THE CONTROLLED CORROSION OF REFRACTORIES BY OIL-ASH COMPONENTS WITH HIGH SODIUM SULPHATE CONTENTS.

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NIGEL CHARLES GRAVETTE, B.Sc(Eng), A.R.S.M.

Department of Chemical Engineering
and Chemical Technology,
City and Guilds College,
Imperial College of Science and Technology,
London, S.W.7.
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ABSTRACT.

Certain components of fuel oil ash have been tested against the refractory oxides silica and alumina. The solubility of alumina in vanadium pentoxide ranges from 1.4% at 750°C to 3.3% at 1050°C. The addition of sodium sulphate to this melt causes the solubility to rise to a slight maximum at 14 mole % Na_2SO_4 and from there decrease steadily to zero in the pure salt. The solubility of silica in vanadium pentoxide ranges from 1.8% at 750°C to 2.9% at 1050°C and the addition of sodium sulphate to this melt causes solubility to decrease until 18 mole % Na_2SO_4, from there it increases to a maximum at 58 mole % Na_2SO_4 and decreases to almost zero in the pure salt. The corrosion rates of alumina and silica in Na_2SO_4/V_2O_5 melts have been studied. The addition of sodium sulphate to vanadium pentoxide increases the corrosivity of the latter. The addition of vanadium pentoxide to sodium sulphate increases the corrosivity of the latter. At compositions between 30 and 70 mole % Na_2SO_4 in V_2O_5 corrosion rates are similar for both refractories. The diffusion coefficients for silica and alumina in these melts have been evaluated and for both systems a maximum occurs at 30 mole % Na_2SO_4. The kinetics of the reaction between sodium sulphate and vanadium pentoxide to produce vanadates have been investigated. Activation energies vary between 20 and 32 kcal/mole. Attempts were made to hot press firebrick to theoretical density. Results show that this should be possible at 1350°C under 1.15 kg/mm^2. The mechanism is viscous flow, above 1100°C with an energy of activation of 55 kcal/mole.

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CONTENTS.

Explanation of Symbols Used.

A	constant	
B	constant	
C	constant	
c	general concentration term.	g/ml.
c_1	concentration in the bulk melt.	g/ml.
c_A	SO_3 available for expulsion from a mixture.	wt.% or mole/
c_{SO_3}	SO_3 expelled from a mixture.	wt.% or mole/l
c_t	concentration at time t.	wt.% or g/ml.
D	Diffusion coefficient.	$cm^2/sec.$
D_i	Diffusion coefficient of species i.	$cm^2/sec.$
d	The bore of a sample tube.	cm.
dc/dt	rate of change of composition at time t.	units vary
E_{vis}	Activation energy for viscous flow.	cal/gmole
E_a	Energy of activation of a process.	cal/gmole
e	exponential.	
k	Rate constant.	units vary
k_o	Boltzmann's constant.	$1.38x10^{-16}$ erg/^{o}C.
L	The flowlength of a sample tube.	cm.
M	Weight of melt passed through a sample.	g.
N	Total weight loss from a sample.	g.
n	The 'order' of a reaction.	
P	Pressure	kg/mm^2
Q	Relative density.	
R	Gas constant.	1.98cal/g mole
T	Absolute temperature	^{o}K.
t	time	sec, min. hr.
v	Velocity	cm/sec.
$\bar{v}$	Plug flow velocity.	cm/sec.
v_i	Velocity of species i under the action of unit force.	cm/sec.
v_o	Velocity along axis of tube.	cm/sec.
w_A	Weight of platinum bob in air.	g.
w_L	Weight of platinum bob in liquid.	g.

Z	Corrosion rate.	g cm^2/sec.
ρ	Density.	g/ml.
η	Viscosity.	g/cm/sec.
τ_c	Critical yield stress.	kg/mm^2.
c_{eq}	Saturation solubility.	g/ml.

CHAPTER 1. INTRODUCTION.

THE PROGRESS OF THE WORK.

The work described in these pages is an attempt to clarify the corrosion of selected pure refractory oxides by constituents of oil ash slags. The Admiralty (now the Ministry of Defence (Navy) sponsored the entire project which began in 1960 when GOLDMAN (see ref, 1) investigated synthetic slags with sodium sulphate contents up to fifty per cent. Described here is the second phase of the work, concerned mainly with synthetic slags containing more than fifty per cent sodium sulphate.

Due mainly to logistics and economics the large naval vessels burn residual fuel oil in their steam raising installations. This heavy fuel is a non-distillate oil which remains after the higher fractions have been removed from crude oil. Residual oil contains metals as organic derivatives of high boiling point i.e. low vapour pressure. When the oil is burned, these derivatives break down. Sulphur containing compounds such as mercaptans and sulphides form SO_2. Some of this SO_2 then combines with the metal breakdown products to form sulphates, which collect on all fireside boiler surfaces. Vanadium is a major metallic impurity in the fuel oil and this forms with the sulphates, mainly sodium, low melting point mixtures which flow down boiler brickwork when at operating temperatures causing considerable corrosion. It is not the direct purpose of this work to investigate methods of minimising this corrosion, but rather to identify the most corrosive agents and thereby clarify the mechanism of corrosion, thus assisting indirectly.

CHAPTER 2. THE IMPURITIES IN RESIDUAL FUEL OIL.

If an impurity is defined as any constituent which is detrimental to use as a fuel, then oil has many (2A, 5, and Appendix 1). These impurities originate from several sources:-

a. Oil soluble or dispersable compounds which occur naturally in crude oil, both as organo-metallic and inorganic compounds from the strata in which the oil formed or the reservoir rock.

b. Solid particles either suspended or dispersed, picked up during recovery, transportation and storage such as sand, rust, wind blown dust, etc.

c. Water-soluble compounds in solution in water emulsified in the crude.

However, to investigate the corrosion of refractories by oil ash slags, it was considered necessary initially to study only three: VANADIUM, SODIUM and SULPHUR.

2.1. VANADIUM.

Vanadium is present in petroleum in its lowest state of oxidation (VO) as an oil-soluble organic complex associated with the asphaltic components of the fuel. It is almost certain that its presence results from biochemical concentration in certain compounds in the organisms from which the oil was derived (6). (This is assuming that oil was formed from marine organisms(7)). Vanadium has been detected in the blood of some contemporary marine animals and vandium porphyrin has been found in crude oil (8,9). However, GARNER et al (8) question that all vanadium and nickel are present as porphyrins. It is known that ethyl alcohol dissolves these porphyrins but when using this solvent their extraction yield was very low. Porphyrins have complicated molecular structures (see Appendix 2) and relatively high molecular weights (about 550 of which V is 51). Similar complexes are iron porphyrin (haematin) and magnesium porphyrin (chlorophyll). Vanadium is associated with the asphaltines of crude oil and these in turn are associated directly with the specific gravity and viscosity. The denser the crude, the more ash it can hold in suspension.

2.2. SODIUM.

Sodium can occur in fuel oil via all three sources listed in the first paragraph of this chapter. As far as this research is concerned, source (c) is not important. Sea water contamination of fuel oil is an important aspect of refractory corrosion and as such is dealt with in Section 2.6. Brine is sometimes associated with the crude from particular wells, (e.g. salt dome). It may be that another source of sodium is the deliberate addition of a base, such as sodium carbonate, to check corrosion in refineries by acidic components of crude (e.g. naphthanic acids).

2.3. SULPHUR.

Sulphur occurs in the majority of crudes to the extent of 0.5 to 3%. The sulphur compounds are mainly complex high boiling point compounds and therefore tend to concentrate in the residue. In a 3% sulphur oil, sulphur compounds probably represent more than 20% of the crude. Sulphur is basic to the crude and chemically associated with the constituent hydrocarbons, occurring in a variety of compounds of differing molecular weights and complexities, such as elemental sulphur, H_2S, organic mercaptans (R-SH), sulphides (R-S-R), etc. It has been suggested that the vanadium complexes are only rendered oil soluble by sulphur linkages between the porphyrin side chains and large hydrocarbon molecules (3).

2.4. RESIDUAL FUEL OIL.

Crude oil contains many valuable compounds, mainly hydrocarbons, which are relatively easy to recover by fractional distillation. There is, however, a limit beyond which the distillation does not progress. This limit depends on economics and local conditions.

The distillation residue, which may represent up to 40% of the original crude, is the basis of the fuel oil burned in large ships. It is possible that this oil may be used with no further treatment. More likely, the residue receives a simple filtration and the addition of some heavy distillate to reduce the viscosity. The oil is then known as "Bunker C Grade". There is no rigid specification for this oil, but the standard generally accepted is :-

Flashpoint	min.	66°C.
Water	max.	1%
Sediment	max.	0.25%
Viscosity	max.	6,500 sec. Redwood 1 at 38°C (100°F).

The Ministry of Defence (Navy) has a much tighter specification (see Appendix 8). This is still a very loose specification but it must be understood that this has to be so. Any tightening of the specification immediately means that firstly the cost increases and secondly its world-wide availability decreases. It is only fair to mention that the majority of fuel supplied is well within this specification. The present cost of Bunker C Grade varies between 20 and 25 pence per gallon (£ 8 to £ 10 per ton). Thus even the simplest purification process greatly affects the price and destroys the economics of using cheap fuel.

2.5. THE NATURE OF ASH FORMING ELEMENTS IN RESIDUAL FUEL OIL.

Naturally, oil companies wish to extract the maximum from a crude oil before abandoning it as residue. Thus the tendency is for improved refining and cracking techniques to reduce the amount of residue available from a crude oil. This has the effect of increasing the ash content of the fuel oil as the same amount of non-volatile ash components concentrate in less residue. This, coupled with the fact that newer sources of crude oil have yielded material with higher concentrations of particular components, (e.g. high vanadium crudes from Venezuela), is tending to cause concern to marine boiler makers and users (10). The inorganic ash forming constituents are virtually unchanged by refining processes. Emulsions break down and the water distills off, but of course, all solids dissolved in the water are left in the residue, often as micro-crystalline suspensions. Porphyrins have been detected in residual fuel oil and it is probable that there are several types of porphyrins which have different thermal cracking characteristics. Sulphur compounds also tend to be of high molecular weight and high boiling point. Thus the majority of them are found in the residue. The ash content of such fuels may be less than 0.01% and up to 0.1%. Variation in ash composition is enormous, depending mainly upon the source. Residues from different processes may be blended together in the refinery from considerations of properties unconnected with the ash composition, e.g. viscosity.

To these inherent ash constituents must be added the amounts picked up during transportation and storage before use. These include fine rust, scale, wind blown dust and a special case in marine use - sea water.

2.6. CONTAMINATION OF BOILER FUEL OIL BY SEA WATER.

Analyses of naval boiler slags demonstrate that large quantities of sodium are entering the combustion chamber. This problem does not occur in land based boilers and the suspicion falls on sea water. In 1939, the fuel oils burned by large ships were completely immiscible with sea water. Vigorous agitation of the two components produced unstable emulsions which separated into two distinct phases immediately motion ceased. Thus it was common practice to mix oil and water and to ballast empty fuel tanks with sea water. Nowadays it is not uncommon for residual fuel oil to accept 120% sea water in semi-stable emulsion. Soft asphalts in the oil act as emulsifying agents and the motion of a ship at sea is quite sufficient to keep 10-20% sea water in a stable emulsion. This may be burned and up to 12% may not be noticed by the engineer.

The causes of sea water in fuel oil are many. Sediment in fuel oil tanks is washed out using sea water. Empty fuel oil tanks may be ballasted with sea water and tanks may be leaky due to accident, poor repair or enemy action. Mishandling and carelessness must also be considered. It is correct to say that ship owners and designers are striving to eliminate contamination by all these causes.

The effects of sea water contamination are :-

a. Loss of thermal efficiency. Clearly 10% water carried means 10% less fuel available and thus the effective range of a ship is reduced. There is a considerable waste of oil in bringing this water to flame temperature. Start-up may prove difficult and the flame may often by extinguished by the action of a pocket of de-emulsified water.

b. Deterioration of furnace refractories. Cases brought to notice indicate that after months of steaming during which the brickwork has remained in a satisfactory condition, the slagging and subsequent failure of the bricks is sudden and unexpected. Firebricks may be reduced to less than one half original thickness and a dark glass-like slag appears on the walls and floor of the furnace (11). The reference quoted, dated 1948, attributes all these troubles to sea water but the situation is not thought to be as clear now.

c. The formation of bonded deposits in gas passages. The presence of 2% sea water can double the quantity of ash in an average fuel oil. A typical stack gas temperature is 150-200°C and thus all ash components which were liquid or vapour at flame temperatures have an opportunity to condense or solidify on the many tube banks through which they flow. Such deposits present a barrier to the conduction of heat into the steam and thus reduce thermal efficiency.

CHAPTER 3. THE ACTION OF FUEL OIL IMPURITIES.

On combustion, the first action of fuel oil impurities is to form an ash. This is not ipso facto a harmful action. Prior to 1940, little effect of fuel oil ash was noticed and in some cases, especially in coal fired boilers, ash affords a degree of protection to metal surfaces. In oil fired boilers the first problem is that oil ash leads to the formation of DEPOSITS on all boiler surfaces. The deposits in turn lead to CORROSION and most boiler malfunctioning problems stem from these two.

3.1. DEPOSITS.

These are the end products of a series of complicated physico-chemical processes occurring in hot gases and on boiler surfaces. Oil is burned with 10% or more excess air and flame temperatures are of the order of 1600°C. At such temperatures many of the possible ash constituents (see Appendix 1) are either molten or vapourized.

The combustion of fuel oil droplets is considered to take place via three indistinct stages:-

1. Evaporation and combustion of higher hydrocarbons.

2. Thermal cracking of heavier hydrocarbons and combustion of lighter fractions followed in turn by the tarry residue.

3. Combustion of the residual carbon matrix.

Compounds with high vapour pressures at flame temperatures are completely vapourized. Other compounds depending on their properties will be solid, liquid or vapour or combinations of the three. Vanadium complexes are decomposed and then oxidised:-

$$\text{V complexes} \rightarrow V_2O_3 \rightarrow V_2O_4 \rightarrow V_2O_5$$

the oxidation is probably not complete until the final burn out of carbon in stage 3. Most V_2O_5 will be vapour at flame temperature. Some reactions forming double oxides and sulphates will occur and these too will be in various physical states. This then is the mixture from which deposition takes place:- oxides of Na, Mg, Ca, Al, Fe, etc, vaporised NaCl and V_2O_5 possibly Na_2SO_4 and $CaSO_4$, silicates, vanadates, SO_2 and SO_3, O_2, N_2, water vapour and CO_2.

3.1.1. THE MECHANISM OF DEPOSITION.

There are four accepted mechanisms of deposition from oil ash gases (5,16). The distinctions between them is not precise and the actual mechanism depends on parameters such as particle size, particle velocity, gas pressure and temperature.

1. Particle Impaction - whereby the inertia of the particle is sufficient to overcome the deflecting drag forces and the particle impinges on the catchment surfaces. This mechanism becomes increasingly important as deposition progresses. Catchment surface area increases as does turbulence due to the rougher surface.

2. Particle Diffusion - whereby particles in the gas stream enter the boundary layer surrounding a tube and are deposited by Brownian motion (random walk).

3. Thermal Diffusion or Precipitation - particles within the thermal boundary layer surrounding a cooled tube are subjected to a thermal force directing them towards the tube. Deposition from this mechanism is expected to be small but may form the base for the intense impacted deposits.

4. Vapour Diffusion. This is the mechanism by which the majority of deposits are initiated (3). The vapourized oil ash constituents are transported across the temperature boundary layer to condense on the tube surface.

Thus it is a molecular process whereas the previous three are particle processes. Particles deposited by the vapour diffusion process are very small and therefore unlikely to move again since the drag on them is very small and the force necessary to move them very large.

These then are the mechanisms by which ash may be brought to boiler surfaces. It is assumed, though references are few, (3-ref.174) that these mechanisms will also apply to refractory surfaces. The contribution by thermal diffusion is probably very small except during start up when refractories are cold. Whether the ash will deposit and build up depends on a number of other factors such as the physical state of the ash (liquid or solid), size of particles and temperature and nature of the surface. Thus the formation of an ash deposit and its degree may very not only with fuel ash composition but also from one boiler to another and even with the load condition.

Whilst it is quite possible for a deposit to form from a dry ash in a very finely divided state, the possibility is very much greater if any of the particles are sticky. It is certain that the larger particles which arrive at a surface by impaction will not deposit unless they are themselves sticky or molten, or the surface is already coated with a sticky material. If the particles and the surface are dry, they will either bounce off or shatter on hitting the surface. Appendix 1 shows that many compounds are liquid at boiler temperatures.

It is incidentally the opinion of reference (18) that by far the greater proportion of solid matter in oil passes through the boilers and fortunately out through the stacks. This opinion is at variance with that of BUSBY (19) who considers that virtually the whole of the vanadium in the fuel oil used eventually enters the glass passing through an oil fired glass tank. Naturally combustion conditions and aerodynamics are different in these two cases, but it would be surprising if this were enough to account for the difference between these two opinions. BROWN and RITCHIE (36) consider that the compactness of a naval boiler leads to higher deposition rates.

3.2. THE NATURE OF THE DEPOSITS.

It is difficult to generalise for all cases, but with naval boilers the opinion of reference (18) is in good agreement with most workers.

On superheater tubes a thin, hard, almost vitreous coating of high vanadium ash about 3 mm thick is formed next to the metal surface. This is often then topped by massive earthy deposits which block gas passages. These are however loosely held and may be soot blown.

The vitreous, nearly black layers of material which are so notoriously difficult to remove are composed of large intermeshed crystals of sodium vanadyl vanadate I, $Na_2O.V_2O_4.5V_2O_5$, which act as a ceramic bond for the hard layers. Other cryxtalline materials present in the hard layers can be observed as small particles enmeshed in a matrix of long needles of the vanadium compound (See Plate 1). In spite of the extreme hardness of these layers, the structure is not dense and water-soluble fractions can be extracted from the interior of the deposits without noticeably affecting the hardness or disturbing the ceramic bonding of the layers.

The composition of these hard layers is invariably $Na_2O.V_2O_4.5V_2O_5$, sometimes mixed with other sodium/vanadium oxides or sodium sulphate. These layers are the most difficult to remove by present cleaning methods if they are

PLATE 1. TYPICAL STRUCTURE OF DENSE OIL ASH DEPOSIT (x 75)

tightly bonded to the metallic surfaces because they are not appreciably soluble in water or dilute acids. This is also the material which when molten is an excellent solvent for most materials used in boiler construction.

The portions of oil-ash deposits which are soft and crumbly are composed of random particles of more or less pure compounds concentrated in clusters. These deposits are easily water washable. Their appearance is as a chalky-white material (sometimes hidden by carbon), usually either sodium sulphate or a mixture of this with sodium metavanadate and/or other oxides which may all colour. It is accepted that sodium suphate binds these deposits (11).

Deposits on refractories are in the form of a smooth, shiny, hard and brown matrix with macroscopic pieces of refractory randomly distributed. In the cold boiler this slag hangs as stubby "icicles" showing that at boiler operating temperatures the whole surface layer was probably molten and running down under gravity. The pieces of refractory which are separate from the actual wall are present primarily as a result of thermal cracking or "spalling" probably accelerated or assisted by the presence of the slag on the surface. There is also the possibility that the slag attacks certain refractory components preferentially thus releasing more resistant particles into the slag.

The colour, composition and condition of the slag suggests that it was first a hard, almost vitreous coating, high in vanadium as described above. This would undoubtedly be molten when the boiler was operational because brick temperatures approach flame temperatures (20). In this condition it would be able to accept and fuse with any other further constituent offered by the furnace gases.

3.3. THE EFFECTS OF DEPOSITION.

The effects of deposits are twofold. Firstly, all deposits have a relatively poor thermal conductivity. Thus there is an additional barrier to the transfer of heat from flame to water. Efficiencies drop and to combat this forcing rates increase. This serves in general to aggravate the problem and deposit build up in the superheater banks can become so bad that gas flow becomes impossible. Removal of such deposits, once formed may be all but impossible by ship's personnel. Complete retubing in repair yards is occasionally preferred to manual cleaning methods because the ultimate cost and effort may be less.

The second effect of deposits is that they lead to corrosion. This fact is more relevant to this research and is treated separately in the next section.

3.4. CORROSION.

As a simplification, corrosion by fuel oil ash arises from the behaviour of alkali sulphates and complex sodium vanadates formed from the reaction of inorganic ash constituents with oxides of sulphur and vanadium oxides from the region of the flame. It is generally agreed that little corrosion occurs without the presence of a molten or semi-molten phase (17,22,2F). When used in this text, the term "corrosion" refers to the undesirable removal of the surface of refractories. This is assumed to take place by chemical reaction or physical dissolution by chemicals which are molten only at boiler operating temperatures.

3.4.1. CORROSION OF SUPERHEATERS.

Over the past decade, maximum steam temperatures have remained roughly constant at about 565°C. (2E). It might therefore be expected that even localised metal temperatures would not exceed 800°C. This is low compared with flame and refractory temperatures but severely damaging metal corrosion is possible. The volume of scientific literature on this subject is amazing and in fact most references given at the end of this work are mainly concerned with metal wastage. As one might expect the number of opinions and counter-opinions are many and the subject will only be briefly discussed here.

There are three mechanisms by which the effective metal thickness is reduced.

A. Surface Oxidation.

Most of the hot gases in the area of the superheater banks is oxidising in nature. Thus the properties of oxide films and their effects on metals and alloys is important. Sometimes such films are protective because they tend to stifle further reaction. Although oxidation never stops completely, the rate of reaction may decrease considerably. Under certain conditions of exposure, and particularly at higher temperatures, most alloys will form a scale which becomes thicker on continued exposure. Such scales may blister, crack or spall depending on their properties and adhesion to the parent metal.

B. Solution by Molten Salts.

This mechanism is effectively accelerated oxidation attributed to the flowing action of molten ash. Vanadium compounds inhibit the formation of, or destroy, the normal protective oxide layer, leaving oxygen-permeable areas of little scaling resistance. The vanadium compounds act as oxygen carriers with the formation of vanadates as an intermediate stage. In a reducing atmosphere no attack by vanadium salts occurred (3 ref.8).

C. Subsurface Attack.

Accelerated corrosion is also attributed to an intergranular penetration process of sulphidation, and perhaps oxidation. This type of attack is NOT evident by visual observation and is usually detected by metallographic examination. It has the effect of reducing the tensile strength of the metal.

3.4.2. CORROSION OF REFRACTORIES.

Failure of a naval boiler due to corrosion of refractories has occurred in as little as fifty hours steaming. Although such events are fortunately rare the problem arises to a lesser extent in all refractory lined boilers.

The most important factors determining the life of a particular refractory material in boilers are:-

1. Operating temperatures.
2. Rate and frequency of changes in temperature.
3. Degree of contamination by slags.
4. Details of design and installation.

Of these, fluctuations in temperature which cause thermal cracking or "spalling" are by far the most common source of trouble (20). Operating temperatures are high in fighting ships as the forcing rates are some six times higher than in power station boilers. Refractory temperatures are likely to be as high as 1500°C. (20). This is higher than many ofthe fusion points mentioned by JONES and HARDY (21 - see Appendix 4). The effect of increase of temperature is to reduce the viscosity of the slag and increase the mobility of individual ions. Also the solubility of the refractory in the melt is increased as are any reaction rates between slag and refractory. These important aspects are considered further in a later chapter. Very steep temperature gradients form in hot faces on heating up a boiler. These are the conditions under which spalling occurs. The presence of a slag on the brickwork does have the effect of modifying the structure of the refractory material and making it more liable to break down under temperature changes. McCLIMONT (10) considers alkali presence very important in the slag acceleration of spalling. Again in fighting ships the problem is worsened by the fact that boiler load may vary from light loading to full power tens of times in one day.

There is no doubt that oil ash slags can flux refractories. JONES and HARDY (21) give the details of an investigation of a ship reporting severe slag attack. After burning 1,430 tonnes fuel oil, $1\frac{1}{3}$ tonnes slag had accumulated on the boiler floor. This slag was molten under steaming conditions. An analysis of a sample of the slag was compared with the analysis of dust collected from the radiant section boiler tubes. Contents of refractory materials, vanadium pentoxide and alkali metals were 81%, 12.5% and 3.6% and 7.8%, 35.3% and 47% respectively. (See Appendix 4). Thus the slag on the floor had fluxed large proportions of refractory material, lowering its fusion point to 1200°C. The authors conclude that vanadium compounds in general are reactive with refractory materials and will cause significant reduction of the fusion point of such materials. These effects are accelerated by the presence of sodium compounds. Fireclay bricks should not be used in furnaces where vanadium bearing fuel oils are used but high alumina and magnesia bricks seem to be suitable.

TAYLOR and BOOTH (23) consider that slag attack results from the chemical reaction between refractory material and ash from the fuel. They suggest that sodium salts and iron oxide are the important constituents.

As always with refractories, porosity plays an important role in the operational behaviour. A reactive fluid slag such as that from a fuel ash with a high alkaline content, drains away and being continually renewed, rapidly erodes the lining. This action increases with increasing porosity. A viscous slag on the other hand, may form a thick coating without removing the firebrick surface. When this occurs, however, there is some contamination of the surface with more fusible compounds which tends to increase the devitrification and consequently the liability for spalling to occur. Thus the resistance to slag attack is greatest when the refractory material is dense and close textured. Such a structure unfortunately offers poor resistance to spalling. Therefore slag resistance is NOT compatible with spalling resistance.

GRAY and KILLNER (11) filled cavities in firebricks with salts from evaporated sea water both alone and with additions of iron rust and vanadyl sulphate. Heating with an oxy- coal gas flame in each case produced, on cooling, a dark, hard, glass-like slag with much evidence of pitting and penetration of the brick. The same test using vanadyl sulphate alone produced no slag, no evidence of attack and only slight penetration of the brick.

In contrast to this, COLLINS and HERBST (3 ref.42) found that in the absence of vanadium, sodium salts/firebrick slags had no effect on kaolin-alumina brick.

Individual bricks are sometimes held in position by metallic or ceramic keys. These are often a source of weakness as failure of the securing devices can lead to collapse of the refractory lining. Permanent volume changes may result in cracks in the working face or open joints and loss of jointing material. Consequent slag attack on underlying insulating bricks can be catastrophic.

It is highly undesirable for refractory surfaces to be swept by flame. This means that wastage will increase due to increased spalling but also if the refractory surface is blanketed by flame, there will be no heat loss from the brickwork by radiation to the tubes. Thus refractory temperatures increase, boiler efficiency decreases and the forcing rate must increase to counteract this effect, only to aggravate the problem. BAKER (43) also considers that flame impingement leads to excessive carbon formation on brickwork. This carbon then penetrates the surface and leads to disintegration by reduction of refractory oxides.

The extent of deposits and the degree of corrosion depend on the fusing temperature of the ash constituents. In recent years constituents having low melting points have been increasing and at the same time general boiler temperatures have increased. The relation between boiler temperature and extent of deposits is particularly noticeable in the case of brickwork (10). In low forcing rate boilers (therefore low furnace temperatures), such as were more common in the past, deposits were virtually non-existent. The simultaneous changes in forcing rates and the nature of fuel oil supplies make it difficult to sort out the relative significance of these two factors.

3.4.3. THE CORROSION OF OTHER SURFACES.

In general, it can be stated that dustlike material deposits in gas passages beyond the boilers and liquid sulphuric acid accumulate when the temperature of the gas stream falls below a certain minimum value which is dependent on the firing procedures. The dustlike deposits usually contain sodium sulphate with various proportions of ferrous sulphate, ferric sulphate, and sodium vanadyl vanadate I. These deposits are usually light and loosely bonded and aside from a high percentage of adsorbed sulphuric acid are essentially composed of unburned carbon.

The sulphuric acid forms from the action of sulphur trioxide on water and may contain sufficient sulphate to qualify as fuming sulphuric acid while the boilers are operating. This rapidly changes to the highly corrosive dilute sulphuric acid on standing or under the influence of a blast of moist air from the blowers when the boilers are down.

3.5. THE EFFECT OF INDIVIDUAL COMPONENTS.

When fuel oil ash troubles were first attributed to vanadium, BOWDING, DRAPER and ROWLING (5) decided to run a test with a fuel containing almost no vanadium. The test rig was a low rated gas turbine but as the results concern deposition only, they are considered relevant. The fuel used contained 4.6 p.p.m. vanadium as V_2O_5 and 1440 p.p.m. sodium as Na_2O, and the rate of deposit build-up was found to be far greater than had been obtained with any previous fuel.

To investigate further the effect of different ash compounds, a series of tests were run using gas oil as the fuel, into which was dissolved in each case a different organo-metallic compound. It was seen that sodium was by far the worst offender in deposit formation (see Appendix 5). This high deposit rate of sodium has been confirmed by other workers (14A,). Other metals tested gave curves which, after an initial rise, levelled off, indicating that an equilibrium condition had been reached.

As the melting point of sodium sulphate is above that of vanadium pentoxide, the authors explained the bonded appearance of the deposits gained by the presence of small quantities of sodium pyrosulphate (M.P. 400°C).

Vanadium on its own is not considered particularly hazardous, but after sodium has led to the formation of deposits, vanadium compounds lower their melting points, reduce viscosity and aggravate corrosion. McCLIMONT (10) states that cases of gross wastage of brickwork due to slag erosion can always be associated with some mishap which has resulted in gross contamination of the fuel oil by sea water (i.e. sodium) reaching the burners.

Sulphur is a problem in all phases of oil refining and utilisation and also a significant factor in high temperature deposition and low temperature corrosion in boilers. Some authors consider that virtually complete removal of the sulphur from residual fuel oils burned under modern boiler conditions may be necessary to reduce this factor to tolerable limits (3). Certainly, sulphur must play a leading role in the formation of sulphates which are found in all boiler deposits especially the light-coloured, water-soluble, friable deposits in superheater tubes. The formation of sulphur oxides and sulphates is discussed at length by many authors (2,3,4) but the highly-corrosive $Na_2O.V_2O_4.5V_2O_5$ (M.P. 560°C) can still be formed from fuel oils containing little or no sulphur.

CHAPTER 4. METHODS OF COMBATTING CORROSION.

The most important fact about naval boilers and gas turbines is that they must be capable of accepting all types of residual fuel oils from all parts of the world regardless of content or quality of ash. This is not so much on account of their cheapness as on their greater availability throughout the world in time of war. All improvements to boiler efficiency and output must be made with full regard for this fact. Thus, any oil treatment plant must be installed on board ship and therefore must be small for small ships unless a treatment for residual oils is discovered that is so cheap and simple that it rapidly becomes universal.

The various methods of combatting corrosion from residual fuel oils may be placed under four broad and often overlapping headings:-

1. REMOVAL OF ASH CONSTITUENTS.
2. USE OF ADDITIVES.
3. DESIGN AND OPERATION IMPROVEMENTS.
4. IMPROVEMENT OF MATERIALS.

4.1. THE REMOVAL OF ASH CONSTITUENTS.

As already mentioned, a great effort is being put into the purification of fuel oil. At present, all processes are ruled out on economic grounds for marine boiler use. However, if the ash content of fuel oils continues effectively to increase and boiler temperatures rise then corrosion and deposition may become severe enough for some purification process to be used. Indeed, it may be argued that the glaringly obvious solution to all oil ash corrosion is to remove all ash forming constituents before use. The strong argument against this point is the scientists archenemy - economics. At the time of writing, all oil purification processes are more expensive than further distillation.

There are four main methods available:-

1. FILTRATION.
2. CENTRIFUGING.
3. SOLVENT TREATMENT.
4. CHEMICAL AND CATALYTIC PROCESSING.

4.1.1. <u>FILTRATION</u>.

Simple filtration applies only to insoluble inorganic components, present in macroscopic sizes such as sand and dirt picked up by careless handling of the fuel and iron scale from storage tanks and fuel systems.

SHIELDS (12) in 1955 indicated that improved residual fuel for gas turbines was economically possible using a rotary vacuum filter and a precoat base of diatomaceous earth and calcined clay filter aids. Results are shown in Appendix 3. The sodium content ofthe oil was greatly reduced. Substantial reductions were achieved in calcium, aluminium, iron, lead, magnesium and total ash. The content of vanadium was little affected. NCG cannot understand why very little reference, complimentary or otherwise, is made to this singularly economic process.

4.1.2. <u>CENTRIFUGING</u>.

Centrifuging is again applicable to inorganic insoluble material only. It is effective in removing water from the fuel and where the water contains dissolved compounds these would also be removed. Thus it is usual for a sequence of water washing to precede the centrifuging.

<u>Water washing</u> can largely remove sodium which is usually present as simple inorganic salts. Such treatment can easily remove 95% of the total sodium present.

Disadvantages of this process, for ship board operation are the space required for the centrifuge and ancillary equipment (minimum 20 cubic metres) and a not inconsiderable supply of fresh water. DEAR (2B) has published results of an electric separating system to replace the centrifuging. At optimum operating conditions the plant achieved a 90% reduction in the sodium content of a typical 6,000 sec. heavy fuel oil. The melting point of the laboratory prepared oil ash was increased by the process by up to 200°C. Cost 2.34 shillings per ton for 520,000 tons of treated oil per annum.

Water washing with dilute alkali is effective in the removal of (a) traces of oxygen compounds such as carboxylic acids and phenols, (b) hydrogen sulphide, (c) mercaptans of low molecular weight.

Water washing with a magnesium sulphate solution is useful in creating a greater density differential between oil and water and thus achieving greater separation. Effective removal of 56 - 98% sodium and 15 - 98% calcium was obtained (13). Cost 5/10d per ton reducing to 2/- per ton on large scale plant. Vanadium is virtually unaffected by water washing but there is evidence that the reduction of sodium to 10 p.p.m. in the fuel oil renders the vanadium almost harmless. CROSSLEY (17) is certain that the complete removal of sodium from fuel oil would prevent external corrosion in superheaters. If water washing with magnesium sulphate is employed, a Mg/V ratio of at least 3 can be easily gained, which further reduces corrosion by vanadium. There is considerable opinion that reduction of the Na/V ratio to 0.3 or less considerably reduces corrosion and deposition (3, 14A). Equally strong are the views that the Na/V ratio is unimportant (2C, 14B). BUCKLAND and

SANDERS (13) reduced the Na/V ratio of a fuel oil from 1.64 to 0.04. This change produced a twelvefold increase in corrosion! All types of water washing produce an emulsion at some stage in the process. A quantity of organic material is always removed together with the water and must be included in economic calculations.

4.1.3. SOLVENT TREATMENT.

The bulk of the ash-forming constituents in residual oil can be separated, together with a large proportion of the fuel by the use of certain selective solvents. These precipitate various colloidal asphaltenes depending on the solvent, its concentration, temperature, etc. For example, liquid propane will precipitate 97% of the vanadium, 99% of the nickel and 86% of the iron in a fuel oil, regardless of its origin, under favourable conditions. The process is, however, wasteful and expensive. Also ship board units are at present out of the question.

4.1.4. CHEMICAL AND CATALYTIC PROCESSING.

Hydrofining or hydrodesulphurisation is concerned with the removal of sulphur from any oil. Of all the processes described here it is probably the most exciting. The oil is treated with hydrogen under mild conditions of temperature and pressure (210 - 370°C and 14 - 70 kg/cm^2) in the presence of a catalyst such as cobalt molybdate. This treatment results in the hydrogenation of certain unsaturated hydrocarbons and in other changes. In particular, the sulphur compounds react with hydrogen to an extent which depends on the nature of the oil and the reaction conditions, forming H_2S which can easily be removed by alkali washing. It is therefore possible to remove sulphur from petroleum distillates and residues to any extent which is economically justified (15). The prospect of treating the complete crude oil before refining and the subsequent on all by-products must be of considerable interest to the oil companies. Already, some local health authorities in NORTH AMERICA, JAPAN and SWEDEN have specified a maximum value for sulphur in fuels in an attempt to reduce air pollution. Figures of around 2.8% are quoted with plans in the future for less than 1%. The economics of hydrofining seem to be marginal. VOORHIES et al (2D) quote the cost for the reduction of a 4.1% sulphur Kinosit crude to (a) 2,5% as 11/6d per ton, (b) 1.0% as 15/7d per ton. It has been suggested that the vanadium compounds are only rendered oil soluble by sulphur linkages between the porphyrin side chains and large hydrocarbon molecules (3). Thus it would be expected that some vanadium should be removed by the centrifuging process separating the alkali wash.

Ion-Exchange methods have been used for the demineralisation of fuel oils. Essentially the process involves preheating the oil to perhaps 110°C and passing it through a bed of cation exchange resin. The resins are of the hydrogen or ammonium type and the process results in the removal of sodium, magnesium and calcium. Details regarding performance and cost are sketchy and the process does not seem to be seriously considered.

Iodine is useful in removing vanadium and small scale tests showed a removal of from 60 to 90% (3). The iodine apparently reacts with the asphaltic portion of the oil, rendering it insoluble and precipitating it with the associated vanadium compounds as a tarry residue. More than 5% iodine is needed and the oil loss on processing is about 15%. Thus the process is very unsound economically and the use of other halogens were not successful (3). VOORHIES, ADAMS, KIMBERLIN and JAHNIG (2D) mention a vague "demetallization process" in which they claim that it is technically feasible to remove as much as 90% of more of the vanadium in a residual fuel oil. The single stage process gives a loss in oil yield of no more than 0.5% and the "reagent" is recoverable. VENEZUELAN crude and residual fuels were tested and they suffered a slight increase in viscosity. Some 75% of the vanadium is readily removed by a "mild treatment" and 20% of the nickel. To remove 90% of the vanadium costs 10/- per ton in a plant treating 4300 tonnes per day.

4.2. THE USE OF ADDITIVES.

The required effect of additives, however applied, is either to affect the physical nature of the ash by reducing its adhesive or fluid powers or to chemically affect various constituents to produce a relatively inert substance. As boilers are normally poor ash collectors, there has been little hesitancy in the use of additives. SAMMS and SMITH (24) have suggested the qualities of the ideal additive:-

(a) It should combine chemically with the corrosive components of the ash to produce compounds of high fusion point.

(b) Its cost must be low compared with fuel costs.

(c) The quantities required must be small.

(d) It must be easily obtainable.

(e) It must lend itself to easy introduction into the boiler.

As with all phases of the fuel oil ash problem, its complexity is aggravated by the particular application in fighting ships. The effects of additives are again reduced in the case of refractories. These two considerations mean higher temperatures and therefore more components will be molten and the task of the additive extended.

Considerations under (c), (d) and (e) have particular reference. While considering these points, it is convenient to divide additives into two groups:-

1. Additions to the oil.
   - a. Oil soluble additions.
   - b. Water soluble additions held in an emulsion.
   - c. Dispersions or suspensions.
2. Additions to the air or boiler.
   - a. Mists or finely divided additions.
   - b. Solid additions.
   - c. Sprays of water solutions.

4.2.1. ADDITIONS TO THE OIL.

In general these are more effective as they are easier to use and upon burning have direct contact with the ash, increasing the possibility of an early and complete reaction taking place.

a. Oil soluble additions.

The advantages to be gained by such additions are ease of addition to fuel and fuel oil/additive mixture stability. Elements selected are usually employed in the form of naphthenates although silicones have been used. Some additives reduce the amount of deposit formed while others modify the deposit into a fusible, more bulky deposit which may be soot-blown or water washed.

Many metals are quoted as being useful in this respect and it is probable that any metal having a high melting point oxide under furnace conditions, could be effective as a deposit reducing or modifying additive. Such additives will be less effective on reffactories due to the higher temperatures. Also oil soluble compounds are expensive and do not appear to be any more effective than other methods of addition.

The special case of ethyl silicate has particular reference to this work. On combustion, fine silica is produced which has the dual ability of saturating the slags on the refractory surface to minimise dissolution and of increasing the viscosity of the slag by the production of silicates.

b. Water soluble additives held in an emulsion.

These produce the same effects as oil soluble additives but have the advantage that cheaper compounds may be used. Saturated aqueous solutions of these are mixed into an emulsion with the fuel oil which is either stable or is kept stable by agitator or ship motion. Naturally, a lowering of thermal efficiency accompanies the combustion of such emulsified fuels.

c. Dispersions.

Some potentially useful materials are cheap, but only in solid form. Substances such as kaolin and dolomite are NOT readily available in oil or water soluble forms. It is possible, however, to add these to the oil as a dry powder, dispersed in the fuel by high energy mixing. Dispersion must be good to give even distribution and a stable suspension, and this action often leads to severe wear on nozzles and fuel pumps. An interesting use of very finely divided silica is quoted by HANSEN (27). The treated silica was added to the oil in the tank trucks on arrival and the resultant pumping from tank to tank was sufficient to keep it in suspension. The cost of treating the oil was 2/- per ton and resulted in the following beneficial effects:- chemical reaction with ash components to form less corrosive or less catalytic compounds e.g. sodium silicate; loosening of the oil ash and raising the melting points of deposits; adhesion of molten ash constituents on the surface of the silica; the cost of the additive treatment was less than the cost of replacing dampers or soot blowers that were previously destroyed by oil ash corrosion.

4.2.2. ADDITIONS TO AIR OR BOILER.

Again, with the object of using cheaper materials, they may be added conveniently and at will either with the combustion air or directly into the boiler.

a. Mists or finely divided additives.

These may be added by a metering device directly into the combustion air. Substances such as kaolin and dolomite have been used with success, but more spectacular is the use of finely powdered metals e.g. zinc (26). This firstly used up excess oxygen thus helping to suppress the formation of V_2O_5 and SO_3 and secondly the zinc oxide formed has a beneficial effect on deposits.

b. Solid additions.

The inspection port in a boiler is a reasonably convenient point for the addition of modifying solids. Distribution of the additives within the furnace is very poor but the cost of the treatment is low.

c. Water solution sprays.

An extra nozzle is installed into the burner wall and a water solution of the required chemicals is sprayed into the furnace. Magnesium, calcium and aluminium salts have been used and included here is the use of a calcium/magnesium oxide slurry which was sprayed directly into superheater tubes. KECK (3, ref.87) found that only small amounts of deposit were formed and these were easily removed.

4.2.3. GENERAL CONCLUSIONS.

The method by which the addition is made is not of the greatest importance. It is presumed that for each case there is a suitable method. Of all the elements tested magnesium is favoured by most, followed by aluminium, calcium, and possibly zinc. These may be used as pure compounds or as natural products, e.g. kaolin and dolomite. However, opinions vary so widely that no instances will be quoted.

Better success is achieved by the use of a combination of methods. TIPLER (3, ref.238) used magnesium naphthenate in oil solution and powdered kaolin, in a gas turbine. The combined effect of the two far exceeded their added effects, and it is suggested that the presence of aluminium silicate favours the formation of additive sulphates. These results are confirmed by Esso Research (3, ref.57) and NILES and SIEGMUND(2G). Zinc vanadate appears to resist sulphation and the presence of zinc oxide with calcium oxide in an additive considerably increased the efficiency of the latter (3, ref.132).

Trade literature (25) describes the use of an oil additive combined with a solid additive to the combustion chamber. The oil additive contains compounds which upon combustion give atomic iron to react with atomic oxygen and suppress vanadium pentoxide and sulphur trioxide formation. Crystals added to the combustion chamber give copper chloride to reduce the ignition temperature of carbon and reduce smut deposits and zinc to reduce corrosion by deposits. During a controlled test an increase of thermal efficiency of 3.5% was gained. The equivalent cost of chemicals was 2½%. Ironically, the use of an alkali metal salt in conjunction with a magnesium additive has reduced corrosion by high vanadium slags. Also boilers burning mixtures of coal and oil show little evidence of metal corrosion (3), thought to be due to the high calcium content of the particular coal.

Some workers (8,4, 3 ref.57) conclude that additives are likely to be the only method of combatting corrosion likely to be cheaper than distillation. However, for additives to be really effective, the type, quantity and method of application would need to be varied with such variables as furnace load, type of fuel and its ash qualities. Unfortunately, it is often the case that the only factor known about a fuel being loaded is its price (10).

4.3. DESIGN AND OPERATION IMPROVEMENTS.

If steam generation is to progress, then improvements in design and operation must be made. These do not always benefit the oil ash corrosion problem, especially the trend for ever-increasing furnace temperatures. Thus, listed here are several methods which have been shown to reduce deposit formation and/or corrosion although often at the expense of efficiency.

4.3.1. FURNACE DESIGN.

The design of the furnace is always changing. Walls consisting completely of refractories are avoided in the attempt to gain the maximum metal area exposed to the hot gases. Designs in operation at the present time include a refractory wall with water tubes just below the surface. Heat conduction to the tubes is assisted by studs which project to the surface. An advanced design of this is the tangent tube wall (see Appendix 6). Both these designs permit cooler surfaces and therefore reduce the corrosion problem. It is possible, however, that deposition is increased. Actual flame impingement on refractory surfaces is particularly harmful and the development of short flame lengths minimises this condition.

Physical removal of deposits whilst the boiler is in operation is possible especially if the deposits have been modified by an addition such as magnesium. Soot blowing with steam has proved far more effective than air alone and steam has been shown to be generally effective in reducing deposit formation probably by increasing the volatility of vanadium pentoxide.

It is possible to consider ash removal from the gas stream but the problems involved are very great. In gas turbine systems such as cyclones, electrostatic separators and filtration by screens of refractory material have been suggested (5). All methods have met with problems which indicate that application of such devices in naval boilers is at present impossible.

4.3.2. COMBUSTION CONTROL.

This is one method of minimization of deposition and corrosion which has not only been proved successful but is also economical. There are two aspects to such combustion control. The first is to minimise the quantity of excess oxygen entering the furnace. In this way the formation of sulphur trioxide is minimised and the tendency for high melting points V_2O_3 and V_2O_4 to form the low melting point V_2O_5 is suppressed. Thus possible deposit material will have higher melting points and will either bounce off furnace surfaces or be only lightly held.

The second aspect is the control of oil droplet size or air mixing conditions to avoid complete combustion of the droplet. A small percentage of the fuel leaves the combustion chamber as solid carbon and takes with it a high percentage of the oil ash. The two aspects are complementary, the presence of elemental carbon indicates in theory that sulphur and vanadium should not be oxidised.

CROSSLEY (17) quotes several examples of EUROPEAN power stations running on low excess oxygen. MERKSEM power station in BELGIUM has been operated for two years on 0.2% excess oxygen in flue gases, without any deposition or corrosion problems. SCHILLING power station in HAMBURG has operated successfully on 0.2% excess oxygen for more than five years.

BOWEN, DRAPER and ROWLING (5) experimented with a gas turbine rig fitted with lower pressure fuel atomisers. They achieved low deposition when burning a fuel known to give high deposits using conventional spray equipment. The low order of deposits was considered due to the presence in the combustion gases of hard, spherical carbon particles, ranging in size from 1-50 microns. Approximately 50% of the ash components were associated with these spheres, which were considered to be the coked residues from incomplete combustion of the larger fuel droplets resulting from the relatively low pressure atomisation (2J, 23). Two functions were served by the spheres; the first being the tie-up of ash components in an innocuous form and the second, the erosion of deposits formed. Combustion loss due to the particles was only 1.1% of the total heat input. The boilers in fighting ships have a large power to volume ratio and the residence time of combustion gases in the furnace is small. Mixing efficiencies are such that near-stoichiometric burning would probably lead to combustion continuing in the stack and the formation of smoke (36). To counter this, a two part furnace has been proposed (2H) and is now functioning. Burning takes place in the first part of the boiler with about 30% deficiency of air at a temperature of 2000°C. About half the heat energy of the oil is then removed in the superheater tube bank. The gas leaves these tubes at approx. 900°C and air is then added to bring the mixture up to stoichiometric proportions. Combustion takes place at 1450°C, the rest of the heat in the fuel being recovered in another section of the boiler.

KEARTON (2E) has also suggested the possibility of preheating with a poor fraction of dirty oil and using the clean fraction for the final stage.

4.4. IMPROVEMENT OF MATERIALS.

General attempts to improve boiler constructional materials will, for convenience, be considered under three headings:-

1. Improvements in metals.
2. Protective coatings for metals.
3. Improvements in refractories.

4.4.1. IMPROVEMENTS IN METALS.

There is a vast amount of literature and research on this topic, as metal wastage is more severe than refractory wastage. Many different systems are described for contacting melt, metal and atmosphere, understandably arriving at opinions which sometimes conflict. This does not necessarily indicate that the several conclusions may not be useful as metals are called to act under various conditions of service in different types of boilers.

High nickel alloys are most resistant to high vanadium attack but are prone to intergranular sulphidic attack by high sodium ash and sulphur atmospheres. Chromium in ferrous alloys up to 30% is resistant to high sodium ash and sulphur attack, but is less resistant to vanadium salts oxidation. This is preferable to high nickel but fabrication of high chromium steels and irons is difficult even by direct casting.

Experience in the Ceramics Laboratories of Imperial College has shown that a combination steel (25% Cr, 12% Ni) is both easy to cast and machine.

Most promising of all alloys used was a 65% Ni, 35% Cr alloy. This was relatively easy to cast and machine and there was no sign of brittleness (intergranular attack) after several dozen runs. There is evidence that even higher chromium alloys will prove still more successful e.g. 50% Ni, 50% Cr; 40% Ni, 60% Cr. (29). A more detailed report of experience with heat resisting alloys is given in Appendix 7.

4.4.2. PROTECTIVE COATINGS FOR METALS.

Corrosion resistant coatings are a means of corrosion proofing relatively low grade alloys. Many of the more resistant alloys are considered too expensive for large scale use; some are not easily worked and some have not the necessary mechanical strength for high temperature, high pressure application.

Three broad methods have been used for surface coating or surface treating such alloys.

1. Electro-deposition of metals e.g. nickel, chromium, platinum. These have been shown to give only partial protection to corrosion by vanadium pentoxide/sodium sulphate mixtures. Differences in thermal expansion between coating and base caused cracking of the coating.

2. Diffusion of an element into the surface of the alloy. Silicon has been proved very effective using this method (3, refs. 101, 153 and 60). Chromium has also been used. Aluminium diffused into carbon steels has been found useful in the Ceramic Laboratories of Imperial College (See also ref.31 and Appendix 7).

3. Ceramic Coatings. Two kinds of coatings for metal surfaces are possible. One is a temporary coating, where the refractory is applied regularly in the hope that it will either modify corrosive agents or be preferentially dissolved. HALL et al. (3 ref.83) used a special nozzle to spray water slurries of various refractories e.g. magnesia,

calcium carbonate, daily into tubes in a land based boiler. This was surprisingly unsuccessful. Perhaps such treatments would only be effective on new metal surfaces. Other workers (4, 3 ref.37) report beneficial changes in deposit structure using such methods, i.e. the deposit is more easily removed by soot blowing.

The second kind of ceramic coating for metals is permanent protection in the form of a graded cermet. Diffusion of silicon and aluminium into the surface of mild steels (see above) may be considered under this heading as the exposed faces will oxidise to silica and alumina at operating temperatures. More exotic is theuse of thicker layers of refractories such as borides, silicides and carbides, but although these bond well to high nickel alloys, they do not show good corrosion resistance (3). Titanium carbide/cobalt cermet has good strength but poor oxidation resistance. This resistance can be provided by a high chromium/barium silicon frit, and in such condition is considered suitable for use in gas turbines (3 ref.209). Generally, cost and application problems will limit any use of cermets to small boiler parts and even then, their value above 800°C is in question (3 ref.120). Flame sprayed alumina is initially effective, but the coating is removed in a comparatively short time (3 ref.101).

4.4.3. IMPROVEMENTS IN REFRACTORIES.

Twenty-five years ago refractories used in marine boilers were normal fireclay bricks supported by simple steel bolts. A major improvement was the use of higher alumina "super" firebricks. These have a higher refractoriness, lower porosity, better spalling resistance and are supplied within finer tolerances. These bricks were used as the main slag and spalling resistance. Other graded refractories were used in various positions in the boiler according to conditions. Better heat and corrosion resisting steels were used as brick keys. Methods such as these ensured that furnace brickwork would remain servicable for the minimum strategic time - 5000 steaming hours, i.e. the approximate time between refits.

It is important to note at this point that small improvements in refractory life over the 5000 hour one are not economical. Increased costs usually accompany such improvements, the benefit of which will not be felt. This is due to the fact that the next useful life of a furnace lining after 5000 hours is 10,000 hours, i.e. the approximate steaming time between TWO refits. It is probable that a furnace lining inspected after 5000 steaming hours would be renewed, even if it were considered capable of a further 3-4000 hours. This would avoid the ship being out of service before the next refit was due.

MONOLITHIC refractories are now used in ships' boilers and these are indicating that with careful installation and use they will achieve the target 10,000 steaming hours. As the name suggests, linings consist of a single layer of rammed mouldable refractory over the normal insulating layers. This unit coat is free from joints and cement and this fact alone is of great assistance in corrosion resistance. Care during the initial installation of this lining is very important for long life (30). A major advantage of mouldable refractories is their ease of repair over small areas. This fact is however only true if the repair is carefully and correctly executed. One disadvantage of mouldable refractories arises from their very nature. In the **unfired** state, the lining will possess a "green" strength mainly due to the presence of moisture. On firing in situ the exposed face will develop a fired strength due to chemical and physical changes. The cool face may retain its green strength but the middle section will have lost its green strength and yet have no fired strength. Thus the centre of a monolithic lining in use is very weak. This problem has been successfully solved by the use of large ceramic keys which project through the weak layer into the first layer (see Appendix 6). Also a disadvantage with rammed linings is the difficulty experienced in their removal. This has led to the development of special tools and to negotiations for special rates of pay both of which contribute significantly to higher costs.

Such factors, however, have no importance in the boiler makers dream - the boiler with no refractories. An installation of this type has the advantages that all surfaces are heat exchange surfaces and research such as this described here can be curtailed.

4.4.4. CONCLUSIONS.

It is obvious that no one method alone will be effective in reducing corrosion to an acceptable level. As boiler design progresses temperatures and forcing rates will increase. Simultaneously, residual fuel oils will effectively contain more possible ash constituents, unless a process such as desulphurization becomes universal to all crudes. Thus minimization of corrosion will probably be a combination of a simple fuel oil treatment such as water washing and the application of balanced oil additives. Improved combustion control will minimise deposition while improved furnace design and materials will receive such depositions with little effect. Ash deposits will be friable and preferably water washable so that partial removal during operation and total removal during shut-down is possible.

CHAPTER 5. THE REACTION BETWEEN SODIUM SULPHATE AND VANADIUM PENTOXIDE.

At temperatures above 480°C vanadium pentoxide decomposes sodium sulphate releasing sulphur oxides, and sometimes oxygen, accompanied by the formation of binary compounds of sodium monoxide and vanadium pentoxide. The nature of the binary sodium-vanadium compound formed depends on the ratio of sodium to vanadium in the original mixture, the temperature to which the mixture is heated and the time the reactants spend at this temperature.

5.1. COMPOUNDS FORMED.

There have been several workers in this system (3,32, 33,34,37,38,39). Their conclusions differ over many points, but they all agree on the following facts:-

1. Sodium sulphate and vanadium pentoxide will react together to form binary oxide compounds, but an addition compound is NOT formed.

2. One of these compounds is sodium metavanadate, $NaVO_3$, formed by reacting an equimolecular mixture.

3. Another compound is sodium vanadyl vanadate I, $Na_2O.V_2O_4.5V_2O_5$, formed from 14.3 mole % Na_2SO_4 but exhibiting a wide range of non-stoichiometry.

4. At least one other vanadate is formed. This probably has the formula $Na_2O.3V_2O_5$ or $5Na_2O.V_2O_4.11V_2O_5$.

5. When reacting sodium sulphate with vanadium pentoxide, the compounds sodium pyrovanadate $2Na_2O.V_2O_5$ and sodium orthovanadate $3Na_2O.V_2O_5$ are NOT formed.

6. Sodium vanadyl vanadate I $Na_2O.V_2O_4.5V_2O_5$ and sodium vanadyl vanadate II $5Na_2O.V_2O_4.11V_2O_5$ (if it occurs) exist as $Na_2O.6V_2O_5$ and $5Na_2O.12V_2O_5$ respectively, in the molten state. On solidification the "extra" oxygen atom is released to give the characteristic "spitting" action well known to vanadium pentoxide in the presence of an alkali(34).

5.1.1. SODIUM VANADYL VANADATE I.

PRANDTL (33) in 1905 suggested the formula $Na_2O.V_2O_4.5V_2O_5$ for this compound. Subsequent workers have concluded that this formula is correct and its range of existence is accepted as from 7.5 to 15.4 mole per cent Na_2O with a stoichiometric value at 14.3 mole %. It is this compound which evolves most oxygen upon solidification, and which is considered particularly damaging to metals (29), probably due to oxygen transfer (23). The probable reaction is:-

$$6V_2O_5 + Na_2SO_4 \longrightarrow Na_2O.V_2O_4.5V_2O_5 + SO_3 + \tfrac{1}{2}O_2 \qquad (1)$$

According to BALDWIN and DAVIS (35A) this reaction will take place above 440°C. If the reaction goes to completion, the weight losses will be 6.5% due to SO_3 and when solid 1.3% due to oxygen.

5.1.2. SODIUM VANADYL VANADATE II.

It is the actual composition of the second vanadyl vanadate that is in doubt. FLOOD and SØRUM (34) in 1943, mainly by careful X-ray analysis concluded that the second compound had the composition $5Na_2O.V_2O_4.11V_2O_5$ (29.4 mole % Na_2O) and rejected various alternative formulae, such as suggested by CANNERI (32). FOSTER, LEIPOLD and SHEVLIN (37) heated mixtures of sodium sulphate and vanadium pentoxide at 870°C and suggested that a 24.2 mole % sodium sulphate mixture formed only a compound with the approximate formula $Na_2O.3V_2O_5$ (25 mole % Na_2O). NILES and SANDERS (3 ref.142) confirmed these findings. POLLARD (18) mentions a compound $Na_2O.2V_2O_5$. LOGAN (39) and BALDWIN (3 ref.12) consider the formula to be $5Na_2O.V_2O_4.11V_2O_5$. PHILLIPS and WAGONER (38) suggest that such a composition is in fact an eutectic between $NaVO_3$ and $Na_2O.3V_2O_5$, but this relies on their assumption that the approximate formula given by FOSTER, LEIPOLD and SHEVLIN is correct.

The purpose of Thornton Research Centre Report M198 (35C) was to establish the empirical formulae of the compounds formed in reactions between sodium oxide and vanadium pentoxide. The oxygen evolution on reacting selected mixtures of sodium metavanadate and vanadium pentoxide was carefully measured. This is equivalent to measuring the tetravalent vanadium content. Careful X-ray analysis helped the workers confirm the results of FLOOD and SØRUM. Thus, for the purpose of this test, sodium vanadyl vanadate II, $5Na_2O.V_2O_4.11V_2O_5$ is considered to be the correct compound. This is not an important decision, however, as firstly this research was only interested in melts and this discussion is concerned with solids and secondly, this author has seen little reference to sodium vanadyl vanadate II being detected in a boiler. The probable reaction for the formation of sodium vanadyl vanadate II is

$$2(Na_2O.V_2O_4.5V_2O_5)+3Na_2SO_4 + \tfrac{1}{2}O_2 \rightarrow 5Na_2O.V_2O_4.11V_2O_5 + 3SO_3 \qquad (2)$$

This is due to the fact that BALDWIN and DAVIS (35A) believe that sodium sulphate and vanadium pentoxide first form sodium vanadyl vanadate I and then, at temperatures above 660°C, providing sufficient sodium sulphate is available, sodium vanadyl vanadate II is formed. If the reaction is complete, the weight losses from the original mixture are 13.8% due to SO_3 and when solid 0.55% due to oxygen. The pure compound contains 29.4 mole % Na_2O and the range of stoichiometry is small but undefined (34).

5.1.3. SODIUM METAVANADATE.

This compound is formed from an equimolecular mixture of sodium sulphate and vanadium pentoxide. BALDWIN and DAVIS (35A) believe that the reaction proceeds via sodium vanadyl vanadates I and II and then only above about 750°C. Thus the probable reaction is:-

$$5Na_2O.V_2O_4.11V_2O_5 + 7Na_2SO_4 + \frac{1}{2}O_2 \rightarrow 24NaVO_3 + 7SO_3 \qquad (3)$$

For the completed reaction the total weight loss due to SO_3 is 24.7%. The compound has a range of stoichiometry from 45.9 mole % Na_2O to 50 mole %. There may be an upper limit to the stoichiometry above 50 mole % but it is not given in the literature quoted.

5.1.4. MIXTURES CONTAINING MORE THAN 50 MOLE % Na_2SO_4.

Providing the reaction takes place at a temperature above 750°C, all the vanadium pentoxide is used up to make sodium metavanadate. NO reaction between sodium metavanadate and sodium sulphate up to 900°C was recorded by BALDWIN and Davis. This author has no evidence for any reaction up to 1050°C. Two further binary oxides between sodium monoxide and vanadium pentoxide, namely sodium pyrovanadate $2Na_2O.V_2O_5$ and sodium orthovanadate $3Na_2O.V_2O_5$ are NOT formed in the presence of sodium sulphate. NILES and SIEGMUND (2G) also found that while reacting barium and calcium sulphates with vanadium pentoxide, the respective orthovanadates and pyrovanadates were NOT formed. However, sodium, calcium and barium pyrovanadates and orthovanadates may easily be prepared by reacting the correct quantity of the respective carbonate with vanadium pentoxide. Thus although much of the work described later concerns melts where the sodium to vanadium ratio is greater than unity, mixtures will contain only sodium metavanadate and sodium sulphate.

5.1.5. SUMMARY.

Compounds formed by completely reacting mixtures of sodium sulphate and vanadium pentoxide are summarized in table 1.

Table 1.

Phase	M.P. °C	Limits Considered	Mole% Na_2O	Estimated Weight loss %	Minimum Temp. of Formatio
V_2O_5	673	Upper limit	2.1	0.62	-
$Na_2O.V_2O_4$ $5V_2O_5$	625	Lower Limit	7.5	2.40	440
		Stoichiometric	14.3	4.98	
		Upper Limit	15.3	5.26	
$5Na_2O.V_2O_4$ $11V_2O_5$	535*	Stoichiometric**	29.4	10.7	660
$NaVO_3$	630	Lower Limit	45.9	21.1	750
		Stoichiometric	50	24.7	
Na_2SO_4	886	-	100	-	-

* Ref. (35) gives the melting point as 590°C.

** Range of solubility not defined but small.

5.2. REASONS FOR THE EXPERIMENTATION.

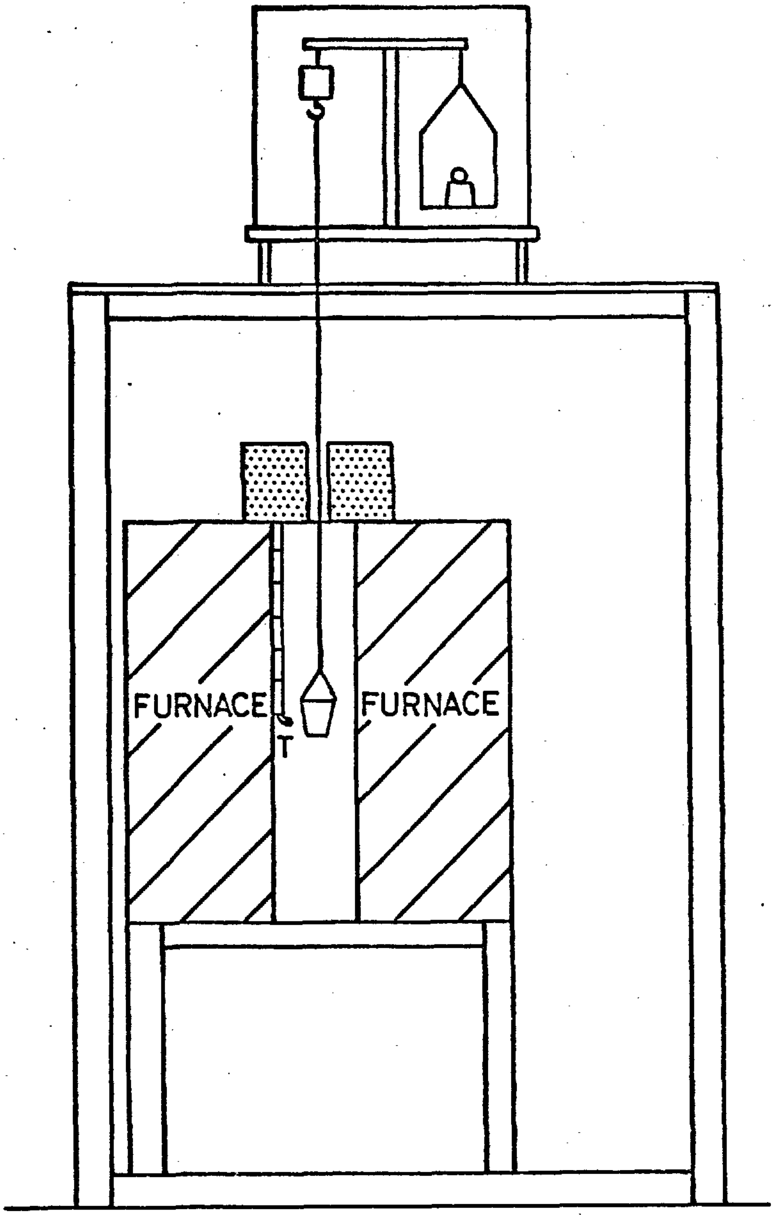
It is one of the functions of this work to test the corrosive action of molten mixtures of sodium sulphate and vanadium pentoxide on refractory oxides. In the molten state, the reaction between the two constituents will have reached a stage depending upon the reaction time and temperature. Sulphur trioxide may have been evolved to an extent which could affect the properties of the melt. For example, above 750°C the equimolecular mixture reacts to the following overall equation:-

$$Na_2SO_4 + V_2O_5 \longrightarrow 2NaVO_3 + SO_3 \qquad (4)$$

If this reaction is complete, then 24.7 wt.% of the original mixture has been lost, leaving a compound which has none of the properties of its present compounds. It was therefore necessary to discover to what extent mixtures intended for use in the high temperature corrosion testing apparatus had achieved equilibrium.

5.3. EXPERIMENTAL METHOD.

Although sulphur trioxide is liberated over a wide range of sodium to vanadium ratio, the ratio itself stays essentially constant. It is therefore relatively easy to follow the progress of a reaction by the weight loss from a reaction mixture. This is conveniently done in a continuous weighing apparatus as shown in Fig.1. The small platinum crucible is suspended on a platinum/rhodium wire from one arm of an analytical balance. The "Chainamatic" type balance is good for this work. The crucible is adjusted to hang free adjacent to the head of a thermocouple situated in a small electrically heated furnace. In the apparatus used, "Kanthal A" was wound on electrical porcelain tubes, the power being supplied from stabilised mains voltage via "Variac" torroidal transformers. Four such apparatuses were built into one assembly shown in plate 2. The thermocouples were platinum/platinum 13% rhodium and they were fed into one calibrated indicator via a thermocouple switch. The difference in temperature between the crucible contents and the thermocouple was found to be about 25°C, which reading was subtracted from the indicated temperature. A clean crucible was weighed empty and then plus mixture on a STANTON A49 analytical balance before being transferred to the continuous weighing apparatus. After taking the new reading on the modified balance the furnace was turned on and the time noted when the contents first became molten. It was possible to lower the crucible into a <u>hot</u> furnace but firstly the weighing of the crucible had to be done very quickly i.e. before the contents reached 480°C and secondly, some melts reacted so vigorously at first that with such rapid heating some melt bubbled out of the crucibles. The former method avoided both of these troubles and all melts were at temperature within 90 minutes. The reaction was investigated at 750,850, 950 and 1050°C and the results are shown in figures 2, 3, 4 and 5.



T= THERMOCOUPLE

FIG. 1 CONTINUOUS WEIGHING APPARATUS

PLATE 2. ASSEMBLY OF FURNACES FOR CONTINUOUS WEIGHING

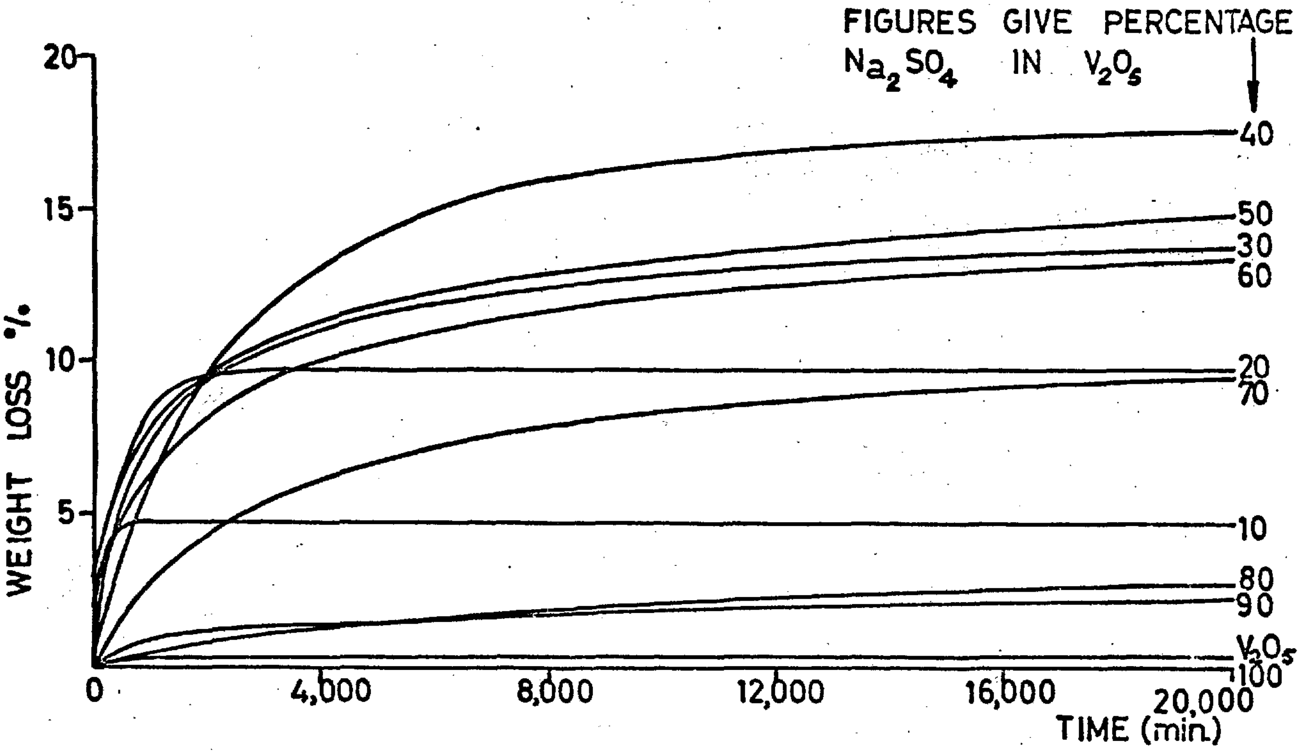


FIG. 2A WEIGHT LOSSES AT 750°C

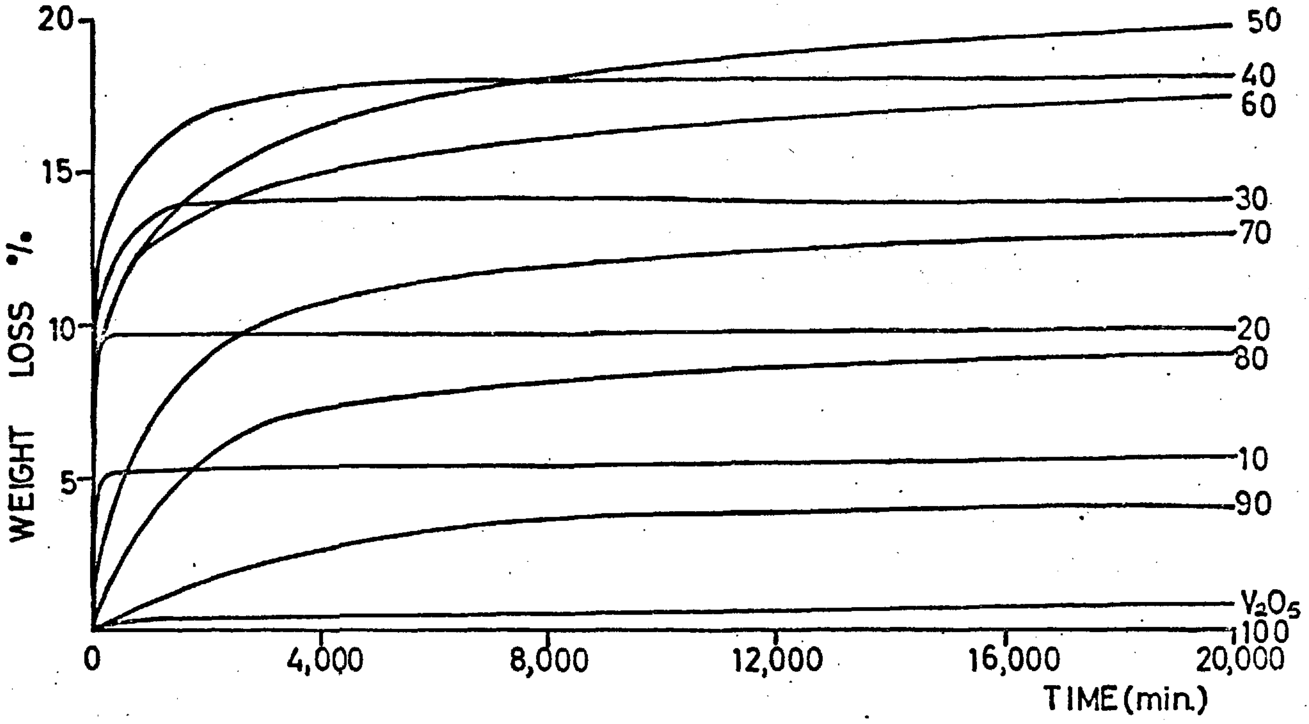


FIG. 2B WEIGHT LOSS AT 850°C

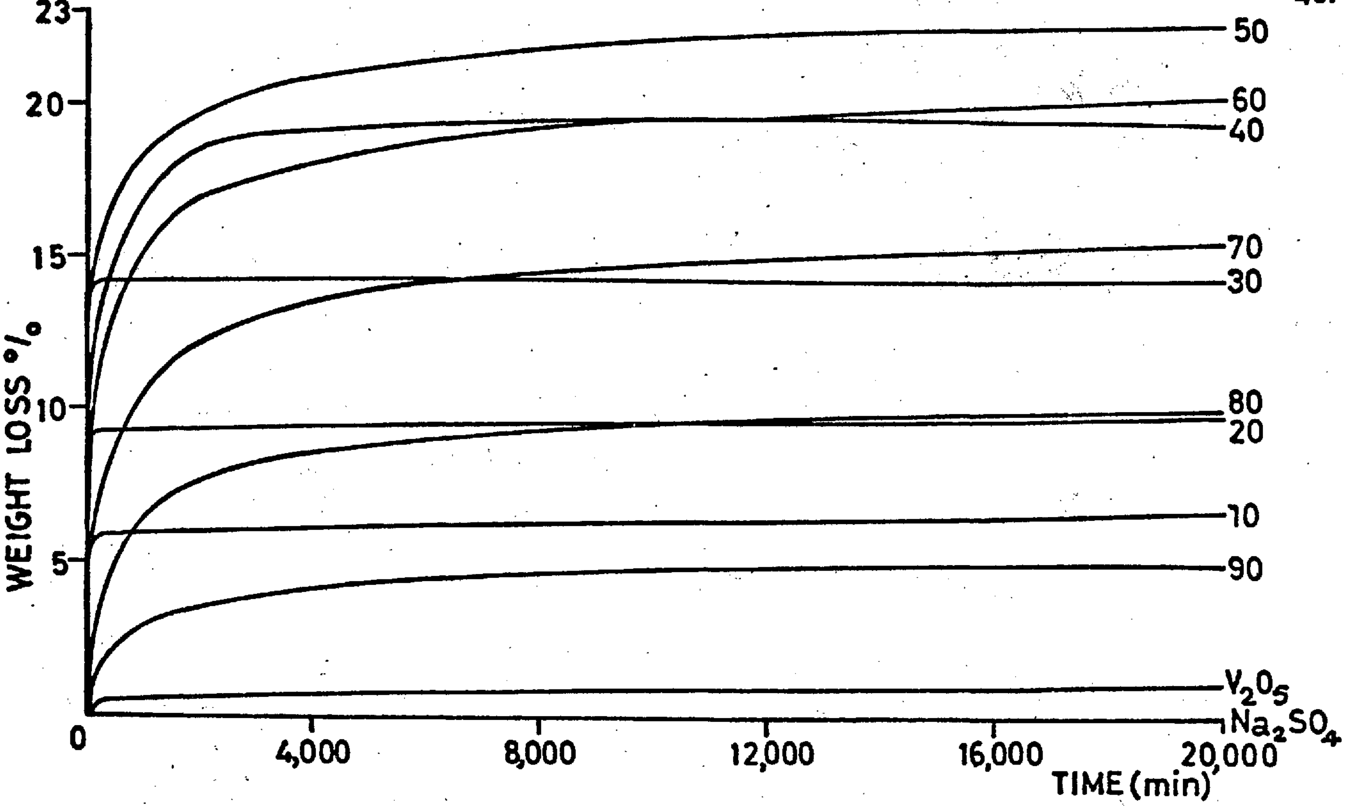


FIG. 3A WEIGHT LOSSES AT 950°C

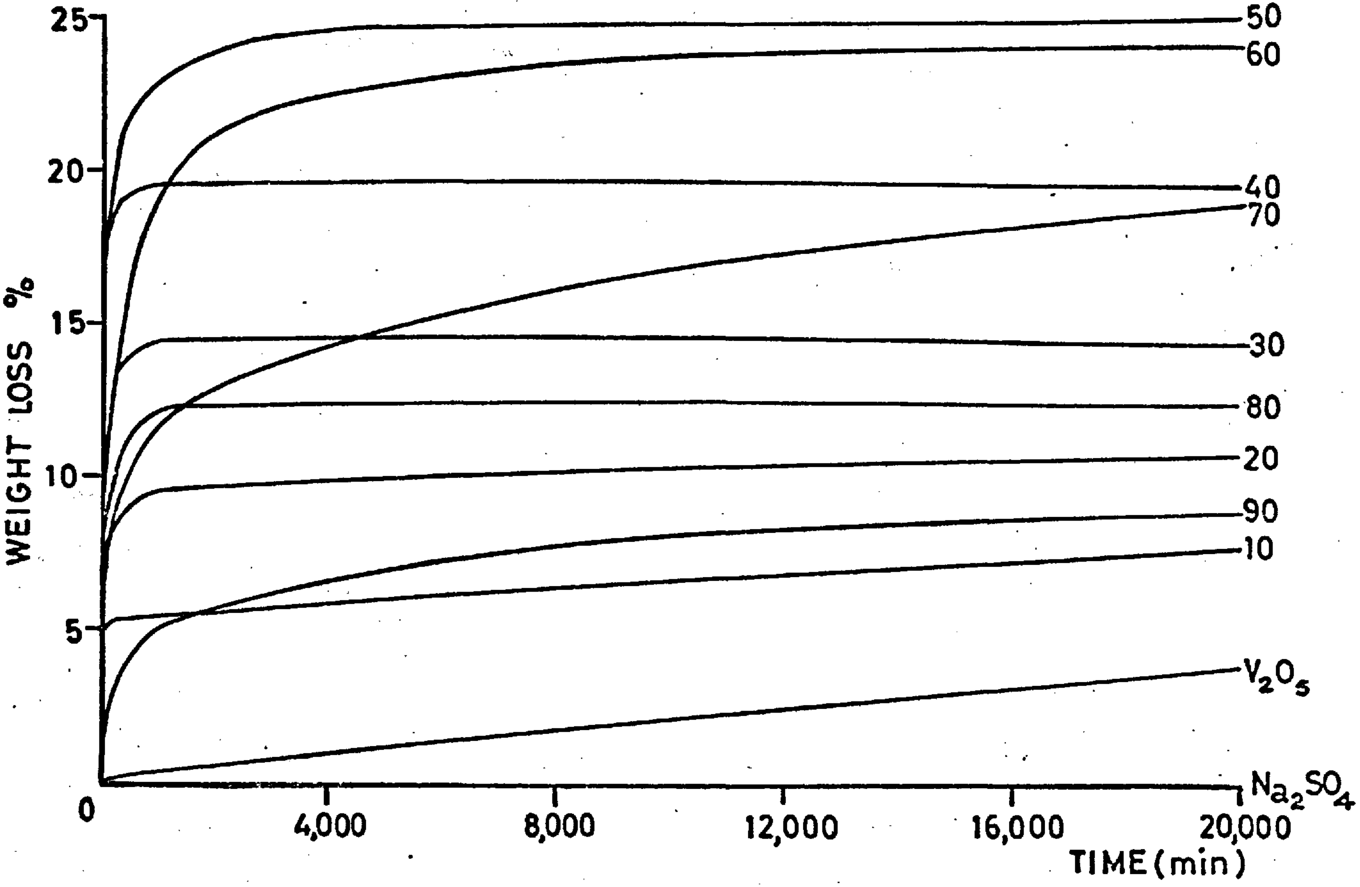


FIG. 3B WEIGHT LOSSES AT 1050°C

5.4. RESULTS.

The results were generally as expected. The weight losses of each mixture at a particular time increasing with increasing temperature.

5.4.1. WEIGHT LOSSES AT 750°C (Fig.2A).

The 10% Na_2SO_4 mixture rapidly reached a steady value at 4.76 wt.%, which is a little above the expected 4.5 wt.% due to SO_3. The 20% Na_2SO_4 mixture also reacted rapidly but took 3,000 min. to achieve a steady value of 9.76 wt %, again above the expected weight loss of 9.21 wt.%. At 750°C, NO other mixture reached its estimated weight loss. Mixtures containing 50 mole % and more of sodium sulphate were slow to react. The reaction for the 50,60 and 70 mole % mixtures was only approximately 63% complete after 20,000 min. (2 weeks) which is understandable as BALDWIN and DAVIS (35A) consider that the reaction to form sodium metavanadate does not occur until 750°C is reached. It is surprising that the weight loss of the 50 mole % mixture is finally below that of the 40 mole % mixture, especially as the 50 mole % mixture has the highest initial rate of loss of weight. This experiment was performed three times and the reproducible results had a maximum error of 5%. The 80 and 90 mole % mixtures were particularly slow reacting, being only 26 and 43% respectively complete at 20,000 min. This is presumably due to the presence of an excess of sodium sulphate which has a melting point of 886°C.

5.4.2. WEIGHT LOSSES AT 850°C (Fig.2B).

At this temperature, three mixtures achieved a steady weight loss. The 10 and 20 mole % mixtures after about 700 min. and the 30 mole % mixture after about 3,000 min. the reactions being 100% complete. After 8,000 min. the weight loss of the 50 mole % mixture exceeded that of the 40%. Again mixtures containing 50 mole % Na_2SO_4 and more were slow to react, being on average of 82% complete at 20,000 min.

5.4.3. WEIGHT LOSSES AT 950°C. (Fig.3A).

After 20,000 min. at 950°C some of the mixtures showed weight losses in excess of the estimated. It was assumed that this excess was due to evaporation. Mixtures of 10, 20 and 30 mole % reached a steady weight loss after about 300 min. and 40 mole % after 8,000 min. These four reactions were all 100% complete. The equimolecular mixture was still reacting at 20,000 min., the weight loss being 22.8% compared with the estimated 24.7% if the reaction is completed. Although the weight losses of mixtures containing more than 50 mole % Na_2SO_4 indicated that the reaction was complete, (for 80 and 90 mole % - almost complete), this was not thought to be correct as some of the weight loss was attributed to loss by evaporation.

5.4.4. WEIGHT LOSS AT 1050°C (Fig.3B).

At this temperature, all the reactions were considered complete at 20,000 min. Any chemical reaction was considered complete for mixtures containing 10-40 mole % Na_2SO_4 after 1,000 min., and for the equimolecular mixture after 6,000 min., but the weight loss from these mixtures continued due to evaporation. Mixtures containing more than 50 mole % Na_2SO_4 were again slower to react but all had exceeded the estimated weight loss by 20,000 min. The difference between the estimated and actual weight loss at 20,000 min was taken to be solely due to evaporation. Rates of evaporation thus calculated are shown in Fig.4B. The probable accuracy of these results is ± 50% or more. It is seen that the evaporation rate of mixtures containing 30-40 mole % Na_2SO_4 is very low. Mixtures containing 60-90 mole % Na_2SO_4 are correspondingly high. It should be noted that the lowest evaporation rate for a mixture is that at 30 mole % Na_2SO_4 i.e. very near the 29.4 mole% of sodium vanadyl

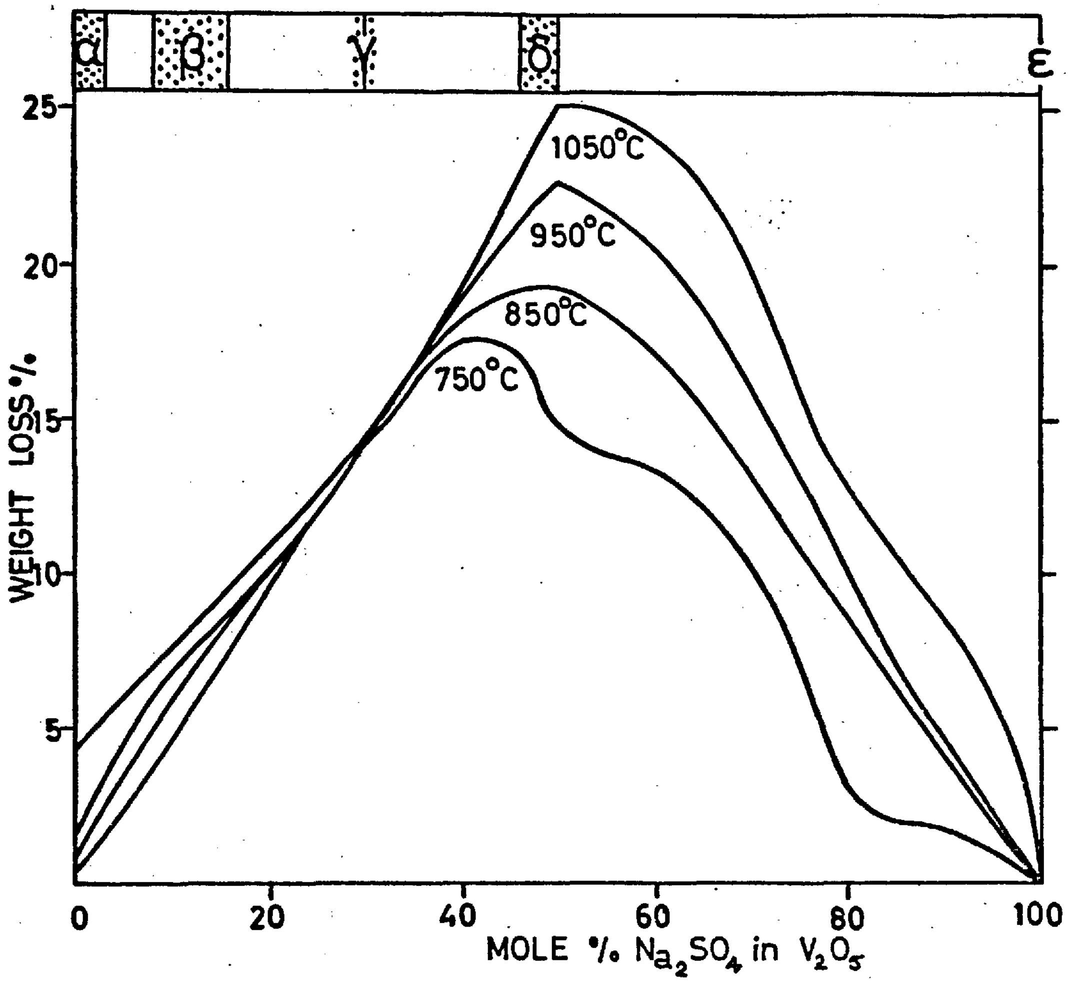


FIG. 4A WEIGHT LOSSES AT 20,000 min. FOR Na_2SO_4/V_2O_5 MIXTURES

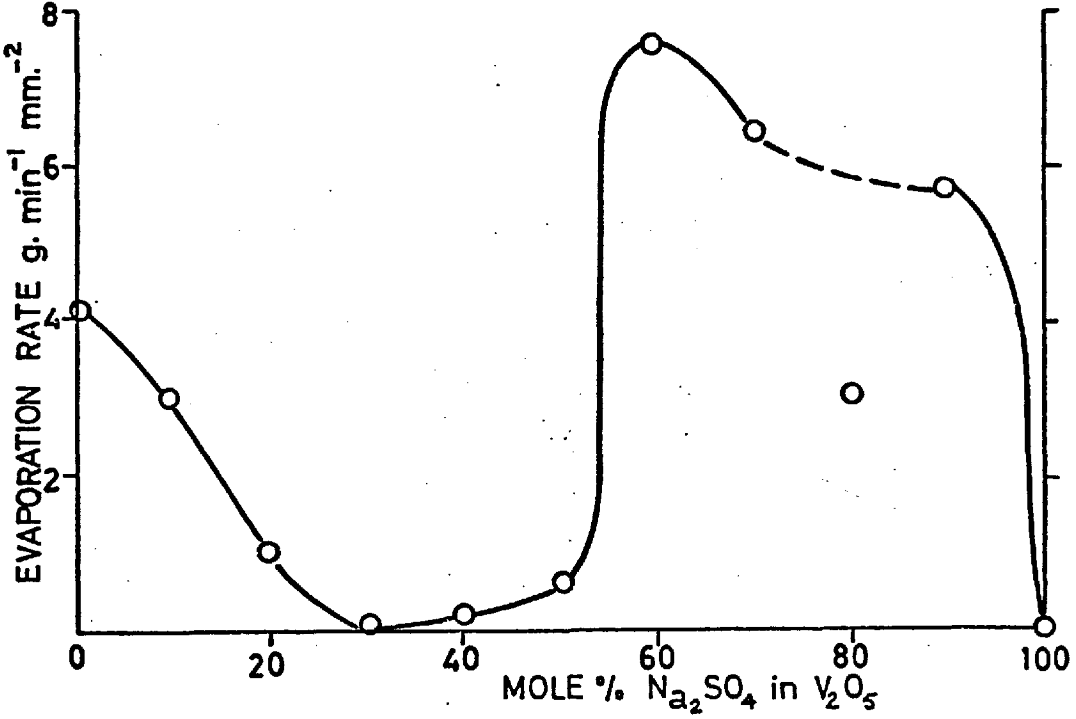


FIG. 4B APPROX. EVAPORATION RATES OF Na_2SO_4/V_2O_5 MIXTURES AT 1050°C vanadate II. PHILLIPS and WAGONER (38) attribute the high evaporation rate of mixtures containing sodium metavanadate to loss of Na_2O. The evaporation rate of V_2O_5 as measured is some 400 times higher than that of Na_2SO_4 although their vapour pressures are of the same order (3, fig.16).

Weight losses recorded at 20,000 min. are plotted in fig.4A with indication of the compounds formed. The consistency of the 30 mole % mixture is notable.

5.4.5. KINETICS OF THE REACTION.

With the amount of data available, various approximate evaluations of the kinetics of the overall reactions occurring are possible. In all the reactions mentioned above, sulphur trioxide is given off. It is therefore convenient to determine the kinetics of these reactions by the rate of evolution of sulphur trioxide. Two assumptions have been made. Firstly that all SO_3 produced by chemical reaction is expelled, i.e. the solubility of SO_3 in the melts is zero. Secondly that the rections involving oxygen are molten at the considered temperatures and so there is no weight change due to adsorption or evolution of this element. Kinetics deduced will be with respect to the changing concentration of sulphur trioxide and apparent activation energies deduced will be for the formation of this compound.

Now the three reactions to form sodium vanadyl vanadates I and II and sodium metavanadate are all of the overall type :-

$$a\ Na_2SO_4 + b\ V_2O_5 \longrightarrow (\text{compound}) + a\ SO_3 \qquad (5)$$

The rate of this reaction is :-

$$\text{Rate} = \text{const.}\ [Na_2SO_4]^{n_1}\ [V_2O_5]^{n_2} \qquad (6)$$

If the initial concentrations of Na_2SO_4 and V_2O_5 are a and b respectively:-

$$\frac{dx}{dt} = k\,[a - x]^{n_1}\,[b - x]^{n_2} \qquad (7)$$

If the initial concentrations are in stoichiometric proportions:-

$$\frac{dx}{dt} = k'\,[a - x]^{n} \qquad (8)$$

Now, the rate of formation of the compound is directly proportional to the rate of formation of SO_3:-

$$\frac{dC_{SO_3}}{dt} = k''\,[C_A - C_{SO_3}]^{n} \qquad (9)$$

or

$$\log \frac{dC_{SO_3}}{dt} = \log k'' + n \log (C_A - C_{SO_3}) \qquad (10)$$

Thus a log dC_{SO_3}/dt against log $(C_A - C_{SO_3})$ should have a slope of n and cut the ordinate at log k''. The rate constant, k'', indicates the dependence of the reaction upon <u>concentration</u> of components (in this case SO_3) at constant temperature. The detailed mechanism by which sodium vanadates are formed is not known and so equation (9) is applied loosely to the overall reaction. Rate constants so gained will apply to the slowest step within the reaction.

There are four possible controlling steps to the reaction between sodium sulphate and vanadium pentoxide:-

1. Energy of mixing of the two components.
2. Diffusion of reactants into, or products out of, the reaction zone.
3. The rate of chemical reaction.
4. Rate of nucleation of SO_3.

The ~~energy~~ rate of mixing of the two components may be discounted as the controlling step as the mixtures were intimately mixed by pestle and mortar before heating. Also, once molten, the liquids are miscible. It is difficult to attribute the controlling reaction to any of the remaining three mechanisms without further knowledge of the system.

Before a chemical reaction can take place, the molecule or molecules involved must be raised to a state of higher potential energy. They are then said to be activated or to form an activated complex. The potential energy hill that must be climbed to reach the activated state is called the Activation Energy and in this text it is assumed to be independent of temperature. If values of k are known for several temperatures, it is possible to relate these with the activation energy by the ARRHENIUS equation:-

$$k = A\, e^{-E_a/RT} \qquad (11)$$

or

$$\ln k = -E_a/RT + \ln A \qquad (12)$$

As the detailed mechanisms of the reactions described are not known, E_a will be called the "apparent activation energy".

Sodium Vanadyl Vanadate I.

The stoichiometric mixture was not studied, but the 10 mole % mixture is within the stoichiometric range for this compound (35) and equation (1) is represented. $\mathrm{Log}_{10} \frac{dC_{SO_3}}{dt}$ versus $\log_{10}(C_A - C_{SO_3})$ for this reaction is plotted in figure 5A, for 750, 850, 950 and 1050°C. Each set of values was assumed to be a straight line and analysed by the method of least squares to give four values for k. These were in turn analysed by the method of least squares to give a value of -10,500 to the slope of the line $-E_a/R$ in equation (8). Thus, for equation (1) with NO oxygen evolution, a 10 mole % sodium sulphate/80 mole % vanadium pentoxide mixture reacting to give $Na_2O.6V_2O_5$, has an apparent activation energy of 20.8 kcal/mole with a judged accuracy of ± 10%.

Sodium Vanadyl Vanadate II.

Whereas sodium vanadyl vanadate I is formed above 440°C, sodium vanadyl vanadate II does not occur until 660°C. It is therefore probable that the apparent activation energy

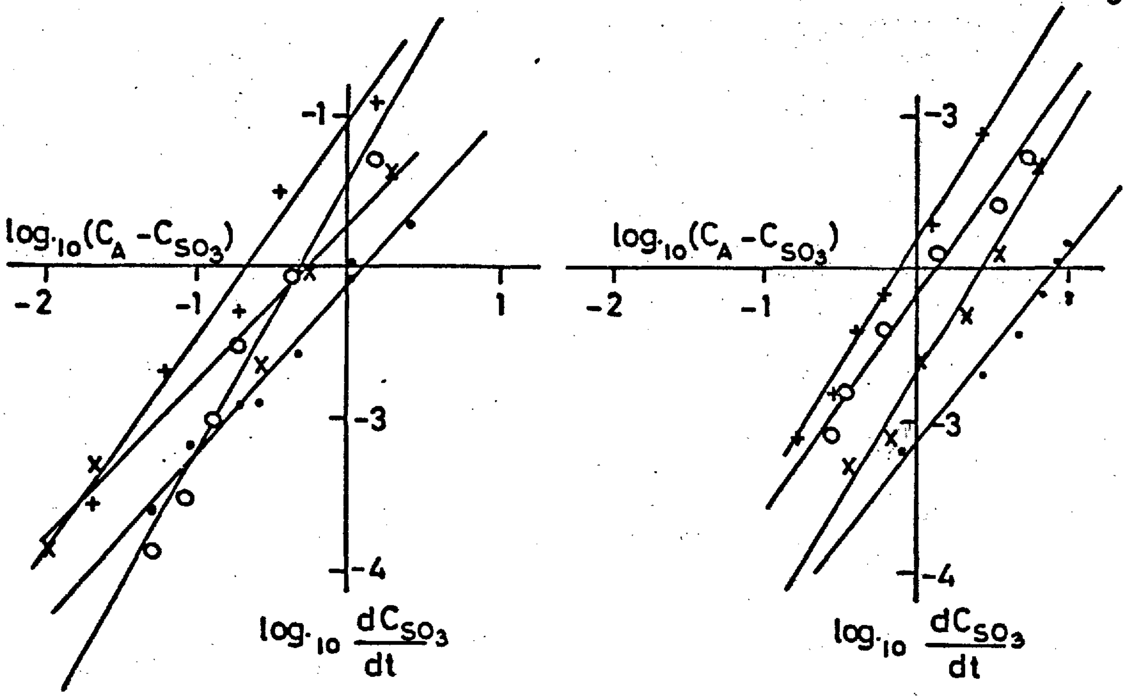


FIG. 5A FORMATION OF $Na_2O.V_2O_4.5V_2O_5$ FIG. 5B FORMATION OF $5Na_2O.V_2O_4.11V_2O_5$

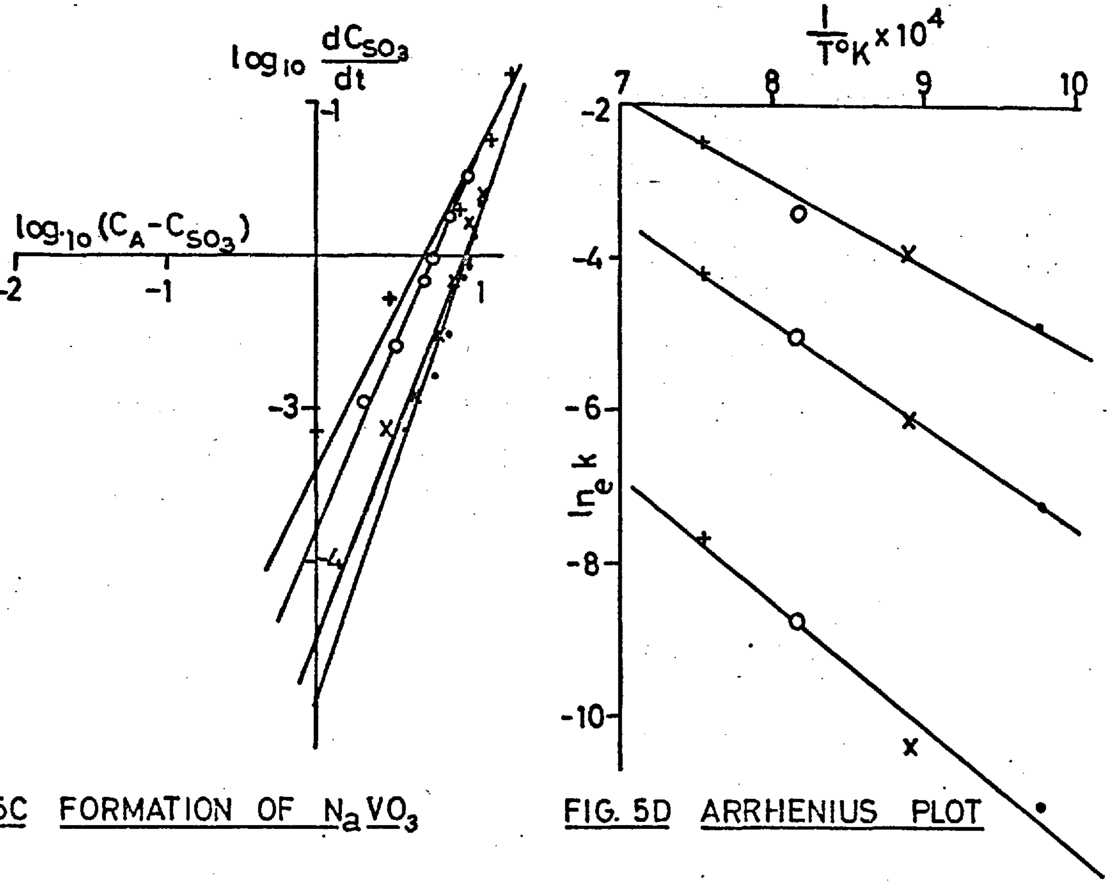


FIG. 5C FORMATION OF $NaVO_3$

FIG. 5D ARRHENIUS PLOT

FIG. 5 KINETIC PLOTS FOR REACTIONS BETWEEN Na_2SO_4 & V_2O_5

for the overall reaction will be higher than that for equation (1) and possible that the rate of reaction will be slower. In fig.5B it is seen that this latter is in fact the case, rate constants for equation (9) being between 1/4 and 1/10 those for equation (1).

$$12V_2O_5 + 5Na_2SO_4 \longrightarrow 5Na_2O.12V_2O_5 + 5SO_3 \qquad (13)$$

Thus, also, for a 30 mole % Na_2SO_4/70 mole % V_2O_5 mixture reacting to the overall equation (9) the apparent activation energy is 27.1 kcal/mole with a judged accuracy of ± 10%. (Note that a 29.4 mole % Na_2SO_4 mixture was NOT studied, but the 30 mole % Na_2SO_4 mixture is very close and may be within the stoichiometric range for this compound).

Sodium Metavanadate.

The equimolecular mixture was studied at 750, 850, 950 and 1050°C. Reaction rates for the overall equation (4) are approximately 50 times smaller than for equation (9). The value for the apparent activation energy is 31.6 ± 3.8 kcal/mole with a judged accuracy of ± 10%.

5.4.6. CONCLUSIONS.

As was to be expected, temperature is of great importance in the reaction between sodium sulphate and vanadium pentoxide. At low temperatures, say up to a maximum 700°C, such as are common in deposits on superheater tubes and economisers, the presence of sulphur trioxide in a deposit will be significant. BROWN and RITCHIE (36) report values of SO_3 from 19.3 to 57.4 wt.% in the deposit on a superheater tube bank in a destroyer. At higher temperatures, such as are experienced by the hot faces of refractories, the SO_3 content will be very small. GRAY and KILLNER (11) report a SO_3 content of 1.50 wt.% in the slag formed on the surface of the brickwork in a cruiser and 0.05 wt.% SO_3 in the dark, glass-like slag on the furnace floor.

Certain assumptions have been made about the kinetics of the reactions between sodium sulphate and vanadium pentoxide. The data published in fig.5 fitted the curves well showing that it was NOT unreasonable to deduce the following overall apparent activation energies from fig.5D:

Sodium Vanadyl Vanadate I	20.8 k.cal/mole ± approx. 10%
Sodium Vanadyl Vanadate II	27.1 k.cal/mole ± approx. 10%
Sodium Metavanadate	31.6 k.cal/mole ± approx. 12%

At a given temperature between 750°C and 1050°C the reaction to form sodium vanadyl vanadate I is more rapid than the reaction to form sodium vanadyl vanadate II from sodium sulphate and vanadium pentoxide. This latter reaction is in turn more rapid than the reaction to form sodium metavanadate. The reaction order, as indicated by "n" in equation (5) had the average values 1.33, 1.46 and 2.56 for the reactions to form sodium vanadate I, II, and sodium metavanadate respectively.

5.5. THE REACTED MELT FURNACE.

The reason for the experimentation just described was that the degree to which oil-ash components had reacted with each other, at a given temperature, was required. Temperatures up to 1050°C were investigated. However, all ash in a marine boiler will have experienced the temperature of the flame, roughly 1850°C (20) for at least a short period. Reactions in the gaseous state take place as the gases cool and eventually deposits are formed. Reactions will continue in the solid or semi-solid state (17).

In the corrosion testing experiments (Chap.8) melts representing sodium sulphate and vanadium pentoxide were to be used. Clearly, the reacted condition of this melt might affect corrosion rates gained e.g. an equimolecular mixture just melted contains 24.7 wt % SO_3 available for expulsion. After 20,000 min at 750°C, this mixture still contains 9.9 wt %

SO_3 available for expulsion, and after 20,000 min at 950°C, 1.9 wt %. If the reaction is complete then the melt is only sodium metavanadate. Considerable quantities of melt in a reacted condition were required (2kg. each mixture). It was decided to attempt to manufacture the required corrodants by passing appropriate mixtures of sodium sulphate and vanadium pentoxide through a flame.

5.5.1. The appartus is shown in plate 3A. The sodium sulphate/vanadium pentoxide mixture was held in a hopper. The base of the hopper was a wire gauze and led out into the air supply of a town gas burner. A vibration mechanism on the lid of the hopper gently shook the mixture through the gauze, into the air stream which carried it into the gas flame. The temperature of the flame was adjusted to be 1850°C by fixing the air/gas ratio to 4.7 i.e. slightly oxidising (40). It was hoped that particles would vapourize and be collected on the water-cooled copper coil placed across the furnace gas-exit.

5.5.2. A 60 mole % Na_2SO_4/40 mole % V_2O_5 mixture was used for the first four runs. This was passed through a 100 mesh sieve before use. The deposits gained were quite large (see plate 3B) representing about 35% original weight and upon analysis gave an average value of 43 mole % Na_2SO_4 and 57 mole % V_2O_5. Sodium metavanadate content, if present, was very small. Thus it appears that there was no reaction between the two components and that the sodium sulphate was somehow being lost. It was considered that burner design was poor and a temperature of about 1500°C more probable. Also the particle size was much too large and probably 5 μ should be the maximum (41). Therefore large particles were less likely to melt completely and were probably bouncing off the copper coil. Sodium sulphate has a melting point some 200°C above that of vanadium pentoxide and so would be more affected by the mechanism.

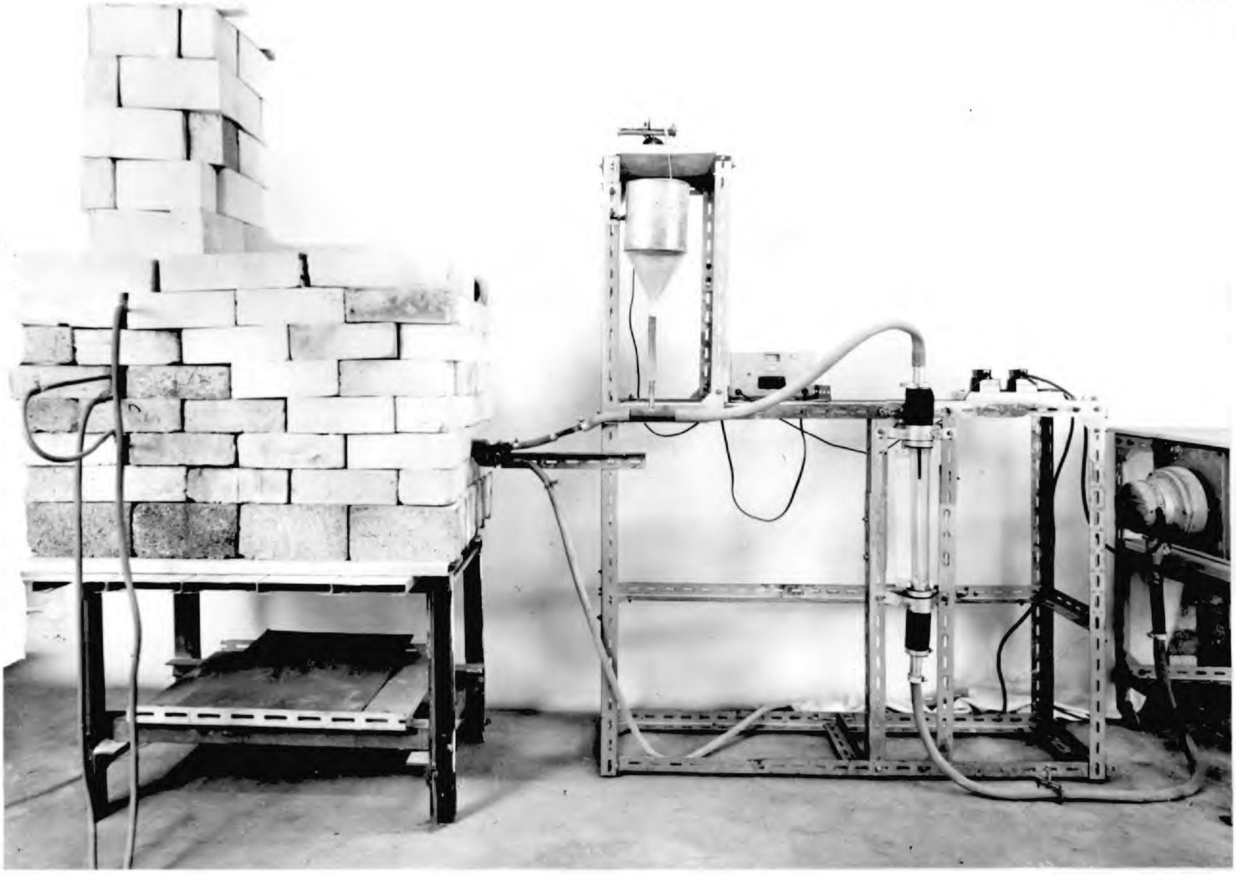


PLATE 3A. THE REACTED MELT FURNACE

PLATE 3B. PRODUCT FROM THE REACTED MELT FURNACE

5.5.3. A new burner was substituted which required a more powerful blower. As a result of the powerful blower and a more turbulent flame, residence time of the particle in the flame decreased as did the yield. Grinding the powders to -5μ proved difficult. The powders caked in a ball mill, and a disc crusher, although effective, allowed much fine dust to escape. Vanadium pentoxide dust is an irritant to the conjunctivae. Using the finer powder the yield dropped further to about 5% although the presence of white fumes in the furnace gases (SO_3?) indicated that a reaction was probably occurring. Eventually this phase of the experimentation was stopped due to the following reasons:-
1. The cost of vanadium pentoxide is relatively high (£5/kg) and thus with a low yield the cost to produce 2 kg of reacted melt would be high. 2. The use of very fine powders meant that a different design of hopper was required. 3. The mixtures take a long time to be ground to -5μ and the presence of V_2O_5 dust is not welcome in the grinding room.
4. This particular time in the experimentation coincided with a decision to use fully equilibriated melts. By this expression it is indicated that, for melts containing 50 mole % and more sodium sulphate, vanadium pentoxide will not be used, but the appropriate amount of sodium metavanadate will be substituted e.g. for a 60 mole % Na_2SO_4 mixture :-

$$60Na_aSO_4 + 40V_2O_5 \longrightarrow 80NaVO_3 + 20\ Na_2SO_4 + 40\ SO_3 \qquad (14)$$

providing that the reaction is complete. Thus, instead of the 60 mole % Na_2SO_4/40 mole % V_2O_5 mixture, an 80 mole % $NaVO_3$/20 mole % Na_2SO_4 mixture will be used. It is more sensible to test an equilibriated melt first and then compare it with a non-equilibriated melt. Also the problem of reacting the components is eliminated as is the slight health hazard of vanadium pentoxide.

CHAPTER 6. REFRACTORIES AND METHODS OF TESTING THEM AGAINST CORROSION.

6.1. THE STRUCTURE AND TYPES OF SILICA GLASS USED.

Silica has many crystalline forms, but it is vitreous silica or silica glass that is of prime interest to this work. The silica structure is built up from tetrahedra with oxygen atoms at each corner equidistant from a silicon atom at the centre. It is different arrangements of these tetrahedra that gives rise to the different structural forms of silica. In the crystalline forms the silica tetrahedra form regular patterns, whereas in the vitreous state they are randomly distributed. Silica glass was used during this work due to its high resistance to thermal shock, non-orientated structure and availability in suitable shapes. Three types of vitreous silica were used:- translucent, transparent and synthetic, sold under the trade names "Translucent Vitreosil", "Transparent Vitreosil" and "Spectrosil" (Thermal Syndicate Ltd

Translucent Vitreosil is manufactured by the electrical fusion of pure silica sand. The rods used in this work were made by heating externally such a fused mass of sand during a drawing operation. Striated bubbles give the rod (or tubing) its characteristic sheen. Transparent Vitreosil is prepared by the fusion of quartz crystal in a flame. Like all vitreous silicas prepared in a water vapour atmosphere, it contains varying concentrations of the hydroxyl radical (usually 0.015 - 0.04 wt.% OH) depending on the fusing conditions and the size of the quartz particles used. "Granularity" is the term given to the result of the establishment of hydroxyl concentration gradients in each small particle as it fuses. Also unless the heating is for long periods well above the melting point, traces of the original crystal shape remain and can affect the optical properties of the glass. Spectrosil is made by the vapour-phase hydrolysis or oxidation of silicon compounds in a flame. Thus granularity defects are absent but hydroxyl content is high (about 0.12 wt %). The maximum chemical impurities so far determined in these three grades are shown in table 2.

Table 2. Chemical Purities of Vitreous Silica (42)
(Maximum levels so far determined p.p.m.)

Element	Translucent	Transparent	Spectrosil
Al	380	60	0.02
B	7	3	0.01
Ca	10	0.4	0.1
Fe	70	1.5	0.1
Na	60	1	0.04
OH	-	400	1200

6.2. THE STRUCTURE AND TYPES OF ALUMINA USED.

In the corundum structure (αAl_2O_3) six oxygen atoms form an octahedral group around the metal and each oxygen atom is surrounded by four metal ions. Each aluminium atom has six practically equidistant oxygen neighbours and the structure is best regarded as a close-packed array of oxygen atoms with aluminium atoms occupying octahedral sites. Another form of alumina is γAl_2O_3 which is metastable and not found in nature. It may be prepared by heating aluminium hydroxide to 1000°C. The particle size is very small and thus is used in the manufacture of sapphire in the Verneuil furnace. On prolonged heating, it converts to αAl_2O_3. The compound $Na_2O.11Al_2O_3$ was originally thought to be a form of alumina and is still called βAl_2O_3. It has a definite structure close to that of spinel and the presence of the large Na(or K) ions is essential to the stability of the structure.

Three types of alumina refractory were used for testing: high purity sapphire and two forms of high alumina refractory. The sapphire was in the form of single crystal rods manufactured by the Salford Electrical Instrument Co. Test pieces for the corrosion testing apparatus were hot pressed alumina manufactured by the Carborundum Co. These were supplied in the form of zero porosity cylinders containing 98.5% Al_2O_3. Main impurities of this standard cutting tool material were magnesia, silica and sodium monoxide. The structure was fine polycrystalline αAl_2O_3 with a probable small percentage of βAl_2O_3. Machining of these and other samples was carried out by F.Yorke and Ptns. Ltd. Other test pieces were made of HILOX 961, a zero-porosity, brown, 96% alumina supplied by Steatite and Porcelain Products Ltd.

6.3. ALUMINO-SILICATES.

A large number of the refractories in use in boilers at the present time can be considered as alumino-silicates. Most of the bricks submitted for use in naval boilers may be considered mineralogically as corundum, mullite and glass. Mullite is the name given to the only compound formed between silica and alumina. The formula is $3Al_2O_3.2SiO_2$ and it is thought by ARAMAKI and ROY (44) to melt congruently at about 1850°C. Mullite was tested by GOLDMAN (1) who found that after reaction with vanadium pentoxide, the mullite surface layer consisted of alumina i.e. the silica had been selectively leached out. His conclusion was that mullite will take on the slagging characteristics of alumina. GAD and BARRETT(45) considered the decomposition of mullite by soda and they concluded that 4% Na_2O was sufficient to completely decompose mullite into alumina and liquid albite at 1400°C. Thus it is reasonably certain that in all melts containing V_2O_5 and Na_2SO_4, mullite will behave very much as alumina. So it was decided not to test mullite as its behaviour could be reasonably predicted and the difficulties encountered by GOLDMAN while testing this material have not yet been overcome.

(the main problem was the manufacture of a non-porous sample, free of hair-line cracks).

6.4. METHODS OF TESTING THE CORROSION RESISTANCE OF REFRACTORIES.

There are very many methods by which refractories may be tested against corrosion. A large portion of these are tailored by industrial research workers to their individual requirements and the data produced is mainly empirical. Laboratory tests are here described under four headings.

6.4.1. Finger or bar tests. Suitable sized sections of a brick, or specially made bars or "fingers" are dipped into the molten slag. Immersion may be complete or more often partial. Tests where the melt is stagnant produce good comparative results. Information about the density of the slagged product, the surface tension of the melt and the activity of the vapour above the melt may be deduced from reactions at the slag line (partial immersion only). A rotating or moving test-piece increases the rate of attack to provide more rapid comparison. Of greater scientific value is the continuous weighing of a sample immersed in the melt. If the surface area undergoing dissolution is known, then comparative rates of attack may be measured which are reasonably reproducible, providing variables such as container size and size, shape and orientation of testpieces are kept constant.

6.4.2. Powdered slag is placed on the cold refractory surface which is then raised to the required temperature. In such tests the refractory is in excess whereas in 6.4.1 the slag is in excess. Finely powdered slag dusted onto a brick surface is liable to be adsorbed giving information about depth of penetration upon sectioning. Repetition of the heating cycle, with or without more slag will demonstrate the effect of slag on spalling characteristics. It is not necessary to dust the whole surface of a testpiece. Sometimes it is preferable to place a pellet of slag on the surface of the refractory, perhaps in a small depression (47). Sectioning through such samples heated to various temperatures provides useful visual information (11) as well as providing samples for petrographic and perhaps X-ray studies.

6.4.3. *Crucible testing*. The simplest form of this method is to weigh a crucible made of the material under test, put in a weighed amount of slag, heat at the test temperature for the required time and pour the melt out. The new weight of the clean crucible gives the quantity dissolved. The disadvantages of this method are the porosity of most materials, the changing composition of the slag, and the difficulty of measuring the surface area undergoing dissolutio Crucibles with a hole in the bottom have been used so that when the slag melts, it runs out. Translation of results gained must be very difficult especially the effects of temperature and time. Most like the method used in this research was that by FITCHETT and RICHARDSON (46). To test magnesite mixer blocks, they cut brick pieces 2.5" x 2.5" x 3" deep. In the top surface of this sample was a "well" 1" deep and 1.25" dia. From the centre of this well and leading to the bottom surface was a "slag passage" of 0.25" dia. Both melt and sample were heated separately to the test temperature when 10 g molten slag were fed into the well every 3 min. for 1 hour. After passing through the slag passage, the molten slag fell through a hole at the bottom of the furnace into a water bath. Comparison of test pieces was primarily visual assisted by the increase in volume of the slag passage measured by filling it with mercury.

6.4.4. *Tests involving a flowing slag* include rotating drum and sloping plate. In the rotating drum test a horizontal cylinder is lined with the refractory under test. Heating is by gas flame from one end while the drum rotates on rollers. When the required temperature is reached, slag is added from time to time until a pool forms, which, as the drum rotates, flows over the refractory surface. At the end of the test the melt is tipped out and the drum allowed to cool. Tests such as thickness loss of refractory, change in melt composition, melt penetration of refractory, etc. may be coupled with comparison in jointing compounds. The disadavantages of this method are that it is expensive to run, the temperature is difficult to control and a series of results can take a long time to complete. Also, dissolving brick changes the slag composition and if several bricks are being tested, one poor brand will alter the result. Approaching even nearer to actual operating conditions in boilers is the spraying of powdered slag onto a vertical (52) or sloping (51) refractory surface. Again, the temperature is difficult to control and results are comparative only.

6.4.5. DISCUSSION.

Generally, corrosion rates of refractories are low. This is beneficial to industry but makes the testing of corrosion difficult. There are many variables, which although easy to control in the laboratory, are often difficult to control in practice. Corrosion products can lead to side reactions which may proceed at comparable rates with the studied rate. Many testing methods are probably necessary due to the many systems and conditions under which refractories are called to operate. All tests suffer from the fact that it is difficult to remove all slag from a specimen after testing. This is mainly due to porosity effects. As the porosity of a refractory increases, so does the surface area over which the reaction can take place. Interconnected pores greatly increase the depth to which a slag can penetrate above that due to normal diffusion. This deeply penetrated slag is most difficult to remove selectively. This complication is partially removed by considering non-porous refractories only. Surface tension changes occur in most refractory/slag systems and the effect of this can often be seen at the slag line. Eddy currents in the melt surface near the refractory arise due to concentration or temperature gradients. The surface tension gradient produces surface movement either towards or away from the refractory surface depending upon whether the surface tension gradient is positive or negative. The eddies produced cause the familiar enhanced corrosion at the slag line. If however, a melt does not wet a refractory, then one would expect the rate of corrosion to be low or zero. Sodium sulphate/vanadium pentoxide melts appear to have a very low surface tension (48). The angle of contact of such melts also appears to be about zero, as they appear to have the ability of climbing out of a crucible. Therefore it is expected that surface tension effects would not be noticed in the corrosion testing apparatus as there is no slag line.

6.5. THE EFFECT OF TEMPERATURE.

Nearly all refractory materials are heat-treated before use. They are chosen for use at higher temperatures because of their resistance to chemical action and fusion. Yet, there is at present, no refractory which is completely inert under all conditions and the very reason for choosing refractory materials i.e. resistance to high temperatures, is very often also the reason for its deterioration. For a refractory in use in an inert atmosphere the only probable danger of increasing temperature is that the fusion or softening point of the material will be approached. If the atmosphere is not inert with respect to the refractory then chemical action will occur. These gas/oxide reacts will be slow or the employer will eitner use a different material or reduce temperature.

Refractories used for slag resistance have this task because they are economically able to resist slag attack. It is unlikely that any refractory will ever resist a slag completely and so materials are chosen to remain useful for a period of time depending upon conditions. To make this period as long as possible, the avoidance of temperatures higher than necessary, cannot be over-emphasized. To balance this statement, the person using the refractories will probably seek high temperatures as generally, efficiencies increase with increasing temperature (especially in a boiler), heat transfer and radiation increase and it is likely that reaction rates and yields will improve.

In systems where a slag is in contact with a refractory, the following parameters are affected:-

6.5.1. Viscosity. The viscosity of liquids is dependent on temperature to a very marked extent, but although the relationship has been the subject of many investigations, no satisfactory simple formula has been suggested to express the connection with any great degree of accuracy. A modified empirical formula is :-

$$\eta = \frac{A}{(1 + BT)^C} \qquad (15)$$

This is applicable to pure liquids only. Note that viscosity decreases as temperature increases. ANDRADE's simplified viscosity/temperature relationship is :-

$$\eta = A\, e^{E_{Vis}/RT} \qquad (16)$$

The quantity E_{Vis} is a measure of the energy barrier that must be overcome before the elementary flow process can occur. The presence of a melt in boilers has already been described as damaging. Thus, raising the temperature reduces viscosity and a mobile melt is able to remove reaction products leaving new areas exposed. Channels in boiler brickwork are sometimes seen wherethe flowing melt has eroded the refractory surface.

6.5.2. Ion mobility. This is the mechanism by which all reactions occur i.e. the movement of an ion from one state to another. This is true whether a reaction be diffusion or reaction controlled. Increasing temperature increases ionic mobility by increasing free energy and this applies equally to the diffusion of reaction products away from the reaction surface. The temperature dependence of the diffusion coefficient (49,50) is given by :-

$$D_i = k_o T v_i \quad \text{— vel/force - ve pri} \qquad (17)$$

6.5.3. Rate of reaction. The ARRHENIUS equation which relates reaction rate and temperature has already been given:

$$k = A e^{-E_a/RT} \qquad (11)$$

Thus the rate of reaction will increase with increasing temperature. The rate at which a refractory is attacked by a melt depends also on the system and concentrations of individual components. However, for one set of concentration conditions, k is dependent only upon temperature. An increase in reaction temperature of 100°C very approximately doubles the rate of reaction.

6.5.4. Solubility. The reason why refractories are attacked by slags is that they are soluble in them and by dissolution the system tends towards a lower energy. Although it is not always the case, increase in temperature usually results in an increase in the saturation solubility of a refractory in a melt. This increases the driving force for the reaction.

6.5.5. Other considerations include the possibility of new reactions due to an increase in temperature; the fusion or structural change in one particular component of the refractory e.g. devitrification of a glassy phase (silica glass above 1050°C) and the reduction in surface tension which means that more refractory surfaces well wetted due to increased capillary action in pores.

CHAPTER 7. THE SOLUBILITY OF Al_2O_3 AND SiO_2 IN $Na_2SO_4/NaVO_3/V_2O_5$ MELTS.

Most refractories are soluble in the melts with which they are in contact. The magnitude of this solubility largely governs the degree of attack as it is the driving force for the dissolution process. GOLDMAN (1) discovered the solubility of alumina in vanadium pentoxide melts containing up to 50% sodium sulphate. He was unable to discover the solubility of silica in these melts because at 721°C, silica was still dissolving after 4 months. Several workers (21, 53, 54, 55, 56) have used cones of mixtures of refractory and slag. These are heated in a furnace at a constant rate of increase in temperature. The temperature at which these cones slump is often quoted as the "fusion point" or"liquidus point" for such mixtures. As slumping temperatures under the stated conditions, they are probably correct, but the condition of the mixture will be far from equilibrium as it is the opinion of the author that at the temperatures quoted, such systems take several hours to approach equilibrium. Therefore the results from these workers is considered of little use to this research, but the following points are of interest. High alumina firebrick and magnesia showed the greatest resistance to corrosion by the ash from a LAGUNILLAS crude as tested by cone slumping(21). KING and SUBER (54) heated an equimolar mixture of alumina and vanadium pentoxide at 650°C. This gave a solid solution of alumina in vanadium pentoxide plus αAl_2O_3. Under the same conditions, silica yielded a solid solution of silica in vanadium pentoxide plus quartz, and baria and strontia gave glasses. McCLAREN and RICHARDSON (56) using X-ray analysis and cone slumping techniques found that V_2O_5 had very little action on refractories, with no evidence of reaction products. However, additions of soda produced greater modification of the refractory phases. This is in agreement with GRAY and KILLNER (11) and to some extent with JONES and HARDY (21). It was decided to complete the solubilities of alumina in melts containing more than 50 mole % sodium sulphate and to attempt to determine solubilities of silica in these melts.

7.1. EXPERIMENTAL TECHNIQUE.

The technique involved is essentially that of heating a sample of refractory in a melt to constant loss of weight. To simplify the process and to facilitate evaluation of results, non-porous, pure refractory oxides were used i.e. sapphire and silica glass. The melts were contained in platinum or platinum/rhodium crucibles heated in small electrical resistance furnaces. These furnaces were constructed of Kanthal 'A' wound on electrical porcelain tubes using vermiculite insulating material. Power was supplied from stabilized mains through a "Variac" torroidal transformer. Temperature was controlled by "Electroflo" ON/OFF type controllers using chromel/alumel thermocouples. Rods of alumina and silica were held in the chucks of stirring motors (see fig.6) which were mounted on a carriage capable of vertical movement on a threaded rod. Operation of an electric motor (the "lifting" motor) at the upper end of the threaded rod caused the rod to ascend out of or descend into the melt. Microswitches determined the position at which the motor stopped, which effect ensured that rods were immersed to approximately the same depth in the melt each time. A time switch was capable of starting the lifting motor (and switching off the st$\overset{\text{irr}}{\text{ar}}$ting motor) after any period up to four hours. This also enabled a rod to be put into the melt at the end of the working day thereby increasing the number of observations per day and shortening the duration of the experiment. The lifting motor was capable of three speeds, the slowest of which enabled alumina rods to enter the

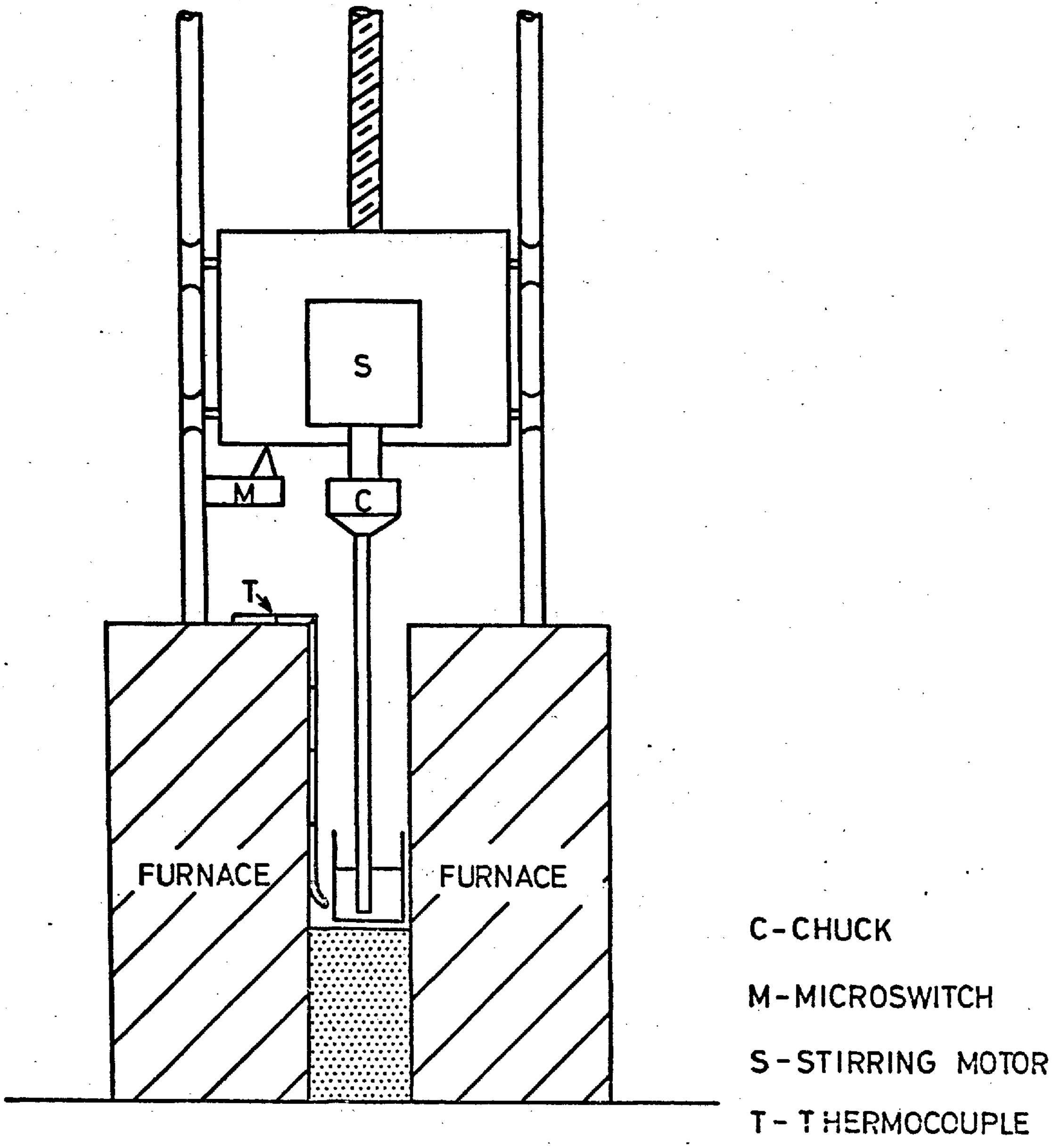


FIG. 6 APPARATUS FOR THE DETERMINATION OF THE SOLUBILITY OF REFRACTORIES

furnace without fear of thermal shock. The stirring motors, only rotated at one speed - 960 r.p.m. These were not always used as some melts dissolved the rods rapidly under static conditions. Three such units were built into one compact assembly shown in plate 4 which included an extractor hood for vapours such as SO_3 and V_2O_5.

7.2. EXPERIMENTAL PROCEDURE.

A platinum crucible was weighed empty and then plus mixture. This was then placed in the furnace and brought to the required temperature. The length of time before the rod first entered this melt depended upon the composition of the mixture and the conditions required. If mixtures of sodium metavanadate and sodium sulphate were used, the experiment could start immediately. Vanadium pentoxide and sodium sulphate mixtures were allowed 4 days at 1050°C which ensured that at least 90% of the available SO_3 was expelled. Some V_2O_5/Na_2SO_4 mixtures were not allowed this time to react and the experiment was commenced immediately the components became molten. This was to enable a comparison to be drawn between a reacted and a "non-reacted" melt. Throughout the solubility experiments B.D.H. 98.5% V_2O_5 and "Analar" Na_2SO_4 were used. The initial period that the first rod spent in a melt depended on temperature and corrosivity of the melt. For silica the time varied between 1.5 min. and 2 hr. and for alumina 1 day and 4 days. The actual procedure for alumina and silica varied and so they will be described separately.

7.2.1. ALUMINA.

As discovered by GOLDMAN, alumina will reach a constant weight loss in a V_2O_5/Na_2SO_4 melt. Therefore, the sapphire rod was lowered into the melt and left stirring for about one day. It was then lifted out, weighed, cleaned and reweighed. The amount of slag lost during the cleaning

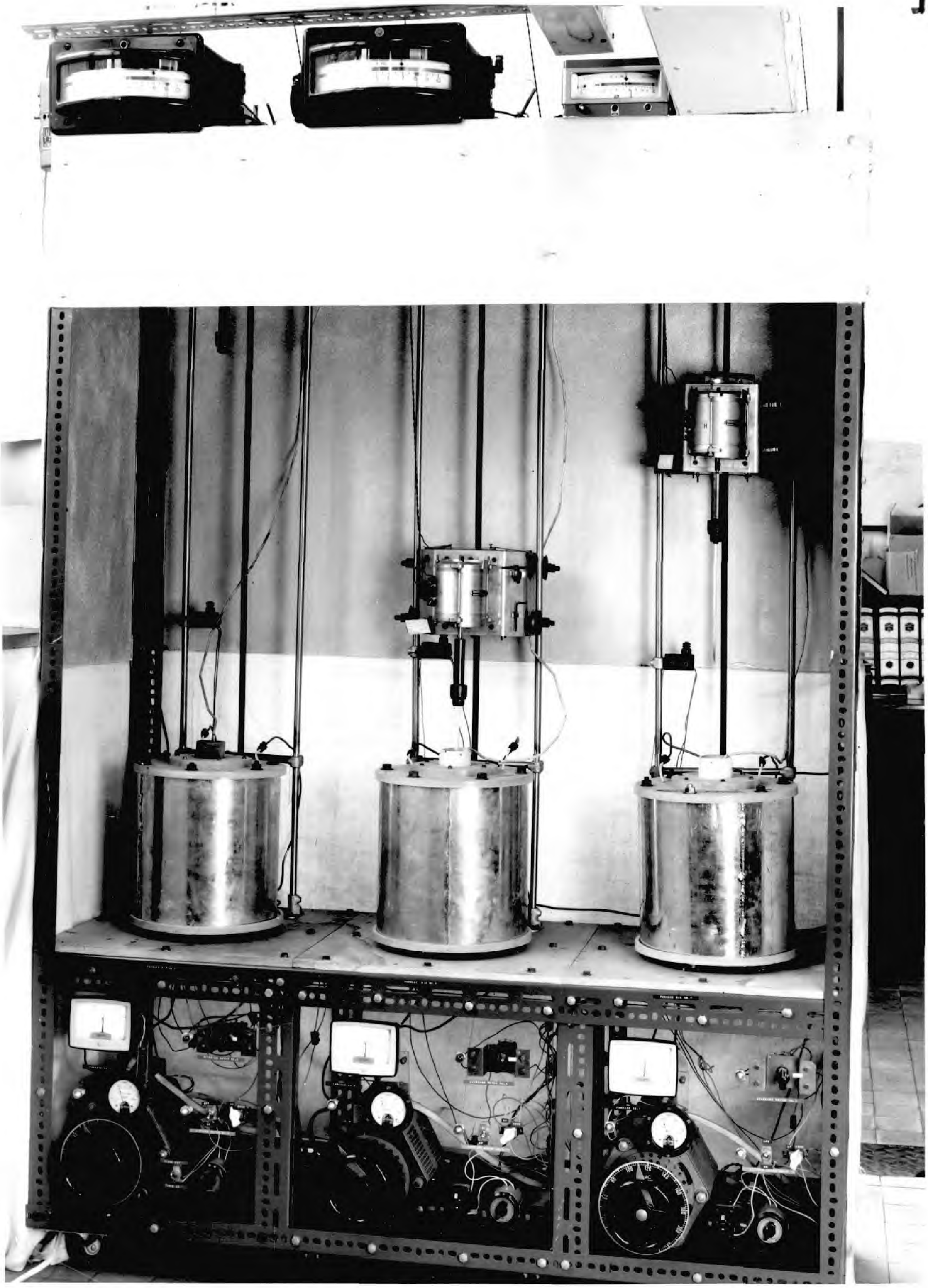


PLATE 4. THE SOLUBILITY TESTING APPARATUS

process was deducted from the amount known to be in the crucible. The rod was then replaced in the melt and this procedure continued until a constant weight loss was achieved. A typical result is shown in fig. 7A. For the system shown, the melt was saturated with alumina after about 60 hr. The temperature was then increased by approximately 100°C and a new constant weight loss measured. To reclean the rods for weighing, cold or warm running water was found to be satisfactory.

7.2.2. SILICA.

GOLDMAN (1) discovered that at 721°C, V_2O_5 dissolved 48 wt.% silica after about four months. This experiment was repeated and the weight loss of the rod plotted against time as the experiment progressed. Two aspects of this graph were noticed. Firstly that although the points followed an approximate straight line, the locus of this line did not pass through the origin. Secondly, the early readings for this system deviated from the straight line more than the later points. Therefore the experiment was repeated taking smaller and smaller intervals of time until the form of the graph shown in fig.7B evolved. The section of the graph marked OA represents the simple dissolution of silica glass in the melt. Such a mechanism should follow an equation of the type:-

$$\frac{dc}{dt} \propto (C_{eq} - C_t) \qquad (18)$$

Plots of dc/dt versus C_t produced approximate straight lines indicating that the assumed equation was being obeyed and enabling C_{eq} to be evaluated. However, silica glass is not the stable phase at temperatures investigated and the line AB represents the steady transfer of silica glass in the rod to cristobalite, which was usually deposited on the crucible walls at the slag line. Thus the silica glass in the rod was using the melt as a method of reaching a lower energy form.

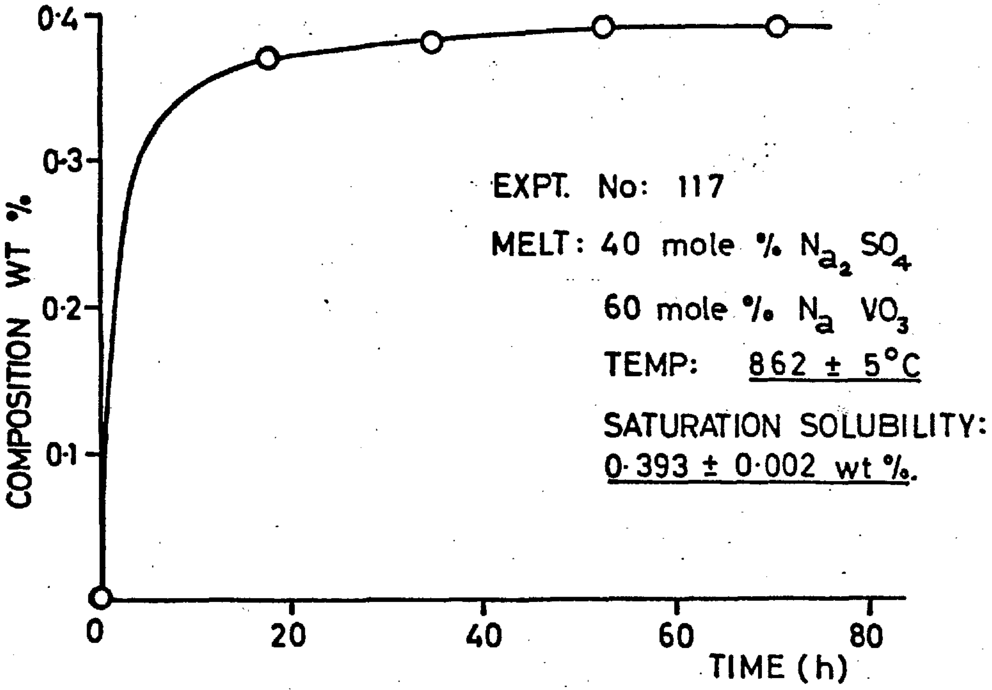


FIG. 7A TYPICAL RESULT FOR THE DISSOLUTION OF ALUMINA

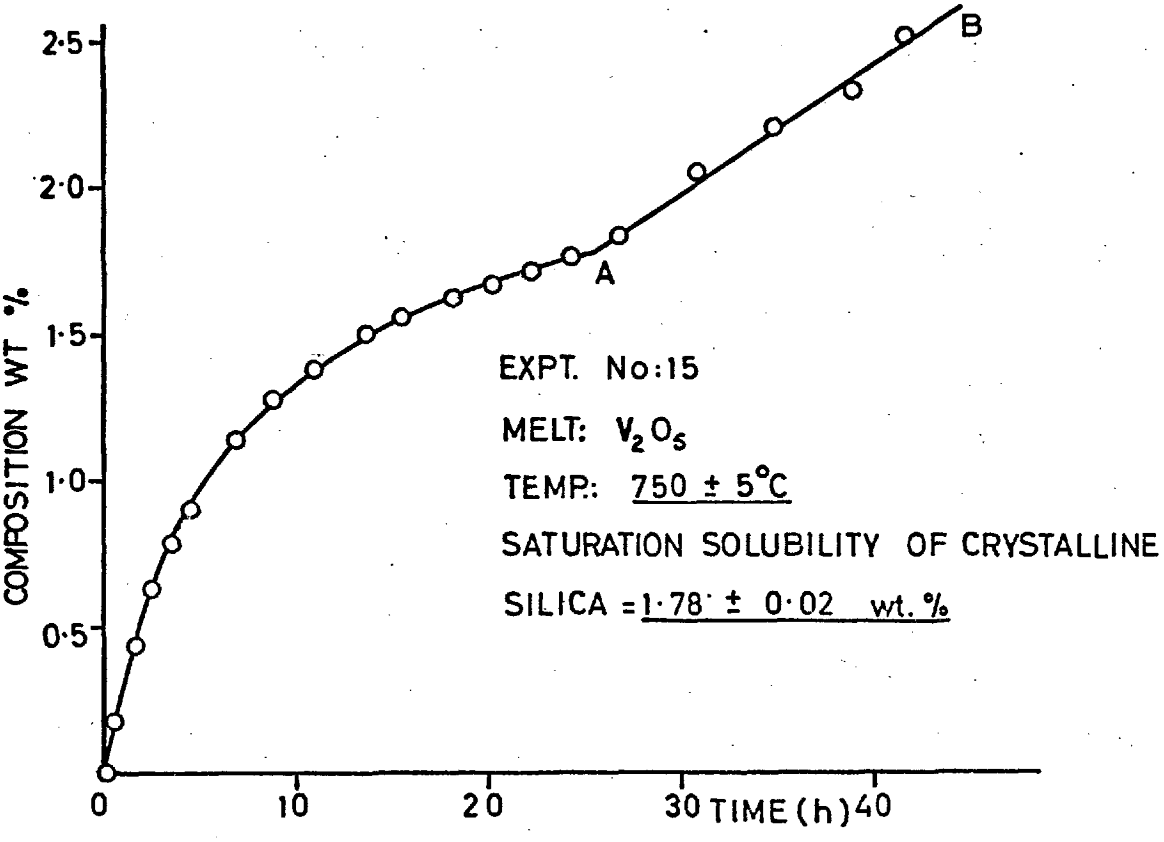


FIG. 7B TYPICAL RESULTS FOR THE DISSOLUTION OF SILICA

Therefore at A the melt was saturated with cristobalite and the values of C_{eq} calculated by equation (18) refer to the apparent saturation solubilities of silica glass. Upon removal of a rod from a melt after reaching point A, small crystals of cristobalite could be seen in the slag on the rod surface. These were presumably picked up from the surface of the melt where they would have been floating.

7.3. RESULTS FOR ALUMINA.

The results are seen in figs. 8A, 8B and 11A. They show that as the percentage of sodium sulphate increases beyond 50 mole %, the saturation solubility of alumina decreases.

7.3.1. SOLUBILITY OF Al_2O_3 in Na_2SO_4/V_2O_5 MELTS (Fig.8A).

In these melts containing more than 50 mole % Na_2SO_4, the solubility of alumina is quite low, being below 2.5 wt.% at 1100°C. GOLDMAN investigated melts containing up to 50 mole % Na_2SO_4 and fig. 8A includes his values for the equimolecular mixture. All these mixtures were allowed four days at 1050°C to expel at least 90% of the available SO_3 before adding any alumina. The 50 mole % Na_2SO_4 mixture is very dependent upon temperature. The 60 mole % mixture is quite dependent upon temperature above 1000°C, but mixtures containing 70 or more mole % Na_2SO_4 are relatively independent of this parameter, e.g. raising the tempreature of the 70 mole % Na_2SO_4 mixture from 700 to 1100°C only causes the solubility to increase from 0.55 to 0.76 wt.%. The addition of sodium sulphate caused the solubility to drop rapidly and the solubility of alumina in Na_2SO_4 is too small to be shown on the graph. Values obtained were: less than 0.0022 wt.% at 915±5°C and less than 0.0027 wt.% at 974±5°C. The reason for quoting these values in the "less than" form is that after 30 hr. the rods began to gain weight due to ionic penetration by sodium sulphate in some form. This fact was proved by

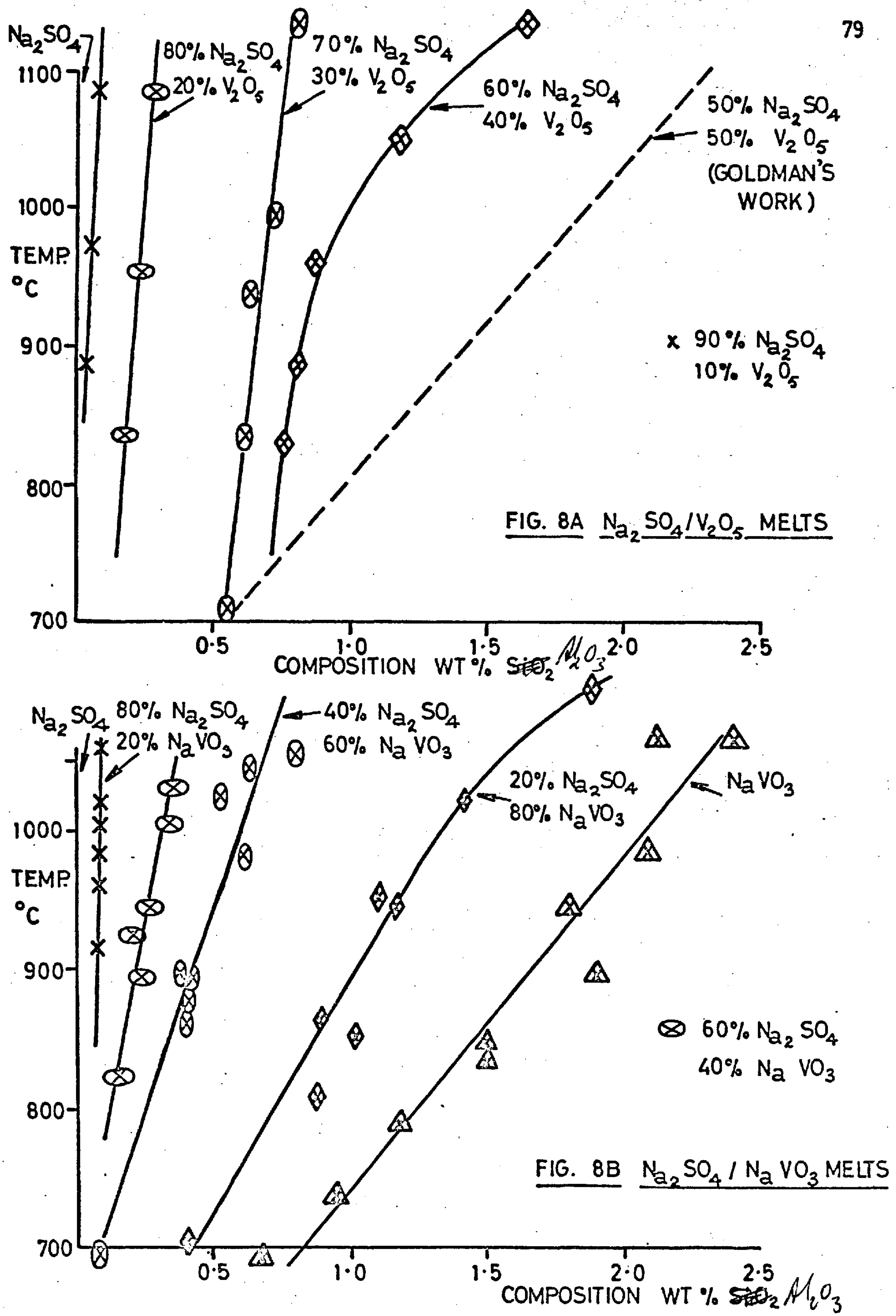


FIG. 8A Na_2SO_4/V_2O_5 MELTS

FIG. 8B Na_2SO_4 / $NaVO_3$ MELTS

FIG. 8 SOLUBILITY OF Al_2O_3 IN MELTS CONTAINING Na_2SO_4

subsequent analysis (by the Analytical Service Laboratory, Imperial College). The values quoted are the maximum thought possible to have been dissolved in 60 hr. ignoring weight gains. Now the single crystal sapphire rods showed no evidence of macrostructure before use. However, in all melts tested, with the exception of pure sodium sulphate, on removal from a melt the rod end that had been immersed had developed flat sides. These were symmetrical about a diameter of the rod and the shape of the faces were reproducible using differe rods in other melts. These were therefore sapphire crystal faces which had been exposed by thedissolution process. This effect indicates that the dissolution mechanism is probably reaction controlled, as concluded by FARUQI (62). This may also be the case with the pure sodium sulphate, but the amount dissolved was so small that such observations were impossible.

7.3.2. SOLUBILITY OF Al_2O_3 in $Na_2SO_4/NaVO_3$ MELTS (Fig.8B).

The melts tested besides pure $NaVO_3$ and Na_2SO_4 had the compositions 20,40,60,80 mole % $NaVO_3$. These melts are equivalent to 10,20,30,40 mole % V_2O_5/Na_2SO_4 melts respectivel at equilibrium. In fig.8A and B comparison is possible between these various melts. It was not expected that the results would be vastly different but it was not known what effect small percentages of available sulphur trioxide would have. It is seen that over some temperature ranges for certain mixtures, the "fully equilibriated" melts accept more alumina. It can be argued that this is solely due to the fact that in fig 8A, percentages are based on the original weight of the Na_2SO_4/V_2O_5 mixture before reaction. $Na_2SO_4/NaVO_3$ melts lose no weight due to chemical reaction. Table 3 compares the saturation solubilities of the two kinds of melts based on the weights that they would have had as unreacted mixtures of Na_2SO_4 and V_2O_5.

Table 3. Solubility of Al_2O_3 in Na_2SO_4/V_2O_5 and $Na_2SO_4/NaVO_3$ Compared.

MELT (mole %)	SOLUBILITY wt.%			
	750°C	850°C	950°C	1050°C
Na_2SO_4	-	-	0.0025	0.0032
90% Na_2SO_4 10% V_2O_5 A	-	0.030	0.052	0.073
80% Na_2SO_4 20% $NaVO_3$ B	-	0.072	0.076	0.079
80% Na_2SO_4 20% V_2O_5 A	0.15	0.19	0.23	0.27
60% Na_2SO_4 40% $NaVO_3$ B	0.09	0.13	0.23	0.40
70% Na_2SO_4 30% V_2O_5 A	0.57	0.61	0.67	0.75
40% Na_2SO_4 60% $NaVO_3$ B	0.14	0.28	0.42	0.63
60% Na_2SO_4 40% V_2O_5 A	0.66	0.76	0.92	1.24
20% Na_2SO_4 80% $NaVO_3$ B	0.44	0.68	0.92	1.24
50% Na_2SO_4 50% V_2O_5 A	0.76	1.19	1.64	2.11
$NaVO_3$ B	0.76	1.09	1.43	1.74

A. Results for Na_2SO_4/V_2O_5 melts based on original weight of the unreacted mixtures.

B. Results for $Na_2SO_4/NaVO_3$ melts based on the weight that these would have had as unreacted Na_2SO_4/V_2O_5 mixtures.

So it is seen that under these conditions the mixtures containing small percentages of available sulphur trioxide, or sodium vanadyl vanadate II dissolve slightly more alumina than completely equilibriated melts. The exception to the statement is the 90% Na_2SO_4/10% V_2O_5 melt. This is presumably due to the fact that sodium vanadyl vanadate II dissolves more alumina than sodium metavanadate (see fig.11A).

7.3.3. THE SOLUBILITY OF Al_2O_3 VERSUS MELT COMPOSITION.

As the sodium/vanadium ratio found in marine boiler slags varies, it is of interest to know how the possible solubility of alumina will vary with this ratio. Conditions will be very different, of course, with many other components in the melt which may either increase or decrease its corrosivity. Fig.11A shows the saturation solubility of sapphire in pure sodium sulphate/vandium pentoxide melts at 750, 850, 950 and 1050°C. (The results for up to 50 mole % Na_2SO_4 were GOLDMAN's work).

Starting with pure vandium pentoxide, the solubility ranges from 1.4 wt.% at 750°C to 3.3 wt.% at 1050°C. The addition of soda increases the solubility until a maximum is reached somewhere between 10 and 16 mole % Na_2SO_4. Further addition of sodium sulphate after this maximum serves only to reduce the solubility. After 50 mole % i.e. at the first appearance of free sodium sulphate in the melt, the solubility drops rapidly to very nearly zero in pure sodium sulphate. Up to 50 mole % Na_2SO_4 the solubilities are all of the same order i.e. approximately between 1 amd 3.5 wt.%. Therefore, it would appear that free sodium sulphate in a melt acts as a modifier. The sodium/vanadium ratio on a superheater tube of a fighting ship in 1967 was approx. 0.9. Therefore, if these results are capable of application to boiler surfaces, this ratio would need to increase to about 4 to have effect. This is unlikely to happen as vanadium contents appear to be increasing while attempts are being made to reduce sodium contamination.

7.3.4. ACCURACY OF THE RESULTS.

Temperature: mostly ± 5°C but some results ±10 and 20°C.
Weighing: each weighing ± 0.0005g. but differences in weighing also ± 0.0005 g.

Example Expt. 117 (Fig.7A).

Temperature	862 ± 5°C.
Loss of weight of sapphire rod A2	0.0904 ± 0.0005 g.
Original weight of mixture	22.9725 ± 0.0005 g.
Loss of slag	0.0335 ± 0.0020 g. (4 weighings)
Evaporation of slag(estimate only)	0.0100 ± 0.0100 g.

Composition = 0.393 ± 0.002 wt.% i.e. less than 1%.

In fig.8A and 8B it is obvious that some points are well outside this very small error limit. Possible further factors affecting the accuracy are : diffusion of sodium sulphate into the sapphire (this is NOT removed by boiling 2N HCl), evaporation of selective components e.g. Na_2O (38), incorrect mixture of components (small errors only), effect of dipping cool rod into nearly saturated melt, melts creeping out of pot, further approaches towards equilibrium by melt, cycling effect of ON/OFF controller, local atmospheres, etc. A more probable error is ± 4%.

7.4. RESULTS FOR SILICA.

The results for silica are given in fig. 9, 10 and 11B. Generally, silica is more soluble in a melt than alumin- Except for high sodium sulphate contents, melts which dissolved much alumina dissolve relatively small amounts of silica and vice versa.

7.4.1. THE V_2O_5 - SiO_2 PHASE DIAGRAM.

As explained earlier, the saturation solubility of silica in vanadium pentoxide was found to be far less than GOLDMAN has indicated. The transfer of silica as a glass in the rod, to cristobalite on the walls of the crucible indicated that at point A on fig.7B the melt was saturated with cristobalite. The various "points A" gained were plotted versus temperature and it was noticed that this was not a smooth curve, but two distinct curves. The junction of the two curves at 855±5°C was recognised as near to the quartz to Tridymite transformation at 867°C. Investigation of precipitates formed at 705, 800, 920 and 1030°C were examined by X-ray analysis (by D.BARHAM). In each case the precipitate was cristobalite. However, samples of quartz crystal heated in the presence of V_2O_5 were found to be stable at 765°C but a slow conversion to cristobalite took place at 900°C. (D.BARHAM by X-ray analysis). Thermal analysis of vanadium pentoxide melts containing small percentages of silica enabled the phase diagram shown in fig.9A to be produced (Thermal analysis work done mainly by D.BARHAM). Thisdiagram has been published under the joint authorship of GRAVETTE, BARHAM AND BARRETT (57). The results from most experiments enabled an apparent equilibrium solubility for silica glass to be caculated. This was always more than the solubility of the crystalline phase by approximately 7 wt.% below 855°C and 12 wt.% above 855°C.

7.4.2. SOLUBILITY OF SiO_2 IN V_2O_5/0-50% Na_2SO_4 (Fig.9B).

The result of adding 10 and 20 mole % Na_2SO_4 to V_2O_5 is to decrease the solubility of silica. It is possible that changes in the slopes of these curves also occurs corresponding to the quartz-cristobalite transformation, but too few results were taken to discover whether this is so. At 30 mole % Na_2SO_4, the melt dissolves approximately the same amounts as did pure V_2O_5. However 40 and 50 mole % Na_2SO_4/V_2O_5 melts dissolved more silica, than those with lower Na_2SO_4 concentrations, at all temperatures investigated. Also the temperature dependence of the saturation solubility increased as Na_2SO_4 concentration increased. The size of the points in fig.9B indicates the approximate estimated error.

7.4.3. SOLUBILITY OF SiO_2 IN Na_2SO_4/50-0 MOLE % V_2O_5 MELTS (Fig.10A).

The scatter of results in this half of the diagram is considerably more than that with melts containing 0.50 mole% Na_2SO_4. This is due to the fact that in high sodium sulphate melts and particularly at high temperatures the silica glass rods devitrified faster than they dissolved. While the rods were in the melt, the devitrified layer was usually coherent

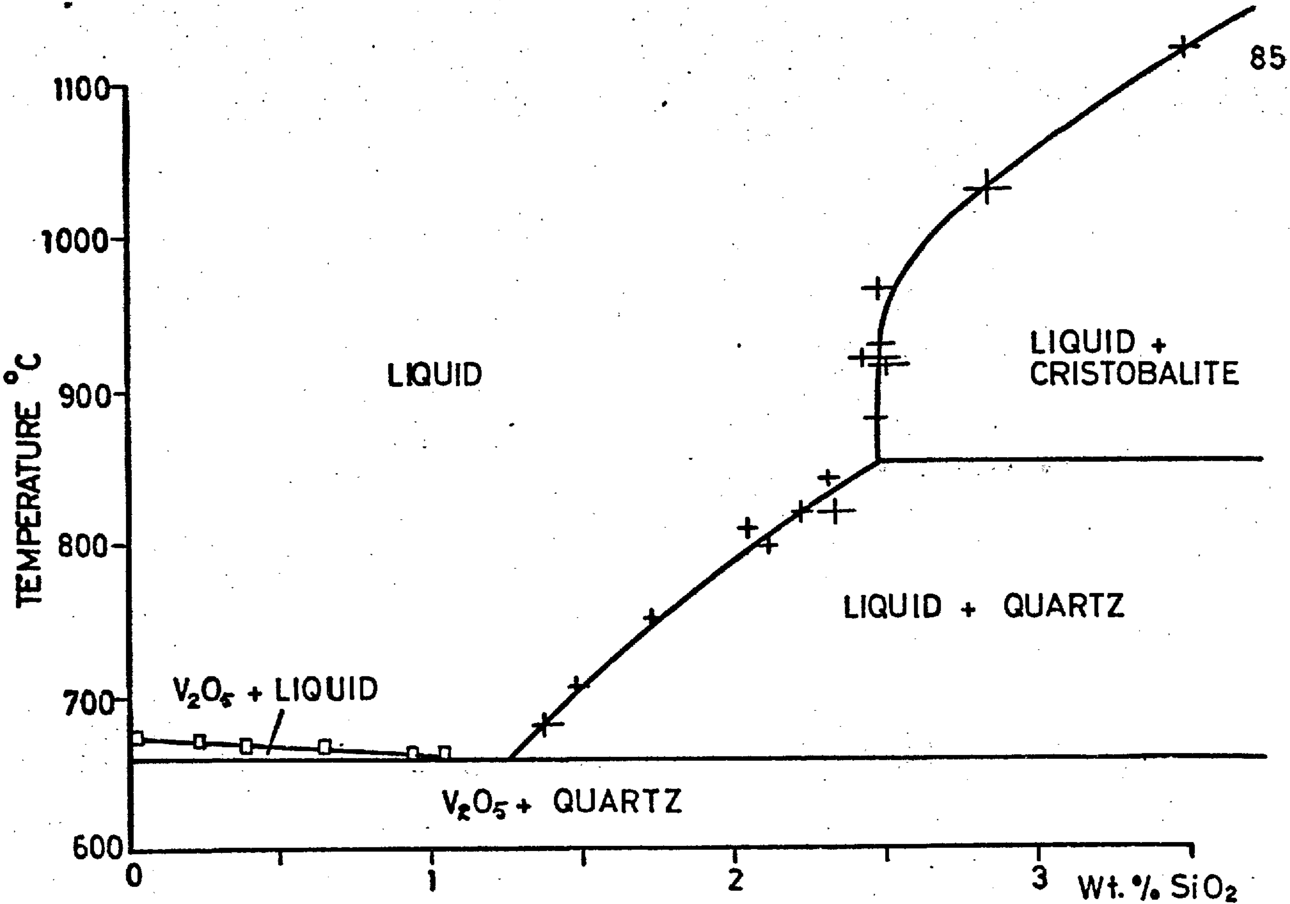


FIG. 9A THE V_2O_5-SiO_2 PHASE DIAGRAM (57)

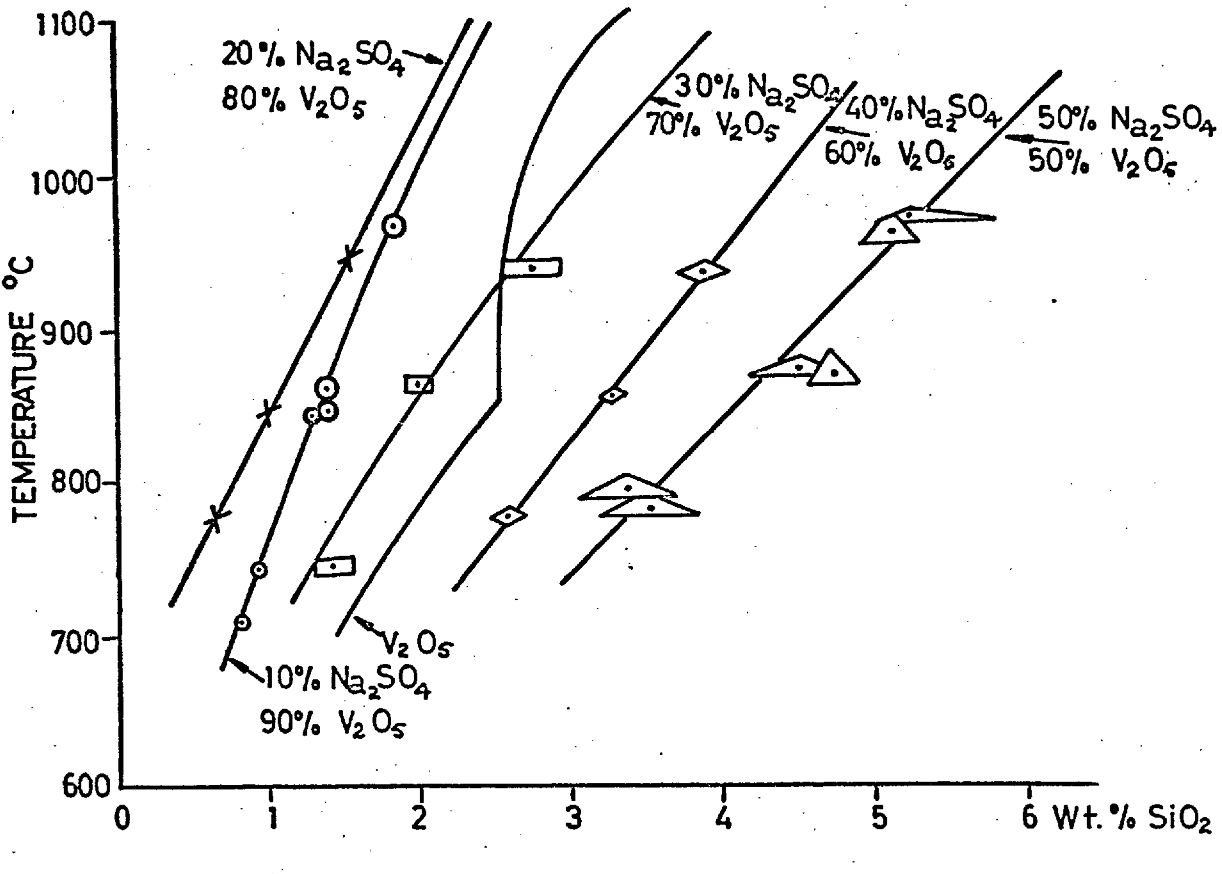


FIG. 9B THE SOLUBILITY OF SiO_2 IN V_2O_5 / 0-50 mde % Na_2SO_4

and whole. On removal from the melt, even with slow cooling, hair-line cracks appeared. If the devitrification product was β-cristobalite (or "high cristobalite"), this would have had a different coefficient of thermal expansion to that of silica glass. The cracks probably appeared when β-cristobalite transformed to α-cristobalite at a temperature between 270 and 180°C. This transformation is accompanied by a 3.7% volume shrinkage. Upon placing such rods into water or HCl solution for cleaning, the devitrified layer and slag often audibly flaked off. This problem of devitrification increased with increasing temperature and increasing sodium sulphate content, although the devitrified layer was more coherent from melts of pure sodium sulphate. If a melt contained enough sodium sulphate and was at a high enough temperature for the rate of devitrification to exceed the rate of dissolution, then the point of inflexion ("A" in fig.7B) did not occur as silica glass was no longer being presented to the melt. Instead a smooth curve was obtained much as that in fig.7A but generally equilibrium was achieved in a much shorter time. The occurrence of devitrification is summarised in Table 4.

At first, when devitrification became a nuisance, the method used to combat this effect was the use of shorter and shorter immersion times for the rods. When using 70 and 80 mole % Na_2SO_4 melts this entailed using dozens of rods. Then one rod was accidentally left in the melt for about 2 hr. and this devitrified layer was found to be more coherent. Therefore, when devitrification was experienced in a system, times of 2 hr. were used at first increasing to 8 hr as equilibrium was approached. These devitrified layers produced from long immersion times were not always coherent, but in most cases an estimate of the silica dissolved was possible by deducting an average slag loss value from the weight of the rod plus slag.

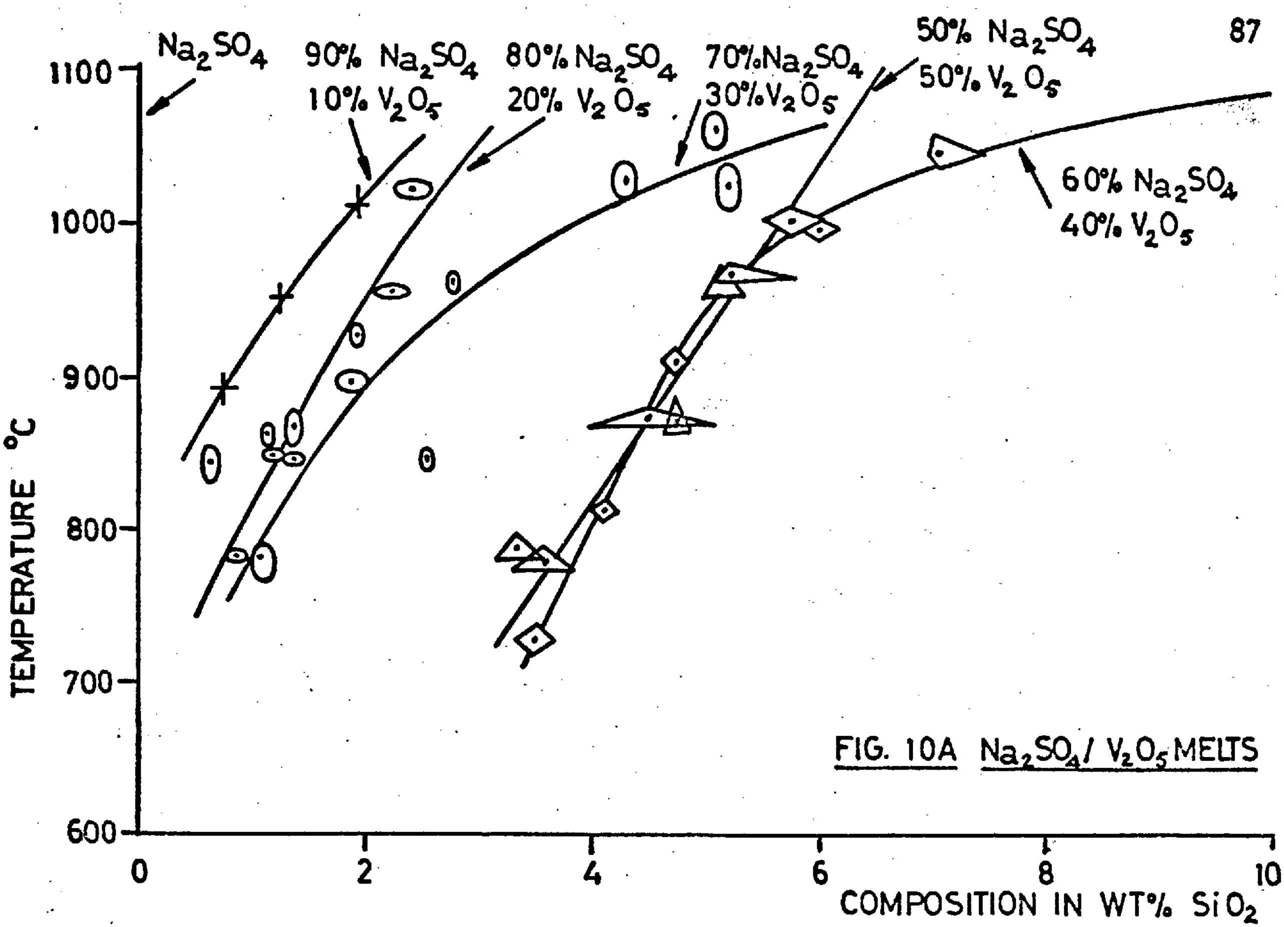


FIG. 10A Na_2SO_4 / V_2O_5 MELTS

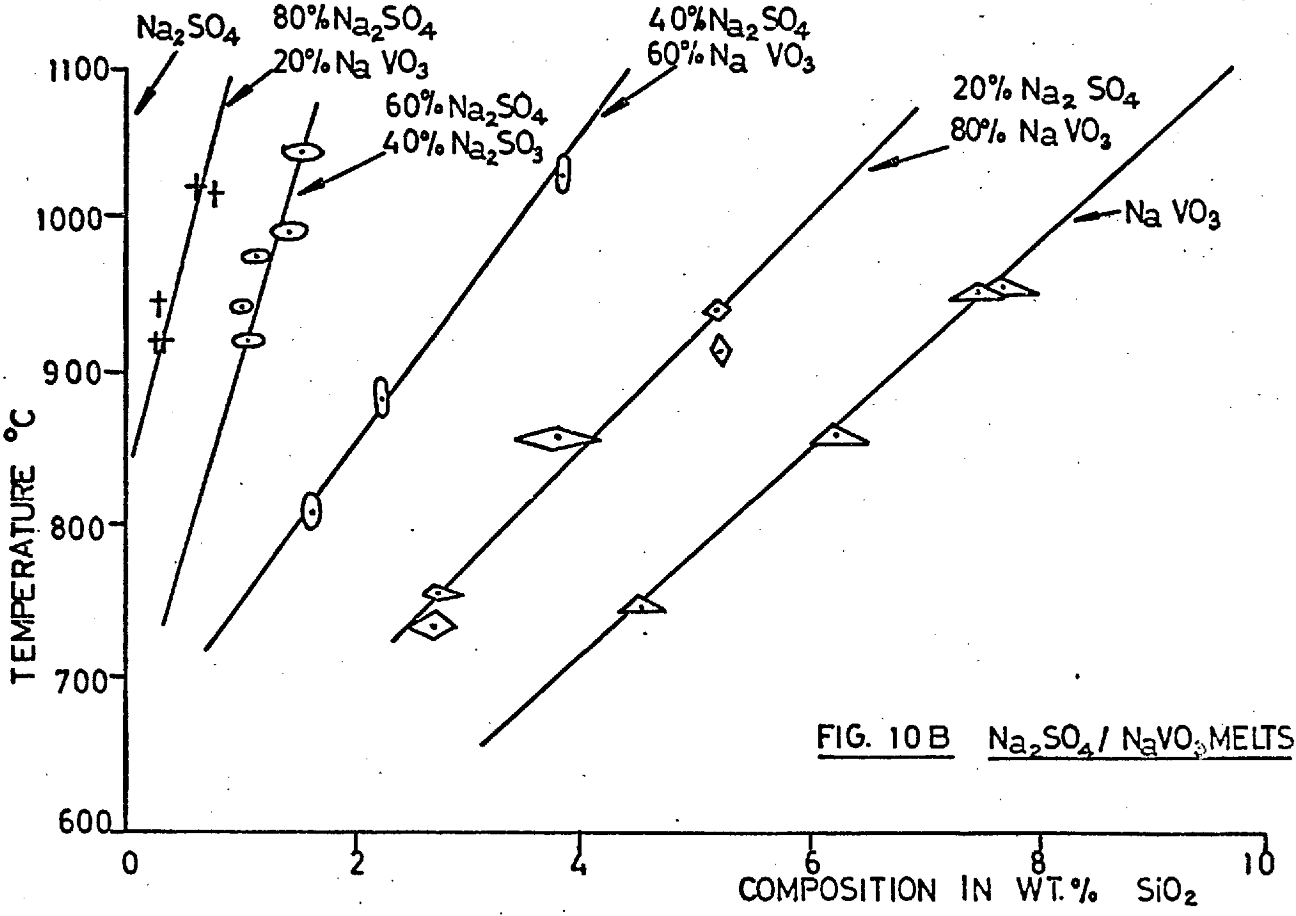


FIG. 10 B Na_2SO_4 / $NaVO_3$ MELTS

FIG. 10 SOLUBILITY OF SiO_2 IN MELTS CONTAINING Na_2SO_4

Table 4.

Occurrence of Devitrification of Vitreous Silica in Na_2SO_4/V_2O_5 Melts.

Melt Composition Mole %		Temp. °C.	Devitrification
Na_2SO_4	V_2O_5		
	100	1175	No devitrification
10	90	970	No devitrification
20	80	950	No devitrification
30	70	938	No devitrification
40	60	936	No definite data
50	50	974 875	Devitrification with some loss of devitrified product
		784	Devitrification of surface layer only
60	40	758	Devitrification with some loss of devitrified product
70	30		Severe devitrification and loss of devitrified product product at all temperatures investigated
80	20		
90	10	1012	Devitrification but NO loss (i.e. surface only)
100		903	Devitrification with loss of product after 53 hr.
		1031	Devitrification with loss of product after 17 hr.

7.4.4. SOLUBILITY OF SiO_2 IN $Na_2SO_4/NaVO_3$ MELTS (Fig.10B).

As with alumina, melts containing 20, 40, 60, 80 and 100 mole % $NaVO_3$ were tested. These are equivalent to fully reacted sodium sulphate mixtures containing 10, 20, 30, 40 and 50 mole % V_2O_5. Melts containing 100, 80 and 60 mole % $NaVO_3$ are seen to be capable of dissolving more silica than their Na_2SO_4/V_2O_5 equivalents. Those containing 40 and 20 mole % $NaVO_3$ dissolved less. This is comparable with the results for alumina where all melts dissolved more. The results in Table 5 compare solubilities in Na_2SO_4/V_2O_5 melts with $Na_2SO_4/NaVO_3$ melts where the latter are considered as being derived from a Na_2SO_4/V_2O_5 mixture.

Table 5.

Solubility of SiO_2 in Na_2SO_4/V_2O_5 and $Na_2SO_4/NaVO_3$ Compared.

MELT (mole %)		750	850	950	1050°C
Na_2SO_4		-	-	0.017	0.058
90% Na_2SO_4 10% V_2O_5	A	-	0.4	1.3	2.4
80% Na_2SO_4 20% $NaVO_3$	B	-	0.09	0.38	0.75
80% Na_2SO_4 20% V_2O_5	A	0.6	1.25	2.0	3.0
60% Na_2SO_4 40% $NaVO_3$	B	0.36	0.6	1.0	1.4
70% Na_2SO_4 30% V_2O_5	A	1.0	1.7	2.9	5.0
40% Na_2SO_4 60% $NaVO_3$	B	0.8	1.7	2.5	3.4
60% Na_2SO_4 40% V_2O_5	A	3.6	4.3	5.1	7.3
20% Na_2SO_4 80% $NaVO_3$	B	2.2	3.2	4.3	5.0
50% Na_2SO_4 50% V_2O_5	A	3.1	4.1	5.1	6.1
$NaVO_3$	B	3.4	4.6	5.7	6.9

For A and B - see Table 3, p. 81.

So it is seen that for all compositions in table 5, except the equimolecular mixture, the "fully equilibriated" melts dissolve less silica than the "near equilibriated" melts. This is similar to the results for alumina in table 3.

7.4.5. THE SOLUBILITY OF SiO_2 VERSUS MELT COMPOSITION (Fig.11B)

In fig.11B it is seen that the composition of the melt greatly affects the solubility of silica. Addition of soda to vanadium pentoxide serves initially to decrease the amount of silica the melt can dissolve (cf. Al_2O_3 which increases). The 10-16 mole % Na_2SO_4 which produced a maximum in the solubility of alumina (fig.11A) may be compared with the 12-18 mole % Na_2SO_4 which produced a minimum in the

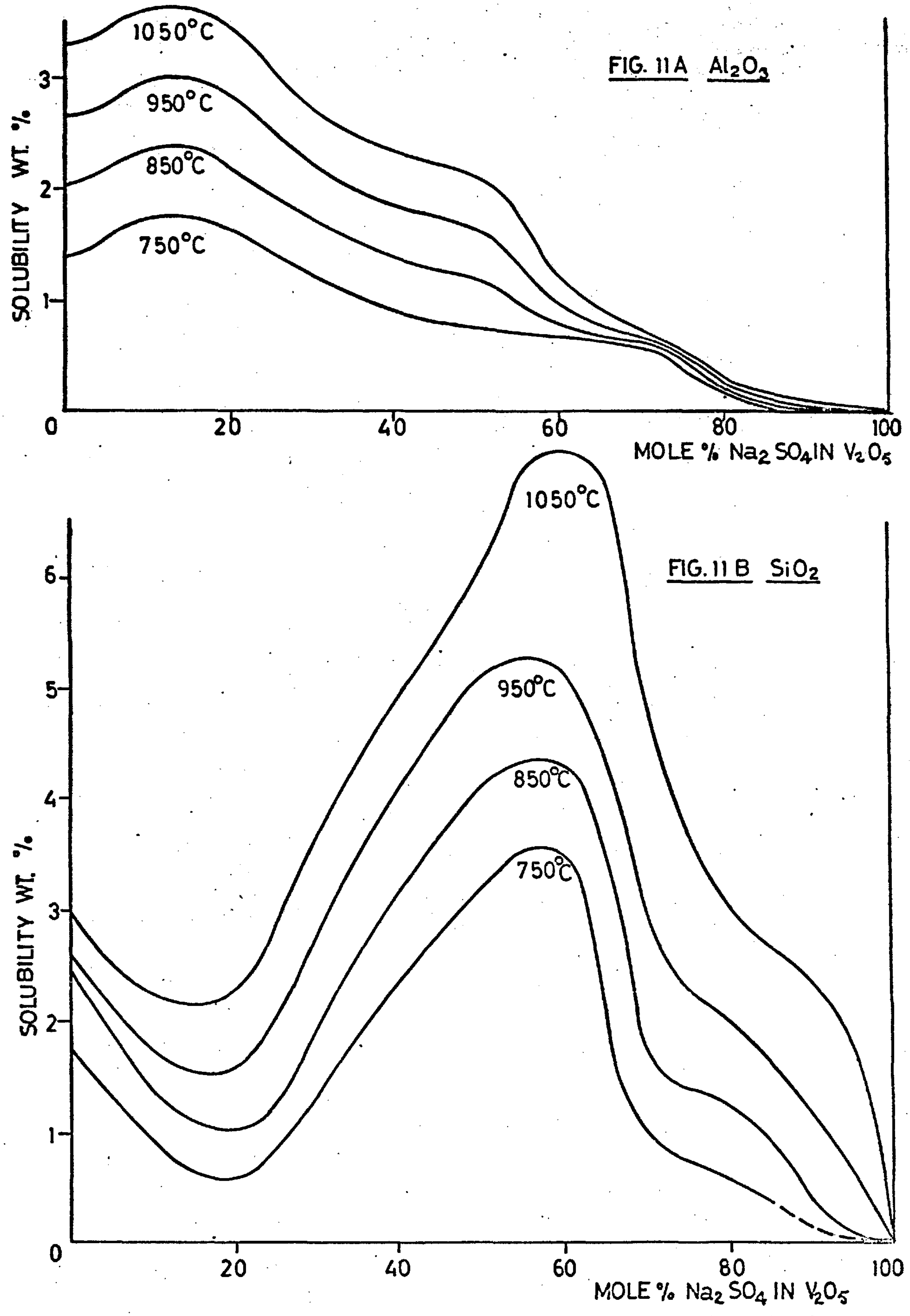


FIG. 11 SOLUBILITY OF Al_2O_3 & SiO_2 IN Na_2SO_4/V_2O_5 MELTS

solubility of silica. The equimolecular mix dissolved more silica than pure V_2O_5 whereas it dissolved less alumina. Also the presence of free sodium sulphate, definitely a modifier for alumina, gives a maximum on the curve for silica. The solubility of silica in pure sodium sulphate is very small, being approximately 0.017 wt.% at 950°C and 0.058 wt.% at 1050°C.

7.4.6. ACCURACY OF THE RESULTS.

The accuracy of the results using silica was far better than expected. The method used, i.e. plotting weight loss against time for a dissolving rod, seemed to invite errors. As the rod dissolved, the surface area undergoing dissolution changed, in some cases the area dropped from about 190 mm^2 to about 50 mm^2 with no apparent deviation of the plot. Also, the rods were not always immersed to the same depth. The microswitch stops ensured that the stirring motor and the chuck were always approximately the same position, but this did not account for differences in the lengths of the rods used. Such variations could change the area undergoing dissolution by 12%. It was very rare for one rod only to be used in an experiment. Usually each time one rod was removed, it was replaced by another. Nevertheless curves gained were remarkably good - fig.7B being a good example (although, naturally, one of the better results). A peculiar feature of this method was found to be as follows:- let us suppose that the curve OA in fig.7B was being followed with good results, then one result was off the line (below OA deviations were never large above the line); then the next result was often quite large, bringing the total quantity of silica dissolved "back" onto the expected curve. As these two results involved two separate rods, this phenomenon appears ridiculous. However, it happened on several occasions and was also noticed by D.BARHAM while he was dissolving silica in molybdenate melts using the same method. No explanation can be offered for this peculiar effect.

Estimated errors:-

Temperature - usually ± 5°C sometimes ± 10 and 20°C.

Weighings - ± 0.0005 for each pair of weighings involving a difference.

Example: Expt. 15 (fig.7B).

Temperature	750 ± 5°C.
At "A" wt. of silica dissolved	0.150 ± 0.002 g.

(only one rod, S9, was used and the error in weighing this many times must be about 0.002 g.)

Melt present at point "A"	8.4887 ± 0.0075 g
Possible evaporation of V_2O_5	0.090 g.

Composition $\frac{0.150}{8.55} = \underline{1.75 \pm 0.03 \text{ wt. } \%}$

Note that error is for a melt where NO devitrification occurred. Melts containing more than 50 mole % Na_2SO_4 suffered from loss of devitrified product and errors varied in each separate experiment. As may be seen from the points in fig. 9B, 10A and 10B errors varied from ± 2 to ± 22%, with melts containing 60, 70 and 80 mole % Na_2SO_4 (and the equivalent 80, 60 and 40 mole % $NaVO_3$) suffering the largest errors.

7.4.7. THE DISSOLUTION OF SILICA IN 60% Na_2SO_4/40% V_2O_5 UNDER DIFFERENT CONDITIONS.

To investigate further, the effect of melt condition on the solubility of silica, it was decided to perform three experiments.

1. Dissolution of silica glass in 60% Na_2SO_4/40% V_2O_5 - the dissolution process to start immediately the mixture was molten. Thus the mixture would contain free V_2O_5 at first, then some sodium vanadyl vanadate I and perhaps some sodium vanadyl vanadate II and sodium metavanadate.

2. Dissolution of silica glass in 60% Na_2SO_4/40% V_2O_5

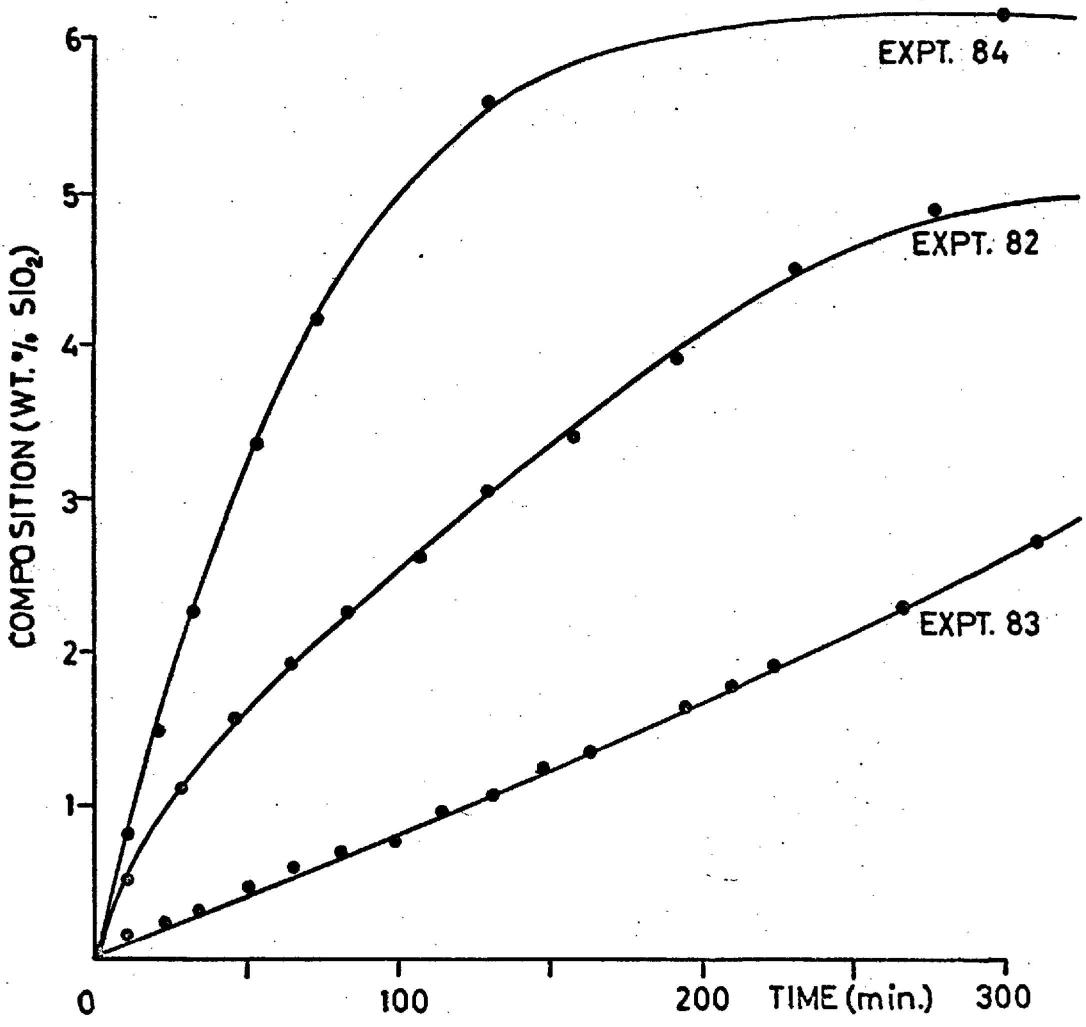


FIG. 12 DISSOLUTION OF SILICA GLASS IN 60% Na_2SO_4/40% V_2O_5

EXPT. 83 60% Na_2SO_4/40% V_2O_5 DISSOLUTION OF SILICA STARTED IMMEDIATELY THE MIXTURE WAS MOLTEN. TEMP. 937 °C

EXPT. 82 60% Na_2SO_4/40% V_2O_5 MIXTURE ALLOWED 10,000 min. AT 950 °C TO APPROACH EQUILIBRIUM BEFORE DISSOLVING SILICA. WEIGHT LOSS OF MIXTURE ABOUT 19·5%. TEMP. 914 °C

EXPT. 84 20% Na_2SO_4/80% Na_2VO_3 (≡ 60% Na_2SO_4/40% V_2O_5 AT EQUILIBRIUM). WEIGHT LOSS 20·3% AT EQUILIBRIUM. TEMP. 916 °C previously stablized for 10,000 min. at 950°C. Thus this melt would contain both sodium metavanadate and sodium vanadyl vanadate II and perhaps others.

3. The dissolution of silica glass in 20% Na_2SO_4/80% $NaVO$ which is equivalent to a fully equilibriated 60% Na_2SO_4/40% V_2O_5 mole mixture.

The results are shown in fig.12. The variation between the melts is surprising. The rate of dissolution in Expt. 84 is approximately twice that of Expt. 82 and six times that of Expt. 83 in the first 100 mins. The slope of the Expt. 83 curve increases with time, due to the formation of sodium metavanadate, which is known from previous experimentation to dissolve silica more rapidly than V_2O_5. Whether the three experiments would have reached the same saturation solubility after a long time was impossible to discover due to the fact that even after about 100 min. devitrification of the glass rods was a problem. In these three experiments, the rods were unstirred as the dissolution is rapid. It is possible that SO_3 bubbles formed on the surface of the rods used in experiment 83 greatly reducing the area exposed to the melt.

7.5. CONCLUSIONS.

The conclusions of the work just described explain why there is a problem of refractory corrosion in marine boilers High vanadium pentoxide melts will dissolve considerable quantities of alumina. Melts containing roughly equal proportions of sodium sulphate and vanadium pentoxide will dissolve considerable quantities of silica. Also, if the glassy phase in the brick contains high proportions of silica, the high sodium sulphate melts will cause this to devitrify.

When alumina dissolves in $Na_2SO_4/NaVO_3/V_2O_5$ melts the alumina reaches saturation solubility in tens of hours, depending on the temperature. When silica dissolves in melts containing up to 50% Na_2SO_4, the composition follows an equation of the type $dc/dt \quad /C_{eq} - C_t)$ until a point is reached where the melt is saturated with cristobalite. After this point, the silica glass uses the melt as a medium for reaching the lower energy form - cristobalite. The addition of up to 12-16 mole % Na_2SO_4 to V_2O_5 causes the solubility of silica to *decrease* and the solubility of alumina to *increase*. Further additions of sodium sulphate up to 55 mole % cause the solubility of silica to *increase* approximately linearly and the solubility of alumina to *decrease*. From 55-100 mole % Na_2SO_4 the solubility of both silica and alumina decreases to a very low level at pure sodium sulphate. V_2O_5 and Na_2SO_4 react together to release SO_3. A melt containing 60 mole % Na_2SO_4 which had reached complete equilibrium dissolved silica approximately six times faster than a melt far from equilibrium. Melts containing 50 mole % and above Na_2SO_4 were found to devitrify silica glass faster than they dissolved it. This problem of devitrification, accompanied by loss of devitrified product, increased with increasing temperature. In most systems, the maximum temperature investigated was about 950°C. Several systems whose higher temperature region was complicated by devitrification were investigated up to 1100°C. This latter temperature is the temperature to which most of the lines produced are extrapolated. It is thought that above this temperature the effect of small increases in temperature will become more and more critical e.g. 60% Na_2SO_4/40% V_2O_5 fig. 8A and 10A. Also concluded here is the fact that chromel/alumel thermocouples should NOT be used for this work. The life of such thermocouples is sometimes as short as one week. When dipped into a melt the life may be only several minutes. Presumably, the presence of V_2O_5 vapour accelerates the oxidation of the metal. The worst effect of such oxidation was the reduction in the cross-sectional area of the current carrying portion of the wire. This acted as a resistance thus reducing the voltage arriving at the controller. The controller would therefore increase the temperature of the furnace to counteract this voltage drop. In this way, temperature rises of 100°C were possible in two days, culminating in the failure of the thermocouple. Alumina sheaths were used for the thermocouple, which increased their definite life to two weeks but still dependent on temperature (and of course the quality of the bead). Finally, to ensure accurate control, a new thermocouple was used for each experiment.

7.6. PROPOSED BASES FOR Al_2O_3/SiO_2 - Na_2SO_4/$NaVO_3$ PHASE DIAGRAMS.

The V_2O_5 - SiO_2 and the V_2O_5 - Al_2O_3 phase equilibrium diagrams have already been published (57,58). Work so far described supplies certain information towards the Na_2SO_4-Al_2O_3, $NaVO_3$-Al_2O_3, Na_2SO_4-SiO_2 and $NaVO_3$-SiO_2 phase diagrams and is shown in fig.13. This figure contains no new information beyond that already described but relevant results have been extracted with the object of supplying, for each system, a basis from which more accurate work could stem. This author does not suggest that the diagrams are complete, but hopes that they might be of use to a future colleague.

7.6.1. Na_2SO_4 - Al_2O_3.

As with the other diagrams in fig.13 this diagram is really part of a more comprehensive phase diagram. Fig.13A can be considered as the sodium sulphate end of a pseudo-binary in the system Na_2O-Al_2O_3-SO_3. It is very probable that these two compounds are stable over very limited ranges of temperature due to the reaction:-

$$Na_2SO_4 + Al_2O_3 \longrightarrow Na_2O.Al_2O_3 + SO_3$$

(N.B. The melting point of $Na_2O.Al_2O_3$ is about 1877°C).
The lowering of the freezing point of sodium sulphate by such

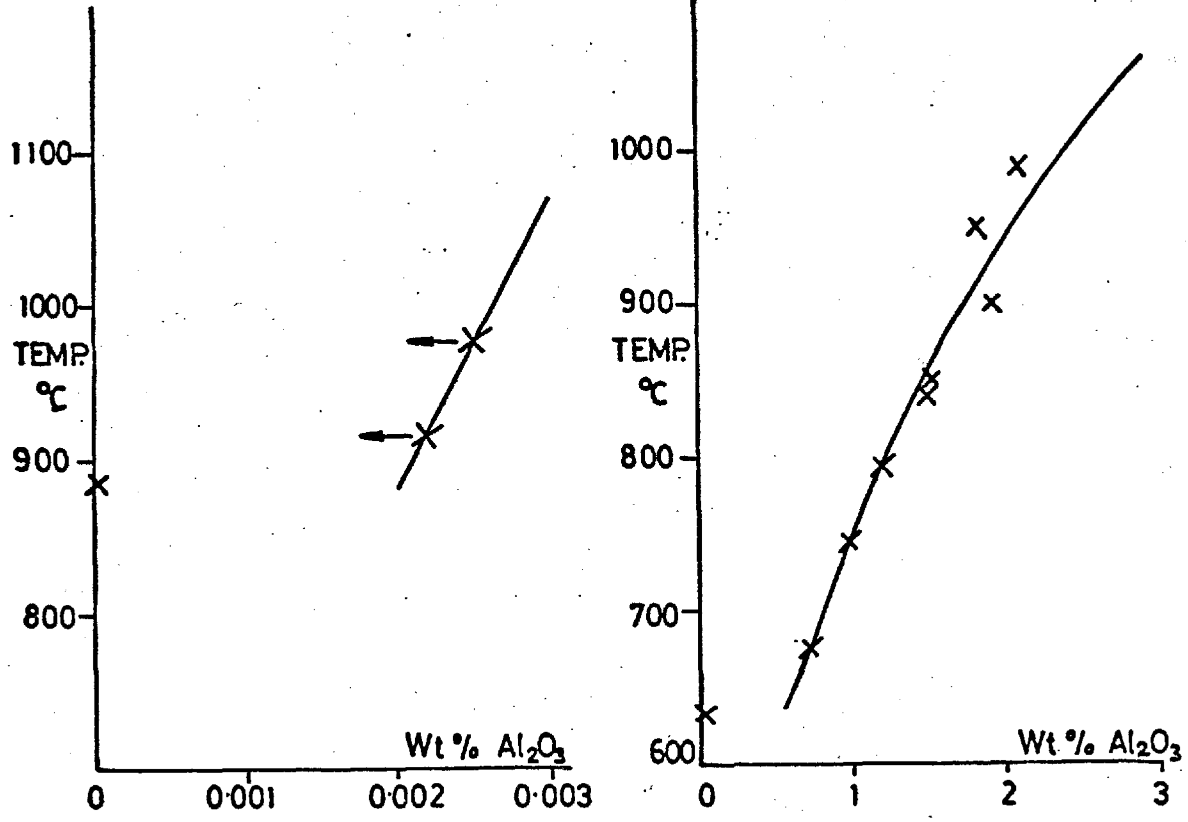


FIG. 13 A $Na_2SO_4 - Al_2O_3$ FIG. 13 B $NaVO_3 - Al_2O_3$

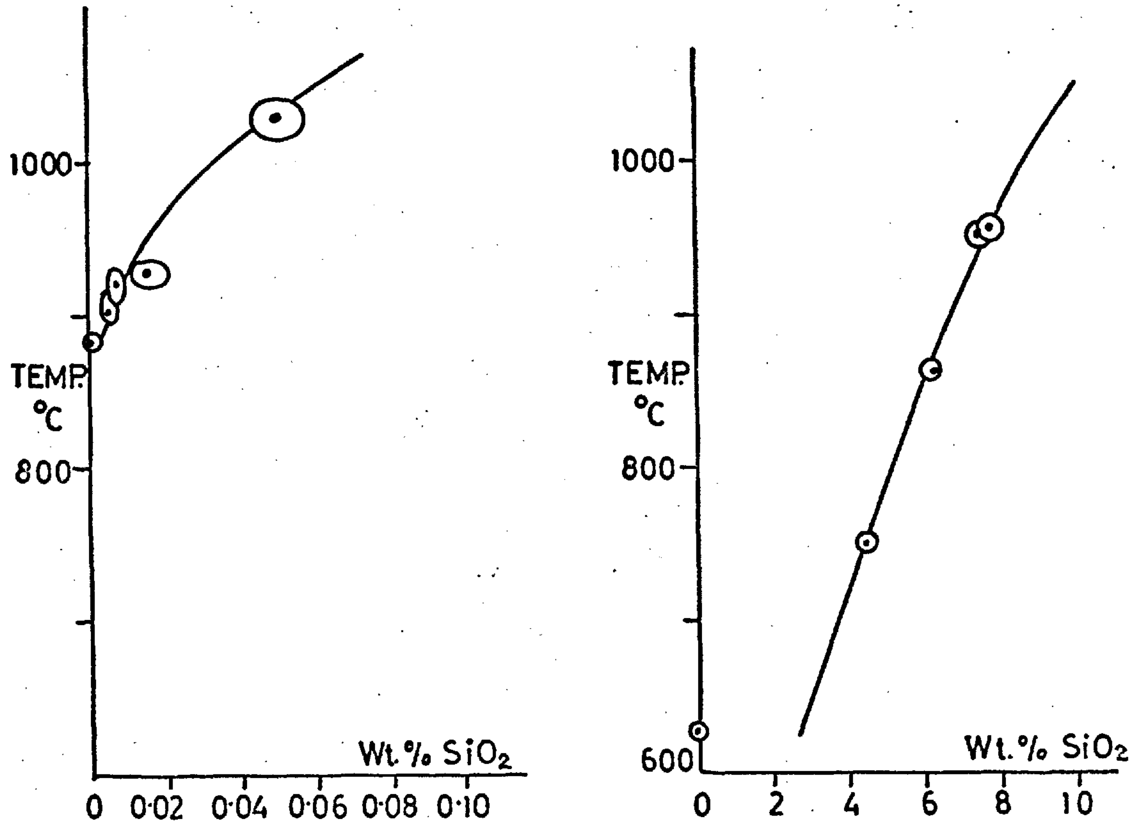


FIG. 13C $Na_2SO_4 - SiO_2$ FIG. 13D $NaVO_3 - SiO_2$

FIG. 13 SOLUBILITIES OF Al_2O_3 & SiO_2 IN Na_2SO_4 & $NaVO_3$

a small quantity of dissolved alumina will be certainly only a degree or two. Therefore the eutectic point will be at a composition of less than 0.0020 wt.% Al_2O_3.

7.6.2. $NaVO_3$ - Al_2O_3.

This is a pseudo-binary in the system Al_2O_3-V_2O_5-Na_2O. The eutectic point is possibly at 0.50 wt.% Al_2O_3 at $627 \pm 2^\circ C$. (M.P. $NaVO_3$ is $630^\circ C$) (35).

7.6.3. Na_2SO_4 - SiO_2.

Here, the SiO_2-Na_2O-SO_3 system is indicated. It is to be expected that at higher temperatures the two components react to give Na_2SiO_3.

$$Na_2SO_4 + SiO_2 \longrightarrow Na_2SiO_3 + SO_3$$

The depression of the freezing point will again be very small, probably $2^\circ C$ maximum at the eutectic composition of approximately 0.002 wt.% SiO_2.

7.6.4. $NaVO_3$ - SiO_2.

As no addition compounds have been found to exist between V_2O_5 and SiO_2 (57) it is reasonable to expect that the $NaVO_3$-SiO_2 system forms a quasi-binary diagram within the SiO_2-V_2O_5-Na_2O phase diagram. The depression of the freezing point of sodium metavanadate might be up to $20^\circ C$ and the eutectic composition is probably between 2-3 wt.% SiO_2.

A search of "Phase Diagrams for Ceramists" by LEVIN, ROBBINS and McMURDIE 1964, produced no evidence to support these results. Na_3AlF_6 dissolved about 13% Al_2O_3 at $1000^\circ C$ and Li_3AlF_6 dissolves about 4% Al_2O_3 at $900^\circ C$. (figs 1698 and 1686). Similar figures have been gained from previous work at Imperial College (57, 58).

CHAPTER 8. THE CORROSION OF SiO_2 AND Al_2O_3 IN Na_2SO_4/V_2O_5 MELTS.

Several slagging tests for refractories were described in section 6.4. Nearly all suffer from the fact that they are empirical i.e. they produce results that are useful for comparison only. GOLDMAN (1) described and erected an apparatus by which non-porous refractory materials may be tested for corrosion. Although this is a severe limitation since conventional refractories are porous, the trend is towards lower porosities and hence this restricted test will become more valuable in time. It can already be applied to grogs of low porosity and to fusion cast refractories. The method used in this research is essentially the same as that originated by GOLDMAN.

8.1. EXPERIMENTAL TECHNIQUE.

The principle employed in the technique is extremely simple:- take a tube of refractory, weigh it, pass slag through it and weigh it again. The loss in weight of the tube, N, divided by the product of the dissolution area, πdl, and the time of flow, t, gives the corrosion rate:

$$Z = \frac{N}{\pi dlt} \qquad (19)$$

In practice, to carry out such a manoeuvre is quite complicated and needs fairly elaborate equipment. In fig.14, a diagram is seen of the essential part to the testing apparatus. The sample under test, "S", was held securely in heat resisting steel castings. The upper end was located directly under theoutlet from a siphon tube, "h", and secured from leaking by a graphite washer, "g". The lower end of the sample was located over a central orifice and again sealed from leaking by a graphite washer. The melt, against which the refractory was to be tested was held in a platinum/10% rhodium pot, "p", in the floor of which was the siphon tube.

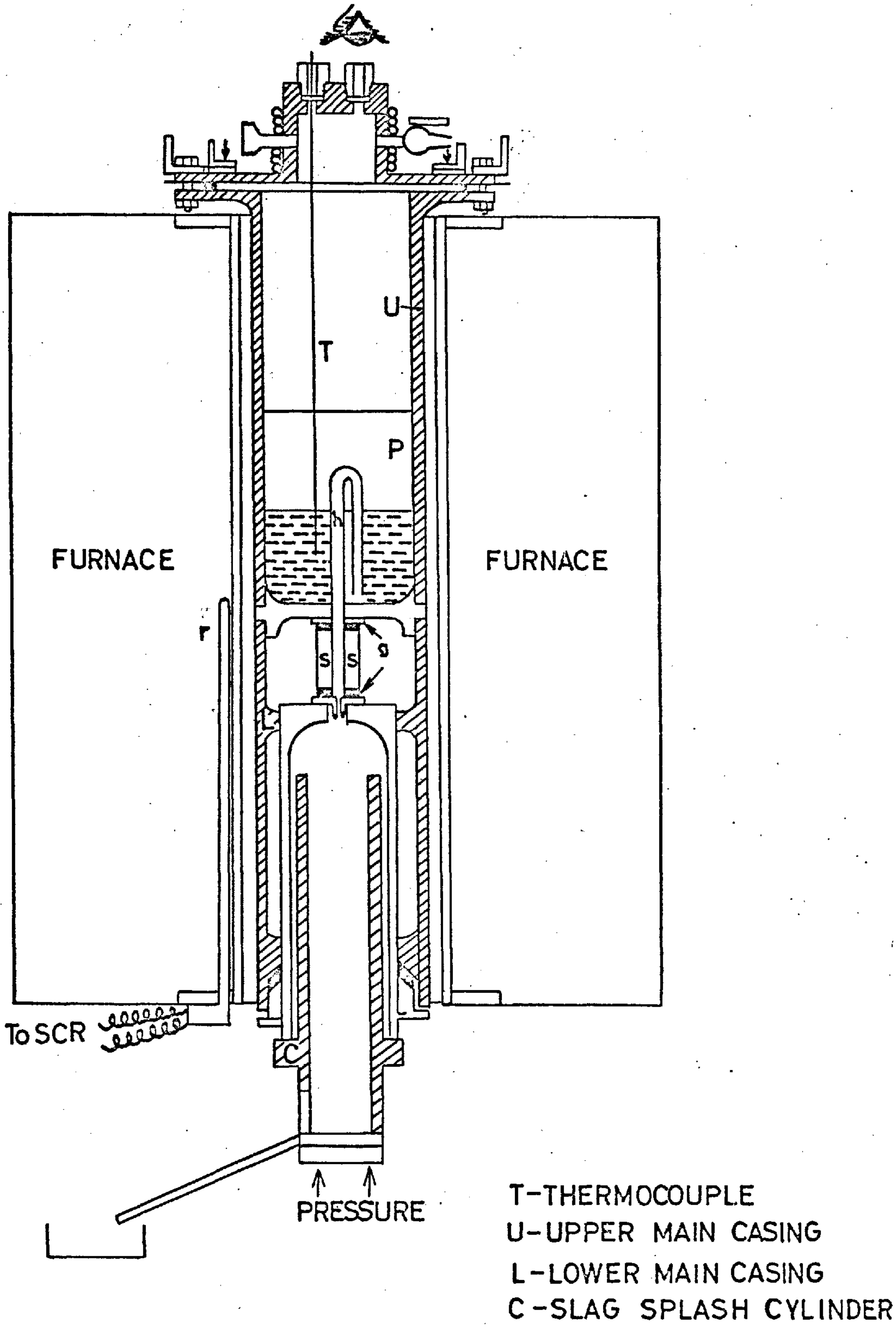


FIG. 14 THE CORROSION TESTING APPARATUS

In this way refractory and melt could be heated separately but in sufficient proximity to ensure that their temperatures were approximately equal. The minimum thickness of the heat resisting steel was 0.25" and such a mass of metal assists generally in achieving even temperature. When the melt was at the required temperature, air pressure above the melt caused it to flow through the siphon tube, sample, central orifice, and eventually out of the bottom of the furnace. Once started the melt would continue to flow without pressure, but usually the pressure was kept constant during a run. The used slag ran down a sloping copper plate and was collected on either a steel or aluminium plate. Supply of power to the furnace was from stabilized mains (240 v. 50 c/s) through a silicon controlled rectifier unit (SCR). This unit employed a platinum resistance thermometer, r , close to the Kanthal A windings around the silica muffle furnace tube. As the temperature of the furnace approached a predetermined value, the SCR cut down the power supplied to the furnace until, in theory, when the required temperature was reached, just enough power was being supplied to the furnace to keep it at that temperature. This effect avoided abrupt fluctuations in the current due to ON/OFF controlling technique and increased the life of the winding. Compressed air was used to increase the pressure above the melt to initiate a run. The pressure was read from a mercury manometer which incorporated two contact wires. When the mercury column rose and touched the two wires, an electric relay closed the air supply. If the pressure dropped, contact was broken and the air supply restored. In this way the pressure in the apparatus, which was fed via a large drum, could be controlled ± 1 mm. Hg. The complete apparatus is shown in plate 5. The temperature of the melt was read from a calibrated indicator fed from a platinum/platinum -13% rhodium thermocouple.

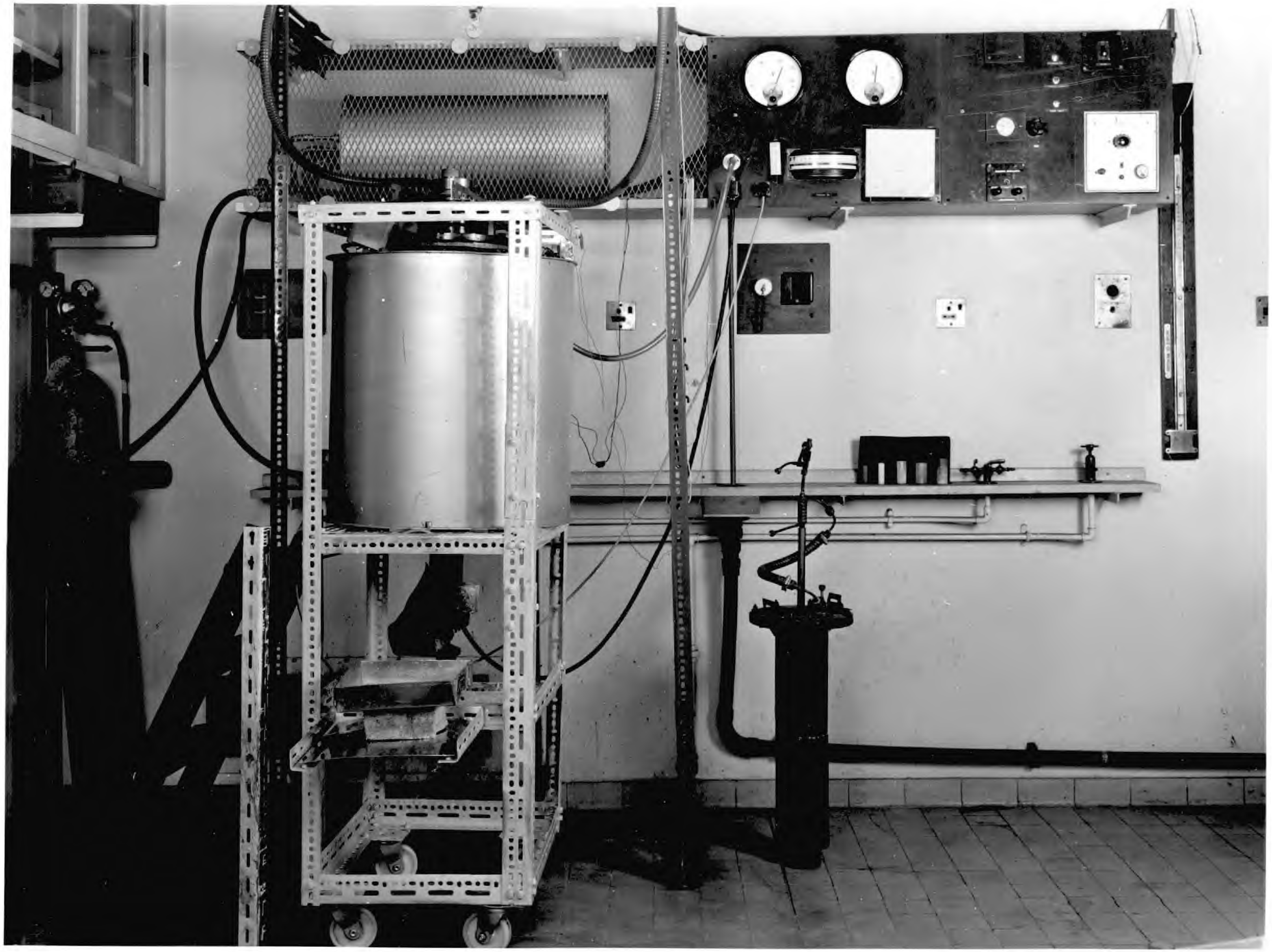
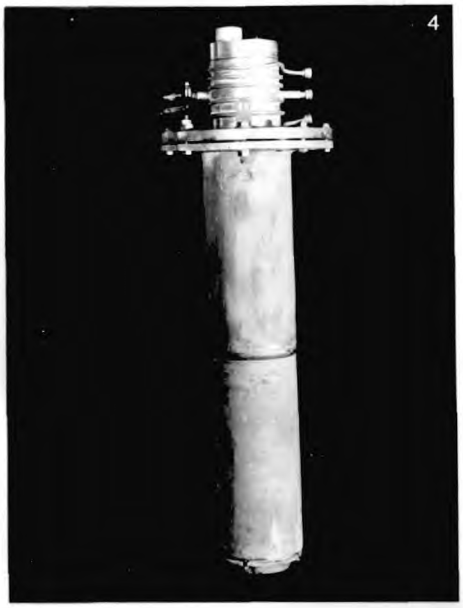
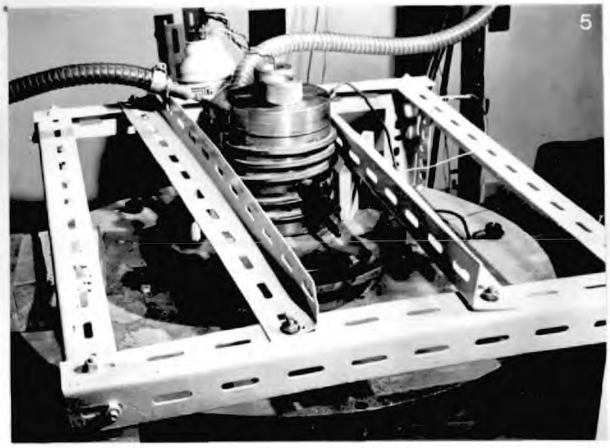


PLATE 5. THE CORROSION TESTING APPARATUS

8.2. EXPERIMENTAL PROCEDURE.

The samples used were tubes of alumina and silica 15-30 mm. O.D., 6-9 mm. I.D. and 40-60 mm. high. The bore of one of these samples was measured and the sample was scrubbed, dried and weighed. Two graphite washers were prepared by pressing flake graphite to about 900 kg/cm^2 (6 t.s.i.) for 1 min. in a small mould. Approximately 1 kg. of the slag to be used was weighed and the upper main casing cleaned to give the situation as in plate 6.1. One graphite washer was located over the outlet from the siphon in the upturned upper main casing. The sample, the second washer and the control orifice were then located over this, (Plate 6.2). After screwing on the lower main casing, the sample support cylinder was slipped in and secured with packing squeezed against it by the packing collar (plate 6.3). The unit was then inverted, the slag added and the services head bolted on. Two of these bolts also secured lifting lugs (plate 6.4). The now complete unit was lifted up and into a furnace by means of pulleys. When in the furnace, angle iron on top of insulating blocks secured the top flange (plate 6.5). Pressure was then applied to the inserted slag splash cylinder via a car jack. The slotted angle frame had a certain flexibility and experience told the operator when enough pressure had been applied by the curvature of the slotted angle securing sections. The following connections were then made: power, control thermometer, frame earth check, castings earth check, compressed air, services head water cooling inlet and outlet. The power was then turned on. Using a silica test piece, maximum power (3,600 watts) could be applied immediately but with alumina the maximum power for the first two hours was limited to 1000 watts. Further increases to maximum power in 3½-4 hr. total time avoided damage due to thermal shock. When the slag became molten, as seen through the window in the services head, the thermo-





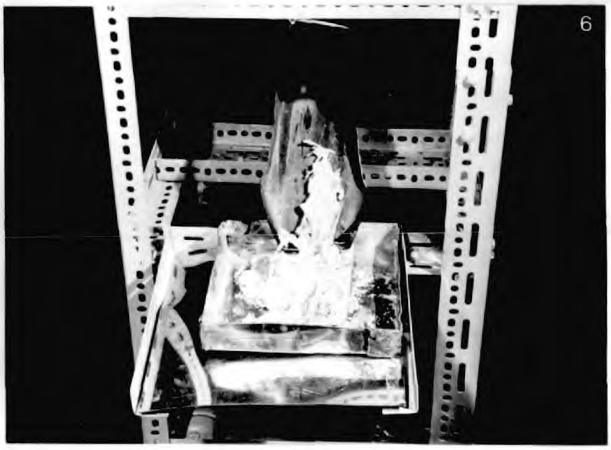


PLATE 6. STAGES DURING A RUN ON THE CORROSION TESTING APPARATUS

couple was lowered into the melt. After the SCR unit had cut the power down to a fairly constant value, a further period of about 30 min. was allowed for equilibrium to be approached. The following procedure was then quite critical: turn on air pressure control, turn on vacuum line, gently shake furnace to even out temperature gradients in the melt, take temperature close air vent tap on services head, open tap from air pressure supply and start watch when first slag appeared at bottom of slag splash cylinder. The watch was stopped when melt ceased flowing through the sample. This was easily detected by the sound of air escaping through the control orifice. The slag solidified, usually into a single piece as seen in plate 6.6. It was necessary to dismantle the cold castings to obtain the sample for cleaning and reweighing. Great care was needed at this stage to retrieve a complete sample. Sometimes, in the initial stages of flow the control orifice would become blocked (usually by a graphite flake) and melt would cease to flow. In such cases, the waiting vacuum line was rapidly connected to the services head air vent tap. The air pressure supply tap was then closed and the air vent tap opened. These movements resulted in air being sucked up through the sample and siphon tube. Replacement of the vacuum by pressure nearly always freed the system.

8.3. RESULTS.

The results are seen in fig. 15, 16 and 17. They show that, at temperatures up to 1050°C, there is little difference between the resistance of alumina and silica to corrosion by Na_2SO_4/V_2O_5 melts. At higher temperatures (say up to 1500°C) alumina will probably be superior to silica as the temperature dependence of the corrosion of alumina is less and alumina does not suffer from devitrification.

8.3.1. ALUMINA.

Fig.15 shows the corrosion rate of alumina in various

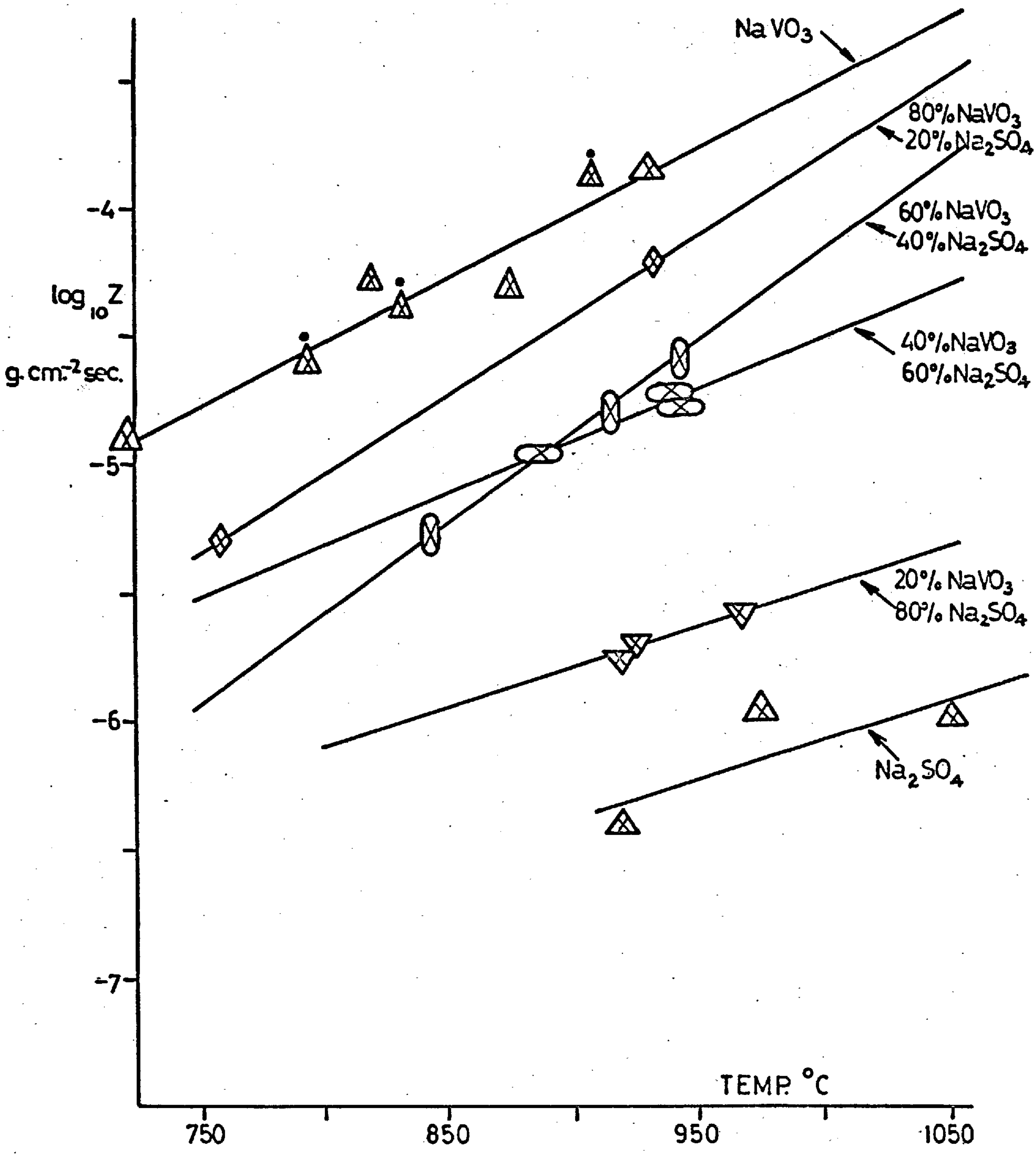


FIG. 15 THE CORROSION RATE, Z, OF Al_2O_3 IN Na_2SO_4/$NaVO_3$ MELTS

$Na_2SO_4/NaVO_3$ melts. It is immediately seen that sodium metavanadate is more corrosive to alumina than sodium sulphate. The results plotted were analysed by the method of least squares. The assumed straight linesso produced indicate that the addition of sodium sulphate to sodium metavanadate lowers the corrosivity of the latter. Results for 60%Na_2SO_4/40%$NaVO_3$ do not follow the general trend of the changing position of the other lines. This may be due to the fact that the three results plotted are too close for the method of least squares to be applied with any accuracy. Attempts to produce further points on this line have, at the time of writing, been unsuccessful. Five further runs using pure sodium sulphate all produced weight gains in the sample which could not be removed by boiling 2N HCl. Similar weight gains occurred at 80 and 60 mole % Na_2SO_4.

8.3.2. SILICA.

The pattern in fig.16 is much the same as with alumina. The addition of sodium sulphate lowers the corrosivity of sodium metavanadate. Again one line is out of keeping with the general trend. The 20 mole % Na_2SO_4 line has a very low temperature dependence and it is thought that there is an error in the result at 746°C. All the remaining lines show a steeper temperature dependence than the corresponding results for alumina. This applies particularly to the result for pure sodium sulphate. However, large weight losses above 950°C using this melt were partly due to devitrification of the bore of the sample. This cloudy layer was loosely bonded and often its presence was not noted until some of the layer was removed. Thus it is thought that the slope of this line is misleadingly high. It is probably nearer to that of the 80% Na_2SO_4/20% $NaVO_3$ line if the effects of devitrification are ignored.

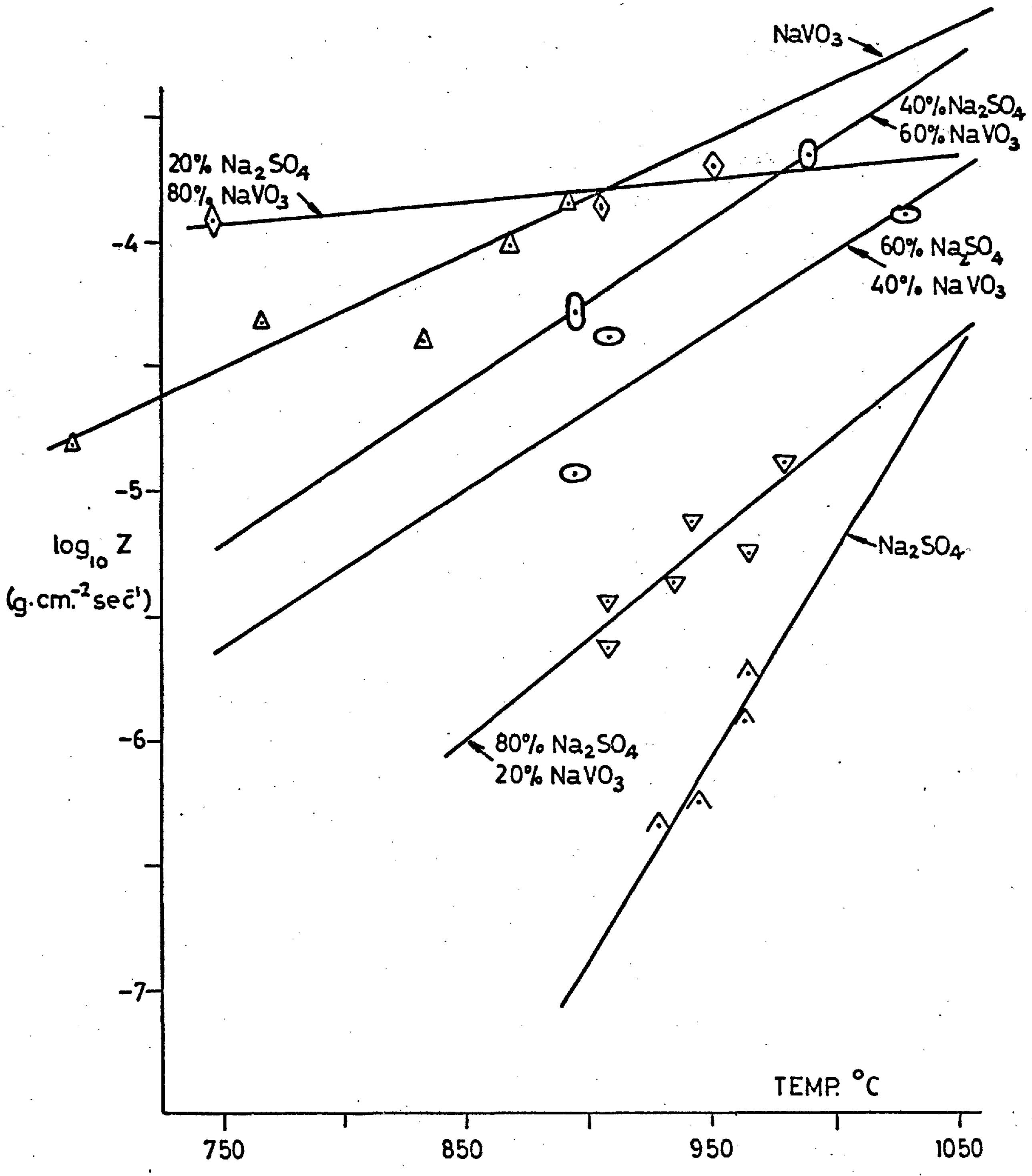
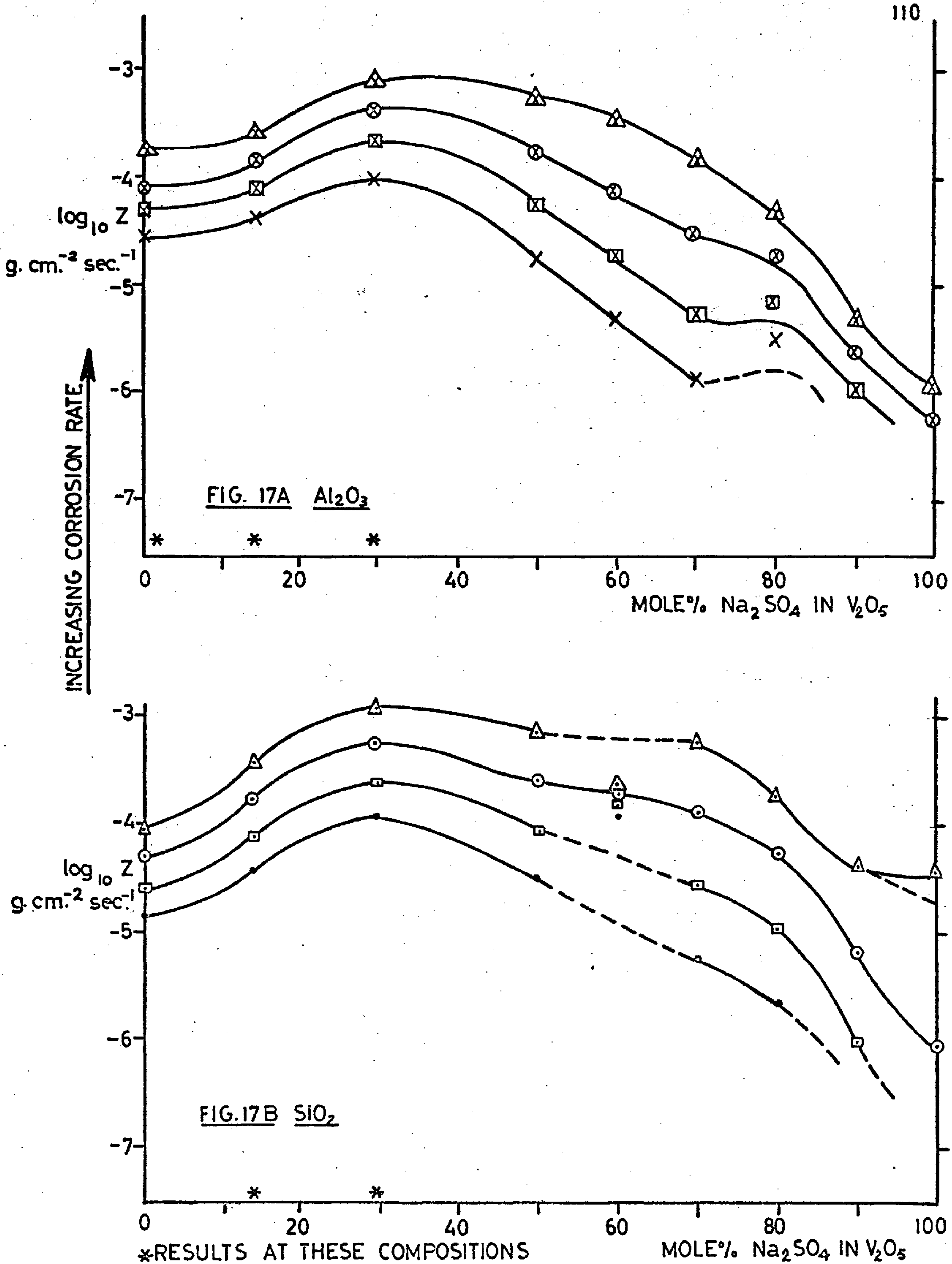


FIG. 16 THE CORROSION RATE, Z, OF SiO_2 IN Na_2SO_4 / $NaVO_3$ MELTS

8.3.3. DISCUSSION.

To enable a comparison to be made between alumina and silica, selected corrosion rates at 750, 850, 950 and 1050°C are shown on the same scale in fig.17. The incomplete curves indicate regions where the results are open to doubt as already explained. Essentially, there is very little difference between the corrosion rates of silica and alumina at the temperatures investigated and such variations as there are are probably within experimental error which is larger at the high sodium sulphate end. The results are plotted on a Na_2SO_4/V_2O_5 base although mainly $Na_2SO_4/NaVO_3$ melts were used at and above 50 mole % Na_2SO_4. Four runs were carried out using a 60 mole % Na_2SO_4/40 mole % V_2O_5 melt stablized for 10,000 min. at 950°C with the object of comparing such results with those using the 80 mole % $NaVO_3$/20 mole % Na_2SO_4 melt. Much more experimentation is necessary, but it would appear that non-equilibrium melts are slightly less corrosive below about 950°C but of similar corrosivity to the fully equilibriated melt above this temperature. No difference in result could be detected using hot pressed 98.5% Al_2O_3 and the HILOX 961 (96% Al_2O_3) specimens. In fig.15, melt $NaVO_3$, the results gained using hot pressed 98.5% Al_2O_3 have a dot over them.

In conclusion, corrosion of refractories is to be expected at all ratios of sodium to vanadium in fuel-oil ash. The corrosion rate of silica and alumina is less in pure sodium sulphate than in pure vanadium pentoxide, up to 1050°C. Melts containing between 30 and 70 mole % sodium sulphate are most damaging and at 1050°C the corrosion rate is relatively independent of the melt composition between these limits. It is not scientifically sound to extrapolate the lines in fig. 15 and 16 to higher temperatures but alumina will resist high sodium and high vanadium melts at higher temperatures better



*RESULTS AT THESE COMPOSITIONS
BY GOLDMAN (1)

THE CORROSION RATE Z OF Al 0 & SiO IN Na SO$_4$/V O$_5$ MELTS than silica, especially as silica glass will devitrify at all temperatures in contact with high sodium sulphate melts. This is an academic argument, however, as silica does not occur free in high alumina firebricks. In such firebricks there is a glassy phase and silica glass could possibly indicate how this might behave.

8.3.4. ACCURACY OF THE RESULTS.

Temperatures were measured on a calibrated indicator to ± 5°C. Time was measured on a stopwatch and dual testing by two separate persons never varied by more than 0.5 sec. The bores of most samples were measured using an internal micrometer. A trial on a nominal 1/4" bore sample produced a maximum error of 2% which included possible variations in the bore. Sample flowlengths in the initial experiments had to be judged. The flow length of the sample equalled the actual length of the sample <u>minus</u> the projections of the early control orifice and siphon tube outlet into the sample, <u>plus</u> the thickness of the two graphite washers. All these quantities could be measured but it was unknown how much the graphite washers compressed in the rig. The probable accuracy of this measurement was about ± 2 mm. (3-5% depending on the length of the sample). Later, the projection on the siphon tube was removed and a new orifice was introduced which located on the outside of the sample rather than on the inside (see fig.18A). This ensured that the whole sample bore was a reaction area, eddies in the melt were minimised and the possibility of small pockets of melt creeping between the orifice projection and the inside of the sample was eliminated. However, good quality graphite washers were necessary to avoid the melt creeping between washer and sample. On these runs the flowlength accuracy was ± 1%.

The weight loss of the samples was nominally the difference between two weighings on an analytical balance i.e. ± 0.0005 g. However, due to chipping, adhering melt, adhering carbon, leaks, etc., the accuracy rarely achieved this figure. One of the better results is given as an exampl

Run 42. Silica Glass and 80% Na_2SO_4/20% $NaVO_3$.

Sample S.11 (Transparent Vitreosil).

Bore	0.654 ± 0.008 cm
Length	6.37 cm.
Flowlength	6.25 ± 0.20 cm
Weight Before	66.6271
Weight After	66.6077
Loss in Weight	0.0194 ±0.0005 g.
Time	264.0 ± 0.5 sec.
Temperature	966 ± 5°C.
Weight of melt passed	990 ± 20 g.

$$Z = \frac{0.0194}{\pi . 0.654 \; . \; 6.25 . 264.0} = 5.72 \pm 0.43 \times 10^{-6} \text{ g/cm}^2\text{sec}$$

i.e. ± about 8%.

The measurement of the weight loss of the sample was a problem throughout the experimentation and is treated separately in the next section.

8.4. ON THE WEIGHT LOSS OF THE SAMPLES.

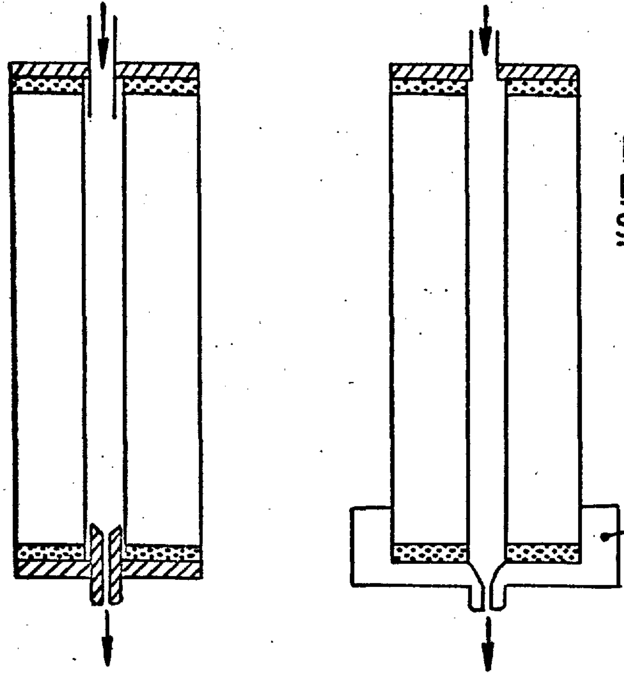
During an experiment using the corrosion testing apparatus, providing that the melt flows steadily through the sample, the most difficult quantity to measure with accuracy is the weight loss of the sample.

8.4.1. General. The following events may occur to make the final weighing inaccurate: a. complete fracture of the sample; b. chipping from the inside edges of the bore; c. chipping from the outside edges of the sample - usually due to careless removal; d. the leaking of a melt between a graphite washer and the sample. This melt flows over the outside of the sample, but not out of the apparatus. These points could be partially solved if instead of weighing the sample, the increase in bore, d, was measured. A typical weight loss is 0.0200 g. which, at a density of say 3 g/cm^3 means a volume loss of 0.0067 cm^3. Now, from the walls of a cylinder 0.66

cm. I.D. and 6 cm. long this leads to an approximate average increase in diameter of 0.00108 cm. Attempts were made to measure the increase in bore of sample A2 by micrometer, travelling microscope and filling the bore with mercury. All these methods detected an increase. Internal micrometers were difficult to use in irregular and sometimes unevenly tapering holes. The mercury method was only accurate to ± 1 drop of mercury which had the same order of volume as the volume increase sought. The travelling microscope could only detect increases in the bore at the end of the samples which was the first region to suffer from chipping. The Metrology Department of Imperial College were able to offer a machine capable of measuring the increases expected. A special probe was manufactured for this machine to enable the whole length of the bore to be measured. Unfortuantely, with such a high length to width ratio, flexing in the probe was greater than the bore increase. Following the advice of Mr.J.G.TWEEDDALE the possibility of using an air gauge tool was investigated.

<u>8.4.2. Air Gauging</u>. An air gauge tool is able to measure very small changes in the dimensions of an object by measuring the change in back pressure sensed in an air jet close to the surface of the object being measured. Thos. MERCER and Co. Lt kindly loaned a unit while the method was being tested. New silica samples were ordered with a bore of 0.635 cm. and an air plug gauge suited to measure them. Upon arrival it was discovered that although the bore of the silica samples was within the tolerance requested, they were outside the range of the air plug gauge. A new plug (and "setting" rings) was ordered and the bore of a sample measured. After corrosion testing the sample it was found that the majority of the bore was again outside the range of the instrument. The coarsest machine manufactured by Thos. MERCER is now installed in the Ceramics Laboratories at Imperial College. Results such as that in fig.18B are gained but the machine still is too

FIG. 18A COMPARISON BETWEEN PREVIOUS (LEFT) & REVISED (RIGHT) SAMPLE SEALING SYSTEMS



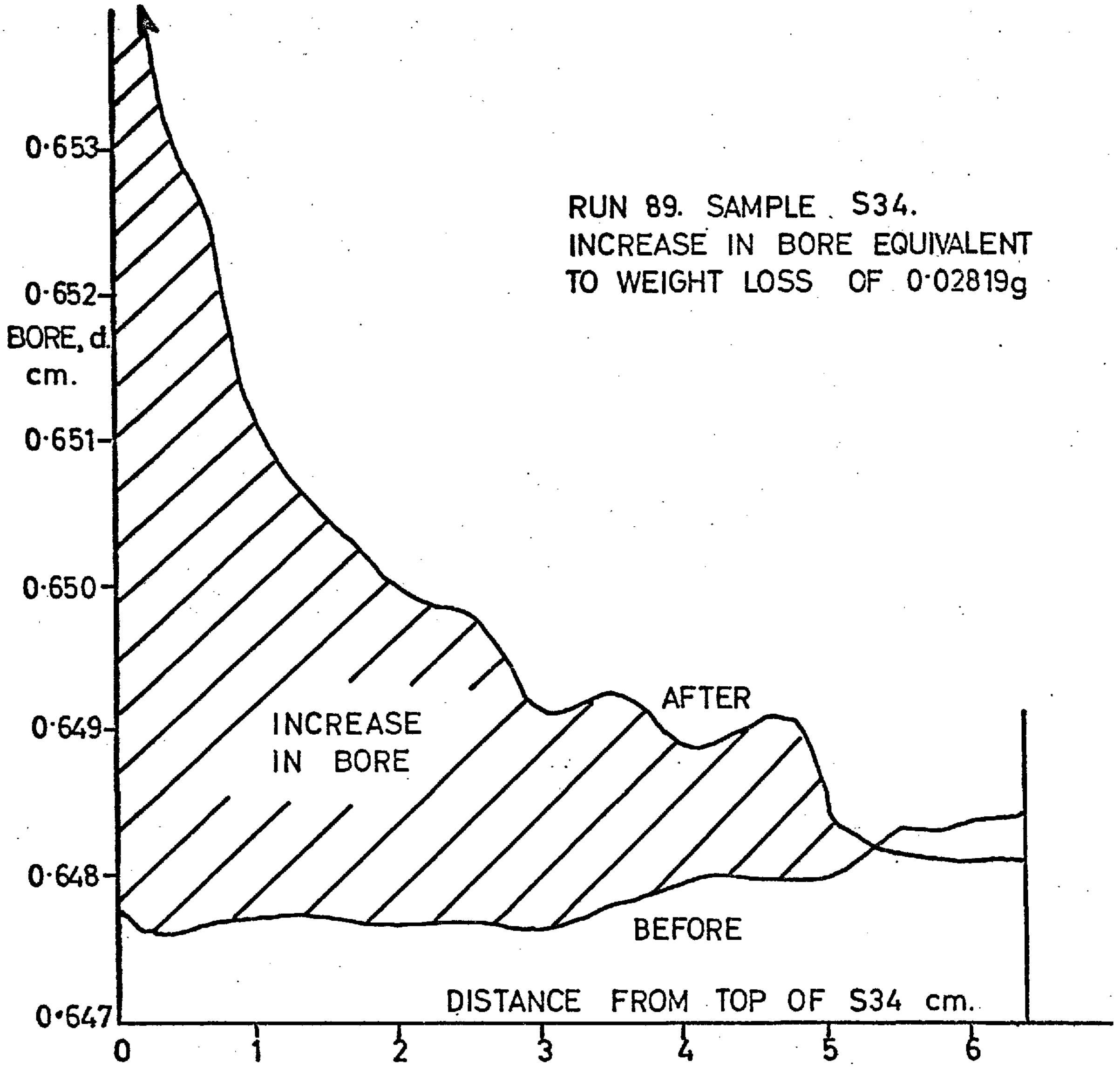


FIG. 18B RESULT OF AIR GAUGING A SILICA SAMPLE accurate for the particular job. It is possible, that if a set of samples was ordered to be drilled, all with the same drill, THOS MERCER could manufacture the largest possible air plug gauge to just slip inside them. Then the whole range of the instrument would be available for any increase in bore.

8.4.3. The Effect of H_2O and HCl on Al_2O_3.

While seeking a small weight loss (approx. 0.0010 g) from a sample, it was discovered that each time of cold water washing, drying and weighing, there was a weight decrease. Therefore the effects of washing several alumina samples was examined. As dilute HCl was sometimes used to remove stubbor slag, it was included in the programme. Samples tested were: A1, A2 and A3 - all 98.5% hot pressed alumina used several times in the corrosion testing apparatus; A4 and Y1 - unused 98.5% and 96% Al_2O_3 respectively; a piece of sapphire rod; a recrystallized alumina crucible and a piece of alumina furnace tube. The tests were:- 1. cold running tap water for 2 days; 2. cold, static, 0.1N HCl for 2 days; 3. boiling 2N HCl under reflux for 1 day. Each test was followed by 1 day or more in a drying oven at 160°C and the samples were allowed 1 hour to cool before weighing.

The results were as follows:- sapphire - no effect; alumina furnace tube - very erratic behaviour due to its porosity, but test 3 produced a weight loss of 30 p.p.m.; recrystallised alumina crucible - test 1 average loss 15 p.p.m test 2 average loss 75 p.p.m., test 3 average loss 240 p.p.m.; all hot pressed alumina samples behaved similarly - test 1 18 p.p.m., test 2 100 p.p.m., test 3 190 p.p.m.; sample Y1 (96% Al_2O_3) test 1 average loss 20 p.p.m., test 2 average loss 55 p.p.m. This latter loss in the weight of Y1 is only 0.2 mg. The comparable loss in say A4 in test 2 was 20 mg., whic was considerably higher even when considering the fact that A4 had a 60% larger surface area. Thus all alumina samples from corrosion testing were washed only in cold water and such washing was kept to a minimum.

8.5. DESIGN IMPROVEMENTS.

This author is convinced that the method described is essentially sound technique. However, to enable its application to be of greater value design improvements must be made with two objectives: firstly the ability to produce more results in less time i.e. increase the population of the results to enable much more definite conclusions to be drawn; secondly to improve sample sealing methods to enable the weigh loss to be determined more accurately. Some improvements have already been described. Future improvements are propose in the form of a redesigned unit for holding melt and sample. Many variations are possible, a selection of which are shown: fig.19. A most important feature is the avoidance of all screw threads in the hot zone. The upper main casing needs to be made of a heat resisting alloy such as Cronite 55 or EV 12 (see Appendix 7). This would, as normal, hold the platinum/10% rhodium pot sealed in position but it is suggested that the highest part of the siphon tube is enlarged to avoid possible solidification of melt in this cooler region. The service head could be sealed onto the upper main casing using a gasket (copper, brass, stainless steel, gold, or any of several high temperature gasket materials). The service head should have more water cooling coils, hard soldered onto the stainless steel. The life of the thermocouple could be increased by using a thicker wire (above 0.4 mm) and using a plug and socket (with low contact resistance) in the head to connect to the indicator rather than the soldered wires now used. The lower main casing could be made of a good heat resisting steel with spares in stainless steel and/or mild steel "PENETRAL" treated (see Appendix 7). A good heat resisting steel must be used for the sample support which coul usefully employ a locating area for the slag splash cylinder. To hold the complete unit in one piece it is suggested that mild steel rods be used until the unit is in place in the cold

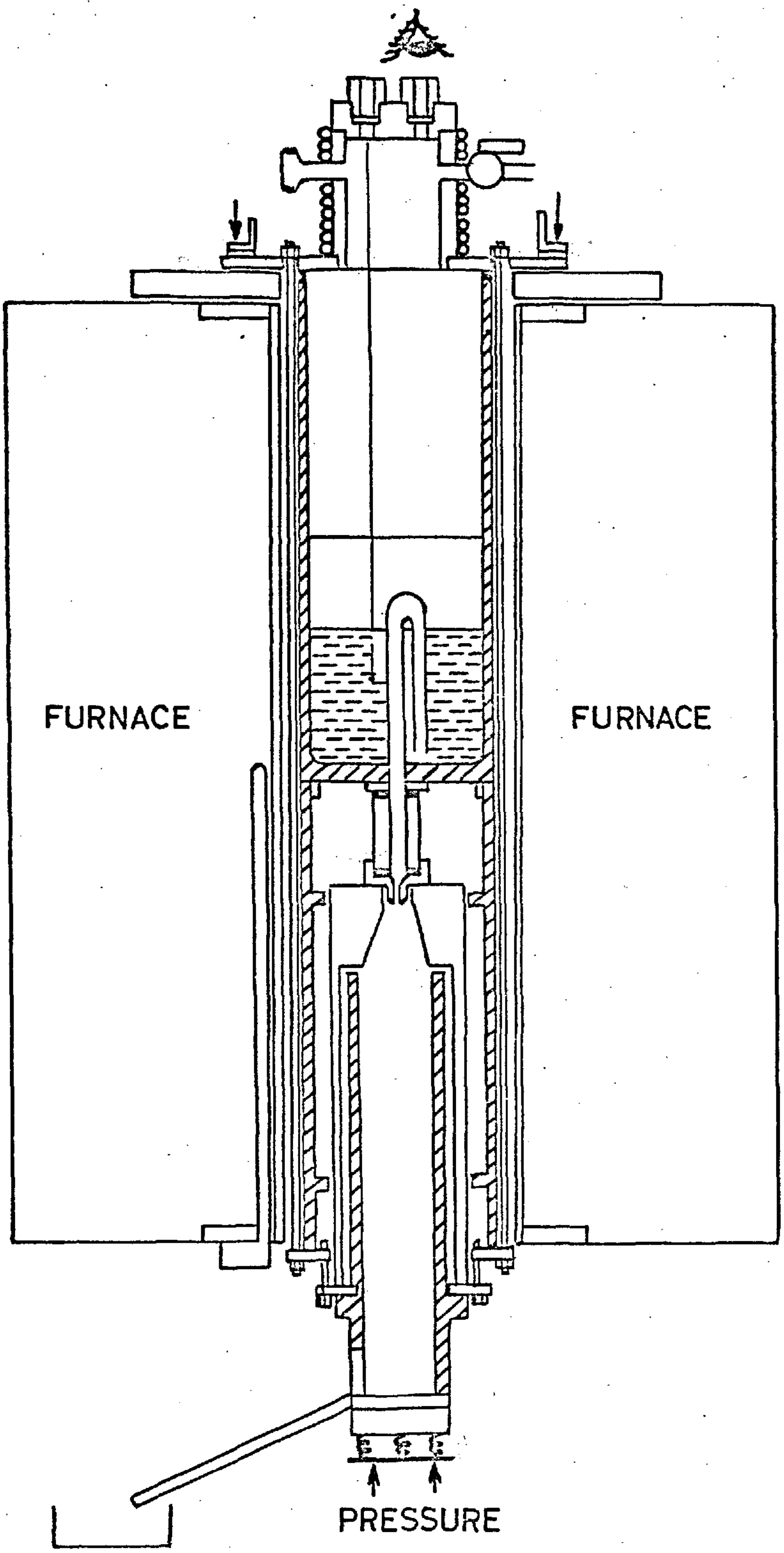


FIG. 19 POSSIBLE FUTURE DESIGN FOR CORROSION TESTING APPARATUS

furnace and under pressure from the car jack. These rods could then be removed. Heat resisting rods of about 1/4" are very expensive and also unable to resist creep at about 1000°C. It is suggested that mild steel tubes are used to make the slag splash cylinders which are then discarded after 10-12 runs.

The dismantling of this design after a run should be very simple and with care, samples could be extended to include any non-porous refractory tube commercially available.

CHAPTER 9. THE APPARENT DIFFUSION COEFFICIENTS OF SiO_2 AND Al_2O_3 IN $Na_2SO_4/NaVO_3/V_2O_5$ MELTS.

Certain information has been presented in the preceding chapter concerning forced convection in a pipe or tube of refractory. On applying several assumptions, analysis of this situation is possible to produce apparent diffusion coefficients. The solution for the analogous problem of heat transfer has been given by LEVEQUE in 1928 (59) and reviewed by DREW (61). The derivation of similar solutions for mass transfer have been given by GOLDMAN (1) and LEVICH(60) The essentials of their analyses are reproduced here.

9.1. DERIVATION OF THE EQUATIONS.

In the flow reactor under streamline flow, the x-axis is taken to be down the axis of the tube and the diffusion coefficient of material in this direction is assumed to be zero. If the denisty of the melt and diffusion coefficient, remain constant at constant temperature, then Fick's Second Law of Diffusion for one diffusing species only reduces to :-

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial y^2} \qquad (20)$$

In this equation the y-axis is at right angles to the x-axis and is assumed to be the only direction in which diffusion occurs. Velocity profiles across such a tube will be parabolic but solution of equation (20) is complicated and inaccurate. LEVEQUE assumed that close to the wall of the tube, the velocity profile was a straight line. If v_o is the maximum velocity at the centre of the tube, then for small values of y measured from the tube wall:-

$$v \approx \frac{4v_o y}{d} \qquad (21)$$

Equation (20) then becomes:

$$\frac{\partial c}{\partial x} = \frac{D\ d}{4v_o\ g} \cdot \frac{\partial^2 c}{\partial y^2} \qquad (22)$$

Upon application of the following boundary conditions:-

At $y = 0$ (i.e. at the tube wall) and $x > 0$, $C = C_{eq}$

At $y = +\infty$ (i.e. beyond the boundary layer) and $x > 0$, $C = 0$

For $x \leqslant 0$, $C = 0$.

Equation (22) may be solved (60) by introducing a dimensionless group, to give the flux due to diffusion:-

$$I_{diff} = 2.01\ \pi\ C_{eq}\ D\ \left(\frac{4v_o\ x^2}{D\ d}\right)^{1/3}\ \frac{d}{2} \qquad (23)$$

In a tube of length, L, through which melt passes for t secs:

$$N = 5.02\ C_{eq}\ (D.L)^{2/3}\ v_o^{1/3}\ d^{2/3}.\ t \qquad (24)$$

Now if $\bar{v}$ is the plug flow velocity:-

$$v_o = \frac{3}{2}\bar{v} \qquad (25)$$

but $$\bar{v} = \frac{4M}{\rho\pi t d^2}$$

$$\therefore \quad v_o = \frac{6M}{\rho\pi t d^2} \qquad (26)$$

and $$N = 6.241\ C_{eq}(DLt)^{2/3}\ \left(\frac{M}{\rho}\right)^{1/3} \qquad (27)$$

or $$D = \frac{0.0641}{L.t}\ \left(\frac{N}{C_{eq}}\right)^{3/2}\ \left(\frac{\rho}{M}\right)^{1/2} \qquad (28)$$

This equation assumes that the concentration of refractory in the bulk of the melt is always zero. If this concentration is not zero then equation (28) may be modified by replacing C_{eq} by $C_{eq} - C_1$. In GOLDMAN's equation (p.86) the numerical constant corresponding to 0.0641 in equation (28) is 0.0781. This is due to the fact that he used LEVEQUE's value of 2.16 in equation (23). LEVICH (60) considers that this should be 2.01. Subsequent treatment of constants which

which includes raising to the power of 1.5 and reciprocation, coupled with GOLDMAN's use of an alternative equation (21) produced this difference. These variations are to be expected in systems where different approaches are made and the assumptions are many. GOLDMAN explained deviations from the LEVEQUE equation in his model experiments by an activity coefficient which modified the C_{eq} "driving force". It is more probable that the LEVEQUE equation is an approximation and that GOLDMAN's results are truly within the absolute errors he states.

In the title to this chapter, the words "apparent diffusion coefficients" appear. This is because when FICK's Second Law is applied to a system, the mechanism to which it is applied must be controlled by a diffusion process. When alumina dissolves in $Na_2SO_4/NaVO_3/V_2O_5$ melts, crystal faces are exposed, indicating that the controlling mechanism is probably the reaction at the solid/liquid interface. Experiments with silica cannot provide such information as silica glass was used. However, the initial dissolution rate of a silica glass rod in a system could be multiplied up to 15 times by stirring the rod at 960 r.p.m. Such figures are not accurately reproducible due to a degree of whip in the rods, but they indicate that for silica the mechanism is probably diffusion controlled.

9.2. EXPERIMENTAL TECHNIQUE.

To evaluate apparent diffusion coefficients uses exactly the same technique, procedure and results as described in Chapter 8. Two extra variables were required for each run, namely, M, the quantity of melt passed through the sample and ρ, the density of the melt at the experimental temperature. M was simply found by weighing the cold solidified slag. The densities of melts up to 50 mole % Na_2SO_4 were given by GOLDMAN. As there is no reaction between $NaVO_3$ and Na_2SO_4 at the temperatures studied the approximate densities of mixtures of these two compounds will be in simple proportions to the percentages of each present.

9.2.1. The density of sodium sulphate was determined by weighing a platinum bob in air and in the molten salt. Results are shown in fig. 21B. The density of sodium sulphate between 890 and 1120°C is given by the approximate formula:-

$$\rho = 2.481 - 0.000467\ T \qquad (29)$$

The accuracies of the experiment are : temperature ± 5°C; weight of platinum bob in air ± 0.005 g; weight of platinum bob in melt ± 0.010 g. due to thermal currents.

Typical result :-

Temperature	988 ± 5°C
Weight of bob in melt	10.389 ± 0.010 g.
Weight of bob in air	11.503 ± 0.005 g.

$$\rho_{Na_2SO_4} = \rho_{Pt} \left(1 - \frac{w_L}{w_A} \right) \qquad (30)$$

$$\rho_{Na_2SO_4} = 2.017 \pm 0.026 \text{ i.e. } \pm 1.3\%.$$

The densities of platinum were calculated from figures given by KAYE and LABY (1959).

9.3. RESULTS.

9.3.1. SILICA.

Apparent diffusion coefficients were calculated for each run on the apparatus using equation (28). The results in fig.20 include some of GOLDMAN's work, i.e. at 0, 14.3 and 29.4 mole % Na_2SO_4. In the case of these three melts C_{eq} was unknown at the time of writing. GOLDMAN's thesis and the data was presented in the form $D\ C_{eq}^{3/2}$. To present the information gathered for each melt on one graph is most confusing as many of the coefficients evaluated are of the same order and the several lines cross in many places. It was considered best to present the information as in fig.20.

There was a great deal of scatter in these results. The plot of $\log_{10}D$ against temperature was assumed to be a straight line and analysed by the method of least squares. Where insufficient information has been gathered, the use of this method can be misleading. Thus in fig.20 are seen several points that do not reasonably fit on a smooth curve. When this occurs the curve is shown incomplete. Points of interest on the graph are the amazing increase in ion mobility as soda is added to V_2O_5, the maximum on the curve between 27 and 32 mole % Na_2SO_4 (sodium vanadyl vanadate II) and the extreme dependence of the apparent diffusion of silica in sodium sulphate upon temperature.

9.3.2. ALUMINA.

Results for alumina in fig.21A were gained from lines produced with much less scatter of points. This is due to the fact that it is much easier to work with alumina. It is rare to get chipping of the bore, and devitrification does not occur. Again, the large increase in ion mobility is seen from the addition of up to 30 mole % Na_2SO_4. At the high sodium sulphate end the results were less reliable. The dependence of the diffusion coefficient in sodium sulphate upon temperature is again seen to be large but these results were produced by extrapolation, aided by two results and are therefore questionable. Results for 0, 14.3 and 29.4 mole % Na_2SO_4 are GOLDMAN's work.

9.3.3. ACCURACY OF THE RESULTS.

This is the most inaccurate of the experiments described in this work. Many parameters were required to be measured, all with errors above 1%. In particular N and C_{eq} have low accuracies and the quotient of these two is raised to the power of 1.5.

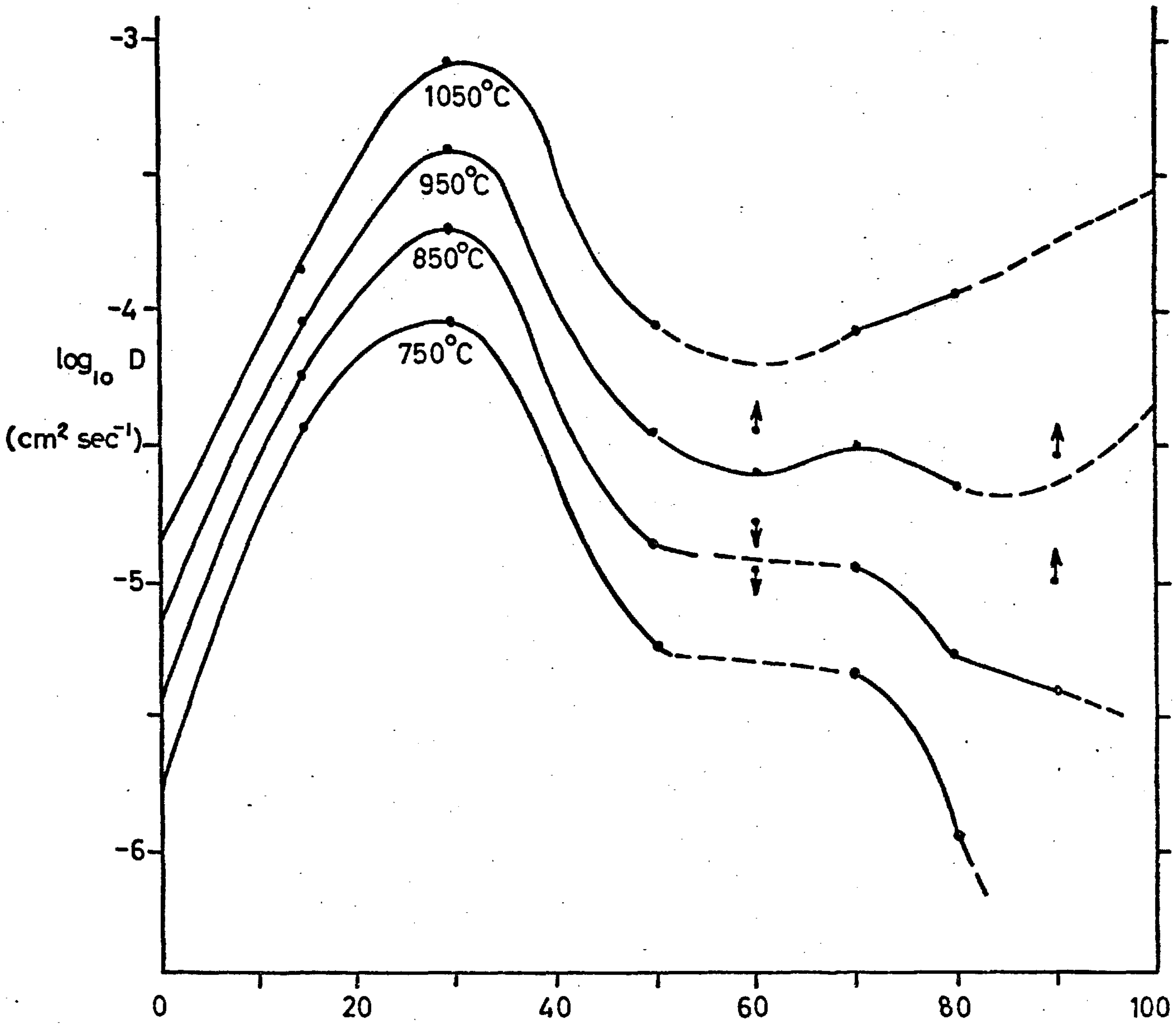


FIG. 20 APPARENT DIFFUSION COEFFICIENT OF SiO_2 IN Na_2SO_4/V_2O_5 MELTS

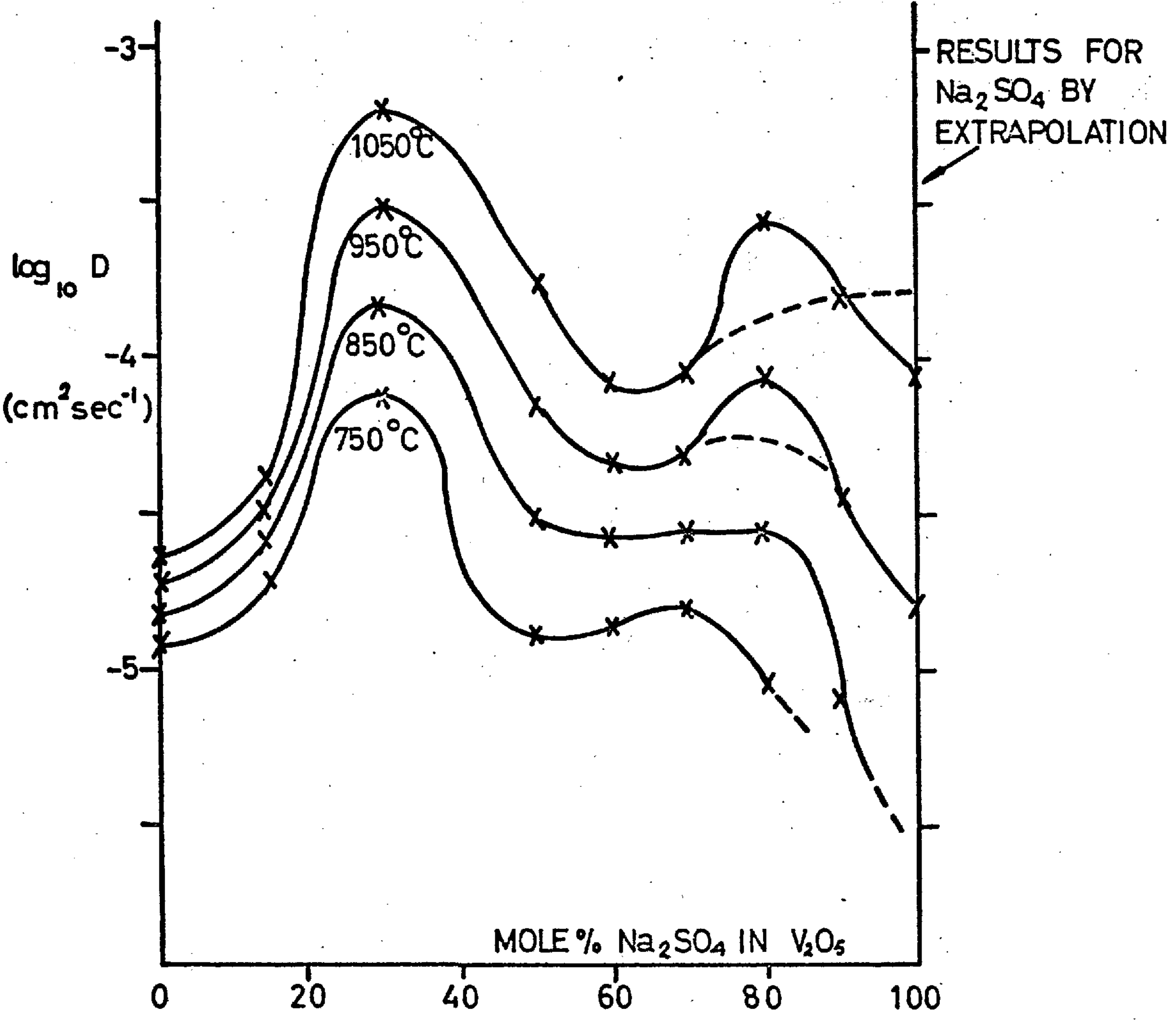


FIG. 21A APPARENT DIFFUSION COEFFICIENT OF Al_2O_3 IN Na_2SO_4/V_2O_5 MELTS

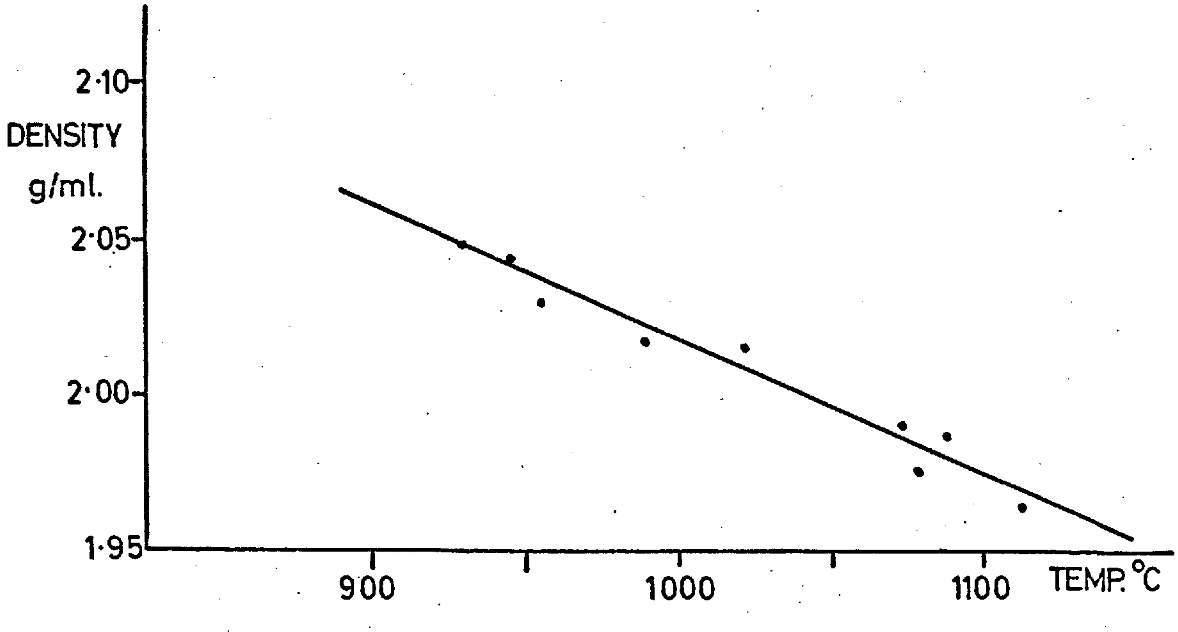


FIG. 21B DENSITY OF SODIUM SULPHATE

Temperature		$\pm$ 5°C
Flow length of tube, L (see section 8.3.4)		$\pm$ 1 to 5%
Time, t		$\pm$ 0.5 sec.
Wt. loss of sample, alumina, usually		$\pm$ 0.0010 g.
silica , usually		$\pm$ 0.0020 g.
Saturation Solubility, C_{eq},	alumina	$\pm$ 1 to 4%
	silica	$\pm$ 2 to 22% (depending on melt and temperature)
Density, ρ		$\pm$ 2%
Weight of melt passed, M		$\pm$ 10 to 40 g.

There is an additional error in neglecting the term C_1 in equation (28). Sometimes this was zero, but for most runs the error introduced is less than 1%. In four runs it was above 1% and in these cases C_1 was subtracted from C_{eq}. There was still an inaccuracy of about 1% in these cases as C_1 was never known really accurately.

Examples: Melt 80% Na_2SO_4/20% $NaVO_3$.

	Alumina	Silica
Run No., Sample No.	84, Y 14	47, S 9
Temperature °C	968 $\pm$ 5	979 $\pm$ 5
Flowlength, L, cm.	4.72 $\pm$ 0.10	5.33 $\pm$ 0.20
Time, t, sec.	204.4 $\pm$ 0.5	160.5 $\pm$ 0.5
Wt. of sample before	27.9814	61.4844
Wt. of sample after	27.9733	61.4602
Loss in wt., N, g.	0.0076$\pm$0.0005	0.0242$\pm$0.0015
Saturation Solubility, C_{eq}, g/ml.	0.00172$\pm$0.00010	0.0113$\pm$0.0012
Density of the melt, ρ, g/ml.	2.066$\pm$0.041	2.062$\pm$0.041
Weight of melt passed, M, g.	790 $\pm$ 20	790 $\pm$ 20
Bulk concentration, C_1, g/ml.	0	0.0001 g/ml.
Diffusion Coefficient, D cm²/sec.	$22.5 \pm 5.9 \times 10^{6}$ i.e. $\pm$ 25%	$8.65 \pm 3.31 \times 10^{-6}$ i.e. $\pm$ 38%

9.4. CONCLUSIONS.

The accuracies estimated in the above paragraph are typical of the system. Some results had better accuracies, some much worse. The worst results of all are in the high sodium sulphate regions where very low weight losses were recorded and the error in measuring these was sometimes of the same order as the weight loss itself. Thus the maximum error is 100% or more and leads to the conclusion that this is not a very good method for the determination of diffusion coefficients. Trends from the graphs 20 and 21A were: the addition of soda to vanadium pentoxide caused a large increase in ion mobility until about 30 mole % Na_2SO_4 was reached. Further additions up to 50 mole % caused the mobility to decrease and from 50-100% Na_2SO_4 diffusion coefficients evaluated were all of the same order. Although the method was not thought to be very accurate, ARRHENIUS plots of $\ln_e D$ versus $1/T^{\circ}K$ produced reasonably straight lines. Apparent energies of activation for the diffusion mechanism were deduced from the slope of the line (see equation 11) and are given in table 6. Estimated errors are ± 15%.

Table 6. Apparent Activation Energies for Diffusion of SiO_2 and Al_2O_3 in Na_2SO_4/V_2O_5 Melts - E_a in kcal/mole.

Melt	SiO_2	Al_2O_3
$NaVO_3$	24.4 **	23.4
80% $NaVO_3$, 20% Na_2SO_4	9.5 (21.2*)	15.6
60% $NaVO_3$, 40% Na_2SO_4	28.1	15.4
40% $NaVO_3$, 60% Na_2SO_4	42.8	30.6
20% $NaVO_3$, 80% Na_2SO_4	24.8 (46.9*)	44.1
Na_2SO_4	61.4	52.0

** GOLDMAN's result for 50% V_2O_5/50% Na_2SO_4 was 19.7 kcal/mole

* Calculated using the incomplete (broken) lines in fig.20.

THOMAS (67) found the diffusion coefficient of Al_2O_3 in various lime-alumina-silica slags to be of the order of 1×10^{-6} cm^2/sec between 1500 and 1600°C.

CHAPTER 10. THE HOT PRESSING OF FIREBRICK.

One of the objects of the present research programme was to test materials other than pure oxides for corrosion resistance. To enable this research to be of greatest value to the sponsors, it was decided to attempt the testing of high alumina firebrick. In the condition supplied for use in marine boilers firebricks have a porosity of up to 27%. Such porosities cannot be accepted by the corrosion testing apparatus. To produce denser samples it was decided to attempt to hot press finely ground firebrick in a carbon mould.

10.1. EXPERIMENTAL TECHNIQUE.

A small, electrical furnace (Kanthal A) was made to fit between the uprights of a hydraulic press (see fig.22). A carbon mould then fitted inside the furnace to allow the simple application of pressure. A measurement was taken, at intervals, of the distance between the press platens, h. The final measurement was then related to the height of the specimen, to enable the changes in density with time to be calculated. Although this method was only really accurate during the last measurement, it was sufficient to indicate the rate of densification. The two errors in this measurement were, changes in h due to thermal expansion of the uprights and changes in the height of the specimen due to thermal expansion of the carbon plungers. The former was considered insignificant as even after several hours, the uprights of the press were never more than warm to the hand (probable expansion 0.005 cm). When hot pressing at 1300°C, the maximum error due to expansion of the carbon was 3%. These experiments were concerned only with the production of a dense end product and so this error was ignored. It was originally thought that due to the presence of a glassy phase in the fireclay brick, considerable densification would be achieved at comparatively low temperatures, say up to 1100°C.

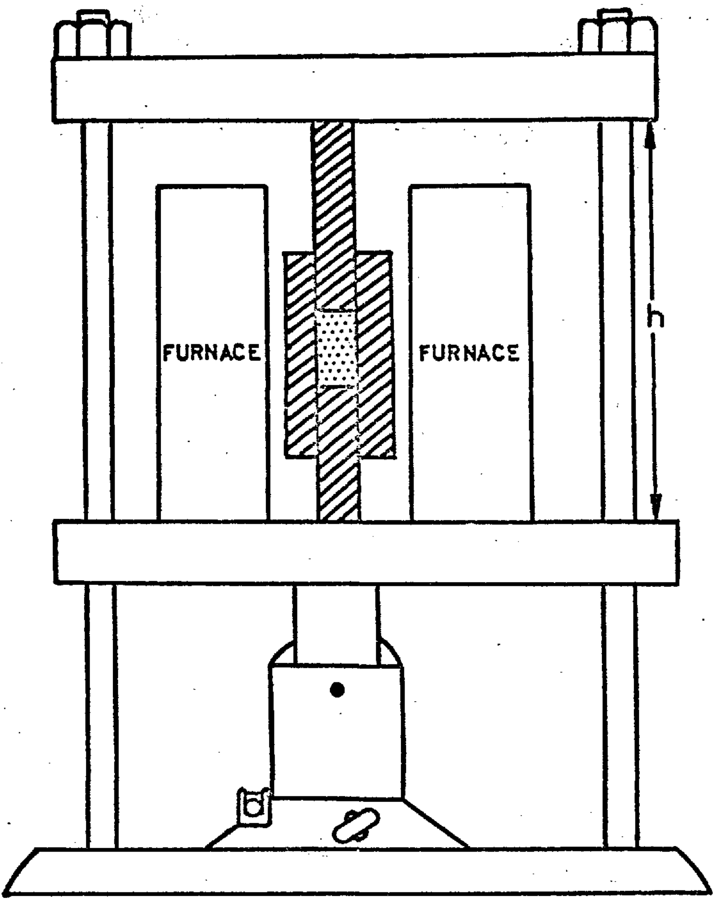


FIG. 22 HOT PRESSING APPARATUS

This was the reason for choosing an electrical furnace. However, it was soon discovered that such temperatures were NOT sufficient and higher temperatures were gained by using the carbon mould as the furnace resistance. A 0-110 volts variable transformer was fed into a fixed 5 to 1 step-down transformer. The output leads from this were taken by copper braiding to the top and bottom carbon plungers where contact was made on mild steel bars. These bars were insulated from the press by asbestos board (see plate 7, p.131) With a power of about 3000 watts, 1300°C was reached in about 45 min. but it was difficult to hold this temperature stable. In all experiments, temperature was indicated by a platinum/rhodium thermocouple bound onto the mould using electrical resistance wire.

10.2. EXPERIMENTAL PROCEDURE.

The moulds used had an internal bore which varied between 2 and 2.5 cm. A sample of ground firebrick was weighed which would give a specimen about 4 cm. high at theoretical density. This was placed in the carbon mould in the cold furnace and subjected to the pressure at which the hot test would be carried out, for one minute. At the end of this time, the distance, h, was measured. The pressure was then removed and the power turned on. In the case of the carbon resistance furnace, the pressure was removed to the minimum possible for good contact between plungers and iron bars. The time was noted for the mould to reach the required temperature and the new value of h taken at this time. Full pressure wss then applied and values of h taken at intervals of 1 to 5 min. It was originally hoped to continue each experiment until changes in h became very small or about 4 hours was reached. In practice most experiments were stopped when the mould broke. It had initially been the intention to press at 3.0 kg/mm^2 (about

PLATE 7 HOT PRESSING APPARATUS

1.9 t.s.i.) i.e. about one half the strength of carbon at these temperatures. After several runs it was obvious that the carbon tubes used could not tolerate these pressures. On reduction of the pressure to 1.5 kg/mm^2 several runs were made that gave useful results. However, more moulds cracked than remained whole and the advice of MORGANITE CARBON Ltd. was sought. They gave the information that the particular tubes being used (EY 8348) were manufactured by an extrusion process which causes weaknesses down the length of the tube. Machining of a tube from CY 9 rod was suggested and using this new material the results of fig.23 were gained.

10.3. MATERIAL USED.

A "NETTLE" brand firebrick (J.G.STEIN and Co.) was chosen as the starting material. This brick was made with keyways for use in marine boilers (supplied by A.M.E.E., Haslar). One half of a normal sized brick was crushed on a bucking plate and then put through a jaw crusher set at about 6 mm. This product was crushed in a disc crusher until it all passed a 14 mesh sieve. The whole powder was then wet milled for 48 hours in a rubber lined ball mill using porcelain balls. It then easily passed through a 350 mesh B.S.sieve. The analysis of a typical "NETTLE" brick is as follows:-

Alumina	42%
Silica	52%

Refractoriness 1760°C.
Density Bulk 2.06; True 2.78 g/ml.
Porosity Apparent 19.0%; True 27.0%.

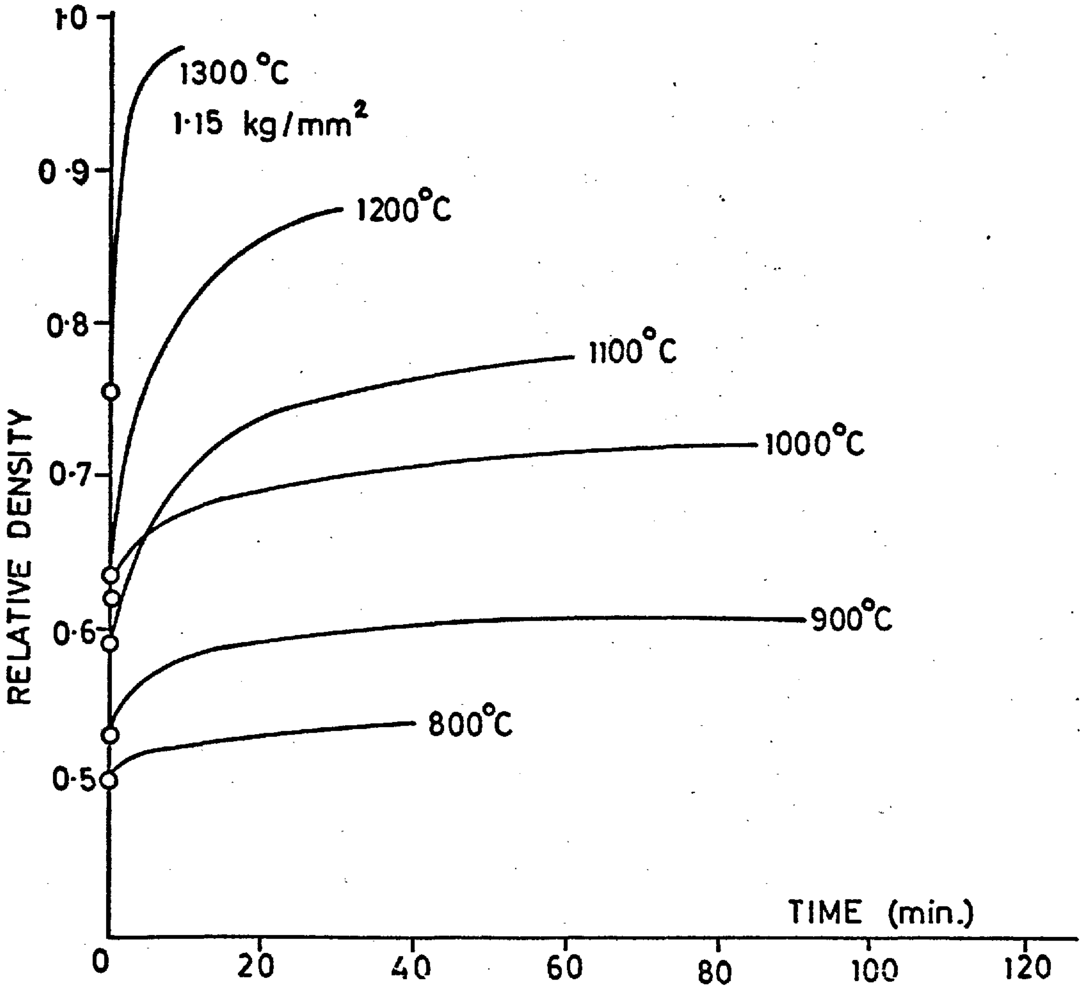


FIG. 23 HOT PRESSING OF "NETTLE" FIREBRICK AT 1·5 kg/mm^2

10.4. RESULTS.

The results of pressing "NETTLE" firebrick at 1.5 kg/mm^2 between 800 and 1200°C and at 1.15 kg/mm^2 at 1300°C are shown in fig.23. At all temperatures the compaction is characterized by an apparent end-point density which increases with increasing temperature. Initially there is a rapid rate of densification, followed by a gradual approach to the end-point density. The initial slope of density versus time increases with increasing temperature. There was always some sintering of the compacted powder which occurred on heating the sample to the test temperature. This initial density also increases with increasing temperature except for the result at 1000°C, which is due to the mould taking 80 min. to reach temperature. According to the graph, it should be possible to hot press "NETTLE" firebrick of the grain size used to approximately theoretical density at about 1350°C and 1.15 kg/mm^2. To perform this experiment successfully, however, will need a design change in mould or furnace or both. The thickness of the mould wall must be increased. At present this is impossible as the resistance of the wall will then be less than the plungers. At present, plungers are only used once due to a high degree of oxidation. A new furnace such as the hot press furnace described by WHITE (63) would be adequate or the possibility of using an induction furnace with a graphite susceptor could be investigated.

According to McCLELLAND (64) the condition that an end-point density exists is :-

$$[1 - (1 - Q'^{2/3}] \ \ln \frac{1}{(1-Q')}) = \frac{P}{\sqrt{2}\,\tau_c} \qquad (31)$$

where Q' is the end-point relative density (relative to theoretical density) produced by a pressure, P, at constant temperature at which τ_c is the critical yield stress. Using this formula and the results in fig.23, τ_c has been estimated for "NETTLE" firebrick and the results are seen in fig.24A.

A smooth curve has been drawn through these points; they must not be extrapolated to room temperature.

If the flow to produce a more dense sample is viscous, then McCLELLAND (64) presents a modified form of the MACKENZIE and SHUTTLEWORTH hot pressing equation

$$\frac{dQ}{dt} = \frac{3P}{4\eta}(1 - Q) \qquad (32)$$

where η is the viscosity at infinite shear rate. MANGSEN et al (65) found that this expression fitted their data for the hot pressing of alumina at times of less than 30 min. This author considers that equation (32) only applies to the hot pressing of "NETTLE" firebrick for the first 6-8 min. and then only at temperatures of 1100°C and above. Such results, plotting (1-Q) against dQ/dt, are shown in fig.24C. The approximate straight lines have a slope of $4\eta/3P$ and it is seen that at 10 min. the points on the 1100°C line are beginning to deviate. This trend was much more marked at 1000°C and below. The approximate viscosities evaluated are:

At 1100°C, viscosity = 1.05 $\times 10^8$ poise.
1200°C, viscosity = 2.5 $\times 10^7$ poise
1300°C, viscosity = 8.9 $\times 10^6$ poise.

The accuracy of these results was difficult to judge. The rate of densification from the graph was better than ± 10%. Pressure varied due to the movement of the platens ± 20%. Q had maximum errors of ± 6% and the temperature was controlled ± 15°C. Therefore the error is ± 36%. This is probably modified by the use of a graph, but increased by an unknown factor depending upon how reliable it was to apply equation (32) to the results.

In chapter 6.5 equation (16) related viscosity and temperature by the ARRHENIUS equation:-

$$\eta = A\,e^{E_{vis}/RT} \qquad (16)$$

Plotting ln η against 1/T in fig.24B gave a good line (as far as can be judged) indicating an activation energy for viscous flow as 55 kcal/mole. This is providing that the hot pressing mechanism proceeds via viscous flow. The error in the figure quoted is probably half that for viscosity, due to the use of a graph i.e. ± 18%. CHAKLADER, CARRUTHERS and ROBERTS (66) found the viscosity of a 42% Al_2O_3, 51% SiO_2 brick to be 1.4×10^{15} poise at 1000°C, 1.8×10^{14} poise at 1100°C and 8.8×10^{12} poise at 1150°C. This is some 10^6 times more t than those results by this author which agree more with the values given in ref. (66) for the glasses likely to be present. They suggest that crystal phases interdispersed in the glassy matrix strongly reinforce the strength of the glass. Such crystal phases have been greatly reduced in size by grinding for the work described in this chapter.

10.5. CONCLUSIONS.

It is possible to hot press finely ground "NETTLE" firebrick at 800°C and above. At all temperatures the compaction is characterized by an apparent end-point density which increases with increasing temperature. It should be possible to approach the theoretical density of the firebrick by hot pressing at 1350°C or higher using a pressure of 1.15 kg/mm^2 or more. A change in the design of the mould and furnace will be necessary to execute this experiment. The approximate critical yield stress of "NETTLE" firebrick has been evaluated giving values ranging from 4.26 kg/mm^2 at 800°C to 0.21 kg/mm^2 at 1300°C. The hot pressing mechanism at 1100° C and above appears to be viscous flow with an energy of activation of the process of 55 ± 10 kcal/mole.

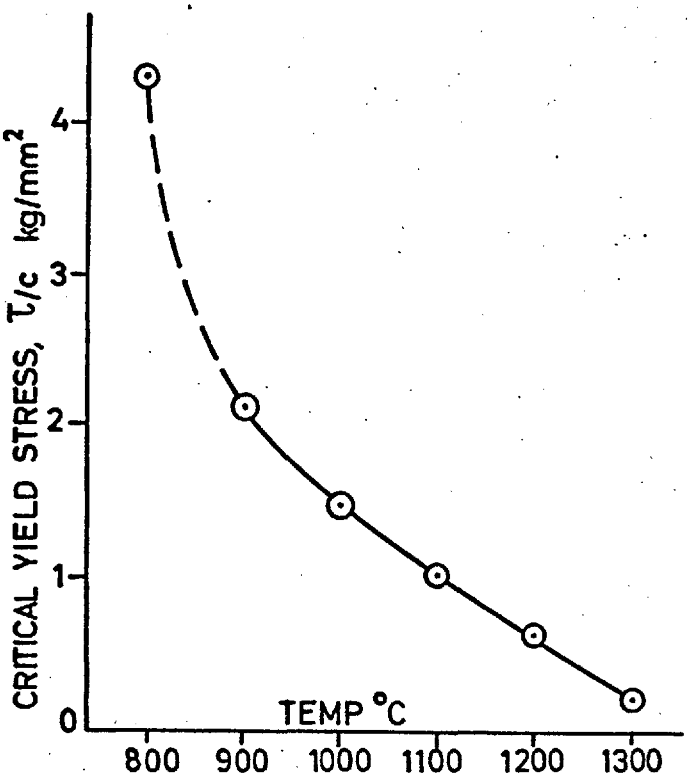


FIG. 24A APPROX. CRITICAL YIELD STRESS OF "NETTLE" FIREBRICK

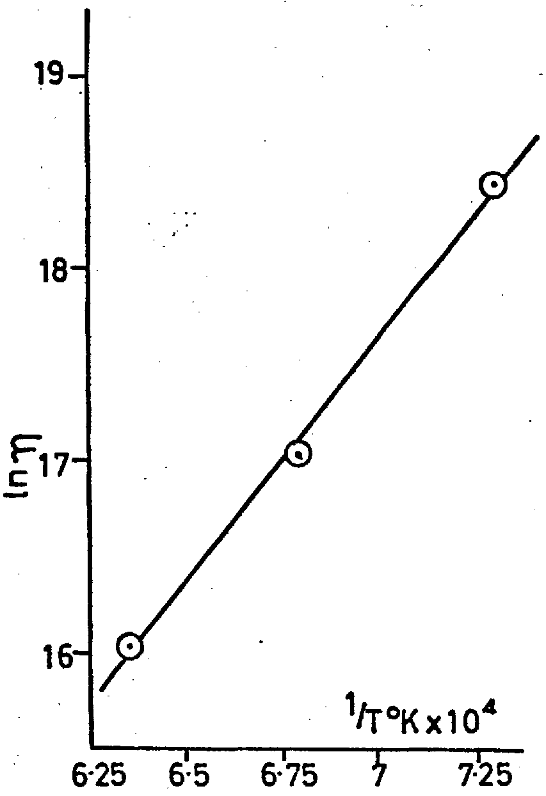


FIG. 24B ARRENIUS PLOT FOR APPARENT VISCOUS FLOW IN "NETTLE" FIREBRICK

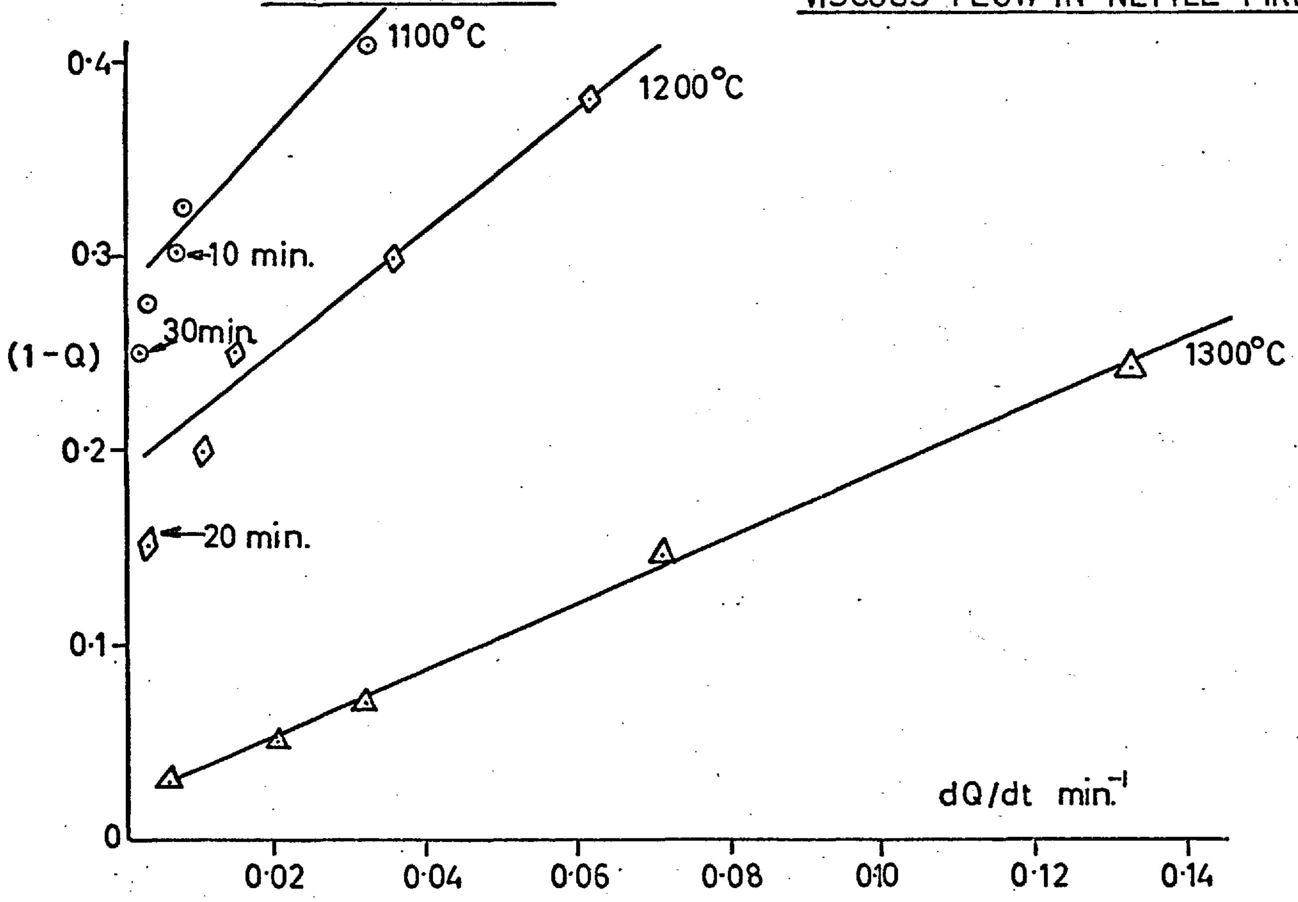


FIG. 24C RATE OF DENSIFICATION OF NETTLE FIREBRICK

CHAPTER 11. GENERAL CONCLUSIONS.

The object of this research was to identify the elements of fuel oil ash which are particularly damaging to marine boiler refractories. It had already been decided that the correct way of fulfilling this object was to treat this dissolution process as an example of mass transfer under streamline conditions. The apparatus permitted a melt, in transit through a refractory tube, to dissolve the tube walls. This method necessarily involved the measurement of concentration gradients near the refractory wall which provides the driving force for the dissolution process. Towards this end, alumina and silica have been tested for saturation solubilities and corrosion rates in sodium sulphate/vanadium pentoxide melts. The main conclusions of the work are:-

1. At temperatures above about 480°C, vanadium pentoxide will decompose sodium sulphate to release sulphur trioxide and form sodium vanadates. The reaction to form sodium vanadyl vanadate I is faster than the reaction to form sodium vanadyl vanadate II which is in turn faster than that to form sodium metavanadate. All reactions are considered to be complete after 20,000 min. at 1050°C. Apparent activation energies for the formation of these three compounds are 20.8, 27.1 and 31.6 kcal/mole respectively with probable errors ± 10-12%.

2. The saturation solubilities of alumina and silica in $Na_2SO_4/NaVO_3/V_2O_5$ melts have been determined, completing the series of experiments started by GOLDMAN. The solubilities of silica and alumina in vanadium pentoxide are approximately equal: 1.8 wt.% at 750°C and 2.9 wt.% at 1050°C for silica; and 1.4 wt.% at 750°C and 3.3 wt.% at 1050°C for alumina. In pure sodium sulphate, both oxides are almost insoluble. However, solubilities of these two oxides in mixtures of Na_2SO_4 and V_2O_5 show quite different behaviour

(see fig.11). The solubility of alumina has a maximum at approximately 14 mole % sodium sulphate (the composition of a compound commonly found in marine boiler slags-sodium vanadyl vanadate I). Silica has a minimum at about 18 mole % and a maximum at 58 mole % sodium sulphate. Thus melts containing up to about 90 mole % sodium sulphate are capable of dissolving considerable quantities of silica and alumina. Melts containing much sodium sulphate can be expected to cause devitrification of the glassy phase which binds brick particles.

3. The corrosion rates of silica and alumina in Na_2SO_4/V_2O_5 melts are approximately equal for a given melt at a given temperature (see fig.17). The corrosivity of pure vanadium pentoxide is increased by the addition of sodium sulphate. Similarly vanadium pentoxide increases the corrosivity of sodium sulphate. Melts containing between 30 and 70 mole % Na_2SO_4 have roughly equivalent corrosion rates at 1050°C for both oxides. No difference in results could be detected using 98.5% Al_2O_3 and 96.0 Al_2O_3 specimens. It is expected that alumina will resist corrosion by such melts above 1050°C better than silica.

4. The apparent diffusion coefficients of silica and alumina in Na_2SO_4/V_2O_5 melts have been evaluated. Results for temperatures between 750 and 1050°C are between 10^{-6} and 10^{-3} $cm^2/sec.$ and show a maximum at approx. 30 mole % Na_2SO_4 for both oxides. The diffusion coefficients at this composition are some 25 times more than in pure vanadium pentoxide. This is presumably due to the corresponding decrease in viscosity. The apparent activation energies for the diffusion of silica increase from 20 to 60 kcal/mole as the melt composition increases from 60 to 100% Na_2SO_4. The corresponding increase for alumina is from 15 to 50 kcal/mole.

5. Attempts were made to hot press "NETTLE" firebrick to theoretical density between 800 and 1300°C. At all

temperatures the compaction was characterised by an end point density which increased with increasing temperature. The approximate critical yield stress of "NETTLE" firebrick was evaluated giving values ranging from 4.3 kg/mm^2 at 800°C to 0.21 kg/mm^2 at 1200°C. The hot pressing mechanism at 1100°C and above appears to be viscous flow with an energy of activation for the process of 55 ± 10 kcal/mole.

11.1. SUGGESTIONS FOR FUTURE WORK.

Suggestions for future work fall into two categories -those of practical value to the sponsor andthose of academic interest.

The sponsor now has information on the solubilities and corrosion rates of alumina and silica in melts consisting essentially of sodium sulphate and vanadium pentoxide up to 1050°C. Firstly the refractories used should be extended to include those commercially available e.g. various alumina based tubes, fusion cast refractories. An attempt should be made at testing firebricks, mouldable refractories and castable refractories hot pressed to theoretical density. Consideration should also be given to the glassy phase which binds a firebrick as this may well exhibit poor corrosion resistance. Secondly, the range of melts should be extended to include other impurities commonly found in boiler slags e.g. nickel oxide, magnesium oxide, calcium oxide and ferric oxide. This could be simply investigated by adding a few per cent of each oxide to the melt which dissolved most alumina i.e. sodium vanadyl vanadate I, and then testing using sapphire rods for solubility measurements and HILOX 961 tubes for corrosion testing. Lastly, the temperature at which the testing is carried out must be increased. This is relatively simple for the solubility experiments. Electrical resistance furnaces can with care reach 1200°C using unprotected, low-cost windings. Molybdenum, platinum or carbon can increase this temperature to beyond that normally experienced in the boilers of fighting ships. The corrosion testing apparatus is probably capable of 1100°C if the heat resisting alloy is chosen (and manufactured) with care. Beyond this temperature the use of refractories is possible in the proposed future design (see fig.19). Although it is academically unsound to extrapolate the corrosion rates to higher temperatures, it is possible to deduce diffusion coefficients from the ARRHENIUS plot at possible refractory temperatures in marine boilers. If C_{eq} is known at such temperatures, then N could be estimated using equation (28). This method would be approximate only but useful, should the corrosion testing apparatus prove difficult to use above 1100°C.

Points of more academic interest include: the further study of the phase diagrams, for which the bases are given in section 7.6; determination of the controlling mechanism for the dissolution of silica and alumina in sodium sulphate/vanadium pentoxide melts; further work to compare the sintering characteristics of firebrick with the hot pressing information gained; and determination of the $NaVO_3/Na_2SO_4$ phase diagram up to about 1500°C.

APPENDICES.

APPENDIX 1.

IMPURITIES IN CRUDE PETROLEUM.

1. Oxygen - usually as carboxylic acids, normally less then 0.1%.
2. Nitrogen - organic compounds, notably porphyrins normally less than 0.1%.
3. Chlorine - crude oil contamination with brine. Up to 1.2%.
4. Sulphur - majority of crudes 0.5-3.0% but seems to be increasing.
5. Vanadium - porphyrin compounds. 1-500 p.p.m.
6. Sodium - crude oil contamination with brine or suspension in microcrystalline state. Up to 500 p.p.m.
7. Iron - porphyrins and finely divided oxides. Up to 100 p.p.m.
8. Nickel - porphyrins. Up to 100 p.p.m.
9. Calcium - minerals in suspension or dissolved in emulsified water. Up to 300 p.p.m.
10. Silicon Aluminium - complex alumino-silicates and sand in suspension. 0-50 p.p.m.
11. Magnesium, Zinc, Copper, Potassium, Lead, Chromium, Silver, Manganese, Titanium, Tin and many others 0-50 p.p.m.
12. Total ash content of crude oil 20 - 1500 p.p.m.

COMPOUNDS OF INTEREST IN OIL ASH CORROSION. (2,3,4,5).

COMPOUND.		MELTING POINT °C.
Aluminium Oxide	Al_2O_3	2050
Aluminium Sulphate	$Al_2(SO_4)_3$	D at 770°C to Al_2O_3
Calcium Oxide	CaO	2572
Calcium Orthovanadate	$3CaO.V_2O_5$	1370
Calcium Sulphate	$CaSO_4$	1450
Ferric Oxide	Fe_2O_3	1565
Ferric Sulphate	$Fe_2(SO_4)_3$	D at 480°C to Fe_2O_3
Ferric Vanadate	$Fe_2O_3.2V_2O_5$	855
Ferric Metavanadate	$Fe_2O_3.V_2O_5$	860
Magnesium Oxide	MgO	2800
Magnesium Sulphate	$MgSO_4$	D at 1124°C to MgO
Magnesium Metavanadate	$MgO.V_2O_5$	835
Magnesium Pyrovanadate	$2MgO.V_2O_5$	670
Magnesium Orthovanadate	$3MgO.V_2O_5$	1190
Nickel Oxide	NiO	2090
Nickel Sulphate	$NiSO_4$	D at 840°C to NiO
Nickel Sulphide	NiS	797
Nickel Pyrovanadate	$2NiO.V_2O_5$	900
Nickel Orthovanadate	$3NiO.V_2O_5$	900
Potassium Chloride	KCl	790
Potassium Sulphate	K_2SO_4	1069
Potassium Aluminium Sulphate	$K_3Al(SO_4)_3$	654
Silicon Dioxide	SiO_2	1710
Sodium Chloride	$NaCl$	801
Sodium Sulphate	Na_2SO_4	884
Sodium Bisulphate	$NaHSO_4$	D at 250 to $Na_2S_2O_7$
Sodium Pyrosulphate	$Na_2S_2O_7$	400 D at 460 to Na_2SO_4
Sodium Vanadyl Vanadate I	$Na_2O.V_2O_4.5V_2O_5$	625
Sodium Vanadyl Vanadate II	$5Na_2O.V_2O_4$ $11\ V_2O_5$	535

COMPOUND		MELTING POINT °C	
Sodium Metavanadate	$Na_2O.V_2O_5$	630	
Sodium Pyrovanadate	$2Na_2O.V_2O_5$	640	*
Sodium Orthovanadate	$3Na_2O.V_2O_5$	850	**
Sodium Aluminium Sulphate	$Na_3Al(SO_4)_3$	645	
Vanadium Trioxide	V_2O_3	1970	
Vanadium Tetroxide	V_2O_4	1970	***
Vanadium Pentoxide	V_2O_5	673	
Zinc Oxide	ZnO	1800	
Zinc Sulphate	$ZnSO_4$	D at 740 to ZnO	
Zinc Vanadate	$ZnO.2V_2O_5$	610 - 650	
Zinc Pyrovanadate	$2ZnO.V_2O_5$	875	
Zinc Orthovanadate	$3ZnO.V_2O_5$	approx. 875	

D = decomposes.

* CANNERI (32) quotes 632°C. THORNTON REPORT (35) quotes 675°C.

** CANNERI (32) quotes 860°C. THORNTON REPORT (35) quotes 1100°C.

*** KING and SUBER (54) quote 1545°C.

APPENDIX 2

THE STRUCTURE OF VANADIUM PORPHYRIN (9)

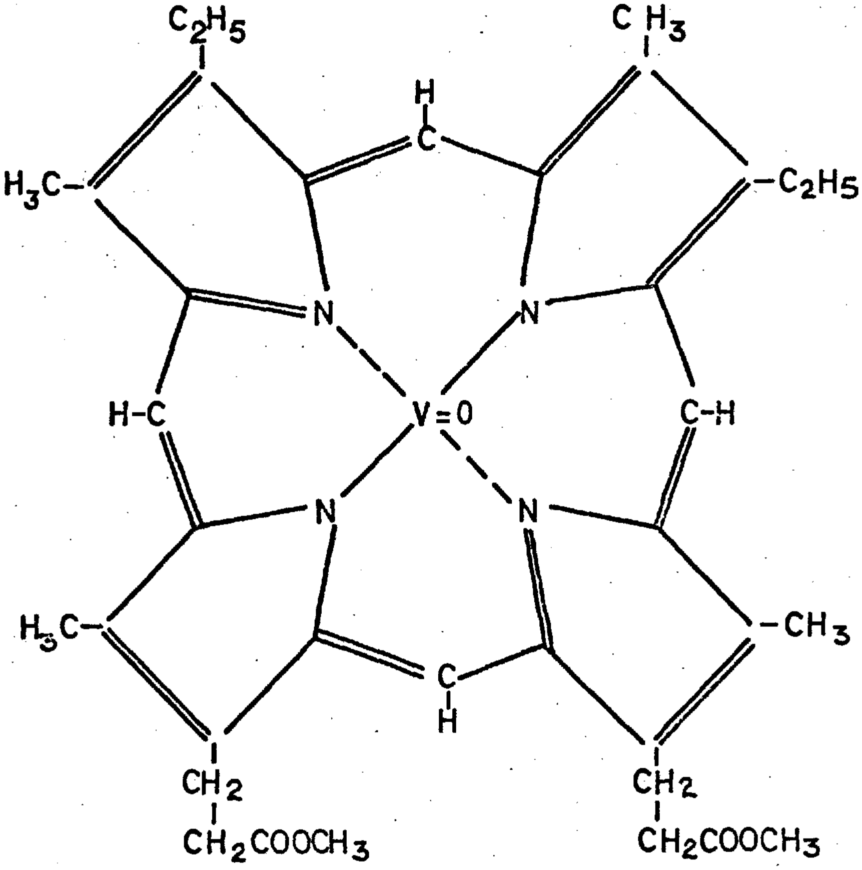


FIG. 25 VANADIUM COMPLEX OF MESOPORPHYRIN IX DIMETHYL ESTER(2)

APPENDIX 3.

RESULTS OF FILTERING A No.6 OIL AS SHOWN BY ASH ANALYSES (12).

Table 7.

Element	Before Filtration ppm in Oil	After Filtration ppm in Oil
Na	217	2
Ca	250	48
Ni	20	14
Al	23	4.1
Fe	47	20.5
Pb	13.6	2
Cr	2.1	2
Mg	18	5.8
V	33	31.8
Cu	8	2
Zn	16	16
Ag	1	1
Mn	2	2
Ti	2	2
Sn	2	2
Total Ash	1,200	260
Sediment % wt	0.086	0.0097

APPENDIX 4.

SLUMPING TEMPERATURES OF VARIOUS REFRACTORIES WITH OIL ASH SLAGS (21).

Table 8.

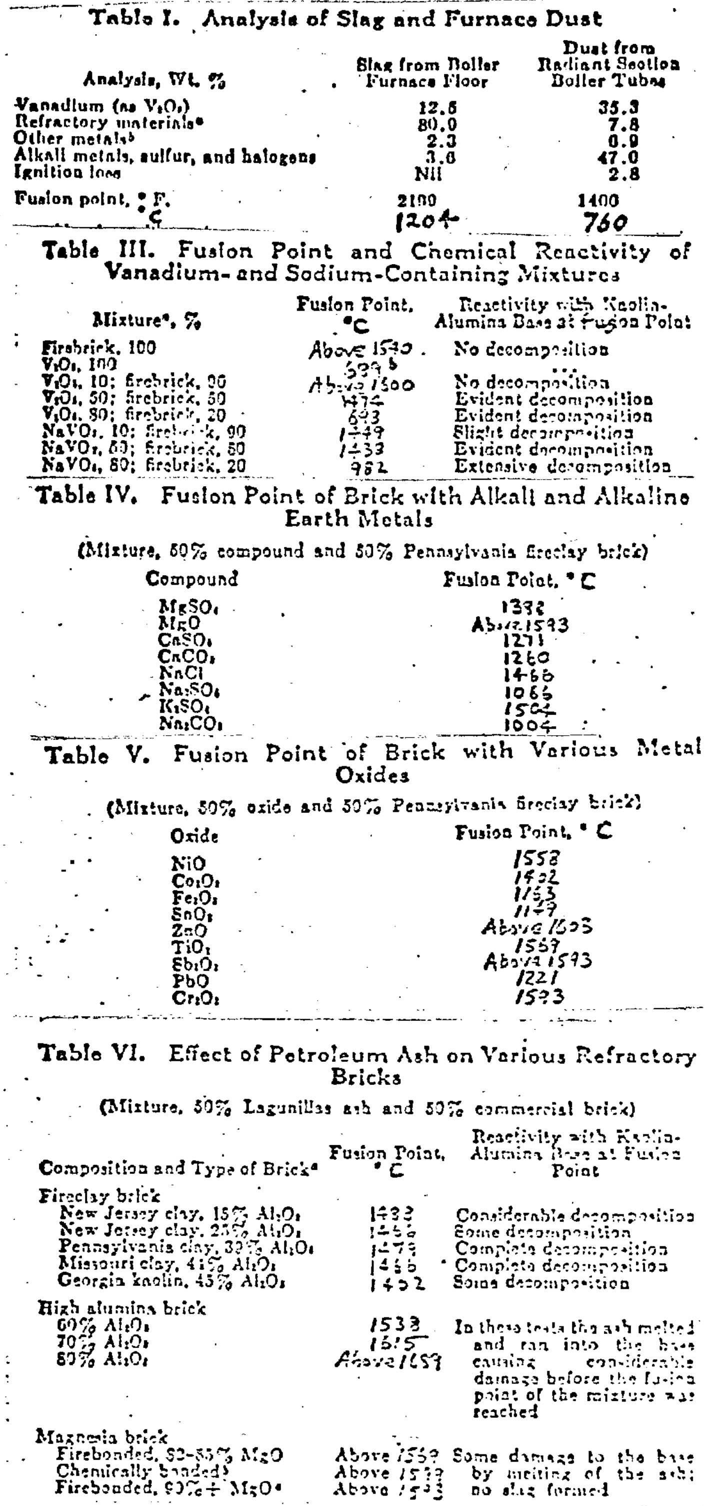


Table I. Analysis of Slag and Furnace Dust

Analysis, Wt. %	Slag from Boiler Furnace Floor	Dust from Radiant Section Boiler Tubes
Vanadium (as V_2O_5)	12.5	35.3
Refractory materials[a]	80.0	7.8
Other metals[b]	2.3	6.9
Alkali metals, sulfur, and halogens	3.6	47.0
Ignition loss	Nil	2.8
Fusion point, ° F.	2100	1400
° C	1204	760

Table III. Fusion Point and Chemical Reactivity of Vanadium- and Sodium-Containing Mixtures

Mixture[a], %	Fusion Point, °C	Reactivity with Kaolin-Alumina Base at Fusion Point
Firebrick, 100	Above 1540	No decomposition
V_2O_5, 100	699 b	...
V_2O_5, 10; firebrick, 90	Above 1500	No decomposition
V_2O_5, 50; firebrick, 50	1474	Evident decomposition
V_2O_5, 80; firebrick, 20	693	Evident decomposition
$NaVO_3$, 10; firebrick, 90	1449	Slight decomposition
$NaVO_3$, 50; firebrick, 50	1433	Evident decomposition
$NaVO_3$, 80; firebrick, 20	982	Extensive decomposition

Table IV. Fusion Point of Brick with Alkali and Alkaline Earth Metals

(Mixture, 50% compound and 50% Pennsylvania fireclay brick)

Compound	Fusion Point, ° C
$MgSO_4$	1388
MgO	Above 1593
$CaSO_4$	1271
$CaCO_3$	1260
NaCl	1466
Na_2SO_4	1066
K_2SO_4	1504
Na_2CO_3	1004

Table V. Fusion Point of Brick with Various Metal Oxides

(Mixture, 50% oxide and 50% Pennsylvania fireclay brick)

Oxide	Fusion Point, ° C
NiO	1558
Co_2O_3	1432
Fe_2O_3	1153
SnO_2	1149
ZnO	Above 1593
TiO_2	1559
Sb_2O_3	Above 1593
PbO	1221
Cr_2O_3	1593

Table VI. Effect of Petroleum Ash on Various Refractory Bricks

(Mixture, 50% Lagunillas ash and 50% commercial brick)

Composition and Type of Brick[a]	Fusion Point, ° C	Reactivity with Kaolin-Alumina Base at Fusion Point
Fireclay brick		
New Jersey clay, 15% Al_2O_3	1433	Considerable decomposition
New Jersey clay, 25% Al_2O_3	1456	Some decomposition
Pennsylvania clay, 39% Al_2O_3	1479	Complete decomposition
Missouri clay, 41% Al_2O_3	1456	Complete decomposition
Georgia kaolin, 45% Al_2O_3	1452	Some decomposition
High alumina brick		
60% Al_2O_3	1538	In these tests the ash melted and ran into the base causing considerable damage before the fusion point of the mixture was reached
70% Al_2O_3	1515	
80% Al_2O_3	Above 1659	
Magnesia brick		
Firebonded, 82-85% MgO	Above 1559	Some damage to the base by melting of the ash; no slag formed
Chemically bonded[b]	Above 1593	
Firebonded, 90% + MgO[c]	Above 1593	

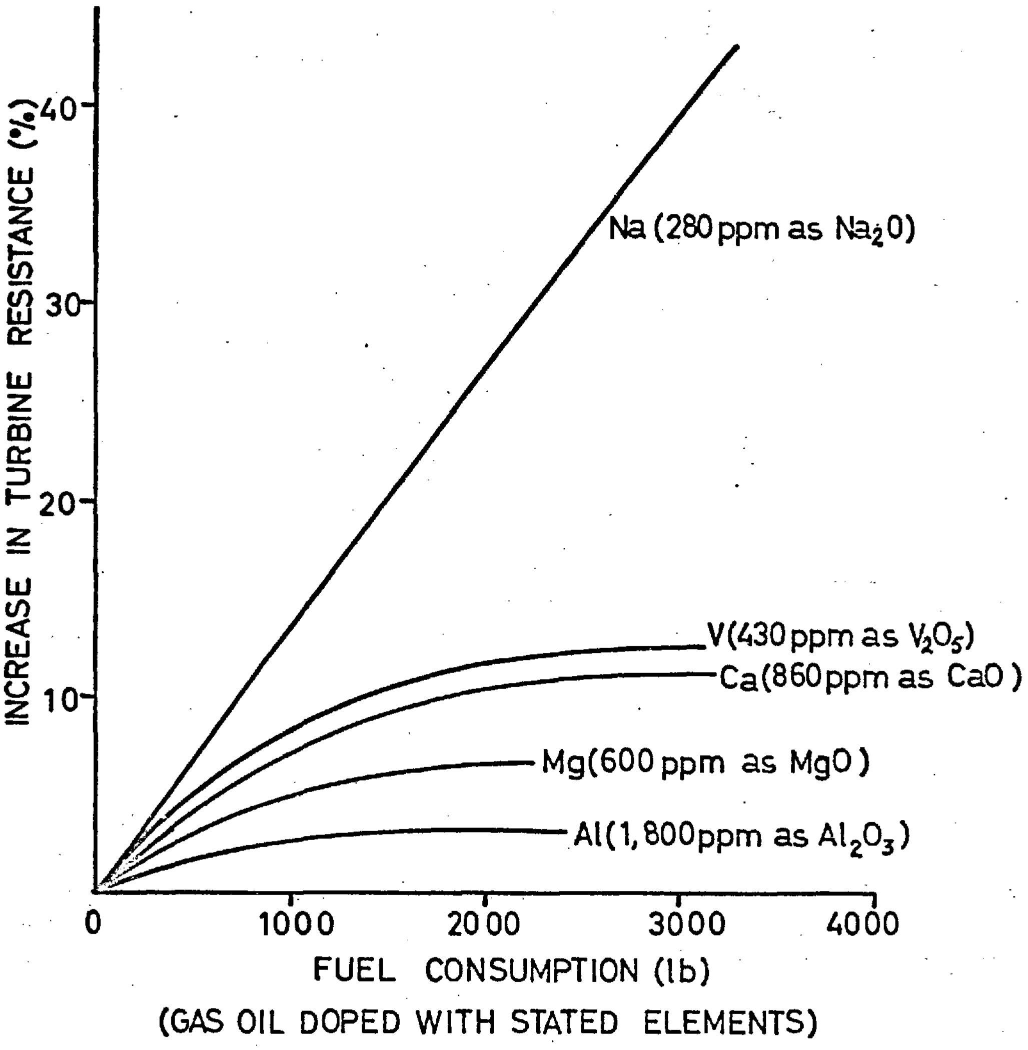
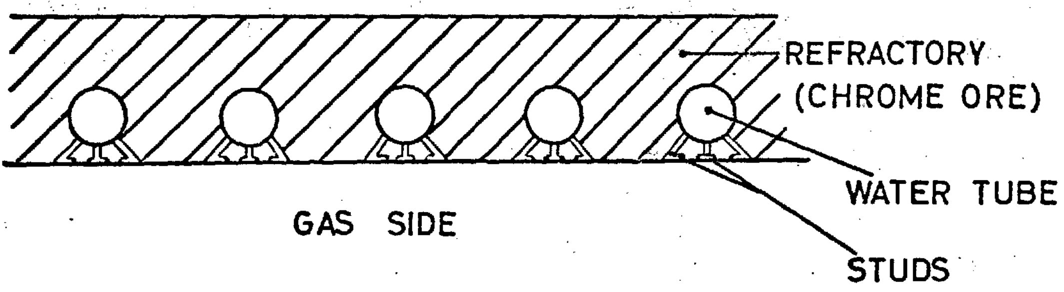
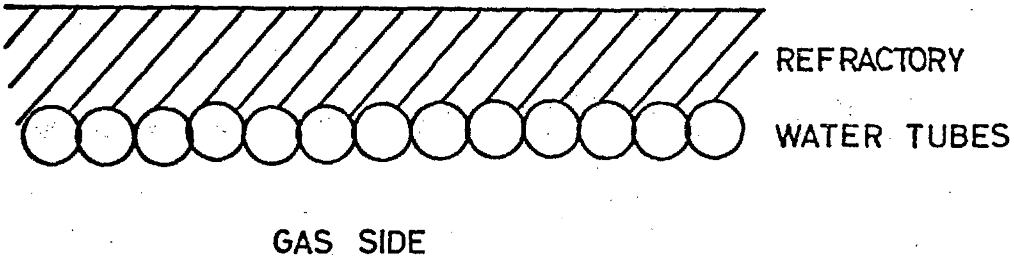


FIG. 26 EFFECT OF INDIVIDUAL ASH COMPONENTS ON DEPOSIT FORMATION(5)

1. STUDDED TUBES



2. TANGENT TUBES



3. MONOLITHIC RAMMED REFRACTORIES

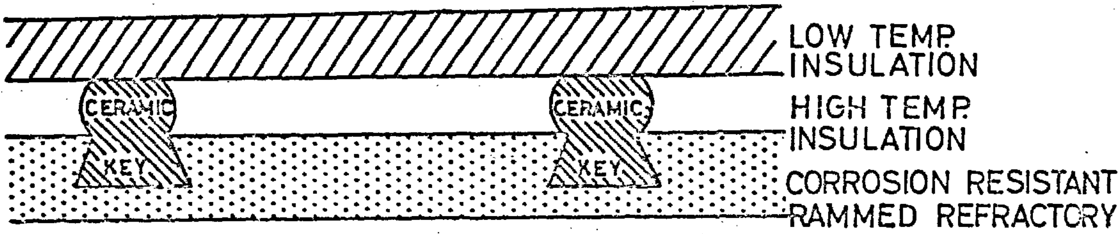


FIG. 27. MARINE BOILER WALLS

APPENDIX 7.

"Experiences in the Ceramics Laboratories of Imperial College with Heat Resisting Alloys."

The upper temperature of the corrosion testing apparatus was limited to the maximum service temperature of the heat resisting alloy castings. Good alloys have a continuous maximum temperature of about 1000°C but for the relatively short duration of a run on the apparatus temperatures of 1070°C were reached without external evidence of deterioration. GOLDMAN used an alloy, CRONITE 55, containing 55% nickel, 18% chromium, 18% iron and other small additions. This was found to give good service up to 950°C, but at temperatures beyond this point deformation, especially of the thinner sections, became a problem, even under light loading (approx. 0.08 kg/mm^2). In later designs, such sections were successfully thickened. Attempts were made at welding the alloy after several runs at higher temperatures. As the electrode touched the metal surface, an area slightly larger than the rod tip fractured from the casting. This was due to intergranular sulphidic attack and the fracture was brittle. In one run at about 950°C, pure sodium sulphate spilled into this alloy and was probably molten on the metal surface for 30 min. The resulting slag was analysed by the Analytical Services Laboratory of Imperial College and found to contain 41.4% $FeSO_4$, 12.9% $Cr_2(SO_4)_3$, 8.5% $NiSO_4$ with the balance Na_2SO_4. Therefore the melt appeared to selectively leach out the iron.

Following the receipt of trade literature and samples, an iron, 30% chromium alloy (EV.300) was tested by placing a small piece in molten V_2O_5. After 24 hours this suffered no external effects. New apparatus parts were ordered in this alloy. However, difficulties in casting thin sections coupled with melting problems, (this alloy attacks mouldable refractories when molten) caused a 25% chromium, 12% nickel steel (EV.12) to be substituted. One set of these castings has now completed fifty or more runs and its conditio is very fair. This alloy has also been successfully electro-moulded.

The weak point in the original design was the screw threads on the joining web, upper main casing and lower main casing (see fig.14). These were always difficult to separate after a run, especially following a slag leak. The problem was lessened by use of dissimilar metals but the life of the web was still considerably less than that of the platinum lining. This factor is important because if the web failed the lining was spoiled and the approximate time to repair this was 3 months. "CORRONEL 230" is claimed to resist oil ash corrosion and high temperatures. Quotations for a disc 5½" in diameter and 1.5" thick in this material were requested from several firms. The estimates ranged from free to £1600! Unfortunately the firm offering their services free was unable to help for at least three months and eventually the problem was solved by casting several such discs in 65% nickel, 35% chromium in the foundry of the Metallurgy Dept., Royal School of Mines, Imperial College. These have given very good service especially since before each run, all threaded surfaces are smeared with a film of graphitized grease. In the proposed new design (fig.19) there are no screw threads in the hot zone.

All parts ordered from firms supplying the heat resisting alloys are subject to large delays. This is mainly because they are "one off" jobs which are disliked by foundrymen. Unfortunately castings are at present the only method of manufacturing large components. Heat resisting alloys in general suffer from brittleness due to high nickel content. This was often found out at cost when castings sealed together following a slag leak were subjected to extensive hammer treatment. To be fair, the conditions imposed upon the alloys here described were quite severe and performances were above those specified in literature.

One further form of heat resisting metal used was mild steel, superficially treated with an aluminium alloy. Mild steel has a good tensile strength at 1000°C (1.6 kg/mm^2) but poor oxidation resistance. The aluminium changes to alumina at high temperatures affording the oxidation resistance These articles have the great advantage that they may be made from cheap materials in the departmental workshop. The subsequent "PENETRAL" process cost about as much again as the original article, and was completed within two weeks. Slag splash cylinders manufactured this way have been very useful. The surface has flaked off in some places but only after several runs and a soaking by liquid slag.

APPENDIX 8.

SPECIFICATION OF RESIDUAL FUEL OIL SUPPLIED TO M.O.D(NAVY).

	Max.	Min.
Flash Point Pensky-Martin closed cup	-	66°C.
Fire Point (if Flash Point is less than 77°C)	-	93
Ash % by weight	0.10	-
Water % by volume	0.50	-
Sediment by extraction % by wt.	0.12	-
Sulphur % by wt.	3.5	-
Inorganic Acidity	NIL	-
Explosiveness	50	
Viscosity at 50°C		
Redwood 1 sec.	200	57
Centistokes	48.6	11.8
S.U.Seconds	225	65
Upper pour point °C	-10	-

APPENDIX 9.

THE APPROXIMATE SOLUBILITY OF PLATINUM IN Na_2SO_4, $NaVO_3$ AND V_2O_5.

Throughout the experimentation, platinum crucibles were used almost without exception. On occasions, recrystallised alumina crucibles were used without success. Some of the crucibles were platinum alloyed with 10 or 13% rhodium. Although these were stronger, they did not seem to resist corrosion any better. As each crucible was weighed before and after each experiment, it is possible to estimate the solubility or order of acceptance of the platinum in the melt. The range of solubility was usually 1-30 mg. platinum in 8-40 g. melt. The solubility in all melts was of the same order and the scatter of the results is considerable. Therefore, the incidental results for Na_2SO_4, $NaVO_3$ and V_2O_5 only are shown in fig.26. These graphs are self-explanatory.

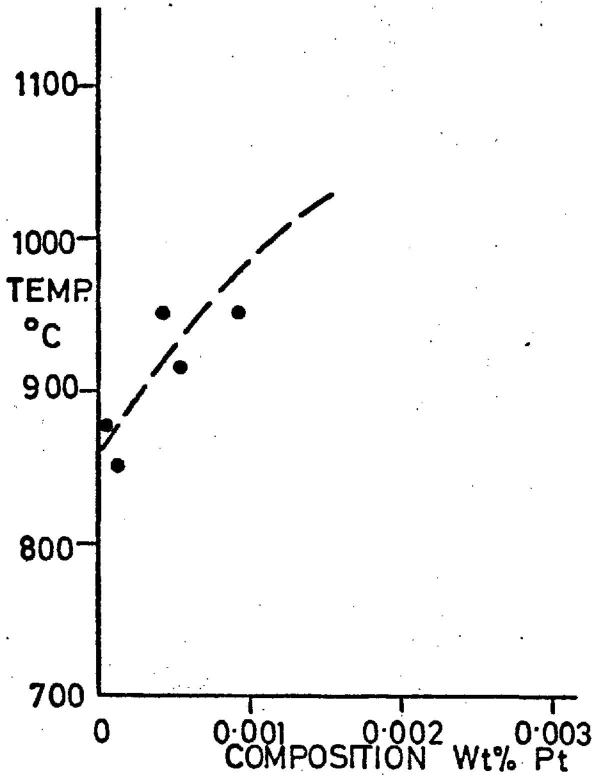


FIG. 28A Na_2SO_4

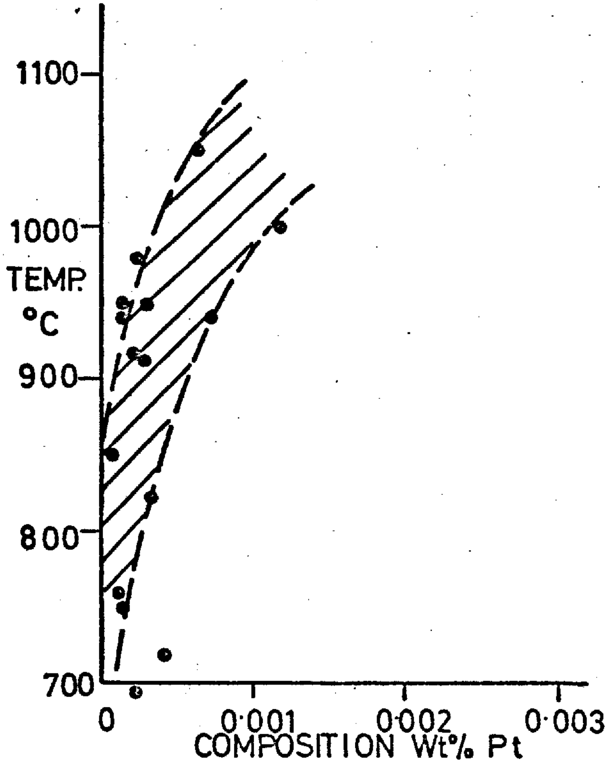


FIG. 28B $NaVO_3$

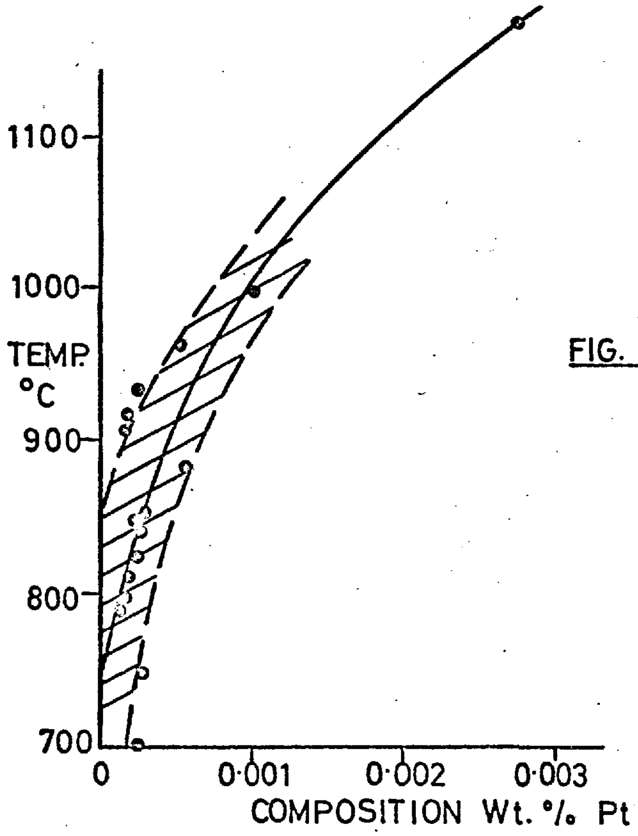


FIG. 28C V_2O_5

FIG. 28 APPROX. SOLUBILITIES OF PLATINUM IN Na_2SO_4, $NaVO_3$ & V_2O_5

REFERENCES.

1. Ph.D.Thesis. M.R.GOLDMAN 1963. Imperial College, London.
   "The Dissolution of Refractories in Vanadium Pentoxide/ Sodium Sulphate melts under controlled conditions".

2. "The Mechanism of Corrosion by Fuel Impurities"
   CEGB 1963. General Editiors JOHNSON & LITTLER
   Published by Butterworths.

   A. Introductory Lecture II. F.A.WILLIMAS & C.H.CAWLEY.
   B. Paper 18. D.J.A.DEAR.
   C. Paper 21. R.GREATOREX.
   D. Paper 19. VOORHIES, ADAMS, KIMBERLIN & JAHNIG.
   E. Introductory Lecture I. C.F.KEARTON.
   F. Paper 38. P.A.ALEXANDER & R.A.MARSDEN.
   G. Paper 22. W.D.NILES & C.W.SIEGMUND.
   H. Discussion by P.EISENKLAM to Paper 15. J.J.McFARLANE.
   J. Paper 14. N.H.SMALL, H.STRAWSON & A.LEWIS.

3. "Literature Survey primarily covering fire-side deposits and corrosion associated with boiler and superheater tubes in oil-fired naval steam raising installations with some references also to similar problems in land-based installations and gas turbines".
   C.J.A.EDWARDS. BP. Research Centre, Sunbury.

4. A Review of available information on corrosion and deposits in coal and oil fired boilers and gas turbines" by Battelle Memorial Institute. Published jointly by Pergamon Press and the American Society of Mechanical Engineers.

5. A.T.BOWDEN, P.DRAPER & H.ROWLING.
   "The Problem of Fuel-Oil Ash Deposition in Open Cycle Gas Turbines"
   Proc.Inst.Mech.Engrs., (A), 1953, 167, 291.

6. D.H.SHAW.
   "Rare Elements as a Key to the Past"
   New Scientist, No.225, 9 Mar., 1961, p.618.

7. R.ROBINSON.
   "The Origins of Petroleum".
   Catalyst 6. Spring 1961, p.41.

8. F.H.GARNER, S.J.GREEN, F.D.HARPER & R.E.PEGG.
   "The Metallic Elements in Residual Fuel Oils"
   J.Inst.Petroleum, 1953, 39, 278.

9. D.A.SKINNER.
   "Chemical State of Vanadium in Santa Maria Valley Crude Oil"
   Ind.Eng.Chem., 1952, 44, 1159.

10. W.McCLIMONT.
"Fuel Problems in Merchant Ships".
J.Inst.Fuel, 1959, 32, 275.

11. C.J.GRAY & W.KILLNER.
"Sea Water Contamination of Boiler Fuel Oil and Its Effect
Trans.Inst.Marine Engrs., 1948, LX No.2, p.43.

12. C.H.SHIELDS Jnr.
"The Filtration of No.6 Fuel Oil to Remove Undesirable Trace Metals".
ASME Paper No.55-A-121. Sept. 1955.

13. B.O.BUCKLAND & D.G.SANDERS.
"Modified Residual Fuel for Gas Turbines"
Trans. of ASME 1955, 77, 1199.

14. "Proceedings of the Australian Symposium on the Inorganic Constituents of Fuel"
University of Melbourne, May 1964.
Summarised J.Inst.Fuel, 1965, 38, 171.

A. Paper 14. C.H.HUMBY & W.TIPLER.
B. Paper 1. M.E.HOW, P.J.STREET & P.J.JACKSON.

15. PORTER & WHITE.
"Modern Petroleum Technology" pp.365-376.
Inst. of Petroleum, London, 1962.

16. T.D.BROWN.
"The Deposition of Sodium Sulphate from Combustion Gases"
J.Inst.Fuel, 1965, 39, 379.

17. H.E.CROSSLEY.
"External Fouling and Corrosion of Boiler Plant"
J.Inst.Fuel, 1967, XL, 342.

18. A.J.POLLARD.
"A Survey of the Chemistry of High Vanadium Oil-Ash Deposits in Naval Boilers".
U.S.Naval Research Labs. Report No.5852, 19 Nov. 1962, AD 291209.

19. T.S.BUSBY.
"A Study of the Effect of Fuel-Oil ASh on Glass Tank Refractories"
Glass Technology, 1963, 4, No.1, 18.

20. W.McCLIMONT, H.M.RICHARDSON & B.TAYLOR.
"Boiler Refractories Operating Temperatures and Recent Developments in Construction".
Trans.Inst. Marine Engrs., 1959, 71, 237.

21. M.C.K.JONES & R.L.HARDY.
"Petroleum Ash Components and their Effect on Refractories"
Ind. Eng. Chem., Nov. 1952, 44, 2615.

22. S.H.FREDERICK & T.F.EDEN.
"Corrosion Aspects of the Vanadium Problem in Gas Turbines"
Corrosion, 1955, 11, 19t - 33t.

23. B.TAYLOR & H.BOOTH.
"Service Performance of Boiler Brickwork - the Causes and Extent of Wastage".
Trans.Inst.Marine Engrs., 1953, 65, 165.

24. J.A.C.SAMMS & W.D.SMITH.
"High Temperature Gas Side Corrosion in Water-Tube Boilers"
BCURA Monthly Bulletin Vol.XXV; No.12, Nov/Dec.1961, part 1, review No.209.

25. "Houseman-Vaps. Combustion Control Process"
Technical Bulletin No.701V The Priory, Burnham, Bucks.

26. J.A.C.SAMMS & W.D.SMITH.
"Further Experiences of High Temperature Gas Side Corrosion in Water-tube Boilers"
BCURA Monthly Bulletin, Vol.XXVI, No.10, Oct 1962, Review No.216.

27. W.HANSEN.
"A Successful Additive against High Temperature Corrosion by Residual Fuel Oil Ash".
J.Inst.Fuel, Aug.1967, XL, p.348.

28. J.E.C.TOPPS.
"An Experimental Study of the Evaporation and Combustion of Falling Droplets"
J.Inst.Petroleum, 1951, 37, 535.

29. G.L.SWALES.
"The Evaluation of Nearly Developed Nickel-Chromium Alloys of High Chromium Content to Combat Fuel Ash Corrosion Problems"
Australian Corrosion Engineering, Vol.7, No.9, Sept 1963.

30. N.W.HINCHLIFFE.
"Boiler Plant Refractories"
British Power Engineering, July 1960, 1, p.77.

31. E.S.NICHOLS, J.A.BURGER & D.K.HANINK.
"Comparative Evaluation of Protective Coatings for High Temperature Alloys"
Soc.Automotive Engrs./ASME, Air Transport and Space Heating, New York, Apr. 1964, paper 843E.

32. G.CANNERI.
"Vanadic Vanadates"
Gazetta Chimica Italiana, 1928, 58, 6.

33. W.PRANDTL.
Ber.Dtsch.Chem.Ges., 1905, 38, 657.

34. H.FLOOD & H.SØRUM.
"Om Vanadylvanadat, en ny type elektriske halvlendere"
Tidsskr. Kemi. Berev., 1943, 5, 55.

35. Thornton Research Centre, Shell Research Lts.
A. Report M.185. D.G.BALDWIN & C.E.DAVIS.
B. Report M.186 D.G.BALDWIN.
C. Report M.198. P.T.DAVIES et al.

36. T.D.BROWN & J.RITCHIE.
"Fuel Oil Ash Deposition in Naval Boilers"
Paper 7 at the Symposium on Combustion in Marine Boilers held jointly by Inst.Marine Engrs. and Inst of Fuel
10 Jan, 1968.

37. W.R.FOSTER, M.H.LEIPOLD & T.S.SHEVLIN.
"A Simple Phase Equilibrium Approach to the Problem of Oil Ash Corrosion"
Corrosion, 1956, 12, 539t.

38. N.D.PHILLIPS & C.L.WAGONER.
"Use of Differential Thermal Analysis in Explaining Minimum Temperature Limits of Oil Ash Corrosion"
Corrosion, 1961, 17, No.8, 102.

39. H.T.LOGAN.
"Corrosion of Type 310 Stainless Steel by Synthetic Fuel Oil Ash"
Corrosion, 1959, 15, No.8, 443t.

40. V.D.LONG.
"Some Aspects of the Fuel Technology of Glassworking"
Glass Technology, 1965, 6, 124.

41. Professor A.G.GAYDON - Private Communication.

42. T.P.BROWELL & G.HETHERINGTON.
"Vitreous Silica for the Scientific Glassblower"
J.Brit.Soc.Scientific Glassblowers, Vol.3, No.1.

43. L.BAKER.
"Design of Marine Water-Tube Boilers"
C.Griffin and Co., London, 1950.

44. S.ARAMAKI & R.ROY.

J.Amer.Ceram.Soc., 1959, 42, 644.

45. G.M.GAD & L.R.BARRETT.
"The High Temperature Breakdown of Mullite and other Alumino-Silicates in the Presence of Alkalis"
Trans.Brit.Ceram.Soc., 1950, 49, 471-491.

46. K.FITCHETT & H.M.RICHARDSON.
"The Properties of Magnesite Mixer Blocks and their Reaction with Mixer Slags"
Trans.Brit.Ceram.Soc., 1961, 60, 627.

47. J.F.HYSLOP.
"A Test for Assessing the Slag Attack of Refractories"
Trans.Brit.Ceramic Soc., 1961, 60, 212.

48. M.SAFDAR.
"Some Aspects of the Dissolution of Refracory Crystals and Glasses in Ionic Melts"
Ph.D.Thesis, University of London, 1961.

49. W.J.MOORE.
"Physical Chemistry"
Longmans, 3rd Ed., 1957.

50. W.JOST.
"Diffusion in Solids, Liquids and Gases"
Academic Press, New York, 1952.

51. L.R.FAULKNER.
"Slagging Action of Fuel-Oil Ash"
Bull.Amer.Ceram.Soc., 1934, 13, [2], 45-46.

52. W.HUGILL & A.T.GREEN.
"The Action of Slags on Refractory Materials. Part 1. The application of certain tests to the study of the action of blast-furnace slags on refractory materials"
First Report on Refractory Materials. Iron and Steel Institute Special Report No.26, 1939, p.295.

53. G.R.RIGBY & R.HUTTON.
"Action of Alkali and Alkali-Vanadium Oxide Slags on Alumina-Silica Refracories"
J.Amer.Ceram.Soc., 1962, 45, 68.

54. B.W.KING & L.L.SUBER.
"Some Properties of the Oxides of Vanadium and their Compounds"
J.Amer.Ceram.Soc., 1955, 38, 306-11.

55. G.LUCAS, M.WEDDLE & A.PREECE.
"The Liquidus of Metal-Oxide/V_2O_5 Systems".
J.Iron and Steel Inst., 1955, 179, 342-7.

56. J.R.McCLAREN & H.M.RICHARDSON.
"The Action of Vanadium Pentoxide on Alumino-Silicate Refractories"
Trans.Brit.Ceramic Soc., 1959, 58, 188.

57. N.C.GRAVETTE, D.BARHAM & L.R.BARRETT.
"An Investigation of the System V_2O_5-SiO_2"
Trans.Brit.Ceramic Soc., 1966, 65, 199.

58. D.BARHAM.
"An Investigation of the System V_2O_5-Al_2O_3.
Trans.Brit.Ceramic. Soc., 1965, <u>64</u>, 371.

59. J.LEVEQUE.
"De Chaleur par Convection"
Ann. Mines (Series 12) 1928, pp.13,201,305,381.

60. V.G.LEVICH.
"Physicochemical Hydrodynamics"
Prentice Hall, 1962.

61. T.B.DREW.
"Mathematical Attacks on Forced Convection Problems - A Review"
J.Amer.Inst.Chem.Engrs., 1931, <u>26</u>, 26.

62. F.A.FARUQI.
Ph.D.Thesis, University of London, 1960.

63. A.E.S.WHITE.
"The Use of Carbon in High Temperature Laboratory Furnaces"

64. J.D.McCLELLAND.
"Kinetics of Hot Pressing".
Powder Metallurgy - Proceedings of International Conf. New York 1960, W.LESEYNSKI (ed) Interscience Publishers 1961, p.157.

65. G.E.MANGSEN, W.A.LAMBERTSON & B.BEST.
"Hot Pressing of Aluminium Oxide"
J.Amer.Ceram.Soc., 1960, <u>43</u>, 55.

66. A.C.D.CHAKLADER, T.G.CARRUTHERS & A.L.ROBERTS.
"The Apparent Viscosity of Refractory Materials at High Temperatures"
6th International Ceramics Congress, Wiesbaden, 1958.

67. A.G.THOMAS.
"Physico-Chemical Aspects of the Corrosion of Refractories by Slags"
Ph.D.Thesis. University of London, 1955.