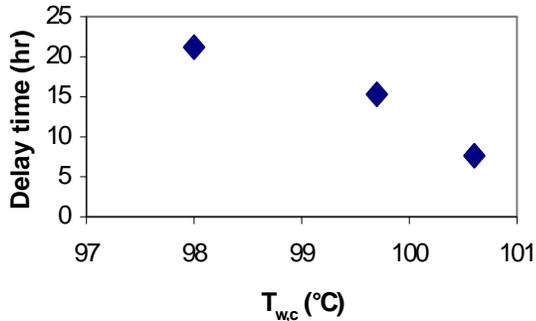
Delay Time

The period of time that elapses between the achievement of supersaturation and the first detection of a fouling deposit has been given different names and will be denoted here as the delay time. The duration of the delay time for a given system is affected by the degree of supersaturation, the temperature level, the velocity and the presence of impurities. The occurrence of a delay time is undoubtedly related to the kinetics of nucleation but its significance is difficult to analyse. It has been shown that $CaSO_4$ nucleation on the heat transfer surface of a non-boiling flow exchanger is a transient nucleation phenomenon (Hasson and Zahavi, 1970). Also, Branch (1991) correlated the reciprocal of the delay time as if it were independent of solute concentration but with an Arrhenius dependence on wall temperature, but Najibi et al. (1997) showed that the delay time is a strong function of the degree of supersaturation and, therefore, cannot be expressed by a zero-order model.

Figure 4 shows how the line representing the reciprocal heat transfer coefficient prior to fouling build-up (horizontal) intersects with the regressed straight line (the region with a constant fouling rate) and thus determines the delay time for each thermocouple. In all of the fouling runs for the present investigation, delay times were observed and measured using this method and then it was possible to see how the delay time varies with velocity and temperature.

**Table 1. Fouling activation energies for calcium sulfate experiments**

Run	$T_{w,c}$ (°C)	$T_{b,x}$(°C)	V (m/s)	ΔE_f (kJ/mol)	A (m^2K/kJ)
507	97-100	70-72	0.29	176	4.25E+19
506	98-100.6	72-74	0.44	313	1.40E+39
510	98-100	73-74	0.62	503	2.83E+65
511	99-100	73-74	0.76	583	2.72E+77
512	99-101	72-74	0.84	1248	4.59E+169

Figure 5 shows the effect of surface temperature on the delay time for TFU 506. It shows that the delay time is a strong function of surface temperature.

Figure 5. Effect of surface temperature on the delay time at V = 0.44 m/s

Figure 6 shows the effect of velocity on the delay time. It is seen that as the velocity increases, the delay time first decreases and then remains approximately constant**.**
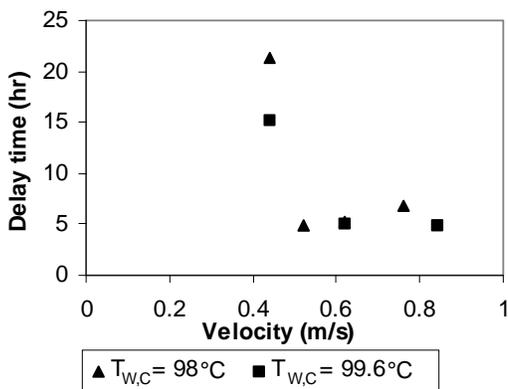
Figure 6. Effect of velocity on the delay time at two different wall temperatures

Conclusions

A systematic study of calcium sulfate scaling in turbulent flow under sensible heating conditions has been initiated. The results obtained thus far show, with some scatter, a maximum initial fouling rate at a given surface temperature over a range of fluid velocities, and an Arrhenius dependence on surface temperature at any given velocity. Overall activation energies are inordinately large and therefore require further investigation. Delay times were found to decrease with increasing surface temperature and fluid velocity below

about 0.5 m/s, but to remain approximately constant at higher velocities.

This study will be continued over a wider temperature range, with deposit analysis.

NOMENCLATURE

A = pre-exponential factor, $m^2 \cdot K/kJ$

d_i = inside tube diameter, mm or m

ΔE_f = fouling process activation energy, J/mol

$\dot{Q}$ = heat flux, kW/m^2

R = universal gas constant, 0.008314 k J/mol·K

R_f = fouling resistance, $m^2 \cdot K/kW$

$\dot{R}_{fo}$ = initial fouling rate, $m^2 \cdot K/kJ$

T = temperature, ºC or K

T_b = bulk fluid temperature, ºC or K

T_o = outside tube wall temperature, ºC or K

T_w = inside tube wall temperature, ºC or K

t = time, s

U = overall heat transfer coefficient, $kW/m^2 \cdot K$

V = bulk fluid velocity, m/s

t_d = delay time, s

Subscripts

c = clean

REFERENCES

Branch, C. A. "Heat transfer and heat transfer fouling in evaporators with kraft pulp black liquor,". Ph.D. thesis, University of Auckland, New Zealand (1991).

Epstein, N., "A Model of the Initial Chemical Reaction Fouling Rates for Flow within a Heated Tube, and its Verification," Heat Transfer 1994, Proceedings of The Tenth International Heat Transfer Conference, Brighton, UK , **4**, 225-229 (1994).

Hasson, D., Zahavi, J., "Mechanism of Calcium Sulfate Deposition on Heat-Transfer Surfaces," I&EC Fundamentals **9,** 1-10 (1970).

Mwaba, M. G., Rindt, C. C. M., Vorstman, M. A. G., Van Steenhoven, A. A., "Calcium Sulfate Deposition and Removal Characteristics on a Heated Plate," Proceedings of an Engineering Foundation Conference on Heat Exchanger Fouling: Fundamental Approaches & Technical Solutions, Davos, Switzerland, July, 2001.

Najibi, S. H., Muller-Steinhagen, H., Jamialahmadi, M., "Calcium Sulphate Scale Formation During Subcooled Flow Boiling," Chemical Engineering Science **52**, 1265-83 (1997).

Rose, I. C., Watkinson, A.P., Epstein, N., "Testing a Mathematical Model for Initial Chemical Reaction Fouling using a Dilute Protein Solution," Canadian Journal of Chemical Engineering **78**, 5-11 (2000).

Wilson, D.I., Watkinson, A. P., "A Study of Autoxidation Reaction Fouling Heat Exchangers," Canadian Journal of Chemical Engineering **74**, 236-246 (1996).