A Study of Fuel Oil Ash Corrosion of Selected Stainless Steels.

A thesis submitted to the University of Surrey for the Degree of Doctor of Philosophy

by

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November, 1974
Fuel oil ash corrosion has been studied using laboratory crucible testing methods on four stainless steels with nominal specifications of 12%Cr, 9% Ni, Type 347 and 25Cr 20Ni. These have been corroded for periods of 1, 5, 24, 48, 72 and 100 hours in a synthetic slag of 70 wt.% V2O5 and 30 wt.% Na2SO4, under atmospheres of either pure oxygen, air or pure argon. A kinetic study has been carried out by measuring the reduction in specimen thickness with time. The specimens have been examined by Electron Probe Microanalysis and Scanning Electron Microscopy techniques and the results presented in the form of scanning electron micrographs with the position of the analysis for the elements Fe, Cr, Ni, V and S indicated.

Samples of eight corroded steels from the Marchwood Power Station 10,000 hour trials have also been studied and the results presented as with the laboratory prepared specimens.

The results from the study indicate that the main mechanism of corrosion is one of sulphidation, but that the rate controlling step is probably determined by the composition and physical nature of the vanadate layers which are produced. Chromium vanadate appears to give a greater measure of protection to the steels than other corrosion products. A mechanism for fuel oil ash corrosion has been given which indicates that the sulphur content of the slag will have the greatest influence in corroding superheater materials, especially if nickel is present as an alloying element.
ACKNOWLEDGEMENTS

The work described in this thesis was carried out in the laboratories of the Department of Metallurgy and Materials Technology under the supervision of Dr. J. Mackowiak and Professor M. B. Waldron. The author would like to express his gratitude and thanks for the constructive advice they have given and to Professor Waldron for the facilities he has provided.

The author would like to express his appreciation to the Esso Research Centre, and in particular to Dr. Hall and Mr. Rosborough, for their advice, encouragement and financial support, which made this work possible.

Thanks are extended to the author's colleagues for their useful discussion and especially to Dr. P. Goodhew, who has given invaluable advice regarding Electron Probe Microanalysis.

Finally, the author wishes to express his gratitude towards his parents and his wife for their encouragement throughout the course of this work.
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## MATERIALS USED

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**ANALYSIS BY FULMER RESEARCH LABORATORIES EXCEPT FOR THE 9% Ni STEEL, BY INTERNATIONAL NICKEL CO.**

### 2. Crucibles supplied by Thermal Syndicate Ltd.,

- **Type Drg. No. A/A3/195**
- **Ref. 3**
- **Height 25.5mm**
- **Diameter 19mm**

### 3. Chemicals for synthetic slag supplied by

- **British Drug Houses Ltd.**
  - Vanadium pentoxide ($V_2O_5$). Assay - Not less than 98.5%
  - Sodium Sulphate (Anhydrous) ($Na_2SO_4$). Assay - Not less than 99%


- **High Purity Argon (Ar)** - Better than 99.999%
- **maximum total impurities do not exceed 200 ppm.**
- **Oxygen (O_2)**

### 5. Araldite Mouting Resin supplied by C.I.B.A. Ltd.,

- **Resin Type** AY103
- **Hardener Type** HY951
1. INTRODUCTION

Fuel oil ash corrosion is a process whereby stainless steels corrode at a rate far higher than would normally be expected from the operating temperature to which they are subjected.

The main reason for this accelerated attack is the presence of a molten ash that forms from the impurities found in the original fuel oil. The main contaminants that constitute the molten ash phase are vanadium pentoxide, sodium sulphate and chloride salts, as well as complex compounds that form by the interaction of the various contaminants. Gaseous contamination is also present in the form of oxides of sulphur, carbon dioxide and other hydrocarbon gases.

Due to the present inability to adequately control this form of corrosion, the normal operating limit of most boiler plants is a steam temperature of 540°C. With the present demand for higher efficiency, thus higher steam temperatures, fuel oil ash corrosion becomes a very serious problem since the life expectancy of the boiler superheater tubes is greatly reduced.

The present work has been undertaken with a view to examine systematically under controlled conditions the corrosion mechanism involved with this form of attack. It is hoped that further information will be produced to find methods of either reducing the corrosion, or suggesting materials which can
withstand the attack.

Dormant immersion tests have been used to simulate the attack using four different stainless steels subjected to corrosion by a synthetic slag having a composition of 70 wt.% vanadium pentoxide and 30 wt.% sodium sulphate, under atmospheres of either pure oxygen, air or pure argon. The corrosion tests have been carried out at a temperature of 675°C with corrosion immersion times ranging from 1 to 100 hours.

A study of actual boiler tubes taken from Marchwood Power Station has also been carried out to obtain a comparison between the laboratory prepared specimens, and those from the Marchwood trials.

The main methods of investigation used throughout this study have been Electron Probe Microanalysis, in conjunction with Scanning Electron Microscopy.

The reduction in the specimen thickness due to corrosion has been used as the measurement for the kinetic study.
2. LITERATURE REVIEW

2.1 Fuel Oil Contaminants

2.1.1 The Origin of ash forming elements

Several theories as to the formation of petroleum have been put forward and in the great majority of cases the origin has been given as organic animal and vegetable matter. The main body of the crude oil is hydrocarbon in nature, however; a process of oxygen removal, hydrogenation, must therefore have taken place. (1)

As well as the main hydrocarbon bulk, the oil also contains many other elements as impurities, which may form a significant fraction of the total oil. (2) The impurities are usually oxygen, nitrogen, chlorine and a very wide variety of metals, usually present as constituents of large compound molecules.

Residual fuel oil is the remaining fraction from the refining of crude oil, diluted to the required viscosity with distillate hydrocarbons, and will therefore contain the main bulk of the impurities from the original crude oil.

Contaminant elements may also be picked up by the crude oil during transportation, recovery and storage of the oil, thus increasing the impurity level of the crude.

A further complication arises with the impurity level when one considers the location of the crude oil source. Vast differences in both the type of impurity elements and their relative amounts can exist depending on the area from which
the oil was obtained.

A comprehensive list of the principal ash forming elements has been given by Thomas\(^2\), while Williams and Crawley\(^3\) give a guide to the impurity elements, determined by ash analysis, found in crude oils from various locations.

2.1.2 The Nature of Impurities in Residual Fuel Oil

Modern refinery techniques and cracking processes have reduced the amount of crude oil residues but have thus increased the impurity content per unit volume within this residue. After dilution with lighter hydrocarbons, a colloidal suspension is formed consisting of high molecular weight organic compounds, and micro-crystalline solids, with the metallic elements mostly found within these organic compounds.

The main elements that appear to produce the corrosive nature of the fuel oil ash are vanadium, sodium, sulphur and chlorine.

**Vanadium**

The vanadium content of crude oils depends on the geographical location from which they are obtained, thus the amount in the residual fuel oil will vary considerably, from nil to 100 ppm \(^3,4\). Vandium exists as a range of complex high molecular weight organic compounds known as porphyrins, thought to originate from various marine flora and fauna \(^4,5\).

**Sodium**

Sodium is present in crude oil, mainly as sodium chloride \(^5,6\)
dissolved in emulsified water or as a suspension in a crystalline state, and can be present up to 100 ppm. (4)

**Sulphur**

All crude oils contain some sulphur but the quantity of this element can vary from as little as 0.5%, up to 7% (3), with 3% not uncommon in the residual fuel oil. (4)

The sulphur is present largely in the form of complex, high boiling point compounds, as in asphaltic constituents. It can also be present as elemental sulphur and hydrogen sulphide. (5)

**Chlorine**

Chlorine is usually associated with sodium as sodium chloride, with contamination levels ranging from 0.1 to 2%, as well as with small quantities of magnesium chlorides. (7)

The presence of sodium chloride is very important in considering corrosion of marine boiler plant due to the high levels of contamination of the fuel oil by sea-water.

**Others**

As previously mentioned, crude oils contain many other contaminants, mostly in the form of organo-metallic compounds. These also include silicon, in the form of silicates, iron and nickel (up to 25 ppm). (4) The total content of these elements in the oil can be 0.2%, depending on the subsequent handling of the crude oil. (3)

### 2.1.3 Melting Points of Compounds found in Residual Fuel Oil Deposits.
The main compounds that have been found in deposits taken from oil fired plants are usually vanadates, oxides, chlorides, sulphates and possibly sulphides. Since it is considered that catastrophic corrosion by fuel oil ash occurs in the presence of a liquid phase, a knowledge of the melting points of these compounds and of the compounds subsequently formed, is useful. Lists of the relevant compounds and their melting points have been published, and a summary is given in Table 1.

It is interesting to note that the majority of the lowest melting point compounds are associated with vanadium. This immediately poses a two fold problem in that both a liquid phase, which can produce accelerated corrosion attack, and vanadium compounds, thought to be very corrosive in themselves, are present.

It has also been found that even lower melting point eutectics exist in the $V_2O_5/Na_2SO_4$, $V_2O_5/Na_2O$ systems. Cunningham and Brasunas found that two eutectics exist at 5 and 50 weight percent $Na_2SO_4$, in the $Na_2SO_4/V_2O_5$ system, with melting points of 619°C and 600°C respectively.

Lucus et al. investigated the change in the melting point of vanadium pentoxide with various oxide additions, and, in the majority of cases it was found that the melting point was reduced with small additions, less than 10 weight percent. The actual reduction in the melting point of vanadium pentoxide...
was however very small, generally $5^\circ C$ being the maximum, with the major metallic oxides, $\text{Fe}_2\text{O}_3$, $\text{Cr}_2\text{O}_3$ and $\text{NiO}$.

![Diagram](image)

*Fig. 1. Na$_2$SO$_4$ - V$_2$O$_5$ System*
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<th>COMPOUND</th>
<th>MELTING POINT °C</th>
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<td>Alumina</td>
<td>Al₂O₃</td>
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<tr>
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<td>Al₂(SO₄)₃</td>
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<td>Calcium Oxide</td>
<td>CaO</td>
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<td>Calcium Sulphate</td>
<td>CaSO₄</td>
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<td>Ferric Oxide</td>
<td>Fe₂O₃</td>
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<td>Ferric Sulphate</td>
<td>Fe₂(SO₄)₃</td>
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<td>Ferric Sulphide/iron Eutectic</td>
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<tr>
<td>Magnetite</td>
<td>Fe₃O₄</td>
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<td>Magnesium Oxide</td>
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<tr>
<td>Nickel Sulphide/Nickel Eutectic</td>
<td>Ni₃/₂/Ni</td>
</tr>
<tr>
<td>Nickel Vanadate</td>
<td>NiO.V₂O₅</td>
</tr>
<tr>
<td>Silica</td>
<td>SiO₂</td>
</tr>
<tr>
<td>Sodium Sulphate</td>
<td>Na₂SO₄</td>
</tr>
<tr>
<td>Sodium Bisulphate</td>
<td>NaHSO₄</td>
</tr>
<tr>
<td>Sodium Pyrosulphate</td>
<td>Na₂S₂O₇</td>
</tr>
<tr>
<td>Sodium Pyrovanadate</td>
<td>2Na₂O.V₂O₅</td>
</tr>
<tr>
<td>Sodium Metavanadate</td>
<td>Na₂O.V₂O₅</td>
</tr>
<tr>
<td>Sodium Vanadyl Vanadate (α)</td>
<td>Na₂O.V₂O₄·5V₂O₅</td>
</tr>
<tr>
<td>Sodium Vanadyl Vanadate (γ)</td>
<td>5Na₂O.V₂O₄·11V₂O₃</td>
</tr>
<tr>
<td>Sodium Orthovanadate</td>
<td>3Na₂O·V₂O₅</td>
</tr>
<tr>
<td>Vanadium Trioxide</td>
<td>V₂O₃</td>
</tr>
<tr>
<td>Vanadium Tetroxide</td>
<td>V₂O₄</td>
</tr>
<tr>
<td>Vanadium Pentoxide</td>
<td>V₂O₅</td>
</tr>
<tr>
<td>Nickel Pyrovovanadate</td>
<td>2NiO.V₂O₅</td>
</tr>
<tr>
<td>Nickel Orthovanadate</td>
<td>3NiO.V₂O₅</td>
</tr>
<tr>
<td>Ferric Metavanadate</td>
<td>Fe₂O₃.V₂O₅</td>
</tr>
<tr>
<td>Ferric Orthovanadate</td>
<td>FeO₂V₂O₅</td>
</tr>
<tr>
<td>Chromium Sulphide</td>
<td>CrS</td>
</tr>
</tbody>
</table>
2.2 COMBUSTION AND DEPOSITION

2.2.1 Combustion of Residual Fuel Oil

The fuel oil enters the boiler in an atomised state thus combustion takes place of the individual fuel droplets. The combustion of these droplets is considered to proceed in two stages, (17):

i. The lighter hydrocarbons are evaporated and burnt, while thermal cracking takes place of the heavier hydrocarbons, resulting in a tarry coke residue.

ii. The tarry coke residue and non volatile compounds are then burnt.

Since the combustion rate of the droplets is inversely proportional to the square of their diameter, then small droplets will be quickly exposed to the flame temperature within the boiler (\(\equiv 1400^\circ C\)). The larger coke residues will require more heating, and, since they tend to contain the majority of the ash forming elements, the rate of release of these elements will be dependent on the combustion rate of the tarry coke residue. (18)

Both large and small droplets will contain vanadium, thus, the oxidation of vanadium, in the smaller droplets, to \(V_2O_5\) will be quicker than that in the larger droplets. During the tarry stage, vanadium probably remains as \(V_2O_3\) and is not fully oxidised to \(V_2O_5\) until this residue has been burnt out. (17)
2.2.2 The behaviour of S, Na, V and Cl before ash deposit formation.

Sulphur

During combustion all the sulphur is oxidised to \( \text{SO}_2 \) and \( \text{SO}_3 \), depending on the oxygen level in the boiler. The \( \text{SO}_3 \) is able to combine with water vapour, which is also present in the gas stream, and may condense on relatively cool surfaces of the boiler, such as air heaters and economizers, causing severe acidic corrosion.\(^{(4,21)}\)

The production of \( \text{SO}_3 \) may arise from three sources;\(^{(11)}\)

i) reactions within the flame, ii) oxidation of \( \text{SO}_2 \) and iii) dissociation of complex sulphates. However, since the sulphate content is very low, no appreciable level of \( \text{SO}_3 \) would be expected to originate from this source except in very localised regions. The main production must therefore be considered to be the flame reactions and the oxidation of \( \text{SO}_2 \).\(^{(11)}\)

The main oxidation reaction of \( \text{SO}_2 \) to \( \text{SO}_3 \) is by atomic oxygen, found within the flame, often with a catalyst present.\(^{(22)}\)

\[
\text{SO}_2 + O + M \rightleftharpoons \text{SO}_3 + M^* \tag{1}
\]

\( M \) is a third body such as \( \text{Fe}_2\text{O}_3 \).

Outside the flame zone the concentration of atomic oxygen decreases and the production of further \( \text{SO}_3 \) becomes increasingly dependent upon intermolecular reactions, such as

\[
\text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_3 \tag{2}
\]

Since the production of \( \text{SO}_3 \) depends on the presence of oxygen, then by reducing the level of excess oxygen in the
combustion chamber, the oxidation of $\text{SO}_2$ can be limited and thus the formation of $\text{H}_2\text{SO}_4$ reduced.\(^{(4,23)}\)

Sulphur oxides may also combine with sodium oxide and iron oxides to produce complexes sulphates, (e.g. $\text{Na}_3\text{Fe(SO}_4^\cdot3\text{)}$), identified by chemical and X-ray analysis, which have been suggested to play an important role in the corrosion of superheater materials in the temperature range of 590 to 650°C.\(^{(24)}\)

**Sodium and Chlorine**

The two elements, sodium and chlorine, are combined together as sodium chloride in the fuel oil and enter the boiler as such. In the combustion process, the compound is rapidly vapourized by one or more of a number of different vapourization processes that exist,\(^{(25)}\) but once complete the elements are present as either $\text{NaCl}$ or $\text{NaOH}$ and $\text{HCl}$. The relative proportions of these compounds is determined by the interaction of the type,\(^{(26)}\)

\[
\text{NaCl (gas) + H}_2\text{O} \rightleftharpoons \text{NaOH (gas) + 2 HCl (gas)} \quad (3)
\]

The NaOH produced and the NaCl remaining will not however condense directly onto plant surfaces, but will react with liquid vanadium pentoxide.\(^{(26)}\)

\[
2 \text{NaOH (gas) + V}_2\text{O}_5 \text{(liquid)} \rightarrow 2 \text{NaVO}_3 \text{(liquid) + H}_2\text{O} \quad (4)
\]

and

\[
\text{H}_2\text{O} + 2 \text{NaCl (gas) + V}_2\text{O}_5 \text{(liquid)} \rightarrow 2 \text{NaVO}_3 \text{(liquid) + 2 HCl} \quad (5)
\]

**Vanadium**

The vanadium in the oil exists as part of the prophyrin molecule in the divalent state. The products from the initial combustion are probably VO and VO\(_2\),\(^{(26)}\) both of which have been
identified in the vapour phase. These however have very low saturated vapour pressures so that they condense to form either \( \text{VO}, \text{V}_2\text{O}_3 \) or \( \text{V}_2\text{O}_4 \), depending on the oxygen level in the gas stream. Further reation takes place as the gas cools, when oxygen is absorbed to form \( \text{V}_2\text{O}_5 \). This in turn may react with gaseous \( \text{NaCl} \) and \( \text{NaOH} \) to produce sodium vanadates, as shown in equations (4) and (5). \(^{(4)}\)

2.2.3 The Mechanism of Ash Deposition

There are numerous factors which influence the deposition of ash particles and these include temperature and pressure of the gases in the combustion stream, concentration and physical state of the particles, speed and direction of the particles and their velocity in relation to the gas stream. The velocity of the particles will be related to their size and the level of the gas stream. The deposition rate will also be influenced by the surface finish, size and shape of the receiving body. \(^{(12)}\)

Four main processes can be considered to occur by which ash deposition takes place \(^{(26,27)}\):

i) "Particle Impaction" — whereby the inertia of the particle is sufficient to overcome deflecting drag forces, thus the particle impinges on the catchment surface.

ii) Particle Diffusion — whereby particles in the gas stream enter the boundary layer surrounding the tube and are deposited by Brownian motion.
iii) Thermal Diffusion - whereby particles in the thermal boundary layer surrounding a cooled tube are subjected to a thermal force which draws them towards the tube where they are deposited.

iv) Vapour Diffusion - whereby the vapourized oil ash constituents are transported across the temperature boundary layer by molecular diffusion and condense on the tube surface.

2.2.4 The Mechanism of Deposit Formation

It has been previously (2.2.1) shown that fuel oils containing impurities when burnt produce atmospheres consisting of solid particles, molten and semi-molten particles and compounds in the vapour phase.

These particles are then deposited on the catchment surface as described in 2.2.3. Once on the surface the particles form into deposits and it has been found by Jacklin et al.\(^{(28)}\) that this formation occurs by three different processes.

1) Precipitation from the Vapour Phase

Depending on the fuel gas temperature and the condensing surface, various products may be formed during the condensation process. This may proceed by either condensation or sublimation:

i) In high gas temperature regions and on surfaces of varied temperature, molten droplets of NaCl or Na\(_2\)SO\(_4\) may condense out.
ii) In high gas temperature regions and surfaces of low temperature, NaFe(SO\(_4\))\(_3\) can form from the reaction of Na\(_2\)SO\(_4\) or NaCl with iron, present in the boiler tubes, and SO\(_3\) in the gas stream.

iii) In low temperature gas and surface regions, sulphuric acid is formed by the reaction of condensed H\(_2\)O and SO\(_3\). The sulphuric acid formed can then react with boiler materials causing severe acidic corrosion.

2. **Sticking of Molten and Semi Molten Compounds**, takes place when they are heated only sufficiently to become just molten or sintered, before they are deposited.

3. **Physical Entrapment of Solid Particles** occurs on molten or sticky surfaces, or on dry irregular surfaces of deposits already formed by methods (1 and 2 above.

### 2.2.5 The Nature of Deposits

**Physical Appearance**

The physical appearance of the three main types of fuel oil ash deposits have been described by many workers.\(^{(9,18,29)}\) These have been identified as alkaline, vanadium and various vanadyl vanadates, with by far the most bulky deposits containing sodium. Work carried out by Bowden et al,\(^{(6)}\) on distillate fuels with additions of metallic salts, showed that rapid deposit build up was encountered when sodium was present. This has also been confirmed by other workers.\(^{(18,30)}\) The appearance of the deposits
has been described as black/brown, grey/white, green/white and green/brown in colour and of solid glassy or granular appearance and strongly bonded to the metal surface.

When vanadium is present as the main impurity, it exists as vanadium pentoxide, or if reaction has taken place with SO$_3$, a compound, such as sodium vanadyl vanadate, may be formed.\textsuperscript{(31)} These deposits are described as thin, hard, black and crystalline.

A thin yellow powdery layer adjacent to the metal surface was identified by Small et al\textsuperscript{(18)} as vanadium pentoxide, by using x-ray diffraction.

In commercial boilers the deposits are generally mixtures of sodium and vanadium in the form of mixed vanadates, vanadyl vanadates and free metallic salts and oxides. These deposits have the general appearance of the high vanadium deposits.

**Order of Deposition**

Since the majority of the impurities are in the vapour state within the flame zone, and tend to have low vapour pressures, therefore on reaching cooler surfaces condensation takes place. Nuclei of less volatile compounds, which may be in the solid or plastic state, will encourage condensation.

Smith\textsuperscript{(27)} has suggested that the majority of ash particles are solid, while only the larger particles retain their plastic state, whereas Jacklin et al\textsuperscript{(28)} maintain that all particles will remain molten until deposition.

Both sodium and vanadium are deposited mainly by condensation and sublimation and results from distillate fuels\textsuperscript{(18)} show that
vanadium compounds will tend to migrate towards the inner layer, although available data does not predict which will actually deposit first.

Workers at Esso Research Centre (23,29,35) have suggested that the slag layer is striated with alternate layers of vanadium rich and sulphur rich compounds. The layer adjacent to the metal surface tends to be vanadium rich, implying that vanadium rich compounds will deposit initially.

**Interdiffusion of Elements**

The usual method of studying interdiffusion of elements has been to burn distillate fuels with additions of metallic constituents as naphthenates. (6,18)

When the initial deposit is sodium, then vanadium is deposited as the second layer, and the compound \( \beta \) vanadyl vanadate, \( \text{Na}_2\text{O}_3\text{V}_2\text{O}_4\cdot5\text{V}_2\text{O}_5 \), is formed. This compound was also formed if the initial layer was vanadium. However, in all cases the innermost layer was found to be vanadium pentoxide, while sodium occurred in the outermost layers. The concentration of sodium was found to increase with increasing distance from the metal surface.

By using corrosion probes inserted into an operative boiler, Holland et al. (23,29) noted in all cases an enrichment of chromium on the deposit side of the interface, with a corresponding decrease in the metal. Nickel was found to be concentrated on the metal side of the interface, whereas iron was evenly distributed in the deposit layer, with some depletion
at the metal interface.

These findings have also been observed by several workers using different systems. (32,33)

Analysis of Deposits

All conventional methods of analysis have been used to analyse fuel ash deposits, chemical analysis, spectrographic analysis, x-ray diffraction, electron probe microanalysis, and metallography.

The actual analysis of fuel oil ashes depends on the quantity of the major impurity constituents in the original fuel, sodium and vanadium, and their relative proportions.

With largely alkaline fuels, the deposits are mainly sulphates and oxides, while with high vanadium fuel ashes, layers of vanadyl vanadates, \( \text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5 \) and \( 5\text{Na}_2\text{O} \cdot 2\text{V}_2\text{O}_4 \cdot 11\text{V}_2\text{O}_5 \), are found with an inner powdery layer of \( \text{V}_2\text{O}_5 \).

Both of these types of fuel ashes will also contain complex oxides and vanadates of the boiler tube metal constituents.
2.3 CORROSION OF MATERIALS IN CONTAMINATED ATMOSPHERES

2.3.1 Introduction

The atmosphere formed by the combustion of residual fuel oil is derived from the main bulk of hydrocarbons, and the contaminants contained in the oil. A mixture of gases is produced all of which can cause corrosion in their own right. These gases include hydrogen, oxygen, carbon dioxide, sulphur dioxide and trioxide as well as NaOH, NaCl and HCl which may be present in the vapour phase.

2.3.2 Oxidation

Oxidation will be the predominant reaction in a system if excess air is present and providing sulphur and chlorine are absent. (12)

The oxidation resistance of metals and alloys has been widely studied and much work published on the subject (38, 39, 40).

Since high melting point refractory metals, W, Ta, Nb, and Mo and alloys are not suitable in oxidising atmosphere, although they have very good strength, alloys based on iron, chromium and nickel have been developed. Although these alloys have satisfactory strength and oxidation resistance up to 1000°C, care must be taken when other alloying additions are used to improve creep resistance and formability. Leslie and Fontana (41) found 'catastrophic oxidation' in a molybdenum containing stainless
steel which they attributed to the formation of volatile molybdenic oxide (MoO$_3$) which disrupted the protective scale. Also, Bradbury et al.\(^{(42)}\) found that vanadium additions to a carbide hardened alloys based on the nickel-chromium-cobalt system also caused severe attack.

Since oxidation resistance is initially due to the existence of an oxide film that forms a protective barrier between the metal and the atmosphere, any build up of stress in this oxide layer that may cause the oxide to crack is detrimental. Iron-chromium alloys form a layer of predominantly Cr$_2$O$_3$ but at high temperatures, and especially under stress conditions, this layer tends to rupture eventually due to the stress build up.\(^{(43)}\)

Nickel additions to the alloy tend to reduce the susceptibility for cracking of the oxide scale without reducing the oxidation resistance of the alloy.\(^{(43)}\) Although the actual reason for this is uncertain it is thought to be due to the nickel oxide in the scale allowing a measure of plasticity or a greater scale-metal interface adhesion.\(^{(43)}\)

### 2.3.3 Effects of steam and oxides of carbon

When a protective oxide scale is present on a metal surface then oxidation can only occur by the diffusion of ions and electrons through the oxide layer, thus steam and carbon dioxide should have little effect on the oxidation rate of the alloy.\(^{(12)}\)
The scaling behaviour of various metals and alloys in an atmosphere of carbon dioxide, containing small amounts of carbon monoxide, was studied by Hancock.\(^{(12)}\) It was found that only the materials that would normally be expected to suffer severe corrosion in a simple oxidation system were affected. High alloy steels behave as under normal oxidizing conditions at similar temperatures.

Eberle and Anderson\(^{(44)}\) also found this to be true when stainless steels were exposed to superheated steam atmospheres at temperatures of 650°C, 750°C and 820°C. It was however noticed that at high temperatures, only those alloys with a high nickel (\(\geq 8\%\)) content did not suffer scale exfoliation.

If sufficiently reducing atmospheres are present, chromium containing alloys may become susceptible to attack. Carbon can diffuse from the surface into the alloy with the result that chromium carbide can be precipitated, thus causing the matrix to be locally depleted of chromium and susceptible to oxidation. This attack is often termed "green rot" and is generally associated with gas turbine alloys operating in the region of 900°C.\(^{(42)}\)

2.3.4. Sulphur Containing Gases

Since most residual fuel oils contain sulphur as a contaminant, the production of SO\(_2\) and SO\(_3\) is inevitable when burning in an excess of air.
Sulphur dioxide will react readily with mild steel at boiler temperatures and it has been shown that the scale consists of alternate oxide/sulphide layers.\(^{(45)}\)

Attack by low level sulphur oxides can usually be overcome by using austenitic stainless steels. Corrosion attack has however been found to increase with increasing sulphur content of the flue gas and also reducing conditions which have a more severe effect.\(^{(46)}\) Ferritic alloys, containing less nickel, appeared to be less susceptible to attack with high levels of sulphur contamination.

In hydrogen sulphide atmospheres a continuous film of CrS can be formed providing sufficient chromium is present and a parabolic rate of oxidation is produced,\(^{(46)}\) (although not as protective as Cr\(_2\)O\(_3\)).

Sulphur can also attack Fe/Ni/Cr alloys by penetration into the metal and the formation of sulphides. This type of attack usually only occurs in high nickel chromium alloys used in gas turbines.

Alexander\(^{(47)}\) published microstructures showing spheroids of chromium sulphide in a matrix of nickel/nickel sulphide eutectic. The eutectic melts at 645°C, which is well below the operating temperature range of turbines but it is still in that of the boiler.

Corrosion by SO\(_2\) has been observed by Viswanathan and Spengler,\(^{(56)}\) to be more severe in 0.2% SO\(_2\), balance N\(_2\), than in pure SO\(_2\) probably due to the insufficient amount of Cr\(_2\)O\(_3\).
initially formed on the surface to protect the bare metal. Sulphides of both nickel and chromium were found by x-ray diffraction and electron probe microanalysis. It is also stated\textsuperscript{(56)} that free oxygen is expected to be highly beneficial in retarding sulphidation in Ni-Cr alloys in SO\textsubscript{2} atmospheres due to the ability to form larger amounts of Cr\textsubscript{2}O\textsubscript{3}.
2.4 CORROSION BY FUEL OIL ASH DEPOSITS

2.4.1 Corrosion by Vanadium Compounds

Corrosion attack associated with vanadium compounds has been considered to occur by three mechanisms:

1) Vanadium compounds act as oxygen carriers
2) The vanadium compounds dissolve the oxide scale
3) Vanadium enters the oxide scale on the metal, increasing the defect mechanisms and allowing accelerated attack.

It is however generally accepted that a liquid phase needs to be present for accelerated attack to occur and it has been found that attack increases with temperature, time of immersion and quantity of slag present.

Mechanisms 1 and 2 above were also confirmed by Amgwert et al. when they observed that the rate of attack was drastically reduced when the atmosphere above the slag was nitrogen. This was also supported by Johnson.

Since the presence of a molten phase is very important for accelerated corrosion to occur, a knowledge of the melting points of the compounds likely to form is invaluable. Many of such compounds with their melting points have been given in section 2.1.3. It is worth noting that within the Na$_2$O/V$_{2.5}$ system, various eutectics exist with very low melting points, well below the operating temperature of both boilers and turbines. The eutectic formed between 5Na$_2$O.V$_{2.4}$·11V$_2$O$_5$ and sodium metavanadate Na$_2$O.V$_{2.5}$ melts at 527°C and most of
the compounds formed between $\text{Na}_2\text{O}$ and $\text{V}_2\text{O}_5$ melt below $675^\circ\text{C}$, the mp of $\text{V}_2\text{O}_5$. However Wickert$^{(51)}$ found that under an atmosphere containing oxides of sulphur, other compounds can form (e.g. $\text{Na}_2\text{SO}_4$, $\text{Na}_2\text{S}_2\text{O}_7$, $\text{V}_2\text{O}_5\cdot2\text{SO}_3$ and $\text{V}_2\text{O}_5\cdot\frac{3}{2}\text{SO}_3$), see table 1. In practice 1.1.5 sodium vanadyl vanadate, $(\text{Na}_2\text{O}\cdot\text{V}_2\text{O}_4\cdot5\text{V}_2\text{O}_5)$ is often found in boiler deposits and Small et al$^{(18)}$ consider this compound to be the most aggressive due to its oxygen carrying ability, the mechanism of which is postulated as:-

\[
\text{SO}_2 + \text{AIR} \rightarrow \text{SO}_3
\]

\[
\text{SO}_3 + \text{Na}_2\text{O}\cdot\text{V}_2\text{O}_4\cdot5\text{V}_2\text{O}_5 \rightarrow \text{Na}_2\text{O}\cdot6\text{V}_2\text{O}_5 + \text{SO}_2
\]

\[
\text{Na}_2\text{O}\cdot6\text{V}_2\text{O}_5 + \text{METAL} \rightarrow \text{METAL OXIDE} + \text{Na}_2\text{O}\cdot\text{V}_2\text{O}_4\cdot5\text{V}_2\text{O}_5
\]

Cunningham and Brasunas$^{(52)}$ confirmed the aggressiveness of the sodium vanadyl vanadate using a mixture of $\text{V}_2\text{O}_5/20\%\text{Na}_2\text{O}$. Pantony$^{(53)}$ has shown that corrosion in vanadium melts depends upon oxygen diffusion into the liquid melt, again confirming the oxygen carrier mechanism.

Because of the evidence which supports the oxygen carrier mechanism it has been reported that the operation of a boiler on low excess air could eliminate or considerably reduce high temperative corrosion.$^{(54,55)}$ Holland and Rosborough,$^{(23)}$ however found under those conditions, only a very limited improvement is gained.

Work carried out by Maksimov$^{(37)}$ on the interaction of vanadium pentoxide with metal oxides and also the reaction of metal with their vanadates, has shown that chromium will be beneficial in preventing vanadium pentoxide corrosion.
The main conclusions made by Maksimov (37) can be summarized as follows:

i) All oxides of the main elements in stainless steels in present usage (e.g. iron, chromium and nickel) will react with vanadium pentoxide, to give the respective metal vanadate.

\[
\text{Fe}_2\text{O}_3 + \text{V}_2\text{O}_5 \rightarrow 2\text{FeVO}_4
\]
\[
\text{Cr}_2\text{O}_3 + \text{V}_2\text{O}_5 \rightarrow 2\text{CrVO}_4
\]
\[
2\text{NiO} + \text{V}_2\text{O}_5 \rightarrow \text{Ni}_2\text{V}_2\text{O}_7
\]

ii) The metal vanadates are generally unstable and will subsequently react with the metal substrate to produce metal oxide and vanadium trioxide.

\[
4 \text{Fe} + 6\text{FeVO}_4 \rightarrow 5\text{Fe}_2\text{O}_3 + 3\text{V}_2\text{O}_3
\]
\[
2\text{Ni} + \text{Ni}_2\text{V}_2\text{O}_7 \rightarrow 4\text{NiO} + \text{V}_2\text{O}_3
\]

The behaviour of chromium is somewhat different in that chromium vanadate, although reactive with some metals, reacts very little with either iron, chromium or nickel.

This leads to the hypothesis that high chromium steels, and ferritic steels especially, will have a superior corrosion resistance to \text{V}_2\text{O}_5 attack. This was confirmed by several workers (23,29).

The effect of the addition of sodium sulphate to the vanadium pentoxide was to increase the fluidity and wetting power of the mixture. This was also suggested by Elliot et al (36).

From these conclusions, the mechanism of vanadium corrosion appears to be as follows:
\[
\begin{align*}
\text{V}_2\text{O}_5 + 2\text{Me} & \rightarrow 2\text{MeO} + \text{V}_2\text{O}_3 \\
\text{V}_2\text{O}_3 + \text{O}_2 & \rightarrow \text{V}_2\text{O}_5 \\
\text{V}_2\text{O}_5 + 2\text{MeO} & \rightarrow \text{Me}_2\text{V}_2\text{O}_7 \\
2\text{Me} + \text{Me}_2\text{V}_2\text{O}_7 & \rightarrow 4\text{MeO} + \text{V}_2\text{O}_3 \\
\text{V}_2\text{O}_3 + \text{O}_2 & \rightarrow \text{V}_2\text{O}_5 \quad (2) \text{ repeated and the cycle continuing.}
\end{align*}
\]

2.4.2 Effect of Sulphates and Sulphidation Attack

Attack by sulphates alone is greatly dependant on the temperature of the system, and little effect is produced below 750°C. If a reducing atmosphere or sub-stoichiometric oxygen conditions are used for a short period initially, accelerated attack takes place below the melting point of the salt. This attack is manifested by sulphide penetration into the metal.

Dean has stated that incandescent carbon particles can promote sulphidation attack by releasing free sulphur from the sodium sulphate.

\[
2\text{Na}_2\text{SO}_4 + 6\text{C} + 3\text{O}_2 \rightarrow 2\text{Na}_2\text{O} + 6\text{CO}_2 + 2\text{S}
\]

Although Drake and Harnett found some sulphidation attack when solid carbon particles were injected into the gas stream, there was however, an overall decrease in the corrosion rate. This is probably due to the reduction in the oxygen level by the formation of carbon monoxide and carbon dioxide.

It has been suggested that corrosion by sulphates in boiler occurs by the formation of pyrosulphates, \( \text{Na}_2\text{S}_2\text{O}_7 \), which melt at
about 395°C, from sodium sulphate in the presence of catalytically
formed SO₃. (51)

\[
\begin{align*}
\text{SO}_2 + \frac{1}{2}\text{O}_2 & \xrightarrow{\text{(Fe}_2\text{O}_3)} \text{SO}_3 \\
\text{SO}_3 + \text{Na}_2\text{SO}_4 & \rightarrow \text{Na}_2\text{S}_2\text{O}_7 \text{ (liquid)} \\
3\text{Na}_2\text{S}_2\text{O}_7 \text{ (liquid)} + \text{Fe}_2\text{O}_3 & \rightarrow 2\text{Na}_3\text{Fe(SO}_4)_2 \\
\end{align*}
\]

Wickert (51) has found that attack by SO₃, in the presence
of sodium sulphate, has a maximum value between temperatures of
600 and 750°C, which seems to agree with the pyrosulphate attack
mechanism, since the stability of the pyrosulphate, although
dependant upon the SO₃ concentration, lies between 590°C and
800°C.

Jonakin (62) and Jackson (61) have both given evidence for
the formation of complex alkali iron trisulphates, supporting
the pyrosulphate mechanism.

As the maximum rate of formation of SO₃ is between 600 and
700°C (owing to the balance between the dissociation reaction
SO₃ \rightleftharpoons \text{SO}_2 + \text{O}_2 and the catalytic effect of SO₃ formation)
it is claimed that, at the oxide/deposit interface in boiler
deposits, where these temperatures are achieved, the complex
sulphates decompose to give SO₃ which diffuses and attacks the
metal. (63)

Goebel and Pettit, (64) studied the effect of Na₂SO₄ on
nickel at 1000°C and showed that a low oxygen activity,
from the formation of NiO, causes the sulphur activity to
increase. Nickel and sulphur, from the slag, combine to give
nickel sulphide which increases the oxide ion activity. This
Accelerated corrosion is not self-sustaining since oxide ions are not produced when conditions in the Na$_2$SO$_4$ are no longer favourable for the formation of nickel sulphide.

Seybolt (65) considers that the accelerated corrosion of chromium-containing alloys occurs by the destruction of the protective oxide film by the sodium sulphate. Sulphidation attack takes place and chromium sulphides are formed, thus depleting the alloy matrix of chromium which is then oxidised.

Further work by Goebel et al. (60) using nickel alloys containing additions of Cr, Al, Mo, W and V showed that in the temperature range 650 to 1000°C corrosion behaviour could usually be characterized by either sodium sulphate induced catastrophic oxidation or sodium sulphate induced accelerated oxidation. In both cases liquid Na$_2$SO$_4$ fluxes dissolve the normally protective oxide layers as previously shown. (64) However catastrophic or self sustaining oxidation occurs when Mo, W and V are present in the alloy since their oxides will decrease the oxide ion activity of the Na$_2$SO$_4$, thus producing melts which are acidic fluxes for oxide scales.

The production of acidic fluxes was also confirmed when vanadium pentoxide was added to the melt separately in tests conducted by Bornstein et al. (67)

2.4.3 Corrosion by Chlorides

The effect of chlorides on corrosion is very important when
marine installations are under consideration. The level of chloride contamination in land based fuel oil burning boilers tends to be low.

The effect of chloride contaminants on sulphate corrosion was demonstrated by many workers, and several mechanisms of attack have been suggested.

1) Chromic chloride is produced, which is volatile, thus is removed from the reaction site. This renders the site free for further chloride attack on oxidation.

\[ 24 \text{NaCl} + 10\text{Cr}_2\text{O}_3 + 9\text{O}_2 \rightarrow 12\text{Na}_2\text{Cr}_2\text{O}_3 + 8\text{CrCl}_3 \text{(vapour)} \]

2) Chlorides have a catalytic effect on the reaction

\[ 4 \text{Fe} + 2\text{SO}_4^{2-} + \text{Cl}^- \rightarrow 4\text{FeO} + \text{S}_4^2- \]

This reaction is considered to take place between sulphates and sub-scale iron, and may be responsible for the formation of a non-protective chromium sulphide layer.

Greenert has shown that very severe corrosion takes place with mixtures of Na_2SO_4 and NaCl under an inert atmosphere.

In general, it is thought that if chlorides are present, then the oxide is disrupted and formation of volatile chromium chlorides probably occurs which will allow internal penetration of the "reduced sulphur environment" and thus cause sulphidation of the metal substrate. If sufficient chromium depletion has taken place, nickel sulphide may possibly form.

2.4.4 Summary

It can be seen that the main fuel oil contaminants are
vanadium, sodium, chlorine and sulphur, and that each contaminant can act as an aggressive corrodent of stainless steel in its own right. Under plant conditions, these contaminants exist and react together, producing corrosive mixtures of far greater severity than could be expected from the single components.

Catastrophic and accelerated corrosion both occur in the presence of a liquid phase, which is produced by the interaction of vanadium pentoxide and sodium sulphate especially. Under a liquid slag, the normally protective oxide layers on the metal are fluxed exposing the underlying metal to attack by either vanadium or sulphur compounds. The actual mechanism of attack is the subject of many papers but controversy still exists as to the exact mechanism. It seems likely that several suggested mechanisms are correct, but the operative mechanism depends on the composition of the steel and the conditions of the particular installation.

Chlorine is less important in land based boilers but becomes extremely important when marine installations are considered.
2.5 THE CHEMISTRY OF THE VANADIUM PENTOXIDE/SODIUM SULPHATE SYSTEM.

2.5.1 Vanadium Pentoxide

Vanadium pentoxide has an orthorhombic structure and is the highest oxide in the vanadium/oxygen system. It does, however, have the lowest melting point within that system, melting at 675°C.

The pentoxide has a low stability range and begins to lose oxygen at about 600°C when heated in a high vacuum. It has been stated, however, that the evaporation of VO₂ involves the formation of V₂O₅ and oxygen. It has also been stated that there is complete miscibility between VO₂ and V₂O₅.

Vanadium pentoxide has the n-type semi-conductive properties in both the liquid and solid states.

Heats of formation up to 2000°C have been calculated and the data produced plotted in relation to 1 mole of vanadium and 1 mole of oxygen. From this data it appears that there is no tendency for the lower oxides to decompose, but, due to the closeness of the free energies of V₂O₅ and VO₂, some oxygen will be lost by the higher oxide at high temperatures.

Thermodynamic data for the V-O system has been published by Allen et al.

2.5.2 Vanadium pentoxide and Sodium Sulphate Mixtures
The first phase diagram produced for this system was by Canneri, (76) who also studied the oxygen evolution properties of Na:V ratios less than unity. He first suggested the name vanadyl vanadates for the crystalline compounds formed from the melt as oxygen was evolved.

This effect was also observed by Prandlt (77) and Flood et al. (78). Flood, Sorum and Krog, using x-ray analysis, showed that five compounds were in fact formed: Na$_3$VO$_4$, Na$_2$V$_2$O$_7$, NaVO$_3$, 5Na$_2$O·V$_2$O$_4$, 11V$_2$O$_5$ (α vanadyl vanadate), and Na$_2$O·V$_2$O$_4$·5V$_2$O$_5$ (β vanadyl vanadate).

X-ray studies conducted by Wadsley (79) on the β compound showed that the sodium atoms are situated in tunnels in the vanadium-oxygen skeleton. X-ray analysis of the Na$_2$SO$_4$ - V$_2$O$_5$ system in air by Pollman (84) also identified the α and β compounds. The β compound has been found as a common deposit both in gas turbines (6,80) and on superheater tubes (10).

Cunningham and Brasunas (15) have shown that maximum corrosion of steel specimens occurred when 20 mole% Na$_2$SO$_4$ and 80 mole% V$_2$O$_5$ molten slags, were used as the corrodenent. These figures lie close to the composition of the β compound, 83 mole% V$_2$O$_5$.

This was verified by Macfarlane, (82) who used the same slag composition, but with different SO$_2$/SO$_3$ atmosphere mixtures. Coats (83) has carried out investigations into the Na$_2$SO$_4$ - V$_2$O$_5$ - SO$_3$ system over a wide range of slag compositions and temperatures. From x-ray analysis, the major constituents
identified, apart from the original reactants, were the $\alpha$ and $\beta$ compounds. It was also noted that in the equilibrium state, excess $SO_3$ was dissolved in the liquid phase.
2.6 THERMODYNAMIC ANALYSIS OF THE SYSTEM

2.6.1 Introduction

With the use of reliable thermodynamic data, it is possible to calculate the equilibria within a boiler plant that may occur at given conditions of temperature, pressure and concentration.

In practice, the residence time of flue gas within the boiler is short, perhaps only 5 seconds in a 200 MW boiler, and it is therefore possible that some reactions will not necessarily reach chemical equilibrium. However, even if equilibrium is not reached, there will be a tendency towards that state of equilibrium and thus data as to the most probable reactions is obtained from such calculations, which should be of use in the analysis of experimental results.

2.6.2 Main Thermodynamic Equations

Assuming a reaction takes place between two gaseous reactants to produce two gaseous products, then the reaction at equilibrium can be represented by

\[ aA + bB \rightleftharpoons cC + dD \]  

At a temperature \( T \) K, the equilibrium constant \( K_T \) is given by:

\[ K_T = \frac{(P_C)^c}{(P_B)^d} \frac{(P_D)^d}{(P_A)^a} \]  

where \( P_A, P_B, P_C \) and \( P_D \) are the equilibrium partial pressures of the reacting species.

The standard free energy change, \( \Delta G_T^o \), for the reaction is
related to the equilibrium constant, $K_P^T$ by

$$\Delta G^O_T = -RT \log_e K_P^T$$  (3)

If, however, the gaseous atmosphere contains consistently other ratios of gases than that given by the equilibrium constant, then

$$\Delta G_T = \Delta G^O_T + RT \ln Q$$  (4)

where $Q = \frac{P_aP_b}{P_cP_d} = \frac{F_aF_b}{F_cF_d}$ and $F$ = the fugacity.

The pressures $P_a$, $P_b$, $P_c$, and $P_d$, are the working pressures in the system, and not the equilibrium pressures.

The standard free energy change, $\Delta G^O_T$, at any temperature $T^O_K$, for any chemical reaction is directly related to the differences between the standard heats of formation, $\Delta H^O_{298}$, of the products and reactants, their standard entropies, $\Delta S^O_{298}$, and the difference of heat capacities, $\Delta C_P$, between 298°K and $T^O_K$, by the equation

$$\Delta G^O_T = \Delta H^O_{298} + \int_{298}^{T} \Delta C_P dT - T \Delta S^O_{298} - T \int_{298}^{T} \frac{\Delta C_P}{T} dT$$  (5)

This is assuming that within the temperature range, from 298 to $T^O_K$, there are no phase changes of reactants and products.

For the reactions which take place between the slag and metal, after slag deposition has taken place, the standard free energies for the reactions again need to be modified. In this case, the reactants and products are most probably not as pure substances, but in the form of alloys and compounds, thus to obtain $\Delta G_T$ values, correction for the deviation from the standard states has to be made using the Van't Hoff Isotherm.
Normally, the $\Delta G_T$ would be calculated from the following equation:

$$\Delta G_T^o = \Delta G_T^o + RT \log_e Q \quad (6)$$

where $Q = \frac{\text{Pressure}}{\text{Activity}} \times \frac{\text{Concentration}}{\text{Pressure}} \times \frac{\text{Activity}}{\text{Reactants}} \times \frac{\text{Concentration}}{\text{Products}}$

Since the activities, in the majority of cases for the system under study, are not available, the values of concentration have to be used as a first approximation,

thus $a_M = \frac{N}{M}$

where $a_M =$ activity of the metal in the alloy

$N_M =$ mole fraction of the metal in the alloy.

For an alloy composition 20 wt% Cr, 25 wt% Ni and 55 wt% Fe,

the value of $N_{Cr} = \frac{0.2}{51.996} + \frac{0.25}{58.71} + \frac{0.55}{55.847}$

Atomic Weight Cr = 51.996

Atomic Weight Ni = 58.71

Atomic Weight Fe = 55.847

thus, $N_{Cr} = \frac{0.2}{51.996} + \frac{0.25}{58.71} + \frac{0.55}{55.847} = 0.21425$

By applying this correction to each of the reactions, the calculated "corrected" $\Delta G_T$ value can be used for the thermodynamic analysis of the system.
2.6.3 Thermodynamic Data for Reactions Occurring in the Flame and Condensed Phases.

The main elements present in the fuel oil which are responsible for the corrosion, are sulphur, vanadium, sodium and chlorine which on combustion will be either oxidised or vapourised. The extent to which oxidation takes place will depend on the operating conditions of the plant, especially with respect to the excess oxygen combustion conditions. Table 2 shows the values for $\Delta G^\circ_T$ for the possible reactions occurring within the range 1100 to 1900 $^\circ$K which have been calculated from previously determined data (108,109,110,111) using equation (4).

From thermodynamic calculations and experimental data obtained, Halstead (26) concluded as follows:

1) Vanadium will initially form VO$_2$(gas), which condenses to form either V$_2$O$_3$ or V$_2$O$_4$, as solid fume. Condensation of V$_2$O$_3$ via the reaction $2$VO$_2$(gas) $\rightarrow$ V$_2$O$_3$(cond) + $\frac{1}{2}$O$_2$, will start at a gas temperature of 1750 $^\circ$K. Condensation of V$_2$O$_4$, via the reaction $2$VO$_2$(gas) $\rightarrow$ V$_2$O$_4$(cond), would begin at 1830 $^\circ$K.

2) The deposited fume will liquefy, due to the formation of V$_2$O$_5$ temp. 675 $^\circ$C, on absorption of oxygen.

3) Chemical reaction between vapour phase sodium species and the fume will begin at a flue gas temperature of 1800 $^\circ$K.

4) NaOH and NaCl will not condense directly onto plant surfaces. Direct condensation of Na$_2$SO$_4$ can occur in systems burning oil
### Table 2

**Thermodynamic Data of the Flame and Condensed Phases**

\[ \Delta G^0_T = A + BT \text{ Kcals} \]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( A )</th>
<th>( B \times 10^{-2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{VO}_2(\text{gas}) + \frac{1}{2}\text{O}_2 \rightarrow \text{VO}_2(\text{gas}) )</td>
<td>-87.95</td>
<td>2.05</td>
</tr>
<tr>
<td>( 2\text{VO}_2(\text{gas}) \rightarrow \text{V}_2\text{O}_5(\text{cond}) + \frac{1}{2}\text{O}_2 )</td>
<td>-172.68</td>
<td>5.33</td>
</tr>
<tr>
<td>( 2\text{VO}_2(\text{gas}) \rightarrow \text{V}_2\text{O}_4(\text{cond}) )</td>
<td>-218.73</td>
<td>7.03</td>
</tr>
<tr>
<td>( \text{VO(\text{gas})} \rightarrow \text{VO(\text{cond})} )</td>
<td>-130.36</td>
<td>3.76</td>
</tr>
<tr>
<td>( \text{NaCl(gas)} + \text{H}_2\text{O} \rightarrow \text{NaOH(gas)} + \text{HCl} )</td>
<td>28.78</td>
<td>-0.13</td>
</tr>
<tr>
<td>( 2\text{NaOH(gas)} + \text{V}_2\text{O}_5(\text{cond}) \rightarrow 2\text{NaVO}_3(\text{cond}) + \text{H}_2\text{O} )</td>
<td>-107.45</td>
<td>1.95</td>
</tr>
<tr>
<td>( 2\text{NaCl(gas)} + \text{V}_2\text{O}_5(\text{cond}) + \text{H}_2\text{O} \rightarrow 2\text{NaVO}_3(\text{cond}) + \text{HCl} )</td>
<td>-48.50</td>
<td>1.60</td>
</tr>
<tr>
<td>( 2\text{NaOH(gas)} + \text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{Na}_2\text{SO}_4(\text{gas}) + \text{H}_2\text{O} )</td>
<td>-164.84</td>
<td>8.04</td>
</tr>
<tr>
<td>( 2\text{NaCl(gas)} + \text{SO}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow \text{Na}_2\text{SO}_4(\text{gas}) + 2\text{HCl} )</td>
<td>-107.29</td>
<td>7.79</td>
</tr>
<tr>
<td>( 2\text{NaVO}_3(\text{cond}) + \text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{Na}_2\text{SO}_4(\text{cond}) + \text{V}_2\text{O}_5(\text{cond}) )</td>
<td>-88.04</td>
<td>6.68</td>
</tr>
<tr>
<td>( 2\text{HCl} + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{Cl}_2 )</td>
<td>-13.98</td>
<td>1.63</td>
</tr>
<tr>
<td>( 2\text{Ni(gas)} + \text{O}_2 \rightarrow 2\text{NiO(\text{cond})} )</td>
<td>-309.83</td>
<td>10.58</td>
</tr>
<tr>
<td>( 2\text{Fe(gas)} + \text{O}_2 \rightarrow 2\text{FeO(\text{cond})} )</td>
<td>-297.08</td>
<td>8.93</td>
</tr>
<tr>
<td>( 2\text{V(gas)} + \text{O}_2 \rightarrow 2\text{VO(\text{cond})} )</td>
<td>-437.04</td>
<td>10.64</td>
</tr>
</tbody>
</table>
with low vanadium but high sodium content, i.e. molar vanadium to sodium ratio less than unity.

5) \( \text{Na}_2\text{SO}_4 \) will be formed in deposits at temperatures below 1000\(^\circ\)K, by the interactions of sodium vanadates with vapour phase \( \text{SO}_2 \) and \( \text{O}_2 \).

6) Both the nickel and the iron present in residual fuel oil will form condensed phase fume in the flue gas at temperatures above 1800\(^\circ\)K.

2.6.4 Thermodynamic Data for Possible Reactions occurring between the liquid Slag Constituents and Superheater Material.

The reactions that must be considered are those between the constituents of the alloy material, generally iron, chromium and nickel and any significant amounts of ther metals, and the constituents of the molten slag. The thermodynamic data at present available, however, does not include the formation of complex metallic vanadates or sulphates which may occur. The data available therefore is limited to the formation of oxides and sulphides of the elements iron, chromium and nickel, which is given in Table 3.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G^0$ in cals.</th>
<th>$\Delta G^0_{948}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2\text{Cr} + S_2 \rightarrow 2\text{CrS}^*$</td>
<td>$-43,000 + 13.4 , \text{T}$</td>
<td>$-53,297$</td>
</tr>
<tr>
<td>$3\text{Ni} + S_2 \rightarrow \text{Ni}_3 S_2$</td>
<td>$-79,240 + 39.01 , \text{T}$</td>
<td>$-42,259$</td>
</tr>
<tr>
<td>$2\text{Fe} + S_2 \rightarrow 2\text{FeS}$</td>
<td>$-71,820 + 25.12 , \text{T}$</td>
<td>$-48,007$</td>
</tr>
<tr>
<td>$3\text{O}_2 + S_2 \rightarrow 2\text{SO}_3$</td>
<td>$-218,440 + 77.34 , \text{T}$</td>
<td>$-145,122$</td>
</tr>
<tr>
<td>$2\text{Cr} + \frac{1}{2}\text{O}_2 \rightarrow \text{Cr}_2 \text{O}_3$</td>
<td>$-267,750 + 62.1 , \text{T}$</td>
<td>$-208,879$</td>
</tr>
<tr>
<td>$3\text{Ni} + \frac{1}{2}\text{O}_2 \rightarrow 3\text{NiO}$</td>
<td>$-175,350 + 70.65 , \text{T}$</td>
<td>$-108,375$</td>
</tr>
<tr>
<td>$2\text{Fe} + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe}_2 \text{O}_3$</td>
<td>$-193,919 + 61.03 , \text{T}$</td>
<td>$-136,062$</td>
</tr>
<tr>
<td>$3\text{Cr} + \text{SO}_3 \rightarrow \text{CrS} + \text{Cr}_2 \text{O}_3$</td>
<td>$-182,530 + 30.13 , \text{T}$</td>
<td>$-153,966$</td>
</tr>
<tr>
<td>$4\frac{1}{2}\text{Ni} + \text{SO}_2 \rightarrow \frac{3}{2}\text{Ni}_3 S_2 + 3\text{NiO}$</td>
<td>$-105,750 + 51.48 , \text{T}$</td>
<td>$-56,942$</td>
</tr>
<tr>
<td>$3\text{Fe} + \text{SO}_3 \rightarrow \text{Fe}_5 + \text{Fe}_2 \text{O}_3$</td>
<td>$-120,609 + 34.92 , \text{T}$</td>
<td>$-87,505$</td>
</tr>
<tr>
<td>$2\text{CrS} + \frac{1}{2}\text{O}_2 \rightarrow \text{Cr}_2 \text{O}_3 + 2\text{SO}_3$</td>
<td>$-438,190 + 126.04 , \text{T}$</td>
<td>$-318,704$</td>
</tr>
<tr>
<td>$\text{Ni}_3 S_2 + \frac{1}{2}\text{O}_2 \rightarrow 3\text{NiO} + 2\text{SO}_3$</td>
<td>$-314,550 + 108.98 , \text{T}$</td>
<td>$-211,237$</td>
</tr>
<tr>
<td>$2\text{FeS} + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe}_2 \text{O}_3 + 2\text{SO}_3$</td>
<td>$-340,539 + 113.35 , \text{T}$</td>
<td>$-233,178$</td>
</tr>
</tbody>
</table>

All from Kubaschewski, Evans and Alcock,\textsuperscript{(111)}

except \textsuperscript{*} from Hager and Elliot\textsuperscript{(113)}
2.6.5 Summary

From the thermodynamic data given in Table 2, it can be seen that the final molten phase likely to be present within the operative boiler would consist of vanadium pentoxide and sodium sulphate. The relative amounts of these two components will depend on the fuel used.

From the data in Table 3 it should be possible to predict the main corrosion products (except the complex vanadates and sulphates) likely to form during fuel oil ash corrosion.
2.7 METHODS OF REDUCING CORROSION BY FUEL OIL ASH DEPOSITS

2.7.1 Introduction

There are many ways in which the reduction of corrosion can be attempted in contaminated combustion atmospheres, and these methods generally fall into one of two groups based on either changing the environmental conditions or changing the material.

Changing of the environmental conditions can be obtained in three ways and these will be reviewed under the following headings:

i) Removal of harmful impurities present in the environment.

ii) Addition of a compound to counteract the harmful impurities.

iii) Changing the combustion conditions to minimise the attack.

The changing of materials to withstand corrosion is an exceedingly difficult problem, since operating conditions and fuel types range from boiler to boiler. Also, there exists an ever increasing demand to increase efficiency, thus increased operating temperature, and therefore new materials must always be sought after. New materials and coatings on existing alloys, will also be considered in this section.
2.7.2 Removal of Ash Forming Impurities.

The problem of corrosion by fuel oil ash could be drastically reduced if ash-forming elements could be removed. Reviews have been carried out on the subject of contaminant removal by Edwards, Williams and Crawley and Samms and Smith. The main conclusion arrived at in each case is the high cost of such a process making fuel oil no longer an economic fuel.

Water washing of fuel oil can however reduce the sodium concentration appreciably and in conjunction with centrifuging the reduction can be 75 - 80% of the total sodium content. Vanadium however cannot be removed by water washing and therefore great care must be exercised if sodium were to be reduced by this process, otherwise the 20% Na₂O/V₂O₅ mixture may be approached by removing sodium to this level. Other methods available for the removal of impurities can be classified in four groups:

1) Filtration, which is mainly used for solid material.
2) Centrifuging, usually used in conjunction with water washing. It only removes material suspended in the oil i.e. sodium.
3) Solvent precipitation which is a very expensive process involving loss of oil and expensive chemicals.
4) Chemical and catalytic processing, which consists of hydrogenation to achieve breakdown of organic molecules,
followed by ion exchange and treatment with halogens.\(^{(9)}\)

The process of impurity removal is therefore not a technological problem but economic, since fuel oil is basically a cheap commodity and further processing costs cannot be justified.

### 2.7.3 Use of Additives

Additives are used to reduce corrosion of stainless steels by either reacting with the molten ash phase and producing a phase with a melting point above the operating temperature of the boiler, or to physically soak up the molten phase and thus remove it from direct contact with the metal.

The most important additive compounds are oxides, hydroxides and carbonates of magnesium and calcium.\(^{(23)}\) These additives can neutralize both the sulphuric acid, which condenses on the cooler parts of the plant, and vanadium pentoxide to form vanadates with melting points in excess of 1000°C.

\[
\begin{align*}
\text{CaO} + \text{H}_2\text{SO}_4 & \rightarrow \text{CaSO}_4 + \text{H}_2\text{O} \\
\text{MgO} + \text{V}_2\text{O}_5 & \rightarrow \text{MgV}_2\text{O}_6
\end{align*}
\]

Daebelar and Smerke\(^{(84)}\) have also found success using MgO addition. Dolomite (\(\text{CaCO}_3 \cdot \text{MgCO}_3\)) has been widely used as an additive\(^{(13)}\) but its efficiency is somewhat dubious. It is claimed that dolomite additions give less corrosion on high chromium alloys but cause increased attack on low chromium alloys.
Inert additives, such as silica (SiO$_2$)\textsuperscript{(54,82)} and Kaolin (Al$_2$O$_3$ \cdot 2SiO$_2$ \cdot 2H$_2$O)\textsuperscript{(86)} have been used but in this case the idea is to add sufficient high melting point inert material to the fuel to swamp the low melting point ash, so that any deposits which form are easily blown off.

The efficiency of additive injection in reducing corrosion varies, possible due to the physical features of the injection process and the nature of the boiler.\textsuperscript{(23)}

The justification for the use of additives must be made on economic grounds and it was suggested in 1967 that the maximum permissible cost of the additive was 2\textsuperscript{1}p per ton of fuel oil.\textsuperscript{(55)} This figure was based on the assumption that the use of the additive would permit the raising of the superheater temperature from 541\textdegree C to 565\textdegree C. The economic efficiency would be lost if this figure, 2\textsuperscript{1}p, was exceeded.

The cost of adding magnesium hydroxide at the rate of 0.05 wt %, was 3.5p/ton of fuel oil, in trials conducted by Holland and Rosborough.\textsuperscript{(23)} Limited success in reducing the corrosion rate was achieved in this trial.

There is reluctance in the part of the oil companies to use additives, in view of the concern now being shown with respect to pollution problems.

\textbf{2.7.4 Control of Combustion}

With both control of combustion and detailed boiler design
it has been suggested that a great deal can be done to minimise corrosion. (87)

Macfarlane (81) has calculated that to reduce or completely stop the formation of $V_2O_5$ at 1400°C, less than 0.05% excess air is required. These conditions would also apply for the prevention of much of the $SO_3$ formation.

Burner design carried out at Lingen Refinery (88) have made it possible to burn oil with less than 1% excess air, and with such a burner no fouling or corrosion problems were experienced after 40,000 hours of operation.

Eisenhlam (89) has suggested a two stage boiler-system in which the first stage burns oil with a 30% deficiency of oil then the existing gases are mixed with further air to bring the oxygen to the stoichiometric level. Actual boiler trials on this system have yet to be carried out.

Trials conducted by Holland and Rosborough, (21) using low excess air operation, 0.2 to 0.3% oxygen above stoichiometric, show no significant effect on reducing the corrosion rate. They, however, put the discrepancy down to the differences in the vanadium to sodium ratio of the fuels employed.

2.7.5 Use of Materials to withstand corrosion attack.

Much work has been carried out on the evaluation of high strength, oxidation resistant alloys, but in many cases the results obtained are contradictory. This is probably due to
the different experimental conditions and experimental methods of evaluating the performance of the steels by the different workers.

The main necessity for good corrosion resistance of steels has been given as:-

1) Minimum chromium content of 20 - 30%. (90)
2) Presence of iron to modify the chromium oxide layer. (91)
3) Low nickel content to reduce the susceptibility of the alloy to the formation of nickel sulphide. (34)

Holland and Rosborough (29) tested a range of steels, in the form of corrosion probes inserted into an operative boiler, and found the 12% Cr MoV., ferritic, alloy had the best corrosion resistance. In later trials (23) on a further range of steels, the 2%Cr, ferritic steel gave even better corrosion resistance. The best performance given by an austenitic steel was the 25Cr 20Ni steel.

The difficulty, however, with the present day materials, austenitic and ferritic stainless steels, is that they are based on alloy systems which melt in the region 1400 - 1500°C. This is, however, at present well above the operating temperatures of boilers in present use but with the demand for greater efficiency much higher temperatures will be necessary. Even though many of the conventional alloys may be able to withstand corrosion attack at these temperatures, strength will become the major consideration.

The use of refractory metals, Nb,Mo,W,Ta, is a possibility
but their oxidation resistance would be very poor in the contaminated atmospheres of the operative boiler. It has been suggested however, that with the use of suitable coatings, (see section 2.7.6), these materials could be used.  

Protective coatings on molybdenum have been tested by Hancock and Downey using molybdenum disilicide as the coating but impact erosion and fatigue conditions in a test turbine caused extensive damage. Failure by thermal shock took place when a diffused nickel chromium layer was tested by Pasman.  

Sintered carbides have been considered as coatings but those of titanium, niobium and tantalum oxidise rapidly at 800 - 1000°C. Only chromium carbide was found to give satisfactory oxidation resistance. Greenert has shown that a cermet of chromium carbide with 15% iron will not resist vanadium containing slags, although it is resistant to sulphate/chloride mixtures.  

Silicon carbide has been shown to resist vanadium pentoxide/sodium sulphate slags but has a low impact strength, thus limiting its application in turbines.

The mechanical and oxidation properties of silicon nitride are relatively good and this material has therefore been considered for use in turbine applications.  

Horn et al have studied the use of ceramic heat exchange tubes, but the difficulties in manufacture were found to be the great drawback except for simple components.
2.7.6 Surface Coatings

The use of corrosion resistant coatings, both metallic and ceramic has found wide application, especially in the gas turbine field. Metallic coatings have been applied in a number of ways, electrodeposition, high temperature diffusion, vapour deposition and flame and plasma arc spraying. The main metallic coatings used are those of silicon, chromium, aluminium, zirconium and beryllium.

Fitzer and Schwab and Richards have produced silicon coatings on various nickel chromium and Nimonic alloys but in most cases the results obtained were inconclusive.

The use of chromium coatings on Nimonic alloys applied by both electrodeposition and vapour phase diffusion has been tested and it is claimed that good corrosion resistance is offered against SO$_2$ and salt spay at 850°C, and sodium sulphate/chloride mixtures. They are however ineffective against both lead salts and vanadium pentoxide. Their resistance to thermal shock is also suspect and spalling has been reported during heat treatment. Aluminised coatings on Nimonic alloys improves the resistance to corrosion by sodium salts, sulphur dioxide, vanadium pentoxide and lead additive attack between 900 and 950°C. Interdiffusion between coating and base metal however takes place at high temperature, this gradually reducing the effectiveness of the aluminised coating. Both beryllium and zirconium were found to be unsatisfactory
for use on stainless steels and Nimonic.

Non-metallic coatings based on silicate glasses have been considered for corrosion protection of turbine alloys at high temperatures. The coatings considered were A418, a barium silicate glass with the addition of chromic oxide, and 'Solaramic', a borosilicate glass. Short term tests showed the coating to be satisfactory but above 900°C softening begins and poor abrasion resistance is noted. Also cracking can occur due to the different thermal expansions of the glass and substrate.

The use of enamels containing Cr₂O₃ were found to be successful in protecting stainless steels up to 1000°C.

The use of surface coating in the protection of refractory metals has been studied for various systems. Rausch evaluated the effectiveness of coatings on tungsten using a thermal shock test. The most promising systems were plasma sprayed HfO₂ - Y₂O₃ and Sr - ZrO₃. A ceramic coating for niobium has been developed by Imperial Metal Industries, in which the niobium is dip coated with titanium, then plasma sprayed with alumina. This coating is then sealed with a silica dipped glaze and the whole fired in vacuum at 1350°C. The coating showed little deterioration under oxidising conditions and is claimed to withstand thermal cycling for 100 hours at 1200°C.

2.7.7 Summary

Due to the recent increase in the price of crude oil many
methods of corrosion reduction such as the use of additives and removal of impurities, are even less attractive economically. It seems likely therefore that new materials must be developed to withstand corrosion for much longer periods of time.
2.8 CORROSION TESTING PROCEDURES

2.8.1 Introduction

Because of the complexity and variety of factors involved in fuel ash corrosion, no one universal testing method can be adopted. It is often necessary to use a number of testing procedures to cover the complete range of factors existing within any given system.

The three main types of corrosion investigation methods are given as (107):

a) laboratory tests,

b) field tests and

c) service tests.

All the main methods available for the study of fuel oil ash corrosion fall into the above three categories and each type of test has been extensively used for the system.

It is considered unnecessary to discuss the development of the various corrosion testing techniques but reference will be made to some of the applications of these techniques.

2.8.2 Service Testing

Service testing is a complex and expensive testing procedure in that the complete plant, or rig, becomes the test specimen. The great advantage of this testing method is that the actual conditions of operation are studied with no artificial
influences introduced. The procedure is by investigation of failures that have arisen during service, in an attempt to find the corrosion mechanism responsible for the failure. This type of testing is probably the most exact for corrosion trials, but a number of drawbacks are apparent.

In these types of test, it would be difficult and very costly to investigate the effect of various factors on the overall rate of corrosion, e.g. the effect of

i) composition of steels,

ii) temperature,

iii) atmospheres,

iv) presence of impurities, and

v) additions to fuels.

The results from this type of test will only be applicable to plants running at exactly the same operating conditions of excess air, temperature and type of fuel, as that used in the test plant. The results from this type of test are generally not very scientific but are of practical value. The problem of expense is very important since the plant requires much space and great care has to be taken in its running and operating. Control experiments or repetition thus becomes an exceedingly expensive operation, which is preferably avoided.

The specimens produced from these types of tests may not be representative of their condition during the corrosion process. Since these structures as a whole are very large, then a very long period of time is necessary for cooling to
take place. During this time diffusion within the scale and between the scale and base metal can occur giving false and misleading information.

Because of the drawbacks, this method of testing is little used and very little development of the method has taken place.  

2.8.3 Field and Rig Testing

Field and rig testing both have the same disadvantages of the service testing method in that it is the end product of corrosion that is examined and possibly misleading information obtained.

Field testing is generally carried out on special specimens placed into the boiler, thus the corrosion medium and testing condition are exactly the same as under service conditions for that particular boiler. This does mean that several different test materials can be compared at one time under the same conditions. Again it must be said that although this method of testing is accurate, if the specimens themselves do not disturb the normal conditions, long periods of time are necessary to obtain sufficient data. This method is often used as a comparison with other testing procedures. The insertion of corrosion probes into an operative boiler to obtain data regarding service conditions has been used to evaluate the performance of a large selection of materials.  

(23, 29, 35)
In the case of rig testing the previously mentioned disadvantages regarding the control of variables (see Section 2.8.2), again arises but with this method, a much wider scope of operational conditions can be evaluated. Rig testing is carried out on specially made samples which are inserted into rigs containing a burner. The burner is run on distillate fuels to which is added the desired contaminants. Large variations of contaminant composition can be introduced onto the specimens under conditions closely resembling those found in service. (24,65)

2.8.4 Crucible Testing

Crucible testing involves the corrosion of small specimens in synthetic ashes under stringent laboratory conditions. The specimens may be completely immersed or only partially immersed in the molten ash, to obtain simultaneous results as to the effect of partial pressure of the atmosphere on the specimens.

This method has the great advantage that there is virtually no limit to the number of variables that can be investigated one at a time, and thus no limit to the type of system studied. Although the method can be used to test corrosion under identical slags found from boiler deposits, it has the major disadvantage that it tends to be static whereas in the boiler, gas flow and particle impingement, temperature fluctuation, and gas compositions for instance, could affect the molten slag and thus the corrosion mechanism.
A further advantage of this method however is that by very rapid cooling of the specimens, its representative corrosion product layers associated with the attack can be studied at room temperature with little fear of misleading results caused by interdiffusion during cooling. Also these specimens can be produced very rapidly thus enabling a larger number of factors to be studied in a shorter time period.

This method has been widely used for corrosion studies, (16,37,65,83,114) and has been the subject of a review by Bishop. (127)

2.8.5 Controlled Atmospheres

In this type of test it is possible to either study the corrosion of a metal in gaseous atmospheres, or the effect of the atmosphere above a molten slag on the kinetics and nature of the corrosion products. Any combination of gas mixtures can be used to simulate boiler condition or to artificially create situations that would not normally be experienced in the boiler. Controlled atmosphere techniques can be extremely useful when carried out simultaneously with both Rig Testing, 2.8.3 or Crucible Testing 2.8.4.

Controlled atmosphere techniques are often used in oxidation studies or two gaseous component reaction studies using thermogravimetric analysis where the effect of atmosphere on the weight change of the specimen in a particular atmosphere
can be automatically measured. Sulphur attack of metal using $H_2S$ gas in mixtures of other gases has been widely studied using this method. \(56,113,115,116\)

2.8.6 Others

Many other corrosion testing procedures have been developed but these tend to be more specific to individual problems. The types of test that can be used in the specialised study of fuel oil ash corrosion include the measurement of electromotive force in fused salt electrochemical cells\(^{33,123}\), electrical measurement of resistance of fused salts\(^{33}\) and determination of the electrical resistance of metallic specimens. A wide selection of testing techniques is given by Romanov\(^{117}\), who describes many actual testing procedures.

2.8.7 Summary

Although a number of techniques for the study of fuel ash corrosion are available, it was considered that in this particular work, only a limited number be used to study all the desirable variables. Since these will include the effect of the composition of the slag, atmosphere and alloy at a constant temperature on the kinetics, it appears that the laboratory crucible testing technique would be the only satisfactory method to investigate all the above factors. Also since the
present work is a continuation of a previous investigation in which laboratory crucible testing was adopted, the present work could then be compared with the previous results.
2.9 ELECTRON PROBE MICROANALYSIS

2.9.1 Introduction and Elementary Theory

Electron probe microanalysis essentially involves a miniaturisation of the classical procedure of x-ray spectrometry, which is based upon the discovery by Moseley (119) that each element has a characteristic x-ray radiation. The basic experiment arrangement is shown in Fig. 2, in which an electron beam, (E), of moderate energy, (5-40 KV), is directed onto the sample (S) to be investigated. The x-rays, (X) emitted from the sample are dispersively analysed by means of a Bragg spectrometer (C). The complete system is maintained in a vacuum.

The spectrometer employs a crystal of known atomic lattice spacing, to diffract the x-rays of different wave lengths through different angles. The wave length of the x-ray, \( \lambda \), diffracted at a given angle, \( \theta \), is related to the lattice spacing of the crystal, \( d \), by the simple equation:

\[
n\lambda = 2d \sin \theta
\]
where \( n \) is the order of diffraction of the spectrum, which is unity under most experimental conditions.

Qualitative analysis of a specimen can be readily made from the measurement of the x-ray spectrum, since the wavelength of an x-ray emission line is little influenced by its state of chemical combination.

Quantitative analysis is obtainable by direct comparison of the x-ray intensities for an element, \( A \), in the unknown sample, \( (I_A) \), and in a pure reference sample \( (I_A)_r \). Providing identical experimental conditions are used, then the weight fraction of \( A \) in the sample is given, to a first approximation, by:

\[
C_A = \frac{(I_A)_S}{(I_A)_r}
\]

For more accuracy with quantitative analysis, complex corrections must be applied. Although this procedure is normally carried out using a computer, the correction procedure has been given in Appendix 1.

2.9.2 The Electron Probe Microanalyser (with special reference to the Jeol JXA - 50A).

The schematic representation of the instrument is shown in Fig. 3, with the spectrometer and solid state detector shown in their correct take-off angle positions of \( 35^\circ \) and \( 38^\circ \) respectively.

The instrument basically consists of an electron gun, which
supplies electrons to be focussed by the magnetic lenses $L_1$ and $L_2$. The focussed beam of electrons impinges on the specimen surface with the production of x-rays as a result. As the x-rays are characteristic of a particular element, their analysis will indicate the element present, and with the correct procedure, the concentration of that element can be determined.

Analysis by a crystal spectrometer is based almost exclusively on fundamental theory of x-ray diffraction, as given in Section 2.9.1. Within the instrument, the specimen, crystal and detector must all lie on the circumference of the same circle, known as the Rowland Circle. The detector should see a focussed spot produced from a spot source on the specimen. Since it is necessary to move the crystal, so that the
detection angle can be changed, the mechanical system used becomes complex to allow the crystal and detector to remain on the Rowland circle. When the crystal is moved, however, the take-off angle varies, thus leading to difficulties in the interpretation of results. To overcome this problem, the Johann system of linear geometry is used. In this system the crystal, and thus the lattice planes, are bent to $2R$, where $R$ is the radius of the Rowland circle. This system overcomes the problem, and is also less sensitive to the specimen position. However, since the whole crystal is not used, the signal at the detector tends to be weaker.

The detector system employed in the JXA-50A is of the proportional flow counter type. The layout of the device is shown in Fig. 4, and consists of a cylindrical metal shell, (the cathode), through which a mixture of 10% argon and 90% methane is slowly passed. The anode consists of a fine metal wire running along the axis of the cylinder. A constant potential is applied between the anode and cathode 1750 to 1950 volts. One end of the cylinder is sealed with

![Fig.4. Proportional Flow Counter.](image-url)
an insulating medium, while the other end is covered with a polypropylene window of high transparency to x-rays. The x-rays enter the cylinder, via the window, and are absorbed by the gas with the net result of multiple ionization or gas "amplification". The electric-field intensity is now high and the electrons produced by primary ionization are rapidly accelerated towards the wire anode. An ever increasing rate of acceleration will be experienced by the electrons since the field intensity is increased as the anode is approached. The energy acquired by the electrons is sufficient to knock further electrons from other gas atoms which can in turn also cause ionization. As a result of this amplification, a very large number of electrons hit the wire anode, causing a pulse of current which is detectable in the external circuit. This pulse leaks away through the large resistance $R_1$, but not before the charge momentarily added to the capacitor, $C_1$, has been detected by the rate meter or scaling circuit connected to $C_1$. At the same time the positive gas ions move toward the cathode, but at a much slower rate due to their larger mass. This whole process, which is extremely fast, is triggered by the absorption of an x-ray quantum. Although this process is very fast, at high count rates especially, a period of time is required for the gas to return to normal and the electronics to readjust themselves. During this period, incoming x-rays are not counted and are lost. This period is termed Dead Time and must be corrected for in accurate quantitative analysis.
As previously mentioned, the JXA - 50A is also equipped with a Solid State Detector, in which the x-rays are analysed by energy dispersion. The detector head is positioned at a take-off angle of 38° to zero tilt. The detector basically consists of a piece of lithium doped silicon which is cooled by liquid nitrogen. A potential of 1500 volts is applied across the silicon. The mode of operation of this detector is best described using a specific example. The energy required to produce one electron-hole pair in silicon is 3.7 eV, thus, if an x-ray of 6.40 KeV, (FeKα), strikes the silicon, the number of electron-hole pairs produced is \( \frac{6400}{3.7} \approx 1730 \). The signal thus produced is then amplified and displayed on the multi-channel analyser in the position of 6.4 KV. Since each element has a characteristic x-ray energy, the position occupied on the multi-channel analyser will be for one particular element only.

Dead time is also associated with this type of detector but in this case the system has inbuilt compensation, thus no correction need be made.

With all types of detector, it is necessary to consider the Minimum Detection Limit (MDL) for a particular element in the system under investigation. This will depend on the ratio of the peak intensity, \( I_p \), of the element, and the intensity of the background, \( I_B \). The limit of detection is generally taken as

\[
I_p - I_B = 2\sigma_B
\]

where \( \sigma_B \) is the standard deviation of the background. On the standard, the peak height will be very large, such that \( I_p - I_B \approx I_p \); thus the MDL will be equal to

\[
\frac{2\sigma_B}{I_p} \times 100\%
\]
Since the intensity is related to time, then

\[ I_p = I \text{ counts/second} \times t \text{ seconds} \]

\[ \therefore \sigma_B = \frac{\sqrt{I_B x t}}{I_B x t} \]

thus the concentration at MDL = \[
\frac{2 \times \sqrt{I_B \text{ c.p.s.} \times \sqrt{t} \times 100}}{I_p \text{ c.p.s.} \times t}
\]

\[
= \frac{2 \sqrt{I_B}}{I_p \times \sqrt{t}} \quad \text{or} \quad \frac{2}{\sqrt{t} \sqrt{I_p}} \sqrt{\frac{I_B}{I_p}}
\]

For maximum efficiency, therefore, \( \frac{I_p}{I_B} \) should be as large as possible and the counting time, \( t \), as long as possible.

A technical summary and the capabilities of the Jeol JXA-50A Microanalyser is given in Appendix II.

2.9.3 Errors in Microprobe Analysis

a) When an electron beam strikes the metal surface, the region from which x-rays are produced is much larger than the actual beam. The total radius, \( r_T \), see Fig. 5, from which x-rays are produced is given by,

\[ r_T = (r_d^2 + r_e^2)^{\frac{1}{2}} \]

where \( r_d \) = radius from point source at which scattered electrons can produce x-rays and \( r_e \) = radius of the electron beam.

The value of \( r_T \) can be reduced by reducing the accelerating voltage, and thus the overvoltage ratio \( \frac{E}{E_k} \) where
Fig. 5. Volume of Material from which X-rays are produced.

![Diagram showing volume of material](image)

\[ E = \text{accelerating voltage of the beam.} \]

\[ E_k = \text{exitation potential of the particular x-ray.} \]

Because of this large region of x-ray production, x-rays will be produced from the specimen in a zone not indicated by the position of the beam. This is manifested either as an apparent concentration gradient, Fig. 6(a) or a false analysis of small particles, Fig. 6(b).

![Diagram showing concentration gradient](image)

(a) Apparent concentration of A.

(b) Particle of X in matrix of Y.

(b) Physical effects within the specimen surface, e.g. grain boundaries, ridges between soft and hard phases after polishing etc., can give the impression of a false composition.

The x-rays produced by the electron beam striking the specimen, A, Fig. 7, can excite x-rays from the second phase, B. The results will then indicate that the region A contains B although it may not be so.
c) When using the crystal spectrometer, it is essential that the specimen, crystal and detector all lie on the Rowland circle. If however the specimen is not mounted flat, then only one particular line on the specimen can lie on the Rowland circle. If the beam is then traversed across the specimen, an apparent concentration gradient will be indicated. This aspect is more important when using the crystal spectrometer than with the solid state detector.

d) An apparent increase in the count rate, or production of a peak, thus increase in concentration, can be seen when the beam is moved across the interface of two compounds. If one of the compounds is mainly composed of low atomic number elements and the other composed of high atomic number elements, on crossing the boundary between the two, from low to high atomic number, the background count will increase. This is due to the background being proportional to the Atomic Number. This is especially important when particles or inclusions are being studied.

e) If the electron beam is left on a single spot on the specimen for a long period, the heat produced by the beam can thermally crack the oil vapour in the vacuum chamber. The
carbon produced will then deposit on the specimen under the electron beam. The gradual increase in thickness of the contamination will give the impression of a slowly falling concentration.

f) Operator Error is probably the most likely cause of differences in analysis. It is therefore absolutely essential that the operating conditions or mode of operation are not changed from specimen to specimen. This is especially true when comparisons are being made between specimens or when the beam is moved from the specimen to the standard material.

g) Less common errors which may need to be considered in particular circumstances are given below:-

1) Smearing - caused, by polishing, can give very unusual effects.

2) Compositional changes occurring during observation caused by the heat generated by the beam. This is especially important with sodium containing glasses and biological samples.

3) Overlaps of crystal positions whereby a first order radiation of one element is the same as an \( n \)th order radiation of another element. This can be quite common when using the solid state detector but tends to be rare on the crystal spectrometer.

4) Extra x-rays can be produced by back-scattered x-rays striking parts of the specimen chamber of the instrument. These will be mainly copper and zinc from the brass used in the construction of the equipment.
2.10 GENERAL SUMMARY

From the literature survey, it can be seen that several mechanisms of attack of stainless steels have been postulated, but which of these mechanisms will actually operate will depend on the steel used and the particular installation under study. It is generally agreed that for accelerated or catastrophic corrosion to occur, a liquid phase must be present. Under operative boiler conditions, a liquid phase is produced by the deposition of molten vanadium pentoxide particles onto the superheater tubes. Reaction of vanadium pentoxide with sodium sulphate, producing complex vanadyl vanadates further reduces the melting point of the slag.

Mechanisms of attack by the molten slag can be subdivided into basically two groups; i) attack by vanadium compounds ii) attack by sodium sulphate.

Vanadium attack has been considered to occur by three mechanisms:

a) Vanadium compounds act as oxygen carriers.
b) The vanadium compounds dissolve the normally protective oxide scale.
c) Vanadium enters the oxide scale on the metal, increasing the defect mechanisms and allowing accelerated attack.

Mechanisms a) and b) have been confirmed by many workers and it seems probable that these mechanisms will occur within the operative boiler.

The mechanism of attack by sodium sulphate is considered
to occur by the initial dissolution of the oxide layer with the subsequent sulphidation of the metal. This may occur by the formation of complex sulphates which, on decomposition, release sulphur trioxide which in turn attacks the metal.

Mechanisms have also been suggested whereby the addition of vanadium pentoxide to sodium sulphate will decrease the oxide ion activity of the sodium sulphate, thus producing a melt which is an acidic flux for basic oxide scales. This produces catastrophic or self sustained oxidation.

Although the postulated mechanisms of attack are quite feasible in their own right, it is conceivable that in the operative boiler, where ever-changing conditions are encountered, each of the suggested mechanisms can occur. The mechanism of attack may therefore not be any one mechanism, but several either operating simultaneously or in a cyclic process.
3. PRELIMINARY WORK

3.1 INTRODUCTION

Preliminary work was carried out in order to gain experience with the possible techniques that could be used, and also to check the accuracy of these techniques.

The main factors which had to be established were:

a) the accuracy of the measurement of the reduction in thickness due to corrosion, (as the rate of corrosion measurement),

b) the reproducibility of the rate of corrosion results,

c) The solubility of the slag constituents in aqueous and other media,

d) the solubility of possible crucible materials in the slag at the experimental temperature.

The experimental methods for the preliminary work, the results obtained and the conclusions from the work are given in this chapter.
3.2 ACCURACY OF THICKNESS MEASUREMENTS.

The method to be used for the measurement of the corrosion rate, was that of specimen thickness reduction. The initial thickness of the specimens was determined using a micrometer screw gauge, and then after corrosion, mounting, cross-sectioning and polishing, the final thickness was measured with a travelling stage micrometer. Both of these instruments could measure to 0.001mm.

Since two different methods were used to measure the dimensional changes, it was thought necessary to check the accuracy with which this could be achieved.

This was carried out by measuring each of three specimens, eight times over the surface with the micrometer screw gauge and the average thickness calculated for each specimen. The specimens were then mounted in Araldite in the manner found, during the project, to be the most appropriate for the actually corroded specimens, sectioned and measured with a travelling stage microscope. The measurements, as obtained from the two instruments, the difference between the two measurements, and the standard deviation, \( s \), of the results from the two methods are given in Table 4.

In all cases, the measurement from the travelling microscope was slightly less than that taken with the screw-gauge micrometer. This difference was probably due to the inability of the screw-gauge micrometer to read the lowest points on the surface.
<table>
<thead>
<tr>
<th>SPECIMEN 1</th>
<th>SPECIMEN 2</th>
<th>SPECIMEN 3</th>
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<tbody>
<tr>
<td>Thickness as measured with Screw-Gauge Micrometer (mm)</td>
<td>Thickness as measured with Travelling-Stage Microscope (mm)</td>
<td>Difference between average Initial and Final Thickness (mm)</td>
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If slight surface roughness was present, the micrometer would give the thickness between the peaks. When measuring with the travelling microscope, it is necessary to measure the smallest thickness (that in the valleys on the surface), since this will be the effective thickness, Fig. 8.

The error however is small and within normal experimental error and can be treated as such.

![Diagram](image.png)

**Fig. 8. Accuracy of Thickness Measurement.**

Due to this constant error, it was found necessary to adopt a standard surface treatment for all specimens, 4.7., thus reducing the possibility of introducing unknown variables.
3.3 SOLUBILITY OF SLAG CONSTITUENTS

Since a large proportion of the slag constituents are soluble in water, (this fact being utilised in the analysis of fuel oil ash deposits), it was necessary to use a non-aqueous coolant for the grinding and polishing operation. As white spirit is a good lubricant for polishing, and has little or no aqueous content, a test was conducted to ascertain if any of the slag constituents would be soluble in it.

A corroded specimen, after having been mounted in Araldite, was left submerged in white spirit for 250 hours. Intermittent stirring was also carried out during the 250 hour period.

A portion of the white spirit was introduced into an accurately weighed specimen tube and the weight of the white spirit found. The specimen tube was then placed on the specimen pan of a Stanton Thermal Balance and, using a very low heating rate, $2^\circ C/min.$, the furnace was heated until the white spirit had completely evaporated.

Having known the initial weight of the spirit, the amount of any residue could be found from the final weight. A control experiment was also carried out, using the standard white spirit, to determine the weight of any non-volatile impurities which may have been present in the spirit.

The results of this test are shown in Table 5.

From these results it can be seen that 0.361% of the original white spirit was impurities, thus the percentage of
### TABLE 5. SOLUBILITY OF SLAG CONSTITUENTS IN WHITE SPIRIT

<table>
<thead>
<tr>
<th></th>
<th>Initial Weight of tube (gms)</th>
<th>Wt. of White Spirit Sample (gms)</th>
<th>Final Weight of tube (gms)</th>
<th>Weight of sample residue (gms)</th>
<th>% of Solid in sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>White Spirit from tube containing corroded metal and slag.</td>
<td>0.96085</td>
<td>0.07605</td>
<td>0.96180</td>
<td>0.00095</td>
<td>1.25 %</td>
</tr>
<tr>
<td>White Spirit only (control)</td>
<td>0.87025</td>
<td>0.06925</td>
<td>0.87050</td>
<td>0.00025</td>
<td>0.361%</td>
</tr>
</tbody>
</table>
soluble constituents of the mounted specimen was 0.89% of the white spirit. This amount, 0.00068 gms is negligible considering the total weight of the original specimen, including the mounting was 5.5 gms, thus the percentage of soluble material in the specimen and mounting medium was 0.012%. Furthermore, when a blank specimen of the mounting material was tested it was found that the weight loss of the material from an initial specimen weight of 4.0719 gms, was 0.0021 gms. This therefore showed that the loss of material from the actual metal and slag system was very much less than the original figure of 0.00068 gms.

Also, when blanks of the mounting material were tested to ascertain whether or not white spirit reacts with or is dissolved in the mounting material, DTA/TGA showed no difference between a sample immersed in white spirit and a control sample which was not immersed in the white spirit. This showed that there is no dissolution of white spirit in the Araldite mounting medium.

Since the metal/slag specimen was immersed in the white spirit for a period of 250 hours, whereas, in practice, during grinding, the total contact time is less than 10 minutes, it can be safely said that the dissolution of the slag/metal in white spirit is negligible and can be ignored.

White spirit was proved to be so satisfactory, that no further coolant/lubricants were tested.
3.4 REPRODUCIBILITY OF KINETIC RESULTS

Once the accuracy of thickness measurement of the specimens was established, it was necessary to determine the reproducibility of results after corrosion had taken place.

This was determined on 6 specimens of one particular steel type, in this case EN58F, corroded under an atmosphere of air in a slag of composition 30wt.% Na$_2$SO$_4$/70wt.% V$_2$O for a period of 24 hours. This assessment of reproducibility was then repeated twice using 6 new steel samples in each case corroded for periods of 12 hours and 36 hours. The specimens were prepared and the experiment run as in Section 4.

The results are shown in Fig. 9 in which the reduction in thickness of the 6 specimens is given and the spread of results shown, for the 3 corrosion times.

From Fig. 9, it can be seen that the overall reproducibility of the results is good since the total spread of results in all cases was 0.01mm $\pm$ 0.005mm.

The reproducibility can also be said to justify the experimental techniques used throughout this project.
Platinum, recrystallised alumina and fused silica were selected as possible materials in which the corrosion tests could be conducted. Since it was necessary to mount the complete crucible, so as not to disturb the specimen and associated slag layers, the prohibitive cost of platinum ruled out its use. The choice was therefore limited to recrystallised alumina and fused silica.

To test the relative merits of using alumina and silica crucibles, equal portions, 3 gms, of 30% Na₂SO₄/70% V₂O₅ synthetic slag were placed in the two types of crucible, which were heated for 24 hours at 675°C. After this period the crucibles were cooled and examined macroscopically.

The examination of the silica crucible showed that a severe attack had taken place, bubbles had appeared on the outside, while the slag had penetrated the inner walls.

The outside of the alumina crucible showed no ill-effects and there seemed to be no penetration into the walls by the slag. On breaking open the crucible, however, there was some penetration by the slag into the walls. This appeared to be as if the alumina was porous to the slag as opposed to being soluble in the slag.

In both the alumina and silica crucibles some creep of slag had taken place over the top of the crucible, but with no detrimental effect except for slag loss.
Recrystallised alumina crucibles were therefore chosen to be used throughout the project.

During subsequent electron probe microanalysis no aluminium was detected within the slag system, thus no alumina or aluminium compounds from the crucible had formed, thus confirming the suitability of this material.
From the preliminary work it was found that the reproducibility of kinetic measurements is good and within the normal experimental error limits.

The actual measuring technique was also found to be satisfactory.

It was also found that the most suitable material for crucibles, in which to carry out the corrosion testing procedures, was recrystallised alumina.

A suitable lubricant and coolant for all grinding and polishing operations was found to be white spirit.
4. APPARATUS AND EXPERIMENTAL METHODS

4.1 INTRODUCTION

At the onset of the project, the majority of the equipment was available, thus little apparatus building was necessary. It was thought, however, that several items needed revising to obtain better performance, reliability and reproducibility.

The choice of materials to be investigated arose from discussion between the author, supervisors and members of the Esso Research Centre, Abingdon, who provided the financial support for this project. Since this project is a continuation of a complete research programme, the materials used and experimental methods were the outcome of the previous results and also from information obtained from the Literature Survey, (Section 2).

The four alloys used, 2 austenitic and 2 ferritic, were chosen to cover the range of iron-chromium-nickel alloys and had specifications of Fe-12\% Cr, Fe-9\% Ni, Fe-18Cr-8Ni and Fe-25Cr-20Ni. The actual analysis of the steels is given in the Materials Section page 13.

A slag having a composition of 70wt.\% V_{2}O_{5} and 30wt.\% Na_{2}SO_{4} was chosen because during the previous project,\(^{(118)}\) this composition was found to give the highest rate of corrosion at 675\(^{\circ}\)C.

The three atmospheres for the tests were chosen so that the effect of oxygen partial pressure could be assessed on
both the kinetics of corrosion of the alloys and the composition and morphology of the corrosion products.

The description of the equipment, experimental method and procedure are given in the sections which follow.
4.2 Furnaces

The furnaces available for the project were of the electrical resistance heating type, using Crucilite rod elements (Silicon Carbide). These were controlled by Ether Transitrol Controllers via platinum/platinum 13% rhodium thermocouples placed adjacent to the furnace tube.

After calibration and positioning of the hot zone, it was found that the temperature, as recorded by a second thermocouple connected to a potentiometer box, at the hot-zone fluctuated by +10°C from the initial setting of 675°C. This amount of fluctuation was completely unacceptable, since reproducibility of results would not be achieved.

At this stage it was decided to replace the Transitrol Controllers with the more modern proportional type controllers. The system chosen, from both cost and operational considerations, was the Ether 'Digi' Type 1972 in conjunction with a Type 2825 Thyristor control assembly. These control units, however, operated via NiCr/NiAl thermocouples, which replaced the original Pt/Pt.13% Rh thermocouples.

With both furnaces operating with the new controllers, the furnaces were calibrated and the hot zone located. In both furnaces, the hot-zone, operating at 675°C, existed over a 2 centimetre range, while the temperature within that range could be controlled at better than +1°C over a period of 100 hours.
Accurate temperature measurement was achieved using a platinum/platinum 13% rhodium thermocouple placed in the centre of the furnace tube in the hot zone.

The temperature distribution within the two furnaces was measured by moving the Pt/Pt 13% Rh thermocouple by half a centimetre steps along the furnace, allowing half an hour for stabilisation then measuring the temperature with a potentiometer at each point. The temperature distribution curves are shown in Fig. 10.

The furnace tubes used were of recrystallised alumina with an internal bore of 47mm and supplied by Thermal Syndicate Ltd. Both ends of the tubes were water-cooled with copper coils, and contained rubber bungs holding copper tubes to facilitate the introduction of any required atmosphere into the furnace tube.

The furnace tube arrangement, with the crucible and specimen in position is shown in Fig. 11.

Continuous recording of the temperature was carried out during experimental runs via the Pt/Pt 13% Rh thermocouple fitted to a Leeds and Northrup Speedomax H chart recorder,
having the facility of a 2mV full scale deflection within the range of 0 to 14mV.
4.3 CORROSION TESTING PROCEDURE

The synthetic slag was prepared by ball milling a 70wt.% $\text{V}_2\text{O}_5$/30wt.% $\text{Na}_2\text{SO}_4$ mixture for 24 hours to produce a homogeneous product. It was found most convenient to produce 100 gms samples of this mixture in one operation.

The steels were in the form of plate and sheet, thus to obtain specimens of approximately equal size and all with the same surface finish, specimens were prepared having dimensions of 10 x 10 x 1.5 to 2.5 mm, and with surfaces dry surface ground. This surface finish was adopted as the standard, even though it had been previously found that the surface finish has little effect on the corrosion rate.

The thickness of each specimen was accurately measured using a micrometer screw gauge, fitted with a ratchet so that equal pressure was always applied and less errors introduced, at this stage.

The specimens were degreased with acetone and placed flat on the bottom, inside the crucible and then covered with 3 grams of the synthetic slag mixture. This ensured that the main region of corrosion attack was the top surface of the specimen, although some corrosion would inevitably take place at the edges of the specimen. The crucible was placed on a silica boat which was then introduced into the cooled end region of the furnace. At this point the gas flow was started, initially at a high rate to purge the furnace tube of its
normal atmosphere. At least 15 minutes was allowed for this purging operation in each case. Oxygen and argon were supplied directly from their cylinders, via the pressure regulation valve and G.A.P. flow meters. Air was supplied from a small air pump, the flow rate again regulated by a G.A.P. meter.

This was followed by the introduction of the silica boat into the hot zone of the furnace, the end plug introduced to seal the furnace tube, and the gas flow rate adjusted to give 0.15 litres per minute, (sufficient to maintain a pressure just above atmospheric).

The outlet gas was passed through a bubble bottle to prevent diffusion of the outside atmosphere into the furnace tube, as well as to check that the gas was actually passing through the furnace.

Corrosion tests were run for periods of 1, 5, 24, 48, 72 and 100 hours for each of the four alloys and under each of the three selected atmospheres.

The arrangement of the specimen in the furnace is shown in Fig. 11.
4.4 POST CORROSION SPECIMEN PREPARATION

After the requisite corrosion period had elapsed, the gas flow was again increased and the furnace tube bung removed. The boat was moved to the cooled end of the furnace and the sealing bung repositioned as quickly as possible so that the possibility of any contamination of the furnace atmosphere during the cooling of the specimen was reduced. The cooling period necessary was approximately 5 minutes, after which time the gas flow was stopped and the boat removed.

4.4.1 Specimen Mounting

The most convenient size of specimen mount was found to be 25 mm. diameter, as this was the size taken by the specimen holder in the Electron Probe Microanalyser, thus, mounting was carried out in 25 mm. soda glass test tubes.

The top 10 mm. of the alumina crucible were firstly broken away so that the specimen and slag, in an undisturbed condition within the remaining portion of the crucible, could be placed in the bottom of the test tube with the crucible base vertical. The test tube was then half filled with pre-mixed Araldite, the mixture being one part hardener to ten parts resin. The Araldite chosen was of low viscosity in the precured stage, thus giving good penetration into the porous slag. The viscosity was further reduced by standing the test tube in a beaker of warm
water \(\sim 60^\circ C\). To ensure complete penetration by the Araldite into the slag, a rotary vacuum pump was connected to the tube to remove the air pockets within the slag. This degassing operation was continued until the liquid Araldite showed signs of boiling, at which point the pump was stopped and the test tube stood in a holder in a vertical position. The crucible was checked to ensure the vertical base position had been maintained, and corrected if required. The Araldite was then left undisturbed for approximately 12 hours so that complete curing could take place. The specimen mounting arrangement is shown in Fig. 12.

Once the Araldite had cured, the glass test tube was broken away and the specimen cut on a diamond slitting wheel. The first cut was made across the diameter of the crucible, such that half the crucible remained within the bulk of the mounting with the metal and slag revealed. A second cut was then made above the crucible so that a mounted specimen 25 mm in diameter and 10 mm thick was produced. The position of these two cuts is shown in Fig. 12.
The identification code was finally engraved on the reverse of the specimen using a Vibrotool.

4.4.2 Grinding and Polishing

Since a large proportion of the slag phase is soluble in water, a non-aqueous coolant was necessary for the grinding operation. White spirit was found to be suitable, (see Section 3.3), and was in fact used for both the grinding and polishing operations.

Grinding was carried out using silicon carbide papers, working to successively finer grits, ranging from 220 grade to 600 grade. Between each change of paper, the specimen was thoroughly washed with white spirit to remove any adherent grit particles.

The polishing operation was carried out using diamond pastes on DP cloth with successively finer grades to produce the final polished specimen. The diamond pastes ranged from 14 micron, as the initial polish, followed by 7 and 1 micron pastes, with the final polish being carried out using ½ micron diamond paste. The specimen was thoroughly washed with white spirit between each change of diamond paste to ensure that no particles remained on the specimen surface to cause scratching of the specimen and contamination of the polishing cloth. After the final polish, the specimen was washed with white spirit and dried with acetone.
Since the main region of interest in the specimen was at the interface of the steel (hard) and slag (soft), it was found that a short polish was best in preventing excessive relief effects at the interface.
4.5 KINETIC STUDY

As described in Section 4.3, the initial thickness of the steel specimens was accurately measured using a screw gauge micrometer to an accuracy of $\pm 0.0002\text{mm}$, and the measurements noted.

The final thickness of the specimen, after corrosion testing, was then measured using a travelling stage microscope, fitted with a micrometer screw gauge. The eye piece of the microscope contained a cross wire which acted as the reference point for the measurement when the specimen was moved by the micrometer on the travelling stage. The accuracy of this method was found to be $\pm 0.0005\text{mm}$ when 6 readings were taken at random positions along the specimens.

In some of the specimens, the slag had infiltrated the metal surface thus the thickness measurement was made between points where solid metal existed, since this would be the effective metal thickness in service conditions.

From the measurements, the decrease of metal thickness was calculated, and the rate of corrosion was obtained from suitable plots.

It is worth noting that using the above method of measurement of metal corrosion, the steel specimen and related slag layers remain undisturbed, for future metallographic examination, e.g. EPMA and microscopy. Other methods, such as weight loss etc., necessitate the complete removal of the slag layers before the measurement can be made.
The main analytical technique used in this research was the Electron Probe Microanalysis of the metal and its associated slag layers. The equipment used also made it possible to examine the specimen microscopically, by producing a Scanning Electron Image of the specimen.

Prior to the examination, the specimens had to be coated with a very thin layer of carbon to ensure complete electrical conductivity over the specimen and mounting material surface. This was carried out by a vacuum deposition technique using an Edwards Coating Unit, (Model 306), in which a controlled arc was struck between two carbon electrodes. The typical current passed was of the order of 50 amps. The specimen was placed below the electrodes at a distance of approximately 8 cms, and a bell jar then put in place. When a vacuum of $10^{-5}$ torr was reached, the arc was struck. It was found that a satisfactory coating was produced after approximately 30 secs, or alternatively when the metal specimens could be seen to lose its shine. At this point the current was stopped and air admitted into the bell jar. The specimen was now ready for examination on the microprobe analyser.

The instrument used for this study was the Jeol JXA-50A fitted with both a Wavelength Dispersive Spectrometer (crystal) and an Energy Dispersive Spectrometer (Solid State Detector - Ortec) systems.
For the whole of the project the Ortec system was used for the detection of the elements iron, chromium, nickel, vanadium and sulphur. For the majority of the work the distribution of the elements present was detected using the Ortec 6200 multi-channel analyser with a selected region of interest, for a particular element, to give a y-modulated line on the cathode ray tube.

The specimen was inserted into the specimen holder such that the surface of the specimen was level and at a distance of 37mm from the final aperture. This ensures that the specimen is in a position for maximum efficiency for x-ray detection, i.e. lying on the Rowland Circle, see Section 2.9.

Once the specimen was in position and the working vacuum, $5 \times 10^{-5}$ torr, obtained, the instrument was ready for use. The accelerating voltage was set at 25 KV followed by the increasing of the gun filament current to a point just before the second saturation peak, as shown by the absorbed current meter. The electron beam was then aligned, using the alignment controls, such that when the absorbed current was at a maximum, the beam was aligned. With the photomultiplier switched on, the brightness increased, and the display mode set to 'picture', a scanning electron image, (SEI), of the specimen could be seen. For use with the Ortec system the specimen current had to be set at approximately $2 \times 10^{-10}$ amps by adjusting the condenser lens. This gave a reading of 20% dead time for the Ortec system.
Focussing of the specimen was achieved via the objective lens control, and a best picture obtained. For the majority of the work the magnification used was X 500 on the screen. This however, corresponds to X 300 when photographs are taken of the cathode ray tube, being due to the camera constant of the particular instrument.

At this time the Ortec 6200 multi-channel analyser could be switched on, which gave a complete spectrum of x-rays for the elements which were present. By selecting a region of interest, i.e. a particular element, within this spectrum, the distribution of that element could be seen, either within the whole CRT image, using x-ray mapping, or along any particular line, using a y-modulated line.

The most convenient method of obtaining the distribution of the elements within the specimen was found to be by the y-modulated line method for each element along the same trace line. The Scanning Electron Image was photographed and the trace line superimposed on it. A particular element was selected and the y-modulated line trace produced was also photographed. This was carried out for each of the elements in turn until the complete distribution pattern was recorded. This procedure was adopted as standard on all the specimens. In each of the electron probe microanalysis traces, the horizontal axis represents the distance across the specimen, while the vertical axis show the concentration of a particular element.
5. RESULTS

5.1 INTRODUCTION

The experimental results obtained from both the kinetic study and the electron probe microanalysis are reported in this chapter, with reference in each case to the appropriate graph and micrograph.

The kinetic results are given in graphical form showing the reduction in specimen thickness versus the corrosion time. Each graph shows the results obtained from one steel under the three atmospheres, either oxygen or air or argon.

The results from the electron probe microanalysis study are presented in the form of a Scanning Electron Image, (S.E.I), micrograph with the position indicated of the trace line, along which analysis was carried out. The metal is shown on the left hand side of each micrograph and in certain cases a region is marked with 'M', indicating the mounting material. Below each micrograph, the distribution is given for the alloy elements and sulphur and vanadium in the form of a y-modulated line trace. For convenience the interface position steel/slag has also been included as a dotted line. The magnification of the micrographs is X300 in each case.

Because of the large number of specimens produced, the description of the micrographs and electron probe microanalysis traces has been given for each steel, rather than for individual specimens.
5.2 DESCRIPTION OF ELECTRON PROBE MICROANALYSIS TRACES AND SCANNING ELECTRON IMAGE MICROGRAPHS.

5.2.1 12% Chromium Steel (Type A)

Specimens corroded for 1 hour

On studying the micrograph for the specimens of 12% Cr steel corroded for 1 hour, Figs. 13, 14 and 15, it is apparent that little in the way of a layered structure exists. Adjacent to the metal surface is a narrow layer, approximately 3µ wide. In the case of the specimens corroded under argon and air the layer is broken away from the metal surface. The narrow layer corresponds to peaks of both chromium and sulphur suggesting the composition to be of chromium sulphide. The remainder of the slag present is of a crystalline nature, corresponding to a high concentration of vanadium. The crystalline structure was similar to that which is characteristic to vanadium pentoxide solidified from the melt. Sulphur was also present in the main bulk of slag, distributed between the vanadium pentoxide crystals.

Specimens corroded for 24 hours

Micrographs of the specimens corroded for 24 hours, Figs. 16, 17 and 18, show that the initial slag layer is much thicker, 25 - 30 µ, and of a duplex structure. The region of the duplex layer adjacent to the metal surface is porous and corresponds to peaks of chromium and sulphur, which again suggests the presence of chromium sulphide. The second region of the duplex layer is much denser and corresponds to the presence of iron
Time: 1 Hour
Atmosphere: Argon

Time: 1 Hour
Atmosphere: Air
Time: 1 Hour  
Atmosphere: Oxygen
Time: 24 hours
Atmosphere: Argon

Time: 24 hours
Atmosphere: Air
Cr Steel (Type A)
Time: 24 hours
Atmosphere: Oxygen
chromium and vanadium suggesting a complex vanadate formation. Again the main bulk of slag consists of the vanadium rich crystalline structure, but the crystals are finer than those seen after 1 hour's corrosion. Sulphur is again present between the vanadium rich crystals.

**Specimens corroded for 100 hours**

After 100 hours corrosion, Figs 19, 20 and 21, the initial slag layer is well formed and up to 50µ in thickness. Again, this layer has a duplex structure with an initial porous region corresponding to chromium and sulphur with a little iron also present. This suggests the formation of a mixed sulphide layer, but mainly consisting of chromium sulphide. In the specimen produced under argon, Fig. 19, a very narrow region of iron and sulphur exists below the chromium and sulphur region. This suggests a region of iron sulphide growth directly on the metal surface. The second region of the duplex layer has a dense structure which corresponds, mainly, to chromium. There is however a decreasing concentration gradient of chromium and increasing concentration gradient of vanadium across this layer. The layer is possibly composed of mixed oxide and vanadate with the oxide region being closest to the metal. A light coloured, dense phase is also present on the metal surface in the specimen corroded under oxygen, Fig. 21. This phase corresponds to a large sulphur peak and a chromium region containing less chromium than is present in the porous layer on the metal surface. This suggests that a second chromium
Time: 100 hours
Atmosphere: Argon

Time: 100 hours
Atmosphere: Air
Time: 100 hours
Atmosphere: Oxygen
sulphide is present, with a different Cr/S ratio. The main bulk of slag, under all three atmospheres was similar to that produced after 24 hours corrosion.

The different stages of attack by synthetic fuel ash appear to be as follows:

Initially a layer is formed composed of chromium sulphide. With increased corrosion time the layer becomes thicker and of a duplex nature with the region closest to the metal composed of chromium sulphide. The second portion of the layer appears to consist of a mixed iron/chromium vanadate.

Under an atmosphere of oxygen, a second, but different, chromium sulphide layer appears to be formed on the metal surface.

The main bulk of the slag consists of crystalline vanadium pentoxide, with sulphur, probably as the original sodium sulphate, present between the vanadium pentoxide crystals.

5.2.2 9% Nickel Steel (Type B)

Specimens corroded for 1 hour

Examination of the micrographs for the 9% Ni steel corroded for 1 hour, Figs. 22, 23 and 24, revealed a mainly crystalline bulk slag with a narrow surface layer, adjacent to the metal. In the case of the specimen corroded under an argon atmosphere, Fig. 22, the layer, of approximately 20 \( \mu \) thickness, appears to be of a dense nature. Under oxygen, Fig. 24 and air, Fig. 23,
Time: 1 hour
Atmosphere: Argon

Time: 1 Hour
Atmosphere: Air
Time: 1 Hour
Atmosphere: Oxygen

Fe

Ni

V

S
atmospheres however, the layer is much less defined and of an amorphous nature. The width of the layer could not be determined since its boundaries were not well defined.

From the EPMA traces it can be seen that in each case there exists a sulphur rich layer on the metal surface which corresponds to regions of iron and nickel which could suggest that it is a mixed, iron/nickel sulphide. A second region can also be seen from the EPMA traces with high concentrations of both iron and nickel as well as vanadium, which suggests a mixed iron/nickel vanadate.

The bulk of the slag is mainly vanadium rich with regions of sulphur existing between the crystals.

**Specimens corroded for 24 hours**

After 24 hours corrosion, a layered structure is very pronounced in the specimens corroded under argon, Fig. 25 and air, Fig. 26, while the specimen corroded under oxygen, Fig. 27, shows the presence of an indefinable amorphous layer. Under all three atmospheres, some infiltration of the slag into the metal can be seen, to a depth of approximately 7μ. The layered structure produced under the argon and air atmospheres shows that at least two distinct phases are present. Adjacent and adherent to the metal surface is a dark, reasonably dense phase, 30μ thick in argon and 25μ in air, with several large pores present within it. The second phase is lighter in colour and appears to be more dense, with a width of approximately 10μ when formed in air, while under argon the width varies considerably,
Time: 24 hours
Atmosphere: Argon

Time: 24 hours
Atmosphere: Air
Time: 24 Hours
Atmosphere: Oxygen
from 16\mu to 40\mu.

The specimen produced under oxygen shows a very indistinct layer, the width of which could not be determined.

The main bulk of the slag shows in each case a very porous, possibly crystalline structure.

The EPMA traces show that sulphur is present in each case at the metal/slag interface. The sulphur peak corresponds to the presence of iron, thus suggesting an iron sulphide layer. A second sulphur peak is also present in each case which corresponds to a large nickel peak, higher than in the original alloy, suggesting nickel sulphide to be present.

A second nickel peak can also be seen corresponding to a region of high iron and vanadium concentration with a small amount of sulphur. This suggests a complex compound containing all the elements iron, nickel vanadium and sulphur, possibly as a vanadate.

The lighter coloured second phase, also seen in the specimens corroded under argon and air, corresponds to a high concentration of both vanadium and iron, with a very much smaller proportion of nickel, suggesting a mainly iron vanadate layer. Although the lighter coloured second phase cannot be seen in the micrograph for the specimen corroded under oxygen, Fig. 29, the EPMA traces, reveal iron and vanadium peaks in a similar position as seen for the specimens produced under air and argon, suggesting that a great similarity exists in the distribution of the elements but not in their morphology.
Also present in the sample corroded under oxygen, are large nickel and sulphur peaks corresponding with each other within the main bulk of the slag. This suggests the presence of a nickel sulphide particle.

The main bulk of the slag again consisted of a large concentration of vanadium, with sulphur present between the vanadium rich regions.

**Specimens corroded for 100 hours**

After 100 hours corrosion, a well established layered structure is formed, as well as a large amount of infiltration of the metal surface by the slag. The specimens produced under oxygen and air, Figs. 30 and 29, respectively, have a very similar appearance, with the initial layer being relatively porous. The specimen produced under argon, Fig. 28, however, shows an initial layer with a dense appearance which has a crystalline outer extremity.

In all cases the infiltrated layer is of the order of 23μ wide and the initial surface layer ranging from 33 - 40μ in thickness.

The EPMA traces show that in all cases the infiltrated layer is very rich in nickel and sulphur, with the nickel level being very much higher than the parent metal. Iron is also present within this region suggesting the infiltration is by a mixed iron nickel sulphide or a nickel matte \((\text{FeS})_x (\text{Ni}_3\text{S}_2)_y\).

The initial slag layer tends to be rich in iron with only
Fig. 28.
Ni Steel (Type B)
Time: 100 hours
Atmosphere: Argon

Fig. 29.
Ni Steel (Type B)
Time: 100 hours
Atmosphere: Air
Time: 100 hours
Atmosphere: Oxygen
small amount of nickel present. Sulphur was detected in isolated regions suggesting particles of iron sulphide. Vanadium was found at the outer edge, furthest from the metal, showing an increasing concentration gradient. This could suggest a sulphide.

In the specimen produced under oxygen, Fig. 30, particles are present at the outer extremity of the initial slag layer. These particles correspond to high concentrations of nickel and sulphur suggesting the present of nickel sulphide.

Immediately before the main bulk of slag, iron and vanadium are present together suggesting iron vanadate. The main bulk of slag is vanadium rich with sulphur present between the vanadium particles. Under argon, however, there seems to be little or no sulphur within the main bulk of slag.

In general it can be said that increasing corrosion time from 1 to 24 hours, increases the thickness of the layers, while from 24 to 100 hours except under oxygen, there is little increase in thickness. Infiltration attack also increases with corrosion time.

The surface layer tends to be composed of iron nickel sulphides, throughout the complete range of corrosion times used.

The remaining layer tends to be of the complex vanadate, probably formed from the reaction of the sulphides, or sulphates, with vanadium pentoxide.
5.2.3 Type 347 Steel (Type C)

Specimens corroded for 1 hour

The specimens produced under atmospheres of argon Fig. 31 and oxygen Fig. 33 are very similar in appearance, in that they both have narrow surface layers present which were broken away from the metal substrate. In each case the layer is of the order of $4\mu\text{m}$ in width. The main bulk of slag shows the porous crystalline type of structure.

The specimen produced under an atmosphere of air Fig. 32, shows that a surface layer is present, again approximately $4\mu\text{m}$ in width, but in this case it is not broken away from the metal. Also the main bulk of slag has an amorphous appearance but with some crystalline particles also present.

In no case there is any infiltration of the metal surface by the slag.

The EPMA traces for the oxygen and argon atmospheres are also very similar as sulphur is present on the actual metal surface which corresponds to slight increases in the concentration of chromium, iron and nickel.

Also the narrow initial layer of slag in both cases corresponds to peaks for all five elements iron, chromium, nickel, vanadium and sulphur which suggests the layer is a mixture of compounds or a complex single compound. The specimen produced under argon Fig. 31, shows a second layer having the same composition on the inner edge of the main bulk of slag.
Time: 1 hour
Atmosphere: Oxygen
This, however, is part of the initial layer which was broken away. The main bulk of slag, in both cases, consists of a high concentration of vanadium with sulphur present between the crystalline structure.

The specimen produced under air, Fig. 32, in fact shows basically the same effect as for the oxygen and argon produced specimens. Sulphur is present on the surface in conjunction with iron chromium and nickel. The initial layer again consists of all five elements, but in this case the layers, as seen from the EPMA traces, seems to be much wider. Also the inner and outer edges seem to have a higher sulphur content and lower vanadium content, while the middle region shows the reverse. The main bulk of slag again consists of a high vanadium concentration, with sulphur between the vanadium rich regions.

**Specimens corroded for 24 hours**

For the specimens corroded for 24 hours, it is necessary to describe the nature of corrosion separately, since very few similarities exist between them.

The specimen produced under argon Fig. 34, shows a duplex initial layer broken away from the metal surface. The region adjacent to the metal surface is dense and approximately $16\mu$ in width. The second region is slightly less dense and approximately $13\mu$ in width. The two layers appear to have cracked probably on cooling almost along their boundary. This is probably due to their different compositions, resulting in
Time: 24 hours
Atmosphere: Argon

Time: 24 hours
Atmosphere: Air
different coefficients of thermal expansion.

The main bulk of slag shows a dense structure also containing regions of dendritic growth. The specimen produced under air, Fig. 35, shows, from its very rough appearance of the metal surface, to have been severely attacked. Infiltration by the slag into the metal surface has not taken place. A narrow light coloured phase is present on the metal surface which seems to be separated from the metal in places by cracks or pores. The width of the layer is less than 2μ. The initial layer of slag has again a duplex nature, but the distinction between the two is difficult to determine. The layer is generally porous and very uneven in width, ranging from almost zero to 26μ. This layer is in part separated from the metal surface layer by large pores. The main bulk of slag is porous and contains a dark dendritic structure in a lighter matrix.

In the specimen produced under oxygen, Fig.36, there is an adherent layer on the metal surface with a very similar appearance to the main bulk of slag. The slag is largely porous and contains a lighter coloured second phase. No infiltration of slag into the metal had taken place.

The EPMA traces for the specimen produced under argon show that no sulphur is present at the metal surface.

The duplex layer consists initially of iron and chromium, the concentration of the latter being higher than in the parent metal. There is also a small amount of vanadium and nickel.
34. Steel (type C)
Time: 24 hours
Atmosphere: Oxygen
This, therefore, could be a mixture of oxides and vanadates or a mixed vanadate. The second region of the duplex layer is mainly composed of chromium and vanadium with very small amounts of nickel and iron also present. The region is probably composed mainly of chromium vanadate.

The dense region of the main bulk of slag has a high vanadium concentration in a dendritic structure with sulphur rich regions between the dendrite arms, probably deposited from the original slag mixture.

The EPMA traces for the specimen produced under air show that the initial narrow surface layer is composed of mainly iron and nickel with some sulphur also present, suggesting iron-nickel sulphides. The layer within the slag shows a very narrow region of iron, nickel and sulphur present on the edge adjacent to the metal. This was probably part of the initial surface layer before the layers broke away on cooling. The slag layer itself is composed mainly of chromium and vanadium suggesting the presence of chromium vanadate, similar to the specimen produced under argon.

The main bulk of slag is again composed of alternate vanadium and sulphur regions.

The specimen produced under oxygen, Fig. 31, shows a narrow surface layer of sulphur, chromium and nickel, probably due to mixed metallic sulphide. This is followed by a narrow chromium and vanadium rich layer with some sulphur also present. This is probably a mixed chromium sulphide and chromium vanadate
layer. The main bulk of slag was again alternate vanadium and sulphur rich regions probably due to the presence of the sulphur rich regions between the dendritic vanadium compounds.

**Specimens corroded for 100 hours**

All the specimens show layered structures but the width of the layers is vastly different.

The specimen produced under argon, Fig. 37, has an initial layer 100μ wide which contains a moderate amount of small sized porosity or second phase. There is no infiltration of the metal surface and no other layer present except the main bulk of slag.

The specimen produced under air, Fig. 38, has a very much narrower surface layer, 13μ in width, which seems to be of a duplex nature. Again no infiltration had taken place and the main bulk of slag contains a dendritic phase, which is the only other region present.

Under oxygen, Fig. 39, the specimen shows two layers, initially a narrow region consisting of a particulate type of structure of approximately 4μ in width, followed by a dense region, 14μ in width, which extends into the main bulk of slag. Again no infiltration has taken place and the main bulk of slag contains a dendritic second phase.

For the specimen produced under argon, the EPMA traces indicate that the very wide surface layer is composed of iron chromium, nickel, all of which show a slight downward concentration gradient, and vanadium with an upward concentration
Fig. 37.
347 Steel (Type C)
Time: 100 hours
Atmosphere: Argon

Fig. 38.
347 Steel (Type C)
Time: 100 hours
Atmosphere: Air
Fig. 39.
347 Steel (Type C)
Time: 100 hours
Atmosphere: Oxygen
gradient. Small sulphur rich particles are also present. The outer edge of the layer shows a region of increased iron, chromium and vanadium concentration with a very low nickel content. However a nickel and sulphur rich region are present adjacent to this layer. The main bulk of slag is composed of alternate sulphur and vanadium rich regions.

The EPMA traces for the specimens produced under oxygen and air show similar compositions. The initial layer in both cases is rich in iron, chromium, nickel and sulphur suggesting a mixed sulphide, while the second region is rich in iron, chromium, nickel and vanadium suggesting a mixed vanadate.

The main bulk of slag is again composed of alternate vanadium and sulphur rich regions. Within the bulk of slag several particles of iron, nickel and sulphur rich particles exist, this suggesting the presence of a further mixed sulphide.

The general pattern therefore is one of increasing layer width with decreasing oxygen potential and increasing time. The general picture of the distribution of elements is an initial mixed sulphide layer, followed by a mixed vanadate layer. Chromium tends to be the most predominant element in the vanadate layers. After longer periods of time, no sulphides were present at the metal surface under an atmosphere of argon.

5.2.4 Type "25Cr 20Ni" Steel (Type D)

Specimens corroded for 1 hour
Time: 1 Hour
Atmosphere: Oxygen

Fe
Cr
Ni
V
S
The micrographs for the specimens produced under all three atmospheres show a very similar appearance, Figs. 40, 41 and 42. There is no layered structure present and the main bulk of the slag shows a great number of very large pores. The slag tends to be crystalline in nature, with an amorphous phase interdispersed between the crystals.

The EPMA traces are also very similar in that all the specimens show very large nickel peaks at the interface. The level of nickel is higher than in the parent metal. The nickel peaks also correspond to large concentrations of iron and sulphur at the interface, suggesting the presence of mixed sulphides. Chromium on the other hand tends to be of higher concentration further into the slag and is associated with vanadium and smaller amounts of sulphur.

**Specimens corroded for 24 hours**

These specimens again show similar appearance under the three different atmospheres, Figs. 43, 44 and 45. The main bulk of slag is much more compact than seen in the specimens corroded for 1 hour. Also, the beginnings of a layered structure can be seen at the metal/slag interface. The presence of a dendritic structure can also be seen within the main bulk of the slag.

The EPMA traces show that the surface layer tends to be sulphur rich with peaks of nickel, iron and chromium also present. Again chromium tends to be associated with vanadium as a second layer. The main bulk of the slag consists of
Time: 24 hours
Atmosphere: Argon

Time: 24 hours
Atmosphere: Air
25Cr 20 Ni (Type D)
Time: 24 hours
Atmosphere: Oxygen
regions of vanadium interdispersed with sulphur.

Specimens corroded for 100 hours

The specimens produced under all three atmospheres have distinct layered structures, Figs. 46, 47 and 48. The specimen produced under argon, however, contains particles of a second phase forming a line parallel to the metal surface. It is also apparent that the thickness of the layers varied under the different atmospheres. Under oxygen, Fig. 48, the layer was only 7μ while under air its width was 17μ and under argon the layer width was 30μ.

In each case the layer structures are duplex with an initial porous, amorphous layer and in each case only 3μ in thickness, while a dense phase constitutes the remainder.

In the specimen produced under argon, Fig. 46, however, the dense phase is longitudinally cracked, probably on cooling. Also this specimen contains particles of a second phase which appears globular, ranging in size from 3 to 6μ, forming a line parallel to and 50μ from the metal surface.

The main bulk of slag in each case is compact and contains a dendritic phase.

The EPMA traces show that, in each case, the narrow, porous amorphous layer coincides with high concentration regions of iron, chromium, nickel and sulphur suggesting a mixed sulphide.

In the case of the specimen produced under air, Fig 47, there exists a nickel peak on the metal surface. This coincides
"25Cr 20Ni" (Type D)
Time: 100 hours
Atmosphere: Argon

"25Cr 20Ni" (Type D)
Time: 100 hours
Atmosphere: Air
Atmosphere: Oxygen

Time: 100 hours

Atmosphere: Oxygen
with a strong sulphur peak, suggesting nickel sulphide, as a small region of adherent slag on the metal surface.

The dense second region of the layered structure corresponds to regions of high chromium and vanadium suggesting the presence of chromium vanadate.

The main bulk of slag is composed of high vanadium and sulphur regions.

The particles seen in the specimen corroded under argon Fig 46, coincide with peaks of iron, chromium and nickel but with neither sulphur nor vanadium. These particles are probably oxides of the metal elements.

In general, therefore, there appears to be a pattern of an increasing layer thickness with increasing time, but decreasing oxygen potential.

The distribution of the elements tends to follow the pattern having an initial sulphide layer, generally containing all the parent metal elements, followed by a layer of mainly chromium and vanadium, probably as the vanadate, and finally the bulk of the slag.

Nickel is present on the metal surface and in all cases the concentration is higher than that of the parent metal. The nickel probably forms part of the sulphide layer.

The bulk of the slag became more compact with increased corrosion time, but the overall distribution of vanadium and sulphur changed little.
5.2.5 Summary

The general picture that arose from the metallographic study was one of an increasing tendency for a layered structure to be produced, with increasing time and/or decreasing oxygen potential. In certain cases under an oxygen atmosphere, no layered structure was produced.

Except for the 12% Cr steel, the thickness of the layered structure was not regular with time.

The general trend regarding the composition of the phases as obtained from the EPMA study, was that the initial layer tended to be a sulphide, the composition of which depended on the alloy composition. For the 12% Cr steel, the initial layer was a chromium sulphide, while for the 9% Ni steel, the initial layer was composed of a mixed iron/nickel sulphide. For the alloys containing both nickel and chromium, the initial layer tended to contain iron and nickel in the sulphide.

The final layers formed tended to be of the vanadate type, and when chromium was present in the original alloy, chromium vanadate was predominant. The "25Cr 2ONi" steel in all cases produced a layer of chromium vanadate with no other elements present. This type of layer was also produced after 24 hours corrosion with the Type 347 steel under all atmospheres. After 100 hours, however, mixed vanadates tended to form.

For both the 12% Cr steel and the 9% Ni steel, iron vanadate with small amounts of the second major alloying element
also present, tended to constitute the final layer.

A summary of the elements present in each layer, and the thickness of the individual layers is given in Table 6. In several cases two or more columns appear to show the same layer composition. This was in fact true but these were present in the specimen as two separate layers. The table is intended to show only the elements present in each layer with no suggestion of the composition of any actual compounds.
<table>
<thead>
<tr>
<th>Steel type &amp; atmosphere</th>
<th>Corrosion time - 1 hour</th>
<th>Corrosion time - 24 hours</th>
<th>Corrosion time - 100 hours</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>11Cr Steel</td>
<td>3h</td>
<td>Fe₃Cr₂S₃, Cr₂S₄</td>
<td>Fe₃Cr₂S₃, Cr₂S₄</td>
<td>The first layer formed is chromium sulphide which initially increases and then decreases in thickness with time. The total thickness of the complete interaction layer increases in thickness with time. In the vanadium-rich region, increasing time leads to a decreasing iron concentration, increasing vanadium concentration, while chromium remains steady. Although the initial layer is Cr₂S₄ after 1 hour, iron diffuses into and through this layer to react with vanadium resulting in mixed vanadates. From 24 to 100 hours, the mixed Fe₃Cr₂V layer increases in thickness.</td>
</tr>
<tr>
<td>Argon</td>
<td>2h</td>
<td>Cr₂S₄, Cr₂S₄</td>
<td>Fe₃Cr₂S₃, Cr₂S₄</td>
<td>-</td>
</tr>
<tr>
<td>Air</td>
<td>3h</td>
<td>Cr₂S₄, Cr₂S₄</td>
<td>Fe₃Cr₂S₃, Cr₂S₄</td>
<td>-</td>
</tr>
<tr>
<td>Oxygen</td>
<td>1h</td>
<td>Cr₂S₄, Cr₂S₄</td>
<td>Fe₃Cr₂S₃, Cr₂S₄</td>
<td>-</td>
</tr>
<tr>
<td>9Cr Ni Steel</td>
<td>3h</td>
<td>Fe₃Ni₅, Fe₃Ni₅</td>
<td>Fe₃Ni₅, Fe₃Ni₅</td>
<td>The thickness of the layers increases with time from 1 - 24 hours, but from 24 - 100 hours, except under oxygen, little increase is seen. After 1 hour the layer thickness increases with increasing oxygen potential, while after 24 hours the thickness decreases with increasing oxygen potential. In all cases, the initial layer was Fe₃Ni₅, while the outermost layer, furthest from the metal, was always Fe₃Ni₅, except after 100 hours in argon where FeV only formed the outermost layer.</td>
</tr>
<tr>
<td>Argon</td>
<td>3h</td>
<td>Fe₃Ni₅, Fe₃Ni₅</td>
<td>Fe₃Ni₅, Fe₃Ni₅</td>
<td>-</td>
</tr>
<tr>
<td>Air</td>
<td>3h</td>
<td>Fe₃Ni₅, Fe₃Ni₅</td>
<td>Fe₃Ni₅, Fe₃Ni₅</td>
<td>-</td>
</tr>
<tr>
<td>Oxygen</td>
<td>3h</td>
<td>Fe₃Ni₅, Fe₃Ni₅</td>
<td>Fe₃Ni₅, Fe₃Ni₅</td>
<td>-</td>
</tr>
<tr>
<td>Type 317</td>
<td>3h</td>
<td>Cr₃Ni₂S₃, Cr₃Ni₂S₄</td>
<td>Cr₃Ni₂S₃, Cr₃Ni₂S₄</td>
<td>When no oxygen is present, after 100 hours the interaction layers are composed of mixed sulphides. These tend to form the layer adjacent to the metal surface. Chromium vanade is the outermost layer after 24 hours, while after 100 hours the outermost layer is composed of iron chromium and nickel vanadate in oxygen, but only iron and chromium in argon and air.</td>
</tr>
<tr>
<td>Argon</td>
<td>3h</td>
<td>Cr₃Ni₂S₃, Cr₃Ni₂S₄</td>
<td>Cr₃Ni₂S₃, Cr₃Ni₂S₄</td>
<td>-</td>
</tr>
<tr>
<td>Air</td>
<td>3h</td>
<td>Cr₃Ni₂S₃, Cr₃Ni₂S₄</td>
<td>Cr₃Ni₂S₃, Cr₃Ni₂S₄</td>
<td>-</td>
</tr>
<tr>
<td>Oxygen</td>
<td>3h</td>
<td>Cr₃Ni₂S₃, Cr₃Ni₂S₄</td>
<td>Cr₃Ni₂S₃, Cr₃Ni₂S₄</td>
<td>-</td>
</tr>
<tr>
<td>25Cr 20H1</td>
<td>Very small</td>
<td>Fe₃Cr₂S₃, Fe₃Cr₂S₄</td>
<td>Fe₃Cr₂S₃, Fe₃Cr₂S₄</td>
<td>In all cases, mixed sulphides form the layer adjacent to the metal surface, while the outermost layer is composed of Cr and V, except under argon after 1 hour when the mixed Fe₃Cr₂V forms. Little or no diffusion of iron or nickel takes place towards the outermost region. Layers tend to increase in thickness up to 24 hours, then decrease. More layers are present under the argon atmosphere than under oxygen or air, and also tend to be thicker.</td>
</tr>
<tr>
<td>Argon</td>
<td>Very small</td>
<td>Fe₃Cr₂S₃, Fe₃Cr₂S₄</td>
<td>Fe₃Cr₂S₃, Fe₃Cr₂S₄</td>
<td>-</td>
</tr>
<tr>
<td>Air</td>
<td>Very small</td>
<td>Fe₃Cr₂S₃, Fe₃Cr₂S₄</td>
<td>Fe₃Cr₂S₃, Fe₃Cr₂S₄</td>
<td>-</td>
</tr>
<tr>
<td>Oxygen</td>
<td>Very small</td>
<td>Fe₃Cr₂S₃, Fe₃Cr₂S₄</td>
<td>Fe₃Cr₂S₃, Fe₃Cr₂S₄</td>
<td>-</td>
</tr>
</tbody>
</table>
5.3 KINETIC STUDY

The results obtained from the kinetic study of the four steels are given in graphical form in Figs. 49 to 52. For each steel, two graphs are shown giving, (a) the reduction in specimen thickness plotted against the corrosion time, and (b) the log reduction in specimen thickness plotted against the log corrosion time. Each graph contains three plots, one for each of the atmospheres oxygen, air and argon, under which the steels were corroded.

From the four graphs, Figs. 49(a), 50(a), 51(a) and 52(a), it can be seen that the "25Cr 20Ni" steel, Fig. 52(a), corroded the least while the most corrosion took place in the 9% Ni steel, Fig. 50(a). The type 347 and 12% Cr steels show similar amounts of corrosion and lie between the other two steels. It can also be seen that for all cases, approximately one third of the total corrosion occurred within the first five hours of the corrosion test time. Although the amount of corrosion taking place varies enormously, from 0.085mm reduction in thickness after 100 hours for steel Type D, Fig. 52(a), to 0.30mm for steel Type B, Fig. 50(a), the actual kinetic law of corrosion in the majority of cases, is very similar when interpreting the results using the general equation: \[ w = k t^n \]

where

\[ w = \text{the reduction in specimen thickness in a given time, } t. \]
\[ k = \text{the rate constant} \]
Fig. 49. 12% Cr Steel (Type A)

(a) Atmosphere

- - - - - Oxygen
- - - - - Air
- - - - - Argon

Corrosion Time (hours)

(b) Atmosphere

- - - - - Oxygen
- - - - - Air
- - - - - Argon

Log. Reduction in Thickness (mm)

Log. Corrosion Time

0 0.69 1.38 1.68 1.86 2
Fig. 50. 9% Ni Steel (Type B)

(a) Log. Reduction in Thickness (mm).

Atmosphere
- O Oxygen
- □ Air
- △ Argon

Corrosion Time (hours)

(b) Log. Reduction in Thickness

Atmosphere
- O Oxygen
- □ Air
- △ Argon

Log. Corrosion Time
Fig. 51 Type 347 Steel (Type C)

(a) Reduction in Thickness (mm).

- Atmosphere
- Oxygen
- Air
- Argon

Corrosion Time (hours)

Log. Reduction in Thickness

Fig. 51 Type 347 Steel (Type C)

(b) Log. Corrosion Time
Fig. 52 - 25 Cr. 20 Ni Steel (Type D)

(a) Reduction in Thickness (mm).

- Oxygen
- Air
- Argon

Corrosion Time (hours)

(b) Log Reduction in Thickness

- Oxygen
- Air
- Argon

Log. Corrosion Time
\[ n = \text{exponential constant} \]

By taking logarithms of both sides of the equation,

\[ \log w = \log k + n \log t, \]

then plotting \( \log w \) against \( \log t \), the value of \( k \) is given by the intercept on the \( \log w \) axis, and \( n \) is given by the slope of the plot.

From the graphs shown in Figs. 49 (b), 50 (b), 51 (b) and 52 (b) the values for \( n \) and \( k \), during the initial corrosion period from 1 to 5 hours are given in Table 7. The value of \( x \), from the alternative equation,

\[ w^x = kt \]

is also given.

It can be seen that in the majority of cases the value of \( n \) lies between 0.5 and 0.33, thus giving a parabolic to cubic mathematical relationship. The great exception is the 9\% Ni steel which shows \( n \) values of 0.237, 0.1 and 0.193, giving a logarithmic type of corrosion behaviour. This steel also has the highest values for the rate constant, \( k \), thus the steel in which the most corrosion took place has the highest rate constant, and the lowest \( n \) values. The "25Cr 20Ni" steel, however, which exhibits the lowest amount of corrosion, has the lowest values for the rate constant, \( k \), and one of the highest \( n \) values.

The 12\% Cr steel, Figs 49 (a) and (b), shows that after 100 hours, identical amounts of corrosion had occurred under all three atmospheres, even though in the early stages of corrosion, up to 60 hours, the specimen corroded under argon
TABLE 7 KINETIC DATA FOR THE LABORATORY PRODUCED SPECIMENS.

<table>
<thead>
<tr>
<th>STEEL</th>
<th>ATMOSPHERE</th>
<th>n</th>
<th>x</th>
<th>( k_{\text{mm.hrs}^{-n}} )</th>
<th>TYPE OF CORROSION RATE</th>
</tr>
</thead>
<tbody>
<tr>
<td>12% Cr</td>
<td>Oxygen</td>
<td>0.36</td>
<td>2.77</td>
<td>0.028</td>
<td>parabolic → cubic</td>
</tr>
<tr>
<td>12% Cr</td>
<td>Air</td>
<td>0.43</td>
<td>2.32</td>
<td>0.020</td>
<td>parabolic → cubic</td>
</tr>
<tr>
<td>12% Cr</td>
<td>Argon</td>
<td>0.57</td>
<td>1.75</td>
<td>0.022</td>
<td>parabolic</td>
</tr>
<tr>
<td>9% Ni</td>
<td>Oxygen</td>
<td>0.237</td>
<td>4.2</td>
<td>0.075</td>
<td></td>
</tr>
<tr>
<td>9% Ni</td>
<td>Air</td>
<td>0.1</td>
<td>10</td>
<td>0.080</td>
<td></td>
</tr>
<tr>
<td>9% Ni</td>
<td>Argon</td>
<td>0.193</td>
<td>5.1</td>
<td>0.063</td>
<td></td>
</tr>
<tr>
<td>Type 347</td>
<td>Oxygen</td>
<td>0.37</td>
<td>2.7</td>
<td>0.016</td>
<td>parabolic → cubic</td>
</tr>
<tr>
<td>Type 347</td>
<td>Air</td>
<td>0.37</td>
<td>2.7</td>
<td>0.023</td>
<td>parabolic → cubic</td>
</tr>
<tr>
<td>Type 347</td>
<td>Argon</td>
<td>0.071</td>
<td>14.1</td>
<td>0.033</td>
<td></td>
</tr>
<tr>
<td>&quot;25Cr20Ni&quot;</td>
<td>Oxygen</td>
<td>0.357</td>
<td>2.8</td>
<td>0.018</td>
<td>parabolic → cubic</td>
</tr>
<tr>
<td>&quot;25Cr20Ni&quot;</td>
<td>Air</td>
<td>0.48</td>
<td>2.08</td>
<td>0.012</td>
<td>parabolic</td>
</tr>
<tr>
<td>&quot;25Cr20Ni&quot;</td>
<td>Argon</td>
<td>0.46</td>
<td>2.15</td>
<td>0.012</td>
<td>parabolic</td>
</tr>
</tbody>
</table>

gave the worst corrosion resistance, while the specimen produced under oxygen gave the best. After 60 hours, however, a complete reversal took place and the specimens under oxygen gave the worst resistance while those under argon gave the best. The initial stages of corrosion follow approximately a parabolic rate law but the rate changes after approximately 24 hours. This is
probably due to a change in the corrosion mechanism occurring under the slag. After a short period it can be seen that the parabolic rate law is again resumed. From the shape of the curves, Figs. 49(a) and (b), on approaching 100 hours corrosion, the trace for argon appears to show an increasing corrosion rate, while that for oxygen and air are decreasing. It is therefore possible that a second reversal would have occurred after the 100 hours period.

The 9% Nickel steel, Figs. 50(a) and (b) gave the worst corrosion resistance of all four steels, under all three atmospheres. During the first hour, a very large amount of corrosion occurred but the corrosion then followed a short period at a parabolic rate.

After this short period, less than 24 hours, however, the specimens corroded under oxygen and air, continued to corrode at a fast rate which was in fact almost linear. The specimen corroded under argon, however, showed a drastic change in its oxidation rate after 24 hours, showing only a very slight increase in corrosion up to 100 hours.

In this case, oxygen appears to have a marked effect on the corrosion of the steel. Oxygen appears to be detrimental to the 9% nickel steel, under the conditions of the corrosion tests, while argon is beneficial in reducing the corrosion, after the initial 24 hours period.

The general corrosion pattern for the Type 346 steel, Figs. 51(a) and (b), is one of a parabolic rate, with slight
variations, probably due to changes occurring within the slag system, followed by a resumption of the parabolic rate. In this case the presence of oxygen in the atmosphere tends to be beneficial in reducing the amount of corrosion that occurs.

In the case of the "25Cr 20Ni" steel, Figs. 52(a) and (b), a parabolic rate occurs throughout the range of times for which the tests were conducted. Little variation can be seen to have occurred throughout the total corrosion period. Also, it can be seen that there is little effect on the corrosion rate by changing the prevailing atmosphere over the molten slag melt.

5.3.1 Summary

From Figures 49 to 52, it can be seen that the order of corrosion resistance of the four steels under laboratory test conditions is firstly the 25Cr 20Ni steel, followed by the type 347 and 12% Cr steels, with the 9% Ni steel showing the worst corrosion resistance. The above order of corrosion resistance can also be correlated to the chromium content of the alloys. The alloy containing the highest chromium content, i.e. the "25Cr 20Ni" steel gave the best results while the alloy containing no chromium gave the worst. The other two alloys gave corrosion resistances lying between these two extremes, with the Type 247 steel, containing 18% chromium, slightly better than the 12% Cr steel. Nickel may be harmful
to the steel unless sufficient chromium is present to subdue its effect.

The variation of atmosphere had little overall effect on the kinetics of corrosion, except in the 9% Ni steel where the specimens produced under argon gave much less corrosion than these produced under air and oxygen.

The corrosion rates, and related information, as given in Figs. 49 to 52, and Table 7, relate only to one temperature, as this work was devised to study the overall corrosion behaviour of the steels at 675°C, under different atmospheres.

A different type of apparatus would have to be devised to study, systematically, the initial rates of corrosion of these alloys at different temperatures and under different atmospheres, so that the energies of activation and meaningful values of k and n could be obtained for a thorough kinetic analysis of these systems.
6. PRELIMINARY DISCUSSION OF RESULTS

From the results obtained from the electron probe microanalysis, metallographic and kinetic studies, it became apparent that the composition of the layers formed gave an indication of the corrosion resistance of the alloy. It has also been shown that the partial pressure of oxygen has a marked effect on the morphology and thickness of the corrosion layers. This, however, does not appear to have a marked effect on the overall corrosion behaviour of the alloys in the same way.

The order of corrosion resistance, after 100 hours corrosion, obtained from Fig. 49 to 52, is given in Table 8, together with the composition of the final layer of slag, before the main bulk of the slag.

From Table 8, it becomes immediately apparent that certain layers may be more protective than others and thus help to retard further corrosion of the alloy. The association of chromium and vanadium, probably as chromium vanadate, CrV\text{O}_4, forming the layer furthest from the metal, was produced in the specimens possessing the most superior corrosion resistance, the "25Cr 20Ni" steel specimens. The specimens having the least corrosion resistance, the 9% Ni steel specimens, produced a layer furthest from the metal composed of iron, nickel and vanadium, probably as the mixed vanadate. The remaining specimens had final slag layers composed of mixtures of the parent metal
TABLE 8. ORDER OF CORROSION RESISTANCE AND CONSTITUENTS OF THE FINAL LAYER OF SLAG IN THE LABORATORY PREPARED SPECIMENS.

<table>
<thead>
<tr>
<th>SPECIMEN AND ATMOSPHERE IN DECREASING ORDER OF CORROSION RESISTANCE</th>
<th>CONSTITUENTS OF THE FINAL LAYER OF THE SLAG</th>
</tr>
</thead>
<tbody>
<tr>
<td>25Cr 20Ni under Air</td>
<td>Cr, V</td>
</tr>
<tr>
<td>25Cr 20Ni under Argon</td>
<td>Cr, V</td>
</tr>
<tr>
<td>25Cr 20Ni under Oxygen</td>
<td>Cr, V</td>
</tr>
<tr>
<td>Type 347 under Oxygen</td>
<td>Cr, Fe, V</td>
</tr>
<tr>
<td>Type 347 under Air</td>
<td>Cr, Fe, Ni, V</td>
</tr>
<tr>
<td>Type 347 under Argon</td>
<td>Cr, Fe, Ni, V</td>
</tr>
<tr>
<td>12% Cr Steel under all Atmospheres</td>
<td>Fe, Cr, V</td>
</tr>
<tr>
<td>9% Ni Steel under Argon</td>
<td>Fe, Ni, V</td>
</tr>
<tr>
<td>9% Ni Steel under Oxygen</td>
<td>Fe, Ni, V</td>
</tr>
<tr>
<td>9% Ni Steel under Air</td>
<td>Fe, Ni, V</td>
</tr>
</tbody>
</table>

It appears from the results, therefore, that a possible protective barrier to corrosion can be formed by the production of chromium vanadate in particular. Mixed vanadates with decreasing chromium contents appear to give less protective layers. This is borne out by the order of corrosion resistance, as given by Table 8, which indicates decreasing corrosion resistance with a decreasing chromium content of the parent alloying elements of the steel and vanadium.
Although it appears that vanadate compounds can retard corrosion, the presence of sulphur, probably as sulphides, at the metal/slag interface, suggests that the actual mechanism of corrosion involves sulphidation attack. The shape of the kinetic graphs, shown in Figs. 49 to 52, indicates that the corrosion process is a combination of processes possibly occurring in a cyclic manner. These processes probably involve an attack by vanadium, or vanadium compounds, and sulphidation, with the oxidation state of the slag governing the mechanism which operates.

Since sulphur is found at the interface of the metal and slag layers formed by corrosion, the main mechanism of attack on the metal is probably sulphidation. In the case of the alloy specimens containing nickel, sulphur was found at the specimen surface mainly in association with the nickel. Although small amounts of iron and chromium were also present, the main compound at the interface was probably nickel sulphide. In the case of the 9% Ni steel, a large region of infiltration by the slag had occurred into the metal surface. The region corresponded to high concentrations of both nickel and sulphur which suggested the formation of nickel sulphide. Also, the infiltrated region had the appearance of being produced by a molten phase, which was probably a nickel/nickel sulphide eutectic, which melts at 645°C.

If, however, the thermodynamics of nickel sulphide
formation are studied, it appears, at first sight, that when iron is present, no nickel sulphide should form.

\[
\begin{align*}
3 \text{Ni} + S_2 &\rightarrow \text{Ni}_3S_2 & \Delta G^\circ_{948} = -42,259 \pm 3 \text{ Kcal} \\
2 \text{Fe} + S_2 &\rightarrow 2\text{FeS} & \Delta G^\circ_{948} = -48,007 \pm 1 \text{ Kcal} \\
2 \text{Cr} + S_2 &\rightarrow 2\text{CrS} & \Delta G^\circ_{948} = -35,297
\end{align*}
\]

and

\[
4\frac{1}{2}\text{Ni} + \frac{2}{3}\text{SO}_3 \rightarrow \frac{1}{2}\text{Ni}_3S_2 + 3\text{NiO} & \Delta G^\circ_{948} = -56,942
\]

\[
3 \text{Fe} + \text{SO}_3 \rightarrow \text{FeS} + \text{Fe}_2\text{O}_3 & \Delta G^\circ_{948} = -87,505
\]

\[
3 \text{Cr} + \text{SO}_3 \rightarrow \text{CrS} + \text{Cr}_2\text{O}_3 & \Delta G^\circ_{948} = -153,966
\]

In both of the above cases, reaction with either elemental sulphur or sulphur trioxide would be preferential with iron to form iron sulphide. The reaction is probably via the sulphur trioxide gaseous phase, produced by the reaction of the original synthetic slag constituents, sodium sulphate and vanadium pentoxide.

\[
\text{Na}_2\text{SO}_4 + \text{V}_2\text{O}_5 \rightarrow 2\text{NaV}_2\text{O}_5 + \text{SO}_3
\]

Since both iron and chromium are also found at the slag/metal interface, but in far smaller concentrations than nickel, then the above reactions are true in practice. However, when iron sulphide is formed, iron oxide would also form and inevitably some nickel oxide also. This then could lead to an exchange reaction between the iron sulphide and nickel oxide which can be represented as follows:

\[
3 \text{NiO} + 2 \text{FeS} \rightarrow \text{Ni}_3S_2 + \text{Fe}_2\text{O}_3 & \Delta G^\circ_{948} = -21,941
\]

To test the practical feasibility of the above reaction, an experiment was devised using a mixture of pure samples of powdered nickel oxide and iron sulphide, then heating to 675°C.
The results and eventual interpretation thereof are given in Section 7.

The oxides that would be formed by such an exchange reaction would most probably be as a dispersed phase as opposed to a continuous layer and would thus offer little protection to the metal substrate. Reaction of the metallic oxides with vanadium compounds, to produce the respective vanadates or mixed vanadates, would then proceed. From the present work it appears that if the production of chromium vanadate could be achieved, then it may be possible to retard corrosion sufficiently to greatly increase the working life of the alloys.

Since it appears that at least two corrosion mechanisms are operating, the conditions under which either of these mechanisms is most favourable must be considered, with respect to both the laboratory prepared specimens and the specimens from the operative boiler, (Section 9).

6.1 Summary

(a) The mechanism of corrosion operating in the laboratory tests appears to be as follows:-

(1) The initially protective oxide layers are slagged off by either vanadium pentoxide or sodium sulphate, to expose the metal substrate.

(2) Sulphidation attack of the metal takes place with
the formation of mixed oxide/sulphide layers.

(3) An exchange reaction of nickel, or nickel oxide with iron or other sulphides, takes place to produce a molten nickel/nickel sulphide eutectic at the metal surface.

(4) The oxides produced, by the exchange reaction, react with vanadium compounds to produce metallic vanadates.

(b) The production of chromium vanadate appears to retard corrosion by acting as a protective barrier to the liquid phases and possibly also to the gaseous phases.

(c) Increasing the chromium content of the alloys tends to reduce the amount of corrosion, probably by the greater capability to form the protective chromium vanadate layer.
7. THE EXCHANGE REACTION OF NICKEL OXIDE AND IRON SULPHIDE.

7.1 Introduction

As mentioned in Section 6, thermodynamic calculations show that nickel sulphide could be formed from the exchange reaction of nickel oxide and iron sulphide, providing no oxygen is present.

The results obtained from the electron probe microanalysis study indicate the presence of nickel sulphide at the interface of the nickel containing alloys, under both oxygen containing and inert atmospheres. The conditions in the immediate vicinity of the reaction site must therefore have been sufficiently altered to make the exchange reaction thermodynamically possible. To investigate this possibility, pure iron sulphide and nickel oxide were reacted under both oxygen and argon atmospheres and the reaction products analysed.

7.2 Method

Small pieces of iron sulphide, supplied as broken plate, were compressed at a pressure of 750,000 KN/m² with nickel oxide powder to form samples, approximately 1cm thick and 1cm diameter. These pellets were then placed in a crucible and introduced into the furnace, then held at 675°C, under either an oxygen or argon atmosphere. After 24 hours, the specimens
were removed, mounted, polished and prepared for electron probe microanalysis, (see Section 4).

The specimens were analysed for the elements iron, nickel and sulphur.

7.3 Results

The results obtained from the electron probe microanalysis have been presented in the form of a micrograph, showing the trace line along which the analysis was carried out, and the line traces for the three elements, iron, nickel and sulphur. The magnification of both micrographs is 960 times.

7.3.1 Iron Sulphide and Nickel Oxide Pellets heated in Oxygen.

From Fig. 53, showing the specimen heated in oxygen, it can be seen that three phases exist. The right hand side of the micrograph shows a dark phase, containing a large number of pores, which corresponds to a high concentration of iron with no nickel or sulphur present. This suggests that the iron is present as the oxide.

The left hand side of the micrograph shows a phase, slightly lighter in colour and of smaller pore size. This region corresponds to high concentrations of both iron and sulphur, suggesting iron sulphide remaining from the original
Fig. 53.
FeS + NiO heated at 675°C for 24 hours in an atmosphere of oxygen.

Fig. 54.
FeS + NiO heated at 675°C for 24 hours in an atmosphere of argon.
The third phase present is much lighter in colour and contains no porosity. It formed a line of globular particles along the boundary line of the other two phases. The electron probe microanalysis showed the particles to contain high concentrations of both nickel and sulphur, with no iron present. These particles therefore appear to be nickel sulphide, and their globular appearance suggesting they were solidified from the molten state.

7.3.2 Iron Sulphide and Nickel Oxide heated in Argon.

From Fig. 54, showing the micrograph and analytical line traces for the specimens heated in argon, it can be seen that only two phases are present. The main bulk of the material is light coloured and contains porosity of different sizes, including some large holes. The region corresponds to a high concentration of nickel, with little or no iron or sulphur present, suggesting the phase was nickel oxide. The actual trace line appears to indicate a low level of nickel. In fact the level of nickel was high throughout the specimen thus little deviation could be seen in the trace line.

The second phase present is slightly darker in colour, appears angular in shape and present throughout the oxide region. The electron probe microanalysis traces show the regions are very rich in nickel and sulphur, suggesting the second phase to be nickel sulphide.
7.4 DISCUSSION

At first sight it appears from thermodynamics that nickel sulphide could form from nickel oxide and iron sulphide by an exchange reaction. However, further thermodynamic calculations showed that if oxygen was present, the iron sulphide would oxidise to form sulphur trioxide, and not react with the nickel oxide.

\[
2\text{FeS} + 3\text{NiO} \rightarrow \text{Fe}_2\text{O}_3 + \text{Ni}_3\text{S}_2 \quad \Delta G_{948}^0 = -21,941
\]

\[
2\text{FeS} + 4\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 2\text{SO}_3 \quad \Delta G_{948}^0 = -233,178
\]

Also even if nickel sulphide could form thermodynamically under oxygen, it would be unstable and also be oxidised.

\[
\text{Ni}_3\text{S}_2 + 4\text{O}_2 \rightarrow 3\text{NiO} + 2\text{SO}_3 \quad \Delta G_{948}^0 = -211,237
\]

Thermodynamically, therefore, the presence of nickel sulphide under a normal oxygen atmosphere is not feasible, since oxidation is far more favourable. Nickel sulphide should however form under an inert atmosphere.

The results have however shown that nickel sulphide does in fact form under both atmospheres. This therefore, suggests that the local conditions prevailing at the nickel oxide/iron sulphide interface were such as to make the reaction possible. This condition could have been achieved in two ways;

i. either the level of sulphur trioxide, produced by the decomposition of the iron sulphide, was sufficient to decrease the oxygen potential to a level below which iron sulphide and nickel sulphide were not oxidised,
ii. or, the diffusion rate of oxygen into the pelleted sample was so low that it could not supply oxygen fast enough to establish a sufficiently high oxygen potential for the oxidation to occur.

For the oxidation of iron sulphide to iron oxide to be thermodynamically possible, the level of oxygen at equilibrium can be calculated as follows:

Assuming the reaction is: $2FeS + 4\frac{1}{3}O_2 \rightarrow Fe_2O_3 + 2SO_3$ and

$$
\Delta G^\circ_{948} = -233.172
$$

then using the Van't Hoff Isotherm we have:

$$
\Delta G_T = \Delta G^\circ_T + RT \log_e \frac{a_{Fe_2O_3} \times (P_{SO_3})^2}{a_{FeS} \times (P_{O_2})^{9/2}}
$$

where $\Delta G_T$ = the Gibbs free Energy at $T$.

then assuming FeS and Fe$_2$O$_3$ are in the pure solid or liquid state

then $a_{FeS} = 1$ and $a_{Fe_2O_3} = 1$

Hence $\Delta G_T = -233.172 + 4.575 \times 948 \times \log_{10} \frac{(P_{SO_3})^2}{(P_{O_2})^{9/2}}$

at equilibrium, $\Delta G_T = 0$

$$
\therefore 233.172 = 4.575 \times 948 \times \log_{10} \frac{(P_{SO_3})^2}{(P_{O_2})^{9/2}}
$$
The equilibrium partial pressure of oxygen for the formation of \( \text{Fe}_2\text{O}_3 \), from the reaction:

\[
2\text{Fe} + \frac{3}{2}\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 \quad \Delta G^\circ_{948} = -136,062
\]

is given by

\[
\Delta G_T = \Delta G^\circ + RT \log_e \left( \frac{1}{(P_{O_2})^{3/2}} \right)
\]

at equilibrium, \( \Delta G_T = 0 \)

\[
\therefore \frac{-136,062}{4.575 \times 948} = \log_{10} \left( \frac{1}{(P_{O_2})^{3/2}} \right)
\]

thus \( P_{O_2} = 1.2178 \times 10^{-21} \) ......................... (2)

Substituting this value of \( P_{O_2} \) into (1)

we have

\[
\begin{align*}
X \quad P_{SO_3}^2 &= 5.781 \times 10^{53} \times (1.2178 \times 10^{-21})^{9/2} \\
&= 6.666 \times 10^{-21} \quad ......................... (3)
\end{align*}
\]

The reaction for the formation of nickel oxide and sulphur trioxide by the oxidation of nickel sulphide is given by;

\[
\text{Ni}_3\text{S}_2 + \frac{4}{2}\text{O}_2 \rightarrow 3\text{NiO} + 2\text{SO}_3 \quad \Delta G^\circ_{948} = -211,237
\]
thus $\Delta G_T = \Delta G^0_T + RT \log_e \frac{(P_{SO_3})^2}{(P_{O_2})^{9/2}}$

Since the oxidation of FeS is thermodynamically more favourable, the level of $SO_3$ and $O_2$ will be governed by the reaction:

$$2FeS + 4\frac{1}{2}O_2 \rightarrow Fe_2O_3 + 2SO_3$$

i.e. $\frac{(P_{SO_3})^2}{(P_{O_2})^{9/2}} = 5.781 \times 10^{53}$ \hspace{1cm} (1)

thus $\Delta G_T = \Delta G^0_T + RT \log_e \frac{(P_{SO_3})^2}{(P_{O_2})^{9/2}}$

$\therefore \Delta G_T = -211,237 + (4.575 \times 948 \times 53.762)$

$= -211,237 + 233,171$

$= +21,934$ \hspace{1cm} (4)

This therefore indicates that under the above-mentioned conditions of equilibrium $SO_3$ and $O_2$ partial pressures, the reaction for the oxidation of nickel sulphide will be reversed, thus

$$3NiO + 2SO_3 \rightarrow Ni_3S_2 + 4\frac{1}{2}O_2 \hspace{1cm} \Delta G_T = -21,934$$

showing that nickel sulphide will form.

When chromium is present, the formation of nickel sulphide by the exchange reaction will also be thermodynamically favourable.

$$2CrS + 4\frac{1}{2}O_2 \rightarrow Cr_2O_3 + 2SO_3 \hspace{1cm} \Delta G^0_{948} = -318,704$$
thus at equilibrium $\Delta G_T = 0$

\[ \therefore \quad 318,704 = 4.575 \times 948 \times \log_{10} \left( \frac{(P_{SO_3})^2}{(P_{O_2})^{9/2}} \right) \]

\[ \therefore \quad \log_{10} \left( \frac{(P_{SO_3})^2}{(P_{O_2})^{9/2}} \right) = \frac{318,704}{4.575 \times 948} = 73.48 \]

\[ \therefore \quad \frac{(P_{SO_3})^2}{(P_{O_2})^{9/2}} = 3.0903 \times 10^{73} \]

Again using this value for the production of nickel sulphide from the oxide, then

\[ \Delta G_T = \Delta G^0 + RT \log_e \left( \frac{(P_{SO_3})^2}{(P_{O_2})^{9/2}} \right) \]

thus $\Delta G_T = -211,237 + (4.575 \times 948 \times 73.48)$

\[ \therefore \Delta G_{948} = -211,237 + 318,704 = +107,467 \]

This again indicates that the nickel sulphide will be formed due to the gettering action of the chromium, as chromium sulphide, producing sufficient $SO_3$, and insufficient $O_2$, to give the reaction:

$$3NiO + 2SO_3 \rightarrow Ni_3S_2 + 4\frac{1}{2}O_2 \quad \Delta G_T = -107,467$$

Providing sufficient chromium sulphide or iron sulphide is present, an increase in the oxygen partial pressure will give a corresponding increase in the sulphur trioxide partial
pressure thus allowing further nickel sulphide to form.

It can therefore be seen from the calculation, that it is thermodynamically possible to form nickel sulphide under the prevailing experimental conditions. It is not surprising therefore, that this compound was found at the interface of the metal and slag in the majority of steels containing nickel, which were subjected to fuel ash corrosion.

At this stage, the experiment was designed only to test the possibility of the formation of nickel sulphide. The experiment did not give further data regarding the direction of movement of the metal species diffusing to form the exchange reaction, and therefore further work should be carried out to establish this point.
8.1 Introduction

The effect of fuel oil ash corrosion has been studied by using corrosion probes inserted into the high temperature regions of a boiler at Marchwood Power Station.\(^{(23,29,35)}\)

The mean mid-wall temperatures of the samples ranged from 590\(^\circ\) C to 635\(^\circ\) C with an exposure time of 10,000 hours.

Sections of the probes have been analysed in the same way as for the laboratory corroded specimens, using electron probe microanalysis and metallographic methods, to ascertain the behaviour of the various alloys in actual service conditions. The results have also been used to compare and contrast the corrosion occurring under laboratory conditions, with that obtained in the working boiler.
The materials used for the Marchwood tests were commercial stainless steels, ranging from alloying additions of 2½% chromium to 25% chromium 20% nickel, with various stabilising additions. The full analysis of the specimens, with the specimen numbering used for this thesis, is given in Table 9.
<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>Type</th>
<th>Steel Analysis</th>
<th>Mean mid-wall temperature of hot gas side</th>
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<tr>
<td></td>
<td></td>
<td>C  Si Mn S P Ni Cr Mo V Ti Nb B</td>
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<td>$2\frac{1}{2}$ Cr-1 Mo</td>
<td>.09 .36 .49 .005 .025 .37 2.16 1.06 .020</td>
<td>615</td>
</tr>
<tr>
<td>16</td>
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<td>635</td>
</tr>
<tr>
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<td>9 Cr-1 Mo</td>
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<td>595</td>
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<td>26</td>
<td>Esshete 1250</td>
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<tr>
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<td>590</td>
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<td>46</td>
<td>&quot;25 Cr 20 Ni&quot;</td>
<td>.08 .83 1.49 .005 .024 26.56 24.37 0.23 .010 .002 0.10 .004</td>
<td>615</td>
</tr>
</tbody>
</table>
8.3 RESULTS

The analytical results have been presented in Figs. 55 to 62 by giving micrographs of the specimens including the slag and interaction layers and showing the trace lines along which the analysis was carried out. Below the micrograph, the distribution traces are given for iron, chromium, nickel, vanadium and sulphur. In this section a description of the micrograph and distribution of the elements is shown for each specimen separately. In each case the magnification of the micrograph is 300 times.

8.3.1 Specimen 15 - 2%Cr.1Mo.

The micrograph, Fig. 55, shows that a small amount of infiltration of the metal surface, by the slag, has taken place, approximately $7 \mu$ in depth. A wide surface layer is present, which is composed of three distinct phases. The main bulk of slag is also present, thus making four distinct layers altogether.

The initial layer of slag, adjacent to the metal surface, is light coloured, very porous in nature and $35 \mu$ wide. This region corresponds to a high concentration of iron, with an increasing concentration of chromium, away from the metal surface. Since neither vanadium nor sulphur are present, it seems likely that the layer consists of mixed oxides.
Fig. 55.
Specimen 15 - 2\%Cr 1Mo
Marchwood Power Station
10,000 hour trials
The colour of the second layer is the same as the first one, but is very much less porous and 24 \( \mu \) in width. This layer corresponds to a high concentration of iron, from electron probe microanalysis found to be the same as that in the initial layer, but with a higher concentration of chromium than was found in the initial layer. This again suggests a mixed oxide region but with a different Fe/Cr ratio.

Existing between the first and second layers, however, the EPMA traces show a slight increase in the chromium concentration which corresponds to a small peak in the sulphur trace. This suggests the presence of a small particle of chromium sulphate or sulphide.

The third layer is very narrow, approximately 4 \( \mu \) in thickness, which again has the appearance of being very dense. This narrow region corresponds to a vanadium peak and at the inner edge, nearest the metal, a high concentration of chromium which decreases towards the main bulk of slag. This suggests a chromium vanadate region, possibly with an outer region of vanadium oxide.

The main bulk of the slag appears to be very porous and contains a very high concentration of sulphur, possibly in the form of sulphates as deposited from the vapour phase, or sulphides as reaction products.
8.3.2 Specimen 16. 12Cr Mo V

The micrograph, Fig. 56, shows little or no infiltration of the metal surface by the slag. The layered structure present on the specimen surface consists of at least three separate regions, with a possible fourth region at the outermost surface. The main bulk of slag is of a crystalline nature and very porous.

The initial slag layer, 17 μ in width, appears to be porous and corresponds to a very high concentration of chromium, higher than the parent metal, with a large amount of iron and sulphur also present. The level of chromium at each extremity of the layer was higher than that in the central region with much lower levels of sulphur in the high chromium concentration regions. The layer is possibly a mixed sulphide with mainly chromium oxide at the extremities.

The second layer is much less porous and corresponds to high concentration levels of both chromium and iron. In this case, however, the chromium level was less than in the initial layer, while that of the iron was higher than the first layer. The layer is probably a mixed iron/chromium oxide.

The outer region of this layer corresponds to an increasing concentration of vanadium, with corresponding decreases of both chromium and iron, suggesting a vanadate region of varying composition across its width.

The main bulk of slag shows a high concentration of
Fig. 56.
Specimen 16 - 12 Cr Mo V
Marchwood Power Station
10,000 hour trials
vanadium, with small amounts of sulphur present between the vanadium crystals.

8.3.3. Specimen 25. 9 Cr 1 Mo.

The micrograph, Fig. 57, shows that little infiltration of the metal surface by the slag has taken place. Three main regions appear to be present in the thick layered structure. Adjacent to the metal surface there is a narrow band containing fine pores. This layer corresponds to a region containing sulphur and iron. Although the nickel content of this steel is only 0.28%, nickel had concentrated within this layer, thus the layer is probably composed of a mixed iron/nickel sulphide.

The second region of the slag appears to be denser and is composed mainly of chromium and iron, although a small particle within this region has a high vanadium content. The main region is probably composed of oxides, while the particle is possibly iron chromium vanadate.

The remainder of the slag is porous in nature and corresponds to high levels of chromium and iron, with two very narrow regions containing a high concentration of vanadium. This region is probably composed of mixed oxide, with inter-dispersed vanadate particles.
Fig. 57.
Specimen 25 - 9Cr 1Mo
Marchwood Power Station
10,000 hour trials
8.3.4 Specimen 26, Esshete 1250

The micrograph, Fig. 58, shows that only a small amount of slag is present on the specimen surface, approximately 17 μ thick. It is composed of three distinct layers and the metal surface is also infiltrated to a depth of 3 μ. The infiltrated region corresponds to peaks of both nickel and sulphur, suggesting the presence of nickel sulphide in the infiltrated region. Adjacent to the infiltrated region, a second layer approximately 2 μ in thickness can be seen. The analysis shows that it is composed of iron, chromium and sulphur, suggesting a mixed sulphide or sulphate.

The outer-most layer, 12 μ in thickness, corresponds to a region of high chromium, vanadium and iron content which suggests it to be composed of an iron/chromium vanadate.

It is possible, and quite probable, that more slag had been present on the trial probe but may have been lost by spalling during cooling.

8.3.5 Specimen 35, 316

The micrograph, Fig. 59, shows that a very small amount of infiltration by the slag into the metal surface had taken place, less than 2 μ, and that this layer is adherent while the remainder of the slag system cracked away from the metal. This narrow layer corresponds to a high nickel peak only, in the
Fig. 58.
Specimen 26 - Esshete 1250
Marchwood Power Station
10,000 hour trials
Fig. 59.
Specimen 35 - 316
Marchwood Power Station
10,000 hour trials

Fe
Cr
Ni
V
S
EPMA trace, suggesting that it is composed of nickel oxide.

The initial layer of slag, adjacent to the infiltrated metal region, appears to be porous and very narrow, approximately 3 μ wide. This layer corresponds to high levels of nickel, chromium and sulphur, suggesting it to be composed of a mixed sulphide or sulphate.

The next layer appears to be dense and corresponds to a high chromium, nickel and vanadium content suggesting a mixed chromium nickel vanadate. However, the level of iron in this 9 μ layer increases across its width thus the outer regions of the layer may be a mixed iron chromium nickel vanadate.

The third layer is very much wider than the initial layers, 40 μ, and is of a porous nature. All across this region, the levels of iron, chromium, nickel and vanadium are very high suggesting a complex mixed vanadate.

The final layer again appears to be dense and is composed of iron, chromium, nickel and vanadium. In this case however, the levels of vanadium and nickel are slightly higher than in the previous layer, while that of iron is lower. This suggests a second vanadate layer but with a slightly different composition as compared with the previous layer.

8.3.6 Specimen 36. 347

In this case, the micrograph, Fig. 60, shows that the only slag present on the metal forms a narrow surface infiltrated
Fig. 60.
Specimen 36 - 347
Marchwood Power Station
10,000 hour trials

V not detected
layer, 10 μ thick. The light coloured region which can be seen on the right hand side of the picture is in fact a portion of the mounting medium, and not the slag.

The EPMA traces show that this single layer is composed only of sulphides or sulphates of iron, chromium and nickel. Vanadium was not detected at all within this specimen.

Further slag was no doubt formed during the test but was probably lost by spalling.

8.3.7 Specimen 45. 321

The micrograph, Fig. 61, shows that some penetration of the metal surface by the slag has taken place to a depth of 10 μ. This region corresponds to a decrease in concentration of both iron and chromium, while a very high nickel concentration is present. Sulphur is also present within this region suggesting that nickel sulphide is either the product of a reaction or is responsible for the infiltration, or both.

Two layers seem to exist in the slag, the first extending from the infiltrated metal surface for approximately 16 μ, while the second, broken away from the initial layer of corrosion products, is 7 μ in thickness.

The first of these two layers corresponds to a high concentration of both iron and chromium, with no other elements detected, suggesting the presence of a mixed oxide.

The second of the layers corresponds to a slight sulphur
Fig. 61.
Specimen 45 - 321
Marchwood Power Station
10,000 hour trials
peak, with very small amounts of chromium and nickel also present suggesting that a small amount of mixed sulphide may be present.

Vanadium was only detected as a small, single peak within the metal specimen. This was possibly due to a slight vanadium pick-up into a small pore from the polishing wheel, since several specimens were prepared together.

8.3.8 Specimen 46. "25 Cr 20 Ni"

The micrograph, Fig. 62, shows that only a very small amount of infiltration of the metal surface has occurred, less than 2 \( \mu \), which corresponds on the EPMA traces to a nickel peak, with a small amount of sulphur also present. The infiltrated layer therefore appears to be mainly nickel oxide, with a small amount of nickel sulphide dispersed in the oxide.

An initial dense layer, 4 \( \mu \) in thickness, is present on the metal surface which corresponds to a region of high chromium and iron concentration, with some vanadium also present. The layer is probably a mixed iron chromium vanadate.

The remainder of the slag of approximately 43 \( \mu \) in thickness, has a porous structure with little change across its width. From the EPMA traces, however, it would follow that three layers are present. Each layer is composed of the elements, iron, chromium, nickel and vanadium, but the relative composition of the layers varies. Each successive layer has an increasing
Fig. 62.

Specimen 46 - "25 Cr 20 Ni"
Marchwood Power Station
10,000 hour trials
vanadium content but decreasing iron content. The concentration of nickel is similar in the first and third layers but less in the middle layer. The concentration of chromium is approximately constant throughout the layers.

The electron probe microanalysis suggests that a variety of vanadates had been formed across the interaction zone.
8.3.9. SUMMARY

The general picture obtained from the results appears to be that the initial layer of slag, adjacent to the metal surface, consists of oxides or sulphides of the parent alloy elements. Sulphur was detected in all the specimens and formed a sulphide layer, either as the first or second layer of slag.

The distribution of vanadium indicates that generally a metallic vanadate formed the outermost layer of the slag, just before the main bulk of the slag. The only specimen in which vanadium was not detected was Specimen 36, Type 347, which showed only a very narrow sulphide rich layer of slag. Vanadium was probably present during the corrosion test but the majority of the slag seems to have suffered spalling during cooling.

A summary of the distribution of the elements in the layers formed on the steels used is given in Table 10. The left hand column describes the composition of the layer nearest to the corroding alloy steel while the other columns indicate successive layers. The thickness of the visible individual layers is also shown.

Although the kinetic results were not studied in the investigation, the results obtained on these specimens by Parker, Rosborough and Virr (35), are given in Figure 63.
<table>
<thead>
<tr>
<th>SPECIMEN NUMBER</th>
<th>CONSTITUENTS AND THICKNESS OF THE LAYERS IN THE SLAG</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>Fe,(O) 16 µ Cr,S 15 µ Fe,Cr,(O) 23 µ Cr,V 8 µ</td>
</tr>
<tr>
<td>16</td>
<td>Fe,Cr,S 16 µ Fe,Cr,(O) 20 µ Fe,Cr,V 3 µ</td>
</tr>
<tr>
<td>25</td>
<td>Fe,Ni,Cr,S 7 µ Fe,Ni,Cr,S 20 µ Fe,Dr,V 26 µ Fe,Cr,Ni,(O) 30 µ Fe,Cr,V 6 µ</td>
</tr>
<tr>
<td>26</td>
<td>Ni,S 3 µ Fe,Cr,S 3 µ Fe,Cr,V 5 µ</td>
</tr>
<tr>
<td>35</td>
<td>Ni,(O) 3 µ Cr,Ni,S 13 µ Cr,Ni,V 13 µ Fe,Cr,Ni,V 30 µ</td>
</tr>
<tr>
<td>36</td>
<td>Fe,Cr,Ni,S 10 µ</td>
</tr>
<tr>
<td>45</td>
<td>Ni,S 10 µ Fe,Cr,(O) 16 µ Cr,Ni,S 4 µ</td>
</tr>
<tr>
<td>46</td>
<td>Ni,(O) 2 µ Fe,Cr,S 8 µ Fe,Cr,Ni,V 13 µ Fe,Cr,V 20 µ Fe,Cr,Ni,V 3 µ</td>
</tr>
</tbody>
</table>
By combining the results obtained by electron probe microanalysis, Table 9, with the relative corrosion resistance of the steels investigated, Fig. 63, it is interesting to consider the relationship between the composition of the final layer of the slag, and the corrosion resistance of the alloy. Table 11 shows, in decreasing order of corrosion resistance, the steels investigated, and the elements present in the final layer of slag. The mean mid-wall temperatures and thicknesses of the final layer have also been included.
### TABLE 11. ORDER OF CORROSION RESISTANCE AND CONSTITUENTS OF THE FINAL LAYER OF SLAG AS FOUND IN THE MARCHWOOD 10,000 HOUR CORROSION TRIAL SPECIMENS

<table>
<thead>
<tr>
<th>SPECIMEN NUMBER, GIVEN IN DECREASING ORDER OF CORROSION RESISTANCE (35)</th>
<th>MEAN MID-WALL TEMPERATURE OF SPECIMENS, °C (35)</th>
<th>ELEMENTS PRESENT IN THE FINAL LAYER OF SLAG</th>
<th>THICKNESS OF THE FINAL LAYER OF SLAG, µ</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 2 1/2 Cr</td>
<td>615</td>
<td>Cr, V</td>
<td>8 µ</td>
</tr>
<tr>
<td>25 9 Cr</td>
<td>595</td>
<td>Fe, Cr, V</td>
<td>6 µ</td>
</tr>
<tr>
<td>16 12 Cr</td>
<td>635</td>
<td>Fe, Cr, V</td>
<td>3 µ</td>
</tr>
<tr>
<td>46 25 Cr 20 Ni</td>
<td>615</td>
<td>Fe, Cr, Ni, V</td>
<td>3 µ</td>
</tr>
<tr>
<td>26 Esshete 1250</td>
<td>625</td>
<td>Fe, Cr, V</td>
<td>5 µ</td>
</tr>
<tr>
<td>45 Type 321</td>
<td>590</td>
<td>Fe, Cr, S</td>
<td>4 µ</td>
</tr>
<tr>
<td>36 Type 347</td>
<td>630</td>
<td>Fe, Cr, Ni, S</td>
<td>19 µ</td>
</tr>
<tr>
<td>35 Type 316</td>
<td>620</td>
<td>Fe, Cr, Ni, V</td>
<td>30 µ</td>
</tr>
</tbody>
</table>
8.4 PRELIMINARY DISCUSSION OF RESULTS

It can be seen from Table 11, that the composition of the final layer of slag is different, and appears to have an influence on the overall corrosion rate of the alloys. It would seem that the most effective layer for reducing corrosion, is composed of chromium vanadate, with little or no other metallic elements present. Other mixed vanadates appear to be less protective, but the mixed iron-chromium vanadate would probably be the second most protective layer after the pure chromium vanadate. The main exception to this theory is Specimen 46, which as seen in Table 11, has a final layer composed of the elements iron, chromium, nickel and vanadium, and appears to be corroding slower than Specimen 26, with a final layer composition of iron chromium and vanadium. This could be connected with the fact that the penultimate layer in Specimen 46 is composed of the mixed iron chromium vanadate, see Table 10, and has a thickness of 20 μ. It is therefore likely that the penultimate layer, in this case, is playing the major role in the protection of the steel.

The mechanical strength of the slag layers, and the final vanadate layer, in particular, may well have had an important influence on the rate of corrosion in the Marchwood trials. During the tests, the operating conditions of the boiler were closely controlled, so that the performance of the alloys would
be studied under specific conditions. If the operating conditions deviated from those required, the corrosion probes were automatically withdrawn from the boiler until the conditions returned to normal. This obviously led to thermal cycling, which would probably be responsible for spalling of the slag layers. Under such conditions it is possible that a protective layer, which was formed on the surface of the alloy, would be disrupted and become non-protective.

The presence of a chromium vanadate layer appears to give good corrosion resistance and also be stable under thermal cycling conditions.

It is therefore, possible that the rate controlling step in the fuel oil ash corrosion of superheated alloys will be the presence of a chromium vanadate layer. The actual corrosion, however, will probably be influenced by sulphidation attack of the alloy, bearing in mind that sulphur was found, in the majority of cases, at the metal/slag interface. Oxidation of the sulphides with the subsequent production of metallic vanadates, as suggested in Section 6, would then form the barriers to corrosion.

It is also worth noting that the 300 series alloys tested, Specimens 35, 36 and 45, Types 316, 347 and 321 respectively, showed the worst corrosion resistance in the tests. The only difference between the three steels is, in fact, the addition of various stabilising elements to the nominal composition of 18% Cr and 12% Ni. Types 347 and 321 gave very similar results.
whilst the Type 316 gave a somewhat higher corrosion rate. This may be due to the relatively high molybdenum content of this steel, 2.49% Mo, which would form volatile oxides. The formation of a significant amount of these oxides could disrupt the slag layers, due to the volume mismatch, allowing further penetration of the slag to the metal surface, thus increasing the overall rate of corrosion.

The variation in the temperature of the corrosion probes may also have had an effect on the relative corrosion resistance of the alloys since the kinetics of the corrosion rate are very temperature dependent.

It is clear, therefore, that before an accurate comparison of the corrosion behaviour could be made between the alloys corroded under laboratory and field conditions, much closer control of the temperature should be made.
8.5 SUMMARY

Under the conditions used for the Marchwood 10,000 hour corrosion trials, the most superior corrosion resistance was offered by the $2\frac{1}{2}$ Cr 1 Mo steel, followed closely by the 9% Cr and 12% Cr steels. The series 300 steels gave the worst corrosion resistance, with the high molybdenum containing Type 316 steel giving the worst results.

The corrosion mechanism of the alloys appears to be the initial removal of the protective oxide layer, either by reaction with vanadium pentoxide or sodium sulphate, both of which can act as fluxes for the metal oxides. The exposed metal surface is then sulphidised producing metal sulphides on the metal surface. This reduces the sulphur potential of the slag, thus increases the oxygen potential which favours oxidation of the sulphides, resulting in the release of further sulphur for attack. The oxides then react with vanadium compounds, to give vanadate layers, of which chromium vanadate appears to be the most protective.

The presence of nickel appears to increase the rate of corrosion, probably due to the formation of a liquid nickel/nickel sulphide eutectic, which promotes, or is responsible for, the infiltration of corrosion products into the alloy surface and thus reduces the effective thickness of the alloy.

The effect of temperatures within the range experienced during the tests, i.e. $590\rightarrow 635^\circ C$, mid-wall, seems, with the
available data,\(^{(35)}\) to have little effect on the corrosion rate. It would be expected that the probes at the highest temperature would corrode at a faster rate than the lower temperature probes.
9. GENERAL DISCUSSION

9.1 Introduction

The object of the research programme was to investigate the corrosion behaviour of selected stainless steels to attack by a synthetic fuel oil ash. Four different steels were chosen so that the effect of nickel and chromium, either alone or in the presence of each other, on the composition and nature of corrosion could be studied. The four steels selected were commercially available and gave the combination of Fe - Ni, Fe - Cr and Fe - Cr - Ni as the main alloying elements. The analysis of the steels is given in the Materials Section, page 13. Using these steels, it was hoped to obtain information as to the behaviour of the alloying elements when subjected to attack at 675°C by \( V_2O_5 \) and \( Na_2SO_4 \).

In addition to the effect of alloying elements, it was considered important to study the effects of the prevailing atmosphere on the corrosion behaviour. Because of the amount of work all the combinations of flux composition, various atmospheres, steel types, corrosion times and temperatures would involve, this work was carried out using only one flux of composition 70wt% \( V_2O_5 \)/30wt% \( Na_2SO_4 \), four steels with nominal specifications of Fe - 9%Ni, Fe - 12%Cr, Type 347 and Type "25Cr 20Ni", and three separate atmospheres of oxygen, air and argon.

It was hoped that additional data would be obtained
regarding the behaviour of alloys during corrosion, and thus explain the rather inconsistent behaviour of the same steels used in different plants.

In this section, the analytical and kinetic results obtained from the laboratory prepared specimens and those from Marchwood Power Station, as well as theoretical aspects of the system, will be considered in an attempt to obtain a theoretical explanation of the behaviour of austenitic and ferritic steels subjected to fuel oil ash corrosion.
9.2 Morphological Features arising during Fuel Oil Ash Corrosion.

On examination of the laboratory prepared specimens, it can be seen that the layer constitution and morphology generally conform to a regular pattern. However, when the prevailing atmosphere is varied, these patterns are often altered. The purpose of the following subsections will be to consider the significance of both the normal behaviour and the atmosphere - affected features, with reference to the present work and relevant published data.

9.2.1 Growth Pattern of Sulphides

When the growth pattern of the sulphides is examined, it can be seen that in the majority of cases, there exists a distinct layer of metallic sulphide on the metal surface with a composition dependant on that of the original alloy.

Since, in each case, the sulphide is formed directly on the metal surface, the original existing surface oxide layer must, prior to sulphide formation, be destroyed or penetrated by sulphur. Also since no oxide was observed on the metal surface beneath the slag and corrosion layer, even under a prevailing atmosphere of oxygen, the atmospheric conditions at the metal/slag interface must be such that the oxygen potential is too low for oxide to form. Under normal conditions,
the stability of the oxide is thermodynamically more favourable than that of the sulphide, See Table 3.

\[
\begin{align*}
2 \text{ Cr} + \text{1.5} \text{O}_2 &\rightarrow \text{Cr}_2\text{O}_3 & \Delta G^0_{948} &= -208,879 \\
2 \text{ Cr} + \text{S}_2 &\rightarrow 2\text{CrS} & \Delta G^0_{948} &= -35,297 \\
3 \text{ Ni} + \text{1.5} \text{O}_2 &\rightarrow 3\text{NiO} & \Delta G^0_{948} &= -108,879 \\
3 \text{ Ni} + \text{S}_2 &\rightarrow \text{Ni}_3\text{S}_2 & \Delta G^0_{948} &= -42,259 \\
2 \text{ Fe} + \text{1.5} \text{O}_2 &\rightarrow \text{Fe}_2\text{O}_3 & \Delta G^0_{948} &= -136,062 \\
2 \text{ Fe} + \text{S}_2 &\rightarrow 2\text{FeS} & \Delta G^0_{948} &= -48,007
\end{align*}
\]

In the majority of cases, the sulphide layer appeared to be of a dense nature, often remaining adherent to the metal surface even after cooling to room temperature. This would suggest that either the growth of the sulphide has taken place at the metal/sulphide interface, due to the diffusion of sulphur to the metal, or, once the sulphide has formed, it acts as a diffusion path across which the metal species can easily diffuse to the outer layers. The sulphide layer would then move with the retreating metal surface, due to the migration of the metal elements into the slag. A third possibility is that the sulphide is molten and will therefore appear dense on solidification.

If the surface sulphide was in the molten state, the question arises of whether or not the layer would remain at the metal surface or rise to the surface of the liquid main bulk
of the slag. In the case of metals' extraction whereby a sulphide matte is produced, e.g. Cu$_2$S·FeS, the mattes are heavier than the slag thus the mattes are found in the bottom of the crucibles. For the sulphides that could be found as a molten phase in the specimens produced in the present work i.e. Ni$_3$S$_2$, or perhaps FeS·Ni$_3$S$_2$, the specific gravities of these compounds are 5.88 and 4.75 respectively. The data available for the specific gravities of the slag constituents is limited to the compounds:-

- $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$: 1.539
- $\text{Na}_2\text{O}$: 2.27
- $\text{Na}_2\text{S}_2\text{O}_7$: 2.658
- $\text{V}_2\text{O}_5$: 3.37

It is therefore reasonable to suggest that the more complex compounds in the steel that are likely to form will have specific gravities lower than those given above for the molten sulphides. It is therefore feasible that the sulphides will remain on the metal surface, providing the surface tension and/or surface irregularities are sufficient to prevent them from flowing to the bottom of the crucible.

In the case of the nickel alloy (Type B), the sulphidation attack has caused substantial penetration of the metal surface. The amount of penetration occurring after 100 hours corrosion, in all three atmospheres, is approximately 25 μ. However, in this case, there is a large difference in the actual amounts of metal corrosion that has taken place, i.e. very much more
corrosion occurring under atmospheres of oxygen and air than under argon. The atmosphere above the slag must thus have a great influence on the sulphidation attack of iron-nickel alloys.

It appears that the previously mentioned theories\(^{66,125}\) regarding the diffusion behaviour of sulphur at the metal surface and the presence of a molten sulphide layer are supported by this work.

In the case of the specimens examined from the Marchwood 10,000 hour corrosion trials, the initial surface sulphide layer tended to be porous with much lower sulphur concentrations at the interface. However, the majority of the specimens showed signs of surface infiltration, with high concentrations of both nickel and sulphur in the infiltrated zone. This again supports the above mentioned theories of the inward diffusion of sulphur. The presence of nickel sulphide at the interface of the alloys is contrary to the diffusion pattern suggested by Spengler and Viswanathan,\(^{125}\) who observed an inner layer of \(\text{Cr}_3\text{S}_4\) with an overlying layer of \(\text{Ni}_3\text{S}_2\) and an outer layer of \(\text{Cr}_2\text{O}_3\) on an 85 Ni/5 Cr alloys. Since the laboratory tests show an inner layer of mixed Fe-Ni sulphides or Fe-Ni-Cr sulphides at the interface, the behaviour as suggested by Spengler and Viswanathan must be greatly dependent on the composition of the alloy, slag and atmosphere of the individual system under investigation.

Let us now consider a possible explanation for the difference
between that found by Spengler et al.\(^{(125)}\) and that found in the examination of the Marchwood specimens in this work, which may also explain the porosity of the surface sulphide layers found in some of the tests. The corrosion process may have occurred in a manner suggested by Goebel et al.\(^{(66)}\), where the oxygen and sulphur potentials in the slag will alternate as compounds are formed, thus reversing the reaction from the direction of sulphide formation to oxide formation and vice versa. In the case of the Marchwood specimens, the mechanism may be as suggested above, whereas in the laboratory tests, vanadates would be formed, as opposed to oxides. If this is the case, then the sulphide at the metallic surface would be subjected to oxidising conditions and thus favour the formation of Cr\(_2\)O\(_3\) or CrVO\(_4\), both being the most stable compounds.

In this work it was observed that the sulphur persists at the metal surface as a mixed Fe-Ni sulphide (in Ni containing steels) and any chromium appears to diffuse outwards from the metal towards the region of higher oxide potential. The surface sulphide layer at the metal/slag interface will therefore be subjected to diffusion of two of its constituent species, i.e. 'S' diffusing inwards, towards the metal and chromium outwards, towards the high oxygen potential regions of the slag. The probable result as seen in the majority of cases, would be a region of high porosity, caused by the Kirkendall effect, being composed of the less mobile ions, Fe and Ni at the interface.
Since this layer tends to be porous in the majority of the Marchwood specimens but dense in the laboratory specimens, it is possible that the level of sulphur present in the slag will influence the actual composition of the inner sulphide layer. It is also possible that time dependent diffusion processes have occurred in the slag system of the Marchwood specimens but have not had time to develop in the laboratory prepared specimens.

In the case of the Marchwood specimens, the total thickness of slag was very much less than that used in the laboratory tests. This, therefore, means that the diffusion path from the prevailing atmosphere to the sulphide layer is short and thus there is a great likelihood of oxidation of the sulphides, reducing the level of sulphur below that normally expected to give stochiometric compound formation. The layer would thus consist of solid mixed oxides and sulphides.

In the laboratory prepared specimens, the level of sulphur was lower than in the Marchwood Trials but the diffusion path across the slag to the metal surface was much greater. The sulphide layer can therefore be rich in sulphur, with the likelihood of molten nickel/nickel sulphide eutectic forming, but be little affected by the prevailing atmosphere during the test. Inevitably, some iron and chromium will also be in solution in the molten sulphide phase, as seen from the EPMA study. Since the sulphide layer is molten, no porosity will be seen, unless caused by a solidification phenomena.
From this discussion of results, it can be seen that any theory of fuel ash corrosion must explain the reason for the presence of a sulphide layer at the metal/corrosion product interface, and the existence of mixed sulphide-oxide regions. The theory should also be able to explain the reason for the formation of certain mixed sulphides, e.g. Fe-Ni-S, and not Cr-Fe-Ni-S.

9.2.2 The Change in Thickness of the Surface Layer with Time.

From the examination of the thickness of the various layers, as given in Table 6, it can be seen that in the majority of cases the initial sulphide layer varies in thickness with increasing corrosion time. This thickness change is, however, not regular with time but increases from 1 to 24 hours and then a decrease is observed from 24 to 100 hours.

In general, the total layer thickness between 24 and 100 hours either increases or remains constant thus the diffusion path for reactants from the main bulk of the slag becomes steady or, with the other cases, greater thus the supply of reactants is in some cases constant and in others slowed down. If the diffusion rate of the reactants from the bulk of the slag is slowed below the outward diffusion rate of the metal species the possible dynamic equilibrium of the surface layer will be upset which could lead to a reduction in the thickness of the layer.
The production of a surface sulphide layer that does not increase with time also found during this work supports the results obtained by Romeo et al (126), who investigated the "Transport of Chromium in Cr₂O₃ scales in Sulphidizing Environments". They reported the existence of a chromium sulphide layer below the chromium oxide, produced by pre-oxidation, and also an external chromium sulphide layer. The inner layer did not increase in thickness, nor was the oxide layer dissolved. All growth took place on the external sulphide layer by diffusion of chromium through the internal sulphide and oxide layers with the oxide remaining as a metastable compound between the two sulphide layers. Since only sulphidising atmospheres were used and sulphide scales produced, the diffusion path would be little affected by the layers produced.

Under the conditions used in this work, other factors, such as reaction of the reaction products with vanadium compounds or the depletion of the reactants, both in the slag and the metal, may be responsible for the reduction in thickness of the initial sulphide layer. It is also worth mentioning that the internal scale thickness may also have been reduced by the eventual change in composition of the slag melt since no replenishment of the slag constituents, Na₂SO₄ and V₂O₅, was carried out, and/or by the change in composition of the metal at the metal/slag interface caused by the diffusion of a single metallic species, probably chromium, from the metal.
From this discussion, it can be seen that the thickness of the corrosion product layers may play a vital role in the mechanism of fuel ash corrosion. The thickness of the layers varies depending on the alloy and atmosphere compositions, thus the diffusion path for any diffusing species will also be affected. In any theory of fuel ash corrosion, consideration must therefore be given to the reason for the differences in the layer thicknesses.

9.2.3 Production of a Layered Structure.

From the scanning electron image micrographs of the specimens produced under laboratory conditions, Figs. 13 to 48, it can be seen that the tendency for layered structures to be produced increases with decreasing oxygen potential. In the case of the chromium steel, after 1 hour corrosion, Figs. 13, 14 and 15, very little layered structure is seen under oxygen Fig. 15, while a distinct layered structure is present under atmospheres of argon and air, Figs. 13 and 14. This situation is even more evident in the nickel steel, where after 1 hour, a layered structure is only produced under argon, Fig. 22. After 24 hours corrosion the layered structures are produced under both argon, Fig. 25, and air, Fig. 26, while still no layered structure is produced under oxygen, Fig. 27. The majority of the Type 347 steel specimens and all the "25Cr 20Ni"
specimens also show the same tendency.

The specimen of the Type 347 steel corroded for 1 hour under an oxygen atmosphere, Fig. 33, shows a layered structure, whereas the specimen produced under air, Fig. 32, does not.

This unusual result cannot be explained from the present work or published data. A possible explanation for the production of layered structures may lie with the oxygen transport ability of vanadium pentoxide, in the mixture of $V_2O_5$ and $Na_2SO_4$, during the early stages of corrosion before complete reaction has taken place between the $V_2O_5$ and $Na_2SO_4$. The excess oxygen present within the melt may cause a stirring action to take place as oxygen is absorbed. The reaction products that may have normally produced a layered structure would then be removed from their reaction site into the bulk of the slag. Another possibility could be that the layered structures may have been produced during the early stages of corrosion, but on cooling, prior to examination, the excess oxygen dissolved in the melt will be released thus causing a large amount of turbulence which could then destroy the layers. This situation would be especially true if the layers produced were very thin and of little mechanical strength. Both of the above explanations could be possible since, on examination of the micrographs, the slag melt appears exceedingly porous. Also, on examination of the melt while solidification took place, it was observed during this work that large volumes of gas were released from the melts under both oxygen and air, while no gas
release was seen under argon.

A third possibility can arise in which the initially high oxygen potential of the slags could prevent the formation of the layered structures by producing a slagging-off process. If one assumes that the oxygen causes oxidation of the metal sulphide layers which are in the form of particles, the products would be dispersed in the slag as opposed to producing a continuous layer of corrosion product. This possibility does not explain the large volume of porosity as seen in these specimens, thus gas evolution may be the most likely reason for the absence of layered structures under atmospheres of oxygen and air.

It can be seen from this discussion that the production of layers of corrosion product depends to a great extent on the oxygen partial pressure in the prevailing atmosphere above the molten slag. The significance of a layered structure may be important to the overall mechanism of corrosion when one considers that a decrease in the thickness of a corrosion rate regulating layer may give the appearance of a breakaway corrosion mechanism, without any break-up of layers having occurred.
The distribution of the elements iron, chromium, nickel, vanadium and sulphur in the laboratory prepared specimens is shown in Figs. 13 to 48 in the form of electron probe microanalysis traces. A summary of the constituents of the individual layers found in each specimen is also given in Table 6. The traces showing the distribution of the elements for the specimens obtained from the Marchwood 10,000 hour field trials are given in Figs. 55 to 62.

From the laboratory results, it becomes immediately apparent that the distribution of the alloying elements of the steel corroded under each atmosphere is similar. In each case, the metal surface is covered by a sulphide layer which is in turn covered with either further sulphides or vanadate layers. The actual composition of these layers is greatly dependent on the original composition of the alloy substrate. With the 12% chromium steel, the sulphide layer tends to be mainly chromium sulphide, while the outer layers are composed of iron chromium vanadate.

In the case of the 9% Nickel steel, both the sulphide and vanadate layers are mixed as iron nickel sulphide and iron nickel vanadate.

With both the Type 347 and "25Cr 20Ni" steels, the sulphides tend to be inner layers of iron and nickel sulphides and outer
layers of chromium sulphide. The vanadate layers tend to be mixed iron nickel chromium vanadate in the Type 347 steel but mainly as chromium vanadate in the "25Cr 20Ni" steel.

The general picture therefore is one of an initial sulphide layer, with overlying layers of sulphide and vanadate.

9.3.1 The Sulphide Layers.

The presence of metallic sulphides at the metal interface as found in this work confirms previous published work (63,65,115,124,125,126). The actual composition of this layer is however still in dispute. In the majority of cases, it has been stated that nickel sulphide would not be found at the metal/slag interface. It has, however, been shown in this work, see Section 7, that nickel sulphide can be formed from both chromium and iron sulphides, in the presence of either nickel oxide or nickel and oxygen. In both cases, an exchange reaction will take place in which the iron sulphide, for instance, is converted to iron oxide and the nickel oxide converted to nickel sulphide. Although it would appear that under normal conditions, in the presence of oxygen, the nickel sulphide should not be formed, due to the higher stability of nickel oxide. The experiments carried out in this work as reported in Section 7, have shown that the local atmosphere conditions must be such as to make the following reaction thermodynamically possible:-
3NiO + 2FeS \rightarrow Ni_3S_2 + Fe_2O_3 \quad \Delta G^{\circ}_{948} = 21,939 \text{ cals.}

This has also been shown to be true from the actual corrosion tests performed on the various steels, since in each case, the sulphide layer contains a high proportion of nickel. Furthermore, in the 9% Nickel steel, large regions of sulphide infiltration into the metal surface have taken place (e.g. See Figs 22 to 30). This type of attack is characteristic of sulphide attack along grain boundaries with the possibility of the formation of a liquid nickel/nickel sulphide eutectic (mp. 635°C) or FeS/Ni_3S_2 eutectic.

9.3.2 The Vanadate Layers.

The vanadate layers contain in each case, with the exception of the "25Cr 20Ni" steel, the major elements from the parent alloy. Vanadium was not found either at the metal/slag interface, or to have penetrated the metal surface.

This behaviour is however contrary to the findings of both Small et al\(^{(18)}\) and Bowden et al\(^{(6)}\), both of whom claim that the innermost layer was composed of V_2O_5. However, the present work is in agreement with Elliot et al\(^{(36)}\), who did not find any inner layers containing vanadium, nor vanadium penetration into the metal.

The composition of the vanadate layers tends to become more complex with time, with respect to the number of elements which diffused out from the steel. This indicates that the
production of the vanadate layers is a function of the outward diffusion of the metal ions through the surface sulphide layer. Alternatively, it may be a function of the decomposition or oxidation of the sulphide layer at the outer surface. From Table 6, it can be seen that the element found furthest into the slag is chromium. This is followed by iron, with nickel being last of all.

It is possible that this pattern can be accounted for by the relative oxidation potentials of the metal sulphides within the sulphide layer. Since the formation of chromium oxide is thermodynamically the most favourable reaction during the oxidation of FeS, CrS and Ni$_3$S$_2$ with oxygen:

\[
\begin{align*}
2\text{CrS} + 4\frac{1}{2}\text{O}_2 &\rightarrow \text{Cr}_2\text{O}_3 + 2\text{SO}_3 & \Delta G^{\circ} &= -318,704 \\
2\text{FeS} + 4\frac{1}{2}\text{O}_2 &\rightarrow \text{Fe}_2\text{O}_3 + 2\text{SO}_3 & \Delta G^{\circ} &= -233,178 \\
\text{Ni}_3\text{S}_2 + 4\frac{1}{2}\text{O}_2 &\rightarrow 3\text{NiO} + 2\text{SO}_3 & \Delta G^{\circ} &= -211,237
\end{align*}
\]
then it is likely that chromium sulphide will be first converted to oxide and then slagged off with vanadium pentoxide to form chromium vanadate.

It is also possible that the diffusion rate of chromium through the sulphide layers is faster than that of both iron and nickel, thus the reaction between chromium and vanadium would take place preferentially. Also, from the distribution of the elements in the slag layers, it would appear that the diffusion rate of iron through the sulphide layers is faster than that of nickel.

This is borne out when the outermost layers produced in
the slag are examined, since these layers tend to contain only iron and chromium. Nickel was only detected in the outermost layers of the slag produced on the 9% nickel steel and also in one isolated case of the Type 347 steel, which was corroded for 100 hours in an atmosphere of oxygen.

From the distribution of the alloying elements, as previously discussed, it can be seen that the sequence of reaction of the main elements of the alloys investigated with sulphur and compounds of sulphur is firstly iron, then nickel and lastly chromium. The sequence of reaction with vanadium compounds is, however, first chromium oxide, then iron oxide and lastly nickel oxide.
9.4 KINETIC STUDY.

From the kinetic results obtained by measuring the reduction of specimen thickness due to corrosion with time, Figs. 49 to 52, it is apparent that no one corrosion rate law is operative for all the specimens. Although the overall picture appears to indicate an approximately parabolic rate law, some of the specimens have corroded by a combination of rate laws.

In the case of 12% Cr steel, Fig. 49, almost identical amounts of corrosion had taken place under each of the three atmospheres after 100 hours exposure time. The routes by which this corrosion took place, however, varied under the different atmospheres. In the initial stages, from 0 to 48 hours, the specimen corroded under oxygen showed less corrosion than under air. The most corrosion had taken place in the specimens corroded under a prevailing atmosphere of argon. At approximately 60 hours of corrosion, however, a reversal took place in which the specimen under an argon atmosphere showed the least amount of corrosion whilst that under oxygen showed the most. If each curve is examined separately, it is seen that an approximately parabolic rate law operates up to a certain time of corrosion, which is followed at longer times by a second parabolic rate. The actual period of time for which the first parabolic law operates varies from 24 hours in the case of the oxygen atmosphere to 48 hours for the argon and air atmospheres.

This could indicate that the corrosion process changes at
some stage, affecting the layers that had caused the parabolic type rate to be produced. Since a parabolic type rate is produced, it would appear that the corrosion most probably occurs by a diffusion controlled process, which breaks down after a certain time, possibly due to either mechanical breaking of the layers, or due to some chemical changes within the slag, which have an influence on the morphology of the layers and thus on the diffusion controlled process.

In the case of the 9% Ni steels, Fig. 50, the actual corrosion rate is very much higher than in the other steels, but again the initial period from 0 - 48 hours appears to be of a parabolic type. However, it is only under an argon atmosphere that any form of protection appears to be offered since under both oxygen and air, the period of corrosion following the initial parabolic rate is linear. It therefore appears that the initial stages of corrosion are similar to that as seen in the 12% Cr steel, Fig. 49, but the second period does not produce any significant diffusion barrier to the corrosion process.

In both the Type 347 and "25Cr 20Ni" steels the kinetic curves, Figs. 51 and 52 respectively, show parabolic rate laws for the corrosion process, but with the Type 347 showing a faster corrosion rate than that observed in the "25Cr 20Ni" steel.

It appears, therefore, that the initial period of corrosion, for all the steels, proceeds according to a parabolic rate law.
In the case of the Type 347 and the "25Cr 20Ni" steels, the parabolic rate law is followed for the total corrosion time used for the present test. With the 12% Cr steel and 9% Ni steel, however, the initial parabolic rate is halted by either mechanical or chemical processes, with the subsequent corrosion following a different rate law. Thus from the preceding discussion, the actual time cycle to produce this change appears to vary depending on both the atmosphere and type of steel used. Although the change in rate law was not observed for the Type 347 and "25Cr 20Ni" steels in these tests, it may be possible that the time periods used for the tests were insufficient to produce this effect, if it exists at all in these steels. Longer corrosion periods perhaps would be necessary to establish this point.

It is also interesting to compare the composition of the final layers of slag and the corrosion resistance of each steel, see Table 8. From this table it is apparent that the composition of the outermost layer of corrosion product may have a considerable influence on the corrosion behaviour of the alloy. This layer could act as a diffusion barrier between the main bulk of the slag which is liquid, and the metal surface. This would also aid in stifling the underlying reaction processes by not permitting the removal of reaction products from the reaction site. The breakdown of such a diffusion barrier could account for the cyclic manner of corrosion as seen in the 12% Cr and 9% Ni steels, Figs. 49 and 50 respectively.
The order of corrosion resistance, from Table 8, indicates that the most corrosion resistant steel in the present work, the "25Cr 20Ni" steel, has a final layer composed of chromium and vanadium possibly as chromium vanadate. On examination of the steels with least corrosion resistance, it can be seen that the final vanadate layer contains more of the elements from the parent alloy but with decreasing quantities of chromium. It is possible therefore, that the criterion for good corrosion resistance may be the ability of a steel to produce a particular layer of "chromium vanadate".

It is interesting to note that in the Marchwood 10,000 hour field trials, the specimen with the highest corrosion resistance, the 2\% Cr steel, also had the "chromium vanadate" final layer, see Table 11. Also in these specimens it can be seen that with decreasing corrosion resistance of the steel there is an increase in the complexity of the final vanadate layer.

The actual order of corrosion resistance as found in the laboratory crucible tests is given in Table 8 while that for the Marchwood trials is given in Table 11. When these two sets of results are compared it is obvious that the corrosion resistance of a given steel is altered under the conditions of the different environment. This fact indicates that the corrosion resistance of any particular steel must depend greatly on the environment in which the test is conducted. This could be one reason why so many inconsistencies are found throughout the literature regarding the corrosion resistance of a particular
alloy, since the corrosion conditions, and in particular the slag and atmosphere compositions may vary from plant to plant.
9.5 THE EFFECT OF ALLOY COMPOSITION ON FUEL OIL ASH CORROSION.

At the onset of the present work, four different alloys were chosen such that the effects of individual alloying elements could be studied alone, and in the presence of each other.

When one considers the behaviour of the individual alloying elements, it becomes immediately apparent that in the 9% Nickel steel (Type A), the rate of corrosion is very high and also large amounts of infiltration of the metal surface have taken place by a sulphide phase. The appearance of the infiltration attack indicates that the surface sulphide layer was in the molten state, probably as a nickel/nickel sulphide eutectic or a mixed iron-nickel-sulphur matte.

With the 12% chromium steel (Type B), no infiltration attack takes place, but fairly large amounts of corrosion occur, although less than with the nickel steel. There are no indications of any molten sulphide phase being present, but since sulphides of both iron and chromium have higher melting points than the test temperature of 675°C, then this situation would be expected.

When nickel and chromium are both present in the steel, as in the Type 347 steel, little or no infiltration occurs and the rate of corrosion is very similar to that of the 12% Cr steel.

With the higher alloy content steel, the "25Cr 20Ni" steel, a substantially lower rate of corrosion occurs than with the
other steels. Also little or no penetration of sulphides into the steel takes place.

It therefore appears that the main alloying element to combat corrosion in iron based alloys must be chromium. In cases where nickel is used to enhance the mechanical properties of alloys, sufficient chromium should also be present in the steel to suppress the formation of a molten nickel/nickel sulphide eutectic at the metal surface.

Although the mechanical properties of alloy steels become increasingly less attractive with increased alloy content, it appears that the higher the alloy content, the better the corrosion resistance.

The actual corrosion mechanism of the different types of alloy appears to be little affected by the alloy composition, although the corrosion products will depend on this composition. The rate of corrosion will be far more important criterion when considering the use of an alloy of a particular composition.
From the previous discussion on the kinetic results obtained from the present work, Section 9.4, it can be seen that the atmosphere above the slag had very little effect on the actual rate of corrosion of a steel. It did however have a significant effect on the morphology of the corrosion products.

The reason for the effect on the morphology without any on the corrosion rate must therefore be considered. In the previous discussion on the morphological features of the specimens, Section 9.2, it was considered that the change in structure of the slag system could be due to the evolution of oxygen, under atmospheres of oxygen and air, which could cause disruption of the layered structures. Under argon, however, more definite layered structures were seen. It is therefore possible that during the actual corrosion test, the structure of the corrosion product layers, and also the corrosion behaviour, were similar under all atmospheres. However, on cooling to room temperature, the evolution of oxygen could cause the disruption of the layered structure; thus, on examination of the specimens, morphological features would be present which may not reflect those which were present during the test.

The exception that does exist in the laboratory prepared specimens is the 9% Ni steel which shows higher amounts of corrosion under atmospheres of oxygen and air than under argon.
This was probably due to the higher oxidation rate of the nickel sulphide surface layer which would release further "sulphur" for more intensive sulphidation attack. The oxide then produced would react with vanadium pentoxide to produce the respective metallic vanadates, which offer little or no barrier to diffusion of corrodents from the molten slag, so that further oxidation can take place. In the chromium-containing steels the vanadate layers will offer a far more effective diffusion barrier than is the case with the nickel steels.

Under an argon atmosphere, the oxidation of the sulphide layer would have to proceed via the direct reaction of oxygen obtained from the vanadium pentoxide, giving mixed oxides and vanadates. The reaction rate in this case is likely to be much lower.

It appears therefore, that in the majority of cases the atmosphere above the slag has very little effect on both the rate of corrosion and the corrosion mechanism.

It is therefore possible that a corrosion mechanism can be postulated which should operate under all the prevailing atmospheres used for the present test programme.
From the study of four different steels corroded under a slag of 70wt.% \(V_2O_5\)/ 30wt.% \(Na_2SO_4\) in atmospheres of either oxygen, air or argon, it appears that there is a similarity in the corrosion behaviour. Although the composition of the reaction products is dependent on the steel composition, the corrosion process by which these are formed is so similar that the overall corrosion mechanism can be conveniently considered to occur by the four steps given below:

1. The protective oxide layers on the as received metal surface are fluxed or rendered permeable by a compound or compounds in the slag.

2. The metal surface is subjected to sulphidation attack by either gaseous or solid sulphur containing compounds resulting in the formation of a surface metallic sulphide layer.

3. The sulphides of the steel alloying elements which are formed on the metal surface can then be oxidised to form a non-continuous layer of oxide and also release "sulphur" for further sulphidation attack.

4. The oxides produced can then react with vanadium pentoxide to form mixed vanadates. The formation of a layer of 'pure' chromium vanadate, \(CrVO_4\), appears to give better protection to the steel than the mixed metallic vanadate layers.

The feasibility of each step of the above corrosion mechanism
will now be considered in turn in the light of the results obtained in this work and also the relevant thermodynamic, kinetic and other published data.

9.7.1 Loss of Protectivity of the Original Oxide Layer.

From the relevant review of the literature it appears that several mechanisms can produce the loss of protectivity of the original oxide layer on the alloy surface. The actual removal of the oxide layer can be considered to occur by either direct reaction with sodium sulphate, vanadium pentoxide or sulphur trioxide. Other workers have also postulated that the initial oxide layer can be rendered permeable by reaction with sodium sulphate and vanadium pentoxide. These reactions may change the physical, as well as the chemical nature of the protective layers.

In the case of the oxide layer reacting with sodium sulphate, Goebel et al have shown that both nickel oxide and chromium oxide can react with sodium sulphate to produce sodium nickelates and sodium chromates. Since the surface oxide layers will consist mainly of chromic oxide, probably as a spinel, e.g. \( \text{Cr}_2\text{O}_3 - \text{FeO} \), in chromium containing steels, or nickel oxide, again as a spinel \( \text{Fe}_2\text{O}_3\cdot\text{NiO} \), in the iron-nickel steels, then the production of the nickelate compounds is feasible. Although the temperature of 675°C used during the laboratory tests was insufficient to produce molten sodium
sulphate, (mp. 880°C), the interaction of vanadium pentoxide (mp. 675°C) with the sodium sulphate would produce complex compounds of lower melting points, such as sodium vanadyl vanadate (mp. 535°C) and sodium metavanadate (mp 630°C). Uncombined \( \text{Na}_2\text{SO}_4 \) and \( \text{V}_2\text{O}_5 \) dissolved in the molten slag could then react to produce the nickelates and chromates.

\[
\text{Cr}_2\text{O}_3 + \text{V}_2\text{O}_5 + 2\text{Na}_2\text{SO}_4 \rightarrow 2\text{Na}_2\text{CrO}_4 + 2\text{SO}_2 + \text{V}_2\text{O}_4
\]

\[
2\text{NiO} + \text{V}_2\text{O}_5 + \text{Na}_2\text{SO}_4 \rightarrow 2\text{Na}_2\text{NiO}_2 + \text{SO}_3 + \text{V}_2\text{O}_4
\]

The above reactions will also release sulphur dioxide for subsequent sulphidation attack of the metal surface.

Although it is feasible to suggest that sodium nickelate and chromate could be produced at the metal surface, their existence could not be established in this work due to the low atomic number of sodium, which produced very inconsistent and unreliable results during electron probe microanalysis.

The reaction of the original oxide layers with vanadium pentoxide has been demonstrated by Maksimov (37), who has shown that metal oxides of iron, chromium and nickel can react with \( \text{V}_2\text{O}_5 \) to produce the metal vanadates:

\[
\text{Cr}_2\text{O}_3 + \text{V}_2\text{O}_5 \rightarrow 2\text{CrVO}_4
\]

\[
\text{Fe}_2\text{O}_3 + \text{V}_2\text{O}_5 \rightarrow 2\text{FeVO}_4
\]

\[
2\text{NiO} + \text{V}_2\text{O}_5 \rightarrow \text{Ni}_2\text{V}_2\text{O}_7
\]

Since these vanadates have melting points above the temperature used for these tests, the vanadate would remain at the metal surface as a solid layer. In this work, no vanadium was detected at the metal surface. It is therefore,
unlikely that this process was responsible for the destruction of the initial layer. From the present work, this process could only be possible if the reaction is very fast and the layer produced was permeable to "sulphur", allowing immediate sulphidation to occur at the metal surface, which would displace the vanadate layers.

The third possibility for the removal of the oxide layer would be by the direct reaction with sulphur trioxide, which could be obtained from the following reaction of sodium sulphate and vanadium pentoxide:

\[
\text{Na}_2\text{SO}_4 + \text{V}_2\text{O}_5 \rightarrow 2\text{NaVO}_3 + \text{SO}_3
\]
The sulphur trioxide then could react with the oxide layer to produce metallic sulphide:

\[
\text{Cr}_2\text{O}_3 + 2\text{SO}_3 \rightarrow 2\text{CrS} + 4\frac{1}{2}\text{O}_2 \quad \Delta G^\circ_{948} = +318,7042 3 3 2 9 4 8
\]

Under normal conditions, this reaction could not take place but if the \( \frac{P_{\text{SO}_3}}{P_{\text{O}_2}} \) ratio was altered, this reaction could be possible.

For the reaction to proceed in the direction indicated, at a temperature of 675°C, the equilibrium ratio of the gases, as calculated from the Van't Hoff Isotherm, (See Section 2.6.2.) is:

\[
\left( \frac{P_{\text{SO}_3}}{P_{\text{O}_2}} \right)^2 = 3.02 \times 10^{73}
\]

Since the oxide layers are destroyed under atmospheres of both oxygen and argon, it does not appear feasible to expect that localised atmosphere at the onset of corrosion would be so drastically altered to allow this reaction to occur. This
implies that if this reaction does occur, then the atmosphere above the slag will normally have no effect on the corrosion process.

The most feasible route for the loss of protectivity of the oxide layer appears to be by the direct penetration of 'sulphur',

\[ \text{16} \text{ sulphur} \text{, or gaseous oxides of sulphur, through the oxide scale. In this work and elsewhere, it has been observed that sulphide layers exist below the oxide scale,} \text{66} \text{ probably being formed by the penetration of the oxide by sulphur containing gases. It has also been observed}^{16} \text{ that if } V_2O_5 \text{ is present in the chromium oxide layer, then oxygen can penetrate the scale. It is therefore also possible that gaseous oxides of sulphur can penetrate the scale and cause sulphidation of the underlying metal.} \]

If the corrosion products from the specimens corroded for 1 hour are examined, Table 6, it can be seen that in all cases the layer adjacent to the metal surface is already sulphur rich, with an overlying layer of either oxide or vanadate. This could indicate that the initial oxide layer may not have been removed, at this stage, but is penetrated by the 'sulphur' causing sulphidation of the alloy substrate. Alternatively, it could be argued that the layer may have been completely fluxed during the first few minutes of corrosion, exposing the metal surface to sulphidation attack, then the oxides and/or vanadates were formed on top of the sulphide scale.
9.7.2 Sulphidation of the Alloy Substrate.

It has been established that during the hot corrosion process, the SO₂/SO₃ content of the gas phase is insufficient to promote direct sulphidation attack on alloys. A film of liquid Na₂SO₄ on the alloy is however a ready source of sulphur at sufficient concentration provided that appropriate reduction reactions take place.

Thermodynamic arguments have for some years been used to show that once sulphides have formed, they will persist and migrate inwards, into the alloy, under oxidising conditions. This effect has only recently been demonstrated by Spengler and Viswanathan and confirmed by this work. Specimens of an 85% Ni - 15% Cr alloy were initially sulphidised for a period of 50 hours in a mixture of 0.2% SO₂ - N₂ at 871°C, then oxidised in 3% O₂ - N₂ at 871°C for 300 hours. The sulphidised specimens had an outer layer of Cr₂O₃, overlying a layer of Ni₃S₂ and an inner Cr₃S₄ layer. For certain of the oxidation tests, the Ni₃S₂ layer had been stripped leaving only the Cr₃S₄ scale. The total sulphur content of the samples was found to be preserved during oxidation. The self regeneration mechanisms of sulphide propagation were considered to be achieved by the following reaction:

\[
2 \text{Cr}_3\text{S}_4 + 9\text{O}_2 \rightarrow \text{Cr}_2\text{O}_3 + 8\text{S}
\]

\[
8\text{S} + 6\text{Cr} \rightarrow 2\text{Cr}_3\text{S}_4
\]

The initial release of sulphur was considered to diffuse
inward to form further $\text{Cr}_3\text{S}_4$. When $\text{Ni}_3\text{S}_2$ was present, as was the case with most of the specimens, it was considered that further $\text{Cr}_3\text{S}_4$ was formed by the reaction

$$\text{Ni}_3\text{S}_2 + 2\text{O} \rightarrow \text{NiO} + 2\text{S},$$

the sulphur diffusing to combine with the chromium.

Although the above reactions may explain the onset of sulphidation attack of the alloy, it has been shown during this work, Section 7, that at $675^\circ\text{C}$ an exchange reaction between nickel oxide and iron sulphide takes place to produce nickel sulphide and iron oxide. This reaction has been shown in this work to be feasible both practically, Section 7.3, and from thermodynamic calculations, Section 7.4. The thermodynamic analysis also shows that the exchange reaction of nickel oxide and chromium sulphide is thermodynamically even more favourable, producing nickel sulphide and chromium oxide. This result is, in fact, the reverse of that reported by Spengler and Viswanathan\(^{(125)}\). The results obtained from the laboratory crucible tests indicate that in the majority of cases, the scale adjacent to the metal surface is composed of mixed iron nickel and sulphur rich phase, with an overlying layer of sulphide containing chromium. The results obtained are therefore contrary to the results found by previous workers and demonstrate that nickel sulphide can be present as part of the inner scale, as well as chromium sulphide.

Once sulphidation attack has started, the subsequent attack on the metal may depend on the oxide ion activity of
the slag system above the alloy. The presence of vanadium in the molten slag reduces the oxide ion activity, thus the sulphide ion activity will be increased, favouring further sulphidation attack of the alloy.

Since the slag medium used throughout the laboratory tests consisted of 70wt.% V₂O₅ and 30wt.% Na₂SO₄, there is a large excess of vanadium in the molten slag to maintain a low oxide ion activity, thus sustaining sulphidation attack. The oxide ion activity, especially at the outer regions of the sulphide scale, may become sufficiently high, due to the reaction of the sulphur in the slag producing sulphides, to oxidise some of the sulphides to produce metal oxides and release sulphur for further sulphidation attack.

9.7.3 Oxidation of Sulphides.

The oxidation of metal sulphides could occur by either direct reaction with oxygen, from the prevailing atmosphere, or from oxygen produced during the formation of complex vanadates. Thus:

\[ \text{Na}_2\text{O} \cdot 6\text{V}_2\text{O}_5 \rightarrow \text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 + 5\text{V}_2\text{O}_5 + \text{O}^\cdot \]

The oxidation of the common sulphides of the elements iron, chromium and nickel are thermodynamically very favourable since the oxides produced are all very stable.

\[ 2\text{CrS} + 4\frac{1}{2}\text{O}_2 \rightarrow \text{Cr}_2\text{O}_3 + 2\text{SO}_3 \]
\[ \Delta G^\circ_{948} = -318,704 \]

\[ 2\text{FeS} + 4\frac{1}{2}\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 2\text{SO}_3 \]
\[ \Delta G^\circ_{948} = -211,237 \]
It is also possible to oxidise the sulphides by less stable oxides, as shown in Section 7.

\[
\begin{align*}
\text{Ni}_3\text{S}_2 + 4\text{O}_2 & \rightarrow 3\text{NiO} + 2\text{SO}_3 & \Delta G^\circ_{948} = -233,178 \\
2\text{CrS} + 3\text{NiO} & \rightarrow \text{Cr}_2\text{O}_3 + \text{Ni}_3\text{S}_2 & \Delta G^\circ_{948} = -107,466 \\
2\text{FeS} + 3\text{NiO} & \rightarrow \text{Fe}_2\text{O}_3 + \text{Ni}_3\text{S}_2 & \Delta G^\circ_{948} = -21,941
\end{align*}
\]

Oxidation may also occur by an indirect method whereby the oxide ion activity of the slag system becomes increased due to a reduction of the sulphur potential by the formation of sulphides. In this way the sulphides being produced will eventually lead to their subsequent oxidation. This however will reduce the oxide ion activity thus increasing the sulphur activity producing more sulphides. This can lead to a cyclic process, unless one of the reactants is removed from the reaction sites, or the system becomes saturated.

In all the above-mentioned cases the oxide produced would tend to be slagged off and dispersed in the molten slag and would thus offer no effective barrier between the alloy and the slag.

The oxides produced by this process, as well as the initial oxide layer, can react with vanadium pentoxide to form metallic vanadates.

9.7.4 Reaction of Oxides with Vanadium Pentoxide, and the Protective Property of the Chromium Vanadate Surface Layer.

The main work carried out on the study of vanadate production and reactions of vanadium pentoxide has been by
Maksimov has shown that vanadium pentoxide can react with both the pure metal to produce its oxide, and then react with the oxide to produce the metal vanadate. Thus:

$$3\text{V}_2\text{O}_5 + 4\text{Fe} \rightarrow 2\text{Fe}_2\text{O}_3 + 3\text{V}_2\text{O}_3$$

$$\text{V}_2\text{O}_3 + \text{O}_2 \rightarrow \text{V}_2\text{O}_5$$

$$\text{V}_2\text{O}_5 + \text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe VO}_4$$

The metal vanadate that forms can further react with the metal to produce a second oxide and vanadium trioxide,

$$6\text{Fe VO}_4 + 4\text{Fe} \rightarrow 5\text{Fe}_2\text{O}_3 + 3\text{V}_2\text{O}_3$$

It was also found that the metal vanadates could react with oxides of other metals and all the above-mentioned reactions are interchangeable with the metals iron, chromium and nickel,

$$6\text{Fe VO}_4 + 4\text{Cr} \rightarrow 5(\text{Fe Cr})\text{VO}_4 + 3\text{V}_2\text{O}_3$$

However, if chromium vanadate, \(\text{CrVO}_4\), was formed, this would not react with any of the common metals.

Lucas et al. (16) however, found that \(\text{CrVO}_4\) was only one form of a complete range of chromium and vanadium pentoxide compounds. If the proportions of \(\text{Cr}\) or \(\text{V}_2\text{O}_5\) were altered from stoichiometric values to give \(\text{CrVO}_4\), then this compound would further react to give other Cr-V-O compounds, thus no protection could be offered by \(\text{CrVO}_4\). The protectiveness of chromium vanadate must therefore be dependent on the system in which the compound is formed.

In both the laboratory crucible tests and the field tests the outmost layers formed on the metal surface tended to be rich
in vanadium with the alloy metals also present probably as mixed vanadates. In the case of the steels offering the lowest corrosion rates, i.e. the highest corrosion resistance, however, this outer layer contained only chromium and vanadium, possibly as chromium vanadate, CrVO$_4$.

Although the actual mechanism by which the alloys are corroded is almost certainly by sulphidation attack, the production of chromium vanadate appears to offer some measure of protection, possibly by excluding reactants from the reaction site and by acting as a diffusion barrier.

Further work would be necessary to establish the nature and protective property of this phase. It is also considered important that further thermodynamic data should be obtained regarding the formation of the appropriate metal vanadates.
10. CONCLUSIONS

In the light of the present work and the relevant literature on the subject of fuel oil ash corrosion, it appears that:

1. The initial mechanism of attack is sulphidation of the alloy surface by reaction with sulphur containing compounds produced in the liquid slag.
2. The overall corrosion mechanism can be summarised as follows:
   i. The original oxide layers on the alloys are rendered permeable to sulphur containing reactants by either vanadium pentoxide or sodium sulphate.
   ii. The sulphidation attack penetrates the metal surface to produce a sulphide layer, while sulphides furthest from the metal surface become oxidised and react with vanadium pentoxide to produce metallic vanadates.
3. The production of a continuous layer of chromium vanadate retards the corrosion process.
4. Chromium is the most beneficial alloying addition in steels to give good corrosion resistance under isothermal conditions.
5. Nickel may be deleterious if used alone as an alloying addition since a liquid sulphide layer can be formed, which can penetrate the metal surface. The layer is either a nickel/nickel sulphide eutectic or an iron-nickel matte.
6. Laboratory crucible testing could give an indication as to a steel's performance in the operative boiler, providing the slag and temperature conditions are similar in both cases.

7. The oxygen partial pressure in the atmosphere above the slag has little influence on the corrosion rate of the steels, but does affect the morphology of the system as seen at room temperature.
11. RECOMMENDATIONS FOR FUTURE WORK.

From the present work, it appears that several areas of investigation could lead to a further understanding of fuel oil ash corrosion. It is therefore recommended that the following could be studied.

1. One of the main weaknesses in the interpretation of experimental results is the insufficient knowledge of the \( \text{Na}_2\text{SO}_4/\text{V}_2\text{O}_5 \) equilibrium phase diagram, especially in the presence of other oxides, e.g. \( \text{Cr}_2\text{O}_3 \), \( \text{FeO} \), \( \text{NiO} \). An investigation should therefore be undertaken to ascertain the effects of these oxides on the melting points, and phases present within the system.

2. Since the experimental work described in Section 7, regarding the interaction of oxides and sulphides, was concerned purely with the feasibility of the production of nickel sulphide within the system, it is considered that further work should be carried out with special reference to the diffusion patterns of the species involved. This work could also be extended to cover oxide/sulphide systems other than the \( \text{FeS}/\text{NiO} \) system as described in Section 7.

3. The present work was designed to study the effects of the elements nickel and chromium alone and in the presence of each other in iron based alloys. Although further information was obtained as to these effects, it is felt that a large field of research is lacking in both the present work and in published
literature as to the effects of iron both above and in conjunction with nickel and chromium. The results from the present work could then be used to compare the effects of nickel and chromium on the corrosion behaviour of iron.

4. From the present work, it has been shown that the steels having the best corrosion resistance form a layer of a chromium/vanadium complex, possibly as chromium vanadate, CrVO$_4$. Further work should be carried out to establish the protective properties of this compound, with special emphasis on its effectiveness as a diffusion barrier to oxygen and gaseous oxides of sulphur.

5. Since the corrosion mechanism, as suggested from the present work, involves the formation of vanadate compounds in the slag, it is considered essential to determine the relevant thermodynamic data as to the formation of these compounds. Such information may then aid in the prediction of the ability of chromium vanadate formation by a particular steel under specified slag and atmosphere conditions.

6. The present work was carried out at only one temperature (675°C), in the 70/30 wt.% V$_2$O$_5$/Na$_2$SO$_4$ slag. Consequently, the results do not lend themselves to the determination of the energy of activation of corrosion, or other kinetic parameters. It is, therefore, considered that it may be useful to repeat selected areas of the present work but at three different temperatures, possibly 625, 650 and 700°C. It may be useful to allow corrosion to continue at a temperature at which the slag is partially liquid and partially solid.
7. As the role of sulphur is of special importance in the corrosion mechanism, it could be interesting to establish if a non-sulphur containing slag, e.g. Na\textsubscript{2}O - V\textsubscript{2}O\textsubscript{5} or NaVO\textsubscript{3}, has the ability to pick up sulphur from an atmosphere containing gaseous sulphides. Also since the mechanism assumes previous theories that sulphur will persist at the metal surface once it is present there, then the above experiment could be utilized to allow an initial sulphide layer to form, then cease the supply of sulphur. This would then confirm or disprove the previous theories as to the persistence of sulphur on a metal surface under a non-sulphur containing slag.

8. The initial stage of the corrosion mechanism involves the loss of protectivity of the original oxide layer. It is considered that vanadium pentoxide or sodium sulphate enters the oxide layer rendering it permeable to reactants in the slag which attack the metal. It is considered important that this process should be further investigated to establish the mechanism of such a process.

9. During this work, the standard thermodynamic free energy values were corrected by substituting the appropriate concentrations of the alloying elements of the metals into the Van't Hoff Isotherm. The activities of the alloying elements (Fe, Cr and Ni) should be determined for more accurate calculations of the equilibria at the steel/slag and steel/atmosphere interfaces.
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APPENDIX I

Quantitative Correction of EPMA Results

The effects which must be corrected are

(a)  Dead time

The X-ray counter is "dead" to incoming pulses for a small time after each pulse. This means that at high counting rates the number of counts is underestimated.

(b)  Absorption

If the mass absorption coefficient of the standard for the radiation being studied is significantly different from the m.a.c. of the specimen, then a direct comparison of the relative count rates will be inaccurate. The magnitude of this effect depends clearly on the m.a.c.'s of each constituent and on the take-off angle at which the X-rays are observed.

(c)  Atomic Number Effect

If the mean atomic number of the specimen is very different from the atomic number of the standard then two effects will arise. Firstly the penetration of the material by the beam will be different, giving a different distribution of X-ray production. The second effect is the altered percentage of primary electrons scattered directly back up the column by collisions with atomic nuclei. This reduces the amount of possible X-ray production.

(d)  Fluorescence

If the characteristic radiation from one element in an alloy is of shorter wavelength (higher energy) than that from another, then the latter can be "fluoresced" by the former. This results in increased counts from the latter element.

A simple study of the data for your system will reveal which of these effects is likely to be important. For most of the effects there is a quick approximate method of correction and a more precise one. Your choice will depend on the absolute accuracy you require.

Correction Procedures

(a)  Dead Time

i) Low count rates  < 1000 c.p.s. - ignore

ii) High count rates:

\[ N = N^1/(1-N^1\tau) \]

\[ N = \text{true counts/sec} \]

\[ N^1 = \text{observed counts/sec} \]

\[ \tau = \text{resolving time. Take } \tau = 2.5 \text{ } \mu\text{sec for JEOL JXA-50A} \]

(b)  Absorption

i) Quick approximation

\[ C_A = K_A \left[ 1 + \frac{\mu_{AB}}{\mu_A} - \frac{\mu_A}{P + \mu_A} \right] \]
where $C_A =$ weight concentration of element A

$$K_A = \frac{A \text{ counts from spec - background}}{A \text{ counts from standard - background}}$$

$\mu_A =$ m.a.c. for A radiation in A

$\mu_{AB} =$ m.a.c. for A radiation in specimen

$$\mu_A = \frac{\mu_A K_A + \mu_A K_B + \mu_A K_C + \ldots}{K_A + K_B + K_C + \ldots}$$

$$P = \sigma \sin \theta \left[ \frac{1 + h}{1 + 2h} \right]$$

$h = 1.2 A / Z^2$

$\sigma =$ Lenard coefficient - see Table 1A

$A =$ Atomic weight

$Z =$ Atomic number

ii) Accurate method:

$$C_A = K_A f(X)_A$$

where

$$f(X) = \frac{1 + h}{(1 + X) \sigma (1 + h (1 + X))}$$

$h = 1.72 \times 10^{-6} A \cdot \sigma V^2 / Z^2$

$\sigma = 2.39 \times 10^5 \sqrt{1.5 - V_e}$

$V =$ Accelerating potential

$V_e =$ Excitation potential for the particular radiation

$X = \mu_A \cosec \theta$

$\theta =$ take-off angle = 35° for JEOL JXA-50 A

$\mu_{AB} = \mu_A C_A + \mu_A C_B + \ldots$ ie. an iterative method is needed

(c) Atomic Number Effect

i) Quick approximation

$$C_A = K_A \left[ 1 + \frac{Z_A - Z_{AB}}{100} \right]$$

where $Z_{AB} = \frac{Z_A K_A + Z_B K_B}{K_A + K_B + \ldots} \ldots$
For $Z > 40$ use $Z_1 = 40 + 0.3 (Z - 40)$

ii) Accurate method

$$C_A = K_A \frac{C_A^{A_1} + C_B^{A_1} + C_C^{A_1}}{\alpha_A}$$

where $\alpha = \frac{S}{R}$ stopping power effective current factor

\[ (1 - R) = \text{backscatter} \]

Both $S$ and $R$ have been tabulated against atomic number $Z$ (see figures 1A and 2A). Read off $R$ for the appropriate value of $V/V_c$ and $S$ for the value $(V + V_c)/2$.

Again an iterative method is needed, getting more complex the larger the number of constituents.

(d) Fluorescence

Fluorescence by both characteristic and "white" radiation will occur but in general the white fluorescence can be ignored. Fluorescence is only likely to be important when there is a quite large concentration of the fluorescing element, since the "efficiency" of fluorescence is quite low. A K line can be excited by another K line and by an L line (K-K and L-K). These two effects must be calculated separately and both corrections applied.

$$C_A = K_A / (1 + \gamma)$$

where $\gamma = C_B J(A) D \frac{\mu_B^{A}}{\mu_B^{A}} \left[ g(x) + g(y) \right]$.

$C_B$ = mass conc. of exciting element (B)

$J(A)$ = function of element being analysed (A) (Table 2A)

$D$ = function of $V$ and $Z_B - Z_A$ (Figure 3A)

$g$ = function plotted in Figure 4A

$$x = \frac{\mu_A^{A}}{\mu_B^{A}} \csc \theta$$

$$y = \frac{\sigma^{A}}{\mu_B^{A}}$$

Again an iterative method will be needed, however this converges very quickly, particularly if your first guesses at $C_A$, $C_B$ etc. are intelligent.

An estimate of whether the effect is large or not can be made by calculating $C_B J(A)$. This is, in general, slightly larger than $\gamma$.

All corrections can be incorporated in single equation, if they are all needed, which will be of the form:
\[ C_A = K_A \frac{f(x)_A}{f(x)_{AB}} \frac{c_i^{\alpha_A}}{\alpha_A} \frac{1}{1 + \gamma} \]

Absorption    At.No.    Fluorescence

References:


Fluorescence: S.J.B. Reed, Brit. J. Appl. Phys. 16 913 (1965)
Fig. 2A.

Fig. 3A.
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<td>32.6</td>
<td>35</td>
<td>33</td>
<td>86</td>
<td>80</td>
<td>0.14</td>
</tr>
<tr>
<td>Au</td>
<td>79</td>
<td>33.1</td>
<td>36</td>
<td>34</td>
<td>87</td>
<td>81</td>
<td>0.14</td>
</tr>
<tr>
<td>Hg</td>
<td>80</td>
<td>33.5</td>
<td>36</td>
<td>34</td>
<td>88</td>
<td>82</td>
<td>0.15</td>
</tr>
<tr>
<td>Tl</td>
<td>81</td>
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<td>37</td>
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<td>89</td>
<td>83</td>
<td>0.15</td>
</tr>
<tr>
<td>Pb</td>
<td>82</td>
<td>34.5</td>
<td>37</td>
<td>35</td>
<td>90</td>
<td>84</td>
<td>0.16</td>
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</tbody>
</table>
JEOL JXA-50A Microanalyser

This is a high resolution scanning electron microscope fitted with one fully focussing X-ray spectrometer plus a lithium drifted silicon energy-dispersive detector. Both quantitative and qualitative analysis is therefore possible.

Details:

Accelerating voltage: 1-50 kV, continuously variable

Lenses: two; one condenser, one objective

Magnification range: 20 to 140,000 X (nominal)

Resolution (electron image): better than 10 nm on suitable specimens

Apertures: final apertures: 0.1, 0.2 or 0.6 mm.

Operating vacuum: $5 \times 10^{-5}$ torr

Specimen facilities: Entry via airlock at a working distance of either 13 mm (high resolution SEM) or 37 mm (X-ray analysis). 25 mm diameter mount is convenient for analysis, 10 mm diameter for SEM or 33 mm diameter for larger specimens.

Specimen manipulation: The specimen can be moved in x, y and z (vertical) directions, motor driven continuously or in steps along the x axis. It can be rotated through $360^\circ$ and tilted up to $45^\circ$ towards the electron collector (not for analysis).

Cameras: Automatic exposure control, numbering device (manual)
Either 120 roll film (reduction 0.6 to 1) or polaroid 5 x 4 positive + negative film, giving a reduction of 0.88 to 1.

Modes of display: i) secondary electron image (SEI)
ii) TV rate SEI
iii) backscattered electron image, topographical (BEI)
iv) backscattered electron image, compositional (BEI)
v) specimen current image (AEI)
vi) y-modulation image
vii) derivative of SEI
viii) X-ray composition mapping
ix) Sum of any two of the above (except ii) and vii)
x) Optical microscope X 300 with polarizers
Analysis facilities:

Spectrometer: fitted with two crystals, usually RAP and Stearate capable of detecting $5^\circ$ to $15^\circ$. Alternatively LIF and PET can be fitted to cover the range $14^\text{Si}$ to $92^\text{U}$. Take off angle $35^\circ$.

output can be displayed on ratemeter, digital scalar, 3-pen chart recorder, as element distribution map on c.r.t. or as y-modulated line on c.r.t.

Solid state detector: Ortec lithium-drifted silicon detector with resolution 170 eV is fitted. Take off angle $38^\circ$ with specimen at zero tilt. X-ray counts from detector can be collected in the memory of ortec 6200 multi-channel analyser. Complete spectrum of X-rays from $11^\text{Na}$ to $92^\text{U}$ can be displayed simultaneously. Output can be to teleprinter, ratemeter or to c.r.t. display as for spectrometer.

Spectra from 2 (or 4) different specimens or areas can be compared. Integral peak areas can be determined.