

PART II  
PARAFFIN WAX DEPOSITION  
AND FOULING

## PART II - PARAFFIN WAX DEPOSITION AND FOULING

### 1. INTRODUCTION

The problem of deposition and fouling by waxy hydrocarbons is of long standing in the oil processing industry<sup>(1,2)</sup>. It is of particular importance in pipeline operations and any subsequent processing stages where cooling occurs. In pipelines, paraffin wax deposition may increase the pressure drop during normal operation and cause major difficulties during restarting after shut-down. When waxy hydrocarbons are cooled in heat exchangers they tend to deposit and cause fouling; increasing the overall heat transfer resistance and pressure drop.

Methods used to reduce paraffin deposition in industry are both mechanical and chemical in nature. Pipelines are frequently cleaned by mechanical 'pigs' that are transmitted with the bulk flow and scrape away the deposits. Chemical additives affect the crystal structure of materials depositing and may reduce their solidification temperature. Deposition and fouling may also be reduced by proper design and operation of pipelines and heat exchangers. This requires knowledge of the deposition behaviour of waxy hydrocarbons in relation to the various process variables such as velocity, concentration and temperature. The present work was performed to investigate the deposition and fouling characteristics of paraffin wax in kerosene solutions.

### 2. PREVIOUS WORK

#### 2.1 Introduction

In the oil industry the formation of any predominantly organic matter in oil well tubing, surface flowlines and other production equipment, is referred to as paraffin deposition<sup>(3,4)</sup>. The deposits consist mainly of n-paraffins with smaller amounts of branched and cyclic paraffins and aromatics<sup>(5)</sup>.

The literature on paraffin deposition deals primarily with flowlines at laminar flow conditions. Some of the literature, however, discusses the various factors affecting deposition, making it relevant to heat transfer and processing conditions. The latest comprehensive review available on paraffin deposition is from 1955<sup>(6)</sup> and prior to that the most thorough examination of the problem is from 1932<sup>(1)</sup>.

## 2.2 Paraffin Wax Solutions

The amount of paraffins in crude oils is usually in the range 1 - 30 per cent<sup>(5)</sup>, indicating the different deposition problems that may be encountered in the oil industry. The cloud point temperature of waxy hydrocarbons is a controlling factor in paraffin deposition. It indicates the amount of wax in solution and is determined empirically<sup>(7)</sup> as the temperature at which wax crystals appear when petroleum oils are cooled under prescribed conditions. Similarly, the pour point<sup>(8)</sup> is the temperature at which hydrocarbon solutions show no movement at standard conditions.

The crystalline nature of paraffin wax has been investigated by a number of workers<sup>(9,10,11)</sup>. Holder and Winkler<sup>(11)</sup> stated that paraffin wax crystals have the appearance of very thin diamond shaped plates consisting of layers of n-paraffins, stacked side by side parallel with the longer axis of the crystal.

The size and number of wax crystals formed in solutions depend on the rate of cooling. Tronov<sup>(12)</sup> stated that a high rate of cooling favoured the formation of a large number of crystals. Rafikov et al<sup>(13)</sup> studying paraffin based petroleum, observed that on rapid cooling many centres of crystallization arise, which lead to the formation of fine crystals. On slow cooling, however, the crystallization process occurs under more uniform conditions and large and more uniformly packed crystals are formed. Surface active components can have an appreciable effect on the nature of paraffin crystallization, leading to a depression of the pour point.

Both empirical and theoretical expressions are available for the solubility of paraffin waxes in petroleum fractions<sup>(C)</sup>.

## 2.3 Deposition Variables

### 2.3.1 Flowrate and time

Jessen and Howell<sup>(14)</sup> studied the effect of flowrate on paraffin deposition in pipes. The main conclusion of their work was that in laminar flow deposition increased with flowrate, reaching a maximum prior to transition to turbulent flow and then decreasing with increasing turbulence. The increase in deposition with flowrate was explained in terms of more particles being carried towards the wall. As the flowrate increased the shear stress at the wall became equal to or exceeded the deposit strength and deposition becomes

less. Paraffin wax deposited at high flowrates was observed to be considerably harder than at low flowrates.

Tronov<sup>(12)</sup> studied the effect of flowrate on paraffin deposition. The experimental results showed that the deposit thickness decreased with increasing velocity and that the deposit hardness, as expressed by the velocity required to remove it from the tube wall, increased with velocity. Tronov stated that studies on paraffin deposition indicated that the build-up of deposits alternates with their partial or total removal, independent of the nature of the surface. Armenski et al<sup>(15)</sup> observed deposit removal following their build-up when analysing the reduction in pipe diameter due to paraffin deposition.

Patton and Casad<sup>(16)</sup> studied paraffin deposition on a cold surface inserted into a well stirred wax solution maintained above its cloud point temperature. They found that deposition increase asymptotically with time. The initial rate of deposition and the asymptotic deposit both decreased with increased stirring. Hunt<sup>(3)</sup> and Patton and Jessen<sup>(4)</sup> found that paraffin deposition increased asymptotically with time.

### 2.3.2 Temperature

Cole and Jessen<sup>(17)</sup> studied how the temperature difference between the solution cloud point and a confining surface affected paraffin deposition. This was achieved by passing a kerosene-wax solution over a chilled copper plate. The amount of paraffin deposited was determined by removing the copper plate and weighing it. The temperature difference between the cloud point and the plate temperature was considered most important in controlling the accumulation. The experimental results showed that both the initial rate of deposition and the final amount deposited increased with the temperature difference. Jorda<sup>(5)</sup> has obtained similar experimental results.

### 2.3.3 Surface Properties

Cole and Jessen<sup>(17)</sup> studied the effect of wettability on paraffin deposition. The wettability of a copper plate was varied by applying different silicone coatings. The contact angles were measured with water. The amount of paraffin deposited for a given temperature difference decreased with increasing contact angle. It was found that the temperature difference and free surface energy acted independently in determining the amount of wax depositing. A low contact angle means a high free surface energy and more wetting. Cole and Jessen concluded that as paraffin wax is deposited on a surface it is held in place by adsorption forces. The adsorption forces are dependent upon the

free surface energy possessed by both the paraffin and the surface. As the free surface energy of the plate is reduced, a resultant decrease in the adsorption forces holding the paraffin to the plate surface takes place. This causes a decrease in the amount of paraffin which can be retained on the plate surface for the flow conditions present. Patton and Jessen<sup>(4)</sup> investigated the effect of wettability on paraffin deposition. They found that deposition increased with increased free surface energy of the deposition surface.

Hunt<sup>(3)</sup> studied the effect of roughness on paraffin deposition and concluded that deposits do not adhere to metals themselves but are held in place by surface roughness. Jorda<sup>(5)</sup> investigated the roughness effect in deposition. Paraffin deposition was found to increase with surface roughness. Patton and Casad<sup>(16)</sup> performed similar studies and concluded that no correlation could be observed between surface roughness and deposition. However, they argued that the adhesion bond at a surface should be proportional to the total contact area and therefore related to surface roughness.

## 2.4 Summary

1. The nature of wax crystals formed in solutions is affected by the rate of cooling and the presence of surfactants.
2. Paraffin deposition increases asymptotically with time.
3. The initial rate of deposition and the asymptotic deposition both decrease with increased flowrate.
4. The initial rate of deposition and the asymptotic deposition both increase with increased difference between the solution cloud point and wall temperature.
5. Increased flowrate increases the strength of paraffin wax deposits.
6. Paraffin deposits are held to deposition surfaces by adsorption forces.
7. Failures can occur in paraffin deposits resulting in random processes of build-up and break-down.

## 3. FOULING STUDIES

### 3.1 Introduction

The present studies are an extension of work carried out by Walker<sup>(18)</sup> on the

fouling characteristics of paraffin wax in kerosene solutions. Walker studied the effect of flowrate, wax concentration, bulk temperature and time on deposition in cooled heat exchanger tubes. A 51/54°C fully refined paraffin wax was dissolved in a commercial grade kerosene. The wax concentration used in the experiments ranged from 4.2 to 26.4 per cent by weight, corresponding to cloud point temperature from 10 to 32°C respectively. The average bulk temperature ranged from 28.9 to 49.5°C. In all of the 46 runs the bulk temperature was kept above the cloud point. At concentrations below 10 per cent the runs were carried out at ~ 30°C and ~ 50°C but at higher concentrations only at ~ 30°C. The Reynolds number of the paraffin wax-kerosene solutions ranged from 5045 to 25451 and experimental times were up to 167 hours.

The experimental results obtained by Walker<sup>(18)</sup> showed that the overall heat transfer resistance did not increase continuously or approach an asymptotic value. Instead, the overall resistance fluctuated about an initial value. These fluctuations and the overall heat transfer resistance itself, were both found to increase with increasing wax concentration, decreasing flowrate and decreasing bulk temperature. A visual examination of the paraffin wax deposits showed them to vary from individual particles to extended areas, depending on the operating conditions. The deposits were also found to be more extensive at the colder downstream end of the heat exchanger tubes.

### 3.2 Experimental

The main purpose of the experimental work was to obtain data for longer periods than achieved by Walker<sup>(18)</sup>. It was hoped that this would show if an asymptotic heat transfer resistance would be reached or that it had been reached in the first few minutes, not detectable on the apparatus.

The experimental work was carried out in the same apparatus as used by Walker<sup>(18)</sup> with minor modifications (see Figure 1). The apparatus was basically a closed circulation loop where an experimental solution could be circulated a constant bulk temperature and flowrate through ten parallel heat exchangers. The exchanger tubes were mounted vertically between horizontal delivery and discharge manifolds and were cooled by constant flowrate water from the mains, flowing counter-current to the experimental solution. The ten simulate heat exchanger tubes were made from copper 13.1 mm ID and 15.00 mm OD having an entry length of 762 mm with a further water-jacketed section 914 mm long. The water jacket was made from 19.1 mm ID copper pipe. The holding tank of the apparatus was 2660 litres stainless steel while all the pipework was made from copper. The

experimental procedure consisted of regularly measuring the inlet and outlet temperatures of the paraffin wax-kerosene solution and the cooling water. The flowrates were also measured. Before starting the extended experimental runs the apparatus was tested for reproducibility as compared with Walker's<sup>(18)</sup> results.

The paraffin wax-kerosene solution used in all the present experimental work was 26.4 per cent wax with a cloud point temperature of 32°C. The Reynolds numbers obtained ranged from 3000 to 13000 and the bulk temperatures from 33 to 43°C. The maximum experimental times reached were 220 hours. In all, 22 experimental runs were obtained.

The temperature and flowrate data were used to calculate the overall heat transfer resistance of each exchanger with time. A computer program was developed for this purpose. Walker<sup>(18)</sup> and Bott and Gudmundsson<sup>(A)</sup> have given the physical property data used in the calculations. Walker<sup>(18)</sup> has given the basic calculation procedures. The overall heat transfer resistance was used as an indication of the change of fouling resistance with time since the wall resistance was low and the water flowrate constant. Most of the experimental results are shown in Figures 2 - 8 where the overall resistance is plotted with time.

The experimental results confirmed the findings of Walker<sup>(18)</sup>. The overall heat transfer resistance did not increase continuously or approach an asymptotic value, even at the extended experimental times of 220 hours. Instead, it fluctuated about an initial value. These fluctuations and the overall heat transfer resistance both decreased with flowrate and temperature.

### 3.3 Temperature Profile

In all the experimental work the solution bulk temperature was maintained above its cloud point temperature<sup>(A)</sup>. The deposition process was therefore confined to the cooled heat exchanger tubes. Clearly, the temperature conditions existing at the exchanger wall govern the deposition process to a large extent. It was decided to investigate the likely temperature distribution (profile) in the experimental heat exchangers at asymptotic conditions.

There are two significant temperatures at which changes take place near a cold deposition wall. At the cloud point wax particles will be formed and at

the pour point the solution becomes solid. It was found for the 51/54°C paraffin wax solution used in the experimental work that the pour point was 3 - 4°C below the cloud point for the concentrations investigated<sup>(A,B,C)</sup>.

A computer program was developed to calculate the velocity and temperature profiles in turbulent pipe flow. The program was developed for the paraffin wax-kerosene solutions used by Walker<sup>(18)</sup> and in the present studies<sup>(A)</sup>. The program was based on the work of Deissler<sup>(19)</sup> and predicted the temperature distribution from the expressions:

(a)  $y^+ < 26$

$$T^+ = \int_0^{y^+} \frac{dy^+}{\frac{1}{Pr} + n^2 u^+ y^+ [1 - \exp(-n^2 \frac{\mu_w}{\mu} u^+ y^+)]} \dots (1)$$

(b)  $y^+ > 26$

$$T^+ = \frac{1}{K} \ln \frac{y^+}{y_1^+} + T_1^+ \dots (2)$$

where:

- $y^+$  = dimensionless distance
- $u^+$  = dimensionless velocity
- $T^+$  = dimensionless temperature
- Pr = Prandtl number
- n = constant
- $\mu$  = viscosity
- $\mu_w$  = viscosity at wall
- K = constant

and  $y_1^+$  is the lowest value of  $y^+$  for which Equation 2 applies and  $T_1^+$  is the dimensionless temperature at that distance. Equation 1 includes the effect of variable viscosity and must be solved iteratively. The dimensionless temperature was defined as:

$$T^+ = \frac{(T - T_w) C_p \tau_w}{q_w u^*} \dots (3)$$



where  $T$  is the temperature at some distance  $y$  from the wall,  $T_w$ ,  $\tau_w$  and  $q_w$  the temperature, shear stress and heat flux at the wall, respectively, and  $C_p$  and  $u^*$  the heat capacity and friction velocity.

From the experimental heat transfer data used to calculate the overall heat transfer resistance in Figures 2 - 8, all the variables in Equations 1 - 3 were known or could be evaluated, except the wall temperature  $T_w$ . In the present analysis the wall temperature  $T_w$  in Equation 3 was taken as the temperature  $T_s$  of some surface that represented the effective boundary of the flow passage. Therefore, the correlations developed for turbulent flow in clean tubes could be applied to the case where a thin layer of wax had deposited. For a given experimental run the solution average bulk temperature was known. The program calculation procedure consisted of finding a surface temperature  $T_s$  that produced a temperature profile that was consistent with the experimental solution bulk temperature.

Walker's<sup>(18)</sup> data and the results obtained in the present fouling studies were used in the temperature profile analysis. Most of the calculations showed that if the surface temperature  $T_s$  was equal or close to the solution cloud point, the temperature profile corresponded well with the experimental bulk temperature. Figure 9 shows the profile for Run B1-5 whose overall heat transfer resistance is plotted in Figure 2.

### 3.4 Comments

The experimental results have shown that paraffin wax fouling in turbulent pipe flow depends on flowrate, temperature and concentration and that the overall heat transfer resistance fluctuates with time. The deposition appears to consist of continuous build-up and break-down processes. To investigate this further a typical experimental Run F38 by Walker<sup>(18)</sup> for which the individual heat transfer coefficients had been calculated, was selected for analysis:

Reynolds number	Re = 14345
Wax concentration	c = 15%
Estimated cloud point	$T_c = 28^\circ\text{C}$
Average bulk temperature	$T_b = 31^\circ\text{C}$
Average overall heat transfer resistance	$R = 2.3987 \text{ (kW/m}^2\text{ }^\circ\text{C)}^{-1}$
Estimated fouling resistance	$R_f = 1.7483 \text{ (kW/m}^2\text{ }^\circ\text{C)}^{-1}$

The standard deviation of the overall heat transfer resistance  $R$  was calculated as  $0.1585 \text{ (kW/m}^2\text{°C)}^{-1}$  from the experimental data of Walker(18). The maximum fluctuation from the average overall resistance was found to be  $0.3100 \text{ (kW/m}^2\text{°C)}^{-1}$ . Therefore, the standard deviation represented a deviation of 9.1 per cent from the estimated fouling resistance and the maximum fluctuation a deviation of 17.7 per cent. The fouling resistance therefore changed by about 4 standard deviations going from minimum to maximum but more typically by only 2 standard deviations. These calculations show that the amount of wax required to break down or build up and give rise to the measured fluctuations in the overall heat transfer resistance, may typically be 10 - 20 per cent of the average wax deposited.

The shear stress at the pipe wall, in the simulated heat exchanger tubes, will increase during deposition because of the reduction in flow area, assuming constant flowrate. From the fouling resistance  $R_f = 1.7483 \text{ (kW/m}^2\text{°C)}^{-1}$  above and the thermal conductivity of a typical wax given by Nelson(2) as  $k = 0.0002387 \text{ (kW/m °C)}$  the average deposit thickness for Run F38 was evaluated  $R_f k = 0.42 \text{ mm}$ . For a tube having ID 13.1 mm this represents a change in diameter of 6.4 per cent resulting in an increase in average velocity of 14.2 per cent and an increase in shear stress at the wall of 30.4 per cent.

For the experimental results plotted in Figures 2 - 8 the solution bulk temperature  $T_b$  and the cooling water bulk temperature  $T_a$  were  $38 - 43^\circ\text{C}$  and  $\sim 7^\circ\text{C}$  respectively. The cloud point temperature was  $T_c = 32^\circ\text{C}$  and the pour point temperature  $3 - 4^\circ\text{C}$  lower. It was shown for the present experimental results that the average fouling resistance was up to 3x the estimated clean tube overall heat transfer resistance. Therefore, the tube wall temperature  $T_w$  was much closer to the cooling water temperature  $T_a$  than the solution temperature  $T_b$ . The tube wall temperature can be estimated from the relationship:

$$T_w = \frac{T_a + (R_o/R_f) T_s}{1 + (R_o/R_f)} \quad \dots (4)$$

derived by considering the heat flux across the tube wall with a deposit. Walker(18) estimated the cooling water (outside) heat transfer resistance  $R_o = 0.0317 \text{ (kW/m}^2\text{°C)}^{-1}$  for Run F38 discussed above. It was shown in Section 3.3 that the surface of the paraffin wax deposit was at the cloud point temperature such that  $T_s = T_c = 28^\circ\text{C}$  and that  $R_f = 1.7483 \text{ (kW/m}^2\text{°C)}^{-1}$ . Taking the cooling water temperature(A) as  $T_a = 6^\circ\text{C}$  the average wall temperature

in Equation 4 was calculated as  $6.4^{\circ}\text{C}$ . Therefore,  $T_w \sim T_a$  in the present experimental work. The inside and wall resistances for Run F38 were  $R_i = 0.6164 \text{ (kW/m}^2\text{C)}^{-1}$  and  $R_w = 0.0023 \text{ (kW/m}^2\text{C)}^{-1}$  respectively.

#### 4. DEPOSITION STUDIES

##### 4.1 Introduction

In Section 3 it was shown that the overall heat transfer resistance did not increase asymptotically with time. However, the deposition studies reviewed in Section 2 showed that in some model systems the deposition increased asymptotically with time, reaching stable values in 1 - 2 hours. It was considered likely that the asymptotic build-up for the paraffin wax-kerosene solutions was too rapid to be detected on the fouling studies apparatus. To study the initial deposition behaviour of the experimental solutions it was decided to construct a special apparatus where the deposition could be observed visually during operation and examined in detail on shut-down.

##### 4.2 Apparatus

The deposition studies apparatus was basically two closed circulation systems where paraffin wax was allowed to deposit on a copper plate cooled with water. See Figure 10. The experimental solution and the cooling water were circulated through rectangular ducts, separated by the deposition plate. The deposition and cooling ducts were similar to the flow cell first used by Cole and Jessen<sup>(17)</sup> and later by Patton and Jessen<sup>(4)</sup>. The present duct, however, had a long entry section on the solution side while the water side just covered the copper plate.

The experimental solution and cooling water systems were basically the same. Both had constant temperature tanks and centrifugal circulation pumps, feeding the respective ducts. The solution and cooling water tanks were 46 litres and 114 litres, respectively, both made of galvanized steel. Steam traced copper pipes were used throughout. The solution and cooling water inlet and outlet temperatures were measured with  $-10$  to  $50 \times 0.1^{\circ}\text{C}$  mercury-in-glass thermometers. Flowrates were measured with orifice meters connected to mercury manometers.

The deposition assembly was designed to simulate the deposition of paraffin wax in heat exchangers. The assembly consisted of deposition and cooling ducts and a copper plate as shown in Figure 11. The assembly was placed vertically in the apparatus. The experimental solution entered at the bottom and the

cooling water at the top, making the flow counter-current. The deposition and cooling ducts were made from 0.5 cm Perspex glued together. The deposition duct was a 1 x 2 cm rectangular channel, 76 cm long. At the downstream end of the duct a 2 x 10 cm area was cut out to fit a copper plate. The inlet and outlet of the deposition duct had 6 cm long tapered sections where the flow area was reduced to 1 x 1 cm. Perspex pipes were drilled into the tapered sections to connect the deposition duct to the pipework of the circulation system. Expansion bellows were fitted between the Perspex pipes and the rigid pipework. The effective entry length before the deposition plate was 51 cm. The velocity distribution in the deposition duct was therefore fully developed before reaching the plate. The 2 x 10 cm surface of the copper plate was flush with the wall of the deposition duct. A paper gasket was used for sealing between the copper plate and the deposition duct. The copper plate was sand blasted on the surface areas facing the deposition and cooling ducts. The blasting medium was described as 30/40 mesh, non-silica. It was hoped that the sand blasted plate would represent conditions more like those existing in the fouling studies heat exchangers rather than a polished surface. The cooling water duct was 12 cm long with tapered inlet and outlet sections 5 cm long each. The tapered sections were filled with wire mesh to promote better flow distribution in the duct. The rectangular duct was 1 x 2 cm at each end but 1.5 x 2 cm where the copper plate was since the Perspex wall thickness was 0.5 cm. The copper plate was therefore not flush with the wall of the cooling duct. The deposition and cooling ducts were bolted together.

#### 4.3 Experimental

For each experimental run the apparatus was allowed to reach its operating conditions by passing the paraffin wax-kerosene solution and cooling water through the bypass lines. The flow streams were then diverted through the deposition assembly at the controlled flowrates. The inlet and outlet temperatures for both streams were measured several times during experiments. At the end of an experiment the solution and cooling water streams were diverted through the bypass lines and the deposition duct drained quickly and followed by the cooling duct. The shut-down procedure took about 30 seconds. The deposition plate was removed by dismantling the cooling water duct from the deposition duct.

Some slurry-like wax solution was left on the deposit as a result of shut-down. This was washed off by gently pouring fresh kerosene over the plate, leaving

the relatively hard wax deposited during the experiment. Any extraneous liquid kerosene left on the plate was carefully removed with filter paper. Great care was taken to follow exactly the same procedures at the end of each run. The amount of deposit on the plate was determined from weighing before and after cleaning. The plate was cleaned with carbon tetrachloride - as the heat exchanger tubes in the fouling studies - and then washed in fresh kerosene before being put back in the deposition duct.

The cooling water temperature was maintained at 15°C and the flowrate at 0.127 kg/s in all the experimental runs. No deposition was observed on the water side of the deposition plate. The temperature of the paraffin wax-kerosene solution was kept 5°C above the cloud point. The temperature drop of the experimental solution and the cooling water across the deposition assembly was negligible. The temperature controllers kept the solution and cooling water temperatures accurate to within 0.5°C from run to run. The solution flowrate in all the runs was 0.116 kg/s. In Run D2 this corresponded to a Reynolds number of about 5200. The solution flow conditions were therefore turbulent.

The experimental results show the effect of time on the amount of wax deposited. Solutions with two different waxes were used; 51/54°C and 57/60°C melting point fully refined paraffin wax in kerosene. Runs D1, D2 and D3 are for 51/54°C wax and are plotted in Figure 12 - 14. They show the effect of varying the wax concentration and bulk temperature while the solution flowrate and the cooling water flowrate and temperature remain constant. Runs D4 and D5 are for 57/60°C wax and are plotted in Figures 15 - 16. They show the amount of wax deposited at two experimental conditions. In Run D6 the effect of flowrate on deposition in 15 minutes was investigated and is plotted in Figure 17. The experimental conditions are given in Table 1. In Figure 18 the first 20 minutes of Runs D1,

TABLE 1

Experimental Conditions in the Deposition Studies

Run	Wax	c (%)	T <sub>c</sub> (°C)	T <sub>b</sub> (°C)
D1	51/54	8.5	18	23
D2	51/54	10.0	20	25
D3	51/54	11.5	22	27
D4	57/60	2.5	20	25
D5	57/60	3.5	23	28
D6	57/60	3.5	23	28

D2 and D3 have been plotted to show the effect of concentration on deposition. Each experimental point was obtained from separate measurements performed in a random order.

#### 4.4 Comments

The experimental results showed the asymptotic nature of paraffin wax deposition; the deposition increased with time to reach a final fluctuating value. This final asymptotic value was reached more quickly at higher concentrations as shown in Figure 18. The deposits were found to cover the deposition plate evenly. The deposits were firm, although the firmness decreased with concentration. At experimental times approaching two hours the deposits were observed to wear off at the leading edge of the deposition plate. In the three runs (D1, D2 and D3) where the 51/54°C wax was used the highest concentration run did not produce the highest final value although it gave the highest initial deposition rate. Evidently the paraffin deposits broke down earlier at higher concentrations. Since the thickness of the deposits increased with time and concentration it suggests that break-down occurs when a certain critical thickness was reached. As expected, deposition decreased with increased flowrate.

### 5. DISCUSSION

#### 5.1 Mechanism

When a solution containing a wax foulant enters a clean tube that is cooled below the cloud or pour point temperature, deposition will occur. As the wax deposits built up the heat flux decreases gradually, due to increased thermal resistance, and fewer wax particles will be formed. This lower particle concentration reduces the number of particles reaching the wall and thereby the deposition. For the experimental conditions adopted in the present studies the wall temperature was always below the pour point and the wax particles came out of the solution inside the boundary layer. It is suggested that a suspension of wax crystals may exist in the boundary layer from the surface of the solid wax, at the pour point temperature  $T_p$ , to a temperature interface represented by the cloud point  $T_c$ . Clearly, the behaviour of the small particles in the boundary layers is important in paraffin wax deposition and fouling.

The average deposit thickness  $x^*$  at asymptotic conditions can be calculated

from  $x^* = R_f^* k$ , as shown in Section 3.4 above, where  $R_f^*$  and  $k$  are the asymptotic fouling resistance and  $k$  the wax thermal conductivity. This has been done in Table 2 and the deposit thickness found to be in the range 0.11 - 0.77 mm. Assuming constant flowrate and friction factor conditions the shear stress at the wall  $\tau_w \propto d^{-4}$  will therefore increase by 7-65 per cent during deposition from clean to asymptotic conditions. These increases and the decrease in heat flux will be the major factors contributing to the asymptotic behaviour of paraffin wax deposition and fouling.

The fluctuating nature of the overall heat transfer resistance in the fouling studies indicated continuous build-up and break-down of the paraffin wax deposits. The strength of wax deposits will depend upon a close and regular pattern of the crystals. As deposition increases with time the likelihood of such a regular pattern being sustained is reduced and eventually a plane of weakness will develop. The wax deposit breaks down and is removed from the tube surface, probably leaving a thin granular layer. The granular layer may represent a well oriented matrix of crystals with few planes of weakness. The creation of planes of weakness and the increase in shear stress at the wall as deposits build up are probably the main factors causing break-down and removal, giving rise to the characteristic wax deposition and fouling.

The present work has shown that in turbulent flow the deposition at asymptotic conditions decreases with flowrate. Heat, mass and momentum transfer all increase with flowrate. While heat and mass transfer are necessary for deposition to occur, the deposition at asymptotic conditions is probably more dependent on momentum transfer in the form of shear stresses at the wall. The transport of material to the surface is therefore not the limiting factor, but the cohesive properties of the particles depositing. Increased temperature and concentration will decrease and increase the number of particles available for deposition, respectively, and also affect their cohesive properties.

## 5.2 Model

The following characteristics of paraffin wax deposition and fouling have emerged from the literature reviewed and the present studies.

1. Initial rate of fouling  $(dR_f/dt)_{t=0}$  and asymptotic fouling resistance  $R_f^*$  decrease with flowrate and increase with temperature difference  $\Delta T$ (5,12,14, 16,17,18,A).

2. Deposit hardness increases with flowrate(12,14).
3. Deposition is heavier at the downstream end of heat exchangers(18).

The various deposition-release fouling models were reviewed in Part I, Section 3. It was stated that these models have met with some success in predicting heat transfer fouling. Such a model will be proposed in the present section to describe deposition and fouling by paraffin wax-kerosene solutions. The model includes a stickability term  $s$  and mass flux towards the wall  $N$ , in the deposition function, as suggested by Watkinson<sup>(20)</sup>. The exact expressions, however, are based on observations related to paraffin wax systems. The release function includes the effect of deposit hardness similar to that of Taborek et al<sup>(21)</sup>. The following deposition-release model is proposed:

$$\frac{dR_f}{dt} = k_1 s N - k_2 \left( \frac{x}{u^*} \right) \tau_w \quad \dots (5)$$

where:  $R_f$  = fouling resistance  
 $s$  = stickability  
 $N$  = foulant mass flux  
 $x$  = deposit thickness  
 $u^*$  = friction velocity  
 $\tau_w$  = shear stress at wall  
 $k_1$  = deposition coefficient  
 $k_2$  = release coefficient

In accordance with the experimental observations it is suggested that the stickability be expressed by:

$$s = \frac{k_3 \Delta T'}{\tau_w} \quad \dots (6)$$

where  $k_3$  is a constant and  $\Delta T'$  the temperature driving force causing deposition.

$$\Delta T' = \frac{T_c - T_w}{T_b} \quad \dots (7)$$

This dimensionless temperature difference applies to systems where the solubility increases with temperature.



The mass transfer of foulant towards the wall may be expressed by the general relationship:

$$N = hc \quad \dots (8)$$

where  $h$  and  $c$  are the mass transfer coefficient and foulant concentration, respectively. The mass transfer coefficient will depend greatly on the nature of the foulant; molecular or particulate. For molecular foulants traditional mass transfer correlations may be used while the situation for particulate systems is more complex, as discussed in Part V, Section 3. It was decided to use the following approximation of the mass transfer coefficient:

$$h = k_4 u^* \quad \dots (9)$$

where  $k_4$  is a constant. This approximation is not without justification. Friedlander(22) gives the Deissler(19) and Landau and Lifshitz(23) expression for mass transfer of small particles in turbulent pipe flow:

$$Sh = 0.112 Re \sqrt{\frac{f}{2}} Sc^{0.25} \quad \dots (10)$$

where the mass transfer coefficient is proportional to the friction velocity as in Equation 9.

The effect of flowrate on deposit strength is included in the model by dividing the release function by  $u^*$  the friction velocity. By substituting Equations 6, 8 and 9 into Equation 5 and putting  $x = 0$  and  $dR_f/dt = 0$  respectively, the following relationships are obtained:

$$\left( \frac{dR_f}{dt} \right)_{t=0} \propto \frac{c \Delta T'}{\rho u^*} \quad \dots (11)$$

$$R_f^* \propto \frac{c \Delta T'}{(\rho u^*)^2} \quad \dots (12)$$

where  $R_f^*$  is the fouling resistance at asymptotic conditions and  $\rho$  the solution density. It should be noted that when the deposition-release models are applied to a single system such as paraffin wax-kerosene solutions at similar concentration and temperature conditions, the exact form of the 'velocity' term (ie bulk velocity  $u$ , friction velocity  $u^*$ , flowrate  $W$ , mass flux  $G$  or

Reynolds number) is not all that important.

The deposition-release model was tested against the experimental data obtained in the fouling studies. To do this the fouling resistance has to be evaluated from the overall heat transfer resistance presented in Figures 2 - 8. This was done by calculating the average overall heat transfer resistance from the experimental data and assuming it to be the overall resistance at asymptotic conditions  $R^*$ . The individual heat transfer resistances on the solution side  $R_i$  (inside) and the cooling water side  $R_o$  (outside) were then calculated for each run from the average Reynolds number and the average bulk temperature. The wall resistance  $R_w$  was readily available from the copper tube thermal conductivity and thickness. See Section 3.4 above. The asymptotic fouling resistance was then obtained from the expression:

$$R_f^* = R^* - R_i - R_o - R_w \quad \dots (13)$$

The inside  $R_i$  and outside  $R_o$  resistances were calculated from a Dittus-Boelter type expression<sup>(24)</sup>. It has been found that the expression used predicts heat transfer coefficients which are about 10 per cent lower than those determined experimentally for commercial tubes<sup>(25)</sup>. A correction of this magnitude was included in the calculation of  $R_i$  and  $R_o$ <sup>(A)</sup>. Table 2 shows the calculated asymptotic fouling resistance  $R_f^*$  for 3 of Walker's<sup>(18)</sup> results and 6 of the present results. The estimated deposit thickness was also calculated from  $x^* = R_f^* k$  as in Section 3.4 above. The experimental data was such that only Equation 12 could be tested. The parameter  $c \Delta T' / Re^2$  has been calculated in Table 2 and plotted against the asymptotic fouling resistance  $R_f^*$  in Figure 19. The wall temperature  $T_w$  used to calculate  $\Delta T'$  was the cooling water temperature  $T_a$ . It was shown in Section 3.4 that  $T_w \sim T_a$  in the present studies.

The deposition-release model (Equation 12) predicts a straight line which goes through the origin. Figure 19 shows that the experimental points fall on a curve that increases sharply at first and then becomes straight. The overall behaviour of the experimental data is therefore in agreement with the model, particularly for values of  $(c \Delta T' / Re^2) > 0.1 \cdot 10^{-6}$ . It is unclear why the experimental curve is not straight at all values of  $c \Delta T' / Re^2$ , unless the asymptotic fouling resistance was estimated too high in Table 2. A straight line may be drawn through the origin and parallel to the experimental curve. The asymptotic fouling resistance will therefore be given by the

TABLE 2  
Experimental Data and Calculated Parameters

Run	Re	c (%)	T <sub>c</sub> (°C)	T <sub>b</sub> (°C)	T <sub>a</sub> (°C)	R <sub>f</sub> <sup>*</sup> (kW/m <sup>2</sup> °C) <sup>-1</sup>	x* (mm)	ΔT <sup>*</sup>	$\frac{\Delta T^*}{Re^2} c$ (%)
F30	20868	9.6	20	28.6	6.1	0.4480	0.11	0.486	0.011 · 10 <sup>-6</sup>
F31	8699	9.6	20	28.4	6.0	1.0142	0.24	0.493	0.063 · 10 <sup>-6</sup>
F32	11741	9.6	20	28.5	6.0	0.7370	0.18	0.491	0.034 · 10 <sup>-6</sup>
B1-5	7635	26	32	42.5	7.1	2.1864	0.52	0.586	0.261 · 10 <sup>-6</sup>
B6-9	13311	26	32	42.8	7.1	1.5359	0.37	0.586	0.086 · 10 <sup>-6</sup>
B10-13	6716	26	32	42.4	6.8	3.0117	0.72	0.594	0.342 · 10 <sup>-6</sup>
C1-14	8890	26	32	38.2	6.9	2.2584	0.54	0.657	0.216 · 10 <sup>-6</sup>
C5-16	6888	26	32	38.2	6.8	3.2116	0.77	0.660	0.362 · 10 <sup>-6</sup>
C8-20	4635	26	32	38.1	6.7	5.6461	1.35	0.664	0.803 · 10 <sup>-6</sup>

Note : All figures are average values

approximate expression:

$$R_f^* = 6 \cdot 10^6 \left( \frac{\Delta T'}{Re^2} c \right) \dots (14)$$

## 6. CONCLUSIONS

1. The deposition of paraffin wax from kerosene solutions onto cooled surfaces increases asymptotically with time.
2. The asymptotic fouling resistance fluctuates at random with time due to deposit build-up and break-down.
3. The amount of wax depositing at initial and asymptotic conditions decreases with flowrate and temperature but increases with concentration.
4. The cohesive properties of wax crystals appear to be important in the mechanism of deposition.
5. Paraffin deposition and fouling may be described by a deposition-release model where the initial rate of fouling and the asymptotic fouling resistance are inversely proportional to friction velocity and friction velocity squared, respectively.

## 7. RECOMMENDATIONS

1. Further work should be carried out to test the proposed deposition-release model, particularly the initial rate of fouling.
2. The increase in pressure drop during asymptotic build-up should be investigated. Shear stresses at the wall could then be related to strength of deposits.
3. The weighing method used to determine deposition may be improved by evaporating the extraneous solvent under vacuum.

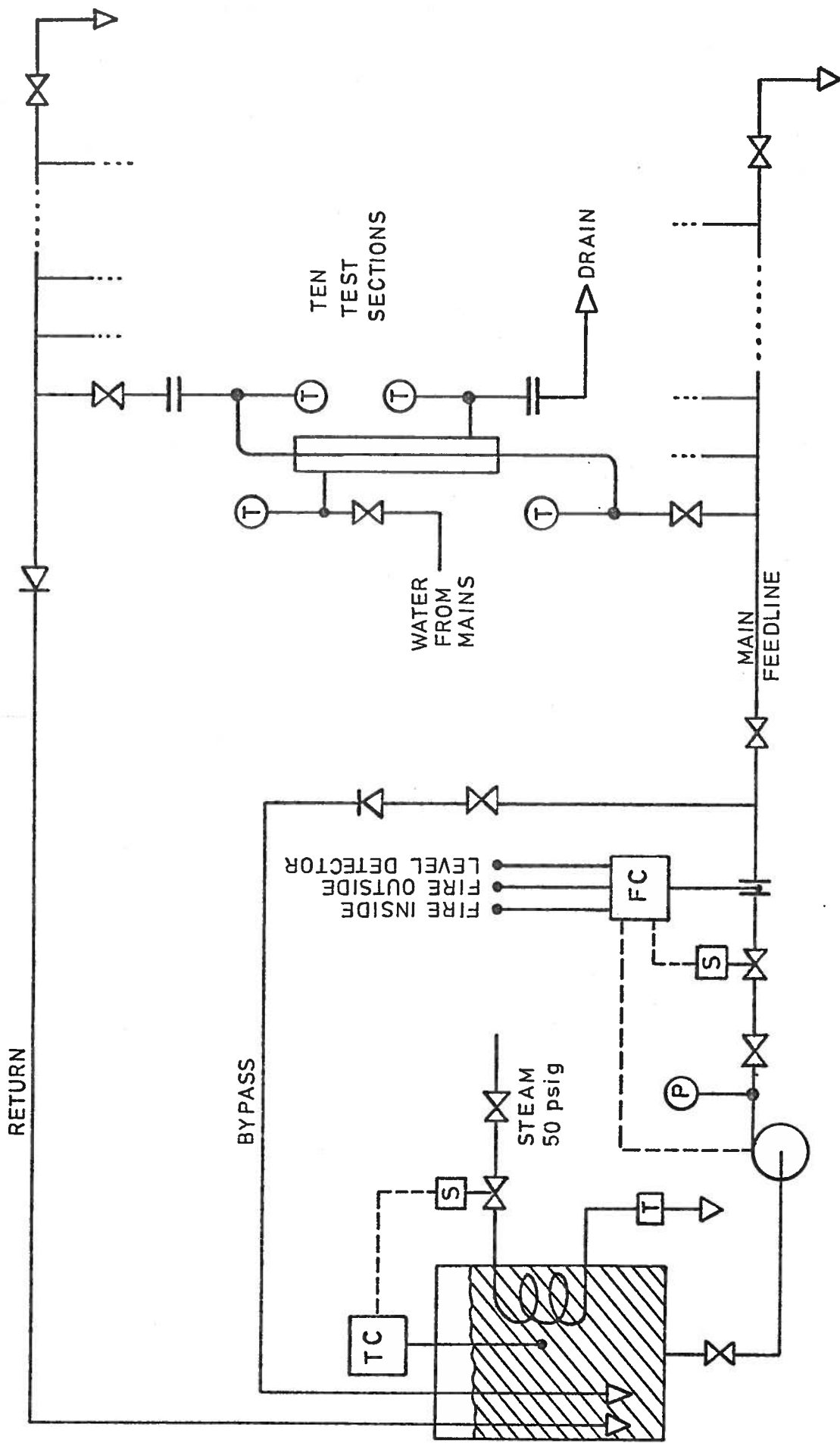


Fig.1.- Flow diagram of the fouling studies apparatus

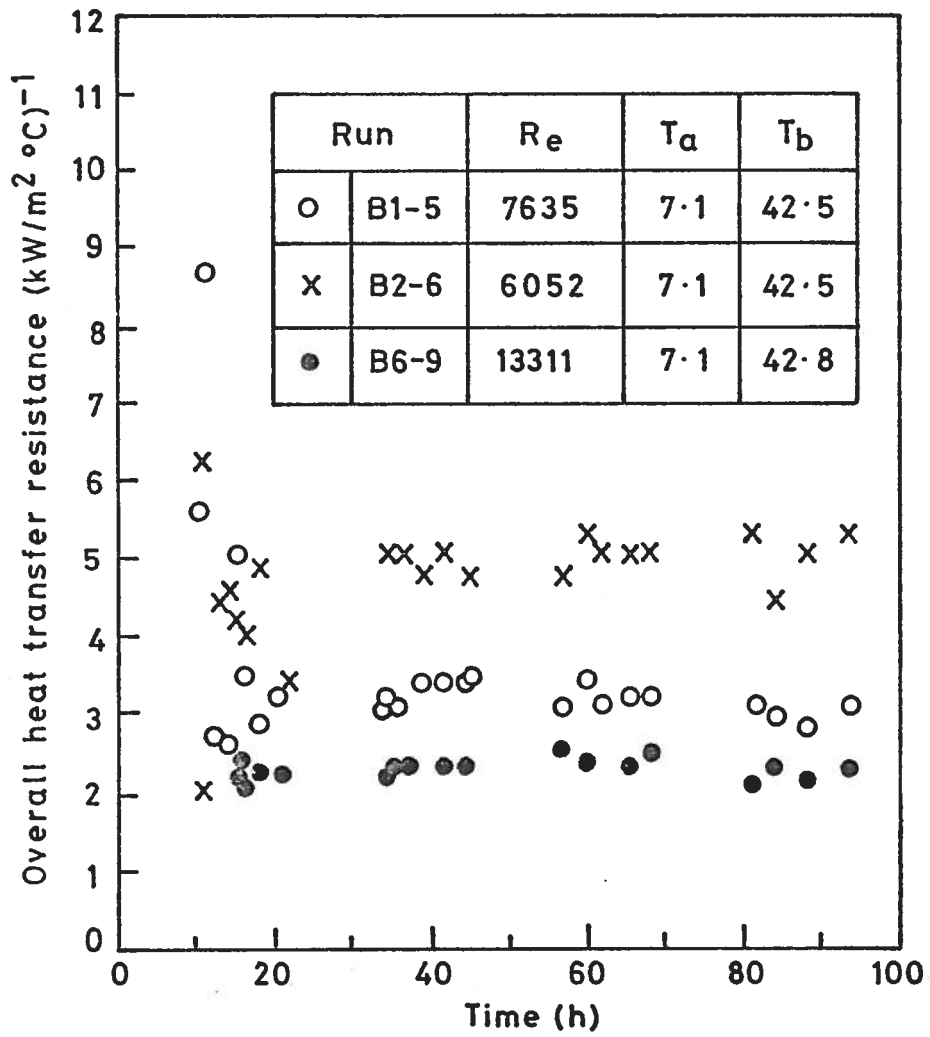


Fig.2.- Heat transfer resistance v time,  
 $T_c = 32 \text{ } ^\circ\text{C}$  and  $c = 26 \%$ .

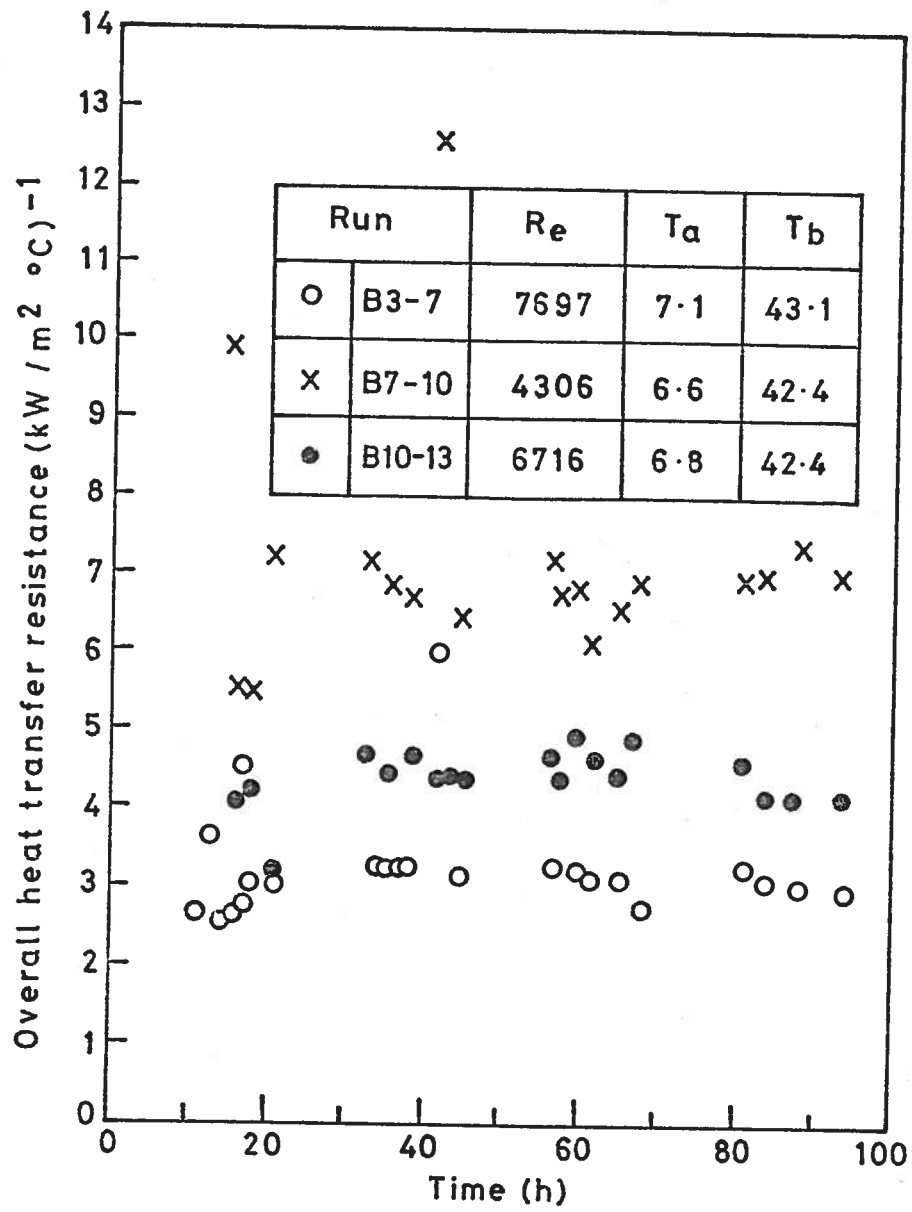


Fig.3.- Heat transfer resistance v time,  
 $T_c = 32\text{ }^\circ\text{C}$  and  $c = 26\%$ .

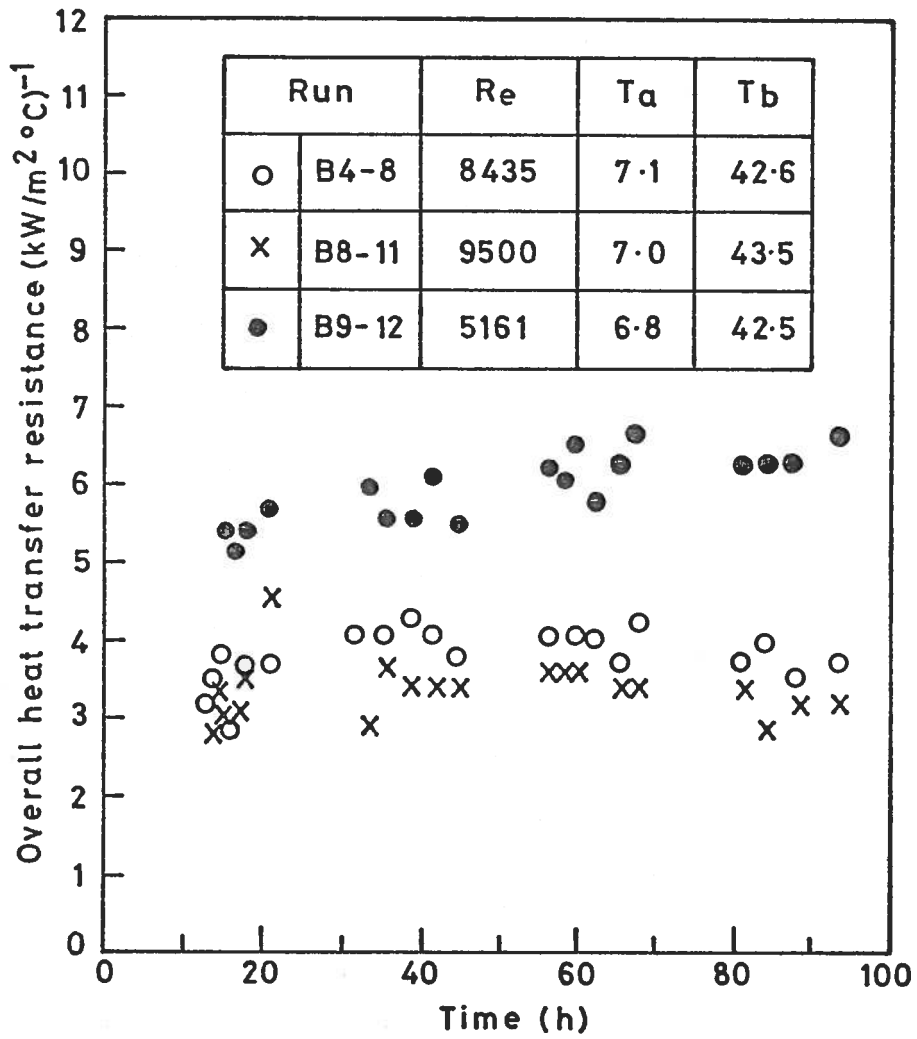


Fig. 4.- Heat transfer resistance v time,  
 $T_c = 32 \text{ } ^\circ\text{C}$  and  $c = 26 \%$ .



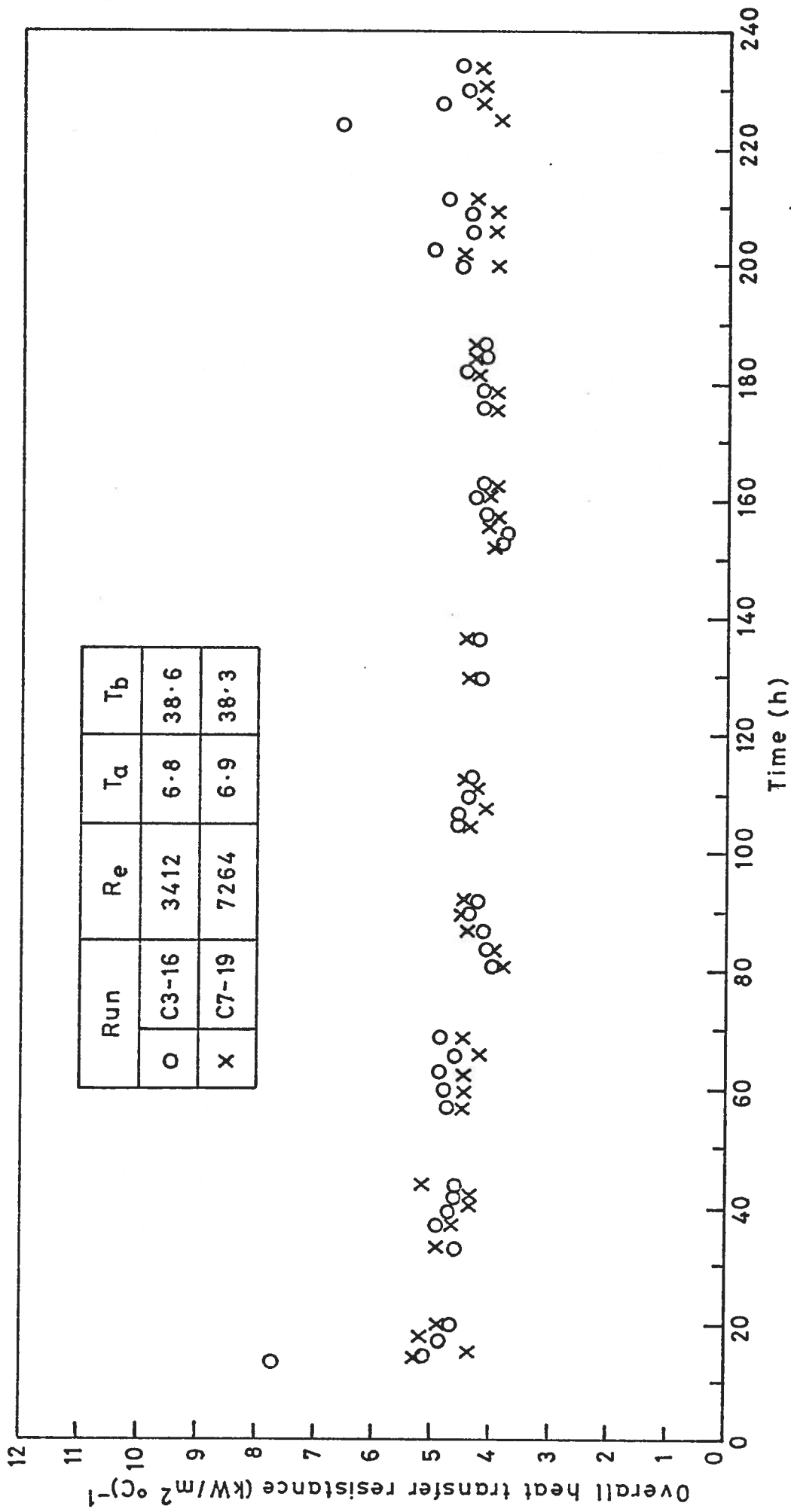


Fig. 5. - Heat transfer resistance v time,  $T_c = 32\text{ }^\circ\text{C}$  and  $c = 26\%$ .

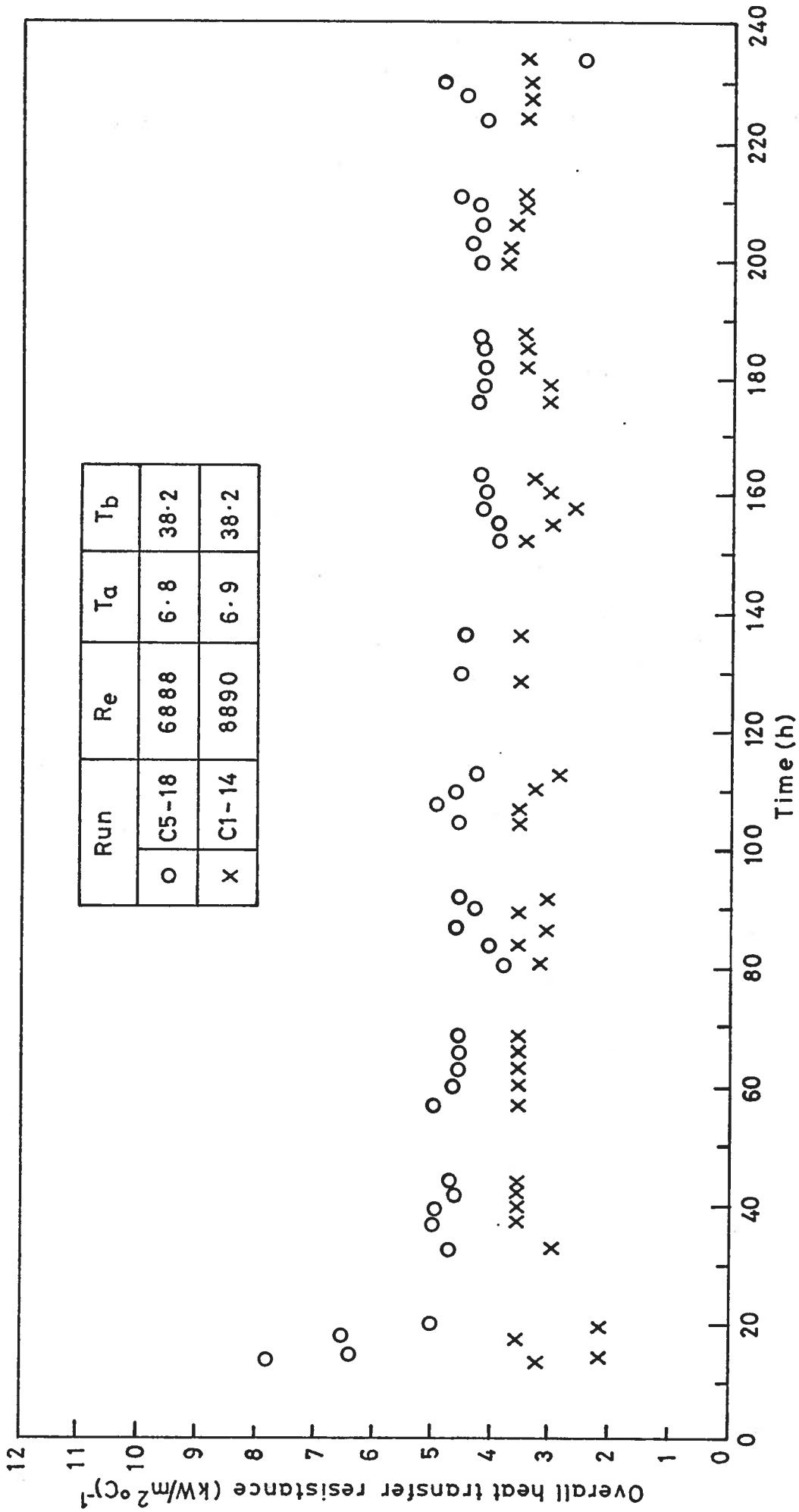


Fig. 6.- Heat transfer resistance v time, T<sub>c</sub> = 32 °C and c = 26%.

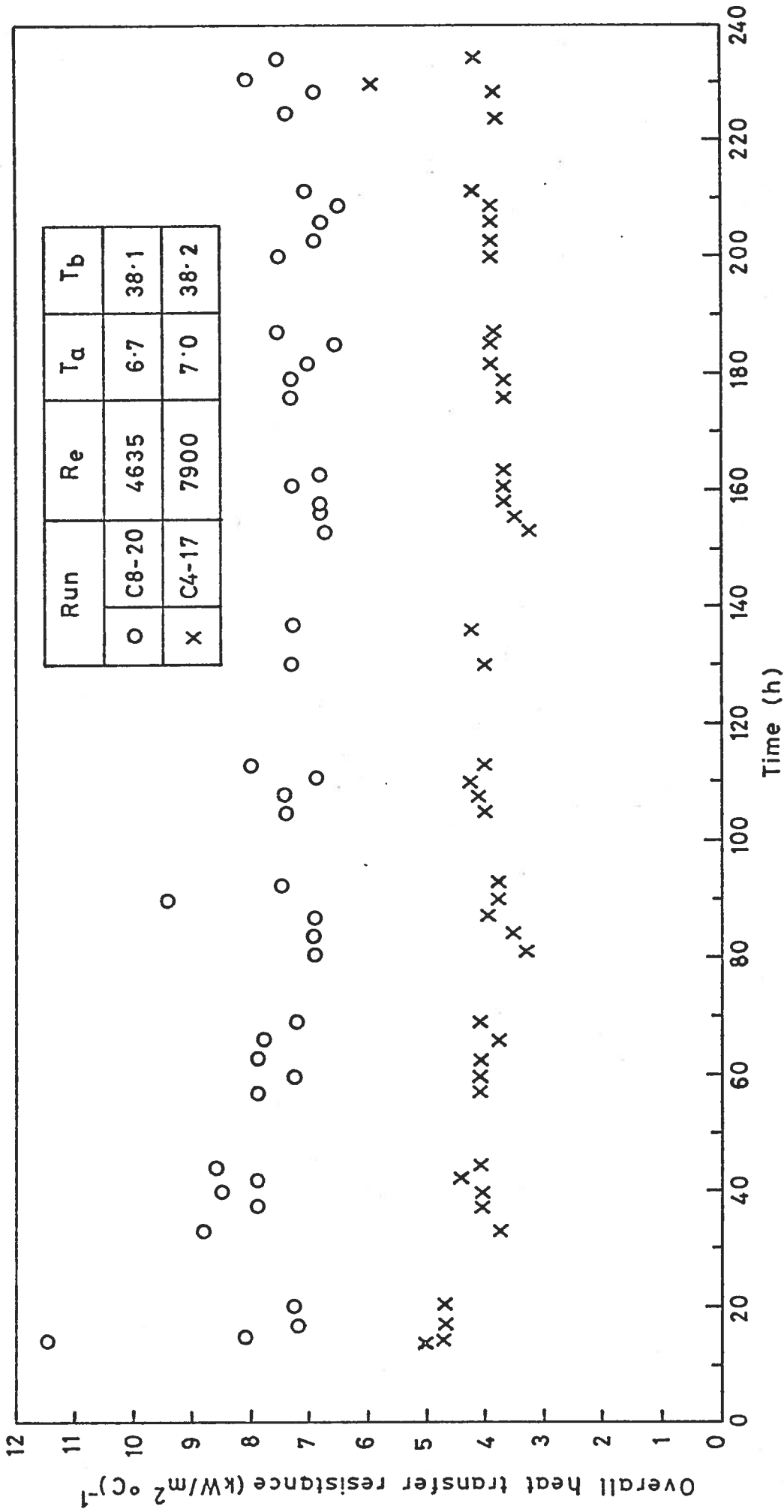


Fig. 7. - Heat transfer resistance v time, T<sub>c</sub> = 32 °C and c = 26%.

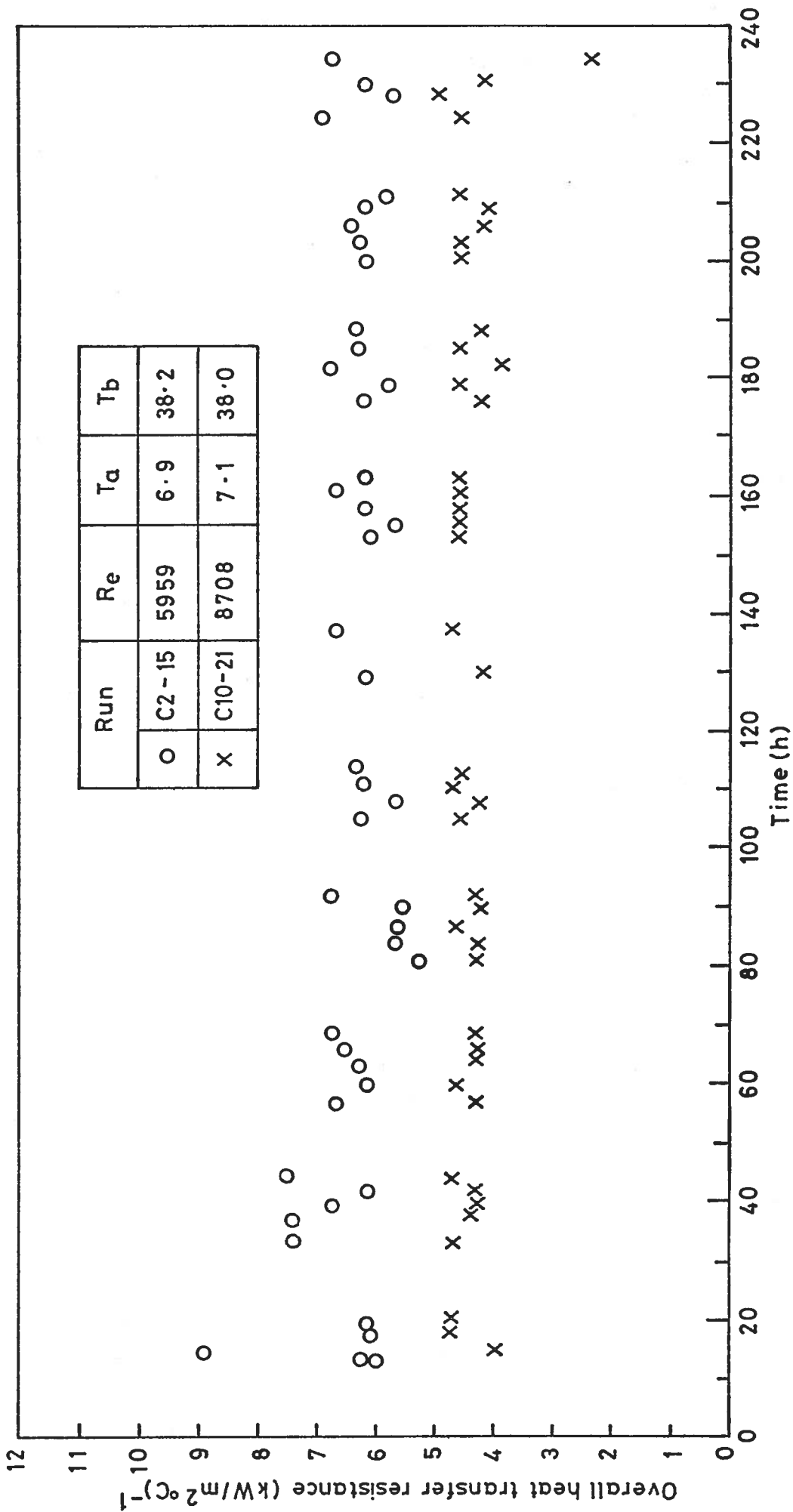


Fig.8. - Heat transfer resistance v time,  $T_c = 32\text{ °C}$  and  $c = 26\%$ .

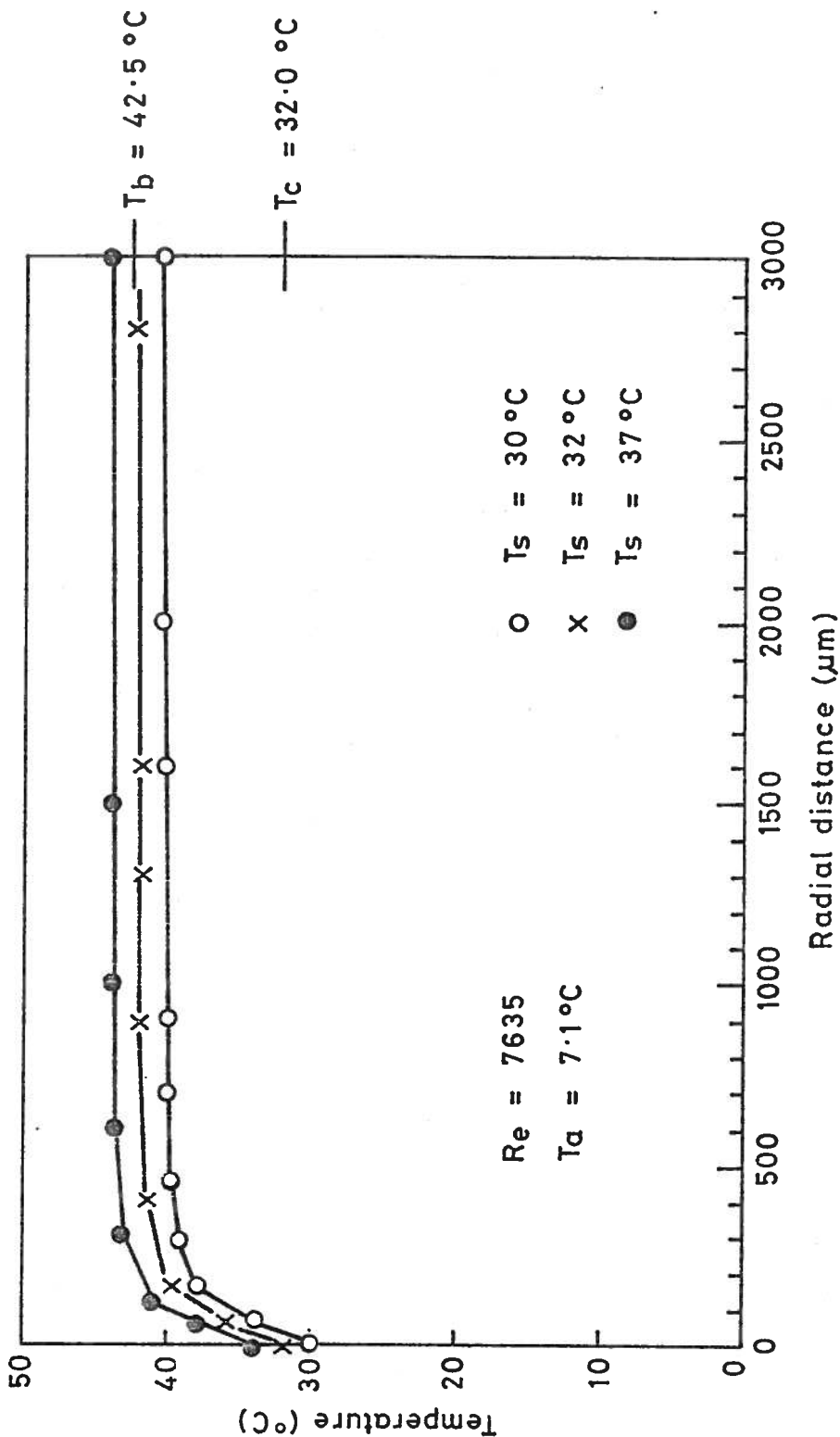


Fig. 9.- Temperature v radial distance at different wall temperatures in Run B1-5.

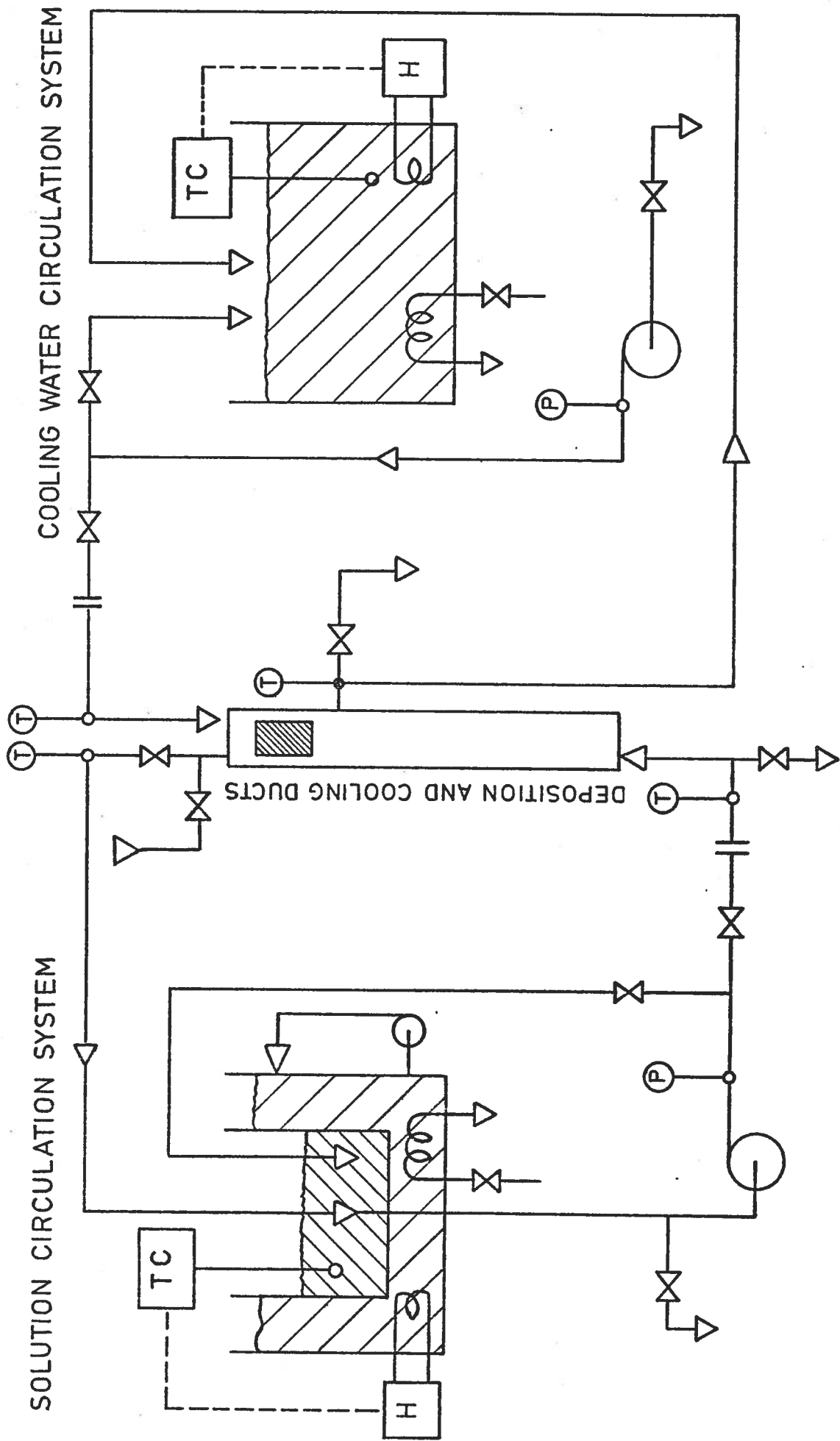


FIG.10. DEPOSITION STUDIES APPARATUS

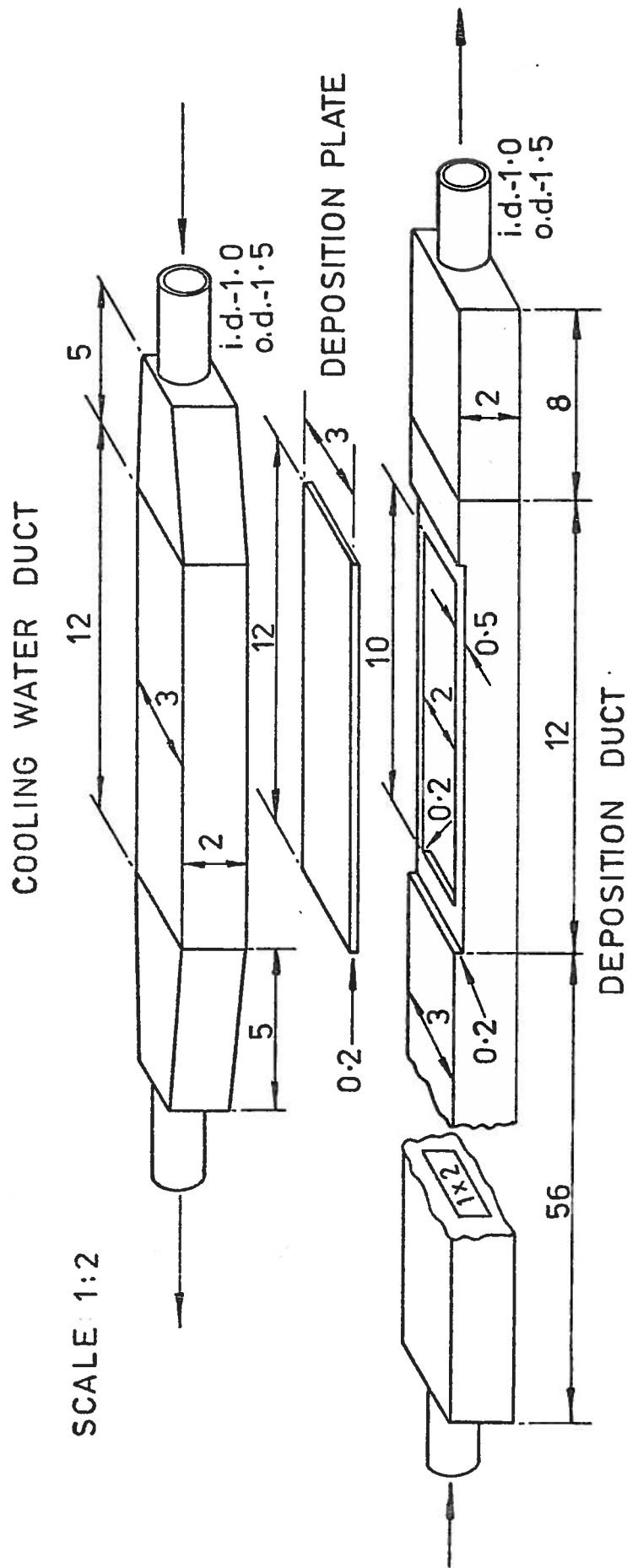


FIG. 11. DEPOSITION AND COOLING DUCTS WITH DEPOSITION PLATE BETWEEN THEM

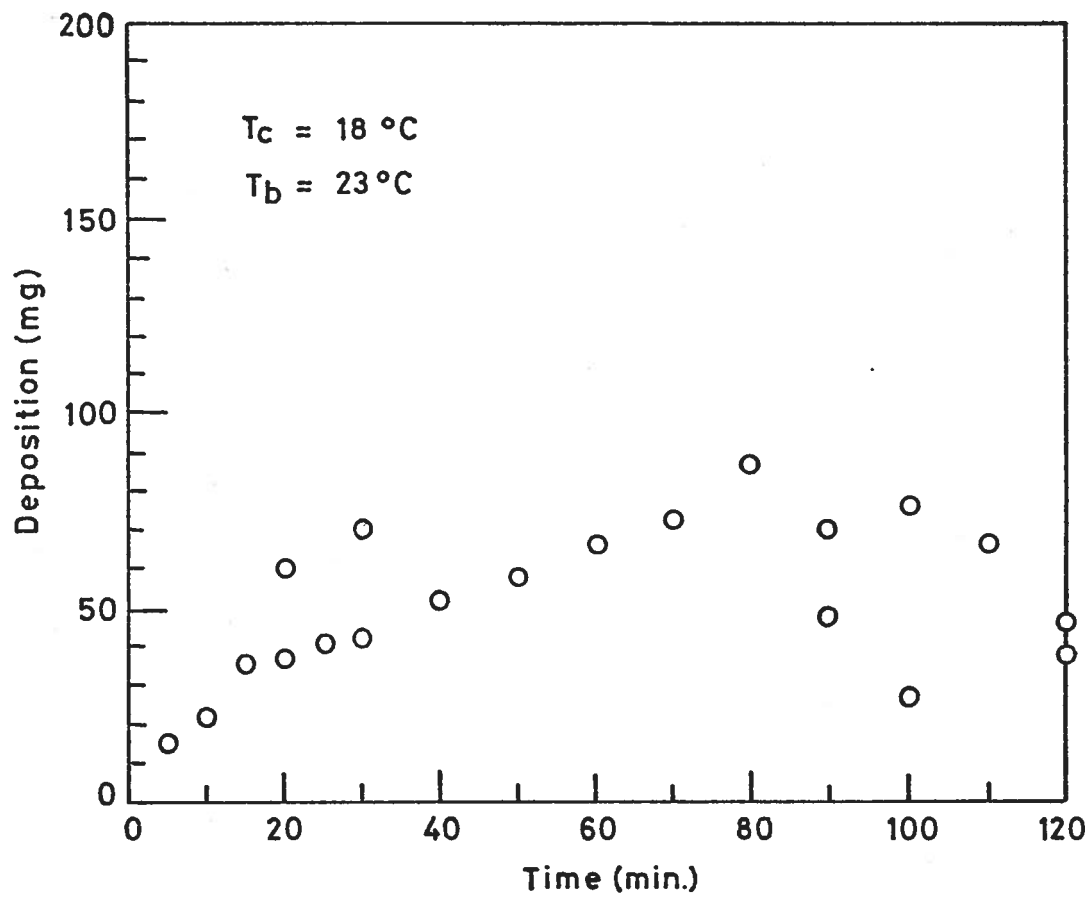


Fig. 12. - Deposition v time in Run D1.



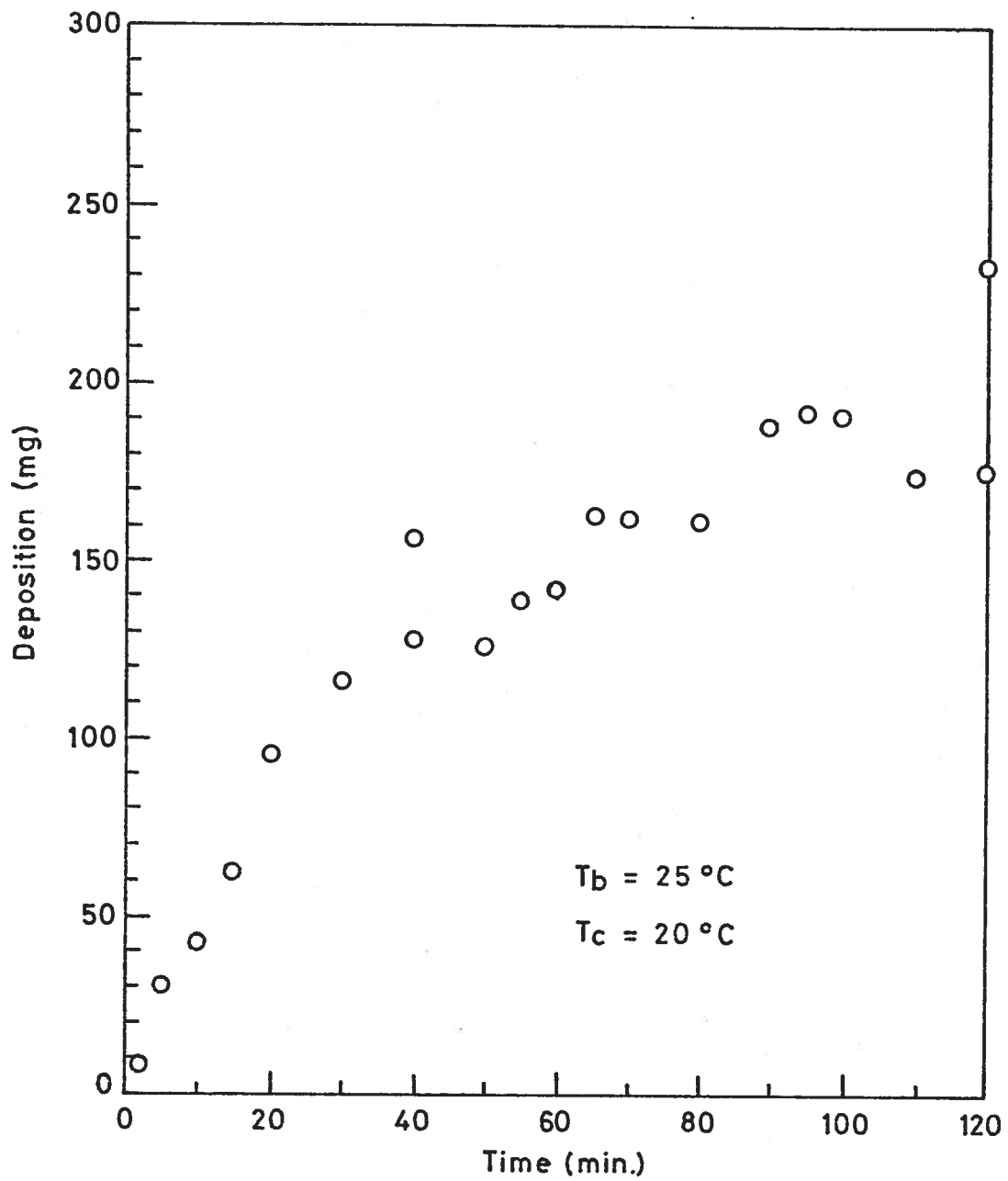


Fig.13.- Deposition v time in Run D2.

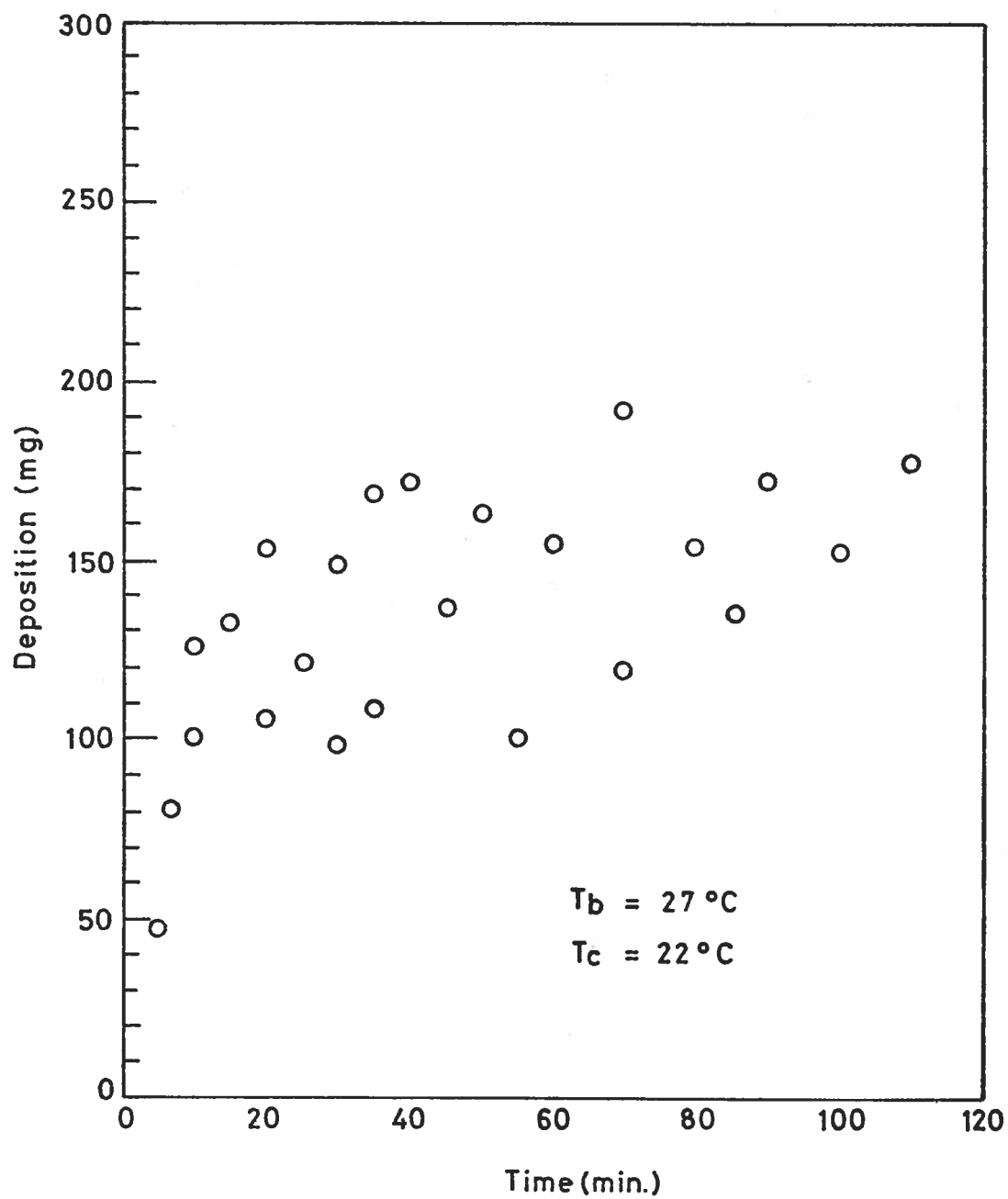


Fig.14.- Deposition v time in Run D3.

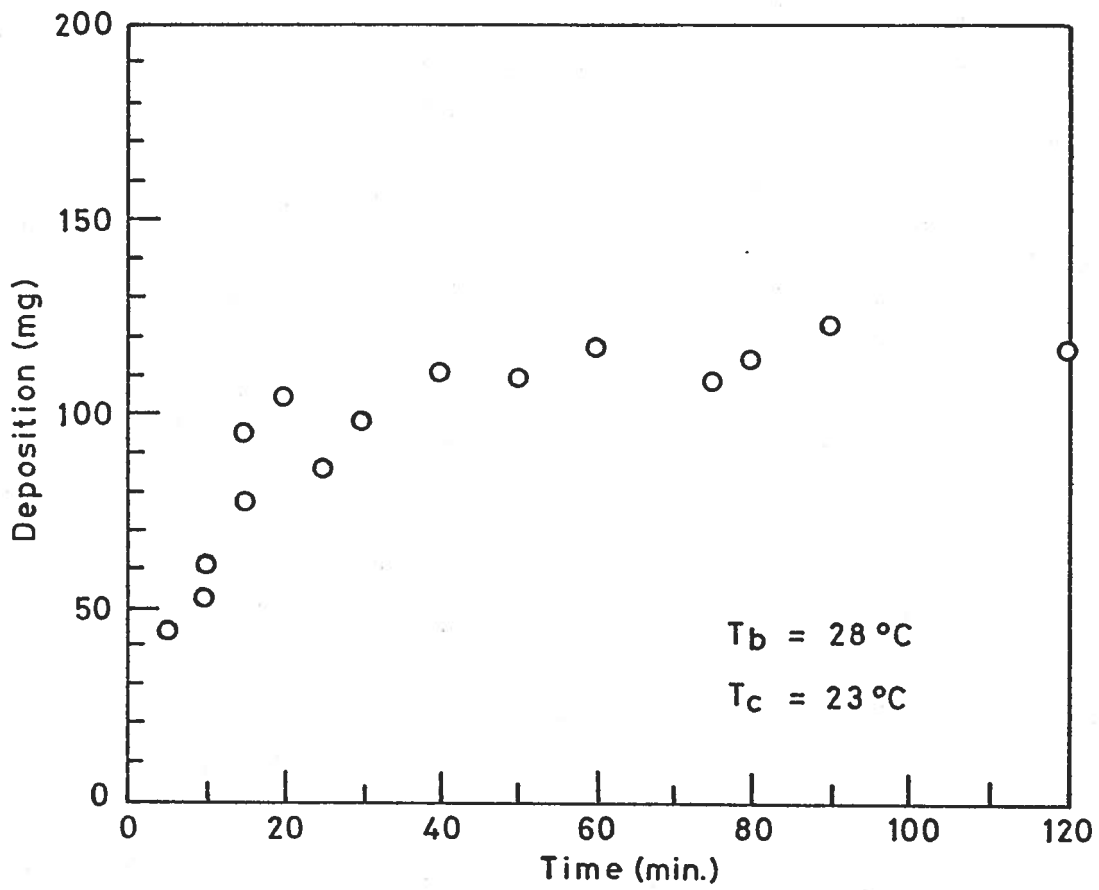


Fig.15.- Deposition v time in Run D4.

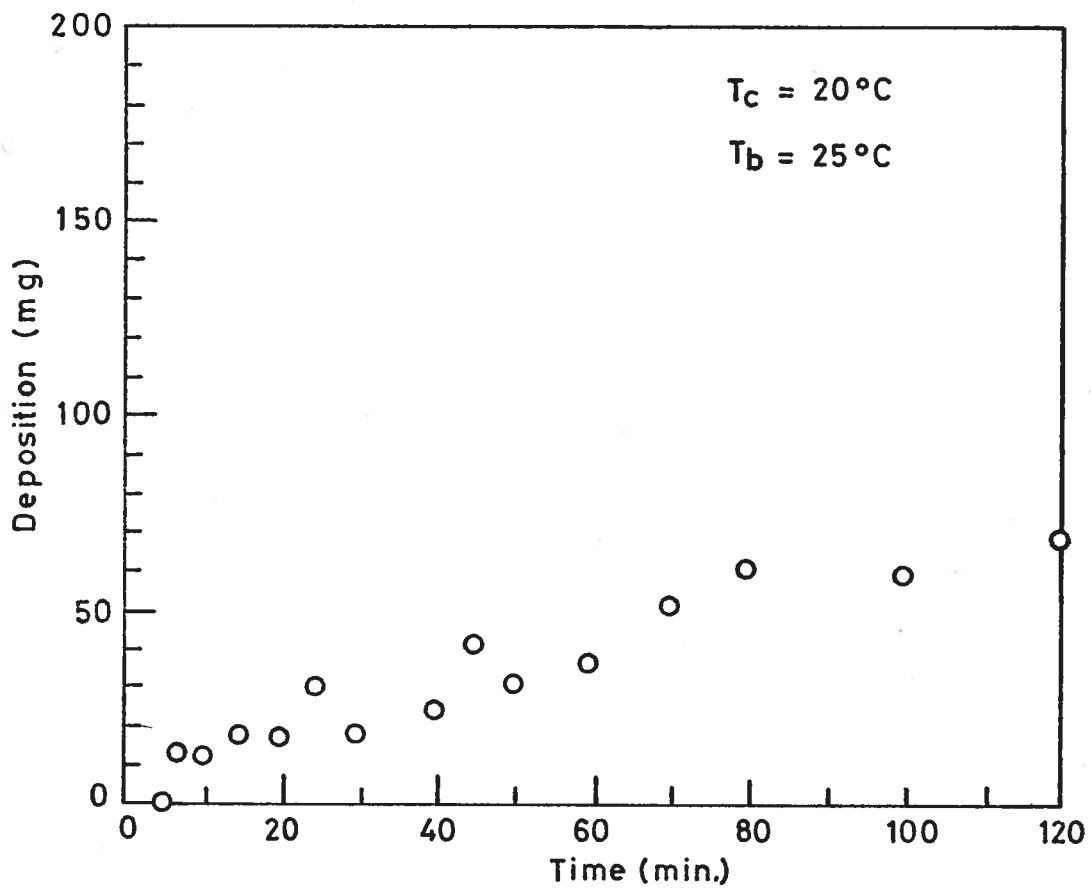


Fig.16. - Deposition v time in Run D5.

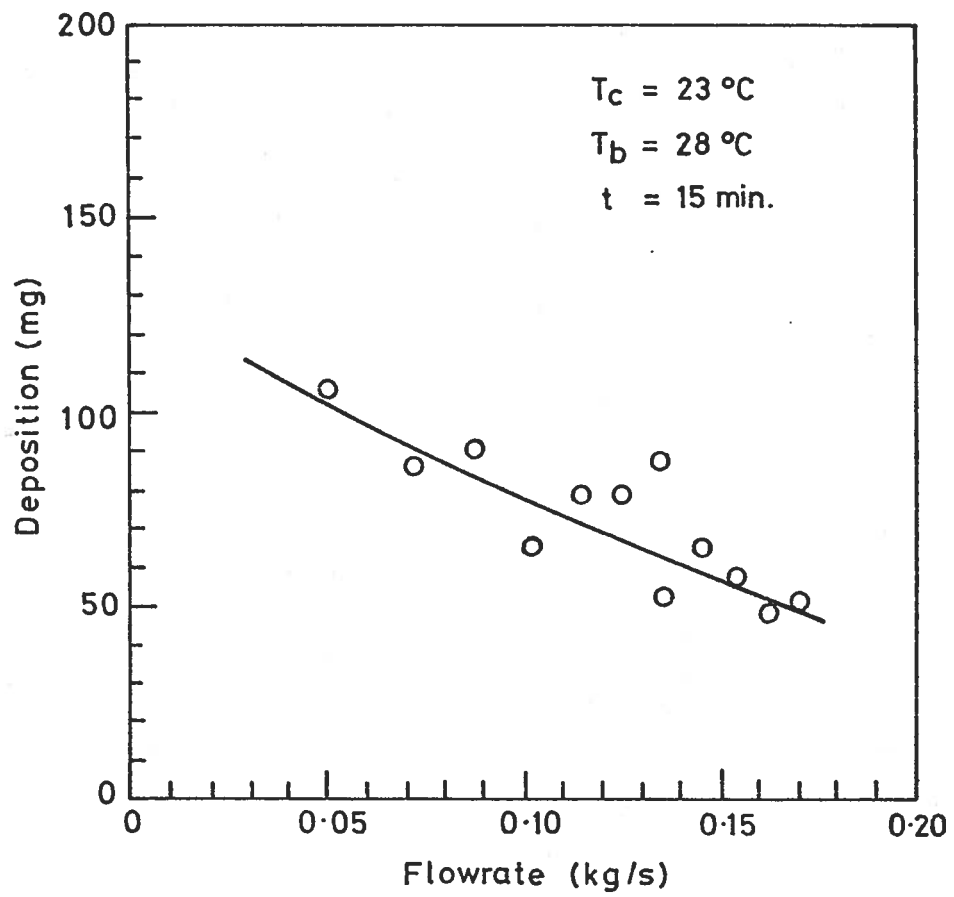


Fig.17 - Deposition v flowrate in Run D6.

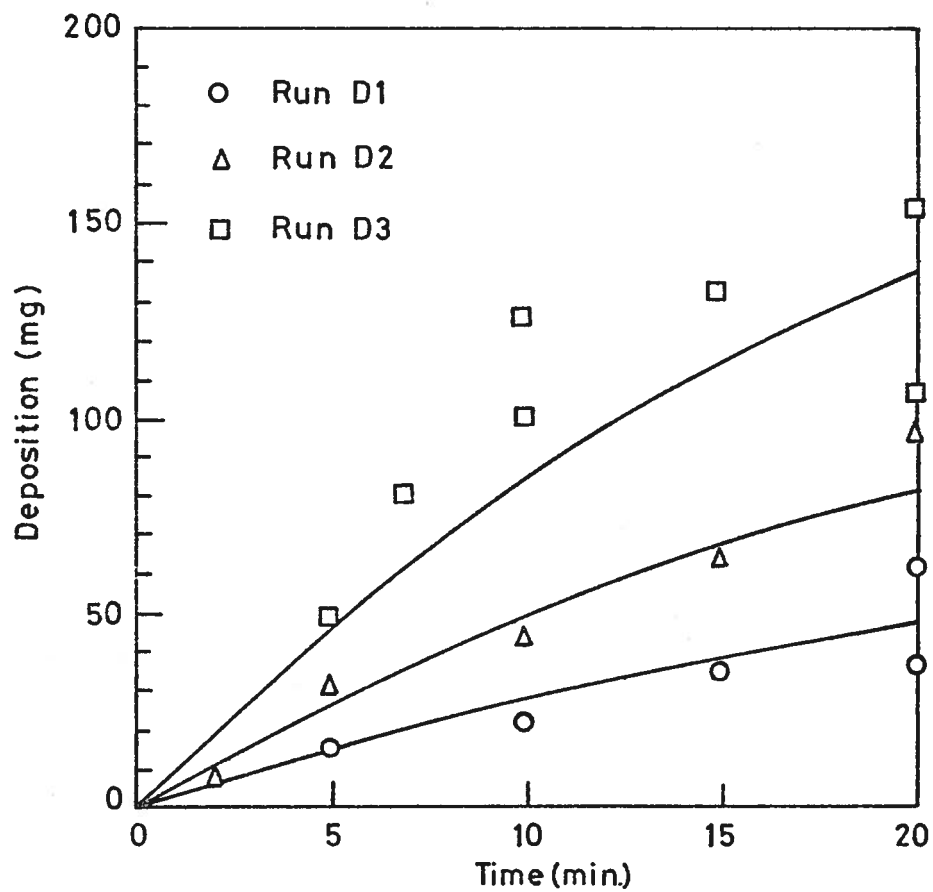


Fig.18. -Deposition v time at different concentrations.

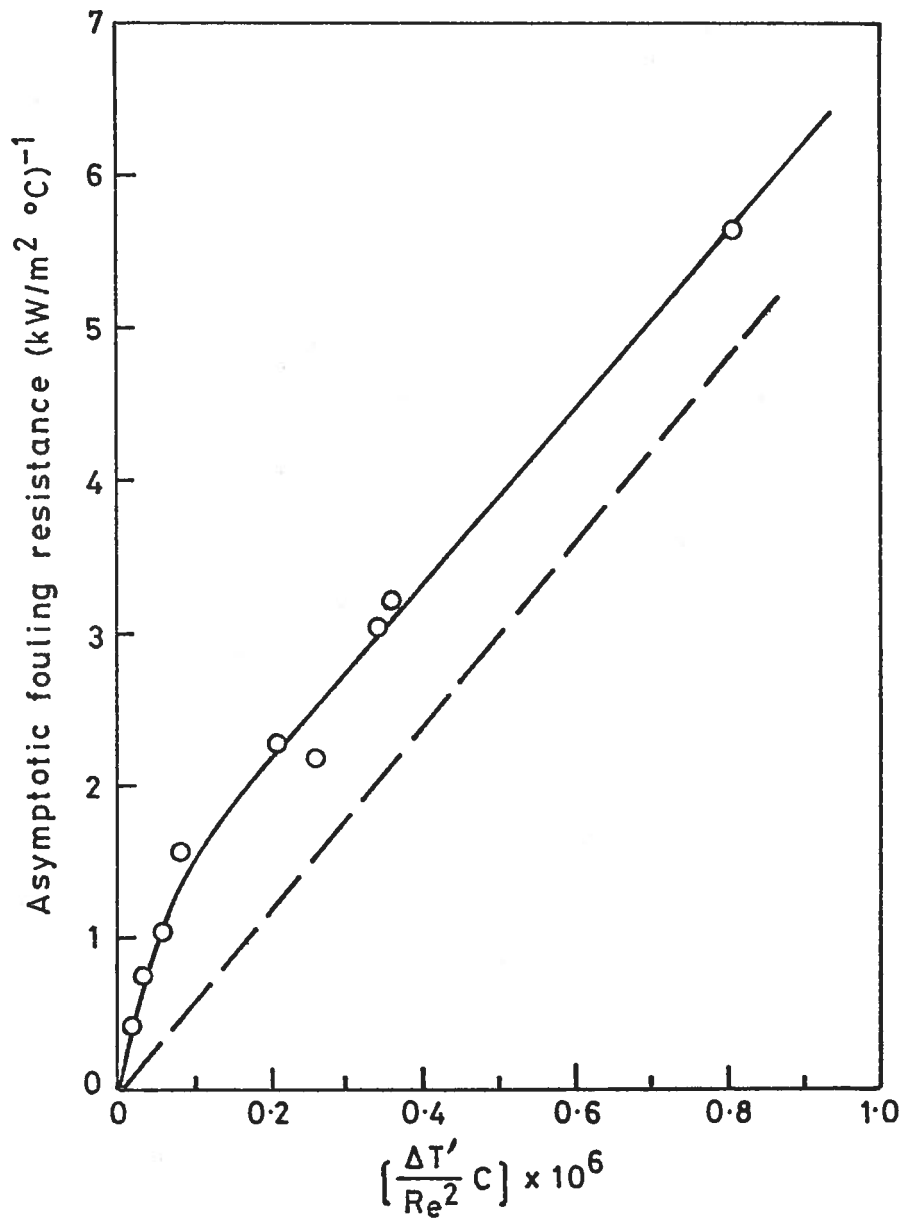


Fig 19 - Asymptotic fouling resistance against model parameter.

NOMENCLATURE

c	:	Foulant concentration (%) or (kg/m <sup>3</sup> )
C <sub>p</sub>	:	Solution heat capacity (kJ/kg <sup>0</sup> C)
d	:	Tube diameter (m)
D	:	Foulant diffusivity (m <sup>2</sup> /s)
f	:	Friction factor (= $\tau_w / \frac{1}{2} \rho u^2$ )
G	:	Solution mass flux (kg/m <sup>2</sup> s)
h	:	Foulant mass transfer coefficient (m/s)
k	:	Deposit thermal conductivity (kW/m <sup>0</sup> C)
K	:	Constant (= 0.36)
k <sub>1</sub>	:	Deposition coefficient
k <sub>2</sub>	:	Release coefficient
k <sub>3</sub>	:	Stickability constant
n	:	Constant (= 0.124)
N	:	Foulant mass flux towards wall (kg/m <sup>2</sup> s)
Pr	:	Prandtl number (= C <sub>p</sub> μ/k)
q	:	Heat flux (kW/m <sup>2</sup> )
R	:	Heat transfer resistance (kW/m <sup>2</sup> <sup>0</sup> C) <sup>-1</sup>
R <sub>f</sub>	:	Fouling resistance (kW/m <sup>2</sup> <sup>0</sup> C) <sup>-1</sup>
Re	:	Reynolds number (= ud/ν)
s	:	Foulant stickability (N/m <sup>2</sup> ) <sup>-1</sup>
Sh	:	Sherwood number (= hd/D)
Sc	:	Schmidt number (= ν/D)
t	:	Time (s)
T	:	Temperature ( <sup>0</sup> C)
ΔT	:	Temperature difference ( <sup>0</sup> C)
ΔT'	:	Dimensionless temperature difference (Eq. 7)
ΔT <sup>+</sup>	:	Dimensionless temperature (Eq. 3)
ΔT <sub>1</sub> <sup>+</sup>	:	Dimensionless temperature at y <sub>1</sub> <sup>+</sup>
u	:	Solution bulk velocity (m/s)
u*	:	Friction velocity (= $u \sqrt{f/2}$ )
u <sup>+</sup>	:	Dimensionless velocity (= u/u*)
W	:	Solution mass flowrate (kg/s)
x	:	Deposit thickness (m)
y	:	Distance from wall (m)
y <sup>+</sup>	:	Dimensionless distance (yu*/ν <sub>w</sub> )
μ	:	Solution viscosity (kg/ms)
ν	:	Solution kinematic viscosity (m <sup>2</sup> /s)
ρ	:	Solution density (kg/m <sup>3</sup> )
τ	:	Shear stress (N/m <sup>2</sup> )

Subscripts

a : Cooling water  
b : Bulk (solution)  
c : Cloud point  
i : Inside  
o : Outside  
p : Pour point  
s : Surface  
w : Wall

Superscript

\* : Asymptotic (except  $u^*$ )

REFERENCES

1. Reistle, C E, "Paraffin and Congealing Oil Problems", Bull USBM, 348, (1932).
2. Nelson, W L, "Fouling of Heat Exchangers", Refiner and Natural Gasoline Manufacturer, 13 (7), 271-276, (July 1934), and 13 (8), 292-298, (August 1934).
3. Hunt, E B, "Laboratory Study of Paraffin Deposition", J Pet Tech, 1259-1269, (November 1962).
4. Patton, C C, Jessen, F W, "The Effect of Petroleum Residua on Paraffin Deposition from a Heptane-Refined Wax System", Soc Pet Engrs J, 333-340, (Dec 1965).
5. Jorda, R M, "Paraffin Deposition and Prevention in Oil Wells", J Pet Tech, 1605-1619, (Dec 1966).
6. Shock, D A, Sudbury, J D, Crockett, J J, "Studies of the Mechanism of Paraffin Deposition and its Control", J Pet Tech, 23-28, (Sept 1955).
7. ASTM D2500-66 and IP 219/67, "Cloud Point of Petroleum Oils".
8. ASTM 97-67 and IP 15/67, "Pour Point of Petroleum Oils".
9. Rhodes, F H, Mason, C W, Sutton, W R, "Crystallisation of Paraffin Wax", Ind Eng Chem, 19, 935-938, (1927).
10. Cruse, W A, Stevens, D R, "Chemical Technology of Petroleum", McGraw Hill, 3rd Edition, (1960).
11. Holder, G A, Winkler, J, "Wax Crystallisation from Distillate Fuels", J Inst Pet, 51 (499), 228-252, (July 1965).
12. Tronov, V P, "Effect of Flowrate and Other Factors on the Formation of Paraffin Deposits", Tr, Tatar. Neft. Nauch-Issled. Inst, No 13, 207-30, (1969), (in Russian).
13. Rafikov, S R, Gutsalyuk, V G, Epelbaum, K E, Yatsenko, E A, Sdobnov, E I, "The Rheological Properties of Paraffin-Based Petroleum", Int Chem Eng, 13 (3), 500-506, (July 1973).
14. Jessen, F M, Howell, J N, "Effect of Flow Rate on Paraffin Accumulation in Plastic Steel and Coated Pipe", Pet Trans AIME, 213, 80-87, (1958).
15. Armenski, E A, Novoselov, V F, Tugunov, P I, "Paraffin Deposition in Short Pipelines", Izv Vyssh. Ucheb. Zaved., Neft Gas, 14(7), 71-73, (1971), (in Russian).
16. Patton, C C, Casad, B M, "Paraffin Deposition from Refined Wax-Solvent Systems", Soc Pet Engrs J, 17-24, (March 1970).
17. Cole, R J, Jessen, F W, "Paraffin Deposition", Oil Gas J, 58 (38), 87-91, (Sept 1960).
18. Walker, R A, "Fouling in Heat Exchanger Tubes", PhD Thesis, University of Birmingham, (1973).



19. Deissler, R G, "Turbulent Heat Transfer and Friction in Smooth Passages", High Speed Aerodynamics and Jet Propulsion, Volume 5, Section E, Convective Heat Transfer and Friction in Flow of Liquids, 288-337, edited by C C Lin, Oxford University Press, (1959).
20. Watkinson, A P, "Particulate Fouling of Sensible Heat Exchangers", PhD Thesis, University of British Columbia, (1968).
21. Taborek, J, Aoki, T, Ritter, R B, Palen, J W, Knudsen, J G, "Predictive Methods for Fouling Behaviour", Chem Eng Prog, 68 (7), 69-78, (July 1972).
22. Friedlander, S K, "Smoke, Dust and Haze : Fundamentals of Aerosol Behaviour", Wiley, (1977).
23. Landau, L D, Lifshitz, E M, "Fluid Mechanics", Addison-Wesley, (1959).
24. Everett, M, "Forced Convection Heat Transfer Inside Tubes - Turbulent Flow", Chem Engr, No 159, (Sept 1969).
25. Gudmundsson, J S, Bott, T R, "Deposition of Silica from Geothermal Waters on Heat Transfer Surfaces", to be published

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- A. Bott, T R, Gudmundsson, J S, "Deposition of Paraffin Wax from Kerosene in Cooled Heat Exchanger Tubes", Paper No 76-CSME/CSE-21, 16th Nat Heat Transfer Conf, St Louis, Mo, (August 1976), to be published Can J Chem Eng, (1977).
- B. Gudmundsson, J S, Bott, T R, "Deposition of Paraffin Wax from Flowing Systems", to be published.
- C. Gudmundsson, J S, Bott, T R, "Solubility of Paraffin Wax in Kerosene", Fuel, 56 (1), 15-16, (1977).