SOME ASPECTS OF MODERN MARINE BOILER WATER TREATMENT

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In recent years there has been a marked increase in the operating pressure and temperature of the boilers used in marine installations. The single boiler concept is also now quite common. These developments have required new thinking on the subject of marine boiler water treatment. The work on which this paper is based was aimed at evolving a total system of boiler and feed water treatment for a fleet of large tankers, so the paper covers not only the chemical aspects of the subject but also the engineering features which are desirable within the feed system. The main trace contaminants likely to be present in a marine feed system are silica, iron and copper. Care must be taken to ensure that the level of contamination is within the limits detailed in the appendix. Silica can cause severe deposits on turbine blades, whereas copper and iron can initiate corrosion within the boiler. Successful boiler water treatment can only be the sequel to successful boiler commissioning, both boiler water treatment and commissioning methods are detailed in this paper.

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INTRODUCTION

In recent years there have been considerable advances in the design of marine steam turbine propulsion systems. Perhaps the biggest changes have been those affecting the boiler plant. The single boiler concept is now quite common; membrane furnace walls are being used and the majority of boiler designs employ an all welded construction method. The operating conditions of the boilers have risen; pressures in the region of 65 kg/cm^2 and temperatures in excess of 500°C are now regarded as the rule rather than the exception.

These advances have required a revision of the methods of boiler water treatment used on board ships fitted with such boilers. Contamination which can be tolerated in the boiler and feed systems of ships operating at lower pressures can give rise to serious problems when the operating conditions of the boilers are increased.

The object of the work on which this paper is based was to evolve a total system of boiler and feed water treatment for a fleet of large tankers with single boiler installations. The operating conditions of the boilers are at a pressure of 63 kg/cm^2 and a temperature of 500°C at the boiler stop valve.

The experimental work mentioned in the paper was carried out at sea on board one of these ships. Full details of the analytical techniques used are given in the appendix.

COMMISSIONING OF NEW MARINE BOILERS

Effective boiler water treatment can only be achieved if sufficient attention has been paid to boiler commissioning.

The following practices and routines will aid the early establishment of correct boiler water conditions.

Only de-mineralized water should be used for pressure testing the boiler. As such water may be saturated with oxygen and carbon dioxide, it is essential that 20 ppm of hydrazine should be present at a pH of 10 to 10·5. This water will give ample protection against corrosion during hydraulic testing and can be left in the boiler prior to commissioning.

Before raising steam, this water should be dumped and the boiler refilled with de-ionized water containing only five ppm of hydrazine.

The successful commissioning of a marine boiler is dependent on the controlled formation of a perfect magnetite layer on the iron surfaces of the boiler. Iron of course tends to oxidize when exposed to air and water. Fortunately one of the oxides is magnetite (Fe_3O_4) which will, if conditions are correct, form a protective oxide layer on the metal, so preventing to a large extent any further oxidation. The problem is to establish the conditions under which such a protective film may be generated and maintained during practical operation of the boiler. These conditions are achieved by the controlled injection of hydrazine during the first steaming hours of the boiler. The hydrazine should be injected into the feed system in carefully controlled amounts and at a controlled pH in order to encourage two reactions.

First it is assumed that after the cleaning of the boiler and its subsequent examination and hydraulic testing certain amounts of Fe_2O_3 (rust) would form on the bare metal structure of the boiler. The introduction of hydrazine encourages the following reaction:

$$6Fe_2O_3 + N_2H_4 = 4Fe_3O_4 + 2H_2O + N_2$$

So any loose rust on the boiler surface will be chemically removed. However, during this phase the boiler water temperature must be raised to 250°C as soon as possible to prevent the formation of further Fe_2O_3 on the boiler.

During these early steaming stages of the boiler the hydrazine should be injected to maintain a hydrazine reserve in the boiler, the pH during this phase should not be allowed to rise above 8·7.

Once the hydrazine reserve has been established, it is assumed that the first reaction is complete. The pH of the boiler should now be raised to at least nine by the injection of small amounts of caustic soda.

The conditions in the boiler should now encourage the following reaction:

$$3Fe + 4H_2O = Fe_3O_4 + 2H_2$$

There will have been a tendency for this to occur at the lower pH, but the reaction will proceed vigorously once the pH has been raised. The hydrazine reserve should be maintained to ensure that the boiler water is oxygen free.

The crystallites which form the magnetite deposit are of colloidal dimensions and the volume of magnetite formed is about twice that of the metal consumed. The result is that vast

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amounts of magnetite will be swept into the boiler water and held in colloidal suspension. The appearance of these colloidal particles is a sure indication that the reaction is proceeding as planned. The solution will be easily recognizable as it has a cloudy black appearance, and normal filtration should fail to separate the particles from solution.

The bulk of the magnetite will, however, adhere tightly to the base metal progressively isolating it from the boiler water until the corrosion rate is practically zero. The course of this reaction can be recorded by measuring the hydrogen content of the steam generated.

Once the reaction has run its course, the boiler water should be dumped as quickly as possible. In this fashion the colloidal particles of magnetite will be flushed out of the system.

Ideally, these first chemical commissioning techniques should be performed during the trials of the alternators or similar auxiliary plant. The boiler should then be shut down, the colloidal boiler water dumped and the boiler refilled with de-ionized water. The boiler can now be put on line again and normal boiler water treatment commenced.

If teething troubles cause an excessive number of boiler starts, the boiler water should be brought up to 250°C as rapidly as possible to protect the magnetite film. If the boiler has to be put in wet storage the hydrazine content of the water should be kept at 30 ppm with a pH of 10·5. After having achieved apparently clear boiler water a reappearance of suspended solids may occur—particularly after reductions in load. If these deposits are dense and can be filtered out of suspension it is most probable that they are aglomerated particles of colloidal matter which have remained in the boiler from the commissioning period. If, however, they are in colloidal form, that is they cannot be filtered out, they are undoubtedly caused by fresh corrosion. This is most likely due to the fact that marginal boiler water conditions existed under full load; on load reduction the amount of water in the boiler would increase and inadequate boiler conditions occur. These off specification conditions result in breakdown of the magnetite film which has then to be restored, hence the appearance of colloidal magnetite in the water.

To prevent this happening care should be taken to ensure that adequate chemical reserves are available in the boiler prior to load fluctuations occurring.

It goes without saying that the maintenance of the protective magnetite film during shutdowns is very important. If the magnetite film is exposed to air and water, the following reaction may occur:

$$4\,Fe_3O_4 + O_2 + 6H_2O = 12\,Fe\,OOH$$

This Fe OOH (a light brown hydroxide) forms as a non-adherent powder. It follows that during shutdown periods the boiler should be blown out whilst still hot, subsequent examination of the boiler should be kept to a minimum, great care being taken to avoid physical damage to the magnetite layer (by hobnail boots, etc.).

If these precautions are observed, the establishment of correct subsequent boiler water conditions will be aided and this in its turn can only result in a longer boiler life with much reduced possibilities for serious internal corrosion.

BOILER AND FEED WATER TREATMENT

Unfortunately the prevention of internal boiler corrosion is not exclusively a chemical problem. The best standards of chemical control will only assist in minimizing the possibility of corrosion. The design and layout of the plant are just as important as the chemical conditioning, if corrosion problems are to be totally avoided.

The chemical tolerances required for boilers operating at pressures in the region of 63 kg/cm² are exacting and experience has shown that there will be occasions when they cannot be strictly maintained. Such occasions are the immediate period after the initial commissioning of the plant and periods during manoeuvring or cargo handling operations.

So, effective corrosion control results from two factors. First, the design of the feed system must be tailored to avoid excessive corrosion occurring in the system and care should be taken to avoid transporting to the boiler the products of the small amounts of corrosion that will inevitably take place.

Second, a schedule of desired chemical criteria within the boiler and feed system must be drawn up, and procedures laid down to enable these values to be easily maintained by the ship's staff. On board ship, such a chemical control specification must inevitably be a compromise between the standards which are theoretically desirable and the standards which the ship's staff can reasonably maintain with the limited analytical facilities available.

BOILER WATER CHEMICAL SCHEDULE

The basic aims of boiler water chemical conditioning are:

1) to provide an environment that will encourage the controlled formation of the protective magnetic film;
2) to prevent any further corrosion occurring after the magnetite film has formed;
3) to prevent deposits forming on the heat transfer surfaces;
4) all the above to be attained whilst maintaining a high degree of steam purity.

The above objectives are achieved by controlling the following chemical criteria.

Alkalinity

The best environment in which to develop and maintain the stable magnetite film on the boiler steel is obtained by keeping the boiler water alkaline. The choice of a suitable alkali is governed by the following factors. Caustic soda is the most aggressive alkali and offers the best guarantee of maintaining an alkali film at the heat transfer surfaces. However, it is possible that hideout of caustic soda could occur, and the localized concentration could be sufficient to cause a rapid corrosion rate. Sodium carbonate is often included as the alkalizing agent in proprietary boiler water compounds. It has the advantage of being easy to handle, but in the boiler it decomposes according to the following reaction:

$$Na_2\,CO_3 + H_2O \rightleftharpoons 2\,Na\,OH + CO_2$$

The exact equilibrium of the reaction will depend on the operating conditions of the boiler. But in all cases its use will result in carbon dioxide being released into the feed system.

In high pressure shore installations it is not uncommon to use only volatile alkalizing agents such as ammonia and hydrazine. However, such treatment methods are not normally used at sea because they require careful supervision and it is uncertain to what extent the volatile alkalies can neutralize the acidic salts which result from slight condenser leakage.

From the above considerations it is apparent that each of the alkalizing agents has its own particular disadvantages. However, the best advice at the present time, for marine drum type boilers operating from a pressure of 63 kg/cm² upwards is to use caustic soda, provided of course that operating experience reveals that caustic hideout is not occurring.

Phosphate Reserve

The sole purpose of maintaining a phosphate reserve in the boiler water is to precipitate any hardness salts which may enter the boiler due to condenser leakage. If the condenser could be guaranteed not to leak there would be no need to use any phosphate treatment. In fact in shore based installations using closed circuit cooling systems this is frequently the case, but at sea it is not usual to take such risks. There are several commercially available phosphates:

Sodium metaphosphate ..	$Na\,PO_3$
Trisodium phosphate ..	$Na_3\,PO_4$
Disodium phosphate ..	Na_2HPO_4
Monosodium phosphate ..	$Na\,H\,PO_4$

Usually the metaphosphate is used, being readily available, easy to handle and stable. Its basic reaction in the boiler is shown below:

$$2\,Na\,PO_3 + 3\,Ca\,CO_3 = Ca_3(PO_4)_2 + Na_2CO_3 + 2CO_2$$

Thus any scale forming constituents are precipitated as a harmless phosphate sludge.

All the boiler water chemicals are injected directly into the boiler, either by themselves or as a proprietary boiler water treatment compound. They should be injected in sufficient quantities to maintain the chemical reserves in the boiler at the values detailed in the appendix. Ideally they should be injected independently as only in this way can there be any guarantee of keeping the boiler water exactly on specification. Many shipowners use a proprietary boiler water compound which will contain a balance of chemicals to give very approximately the correct alkalinity and phosphate reserve in the boiler. One of the advantages of these compounds is that they contain the fringe additives such as anti-foaming agents and sludge conditioners that would otherwise have to be added separately. Their big disadvantage is that when using them it is virtually impossible to keep the boiler water exactly on specification at all times. The ideal compromise is to use caustic soda to give the correct alkalinity and then use a proprietary phosphate compound, which will contain the anti-foaming additives, to get the correct phosphate reserve.

FEED WATER CHEMICAL SCHEDULE

Oxygen Scavenging—The Use of Hydrazine

The sole purpose of continuous hydrazine injection is to scavenge excess oxygen from the feed system. The rate of hydrazine injection is generally controlled to maintain a slight reserve of hydrazine in the boiler, the presence of this reserve being taken as a sign that no oxygen is present. The amount of hydrazine that will have to be injected depends very clearly upon the efficiency of the de-aerator.

On modern ships the de-aerator should work very efficiently when the plant is at full load. However, when manoeuvring or in port there may be significant amounts of oxygen in the feed system. It is at these times that particular attention will have to be given to the rate of hydrazine injection. If free oxygen is allowed to remain dissolved in the feed water, it will cause severe corrosion of the pre-boiler systems. The oxygen is forced out of solution as the temperature increases so economizers are particularly prone to oxygen corrosion. In cases of severe oxygen contamination, then even the boiler drums and tubes may be attacked. The basic reaction of hydrazine is:

$$N_2H_4 + O_2 = 2H_2O + N_2$$

This reaction removes the oxygen but does not increase the dissolved solids content of the boiler water. The big drawback to the use of hydrazine is that the excess which is allowed to exist in the boiler decomposes to form ammonia.

The reaction being:

$$3\,N_2\,H_4 = 4\,N\,H_3 + N_2$$

Some of the feed water treatment specialists who supply hydrazine infer that this is an advantage because it tends to raise the pH value of the feed water. However, as can be shown, it is a rather dubious advantage.

Experiments were performed on board a ship at sea in order to trace the effects of this ammonia. It was found that the ammonia reached every corner of the feed system.

Table I shows typical ammonia concentrations at various points in the feed system which resulted from maintaining a hydrazine reserve of 0·1 ppm in the boiler.

The effect of this ammonia is mentioned in the section on copper contamination, where it is shown that there is a definite link between the ammonia content of the feed water and the degree of copper corrosion in the system.

In view of this fact it is essential that the injection of hydrazine is strictly controlled, and there is a very strong case for injecting the hydrazine into the turbine cross over pipe rather than into the de-aerator outlet as is normally the case. Injecting the hydrazine into the cross over pipe of the turbine will dramatically reduce the amount of copper corrosion products reaching the boiler.

This practice should not involve injecting significantly different amounts of hydrazine to maintain the same hydrazine reserve in the boiler. The oxygen scavenging properties of hydrazine are affected by the temperature. Whilst the reaction will proceed slowly at condensate temperatures, it will not proceed with vigour until after the temperature has been raised in the de-aerator. Because of this, the oxygen scavenging reaction is not significantly affected even though the position of the hydrazine injection has been altered. Of overriding importance is the need to inject no more hydrazine than is necessary to maintain the lowest detectable reserve in the boiler.

TABLE I—AMMONIA CONCENTRATIONS IN THE FEED SYSTEM RESULTING FROM 0·1 PPM HYDRAZINE RESERVE IN THE BOILER

Sample Point	NH_3 ppm
Main condensate	0·5
Drain tank outlet	0·6
Air heater drains	0·55
L.P. heater drains	0·5
De-aerator outlet	0·5
Main boiler water	0·2
Distilled water tank	0·18
Distiller output	nil

No useful purpose is served by maintaining a hydrazine reserve in the boiler above this detectable minimum.

The use of other chemical oxygen scavengers such as sulphites, etc., is not recommended due to the increase in total dissolved solids in the boiler water caused by their use, and the fact that they do not protect the economizers which are particularly prone to oxygen corrosion.

The Use of Volatile Amines

Corrosion in boiler feed systems is often the result of carbonic acid attack. So it is modern practice to take precautions which ensure the chemical removal of any residual carbon dioxide which may be present in the condensate. This in effect means that the pH value of the feed water must be raised to at least 9·0 to ensure that no free carbon dioxide is present. At one time ammonia was recommended for this purpose but large quantities are required to raise the pH significantly above 8·5. In any case the ammoniacal compounds so formed tend to be unstable and can break down to re-release the carbon dioxide. A further disadvantage is that modern feed systems contain a high percentage of copper alloys, which tend to be corroded by high concentrations of ammonia.

The neutralization of carbonic acid can be safely accomplished by certain volatile amines such as monocyclohexylamine $C_6H_{11}NH_2$.

When this amine is injected into the boiler it volatilizes with the steam and combines with any carbon dioxide in the condensate to neutralize its acidity.

It is difficult to get any firm evidence as to how effective the amines are, mainly because no accurate suitable analytical techniques are available for use on board ship to detect carbon dioxide in concentrations below one ppm; nor is taking samples for shore analysis a suitable alternative, due to the trace level of the contamination being sought and the ever present possibility of contamination of such a sample during transport.

However, as a result of trials on board ship at sea, there is evidence, mainly from the pH/conductivity/ammonia values of the condensate, that small amounts of free carbon dioxide will be present if amine injection is not used. So the use of volatile amines must be regarded as an essential component of the feed water treatment schedule. In order to simplify the application of the treatment it is advisable to inject the amine *via* its own independent injection system.

De-ionization Plants in Marine Feed Systems

In high pressure boiler feed systems every effort must be made to ensure that no contamination enters the system in the make up feed water. Generally, all this water will have been produced on board ship in vacuum type sea water distillers. It is now usual to pass this raw distilled water through an ion exchange column before it enters the feed system.

De-ionization is a process whereby mineral salts and other such contaminants can be removed from water. Only those substances which ionize in water can be removed by this process. Total de-ionization involves two ion exchange reactions, the cations, such as calcium, sodium, magnesium, ammonia are removed by a hydrogen cation exchanger. The anions such as chloride, sulphate, silicate, carbon dioxide are removed by an anion exchanger. For effective silica removal a highly basic anion material is required. The exchange materials used in modern plants are usually organic exchange resins. The cation exchange resin used at sea is usually of the sulphonic acid group, the trade names of such resins are Amberlite 120 and Zeo-carb 225. The anion resin used at sea is generally a strongly basic type such as Amberlite 400 or Deacidite FF.

The conventional method of de-ionization used to be, first to pass the water to be treated through a column of cation exchanger and then through a column of anion exchanger. The cation material exchanges hydrogen for all metallic ions and the resultant acids and any carbon dioxide or silica are removed by the anion material.

It has always been realized that by passing the water to be treated through a mixture of cation and anion resins a much purer water could be obtained. This is explained by the fact that during such mixed bed treatment the water comes repeatedly into contact with grains of cation and anion resin and is thus subjected to a series of treatments. The drawback to such mixed bed systems was that the resins must be separated from each other for regeneration. Only fairly recently have cation and anion resins of different specific gravity been produced, thus enabling them to be easily separated by differential flotation.

These mixed bed ion exchange units are now considered standard components in a marine feed system. But it is important that the design of the unit, and the balance of cation and anion resin should be exactly tailored to the ionic load of the water that the unit will have to treat. If this is not done then the unit will be depleted before it has treated its theoretical throughput.

Unfortunately there is a tendency for marine engineers to assume that the main contaminant in the distilled water produced by the evaporators is sodium chloride. As a result ion exchange columns are often installed which are designed to treat a balanced ionic load, that is the exchange capacity of the cation resin is the same as the anion resin. Experience at sea has shown that salt is in fact not the main contaminant of the distilled water produced by evaporators once they are steadily on line. Table II shows the analyses of typical distilled water produced in a vacuum type sea water evaporator.

TABLE II—ANALYSES OF TYPICAL DISTILLED WATER SAMPLES

Sample No.	1	2	3
CO_2 ppm as such	12	14	18
Fe ppm	0·01	0·01	0·01
Cubic ppm	0·2	0·2	0·25
Total $S_1 O_2$ ppm	0·04	0·04	0·04
Na ppm	0·38	0·40	0·30
pH	6	6	5·4
Conductivity $\mu\Omega$	6	6·5	7·0

The sodium content of the distilled water stays fairly constant, but there are big changes in the carbon dioxide content according to the operating conditions of the plant. The important point is that the main containment in the water produced by the evaporators is, in fact, carbon dioxide, so the balance of the resins in the ion exchange unit must be tailored to meet the heavy anion load that will be imposed upon it by this carbon dioxide. Ideally, the ion exchange plant should consist of a column of anion resin, to remove carbon dioxide and silica, followed by a mixed bed column to remove the traces of metallic salts. Alternatively the water could be passed through a de-gassing column prior to treatment in a mixed bed ion exchange column; however, the efficiency of a de-gassing column at the low carbon dioxide concentrations involved has yet to be proved.

Feed System Contamination Detection

It is obviously important to have an effective detection system to give warning when feed system contamination is occurring. The principal source of such contamination is the main condenser, but other potential sources such as evaporator coil drains should not be forgotten. The conventional method of detecting such leaks is to use conductivity cells fitted at strategic points in the feed system. Whilst the meters of such cells may be calibrated in parts per million or grains per gallon of salt, the meter is actually measuring the conductivity of the water. To understand the limitations and drawbacks of such systems a working knowledge of the theory of the conductivity of dilute solutions is essential.

The conductivity of a solution depends basically upon the concentration of the free ions in the sample. Most substances ionize when they are in solution—that is to say that salt, sodium chloride, Na Cl, becomes in solution Na + ions and Cl − ions. The conductivity of a solution will then depend upon the degree of ionization that has occurred. The percentage of dissociation of a salt in solution into ions varies with the dilution, in very dilute solutions nearly all the salt will be ionized, but stronger solutions will not ionize to the same degree. It follows then that the relationship conductivity/concentration is not a straight line law, but a curve which tends to flatten out at high concentrations. Numerous measurements have been made of the conductances of salt, acid and alkaline solutions, the values of the equivalent conductances at various dilutions of the solutions which interest the marine engineer are shown in Table III.

TABLE III—EQUIVALENT CONDUCTANCE OF VARIOUS SOLUTIONS

Number of litres containing one gram equivalent	1	10	20	500	2000	α
H Cl	300	350	358	375	378	380
Na Cl	74	92	96	105	107	109
Na OH	164	193	198	213	215	218
NH_4 OH	0·89	3·3	4·6	21	38	238

Note: Conductances are in reciprocal ohms at 18°C

Table III shows that the equivalent conductance increases with dilution until it approaches a constant value in very dilute solutions. This is due to the fact that in dilute solutions, a greater degree of ionization occurs and it is this ionization which ultimately influences the conductivity of the solution. Another important factor is that the equivalent conductances at various dilutions of different salts have values very close to each other. Strong acids and alkalis, however, are always better conductors than salts.

As has been said, on conventional ships the salinity cells do in fact measure the conductivity of the water, the meter, however, is often calibrated not in conductance units but directly in salt concentration in parts per million. It has been calibrated on the assumption that any conductivity in the water will be due to salts in solution. For older ships this is a fair assumption because all salts have a very similar conductivity.

However, on modern ships with high pressure boilers, pH improvement of the feed water is practised to prevent feed system corrosion products reaching the boiler. To achieve this chemicals are deliberately injected into the feed system. As a result the following contaminants may be present in the feed water at the main condenser outlet:

Ammonia as NH_4OH	..	due to thermal breakdown of the hydrazine in the boiler;
Hydrazine as N_2H_4	..	depending upon the position of the hydrazine injection;
Amine as $C_6H_{11}NH_2$	..	injected to chemically scavenge carbon dioxide.

The total conductivity of a dilute solution containing several contaminants is now approximately equal to the sum of the conductivities of the individual contaminants. If the feed water chemicals are being injected into the system in their prescribed amounts the following concentration of contaminants could be expected in the condensate at the condenser outlet:

Ammonia 0·5 ppm	conductivity	..	4·0 m mho
Hydrazine 0·05 ppm	conductivity	..	0·5 m mho
Amine 0·1 ppm	conductivity	..	1·0 m mho
Base distilled water	conductivity	..	2·0 m mho
	Total conductivity	..	7·5 m mho

There is a total conductivity of about 7·5 m mho, the concentration of salt solution to give this conductivity is about 4·0 ppm. Thus, if the condensate with the above specification were being monitored by a conventional salinity cell, it would be well into the alarm condition. It is normal to assume two ppm as the maximum Na Cl in the condensate before giving an alarm; this would have a conductivity of about 4·0 m mho at 20°C.

It can be seen that conductivity alone does not give any indication of feed system salt contamination if the feed water is being treated for pH improvement by the use of amines and ammonia.

Clearly this situation must be appreciated and some method adopted to overcome the problem of how to give an accurate warning of condenser leakage. There are several ways of doing this. If all pH improvement and hydrazine injection were to be stopped, the conductivity of the condensate at various points in the feed system would be basically as follows: condenser outlet 2·5 m mho, drains tank outlet 3·0 m mho, low pressure heater drains 2·5 m mho, condensate drains from the steam air heater 4·0 m mho, de-aerator outlet 3·0 m mho. The base conductivity of the plant would be 2·5 m mho at the condenser outlet. This conductivity would be due to contaminants in the steam and would represent a zero condenser leakage condition. So one method often suggested is to merely assume the base conductivity of the plant when feed water treatment is being practised at a higher level than the 2·5 m mho which is a reasonable base conductivity for a system with no feed chemical dosing. This method finds little favour because there could be no guarantee that the level of ammonia and amine in the system would always be exactly the same. Also, for the same concentration in parts per million ammonia solutions have higher conductivities than salt solutions, so a salt leakage into the system could be masked by the ammonia.

A more reliable method is to fit an ion exchange column just in front of the salinity cell. This is in the form of a column of cation exchange resin. This resin has two actions: firstly, it removes the amines and ammonia totally from solution;

$$R\text{–}H + NH_4O\,H = R - NH_3 + H_2O;$$

and secondly it converts any salts in solution into the acid form.

$$R\text{–}H + Na\,Cl = R - Na + H\,Cl.$$

Thus, the resin has removed the ammonia contamination completely and converted the salt content to hydrochloric acid. The table of conductances shows that the effect of this resin on the conductivity of the water before and after the ion exchanger will be as follows: that portion of the conductivity caused by the ammonia will be removed and that portion of the conductivity caused by the salt will be increased by a factor of approximately three (this is because equivalent dilute solutions of H Cl are assumed to be approximately three times more conductive than equivalent dilute solutions of Na Cl). This fact means that the indicator of any salinity cell fitted with such an ion exchange column has to be recalibrated, i.e. if a full scale deflexion before fitting a column were equal to 30 ppm of Na Cl, after fitting the column it will be 10 ppm.

Such columns work well but they do require attention at the plant design stage and subsequently require maintenance. The flow of water through the cell must be limited to about two gallons per hour—this is to avoid premature exhaustion of the resin. The exchange column must also be positioned so that it is easy to change the resin which should be protected by an inlet filter of cotton wool. Ideally a small rotameter should be fitted to allow the water flow to be adjusted by means of a needle valve.

Alternatively, adequate indication of condenser leakage can be obtained by using conventional salinity cells and fitting one additional cell to the low pressure heater drains. So long as no condenser leakage occurs the conductivity of the drains from the low pressure heater is very close to that of the main condenser outlet, ammonia and amines effect each sample equally. If the conductivity of the main condenser outlet increased significantly then it would be a sure indication that the condenser was leaking.

There is one further system of detecting condenser leakage that should be mentioned for the sake of completeness. This system uses a pH type meter, but fitted with a special electrode sensitive only to sodium ions. It works on the same principle and is, in fact, identical to a conventional pH meter where of course the electrode is sensitive to hydrogen ions.

However, it would seem wiser to keep to a simpler system for the all important task of condenser leak detection. It is ironical but true that in the long term, the only sure way to detect slight condenser leakage is to keep a regular check on the chloride content of the boiler water.

TRACE CONTAMINATION IN MARINE FEED SYSTEMS

Silica

Turbine blade deposits are nothing new to marine engineers, the factors which influence their formation are varied, but in all cases the final result will be the same. They cause a distortion of the original shape of the blade or nozzle surface and, having a rough textured surface, also cause increased steam friction. The final result will be a loss of efficiency in the turbine. Such non-selective carry-over of boiler water solids generally occurs in turbines operating at low pressures.

However, there is one type of turbine blade fouling which is different from all others, this is the selective carry-over of silica. Turbine deposits in which silica is a predominant constituent rarely occur at low pressures. The problem becomes increasingly severe with increases in boiler pressure and, at pressures above 60 kg/cm², the turbine blade deposit, which contains a high proportion of silica, is the rule rather than the exception.

The exact nature of the phenomenon by which silica present in boiler water can be deposited on turbine blades is not fully understood; suffice to say that the silica can go into solution in the steam and tends to do this more readily with increases in pressure. The pH value of the boiler water is a further factor which appears to influence the rate at which silica will go into solution in the steam; increases in pH give a decrease in silica carry-over.

Operational experience in shore installations has resulted in the publication of certain recommendations for the permissible level of silica in boiler water at different pressures. Pressure alone is the real determining factor when deciding on the upper limits of this permissible silica contamination.

The boilers on the ships in question operate at 63 kg/cm² and at this pressure the generally accepted figure for the maximum level of silica permitted in shore boilers is ten parts per million.

In order to establish the level of silica likely to be found in a marine boiler, tests were performed at sea during the commissioning trials of a ship and during a subsequent voyage after the feed system had settled down.

During the trials, the silica contamination found in the boiler water and at various points in the feed system were as shown in Table IV.

TABLE IV—FEED SYSTEM SILICA CONTAMINATION DURING SHIP TRIALS

Day no.	1	2	3	4	5	6	7
Main boiler	2·2	4·5	8·0	16·4	28·0	34·0	38·0
Main condensate	0·3	0·3	0·3	0·3	0·3	0·3	0·3
Drains tank outlet	0·2	0·2	0·2	0·2	0·2	0·2	0·2
De-aerator outlet	0·25	0·25	0·25	0·25	0·25	0·25	0·25

It was felt that the sharp increase in the boiler water silica level during the trials could not have resulted from the trace contamination detected in the feed system.

Subsequent examination of the boiler internals revealed that the main contamination had resulted from debris left in the boiler during its erection. On analysis, the sludge found in the boiler after the trials proved to be 20 per cent silicous matter—that is, refractory materials and silicate dust.

Between commissioning and acceptance trials the boiler was repeatedly washed out in an attempt to completely purge any silicate materials. However, even when the ship sailed on her maiden voyage the silica content of the boiler water was still fairly high at eight parts per million. Some contamination was possibly being picked up from various components of the feed system.

Whilst the contamination stayed steady at this level, in fact it proved mysteriously difficult to lower it by routine blowing of the boiler. However, as the contamination was below the generally accepted shore standards, it was at that time considered that silica fouling of the turbine would not occur. There was no silica in the make up feed water produced by the ship's evaporators, and as sufficient attention had been paid to lowering the base silica level during commissioning to below ten ppm no recontamination should occur.

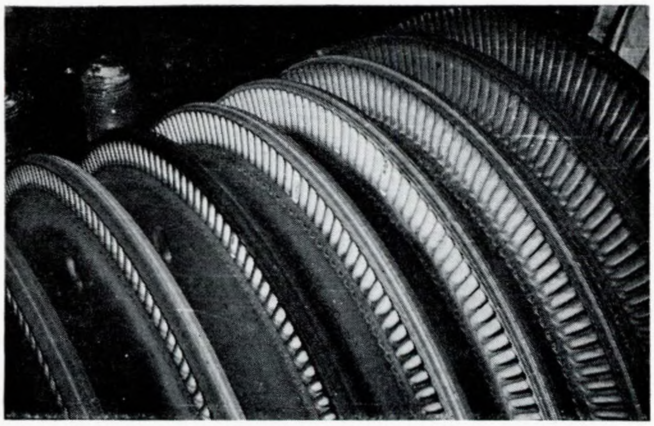


FIG. 1—*Turbine rotor fouled with silica deposit*

Unfortunately silicate fouling of the turbine rotors did occur on several ships, Fig. 1 shows such a rotor. The deposit started at the third stage of the H.P. rotor and extended through the rest of the turbine. As predicted, the deposit proved particularly difficult to remove. Analysis of the deposit showed that it was a complex silicate salt, sodium aluminium silicate, 2 Na_2O, Al_2O_3, 6 SiO_2. It must clearly have been formed by the reaction of the sodium salts in the boiler water treatment compounds with the refractory debris originally left in the boiler.

It appears that carryover of silica is influenced not only by the degree of contamination in the boiler, but also by the physical design of the boiler plant. As a result of these experiences, it is felt that the standards acceptable for shore boilers are not automatically applicable to marine installations. It seems wise to establish an upper limit for silica contamination at about four parts per million. At this lower level rotor fouling is unlikely to occur. Moreover, it is not particularly difficult to establish this low level provided sufficient attention is paid to the commissioning procedures during the initial commissioning period and subsequently after any boiler shutdowns for refitting purposes.

Iron

Iron contamination in the feed system usually consists of fine particles of iron oxides or hydroxides suspended in the feed water. These result from the corrosion of various iron parts of the feed system by the chemical action of oxygen and water.

The degree of contamination depends to a large extent on the layout of the feed system and its associated steam ranges.

The corrosion products of iron which may possibly be found in a marine feed system are shown in Table V.

TABLE V—CORROSION PRODUCTS OF IRON

Mineral name	Chemical name	Formulae	Colour	Behaviour
Magnetite	triiron tetroxide	$Fe_3 0_4$	Black	Melts at 1600°C
—	iron hydroxide	$Fe(OH)_2$	White	Decomposes at -100°C to form $Fe_3 0_4$ and H_2
Wustite	iron monoxide	FeO	Black	Decomposes to $Fe_3 0_4$
Haematite	iron oxide	$Fe_2 0_3$	Brick Red	Can form $Fe_3 0_4$ if temperature and pressure are correct
Gothite	hydrated iron oxide	Fe OOH	Yellow	Dehydrates to $Fe_2 0_3$

The initial corrosion product most likely to be found is the iron hydroxide, $Fe(OH)_2$, which is generated by the action of water on steel below a temperature of 50°C. The reaction is, $Fe + 2 H_2O = Fe(OH)_2 + H_2$. This product has a fairly high solubility but above 50°C it is converted to magnetite, Fe_3O_4, according to the reaction, $3Fe(OH)_2 = Fe_3O_4 + H_2 + 2H_2O$.

Thus, it can be seen that regardless of the initial corrosion product, in a marine feed system all the products of iron corrosion will enter the boiler as magnetite, Fe_3O_4.

When the magnetite particles are swept back to the boiler, they have the following effects: first their presence may be incorrectly diagnosed as being caused by a breakdown of the protective magnetite film in the boiler. Secondly, the particles will tend to aglomerate and form pockets of loose deposit in the headers of the boiler, or become deposited as a film of scale in the steam/water phase section of the generating tubes. Such deposits in the headers and water phase sections of the boiler are one of the contributory factors required for the initiation of hot water oxidation. The deposits in the steam phase section of the generating tubes will result in an alteration in the heat flux in that area, which may result in a failure of the basic protective magnetite layer. So, the presence of any iron compounds in the feed system not only indicates that corrosion is occurring in the system, which fact is itself disturbing, but requires that positive measures be taken to ensure that none of the corrosion products reach the boiler, where their indirect effects may be far more serious.

In order to assess the extent of iron corrosion occurring in a marine feed system, chemical analyses and particle size determinations were carried out on board a ship at sea. The results are shown in Tables VI and VII. The chemical analyses were according to the method detailed in the appendix, and the particle size determinations were performed using a Millepore filter fitted with a 0·8 micron membrane.

TABLE VI—FEED SYSTEM IRON CONTAMINATION

Sample point	Total Iron/ppm	
	Before Fitting Filter	After Fitting Filter
Main condensate	nil	nil
Drain tank outlet	0·02	0·0025
Air heater drain	0·005	0·005
L.P. heater drain	0·005	0·005
De-aerator outlet	0·005	0·0025
Evaporator distillate	0·003	0·0025
Distilled water tank	0·003	0·003

TABLE VII—PARTICLE SIZES OF IRON CONTAMINATION

Class Size in Microns	Per cent less than Stated Class Size	
	Sample From	
	De-aerator	Atmospheric drain tank
30	—	100
20	—	82
15	100	60
10	80	43
7	56	29
5	38	18
3	18	9
Approximate median size	6 micron	11·0 micron

The chemical analyses indicated that whilst the degree of corrosion was not high, it was persistent. It was mainly occurring in the cargo pumping steam systems, deck steam lines and similar systems and was entering the main feed system *via* the atmospheric drain tank. In fact the corrosion products often settled to the bottom of this tank and were only swept into the main feed system when the water in the tank was agitated by any drains returning in bulk due, for instance, to the starting of a cargo pump.

The particle size determinations showed that the bulk of the particles was larger than five micron. Because of these two facts it was decided that the problems of iron corrosion could best be avoided by fitting a full flow filter, size five micron, to the outlets from the atmospheric drain tank discharge pump.

The effects of fitting this filter are shown in Table VI. With this filter in use, the levels of iron found were well below the generally accepted industrial standards for boilers operating at 68 kg/cm^2; such standards usually have 0·05 ppm as the upper limit of acceptable iron contamination in the feed water.

Copper

Much has been written and said in the past about the presence of copper in high pressure boiler feed systems. No two authorities seem able to agree as to the contribution copper deposits on boiler tubes have on the corrosion pattern in the boiler.

In the opinion of the author there are two completely separate copper initiated corrosion failure mechanisms which can occur in boiler tubes. They are totally distinct, the only common factor is the required presence of copper to initiate the reaction.

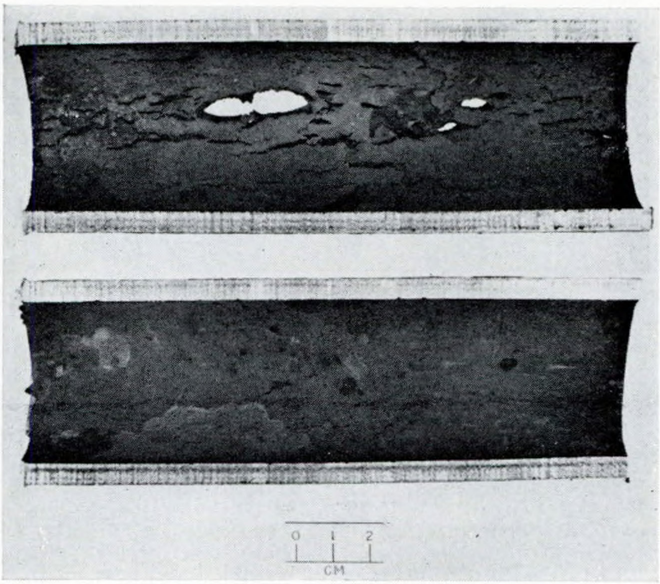


FIG. 2—*Boiler generating tube failed in service*

A practical example will help to illustrate these failure mechanisms. Fig. 2 shows a boiler generating tube which failed in service; numerous pits, cracks and ruptures are evident. The inner surface of the tube was covered by a brown powdery deposit which covered a darker more adherent scale. The results of an X-ray diffraction analysis of the deposits are shown in Table VIII.

TABLE VIII—X-RAY DIFFRACTION ANALYSIS

Deposit or Scale	Compounds Present
Brown powdery deposit on water side of tube	$Fe_3O_4 + \alpha Fe_2O_3 + \gamma Fe_2O_3 . H_2O + Fe_{0.93}O$ + very weak unidentified lines
Brown deposit on crack surface	$Fe_3O_4 + \alpha Fe_2O_3 + \gamma Fe_2O_3 . H_2O + Fe_{0.93}O + \alpha Fe$
Dark adherent scale	$Fe_{0.93}O$ + copper + Fe_3O_4
Coppery deposit (associated with dark scale)	copper

When the outer powdery scale was removed, particles of copper were found embedded in the darker more adherent scale. It seemed fair to assume that this powdery scale had become deposited on the surface as a result of the failure and was not present prior to the failure. At the higher resolution shown in Fig. 3, the deposits of copper are shown to be standing proud on the scale. Typical cracks which have only partially penetrated the tube wall are shown in Fig. 4. It was noticeable that copper deposits were present on the walls of these cracks and in the grain boundaries at the surface of the ruptured tube. The presence of these copper deposits was confirmed by electron probe analysis;

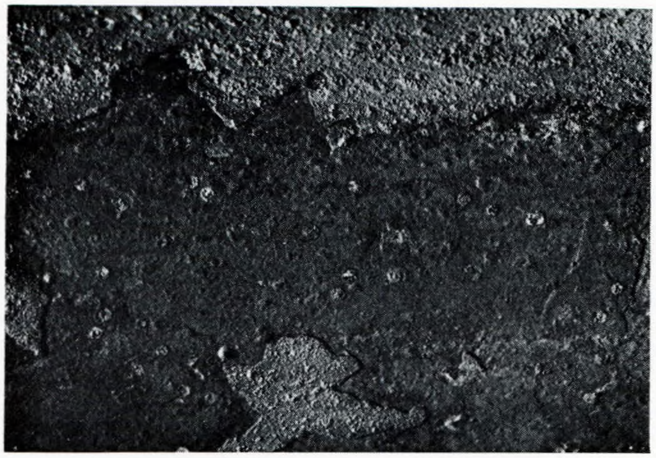


FIG. 3—*Four times magnification of tube shown in Fig. 2*

the actual distribution of the copper and iron at the grain boundaries and on the walls ot the cracks are shown in Fig. 5.

In addition to these copper deposits, microscopic examination indicated the presence of pits and further associated copper deposits on the water side of the tube. A section through one of these deposits is shown in Fig. 6, which reveals that the deposit is in fact copper in zones A and B embedded in the iron oxide scale.

Samples of the tube material were removed from the outer surface of the tube on the side opposite to the ruptures. These metal samples were spectrochemically and chemically analysed, with the results shown in Table IX.

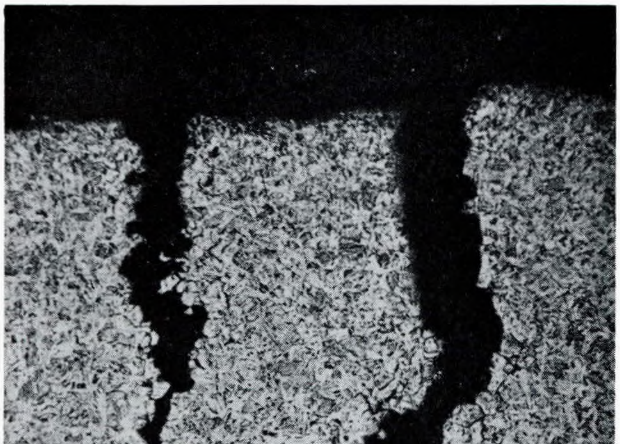


FIG. 4—*Typical cracks partially penetrating the failed tube—cracks initiated from the inner wall—magnification ×50*

TABLE IX—ANALYSIS OF BOILER TUBE MATERIAL

Element Determined	Per cent Weight Present of Element
Carbon	0·12
Silicon	0·07
Sulphur	0·040
Phosphorus	0·024
Manganese	0·53
Nickel	0·16
Chromium	0·06
Molybdenum	0·07
Copper	0·30
Tin	0·01

The boiler tube material has a basic copper content which is higher than normal. In fact, specifications for boiler tubes do not generally cover the copper content and even if a figure were specified, it would possibly be higher than 0·30 per cent. However, it is thought that this relatively high copper content can make a tube susceptible to embrittlement, particularly if exposed to excessive temperature. Such a type of failure is often referred to as 'hot shortness'.

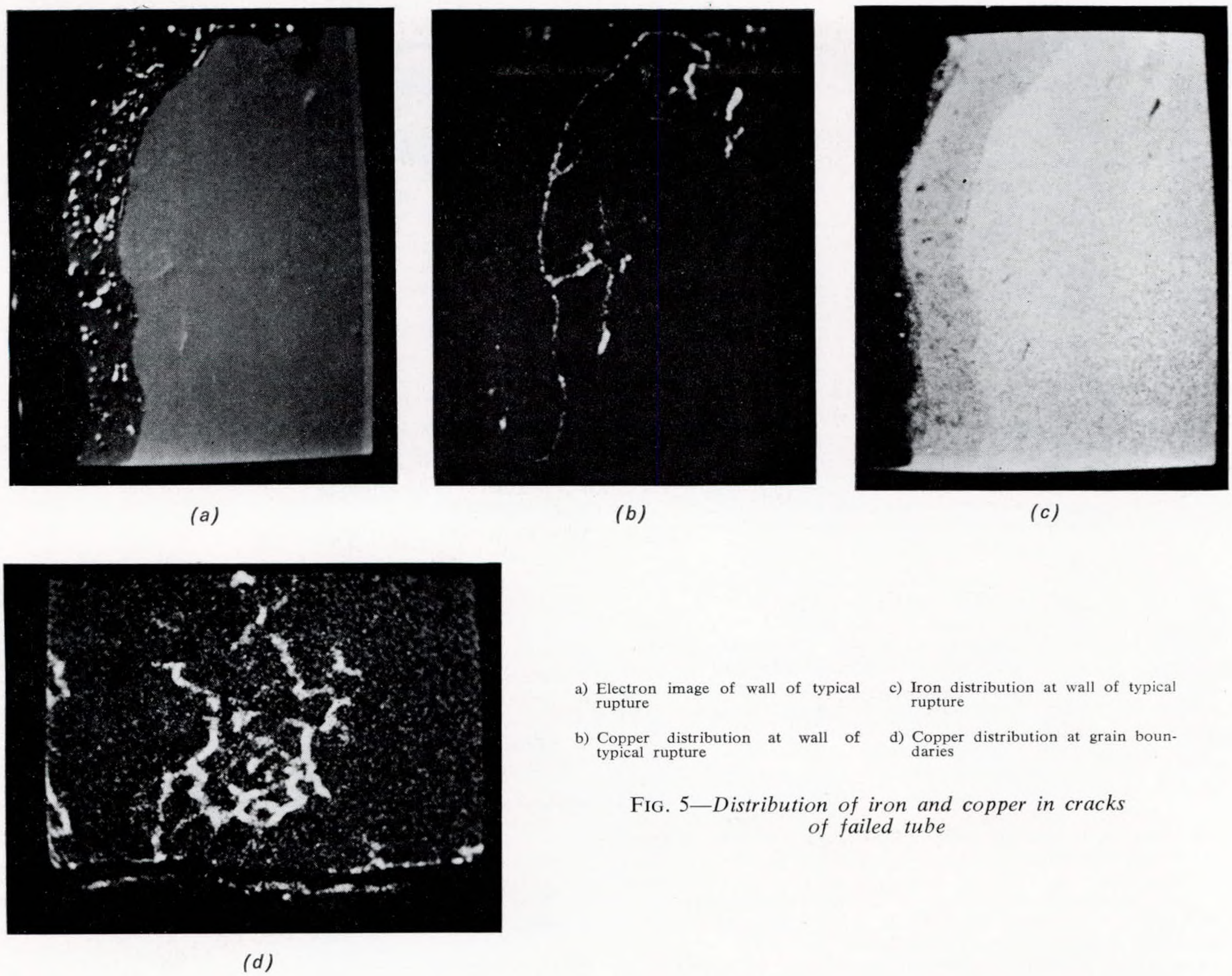
Hot shortness is normally defined as a brittleness in metal at certain ranges above normal room temperature. It is manifested by a loss of ductility and a liability to crack at the particular temperature. It is usually associated with the segregation at high temperatures of a molten or semi-molten phase in the grain boundaries. In steels, hot shortness in susceptible alloys generally occurs following exposure to temperatures in the range 1000-1300°C. The most common cause of hot shortness in steels is the presence of a certain amount of residual copper as a 'tramp' element. It appears that copper bearing steels may develop hot shortness in two ways. At high copper concentrations the solubility of the copper in the steel may be exceeded, and the copper segregates in the grain boundaries causing the brittleness. At lower copper concentrations hot shortness can develop by the following more complicated mechanism.

When the surface layers of a copper bearing steel are oxidized, the iron is oxidized more readily than elements such as copper or nickel, which will accumulate in the metallic state in thin layers adjacent to the steel. A layer of copper formed in this way can be seen in Fig. 7. Oxidation by steam and water favours the formation of copper enriched layers, and this is probably why such layers are only apparent on the inside of the tube. If at any time after the formation of this layer the steel is exposed to stress at very high temperatures then the molten copper will penetrate the grain boundaries leading to an intergranular fracture. It would also be possible for failure to occur by first exposing the steel to a high temperature so that copper penetration occurs so embrittling the steel, and then to a high stress at a lower temperature.

The pitting which is apparent on the water side appears due to deposited copper and not oxygen. Most of the pits, Fig. 7 is typical, contained deposits and corrosion products, and on top of these were particles of metallic copper. It is unlikely that this copper is residual copper from the steel, it is far more likely to be copper deposited from elsewhere in the feed system.

It may seem a remarkable coincidence that copper corrosion and deposition should occur in a boiler system in which the boiler tubes also have a high copper content, but the fact that the copper is on top of the scale in the pits means that this is the more likely explanation for the pitting. In other words pitting and embrittlement are really two separate phenomena, the only common feature being that both require the presence of copper.

So, there is a very strong case, not only to limit the copper content of the boiler tube to avoid possible embrittlement of the metal, but also to keep the copper corrosion products of the feed system out of the boiler where they could cause pitting of the boiler tubes.



a) Electron image of wall of typical rupture

b) Copper distribution at wall of typical rupture

c) Iron distribution at wall of typical rupture

d) Copper distribution at grain boundaries

FIG. 5—*Distribution of iron and copper in cracks of failed tube*

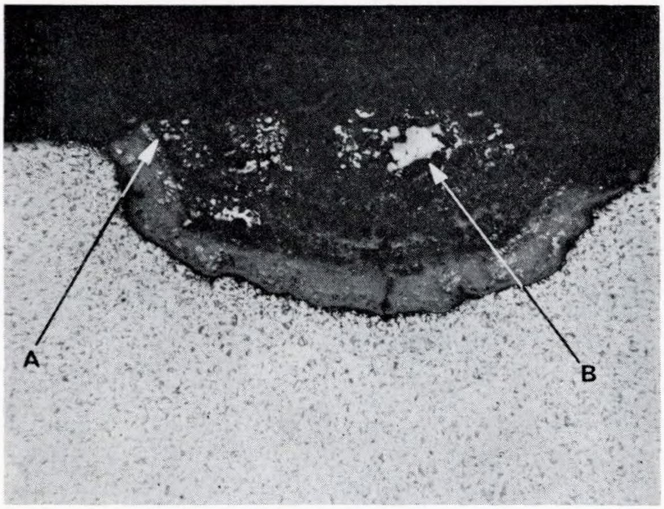


FIG. 6—*Copper deposits in the scale—typical section of corrosion pit—magnification ×75*

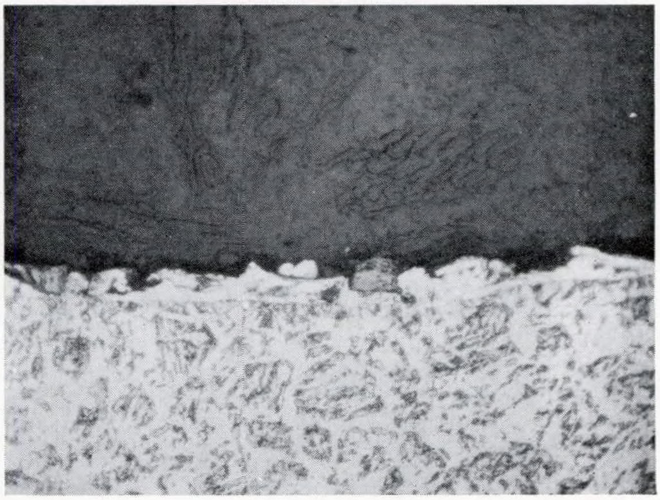


FIG. 7—*Copper layer on inner tube surface—caused by oxidation of parent metal*

Some analytical work was undertaken on a ship at sea to see what quantities of copper corrosion products were present in the feed system and to trace the source of this contamination. Table X shows the copper content detected at various points in the feed system under steady full load steaming conditions, when hydrazine was being injected into the de-aerator outlet.

TABLE X—FEED SYSTEM COPPER CONTAMINATION

Sample Point	Copper ppm	Transported to Boiler per Year Kilogram
Boiler	0·043	—
Main condensate	0·018	9·7
Drain tank outlet	0·04	3·7
Air heater drain	0·035	0·87
L.P. Heater drain	0·04	1·89
De-aerator	0·02	13·95
Evaporator output	0·20	—
Distilled water tank	0·19	—

Using the flow figures from the plant heat balance, the amount of copper transported to the boiler per year (360 operational days) was estimated and is shown in Table X. The figures tallied to a remarkable degree of accuracy. The total of the main condensate and the drain tank comes to 13·4 kg/year, whereas the de-aerator outlet gives 13·96 kg/year; such figures are well within the limits of reasonable experimental accuracy. The difference between the figures for the air heater and the L.P. heater drains and the final drain tank figure was assumed to be due to drains from the fuel oil and domestic heating circuits which were not measured. The nett conclusion was that approximately 14 kg of copper were being transported to the boiler per 360 days of full ahead steaming. During the tank cleaning operation no radical alteration in the basic pattern of copper contamination was detected. The only other possible source of copper contamination was the deck steam lines. Samples of water drains were taken from the deck steam line whilst the line was shut down; they contained up to 0·34 ppm of copper. However, it is doubtful whether any significant quantities of drains with such high copper contents would be returned to the feed system when steam was put on the line. It was concluded that the amount of copper contamination returning from the deck line was certainly no more and probably far less than the quantities returning from the feed system whilst at sea.

One of the basic causes of the copper corrosion occurring in the main feed system appeared to be the ammonia content of the steam. This ammonia resulted from the chemical breakdown of the hydrazine reserve which was being maintained in the boiler.

At one stage in the investigation, the hydrazine treatment was stopped and the hydrazine reserve in the boiler allowed to disappear.

Table XI shows the effect this had on the copper content at key points in the feed system.

After the hydrazine injection had been stopped two days were allowed to elapse, but as can be seen there were strong traces of ammonia around the system. As the ammonia levels fell so did the levels of copper contamination.

It was thought that the ammonia/copper corrosion mechanism was somehow dependent upon the trace quantities of oxygen and carbon dioxide which could exist in the condenser atmosphere. In order to try to upset this complex corrosion mechanism, it was decided to try injecting the hydrazine into the turbine cross-over pipe rather than into the de-aerator outlet. The amount of hydrazine injected was adjusted to keep as near as possible the same level of hydrazine reserve in the boiler as had been maintained when the injection was being put into the de-aerator outlet. With the hydrazine being injected into the cross-over pipe, two days were allowed to elapse before taking a further set of copper analysis around the feed system. The results of this analysis are shown in Table XII, which shows the pertinent comparisons for the condensate.

TABLE XI—EFFECT OF HYDRAZINE ON COPPER CORROSION AND AMMONIA CONTENT OF THE FEED SYSTEM

Sample Point	Hydrazine Injection			
	After de-aerator		Stopped	
	Cu ppm	NH_3 ppm	Cu ppm	NH_3 ppm
Main boiler	0·0425	0·2	0·040	0·15
Main condensate	0·0175	0·5	0·010	0·3
Drain tank outlet	0·040	0·6	0·034	0·3
De-aerator outlet	0·020	0·5	0·013	0·3

TABLE XII—COPPER CONTAMINATION RESULTING FROM DIFFERENT POSITIONS OF HYDRAZINE INJECTION

Injection Position of Hydrazine	Main Condensate			
	pH	NH_3 ppm	N_2H_4 ppm	Cu ppm
After de-aerator	8·5	0·5	0	0·018
Injection stopped	7·9	0·3	0	0·01
Turbine cross-over	9·1	0·5	0·1	<0·005

The results showed that the amount of copper in the condensate could be dramatically reduced when the hydrazine was injected into the turbine cross-over pipe. It seems that the corrosive effect of the ammonia on the copper components of the feed system is influenced by the presence of small concentrations of oxygen or carbon dioxide in the condenser. The presence of hydrazine as such in the condenser seems to inhibit this corrosive mechanism.

ACKNOWLEDGEMENTS

The author wishes to acknowledge the help received from the staff of the Analytical Services Division of the Shell Research Laboratories, Thornton, near Chester, who advised on the analytical techniques detailed in this paper.

Appendix I

BOILER AND FEED WATER TREATMENT SCHEDULE FOR MARINE BOILERS OPERATING AT 63 ATA AND 510°C

	Feed Water	Boiler Water
Alkalinity	approximately 5 ppm	$40\,^{+20}_{-0}$ ppm as $CaCO_3$
Phosphate	—	$15\,^{+5}_{-0}$ ppm as PO_4
Hydrazine	—	$0{\cdot}05\,^{+0{\cdot}5}_{-0}$ ppm as N_2H_4
pH value	$9{\cdot}0\,^{+0}_{-0{\cdot}5}$	$10{\cdot}5\,^{+0{\cdot}5}_{-0}$
Chlorides	—	maximum 50 ppm as $CaCO_3$
Dissolved oxygen	0·007 ml/litre	—
Total dissolved solids	—	maximum 400 ppm
Copper	maximum 0·02 ppm as Cu	—
Iron	maximum 0·05 ppm as Fe	—
Silica	—	maximum 4 ppm as SiO_2

The above values are obtained by the application of a simple "four point plan", that is, four desired values in the feed system each value maintained by the application of a single treatment. These would be as follows:

Boiler Water: Alkalinity—controlled by injection of caustic soda;
Phosphate—controlled by injection of a phosphate compound;
Hydrazine—controlled by the individual injection of hydrazine;
Feed Water: pH— controlled by individual injection of amine.

Note: the hydrazine should be injected into the turbine cross-over pipe at sea, and into the de-aerator outlet in port;
the amine should be injected into the de-aerator outlet;
a 5 micron filter should be fitted into the discharge line of any drain tank in the feed system;
make up feed water to pass through an ion exchange plant before entering the feed system.

Appendix II

THE DETERMINATION OF IRON IN FEED WATER

Note:

At the sampling stage sufficient hydrochloric acid should be added to render the solution 0·1N with respect to the acid (i.e. 10 ml of concentrated hydrochloric acid/litre of sample) and the sample allowed to stand 24 hours before testing.

Procedure:

Measure 200 ml of feed water by means of a measuring cylinder into a 500 ml separating funnel. Adjust the acidity of the water to 0·25N by adding 5 ml of 6N hydrochloric acid. Mix contents. Using a measuring cylinder add 10 ml of iron re-agent 1 (see notes), mix and allow to stand for a few seconds. Add 25 ml of iron re-agent 2 by means of a measuring cylinder, mix, and allow to stand again for a few seconds. Pipette 10 ml of iron re-agent 3 into solution mix and stand for 1 minute. Pipette 10 ml of chloroform into the solution, shake *vigorously for 2 minutes* and allow to stand. Filter a portion of the lower layer through a Whatman phase-separating paper into the instrument cell. Measure the optical density against pure chloroform on an Eel Colorimeter equipped with a 624 filter. Run a blank determination on 200 ml of de-ionized water and determine the optical density against pure chloroform on the Eel Colorimeter. Subtract the blank optical density from the sample optical density and relate the corrected optical density to iron content from a calibration graph, prepared by performing this analysis on standard iron solutions of known concentration.

Iron content in μg/litre = μg of iron found × 5

Iron Re-agent: (hydroxylamine hydrochloride 10 per cent *W/V*)

Prepare by dissolving 100 g of hydroxylamine hydrochloride (A.R.) in 1 litre of de-ionized water. The iron present in the re-agent is removed by adding 20 ml of bathophenanthroline solution and extracting the ferroin bathophenanthroline complex with successive 50 ml chloroform washings. Four washings are normally adequate to remove all the coloured complex. This re-agent is stable for 3 months.

Iron Re-agent 2: (saturated sodium acetate)

Dissolve 500 g of sodium acetate (hydrated A.R.) in 1 litre of de-ionized water. Remove iron present in the re-agent by adding 20 ml of iron-free hydroxylamine hydrochloride solution, then adding 20 ml of bathophenanthroline solution and extracting the ferroin bathophenanthroline complex with successive 50 ml chloroform washings. Four washings are normally adequate to remove all the coloured complex.

Iron Re-agent 3: (bathophenanthroline solution)

Dissolve 33 mg of bathophenanthroline (4, 7-diphenyl 1-10 phenanthroline) in 50 ml of industrial methylated spirit and make up to the mark with de-ionized water in a 100 ml graduated flask.

Appendix III

THE DETERMINATION OF COPPER IN FEED WATER

Note:

When sampling sufficient hydrochloric acid should be added to render the solution 0·1N with respect to the acid (i.e. 10 ml of concentrated hydrochloric acid/litre of sample) and the sample allowed to stand for 24 hours before testing.

Procedure:

Measure 200 ml of feed water by means of a measuring cylinder into a 500 ml separating funnel. Adjust the acidity of the water in the separating funnel to 0·25N by adding 5 ml of 6N hydrochloric acid. Mix contents and allow to stand for approximarely 1 minute.

Pipette 10 ml of the copper re-agent 1 (see notes) into the contents of the separating funnel and shake contents *vigorously for 2 minutes.* Allow the layers to separate and filter the organic extract through a Whatman phase-separating paper into the instrument cell. Measure the optical density against pure chloroform on an Eel Colorimeter equipped with OB10 filter. A blank determination should be made using 200 ml of de-ionized water and the optical density compared to that of pure chloroform. Subtract the optical density of the blank from that of the sample and relate the corrected optical density to copper content from a calibration graph, prepared by performing this analysis on standard copper solutions of known concentration.

copper content in μg/litre = μg of copper found × 5

Note:

(zinc dibenzyldithiocarbamate, 0·2 per cent *W*/*V* in $CHCl_3$)

Copper Re-agent 1:

Prepare a 0·2 per cent *W*/*V* solution of zinc dibenzyldithiocarbamate in chloroform. The re-agent should be prepared freshly every week.

Appendix IV

THE DETERMINATION OF REACTIVE SILICA IN BOILER WATER

Procedure:

1) Measure 100 ml of sample into a measuring cylinder and pour into a 4 oz polythene bottle;
2) Add 2·5 ml of silica re-agent 1 (see notes) to the bottle, mix contents and stand for *10 minutes;*
3) Add 2·5 ml of silica re-agent 2 and again mix contents and allow to stand for *5 minutes;*
4) Add 2 ml of silica re-agent 3, mix contents and stand for *20 minutes* prior to measuring the optical density on the Eel Colorimeter using red filter O.R.1. Carry out a blank on the re-agents + 100 ml de-ionized water and subtract the optical density obtained against pure chloroform from that obtained for the sample against pure chloroform. Read off the silica content of the sample from the calibration graph, prepared by performing this analysis on standard silica solutions of known concentration.

Notes:

Silica Re-agent 1: (ammonium molybdate/sulphuric acid solution)

Dissolve 89 g of ammonium molybdate $(NH_4)_6Mo\ O_{24}4H_2O$ (A.R.) in 800 ml of de-ionized water at room temperature (solution a).

Add cautiously 62 ml of concentrated sulphuric acid (A.R.) to 100 ml of de-ionized water in a beaker and allow to cool (solution b).

Add solution b) to solution a) with stirring, cool, transfer to a 1 litre graduated flask and make up to the mark. Store the solution in a polythene bottle. It is stable for at least three months, and if a blue colour does appear in the solution it need not be rejected until the re-agent blank becomes relatively large, i.e. 0·2 reading on the Eel Colorimeter.

Silica Re-agent 2: (tartaric acid)

Dissolve 280 g of tartaric acid ($(CHOH\ .\ COOH)_2$ A.R.) in 800 ml of de-ionized water and dilute to the 1 litre mark in a measuring cylinder. Store the solution in a polythene bottle. It is stable for at least three months.

Silica Re-agent 3: (Ansa reducing agent)

Dissolve 2·4 g of sodium sulphite ($Na_2SO_37H_2O$ (A.R.)) in 10 ml of de-ionized water. In this solution dissolve 0·2 g of 1-amino-2-naphthol-4-sulphonic acid ($NH_2C_{10}H_5(OH)\ SO_3H$ (BDH extrapure grade)). Dilute to approximately 90 ml and add 14 g of potassium metabisulphite ($K_2S_2O_5$ (A.R.)). When dissolved, dilute to the 100 ml mark in a 100 ml measuring cylinder. Store the solution in a polythene bottle. It is necessary to prepare this re-agent freshly each week.

Appendix V

THE DETERMINATION OF AMMONIA IN BOILER WATER

Procedure:

Measure 50 ml of water into a 4 oz polythene bottle. Pipette 1 ml of re-agent 1 into solution and mix contents. Pipette exactly 0·5 ml of re-agent 2 into the bottle, stopper, and again mix contents. Then pipette 10 ml of re-agent 3 into the sample solution, mix contents and quickly add 5 ml of re-agent 4. Shake contents and stand for 30 minutes ±1 minute. Measure the optical density against de-ionized water on an Eel Colorimeter equipped with a 607 filter. Run a blank determination on 50 ml of de-ionized water and determine the optical density against de-ionized water on the Eel Colorimeter. Subtract the blank optical density from the sample optical density and relate the corrected optical density to ammonia content from a calibration graph, prepared by performing this analysis on standard ammonia solutions of known concentration.

Re-agent 1: (ethylenediaminetetraacetic acid disodium salt 6 per cent *W*/*V*)

Dissolve 30 g in approximately 400 ml of de-ionized water and dilute to 500 ml. This solution is stable for three months.

Re-agent 2: (acetone A.R.)

Re-agent 3: (sodium phenate solution)

Add 25 ml of re-agent 5 (5N sodium hydroxide) to 12·5 g of phenol in a beaker. Transfer to a 100 ml graduated flask and make up to mark with de-ionized water. This solution should be sealed tightly and stored in the dark. We have found it to be stable for three days but it is advisable to prepare freshly each day.

Re-agent 4: (sodium hypochlorite aqueous 1 per cent *W*/*V* available chlorine)

Re-agent 5: (sodium hydroxide 5N)

Dissolve 200 g of sodium hydroxide in water (*CAUTION*). Cool rapidly to room temperature, transfer to a 500 ml graduated flask and dilute to the mark with de-ionized water. Store in a tightly sealed polythene bottle. When stored in the dark the solution is stable for one month.

Note 1:

Sodium hypochlorite solution is available commercially containing 10 to 14 per cent *W*/*V* available chlorine. This concentration of available chlorine can vary considerably and must be checked by determination of the available chlorine (the iodometric method is suitable).

Discussion

MR. T. KAMEEN, M.I.Mar.E., endorsed the author's views regarding individual dosage of specific chemicals according to the conditions of the water at the time of testing but was not entirely in favour of mixed or blended dosing, although this probably had advantages when skilled staff were not available.

He suggested that more emphasis should have been given in the paper to pre-commissioning cleaning of the whole steam/water system, the importance of which could not, in his opinion, be over-stressed. Many problems encountered in the operation of boilers were associated with the plant in the shutdown condition; had the author any experience of simmering coils where a head of steam could be retained in the boiler and so assist in obviating in particular, oxygen attack?

The author had suggested the use of anti-foam and coagulating agents; as such materials were of quite varied composition was it possible that adverse side effects could occur when using those agents? With regard to oxygen in feed water, the author had suggested that excessive quantities of hydrazine were required to provide enough ammonia to raise the pH to about 8·0—his companies experience was that with normal hydrazine treatment little or no difficulty was found in maintaining the pH between 8·5 and 9·0. He was unfamiliar with the concept that hydrazine should be injected into the cross over pipe and would like to know if the author had much experience of this. Were there any dangers involved? His companies experience had shown that the important factor was to ensure injection of hydrazine at a point in the system which was hot enough to ensure complete dispersion; he would have thought that the suggested method might have serious repercussions on non-ferrous parts of the L.P. turbine and condenser.

He thought that conductivity cells should be used as an indication of the rate of change and not so much as an exact measure of contamination.

Where did the author think silica contamination was coming from? He had always been of the opinion that copper in boiler deposits came from the feed system and was in such relatively small quantities in the steel as to be ignored. His company had always associated ammonia with the reaction.

The paper suggested that when hydrazine dosage was stopped for a short period, a reduction in ppm of ammonia in the feed system was noted, together with a reduction in the amount of copper which, in effect, confirmed that the attack on the copper in the system was due to ammonia being present together with oxygen and/or CO_2. A total T.D.S. figure of 400 was quoted in the paper, yet if one totalled the recommended maxima for other chemicals the T.D.S. was well below 400; which did the author think the most important?

Finally, from the paper there would appear to be a tendancy to make steam plants chemical laboratories—he knew this was not the intention, but was considering the situation of a ship's officer confronted with toxic chemicals and such materials as amines, monocyclohexylamines and morpholines.

CAPTAIN R. M. INCHES, R.N., M.I.Mar.E., endorsed the idea behind the author's paper. The Royal Navy had been using marine boilers with operating conditions as therein described for about ten years, and had confirmed that, as compared with previous requirements, feed water treatment had to be re-thought both quantitatively and qualitatively. Qualitatively the treatment had to be related much more precisely to the disease; quantitatively, the total dosage must be kept to a minimum.

The Royal Navy had transferred from the use of U.S. Navy boiler compound to the type of treatment described in the paper: the former had a relatively high alkaline content which might have influenced the final decision of the navy to use the phosphate compound, tri-sodium phosphate, rather than that mentioned by the author. How had the author's company made their selection?

Oxygen scavenging was only applied to fossil fired boiler systems working at even higher pressures than those mentioned: he did not disagree with the author, for when they had used hydrazine they had been very satisfied with its performance. Could the author confirm a row heading in Table II—ppm—which he assumed referred to chlorine?

He understood that in Table VI the contamination was below the acceptable limit, even without the filter. Would the author expand on what this table referred to and further explain the addition of the filter to the system?

The information on copper corrosion was of great interest and whilst he accepted the content of this section, he thought it a good idea to inject the hydrazine where it was most efficient before it went to that part of the system where it was liable to be broken down.

He recalled reading some time ago that there was a kind of temperature threshold for copper corrosion at a temperature of about 80°C. He deduced from this that for parts of the feed system normally running above that temperature, copper bearing materials should not be used. This seemed an effective method of dealing with the problem.

Could the author comment on this?

On the whole, naval experience confirmed the values in relation to the figures in Appendix I. They had kept a slightly higher phosphate level, perhaps because of the use of tri-sodium phosphate. The maximum for T.D.S. was, in fact, higher than that quoted, but once a feed system had settled down, it was thought it should be possible to run at a substantially lower figure, about 250. He was of the opinion that unless the average T.D.S. in a system could be brought down to somewhere near half the maximum quoted, there was some reason for concern.

MR. D. COCHRANE, M.I.Mar.E., said as there was a fairly wide-spread tendency to add hydrazine to the condensate to maintain pH 9, without giving due regard to copper pick-up, he welcomed the authors detailed study on the necessity of controlling the use of hydrazine to minimize corrosion of non-ferrous metals.

A recent case had concerned boiler tube failures on a series of similar ships, in which samples of sludge and scale on tubes showed 50 to 70 per cent copper oxide. Investigation revealed high oxygen and resultant high pH in the feed water system, due to the addition of hydrazine. This caused corrosion of non-ferrous heater tubes, eventually leading to deposits on the boiler tubes, promoting electrolytic corrosion, over-heating and eventual failure.

A chemical cleaning programme was now being instituted on each of the shops to include a copper removal process.

The transport of copper to boilers appeared to be gradual and take place over a number of years before the effects became obvious: this transportation was becoming increasingly associated with boiler tube corrosion and failure. Others, including the author, had drawn attention to high copper content areas in mild steel tubes where pitting had occured in service.

Until recently, affects associated with the presence of copper were considered more common with the higher pressure range of boilers such as those used in power stations, but over the last 12 months he had known of six large marine boilers which had required chemical cleaning using a copper removal process. One notable side result had been the elimination of phosphate hide-out which had previously been experienced.

Regarding the authors detection of refractory debris causing silica deposit on turbine blading, had pre-commission cleaning been carried out on that particular installation? During pre-commission cleaning problems there were opportunities for inspection when debris was usually detected. This debris could be removed by:

a) after alkali boil-out;
b) following neutralizing of the acid process.

The author had stated that successful water treatment could only be the sequel to successful commissioning; Mr. Cochrane submitted that successful commissioning was the sequel to effective pre-commission cleaning. Its purpose was to remove traces of surface rust and loose mill-scale and to establish, in the passivation process, the first fine magnetite protective film. It was a natural prelude to the boiler commissioning programme which should follow immediately.

The author had not specifically mentioned chemical pre-commission cleaning. When properly planned, pre-commission cleaning dovetailed with the commissioning programme, and would reduce the vast amounts of colloidal Fe_3O_4 in suspension which the author had experienced. Mr. Cochrane thought that this set a high initial standard of cleanliness and was well worthwhile. The hydrazine passivation which was part of the process, established the first Fe_3O_4 magnetite film to protect the boiler metal.

It was recommended that pre-commission cleaning should include boilers, feed system pipework and steam pipework.

In 12 years experience of pre-commission cleaning of marine boilers he had noticed an improvement in construction cleanliness standards; but occasionally welding rods, machine cuttings, weld paper shields and general debris were still found in a number of boilers. The sludge which was found in the boiler bottom headers after cleaning usually contained about 10 per cent silica and 90 per cent Fe_3O_4.

The author had emphasized care in maintaining contaminent levels below the specified limits—obviously this could only be carried out by testing for silica, iron and copper. Such tests took about 30 minutes each under laboratory conditions. How frequently would the author recommend testing, considering the incidence of failures attributed to contaminants and (probably equally important) the already multifarious duties of hard-pressed ships' engineers?

The 1968 revision of BSI 1170 recommended these tests be taken every three to six months. Would the author give his views on this?

In connexion with BSE 1170, the 1968 revision was made when data on marine boilers in the pressure range covered by the author was comparatively scarce and it included for the first time reference to hydrazine and amines. It was noted that the figures in Appendix I generally coincided with the 1968 revision of BSI 1170—Table V—which covered 'recommended boiler water characteristics' 60 bar up to and including $8\frac{1}{4}$ bar (850–1200 lb/in²).

Would the author comment on any comparison?

MR. R. SUNDBY said judging from experience of high pressure stationary steam plants it was to be expected that similar recommendations would become an accepted standard by boiler manufacturers, boiler chemical suppliers, ship owners and builders and turbine manufacturers as well as such organizations as The British Standards Institution. A co-ordination of the feed water treatment recommendations of the groups mentioned was of utmost importance for the safety and availability of high pressure steam plants (50 bar and higher) and should be brought about as soon as possible.

The problem of commissioning new boilers needed further investigation; the aim of this work should be specific recommendations for the commissioning periods of new boilers as well as starter periods of older boilers after longer periods of standstill.

He thought that the author's remarks on boiler water treatment methods should be emphasized. Separate simple chemicals should be used preferably; the use of codes in the water analysis reports should be avoided unless the code was clearly explained in the instruction manual; the chemicals used should be clearly specified; the use of sodium carbonate should be avoided as the CO_2 gas produced gave corrosion risks in the turbine and condensate system.

Additionally, emphasis should be placed on external water treatment, i.e. purification of make up water and condensate, in order to minimize the need for internal water treatment, i.e. boiler chemical addition.

The problem of silica contamination was normally as stated, solely a commissioning problem. However, the risk of silica deposits in the turbine during normal running should not be overlooked as this risk increased not only with pressure but also with decreasing alkalinity and salt content. The silica content in high pressure boilers should therefore be checked regularly.

Condensate filtration for the removal of iron oxide particles should be recommended as a standard.

Some modern recommendations gave lower maximum allowable iron contents in the feed water than the 50 ppb mentioned in the report. One boiler chemical manufacturer, for example, gave a maximum value of 10 ppb.

The serious effects of iron oxides reaching the boiler had been mentioned and it should be added that iron oxide deposits in the turbine gave other negative effects and being water insoluble were very troublesome to remove.

The investigation into the variation in copper contamination with the ammonia concentration in the system was very valuable. Copper, although being mainly a boiler problem, might also, under certain circumstances, be transported to the turbine and cause corrosion attacks.

In connexion with the effect of high ammonia concentrations, the increase in copper contamination was not the only negative effect as ammonia could cause stress corrosion cracking in mechanically stressed brass components like the condenser tubes. There was a significant risk of stress corrosion cracking in the air cooler part of the condenser where ammonia and oxygen were present; even when the ammonia concentration in the condensate was below 1 ppm NG_3. The risk of stress corrosion cracking would also decrease when hydrazine was injected directly in the steam.

The reported results of hydrazine injection in the steam were interesting. It was, however, doubtful whether the recommendation to inject all the hydrazine in the steam was the best solution. It would probably be easier to balance the hydrazine reserve and the ammonia concentrations throughout the system by injecting hydrazine in the steam as well as in the feed water. One factor which would affect the choice of injection points would be the degree of chemical filtration of the condensate.

Which type of hydrazine was injected? Had the author compared activated and conventional hydrazine?

Activated hydrazine would probably be beneficial when injected directly in the steam, since the reaction rate of activated hydrazine would be significantly higher than that of conventional hydrazine at the low temperatures in the condenser.

MR. D. SHORT, thought that chemical cleaning of marine boilers was an important ancillary to correct boiler feedwater treatment; correct pre-service cleaning of boilers would certainly prevent the type of silica deposits that were currently being observed on turbines. Normal cleaning cycles involved treatment with both alkali and acid and this combined with adequate flushing between stages would remove all the debris which was the principal cause of the turbine silica deposits.

Regular in-service chemical cleaning was also important for marine boilers. Copper removal could be effected by well defined methods which involved the use of an oxidizing agent in ammoniacal solution. It was to be noted that the latter solution was also present in the condenser and feed system of a boiler during its normal operation, although in concentrations far lower than for cleaning; as such it was not difficult to understand why copper was slowly transferred to the boiler.

It was interesting to note that Mr. Sunby had referred to the possible use of activated hydrazine. This chemical would be more suitable in idle boilers where corrosion resulting from the presence of dissolved oxygen was greater than when the units were working normally. It was felt that the importance of maintaining non-corrosive water conditions at all times in the life of a boiler, particularly a single marine boiler had not been stressed sufficiently. The procedures to be adopted during a boiler's downtime were not well defined and as such, investigation into the use of newer products such as activated hydrazine was worthwhile.

By which method had the turbine blades been freed of silica deposits? It would be ideal if such deposits could be removed *in-situ* by a chemical method, but it was probable that mechanical cleaning had been undertaken.

MR. C. W. DUKES, M.I.Mar.E. said in connexion with the hydrazine injection system described, in view of the rate of oxygen scavenging in the feed system being extremely slow—at least prior to the de-aerator— it was doubtful if in the low temperature phase of the condensate system any scavenging took place. Had experiments with hydrazine injection into the turbine cross over pipe (which had had the effect of reducing the copper content in the feed) been carried out using an activated hydrazine which could scavenge oxygen at much lower temperatures than ordinary hydrazine? If not, it seemed reasonable to reduce feed system corrosion even more by the use of activated hydrazine.

With regard to the use of a volatile amine in conjunction with hydrazine to raise the condensate pH value and so provide CO_2 scavenging, it would appear from normal boiler and feed water tests that the pH value of the feed obtained would be due to ammonia and amine, and without elaborate testing it would not be possible to determine the degree to which the pH was being affected by each component. Would the author comment on this?

In view of the difficulties associated with ammonia in the feed system when using hydrazine, had the author considered a system where only a volatile amine was used to the feed and any excess oxygen which might pass to the boiler was dealt with in the boiler water by maintaining a small reserve of tannins known for their oxygen scavenging properties.* This system would eliminate difficulties with ammonia but still provide for CO_2 scavenging and raising of the feed water pH.

There was also some basis for believing that with such a system the silica problem would be reduced and feed system contamination detection somewhat simplified. Caustic would still be used for alkalinity control of the boiler water.

The use of hydrazine tended to give an initial high pH to the condensate as compared with amine which had a much better distribution ratio, and therefore the use of amine on its own to the feed system would ensure a more uniform and stable pH value throughout the feed system.

Finally, he agreed with the author's comments on not using a single powder treatment for phosphate and alkalinity control in the system as this invariably meant that separate compounds had still to be added from time to time to adjust values, thus defeating the origional idea of simplicity put forward in favour of a single compound treatment.

Mr. A. N. S. Burnett, M.I.Mar.E., asked the author how his company ensured cleanliness in the shipyard during machinery installation. How would a smaller company cope with this operation?

Regarding the maintenance of those standards put forward by the author in connexion with high pressure boilers, how did his company ensure that those standards were maintained on every ship? In his experience the wrong chemicals had been used on occasions because of their similarity in appearance.

Mr. Burnett hoped the author could give some idea of the time out of service if any of the faults which he indicated occurred, and if so, what were maintenance cost limits?

On the question of pH meters, were these in use by the author and his associates, and if so of what type were they?

Probably a number of shipowners wanted to change from Diesel to steam in their large ships, but were hampered by the fact that staff were familiar with Diesel operations. How did the author think that conditions were going to change in a short space of time for this complicated structure, whilst maintaining a high standard of service in ships?

Would the author outline whether he and his company would consider a simplification of what appeared in the paper or would he advocate going ahead with the complicated routines on board ship? Would he prefer to see simpler installations with simpler feed water treatments?

Mr. R. E. Knowles, M.B.E., M.I.Mar.E., asked if it was not important in the case of high pressure units to select for example the right kind of tube? Had the author, in the light of his experience on boiler water treatment, any opinion on the use and comparativeness of cold finished seamless, hot finished seamless or electric resistence welded tubes? It would appear that the cold drawn seamless tube, annealed properly, such that a strong stable oxide film was retained on the water surfaces, was more suitable to sustain the kind of treatment referred to in the paper than perhaps hot finished seamless or ERW tubes.

The author's remarks about keeping subsequent examinations of the boilers to a minimum, was, of course, dependent on the standard of treatment carried out, notwithstanding of course that whilst certain inspections were mandatory it was really a question of good housekeeping as to the degree of intermediate inspections the owner of the ship considered necessary.

The argument in favour of the preferential use of caustic soda as opposed to ammonia based compounds was interesting. Investigation into boiler explosions on land brought to light the phenomenon known as hydrogen embrittlement where, on occasion, full section tube wall failure had occured, particularly when ammonia had formed part of the feed water treatment.

Phosphate compounds, whilst inhibiting hardness, could also be troublesome and, even though anti-foaming compounds were added, there had been evidence of interference with water level and indicating devices due to the build-up of sludge.

The need for a highly efficient de-ionization plant with a highly rated water tube boiler installation could not be overstated. If, and when, nuclear ships became more commonplace, such plants would be an absolute necessity.

He recalled a particular vessel, *Savannah*. This ship had a highly sophisticated de-mineralizing and de-ionization system dictated by the need to ensure that the water in the primary circuit was not at any time contaminated with sea water, stainless steel being susceptible to chloride cracking when under stress.

The section on copper was very interesting and one wondered to what extent copper infusion had a bearing on boiler failures in the past, particularly when ammonia was present in the feed water. That copper based fittings were not used in ammonia refrigerators was indicative of the incompatibility of those two substances.

Finally, was there a similarity in what had been known to be hydrogen embrittlement and copper indicated embrittlement?

Mr. G. S. Solt commented on the increased sophistication in boiler pressure techniques which was bringing land-based and marine-based problems closer together. He thought closer co-operation between the two industries desirable. The point of the discussion had been that absolute purity in boiler feed water could be maintained by clean manufacture; by chemical cleaning before commissioning and by clean-up in the circuit itself, in particular by the use of a high class deaerator and by the treatment of the distillate and of the condensate. All this cost money, but, within reason, paid off. One of the most extreme examples was shown by a gentleman in North Germany who maintained that he would put nothing in his once-through boilers but water. He would not use any chemicals, hydrazine or phosphate or anything else; however he had a huge de-ionization plant and the performance of his boilers was remarkably good. By improving the quality of the boiler contents it was generally possible to avoid a great deal of trouble.

Was Mr. Owen being sincere when he said that he did not foresee marine boilers going to higher pressures?

Mr. Solt suggested that the major impurities in boilers arose during and shortly after commissioning; the silica problem was short term and so was that of iron contamination and therefore it would be possible to provide temporary clean-up plant which might be used only during primary commissioning and again after a major shutdown when corrosion problems had taken place during the shutdown.

Finally, on the difficulty of analysing iron, it was possible to monitor iron by a membrane filter—a Millipore filter. A

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* Certain tannins were also known for their film forming properties and could form and maintain a film in the water spaces of the boiler which was highly resistant to corrosion.

trade name was the best known, but there were other perfectly good membrane filters which gave an easy estimation of the amount of iron in a boiler water.

MR. G. VICTORY, Member of Council, I.Mar.E., and the chairman of the meeting, asked if enough was being done to obviate the need for treatment to remove boiler deposits? For example, on the question of iron content resulting from cargo pumping steam systems entering the system at the atmospheric drain tanks, was that reasonable in present times? Considering the difficulties of assessing condenser leakage, should condensers be made in the way they were at present? Should it be possible to have a leakage in a condenser, or should the outlet tube be supported in such a way that the support permitted an inspection? The first time he had come across migration with iron and copper was in 1950, so this problem had been present for 20 years and his company had found that the C.E.G.B. was able to show that their treatment did produce much better results than the previous type of purely chemical treatment.

Correspondence

MR. B. TODD, M.I.Mar.E., in a written contribution said he was interested in the comments made by Mr. Owen regarding the presence of copper in intergranular cracks in boiler tubes, as he had investigated similar failures in high pressure marine boilers and found similar copper-filled cracks.*

Initially, he had favoured the theory of intergranular cracking due to the concentration of copper in the sub-scale during hot working but rejected this for the following reasons:

a) such cracking would be related to the high temperature austenitic grain size and not the ferrite and pearlite structure produced when the steel was cooled after working. From Fig. 4 the cracks appeared to follow the ferrite and pearlite grain boundaries;

b) copper-filled cracks should be present in other parts of the tube apart from the area of failure. In the case of the tubes he had examined no such cracks could be found. Did Mr. Owen find such cracks in the cooler, less heavily stressed parts of the tube?

c) there were many cracks in the region of the failure but only a few of these contained copper.

Further investigation showed that cracks only occurred in regions of high heat flux and it seemed more likely that the cracks were caused by stress corrosion due to concentrations of sodium hydroxide on the tube surface produced by overheating. Careful attention to combustion conditions reduced the frequency of failures.

Had the failures the author mentioned occurred in areas of high heat flux?

Whilst copper-containing steels were prone to cracking during hot working this tendency could be counteracted by adding small amounts of nickel and a nickel/copper ratio of 1:2 was normally sufficient. The analysis of the tube given in Table IX showed that a nickel content of about this amount and this steel would not be particularly prone to hot cracking.

In discussing copper pick-up in condensers no distinction was made between the alloys normally used in marine condensers in their tendency to corrode in ammoniacal condensate but it was likely that real differences did exist even though data on this was sparse. Tests carried out by Tice and Venizelos† showed average corrosion rates (mils per year penetration) of 1·9, 1·0, and 0·35 for aluminium brass, 90/10 cupro-nickel and 70/30 cupro-nickel respectively, in a solution containing 500 ppm of ammonia. These corrosion rates increased when carbonate was added to the solution. Although this solution was much higher in ammonia than the feed-water, it might approximate to the composition of ammonia in condensate in the air extraction section of the condenser where incondensable gases accumulated and where use of alloys of higher resistance to condensate attack was warranted. In this connexion, whilst agreeing with the remarks of Mr. Sunby on stress corrosion cracking of tubes in ammonia he would emphasise that these referred to brass alloys. The cupro-nickels were not susceptible to stress-corrosion in ammoniacal environments and this was one factor which often lead to their selection for condenser tubes in ships with hydrazine biler water treatment.

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* B. Todd. "The Metallurgist in the Shipping Industry" The Metallurgist. December. Vol. 3, No. 12.

† E. A. Tice and C. P. Venizelos. "Corrosion Behaviour of Condenser Tube Alloy materials". Power, November 1963.

Author's Reply

Mr. Owen said he agreed to a certain extent with Mr. Kameen's remarks concerning boiler water chemistry. It was true that ship's engineers did not need to have a detailed knowledge of boiler water chemistry in order to apply the daily treatment. However, he believed that it was wise to make the detailed chemistry available to those engineers who were interested enough to study it. There was little doubt that in the event of an emergency, the engineer with some chemical knowledge would be in the best position to take corrective action.

He agreed that pre-commission cleaning was all important if correct boiler water conditions were to be easily established and possibly he had not emphasized this as much as he should have done. As far as possible, the pre-commission cleaning should include not only the boiler, but all the feed system pipework and the distilled water storage tanks. The objectives of the cleaning should be to purge the system of all loose iron oxides, refractory material and so on. The commissioning must be carefully planned and it was logical that the final sequences should involve raising steam on the boiler and the controlled establishment of the protective magnetite oxide film. Mr. Kameen had mentioned the subject of the preservation of the auxiliary or reserve boiler when it was shut down. This problem was particularly applicable to many of today's very large tankers fitted with only one main boiler; on such ships it was to be hoped that the reserve boiler would spend much of its life in the shutdown condition.

The author had not had any experience of the simmering coils mentioned by Mr. Kameen, nor did he suspect that they would be particularly effective for long periods. Instead he proposed a "circulating wet lay-up system". This involved taking a supply of hot de-aerated water from the de-aerator outlet and passing it *via* suitable lines to a special connexion on the superheater of the shutdown boiler. This water should be allowed to fill the superheater and flow into the steam drum; a further special connexion on the water drum returning the water to the feed system, usually *via* the atmospheric drains tank. Obviously, precautions should be taken to ensure that the superheater and the steam drum were full of water and not air-locked. This system had several advantages over other non-circulating systems. It required no attention from the ship's engineers, provided that the normal feed water treatments were being observed, then the de-aerated hot water with a slight hydrazine reserve, which was available at the de-aerator outlet, effectively protected the laid-up boiler, which in fact became an integral part of the feed system. The boiler was also ready for instant use, if required, the circulating water flow might be increased from its normal rate of about 100 gallons/h in order to warm through the boiler ready for raising steam. The author was of the firm opinion that a "circulating wet lay-up system", as described, was far superior to any dry or static wet lay-up system.

Mr. Kameen had mentioned, as had other contributors, that he had found no difficulty in raising the feed system pH to between 8·5 and 9·0 when using hydrazine. The author agreed with this, but thought that whilst this was possible, it was not altogether wise. In view of the dangers of using excessive amounts of hydrazine, it seemed wiser in his opinion, to regard hydrazine only as an oxygen scavenger and to use amines as pH improvers. Concerning the injection of hydrazine into the turbine crossover, the author could only claim about one year's experience with this practice, but during this time it had never given rise to any problems and none were anticipated.

Several contributors, had questioned the source of the silica contamination found in marine boilers. The main source of this contamination was from the insulating materials used around the engine-room. Since the use of asbestos was now restricted, silicate materials were being increasingly used, and inevitably these materials found their way into the feed system during the construction period; silicate materials were also used to form the cores, etc. during the casting of the valve bodies in the feed system. This was a further source of silica. All these products tended to be swept back to the boiler during the first few days of steaming.

Captain Inches had raised several issues, including the question of which phosphate compound to use. This subject of phosphate selection was rather complex and was unfortunately often influenced by economic as well as scientific issues. Basically, however, it depended on what was required from the phosphate. In the author's view, it should only be used to combat hardness salts which entered the feed system due to condenser leakage, and in this case the monosodium phosphate was adequate. If alkalinity was also required, then trisodium phosphate would be a better choice.

Captain Inches, in common with other contributors, had raised the subject of Table IV. It was true that even before fitting the filter, the degree of iron contamination was nominally below the generally accepted industrial standards. The point here, was that whilst this was true, it had been found that the level of iron contamination fluctuated violently and could rise suddenly if some machinery were started up, thus causing a sudden increase in the quantity of drains returning to the atmospheric drains tank. This increase was caused in part by the agitation of iron corrosion compounds which tended to settle to the bottom of this tank when only nominal amounts of drains were returning. So, the real purpose of fitting the filter was to prevent these larger quantities of iron corrosion products being carried into the feed system as a result of any feed system disturbance. Of course, there was also the advantage that they lowered the normal level of feed system iron contamination.

Captain Inches had questioned Appendix I, particularly the reference to the total dissolved solids level in the boiler. The author had only intended that those parameters marked with a tolerance should be used as control values. The remaining parameters, such as chlorides, T.D.S., were marked with maximum values, which should not be exceeded under any circumstances. Clearly, under normal circumstances, the level of chlorides should be well below the maximum permitted value, and likewise for T.D.S.

Mr. Cochrane had raised the subject of phosphate hide out. The author's opinion was that phosphate hide out would not occur in a healthy boiler, but would very likely occur in a boiler in which copper corrosion cells existed. In fact, the appearance of phosphate hide out could be regarded as a sure sign that corrosion was occurring. Concerning the frequency of testing for silica, iron and copper, the author agreed that these tests should be regarded as laboratory tests and would suggest that ships should land suitably packed samples for testing at approximately four-monthly intervals.

The comments by Mr. Sundby were particularly welcome, as they represented the thoughts of a major turbine builder on the subject of boiler water treatment, which perhaps would serve to emphasize that boiler water treatment was a subject which influenced not only the boiler but also the turbine. The author agreed that the manufacturers of boiler water treatment compounds should give more thought to naming their products. Mysterious names and codes did not help the superintendent or ship's engineers to understand exactly what a product was supposed to do. Nor were frequent changes of name very helpful; one manufacturer had, for instance, changed the names of his products at least two times in as nearly as many months. Mr. Sundby had also mentioned the subject of ammonia stress cracking in condenser tubes. It was quite true that this could occur, particularly in the air cooler sections of the condenser where high concentrations of ammonia would exist, even when the ammonia level in the condensate was below 1 ppm. However, it must be pointed out that only brass based tubes were liable to such cracking; cupro-nickel tubes were not. The author appreciated Mr. Sundby's comment on the position of the hydrazine injection and agreed that his suggestion to inject the hydrazine in two positions, so enabling a balance to be kept throughout the feed system between the hydrazine and ammonia concentrations, was technically sound. However, from the point of view of simplicity the author still felt his recommendation was correct. That was, hydrazine should be injected into the turbine crossover pipe whilst at sea and into the de-aerator outlet whilst in port.

Both Mr. Sundby and Mr. Short had mentioned activated hydrazine. This was hydrazine to which a catalyst had been added so lowering the temperature at which the hydrazine would actively scavenge oxygen. The author's opinion was that such activated hydrazine could be of use for the protection of laid-up boilers, but even for these boilers a circulating wet lay-up system, as already described was preferable. For normal use plain hydrazine was not only acceptable but preferable, because when injected into the turbine crossover pipe the hydrazine remained semi-dormant in the feed system and only reacted vigorously after the temperature had been raised in the de-aerator. In this fashion, the bulk of the oxygen was removed by the de-aerator, and the hydrazine only had to remove the traces that remained. Consequently, the amount of hydrazine required was kept as low as possible. This was surely a good thing.

Mr. Dukes questioned how it would be possible without elaborate testing to determine how the pH of the feed system was being influenced by the amine and the ammonia (which resulted from the hydrazine injection). The simple answer was that it was impossible to determine. However, the author's contention was that hydrazine should only be used to scavenge oxygen, so if the minimum detectable reserve was maintained in the boiler, then the feed system pH would be influenced very little by any ammonia, so the bulk of the feed system pH correction would then be achieved by amine injection.

The use of tannins would, the author thought, always be regarded in these modern times with some scepticism; their mode of action was not clearly understood, and it seemed wiser to stick to conventional chemicals whose function could be clearly defined.

Mr. Burnett had raised the question of pH meters. It was a fact that if feed water treatment techniques as described by the author were to be followed then an accurate, reliable pH meter was essential. The ships to which the author referred in his paper were fitted with continuous in-line recording pH meters of varied manufacture. Whilst they generally performed satisfactorily they did need repeated servicing, no one type of meter being better than another in this respect. In view of this, it might be wiser to consider using a laboratory type pH meter which would be used for making spot checks on the feed system at the same time that the normal boiler water tests were made.

Mr. Todd's written contribution was exceptionally interesting and the author valued his comments. When examining failed boiler tubes, it was a matter of obtaining as much chemical evidence as possible, and then finding a theory which fitted all the facts. On reading Mr. Todd's contribution the author had to admit that stress corrosion cracking was certainly a possibility, but on balance the author still favoured his own theory for the following reasons. In general, the failures of the type shown in the paper had occurred in overheated tubes, but the overheating in all cases had been so quick that stress corrosion could hardly have been the cause of failure. Whilst the author had not examined every crack in every failed tube, in fact every crack probed had contained some copper. The author still maintained that whilst the prime cause of failure was overheating, and/or over-stressing, the true reason for the failure was the intergranular copper structure. Surely, if a normal boiler tube was subjected to a nominal degree of overheating for a brief period then failure should not occur; if it did occur then there was a definite reason for the failure, and in the author's opinion from the evidence shown in the paper, intergranular cracking due to the copper concentration was a prime cause of such failures.

Related Abstracts

Westinghouse Simplified Steam Plant

In the past, the responsibility for steam plant design has primarily resided with design agents and shipyards. Standard industry practice has been to manufacture what was asked for. Over the last decade, however, major changes have overtaken the marine power industry. This is the age of competing propulsion plants and it has become clear that the major burden of the competition now rests with the machinery designers. Westinghouse has recognized this challenge and is taking positive steps to meet it.

The article represents a brief synopsis of the highlights of a recently-completed study concerned with simplifying marine steam propulsion plants to achieve minimum life cycle costs while providing maximum reliability and maintainability.

Two basic power plants have been studied:

1) A single-shaft power plant rated at 50 000 shp. With small modifications, any power in the range 40 000 to 70 000 shp can be provided. The single-shaft plant is suited to large tankers, and large container ships in the 25-knot speed range. For this plant, the reduction gear is specially tailored to the requirements of the application.
2) A two-shaft power plant rated at 120 000 shp. Lower ratings to 80 000 shp and higher ratings to 140 000 shp are possible. This plant is suited to large container ships in the 30-kn and upwards speed range.

Both plant designs incorporate a number of features which, though standard in other applications, are new to the marine industry. Westinghouse believes these features will significantly enhance the reliability and performance of steam propulsion plants.—*Davis, A. W.: Marine Engineer and Naval Architect, November 1970, Vol. 93, pp. 538–540.*

255 000 dwt Tanker

The first of three supertankers to be built for Texaco Overseas Tankship Ltd. by the Odense Steel Shipyard Ltd., is nearing her completion and was christened *Texaco Denmark* at the Lindo Department of the builders.

With a deadweight of about 255 000 tons, the vessel is the biggest so far from any Scandinavian shipyard and is built as a single-screw tankship under the supervision of American Bureau of Shipping to Class A1 (E) "Oil Tanker" Pt. Higher Tensile—✠ A.M.S.

The vessel has one continuous deck and all accommodation and machinery is arranged aft. The cargo section is divided into five centre tanks and five wing tanks each side, by two longitudinal and six transverse oil-tight bulkheads. The aftmost wing tanks have sludge tanks and No. 2 port and starboard wing tanks are used exclusively for water ballast. Water ballast is also carried in the forepeak.

In addition to the machinery space, the main pump room, wing tanks for water ballast and fuel oil, lubricating oil tanks and fresh water tanks are also arranged aft together with afterpeak for ballast water, steering gear compartment and storerooms.

Of all-welded steel construction, the vessel is longitudinally framed with all longitudinal strength elements being continuous. Special high tensile steel plates are used, allowing a reduction of plate thickness.

The superstructures and casings are of all-welded, well stiffened construction with built-in web bulkheads as an extension of casing sides and strong girders to prevent vibration.

The cargo oil tanks are provided with oil-tight hatches with coamings of 32 in height, while breakwaters afford protection to the cargo oil manifolds and the aft deckhouse.

Propulsion is by a Stal-Laval steam turbine developing 32 000 shp at a propeller shaft speed of 86 rev/min. The astern turbine is incorporated in the low pressure turbine and develops 15 600 shp at 52 rev/min of the propeller shaft. The turbines are coupled to the propeller shaft through double reduction gears.

In normal service the steam is led from the nine-stage high pressure turbine to the eight-stage low pressure turbine and on to the condenser. The pipe arrangement, however, enables each turbine to be operated separately with the other disconnected in case of failure.

The steam for the turbines is generated in a Combustion Engineering watertube type V2M9 boiler which has an evaporation rate of 120 tons/h. The boiler has a superheater and regenerative air-preheater and is arranged for oil-firing with forced draught. A Combustion Engineering type V2M8 auxiliary boiler with an hourly output of 32·5 tons which is likewise arranged for oil-firing wtih forced draught is installed as a standby unit.

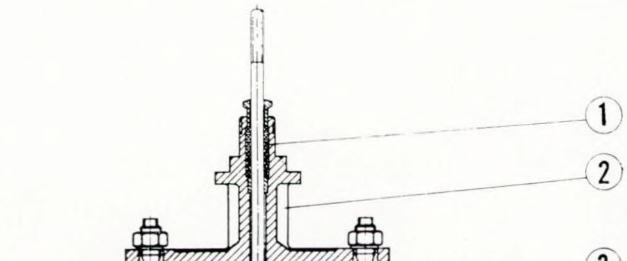
Principal particlars :

Length o.a.	1131 ft 2 in
Length b.p.	1085 ft 0 in
Breadth moulded	170 ft 0 in
Depth moulded	84 ft 0 in
Summer draught	65 ft 10 in
Capacity of cargo oil tanks ...	11 121 235 ft^3
Propulsive power	32 000 shp
Speed on loaded trials	15·75 kn

—*Shipbuilding International, November 1970, Vol. 13, p. 16.*

High Capacity Combined Steam Reducing and Desuperheating Valves

The large tankers now in general use are generally fitted with turbine-driven cargo pumps of high capacity. Although there is a tendency to use steam at full main boiler conditions for the cargo pumps now that these are of such great power, it is more usual to use steam of lower quality calling for reduction in pressure and in temperature. Similar low-grade demands are made by the needs for cargo heating systems where these are not supplied through a steam/steam generator. The Eurocontrol steam reforming valve A40 is able to perform pressure and temperature reductions simultaneously. Examination of the drawing shows that this consists of a double seated valve with centre steam admission having plug, spindle and seats of material equivalent to BS En56 C and A respectively. The spindle is hollow and extended downwards to form a connexion with ports above the upper seat and below the lower one, through which water for desuperheating can be delivered. The valve characteristics are logarithmic as standard and the maker's Numotor pneumatic actuator or a Kalle hydraulic actuator can be used. These valves are made with nominal pipe diameters from 50 to 350 mm for throughputs (rated cubic metres per hour) of water from 12·5 to 2200.—*Marine Engineer and Naval Architect, November 1970, Vol. 93, p. 557.*



1) Packing
2) Cooling fins
3) Flange jointing
4) Top-valve guide bush
5) Plug
6) Seat
7) Water control plug

Arrangement of A40 reducing and desuperheating valve

Electronic Speed Control of Steam Turbines

Electronic control systems have been in use for many years in the aircraft industry and are now finding applications in the marine gas and steam turbine field. Ultra Electronics Ltd. have recently provided UEL systems for a number of new ships including the *Esso Northumbria* class 253 000 dwt British-built tankers and Cunard's *Atlantic Causeway* class container ships.

One of the first applications in marine turbine control has been the introduction of electronic overspeed protection systems. Electronic systems offer many advantages over mechanical protection systems. Accuracies are usually better than one per cent of turbine rated speed and very rapid response is possible, enabling an overspeeding turbine to be protected far faster than mechanical systems allow.

Electronic overspeed switches can be fitted very easily to new or existing installations. All that is required is a pulse probe magnetic transducer fitted in close proximity to a suitable gear wheel driven from the turbine shaft. Any existing gear can be used provided it is made of a ferrous material and that the passing frequency of the gear teeth at 100 per cent rated speed lies between 1 KHz and 20 KHz.

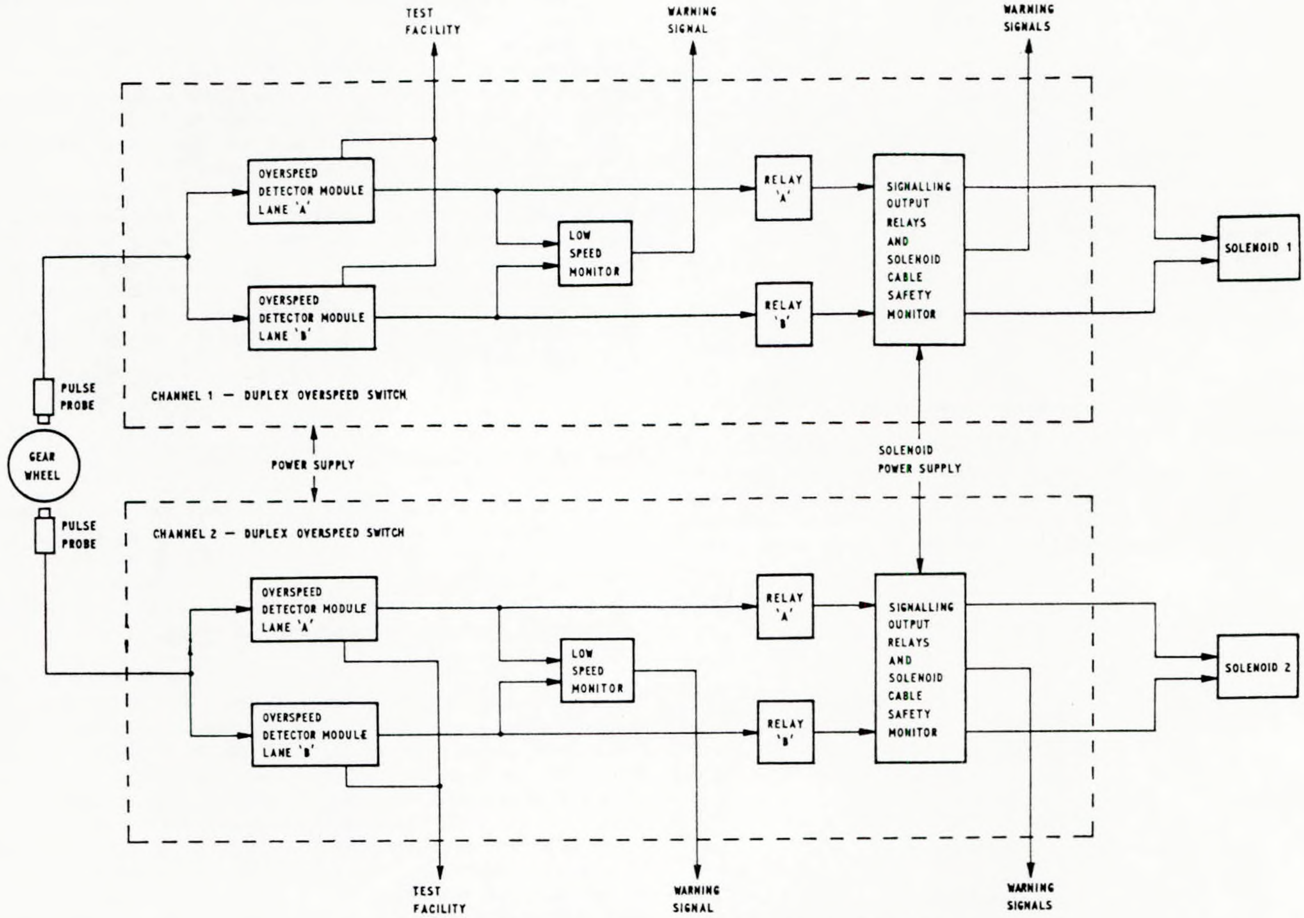
The pulse probe signal is fed to the electronic control box which may be mounted in any convenient position. The control box continuously monitors the turbine speed and if the pre-determined trip level is reached a relay is operated, the contacts of which can be used to operate steam shut-off valves or initiate any other required action. Further contact sets can be made available for a central warning system and hence faults in one part of a multiplex equipment can be isolated with minimum risk or disturbance.

The twin-duplex overspeed switch has been designed to prevent overspeeding of boiler feed pump turbines. The system consists of two pulse probe signal sources sensing shaft speed from the same ferrous toothed wheel, the twin-duplex overspeed switch and the required output facilities.

The twin-duplex overspeed switch comprises two identical duplex channels. Each channel is separately housed and has an independent pulse probe signal input, solenoid valve outputs and signalling outputs. A 36-0-36 V d.c. power supply is used, energizing each channel with 36 V taken from opposite sides of the supply. A 50 V d.c. power supply is used to energize each solenoid continuously through its respective duplex channel. Within each channel the electronic overspeed detection circuitry is duplicated, and comprises two lanes, A and B.

The pulse probe input signal is shared between the two lanes and the relay output from each lane is supplied direct through separate connectors and cables to the solenoid valve.

If two lanes of one channel agree that an overspeed exists, then a trip is caused by the action of the solenoid driven by that channel. This occurs without reference to the other channel and its solenoid.



Schematic diagram of twin-duplex overspeed switch

The logic of the twin-duplex system is:
Trip If either Lanes A and B of Channel 1 command.
or Lanes A and B of Channel 2 command.

Relay contacts are available to operate lamps or flags to indicate the state of each lane. A further set of contacts are available for a computer monitor.

The trip point of the unit is set at 110 per cent turbine running speed, and can be internally adjusted between 100 per cent and 120 per cent turbine running speed. The accuracy of the trip point is ±1 per cent of the trip frequency.—*Becraft, D. and Harrison, S. L.: Marine Engineer and Naval Architect, November 1970, Vol. 93, pp. 546–548.*

On-Load Cleaning of Steam Turbine Blading

The paper describes how, by programmed reduction of steam pressures and temperatures, the saturation point in the blade system of a steam turbine may be moved towards the inlet end, thus progressively washing off soluble blade deposits.

The condition of steam wetness, produced in the blades, results from the heat drop and it is pointed out that having the machine on load is an essential part of the process. The effects of pressure and temperature variations on turbine expansion and vibrations are also considered.—*Paper by Keogh, F. G., presented at an ordinary meeting of the Institution of Mechanical Engineers, 6 January 1971, Vol. 185 15/71.*