

The Effect of Heat Transfer
on Corrosion in Boiling Media

by

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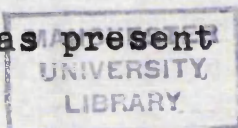
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Abstract

An apparatus was designed to study the effect of heat transfer on corrosion in boiling solutions. This enabled the separation of the effects of heat transfer and surface temperature. Previous workers had suggested that surface temperature was the important factor rather than heat transfer, but no work had been reported which had made a separate study. Boiling conditions, however, allowed large increases in heat transfer rates to occur with only small changes in surface temperature. Runs were initially carried out using mild steel specimens in aerated and deoxygenated distilled water using an inductively wound electrical heater. Problems arose due to induced currents, but these were eventually overcome using a non-inductively wound former. A comparison of the results of runs with various forms of heating indicated that the induced currents had little or no effect on the corrosion processes involved. The main series of runs was then continued and experiments were performed with the same agents but for varying times of exposure. Similar runs were performed with copper specimens, an electropositive metal as opposed to steel, which was electronegative. Having drawn conclusions from a comparison of the two series of experiments, runs were performed using copper specimens in different concentrations of sodium chloride solution. Results indicated that, for steel, while oxygen was present the corrosion rate was



independent of heat transfer rates, and therefore surface temperature was probably the controlling factor. However, with copper it was found that the corrosion rate varied with heat transfer in the presence of oxygen and this was thought to be due to the formation of stable oxide films on the surface at higher heat flux rates, and therefore both heat transfer and surface temperature were important. Results in chloride solutions indicated that the transfer of the chloride ions to the surface was a controlling factor in the processes and at higher heat transfer rates the corrosion rate increased, due to increased mass transfer.

The Author

The author was awarded the degree of B.Sc.Tech. with Honours. (2:1) in Chemical Engineering in June 1962 after three years full time study in the Department of Chemical Engineering, Faculty of Technology, University of Manchester.

Since that time he has been engaged in full time research in the Corrosion Science Group within the Department of Chemical Engineering and has held a Research Studentship awarded by the Science Research Council, (late D.S.I.R.).

Declaration

This is to declare that no part of this work has been published in a thesis for a degree at this or any other University.

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Contents

		Page
<u>Chapter 1</u>	An introduction	1
1.1	An introduction to corrosion	2
1.2	An introduction to heat transfer & boiling	5
	1. Conduction	5
	2. Convection	6
	3. Radiation	6
	4. Boiling	8
	5. Mechanism of Nucleate boiling	9
1.3	An introduction to Heat Transfer and Corrosion	10
<u>Chapter 2</u>	The design and method of operation of the Apparatus	21
2.1	Introduction	22
2.2	The heat supply system	23
2.3	The vessel	25
2.4	The specimens	27
2.5	Measurement	29
	1. Surface temperature	29
	2. Heat Transfer rates	33
	3. Electrode potential	33
	4. pH of the solution	34
<u>Chapter 3</u>	Start up and preliminary experiments	35
3.1	Introduction	36
3.2	Specimen treatment	36
3.3	Start up	38

		Page
3.4	Experimental procedure in preliminary Runs	39
3.5	Results of preliminary runs	40
	1. Potential measurement	40
	2. Weight loss measurement	41
	3. Temperature measurement	41
	4. pH measurement	41
	5. Visual observations	42
3.6	Conclusions and discussion	43
	1. Potential-time curves	43
	2. pH changes	44
	3. Weight loss versus heat flux	45
	4. General discussion	46
<u>Chapter 4</u>	Experiments in Deoxygenated solutions	52
4.1	Introduction	53
4.2	Design and construction of the modifications	53
	1. The packed tower	53
	2. Oxygen concentration measurement	56
4.3	Method of operation of the apparatus	57
4.4	Results	58
	1. Potential time curves	58
	2. Weight loss measurement	58
	3. pH measurement	59
	4. Visual observations	59
	5. Oxygen concentration measurement	59
	6. Surface temperature measurement	59
4.5	Conclusions and discussion	60

		Page
<u>Chapter 5</u>	The change of corrosion rate with time	63
5.1	Introduction	64
5.2	Experiments with various forms of electrical heating	64
	1. Alternating current experiments	66
	2. Direct current experiments	66
	3. Results	67
5.3	Experiments with time as a parameter	68
	1. Experimental	68
	2. Results	68
	Potential readings	69
	Weight loss curves	69
	Oxygen concentration measurement	69
5.4	Conclusions and discussion	70
<u>Chapter 6</u>	Runs using copper specimens in various solutions	72
6.1	Introduction	73
6.2	The specimens	73
6.3	Experiments in aerated distilled water	74
	1. Results	75
	a) Potential measurement	75
	b) Oxygen concentration	75
	c) Weight loss determinations	75
	d) Visual observations	76
	e) pH measurement	76
	Conclusions and Discussion	76

	Page
6.4 Experiments in aqueous sodium chloride solutions	80
1. Results	81
a) Potential measurement	81
b) Weight loss determinations	81
c) Visual observations	82
d) pH determinations	82
2. Conclusion and discussion	82
<u>Chapter 7</u> Overall conclusions and discussion	86
Suggestions for future work	89
<u>Appendix 1</u> Determination of surface temperature and heat transfer rates	90
A.6.1 Introduction	91
A.6.2 Measurement of surface temperature	91
A.6.3 The calculation of heat transfer rates	93
<u>Appendix 2</u> Results of preliminary runs	96
A.6.1 General	97
A.6.2 Particular results	97
<u>Appendix 3</u> The design of the packed column	102
<u>Appendix 4</u> Calibration of the oxymeter	106
<u>Appendix 5</u> Results of experiments with deoxygenated solutions	109
1. General	110
2. Particular results	110
<u>Appendix 6</u> Results with time as a parameter	118
A.6.1 Runs with various forms of heating	119

	Page
1. Alternating current	119
2. Direct current	120
A.6.2 Runs with time as a parameter	121
1. Aerated solutions	121
a) Weight loss	121
b) Oxygen concentration	121
2. Deoxygenated solutions	122
a) Weight loss	122
b) Oxygen concentration	122
<u>Appendix 7</u> Results of runs using copper specimens	123
A.7.1 Aerated solutions	124
1. Weight loss	124
2. Oxygen concentration	124
A.7.2 1gr/ltr sodium chloride solution	125
A.7.3 10gr/ltr sodium chloride solution	125

Chapter 1

An Introduction

1. An Introduction to Corrosion

Corrosion has been defined as the destruction of a substance by chemical or electrochemical agencies. The destruction of metals - such as iron or steels - are probably the best known examples.

To illustrate the mechanism of metallic corrosion, consider a metal, m , immersed in an aqueous electrolyte. Due to various factors, some zones of the metal will become anodes, some will become cathodes. The anode reaction will result in the formation of metallic ions and a number of electrons, depending on the valency of the metal. The reaction may be symbolised thus:-



The formation of anode areas is favoured by the absence of dissolved oxygen in the immediate area and the absence of protective oxide films on the surface.

For the cathode reactions there are alternatives. If no oxygen is present, hydrogen gas may be liberated, and the reaction symbolised thus:-



If oxygen is present, hydroxyl ions are produced by the combination of oxygen, water and available electrons. The

reaction may be symbolised thus:-



Although some authorities symbolise the reaction as:-



The reduction proceeds in stages, hydrogen peroxide being an intermediate product. The presence of oxide films, dissolved oxygen close to the surface, and metal electrolyte interfaces with the power to catalyse reactions 1(ii) and 1(iii) will favour cathodic behaviour.

Electrons produced by the anodic reaction 1(i) and remaining at the metal surface will transfer to the cathode via the metal and take part in the cathodic reaction (ii) or (iii). Due to the passage of this current polarisation may occur at the cathode and/or the anode resulting in a tendency for their potentials to approach each other.

Evidence for the electrochemical nature of aqueous corrosion was provided by Thornhill and Evans¹. They distinguished between anodic and cathodic areas on a partially immersed zinc plate in N/100 sodium chloride solution, and observed that attack only occurred at areas which were at that time anodic. Accurate measurements of the currents flowing on a single metal specimen were carried out by Hoar and Evans² using steel specimens in potassium chloride.

solutions. They also established that calculations expected weight loss from measurements of the potential difference and current flow between the anode and cathode were in very close agreement with the observed weight loss. Agar and Evans³ performed similar work with zinc and came to the same conclusions.

For a reaction to occur spontaneously there must be a decrease in the free energy between initial and final states. However because there is a decrease in free energy, it does not necessarily follow that the reaction will occur spontaneously. There may be an intermediate activated state of higher energy creating a barrier which must be overcome. Consider the reaction:-



to be exothermic. Generally heating such a system introduces two factors, the addition of energy to the system and an increase in temperature. An increase in the energy of the system, by Le Chatelier's Principle, would be expected to move the reaction equilibrium to the left - causing a reduction of the corrosion. An increase in temperature would cause an increase in the reaction rate causing an increase in the corrosion at a give time. Generally speaking the effect of the increased reaction rate is the more

important factor, and corrosion would increase with an increase in heat transfer. If the reaction 1(i) was endothermic the addition of energy to the system would cause a shift of the equilibrium to the right, increasing corrosion. An increased temperature would lead to an increase in the reaction rate, and the overall corrosion would be expected to be greater.

Boiling produces different conditions from heat transfer without phase change, since large changes in heat input result in small changes in temperature and the increase in the reaction rates would be correspondingly smaller. Thus, depending on the extent of the change of the reaction rates for exothermic reactions an increase in heat transfer might result in a decrease in corrosion, and for endothermic reaction an increase might be expected.

This considers only the anodic half cell, the cathodic reaction may also be affected by heat transfer depending on the prevailing conditions.

Let us now consider the modes of heat transfer which would result in this boiling state.

2. An Introduction to Heat Transfer and Boiling

There are three basic modes of heat transfer. Namely:-

1. Conduction

Conduction is the transmission of heat from one part of

a homogeneous opaque solid to another, under the influence of a temperature gradient without appreciable displacement of the particles.

2. Convection

Convection is the transmission of heat by the mixing of parcels of fluid at different temperatures with one another. This mixing may be caused naturally, such as mixing due to density differences resulting from temperature differences within the fluid, or mixing by forced means, such as mechanically stirring. Heat energy may be transferred simultaneously by conduction, and in transparent media by radiation.

3. Radiation

Radiation is the transmission of heat by the emission of radiant energy in all directions. When this energy strikes another body it may be reflected, transmitted or absorbed. In the case of the latter the amount of energy absorbed is transferred quantitatively into heat.

For the work in this thesis the most important mode of heat transfer is convection, which will be dealt with in more detail.

Heat transfer rates from a solid surface to a fluid have been defined⁴ by the equation

$$q_c = h_m A(t_w - t)$$

where q_c = heat transfer rate

h_m = coefficient of heat transfer from the surface of the solid to the fluid, excluding radiation.

t_w = surface temperature

t = bulk temperature of fluid

The coefficient of heat transfer, h_m , depends on several factors, such as the properties of the fluid, the dimensions of the apparatus, the fluid velocity past the surface and the temperature potential, Δt . These conditions may vary at different parts of the surface and therefore the heat transfer rate may also vary from point to point. Consider the aspect of fluid velocity past the surface. Under isothermal conditions workers^{5,6} have shown the nature of flow of fluids past cylindrical models. Eddies form at the rear of the cylinder, eventually become too large and are swept downstream. An idealised drawing of the flow pattern is shown in Fig.1.1. From this it can be inferred that for a fluid flowing at right angles to a heated tube the coefficient of heat transfer will not be uniform around its perimeter. Work by Drew and Ryan⁷ established the local rate of heat flow plotted radially around a cylinder. The plot is shown in Fig.1.2. From this it can be seen that maximum heat transfer occurs at the leading and trailing sections of the tube. The value at the sides being approximately 40% of the maximum. For

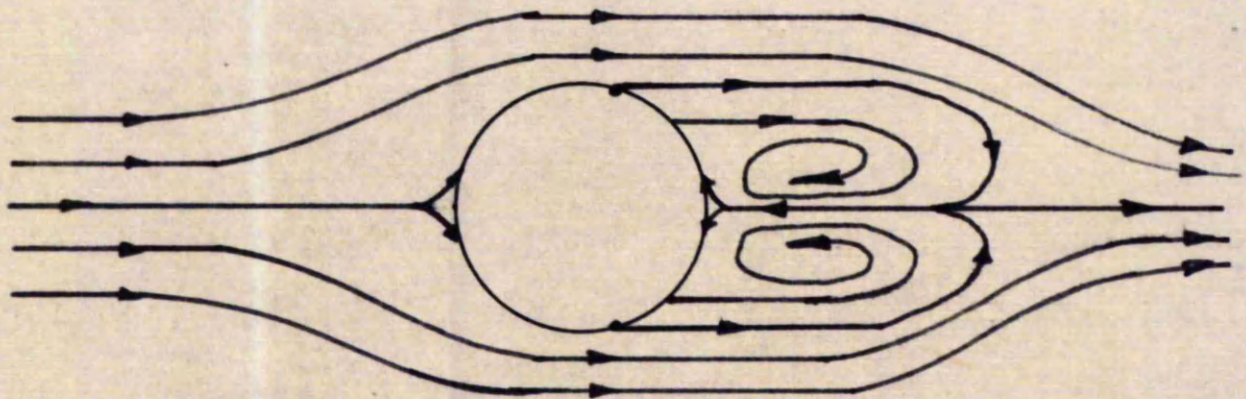


FIG 1.1. Idealised flow patterns of a fluid passing perpendicular to a cylinder.

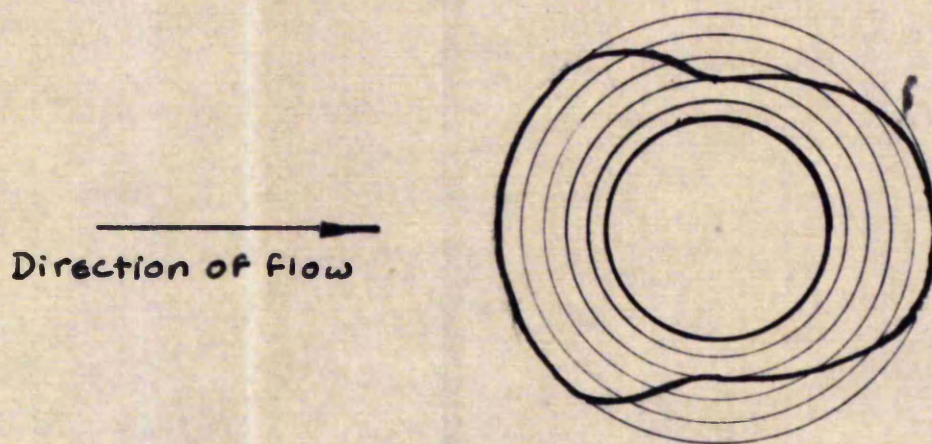


FIG.1.2. Distribution of heat flow per unit area passing perpendicular to a cylinder.

practical purposes an average coefficient is more convenient but this distribution should be borne in mind.

4. Boiling Liquids

When the vapour pressure of a liquid is equal to that of the atmosphere bubbles of vapour are formed and the liquid is said to boil. Consider the boiling of a liquid at a heated surface submerged in a pool of the liquid. Several workers observed the existence of various regimes of boiling. Data was presented by Drew and Meuller⁸ and can be summarised in Fig.1.3. The regimes shown in the diagram may be defined as follows.

AB Natural convection

The water is being superheated and evaporation occurs only at the surface of the pool.

BC Nucleate boiling

Bubbles of steam form at active sites on the heated surface and rise through the pool.

C The critical Δt

At this point the heat flux goes through a maximum and is the limit of the nucleate boiling regime.

CD Partial film boiling

Part of the surface is insulated with a vapour film, the heat flux decreases as Δt increases and more of the surface is insulated by the film.

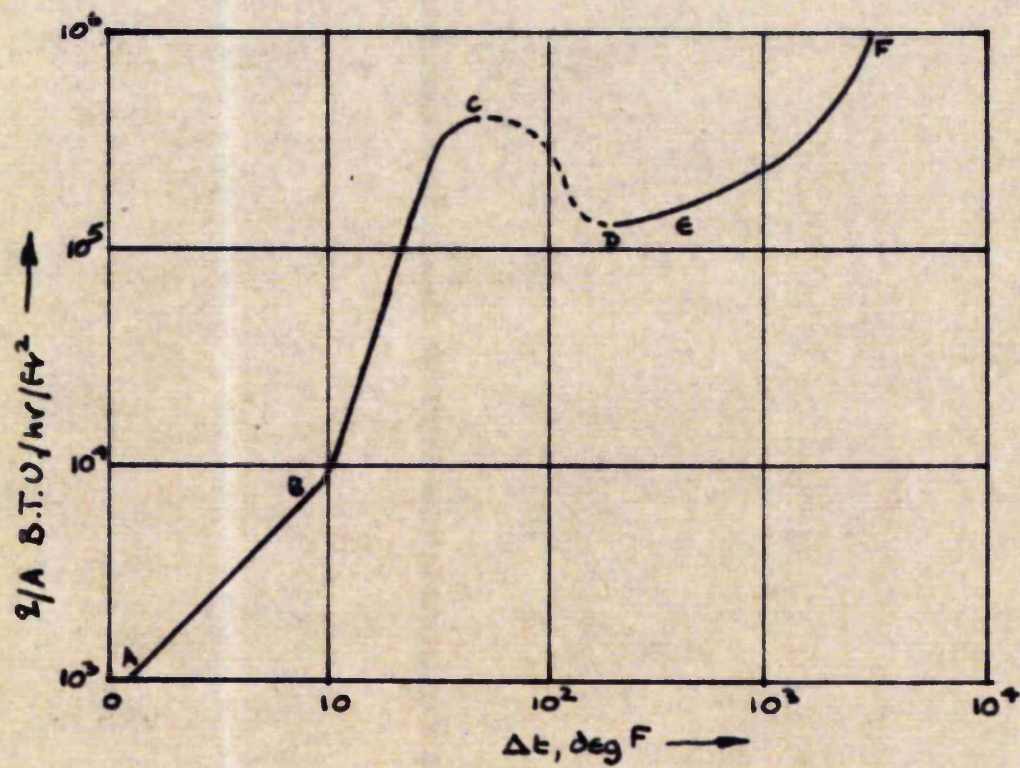


FIG 1.3. Boiling of water at 212°F on an electrically heated platinum wire.

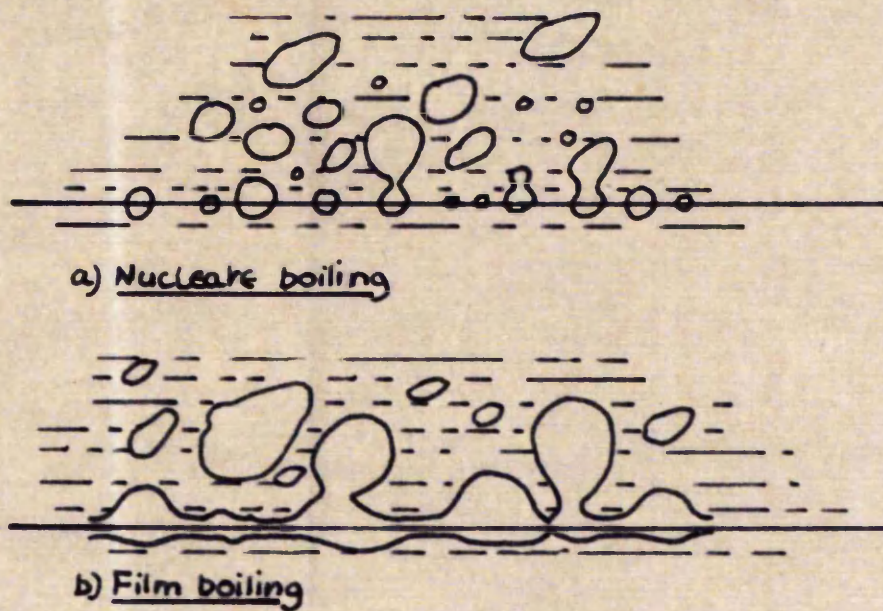


FIG 1.4. Comparison of nucleate and film boiling

D The Leidenfrost point

The heat flux goes through a minimum as all the surface is covered with the vapour film.

DEF Film boiling

Heat is transferred through the film by conduction and radiation.

F corresponds to the melting point of the wire. The difference between film and nucleate boiling is shown in Fig.1.4.

5. The Mechanism of Nucleate Boiling

The vapour pressure over a small concave liquid surface, such as a steam bubble in water is less than that over a flat liquid surface at any given temperature. Therefore for a given pressure the liquid must be hotter to evaporate into a small vapour bubble than into the vapour space above the liquid. Due to this bubbles tend to form at active sites on the heating surface where conditions of temperature and surface are favourable. Depending on the nature of the surface, different degrees of superheat will be required. The rougher the surface, the more sites there are available and therefore the lower the Δt required. In the water boiling at atmospheric pressure Cooper⁹ found that overall heat transfer coefficient in a submerged tube evaporator was larger with iron than with copper tubes, indicating the

increase in number of sites on the, rougher, iron tube more than compensated for the decreased thermal conductivity.

The heat transfer range of the work in this thesis falls within the nucleate boiling region.

3. An Introduction to Heat Transfer and Corrosion

The importance of the effect of heat transfer on corrosion processes has been known for some time. Speller¹⁰ discusses methods of preventing corrosion in hot water heating systems, advocating such things as the control of oxygen concentration and the pH of the water. However little systematic study¹¹ was made until the work of Groves and Eisenbrown in 1959. In their work an external heating source kept the surface temperature of metal specimens above that of the solution, thus transferring heat from one to the other. The apparatus was as shown in Fig.1.5. The specimens were in the form of stainless steel discs clamped to the base of the corrosion vessel in close contact with a flat ground soldering iron element of 550 watt. The solution used were various concentrations of chemically pure sulphuric acid - the boiling points ranging between 215^o F and 235^o F. An external heating coil maintained the temperature within and a condenser was used above the solution surface. Measurements taken during the runs were solution temperature and metal temperature,

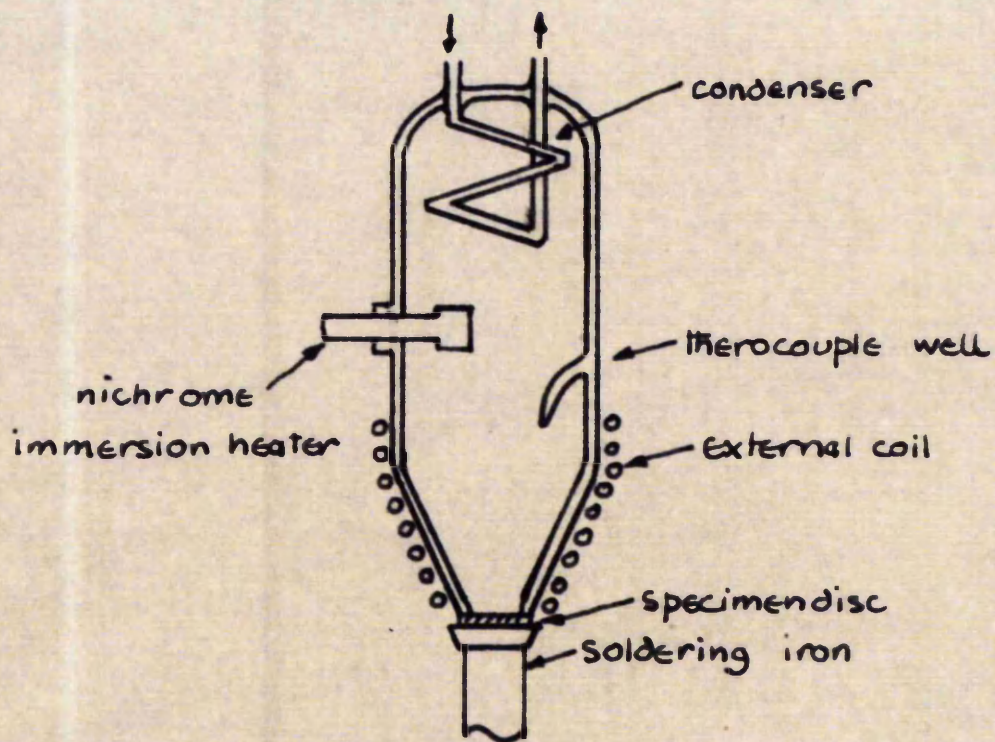


FIG 1.5. Apparatus due to Groves and Eisenbrown.

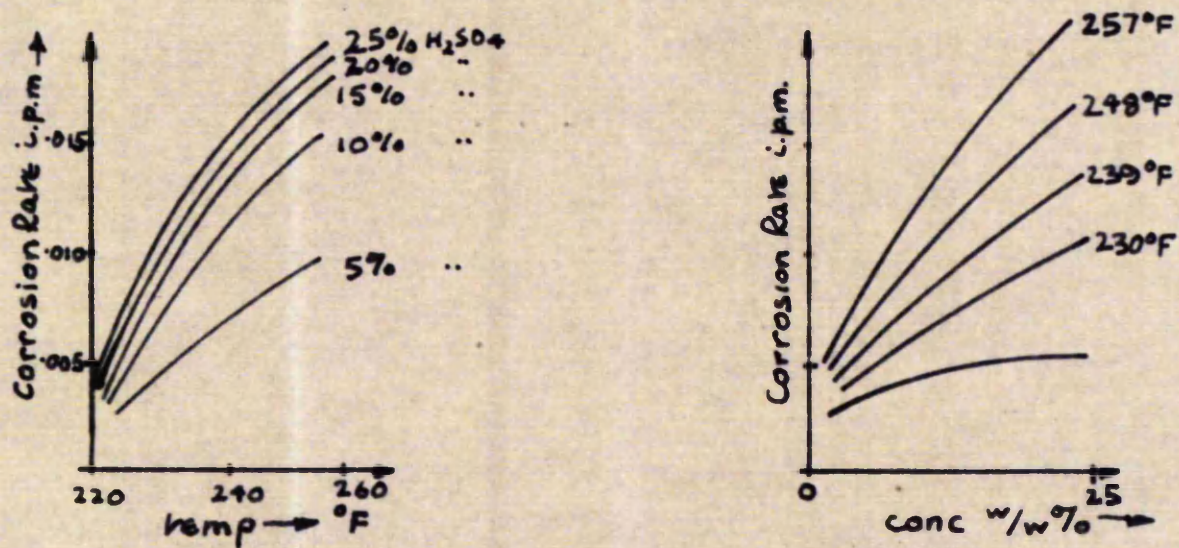


FIG 1.6. a) Corrosion of Carpenter 20C-b. steel versus Surface temperature.
b) Corrosion of Carpenter 20C-b. steel versus Acid concentration.

the latter being measured by means of a thermo-couple placed in a hole drilled edge to centre in the specimen. The solution was changed every forty eight hours during a run to prevent accumulation of the corrosion product. After each run the specimens were reweighed and the weight loss calculated. The specimens underwent stringent procedures of pre run preparation to ensure reproducibility, and runs were of ten days duration. The results, shown in Fig.1.6, were plotted in the form of graphs which indicated an increase in corrosion with increasing metal surface temperature for a given acid concentration, and an increase in corrosion with increasing acid concentration for a given surface temperature.

Three further types of apparatus for studying heat transfer corrosion problems were discussed by Fisher and Whitney¹². The first apparatus was as shown in Fig.1.7. The specimen was in the form of a cast iron rod which was clamped between two large, low resistance electrodes, connected to a half kilowatt transformer. Thus heat was generated by passing an electric current through the specimen. The corrosive media used were molten inorganic salts, whose temperatures were maintained by an external heating source. Mild stirring was provided. The technique was satisfactory practically, but academically it was lacking, since it considered only heat transfer rates and not surface

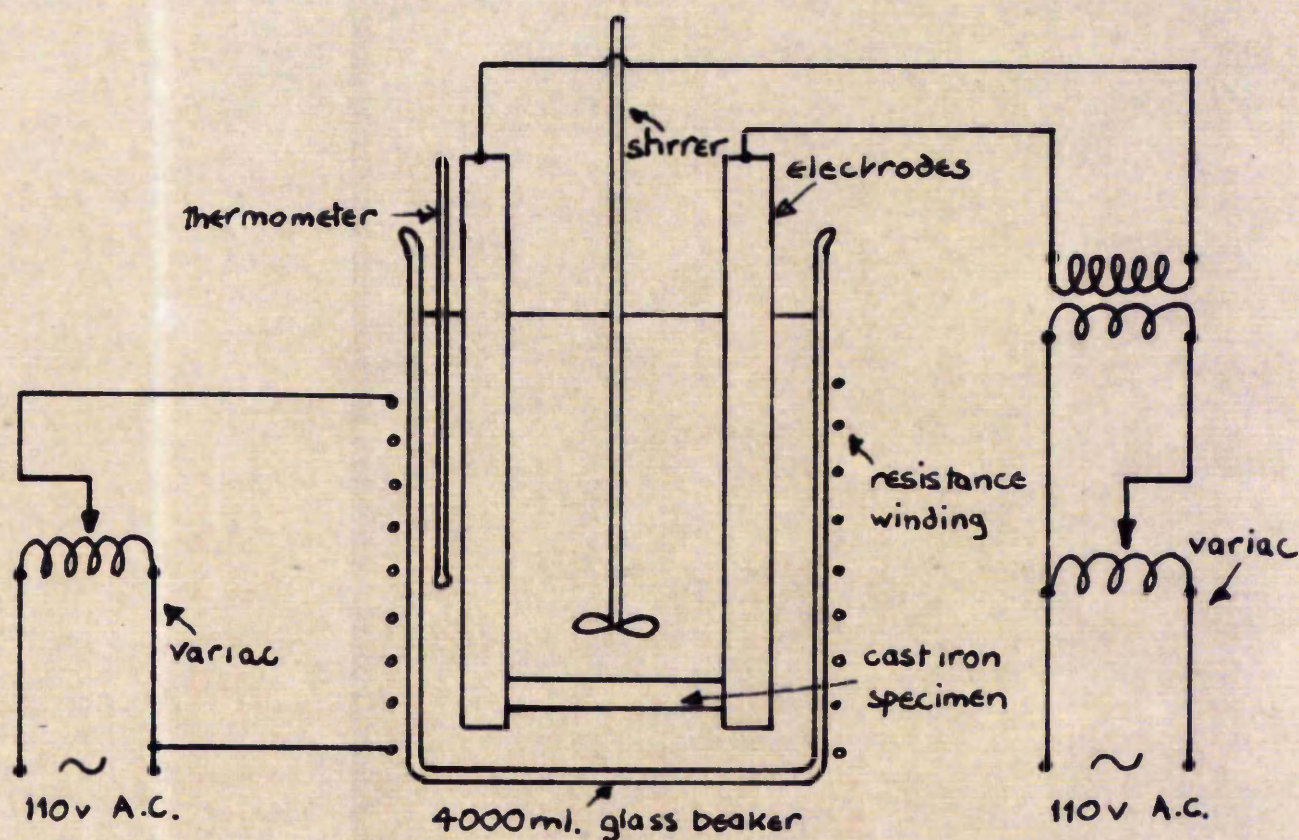


FIG 1.7. Resistance heating apparatus due to Fisher and Whitney

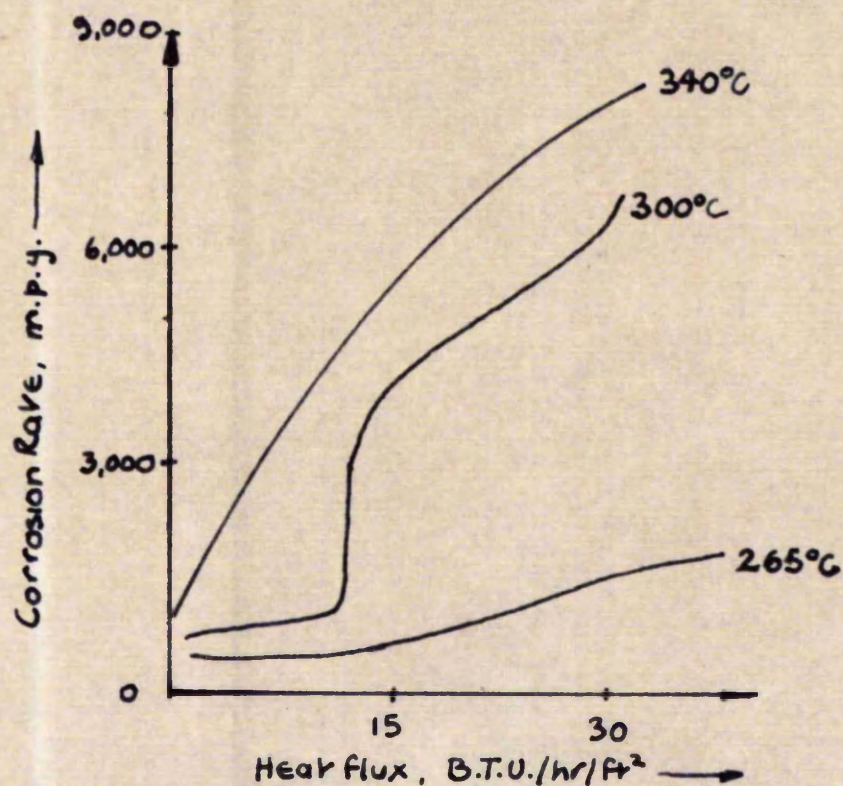


FIG 1.8 Results of Resistance heating Apparatus for cast iron in molten salt.

temperature, no attempt being made to measure it. Other shortcomings were

1. In a conductive environment electrical leakage would occur.

2. Heat distribution was not uniform, the temperature being higher at the middle.

3. Voltage corrections were high in comparison with current corrections.

All the above lead to inaccuracy in the heat flux calculations. Factors not considered in the paper are those of electron excitation and the effect of alternating current on the system. Evans¹³ states that, often, alternating current acting alone produces little corrosion, the cathodic half period replacing the metal which passed into solution during the anodic half period. This is only true at high frequencies, and at low frequencies the damage due to a given current increases. Hohn¹⁴ observed that if impurities were present these may well be deposited during the cathodic half period and therefore the damage done during the anodic half period would only be partially repaired. Also a self stifling process might be disturbed by continuous change from oxidation to reduction, producing volume changes in the product which could lead to porosity in a normally stifling film. Torigoe¹⁵ making a study of the effect of alternating

current on the corrosion process of iron found that for small impressed alternating currents the corrosion current was increased in acid solutions, but little changed in neutral solutions. Thus it can be seen that using direct electrical heating is - to say the least - suspect.

The results of the "resistance specimen" apparatus are shown in Fig.1.8. Fisher and Whitney observed that the heat flux was critical at approximately 9,000 - 12,000 BTU/hr.ft² when the salt temperature was 300 C. At a salt temperature of 265 C no critical heat flux was observed. This would tend to imply that the surface temperature rather than heat flux was the important factor in corrosion control. The author suggests that the critical heat transfer rate corresponds to the beginning of salt dehydration.

The second apparatus described uses a tubular specimen heated from within by a 300 watt quartz heater as shown in Fig.1.9. The heating system is much more satisfactory. The heat flux is easily controlled and there is no problem from current leakage or electron excitation. It also serves as a quick and ready method of testing tubular stock. No surface temperature measurements were taken, which was a severe limitation, but it would have proved difficult to have made the measurements, radiation from the quartz heater being the main objection. Also such a heavy specimen,

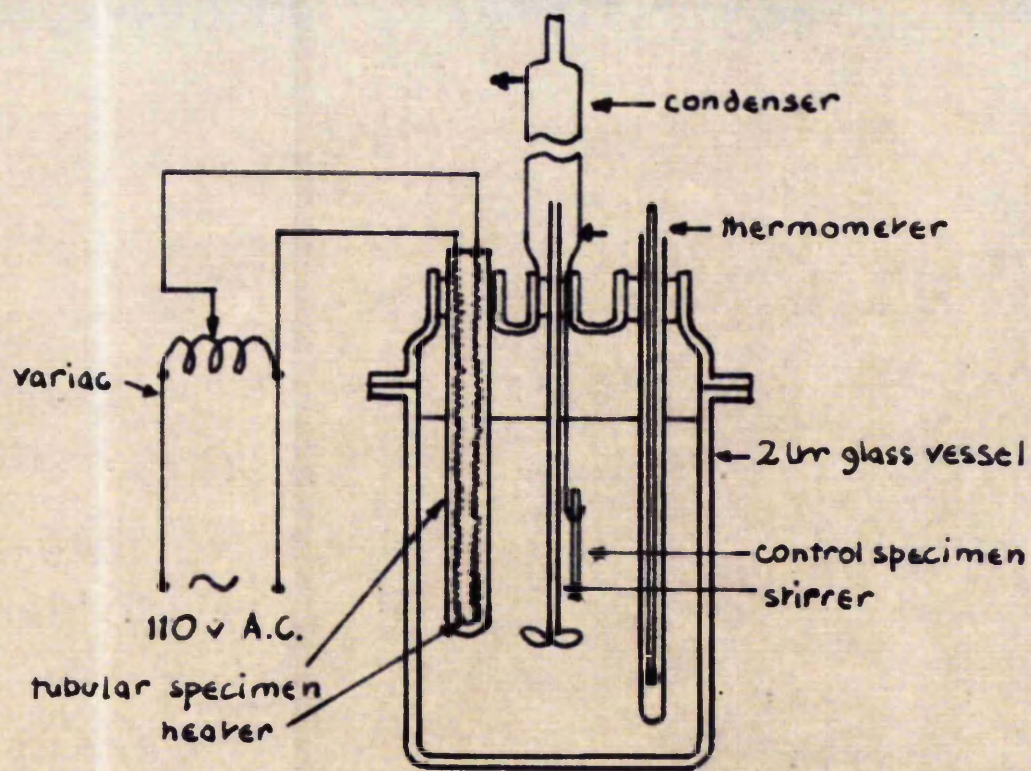


FIG 1.9. Tubular specimen apparatus due to Fisher and Whitney

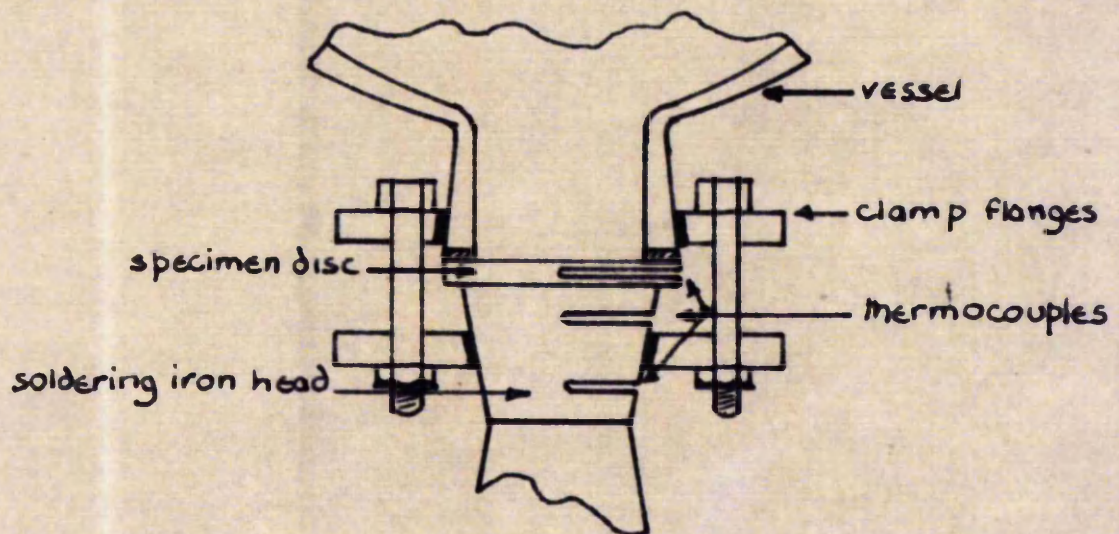


FIG 1.10. Modifications to disc specimen apparatus due to Fisher and Whitney

approximately 150 grams would render weight loss determinations inaccurate. Tests were carried out on 316 Stainless Steel in phosphoric acid. Once again the workers inferred that surface temperature was the important factor, and suggested that immersion tests at a given elevated temperature would give useful information, this though seems to be rather begging the question since from observations it seems more likely that it is the surface temperature relative to the bulk temperature of the solution that is the important factor.

The third system described was the modified disc apparatus shown in Fig.1.10. The apparatus is basically similar to that of Groves and Eisenbrown¹¹, with some modification. Two thermocouple holes were drilled in the head of the soldering iron to enable heat flow calculations to be made. A hole was also drilled in the specimen so that metal surface temperatures could be calculated from its temperature at the centre, the heat flux through it, its thickness and thermal conductivity. For this the standard Fourier equation for heat conduction was used. The heat flux was determined experimentally by cooling and heating curves at various settings on the variac. Readings from the thermocouple in the head were also used to calculate heat flux but required correction for radiation losses. They performed tests in phosphoric, nitric and sulphuric

acid, and came to similar conclusions to the previous work, establishing surface temperature as the important factor. Fisher and Whitney considered that of the three systems the modified disc apparatus was the most satisfactory, stating its advantages as

1. Speed

Specimens were small, therefore quick accurate weight losses determinations were possible. Normal runs were of ten days duration, to allow the development of a type of attack, though for higher heat fluxes twenty four hours would have been sufficient.

2. Accuracy

The reactants used were pure, therefore accuracy depended on the equipment. Using electrical heating left the heated side of the specimens unaffected, and only the test side changed during runs. Steam, oil and other forms of heating produced contamination or corrosion in unwanted areas.

3. Reproducibility

This was of a high order, due to a certain extent to:-

4. Simplicity

The apparatus was simple to set up and run.

5. Plant simulation

The method established heat transfer surfaces within the corrosive media - missing in normal immersion techniques.

They considered its main limitations to be

1. Surface temperature

This proved impracticable to measure and had to be calculated.

2. Velocity

Although agitation was provided to remove corrosion product from the surface, a systematic study of the effect of velocity was not possible.

¹⁶
Kerst performed work with steel specimens in pilot plant cooling towers and noted that specimens under heat transfer conditions corroded at more than eight times the rate of a specimen merely immersed in the same solution.

¹⁷
Groves, Eisenbrown and Sharfstein using the disc technique for various steel indifferent concentrations of acetic, formic and phosphoric acids, showed that some steels were more affected by heat transfer than others, and suggested that this may be due to the nature of the oxide films, high chromium and molybdenum content in the film being most resistant.

¹⁸
Fisher in a later paper compared the modified disc apparatus with further apparatus using much higher solution temperatures and heat fluxes. The temperature sensitivity of the processes was still indicated but the character of the corrosion changed, severe pitting being exhibited.

19

Illingworth designed an apparatus to study simultaneous heat transfer and flow. From the work it was still impossible to completely separate the effects of heat flux and surface temperature, but considered as had the previous workers that the surface temperature rather than the heat flux was the controlling factor. The size of specimen used rendered it impossible to establish the thermal boundary layer and it was therefore impossible to reach rigid conclusions as to the effect of flow.

11,12,18,19

These workers proposed that the metal surface temperature was the controlling factor in the corrosion processes. Other workers, in the field known as thermogalvanic corrosion, observed that this was not necessarily the case. Thermogalvanic or 'hot spot' corrosion refers to cases where potential differences are established within a metal having parts at differing temperatures in contact with a solution. Berry²⁰ and Tyrell²¹ working with copper and silver observed that the colder electrode was the anode of the cell in early work in this field.

22

Buffington considered the system as analagous to a thermocouple with the electrolyte as one half of the couple, and assuming this calculated from standard data the expected thermogalvanic potentials on various metals, including iron and nickel.

Work was performed on iron in various solutions by²³ Uhlig, who noted that, in 3% sodium chloride solutions, the potential difference was 24 mv for a 75 °C difference in temperature. In sulphate solutions it was observed that the polarity of the cell depended on the ferrous/ferric ion ratio. For high ferrous/ferric ion ratios the hot electrode was anodic and vice versa.

Breckheimer and D'Ans²⁴ did work with iron in potassium chloride solutions and observed that the hot electrode was anodic for all concentrations from 0.001N to 3N solutions. The addition of potassium nitrate caused passive films at the hot electrode and a reversion of polarity occurred.

Gerasimov and Rozenfeld²⁵ studied copper, iron, nickel and lead in various sodium chloride solutions. The experimental variables included pH, cold electrode area and agitation near the cold electrode. It was noted in all cases that the hot electrode was anodic and that the system was under cathodic control. Therefore increasing the cold electrode or agitation near to it increased the corrosion rate, in some cases by as much as 10 - 100 fold.

Breckon and Gilbert²⁶ found no relation between severity of attack on Admiralty Brass and the hot spot temperature but noted that the cold electrode area was an important factor and in similar work Bem and Campbell²⁷ also came to the

conclusion that the area ratio was a controlling factor.

Shatalov, Marshakov and Kalnzhina²⁸ performed work with several metals and alloys in their sulphate solutions and at various pH values. It was observed that cathodic control predominated in normal (hot anode) couples but anodic control was more characteristic of reversed (cold anode) couples. It would therefore appear that whatever the process the cold electrode is the controlling factor.

Boden²⁹ in more recent work also established the area of the cold electrode as a controlling factor, whether anodic or cathodic. He derived equations from electrochemical theory for the reaction mechanisms and compared these with the practical work, and noted that the corrosion rate of a given couple could be predicted from the equations, though local cells in any one electrode had also to be taken into account.

The field of corrosion and heat transfer appeared, then, to divide itself into two main studies. Thermogalvanic corrosion where the metal surface temperature varied from point to point and local cell corrosion where all the corroding surface was at the same temperature. It was decided to study the latter and to use heat transfer rates such that boiling would occur on the corroding surface. Although this introduced another factor, that of vapour

bubbles produced on the surface, it presented the opportunity the effects of heat transfer and surface temperature since large heat flux changes would result in comparatively small surface temperature changes. The remainder of the thesis is a report of that work.

Chapter 2

The design and method of operation of the apparatus

1. Introduction

Previous workers^{11,12} in this field had all used as a heat source, the principle of a soldering iron element clamped to the specimens at the bottom of a vessel. It was thought that such apparatus suffered from several disadvantages^{11,12}. Firstly in the case of the disc apparatus, location of the specimens at the bottom of the vessel could lead to a build up of loose corrosion product on the surface of the specimen, unless agitation was employed, which would itself introduce another variable. Secondly, the specimens were not very representative of heat transfer surfaces found in industry. Thirdly, the specimens were inaccessible to probes intended to take measurements such as electrode potential and surface temperature. The apparatus employed¹⁹ by Illingworth overcame these problems to a certain extent, but also assumed, as had others, that axial heat flow occurred through the specimens, and that all the surface was isothermal under conditions of constant heat flux. This was considered to be unlikely, for it is very difficult to ensure both conditions simultaneously.

¹²
Fisher and Whitney listed the advantages of the modified disc apparatus, and it was decided to re-design from first principles an apparatus which had these advantages and at the same time eliminated the disadvantages outlined above.

One feature which was considered to be essential was a method of directly measuring surface temperatures. Another variable of obvious importance was oxygen concentration of the solutions and although not included in the original apparatus, it was allowed for in the design.

2. The Heat Supply System

One method of ensuring constant temperature and heat flux over the surface of the specimens was to have a heat source of large thermal capacity in comparison to the specimens. Two readily available heat sources were considered - steam and electricity. The requirements were for the system to be adaptable capable of running for long periods with little attention, and capable of providing high heat fluxes with no unwanted side effects on the specimens. The steam lines available were of insufficient pressure for the heat flux range required and it was decided that a separate boiler would be an unnecessary complication. Also the use of steam would necessitate a protective treatment of the back surface of the specimens if weight loss determinations were to be of use.

Electrical methods of heating prevented all but the last of these problems, and due to the ease with which high temperatures can be obtained with this form of heating this

problem could be overcome. As already stated a large heat source was to be used, mainly to obtain an even distribution of heat, but also to act as an auxiliary heater. For this the obvious method was a coil which had to be completely insulated from the corrosive solutions to prevent short circuiting. This was best done by some form of sheath completely covering the coil, with the solution on the inside or outside of this sheath.

Since it was required to probe the corroding surface during experiments it was decided that the former method was unsatisfactory, whilst in the latter the sheath could either be the specimen itself or some inert sheath with the specimens retained on the outside of this. If the sheath served as a specimen, high temperature gradients would occur across part of the tube, although the specimen would be so large as to lead to inaccurate weight loss determinations. An inert sheath would reduce temperature gradients and present sealing problems for the sheath side of the specimens, but the specimens would be small, easy to prepare and handle, and internal oxidation would be prevented.

Trials were made of both methods and that employing an inert sheath was found to be more satisfactory. The sheath used was a smooth surfaced silica glass tube, since it fulfilled the requirements of withstanding high temperatures,

was a good electrical insulator and non-porous.

The trials showed that it was unnecessary to seal behind the specimens, since with the method used little corrosion occurred on the rear surface.

The system used may be summarised as follows:-

The element used was wound upon a fire bar type former of $8\frac{1}{2}$ " total length, $\frac{3}{5}$ " outside diameter, and 20 turns/inch. with Nichrome V resistance wire, nominal resistance 2.98 ohms/yard total resistance, 28.2 ohms.

The end fixings on the former were alloy caps internally threaded to match the former and machined to just smaller than the internal diameter of the silica tube, reducing heat loss past them.

The connections were by, $\frac{1}{8}$ " diameter mild steel rod, bolted to the end caps on the former and passing through caps at each end of the silica tube, further reducing heat losses.

The tube was of Vitriosil pure fused silica, satin smooth finish, $14\frac{1}{2}$ " total length, 17.5 mm internal diameter, 1.6 - 2.2 mm wall thickness.

The system was as shown in Fig.2.1. A variac was used to control the heat flux.

3. The Vessel

The vessel had to be large enough, so that during a run

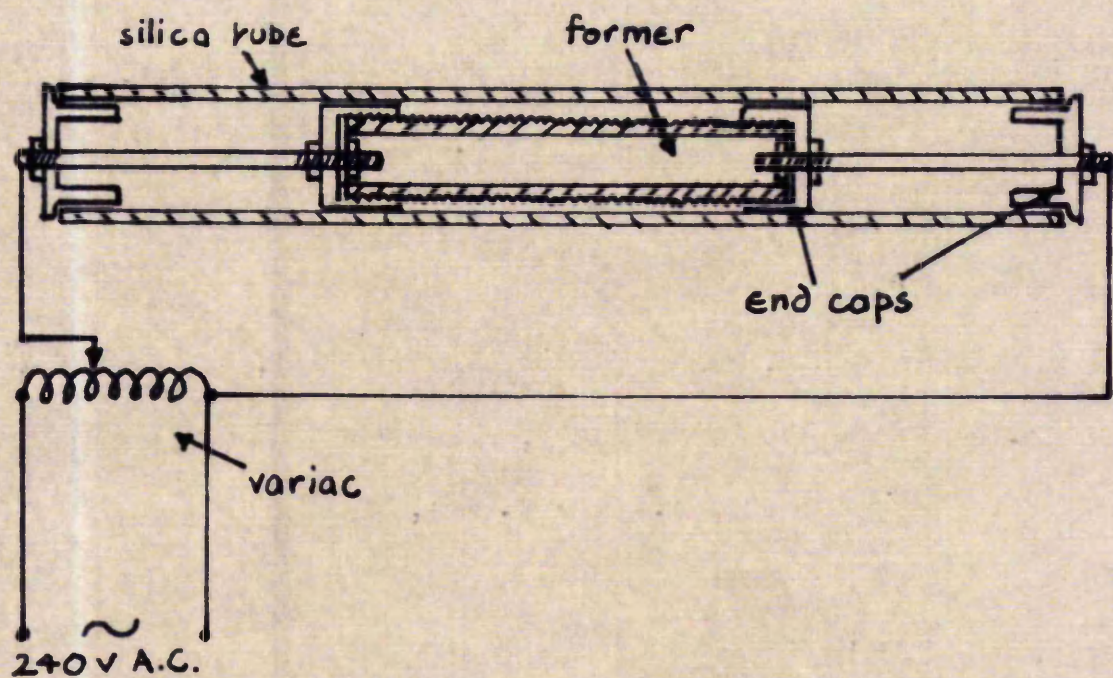


FIG 2.1. Heating system for original apparatus

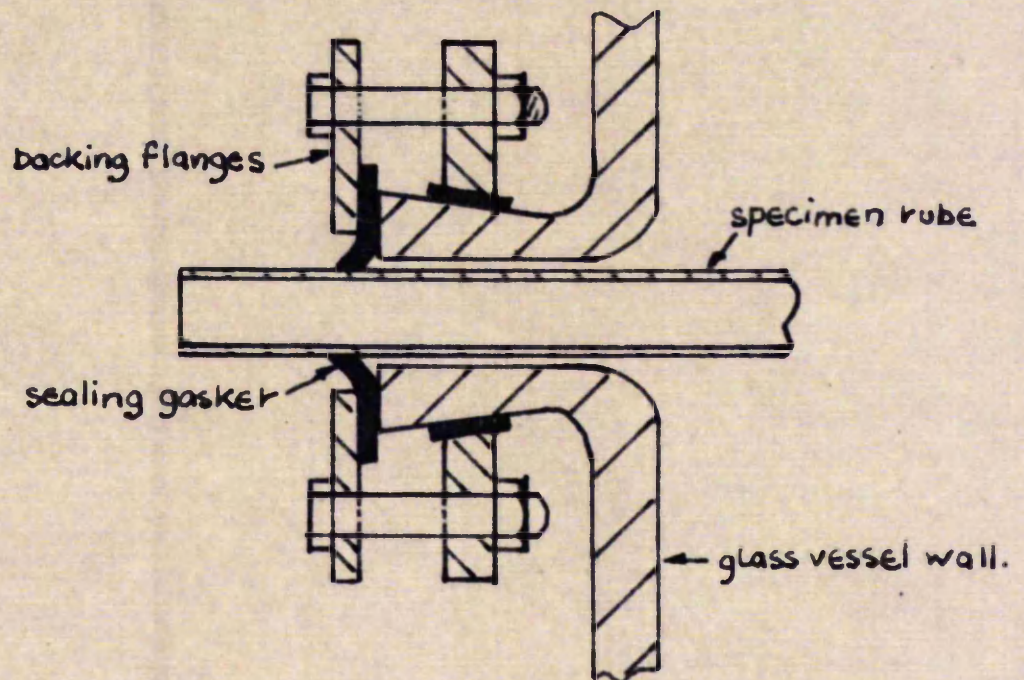


FIG 2.2. System for sealing specimen tube in vessel.

concentration changes were negligible. A condenser was also required to condense steam formed during a run. The specimen tube had to be positioned and sealed. Some provision had to be made for the introduction of the surface probes, and also provision made for cleaning the inside of the apparatus.

For reasons of adaptability the apparatus was assembled from Q.V.F. glass ware, and as the element was 7" in length the vessel was based on 9" Q.V.F. tubing. A vessel constructed of this, giving a reasonable boiling pool above the specimens would contain approximately 15 litres of solution. Uhlig³⁰ suggested that for the concentration of corrosion product to be negligible 5 litres/dm² of the specimen surface area was required. If eight specimens, described later, were used per run the ratio would be 30 litres/dm² and was considered to be satisfactory.

The condenser fitted was a 1½" Q.V.F. condenser, which operated at total reflux and was open to the atmosphere. The specimen tube was positioned in two 1" Q.V.F. buttress ends set in the 9" Q.V.F. tube. The tube was sealed by a neoprene rubber gasket, tightly fitting to the silica tube and clamped to the buttress ends using a brass backing flange as shown in Fig.2.2.

Making fixed electrical contact with each of the

specimens proved impracticable. The method used employed a surface probe, described later, which was pressed against the specimen, passing through a rubber sealing gland, covering a 4" buttress end and clamped by a backing flange at the front of the apparatus. The 4" buttress end also facilitated internal cleaning of the apparatus. A side arm for filling the vessel and a tap for draining were also included. The vessel was as shown in Fig. 2.3.

4. The Specimens

The first experiments were conducted using mild steel specimens, exposed to distilled water. The specimens had to be small and easily made for reproducibility. As mentioned before they were required either to fit closely to the silica tube, or be sealed to it in some manner, in order to prevent seepage behind the specimens, so causing unwanted corrosion. The method eventually found to be extremely satisfactory employed specimens in the form of a split annulus, as shown in Fig. 2.4. In order to obtain a good, close fit to the tube the specimens were made of slightly smaller diameter than the silica tube and when in position were lightly sprung, achieving a close fit. Seepage behind the specimens was then negligible.

The specimens were prepared from solid drawn mild steel

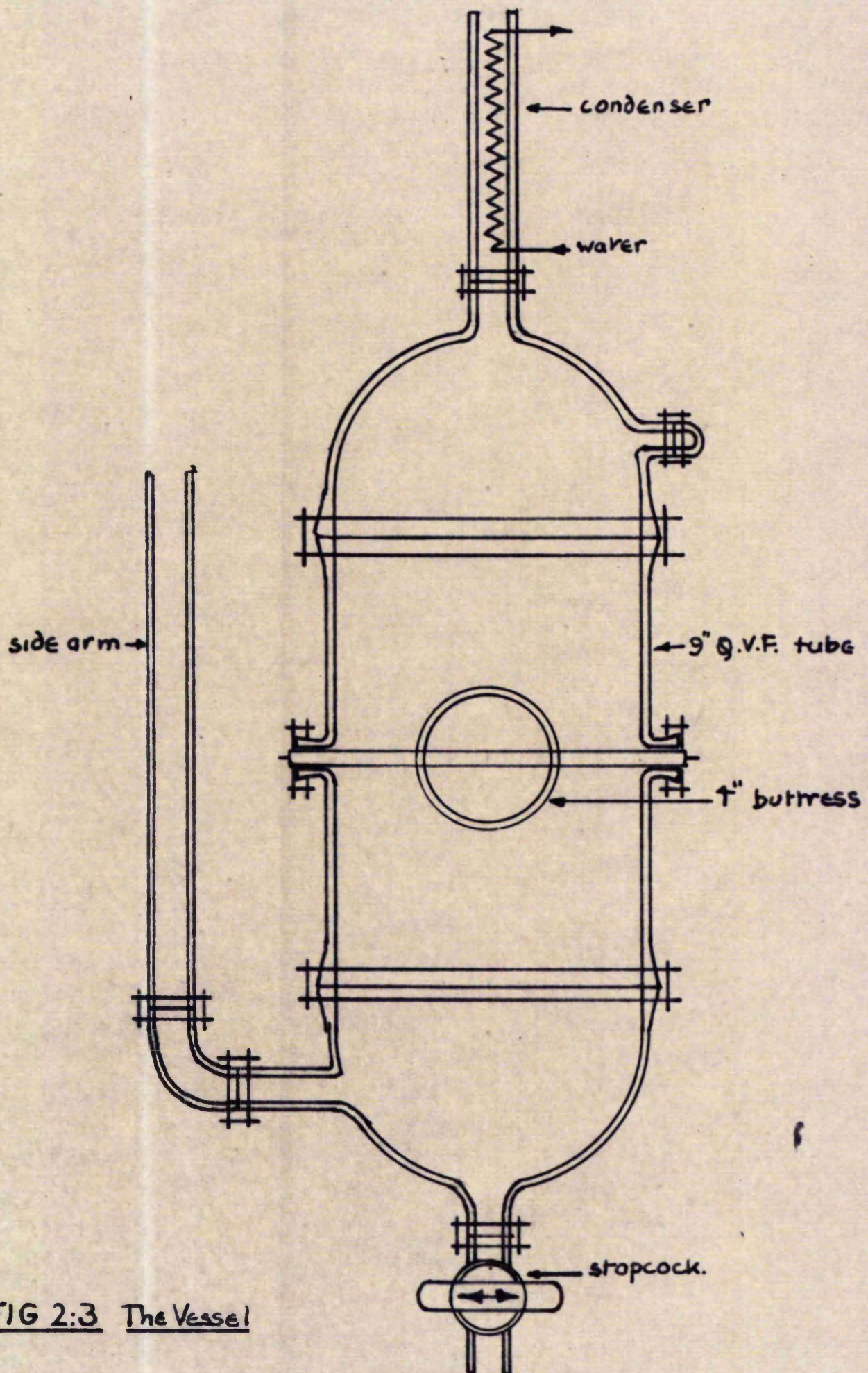


FIG 2:3 The Vessel

tubing, to eliminate composition changes within the metal, the chemical analysis of which was given as

Carbon	0.13%
Manganese	0.36%
Phosphorous	0.039%
Silicon	0.097%
Sulphur	0.04%

Iron Remainder, except for trace amounts of chromium and nickel.

The tube was $\frac{7}{8}$ " outside diameter of 20 S.W.G. wall and was brought to a polished finish in a lathe using medium and fine grades of emery cloth and four grades (100, 220, 440, 600) of Stewers paper. The polished tube was cut into approximately $\frac{1}{2}$ " lengths on a lathe, ground to exactly $\frac{1}{2}$ " lengths and sliced to give the split annulus required.

In this state the specimens were too small to fit onto the silica tube and they had to be stretched a certain amount. This was done in conjunction with heat treatment in order to remove stresses etc. caused during manufacture of the tube or preparation of the specimens. The specimens were pressed onto a mild steel bar, diameter approximately 0.01" smaller than that of the silica tube. A normalisation process was then applied. This involved heating the specimens to 870 °C for three hours in a tube furnace under a nitrogen atmosphere, shown in Fig.2.5. The specimens were kept

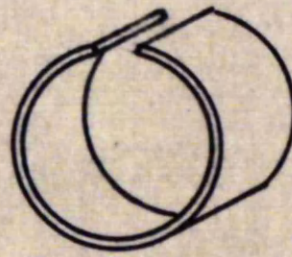


FIG. 2.4. Split annulus specimen

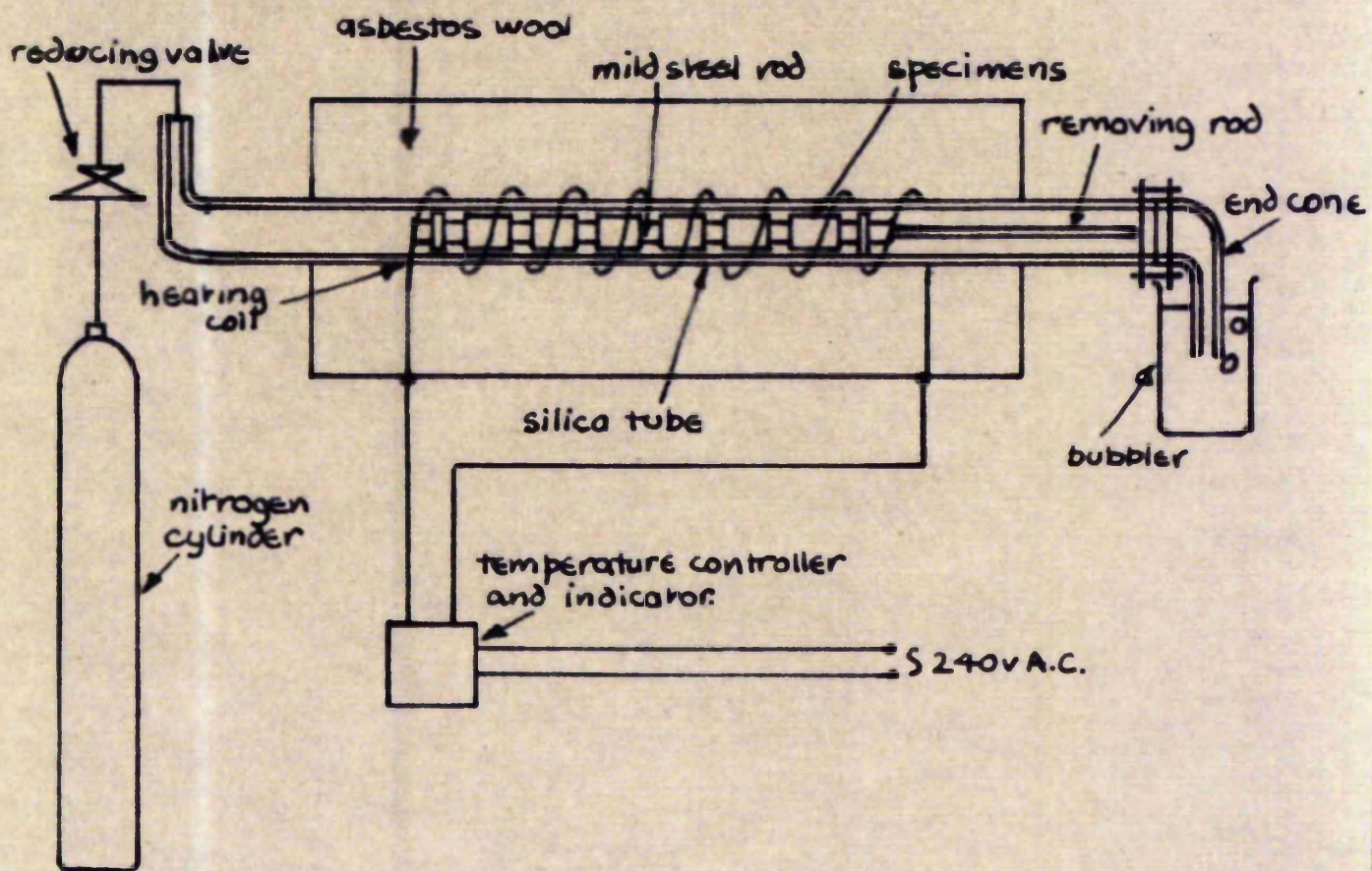


FIG 2.5. Specimen heat treatment furnace.

away from the tube surface by flanges, one removable, at each end of the mild steel bar. The bar was tapered at one end to allow the specimens to be pressed on easily. The bar was pushed to the centre of the furnace by a $\frac{1}{4}$ " diameter mild steel rod screwed into the bar.

After heat soaking for three hours the specimens were air quenched, removed from the bar and placed in a desiccator to await further treatment immediately prior to a run.

5. Measurement

Apart from weight loss the measurements taken during the initial experiments were surface temperature, electrode potentials and the pH of the solution.

1. Measurement of surface temperature

Previous workers, e.g. Illingworth¹⁹ calculated metal surface temperature from the equation

$$T_1 - T_2 = q/h \quad \dots 2(1)$$

where:

T_1 = surface temperature

T_2 = bulk liquid temperature

q = heat flux

h = heat transfer coefficient

The difficulty with this method lies in obtaining a suitable value of 'h'; most of the equations predicting heat transfer apply to established conditions of flow and heat transfer and their application to such small heat transfer surfaces is invalid, although Illingworth admitted this and to a certain extent justified himself by claiming that the results did give an indication of surface temperature.

Fisher and Whitney¹² in their modified disc apparatus used Fouriers equation to calculate the surface temperature

$$\frac{dQ}{dt} = kA \frac{dT}{dx} \quad \dots 2(ii)$$

where:

$$\frac{dQ}{dt} = \text{rate of heat transfer}$$

$$k = \text{thermal conductivity}$$

$$A = \text{area perpendicular to direction of heat flow}$$

$$\frac{dT}{dx} = \text{temperature gradient}$$

Knowing the heat flux, the thermal conductivity of the metal and its temperature at the centre they calculated the surface temperature. This is far more satisfactory but still assumes ideal conditions, such as axial heat flow, etc. Clearly, direct surface temperature measurement would

be a great advantage, though the difficulties are considerable. Methods of measuring the surface temperature of solids are reviewed by Coxon³¹. For low temperature work, thermocouples are suggested as the most suitable. The thermocouple must be in equilibrium with the surface of the hot body and its introduction must not alter the temperature of the surface. Two methods of overcoming these problems are well known.

Firstly the measuring device is made thin to resemble part of the surface, and has the same emissivity etc., and secondly the device is of small area, insulated on the outside, so that although it changes the heat loss conditions in its immediate neighbourhood, lateral conduction in the body causes almost no temperature difference.

As several specimens required temperature measurement in a single run the first method is impracticable. Thus the method employed must be, generally, a small thermocouple in close contact with the heated surface. Another point in favour of this method was that since the surface was being studied from a corrosion aspect as little interference as possible with the surface is desirable. For this reason it is also impossible to drill holes or make grooves in specimens for corrosion experiments. Taking all this into account, the best method appeared to be a small thermocouple

which could be pressed against the surface when readings were required and removed immediately so that no galvanic couples were established, which might alter the corrosion processes. It was therefore decided to use 'Thermocoax' sheathed Chromel/Alumel wire sealed in capillary glass tubing and sealed with Araldite. See Fig.2.6. The measuring circuit was as shown in Fig.2.7.

It was realised that with this system some radial heat transfer was bound to occur and true temperature readings would not be obtained. A method of calibration of the thermocouple was developed which allowed surface temperature to be calculated for a given thermocouple reading.

Three holes were drilled laterally in a specimen, approximately $\frac{1}{4}$ " in depth, one being near the inside surface, one in the middle, and one near the outside surface, as shown in Fig.2.8. 'Thermocoax' sheathed thermocouple wires were inserted in the specimen, and sealed in Araldite so that they were electrically insulated from the metal specimen. From these the temperature gradient across the specimen thickness could be determined and by extrapolation the surface temperature obtained. Used in conjunction with the thermocouple probe, a reading for any given surface temperature could be obtained. Calibration figures are given in appendix 1.

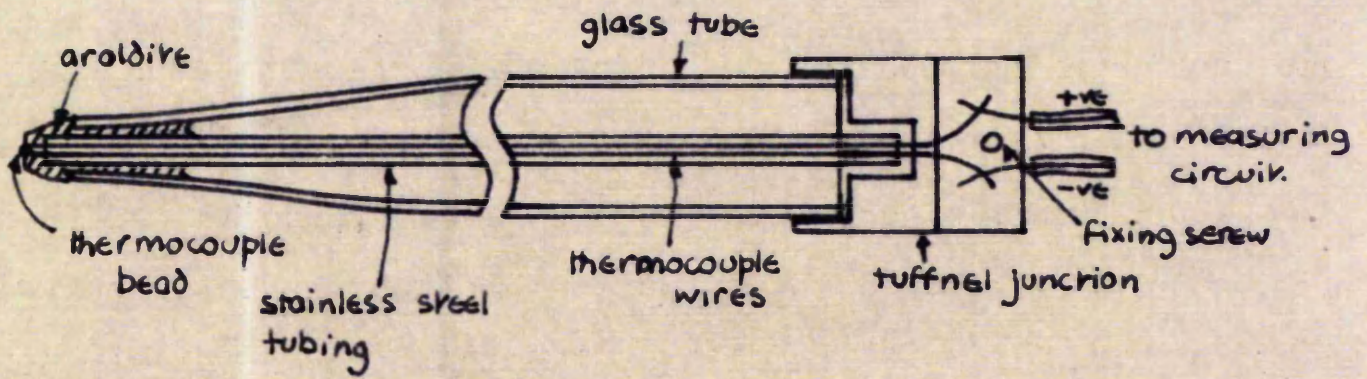


FIG 2.6. Construction of thermocouple probe.

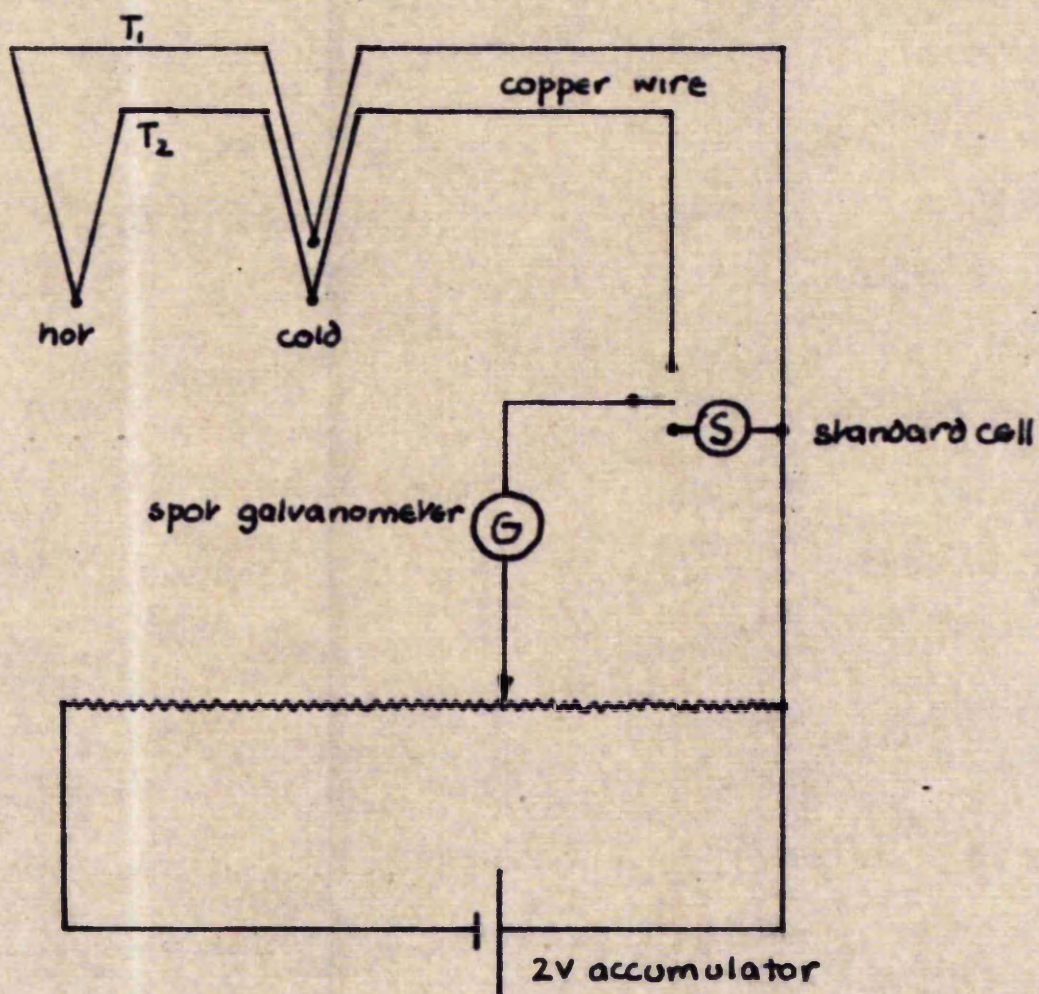


FIG 2.7. Thermocouple measuring circuit.

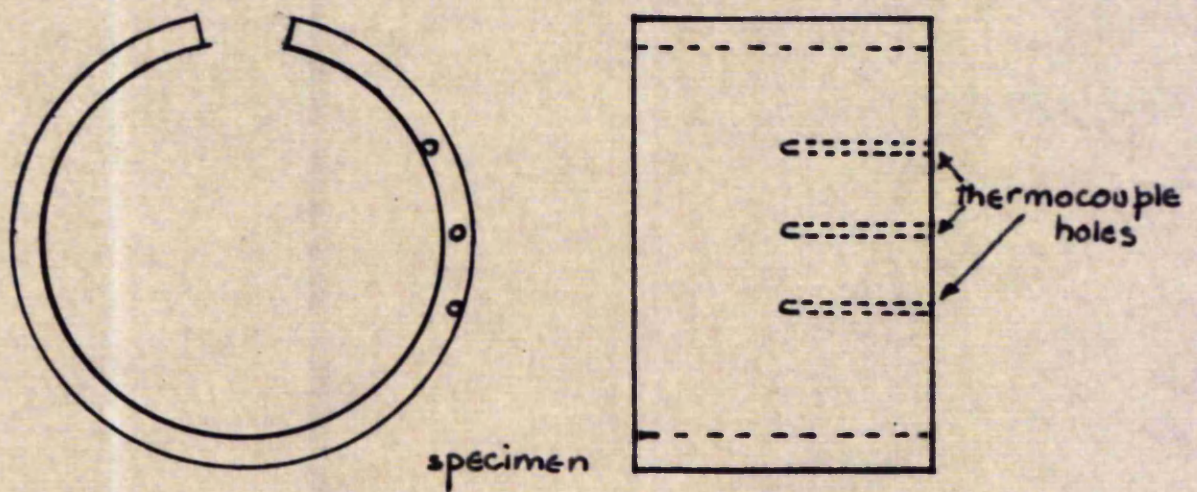


FIG 2.8. Specimen drilled to take calibration thermocouples.

ii. Measurement of heat transfer rates

At the time when preliminary runs were conducted no satisfactory method of determining heat transfer rates was established. At a later stage in the investigation a system was proved to be satisfactory and with temperature readings taken during preliminary runs it was possible to calculate heat transfer rates. The method is fully described in appendix 1. The heat input to the winding was calculated from the voltage and amperage readings across the winding.

iii. Measurement of electrode potential

In order that these measurements could be taken an electrical contact between the specimen and the measuring device was required. As several specimens were to be used in one run it proved impracticable to have a directly attached contact with each one. The method used for this contact took the form of a probe, as shown in Fig.2.9. It consisted of a mild steel rod 1/16" in diameter sealed in a glass tube. The part of the rod protruding beyond the glass was sealed with Araldite so that only the end surface was exposed. This could be passed through the 4" rubber diaphragm and pressed against the surface of any of the specimens.

When readings were not being taken the tip would have been exposed to the corrosive media and could have formed a

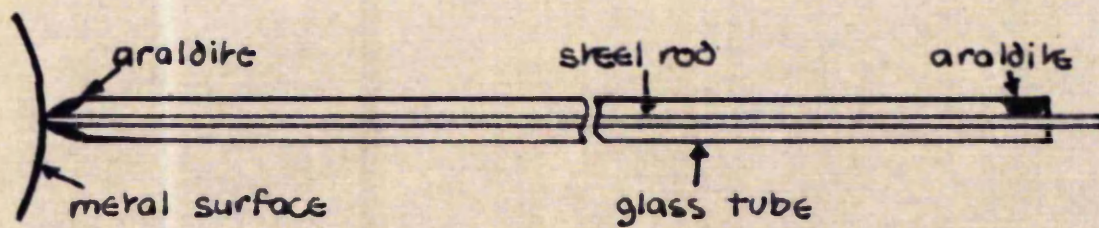


FIG 2.9. Potential surface probe

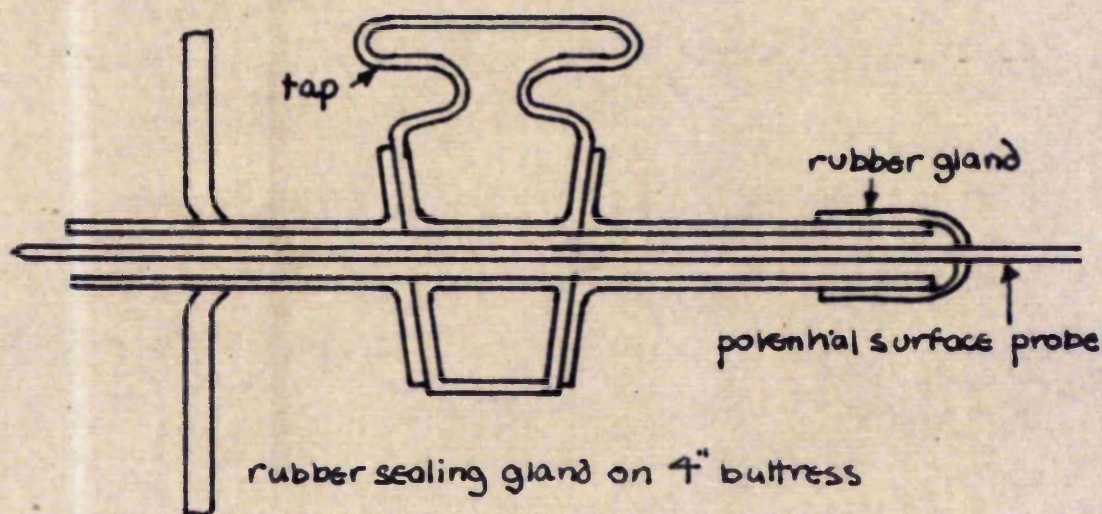


FIG 2.10. Sealing system for potential surface probe.

non-conductive film which could have altered the potential reading obtained with the time exposed. A method was therefore devised in which the probe could be removed after each series of readings so that it could be cleaned. This was arranged by means of a tap and sealing gland, as shown in Fig.2.10. With this method the probe could be introduced with no loss of water from the system.

The reference half-cell was an external saturated calomel electrode connected by means of a liquid bridge containing the corrosive media. The bridge consisted of a glass tube, drawn at the specimen end to a fine capillary. This tube was connected to the glass funnel containing the saturated calomel electrode, by a plastic tube containing a wick, in order to reduce the possibility of air bubbles interfering with the readings. The potentials were measured with an E.I.L. 23A high impedance millivoltmeter, and the full circuit was as shown in Fig.2.11.

iv. Measurement of the pH of the solution

The pH of the corrosive media, distilled water for preliminary runs, was measured using an E.I.L. 23A pH meter, with a glass electrode and a saturated calomel electrode as half cells. The meter was standardised frequently using buffer solutions of pH 4.00 and pH 9.15. The electrodes were thoroughly washed in the corrosive media and then the pH determinations made.

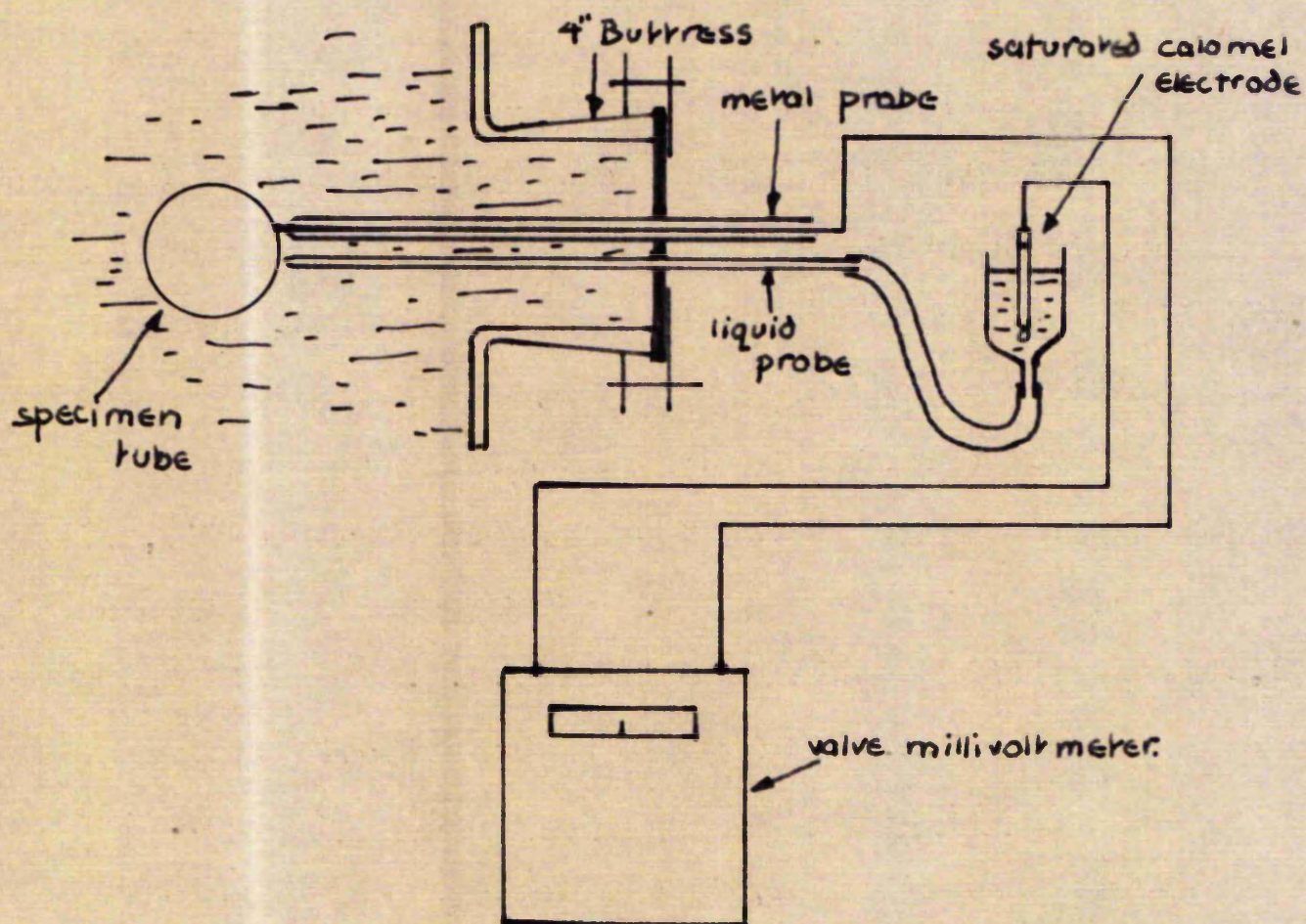


FIG 2.11. Potential measurement circuit

Chapter 3

Start-up and Preliminary Experiments

1. Introduction

The treatment of specimens immediately prior to and after runs is discussed.

The equipment was usually tested using tap water as the corrosive medium and a problem of taking potential measurements, due to the heating method, arose. This problem is considered and a temporary method of taking readings was used until a more satisfactory method of heating could be found. A solution to this heating problem is discussed.

The results obtained from the preliminary runs using the original heating method are recorded and suggestions offered in explanation of the phenomena.

2. Specimen Treatment

Specimens were prepared as described in an earlier chapter, and after the normalisation process the specimens, now covered with an oxide film, were stored in a dessicator. This film had to be removed before corrosion tests could commence. Similarly, after corrosion a method of removing the corrosion product had to be used, so that weight loss determinations could be made. In the latter case it is essential that metal is not removed during the process, or at least kept to a minimum and allowances made in the weight loss determinations. Several chemical methods are available

for removing corrosion products³², and the method decided upon was the use of Clarke's solution³³. This is a solution of 2 gm stannous chloride and 2 gm antimonious oxide in 100 ml concentrated hydrochloric acid, the additives serving as inhibitors to the metal dissolution process. In practice it was found that all the corrosion product was removed by the solution in less than a minute. Blank tests were performed, immersing the specimens for up to fifteen minutes, and weight loss determinations were then made. The weight loss during blank tests was negligible in comparison to the loss in a normal corrosion run.

This method, though, leaves a small deposit of antimony on the surface, which, while having negligible effect on weight loss determinations could affect the corrosion processes. Therefore it was decided to use concentrated hydrochloric acid to remove the oxide film caused by the heat treatment prior to a run, producing a reproducible etched surface on the specimens. After treatment with the acid solutions, in each case the specimens were washed in distilled water, rubbed dry with a soft cloth, immersed in carbon tetrachloride to remove grease films, dried and carefully weighed.

Specimens were treated immediately prior to a run and were then carefully placed, with as little contact as

possible, on the silica sheath. To prevent cracking of the silica tube the specimens were first placed on a mild steel rod fractionally larger than the silica tube and from there moved onto the sheath. The heating coil was then fixed inside the sheath and the whole bar fixed into the vessel.

3. Start-Up

Runs were initially carried out using tap water as the corrosive medium, with a small number of specimens and the slit in the specimens in various positions. Weight loss determinations indicated that there was no significant difference with respect to slit position. Therefore the slit was in future runs arbitrarily placed at the top.

During these runs it proved difficult to measure the surface potential, and absurdly high readings were obtained when the current was flowing through the heater. Reasonable readings were obtained if the current was switched off immediately prior to any reading. To find the cause of this effect, the system was simulated on bench scale and several experiments were performed. The specimens were replaced by a length of iron wire, and the heating coil was replaced by a large number of turns of copper wire wound around the specimen. These experiments established that, due to the heating coil, currents were being induced in either the

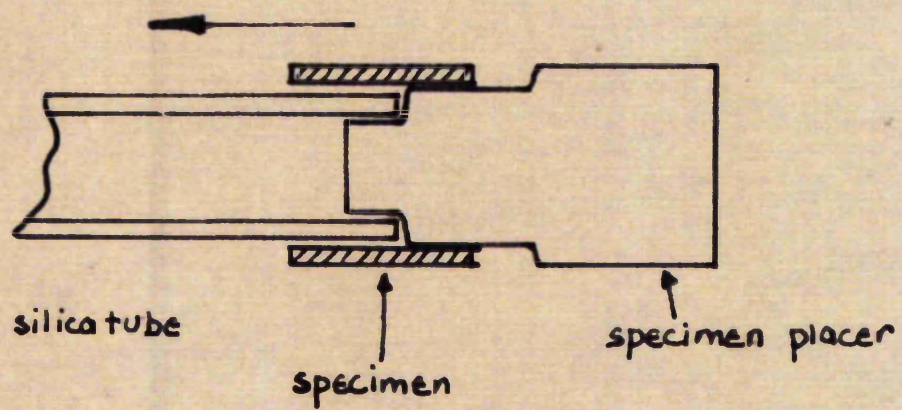


FIG 3.1. Specimen placer

specimens or in the probes. These currents were being transformed into a D.C. signal in the first valve stage of the millivoltmeter. The most likely pick-up point was in the high resistance of the solution between the specimen and reference electrode.

Obtaining a reasonable reading, if electricity was to remain the heating media, could be done in two ways. The A.C. component in the measuring circuit could be shorted prior to the millivoltmeter or a non-inductive winding could be used for the heating coil. The former method would merely mask the effect and if the induced currents had an effect on the corrosion processes, which Torigoe¹⁵ suggested they may, then the corrosion results would be suspect. Using a non-inductive winding as the heater was thought to be the better method. Initially runs were performed using the inductive winding until the other was obtained. Comparisons were made of the results with each winding. During these runs surface potential readings were obtained by switching off the heater immediately prior to taking a reading.

4. Experimental Procedure in Preliminary Runs

Distilled water was used as the corrosive medium.

Eight specimens were used in each run. Six under conditions

of heat transfer, and two as blank specimens - not on the heated part of the tube. The specimen tube was fixed into the vessel and the vessel filled via the side arm until the water was approximately nine inches above the specimens. The water to the condenser was turned on, and the heating current was switched on and maintained at a set value.

Potential readings were taken periodically throughout the run via the front sealing gland. They were taken frequently at the start of any run and every half hour once the system had settled down with the exception of the overnight period.

Temperature readings were taken periodically throughout the run, again at every half hour once the system had settled down.

Runs were of 24 hours duration and at the completion of a run, the specimens were treated as described earlier, weighed, and stored in a desiccator for later examination.

5. Results of Preliminary Runs

1. Potential measurements

At any one time within a given run the potentials of different specimens were almost equal, the two outer specimens having a lightly lower potential than the others. This was in the order of 2-3 mV difference in 600 mV and was

thought to be negligible. Potentials are quoted as negative to a standard calomel electrode.

Within a given run the specimen potential varied with time in a manner typified by the example shown in Fig.3.2.

The average final potential of a run showed an increase with increased heat transfer rates. See Fig.3.3.

ii. Weight loss measurements

Within a given run there appeared to be some bias with respect to position on the specimen tube. The trend is indicated in Fig.3.4. The weight loss by the centre and outside specimens was less than the regions between. Due to the scale used the effect is exaggerated in the diagram, the deviation between maximum and minimum weight loss was in the order of ~~3%~~ 20% in the worst case recorded

The average weight loss of both heated and unheated specimens plotted vs heat transfer rates are shown in Fig.3.5.

iii. Temperature measurement

The surface temperature of the metal increased rapidly at the start of any run and then steadied down to a value held for the remainder of the run. A typical example is shown in Fig.3.6.

iv. pH measurement

The pH of the solution was measured prior to each run

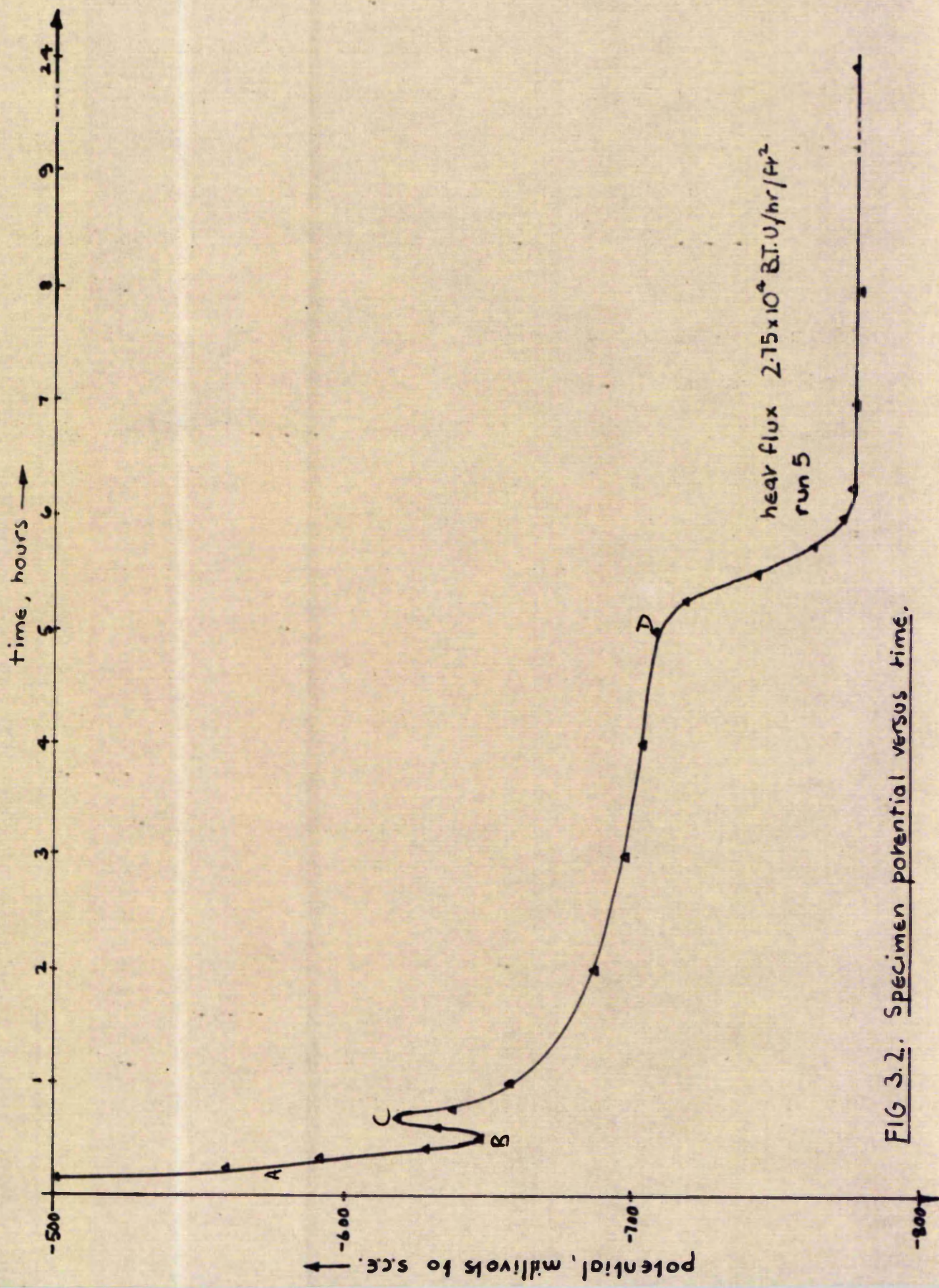


FIG 3.2. Specimen potential versus time.

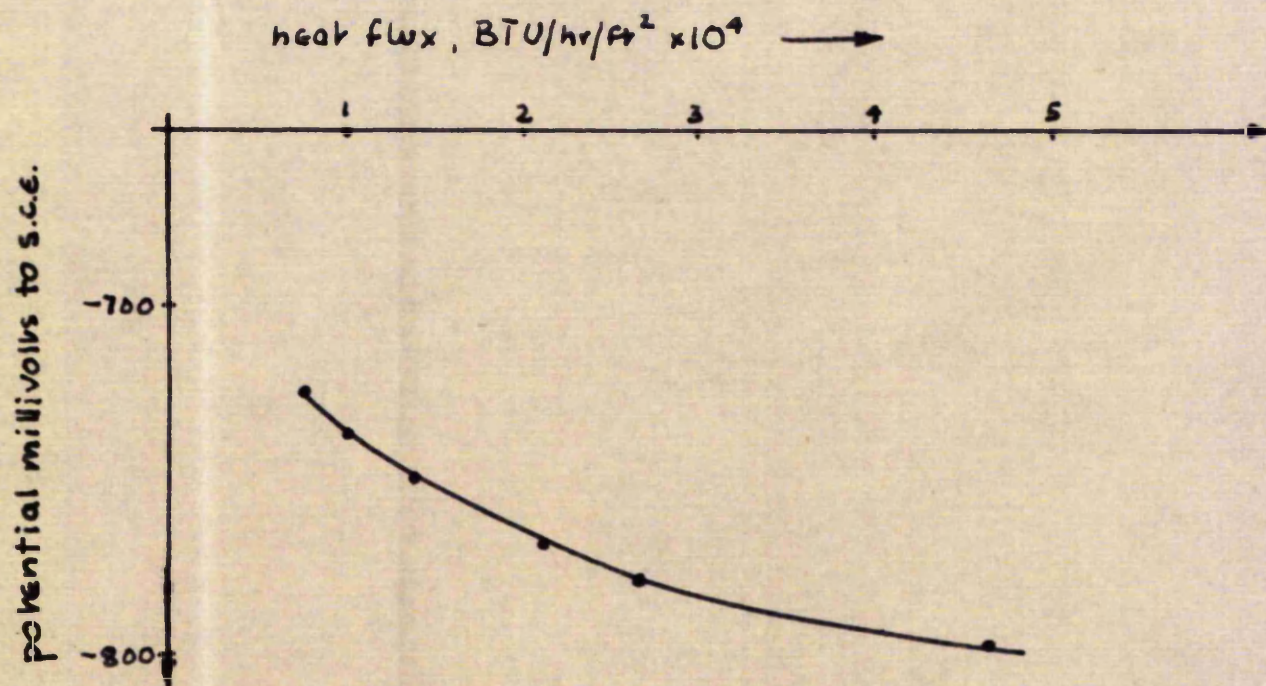


FIG 3.3. Final potential versus heat flux

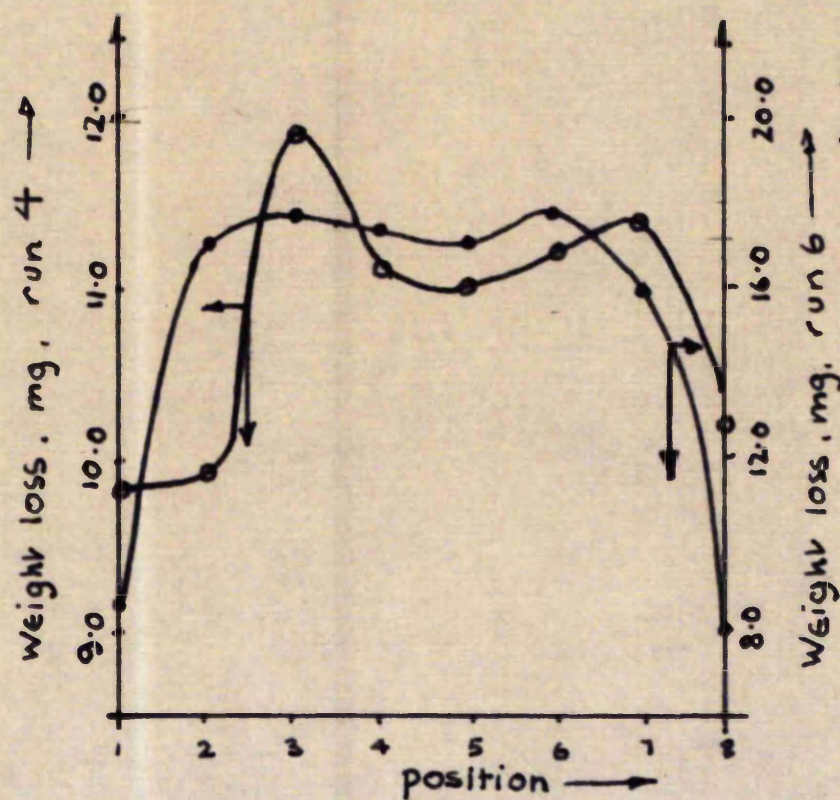


FIG 3.4. Weight loss versus position on tube

Run 4, ○, Heat Flux 4.70×10^4

Run 6, ○, Heat Flux 2.2×10^4
 BTU/hr/ft^2

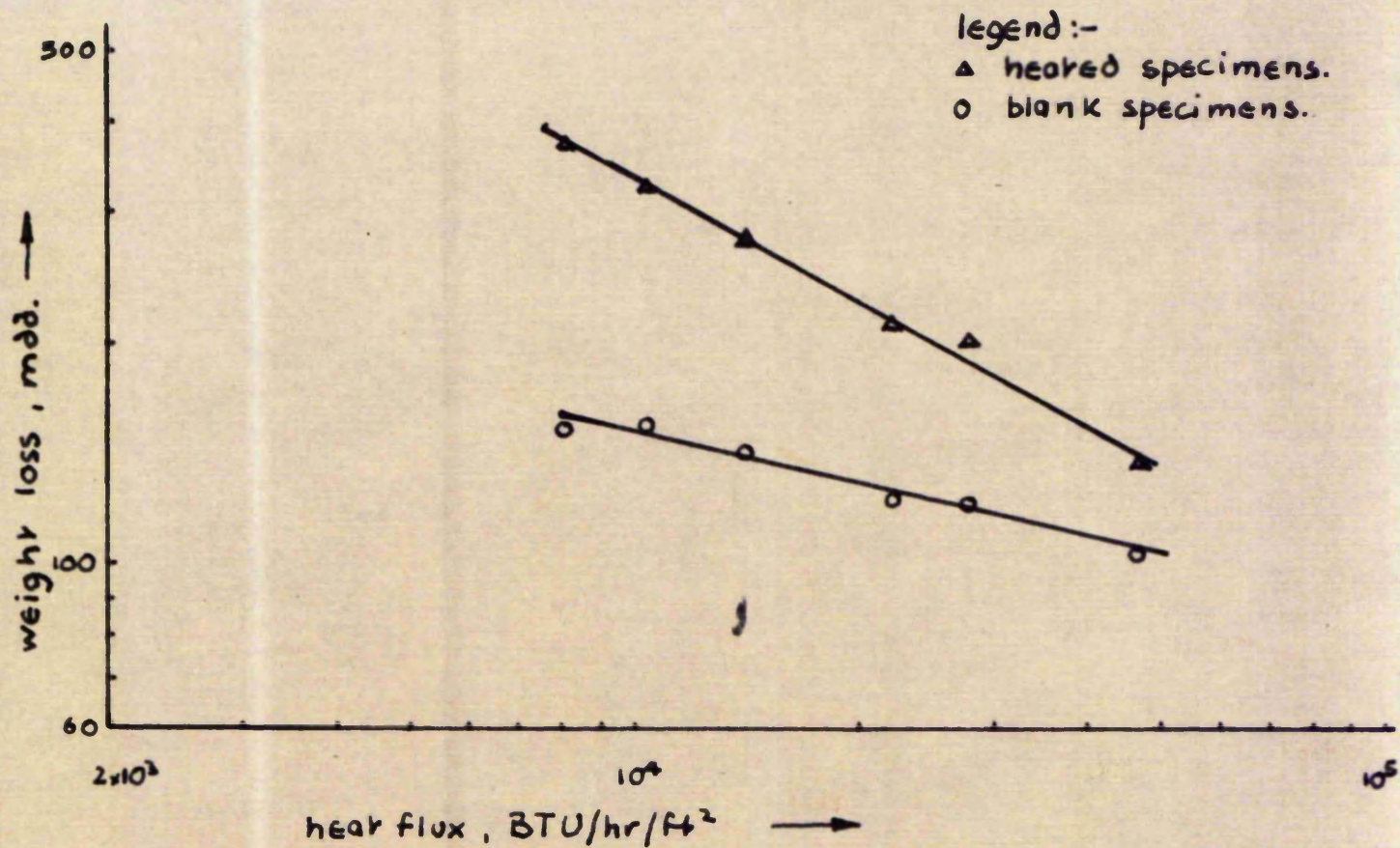


FIG 3.5 Log-Log plot, weight loss versus heat flux

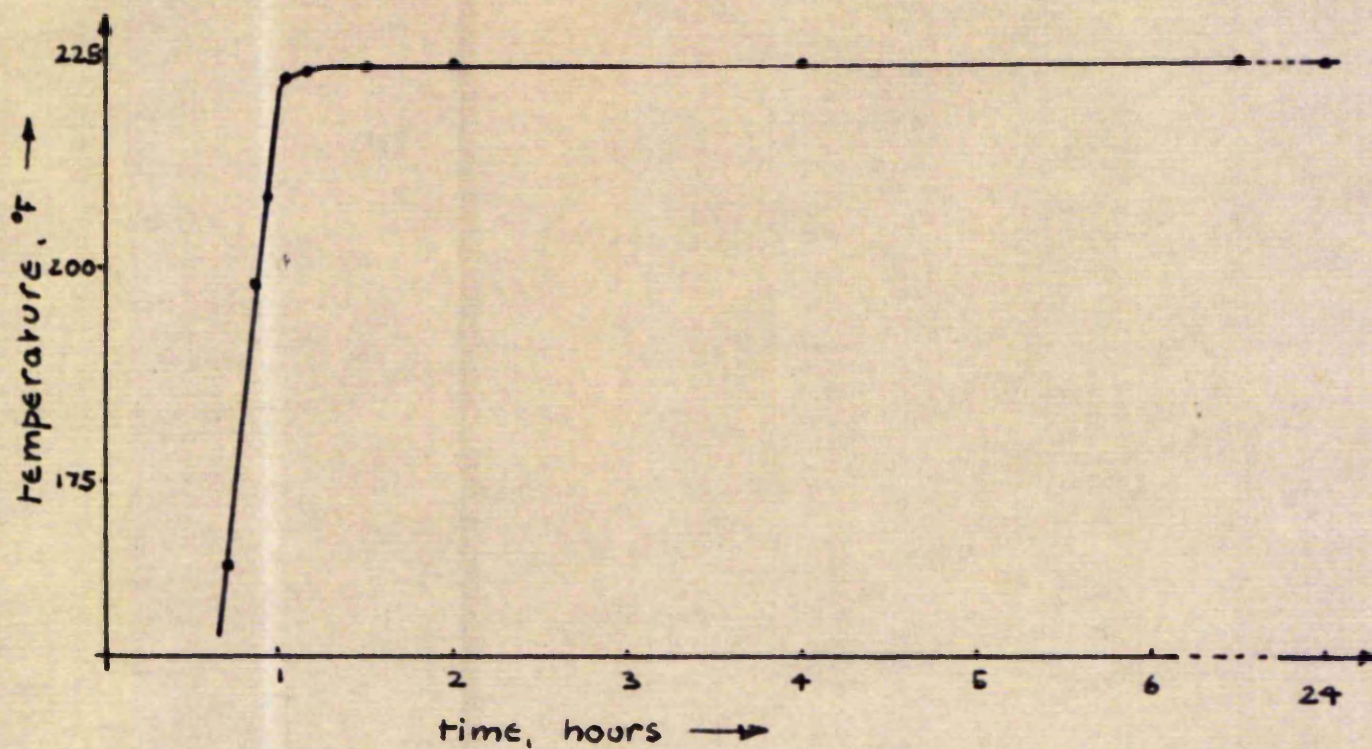


FIG 3.6. Surface temperature versus time

and was in the order of pH 5.2 to 5.3. After a run a sample of water was retained, allowed to cool and its pH measured. This was found to vary between pH 6.8 and 7.1 but the variance was random and bore no relation to heat transfer rates. This was thought to be due to difficulties in obtaining a representative sample from such a massive liquid source. The results are included in Appendix 2.

v. Visual observations

Prior to a run all specimens had a similar surface, a dull matt sheen on a smooth, regular surface. At completion of a run the specimens were all coated with a black corrosion product. On the specimens which had undergone heat transfer were scores, made in the same direction as the bubble paths during a run. This was much less noticeable on the blank specimens. Bubbles were formed at various points on the surface, then rolled up the sides of the specimen, and left the surface near the top, as shown in Fig.3.7. The severity of the scoring was greater with lower heat as shown in the photograph Fig.3.8. Pitting also occurred at the bottom of specimens where numerous bubbles formed and remained stationary for some time, particularly during the first part of runs. Pitting was also greater at lower heat fluxes, see photograph Fig.3.9.

As stated the specimen surface at the beginning of a

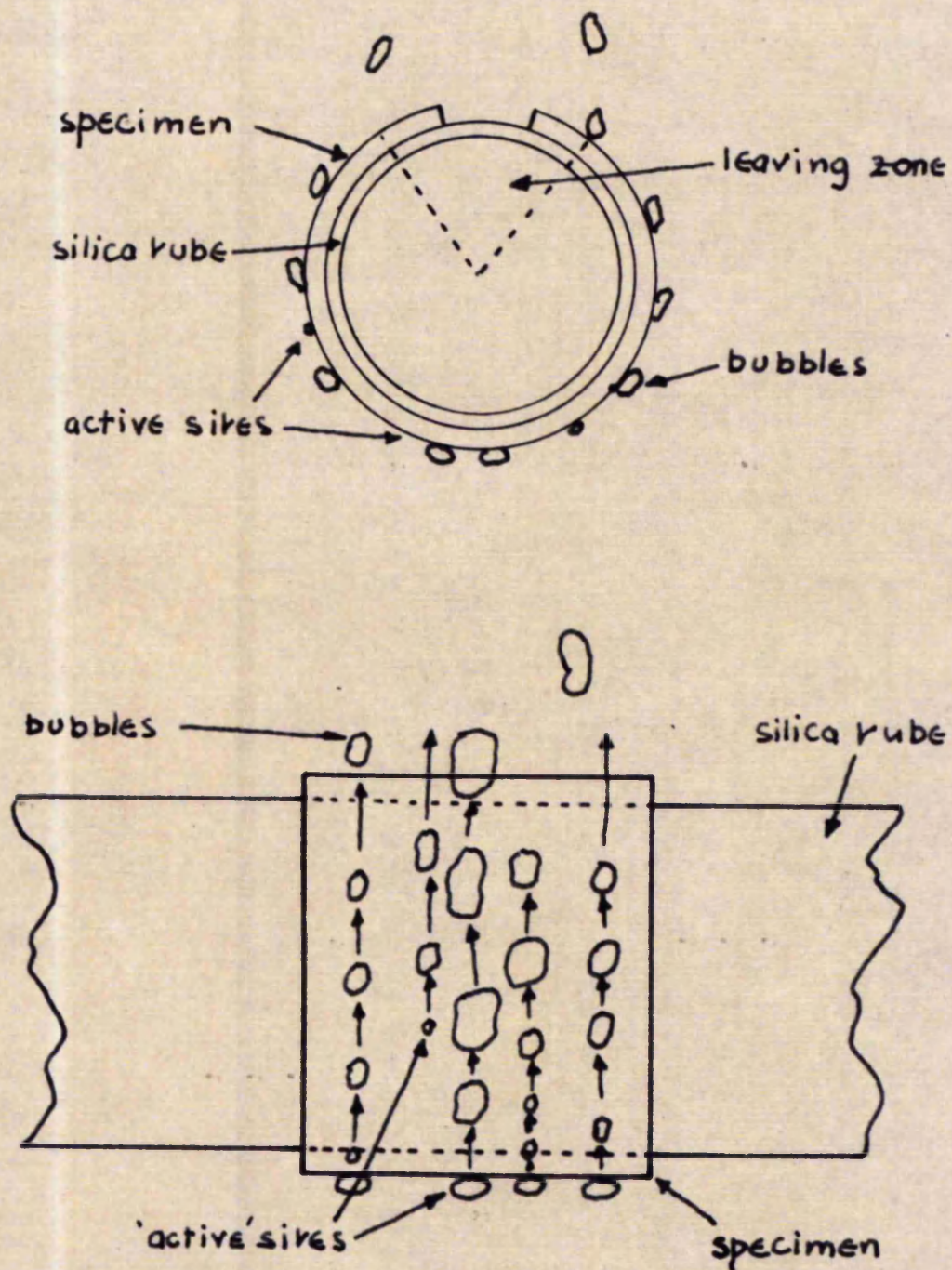


FIG 3.7. Formation of bubbles on specimen

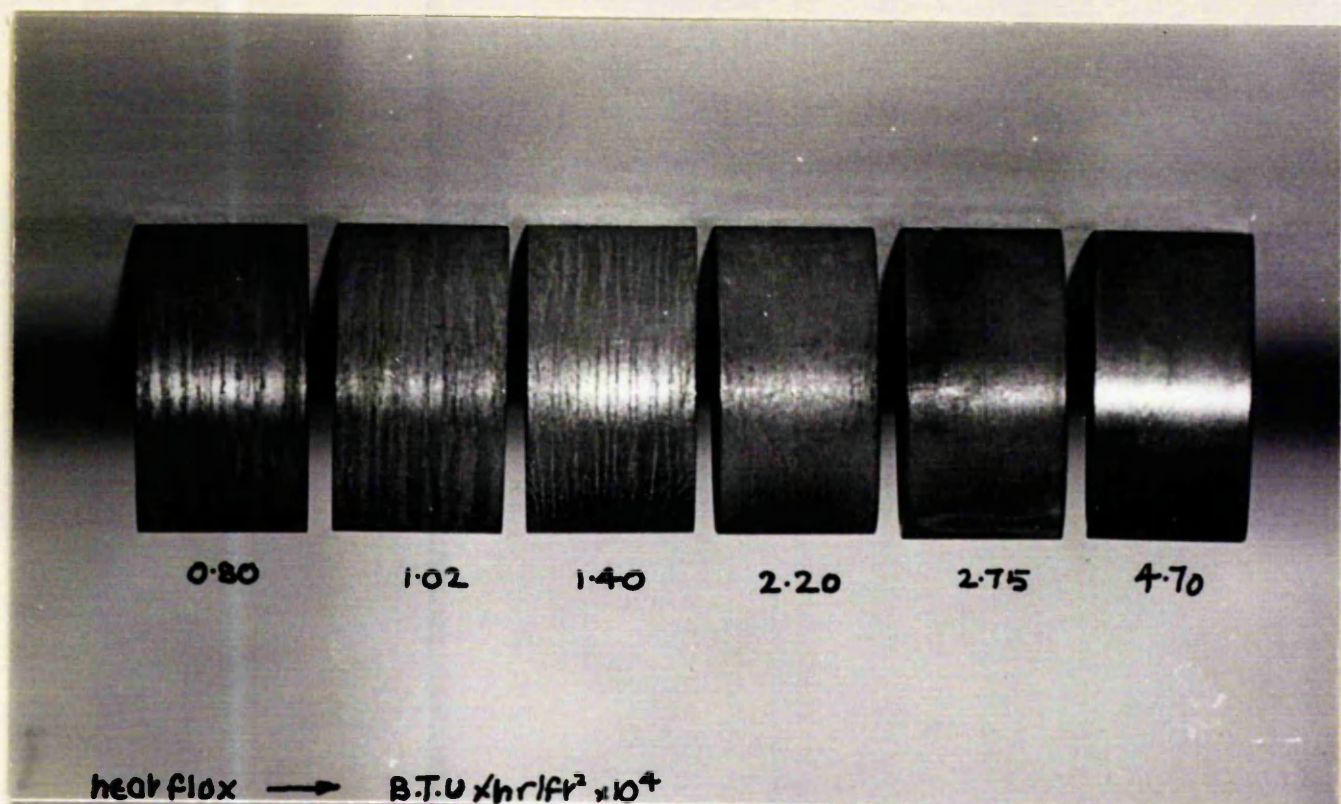


FIG 3.8. Corrosion patterns of mild steel , showing side of specimens

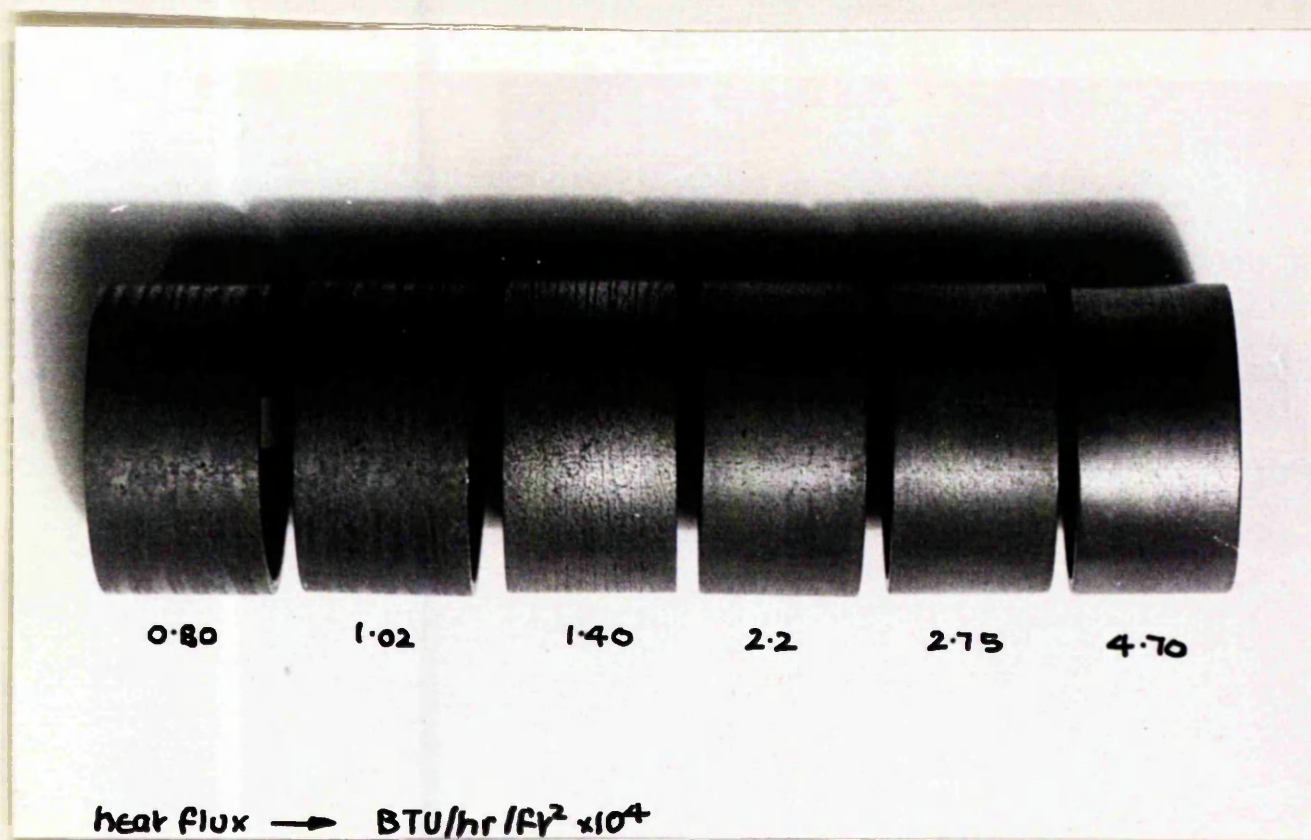


FIG 3.9. Corrosion patterns of mild steel , showing bottom of specimens

run was a matt sheen. As soon as the run started bubbles formed on the surface and rose up the sides marking the surface. After a while a brown deposit developed over the surface which slowly, as the run progressed became darker until it became the black product mentioned above. At low heat fluxes the brown deposit persisted for much longer than at higher heat fluxes.

As boiling commenced a hot/cold water interface developed around the heater tube and spread as boiling became established until it was a flat layer just below the specimen tube. As boiling continued the layer progressed down the vessel and after a time - which varied with the heat flux - reached the bottom of the vessel. The darkening of the corrosion product coincided approximately with the formation and movement of this layer.

6. Conclusions and Discussions

1. Potential time curves

The potential time curves seem to divide themselves into three distinct sections - see Fig.3.2. Before the heater current was switched on the specimens maintained a potential of 350 mV negative to a standard calomel electrode. When heating commenced the potential changed immediately to 550 mV and steadily decreased while deaeration occurred,

without boiling, and section AB may be considered to be essentially a deaeration section. At point B the hot cold interface previously mentioned formed and at Point C had flattened out below the specimen tube. By point C boiling was well developed and the potential continued to fall and at point D appeared to be attaining a reasonably steady value. At this point the hot cold interface reached the bottom of the vessel, which in the run on which Fig.3.2 is based occurred after approximately five hours. The potential suddenly decreased and attained after a short time a potential which was maintained for the remainder of the run.

11. pH changes

The increase in pH, which occurred in all cases, could be due to two distinct causes. At the commencement of a run the distilled water used had a potential of approximately 5.2, probably due to dissolved gases such as carbon dioxide. As the run proceeded the carbon dioxide would be desorbed and the pH of the water should then be approximately 7.0. Boiling separate samples of water showed this to be the case. In some cases however pH values greater than 7.0 were observed which must be due to some other cause. The most likely explanation is that a reaction which either produced hydroxyl ions or removed hydrogen ions was involved in the corrosion process.

iii. Weight loss vs heat flux

The plot of weight loss vs heat flux is shown in Fig.3.5. This indicates a decrease in corrosion with increased heat transfer, and is a contradiction to the observations of ^{11,12,19} other workers in non boiling regions. From thermodynamic considerations it was stated in chapter 1 that boiling conditions offered different circumstances to non boiling heat transfer conditions in as much that large changes in heat transfer rates produced relatively small changes in surface temperature. The dissolution and oxidation of iron in aqueous media are exothermic processes, thus by Le Chateliers principle the introduction of heat energy to the system would shift the reaction equilibrium in such a way as to cause less metal to react. The increase in temperature associated with an increase in heat transfer is shown to be small - see appendix 1 and it could be suggested that the resultant increase in reaction rate was not sufficient to offset the shift in equilibrium and therefore lower corrosion rates occurred at higher heat fluxes.

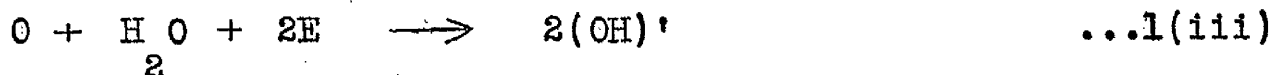
Another explanation for this phenomenon could be oxygen availability at the surface. At low heat fluxes complete deaeration of the solution was a slow process and continued for several hours as the hot cold water interface moved down the vessel and therefore at low heat fluxes oxygen was available at the surface for longer periods than at higher

heat fluxes, where deaeration was more rapid. It has been suggested³⁴ that at low oxygen concentration oxygen will act as an accelerator for the corrosion processes in iron in high temperature waters, and thus the presence of oxygen for longer periods at lower heat fluxes would lead to the higher rate of corrosion observed.

A third possibility was that in some manner the steam bubbles produced on the surface during boiling protected the metal surface and with greater covering by the steam bubbles at higher heat fluxes corrosion is reduced.

iv. General Discussion

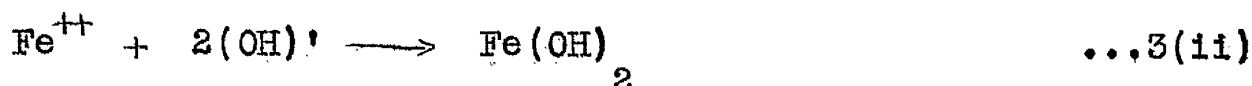
Of the explanations offered above it was thought that the second was the most important, and when the weight loss vs heat flux curves are considered together with the visual observations and the potential time curves this explanation is supported. The solutions used were of neutral pH, prior to a run having a pH of approximately 5.2 and after a run a value of approximately 7.0. It has been suggested^{35,36} that in aerated neutral solutions the predominant cathode reaction is the oxygen reduction reaction



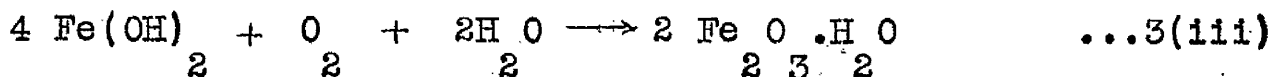
The corresponding anode reaction was the dissolution of iron to ferrous ions.



At the boundary of anodic and cathodic areas ferrous ions react with the hydroxyl ions to produce ferrous hydroxide.



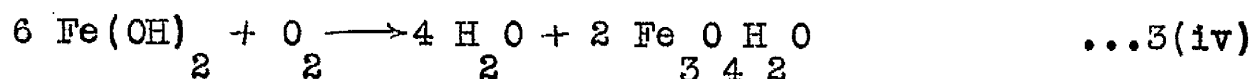
In the presence of dissolved oxygen the ferrous hydroxide is oxydised to the ferric state



This product, ferric hydroxide, is usually rust or brown in colour and was probably the product formed on the specimens in the early part of all runs. The oxygen content of the heated water would be replenished from the cold water below the hot/cold water interface as it moved down the tube, and the reaction potential would remain reasonably constant once the reaction mechanism was established, decreasing slightly as the oxygen content decreased. This was in agreement with the potential time curves obtained during runs as shown in section D.E. in Fig.3.2.

Also as the run proceeded the decrease in oxygen concentration would change the mechanism of the reactions. The metal dissolution reaction, 3(1) and the ferrous hydroxide

formation 3(ii) would remain unaffected by the oxidation reaction would be modified to



Thus with restricted oxygen availability the corrosion product would be black magnetite. The darkening of the corrosion product observed as the run progressed would be explained by this modification in the mechanism.

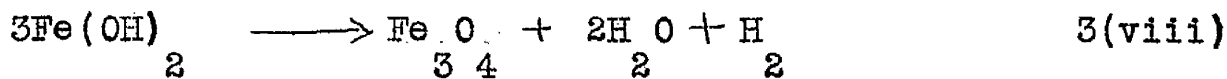
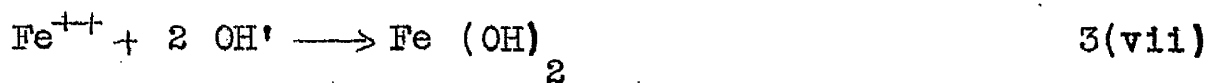
At point D in Fig.3.2. The hot/cold water interface reached the bottom of the vessel and no more oxygen was available for either anode or cathode reaction and an alternative cathode was required if corrosion was to continue. Under these conditions the most likely reaction would be a hydrogen evolution reaction



The potential of this reaction is lower than that of the oxygen reduction reaction and therefore a fall in the electrode potential of the system would be expected. This is in agreement with observed results which indicated a

sudden fall in the potential as the last of the oxygen was desorbed. The potential steadied and maintained the value until the end of the run, it was therefore assumed that there were no further changes in the process mechanisms.

Potter³⁷ has observed that mild steel specimens immersed in high temperature oxygen free water developed a magnetite, Fe₃O₄, film on the surface. The suggested mechanism, has as before ferrous hydroxide as an intermediary.



The experimental observations were in agreement with this mechanism. The black corrosion product, which developed as deaeration proceeded, persisted until the end of the runs.

Another factor in support of this was the weight loss of the blank specimens which followed a similar trend in weight loss to the heated specimens. Since the blank specimens were not being heated it would imply that a factor other than heat transfer was the controlling factor. The oxygen concentration and availability would explain this completely.

The division of the surface into anodic and cathodic sites - the pits and scars mentioned previously - can be explained. Bubbles of gas or vapour formed in a liquid tend to form at active sites³⁸ where conditions of temperature and surface are ideal. Thus both in deaeration and in boiling, oxygen and steam bubbles are formed at these specific points. This was noted during runs. Where steam bubbles formed an area of differential aeration would be established³⁹ and the area beneath the bubble, starved of oxygen, would become anodic to the rest of the surface, and a pit would form. Pits were observed both at the bottom of the specimen where many bubbles were formed and for a time were stationary, and at the top where the bubbles left the surface. Similarly as the bubbles rose up the sides of the specimen the bubble path would be anodic, which would explain the vertical scars on the surface.

The small peak, BC, in the potential time curve, was thought to be due to a change of mechanism. Initially cold water was being heated, and oxygen desorbed on the surface of the specimens, and differential aeration cells would establish themselves at the active sites. At an active site the bubble formed would remove oxygen from its immediate environment, and thus the area would tend to become anodic, see Fig.3.10, since oxygen is required for

the cathodic reaction. Most of the bubbles tended to remain on the surface until the small peak BC Fig.3.2 was reached. At this point bubbles started to rise up the sides of the specimen leaving dark scores in their path. As they moved the area in the path would have oxygen available and the cathodic reaction would be depolarised in the areas around the bubble⁴⁰ thus causing an increase in the potential see Fig. 3.11. As the hot/cold water interface became established, at point C Fig.3.2, the oxygen availability at the surface would decrease due to the lower solubility of oxygen in hot water and the removal of the previously stationary air bubbles on the surface. This would cause polarisation of the cathodic reaction and the potential would decrease once more, and would continue to do so until point E, when, presumably the hydrogen evolution reaction became the cathodic reaction in the absence of oxygen.

These explanations satisfy all the experimental observations, and so it was decided to find the effect of performing runs in oxygen free solutions. This would be a further check on the explanation, and would at the same time eliminate another variable, in particular a variable which was not constant throughout any given run.

Chapter 4

Experiments in de-oxygenated solutions

1. Introduction

The design and construction of the modifications to the original apparatus are discussed. The method of measuring the oxygen concentration of the solutions is shown. The method of operating the apparatus is described, where it differs from the preliminary experiments. The results and conclusions from the experiments are discussed and suggestions made for future work.

2. The design and construction of the modifications

1. The Packed Tower

Modifications were made with as little disturbance of the original apparatus as possible, the side arms included in the first design making this possible. A convenient method of de-oxygenating the solutions was by scrubbing with an inert oxygen free gas, such as nitrogen, in a packed column. During the de-oxygenation it had to be arranged that the specimens did not come into contact with the solutions, but during this section of the run the specimens had to be sealed into the corrosion vessel, and the system made airtight before de-oxygenation commenced, so that the system could be purged of oxygen. For this reason the solution coming from the packed column was fed into a containing vessel above the corrosion cell, with an overflow



to the latter so that the solutions could circulate continually. At the end of de-oxygenation the corrosion cell was filled from the vessel above and the corrosion section of the experiment was started.

One problem of de-oxygenating the solutions was in reducing the possibility of oxygen adsorption by the solutions from the surrounding atmosphere via rubber tubing etc.

⁴¹
Potter in a study on this problem came to the conclusion that neoprene rubber would prevent most of this adsorption and therefore the Q.V.F. gaskets used were made of this. Elsewhere rubber was kept to a minimum. As a further precaution the circulation of the solution was by nitrogen lift pumps, which kept the whole system under a slight positive pressure of nitrogen. The nitrogen was passed through the whole system prior to passing through the column to ensure that oxygen was purged from all parts.

A rigid design of the column was not considered necessary and was considerably over designed to ensure as complete de-oxygenation as possible. The calculations are shown in Appendix 3. The column was three inches in diameter and two feet six inches in height packed with $\frac{1}{2}$ " ceramic Raschig rings.

The level of the solution in the corrosion vessel was to be kept below the specimen tube to avoid wetting and therefore the solution from the column was fed to a 20 litre

aspirator above the corrosion vessel. Connecting this vessel to the corrosion vessel was an overflow system which returned the solution to the latter below the surface in order to avoid splashing. At the end of de-oxygenation the solution was fed into the corrosion vessel by opening a tap in the overflow system (see Fig.4.2.)

Badger and Banchero⁴² suggested that for air (or nitrogen) lift pumps that the ratio $\frac{H_s}{1+s+H_e}$ should be not less than

0.66, if reasonable efficiency is to be obtained where

H_s = submerged height,

H_e = lift height, as shown in Fig.4.1. Therefore, since

the lowest level was fixed at below the specimen tube, three stages were required to obtain the necessary lift. The aspirator into which one line discharged acting as the submerged line for the next stage. The nitrogen supply was from white spot grade compressed nitrogen cylinders.

Separate lines went to each of the lift. The nitrogen effluent from the first two stages passed from the pumps into the corrosion vessel to purge all the oxygen present. From the vessel it was passed counter current to the solutions through the packed column and discharged to the atmosphere via a bubbler at the top of the column. The nitrogen from

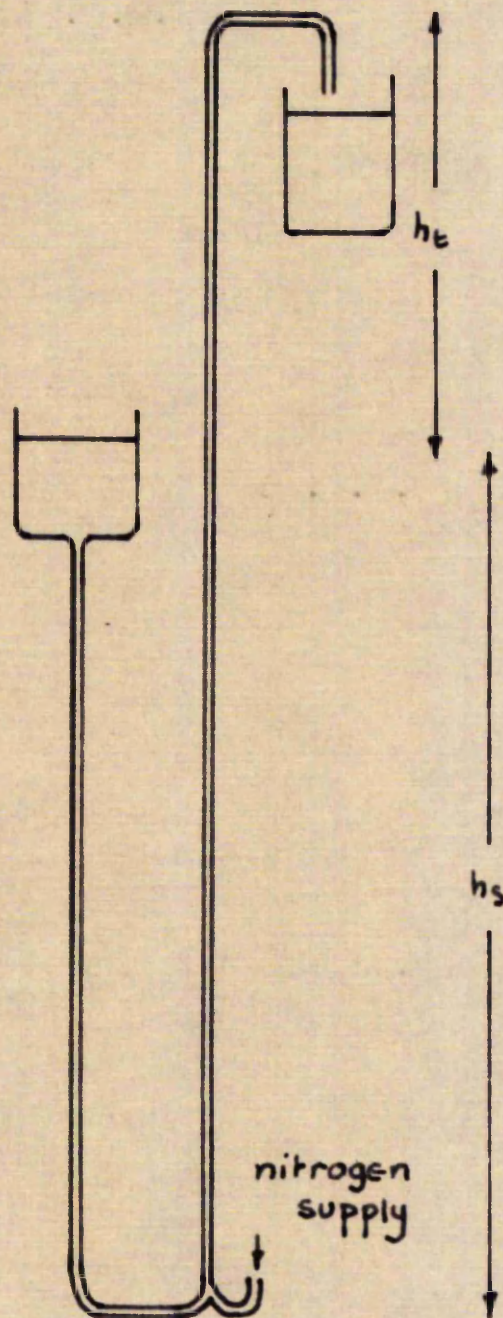


FIG 4.1. Nitrogen lift pump.

the third stage was discharge directly via the bubbler. Thus the whole system was purged with nitrogen and there was little opportunity for oxygen to enter the system. The airtightness of the system was tested by completely filling with water and all leaks were sealed under these conditions. The complete flow system is shown in Fig.4.2.

ii. Oxygen concentration measurement

The oxygen concentration was measured by at Magna Coporation Oxymeter, model 1070, which used as its working principle the electrochemical reduction of oxygen. The current between anode and cathode being a measure of the concentration. The sensor assembly consisted of an anode and cathode mounted on an inert plastic body. This was dipped into an electrolyte and covered with a plastic membrane which would allow only oxygen and some other gases to permeate. The membrane was smoothed carefully over the electrodes then sealed by means of an "O" ring and sleeve, as shown in Fig.4.3. This was directly connected to the indicator which consisted of a meter and two controls. One, the range control, allowed the selection of the desired microameter scale, abitarily graduated from "0-20" and "0-100". The other, the adjust control, was used for calibrating the system. Calibration of the system and the calculation of oxygen concentration from the readings are shown in Appendix 4. Samples of the solution were taken via the 4" sealing gland through a cooling coil to the

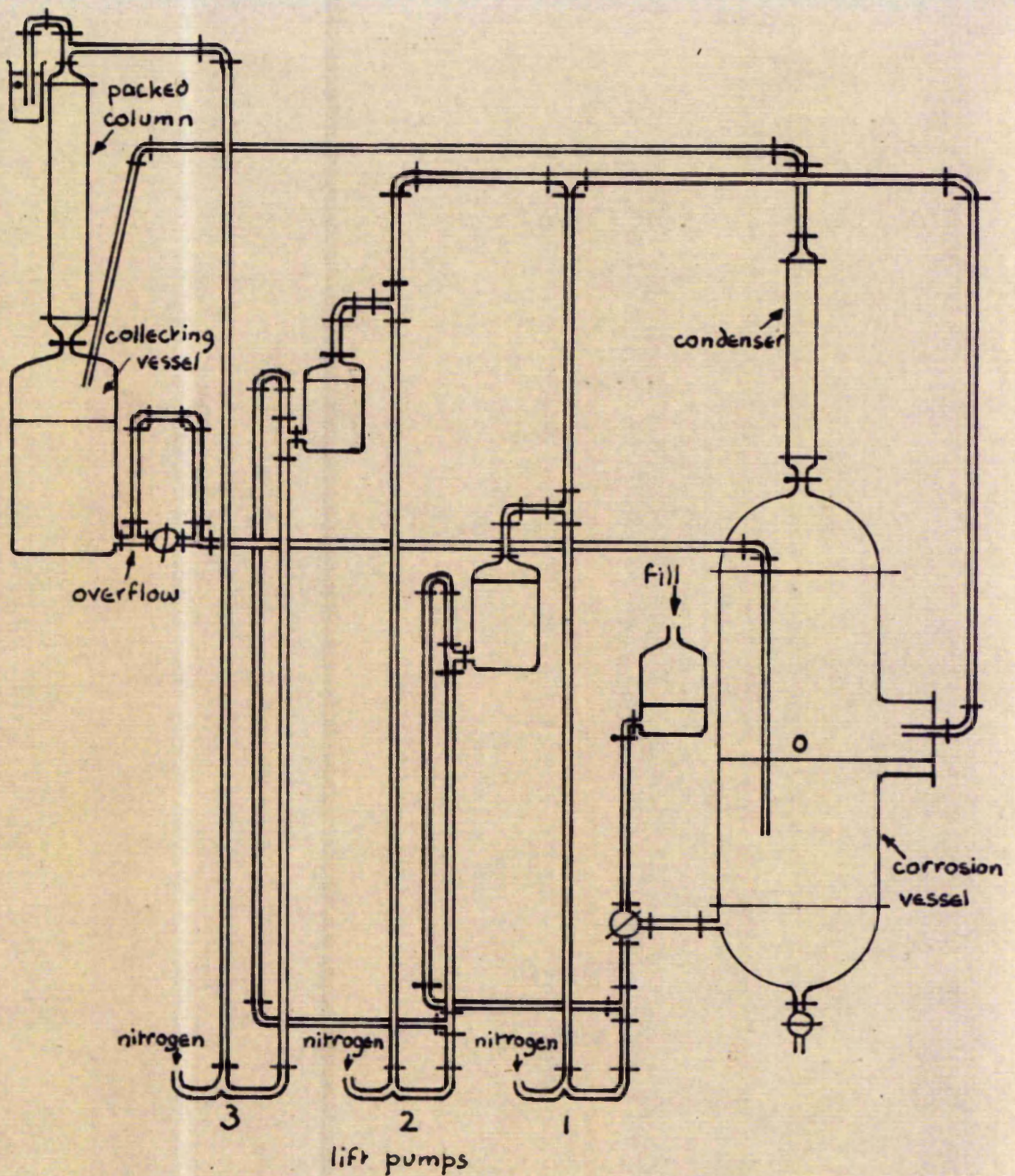


FIG 4.2. Flow system for deoxygenation apparatus

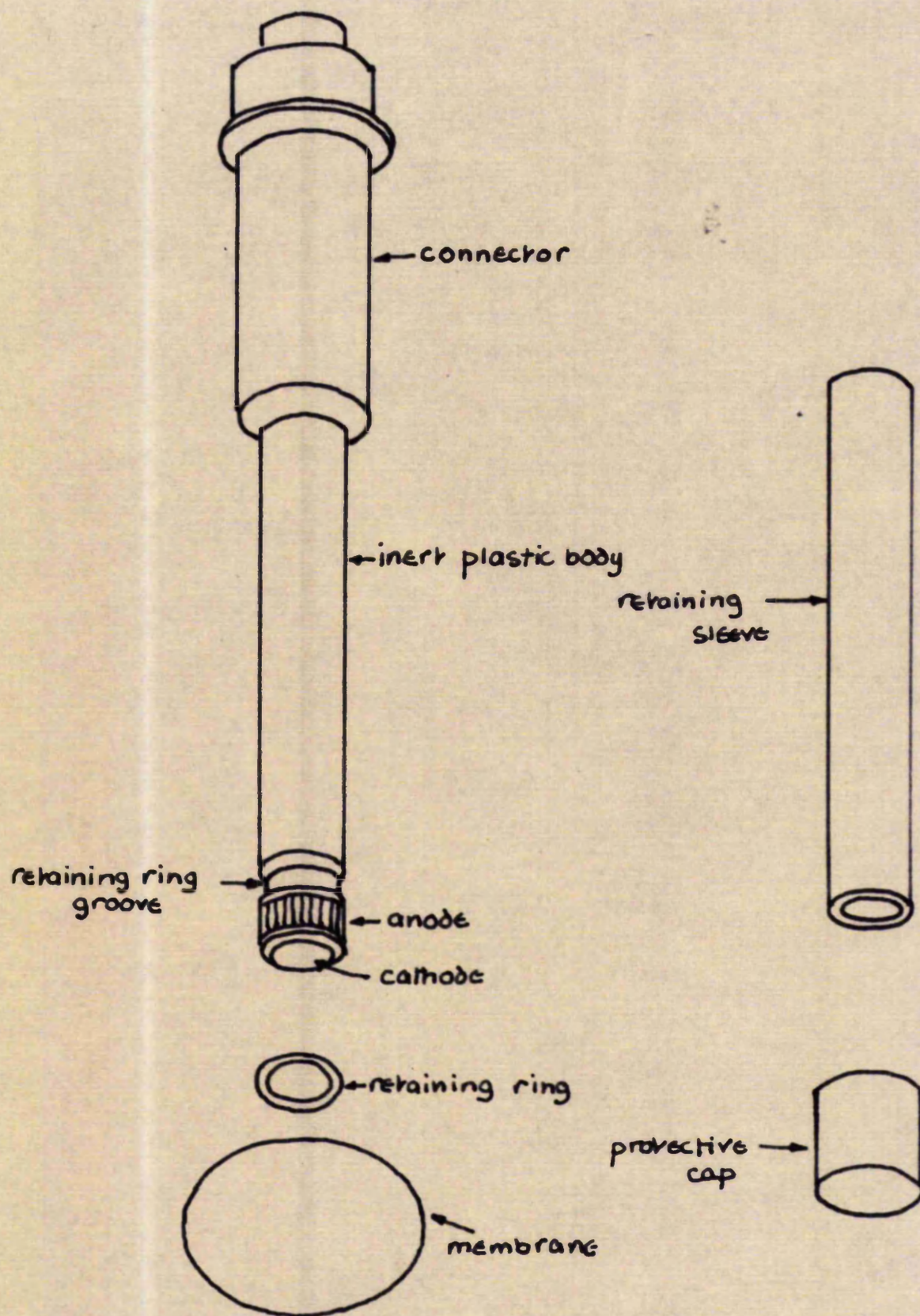


FIG 4.3 Oxygen meter sensor assembly.

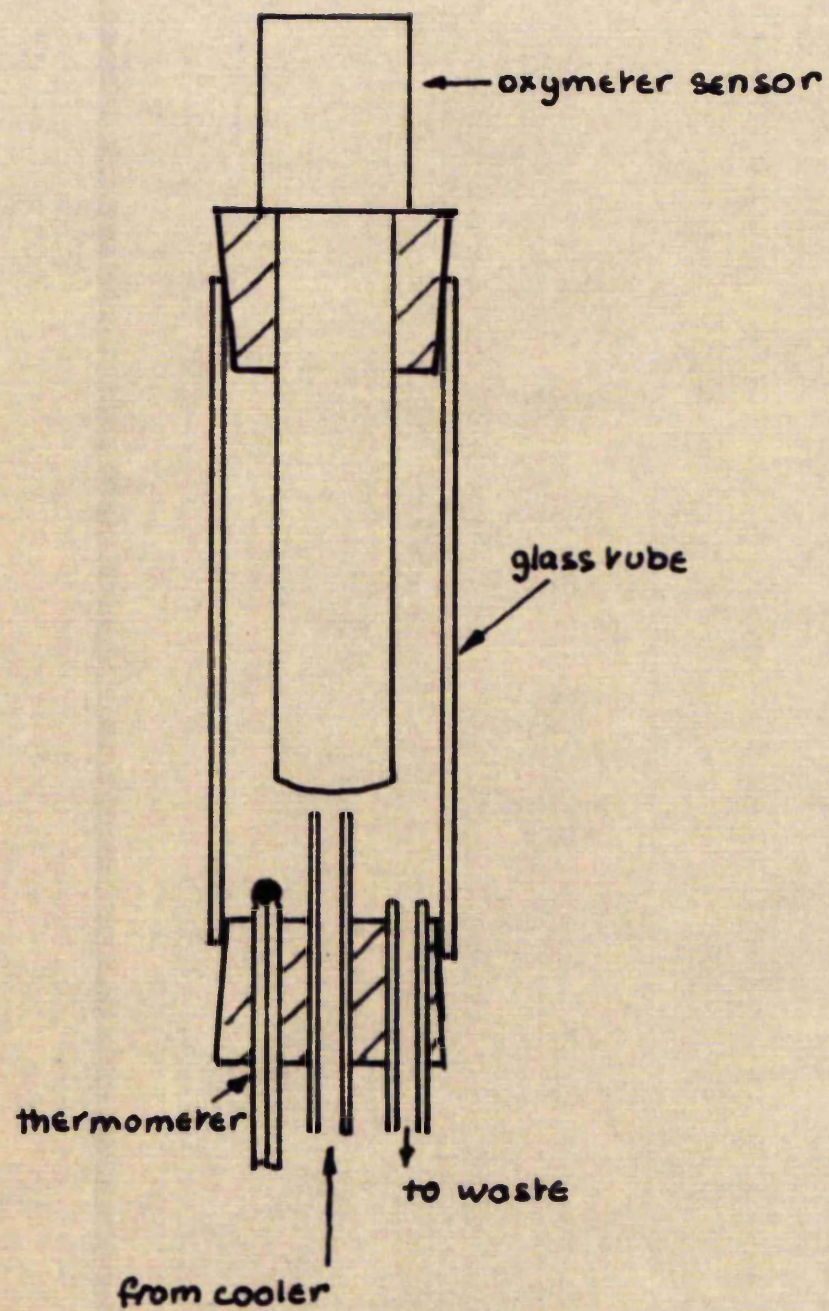


FIG 4.4. Oxygen concentration measurement sampling vessel.

oxymeter fixed in a vessel shown in Fig.4.4. The solution temperature in the vessel was measured.

A photograph of the whole apparatus is shown in Fig.4.5.

3. Method of operation of the apparatus

Specimens were treated, prior to runs, in exactly the same manner as in the preliminary runs. After sealing the specimens in the vessel, as described in chapter 2, the solution, once again distilled water, was poured into the filling vessel and from there allowed to fill the corrosion vessel until the level was just below that of the specimen. The first lift pump was then turned on and the solution pumped to the first aspirator. More solution was fed into the corrosion vessel to maintain the level. When the first aspirator was full the second lift pump stage was started and controlled such that the level in the first aspirator was maintained. Similarly when the second aspirator was full the third stage was started. The solution after the third stage was passed down the packed column, counter current to the nitrogen flow. The solution was then collected in the large aspirator until there was sufficient in the system for the corrosion section of the run. The feed vessel was then isolated and the system run for six hours, solution being returned to the corrosion vessel from the main aspirator.

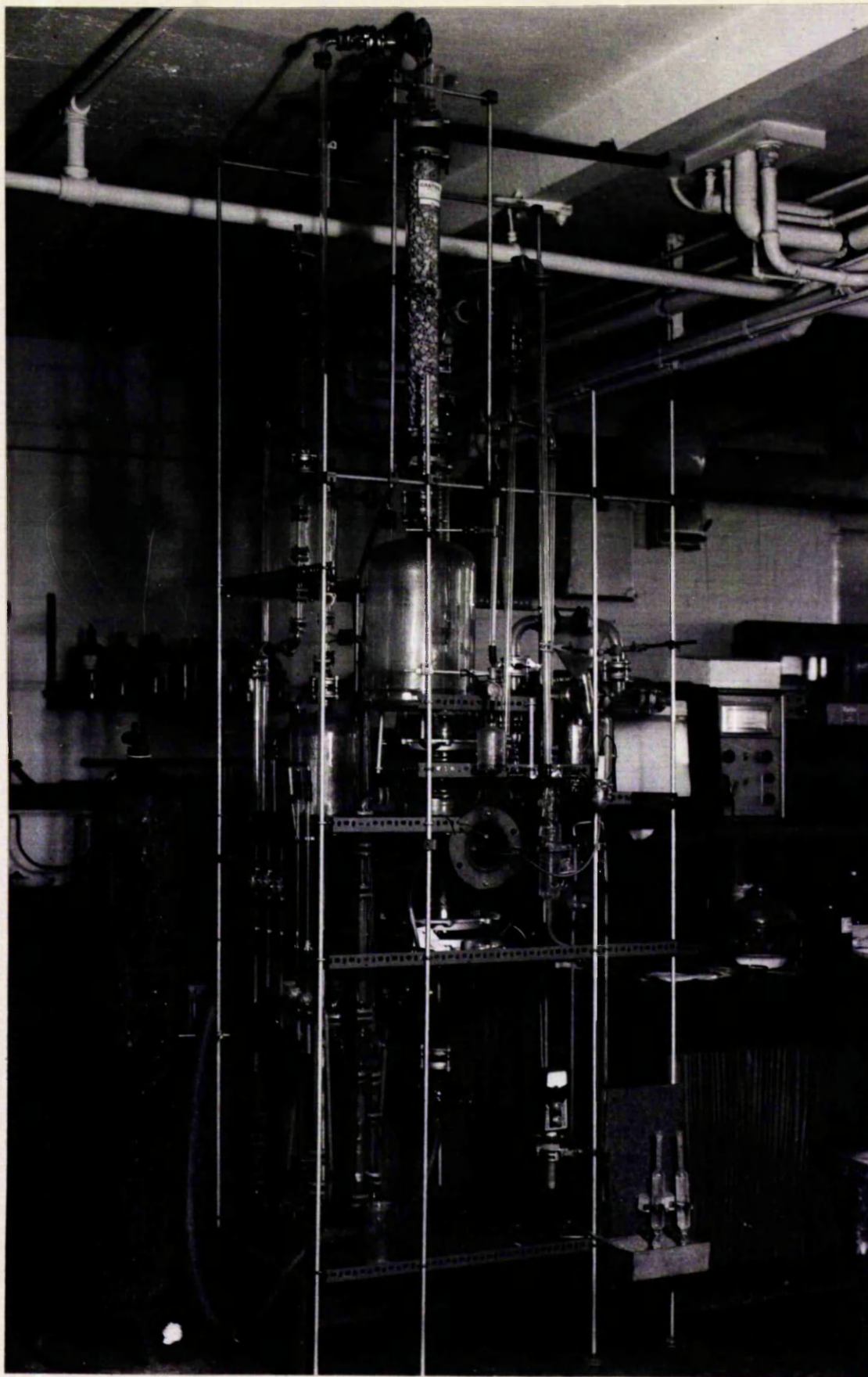


FIG. 4.5. General view of Apparatus

After six hours the lift pumps were stopped, and the solution fed into the corrosion vessel. A sample was passed through the oxygen measurement vessel and was allowed to overflow for a time. The meter was then fixed in position and the solution run through the system until a steady reading was obtained, which was recorded. The level of the solution in the corrosion vessel was adjusted to nine inches above the specimen tube and the procedure described in chapter 2 was continued for the corrosion section of the run.

Results

i. Potential-time curves

As in previous experiments the potentials of all specimens at any one time were equal. The potentials varied with time in a given run in the manner shown in Fig.4.6. Comparison with Fig.3.2 showed the specimens to be at a lower potential for the first few hours of the run and also the lack of an equivalent peak to BC in Fig.3.2. The average final potential again decreased with increased heat transfer, see Fig.4.7, having similar values to the corresponding aerated solution runs.

ii. Weight loss measurement

The weight loss in all cases was lower than that in the corresponding run in aerated solutions. With respect to heat transfer rates the weight loss varied little, decreasing

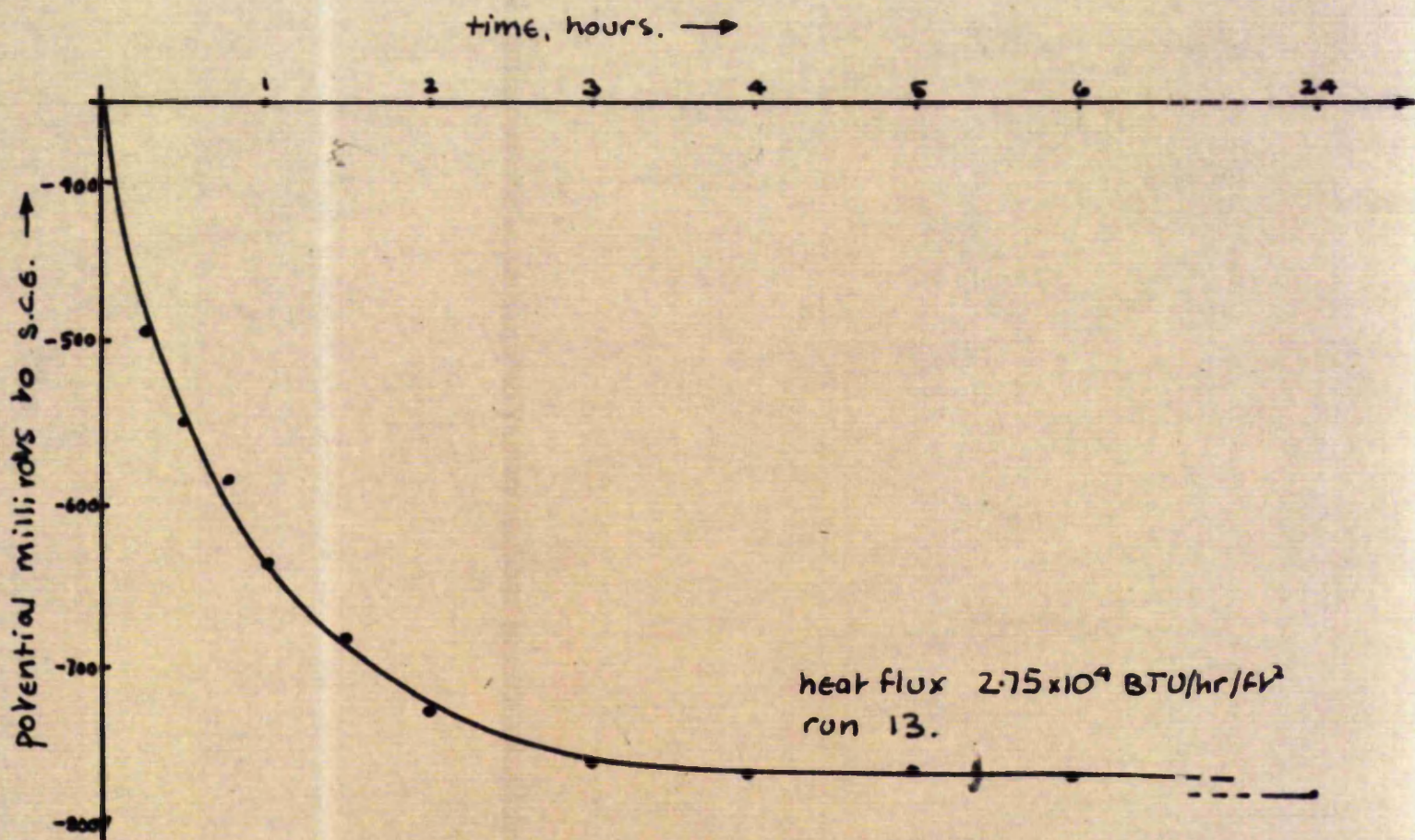


FIG 4.6. Specimen potential versus time

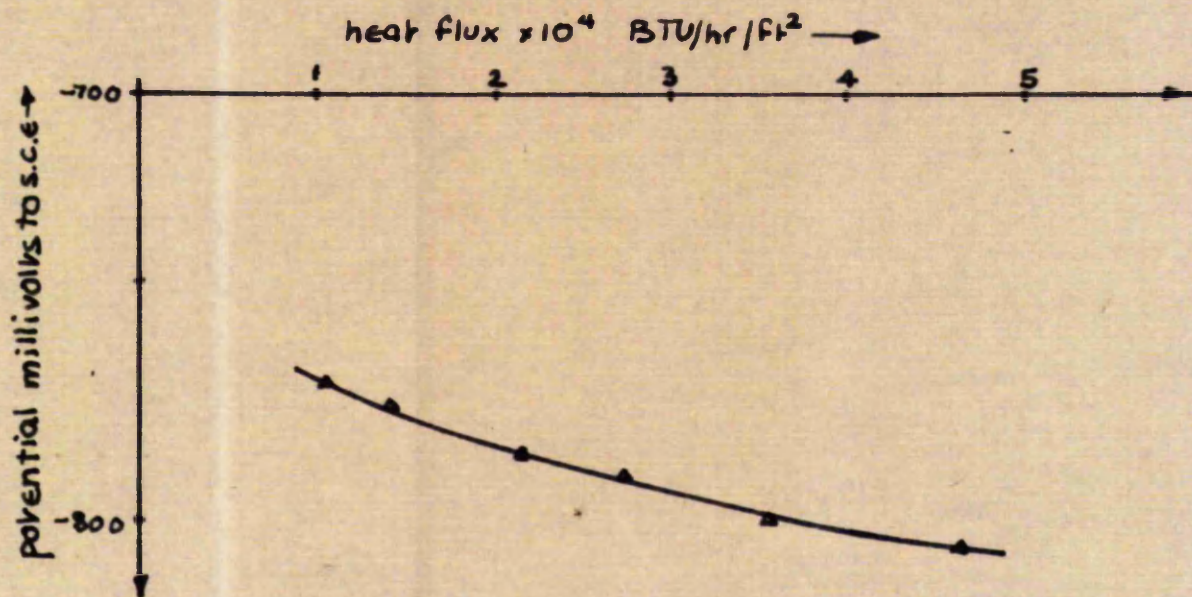


FIG 4.7. Final specimen potential versus heat flux

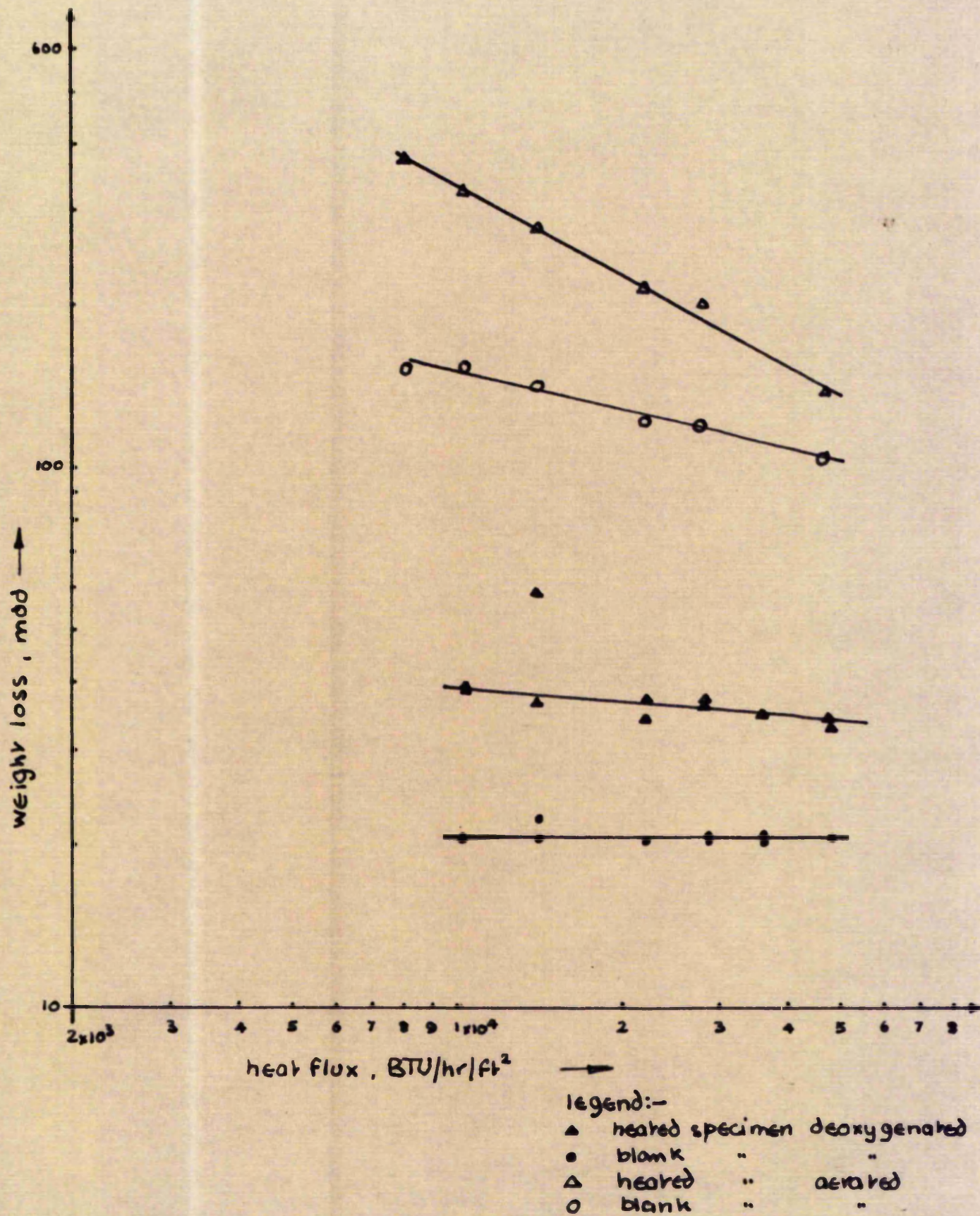


FIG 4.8. Log-log plot weight loss versus heat flux

slightly with increased heat transfer as shown in Fig.4.8.

iii. pH measurement

Samples of solution were taken after de-oxygenation and were found to have pHs of 6.9 - 7.0. Samples taken at the end of a run were cooled, and the pH measured. Values of approximately pH 7.0 were obtained in all cases.

iv. Visual inspection

Prior to a run all specimens were in the same condition as in aerated solutions. At low heat fluxes some streaking occurred, though very little. The surface was duller than at the start of a run but corrosion product was slight. At high heat fluxes a small amount of a grey/gold deposit was noted on the surface, which was slightly darker at the bottom of the specimens.

v. Oxygen concentration measurement

Oxygen concentration was measured after de-oxygenation and at the end of each run. Prior to heating the oxygen concentration was approximately 0.03 p.p.m. At the end of each run the oxygen concentration was hardly measurable but certainly less than 0.02 p.p.m.

vi. Surface temperature measurement

The surface temperature versus time curves followed almost identical trends to the preliminary runs, reaching the same final temperature for the corresponding heat flux

(calibrated at a later date).

The full results of de-oxygenated runs are shown in Appendix 5.

Conclusions and Discussion

The comparison of the weight loss of the first and second series of runs shows a marked decrease in the de-oxygenated solutions. Thus it would appear that the suggestion in chapter 3, that oxygen was an important factor, was correct. The potential held by the specimens was almost the same as the potential of the specimens in the latter stages of the corresponding aerated run. It is therefore thought that the mechanism is the same. As suggested, in the absence of oxygen, which in the second series of runs is established and in preliminary runs assumed, the mechanism would be.

The anodic reaction, the dissolution of iron:-



The cathodic reaction, a hydrogen evolution reaction:-

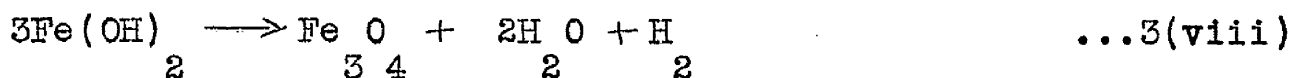


The reaction at the boundary between anodic and

cathodic areas:-



and possibly continuing to:-



The last two reactions producing the corrosion product noticed in these experiments.

The weight loss versus heat flux curves indicate in this series of runs that the change in heat transfer rates has little effect on the corrosion rate, as shown in Fig.4.8. It has already been shown that the surface temperature varies little under boiling conditions, and it is thought that this may well be the controlling factor in the corrosion processes involved with heat transfer. The work of Illingworth¹⁹ showed an increase in corrosion with increased heat transfer over a similar range of heat transfer rates to the present work. However the surface temperature changed in non boiling conditions by 150^o F over the heat transfer range, whereas, over a similar range the change is 6^o F under boiling conditions. Thus if surface temperature were the controlling factor, little change in the corrosion rate under boiling conditions would be expected, though if it were the only factor a slight increase rather than decrease in corrosion

rate would be expected with increased heat transfer. The other factor is possibly the introduction of energy to the system altering the reaction equilibrium as suggested in chapter 3.

From the first and second series of runs it is indicated that oxygen plays an important role in the corrosion process. Though in aerated runs its extent cannot be estimated without further experiments since oxygen concentration is not constant throughout the runs. Therefore the first two series of runs were repeated, with time as a parameter, to separate these effects.

Chapter 5

The change of corrosion rate with time

1. Introduction

Prior to this series of runs the non inductively grooved former was available and trials with various forms of heating were performed and conclusions drawn. The experiments with time as a further parameter are recorded and the results are discussed.

2. Experiments with various forms of electrical heating

It was mentioned in chapter 3 that a problem had arisen in taking surface potential measurements. If the heater current was switched on absurd readings, in the order of 4volts negative to a saturated calomel electrode, were obtained. The method used for the first two series of runs was to switch off the heater current immediately prior to any potential reading. Trials were made, and it was established that the readings were due to currents induced in either the specimens or the probes to the surface. These currents were being rectified in the first valve stage of the millivoltmeter, causing the absurd readings. These signals could be shorted out, but this was thought to be masking the problem, since the currents would still be flowing within the corrosion cell and may be affecting the corrosion processes. A method was therefore required to remove or cancel these currents. Two methods were considered as

feasible, these being the use of a non-inductive winding, with either alternating or direct current, as the heater. With alternating current the currents should cancel each other and the nett induced current would be zero. Using direct current in the form of a coil would produce a magnetic field, but with a non inductive winding the fields would cancel and the nett field would be zero. The non inductive former was constructed of a star shaped section aliminous porcelain rod, 16mm in "diameter", 8" in overall length, with the central 7" inches, grooved externally at ten turns per inch with a two start thread, the grooves approximately 0.75mm wide and 1.0mm deep. The Nichrome V resistance, as used for the previous experiments, was wound in one direction for the total length of the former, fixed at the end, and then wound back, as shown in Fig.5.1. The resistance of the coil was 30.5 ohms. Fine bore steel tubing was pushed over the wire used as leads to the coil and crimped onto it, reducing the resistance of the leads, and the whole system was covered with silica cement and baked in an oven. A similar silica tube was used as in the preliminary experiments, but since both electrical connections were at one end, the other end of the tube was sealed, which greatly facilitated placing the specimens on the tube. The tube, apart from the section occupied by the former was filled

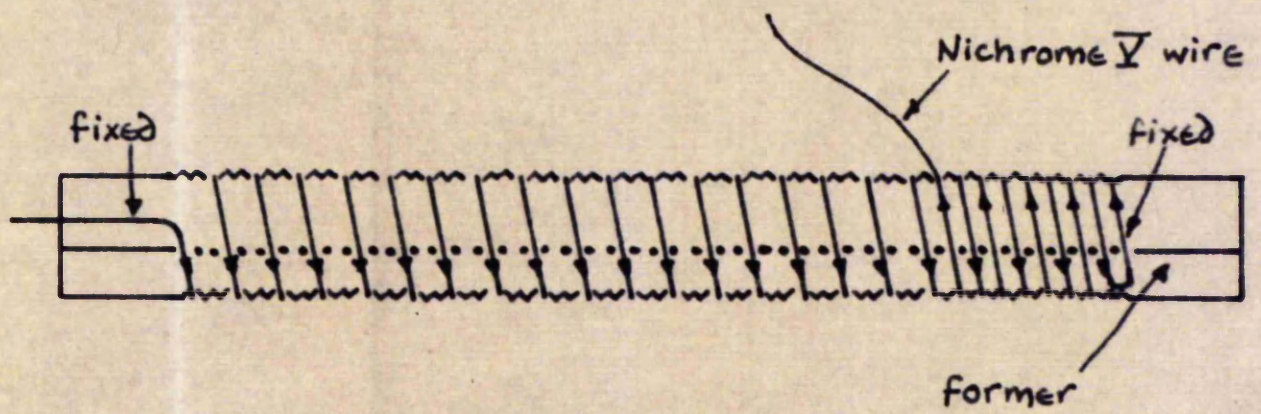


FIG 5.1. Non inductive winding on two start thread former

with asbestos wool, to reduce heat loss along the tube. The specimen tube in this form was used for both alternating and direct current.

i. Alternating current experiments

The circuit was the same as for the previous series of runs, with the exception of the heater, as described. The voltage across the heater was controlled by the variac and the system was as shown in Fig.2.1. Runs were performed at various heat fluxes in aerated solutions for twenty four hours and the weight loss results, and potential results compared with those using the inductive winding. Potential measurements were still slightly sensitive to the switching off and on of the heater - varying by 2-3mv.

ii. Direct current experiments

For the power requirements it was decided that the best method would be to rectify mains AC, using a full wave rectifier. The D.C. ripple was removed using electrolytic condensers across the rectifier output. The rectifier was a silicon bridge rectifier, rated at 400 P.I.V. and 10 amps maximum current. The smoothing condenser, was a bank of eight 500 μ F electrolytic condensers, rated at 350 v. The voltage and current of both rectifier input and output beyond the smoothing condensers was measured. The full circuit is shown in Fig.5.2. Runs were performed at various

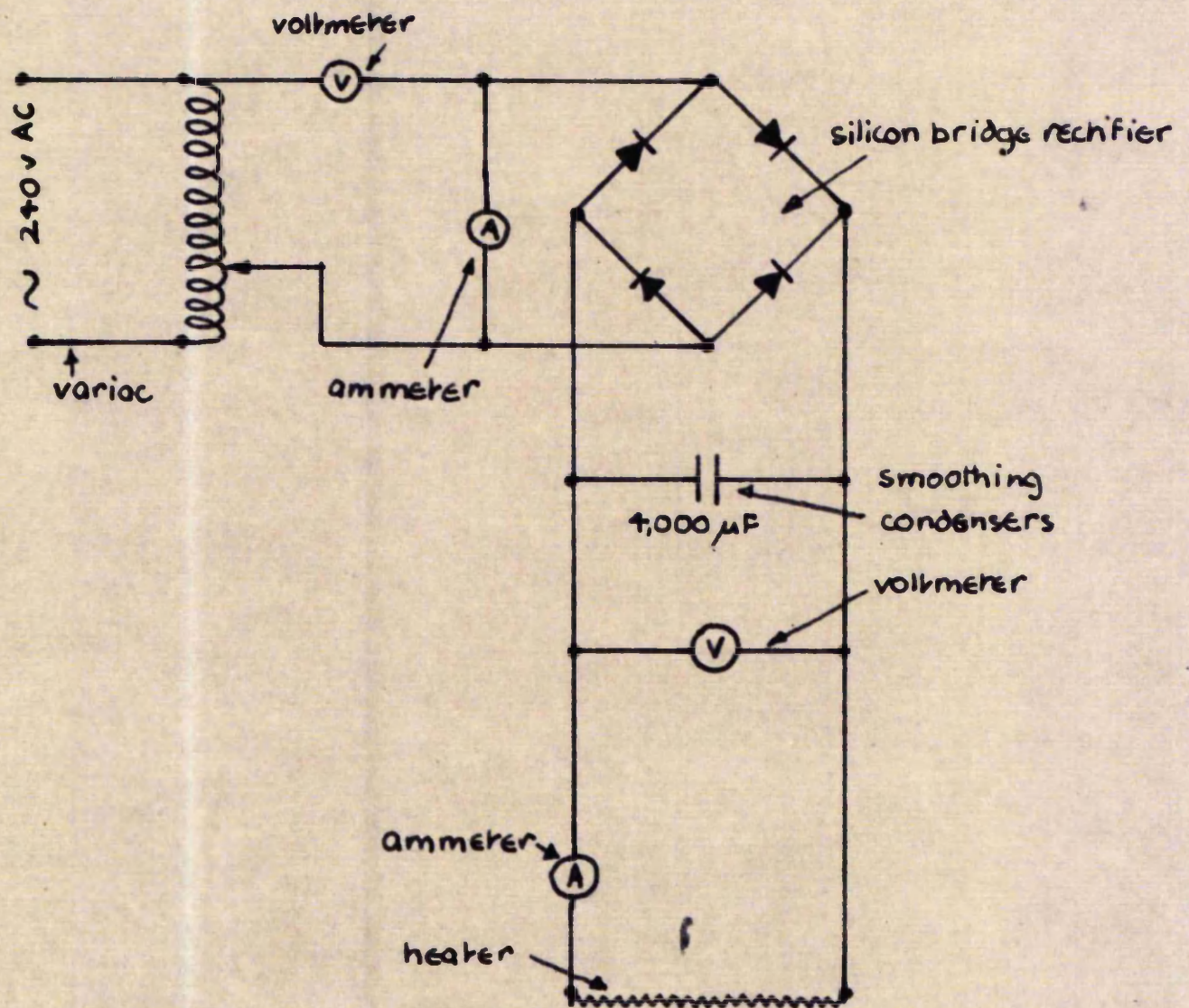


FIG 5.2. Direct current heater circuit.

heat fluxes, though due to the power dissipated in the condensers this was kept to lower rates. Weight loss and Potential readings were taken and compared with previous experiments. The heater had no effect on the potential measurements.

iii. Results

Weight loss vs heat flux curves for the various runs are shown in Fig.5.3. The curves are compared with the curve obtained from the inductive winding and it was found that there was no significant difference between the heating methods. This would indicate that the induced currents were having little or no effect on the corrosion processes.

Similarly the potential time curves were compared. The readings obtained using the non inductive A.C. circuit were slightly higher than readings obtained with the heater switched off and compared well with the readings obtained in previous runs, see Fig.5.4. The difference in reading could be eliminated by using a small condenser across the input to the millivoltmeter. This suggestion was rejected in chapter 3 since it was thought that this was merely masking the problem, but as it had now been shown that the induced currents were having little or no effect, it was decided that shorting the A.C. component was justified, in order to obtain a continuous correct reading. For the remainder of the runs it was decided to use the non inductive

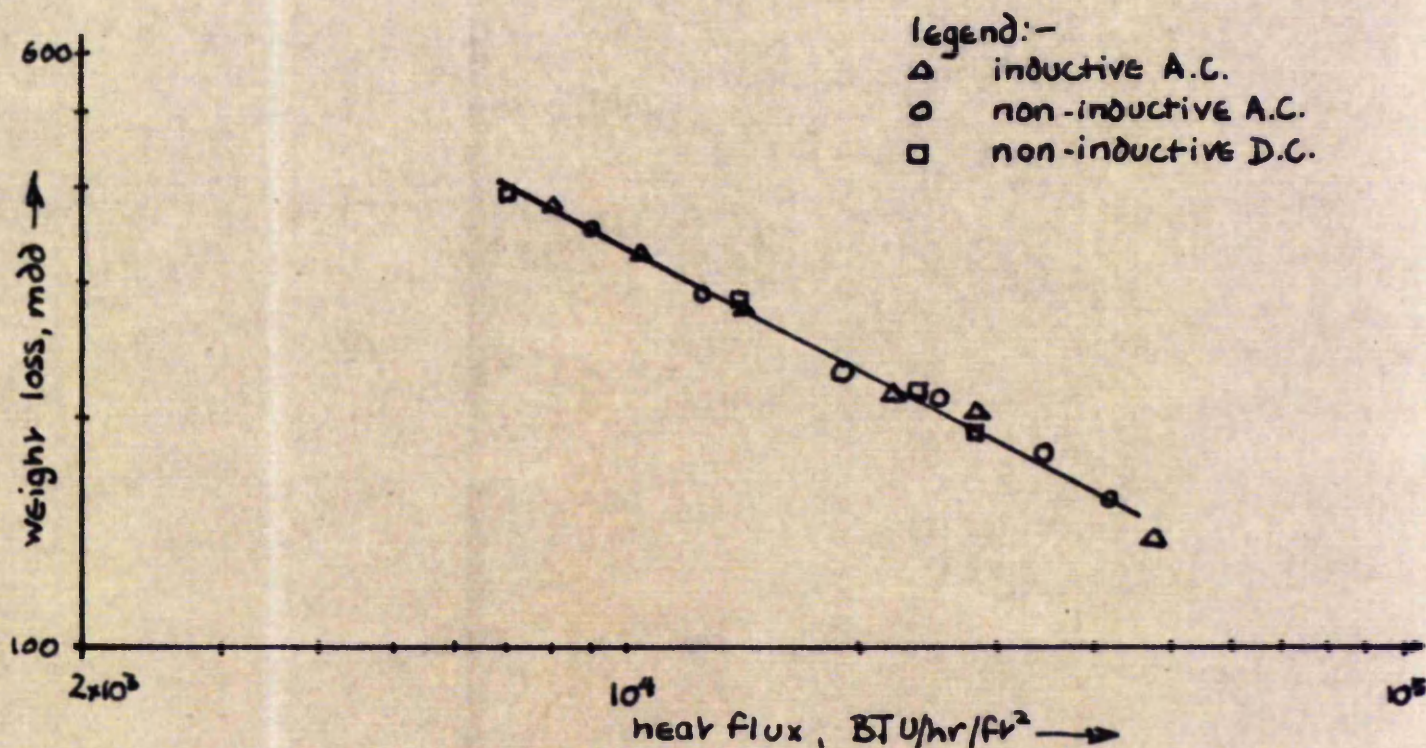


FIG 5.3 Log-log plot weight loss vs heat flux for various heating systems

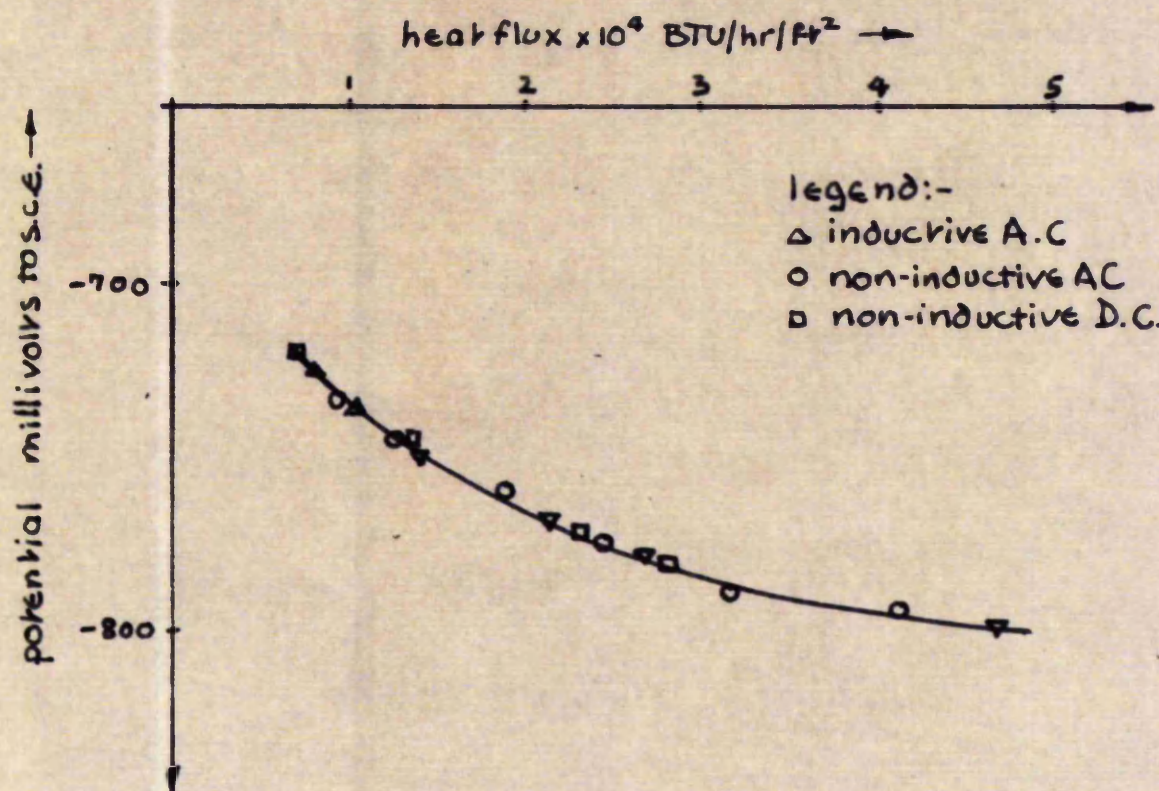


FIG 5.4 Final potential versus heat Flux for various heating systems.

winding because continuous potential readings could be taken. Alternating current was used because it had greater range than direct current.

3. Experiments with time as a parameter

i. Experimental

The same procedure was used as in previous experiments, depending upon whether aerated or de-oxygenated solutions were used. The use of the new heater allowed continuous potential readings to be taken however and these were recorded on a sunvic high impedance recorder with an external rheostat for calibration purposes. A reading was obtained on the meter and the rheostat adjusted until the same reading was indicated on the recorder and a check repeated at the other end of the scale.

The specimens were exposed to the solutions for a given length of time, which was recorded. They were removed and weight loss determinations made. Potential, temperature and oxygen concentration readings were taken and comparisons made with previous runs.

ii. Results

Potential Readings

The readings compared satisfactorily with readings from the corresponding runs from the previous series, and are

shown in Fig.5.4.

Weight loss curves

Weight loss vs heat flux for twenty four hour runs compared satisfactorily with previous results, which was an indication of the reproducibility of the system. Comparisons are shown in Fig.5.3. Weight loss versus time curves are shown in Fig.5.5.. For all heat fluxes in aerated solutions, the initial rate of corrosion was the same. At a time, which, for any given heat transfer rate coincided approximately with the hot cold interface reaching the bottom of the corrosion vessel, the corrosion rate altered to a lower value, which was once again approximately the same for all heat fluxes. Comparison showed the corrosion rates during latter part of runs in aerated solutions to be approximately the same as the corrosion rate throughout de-oxygenated runs.

Oxygen concentration measurements

Once again, as in the case of pH, difficulty was experienced in obtaining a representative sample, but trends were indicated as shown in Fig.5.6. Initially oxygen concentration in aerated runs decreased from the initial value to a value which was held for some time and then the oxygen concentration decreased almost to zero. Full results are shown in Appendix 6.

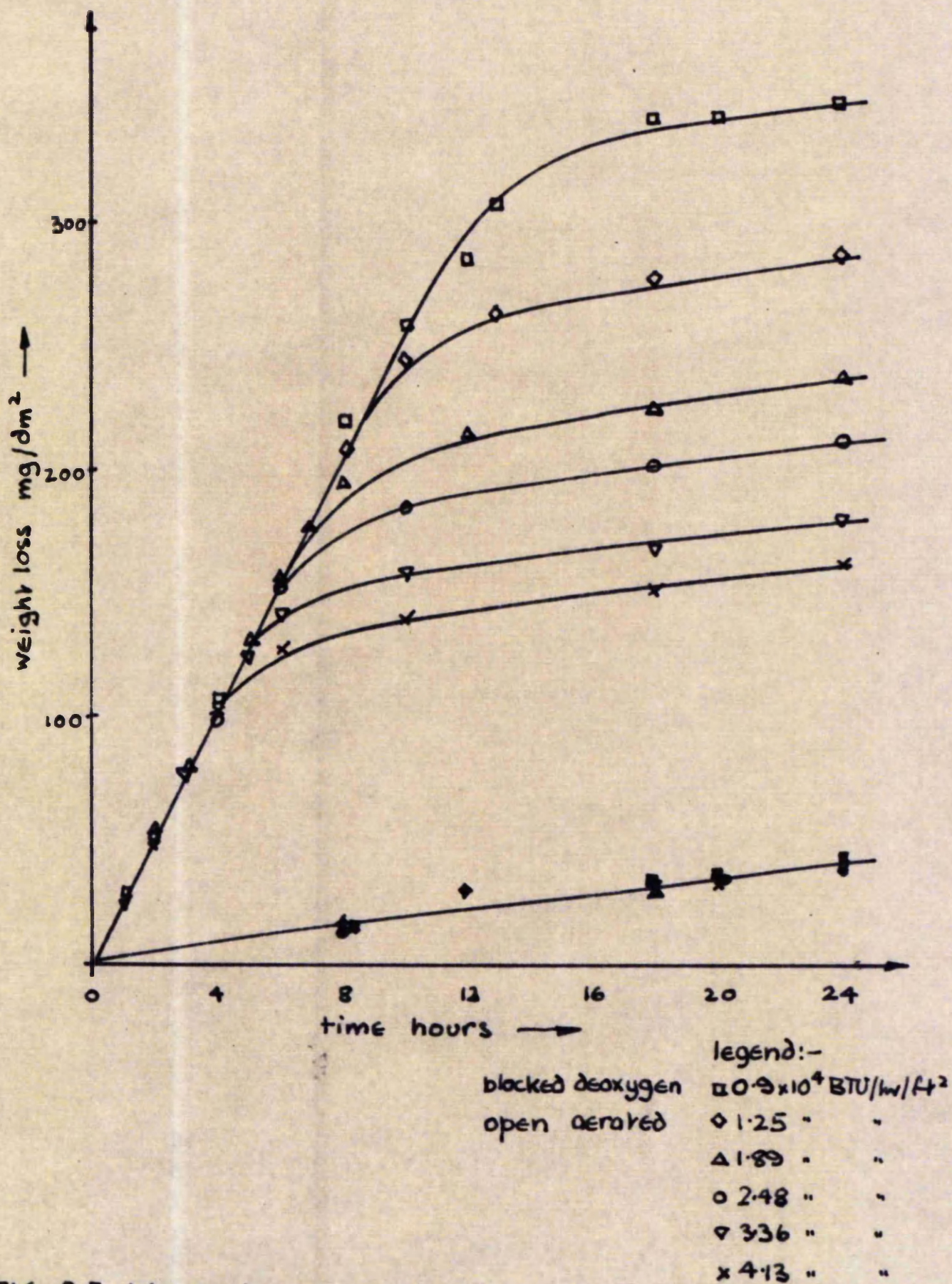
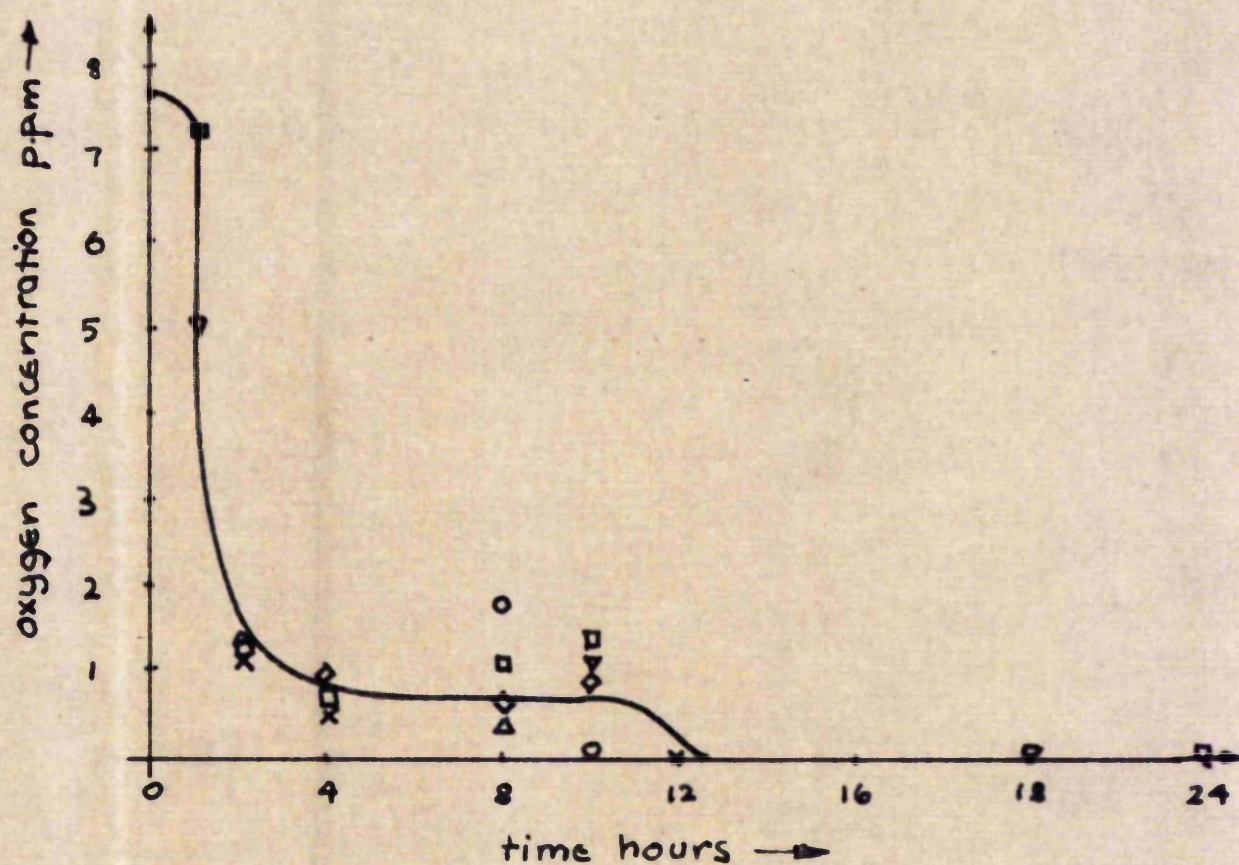


FIG 3.5 Weight loss versus time

Conclusions and Discussions

From Fig.5.5. it would appear that the process in the first part of the runs in aerated solutions was independent of the heat transfer rate. Increasing the heat transfer had no effect on the corrosion rate. Oxygen concentration measurements, although far from accurate, indicated that for all runs the oxygen concentration in the solutions was the same during^{the}/early part. See Fig.5.6. This would be the oxygen concentration of the solution at boiling temperatures in equilibrium with the cold solution below the interface. Once the interface reached the bottom of the vessel the oxygen concentration would fall, since no more oxygen would be available. Thus since the oxygen concentration was almost the same irrespective of heat flux it was thought fair to compare the corrosion rates directly, and it could be seen from the initial slope of the aerated run curves that the increase in heat flux had a negligible effect on the corrosion rate. This had already been shown to be the case in deoxygenated solutions where a small decrease in corrosion rate was noticed with increasing heat transfer.

Thus it is concluded that temperature rather than the transfer of heat is the important factor in heat transfer and corrosion of mild steels in distilled water. The slight decrease in the corrosion rate could be explained by the



legend:-

□	0.9	$\times 10^4$ BTU/hr/ft ²
◇	1.25	" "
Δ	1.89	" "
○	2.48	" "
▽	3.36	" "
x	4.13	" "

FIG 5.6. Oxygen concentration versus time

change of equilibrium of an exothermic reaction due to the energy introduced to the system by heat transfer.

With this in mind it was decided to broaden the field of study by performing experiments with another metal, and assessing the effect of this change.

Chapter 6

Runs using copper specimens in various solutions

1. Introduction

Mild steel specimens were used in all the preceding experiments and, having drawn certain conclusions about the processes involved, it was decided to change the metal used for the specimens. Mild steel is an electronegative metal and it was decided to use a metal somewhat different in character. The corrosion processes of copper, an electropositive metal, vary from the processes of iron and steel, and it is a widely used metal. It was therefore decided to use copper specimens for future work.

The preparation of the specimens is discussed. Experiments were performed in aerated distilled water and in aerated chloride solutions. The results are given and the conclusions discussed.

2. The specimens

The copper specimens were made from copper tubing $\frac{3}{4}$ " in internal diameter and 19 SWG wall thickness. The copper was manufactured to B.S. 659 and B.S. 1172, having an analysis:-

antimony	≧ 0.005%
arsenic	≧ 0.05%
bismuth	≧ 0.003%
iron	≧ 0.03%
lead	≧ 0.01%
nickel	≧ 0.1%

tin	$\nless 0.01\%$
tellurium, selenium	$\nless 0.02\%$
phosphorous	$\nless 0.080\%$ & $\nless 0.015\%$

Total impurity excluding silver, nickel, arsenic and phosphorous 0.060%. The remainder, not less than 99.85% copper, silver counting as copper.

The mechanical preparation of the specimens was the same as for the steel specimens. The specimens were then stretched and heat treated simultaneously but at a lower temperature than for steel, 440°C , for three hours under a nitrogen atmosphere, followed by an air quench. The oxide film, caused by the quench, was removed with 50% hydrochloric acid. For removing the corrosion product after exposure it was found that 50% hydrochloric acid was once more suitable, since blank tests showed that it removed negligible copper in the time required to remove the corrosion product. After cleaning with acid the specimens were rinsed in distilled water, dried, washed in carbon tetrachloride, rubbed dry with a soft cloth, and then weighed.

3. Experiments in aerated distilled water

Runs were performed in exactly the same manner as for steel specimens, for various heat transfer rates and times of exposure. Readings such as potential measurement, pH of the solutions, oxygen concentration and weight loss determinations were made as well as visual inspection of the specimens.

i. Results

a. Potential measurement

The potential of the specimens was, before heating approximately 50 mV negative to the saturated calomel electrode. Upon heating the potential increased rapidly, the rate depending on the heat flux. At high heat fluxes the potential increased more rapidly to a maximum and then decreased to a value which became steady after a number of hours. At lower heat fluxes the rate of increase was less but the maximum was at a higher potential than at higher heat fluxes. The specimen potential then decreased as for high heat fluxes but the final value was higher. The plots are shown in figs. 6.1 and 6.2.

b. Oxygen concentration

As for steel the measurements were not consistent but showed very similar trends. The plot is shown in fig. 6.3.

c. Weight loss determinations

The weight loss curves are shown in figs. 6.4 and 6.5. As for steel in aerated solutions increasing the heat flux decreased the amount of corrosion, but with copper the corrosion rate was different for different heat fluxes throughout the run, whereas with steel the corrosion rate was the same, independent of the heat flux, for a considerable time within a run (c.f. fig. 6.4 and 5.5).

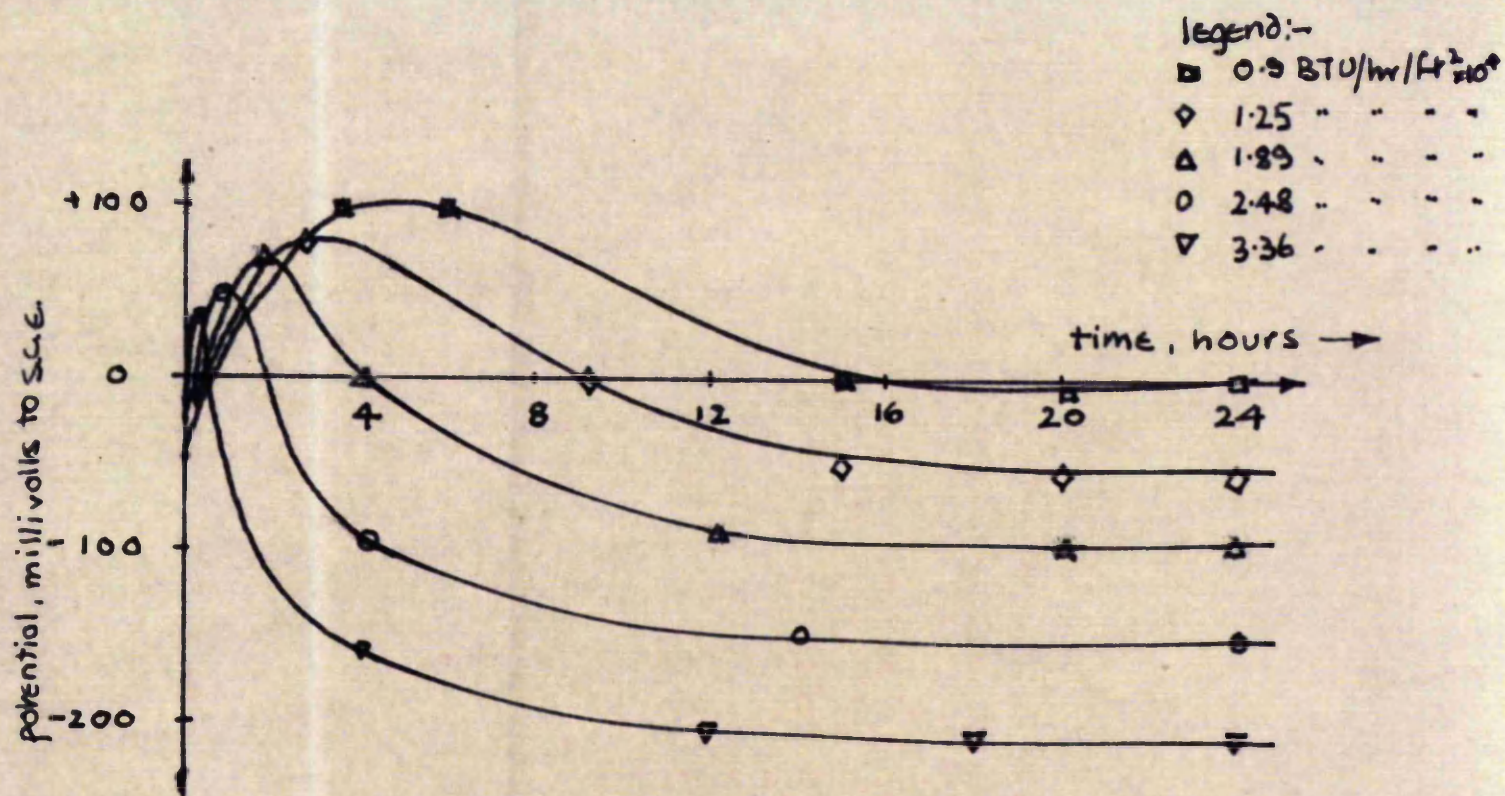


FIG 6.1. Potential versus time

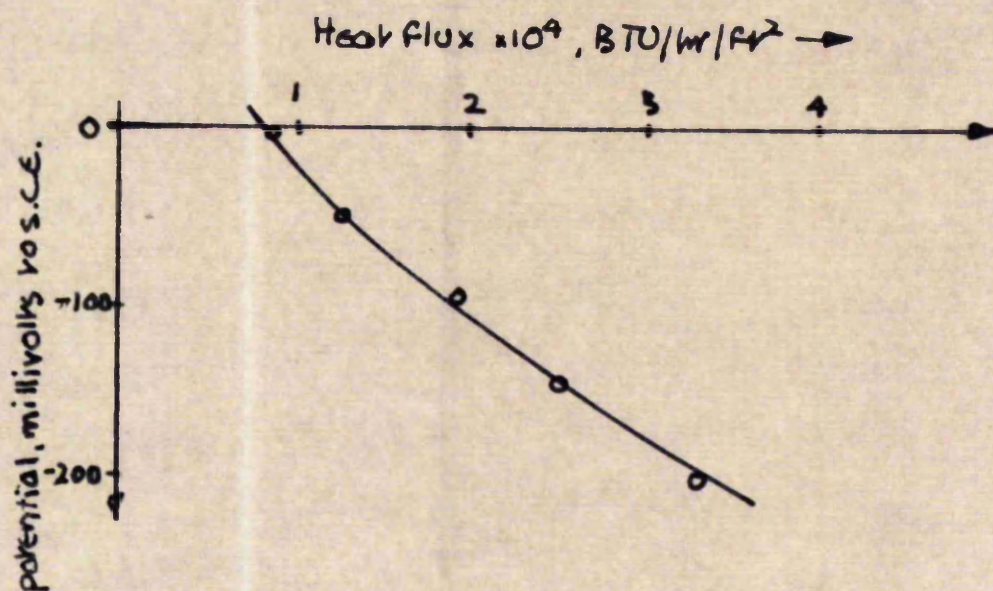


FIG 6.2. Final potential versus heat flux

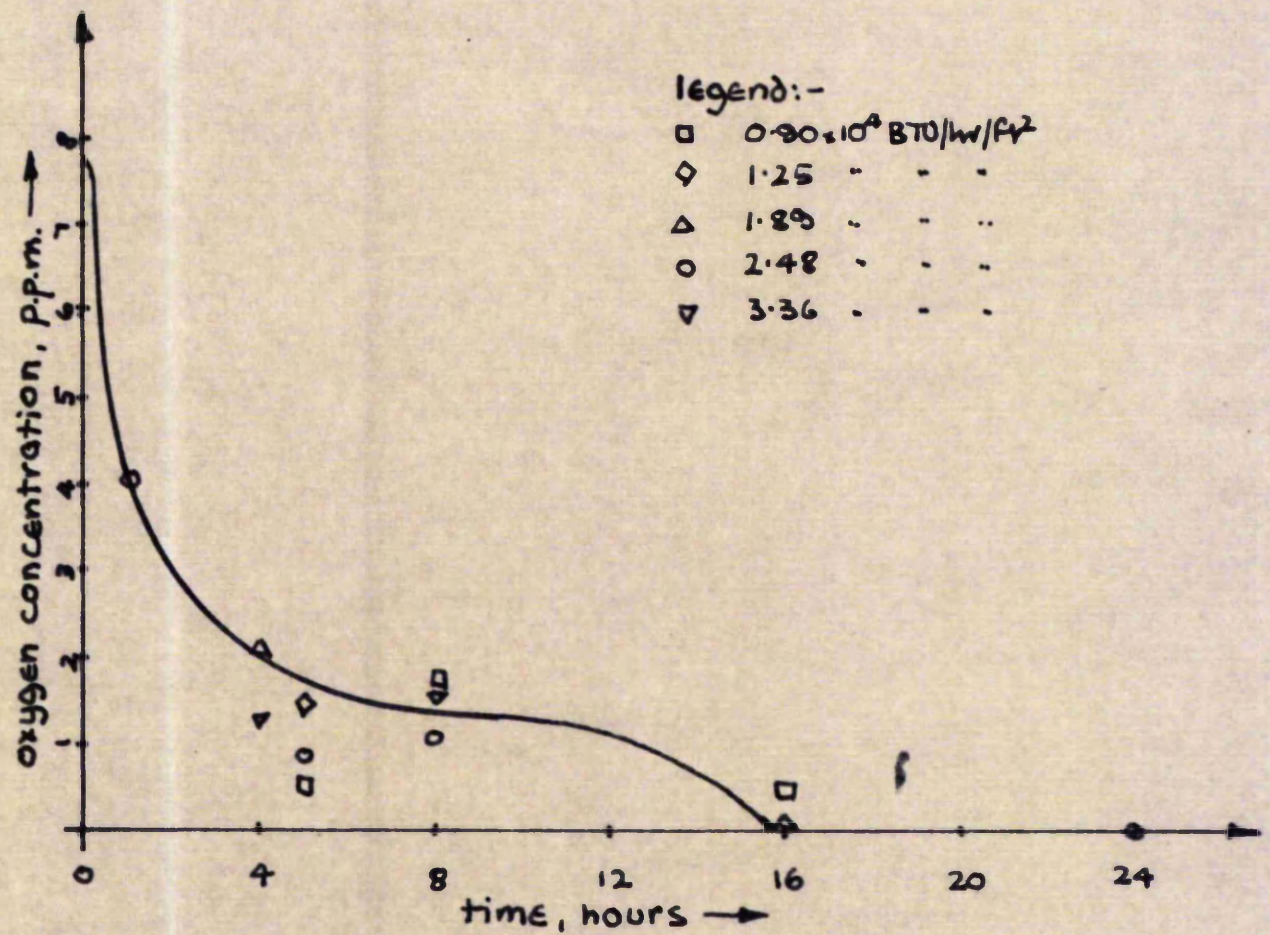


FIG 6.3 Oxygen concentration versus time →

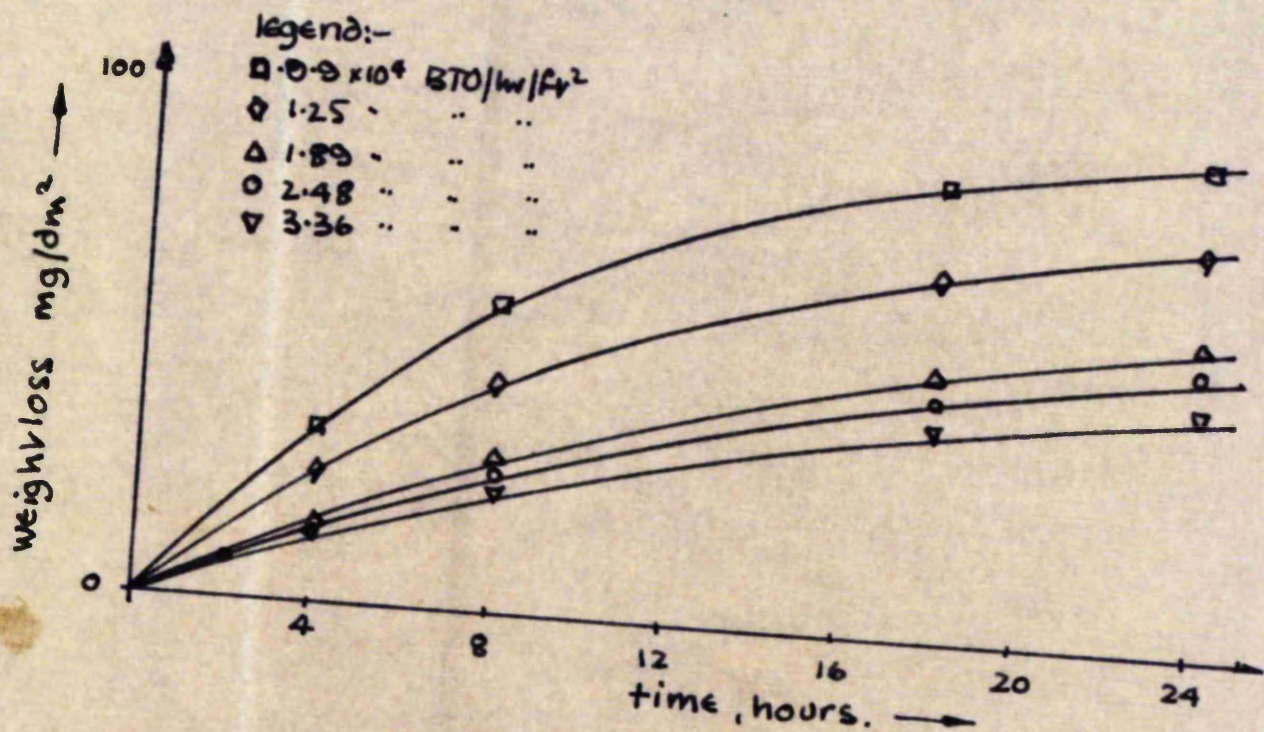


FIG 6.4. Weight loss versus time.

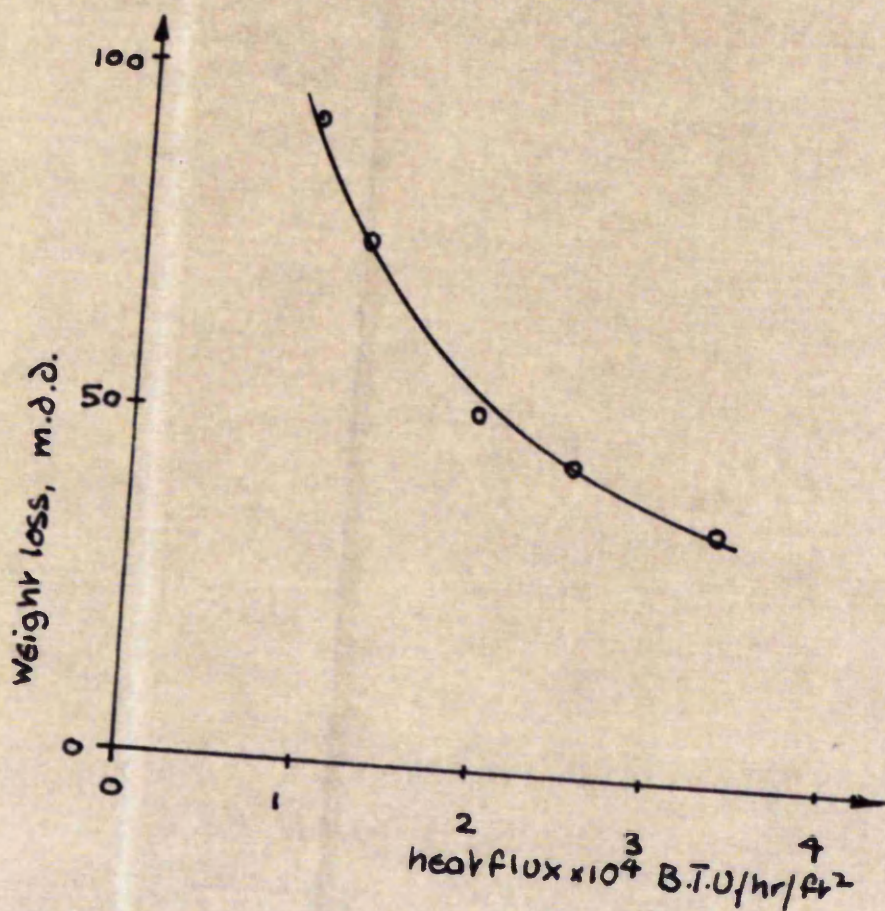


FIG 6.5. Weight loss versus heat flux for 24 hr runs.

d. Visual observations

At the start of any run the specimens possess a smooth matt sheened surface. As heating proceeded the specimens became covered with a dark film which was retained even after twenty four hours. Specimens when removed after a short time of exposure had, at low heat fluxes, small red deposits on bare metal at the bottom of the specimens, and the dark deposits on the sides. After longer periods of exposure the red deposits were larger and there was less bare metal. At higher heat fluxes the dark deposit was more general and only small amounts of the red deposit and bare metal were observed. The deposits on the specimens are shown in fig. 6.6.

pH measurement

The measurement of pH once again proved difficult to perform accurately since the sampling method was not satisfactory. Trends however were observed which as before indicated an increase in the pH from an initial value of approximately 5.3 to a value of approximately 7.1 after boiling had become established.

The results are shown in Appendix 7.

Conclusions and Discussion

As in the case of steel specimens, the corrosion over a period of twenty four hours decreased with increased heat transfer, but a breakdown of the corrosion rate with time

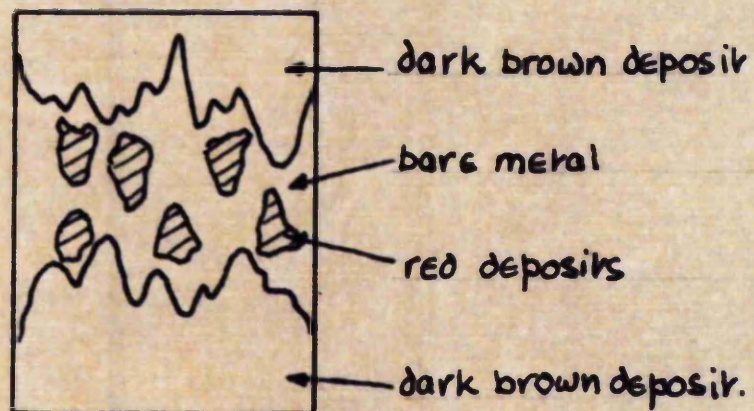


FIG. 6.6. Corrosion patterns on copper specimens.

indicated a difference in the processes. A comparison of figs. 5.5 and 6.4 shows this difference.

Initially steel specimens in aerated solutions corroded at the same rate irrespective of the heat flux, but with copper specimens the corrosion rate varied with heat flux from the beginning of all runs. Brown, Roetheli and Forrest⁴³ state that the initial rate of corrosion of an electropositive metal, such as copper, in agitated aerated solutions of given oxygen concentration varies with the nature of the metal and the corrosion rates are low. For electronegative metals however, such as steel high corrosion rates are observed after a brief period and the corrosion rate is independent of the nature of the metal, the corrosion rate being controlled by the rate at which oxygen can be supplied to the cathode. Thus, considering this relative to the present work, in the case of steel, during the deaeration of the solution the stirring of the solution due to the convection currents will assist the provision of oxygen at the surface. The heat transfer will cause two opposing effects, firstly at high heat fluxes the stirring effect will be greater which will replenish the oxygen at the surface more readily than at lower heat fluxes, and secondly the increased temperature of the solution will cause a decrease in the oxygen concentration near the surface, thus it could be suggested that oxygen availability at the metal surface will be approximately the same for all heat

fluxes, provided that oxygen is available from the bulk of the solution. This suggestion is supported by the results obtained for steel specimens where the initial corrosion rate, dependent on oxygen availability, is the same for all heat transfer rates. In the case of copper the controlling factor of the initial reaction is the nature of the metal rather than oxygen availability⁴³. It has been shown⁴⁴ that on the immersion of copper specimens in aerated solutions a cuprous oxide film is formed on the surface, this film tending to exhibit inhibitive properties, and the surface is divided into anodic and cathodic areas, the anodic areas being pores, exposing bare metal in the oxide film, the cathodic area. At high heat fluxes it was thought that the higher metal surface temperature relative to the solution during the first few minutes of any run would result in a faster reaction rate to produce this inhibitive film on the anode areas. This is supported by the more rapid increase in potential at high heat fluxes, during the early stages of runs. This rapidly formed film would inhibit further corrosion of the specimens and therefore the corrosion rate at high heat fluxes would be lower than at lower heat fluxes. This explanation satisfies the experimental observations. As oxygen is removed from the solution by boiling, it would not be present to maintain the oxide film and the potential would become more anodic. As in the case of experiments with steel specimens the removal of oxygen occurred more rapidly at higher

heat fluxes and therefore the potential would decrease earlier than at low heat fluxes.

The suggested processes are:-

The cathodic reaction - the oxygen reduction reaction



The anodic reaction - the dissolution of metal to its ions



The presence of oxygen in the solution, apart from its reaction at the cathodic areas, will favour the oxidation



This reaction can take place in solution, oxygen acting as the electron acceptor. Thus while oxygen is present, a greater corrosion rate would be expected, due to this depolarisation and since oxygen is present for longer periods at low heat fluxes, the weight loss from the specimens would be greater. Oxygen would then, act as both an anodic and cathodic depolariser, and this would explain the lack of streaking on the specimens since the presence of oxygen itself would not determine whether an area was anodic or cathodic.

The use of aerated distilled water had the disadvantage

of presenting a medium which was not constant throughout the run, the main corrosive agent, the dissolved oxygen, being boiled out of solution. Also, as shown for the case of steel specimens two opposing effects due to heat transfer occur, (i) increased mass transfer due to convection, and stirring by the bubbles and (ii) the decrease in solubility of oxygen near to the surface, at higher heat fluxes. It was therefore decided to introduce a variable which would alter these factors. Experiments were performed in sodium chloride solutions, whose solubility near to the metal surface would increase at higher temperatures, and therefore an increase in the heat transfer rates would increase the chloride availability at the surface by both mechanisms.

4. Experiments in aqueous sodium chloride solutions

Runs were performed in aerated sodium chloride solutions at two concentrations, 1 gr/ltr and 10 gr/ltr. Analar grade sodium chloride was weighed and mixed in the correct proportions in distilled water. This was then introduced to the system in the manner used in previous runs. Experiments were then performed at various heat fluxes and for various times of exposure. The measurements taken in previous runs were also taken in this series.

i. Results

a. Potential measurement

Initially the potential of the specimens altered from a value of about 50 mV negative to a saturated calomel electrode to a value which was dependent on the heat transfer rate, this change occurred in a few minutes. The higher the heat flux used the higher the value of the potential, as shown in Fig. 6.7 and 6.9. As the run proceeded the potential decreased at a rate dependent on the heat transfer rate, higher heat fluxes leading to a greater rate of decrease of the potential. The potential levelled out as the runs progressed and in the case of higher heat fluxes a slight increase was observed. The final potential increased with increased heat transfer as shown in Figs. 6.8 and 6.10. Increasing the sodium chloride content of the solutions caused a decrease in the potential at all stages of the runs as a comparison of the results will indicate.

b. Weight loss determinations

The weight lost by the specimens with respect to heat transfer rates showed different trends to all previous runs. Increasing heat transfer rates from low values initially, as in previous runs, caused a decrease in the corrosion rate but as the heat flux was further increased a minimum weight loss was reached and the corrosion rate increased. Further increase in heat flux caused a further increase in the weight loss. Increased sodium chloride concentration caused an

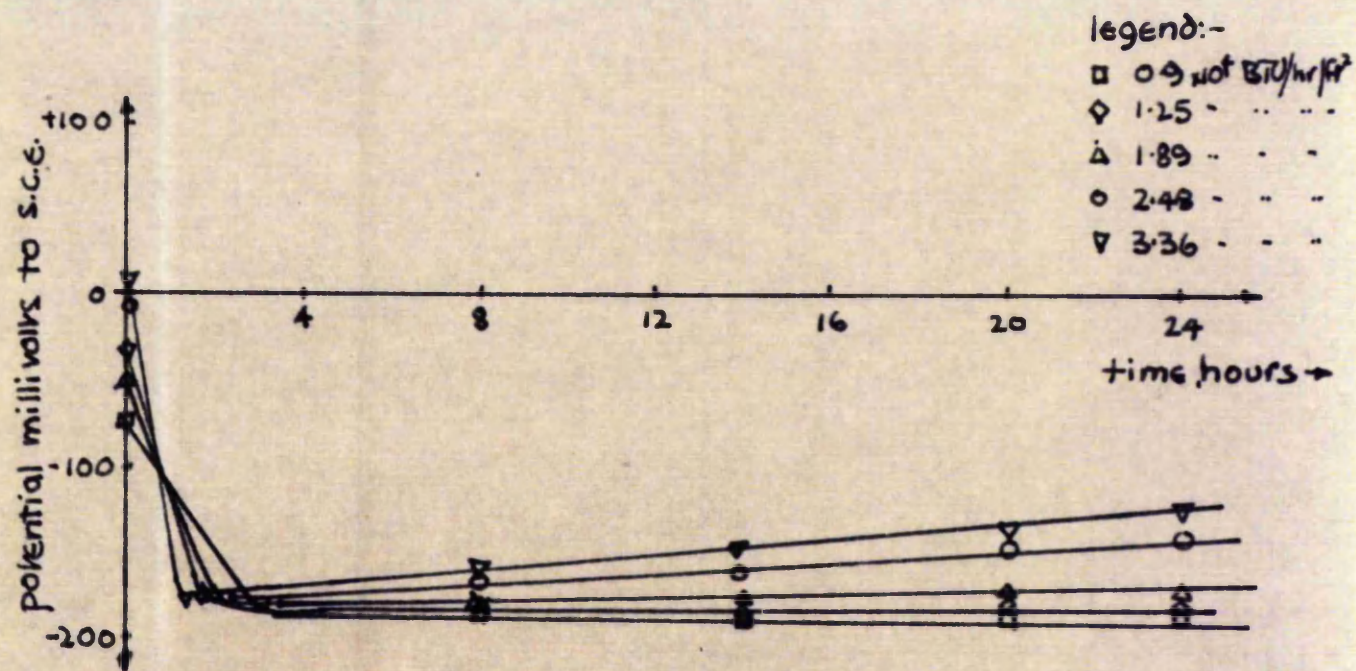


FIG. 6.7. Potential versus time in 1 g/m/ltr NaCl solution

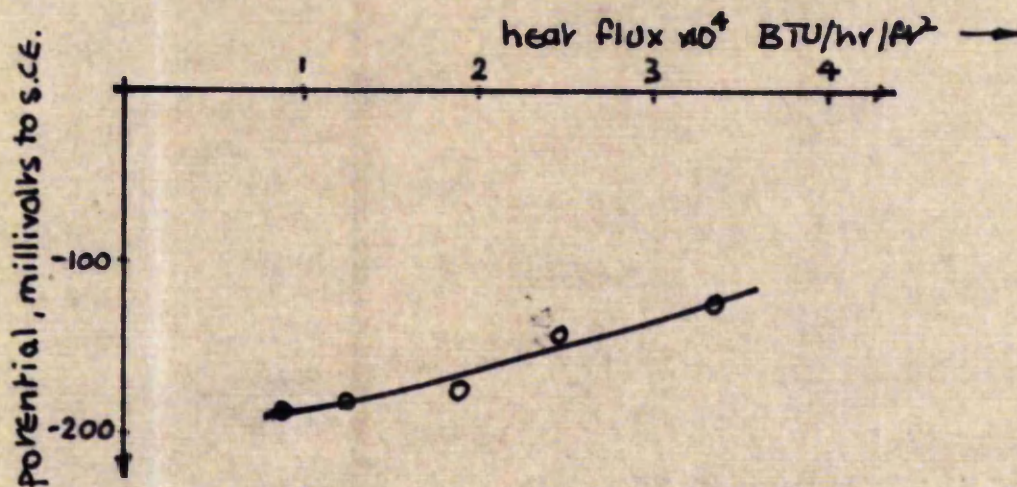


FIG 6.8 Potential versus heat flux in 1 g/m/ltr NaCl solution

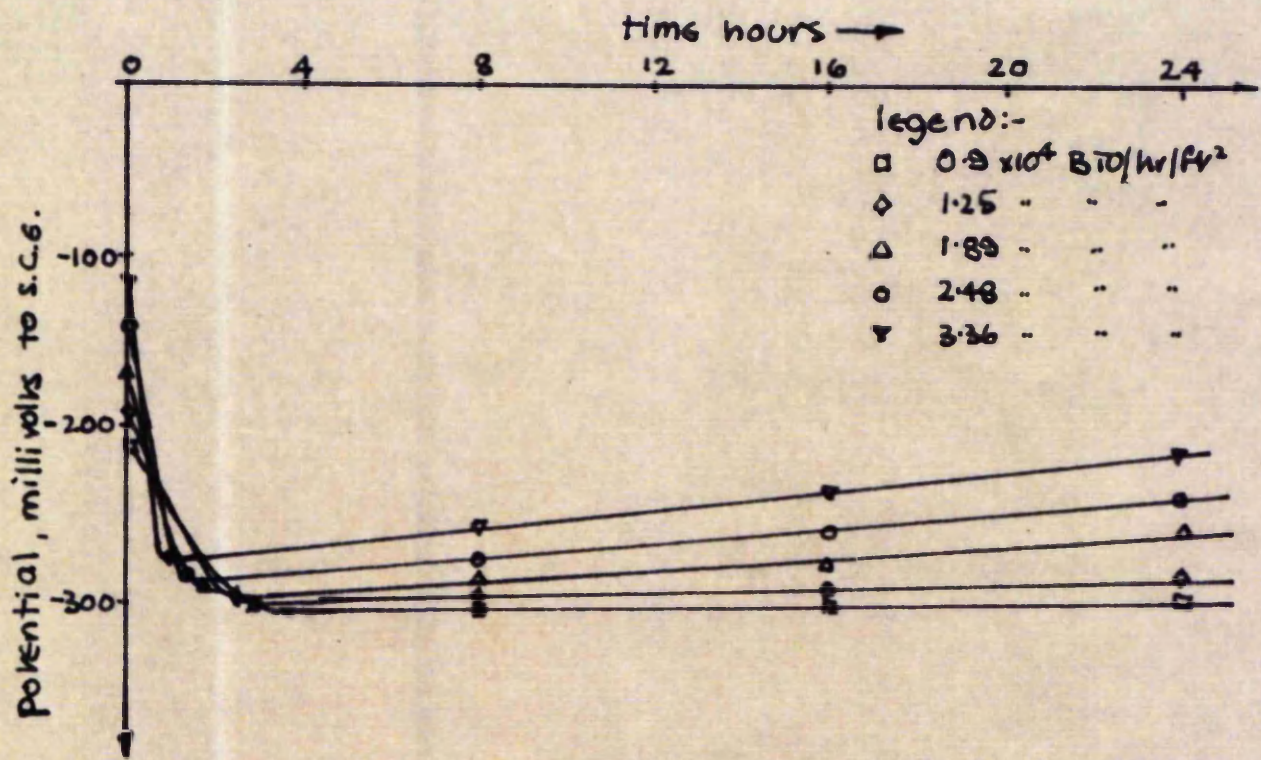


FIG 6.9 Potential versus time in 10 g/L NaCl solution

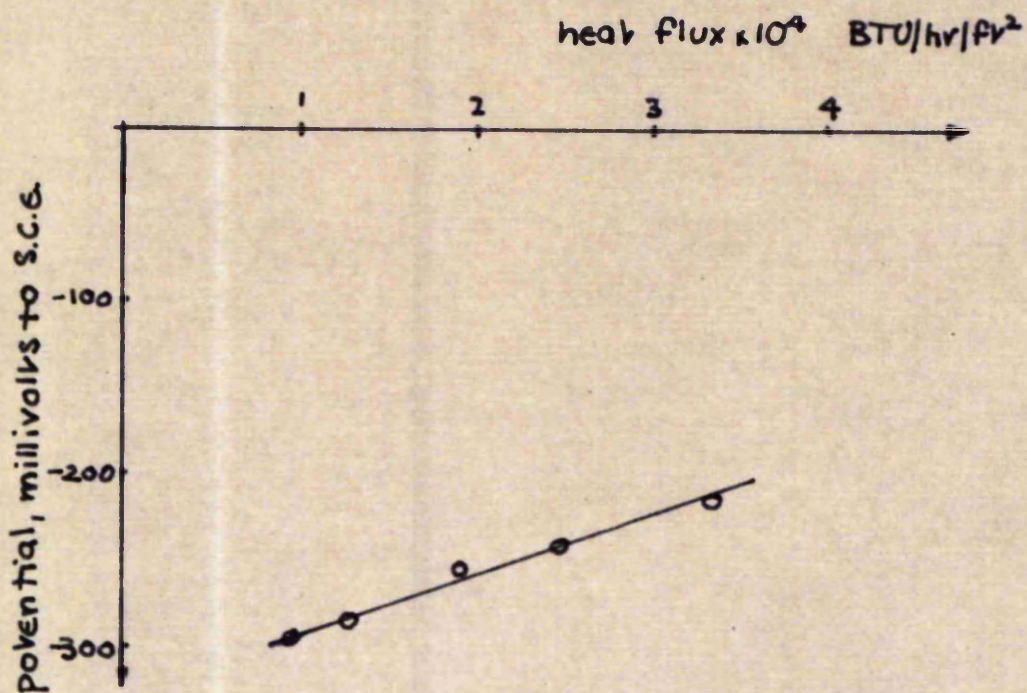


FIG 6.10. Potential versus heat flux in 10 g/L NaCl solution.

increase in the corrosion rate. The trends are shown in Figs. 6.11, 6.12 and 6.13.

c. Visual observations

The dark film, noted in chloride free solutions, was observed in both concentrations of sodium chloride. The attack was much more general than in previous runs and no streaking was observed on any of the specimens. The film was formed almost immediately and persisted for some time, but was slowly removed, particularly at high heat fluxes, as the runs progressed.

d. pH determinations

Similar trends and values to those of previous runs were obtained, reaching, after twenty four hours, a value of approximately 7.3 at all heat transfer rates.

The full results are shown in appendix 7.

2. Conclusions and discussion

The weight loss versus heat flux curve indicated a trend not observed in previous experiments. Between low and intermediate heat fluxes the weight loss decreased with increased heat transfer. A minimum value occurred and at higher heat fluxes weight loss increased with increased heat transfer. Increasing the sodium chloride concentration of the solution increased the weight loss at any given heat flux, and the minimum weight loss occurred at a lower heat flux.

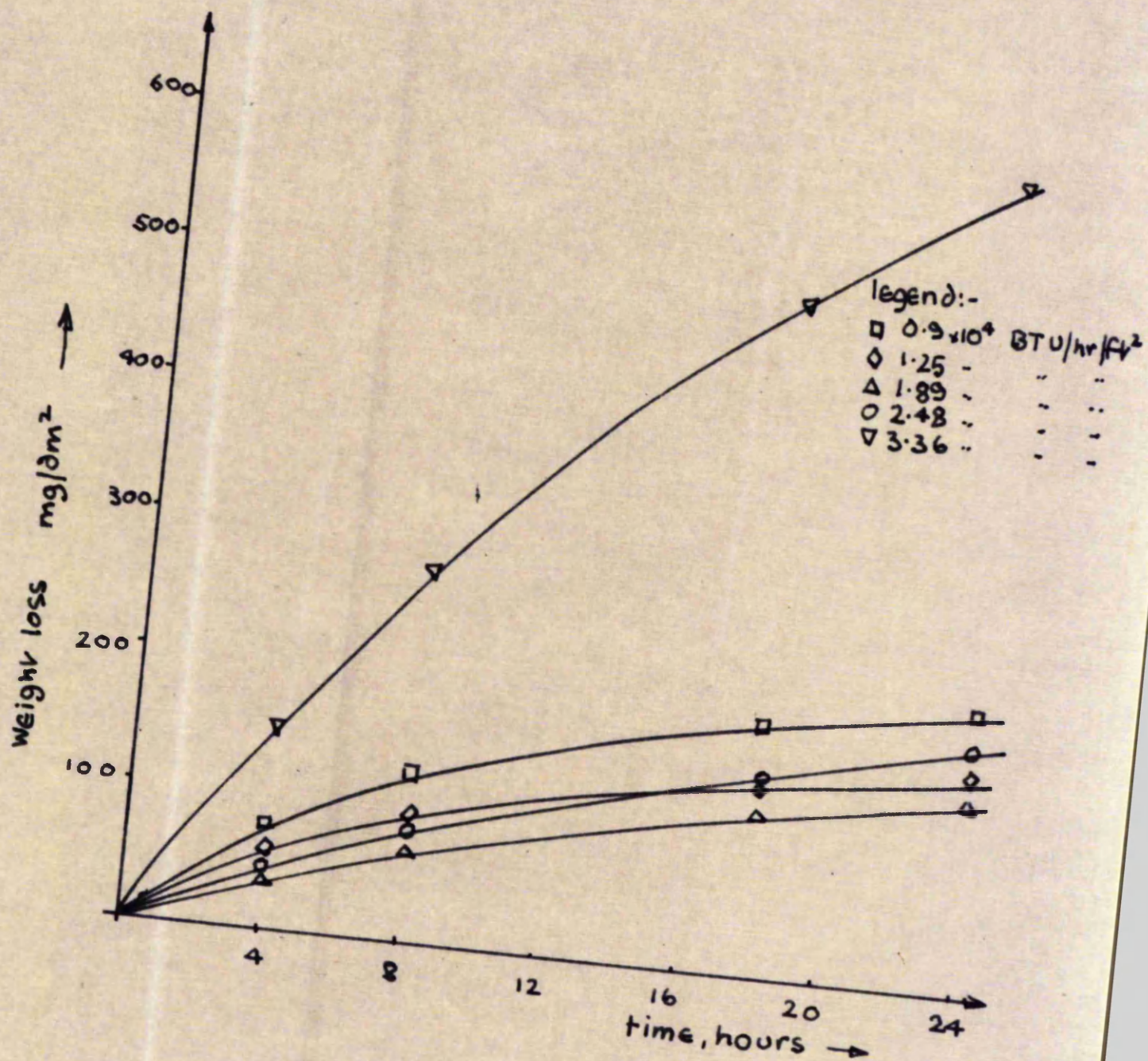


FIG 6.11. Weight loss versus time

in 1gram/ltr NaCl solution

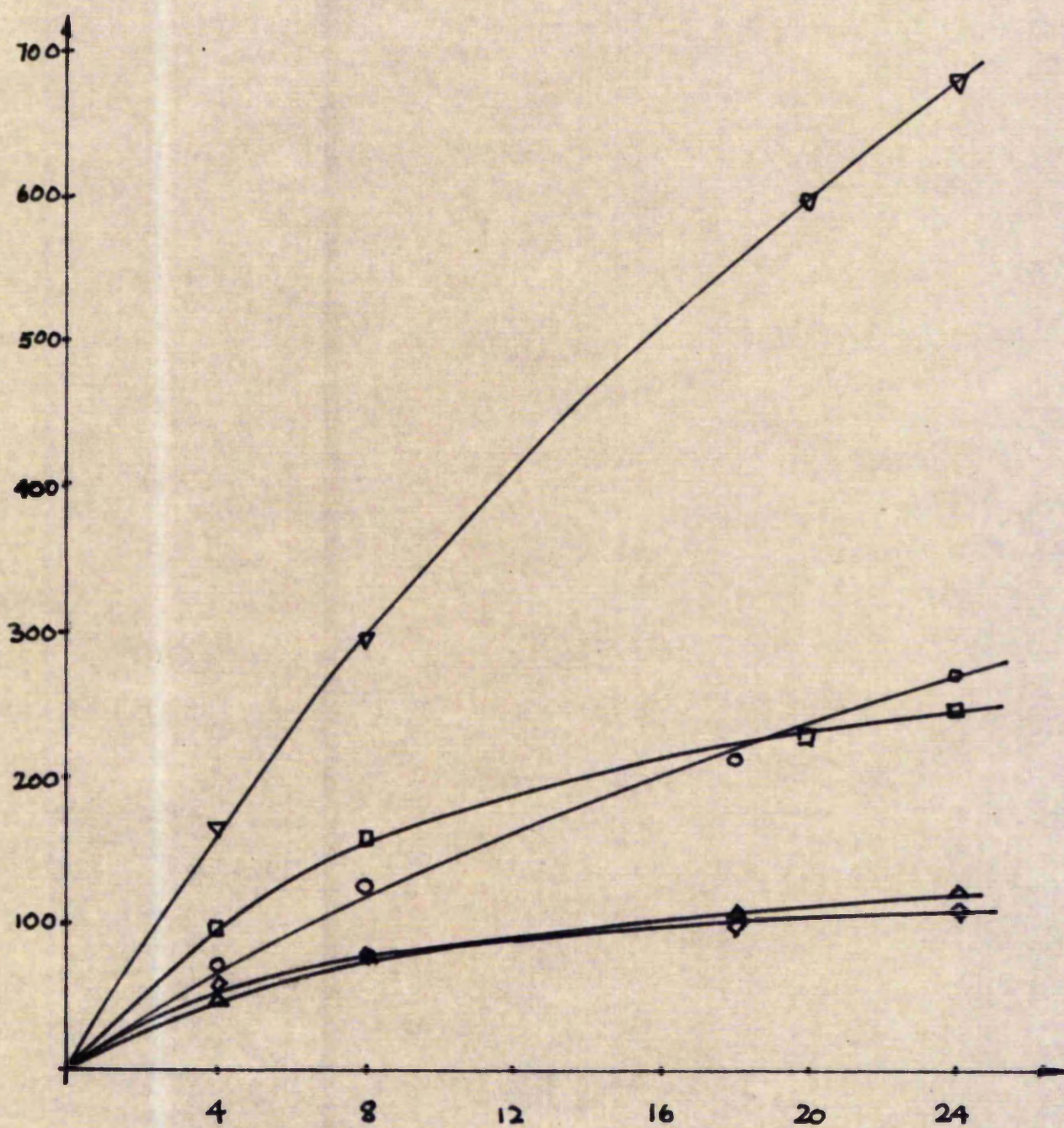


FIG 6.12. Weight loss versus time

in 10g/L NaCl solution

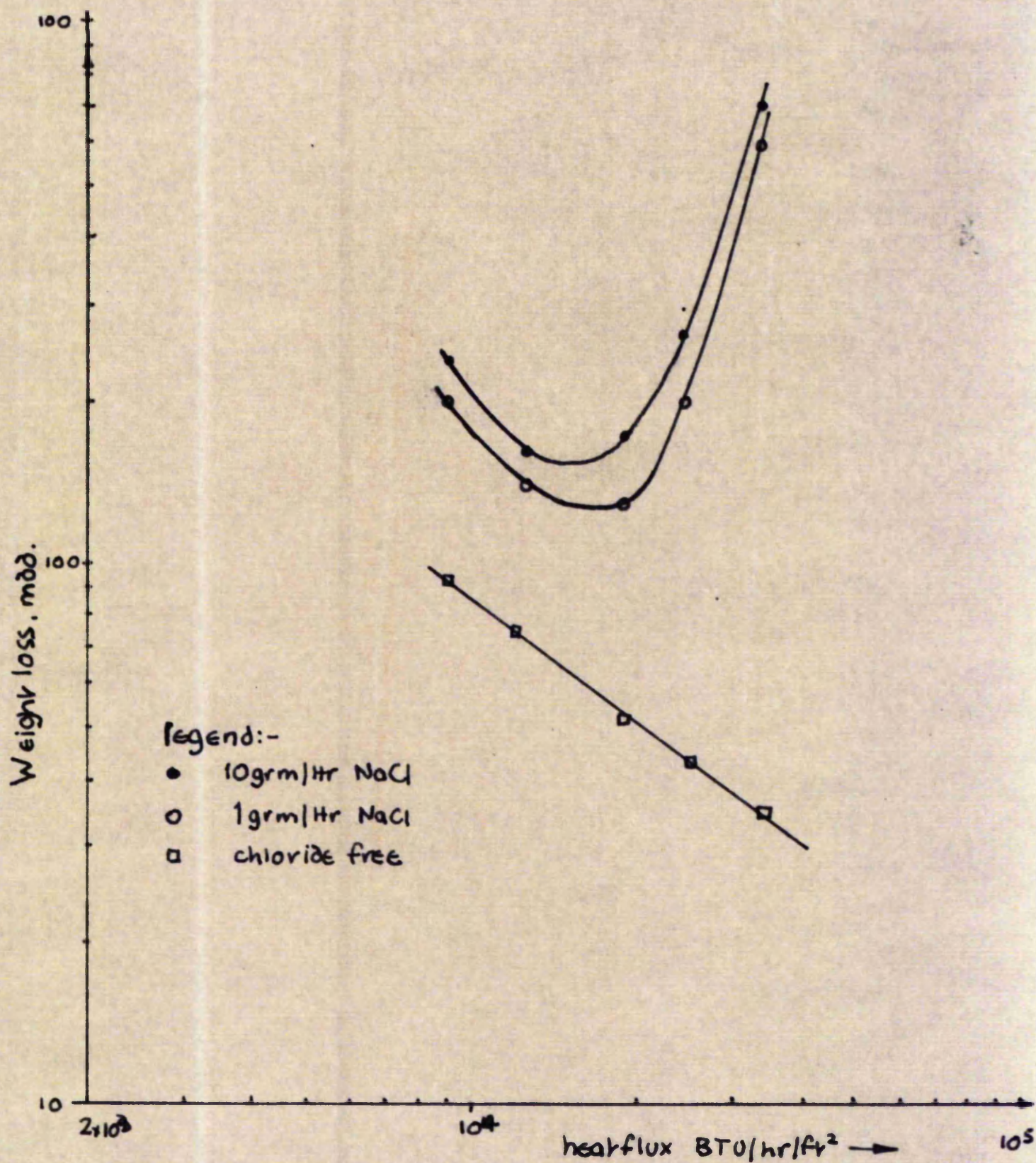


FIG 6.13 Log-log plot, weight loss versus heat flux for 24 hrs.

In this system there were two factors. Initially oxygen was available at the surface and as the runs progressed this was removed by deaeration, the rate of removal being dependent on the heat transfer rate. The chloride ions however were not removed by the heat transfer, and were present throughout the run. It can be seen from Figs. 6.11 and 6.12 that the initial rate of corrosion varied considerably with heat transfer. This was also the case in chloride free solutions, but under those conditions the rate of corrosion decreased with increased heat transfer, throughout the heat transfer range. In chloride solutions, however, the corrosion rate decreased with increasing heat transfer at low heat fluxes but at higher rates the corrosion rate increased. The suggestion put forward for this phenomena in chloride free solutions was that at high heat fluxes more oxygen was available, due to deaeration during the first few minutes of the run, than at lower heat fluxes, and this caused most of the surface to be covered by an oxide film exhibiting inhibitive properties. This film would be maintained by the oxygen in the solution and corrosion would be decreased. The presence of chloride⁴⁵ alters this situation. Gatty and Spooner state that chloride ions in the solution will have the effect of breaking down this oxide film and rendering the copper available for attack. The breakdown is more severe in acid solutions since in neutral solutions the higher pH helps to maintain the oxide

film, but under the severe conditions in the apparatus it is possible that this might occur. At higher heat fluxes the mass transfer of chloride ions to the surface would be greater both due to agitation caused by convection and bubbling, and due to the higher solubility of chloride ions at the inter-phase. Thus at low heat fluxes the oxide film would form slowly and corrosion would occur, at intermediate heat fluxes the oxide film would form fairly rapidly and have an inhibitive effect, yet the breakdown due to chloride ions is not appreciable, and at high heat fluxes the inhibitive oxide film is destroyed by the chloride ions. Two other facts support this explanation. Firstly, after oxygen has been desorbed from the solution a corrosion rate is established which increases with increasing heat transfer, this can be shown by considering the slopes of the weight loss versus time curves Figs. 6.11 and 6.12. From this it can be inferred that the processes involving the chloride ions are sensitive to heat transfer and that the attack is more severe at high heat flux rates. Secondly, a study of the effect of sodium chloride concentration indicates that at higher concentrations the minimum in the weight loss versus heat flux curve occurs at lower heat fluxes. If the effect were due to the mass transfer of chloride ions to the surface then this would be the expected result, since at higher concentrations less agitation would be required to transport the ions to the

metal surface. Further support was the apparent removal or at least lessening of the film as the runs progressed. From these considerations it was thought that heat transfer directly, rather than just the increase in temperature associated with it, was an important factor in the processes.

Chapter 7

Overall Conclusions and Discussion

Several factors have been studied in this work. Previous workers in this field did not separate the effects of heat transfer and specimen surface temperature. This has been done to a certain extent since boiling conditions presented the opportunity to increase heat transfer rates considerably with only small increases in surface temperature. These separated effects have been applied to both electropositive and electronegative metals and conclusions have been drawn as to which factor is the more important. It was found that for an electronegative metal, such as steel, and in the oxygen concentrations range used, the rate of corrosion was independent of heat transfer rates providing that oxygen was available at the surface for the cathode reaction. Previous workers had found that in similar environments increasing the surface temperature increased the corrosion and it was therefore indicated that surface temperature rather than heat transfer is the more important factor. For an electropositive metal, such as copper on the other hand, the corrosion rate in aerated distilled water, seemed to be dependent on heat transfer since the corrosion rate over the first few hours of the run decreased with increased heat transfer. However, this was finally thought to be a temperature effect, the higher surface temperatures in high oxygen concentrations in the first few minutes of a run forming a more inhibitive film on the metal surface at higher heat fluxes. This effect was

34

also observed on iron where at high temperatures and oxygen concentrations inhibitive films were formed. The two-fold role of heat transfer, which tended to increase the surface temperature only slightly in the case of boiling conditions, and the increase in the mass transfer to and from the surface by convection and agitation, would cause, in the case of dissolved oxygen, little change in its availability at the surface. The increased temperature would cause a decrease in the oxygen concentration near the surface due to its lower solubility, increased agitation would cause more oxygen to be transported to the surface, and the effects would tend to cancel. It would therefore be expected that unless a particularly inhibitive film was formed the corrosion rates would vary little with increased heat transfer. Large increases in temperature, observed in non-boiling conditions would cause considerable increases in reaction rate, again assuming no inhibitive film to be formed. Thus it is thought that temperature, rather than heat transfer as such is the important factor in the corrosion of metals in oxygenated waters.

As indicated the solubility of oxygen decreases with increased temperature, whereas the solubility of such salts as sodium chloride increase with increased temperature. Thus the two-fold effects of heat transfer would both tend to increase the transport of ions to the surface, and the

reaction rate would be expected to alter with heat transfer if availability was a controlling step. Experiments in chloride solutions showed this to be the case, and it is thought that both heat transfer and temperature are important factors.

Suggestions for future work

It was thought that the reason for the initial decrease of corrosion with increased heat transfer in aerated chloride solutions was due to the formation of a inhibitive oxide film. Runs could be performed in more acidic solutions where this film would be less stable, and more alkaline solutions where it would be more stable and a study made of the minimum point in the weight-loss vs heat-flux curve relative to the pH of the solution. Runs with salts of oxydising acids, such as nitrates could be used to establish the importance of the oxide film on copper when increased transport may help to maintain the film. The above suggestions are work which could be carried out without changing the basic apparatus. A change which would be of further interest would be to extend the heat transfer range in the film boiling region and the effect of this assessed, where the same heat transfer rate could result in different surface temperatures.

Appendix 1

The determination of surface temperature
and heat transfer rates

1. Introduction

The apparatus described briefly in Chapter 2 was, as stated not used at that time, although the system is mentioned there for the sake of completeness. Surface thermocouple probe readings were taken during the preliminary run and were converted to surface temperatures and heat transfer rates at a later date, and these are the figures used in the graphs. A cross check using the silica tube was made, which as shown, justifies the action.

2. Measurement of the surface temperature

The system was described in Chapter 2. The specimen drilled laterally at three points, and containing thermocouples was heated in the corrosion cell in distilled water. Readings were taken, for various heat fluxes, of both the thermocouples set in the specimens and the surface probe, pressed against the specimens and silica tube. These readings are shown in Table 1. The heater used for the calibration was the non-inductively wound former used in all later work. Readings were taken on three separate occasions using distilled water as the solution. The average of the three runs was the value used. Conversion to degrees Fahrenheit from millivolts⁴⁶ was due to charts by Leeds and Northrop. All readings were made relative to cold junctions immersed in melting ice.

The thickness of the specimen and the distance between

Table 1

Temperature measurement of mild steel specimens at various heat transfer rates.

Readings in mV and F.

Heat flux		Sunken thermocouple readings						Probe readings	
		inner		middle		outer		Spec	Silica
volts	amps	mV	°F	mV	°F	mV	°F	mV	mV
100	3.4	4.314		4.312		4.310		4.304	
		4.315	221.53	4.312	221.39	4.309	221.28	4.305	4.313
		4.314		4.313		4.310		4.304	
120	4.0	4.364		4.357		4.347		4.330	4.340
		4.366	223.69	4.357	223.36	4.348	222.90	4.328	
		4.365		4.358		4.346		4.322	
150	5.0	4.405		4.390		4.373		4.350	4.364
		4.405	225.44	4.387	224.80	4.374	224.04	4.355	
		4.404		4.391		4.374		4.349	
170	5.7	4.447		4.426		4.403		4.371	
		4.449	227.26	4.425	226.35	4.403	225.36	4.374	
		4.445		4.426		4.402		4.370	4.382
200	6.7	4.484		4.462		4.429		4.384	
		4.484	229.05	4.462	227.89	4.428	226.50	4.383	4.403
		4.486		4.463		4.428		4.384	
220	7.4	4.4518		4.484		4.447		4.397	
		4.4520	231.40	4.485	228.37	4.448	227.25	4.396	4.416
		4.4520		4.486		4.446		4.398	

the thermocouple positions were measured with a travelling microscope. The distances are shown in Fig.A.1.1. From the above measurements a temperature profile across the thickness of the specimens could be established for any given heat flux under steady conditions. A thermocouple reading had been obtained by the surface probe simultaneously and from this it was possible to calibrate the surface probe. The calibration curve is shown in Fig.A.1.3 together with the standard curve, constructed for more accurate determination of the sunken thermocouple temperatures. From this curve the surface temperatures during runs could be established. The discrepancy between actual and expected readings is probably due to cooling of the thermocouple probe bead tending to result in a low reading.

3. The calculation of heat transfer rates

From Fig.A.1.2, by extrapolation, the temperature drop across the whole thickness of the specimen could be found, thus the temperature gradient across the specimen was calculated. Using Fouxriers Equation

$$Q = -kA \frac{dt}{dx}$$

where Q = rate of heat transfer BTU/hr

k = thermal conductivity BTU/hr/ft²/°F

A = surface area perpendicular to the direction of heat flow ft²

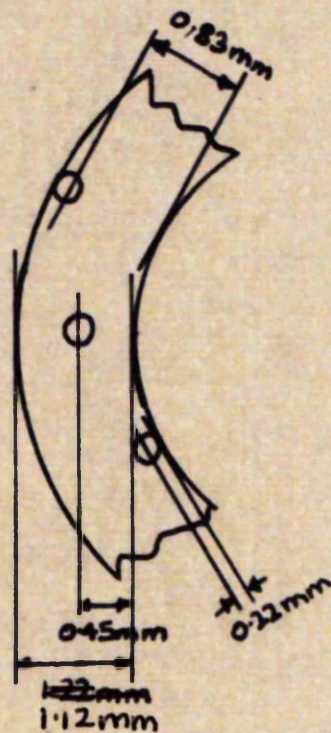


FIG A.1.1. Position of thermocouple wells in specimen

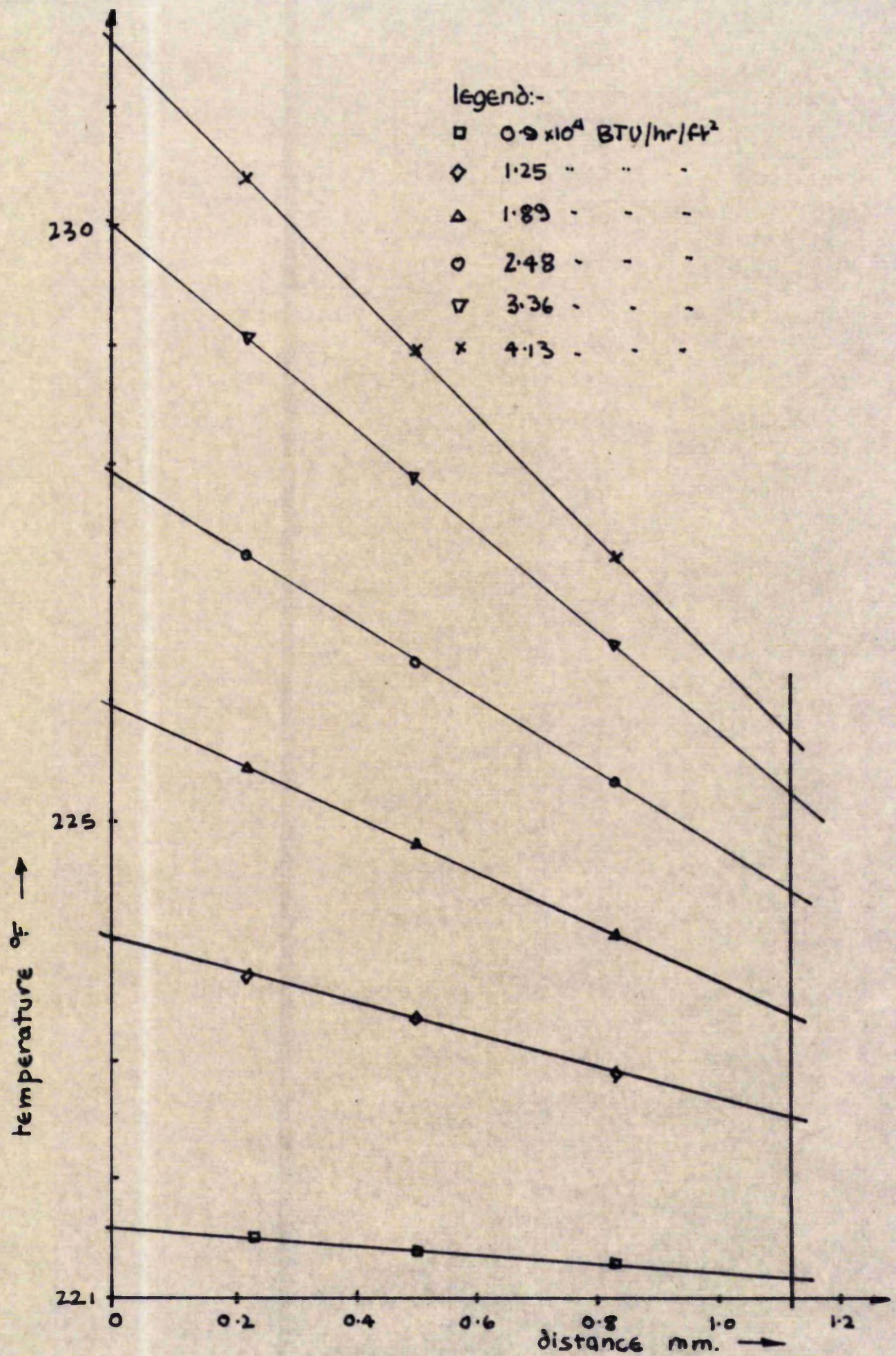


FIG A.1.2. Specimen thickness versus temperature

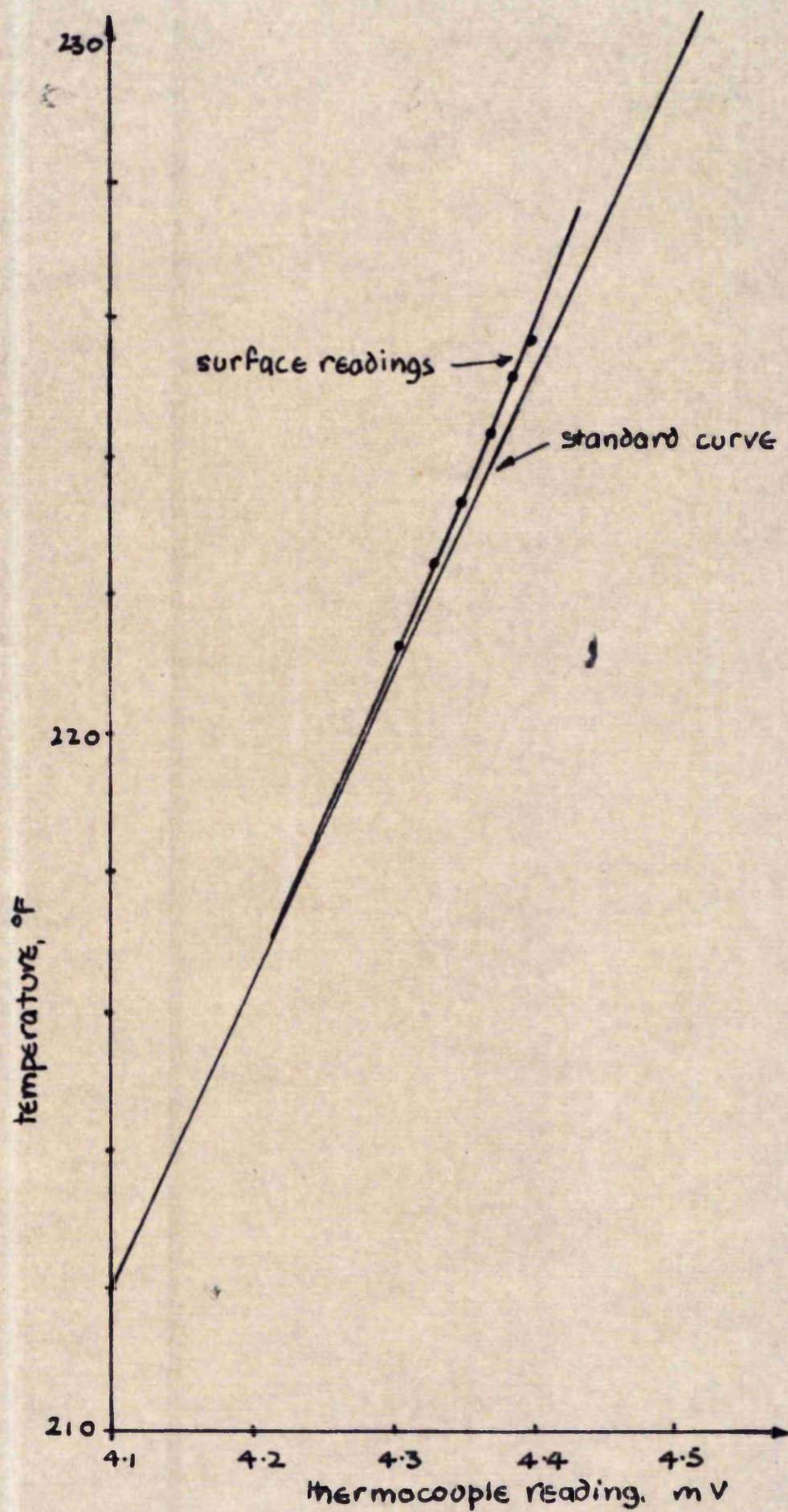


FIG A.1.3. Thermocouple readings versus surface temperature

$\frac{dt}{dx}$ = rate of change of temperature with distance $^{\circ}\text{F}/\text{ft}$

For the conditions the thermal conductivity of the steel was 26.0 BTU/hr/ft²/ $^{\circ}\text{F}/\text{ft}$.

Consider 1 sq.ft. The specimen thickness was measured (Fig.A.1.1) and found to be 1.12 mm.

$$\begin{aligned} \text{Thus, } Q &= -26.0 \cdot 1 \cdot \frac{\Delta t}{0.112} \times 2.54 \times 12 \\ &= -7080 \Delta t \quad \text{BTU/hr/ft}^2 \end{aligned}$$

Therefore for any given temperature drop, the heat transfer rate could be calculated. The results are shown in Table 2.

Table 2

Calculation of Heat Transfer Rates

Heater		Δt	Q
Volts	Amps	$^{\circ}\text{F}$	BTU/hr/ft ²
100	3.4	1.27	0.90×10^4
120	4.0	1.53	1.25×10^4
150	5.0	2.57	1.89×10^4
170	5.7	3.50	2.48×10^4
200	6.7	4.75	3.36×10^4
220	7.9	5.85	4.13×10^4

The heat transfer rates calculated have a corresponding surface temperature. Thus a graph can be plotted of heat flux vs surface temperature and from the surface temperature measurements taken during runs it was possible to establish

the value of the heat transfer rates. The plot is shown in Fig. A.1.4.

The apparatus used for these calculations was not working satisfactorily at the time of the preliminary runs. The thermocouple probe was, however, satisfactory and a cross check was used to enable the results obtained later to be justifiably used to determine the heat transfer rates in early runs. Surface temperature measurements of the silica tube were made during the preliminary runs. For the tube it was assumed that at the centre the heat flux could be calculated from the electrical energy input to the heater and that no loss occurred. A temperature profile showed no temperature variance for the central six inches of the seven inches heated, therefore the assumption was reasonable. Thus a plot of heat transfer rates vs surface temperature could be obtained for the silica tube. A similar curve was obtained at the time of heat transfer determinations. The two are plotted in Fig.A.1.4. The agreement between them is satisfactory and therefore it was thought that using the temperature vs heat flux curve for preliminary runs was justified. The voltage vs current curves used in the calculations are shown in Fig.A.1.5.

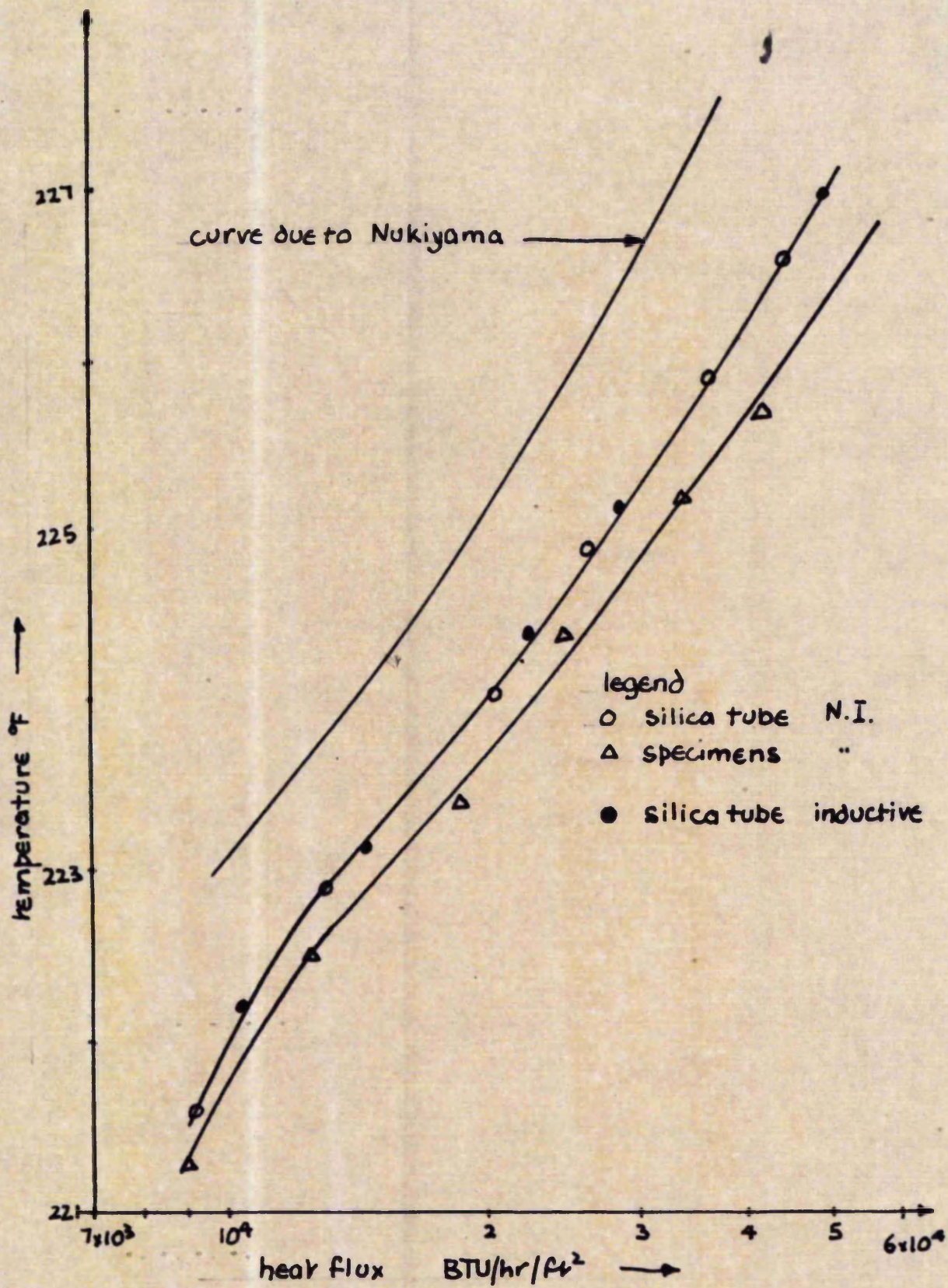


FIG A.1.4. Heat flux versus surface temperature

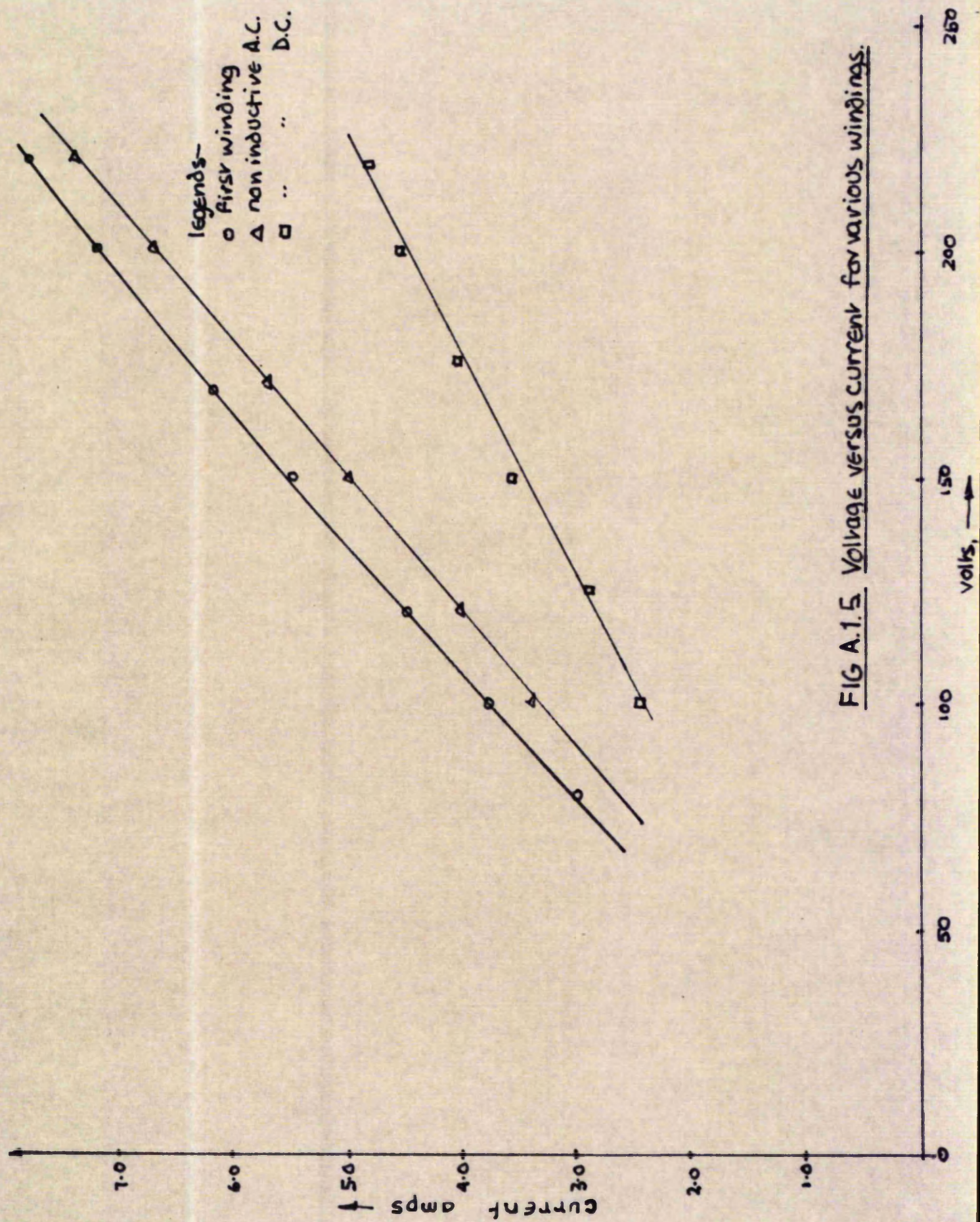


FIG A.1.5 Voltage versus current for various windings.

Appendix 2

Results of preliminary runs

1. General

Eight specimens were used in each run, six under conditions of heat transfer, and two beyond the heated section. The corrosive solution was distilled water. The exposed area of the specimen was 1.263 in^2 . Blank (unheated) specimen results marked * .

2. Particular Results

Run 4

Heater:- voltage 220v
current 7.8A

pH:- initial 5.2
final 7.0

Weight loss:- 1* 2 3 4 5 6 7 8*
mg. 8.6 9.9 11.9 11.1 11.0 11.2 11.4 8.0

Average loss:- heated 11.3 mg 139 mdd
blank 8.3 mg 102 mdd

Heat flux:- $4.70 \times 10^4 \text{ BTU/hr/ft}^2$

Potential (-ve to satd c.e.)

time mins	Pot mV	time mins	Pot mV	time hrs	Pot mV
0	350	35	640	3	780
1	450	40	650	3 $\frac{1}{4}$	790
5	500	45	660	4	800
10	550	60	680	5	800
15	580	120	715	7	805
20	640	135	720	8	800
25	655	150	730		
30	630	165	760	24	800

Temperature ($T_1 T_2$.mV rel.to 0°C)

time min	Temp mV	time hrs	Temp mV
8	1.701	1	4.396
13	1.723	2	4.398
18	2.904	4	4.399
23	3.825	6	4.402
28	4.280		
33	4.385		
38	4.390		
43	4.390	24	4.401

Run 5

Heater:- voltage 170v

pH:- initial 5.2

current 6.1A

final 6.8

Weight loss:- 1* 2 3 4 5 6 7 8*
mg. 9.7 15.7 17.2 16.5 15.8 17.0 15.4 9.8

Average loss:- heated 16.3mg 200 mdd

blank 9.75mg 120 mdd

Heat flux:- 2.75 BTU/hr/ft²

Potential:-

time mins	Pot mV	time mins	Pot mV	time hrs	Pot mV
0	350	35	635	5 $\frac{1}{4}$	720
1	450	40	625	5 $\frac{3}{8}$	745
5	495	45	640	5 $\frac{3}{4}$	765
10	500	60	660	6	775
15	560	120	690	6 $\frac{1}{4}$	780
20	595	180	700	7	780
25	630	240	705	8	780
30	650	300	710	24	780

Temperature:-

time mins	temp. mV	time mins	temp mV
8	1.698	48	4.362
13	1.983	53	4.362
18	2.541	58	4.366
23	2.814	120	4.364
28	3.327	150	4.370
33	3.744	240	4.374
38	3.752		
43	4.354	24hrs	4.375

Run 6

Heater:- voltage 150v

pH:- initial 5.3

current 5.5A

final 7.1

Weight loss:- 1* 2 3 4 5 6 7 8*
mg 10.2 17.0 17.7 17.3 17.0 17.7 16.9 9.8

Average loss:- heated 17.3 mg 212 mdd

blank 10.0 mg 123 mdd

Heat flux:- 2.2 BTU/hr/ft²

Potential:-

time mins	Pot mV	time mins	Pot mV	time hrs	Pot mV
0	350	55	640	7 $\frac{1}{4}$	695
1	420	60	625	7 $\frac{1}{2}$	700
5	470	75	635	7 $\frac{3}{4}$	720
15	540	90	650	8	840
25	580	2	660	8 $\frac{1}{4}$	860
40	635	4	685	8 $\frac{1}{2}$	865
45	645	6	690	9	870
50	645	7	695	24	870

Temperature:-

time mins	temp mV	time mins	temp mV
8	1.592	68	4.333
13	1.876	90	4.342
23	2.042	120	4.354
33	2.751	240	4.360
43	3.004	360	4.363
53	3.742		
58	4.002		
63	4.328	24hrs	4.364

Run 7

Heater:- voltage 120v

pH:- initial 5.3

current 45A

final 6.9

Weight loss:- 1* 2 3 4 5 6 7 8*
mg 11.4 23.0 24.1 22.6 22.8 23.0 21.1 11.6

Average loss:- heated 22.8 mg 280 mdd

blank 11.5 mg 142 mdd

Heat flux:- 1.4 x 10⁴ BTU/hr/ft²

Potential:-

time mins	Pot mV	time mins	Pot mV	time hrs	Pot mV
0	350	55	635	5	675
1	400	60	640	6	680
5	450	65	635	8	685
10	480	70	630		
15	520	75	625		
30	580	90	635		
45	620	120	650		
50	625	180	665	24	750

Temperature:-

time mins	temp mV	time hrs	temp mV
8	1.547	2	4.324
28	2.261	4	4.331
48	3.317	6	4.338
68	3.839		
73	4.191		
78	4.280		
83	4.302		
90	4.322	24	4.337

Run 8

Heater:- voltage 100v

pH:- initial 5.2

current 4.0A

final 7.1

Weight loss:- 1* 2 3 4 5 6 7 8*

mg 12.3 26.7 27.2 26.5 26.9 27.1 26.9 12.3

Average loss:- heated 26.9 mg 329 mdd

blank 12.3 mg 152 mdd

Heat flux:- 1.02 x 10⁴ BTU/hr/ft²

Potential:-

time mins	Pot mV	time mins	Pot mV	time hrs	Pot mV
0	350	70	630		
1	390	75	635		
5	440	80	635		
10	470	90	630		
15	500	120	640		
30	560	180	650		
60	620	300	660		
65	625	480	665	24	735

Temperature:-

time mins	temp mV	time mins	temp mV
8	1.411	98	4.281
28	2.014	120	4.299
48	2.907	240	4.314
68	3.410	360	4.315
78	4.101		
83	4.165		
88	4.143		
93	4.264	24hr	4.318

Run 9

This run was below the boiling range.

Heater:- voltage 80v

pH:- initial 5.2

current 3.0A

final 6.9

Weight loss:- 1* 2 3 4 5 6 7 8*

mg 12.3 29.4 31.3 30.4 30.6 31.1 30.3 12.4

Average loss:- heated 30.5 mg 374 mdd

blank 12.3 mg 152 mdd

Heat flux:- 0.80×10^4 BTU/hr/ft²

Potential:-

time mins	Pot mV	time mins	Pot mV
0	350	85	625
1	380	90	630
5	420	95	625
15	450	100	625
30	550	120	640
60	600	240	650
75	615	480	655
80	620	24hr	725

Temperature:-

time mins	temp mV	time mins	temp mV
8	1.420	108	4.174
28	2.001	123	4.277
48	2.632	120	4.279
68	3.157	240	4.280
88	3.624	360	4.281
93	3.816		
98	3.901		
103	4.060	24hr	4.281

Appendix 3

The design of the packed column

Design of the packed column

Since both the collecting vessel from the column and the column itself had to be above the corrosion vessel, height was limited. The maximum height of the column was 2.5ft. Raschig rings were to be used, and $\frac{1}{2}$ " rings were available and therefore used.

Assume the water to be saturated with oxygen at commencement

\therefore At entering oxygen concentration at $25^{\circ}\text{C} = 1.63 \times 10^{-5} \text{ mol\%}$

The maximum oxygen concentration obtainable by scrubbing with white spot nitrogen is defined by the oxygen concentration in the nitrogen which is, maximum 20 p.p.m. $= 2 \times 10^{-5}$

Henry's constant for oxygen at $25^{\circ}\text{C} = 4.01 \times 10^{-4}$

\therefore Oxygen concentration could be reduced to

$$4.01 \times 10^{-4} \times 2.0 \times 10^{-5} = 8.02 \times 10^{-9}$$

Let us assume a reasonable figure, 1×10^{-8}

Consider two liquid passes per hour $= 24 \text{ galls/hr}$

$$= 4,900 \text{ lb/hr/sq.ft.}$$

47

Due to Chilton

$$K_L = \frac{D}{a} \propto \left[\frac{L}{\mu} \right]^{1-n} \left[\frac{\mu}{\rho D} \right]^{0.5}$$

$D = \text{diffusivity} = 4.64 \times 10^{-4} \text{ ft}^2/\text{hr}$

$a = \text{specific area} = 115 \text{ for packing}$

$L = \text{flow rate} = 4,900 \text{ lb/hr/ft}^2$

$$\begin{aligned}\mu &= \text{viscosity} = 2.42 \text{ ft.lb/hr} \\ \rho &= \text{density} = 0.0892 \text{ lb/ft}^3 \\ K_L &= \text{mass transfer coefficient}\end{aligned}$$

For the packing used, due to Norman⁴⁷

$$\alpha = 280$$

$$n = 0.35$$

$$\begin{aligned}\therefore K_{La} &= 4.64 \times 10^{-4} \cdot 280 \left[\frac{4,900}{2.42} \right]^{0.65} \left[\frac{2.42}{0.0892} \right]^{0.5} \\ &= 433\end{aligned}$$

Now due to Norman⁴⁸

$$Z = \frac{\text{Im} (X_1 - X_2)}{\rho m K_L a \Delta X_{1m}}$$

The change in oxygen concentration from, 1-2 is negligible therefore the equation reduces to

$$Z = \frac{\text{Im}}{\rho m K_L a \ln \frac{X_2}{X_1}}$$

∴ substituting and rearranging

$$\ln \frac{X_1}{X_2} = 13.7$$

From this it can be seen that the concentration required could be obtained from one pass, but to ensure the concentration the apparatus was run for six hours, or twelve passes.

Appendix 4

Calibration of the Oxymeter

The meter scale units were arbitrary, but the readings obtained for any particular setting of the 'adjust' control were proportional to the partial pressure of oxygen in the fluid. The partial pressure, in turn, is related to the oxygen concentration and the relationship is fixed for a particular solution at a given temperature and pressure. An obvious method of calibrating the meter was to insert the sensor in a fluid of known concentration of oxygen and to adjust the meter to a convenient multiple or fraction of that value. One readily available fluid of relatively constant and known oxygen concentration is air. The partial pressure of air is nearly always approximately 20.9% of the total atmospheric pressure. The partial pressure of oxygen in air is also equal to the partial pressure of oxygen in a liquid saturated with air. Thus it was thought to be a convenient calibrating fluid. The saturation concentration of solutions varies with temperature, as shown in Fig.A.4.1, therefore the temperature of the air had to be known when calibration was made.

As an example the air saturated oxygen concentration in fresh water at 30°C is 7.7 p.p.m. as indicated by Fig.A.4.1. If the instrument is calibrated to 77 on the 10-100 scale when the sensor assembly is exposed to air at 30°C, any subsequent determination in fresh water would indicate a concentration of one-tenth of the reading on the meter.

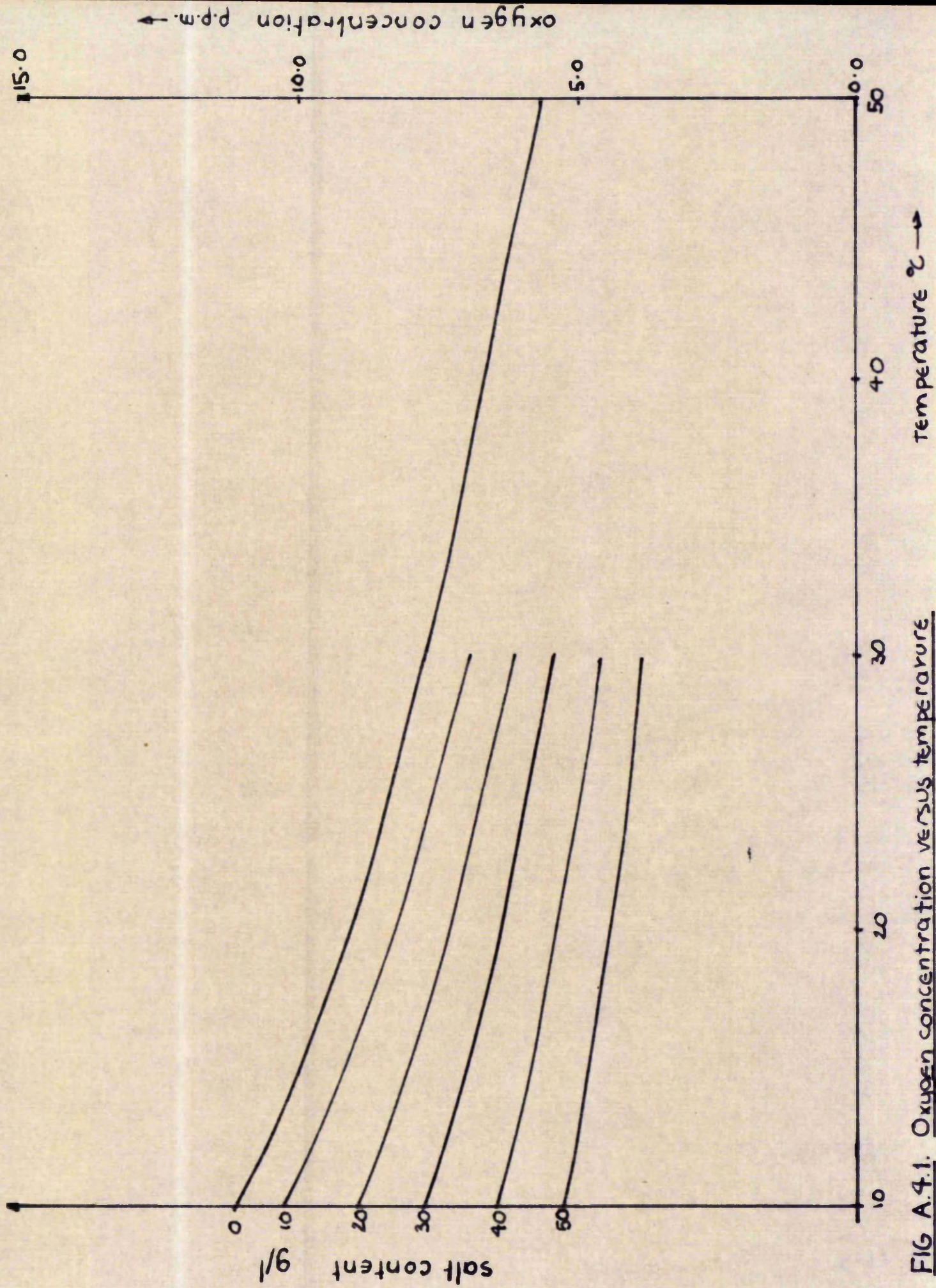


FIG A.4.1. Oxygen concentration versus temperature

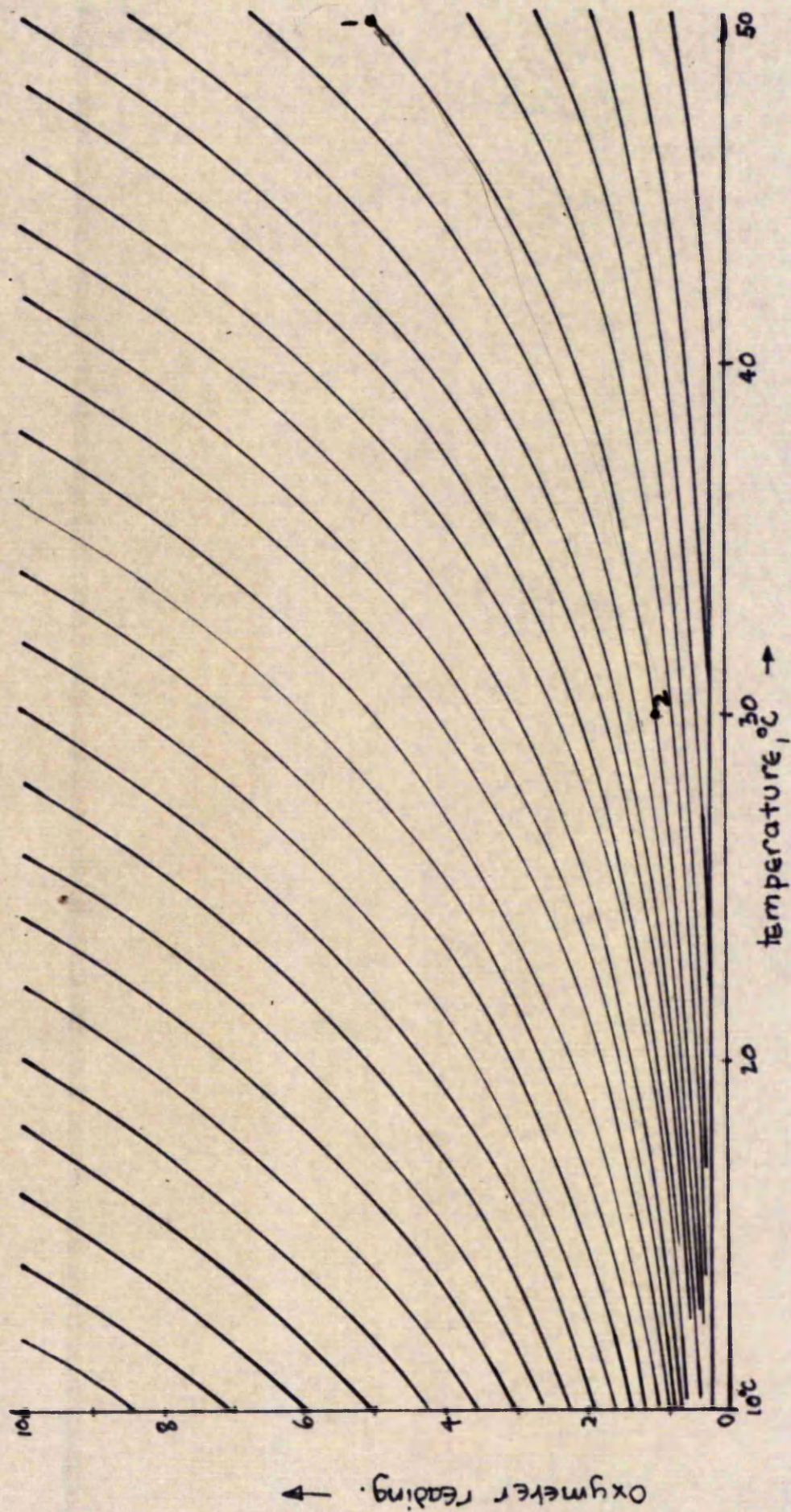


FIG A.4.2. Temperature correction chart.

If the fluid to be measured for oxygen was at a different temperature than the air used for calibration a correction was necessary and was obtained from Fig. A.4.2. For example to correct a reading of 5.0 obtained at 50°C, to a calibration temperature of 30°C, the intersection of the reading line and measuring temperature line. (1) was found and moved parallel to the diagonal curve, toward the calibration temperature, the intersection (2) gave the corrected reading, (1.0). This was then used in the calculation.

The general equation for the calculation was

$$C = \frac{R_c}{M} \cdot S$$

M

where C = oxygen concentration (p.p.m.)

R_c = corrected meter reading

M = meter reading at calibration

S = oxygen concentration in calibrating fluid (p.p.m.)

Thus if the meter was calibrated to 100 at 30°C and a reading of 5.0 was obtained at 50°C in the solution to be measured, the concentration would be

$$R_c = 1.0 \quad (\text{Fig. A.4.2})$$

$$S = 7.7 \quad (\text{Fig. A.4.1})$$

$$M = 100$$

$$\therefore C = \frac{1.0 \times 7.7}{100} = .077 \text{ p.p.m.}$$

Appendix 5

Results of experiments with Deoxygenated Solutions

1. General

Five specimens were used in each run. Four under conditions of heat transfer, and one blank specimen. The corrosive solution was deoxygenated distilled water. The temperature readings were the same as the corresponding run in aerated solutions, therefore only the final temperature is recorded.

2. Particular Results

Run 10

Heater:- voltage 200v pH:- initial 6.9
 current 7.2A final 7.0

Weight loss:- 1* 2 3 4 5
mg 1.7 2.7 2.9 2.8 2.8

Average loss:- heated 2.8 mg 34.4 mdd
 blank 1.7 mg 21.0 mdd

Heat flux:- 3.6 x 10^4 BTU/hr/ft²

Oxygen concentration:- initial 0.03 p.p.m.
 final not measurable

Potential:-

Temperature

time mins	Pot mV	time mins	Pot mV
0	350	2	750
15	490	4	775
30	555	6	785
45	580	8	790
60	620		
90	695	24	800

final 4.390 mV
 225.4°F

Run 11

Heater:- voltage 100v

pH:- initial 7.0

current 4.0A

final 7.1

Weight loss:- 1* 2 3 4 5

mg	1.6	3.4	3.0	2.9	3.4
----	-----	-----	-----	-----	-----

Average loss:- heated 3.2 mg 39.3 mdd

blank 1.6 mg 19.8 mdd

Heat flux:- 1.02 BTU/hr/ft²

Oxygen concentration:- initial 0.03 p.p.m.

final not measureable

Potential:-

Temperature :-

time	Pot	time	Pot
mins	mV	hr	mV

final 4.318 mV

220.0°F

0	350	2	640
15	440	4	720
30	500	6	745
45	525	8	750
60	540		
90	585	24	765

Run 12

Heater:- voltage 120v

pH:- initial 7.0

current 4.5A

final 7.0

Weight loss:- 1* 2 3 4 5

mg	1.9	4.9	4.9	4.5	4.8
----	-----	-----	-----	-----	-----

Average loss:- heated 4.8 mg 59.0 mdd

blank 1.9 mg 23.2 mdd

Heat flux:- 1.4×10^4 BTU/hr/ft²

Oxygen concentration:- initial 0.04 Temperature:- 4.338mV
final 0.02 final:- 222.8°F

Run 13

Heater:- voltage 170v pH:- initial 6.9
current 6.1A final 7.0

Weight loss:- 1* 2 3 4 5
mg 1.7 2.9 3.0 2.8 2.9

Average loss:- heated 2.9 mg 35.7 mdd
blank 1.7 mg 21.0 mdd

Heat flux:- 2.75 BTU/hr/ft²

Oxygen concentration:- initial 0.03
final not measurable

Potential:-

Temperature:-

time mins	Pot mV	time hr	Pot mV
0	350	2	735
15	495	4	770
30	555	6	775
45	590	8	770
60	635		
90	685	24	790

final 4.374 mV
224.6°F

Run 14

Heater:- voltage 150v pH:- initial 6.9
current 5.5A final 7.0

Weight loss:- 1* 2 3 4 5
mg 1.6 3.2 2.8 2.9 3.1

Average loss:- heated 3.0 mg 37.0 mdd

blank 1.6 mg 19.8 mdd

Heat flux:- 2.2 x 10^4 BTU/hr/ft²

Oxygen concentration:- initial 0.03

0.01

Potential:-

Temperature:-

time mins	Pot mV	time hr	Pot mV
0	350	2	675
15	470	4	745
30	505	6	760
45	540	8	770
60	575		
90	630	24	785

final 4.363 mV

224.1°F

Run 15

Heater:- voltage 150v

pH:- initial 7.0

current 5.5A

final 7.0

Weight loss:- 1* 2 3 4 5

mg 1.7 2.9 2.8 2.8 2.8

Average loss:- heated 2.8 mg 34.4 mdd

blank 1.7 mg 21.0 mdd

Heat flux:- 2.2 x 10^4 BTU/hr/ft²

Oxygen concentration:- initial 0.03

final not measurable

Run 16

Heater:- voltage 220v

pH:- initial 7.0

current 7.8A

final 7.0

Weight loss:- 1* 2 3 4 5.

mg	1.6	2.8	2.4	2.7	2.9
----	-----	-----	-----	-----	-----

Average loss:- heated 2.7 mg 33.2 mdd

blank 1.6 mg 19.8 mdd

Heat flux:- 4.7×10^4 BTU/hr/ft²

Oxygen concentration:- initial 0.02.

final not measurable

Potential:-

Temperature:-

time	Pot	time	Pot
mins	mV	hrs	mV

final 4.400 mV

225.9°F

0	350	2	765
15	510	4	785
30	580	6	790
45	605	8	790
60	650		
90	720	24	805

Run 17

Heater:- voltage 120v

pH:- initial 6.9

current 4.5A

final 7.0

Weight loss:- 1* 2 3 4 5

mg	1.6	2.9	3.0	3.1	2.9
----	-----	-----	-----	-----	-----

Average loss:- heated 3.0 mg 36.9 mdd

blank 1.6 mg 19.8 mdd

Heat flux:- 1.4×10^4 BTU/hr/ft²

Oxygen concentration:- initial 0.04

final 0.01

Potential:-

Temperature:-

time mins	Pot mV	time hr	Pot mV
0	350	2	655
15	455	4	735
30	500	6	750
45	530	8	755
60	560		
90	605	24	765

final 4.336 mV

222.7°F

Run 18

Heater:- voltage 220v

pH:- initial 7.0

current 7.8A

final 7.0

Weight loss:- 1* 2 3 4 5
mg 1.7 2.8 2.6 2.6 2.7

Average loss:- heated 2.7 mg 33.2 mdd

blank 1.7 mg 21.0 mdd

Heat flux:- 4.75×10^4 BTU/hr/ft²

Oxygen concentration:- initial 0.03

final not measurable

Temperature:- 4.402 mV 225.9°F

Run 19

Heater: voltage 200v

pH:- initial 6.9

current 7.2A

final 7.0

Weight loss:- 1* 2 3 4 5
mg 1.7 2.9 2.7 2.7 2.8
Average loss:- heated 2.8 mg 34.5 mdd
blank 1.7 mg 21.0 mdd
Heat flux:- 3.6 x 10⁴ BTU/hr/ft²
Oxygen concentration:- initial 0.03
final 0.01
Temperature:- 4.392 mV
final 225.4^oF

Run 20

Heater:- voltage 100v pH:- initial 6.9
current 4.0A final 7.0
Weight loss:- 1* 2 3 4 5
mg 1.7 3.3 3.0 3.1 3.1
Average loss:- heated 3.1 mg 38.2 mdd
blank 1.7 mg 21.0 mdd
Heat flux:- 1.02 x 10⁴ BTU/hr/ft²
Oxygen concentration:- initial 0.04
final not measurable
Temperature:- 4.320 mV
final 220.0^oF

Run 21

Heater: voltage 170v
current 6.1A

pH:- initial 7.0
final 7.0

Weight loss:- 1* 2 3 4 5
mg 1.6 3.0 2.8 2.9 3.0

Average loss:- heated 2.9 mg 36.7 mdd
blank 1.6 mg 19.8 mdd

Heat flux:- 2.75 x 10^4 BTU/hr/ft²

Oxygen concentration:- initial 0.03
final not measurable

Temperature:- 4.374 mV
224.6 °F

Appendix 6

Results of runs with time as a parameter

1. Runs with various forms of heating

i. Alternating current - 24 hrs duration

Potential readings made with condenser across input.

Run 22

Heater:- voltage 100v, current 3.4A, Heat flux 0.9×10^4 BTU/hr/ft².

Average weight loss:- 27.6 mg; 350 mdd

Final potential 735 mV non boiling

Run 23

Heater:voltage 120v, current 4.0A, Heat flux 1.25×10^4 BTU/hr/ft².

Average weight loss:- 22.6 mg; 287 mdd

Final potential 745 mV

Run 24

Heater: voltage 150v, current 5.0A, Heat flux 1.89×10^4 BTU/hr/ft².

Average weight loss:- 18.9 mg; 240 mdd

Final potential 760 mV

Run 25

Heater: voltage 170v, current 5.6A, Heat flux 2.48×10^4 BTU/hr/ft².

Average weight loss:- 16.9 mg; 214 mdd

Final potential 775 mV

Run 26

Heater: voltage 200v, current 6.7A, Heat flux 3.36×10^4 BTU/hr/ft².

Average weight loss:- 14.3 mg; 183 mdd

Final potential 790 mV

Run 27

Heater: voltage 220v, current 7.4A, Heat flux 4.13×10^4 BTU/hr/ft².

Average weight loss:- 12.1 mg; 153 mdd

Final potential 795 mV

ii. Direct current - 24 hrs duration

Run 28

Heater: voltage 100, current 2.4A, Heat flux 0.70×10^4 BTU/hr/ft².

Average weight loss:- 30.7 mg; 387 mdd

Final potential 720 mV non boiling

Run 29

Heater: voltage 150v, current 3.6A, Heat flux 1.38×10^4 BTU/hr/ft².

Average weight loss:- 22.5 mg; 286 mdd

Final potential 745 mV

Run 30

Heater: voltage 200v, current 14.5A, Heat flux 2.39×10^4 BTU/hr/ft².

Average weight loss:- 17.1 mg; 217 mdd

Final potential 770 mV

Run 31

Heater: voltage 220v, current 4.8A, Heat flux 2.80×10^4 BTU/hr/ft².

2. Runs with time as a parameter

1. Aerated solutions

a. Weight loss

Weight loss (mg/dm^2) for a time of exposure (hrs) at a given heat flux ($\text{BTU}/\text{hr}/\text{ft}^2$).

Time hrs	Heat flux $\text{BTU}/\text{hr}/\text{ft}^2 \times 10^4$					
	0.90	1.25	1.89	2.48	3.36	4.13
1	27	-	-	-	25	-
2	-	54	-	52	-	53
3	-	-	77	-	80	-
4	104	109	-	99	-	103
5	-	-	132	-	124	-
6	-	156	-	153	141	127
7	-	-	176	-	-	-
8	219	208	195	-	-	-
10	258	244	-	186	157	140
12	283	-	214	-	-	-
13	309	263	-	-	-	-
18	343	277	225	202	167	151
20	342	-	-	-	-	-
24	350	287	240	214	183	153

b. Oxygen concentration. Concentrations (p.p.m.)

Time hrs	Heat flux $\text{BTU}/\text{hr}/\text{ft}^2 \times 10^4$					
	0.90	1.25	1.89	2.48	3.36	4.13
1	7.3	-	-	-	5.0	-
2	-	1.4	-	1.3	-	1.2
4	0.7	1.0	-	1.8	-	0.5
8	1.1	0.7	0.4	-	-	-
10	1.4	0.9	-	0.1	1.2	NM
18	0.03	NM	NM	0.08	NM	0.01
24	NM	NM	0.01	NM	NM	NM

N.M. = not measurable

2. Deoxygenated solutions

Weight loss

Weight loss (mg/dm^2) for a time of exposure (hr) at a given heat flux ($\text{BTU}/\text{hr}/\text{ft}^2$)

Time hrs	Heat flux $\text{BTU}/\text{hr}/\text{ft}^2 \times 10^4$					
	0.90	1.25	1.89	2.48	3.36	4.13
8	15	-	14	12	-	-
12	-	20	-	-	23	20
18	33	-	30	-	29	-
20	-	37	-	36	-	34
24	40	40	39	37	36	37

Oxygen concentration

As for previous runs, in deoxygenated solution, readings were extremely low and are not recorded.

Appendix 7

Results of runs using copper specimens



Results of runs using copper specimens

I Aerated solutions

i. Weight loss mg/dm^2

time hr	Heat flux x 10^4 . BTU/hr/ft ²				
	0.9	1.25	1.89	2.48	3.36
1	-	-	-	10	-
4	-	-	19	-	13
5	37	32	-	10	-
8	63	49	31	25	19
18	83	68	45	39	33
24	94	75	52	46	36

ii. Oxygen concentration p.p.m.

time hr	Heat flux x 10^4 . BTU/hr/ft ²				
	0.90	1.25	1.89	2.48	3.36
1	-	-	-	4.1	-
4	-	-	2.1	-	1.2
5	0.5	1.4	-	0.9	-
8	1.8	0.9	1.3	1.1	1.6
18	0.5	NM	NM	NM	NM
24	NM	NM	NM	NM	NM

NM - not measurable

II 1 grm/ltr Sodium Chloride solutions

Weight loss mg/dm^2

time hr	Heat flux x 10^4 . BTU/hr/ft ²				
	0.9	1.25	1.89	2.48	3.36
4	75	55	33	44	148
8	123	89	62	78	269
18	184	134	117	146	491
24	203	160	136	180	590

III 10 grm/ltr Sodium Chloride solutions

time hr	Heat flux x 10^4 . BTU/hr/ft ²				
	0.90	1.25	1.89	2.48	3.36
4	96	57	51	72	167
8	158	78	77	125	296
18	-	100	109	214	-
20	231	-	-	-	597
24	248	108	120	271	679

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