AN INVESTIGATION INTO THE MODE OF GROWTH
AND PHYSICAL PROPERTIES OF WATER FORMED
SCALES ON VARIOUS HEATING SURFACES.

THESIS
submitted to the Faculty of Engineering,
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Doctor of Philosophy

by

John Freeborn.

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ABSTRACT.

The work described in this thesis is concerned with some physical and crystallographical aspects of the formation and properties of water-formed scales. It consists mainly of a study of the growth and physical properties of calcite crystals formed under the special conditions of scale formation. Three main aspects of scale and its properties are dealt with. These are:

Part 1) The initiation of scale formation at a heating surface where boiling is taking place.

Part 2) The physical properties of calcareous scale when it has been allowed to grow beyond the initial stage.

Part 3) Some crystallographical aspects of the further growth of calcite under the specially rapid conditions of scale formation.

Part 1), concerned with the initiation of scale formation, shows that the crystalline ring formations first observed by Partridge with calcium sulphate solutions are also obtained when using a range of other solutions. A variety of other formations based on Partridge's rings were also discovered. A dynamic mechanism is advanced to explain these formations.

Part 2) describes tests evolved to test the adherence, crystal size and other properties of scale in the bulk,
The effect on these properties of varying the material and also the texture of the heating surface is investigated. The results lead to a theory of adherence based on mechanical interlocks and bonds between the scale and the heating surface. A section is concerned with cohering forces in the scale itself and a mechanism of cementitious action is proposed that is similar to the setting of gypsum plaster.

Part 3) is concerned with the orientation effects on further scale growth of single calcite crystal substrates attached to a heating surface. A number of different faces of calcite (100), (111), and (211) were used as the substrate and further growth of scale on them was found to be orientated with respect to the substrate crystal and to exhibit different habit formations according to the crystal face. In two cases evidence indicated that the structure of the growths was not that of a simple parallel overgrowth, but was orientated at $90^\circ$ to the structure of the substrate.
INTRODUCTORY SECTION

The subject of this thesis was sponsored by a water treatment firm which specialises in the field of water-formed scale prevention. The subject was chosen because very little is known of the mechanism of scale formation or the effect on scale properties of various physical factors. This is so despite the fact that an immense amount of work has been done by different people on the subject of the prevention of scale by chemical methods. The reasons for this lack of interest in physical properties become apparent when one considers the historical background of scale formation and prevention. However, lately methods of water treatment, electrical and ultrasonic methods being examples, which affect the crystal growth of scale directly, have been evolved. For a proper understanding of these recent methods it is advantageous to know more of the purely physical factors of growth, hence the subject of this thesis arises quite naturally and it is hoped that the work presented here will be of some assistance to those engaged in the field of physical water treatment.

Water formed scale consists of a number of chemical compounds which are formed by thermal action when water is heated. It is precipitated in such places as boilers, both steam and hot water, calorifiers, water heaters, kettles; in short wherever hard water is heated.
The disadvantages of scale are well known. Principally they are:-

1. Blockage of internal waterways necessitating periodical cleaning.

2. Overheating of scaled heat exchange surfaces with consequent damage, caused by the low thermal conductivity of scale.

3. Reduction in efficiency of heat exchange surfaces due to the low thermal conductivity coating of scale.

Scale has been a real problem for approximately two hundred years since the invention of the steam engine which requires a steam boiler to run it, and of the domestic hot water system which needs a hot water boiler and associated pipework. The first definition of scale formation, however must considerably antedate this time as it is given in terms of the four basic elements of mediavel times. It is:-

Fire + Water = Earth + Air

this equation applying particularly to steam boilers or kettles where earth refers to scale, and air to steam. The invention of the steam engine with its associated boiler marked the advent of scale as a problem of industrial importance, the simple low pressure boilers of that era were just as prone to scale-up as the more sophisticated boilers of today. They were
kept clear by manual means at intervals. It has been said that the first means of treating water to prevent scale was discovered accidentally when some of James Watt's (3) workmen put some potatoes in a boiler for their meal and then forgot them. When later cleaning out the boiler, they found the scale to be sludge-like instead of hard and hence it was easy to clean out the boiler. From this beginning sprang the science of internal water treatment which is still very much with us at the present time. By 1839 a great deal was known about scale and its prevention, and an interesting book by Robert Armstrong (4) gives a striking picture of the situation around that time. According to Armstrong, scale consists 9/10 of carbonate of lime (CaCO₃) and 1/10 sulphate of lime (CaSO₄). His account of how carbonic acid gas (CO₂) is driven off in the process of heating the water thus causing deposition, corresponds exactly to our beliefs today. His descriptions of explosions vividly show the magnitude of the problem caused by scale at that time. Explosions due to the insulating effects of scale causing the metal of the boiler to become overheated with resultant fracture are described as of "everyday occurrence". Monday mornings are described as particularly bad in the Manchester area as the stokers were in a hurry to raise steam in
boilers that had become cold over the weekend hence they lit large fires which caused the boiler metal to overheat with subsequent explosions when steam pressure was raised. The explosions were very damaging to property and caused occasional loss of life.

Government action was eventually taken and the Boiler Explosions Acts of 1862 and 1890 were passed which called for a Board of Trade enquiry for every boiler explosion. The Factory and Workshop Act of 1902 made it compulsory for each boiler to be inspected regularly by a competent person in addition to being fitted with a safety valve, pressure gauge and water gauge. Even at the present time however, occasional accidental explosions take place due to scale formation. In 1954 a hot water tank in a factory exploded killing one person. The cause of the explosion was overpressure of steam generated from the water in the tank by heating steam when the relief opening had become choked with scale\(^5\). In 1955 two shipboard boiler explosions took place, one on the "George Cousins" a steam trawler \((6)\), the other on the motor vessel "San Cirilo" killing eleven people\(^7\). Both these explosions are described as having been due to excessive scale formation causing overheating and failure of the metal of the boiler.

Further reports of failure come to light from time to time as can be seen by referring to Insurance Company
The most common salts found in water are given by Taylor as:

- Sodium chloride,
- Calcium bicarbonate,
- Magnesium sulphate,
- Calcium sulphate,
- Magnesium bicarbonate.

The actual constitution of any particular water supply will depend on the geological source. Waters are said to be hard or soft depending on the amount of soap needed to produce a lather. A soft water needs little soap to produce a lather, whilst a hard water will need relatively more. The hardness is dependent on the amount of the various chemicals present as listed above. Hardness is divided into two parts - temporary and permanent.

Temporary hardness is that portion removed by boiling and is caused by the bicarbonates of calcium and magnesium which on boiling break down and liberate carbon dioxide gas, precipitating the less soluble carbonate.

Permanent hardness is that hardness remaining after boiling. It is the hardness salts in water that are the source of scale.

Scale can form in a number of well established ways; and which way occurs in practice will depend on the particular chemicals in the water, the rate of heat transfer and the circulation of water past the heating surface. These different ways of scale precipitation can be listed as follows:
1) Scale caused by chemical action brought about by the increase in temperature when water is heated.

2) Scale caused by evaporation of water as in a steam boiler until the solubilities of the scale forming salts in solution are exceeded with consequent precipitation.

3) Scale caused by a decrease in solubility of salts in solution with rise in temperature as the water is heated.

4) Scales caused on heat exchange surfaces where ebullition is taking place by deposition at the triple interface of steam bubble, water and heating surface.

1) A good example of scale caused by chemical action as the temperature is raised is the case of calcium carbonate scale which is formed when the bicarbonate in the water breaks down to carbonate ion and carbon dioxide as shown in the equation (under:)

$$\text{Ca}^{++} + 2\text{(HCO}_3\text{)}^- \overset{\text{heat}}{\longrightarrow} \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2$$

as calcium carbonate has a fairly small solubility, about 20 p.p.m., it will be precipitated.

2) In steam boilers, recirculated cooling systems using atmospheric cooling towers, indeed in any place where water is evaporated, the concentration of the salts in solution will gradually increase until such time as the solubility limits are exceeded and a condition of supersaturation sets in. Precipitation of scale then occurs until the concentration of salts falls to saturation level.

3) This method of scale formation is closely allied to that of No. 2). The way in which the solubility limit is reached is however quite different.
Suppose that the solubility of the scale forming salt under consideration decreases with rise in temperature. Then if at ambient temperatures the water is nearly saturated with respect to a particular salt, rise in temperature alone will bring about a condition of supersaturation with consequent deposition of scale. Several common scale forming salts have this characteristic negative solubility slope with temperatures, examples being calcium sulphate and calcium hydroxide.

4) On some heat exchange surfaces ebullition, that is steam bubble formation, occurs. Each bubble forming at the heating surface is composed of steam arising out of the evaporation of water. If the bubble formation is quick enough then the water which is evaporating to form the bubble will become locally concentrated with respect to its salt content with consequent precipitation of scale. Whether this scale redissolves or not when the steam bubble leaves the surface depends on the rate of bubble formation. When this rate is fast, more scale is formed than can be washed away and redissolved by the water present. It has been shown that the scale is precipitated at the triple interface of water, steam and heating surface.

These four methods of precipitation of scale forming salts explain the presence of scale forming precipitates in the water. It is of interest to note that this material has been recognized as crystalline in nature for a long time. However there is no explanation implicit in these four phenomena as to why:
a) the scale particles adhere to the heating surface.

b) the scale particles adhere to each other to extend the layer of scale and cause it to get thicker. Furthermore, it is true to say that little work has been done on these questions.

The reasons for this apparent lack of interest in the structure and properties of the scale itself become evident when it is realised that whilst the precipitation of scale forming material at a heat exchange surface can be expressed in chemical terms the actual growth mechanism of the scale cannot. The scale particles are crystalline in nature and the forces holding these particles together to form scale are much more the interest of Crystallographers than of Chemists. Because crystallography is comparatively a young science, the discovery of X-ray diffraction in 1913 by Von Laue marking the beginning of modern crystallography, little attention as yet has been paid to some of its practical applications of which scale formation is one. It is hoped that the work described in this thesis will at least indicate what powerful tools crystallographic methods can put in the hands of research workers in this field.

Hence so far as scale prevention goes most work has been done by Chemists and this work has centred on preventing scale by affecting the chemical processes of precipitation. The result has been a number of processes listed below which stop scale formation by preventing the
precipitation of scale-forming material. It is not, therefore, surprising that with these processes, developed in the last century, there is no need to take into account the crystallographical aspects of scale growth. These processes are as follows:

a) Base exchange softening. In this process the calcium salts in the water are changed into their sodium salt equivalents by passing the water through a bed of chemicals called zeolites. The sodium salts resulting are not normally scale forming as they are extremely soluble. The reaction can be represented as follows:

\[
\text{Ca} (\text{HCO}_3)_2 + 2\text{NaR} \rightarrow \text{CaR}_2 + \text{Na}_2 (\text{HCO}_3)_2
\]

\[
\text{CaSO}_4 + 2\text{NaR} \rightarrow \text{CaR}_2 + \text{Na}_2\text{SO}_4.
\]

The first term in each equation represents the scale forming salt, the second term the zeolite. After a time the zeolite is exhausted and has to be regenerated by passing a salt (NaCl) solution through it.

b) Lime soda softening. Here the water is softened first by adding slaked lime to it when the following action takes place.

\[
\text{Ca} (\text{HCO}_3)_2 + \text{Ca} (\text{OH})_2 \rightarrow 2\text{CaCO}_3 + 2\text{H}_2\text{O}
\]

the calcium carbonate being nearly insoluble precipitates and is collected in a settling tank. Calcium sulphate hardness is dealt with by adding soda (Na$_2$CO$_3$) when the following action is

\[
\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + \text{Na}_2\text{SO}_4
\]

again the calcium carbonate settles out whilst the sodium sulphate is non-scale forming.
c) Distillation - here the salts in solution are removed by generating steam from the hard water. The steam is condensed to form pure water free from scale forming material.

All these processes stop scale absolutely. Unfortunately their complexity and cost often prevent their use in small installations where it is often more convenient to periodically clean the plant of scale by mechanical or chemical means than it is to prevent the scale forming. This state of affairs is not entirely satisfactory and as a result interest has been shown in other methods of dealing with scale. These methods are as follows:

1) Electrical methods which do not affect the chemical reactions causing precipitation of scale forming material but do affect the manner in which the crystalline particles lock together.

2) Chemicals which added to the water again do not prevent precipitation but do prevent the bonding which normally goes on to form a coherent mass of scale.

3) Ultrasonic methods where ultrasonic vibrations in the water physically break-up the scale as it forms.

4) By designing apparatus with flexible heat exchange surfaces whose flexing under normal service conditions prevent the brittle scale becoming permanently attached.

It can readily be seen that these processes are generally different from those in the previous list in
that they do not affect the precipitation reactions but they do affect the growth mechanism of the scale. The design of equipment to put these methods of scale prevention into operation has been entirely empirical and it is true to say that all of them have been evolved through trial and error. It is believed that only when the mechanism of growth, adherence and such like other physical factors are investigated using crystallographical techniques will these latter processes be explained and reach the same state of development as have the older processes for preventing precipitation of scale.
PART I - THE INITIATION OF SCALE FORMATION

INTRODUCTION

The work in this section is concerned with initial deposits that occur on a heating surface where ebullition is taking place. This is an extremely common type of heat transfer. Work has been done in this field in the past. Partridge \(^1\) was the first to consider this type of deposition on a polished and plated heating surface. His work was concerned with calcium sulphate only. He advanced a theory to account for the formations he observed. This type of deposit has also been observed by M. V. Griffiths \(^3\) who obtained photographs similar to those of Partridge. Mesler in a private communication to the author has also reported similar deposit formations in the course of a study of the local variations of heating surface temperature with time under steam bubbles \(^4\). Other work has been done on the initiation of scale formation by Clark, Bunn, Turner, Gray and others but these workers have not been directly concerned with the ring type of formations investigated here. Their work concerns analysis of deposits, ambient temperature precipitation by corrosion cell mechanism and chemical additions to affect the physical forms of the resulting scale.
The work below is concerned with the ring formation occurring under steam bubbles in an apparatus in which the following conditions were controlled:

1) Flow rate of the scale forming water over the heating surface.
2) Chemical content of the scale forming water.
3) Heat input to the heating surface.
4) Surface finish of the heating surface.

APPARATUS

An apparatus was constructed so that the scale formation could be watched using a microscope as it was forming.

The heating surface consisted of part of a flat Monel metal plate which formed the basis of the apparatus. On the polished side a hollow rectangular rubber gasket and a microscope slide were clamped by two metal straps. The space between the Monel plate and the microscope slide formed a cell \((2\frac{1}{2}" \times 3\frac{1}{4}" \times 3/16")\). The solution under test was led in at one end of the cell by three small holes which connected to a pipe at the back of the Monel plate. Solution left the cell through three similar holes at the other end of the cell. The Monel plate was heated by a flat electric element clamped against it on the opposite side to the cell. The maximum rating of the element
was 75 watts at 50 volts input. A support post for
the complete cell was attached to the rear of the heating
element clamp plate. Solution under test was fed into
the cell from a small tank on a stand. The outlet pipe
from this tank contained a regulating needle valve to
to control the flow to the cell. The solution after passing
through the cell could be passed into a measuring cylinder
where the flow could be measured. The electrical supply
for the heating element was taken from the laboratory
supply and could be varied by a series sliding resistance.
The current flow and voltage at the element measured
with an ammeter and voltmeter. The formations on the
heating surface were observed by a Cooke, Troughton and
Simms microscope adapted by removing the substage assembly
and tilted so that its axis was in a horizontal plane.
The heating surface was illuminated for observational
and photographic purposes by a beam of light at about 20°
to the normal of the heating surface. Photographs were
taken using a Beck microscope camera mounted on the
microscope using Ilford 35 mm FP3 film. Diagrams of the
test cell and of the general set-up are shown in Figures
1 and 2.
FIGURE 1. TEST CELL

Scale at full size.

Terminal block

Test surface

Outlet pipe

Electric heater

Support post

Inlet pipe
FIGURE 2. GENERAL ARRANGEMENT.

Solution tank.

Regulating valve.

Diagrammatic.

Circuit diagram

Test cell

Microscope.
METHOD

Preparation of test solutions.

Solutions used in these experiments were:

1) Calcium sulphate (saturated solution);
2) Magnesium hydroxide (saturated solution);
3) Sodium chloride (saturated solution);
4) Calcium hydroxide (saturated solution);
5) Tap water as available in the laboratory;
6) Calcium bicarbonate 100 and 20 parts per million.

The solutions of calcium sulphate, magnesium hydroxide, sodium chloride and calcium hydroxide were obtained by crushing selenite gypsum and brucite in the first two cases and adding excess to distilled water. The latter two solutions were obtained from laboratory chemicals. All solutions were boiled with excess solute and cooled to 20°C, at which temperature they were used. The calcium bicarbonate solutions were made up by suspending the requisite amount of calcium hydroxide in distilled water and then passing gaseous carbon dioxide through it until clear. The solution was heated to 50°C, to standardize the free carbon dioxide content, and cooled to 20°C, at which temperature it was used. These chemicals were chosen as they are to be found regularly in public water supplies, and also furnish examples of compounds with both negative and positive solubility slopes with temperature. The heating surface was
prepared by emery-papering it with successively finer grades of emery paper and finally a mirror polish was obtained using metal polish on Svelte cloth. The procedure followed with each solution was first to establish a definite rate of flow through the apparatus, after which the heater was switched on and observation of the polished surface begun. The heater input energy was maintained at 62.5 W throughout. When the initial scale had formed on the heating surface, the apparatus was switched off and cleaned. Another rate of flow was then selected and the procedure repeated. As pure solutions were used, chemical analysis of the deposit was not necessary except for tap water. The crystal structure of each deposit was obtained by X-ray diffraction techniques. All deposits were photographed.

The results obtained were as follows:

1. **Calcium Sulphate**

   At very low rates of flow (60-135 cm/h) rings of crystals were deposited as described by Partridge, namely each bubble on detachment left behind a ring of crystals. Often the same spot served for the generation of streams of bubbles building up a disc-like deposit within the original rings of crystals. At slightly higher rates of flow (200-450 cm/h) a new phenomenon was observed. As each bubble formed a ring of crystals formed at its contact circle with the heating surface. The bubble grew until its buoyancy was sufficient either to cause
its detachment from the surface or to cause it to slide upwards on the surface until it had moved about one-third of a diameter of the ring, when it reattached and deposited a new ring of crystals; this process was repeated until a ladderlike pattern was obtained, each ring being fractionally greater than its predecessor. After a number of crystal circles had been generated in this manner the bubble had sufficient buoyancy to proceed continuously up the slide leaving two lines of deposit until it appeared to break away completely from the heating surface. Figs. 3 and 4 show the resultant ladder network. Here again bubbles were generated at fairly constant centres and steams of bubbles rose up the ladders depositing more and more material. As the flow rate increased this mode of formation reverted to the original type of single rings as experienced at very low flows. With increasing flow (600 cm/h) less and less deposit occurred until it was observed that as each bubble detached its rings of crystals immediately redissolved until a flow was reached at which very few bubbles were formed at all and those that did form tended to remain stationary on the surface.

2) Magnesium Hydroxide.

At no flow rate was any deposit formed on the heating surface.
3) **Sodium Chloride**

At no flow was any deposit retained on the heating surface. It was seen, however, that where bubbles formed a ring of deposit was also formed at the triple interface. These rings of deposit did not remain on the surface when the bubble became big and buoyant enough to move away, but detached themselves with the bubbles and apparently redissolved. This effect was soon obscured by a snowstorm-like cloud of crystals thrown out of the body of the fluid as solubility limits were exceeded. At the highest flow rates no precipitation at all was seen.

4) **Calcium Hydroxide**

With this salt, ring and ladder formation were clearly observed, and the deposit adhered to the heating surface. At flow rates of 130-220 cm/h ring and ladder formations were observed together (figure 5). There was however a tendency for the ladder formations to be formed nearer the solution inlet than the rings. These rings and ladders were less distinct than those obtained with calcium sulphate and the method of growth appeared different in that the hydroxide rings filled in quickly to give plaque-like deposits. It was also noticed that if the deposit, when dry, was rubbed with the finger, most of it came away easily leaving the original rings and ladders, showing that the adherence of the initial deposit was greater than that formed subsequently within the rings. As the
In this and following photographs flow is indicated by an arrow at the top.

Fig. 3. Calcium sulphate

Fig. 4. Calcium sulphate

Fig. 5. Calcium hydroxide

Fig. 6. Calcium hydroxide
Fig. 11. *Calcium bicarbonate*

Fig. 12. *Calcium bicarbonate*

Fig. 13. *Calcium bicarbonate*
flow increased to 528 cm/h the ladder formations were not so apparent, a ring tracery only being produced, (Fig. 6). At fast rates of flow (1048 cm/h) rings were seen together with V trails, that is ladders without the steps.—Also, one example of cotangential formation was observed (Fig. 7).

5) Tap Water

An analysis of the laboratory tap water used is given on page 28. At lower flow rates (230-430 cm/h) ring and ladder deposits occurred (Fig. 8) and here also the ladder formations were nearer the inlet than the rings.

Certificate of analysis of a sample of water marked —

College Laboratory tap water.

This sample of examination gave the following results:—

<table>
<thead>
<tr>
<th>Component</th>
<th>Parts/million</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total solid matter</td>
<td>370</td>
</tr>
<tr>
<td>dried at 100°C</td>
<td></td>
</tr>
<tr>
<td>Hardness, temporary</td>
<td>172</td>
</tr>
<tr>
<td>Hardness, permanent</td>
<td>107</td>
</tr>
<tr>
<td>Total alkalinity, CaCO₃</td>
<td>192</td>
</tr>
<tr>
<td>Chlorides, Cl</td>
<td>38</td>
</tr>
<tr>
<td>Sulphates, SO₄</td>
<td>60</td>
</tr>
<tr>
<td>Carbonates, CO₃</td>
<td>115</td>
</tr>
<tr>
<td>Calcium, Ca</td>
<td>101</td>
</tr>
<tr>
<td>Magnesium, Mg</td>
<td>6</td>
</tr>
<tr>
<td>Carbon dioxide, free</td>
<td>none</td>
</tr>
<tr>
<td>pH value</td>
<td>7.7</td>
</tr>
</tbody>
</table>
These rings were well defined on examination; with high power the crystals were just discernible as having the calcite shape. At the higher rates of flow (793 cm/h) it was seen that the bubbles were sliding smoothly up the heating surface and leaving a continuous V-shaped trail of deposit. This streamed out from that part of the triple interface whose tangents were a few degrees below the horizontal diameter. Each bubble increased in size as it rose, hence the widening of the trail which continued forming until the bubble had sufficient buoyancy to detach itself from the surface. Also at this flow ordinary ladders were formed. Higher flow rates (1135 cm/h) gave lighter deposits of predominantly ladderlike formations (figure 9). At the highest flow (1185 cm/h), no deposit was formed.

6) Calcium bicarbonate.

At the flow of 220 cm/h only ring tracery was formed. As the flow rose to 270 and 300 cm/h, both rings and ladders were formed, with ladders predominating slightly (figure 10). At 280 cm/h, equal quantities of rings and ladders were formed (figure 11). At 990 cm/h rings only were slowly formed on top of an extremely thin greenish-yellow film that formed evenly over the heating surface and consisted probably of corrosion (figure 12). At flows higher than 990 cm/h, this green film was all
that was formed. The above observations all apply to a solution strength of 100 parts per million. One run using solution strength of 20 parts per million was carried out and whilst the general rate of deposition was so slow as to cause this concentration to be abandoned in favour of 100 parts per million, it was seen that two novel formations had occurred. These deposits consisted of multiple concentric rings (figure 13).

CONCLUSIONS.

These experiments throw light on to the initiation of scale deposits in one common type of scale formation, i.e., the formation which occurs at a heating surface that is hot enough to cause boiling in the scale-producing fluid.

This initial formation consisted of the crystallizing material precipitated at the junction of a bubble with the scale-producing solution and the heating surface. This triple interface formation was of five types:-

1. Plain rings of deposit formed at the edge of one bubble that grew until its buoyancy overcame the forces attaching it to the heating surface. The bubble upon detachment rose straight to the surface without touching the heating surface again.

2. Ladderlike formations where a bubble deposited an initial ring then moved up the surface by a fraction of its diameter when it again became stationary and deposited a fresh ring. This procedure was repeated a number of times, and
at each step the bubble became fractionally bigger, hence the edges of the formation were V-shaped.
More than one bubble made the journey up the ladder, and each bubble added to the original steps in the ladder. In most cases the ladder ended abruptly when the depositing bubble broke completely away from the surface. In some cases the bubble, after making the journey up the ladder did not break completely from the surface, but slid up with a uniform motion leaving two continuous lines of deposit.

3) V tracks of the same outer shapes as the ladder formations but lacking the steps. Here the bubble was initially stationary until it had grown high enough for its buoyancy to start its ascent as in the case of ladders. Once the ascent was started, however, it continued smoothly and left two tracks. The distance between the tracks increased as the bubble rose. The tracks originated from that part of the triple interface whose tangents were a few degrees below the horizontal diameter of the bubble. Here again, more than one bubble made the journey, each bubble adding to the original deposit.

4) Co-tangential ring deposits. These deposits were initiated from one bubble which grew until bigger than average, when it detached itself, leaving a large ring. Successively, small co-tangential rings were then formed in quick succession within the initial ring. This type of formation was very rare and may have been an example of suppressed boiling.

5) Concentric ring deposits. These deposits were seen only twice with 20 parts per million calcium bicarbonate and were not observed in process of formation hence the mechanism is unknown. It could

* NB. pagination incorrect, there is no page 31.
have had a mechanism similar to 4) and perhaps be a further example of suppressed boiling. Alternatively, small rings could have formed first, followed by larger rings from larger bubbles, possibly being the result of a local temperature rise in the heating surface. Both the observed formations had a V-shaped track leading up from the centre, which apparently indicates the route taken by the bubbles on leaving the surface.

The five types of deposit did not all occur with every salt tested. The frequency of occurrence is noted in Figure 14. Also there was a relation between the rate of flow and the type of deposit. This is indicated in Figure 15.

The non-appearance of any deposit from the solution of magnesium hydroxide may be due to the fact that this salt is considered to be deposited indirectly by the action of soda-lye or magnesia\(^{(16)}\), which chemical mechanism was not provided in these tests. The theory of scale formation in association with bubbles has been indicated by Partridge.\(^{(1)}\) The fact that rings of deposit were observed with solutions of sodium chloride strongly bears out his theory that evaporation takes place at the triple interface. With this salt, whose solubility increases with temperature, a temperature rise in the solution as it nears the heating surface could not precipitate a deposit, as with calcium sulphate, for example,
<table>
<thead>
<tr>
<th></th>
<th>Calcium Sulphate</th>
<th>Calcium Bicarbonate</th>
<th>Calcium Hydroxide</th>
<th>Sodium Chloride</th>
<th>Magnesium Hydroxide</th>
<th>Tap Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plain Rings</td>
<td>$&gt;10^2 &lt; 10^4$</td>
<td>$&gt;10^3 &lt; 10^4$</td>
<td>$&gt;10^2 &lt; 10^3$</td>
<td>$&lt; 10$</td>
<td>$0$</td>
<td>$&gt;10^3 &lt; 10^4$</td>
</tr>
<tr>
<td>Ladders</td>
<td>$&gt;10^2 &lt; 10^3$</td>
<td>$&gt;10^2 &lt; 10^3$</td>
<td>$&gt;10 &lt; 10^2$</td>
<td>$0$</td>
<td>$0$</td>
<td>$&gt;10^2 &lt; 10^3$</td>
</tr>
<tr>
<td>V Tracks</td>
<td>$&gt;10 &lt; 10^2$</td>
<td>$0$</td>
<td>$&gt;10 &lt; 10^2$</td>
<td>$0$</td>
<td>$0$</td>
<td>$&gt;10 &lt; 10^2$</td>
</tr>
<tr>
<td>Cotangential rings</td>
<td>$0$</td>
<td>$0$</td>
<td>$&lt; 10$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
<tr>
<td>Concentric Rings</td>
<td>$0$</td>
<td>$2$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
</tbody>
</table>

**Frequency of occurrence of five types of deposit on a heating surface of 2.06 in².**

*Figure 14.*
<table>
<thead>
<tr>
<th>Flow Rate (cm/hr)</th>
<th>0</th>
<th>200</th>
<th>400</th>
<th>600</th>
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<tr>
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<tr>
<td>Calcium Bicarbonate</td>
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<tr>
<td>Calcium Hydroxide</td>
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<tr>
<td>Calcium Sulphate</td>
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</tbody>
</table>

**Relationship between Rate of Flow past heating surface and Type of Deposit**

*Figure 15.*
hence evaporation must have taken place for a deposit to occur at all, and this could only happen by evaporation taking place into the steam bubble. The question of the mechanism causing the deposits has not been fully resolved. This mechanism could either be static or dynamic. In the case of the static mechanism steam would be generated at the triple interface and would form the bubble. The deposit would arise as a result of the evaporation of this steam, and would at the most be proportional to the volume of the bubble. The growth of the deposit would be the result of successive bubbles, each leaving a further increment. In the case of the dynamic mechanism water would be continuously evaporated into the bubble, and at the same time continuously condensed at the outermost surface of the bubble where the solution bulk is cooler than at the heating surface. Thus deposit would be continuously deposited during the life of the bubble, and the amount would not depend upon the volume of the bubble. Thus, the dynamic theory would allow for a considerable amount of deposit to be precipitated under each bubble. The hypothetical picture of this is as shown in Fig 16. The amount of deposit will depend upon the following factors:

1. Amount of water evaporated at the triple interface. It is known that the
heating surface temperature under the bubble is higher than that of the general heating surface. As the bubble is formed a weight of deposit is produced proportional to the amount of water evaporated into the bubble and being condensed at the outermost region. It is possible that a large amount of deposit dependent upon the life of the bubble will be thrown down.

2. Amount of water evaporated at the double interface. The hot spot in the heating surface under the bubble may cause superheating of the steam in the bubble. As this superheated steam circulates in the bubble, it will come into contact with the solution and cause further evaporation into the bubble. This evaporation will cause precipitation on the surface of the bubble, and this unattached precipitate will either coalesce with the material on the heating surface or remain in the liquid and give rise to the dudge that is often found in steam boilers.

3. The solubility slope of the salts in solution. Because the heating surface is at a higher temperature than the solution, there will be a temperature gradient in the latter. Therefore, any increase or decrease in solubility of the salts in solution with temperature will have an effect upon the precipitation occurring at the heating surface. Thus, in the case where no bubbles are forming, precipitate will tend to be thrown down from a solution with a positive solubility slope. In the case where bubbles are forming, a negative solubility will increase the amount of deposit at the triple and double interfaces and positive solubility slope will lessen this amount.
General solution.

**Dynamic Mechanism of Scale Formation**

- Steam condensing at outermost coolest region of bubble.
- Volume of superheated steam due to elevated temp. of heating surface causing evapo. into bubble and resultant crystallisation.
- Evaporation into bubble at triple interface with resultant deposit.
- High temp. area causing crystallisation of salts with negative solubility slope.

Heating surface at general temperature.

Heating surface at elevated temperature.

Figure 16.
If the observed deposit were due to the static mechanism alone, then the amount formed per bubble would be easy to calculate, since it only involves a knowledge of the bubble volume and the concentration of the salt in solution. Assuming a bubble to be $1/32"$ in diameter the amount of solid precipitated from a saturated solution of calcium sulphate (1700 parts per million at $100^\circ$C) would be approximately $1 \times 10^{-12}$ lb. weight which occupies a volume of $22 \times 10^{-12}$ in$^3$, which could be represented by a cube of side $2.8 \times 10^{-4}$in. Thus it may be seen that if one bubble could be observed and the amount of material deposited measured, the precise mechanism could be established. This was not achieved in the present experiments, as bubbles streamed out from one point at high speed making it impossible to see how much deposit each bubble caused. High-speed cinematography might decide this issue. The occurrence of different types of formation, e.g., rings and ladders, together, shows that the type of formation is dependent on factors other than flow, and it is felt that temperature is one of these factors. In the apparatus only the central portion was heated and as cold solution was introduced at one end temperature gradients must have existed with the inlet area being the coolest part. Several times
ladders formed near the inlet, and rings further up, and hence as other conditions were the same it can be seen that the temperature was affecting the mode of formation. It is felt that useful results will be obtained by extending these tests so that the temperature of the surface was known as well as the energy input.
PART II

Physical Properties of Developed Layers of Calcareous Scale.

Part I deals with the initial formation of scale on to its heating surface. The logical follow-up to this is to study the properties of scale in the bulk and to examine the effect on these properties of different types of heating surface. Hence it was decided to investigate the following properties of the scale:

1. The adherence to the heating surface.
2. The crystal size.
3. The crystallographic structure and chemical composition.
4. The structure as revealed by microphotography and microradiography.

Further it was decided to examine the effect on these properties of varying the texture and material of the heating surface. This programme called for the production of thicker layers and larger amounts of scale than the small cell apparatus could conveniently produce. In addition the small cell apparatus did not have a readily exchangeable heating surface and further the area of heating surface was so small as to make the introduction of different textures difficult. Thus the small cell apparatus was not suitable and a scale making apparatus was designed and built to incorporate the following features.
1. Larger and thicker quantities of scale to be produced per run by using a much larger heating surface and running each test for several hours.

2. The heating surface to be easily demountable from the apparatus to facilitate photography and measurements of the scale after formation.

3. The heating surface to be steam-heated so as to give even uniform heating right over the entire surface.

4. Different heating surface materials to be available and the heating surface to be large enough to incorporate different surface textures.

An apparatus to fulfil the above requirements was designed and manufactured in the Crystallography Section of the Battersea College of Technology. Drawings are given below (figs. 17 & 18). The heating surface was the external surface of a cylindrical tube of mild steel four inches in external diameter and six inches in length. A dozen of these cylinders were cut from a length of boiler tube, and turned in a lathe and finished smooth with emery paper on their external surfaces. Samples of these tubes were sent away to be electroplated in copper, nickel and chromium, thick non-porous coatings being specified. In addition, one tube was vitreous enamelled with a high glaze white enamel. For the actual test runs the surface texture was adjusted as described below. The cylindrical heating
surface could be made up into the test cell by clamping flanges over its open-ends, the flanges being made steam tight with rubber gaskets and secured by one through-bolt and nut through the centre of the cell. The uppermost flange had a \( \frac{3}{4} \) inch stud coupling for the heating steam entry and also a tapping for a steam pressure gauge. The bottom flange had a \( \frac{3}{4} \) inch stud coupling for the steam and condensate outlet. The cell was suspended in the centre of a five gallon mild steel drum by means of a horizontal supporting beam which passed through a hole in the centre bolt and rested on the sides of the drum. Water was admitted at the bottom of the drum via a copper pipe leading from a constant head flow device. Inlet water temperature was measured by a thermometer incorporated in a pocket integral with the copper pipe. After being boiled the water left the drum from an overflow pipe at the top of the drum, another thermometer being situated in this pipe. A water preheating coil of 3 turns of \( \frac{3}{4} \) inch diameter copper pipe was coupled to the steam and condensate exit from the test cell. The function of this coil was to preheat the water entering the drum so that vigorous boiling occurred all over the test cell surface. By using this coil much thicker layers of scale could be obtained in the same time than was otherwise the case.
The bottom pipe from the steam coil was led out of the drum through a rubber bush from whence it went to an isolating valve and a steam trap. The steam trap was of the thermostatic type and whilst allowing water to pass, would not let steam through, thus conserving heat. Thermometer glands were incorporated in the drum to enable the temperature gradient in the water to be measured. Steam was admitted to the interior of the test cell via the inlet steam pipe from the steam boiler. The boiler used was a Perkins "Patomic" model capable of producing 100 lb. of steam per hour at up to 50 p.s.i.g. The boiler was oil-fired and steam pressure was automatically regulated by a pressure-stat which controlled the amount of oil flowing to the oil-burner. Pressure regulation was ± 1 p.s.i.g. and the pressure could be adjusted by varying the setting of the pressure-stat.
PROCEDURE

Preparation of Specimens.

As previously stated, it was decided to build up the scale on different metal surfaces, each surface to have varying degrees of surface finish.

The different metal surfaces chosen were:

- mild steel,
- copper,
- nickel,
- chromium.

These metals are typical materials used for heat exchange in current industrial practice and hence have other than purely academic interest. One non-metallic surface was also tried, this being glass which again is used industrially. Some tests were done with steel cathodically protected. In these cases a platinum ring anode was placed around the steel specimen. Direct current passed between the anode and the steel and was regulated so that a voltage of 1.8 as measured with a valve voltmeter was maintained between the platinum and the steel, the platinum being positive.

Each surface was tried with a number of different finishes. One of these was a mirror finish and all the others were produced by using various grades of abrasive papers.

All the specimen heat exchange surfaces were 4 inches outside diameter and 6 inches in length. A number of specimens were cut from a length of boiler tube and samples were sent away to be copper, nickel and chromium plated, in addition one sample was vitreous enamelled with a high glaze white enamel.
The surfaces of the metal surfaced specimens were all prepared in the following manner. The whole surface of each cylinder was buffed and polished to a mirror finish initially using a power rotary buffing machine followed by metal polish on a "Svelte" cloth. Each cylinder was divided into a number of approximately equal horizontal bands at right angles to its axis. One band on each cylinder was left in its polished state whilst the others were roughened with various grades of emery paper. The emery scratches were all in the same circumferential direction. One series of test runs was done with textures produced by emery paper of grades F, 1, 1½, 2, 2½, and 3. It was found however that these textures which were all fairly coarse did not affect the adherence from grade to grade so in the final series of test runs textures produced by emery paper of grades M, 0, 00, and 000 were used, these particular grades being found to have a significant effect on the adhesion of the scale to the heating surface.

Setting up of Apparatus.

The prepared specimen was clamped between the two iron flanges and secured with the single through-bolt all joints being made steamtight with rubber gaskets. The preheating coil was attached to the lower flange and the whole assembly mounted in the cylindrical drum. Steam and water connections were made up as shown in figure 18. Water from the constant head apparatus was then allowed to fill the drum.

Whilst this setting up was being done the steam boiler
had been lit so that steam was available as soon as required. Immediately the drum was full of water the steam was turned on and the test run commenced. The pressure of steam in the test cell was kept constant at either 25 p.s.i.g. or 40 p.s.i.g. according to the test run, this being accomplished automatically by a "Danfoss" pressure-stat which regulated the oil supply to the burner of the boiler. The pressure-stat had an operating differential of ± 1 p.s.i.g. so that steam pressure was always in the range of 24-26 p.s.i.g. or 39-41 p.s.i.g. In the second series of test runs were carried out at 5 p.s.i.g.

The boiling of the water in the drum was initially adjusted to be quite brisk by regulating the flow of water from the constant head apparatus. Once set, the flow was kept constant for a complete series of test runs. Each test run occupied a time of 8 hours. The normal overflow of boiling water from the drum was allowed to run to waste except for a period during the run when the flow was measured by weighing the amount collected in a given time. The flow was 10 g.p.h. at 25 p.s.i.g. and 15 g.p.h. at 40 p.s.i.g.

After 8 hours test run the main steam valve was shut off and the boiler shut down. The water supply to the drum was stopped and the drum drained. All steam and water connections were disconnected.
and the specimen carefully removed and dismantled from its flanges. Tests on the specimen were then carried out as described in the separate sections below. The rest of the apparatus apart from the specimen was prepared for the next run by cleaning with hydrochloric acid.

Check readings were taken during each run to ensure that conditions from run to run were identical.
ADHERENCE TESTS.

INTRODUCTION

A fundamental property of scale is its ability to adhere to the heating surface which is causing its precipitation. It is this property which largely determines the difficulties experienced by operators of industrial plant, such as boilers and calorifiers, when they use a scale forming water. In past experience it has been usual, either to tolerate the scale building-up until the plant can be cleaned at periodical intervals, or, to prevent scale occurring at all by removing the scale forming salts from the water by chemical and physical treatments. In these circumstances the adherence value of the scale to its heating surface has not been of great use and consequently little work has been done to determine the factors affecting adherence. In the past few years water treatments have been developed which do not remove the scale forming salts from solution but affect the physical properties of the scale as it is formed. Because of this, it is now felt that the adhesive power of the scale is now of some importance and might lead even to a method of testing the efficiency of the newer water treatments.
The first problem was to find a method of measuring the adherence of the scale to the heating surface. Literature research indicated that no specific test for scale adhesion had been evolved but a number of methods of testing the adherence of other types of film to their substrates have been evolved.

These methods are as follows:

1. Heaven's method developed by O.S. Heaven\(^{(17)}\) for metallic films on transparent substrates in 1950. In this method a hard metal ball attached to the bottom of a vertical rod is drawn across the film being tested. The vertical loading on the ball is increased by small increments until the film is just removed from the substrate. For this method to work the film must be ductile and the substrate transparent. The method was analysed by Benjamin and Weaver\(^{(18)}\), who showed that the vertical force induced a shearing face between the film and the substrate.

2. A method of determining the adherence of paint and varnishes to a surface has been developed by the Interchemical Corporation\(^{(19)}\). Here a standard chisel is used to split the paint away from its surface the force on the chisel being a measure of adherence.
3. Buffing the film until it is removed has also been tried, but has not been found reliable due to burnishing effects. In addition results obtained are peculiar to the machine being used.

4. Beams Erezeale & Bart have developed a method in which films are deposited on a rotor which is suspended and rotated in a magnetic field at increasing speeds. At a certain speed the centrifugal force generated in the film is sufficient to cause it to part from the rotor. The expression 

\[ \frac{4 \pi^2 N^2 R^2 d}{h} = T + \frac{AR}{h} \]

where \( N \) - rotor speed, \( R \) - Rotor radius, \( d \) - density of film, \( T \) - tensile strength, \( A \) - adhesion and \( h \) - film thickness, gives the relation between the various quantities. By using circumferentially disconnected films \( T \) becomes zero and \( A \) can be determined directly.

5. Moses & Witt have induced tensile forces between a film and its substrate by using ultrasonic vibrations.

6. Belsen & Hicklen attached probes to the film and mounted the specimen and probe into a tensile test machine. They then measured the forces to remove the probe and hence arrived at the adherence directly. The method was used on sputtered metal film and the probes were soldered to the metallic film with a low melting point solder.
TENSILE TEST PROBE

SHEAR TEST PROBE

DETAILS OF ADHERENCE TEST PROBES

Scale: 0' 1' 2'

Figure 19.
DETAILS OF JIG AND SET-UP FOR TENSILE ADHERENCE TEST

Scale: 0 11"  2"  13"

Figure 20.
In the present case two methods of testing the adherence were tried. The first was a direct method, in principle similar to Belsen & Hicklen. In this method steel probes were attached to the scale surface and removed in a tensile test machine. The second method was indirect and was evolved from Heaven's method. Instead of a steel ball a tungsten carbide edge was drawn across the scale film the vertical load being increased until the scale was just removed.

**DIRECT METHOD OF ADHERENCE TESTING.**

In this method mild steel probes which had a surface area of \( \frac{1}{4} \) of a square inch were glued to the surface of the scale. The specimen with probe was fixed in a special jig and mounted in a tensile testing machine. The adherence could thus be measured directly by recording the loading in the tensile testing machine when the probe was wrenched off the specimen. Two types of probe and jig were used. One type of probe was removed from the scale in a direction perpendicular to the specimen surface whilst another type was removed in a direction parallel to the specimen surface. The first type measured the tensile adherence that is the force per unit area needed to detach the scale from the surface in a direction normal to the surface. The second type measured the shear adherence that is the force per unit area necessary to remove the
scale from the specimen in a direction parallel to the surface. The actual details of both probes and jigs are shown in figs. 19, 20, 21 together with the method of mounting in the testing machine. The probe cases were attached to the surface of the scale using "Araldite" adhesive. This particular glue is a proprietary brand of a cold curing epoxy resin. It comes in two parts which are mixed together and then applied to the surfaces to be joined. The glue gells within an hour or two but has to be left for at least twelve hours before any strength develops. In all cases the surface of each probe was given a light grinding to make sure the surface was clean and rough enough to ensure good adhesion to the scale surface. After the glue had set the complete specimen was mounted in the jigs as shown in fig. 20, if it was a tensile adherence test or alternatively as in fig. 21 if it was a shear adherence test. The testing machine used for pulling the probes off the specimens was an "Avery" tensile testing machine type No. 7106-222. In this machine load is applied to the bottom end of the specimen through a hydraulic ram, an electrically driven swashplate pump supplies the necessary oil for the ram and by using a system of bye-pass valves loads can be applied quickly or slowly as desired.
The upper end of the specimen is attached to a system of levers and weights which measure the pull. The actual pull in lbs. weight is shown by a large indicating dial fitted with a maximum reading indicator. The machine has three ranges of pull, these being 0-500, 0-1,000 and 0-2,500 lb. wt. each range being selected by pulling appropriate dead weights on the levers.

The sealed specimen mounted in its jig was loaded into the testing machine and load applied slowly until the probe broke away from the specimen. This load, which was automatically recorded by the machine, was noted. The probe did not in all cases remove an area of scale equal to its own area (a ¼ of a square inch). This was due to the glue soaking into the scale to a small extent round the probe edges. Hence a rather larger area of scale than a ¼ of a square inch was quite often removed. Where this occurred the actual area of scale was estimated and this value used in subsequent calculations.
RESULTS.

TENSILE ADHHERENCE TESTS

<table>
<thead>
<tr>
<th>Metal of Heating Surface</th>
<th>Nature of Finish (emery grade)</th>
<th>Adherence lb/sq.in.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>COPPER</strong> (electro plated)</td>
<td>Polished F</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>200</td>
</tr>
<tr>
<td></td>
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</tr>
<tr>
<td></td>
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</tr>
<tr>
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<td>496</td>
</tr>
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<td>908</td>
</tr>
<tr>
<td></td>
<td></td>
<td>480</td>
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<tr>
<td><strong>STEEL</strong> (cathodically protected)</td>
<td>Polished F</td>
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</tr>
<tr>
<td></td>
<td>1</td>
<td>168</td>
</tr>
<tr>
<td></td>
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<td>168</td>
</tr>
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</tr>
<tr>
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<td>244</td>
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<tr>
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<td></td>
<td>240</td>
</tr>
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<td></td>
<td>720</td>
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<tr>
<td><strong>CHROMIUM</strong></td>
<td>All grades</td>
<td>0 since scale flaked off.</td>
</tr>
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</table>
RESULTS.

TENSILE ADHERENCE TESTS

<table>
<thead>
<tr>
<th>Metal of Heating Surface</th>
<th>Nature of Finish (emery grade)</th>
<th>Adherence lb/sq.in.</th>
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<td>3</td>
<td>380</td>
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</table>
RESULTS.

SHEAR TEST ADHERENCE.

<table>
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<th>Metal of Heating Surface</th>
<th>Finish of Heating Surface (emery grade)</th>
<th>Adherence lb/sq.in.</th>
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</thead>
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<td>596</td>
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<td>2½</td>
<td>1340</td>
</tr>
<tr>
<td>COPPER (electro plated)</td>
<td>Polished</td>
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</tr>
<tr>
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<td>1½</td>
<td>1208</td>
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<td>2</td>
<td>756</td>
</tr>
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<td></td>
<td>2½</td>
<td>792</td>
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<td>STEEL (cathodically protected)</td>
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</tr>
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<td>228</td>
</tr>
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<td></td>
<td>2</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>2½</td>
<td>40</td>
</tr>
<tr>
<td>CHROMIUM</td>
<td>All grades</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>since scale flaked off.</td>
</tr>
</tbody>
</table>
Graphs of Shear Adherence against Surface Finish

Figure 22.
Graphs of Tensile Adherence against Surface Finish.

Figure 23.
Discussion General

The results, figures 22 and 23, whilst exhibiting a considerable degree of consistency do show some scatter and remained erratic even when the tests were repeated and the results averaged. All the other tests carried out on the scale i.e., chemical compositions, grain size etc., showed a much greater degree of consistency. Thus it would appear that the adherence values also were more consistent than indicated in the results. Hence the method of testing the adhesion was considered responsible for the erratic values obtained and it seems likely that the glue used to attach each probe to the scale surface was soaking right through the scale, which was porous, and adhering to the metal of the heating surface directly, thus artificially increasing the values obtained. Naturally this led to the testing of other types of glue based on materials other than epoxy resins but no glue could be found that was strong enough to ensure that the scale was wrenched off the heating surface. It was found that the probe always came away without removing the scale. As the epoxy resin glue was the only adhesive available that was strong enough, attempts were made to continue with its use and incorporate a barrier between the glue and the heating surface. The first attempt at this used
oil poured onto the scale the excess being wiped off, the probe then being stuck on. Unfortunately this process ruined the adhesion between probe and scale completely. Beeswax was fixed in place of the oil, the specimen being heated slightly to allow the beeswax to sink below the outer surface of the scale. Results with this were little better than with the oil.

In addition to the above cause of scatter it was felt that particularly in the shear test the weight of the specimen which as can be seen from fig. 21 was acting off the axis of pull and was causing a small torque on the probe. This small torque may have been sufficient to affect the lower values of adherence as the probe would tend to lift slightly at one edge. Despite these factors, results were obtained for the tensile adherence which were of interest even if the actual values are not dependable. From the graphs of tensile adherence against surface finish it can be seen that in the case of the plain mild steel surface the adherence values appear to be tending upwards as the finish of the specimen gets rougher, and this rise is of the order of 20%. The values however are all much higher than those obtained for the same steel surface cathodically protected from rusting where again there was only a slight tendency for adherence to rise with
roughness of surface finish of the order of 20%. This effect of the cathodic protection to interfere with the bonding between scale and heating surface shows some justification for the Cumberland process of scale prevention which was used commercially circa 1918. In this process metallic anodes were placed in the boiler primarily to prevent corrosion. In addition it was claimed that the resulting slight galvanic currents prevented the formation of hard scale.

It is considered that the lessening of the adhesion is due to the fact that the cathodic protection prevents the steel surface rusting. As no rusting occurred there was no local pitting for the scale to key into as it is formed and thus get a grip on the surface. This view is reinforced by the fact that on a plain steel surface rusting had occurred under the scale. Further some of this rust was detached with the scale when the probes were wrenched off showing how intimately the scale had grown into the surface.

The results for copper and nickel straddle those obtained for steel and thus it would seem that the actual metal, of the heating surface makes little difference to the adherence values obtained. Again there are the same indications that the values of roughness chosen did not alter the adherence much except when the surface was polished when zero values
are perhaps a little artificial as in these cases the scale had flaked off in the specimen as it was removed from the apparatus. Had it remained attached even very lightly, the procedure involved in gluing the probes onto the specimen would have raised the values obtained due to the glue soakage. These remarks also apply to chromium where the scale flaked off on all the grades of surface used.

Because the grades of emery used apparently made little difference to the adhesion it was decided that in the next series of experiments a different range of emery grades would be used and it was found that the new grades which were all finer than grade F used in the present series did not make a considerable difference to the adhesion.

So far as the shear adherence values obtained go the same general picture is shown as for the tensile adherence and the values obtained are of the same order. Greater scatter is shown due to the fact that fewer shear tests were done than tensile tests the points on the graph are not the average of several results. Fewer tests were carried out due to the fact that using the shear type probes only one could be glued to the specimen at a time whereas with the tensile tests up to six probes could be glued to the specimen at a time.
INDIRECT METHOD OF ADHERENCE TESTING.

The specimens used in these tests were similar to those used in the previous tests, but the surfaces were prepared with emery papers of grades 000...00 0 and M in addition to a polished surfaces only. However with the glass specimens breakage was frequent and only two results were obtained. The finer grades of emery produced adherence figures which were not measurable by direct means due to the factors mentioned in the discussion on the direct method. For this reason another method of measuring adhesion indirectly was evolved. This indirect method here described was inspired by Heaven's method of measuring the adherence of ductile evaporated films on transparent substrates\textsuperscript{(17)}. As scale is brittle and the heating surfaces were opaque, Heaven's method had to be considerably modified and in the modified form the theory developed by Benjamin & Weaver\textsuperscript{(18)} for the original no longer applies. In essence the present instrument consists of a tungsten carbide tip which is loaded incrementally until a horizontal force applied to the tip causes the scale just to be removed, when the carbide tip is moved horizontally. The instrument which was designed and built at Battersea College of Technology can be understood by
referring to figs. 24-25. The scale to be tested was formed on the specimen surface in the manner previously described. The specimen was mounted on the shaped supports on the basal platform. A clamp was available rigidly to secure the specimen to the basal platform. The tungsten carbide tip was mounted in a universally swivelling holder so that the angle of the leading face of the tip to its direction of motion could be set to that desired. The holder also enabled the leading edge of the tip to be set parallel to the scale surface. The tip moves in a horizontal arc of a circle parallel to the scale surface and is mounted on free end of a robust girder arm. The vertical bearing of the girder arm consists of two ball-bearings mounted in a hub. The shaft of this bearing is bolted to two horizontal angle girders, which are themselves bolted to the two upright columns of the instrument. The free end of the girder arm is constructed from a solid block of steel with a horizontal hole in which the vertical support for the carbide tip can slide. Two screws clamp the support so that the tip can swing at any pre-set radius from 6 - 12 inches. The tip holder can slide vertically in the vertical support and has fitted to its uppermost end a scale pan by means of which vertical loading can be applied to the tip. The weight of the tip
holder is counterbalanced by a coil spring and clamping collar. This collar is set to a position where the tip will just touch the scale without exerting any force on it. Horizontal pull or force can be applied to the carbide tip from a stirrup attached to the holder. A cord from the stirrup goes via a pulley to a further scale pan on which the weights necessary to provide the horizontal force are placed.

Procedure

The instrument was used in the following manner. The specimen was mounted on the instrument platform so that the carbide tip could cut squarely into the scale for a distance of travel of approximately 1/4". The angle that the leading face of the tip made with the scale was adjusted to that required, which in the case of these tests was 50°. Various angles were tried and the range of 20° - 75° have been found to give substantially the same results as 50°. Below 20° the tip tends to slide over the surface and above 75° interference between the trailing face of the tip and scale debris occurs. Also the leading edge of the tip, that is the one that touched the specimen surface, was adjusted to be parallel to the scale surface. Both these latter adjustments were made by
moving the universally swivelling tip holder. The vertical position of the tip was adjusted by varying the position of the counterbalancing spring collar on its rod until the tip was just touching the scale surface but without disturbing the scale when it was swung to and fro. This last adjustment was carried out with the vertical load scale pan empty so that any weight put into the pan after setting the instrument up was the actual vertical force applied to the scale.

After the instrument was set up as above the vertical load was applied in small increments of a few ounces at a time by loading weights in the scale pan. After each small increment a horizontal pull was applied causing the tip to move over the scale. At a definite vertical load it was found that the tip instead of moving over the scale cut into and removed it from the underlying metal surface when the horizontal pull was applied. The specimen was then moved so that a fresh surface of scale was presented to the tip. With the same vertical load on the tip weights were put into the horizontal pull scale pan until the tip just moved stripping the scale from the metal surface. The two forces namely the vertical load and the horizontal pull were then
noted together with details of the type of surface (nickel, copper, smooth, rough etc.) on which the scale was adhering.

Mechanism.

As mentioned the theory of Benjamin and Weaver is not applicable in this case. The general mechanism of the action of the tip is probably similar to that of a cutting tool operating on a brittle material such as cast iron or marble. The theory of the cutting action of tools when the work material deforms plastically has been investigated by Merchant and others and in general seems to be fairly well understood, although the mechanism of plastic flow varies greatly with different materials. No such general theory of cutting exists for brittle materials and in fact any general theory is probably impossible as the mechanism of brittle fracture varies too widely to be covered by any one theory. For example, some materials crumble during machining, some cleave and others flow slightly before fracture. However, it may be possible to devise approximate treatments to fit special cases and the following analysis is offered as a possible explanation of the mechanism involved between tip and the scale. Assuming this analysis to be substantially correct then the
adherence figure obtained will be a function of the shear adherence of the film to the substrate. This adherence is not necessarily the same as the adherence normal to the surface (tensile adherence). It is felt that the shear adherence is an extremely useful value as in practical cases of scale formation the naturally occurring forces available to remove the scale are those due to the action of differential coefficient of expansion and water circulation along the surface both of which are parallel to the surface. Two types of mechanism were seen to take place and which mechanism occurs in any particular case is believed to depend upon whether the adherence of the film to the substrate is greater than or less than the mechanical strength of the film itself.

The first type of mechanism occurs where the adherence of the scale film to the substrate is greater than the crushing strength of the film. In this case, as the test proceeds the tip tends to ride over the layer of scale film next to the substrate and crush the upper layers of the film to a powder until enough vertical load is applied to keep the tip in contact with the substrate. When this happens the complete film will be removed and the horizontal force will be a measure of the crushing strength of
a column of scale and also of the adherence of the innermost layer of the scale film to the substrate. In addition there will also be a friction term to allow for the friction between the tip and the substrate. Referring to fig. 26.

\[ V = \text{vertical load (oz.)} \]

\[ H = \text{Horizontal pull (oz.)} \]

\[ N = \text{reaction of scale on tip (oz.)} \]

\[ A = \text{adherence of scale to substrate (oz.)} \]

\[ F = \text{friction force arising between tip and substrate (oz.)} \]

\[ V_T = \text{vertical reaction of tip on substrate (oz.)} \]

The second mechanism occurs when the adherence is less than the crushing strength of the film. In this case the film tends to be detached from the substrate in complete pieces or chips without being crushed to a powder. Where the adherence is so low as to be almost non-existent whole areas of scale slide off the substrate without any breakage of the film. This occurred on specially prepared substrates where the adherence was extremely low due to the high polish and other factors. In most cases however the adherence was sufficient to retain the film in position except for the area in the path of the tip where a series of plate-like chips were removed. In this case the horizontal pull is felt
to be a measure of the adherence plus a shear force term necessary to detach each chip from the surrounding film. Also a friction term will be necessary to allow for the contact of the tip with the substrate. See figure 27.

\[ V = \text{vertical load (oz.)} \]
\[ H = \text{horizontal pull (oz.)} \]
\[ N_1 = \text{reaction of chip on tip (oz.)} \]
\[ F = \text{friction arising between tip and substrate (oz.)} \]
\[ V_1 = \text{vertical reaction of tip on substrate (oz.)} \]
\[ A_1 = \text{shear adherence of scale to substrate (oz.)} \]

In both the above cases it can be seen that the horizontal pull does not measure the adherence only. As in practice scale chips and powder are formed, both the above extreme cases are taken into account in the following equation:

\[ H = F + A' + C + S \quad \ldots \ldots \ldots \ldots \quad (1) \]

where \( H \) - horizontal pull applied to carbide tip (oz.)
\( F \) - frictional force arising between tip and substrate (oz.).
\( A' \) - the force due to the shear adherence which is equal to the shear adherence of the scale (lb/in.) multiplied by the width of the tip (in.).
\( C = N \cos \phi \) - the crushing force to break up the column of scale in the way of the tip. This force is equal to the crushing strength
of the scale \((\text{lb./in}^2)\) multiplied by the product of the width of the tip (in.) times the thickness of the scale (in.).

\[ S = N_1 \cos \theta \]  

the shear force to detach a chip from its surroundings this force is equal to the shear strength of the scale \((\text{lb./in}^2)\) multiplied by the product of the thickness of the scale times twice the length of the chip.

Of these terms, \(F\) the friction force, \(G\) and \(S\) the crushing and shear strength factors of the scale, have been neglected in the graphs of the results figures 28 to 35 for the following reasons:-

The friction force term \(F\) is small due to the method of taking readings. In the method used the vertical load \(V\) is increased in small increments until the scale is just removed when the carbide tip is moved horizontally. Under these conditions little vertical force exists between the substrate and tip, and is therefore ignored in the results.

The forces \(G\) and \(S\) have been neglected as in all cases the scale was very thin and the forces needed to crush the scale and shear the chips from the surrounding layer, were therefore small. In any case it would be expected that, as the type of scale
and thickness was sensibly constant throughout the tests, these forces would remain constant and the shape of the curves obtained would have been the same in both cases.

**RESULTS.**

The experimental results are as laid out in the following tables. These results are also shown as graphs in figs. 28 to 35.
<table>
<thead>
<tr>
<th>Metal of Heating Surface</th>
<th>Temperature of Heating Surface</th>
<th>Surface Finish (emery grade)</th>
<th>Adherence lb. wt./inch.</th>
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## RESULTS

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<tr>
<th>Metal of Heating Surface</th>
<th>Temperature of Heating Surface</th>
<th>Surface Finish (emery grade)</th>
<th>Adherence lb.wt./inch.</th>
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Graphs of Adherence against Surface Finish for Copper.

Figure 28
Graphs of Adherence against Surface Finish for Copper

Surface Finish (micro-inches CLA)
Graphs of Adherence against Surface Finish for Nickel

Figure 30.
Graphs of Adherence against Surface Finish for Nickel.

Figure 31
Graphs of Adherence against Surface Finish for Steel.
Graphs of Adherence against Surface Finish for Steel.

Figure 33
Adherence of Scale to a Glass Heating Surface.

Figure 35.
DISCUSSION.

The effects on adhesion of changes in surface finish and surface heating temperature are clearly seen in the graphs figures 28 to 35.

The results for copper show a uniform rise in adherence for all the temperatures used. The adherence rose from 23 lb/inch on the polished band to 55 lb/inch on the M grade emery band at the highest surface temperature. At the lower surface temperatures there is a significant fall in adhesion for any given roughness. It is considered that the values obtained for the polished band in the case of the 267°F heating surface and for the polished and 000 emery bands at the lowest surface temperature are possibly incorrect and should have been higher. This is because trouble was found in obtaining these values as the scale flaked off these bands to a large extent. This flaking probably occurred due to contraction of the specimen surface relative to the scale as the specimen cooled together with a contraction as the steam pressure in the cylinder was let down. Where the adherence was already low these factors always seemed sufficient to cause the scale to flake off. The suggested true values for these adherence figures can be read from
the curves in figure 28 by extrapolating back the flat portions of the curves (shown dotted) thus making the shape of the curves similar to that for the higher heating surface temperature. The rise of adhesion with surface temperature is quite marked and it is suggested that this rise occurs due to the fact that at the higher surface temperatures the temperature of the film of water next to the heating surface is higher and more precipitation of scale crystals will occur next to and in contact with the surface. Under these conditions more of the mechanical interlocking points in the surface will be occupied by scale and adhesion will rise. The rise in adherence with increasing roughness is almost certainly due to the increase in the number of mechanical interlocks available for the scale to grip on the rougher surfaces. The evidence for the existence of these keying points is quite extensive and is discussed at length in the section entitled "The Mechanism of Adherent Action", page 98.

Figure 29 shows the adherence values plotted against the C.L.A. (centre line average) values of the various emery grades. The same general form of curve is obtained.

The curves obtained for nickel are shown in figures 30 and 31. A tendency for the curves to be similar
to those of copper is clearly seen except that at 287°F. where zero adherence values were consistently obtained over all grades of emery. Apart from this values are somewhat lower at all points and it is felt this is due to the fact that less corrosion occurred on the nickel surface than on the copper. Corrosive activity leads to pitting of the surface and thus provides more keying points.

The consistent zero values obtained at the highest heating surface temperature are somewhat puzzling. It seems possible that the surface may have been contaminated although every precaution was taken against this. In addition the higher temperature may have caused greater contraction during cooling leading to rupture of the bonds between scale and substrate.

The results for steel are quite different to those of nickel and copper as can be seen by referring to the graphs 32 and 33. Here the adhesion stayed sensibly constant over all grades of emery tried but was slightly less on the polished section. There seems little doubt that the increase of adherence on the finer grades of emery was due to the fact that the steel specimen became quite rusty during the eight hours test run in boiling water. The rust without doubt was providing extra keying points for the scale to lock into.
This was clearly seen when the scale chip was removed from the specimen when it was found that rust had penetrated into the scale giving the underside of the scale a speckled appearance of brown rust spots on the off-white background of the scale itself. The appearance of the underside of the scale and of the steel specimen showed uniform rusting over the whole part that had been prepared with emery and it is of interest to note that adherence values rose to a nearly uniform level over the whole of this part of the specimen whereas it might be expected that the whole range of adherence values would be increased uniformly over the various grades of emery prepared surface. This would give a graph of adherence against surface finish with a slope similar to the copper and nickel but with all the ordinates uniformly elevated. That this did not occur shows that on the finer grades of emery the rusting was adding to the number of keying points. On the roughened grade (M) however, the rusting was destroying the existing keying points that resulted from the action of preparing the surface and replacing them with new keying points provided by local pitting on the same magnitude as the existing ones were being destroyed. The net result was to
provide a surface uniform over the whole steel surface so far as adherence was concerned. The polished band did not show such big values of adherence and neither had it rusted to the same extent as the emery prepared bands. This was probably due to a mechanical protection given to the surface by a microscopic film of buffing compound used for polishing.

**Chromium Surfaces.**

The adherence values obtained here were very low indeed reaching a maximum of 5½ lb weight/inch. This value was so low that the scale could be easily removed by scratching with a finger nail. The scale had in fact flaked off to a large extent. The values obtained were uniform over the whole surface of the specimen excepting where it had flaked as it was found impossible to get a surface texture comparable to those on nickel, copper and steel. This was due to the extreme hardness of the chromium plate, being 9 on Moh's scale of hardness which was comparable to the hardness of the emery grains themselves. The number of keying points produced by the action of rubbing the surface with the emery paper was therefore very small and hence the adherence from this cause also small. In addition, little corrosive action takes place when chromium is immersed in boiling water,
so there is no adhesion arising from the presence of corrosion pits.

Glass Surface.

The adhesion of scale on glass surface was very small indeed for such scale films as could be deposited. Had the same thickness of film been obtainable results might have been higher, but due to the low thermal conductivity of the glass even twice the normal time of run (8 hours) was insufficient to produce more than $0.04 \times 10^{-3}$ inch of scale compared to the normal thickness of up to $5 \times 10^{-3}$ inch produced on metal surfaces in 8 hours run. The amount produced appeared only as a transparent bloom over the glass surface. In view of the difficulty in producing a reasonable layer of scale in the time available little was done to produce different surface textures. At the higher test temperature the greater steam pressure caused the specimens to blow up. In view of this trouble, vitreous enamel on a steel cylinder was used as a surface. Vitreous enamel is a type of glass and it was thought this might be of interest. However, when the surface was to be prepared it was found that the glazed outer layer was very thin and the material under the glass was quite friable and the emery did not produce at all the texture required. Glass and
vitreous enamel therefore were not really successful experimental subjects in this series of tests.

These tests indicate that the adherence of this particular type of calcareous scale (almost pure calcite) is very dependent on the texture of the heating surface, being greater with increase in roughness. The maximum values of adherence for all types of surface material were of the order of 70-80 lbs. wt/in. which is surprising considering the vastly different nature of say steel and nickel surface. This maximum values is probably regulated by the strength of the scale itself.

**THE MECHANISM OF ADHERENT ACTION.**

The atoms of a solid can be held together by four types of bond.

1. Ionic, in which the atoms, having unlike charges are held together by electrostatic forces.
2. Molecular, in which molecules are held together by Van der Waals forces.
3. Homopolar in which neutral atoms share electrons.
4. Metallic in which metal ions are surrounded by a cloud of freely moving electron.

No matter what kind of force holds the material
together there is a field of force around each ion, atom or molecule. At the surface of the solid these force fields reach out into space. If these forces attract atoms of the same material they are called cohesive forces. If they attract atoms of a different material they are called adhesive forces and if they attract atoms of a gas they are called adsorptive forces.

In this discussion only adhesive forces are considered. In addition to adhesive bonds arising from the four types of bond stated above, they can also arise from mechanical interlocking of the particles being deposited, into the surface of the solid where the texture of this surface is suitable as also must be the method of nucleation and growth of the particles being deposited.

Thus in the case of scale there would seem to be only four hypothetical ways in which it can adhere to the heat exchange surface. These are as follows:

(a) Mechanical interlocking in which the scale is deposited in intimate contact with the surface deformities of the heat exchange surface. The scale thus fills up the microscopic grooves and craters and surrounds the projections of the surface. If any of the grooves or craters are overhung or if any of the projections have rough sides into which the scale can grow then keying points arise from which it is impossible to
remove the scale without breaking it or the heating surface. Where this occurs the adhesive bonds are called mechanical interlocking forces.

(b) Adhesion in which the crystallographic structure of the metallic heating surface is of the size and type to match one of the crystallographic planes in the scale crystal. Deposition thus takes place in such a way that the adhesive forces are due to the atomic forces reaching out from the heating surface. This is known as epitaxial growth and is very common in electrodeposition.

(c) Corrosive action of the heating surface, caused by chemicals and gases in the water and aided by the heat present may produce corrosion craters and pits in the surface. These may be suitable keying points for mechanical interlocking to occur.

(d) Corrosive action in which the surface corrodes and a layer of corrosion product may form which is suitable for epitaxial growth of the scale layer.

There can be little doubt that the adhesive bonds in these experiments arose from cases (a) and (c) above. For nickel and copper where little corrosion was going on primary interlocking of the scale to the heating surface was occurring. For steel a secondary interlocking of the scale into the rusty surface was also occurring.

The reasons leading to this belief are as follows:-

(i) Optical examination of the heating surface under polarised light after the scale had been removed
always revealed a small amount of scale embedded in the surface. This scale was often in the form of lines parallel to the emery scratches. Examples of this effect are shown in figures 36 and 37. The scale had become so well keyed to the surface that it had resisted all the forces involved in measuring the adherence and had broken out of the bulk of the scale rather than become detached from the heating surface. This material was found to be embedded in the scratches caused by the emery. The photograph of the glass surface in figure 37 shows what occurs when no scratches are present and the surface is smooth. It can be clearly seen that the lines of crystals are in the same direction as the movement of the carbide tip; there was no tendency for lines of crystals to form at right angles to the line of motion of the tip. To account for the keying action, consider one of the scratches and its method of formation. Initially the scratch will be formed by just one grain of emery being drawn across the surface and the sectional shape of the scratch could well be a groove with little in the way of keying points. However, the original grain of emery is just one of many thousands in the sheet of emery paper and after it has passed many other grains will pass along or near the scratch, some of them will form other scratches near to the first one, possible sharp ridges being formed.
Photographs of Scale in Surface Scratches.

Figure 36
Arrow indicates direction of carbide tip

Photographs of Scale in Surface Scratches.

Figure 37
between scratches. Other grains of emery will tend to bend these ridges to one side or the other forming an overhang into which the scale can form and obtain its adhesion to the surface. Additionally to this type of keying point single projections will be formed on the surface by the gouging action of some of the emery grains, the actual grain of emery digging into the surface and ploughing up a projection, the emery then breaking, leaving the projection to serve as a keying point. Other asperities will be made by the action of emery grains detached from the paper rolling between paper and heating surface. A few of the emery grains will be lodged into the surface itself and may themselves cause keying points. Attempts were made to verify this hypothesis directly by examining the metal surface of the various specimens using the optical microscope – these attempts were unsuccessful due to smallness of the scratches and the lack of depth of focus of the microscope. Resort was then made to examination by electron microscope. In this method the surface was too thick for the electron beam and a slightly flexible plastic replica of the surface was made in "Bexfilm". This flexible plastic was used so that on stripping from the heating surface the replica would be able to detach itself from the keying points.
Electron microphotographs of specimen surfaces.

Figure 38.

Copper (grade M).
Magnification X 4,000.

Copper (grade 0).

Nickel (grade 000).

Copper (grade 00).
Nickel (grade M).

Magnification X 4,000.

Steel (grade 00).

Steel (grade 000).

Electron microphotographs of specimen surfaces.

Figure 39.
Steel (grade 0)

Copper (grade 000)

Magnification X 4,000.

Electron microphotographs of specimen surfaces.

Figure 40.
without breaking. The "Bexfilm" was then placed in a vacuum chamber and a carbon film was evaporated onto it. The "Bexfilm" was then dissolved away leaving the thin carbon replica of the original heating surface. The carbon replicas were mounted and examined using the Akashi Model TRS-50E1 electron microscope. The magnification, approximately 4,000, was sufficient to show all types of keying point referred to above.

Samples of the microphotographs are shown in figures 38, 39 and 40. These keying points were in themselves sufficient to cause adhesion in the cases of copper and nickel. For steel, however, rusting occurred in the heating surface. The process of rusting caused the surface to become irregular and covered with corrosion pits that formed keying points in addition to those arising from the process of emerying. That the scale adhered to the rust was evident because when the scale was detached from the steel heating surface particles of rust were found embedded in it.

Examination of replicas of the underside of the scale using the electron microscope, approximately 10,000 magnification, revealed crystals of a size comparable to the size of the scratch marks - see figure 41 - so there appears to be little doubt that the scale was able to form in and around the keying points so that no bridging occurred. Whilst the grains are difficult to measure, an estimated size is of the order of
Nickel (grade 00).

Copper (grade M).

Magnification X 10,000.

Nickel (grade 0).

Copper (polished).

Electron microphotographs of undersides of scale chips.

Figure 41.
500Å° and this is small enough to account for the somewhat broad background rings in the Debye-Scherrer diffraction patterns shown in figures 63 and 64. It would appear from the above that all the conditions necessary for mechanical interlocking were present and whilst there is a strong support for this theory from the above evidence it was realised that adhesion due to atomic forces as in (b) above could account for the results under certain circumstances.

Now it can be seen quite readily that if atomic scale forces as occur in epitaxy were responsible for the adhesion then the adherence per unit area would be the same for any given metal. Hence under these conditions of adhesion then the adherence per unit area would be directly proportional to the increase in surface area of the specimen caused by roughening its surface (emery). To check the increase in surface area some experimental work was done. Profiles of the various surfaces were obtained using a "Talysurf" texture estimating instrument. The main function of this instrument is to measure the C.L.A. value of the surface. The C.L.A. value is defined by British Standard 1134:1961 as the "Numerical assessment of the average height of the irregularities constituting surface texture" and this value does not give an estimate of the increase in surface area. However, the machine gives in addition to this value a graphical record of the surface profile from which the increase in area can be worked
"Talysurf profile records for nickel surfaces."
"Tolysurf" profile records for copper surfaces.
Actual "Talysurf" profile record.

Diagram showing true surface profile of copper surface prepared with M grade emery.

Figure 45.
out. These graphical profiles were obtained for the copper, nickel and steel surfaces dealt with and are shown in figures 42, 43 and 44. It must be pointed out that these profiles are not to scale since the vertical magnification varies from 20,000 in the case of the polished surface to 2,000 for the grade M emery paper whilst the horizontal magnification was always 100.

A true profile was drawn for the roughest surface of all, namely copper finished with M grade emery using the "Talysurf" graph as a basis and this is shown in figure 45. From figure 45 it can at once be seen that the increase in surface area compared to the polished surface is only of the order of a few per cent (5%). All the other textures used were smoother than this one therefore the increase in area over the polished specimens was even less than the one measured. Were the adherence due to the atomic forces rather than the mechanical interlocking forces then the adherence should have stayed constant within a few per cent over every grade of emery surface tried. In fact the adherence was rising by a factor of some 3-4 times for nickel and copper, even ignoring the polished surface values, which may be erroneous for reasons previously explained. Even for steel the rise in adherence was much greater than the rise in surface area. It might be argued that the
"Talysurf" which has a stylus radius 0.0001 inch was not recording increases in roughness due to submicroscopic changes in the surface texture, these changes leading to increases in surface area comparable to the increases in adherence.

There is no reason to believe this argument because with the emery prepared surfaces the actual grains of emery would lead to the same submicroscopic texture no matter what their size and it was the size that determined the microscopic texture seen in the "Talysurf" profile. In passing, it is worth mentioning that the nature of the "Talysurf" instrument prevents the surface profile record showing the overhangs so necessary for mechanical interlocking. This is because the stylus of the instrument can only move in a direction dictated by the mechanics of the instrument - one direction of the stylus head parallel to the surface together with perpendicular movement relative to the stylus head. Thus any overhangs will be shown as vertical lines on the profile. There are plenty of these vertical traces on the profiles taken.

A further reason against the epitaxial theory arises from the work described in a Part III where conditions were far more favourable to this form of growth than in the present section. Scale was deposited by thermal action into prepared flakes of calcite. Even under
these conditions growth with a preferred orientation occurred only for a distance of about $2 \times 10^{-3}$ in from the surface of the calcite crystal. This being so, it is unlikely that epitaxy would occur on metal surfaces of such a different nature to the calcite structure of the scale.
CRYSTAL SIZE TESTS.

In industrial practice scale is deposited with various characteristics according to the conditions of formation (i.e. temperature and circulation etc). One of these characteristics is the size of the crystals making up the aggregate of which scale is composed. It was felt that the crystal size might have an important influence on the physical properties of the scale, in particular the cohesion of crystals to each other and the adhesion of the crystals to surfaces of various roughnesses. In view of this it was decided to make measurements of crystal size in the scale samples obtained in the present experiments. Hence any effect the differing conditions in the experiments had on crystal size would be brought to light and could be correlated with the other results.

Several methods are available for the measurement of crystal size, i.e. visual comparison against a standard breaking and sieving etc., but it was decided to use an X-ray method for the following reasons:

(a) The sample need not be broken up, thus preventing an alteration in the size after formation.

(b) The ease of the X-ray method which calls for only a simple procedure to produce a picture, which can be compared directly with a standard.

(c) The fact that the structure of the crystalline
material could be identified at the same time as crystal size determination from the photographs.

The basis of this method depends upon the fact that crystal size affects the degree of spottiness and also the size of the spots obtained in the Debye-Sherrer diffraction rings on the film when the scale specimen is X-rayed.

The size of each spot, called the \( \text{image length}^{(20a)} \) depends upon the divergence of the primary X-ray beam, the size and shape of the focal spot on the target of X-ray beam. On the other hand the degree of spottiness, that is the number of spots in a ring, depends on the number of grains in the volume of specimen irradiated by the X-ray beam amongst other factors. Neither of these two methods permits easy absolute measurements but the latter method can easily be used in practice by adopting a procedure involving comparison with the results obtained from calibration specimens and this was the method used here. Calibrated specimens were made up by crushing calcite crystal and sieving the resultant powder through a series of progressively finer sieves. The sieves were in accordance with British Standard 410:1943 table 2 (fine wire mesh special test sieves). Samples of calcite caught between each pair of mesh sieves were made into flake specimens by folding the powder between
two sheets of cellophane glued around the edges. These standard specimens were mounted in a "Unicam" cylindrical camera and X-ray photos taken using copper radiation with a Ni. filter and $2^{10}_0$ oscillation. Powder from each sample was also examined through the microscope and photographed so that the size of the particles in each sample might be determined absolutely rather than depending solely on the sizes of the apertures in the sieves. The resultant X-ray photos and micro-photographs are shown in figures 46 - 52. The size of the crystals in the micro-photographs was measured by direct comparison with a scale photographed under the same conditions (magnification) as the samples in order to obviate any error in the stated magnification of the microscope.

**TRUE CRYSTAL SIZE OF SIEVED SAMPLES.**

Magnification (true of final photos.)

- $x 26.5$ for Figures 49, 50, 51 and 52.
- $x 107.5$ for Figures 46, 47, and 48.
### TABLE 1.

<table>
<thead>
<tr>
<th>Mesh No. B.S.</th>
<th>Length on Photo</th>
<th>Width on Photo</th>
<th>True Length Microns</th>
<th>True Width Microns</th>
<th>Average Part. Size Microns</th>
<th>Length to Breadth Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>4.1</td>
<td>2.0</td>
<td>38.1</td>
<td>18.6</td>
<td>28.4</td>
<td>2.05</td>
</tr>
<tr>
<td>350 300</td>
<td>7.86</td>
<td>3.65</td>
<td>73.2</td>
<td>33.9</td>
<td>53.5</td>
<td>2.16</td>
</tr>
<tr>
<td>300 240</td>
<td>9.8</td>
<td>6.6</td>
<td>91.2</td>
<td>61.4</td>
<td>76.3</td>
<td>1.48</td>
</tr>
<tr>
<td>240 200</td>
<td>2.57</td>
<td>1.85</td>
<td>97.0</td>
<td>69.3</td>
<td>83.4</td>
<td>1.39</td>
</tr>
<tr>
<td>200 150</td>
<td>3.93</td>
<td>2.85</td>
<td>148.0</td>
<td>107.5</td>
<td>127.8</td>
<td>1.38</td>
</tr>
<tr>
<td>150 100</td>
<td>5.6</td>
<td>3.78</td>
<td>211.0</td>
<td>142.5</td>
<td>176.8</td>
<td>1.49</td>
</tr>
<tr>
<td>100 72</td>
<td>10.8</td>
<td>5.7</td>
<td>408.0</td>
<td>215.0</td>
<td>311.5</td>
<td>1.89</td>
</tr>
</tbody>
</table>
X-ray diffraction pattern from particles below.

Calcite particles after passing through a No. 350 mesh sieve. Magnification - X 107.5.

Grain Size Calibration Pictures.

Figure 46.
X-ray diffraction pattern from particles below.

Calcite particles retained on 350 mesh after passing 300 mesh.
Magnification = X 107.5

Grain Size Calibration Pictures.

Figure 4-7.
X-ray diffraction pattern from particles below.

Calcite particles retained on 300 mesh after passing 240 mesh. Magnification = X 107.5.

Grain Size Calibration Pictures.

Figure 48.
X-ray diffraction pattern from particles below.

Grain particles after passing 240 mesh and retained on 200 mesh. Magnification X 26.5.

Grain Size Calibration Pictures.
X-ray diffraction pattern from particles below.

Calcite particles retained on 200 mesh after passing 150 mesh. Magnification = X 26.5.

Grain Size Calibration Pictures.

Figure 50.
X-ray diffraction pattern from particles below.

Calcite particles retained on 150 mesh after passing 100 mesh.
Magnification = X 26.5.

Grain Size Calibration Pictures.

Figure 60.
X-ray diffraction pattern from particles below.

Calcite particles retained on 100 mesh after passing 72 mesh. Magnification = X 26.5.

Grain Size Calibration Pictures.
RESULTS

Variation of Crystal Size over each Specimen.

Initial runs with varying surface textures were found to have no variation of crystal size over the whole surface. This was determined by taking X-ray diffraction pictures of samples from each different surface texture. This being the case only one scale sample was X-rayed from each specimen in all subsequent runs. A rough check to see if the crystal size altered over the specimen surface in subsequent runs was carried out visually using the optical microscope. No indication of any variation in crystal size was ever seen.

The following table, figure 53, gives the crystal size obtained from one typical scale sample taken from each specimen cylinder.

Examples of the X-ray diffraction pictures taken from some of the scale specimens are shown in figures 63 and 64.
<table>
<thead>
<tr>
<th>Material of Heating Surfaces</th>
<th>Temperature of Heating Surface °F</th>
<th>Grain size microns</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Individual</td>
</tr>
<tr>
<td>STEEL</td>
<td>230</td>
<td>76.3</td>
</tr>
<tr>
<td></td>
<td>267</td>
<td>53.5</td>
</tr>
<tr>
<td></td>
<td>287</td>
<td>76.3</td>
</tr>
<tr>
<td>NICKEL</td>
<td>267</td>
<td>53.5</td>
</tr>
<tr>
<td></td>
<td>287</td>
<td>76.3</td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>53.5</td>
</tr>
<tr>
<td>COPPER</td>
<td>267</td>
<td>53.5</td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>76.3</td>
</tr>
<tr>
<td></td>
<td>287</td>
<td>53.5</td>
</tr>
<tr>
<td>CHROMIUM</td>
<td>230</td>
<td>83.4</td>
</tr>
<tr>
<td></td>
<td>287</td>
<td>28.0</td>
</tr>
<tr>
<td></td>
<td>267</td>
<td>76.3</td>
</tr>
<tr>
<td>GLASS</td>
<td>267</td>
<td>76.3</td>
</tr>
<tr>
<td></td>
<td>287</td>
<td>53.5</td>
</tr>
</tbody>
</table>

Figure 53.
DISCUSSION

The calibration specimens obtained by the sieving show very close agreement as regards their width with the mesh size of the sieves. This can be seen from the following table.

<table>
<thead>
<tr>
<th>Mesh No. of sieve that particle passed through.</th>
<th>Nominal aperture of sieve mesh.</th>
<th>Width of crystal (average).</th>
</tr>
</thead>
<tbody>
<tr>
<td>72</td>
<td>211</td>
<td>214</td>
</tr>
<tr>
<td>100</td>
<td>152</td>
<td>142</td>
</tr>
<tr>
<td>150</td>
<td>104</td>
<td>107</td>
</tr>
<tr>
<td>200</td>
<td>76</td>
<td>70</td>
</tr>
<tr>
<td>240</td>
<td>64</td>
<td>61</td>
</tr>
<tr>
<td>300</td>
<td>53</td>
<td>34</td>
</tr>
<tr>
<td>350</td>
<td>44</td>
<td>19</td>
</tr>
</tbody>
</table>

The figure of 19 obtained as the average width of the crystal passing through the finest mesh (350) is naturally smaller than the nominal mesh size because this sample contained all the sizes of crystals less than the mesh width. From the dimensions given for the calibration crystals in Table I it will be seen that the length to breadth ratio varies from a minimum 1.38 to 1 to a maximum of 2.05:1. The length to breadth ratio of the crystals in the scale as discovered and discussed in the microradiography section varied.
X-ray diffraction pattern of scale from a steel heating surface.

X-ray diffraction picture of scale from a copper heating surface.

Figure 63.
X-ray diffraction pattern from scale formed on a chromium heating surface.

X-ray diffraction pattern of scale from nickel heating surface.

Figure 64.
to approximately 1:1 according to the material of the heating surface. Ideally the shape of the crystals in the calibration specimens should have been identical to that of the crystals in the scale. That this was not so must introduce an error into the results. The error will not be as great as might be expected when it is realised that the number of spots in the Debye-Sherrer rings of the diffraction pattern is given by

\[ N = \frac{1}{2} \left( \frac{A t}{v} \right) P \cos \theta (\alpha' + \alpha) \]

where:
- \( A \) = cross-sectional area of beam.
- \( t \) = effective penetration of beam.
- \( v \) = volume of crystal.
- \( P \) = multiplicity factor.
- \( \alpha' \) = divergence of beam.
- \( \alpha \) = angle over which crystal reflects.

The two sets of conditions for the calibration and the scale X-rays were identical so that in this case the variable causing the spottiness of the ring to alter was the reciprocal of the volume of the crystals. Thus the results obtained indicated that the volume of crystals in the calibration and scale specimens was comparable when the spottiness of the Debye-Sherrer ring was comparable. This is assuming that the overall density of the two specimens was the same. Hence it would be quite possible to work out the size of any given crystal in the scale if the shape
of the given crystal was known from optical or radiographic examination. This was not done as it was felt errors would be introduced in calculating the volumes of the calibration crystals which were not completely regular in shape.

Regarding the results obtained for the steel specimens the crystal size stayed fairly constant for all tests done only varying by one grade in the calibration scale. It would appear then that the temperatures used of the heating surface were not sufficiently different to alter the crystal size appreciably.

The results obtained for nickel heating surfaces covered the same range of crystal sizes as for steel, in fact they were the same with the exception of the 230°F result where the grain size was smaller than with the steel.

The results obtained from the copper surfaces again covered the same range of grain sizes as for steel and nickel.

The chromium surface results showed the greatest scatter of all the different surfaces. There is certainly a tendency here for the crystal size to become smaller as the heating surface temperature rose.

The results from the glass surfaces show a difference of only one grade of the calibration sample.
It would seem from these results that overall the change in heating surface ranging from steel which easily corroded, to copper which tarnished slightly, to nickel which tarnished rather less than copper, to chromium which suffered little, if any, corrosion to glass which is sensibly inert, produced little real change in crystal size. Also the variation in surface texture over each surface was found to have little effect. The average crystal size for each surface — see last column of the Table shown in figure 53 — varied little and it is fairly clear that the conditions under which all these experiments were done were not varied enough to produce any great crystal size change. That this was so is a clear demonstration of the huge variation in heat exchange conditions which must occur over industrial apparatus where, in the writer's experience, crystal sizes from several millimeters measured directly down to $10^{-5}$ m.m. as estimated from X-ray diffraction patterns are found. The reasons for this change in crystal size must obviously be due to the factors other than the material of the heating surface or the texture. These other factors may well arise from difference in chemical composition of water, the temperature of heating surface and whether ebullition is taking place or not, the circulation of water to the heating surface and perhaps time where other conditions are such
as to encourage growth of existing crystals rather than formation of new crystals.
CHEMICAL COMPOSITION & CRYSTALLOGRAPHIC STRUCTURE.

Samples of the scale produced on the various heating surfaces and under the various conditions were collected and chemically analysed in a commercial laboratory.

The samples yielded the analyses as given in the table on page 139.

These results are the analyses as received and the probable constitution as follows, this being worked out from the molecular weights for the analysis for chromium at 267°F.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃</td>
<td>95.9%</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>1.7%</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>1.0%</td>
</tr>
<tr>
<td>Mg(PO₄)₂</td>
<td>1.4%</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>Trace</td>
</tr>
</tbody>
</table>

The above analysis is typical since very little variation occurred when the heating surface was altered, in fact the variations were within the experimental limits of the analytical procedures used except for the iron heating surfaces when approximately 0.5% of rust was detected.
<table>
<thead>
<tr>
<th>Temp. of Heating Surface, °F</th>
<th>Material of Heating Surface</th>
<th>Loss on Ignition</th>
<th>Iron as Fe$_2$O$_3$</th>
<th>Calcium as CaO</th>
<th>Magnes. as MgO</th>
<th>Sulphate as SO$_3$</th>
<th>Phosphate as P$_2$O$_5$</th>
<th>Unestimated.</th>
</tr>
</thead>
<tbody>
<tr>
<td>267</td>
<td>Copper</td>
<td>42.7</td>
<td>trace</td>
<td>54.2</td>
<td>0.8</td>
<td>1.9</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>287</td>
<td>Copper</td>
<td>42.2</td>
<td>trace</td>
<td>54.2</td>
<td>0.8</td>
<td>1.9</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>230</td>
<td>Copper</td>
<td>42.5</td>
<td>trace</td>
<td>54.0</td>
<td>0.8</td>
<td>1.8</td>
<td>0.6</td>
<td>0.3</td>
</tr>
<tr>
<td>267</td>
<td>Nickel</td>
<td>42.6</td>
<td>trace</td>
<td>54.1</td>
<td>0.8</td>
<td>1.9</td>
<td>0.6</td>
<td>None</td>
</tr>
<tr>
<td>287</td>
<td>Nickel</td>
<td>42.2</td>
<td>trace</td>
<td>54.5</td>
<td>0.7</td>
<td>1.9</td>
<td>0.6</td>
<td>0.1</td>
</tr>
<tr>
<td>230</td>
<td>Nickel</td>
<td>42.3</td>
<td>trace</td>
<td>54.1</td>
<td>0.8</td>
<td>1.8</td>
<td>0.7</td>
<td>0.3</td>
</tr>
<tr>
<td>267</td>
<td>Steel</td>
<td>42.8</td>
<td>0.5</td>
<td>53.6</td>
<td>0.8</td>
<td>1.5</td>
<td>0.6</td>
<td>0.2</td>
</tr>
<tr>
<td>287</td>
<td>Steel</td>
<td>42.5</td>
<td>0.8</td>
<td>54.6</td>
<td>0.8</td>
<td>1.3</td>
<td>0.6</td>
<td>0.1</td>
</tr>
<tr>
<td>230</td>
<td>Steel</td>
<td>42.2</td>
<td>0.6</td>
<td>53.8</td>
<td>0.7</td>
<td>1.9</td>
<td>0.5</td>
<td>0.3</td>
</tr>
<tr>
<td>Chromium at 267</td>
<td></td>
<td>42.2</td>
<td>trace</td>
<td>54.4</td>
<td>0.8</td>
<td>1.7</td>
<td>0.8</td>
<td>0.1</td>
</tr>
<tr>
<td>Chromium at 287</td>
<td></td>
<td>42.4</td>
<td>trace</td>
<td>54.2</td>
<td>0.7</td>
<td>1.8</td>
<td>0.7</td>
<td>0.2</td>
</tr>
</tbody>
</table>
The high figure of 95.9% CaCO$_3$ is good evidence that the type of scaling involved here is due mainly to thermal decomposition of the temporary hardness salts. The elevated temperature of the water was causing bicarbonate ion ($\text{HCO}_3^-$) to break down according to the equation:

$$\text{Ca(HCO}_3\text{)}_2 \xrightarrow{\text{heat}} \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2$$

The calcium carbonate being nearly insoluble is precipitated as scale. The presence of calcium and magnesium sulphates would not normally be expected under these conditions as the limit of solubility approximately (1200 p.p.m. for CaSO$_4$) was never exceeded or even approached as there was only 60 p.p.m. total of sulphate ion in the original water. The presence of these salts in the deposit is undoubtedly due to the type of boiling that was taking place, this was of the steam bubble type discussed in the first part of this thesis. Under these conditions local deposits of several salts must have formed at the triple interface of bubble, heat exchange surface and water and following collapse of the steam bubble there would have been a tendency for the soluble deposits to be redissolved, but presumably the speed of circulation was insufficient to redissolve them faster than the rate of formation. It is also possible that redissolution was slowed by the mechanical protection of the insoluble calcium carbonate deposit which was stopping the water circulating freely round the more soluble salts.
The analysis of the raw tap water fed into the apparatus is shown below and beside it for comparative purposes is shown the analysis of the water leaving the apparatus after being boiled.

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Raw tap water entering apparatus (P.P.M.)</th>
<th>Water after leaving apparatus (P.P.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness temporary</td>
<td>172</td>
<td>100</td>
</tr>
<tr>
<td>Hardness permanent</td>
<td>107</td>
<td>88</td>
</tr>
<tr>
<td>Total alkalinity CaCO₃</td>
<td>192</td>
<td>120</td>
</tr>
<tr>
<td>Carbonates, CO₃</td>
<td>115</td>
<td>72</td>
</tr>
<tr>
<td>Sulphates, SO₄</td>
<td>60</td>
<td>56</td>
</tr>
<tr>
<td>Chlorides, Cl</td>
<td>38</td>
<td>41</td>
</tr>
<tr>
<td>Calcium, Ca</td>
<td>101</td>
<td>64</td>
</tr>
<tr>
<td>Magnesium, Mg</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>Free carbon dioxide</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>pH value</td>
<td>8.7</td>
<td>8.8</td>
</tr>
</tbody>
</table>
Percentage reduction in temporary hardness - 41.8%
" " " permanent " - 17.7%
" " " carbonates " - 37.4%
" " " sulphates " - 6.7%
" " " calcium " - 36.7%

From the percentage reduction table it can be seen that six times as much carbonate was being thrown out of solution as was sulphate. It can be seen that only about half the temporary hardness was deposited. This was because the reaction
\[ \text{Ca} (\text{HCO}_3)_2 \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \]

is not instantaneous and the water passed through the apparatus before the reaction reached completion. Independent tests done in which the fall of temporary hardness against time of boiling was measured showed that with the water used boiling for 20 minutes would be necessary completely to eliminate the temporary hardness.

Approximately 10 gallons of water flowed through per hour and the sectional area between the cell and the walls of the drum was 0.46 square feet. These figures give a time of flow for each particle of water past the 6 inches of the cell of 8.5 minutes. That is to say that the water was boiling for a period of 8.5 minutes and in that time deposited 41.8% of its temporary hardness. These figures agree very well with
the figure of 20 minutes mentioned above.

Other workers have noticed that speed of circulation has an effect on quantity of scale formation (13).

From the analysis it can be seen that the chloride ion content in the water leaving the apparatus was greater than that entering. This may have been due to slight concentration there due to steam evolution or residual amount of chloride ion from the acid used to clean the apparatus, but in any case, the rise is small and may even have arisen from slight errors in analysis.

The structure of the deposit shown by X-ray diffraction patterns was always that of calcite which is one of the three forms of calcium carbonate mentioned in the A.S.T.M. index of X-ray powder data. The other two forms are aragonite and vaterite, both of which have been reported as constituents of scale though generally together with the calcite form.

The presence of the other salts found in the chemical analysis of the deposits was not detected using the X-ray diffraction technique. This is because 10% or more of the sample has to consist of say, calcium sulphate, for it to be observable in the diffraction pattern. Here as indicated the amount of salts other than calcium carbonate were much less
than this figure in all amounting to some 4% of the total. It is possible to identify amounts of this order by concentrating the various parts using chemical methods. There is a standard method of doing this\textsuperscript{[27]}.

The X-ray diffraction pictures from which these conclusions were drawn are those shown in figures in the section dealing with grain-size of the deposits.

It is felt that all the above results as regards chemical composition and structure indicate that the variables introduced, i.e., surface finish and material, had little or no effect on the scale produced under the conditions of these experiments.
This section of the work was undertaken to explore the internal structure of the scale. Knowledge of this will lead to conclusions regarding the cohesive forces that hold scale together. It has already been shown that the scale is in the form of a randomly oriented polycrystalline mass by X-ray diffraction techniques, and further, that the adhesive forces bonding the scale to the heating surface are of a mechanical interlocking type. Hence knowledge of the internal factors on which the subsequent growth of the scale depends will add to the general picture of scale formation and particularly to those aspects which deal with the growth of scale on scale.

Microradiographic techniques were necessary as the internal structure of the scales as prepared in these tests was too fine to be seen using normal radiographic methods. Scale is porous and it might be thought that microphotography would enable the structure to be elucidated. However due to the very small depth of focus of the light microscope refraction from the crystals and diffraction effects from the illuminating source little information except from the scale surface could be obtained. Electron microscopy was difficult to apply because of the large absorption in the crystals. Thus
micro-radiography is a compromise between optical microscopy and electron microscopy.

The principle of microradiography is simple, in that a radiograph of a thin specimen in contact with an emulsion is taken, this radiograph is then examined using an optical microscope. It can be seen from this that where the structure of the specimen is fine and much consequent magnification is necessary, a very fine grain film has to be used. For this particular problem a Lippman emulsion was used, this being the finest grain emulsion obtainable. The particular plates used were cut from "Kodak Maximum Resolution" plates.

The choice of radiation depends very much on the specimen as absorption edge effects may be important. For instance, white radiation may be used where the specimen are markedly different and good resulting contrast will be obtained. In other cases, particularly metallic alloys, a particular wavelength may give good contrast between materials whose atomic numbers and hence absorption coefficients are close, if the wavelength is chosen with due regard to the position of the critical absorption edges. For example, in the case of iron and manganese the absorption edges are 1.74Å and 1.89Å respectively so, Co. Kα radiation (λ = 1.79Å) gives good contrast between the two. In this particular case,
radiation at 9kV was used and gave excellent results. Further details of microradiographic procedure are given in "A Further Handbook of Industrial Radiology" (28).

The camera used in the present experiments is a refined edition of one shown in "A Further Handbook of Industrial Radiology" (28) and a dimensional drawing, figure 56, and a diagram, figure 57, are given. This camera was designed and produced in the Crystallography Section of the Battersea College of Technology. From the diagram it may be seen that the whole camera can be clamped directly to the window of a Phillips diffraction X-ray tube by means of four screws through securing holes in the front plate. The axial centre-line of the camera body is at $7\frac{1}{2}^\circ$ to the front plate so the X-rays leaving the tube may travel squarely along the centre-line of the camera. A spring loaded shutter operated by the shutter operating knob is incorporated to keep light out of the camera during transport. The specimen and photographic plate are held against an internal mounting plate by means of a spring loaded clamping plate. A thin layer of sponge rubber is placed between the specimen and a mounting plate thus preventing specimen fracture. The back cover of the camera, normally held in place with a wire clip, can be removed for loading.

The method of use was as follows. The scale specimen...
was a chip obtained from one of the specimen cylinders used in the large cell apparatus. Thus scale from various types of surface was used. The scale was thin enough (approximately $5 \times 10^{-3}$ in.) to give a radiograph without any attempts being made to make it thinner. A photographic plate 1" square was cut from one of the Kodak M.R. plates and the specimen and photographic plate were placed in the camera as shown in figure 57. These operations were carried out in the darkroom using a red safelight to prevent light affecting the Lippman emulsion. With the shutter closed the loaded camera was taken to the X-ray set and screwed into its position over the X-ray tube window. The camera shutter was opened and the X-ray controls set to 9kV at 12mA tube current. An exposure of 5 minutes in all cases was given. Other tube voltages and exposure times were tried but those mentioned gave consistently good results so were always used. After exposure to X-rays the plates were developed and fixed with care using constant agitation. The final radiographs were examined directly under the optical microscope using transmitted light where it was found that magnifications of up to X 400 could be used before grain in the emulsion became at all noticeable. Microradiographs were taken at various magnifications up to X 400 using Ilford FP3 film in
1. Shutter operating rod.
2. Plate securing screw.
3. Cover.
5. Cover securing clip.
7. Photographic plate.
8. Shutter operating knob.
10. Front plate.
11. Shutter.
12. Specimen.
13. Sponge rubber.
15. Securing holes.

MICRO - RADIOPHGRAPHTY CAMER.

Scale - 0 1" 2"

Figure 57

Produced - B.C.A.T.
Designed - Crystallography Dept.
Drawn - J. Subramanian.
March 1
the Beck microscope camera. Exposure was determined empirically and the negatives obtained enlarged using normal photographic techniques. The overall magnification in each case is given under the photographs reproduced on page — 152. A point to note with these photographs is that they are negatives; that is, the crystalline matter appears as white against a dark background. This is due to the threefold process whereby the radiograph is a negative, the microphotographic film is positive and hence the final print will be negative. As the structure is quite discernible in the negative print it was not felt necessary to introduce another process to obtain positive prints.

---

RESULTS

Tests were carried out on scale samples from the following test cylinders. These cylinders being taken from ordinary test runs.

1. Plain polished steel.
3. Copper electro-plated steel.
4. Vitreous enamelled steel.

The photographs are shown in figure 58.

---
Nickel - X 500 magnification.

Vitreous enamel - X 500 magnification.

Copper - X 125 magnification.

Steel - X 500 magnification

Microadiographics of scale from various surfaces.

Figure 58.
DISCUSSION

Scale from Polished Steel.

The crystalline form of the individual crystals is acicular with a ratio of length to breadth of from approximately 7 to 1 down to 3 to 1. No observable facets were seen, the exterior surfaces of each crystal being apparently rough with indications of curving towards the ends of some, a small number were pointed. The crystals appeared to be randomly oriented, no preferred direction being observed. They were extensively interwoven with each other although this did not seem to affect their shape where crossing occurred. Extensive porosity was seen and in some places this appeared to penetrate almost entirely through the thickness of the scale.

The length of the longest crystal was approximately 60 microns whilst the average length was some 36 microns. The thickness average 7.5 microns.

Scale from Nickel Plated Surface.

This structure was similar to that of the scale from the polished steel surface. Acicular crystals with irregular outer surfaces tending towards points at either end were seen. The same extensive interlacing and marked porosity was also seen. The size of the
individual crystal grain was of the same order as that from the polished steel, that is to say, some 36 microns average length, and average thickness of 7.5 microns. There were slight indications on a good proportion of the crystals that there were longitudinal fissures or cracks.

**Scale from Copper Plated Surface.**

This structure was somewhat different to the first two samples in that the shapes of the crystal grains was not uniformly acicular although many acicular crystals were seen. A great number of the grains were irregularly shaped having no discernible facets, and very rough faces with feathery outgrowths in all directions. Extensive interlacing had occurred and again the whole sample was extremely porous with the porosity extending right through the samples in many places. The crystal size for the acicular grains was comparable to the previous sample, 36 x 7.5 microns whilst the size of the irregular grains was of the order of 30 microns x 45 microns.

**Scale from Vitreous Enamelled Surface.**

The sample appeared as a more loosely formed mass compared to the previous three. The grain size was of the same order as the previous three. There were two types of grain, a triangular version - 24 microns x 24 microns, and a fine acicular version some 30
microns by 3 microns. This sample was more porous than any other and there was again extensive interlacing.

GENERAL

Bonding forces and setting action.

It can be seen that in all cases the structure obtained was that of an interlaced mass of randomly oriented crystals. The crystals appear discrete from one another even at their crossing points and there seems little doubt that the coherent forces arise purely from mechanical interlocking. This bonding would appear to be similar to that of gypsum plaster, although the mechanism of setting is undoubtedly different. In the setting of plaster, water is added to the hemihydrate $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ which is five times as soluble as the dihydrate. The hemihydrate dissolves and forms a supersaturated solution from which the dihydrate is precipitated as an interlaced mass of crystals\(^\text{(29)}\). This mechanism of setting was first put forward by Lavoisier in 1765, and the crystalline interlocking theory was first put forward to explain the cementitious action of Portland cement by Le Chatelier in 1892\(^\text{(30)}\), and whilst it is no longer acceptable for Portland cement it is still accepted for the setting of gypsum plaster.
According to Bernal and Jeffrey\(^{(31)}\) the setting of cement can be considered as a process in which calcium silicate hydrate crystals grow out of the cement grains. The crystals which become buckled and folded meet each other and where this occurs and the lattice position of each is similarly oriented then intergrowth occurs. This gives a strong structure throughout the mass.

Another theory of the setting mechanism states that the minute particles due to their high surface energy coalesce into aggregations of a few microns diameter. Some of these aggregations may be similarly oriented and cross connections grow between them.

As mentioned before the deposits of scale in the present cases were all calcium carbonate with the calcite structure. The mechanism of crystallisation and deposition is due to the thermal decomposition of calcium bicarbonate in the water causing the more insoluble calcium carbonate to precipitate on the hot heating surface. As the water is hottest at the heating surface, deposition will occur at the heating surface and the crystals of scale will be in very close proximity to each other. From the photographs alone there does not appear to be any intergrowth and thus the most likely type of coherent bond is that mentioned for gypsum plaster based on mechanical interlocking.
To establish this completely however would in the author's opinion need very delicate electron diffraction techniques.

**COMPARISON OF RESULTS WITH CRYSTAL SIZE MEASUREMENTS.**

The micrographs obtained in these experiments although primarily aimed at showing the structure, can also be used to determine the crystal size in the scale. It is of interest to compare the grain sizes obtained here with those obtained from the X-ray diffraction photographs. The general conclusion reached from the diffraction photographs that the grain size remained constant over the different surfaces tested is fully confirmed here. There is also fair agreement between the average sizes obtained in both sets of experiments the tendency being for the average results here to be somewhat less than those in the X-ray diffraction experiments. This indicates that the particles seen in the photographs in this section were complete crystals in themselves and not composed of two or more individual crystallites.
PART III.

FURTHER GROWTH OF SCALE.

Introduction

Following the work done on the initiation of scale formation it was decided to study the further growth of scale on top of an initial deposit in order to determine whether the initial scale layer affected the subsequent growth in any way.

For this series of experiments laboratory tap water was used as the scale forming solution. This particular water used under the conditions described below yields a calcium carbonate scale arising from the bicarbonate and calcium ions in solution. These ions break down on heating to form $\text{CO}_2$ gas and a sparingly soluble $\text{CaCO}_3$ precipitate. The structure of the calcium carbonate is that of the mineral calcite. This type of scaling arising from the temporary hardness in the water is very common in industrial apparatus and hence it was thought well worth while to investigate it. In order to facilitate examination of the newly formed deposit the initial layer was prepared where necessary so that the further growth took place on a plane surface.

Initially flakes of polycrystalline calcite scale were used as the initial layer. These were prepared by
grinding flat and washing. Subsequently flakes of calcite were used, these being prepared so that definite crystal faces (111) (100) etc. were used as the substrate for further growth. Finally flakes of glass were used to study the effect of an amorphous substrate on further growth.

Apparatus.

The apparatus here was an enlarged and improved version of that used in Part I, see figures 59 and 60. The basic heating surface was the chromium plated sole-plate of an electric iron. The initial deposit of chips was glued to the sole-plate and water was passed over them. A cell to contain the water was built up by means of a 3/16" thick metal cavity wall plate cut to the exterior shape of the sole-plate and about ½" in width. This plate formed the walls of the cavity. A sheet of shaped plate glass, with rubber gaskets on each side, formed the outer surface of the cavity. A metal clamping plate was fitted on top of the glass and screws passed through this and the cavity wall plate to tapped holes in the sole-plate. Water was admitted at the bottom of the cell and left out of the top through small holes drilled through the cavity wall plate. Copper pipes were brazed to the exterior of the holes for connection to the water supply.
Two water exit holes were provided to prevent steam pressure build up in the cell interior. Water was admitted to the cell through a copper pipe coming from a constant head apparatus which could be raised and lowered to regulate the water supply to the cell. The supply could be further regulated by a needle valve fitted in this pipe.

Hot water and steam from the cell was led out through a Liebig condenser, the output from which could be directed into a measuring cylinder in order that the water flow through the cell could be measured. The cell was mounted with the sole-plate in a vertical plane and water admitted at the bottom. The cell was heated by a 750 watt (maximum) electric element as originally supplied with the iron. Current for the element was supplied from the laboratory main electric supply via an adjustable auto-transformer of the Variac type. Provision was made for connecting meters in circuit to measure the energy input to the sole-plate.
EXPERIMENTAL METHOD.

Specimen preparation.

Scale chips - chips of polycrystalline calcite scale were prepared from a bulk sample. The finished chips were 1mm. thick by 5mm. square with plane faces. The chips cut roughly from the bulk sample with a hacksaw and finished by grinding on dry emery papers of successively finer grits, the last grinding being with 000 emery paper. An X-ray diffraction photograph was taken to confirm the calcite structure and the polycrystalline state.

(100) chips - these specimens were prepared so that the water would be in contact with a (100) face of a calcite crystal. As calcite has extremely good cleavage along the 100 form the chips were prepared by cleaving suitable crystals of Iceland Spar. The crystals were cleaved by resting a razor blade edge on the bulk crystal parallel to a cleavage plane and then tapping the razor blade. A little practice enabled one to cleave the crystal very easily and no trouble was experienced in getting as many flakes as required of dimensions 1mm. x 5mm. square approximately.

(111) chips - these specimens were prepared so that a (111) face was in contact with the water. As no crystal showing a sufficiently good (111) was available, the flakes were ground in the following manner. A cleavage
rhomb of Iceland Spar was cleaved from a bulk crystal, its size being approximately 5mm. x 5mm. x 5mm. The rhomb was set in a block of plastic mounting media (acrylic resin) so that the trigonal axis was at right angles to the surface of the resin and a corner of the crystal projected out of the surface of the resin. The back of the plastic mounting was then filed into a tabular form capable of being gripped in the chuck of a universally swivelling head. The swivelling head was mounted in a machine which allowed it to move freely up and down, rotate vertically and move horizontally in the arc of a circle.

The swivelling head was allowed to come to a position where the crystal point was resting on a horizontal piece of plate glass. The crystal point and its reflection were then observed in a telescope (cathetometer). The position of the crystal was then adjusted by means of the universal head until the angle between each of the three edges and its reflection was equal as observed in the cathetometer which had a protractor scale in its eyepiece, the crystal being rotated to bring each edge and its reflection successively to a maximum. This procedure oriented the crystal so that its trigonal axis was at right-angles to the horizontal plate glass surface and therefore the potential (111) plane was parallel to the plate glass.
The crystal was then ready for grinding which was done by mounting emery paper on the plate glass and moving the swivelling holder in a horizontal arc or a circle by hand whilst maintaining contact between the crystal and the emery paper. The grinding was carried on using successively finer grades of emery paper (M 000) until a facet of the right size had appeared on the crystal. This facet was then polished using metal polish impregnated into "Svelte" cloth on the plate glass surface. The crystal in its block of mounting medium was then removed from the machine and a flake about 2mm thick was cut off with a fine hacksaw parallel to the (111) facet. The flake was then ground on emery papers until it was 1mm thick. This finished the preparation of the specimen which was then tested to see if a true (111) face had been obtained. The testing was done by examining the interference figure obtained using convergent light between crossed polaroids on a microscope, the specimen being mounted with its polished face in contact with a microscope slide.

As in calcite the (111) plane is perpendicular to the principal optic axis a uniaxial interference picture should be seen under these conditions. The specimen was rotated on the microscope stage and if the
uniaxial figure stayed in the same position during rotation the specimen was accepted for use.

It was found that with practice calcite flakes with a (111) face could with care be prepared by this method and that the polished faces were comparable so far as surface finish was concerned with natural faces.

(211) chips - these specimens were prepared so that the scale build up on a (211) face could be examined. The (211) form of calcite consists of a set of faces parallel to the principal trigonal axis and making up a hexagonal prism. This form is often found well developed on natural crystals of "nail head" Spar and such a crystal was selected from which to make specimens. Specimens were cut from the Spar by means of a fine hacksaw following which the underside of each was filed and ground till a final thickness of 1mm. was reached.

Glass specimens - these were made from a sheet of glass, each specimen being cut to 5mm. x 5mm. x 1mm. approximately.

Runs were done first with plain glass surfaces, secondly with the glass surface scribed with a diamond point engraving tool and lastly with the surface scratched with a 320 grade emery paper.
DESCRIPTION OF TEST RUNS.

The test runs were done keeping all the operating conditions of each test as near identical as possible, with the exception of the duration of test and the type of specimen.

For each run, six specimens were used and these were glued to the middle of the sole-plate in a vertical line with the spacing shown in figure 61. "Araldite" epoxy resin glue was used to glue each specimen to the sole-plate. This glue consists of two parts, a resin and a hardner. Normally equal parts of resin and hardner are mixed but it was found in this case that these proportions gave a bond between specimen and sole-plate that was too hard to break without damaging the specimen. Therefore excess resin was used as this gave a weaker, more flexible, bond which could be easily broken when it became necessary to remove the specimens. The sole-plate was cleaned and polished with metal polish to a mirror finish before each run. After the specimens were glued into position the cell was built up with the cavity wall plate and front glass, figure 61. The input cold water pipe was then joined to the constant head apparatus output pipe a compression coupling being used and the output pipe was connected to the Liebig condenser. The cell was filled with water and the
electric current switched on. The water came to the boil after a minute or so and the flow was regulated by means of the needle valve so that the boiling line was just below the uppermost specimen. Hence the top two specimens were in the hottest part of the cell and were immersed in a mixture of boiling water and steam. The other four specimens were at various temperatures the lowest being the coldest and in most runs this particular specimen was so cold as to have no further growth. Thus each run gave results for a range of different temperatures and it was found that the type of growth did depend on the temperatures of the specimen. After boiling had commenced the flow from the output of the Liebig condenser was checked by means of a graduated measuring cylinder. The function of the Liebig condenser was to condense and cool the steam and water issuing from the cell so that it could be measured. When the period of time specified for the run had elapsed the electric current was switched off, the water connections were uncoupled and the cell drained. The specimens were removed from the sole-plate by slicing through the adhesive layer with a razor blade and were then ready for study of their further growth.

The specimens were examined under an optical
microscope and photo-micrographs were taken under standard conditions of magnification. A fine grain film FR3 was used for the negatives. Examples of the photos obtained are shown in figures 69 to 81. The photographs all have a magnification of X 400. As the optical microscope had a depth of focus much less than the height of most of the overgrowths obtained it was impossible to see clearly the whole extent of the overgrowth. Because of this, attempts were made to examine them under the electron microscope which has a much greater depth of focus. As the growths were opaque to the electron beam, attempts were made to replicate these growths. These attempts ended in failure due to the overhung nature of the growths which prevented proper stripping of the replicating film.
Figure 61

Front and Side Elevation of Cell

Scale: 3" 1" 1/2" 3"

- Steam and hot water outlet
- Clamping plate
- Rubber gasket 1/4" thick
- Plate glass window 1/4" thick
- Rubber gasket 1/4" thick
- Cell plate 3/4" thick
- Graphite asbestos gasket 1/4" thick
- Heating surface
- Total cell depth 3/4"
- Cold water inlet
DISCUSSION

(100) flakes.

The type of growth on the (100) face of calcite flakes was found to depend mainly on the position of the flake on the heating surface and also upon the length of time the flake was boiled.

Dealing first with the flakes in No. 1 position (see figure 69). This was the hottest position and the flakes were immersed in a mixture of boiling water and steam. When boiled for a period of two minutes a fine precipitate of crystals was fairly evenly deposited. These crystals had no obvious shape as can be seen from the photograph. They were about 2.5 microns in length. Boiling for a longer time up to 5 minutes gave the same type of deposit, but the crystals were larger, about 4 microns in length. Boiling for 7, 10, and 15 minutes produced three types of deposit.

1. An even deposit of oriented triangular crystals with a pair of Vee shaped rootlets extending from the apex.
2. A crusty deposit completely covering the surface in places.
3. An occasional overgrowth of a cluster of crystals randomly oriented apparently lying on top of the other deposits.
1. With regard to the triangular form with rootlets extending fan-wise from an apex an idealised form of this is shown in the drawing figure 70, placed as observed in correct orientation to the two cleavage edges of the basal crystal. See also figure 71. The line drawn bisecting the angle made by the rootlets also bisects the angle between the two cleavage edges of the base crystal. As the (110) plane is the most common of the four observed twin planes of calcite it might be argued that the rootlets form a twin about the (110) plane and taken in conjunction with the base crystal form a type of triplet. Were this so, one would expect the angle between the rootlets to be of the order of 52°30' if the rootlets represent the normal habits of twinning calcite, that is the prismatic or scalenohedral forms with the principal axis along the centrelines of the rootlets.

This angle is however of the order of 78° and as this is so much greater than 52°30' it would apparently put this theory out of court unless it could be shown that the rootlets were not the prismatic or scalenohedral forms, which is unlikely if the crystal is twinned on the (110) plane as these two forms are the commonest twin forms observed.
Further the angle 78° is not considered to be near enough any of the other angles involved in the three laws of twinning for calcite, these angles being: –
180° for the (111) twin,
90°46' and 89°14' for the (100) twin,
and 53°46' and 126°14' for the (111) twin.

This being so it is considered that the rootlet form is not twinned at all with respect to itself, even though the form of the rootlets immediately suggests twinning on first glance. It is felt that the angle 78° is too close to the rhombohedral cell angle for calcite, which is 78°5' for there to be no connection. It is considered probably that the rootlets taken together form part of rhombohedral habit based on the form (100) and that the conditions of growth have restricted filling in between each pair of rootlets leaving the apparently twinned habit. Assuming this to be correct the rootlets formed part of a rhombohedral habit (100) oriented at 90° to the base crystal so that a twinning condition existed based on the (100) plane of the base crystal between the rootlet form and the base crystal.

2. With regard to the crusty deposit which in places completely covers the base crystal surface, the photograph figure 71, shows the triangular form with rootlets to merge into the crust strongly giving the impression
that the two are closely related. This impression was borne out when the specimen was examined between crossed nicols on a polarising microscope when the extinction was uniform over the whole surface showing that the crusty deposit was oriented with respect to the base crystal in the same manner as the triangular crystals. There was no tendency for the parts of crusty deposit to unite and form a single crystal layer spread over the base crystal, nor was there any indication that the crust itself could promote further oriented growth on top of itself.

3. The clustered overgrowth - this deposit consisted of small polycrystalline formation lightly in contact with the oriented growth adjacent to the base crystal face. There were no orientation effects. They occurred only occasionally. The individual crystals in the clusters did not exhibit any particular habit.

With regard to the flakes in the other positions it was found that growth was almost identical to that obtained on the No. 1 flake so far as No. 2 flake was concerned. There is shown in the photographs (figure 72) for this position one ring of the oriented crystals which strongly resembles the boiling rings found in Part I
of this thesis. These rings were found only occasionally in these experiments. The lack of them was due to the insulating effect of the calcite flake on the heating surface which was preventing sufficient heat penetrating to cause steam bubble formation. Thus the surface of the calcite reproduced the conditions met in practice on scaled heat exchange surfaces.

On No. 3 flake the general deposit obtained was quite similar in nature to that obtained on Nos. 1 and 2 flakes see figure 73. The general impression is from the photograph that the sizes of the individual deposit particles were somewhat smaller than those obtained on the Nos. 1 and 2 flakes.

The photographs, figure 73, for the shortest time of boiling, two minutes, shows a plain oriented rhombohedral habit in places.

On the No. 4 flake the deposit particles were not only small, but the rootlets were less well developed. Another ring formation, see photographs figure 74, was also seen. The rhombohedral form was seen on the flake with the shortest time of boiling.

The Nos. 5 and 6 flakes showed a much finer deposit, amongst which the rhombohedral form could be made out.
(111) flakes.

Here as in the case of the (100) flakes several types of deposit were seen and these were as follows:

a) A very light scattering of very small crystals whose habit was not discernible.

b) An oriented overgrowth of plain triangular crystals.

c) A crustlike deposit covering whole areas of the crystal.

d) A random cluster-like growth only occasionally appearing on top of the other deposits.

Dealing first with the flakes in No. 1 position figure 75, boiling for 2 minutes gave a deposit as in a) above of a fairly even scattering of very small crystals of estimated average size 2 microns. There was no discernible habit the crystals appearing to have rough surfaces.

On increasing the time of boiling to five minutes a great change in the habit took place. The predominant shape seen was of an equilateral triangle and these were all oriented in the same direction and in size about 4 microns. There were also a few different growths, similar to that found on the (100) flakes, but with the rootlets not so well distinguished. These few growths did not appear oriented. On further boiling up to 15 minutes the plain triangular form was not so evident as the individual
crystals tended to coalesce to form a crust-like deposit as mentioned in c). The size of the individuals had not increased with the extra boiling time. The randomly oriented clusters on top of the crust were noticed as in the case of the (100) flakes.

The No. 2 flake. This position gave almost identical results to those obtained with the No. 1 flake. In particular the flake boiled for 5 minutes gave a deposit which included a stepped line of triangular crystals. See photograph figure 76. Possibly there was a scratch in the crystal along this line nucleating oriented growth better than on other parts of the crystal.

In the case of No. 3 crystal no triangular growth was seen on the flakes boiled for 2 and 5 minutes, only a thin deposit of very small crystals. A good growth of oriented triangular crystal was seen on the flake when boiled for 15 minutes, see photograph figure 76.

For the No. 4 position flakes, the growths were very similar to No. 3, except that the deposit on the flake boiled for 15 minutes was somewhat more spread out. All the Nos. 5 and 6 flakes showed no deposit after a period of boiling up to fifteen minutes.

It is considered that the plain triangular form is a parallel overgrowth of the base crystal. This is immediately suggested by the fact that these overgrowths
are triangular in shape suggesting a triad axis coming through them perpendicular to the base crystal surface. As the base crystal has a triad axis in this position the inference that the growths are parallel overgrowths is at once apparent.

(211) flakes.

The form (211) is the hexagonal prism which appears in nature in "nail head" Spar.

The types of growth seen were much the same as for the (111) faces, namely:—

a) A light scattering of small crystals.
b) An oriented overgrowth.
c) A crustlike deposit on whole areas of the crystal.
d) A random cluster-like growth appearing on top of the other deposits.

Dealing as before with the flakes in No. 1 position, boiling for 2 minutes gave a uniform covering of small crystals some of rhombohedral habit. They did not appear oriented (see photograph figure 77). On increasing the boiling time to 7 minutes, the habit changed to a multi-rhombohedral form (photograph figure 77) two or more rhombohedra could be seen growing out of an indeterminate crystal. Some of these, particularly those with twin rhombohedral outgrowths appeared oriented in the direction with respect to the base crystal. Again with these there
is the apparent suggestion of twinning as observed in the case of the (100) flakes though it is thought that further investigation would be necessary before this hypothesis could be verified. On boiling for a longer period (10 minutes) nearly all trace of the rhombohedral clusters disappeared leaving only a well oriented deposit consisting of vaguely rhombohedral crystals with a fan-like growth spreading out from one of the acute angled corners (see photograph figure 77). Unfortunately, the angles show no consistancy and it is not possible to advance any theory as to the habit from any angular measurements. Referring to figure 70 which shows a sketch of one of these growths it can be seen that there may well be a crystallographical mirror plane as shown bisecting the growth. This mirror plane may coincide with a mirror plane in the base crystal. The trigonal axis of the base crystal is in the same direction as its mirror plane. However, the trigonal axis in the overgrowth judged on the rhombohedron is certainly not in the direction of the mirror plane. The direction would appear to be at right angles. If the direction is at right angles then there is a basis for thinking that the orientation of these deposits bears the same relation to the (211) plane as in the case of the (100) plane where the deposit also was oriented at 90° to the base crystal structure.
As the period of boiling was increased to 15 minutes a crusty deposit formed on the base crystal somewhat similar to that found on the other planes. Again on this crust occasional random clusters of crystals were seen.

Much the same type of growth appeared on Nos. 2 and 3 flake as on No. 1. With the other flakes very little deposit occurred.
PLAIN GLASS SPECIMENS.

As mentioned before, plain glass flakes were also used as a base for further growth, as it was thought that this material would provide a good example of an amorphous substrate with no orientating effects at all on the growths precipitated by heating the water.

In general, with glass, it was found that there was less tendency for crust-like deposit to form in the longer periods of boiling. The crystal size for the topmost flakes was considerable larger than that obtained on the calcite flakes. On the bottom two flakes little growth at all formed. On the three topmost flakes almost identical deposits occurred over all the boiling times selected. (See photographs figure 78).

After two minutes boiling a light scattering of well developed primary rhombohedra were seen, their size being approximately 7.5 microns. On boiling for a further period up to 5 minutes these rhombohedra tended to increase in size and grow less distinct with a suggestion of overgrowth on some of them. On increasing the boiling time to 7 minutes it was found that each crystal had developed into a cluster of crystals of average number about 4. There was a strong impression that the clusters were formed of rhombohedra. As the boiling time increased to 10 and then 15 minutes, the clustered form modified
and developed into all the types seen on the (100), (111) and (211) flakes. These were as follows:-

a) triangular form with plain rootlets;
b) equilateral triangular form;
c) rhombohedral form with fan-tail outgrowth.

Whilst all these types are discernible it is worth noting that they are not so symmetrically formed as on the ones grown on the calcite flakes. The crystal substrates are not only capable of suppressing completely those forms that are not compatible with them, but can also enhance the apparent symmetry or perfection of the form they do favour. As would be expected on glass there was no tendency for any of the forms to show a preferred orientation.

On specimen 4 the same type of growth was seen as on Nos. 1, 2 and 3 but it tended to be more thinly spread over the surface flakes. For specimens 5 and 6 little growth developed and what there was gave the impression of rhombohedra.

SCRATCHED GLASS SPECIMENS.

A few runs were done with scratched glass specimens in one of which the specimens were scratched with 320 grade emery paper and in the other two the specimens had fine parallel lines engraved on them with a diamond pointed
engraving tool. These runs turned out to be an exercise in nucleation.

The results for the specimens scratched with 320 grade emery paper, are shown in figure 79. As can be seen from the photographs very similar deposits to those on the plain glass specimens were obtained. The three forms of crystal can all easily be picked out. The difference here is that the deposit instead of being evenly spread over the surface as before is now restricted to the scratches so that lines of crystals appear. There was no preferred orientation of the deposit, nor was there any tendency for individual scratches to favour the growth of any one of the three types of deposit. The lower specimens showed the plain rhombohedral growth and this was restricted almost entirely to the scratches. On the lowest specimen No. 6, no discernible growth occurred. This experiment certainly showed nucleation was associated with scratches and it was thought worth while to do further work in which the scratches were bigger and more spaced out to determine if possible what parts of the section of scratch was influencing nucleation. Hence several glass specimens were engraved with a diamond point tool, giving individual scratches of larger dimensions than those produced by the emery paper. A picture of the engraving point is shown in figure 80. As can be seen the point
is in the shape of a circular cone with an apex angle of 90°. The scratches produced were of two types:

a) A scratch which was rough and jagged, the glass breaking and splintering as the engraving point was drawn across it.

b) A scratch with very smooth sides and edges, where the glass had broken away in a series of conchoidal chips.

On boiling for two minutes the type of deposit precipitated was a primary rhombohedron as for all the other glass specimens. The effect of the jagged scratches was to greatly encourage crystallization. The crystals formed in clusters and rows on every available sharp point and edge along the scratch, see figure 80. The effect of the scratches with conchoidal fractures was just as marked, but in the opposite sense. No deposit occurred on the smooth sides of the scratch even though there was some on the surrounding area, see figure 80. One photograph in figure 80 is extremely interesting in that the scratch had one side jagged and the other conchoidal. On the jagged side can be seen the clusters and rows of crystals in every nook and crevice whilst on the other side, nothing. Figure 81 shows this dual effect very clearly due to the fact that the photographs were taken between crossed nicols, the calcite rhombs appearing as white specks against a black background. The author believes this to be an example of heterogeneous nucleation
and that this is the starting point from which adhesion arises. This is more fully explained in the general conclusions. The specimen in the lowest position showed no discernible deposit. On increasing the boiling time to 7 minutes the general surface of the top specimen became covered with the rhombohedral clusters found on the plain glass specimens, figure 81, whilst a crusty deposit formed on the edges of the scratches completely occupying them. The lower specimens showed the rhombohedral growth found when the boiling time was two minutes.

GENERAL CONCLUSIONS

All experiments performed in this series of tests indicated that the most favoured initial form of crystallization is that of the rhombohedron with the possible exception of the deposits on the (111) face which was indeterminate in the early stages. Initially the rhombohedron is quite small and fairly well developed. If the conditions favour further growth these rhombohedra grow bigger and the faces and edges become rougher, the crystals then develop outgrowths eventually developing into rootlets or fan-tails. This appears to be the end point so far as the individual growths are concerned. Figure 82,
shows pictorially the development of the various growth forms. After the individuals have reached full development further boiling causes the whole lot to coalesce into a crust-like growth completely covering the substrate. Beyond this, random clusters begin to appear resting on top of the crust. The effect of using specific crystal faces \((100)\) etc. was intensely to favour one of the end forms and to suppress the others. In addition there was a strong orienting effect noted. Attempts were made as described to identify these various types of deposit. That they were all calcite was confirmed from their X-ray diffraction patterns.

As indicated in the initial discussion on \((100)\) faces there is some reason to believe that the rootleted end-form is oriented at \(90^\circ\) to the substrate, thus making the rootleted growth and the substrate the two parts of a type of twin crystal. In figure 83 the crystal lattice arrangement for this type of overgrowth is shown. The substrate lattice is indicated in continuous black lines each intersection representing the position of a calcium atom. The overgrowth lattice shown by dashed lines is identical to the substrate but rotated \(90^\circ\) about the point at the bottom right hand corner. As can be seen this rotation begins near coincidence at the other points indicated on the "super"lattice which is of rectangular form and nearly square.
In this arrangement it would be expected that the bonding between the substrate and overgrowth would be much weaker than the bonding holding the rest of the crystal together, this being so because coincidence occurs at four points instead of 50 points in each unit of the "super" lattice. This would lead to a strongly defined cleavage plane between overgrowth and substrate.

Evidence for this cleavage plane was found as it was easy to remove the overgrowths by gently rubbing the coated substrate to give a perfect cleavage plane. No damage due to tearing out of the substrate was seen and the substrate surface was in good condition indicating that the overgrowths had broken away from the substrate at the original surface.

It is not known why these overgrowths should be so oriented to the substrate and not plain overgrowths. It is felt that for this type of growth to be initiated at all that there would have to be complete crystallite particles floating in the liquid near the substrate surface. The minimum size of one of these particles would be that corresponding to one unit of the "super" lattice. Were the crystallites smaller than this it is difficult to see how they could be oriented in this manner on the substrate. There is no doubt that these floating crystallites were present due to the thermal decomposition.
extending beyond the heating surface well into the body of the water. In fact growths were found attached to the glass cover of the cell and this was an area where they could scarcely have been formed. Possibly in the process of deposition the crystallites favoured the orientation at $90^\circ$ because the potential energy barrier that they needed to overcome to get into the more stable simple overgrowth position was too great and they therefore favoured an orientation requiring lesser energy to attain.

Beyond this it is difficult to go using the ordinary optical methods of measuring angles mainly because the crystals were so small and visible only under a high power microscope. More experimental work would be needed to extend the ideas put forward. One avenue of approach would be to employ micro-beam electron diffraction techniques. Apparatus of this type was not available to the author. As regards ordinary scale formation, the conclusion from these experiments is that under these conditions of boiling, a fine grained polycrystalline mass of scale will be built up, the particles of which will be randomly oriented. Numerous boiler scale samples examined by the author confirm this.

The experiments described in this section are all exercises in particular aspects of crystal growth. According
to Mullins the deposition of any crystalline phase can be broken down into three distinct steps. These are:

1. Achievement of supersaturation.
2. Formation of nuclei.

In the cases described here, Step 1, the achievement of supersaturation, was never any problem as the mere heating of the water rendered it solubile, no concentration being necessary. This of course arises from the instability of the soluble bicarbonate. Step 2, the formation of nuclei, is the next step to be considered.

Nucleation can occur in one of two ways:

a. Spontaneously, this being called homogeneous nucleation.

b. Artificially, this being called heterogeneous nucleation.

In homogeneous nucleation the nuclei are generated from the supersaturated solution itself, no foreign particles being present to serve as starting points on which nuclei can form. The mechanism is probably as follows. Collisions between a small number of molecules initiate the formation of sub-nucleus. This is analogous to the formation of water drops nuclei from a vapour. The ability of the sub-nucleus to grow or to redissolve is governed by its size or radius assuming it to be spherical.

For a vapour the excess vapour pressure (Pc) can be written:
\[ P_c = P_p + \frac{2T_p}{r} \]

where

- \( P_p \) = surrounding vapour pressure
- \( T \) = surface tension
- \( \epsilon \) = density of vapour phase
- \( \rho \) = density of liquid phase
- \( r \) = radius of droplets

In general \( Q \) is negligible. Where \( r \) is small the drop will evaporate but when \( r \) is large it will continue to grow. Therefore in homogeneous nucleation the random collisions of atoms must result in a nucleus above a certain size before the growth of the nuclei can continue to form a solid crystal phase. If however there are particles present in the vapour phase or if roughnesses or asperities exist on surface in contact with the vapour then the random collisions of atoms around these particles or asperities can result in nuclei being formed which are large enough to be stable and therefore growth will be greatly encouraged at these points. This process where particles and rough surfaces aid nucleation is known as heterogeneous nucleation. This theory accounts for the formation of scale in the various rough surfaces generated by the action of emery papers on the heating surface. It also accounts for the formation found in the jagged scratches made by the diamond engraving tool on the glass surface.
Subsequent crystal growth following nucleation can be grouped according to Mullins under the following headings:-

Surface energy,
Diffusion,
Absorption.

The surface energy theory by Gibbs assumes that the growing crystal will assume such a shape that its surface energy will be least for its volume. Curie used this idea to work out the end form of several crystals. Wulff extending this theory showed that the crystal should form a polyhedron such that the distance from a point inside the crystal to its faces should be proportional to the free energies of the faces. Soehnke introduces the idea that the faces with the least surface energy are those with the greatest reticular density thus tying the Bravais theory of crystal growth to the surface energy theory.

In the diffusion theory of crystal growth first proposed by Noyes & Whitney it is considered that growth is primarily a diffusion process and an equation was proposed in which $\frac{dm}{dt} = K A(C - C^e)$.

Where $\frac{dm}{dt}$ - rate of mass transfer.
$K$ - coefficient of mass transfer.
$A$ - area of surface.
$C$ - supersaturation.
$C^e$ - equilibrium saturation.
Berthoud and Valeton introduced the idea of a two step process whereby solute in the first step diffused onto the crystal face. In the second step a reaction set in by which this material was incorporated in the crystal face.

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In the adsorption layer theory first suggested by Volmer modified by Kossel and others it was considered that atoms in the vicinity of the crystal will attach themselves in positions where the attractive forces are greatest. These positions occur at steps in the crystal structure and the crystal face will grow layer by layer. Before a new layer can grow a step must be formed on the existing face. A two dimensional nucleus is assumed to be formed on the face and this serves as a step for continued growth of the layer. It is not considered that many crystals grow by this method of two dimensional nuclei forming on a face, and it is considered that most crystals grow from faults or dislocations on the growing face. Frank has suggested a type of dislocation which is self-perpetuating as each layer is formed. This is the well known screw dislocation by which the crystal face can be considered to grow up a "spiral staircase" and the need for continued formation of new nuclei or faults is obviated.

---
In the experiments described in this section the habits obtained were different being apparently controlled by the substrate. This fact would appear to rule out the surface energy theory as the growth controlling mechanism here. If the surface energy was responsible for the final habit then this habit should have been the same in all cases. According to Patel and Goswami\(^{34}\) the etch pits that appear on the cleavage faces of calcite originate from dislocations on the surfaces. It seems possible that the growths seen in these experiments grew from these dislocations each growth continuing to enlarge and penetrate into the body of the liquid until conditions became more and more turbulent and prevented their further development. Additional deposition then became random. The nucleation of the random growth could have been of the homogeneous variety as the surface texture nucleating points were by this time completely occupied and in addition the scale on the surface seemed to be independent of the random deposit.
After 2 minutes.  After 5 minutes.

Magnification X 400.

After 7 minutes.  After 10 minutes.

Scale deposited on (100) face in No. 1 position.

Figure 69.
THE RELATIONSHIP OF THE OVERGROWTHS TO THEIR BASAL CRYSTALS.  [FIG. 70]
Photograph showing orientation of growth with respect to cleavage edges of base crystal.

Photograph showing rootlet form merging into crust deposit.

Scale deposited on (100) face in No. 1 position.

Magnification X 400.

General view.

Figure 71.
After 2 minutes.  After 5 minutes.  
Magnification X 400.

After 10 minutes.  Ring formation after 15 minutes.

Scale deposited on (100) face in No. 2. position.

Figure 72.
Scale deposited on (100) face in No. 3 position.

Figure 73.
After 2 minutes.  

After 5 minutes.

After 7 minutes.  

After 10 minutes.

Scale deposited on (100) face in No. 4 position.

Figure 74.
Scale deposited on (111) flake in No. 1 position.

Figure 75.
Figure 76.

No. 2 after 2 minutes.

No. 2 after 5 minutes.

No. 2 after 10 minutes.

No. 3 after 15 minutes.

Magnification X 400.

Scale deposited on (111) face in Nos. 2 & 3 positions.

Figure 76.
Scale deposited on (211) faces in Nos. 1 & 2 positions.
After 5 minutes.  
After 7 minutes.  
After 10 minutes.  
After 15 minutes.  
Magnification X 400.

Scale deposited on plain glass specimen No. 1.

Figure 78.
After 2 minutes.  
Magnification X 400.

After 7 minutes.

After 10 minutes.

After 15 minutes.

Scale deposited on glass specimens scratched with 320 grade emery.

Figure 79.
Diamond engraving point.

After 2 minutes.
Jagged scratch.

Conchoidal scratch.

Part conchoidal, part jagged scratch.

Scale deposited on glass specimens engraved with a diamond tool.

Figure 80.
After 7 minutes.

Conchoidal scratch deposits. Jagged scratch deposits.

After 2 minutes.

After 7 minutes.

After 7 minutes.

Scale deposited on glass specimens engraved with a diamond tool.

Figure 81.
glass, (2TT) and (100) faces.

2 minutes.  →  5 minutes.  →  7 minutes.  →  15 minutes.

(111) face.

DEVELOPMENT OF GROWTH FORMS.

Magnification = x2,000 approx.

Figure 82
APPENDIX

SOME PROPERTIES OF CALCIUM CARBONATE.

Calcium carbonate is one of the most common naturally occurring minerals, being second only to quartz.

There are three crystalline forms, these being:

- Calcite - trigonal
- Aragonite - orthorhombic
- Vaterite - hexagonal

Of the three crystalline forms calcite is the most common being found in limestone, marble and chalk in massive quantities. There are according to Miers\(^{35}\) over two hundred recorded forms of the crystalline variety. Some well known sources are in:

ICELAND - where Iceland spar is found this being an optically clear variety formerly much used in Nicol prisms on account of its high birefringence. It is found in two main habits, Rhombohedral (110) bevelled by (410) and (20\(\bar{1}\)) and Scalenohedral (20\(\bar{1}\)) terminated by (410) and (100).

ENGLAND - in Derbyshire & Cumberland where in the veins of Carboniferous Limestones crystals based in prismatic form (2\(\overline{1}\)I) and on the scalenohedral form (20\(\bar{1}\)) are found.

AUSTRIA - prismatic (2\(\overline{1}\)I) and tabular (11\(\Phi\)) forms are found in the mines in the Harz Mountains.

AMERICA - scalenohedra (20\(\bar{1}\)) are found in Missouri.
Calcite frequently occurs in incrustations in boilers and other heat exchange apparatus due to the instability of solutions of calcium bicarbonate on heating.

The crystallographic structure of calcite was first determined by Bragg in 1914, the space group being $D_{3d}^{6} - R	ext{3c}$ similar to the sodium nitrate structure and containing 6 - (CaCO$_{3}$) units per unit cell. The rhombohedral unit cell dimensions are 6.4125 Angstrom units with an angle of 101°55'.

---

Some other properties of calcite are:

Density - 2.711 at 25°C.

Refractive indices

$E = 1.487$
$W = 1.659$ with negative optical sign.

Linear coefficients of expansion

$2.10 \times 10^{-5}$ parallel to C axis.
$-0.380 \times 10^{-5}$ perpendicular to C axis.

Cleavage is extremely good on the (110) form. Twin varieties - according to Miers there are four laws of twinning, these being:

1. on (111) giving rise to double ended scalenohedra with equatorial planes of symmetry and re-entrant angles.

2. on (100) when the principal axis will be at 90°46' and 89°14'.
3. on (110) this being the most usual law of twinning for calcite. The principal axes will be at 52°30' and 127°30'.

4. on (111) when the angles between the principal axes are 53°46' and 126°14'.
SOLUBILITY

The solubility of calcite is dependent on temperature and the pressure of carbon dioxide, the higher the pressure the higher the solubility.

The figures given below were determined by Frear & Johnston (1929) for aqueous solutions at 25°C.

<table>
<thead>
<tr>
<th>Partial pressure of CO₂ in atmosphere</th>
<th>0.00032</th>
<th>0.001</th>
<th>0.01</th>
<th>0.1</th>
<th>1.0</th>
<th>10.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Millimols of CaCO₃ per Kgm. H₂O.</td>
<td>0.52</td>
<td>0.78</td>
<td>1.7</td>
<td>3.9</td>
<td>9.0</td>
<td>22.5</td>
</tr>
</tbody>
</table>

Frear & Johnston state that the temperature coefficient of solubility is, within the accuracy of the experiments independent of the partial pressure of carbon dioxide particularly in the range 0.0003 to 1.0 atmosphere. Consequently it suffices to give the ratio r of solubility at t° to 25°C.

<table>
<thead>
<tr>
<th>t°</th>
<th>0°</th>
<th>10°</th>
<th>20°</th>
<th>25°</th>
<th>30°</th>
<th>50°</th>
</tr>
</thead>
<tbody>
<tr>
<td>r</td>
<td>1.8</td>
<td>1.4</td>
<td>1.1</td>
<td>1.0</td>
<td>0.9</td>
<td>0.6</td>
</tr>
</tbody>
</table>

These values of r lie on the line:

\[
\log r = \frac{830}{T} - 2.78
\]

This formula when extrapolated yields results in harmony with analyses of boiler deposits.
REFERENCES.

The references below are given in the order in which they appear in the text.


11. Ibid. Volume XV No. 9 pages 165 and 178.
20. Ibid.
The author wishes to acknowledge gratefully the following for help in this thesis:

Aquastat Limited - who sponsored the work in the first instance and helped to finance it.

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INITIATION OF BOILER SCALE FORMATION

By J. Freeborn* and D. Lewis†

This paper describes part of a programme of fundamental study of scale formation. The work described here is concerned with the initiation of scale formation at a heating surface where boiling is taking place. The crystalline ring formations first observed by Partridge (1) with calcium sulphate solution were seen using a range of other solutions under various flow conditions. A variety of other formations based on Partridge's rings were also observed. The theory advanced by Partridge that these deposits are due to evaporation at the triple interface of steam bubble, heating surface and solution was in general confirmed. A dynamic mechanism is proposed to explain these formations.

The problem of scale formation has been of increasing importance to engineers ever since the time when steam began to be used industrially, certainly since the time of Watt. Nowadays all but a tiny fraction of our national requirements of power, heat and light are derived from steam. Modern conditions make the problem of scale formation so great that major steps have to be taken to avoid it. These steps on the industrial front consist mainly of complex and costly processes, such as base exchange and distillation, which remove the scale-forming salts from the water. On the domestic front there is no method cheap enough or simple enough for universal application and millions of householders have to suffer the effects of scale rather than employ the expensive means available to prevent it. This picture is well known and inventors have taken out hundreds of patents covering novel methods of scale prevention. These patents have culminated in a few dozen processes being marketed, using chemical, electrical, magnetic and ultrasonic principles. Most of these processes have achieved only a limited success. One of the reasons for this partial success is that very little is known about the physical mechanism of scale formation, so that attempts to solve the problem are frustrated by lack of understanding of the fundamental processes involved. Almost the only work along these lines is that of Partridge (1) in 1931, and concerns the formation of calcium sulphate scale only. As a result of his observations he proposed a mechanism to explain the origin of the rings that occurred on the heat-transfer surface, based on local overheating behind the steam bubbles formed. The theory being that, due to the local increase in temperature of the heating surface under the bubble, fast evaporation at the triple interface of heating surface, steam and water would throw down a deposit which deposit would tend to remain if the solubility slope of the salt with temperature were negative but would tend to be redissolved if the solubility slope were positive.

Other work on scale formation has been carried out notably by Clark, Bunn, Turner, Gray and others but this other work concerns analysis of deposits, ambient temperature precipitation by corrosion cell mechanism and chemical treatment of water to affect the resultant formation. The present work extends Partridge's discoveries to cover a few examples of salts commonly met with in natural waters and it will be shown that although other types of initial deposit than Partridge rings were obtained, the theory proposed by him seems to explain these also in an entirely satisfactory manner. The formation of scale can be divided into groups as under:

1. Deposition at a heat-transfer surface which is hot enough to cause boiling in the liquid, e.g., domestic kettles, steam boilers.
2. Deposition at a heat-transfer surface that is hotter than the liquid, but not hot enough to cause boiling, e.g., domestic hot water boilers.
3. Deposition at a heat-transfer surface that is colder than the scale-forming liquid, e.g., hot water pipes, radiators.
4. Deposition at a surface at the same temperature as the scale-forming liquid, e.g., baffle plates in heat-exchange apparatus.

The work described below is concerned only with the type of formation listed under (1) above. Thin deposits of various salts were formed in an apparatus in which the following conditions were controlled:

1. Flow rate of solution;
2. Chemical content of solution;
3. Energy input to heating surface;
4. Surface finish of heating surface.

The MS. of this paper was first received at the Institution on 21st November 1960 and in its revised form, as accepted by the Council for publication, on 16th August 1961.
† Battersea College of Technology, London.
‡ A numerical list of references is given in the Appendix.

JOURNAL MECHANICAL ENGINEERING SCIENCE
The apparatus was constructed so that the scale formation could be watched using a microscope. It consisted of a Monel plate polished to a mirror finish on one side. The finish was obtained by emery-papering the Monel sheet with progressively finer grades of emery, the final polish being obtained by using metal polish on svelte cloth.

In the polished side a rubber gasket and microscope slide are clamped so that a compartment was formed whose dimensions were 3 \(\frac{3}{4}\) in. wide, 2\(\frac{1}{4}\) in. long and 1\(\frac{3}{4}\) in. deep. The solution under test was led into this compartment through three small holes at one end, and out through similar holes at the other end. The Monel plate was heated by a flat electric element clamped against it on the opposite side to the compartment. The maximum rating of the heater was 50 volts 1.5 amp. The complete cell (Fig. 1) was mounted with its length vertical, so that the observed surface was in a vertical plane, the solution inlet being at the bottom and outlet at the top. Solution flow was regulated by a gravity-operated drip-feed device as shown in Fig. 2. Solutions tested were:

1. Calcium sulphate (saturated solution);
2. Magnesium hydroxide (saturated solution);
3. Sodium chloride (saturated solution);
4. Calcium hydroxide (saturated solution);
5. Tap water as available in the laboratory;
6. Calcium bicarbonate 100 and 20 parts per million.

The solutions of calcium sulphate, magnesium hydroxide, sodium chloride and calcium hydroxide were obtained by crushing selenite gypsum and brucite in the first two cases and adding excess to distilled water. The last two solutions were obtained from laboratory chemicals. All solutions were boiled with excess solute and cooled to 20°C, at which temperature they were used. The calcium bicarbonate...
solutions were made up by suspending the requisite amount of calcium hydroxide in distilled water and then passing gaseous carbon dioxide through it until clear. The solution was heated to 50°C, to standardize the free carbon dioxide content, and cooled to 20°C, at which temperature it was used. These chemicals were chosen as they are to be found regularly in public water supplies, and also furnish examples of compounds with both negative and positive solubility slopes with temperature. The procedure followed with each solution was first to establish a definite rate of flow through the apparatus, after which the heater was switched on and observation of the polished surface began. The heater input energy was maintained at 62.5 W throughout. When the initial scale had formed on the heating surface, the apparatus was switched off and cleaned. Another rate of flow was then selected and the procedure repeated. As pure solutions were used, chemical analysis of the deposit was not necessary except for tap water. The crystal structure of each deposit was obtained by X-ray diffraction techniques. All deposits were photographed. The results obtained were as follows:

(1) Calcium sulphate
At very low rates of flow (60–135 cm/h) rings of crystals were deposited as described by Partridge, namely, each bubble on detachment left behind a ring of crystals. Often the same spot served for the generation of streams of bubbles building up a disc-like deposit within the original rings of crystals. At slightly higher rates of flow (200–450 cm/h) a new phenomenon was observed. As each bubble formed a ring of crystals formed at its contact circle with the heating surface. The bubble grew until its buoyancy was sufficient either to cause its detachment from the surface or to cause it to slide upwards on the surface until it had moved about one-third of a diameter of the ring, when it re-attached and deposited a new ring of crystals; this process was repeated until a ladderlike pattern was obtained, each ring being fractionally greater than its predecessor. After a number of crystal circles had been generated in this manner the bubble had sufficient buoyancy to proceed continuously up the slide leaving two lines of deposit until it appeared to break away completely from the heating surface. Figs 3 and 4, Plate 1, show the resultant ladder network. Here again bubbles were generated at fairly constant centres and streams of bubbles rose up the ladders depositing more and more material. As the flow rate increased this mode of formation reverted to the original type of single rings as experienced at very low flows. With increasing flow (600 cm/h) less and less deposit occurred until it was observed that as each bubble detached its rings of crystals immediately redissolved until a flow was reached at which very few bubbles were formed at all and those that did form tended to remain stationary on the surface.

(2) Magnesium hydroxide
At no flow-rate was any deposit formed on the heating surface.

(3) Sodium chloride
At no flow was any deposit retained on the heating surface. It was seen, however, that when bubbles formed a ring of deposit was formed at the triple interface. These rings of deposit did not remain on the surface when the bubbles became big, and buoyant enough to move away, but detached themselves with the bubbles and apparently redissolved. This effect was soon obscured by a snowstorm-like cloud of crystals thrown out of the body of the fluid as solubility limits were exceeded. At the highest flow rates no precipitation at all was seen.

(4) Calcium hydroxide
With this salt, ring and ladder formation were clearly observed, and the deposit was adherent to the heating surface. At flow rates of 130–220 cm/h ring and ladder formations were observed together (Fig. 5, Plate 1). There was, however, a tendency for the ladder formations to be formed nearer the solution inlet than the rings. These rings were softer and ladders were less distinct than those obtained with calcium sulphate, and the method of growth appeared to be different in that the hydroxide rings filled in quickly to give plaque-like deposits. It was also noticed that if the deposit, when dry, was rubbed with the finger, most of it came away easily leaving the original rings and ladders, 100 pa showing that the adherence of the initial deposit was greater to that formed subsequently with the rings. As the gas flow increased to 528 cm/h the ladder formations were not so apparent, a ring tracer only being produced (Fig. 6, Plate 1). At fast rates of flow (1048 cm/h) rings were seen together with V trails, that is, ladders without the steps. Fig. 1 Also, one example of cotangential formation was observed (Fig. 7, Plate 2).

(5) Tap water
An analysis of the water used is given in Table 1. At lower flow rates (230–430 cm/h) ring and ladder deposits occurred (Fig. 8, Plate 2) and here also the ladder formations were the nearer the inlet than the rings. These rings were well defined on examination; with high power the crystals were just discernible as having the calcite shape. At higher rates of flow the deposit was smooth and thin, a tracer being produced.

<table>
<thead>
<tr>
<th>Table 1. Certificate of analysis of a sample of water marked College Laboratory tap water</th>
</tr>
</thead>
<tbody>
<tr>
<td>This sample on examination gave the following results:</td>
</tr>
<tr>
<td>Total solid matter, dried at 100°C</td>
</tr>
<tr>
<td>Hardness, temporary</td>
</tr>
<tr>
<td>Hardness, permanent</td>
</tr>
<tr>
<td>Total alkalinity, CaCO₃</td>
</tr>
<tr>
<td>Chlorides, Cl</td>
</tr>
<tr>
<td>Sulphates, SO₄</td>
</tr>
<tr>
<td>Carbonates, CO₃</td>
</tr>
<tr>
<td>Calcium, Ca</td>
</tr>
<tr>
<td>Magnesium, Mg</td>
</tr>
<tr>
<td>Carbon dioxide, free</td>
</tr>
<tr>
<td>pH value</td>
</tr>
</tbody>
</table>
INITIATION OF BOILER SCALE FORMATION

(1) V tracks of the same outer shapes as the ladder formations but lacking the steps. Here the bubble was initially stationary until it had grown big enough for its buoyancy to start its ascent as in the case of ladders. Once the ascent was started, however, it continued smoothly and left two tracks. The distance between the tracks increased as the bubble rose. The tracks originated from that part of the triple interface whose tangents were a few degrees below the horizontal diameter of the bubble. Here again, more than one bubble made the journey, each bubble adding to the original deposit.

(2) Concentric ring deposits. These deposits were seen only twice with 20 parts per million calcium bicarbonate and were not observed in process of formation hence the mechanism is unknown. It could have had a mechanism similar to (4), and perhaps be a further example of suppressed boiling. Alternatively, small rings could have formed first, followed by larger rings from larger bubbles, possibly being the result of a local temperature rise in the heating surface. Both the observed formations had a V-shaped track leading up from the centre, which apparently indicates the route taken by the bubbles on leaving the surface.

The five types of deposit did not all occur with every salt tested. The frequency of occurrence is noted in Table 2. Also, there was a relation between the rate of flow and the type of deposit. This is indicated in Fig. 14.

The non-appearance of any deposit from the solution of magnesium hydroxide may be due to the fact that this salt is considered to be deposited indirectly by the action of soda-lye or magnesia (2) which chemical mechanism was not provided in these tests. The theory of scale formation in association with bubbles has been indicated by Partridge (1). The fact that rings of deposit were observed with solutions of sodium chloride strongly bears out his theory that evaporation takes place at the triple interface. With this salt, whose solubility increases with temperature, a temperature rise in the solution as it nears the heating surface could not precipitate a deposit, as with calcium sulphate, for example, hence evaporation must have taken place for a deposit to occur at all, and the only place at which this could take place was into the steam bubble. The question of the mechanism causing the deposits has not been fully resolved. This mechanism could be either static or dynamic. In the case of the static mechanism steam would be generated at the triple interface and would form the bubble. The deposit would arise as a result of the evaporation causing

CONCLUSIONS

These experiments throw light on to the initiation of scale deposits in one common type of scale formation, i.e., the film formation which occurs at a heating surface that is hot enough to cause boiling in the scale-producing fluid.

(1) Plain rings of deposit formed at the edge of one bubble that grew until its buoyancy overcame the forces retarding its ascent to the heating surface. The bubble upon detachment rose straight to the surface without touching the heating surface again.

(2) Ladder-like formations where a bubble deposited an initial ring then moved up the surface by a fraction of its diameter when it again became stationary and deposited a fresh ring. This procedure was repeated a number of times, and at each step the bubble became fractionally bigger, hence the edges of the formation were V-shaped. More than one bubble made the journey up the ladder, and each bubble added to original steps in the ladder. In most cases the ladder ended abruptly when the depositing bubble broke completely away from the surface. In some cases the bubble, after making the journey up the ladder did not break completely from the surface, but slid up with a uniform motion leaving two continuous lines of deposit.

(3) V tracks of the same outer shapes as the ladder formations but lacking the steps. Here the bubble was initially stationary until it had grown big enough for its buoyancy to start its ascent as in the case of ladders. Once the ascent was started, however, it continued smoothly and left two tracks. The distance between the tracks increased as the bubble rose. The tracks originated from that part of the triple interface whose tangents were a few degrees below the horizontal diameter of the bubble. Here again, more than one bubble made the journey, each bubble adding to the original deposit.

(4) Concentric ring deposits. These deposits were initiated from one bubble which grew until bigger than average, when it detached itself, leaving a larger ring. Successively, smaller concentric rings were then formed in quick succession within the initial ring. This type of formation was very rare and may have been an example of suppressed boiling.

(5) Concentric ring deposits. These deposits were seen only twice with 20 parts per million calcium bicarbonate and were not observed in process of formation hence the mechanism is unknown. It could have had a mechanism similar to (4), and perhaps be a further example of suppressed boiling. Alternatively, small rings could have formed first, followed by larger rings from larger bubbles, possibly being the result of a local temperature rise in the heating surface. Both the observed formations had a V-shaped track leading up from the centre, which apparently indicates the route taken by the bubbles on leaving the surface.

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Table 2. Frequency of occurrence of the five types of deposit on a heating surface of 2.06 in²

<table>
<thead>
<tr>
<th></th>
<th>Calcium sulphate</th>
<th>Calcium bicarbonate</th>
<th>Calcium hydroxide</th>
<th>Sodium chloride</th>
<th>Magnesium hydroxide</th>
<th>Tap water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plain rings</td>
<td>&gt; 10^3 &lt; 10^4</td>
<td>&gt; 10^3 &lt; 10^4</td>
<td>&gt; 10^2 &lt; 10^3</td>
<td>&lt; 10</td>
<td>0</td>
<td>&gt; 10^3 &lt; 10^4</td>
</tr>
<tr>
<td>Ladders</td>
<td>&gt; 10^2 &lt; 10^3</td>
<td>&gt; 10^2 &lt; 10^3</td>
<td>&gt; 10 &lt; 10^2</td>
<td>0</td>
<td>0</td>
<td>&gt; 10^2 &lt; 10^3</td>
</tr>
<tr>
<td>V tracks</td>
<td>&gt; 10 &lt; 10^2</td>
<td>0</td>
<td>&gt; 10 &lt; 10^2</td>
<td>0</td>
<td>0</td>
<td>&gt; 10 &lt; 10^2</td>
</tr>
<tr>
<td>Cotangential rings</td>
<td>0</td>
<td>0</td>
<td>&lt; 10</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Concentric rings</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Fig. 14. Relation between flow and type of deposit
his steam, and would at the most be proportional to the volume of the bubble. The growth of the deposit would be the result of successive bubbles, each leaving a further increment. In the case of the dynamic mechanism water would be continuously evaporated into the bubble, and at the same time continuously condensed at the outermost surface of the bubble where the solution bulk is cooler than at the heating surface. Thus deposit would be continuously deposited during the life of the bubble, and the mount would not depend upon the volume of the bubble. Thus, the dynamic theory would allow for a considerable mount of deposit to be precipitated under each bubble. The hypothetical picture of this is as shown in Fig. 15. The amount of deposit will depend upon the following factors:

1. Amount of water evaporated at the triple interface. It is known that the general heating surface temperature is above that of the liquid, and that the temperature under the bubble is higher than that of the general heating surface. As the bubble is formed a weight of deposit is produced proportional to the amount of water evaporated into the bubble and being condensed at the outermost region. It is possible that a large amount of deposit dependant upon the life of the bubble will be thrown down.

2. Amount of water evaporated at the double interface. The hot spot in the heating surface under the bubble may cause superheating of the steam in the bubble. As this superheated steam circulates in the bubble, it will come into contact with the solution and cause further evaporation into the bubble. This evaporation will cause precipitation on the surface of the bubble, and this unattached precipitate will either coalesce with the material on the heating surface or remain in the liquid and give rise to the sludge that is often found in steam boilers.

3. The solubility slope of the salts in solution. Because the heating surface is at a higher temperature than the solution, there will be a temperature gradient in the latter. Therefore, any increase or decrease in solubility of the salts in solution with temperature will have an effect upon the precipitation occurring at the heating surface. Thus, in the case where no bubbles are forming, precipitate will tend to be thrown down from a solution with a negative solubility slope, or taken up by a solution with a positive solubility slope. In the case where bubbles are forming, a negative solubility will increase the amount of deposit at the triple and double interfaces and positive solubility slope will lessen this amount.

If the observed deposit were due to the static mechanism alone, then the amount formed per bubble would be easy to calculate, since it only involves a knowledge of the bubble volume and the concentration of the salt in solution. Assuming a bubble to be of diameter, which occupies a volume of \( 1 \times 10^{-12} \) lb weight which could be represented by a cube of side \( 2.8 \times 10^{-4} \) in. This it may be seen that if one bubble could be observed and the amount of material deposited measured, the precise mechanism could be established. This was not achieved in the present experiments, as bubbles streamed out from one point at high speed making it impossible to see how much deposit each bubble caused. High-speed cinematography might decide this issue. The occurrence of different types of formation, e.g., rings and ladders, together, shows that the type of formation is dependent on factors other than flow, and it is felt that temperature is one of these factors. In the apparatus only the central portion was heated and as cold solution was introduced at one end temperature gradients must have existed with the inlet area being the coolest part. Several times ladders formed near the inlet, and rings further up, and hence as other conditions were the same it can be seen that the temperature was affecting the mode of formation. It is
felt that useful results will be obtained by extending these tests so that the temperature of the surface was known as well as the energy input.

Further work is in progress on the mechanism of scale adhesion and this will appear in a later paper.

ACKNOWLEDGEMENTS
Thanks are due to Aquastat Ltd for sponsoring and largely financing this work which was carried out by the authors in the Crystallography Department of Battersea College of Technology. Thanks are also due to Mr D. J. White for technical assistance.

APPENDIX
REFERENCES
(2) Mellor, J. W. 1923 'Treatise on inorganic chemistry', vol. 4, p. 291 (Longmans).
This and following photographs flow is indicated by an arrow on the top.

**Fig. 3. Calcium sulphate**

**Fig. 4. Calcium sulphate**

**Fig. 5. Calcium hydroxide**

**Fig. 6. Calcium hydroxide**
Fig. 7. Calcium hydroxide

Fig. 8. Tap water

Fig. 9. Tap water

Fig. 10. Calcium bicarbonate
Fig. 11. Calcium bicarbonate

Fig. 12. Calcium bicarbonate

Fig. 13. Calcium bicarbonate