

PART II

SEA-WATER CONTAMINATION OF BOILER FUEL OIL

by

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PART II—ITS EFFECTS

The effects of sea-water contamination of fuel oil may be numerous, the most important of which are :—

- (i) Loss of thermal efficiency.
- (ii) Deterioration of furnace refractories.
- (iii) The formation of bonded deposits in gas passages.

The first of these has a very obvious effect—the effective range of a ship is reduced by the presence of water in the fuel oil, 10 per cent of water present means 10 per cent less fuel available. It also means a waste of oil in steaming due to some of the available heat units being used to bring the water in the oil to the temperature of the gases.

The deterioration of furnace refractories occasioned by the presence of sea-water is of great importance and has not yet received the consideration which it deserves.

The formation of bonded deposits in the gas passages of the tube banks is also of great importance. Such deposits may not become evident until they have accumulated sufficiently to impede the passage of the furnace gases through the tube banks, and at least one case is known where a reduction of the power of the boiler had to be accepted owing to inability to burn the requisite amount of fuel with the fan power available.

Deterioration of Furnace Refractories

In recent years the occurrence of the failure of furnace refractories in the boilers of H.M. ships due to deterioration by slagging has become prominent. Various suggestions to account for this have been put forward, such as the use of a fuel oil containing vanadium compounds, long periods of high-power operational steaming, extension of periods between refits, etc.

The cases which have been 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.

From this it is reasonable to assume that the failure is not due to the type of fuel oil now in common use in so far as its constituents are concerned, but that it is caused by the introduction into the furnace of some matter capable of reacting with the firebricks.

Sodium chloride would have such an effect and is a most likely substance to be introduced owing to the causes already outlined.

Examinations of furnaces where slagging has occurred show the brickwork to be in various stages of deterioration. Firebricks taken from a furnace for

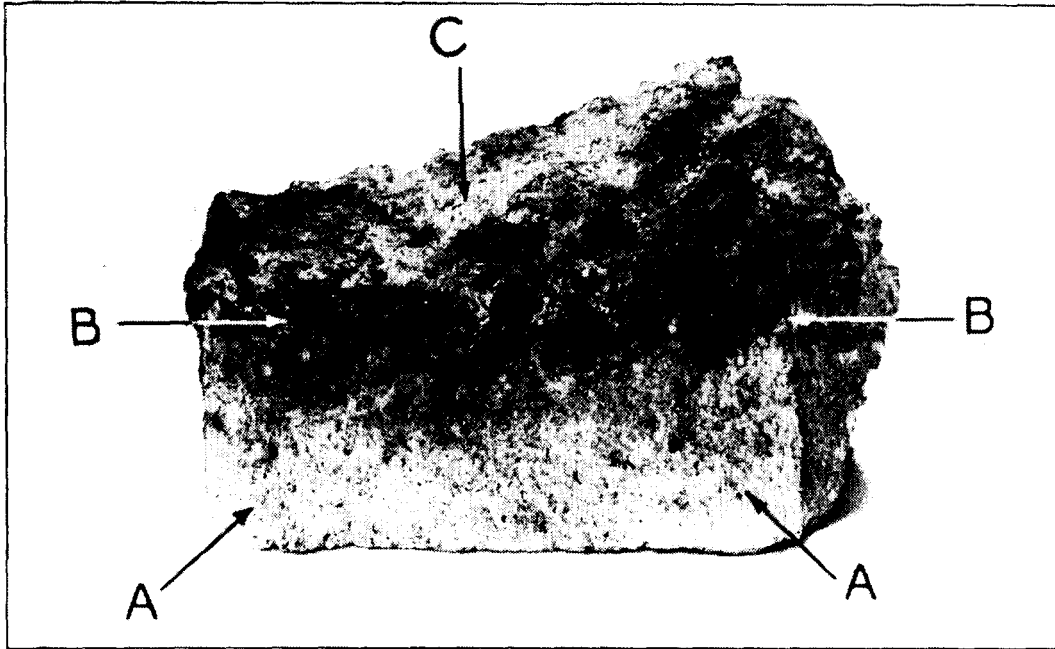


FIG. 1.--A. UNAFFECTED BRICK. B. PARTLY AFFECTED BRICK. C. SLAG OR INCRUSTATION ON THE SURFACE OF THE BRICK

examination during the early stages of slagging have shown dark incrustation on the surface of the bricks. Underneath this incrustation the bricks are found to be discoloured by some matter which has penetrated the brick, the discoloration fades off towards the surface of the brick remote from the furnace.

In cases where the slagging has reached an advanced stage the thickness of the firebricks, particularly on the side and back walls of the furnace, have been found to be reduced to less than half their original thickness. In such cases the surface of the brickwork on the walls is coated with dark glass-like slag while the floor is covered with a similar substance, which in some cases is of the order of one inch thick. Wherever the slagging has reached an advanced stage, that formed on the brickwork of the furnace walls will have run down on to the floor and has been observed to flow with the motion of the ship, as a mass of molten material.

In investigating this problem three cases of firebrick deterioration reported from the Fleet have been given special attention.

Cruiser "X"

In this cruiser the brickwork had not shown any undue signs of slagging after some 5,000 hours steaming, but after normal repairs to the brickwork subsequent steaming caused it to deteriorate very rapidly by heavy slagging. This failure necessitated the renewal of all the brickwork. The Engineer Officer stated: "The condition of brickwork seems to have worsened very suddenly during the period when oil fuel received during the latter part of August was being burnt."

A sample of fuel oil received from this ship was found to contain 11.6 per cent of sea-water. No special mention was made of any difficulty being experienced in burning this water-contaminated oil, from which it was inferred that the presence of the sea-water in the fuel oil was unknown to the ship's officers.

Although there is no direct evidence, it is probable that the oil was not con-

taminated to this extent when supplied to the ship but came into contact with sea-water in one or more of the ship's tanks where emulsification took place.

Cruiser "Y"

In this cruiser "Y" the slagging of the brickwork and subsequent failure was also comparatively sudden. Specimens of the bricks were received, and an average brick was selected from which samples taken at the positions shown in Fig. 1 were chemically examined and the results are given in Table I.

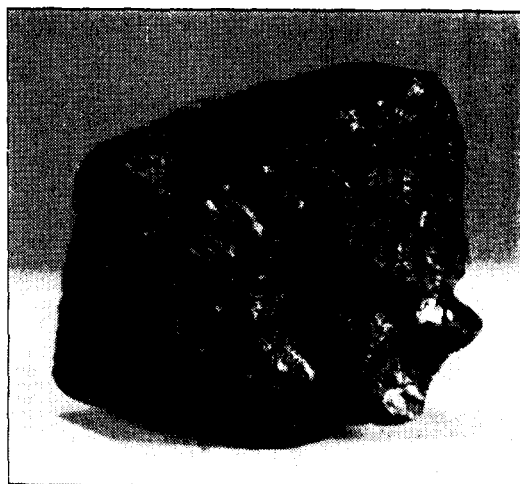


FIG. 2.—A SAMPLE OF THE GLASS-LIKE SLAG FROM THE FURNACE FLOOR OF CRUISER "Z"

TABLE I

	Cruiser "Y"			Cruiser "Z"
	Sample "A" Unaffected brick	Sample "B" Partly affected brick	Sample "C" Slag or incrustation	Dark glass-like slag
Loss on drying at 110 deg C. per cent	0.75	0.21	0.69	0.10
Further loss on ignition	1.25	0.15	0.05	0.30
Results calculated on dried material				
(1) Soluble in water per cent	1.30	1.47	11.65	0.50
(2) Insoluble in water but soluble in HCl	1.50	2.53	62.90	42.40
(3) Insoluble in water and in HCl ..	97.20	96.00	25.45	57.10
Analysis of matter soluble in water				
Silica calculated as SiO ₂ ... per cent	1.30	1.47	< 0.01	0.06
Iron Fe ₂ O ₃			< 0.01	0.02
Aluminium Al ₂ O ₃			< 0.01	0.13
Sulphates SO ₃			6.25	0.08
Alkalis Na ₂ O			5.40	0.21
Analysis of matter insoluble in water but soluble in HCl				
Silica calculated as SiO ₂ ... per cent	1.50	2.53	2.60	1.07
Iron Fe ₂ O ₃			48.24	2.20
Aluminium Al ₂ O ₃			3.07	25.01
Titanium TiO ₂			0.35	1.07
Vanadium V ₂ O ₅			0.26	1.79
Calcium CaO			1.20	1.00
Magnesium MgO			1.20	0.20
Sodium Na ₂ O			3.34	9.15
Potassium K ₂ O			0.63	0.73
Sulphates SO ₃			1.50	0.05
Analysis of matter insoluble in water and in HCl				
Loss on ignition per cent	1.15	0.15	0.05	0.30
Silica calculated as SiO ₂	50.71	47.38	15.20	47.13
Iron Fe ₂ O ₃	3.00	3.20	1.92	6.60
Aluminium Al ₂ O ₃	41.24	43.76	8.33	2.06
Titanium TiO ₂	1.20	1.10	0.25	0.12
Vanadium V ₂ O ₅	Nil	Nil	0.10	0.89

Cruiser " Z "

In this case the brickwork in general showed heavy slagging and the floor of the furnace was evenly covered with a dark glass-like slag something over one inch in thickness, the smooth surface gave ample proof that the whole mass had been molten. Fig. 2 shows a sample of the slag and the results of the chemical examination are given in Table 1.

Description of Samples of Brick from Cruiser " Y "

The bricks in general were coated on the surface exposed to the heat with a slate coloured slag or incrustation. Underneath this slag was a greyish honeycombed layer, while the intermediate portion of the bricks had a brownish discolouration which was most marked near the heated surface. The portion of the bricks remote from the furnace was normal in appearance.

By visual examination it would appear that a fluxing material had come into contact with the brick surface which, at high temperatures, reacted to form a fusible mixture of slag or incrustation. This slag or incrustation, when molten, appears to have penetrated into the firebricks causing the discoloration.

Consideration of the Results of Analysis

Sample " A " has the composition of a normal firebrick and has not been affected.

Sample " B " shows an increase in the amount of sodium compounds present.

Sample " C " shows that the amounts of silica and alumina have decreased and the amounts of compounds of iron, sodium and sulphur have increased considerably and a small amount of vanadium compounds is also present.

Samples " A " and " B " are practically unaffected by treatment with hydrochloric acid whilst sample " C " is decomposed by the treatment, which indicates that the surface of the firebrick nearest the furnace has undergone a complete change.

The presence of a relatively high percentage of sodium compounds suggests that sea-water has been introduced into the furnace at some time. The sodium chloride would, at high temperatures, combine with the firebrick forming a mixture of fusible aluminates and silicates on the face of the firebricks. Sample " C " consists of such a mixture. This material, when molten, would penetrate into the firebrick which would account for the presence of the sodium compounds found in sample " B " and the discoloration of the refractory material.

The amount of vanadium compounds is relatively small and would, of course, arise from the fuel oil burnt. The presence of only 0.3 per cent of vanadium, calculated as vanadium pentoxide, suggests that the slagging has occurred over a relatively short period.

The amount of iron compounds in this sample is considerably greater than is normally found in slags of this type and it is difficult to see how such an amount can have got into the furnace other than by being introduced with the fuel oil as finely divided iron rust.

The report on the sample of fuel oil used by the ship showed the water content to be 0.9 per cent but did not show whether there was any iron rust in the oil. The 0.9 per cent of water present, even if it had consisted entirely of sea-water, is not considered to be sufficient to have caused the amount of slagging which had taken place in such a short time. It would appear therefore that the slagging was caused by a fuel oil used previously and containing a much higher percentage of sea-water and not by that in use when the sample

was taken. If this assumption is correct the iron present could be accounted for by rusting of the tanks and pipes by the sea-water in the water-contaminated fuel.

Chemical Reaction of Slag Formation

The acid character of fireclay bricks is not appreciable unless the bricks are at a high temperature, but it is then found that they combine with alkalis (soda, potash, etc.), or salts (chlorides, sulphates and carbonates) at a rate which depends upon their porosity. At high temperatures the silica and alumina of the firebrick turn out the acid radical from various salts, forming a new salt (alumino-silicate or silicate), and set the hydrochloric, sulphuric, or any other acid free, usually in the form of a gas. The alumina and silica of which the firebrick is composed, will, therefore, at high temperatures, readily decompose any sodium chloride introduced into the furnace as sea-water, producing silicates and/or aluminates. The temperature of formation of these may be lower than the fusion temperature of the components. Various stages may, therefore, occur—the reaction stage, when combination of the firebrick and salt is taking place, forming a semi-solid mass, to the stage when the mass is molten and flows. Firebricks are of a coarse-grained texture and, therefore, have a high degree of porosity, the molten slag penetrates the bricks, carrying with it any excess of salt which may be present, where further reaction takes place affecting the chemical composition of the substance of the brick, which results in changes of the coefficient of expansion and contraction of the various constituents, so that the different parts of the brick expand and shrink differently and soon begin to disintegrate. The molten slag also flows down the walls and may completely cover the brick floor of the furnace.

The presence of certain substances in the molten magma may promote crystallisation, the presence of a vanadium compound for instance, derived from the vanadium content of the fuel oil, promotes the separation of crystals when mixtures of alkali, silica and alumina are fused together. This may cause the slag to crack along the lines of the crystals.

The presence of iron compounds in a furnace may result in the formation of iron silicates which when molten readily penetrate refractory materials.

Description of Laboratory Tests

Laboratory tests were made to show the formation of slag under controlled conditions. Firebricks were prepared by chipping out a cavity approximately $1\frac{1}{2}$ in dia. and $1\frac{1}{2}$ in deep, so as to hold any added matter while being subjected to heat from a blowpipe, using coal gas and oxygen. Tests were made using :—

- (i) Salts from evaporated sea-water.
- (ii) Vanadyl sulphate.
- (iii) Salts from evaporated sea-water plus iron rust.
- (iv) Salts from evaporated sea-water plus vanadyl sulphate.

In the tests (i), (iii) and (iv) when the mass became molten, evidence of the chemical action with the firebrick was given by hot spots appearing in the melt as a result of the reaction taking place.

After heating for about 30 minutes the melt became very fluid and, on cooling, a dark hard glass-like slag remained. On breaking these test bricks it was found that penetration had taken place showing darkening of the firebrick, the darkening being more intense at the surface at which the heat was applied. In the cavity pitting was evident where the brick had suffered attack.

In the test (ii) the vanadium oxide formed by the heating had melted and



FIG. 3.—SPECIMEN OF BONDED DEPOSIT

penetrated only slightly into the brick but there no slag was formed and the brick did not show evidence of attack.

The brick used in test (ii) was then divided, sodium chloride was added to one half of the cavity, and further heat was applied to this portion. The firebrick was found to react with the sodium chloride resulting in the characteristic honeycombing of the brick and the formation of the usual glass-like slag. On breaking this portion of the brick deep penetration was found to have occurred.

Conclusions

That all the evidence to date indicates that the slagging of furnace brickwork in the boilers of H.M. ships is primarily caused by sodium chloride reacting with the silica and alumina of the firebrick at high temperatures.

That the sodium chloride is introduced into the furnace in the form of sea-water emulsified with the fuel oil.

That a higher grade quality of firebricks made from material found in this country, although likely to increase the resistance to normal wear and tear, is not likely to offer greater resistance to the action of sea-water under high temperature conditions.

That cases of brick failures due to excessive slagging are likely to continue unless the entry of sea-water into the furnace is eliminated.

The Formation of Bonded Deposits in the Gas Passages

The formation of deposits in the gas passages through the tube banks and the superheaters of the boilers of H.M. ships is a problem which came to light during the war period; cases were found where the deposit had collected to such an extent that the gas passages were very seriously choked. The deposits were found to be caked or bonded together by some binding material to form a solid mass and to render their removal by mechanical means, such as saws, extremely difficult if not impossible.

Although, in general, the trouble was not discovered in H.M. ships until late in the war period it had previously been experienced in the case of coal-fired boilers. An interesting paper was read by J. R. Rylands and J. R. Jenkinson at a joint meeting of the Institutions of Mechanical and Electrical Engineers, held in London on 4th November, 1943, on "Bonded Deposits on Economiser Heating Surfaces."

Rylands and Jenkinson showed that the deposits with which they were dealing (*i.e.*, those found on the economisers of coal-fired boilers) consisted of the materials found in the ash of coal in combination with the sulphur compounds resulting from the burning of coal, the binding agent being aluminium sulphate.

The bonded deposits found up to date in H.M. ships not only differ in composition from those found in coal-fired boilers and dealt with by Rylands and Jenkinson, but they differ in a very important respect. Sodium sulphate, the compound which constitutes the major portion of these deposits, is not a constituent of the fuel oil used. The temperature conditions at the points affected in the case of H.M. ships are too high to allow the process of formation referred to by Rylands and Jenkinson to operate.

Samples of bonded deposits obtained from various ships were chemically examined and were all found to be similar in composition. Fig. 3 shows a specimen of bonded deposit taken from the tubes of a superheater in one of H.M. ships, and Table II gives the results of analysis of two typical samples.

TABLE II

Loss on drying at 212 deg F.	Per cent 0.17	Per cent 0.22
<i>Analysis of material dried at 212 deg F.</i>		
Soluble in water	Per cent 70.70	Per cent 74.00
Insoluble in water	29.30	26.00
<i>Analysis of matter soluble in water</i>		
Silica calculated as SiO_2	Per cent below 0.10	Per cent below 0.10
Iron Fe_2O_3 0.10	.. 0.10
Aluminium Al_2O_3 0.10	.. 0.10
Calcium CaO	1.50	2.57
Magnesium MgO	1.00	1.00
Nickel NiO	0.35	below 0.10
Vanadium V_2O_5	below 0.10	.. 0.10
Sulphate SO_3	35.70	42.25
Chlorides	Trace	Trace
Sodium Na_2O	22.04	23.35
Potassium K_2O	3.20	1.83
<i>Analysis of matter insoluble in water but soluble in hydrochloric acid</i>		
Iron calculated as Fe_2O_3	Per cent 4.94	Per cent 4.27
Aluminium Al_2O_3	below 0.10	below 0.10
Calcium CaO 0.10	0.30
Nickel NiO	1.60	5.71
Vanadium V_2O_5	14.80	5.80

The matter insoluble in water and in hydrochloric acid consisted of compounds of silica, iron, vanadium and nickel.

This analysis shows up three important points, namely :—

- (i) 70 per cent of the deposit consists of material which is soluble in water.
- (ii) The soluble in water portion consists mainly of sodium sulphate.
- (iii) There are no compounds of iron present which are soluble in water, *i.e.*, iron sulphate.

The absence of water soluble iron compounds indicates that the iron is present in the form of oxide and not sulphate.

In view of the high percentage of matter soluble in water it is to be expected that these deposits can be removed by water treatment and this has been found

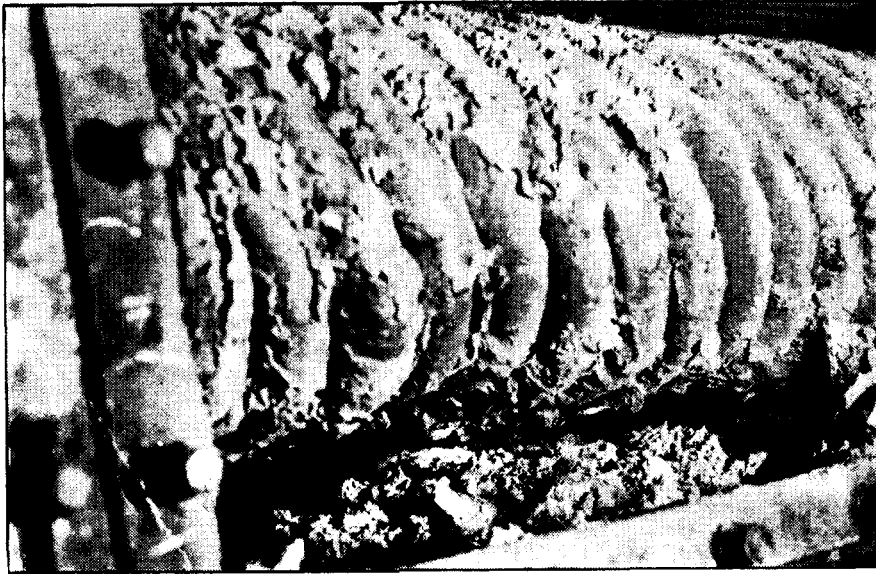


FIG. 4

in practice to be the case. In an aircraft carrier these deposits, which had seriously choked the gas passages through the tube banks, were removed by means of water lancing and saws, except for the matter insoluble in water.

After lighting up the boiler the insoluble matter dried off and was easily removed by soot blower action; this indicates that without the material which is soluble in water the remainder of the deposit does not bond or adhere to the tubes.

This was confirmed in the laboratory where it was found that the bonded deposits readily fuse and melt when heated in a muffle furnace at light red heat, but when the sodium salts are removed by washing, the remainder, *i.e.*, the matter insoluble in water, when maintained at light red heat does not fuse or melt but remains as an amorphous powder.

Fig. 4 shows the superheater tubes of an aircraft carrier choked by bonded deposits, while Fig. 5 shows the same tubes after water washing.

It has, therefore, been shown both on board ship and in the laboratory that the sodium salts are the binding agents.

The gas temperatures in an Admiralty three-drum boiler steaming at high powers are of the order of 2,900 deg F. in the furnace, 2,200 deg F. at entry to the superheater and 1,600 deg F. at exit from the superheater. As the melting point of sodium sulphate is approximately 1,600 deg F. it will be seen that particles of sodium sulphate held in the gas stream will be in the molten state throughout the major part of their passage through the tube banks. These molten particles will, on making contact with the metal surfaces of the tubes, be cooled sufficiently to solidify the portion in contact with the tube whilst the surface exposed to the temperature of the hot gases will be molten, thus offering the necessary sticky surface to which further material will adhere and bond. Of the compounds found in the bonded deposits sodium sulphate is the only one which has the properties necessary for cementing the material together and, therefore, for forming these bonded deposits.

Consideration of the analyses of the ash of fuel oils given in Table III and the analyses of bonded deposits given in Table II offers some interesting evidence regarding the source of the sodium sulphate in the deposits.

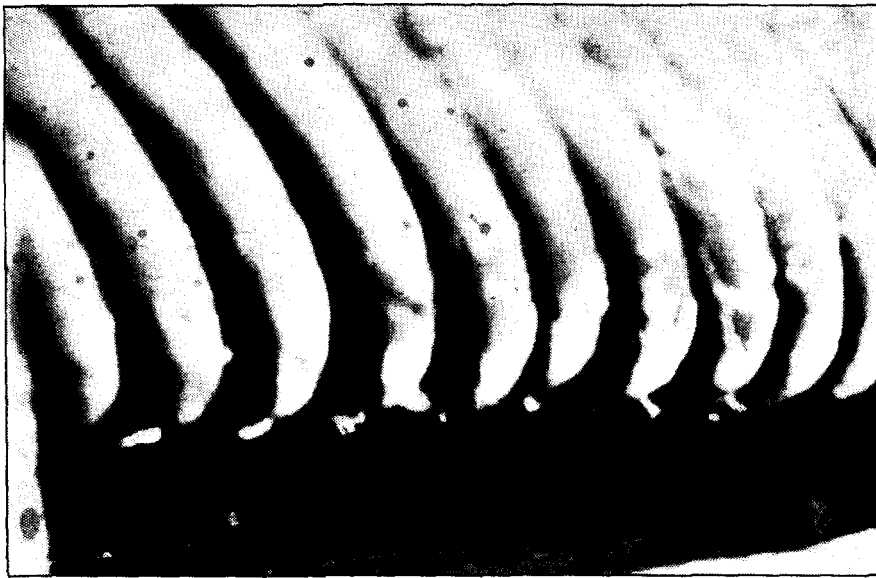


FIG. 5

TABLE III

Crude Oil (filtered)			
	<i>A</i>	<i>B</i>	<i>C</i>
Ash Content per cent	0.005	0.003	0.006
Analysis of ash calculated as percentage of ash :			
SiO ₂	52.8	18.1	12.1
Fe ₂ O ₃ , Al ₂ O ₃ , TiO ₂	13.1	37.1	18.1
CaO	6.1	8.7	12.7
MgO	9.1	3.8	0.2
V ₂ O ₅	14.0	24.9	38.5
NiO	1.4	5.3	10.7
SO ₃	2.6	1.0	7.0

During the processing of the crude oil in the refinery the lighter fractions are distilled off and the fuel oil, which is the residue and amounts to approximately 45 per cent, will, therefore, have an ash content of twice the amount shown in Table III plus any material picked up during the processing, of which the bulk will most probably be iron.

The composition of the ash of the fuel oils given in Table III shows that there are no sodium compounds present, although the composition of the ash of fuel oils from different sources may vary somewhat ; where traces of sodium compounds are found the amount is so small as to be negligible in so far as it could affect the building up of these bonded deposits. It therefore becomes necessary to explain the presence of the sodium compounds in the bonded deposits, and the only explanation which can be found is that they are introduced with the fuel oil as sea-water contamination.

It is a well-established fact that the present day fuel oil readily forms a stable emulsion with sea-water and there is evidence to show that much of the fuel oil burnt in H.M. ships during the war period was contaminated with sea-water, the main source or causes of this contamination, as already stated, being leaking oil tanks, ballasting, displacement of oil by sea-water, and the supply of wet oil from tankers.

Having shown how the sodium compounds become associated with the fuel oil with which they are introduced into the furnace, it only remains to explain the conversion of the sodium chloride, the main salt of sea-water, into sodium sulphate.

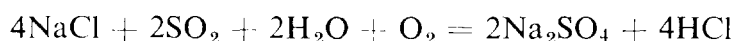
At this stage it may be desirable to refer to views which have been expressed by some investigators and which the authors consider to be unfounded. It has been suggested that the conversion of the sulphur dioxide in the furnace gases to sulphur trioxide is an essential feature of the subsequent formation of sodium sulphate. It has also been suggested that a catalyst is necessary to cause this conversion and that the vanadium compounds present in the ash of the fuel oil act as the catalyst. Supporters of this theory seem to consider the presence of vanadium compounds to be a pre-requisite condition to the formation of sodium sulphate, and suggest that without this catalytic action of the vanadium compounds the sodium sulphate would not form.

We would point out that the oxidation of sulphur dioxide to sulphur trioxide does not require a catalyst under the conditions which obtain in the furnace. If, however, a catalyst were required to accomplish the oxidation, oxide of iron is in plentiful supply in the furnace and its action as a catalyst is well known. There would, therefore, seem to be no evidence to support the contention that the presence of vanadium compounds is an essential or even a contributory feature in the formation of these bonded deposits.

In the gases resulting from the burning of fuel oil, sulphur dioxide, water vapour and oxygen are present, for it is unfortunately necessary to steam with some degree of excess air to ensure a smokeless funnel. These, together with the sodium chloride from the sea-water, supply everything necessary for the formation of sodium sulphate. The conversion is a straightforward chemical reaction and is not dependent upon the complicated stages necessary in the formation of bonded deposits on the economiser heating surfaces of land boilers, which has been explained in detail by Rylands and Jenkinson, nor is the presence of a catalyst necessary.

Although sulphur dioxide alone does not itself decompose sodium chloride yet, if mixed with air and steam, sulphur dioxide will completely convert sodium chloride into the sulphate.

The reaction is :—



Having provided sufficient evidence to support the theory that bonded deposits found in the boilers of H.M. ships, are due to sea-water contamination of the fuel oil, it now remains to suggest the mode of formation of these deposits.

When fuel oil contaminated with sea-water is burnt in the furnace the water is vaporized and the solids which were in solution now exist as dust suspended in the gas stream, together with the natural ash of the fuel oil. The size of the droplets of fuel oil sprayed into the furnace are themselves small and it, therefore, follows that any sea-water which enters the furnace with the fuel oil as an emulsion must, when vaporized, leave its salts in minute particles. In this state they will readily react with the gases surrounding them, the sodium chloride being converted to sodium sulphate, in accordance with the reaction referred to. The temperature of the gases in which they are held in suspension is much above the melting point of sodium sulphate and, therefore, the particles will be in the molten state. As minute molten particles they will be carried in the gas stream and, as they meet, they will join together and so increase in size, in the same way as minute particles of water in the clouds join together to make raindrops.

Whilst the droplets remain minute they will be held by the gas stream and most of them will pass between the fire-row tubes. As the gas stream passes the tubes a turbulence is set up which results in the droplets colliding, causing them to unite still further.

When larger drops have formed they will less readily be carried by the gas stream and their progress will more readily be interrupted by obstructions, hence the impingement of the molten drops on the boiler tubes.

The generator tubes and those of the superheater are well below the melting point of sodium sulphate, and wherever these molten particles impinge on these tubes they will flatten out, and the portion in contact with the metal surface will solidify, but the portion exposed to the hot gases will remain molten wherever the gas temperature is above the melting point of sodium sulphate, will offer a sticky surface to which further molten particles and dust will adhere.

It is clear that molten particles and the dust which collects on the sticky surface will not only adhere but will bond.

As the thickness of the deposit increases, the surface will be less influenced by the cooling effect of the tubes and, consequently, the surface layer will be more fluid and will offer a larger area upon which further particles can build up ; and thus the rate of build up will increase progressively.

Practical Considerations

Apart from the chemical aspect the following practical considerations would appear to have a considerable bearing in supporting the theory that sea-water introduced with the fuel oil as an emulsion is responsible for the formation of bonded deposits.

The phenomenon is new, it only having come into prominence in H.M. ships during the latter part of the 1939-45 war.

Serious cases of choking of the gas passages by bonded deposits have been reported from battleships, aircraft carriers, cruisers (modern) and cruisers (old). No evidence has come to their knowledge regarding experience in destroyers.

All the classes mentioned have had occasion either to displace oil by water, or to ballast the fuel tanks with sea-water, and in many cases, especially in the old cruisers, much trouble has been experienced from leaky fuel tanks. In addition there is little doubt that much wet oil was supplied to ships during the war period.

It has already been stated that the fuel oil latterly supplied to the fleet readily emulsifies when brought into contact with sea-water, and that it is possible to burn oil containing even up to 10 per cent of water without much evidence at the burners. Under these conditions there will be a continuous supply of salts of sodium to the furnace.

Why were bonded deposits not experienced in the years before the war ? This might be attributed to the fact that war-time conditions reduced the number of occasions on which external cleaning could be carried out. This suggestion might apply so far as the gas passages which can be reached by saws are concerned, but on the other hand there are numerous parts of the tube banks which cannot be effectively cleaned by saws and are only exposed on occasions of withdrawal of superheaters during periods of drill tests, retubing, etc. It is safe to say that examination of boilers at these periods did not formerly reveal accumulations of deposits of this nature in those parts of the boilers which could not be effectively cleaned by the normal methods.

The gas temperatures of modern boilers are no doubt higher than in pre-war boilers but the increase is not great, nor is this a contributory factor. What

then is the difference between pre-war conditions and war-time conditions which has caused the formation of bonded deposits ?

Before the war water displacement and ballasting was not employed, furthermore the fuel tanks were normally free from leakage, and the oil supplied presumably met the specified water content of not more than one half per cent.

Of much greater importance is the fact that the type of oil supplied up to 1942 did not emulsify when brought into contact with sea-water. If leakage into tanks occurred, the water readily separated and settled, and could be discharged overboard, or if it did reach the burners they usually became extinguished immediately.

These practical considerations would, therefore, appear to support the findings of the chemical investigation.

There can be no doubt that the bonded deposits found on the generators and superheaters of the boilers of H.M. ships are due to the contamination of the fuel oil by sea-water held in suspension in a finely divided state, and it is clear that the formation of these deposits can only be prevented by ensuring that the fuel oil reaching the burners is free from sea-water contamination.

Methods of Detecting the Presence of Water Contamination of Fuel Oil

Attention has been drawn to the fact that an emulsion can be diluted by adding more of the liquid which forms the outer or continuous phase, and that such dilution, whilst reducing the percentage of sea-water in the emulsion does not reduce the total amount of sea-water present. Obviously a ship steaming for 1,000 hours on oil containing 1 per cent of sea-water will put the same amount of sodium chloride into the furnace as when steaming for 100 hours with oil containing 10 per cent of sea-water.

It is, therefore, very necessary to have some means suitable for use on board ship, for detecting the presence, and estimating the amount of water in fuel oil.

In the days when fuel oil and water did not form a stable emulsion this could be done by using one of the several types of water-detecting pastes. These pastes are a mixture of water soluble matter such as glycerine or a concentrated sugar solution into which a coloured pigment has been incorporated to form a smooth paste. When a sounding tape or a piece of metal is smeared with such a paste and lowered into a vessel containing a layer of oil and a layer of water, the water soluble matter in the paste goes into solution in the water and as the coloured pigment has nothing to hold it on to the metal it falls away leaving a clean surface. The portion immersed in the oil being unaffected by the oil remains intact, thus leaving a clear line of demarkation giving the position of the interface.

Now, however, the position is vastly different as the water present may not be free but held in a fine dispersion throughout the oil as an emulsion, which behaves in the same manner as oil when water-finding paste is immersed in it. In cases where the water is held in large droplets the water-finding paste may have a slightly mottled appearance which is not easily detected, particularly when the line of demarkation is searched for by wiping off the oil with the fingers or some similar method.

In general, water-finding pastes are suitable for detecting the presence of free water but they do not show water held in suspension in the oil in the form of an emulsion.

There is a standard laboratory method for the determination of water content of petroleum products such as fuel oil. The method depends upon heating the sample with a petroleum spirit of a high boiling range ; the petroleum spirit

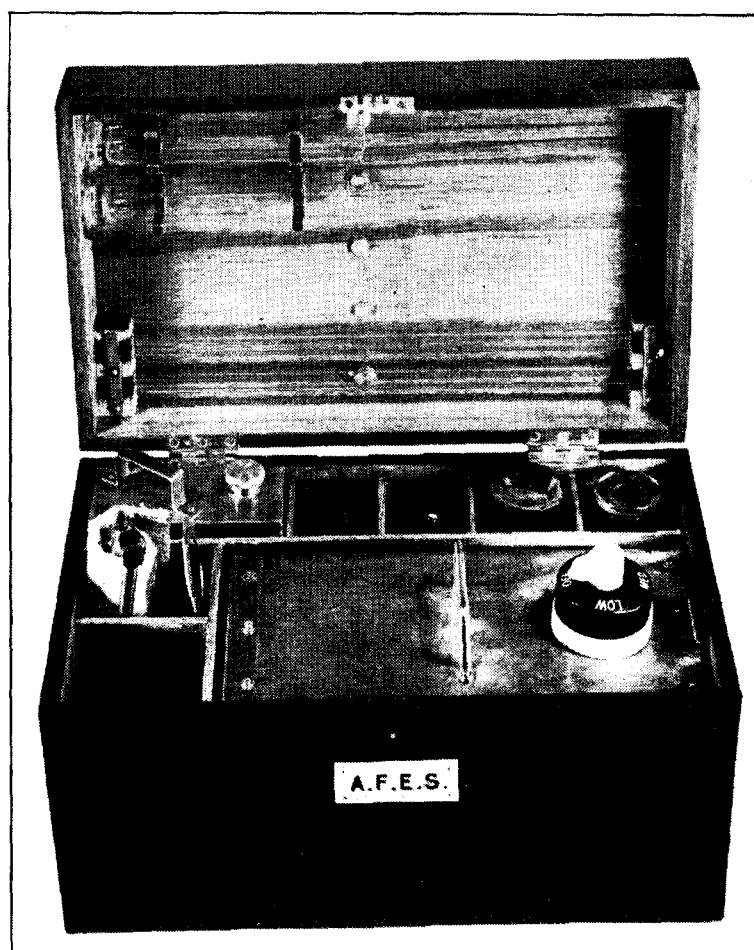


FIG. 6.—APPARATUS STOWED IN BOX

acts as a carrier, the vapours from the mixture pass into a condenser, and the condensed liquids flow into a graduated receiver where they readily separate. When the receiver is full the petroleum spirit overflows back into the petroleum spirit/oil mixture, heating is continued until the volume of the water in the receiver remains constant for five minutes.

This apparatus normally used in the laboratory consists entirely of glass. The condenser is of the water cooled glass-tube reflux type and, therefore, requires running water for the cooling operation.

The apparatus, although simple to manipulate, is unsuitable for use on board ship, the glass portions are too fragile and the necessity of providing running water to the condenser would present a difficulty. There is also the objection that when the test is completed there remains a mixture of petroleum spirit and oil which is not only highly inflammable but is also a nuisance to deal with. In the laboratory the petroleum spirit is recovered by distillation but this is not a practical proposition on board ship.

The authors have designed an apparatus suitable for use on board ship, and have developed a method which is a modification of the standard laboratory method. It is free from the disadvantages referred to above and gives results which are comparable with those obtained by the standard laboratory method.

The apparatus consists of a conical shaped, flat-bottomed copper flask, approximately 500 ml capacity, the neck of the flask is threaded to fit into a coupling by means of which a swan-necked tube is fitted on to the flask ; at the

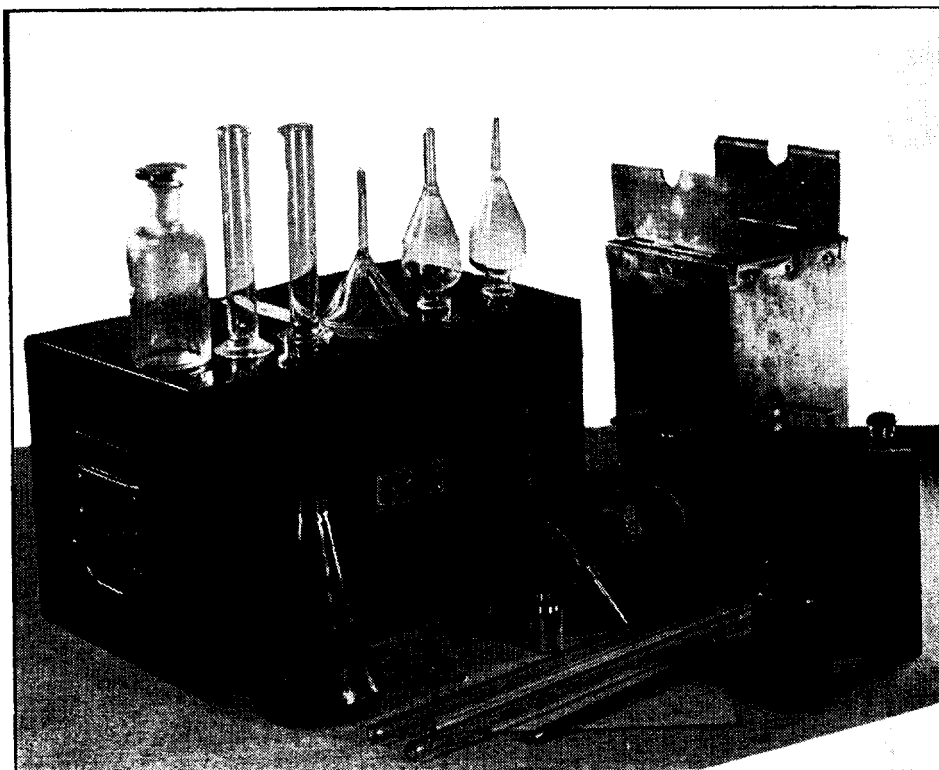


FIG. 7.—COMPONENT PARTS OF APPARATUS

other end of this tube is a gland connection to hold a boiler gauge glass. The free end of the boiler gauge glass is inserted in the neck of a graduated receiver.

The apparatus functions as a distillation apparatus, the copper flask being the distillation flask, the gauge glass the condenser, which is air cooled, and the graduated receiver collects the distillate and provides the means for measuring.

The heat is obtained by means of three electrical elements held between two metal plates and connected in parallel to a three heat snap switch indicating low, medium, high and off positions. The hot plate and switch are set in a lagged copper box which also functions as a draught shield. The apparatus is shown in Fig. 6, 7 and 8.

The procedure for making a determination of the water content of a sample is as follows :—

50 ml of the sample is measured in the graduated cylindrical measure and poured into the distillation flask. The measuring cylinder is rinsed out with successive portions of about 10-15 ml of petroleum spirit, using in all approximately 50 ml, and these washings are added to the flask.

The apparatus is next assembled as shown in Fig. 8. The switch is turned to the medium position until distillation begins, as indicated by condensate appearing in the gauge glass, when the switch is turned to "low" to prevent to rapid ebullition. When the lighter fractions have distilled over distillation will slow down. The heat should then be increased, with the switch at the medium and finally at the high position until distillation is complete, when the volume of the liquids in the graduated receiver should be approximately 50 ml.

If the sample under test contains water the liquids in the graduated receiver will be in two layers, the bottom layer being water and the upper layer consisting of the condensed petroleum spirit. The volume of this water is read off

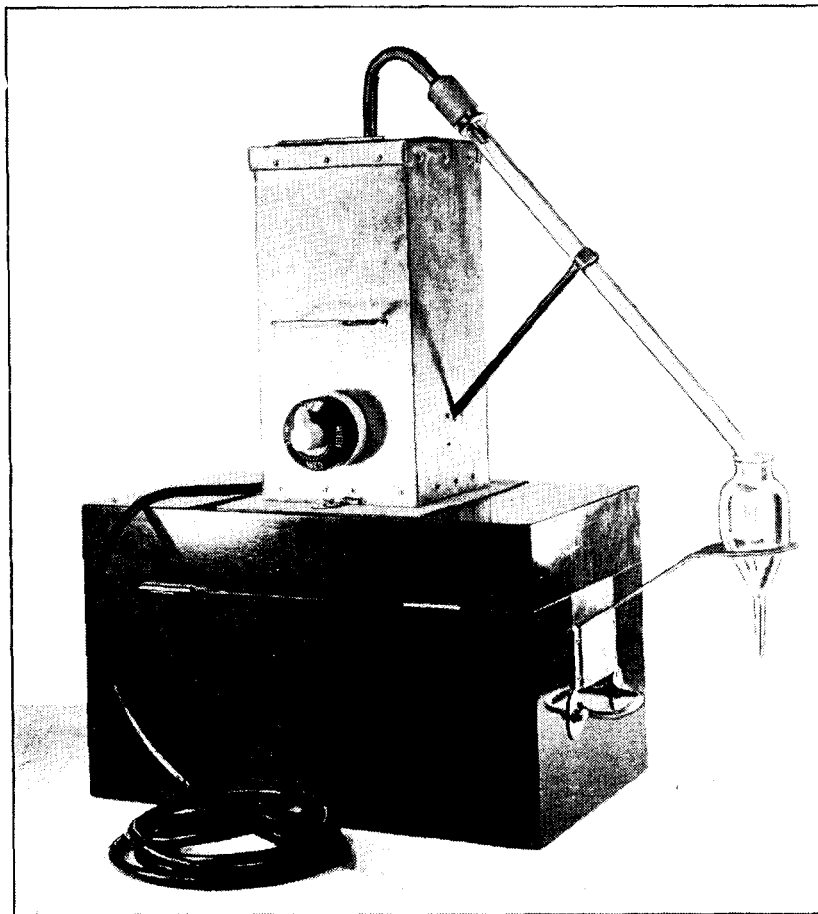


FIG. 8.—APPARATUS ASSEMBLED FOR USE

and this figure when doubled gives the water content of the sample as a percentage by volume.

The receiver is not graduated to measure accurately amounts greater than 3 ml corresponding, in this test, to 6 per cent of water, and normally on board ship no great accuracy is required in the case of an oil containing more than 6 per cent of water. Should, however, a greater accuracy be required for amounts over 6 per cent this can be obtained by repeating the test, using a smaller amount of the sample.

50 ml of the petroleum spirit should be taken for every determination irrespective of the amount of oil used.

An average time to complete a test is 30 minutes when starting from cold.

If the apparatus is being used in a compartment where the temperature is so high that the condensation is inefficient and vapour is passing out of the water gauge glass, an air current from a table fan played on to the gauge glass will effect a considerable improvement.

This apparatus has been used on board ship on many occasions and no difficulties have been met with. Even in rough weather where there has been considerable movement of the ship the method of securing the apparatus has proved satisfactory.

Sampling

This paper would be incomplete without reference to one of the most important aspects, namely that of sampling. It is extremely difficult to obtain a sample which is wholly representative of the contents of a tank.

Experience has shown that "layering" takes place in a tank of fuel oil contaminated with water, and conditions are met with which are contrary to natural laws. Being heavier than oil it would be expected that water would fall through the oil, finding its way to the bottom, but this is not always the case, especially when the viscosity is high and the settling period is short.

There are several forms of apparatus in use for taking samples of oil from a tank, most of which are lowered into the tank to the required depth and, by means of a sharp tug on the line an opening or closing device is operated; it is difficult under these conditions to say with certainty the precise depth at which the sample has been taken. In some cases the sampling pot is open on immersion and is closed by a tug on the line when the required depth is reached, and there is no guarantee that when the device is closed the oil entrapped is representative of the oil at the depth at which the apparatus closed.

An effective sampling vessel has been developed at the Admiralty Fuel Experimental Station and although it requires a jerk to operate the valve, the opening mechanism is so sensitive that it operates by lightly striking the supporting line, and samples can be taken from any required depth within an accuracy of something of the order of one inch. This apparatus has the advantage that, by having a balanced inlet valve to counteract the differing head of oil, the container can be lowered to the required depth before the valve is opened, and the valve closes as soon as the container is filled, thus ensuring that the contents are wholly representative of the oil at the point at which it is desired to take the sample.

In conclusion the authors wish to express their gratitude to Dr. A. S. C. Lawrence, now of Sheffield University, for his valuable help and useful criticism in the preparation of this paper.
