

## MARINE BOILER FEED WATER TREATMENT — CURRENT PRACTICE AND FUTURE DEVELOPMENTS

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### INTRODUCTION

In this paper the authors have not attempted to enter deeply into the fundamentals of marine boiler water treatment which they consider to be adequately covered in standard works on the subject, in particular BSS 1170 : 1968. They have, in fact, assumed a working knowledge of the subject and concentrated more on some of the controversies and difficulties which can arise from current considerations of the subject and conclude with a review of future trends and the concept of automation in this field.

As the rating of steam boilers has increased throughout the years, so has the mere desirability of boiler feed water treatment become a necessity. No longer can the insertion of a sack of potatoes, a horse's head or oak logs into the boiler manhole before sealing, be considered as having much bearing on modern scientific treatment, even if our forebears were, knowingly or unknowingly, already experimenting with the effects of organic materials in countering the effects of impurities in raw feed water.

The history of present marine boiler water treatment can probably be said to have been started on a more logical basis by the work of Commander Solberg, of the US Navy Department, in the 1930's. Cdr. Solberg's work included producing artificial scales from samples of water and trying the effect of various additives on the resultant deposit. One of the most effective he found was starch and, in fact, his mixture of sodium carbonate, sodium phosphate and starch was used for marine boilers for many years as the basic boiler treatment which would precipitate the scale forming salts as a non-adherent free flowing sludge. It was then known as the US Navy Compound and during the 1939-45 war its use was extended to the Royal Navy to whom it was eventually known as Boiler Compound, Navy, or BCN powder for short. This type of treatment, containing as it does combinations of phosphate and alkali in the correct proportion to deal with evaporated salt water make-up, has in effect been the basis for marine treatment for many years and only now, as the authors hope to show later, is some consideration being given to alternative products and processes.

With all the literature available to us and the long lists of troubles which can be expected as a result of incorrect boiler treatment, it is perhaps a little sobering to consider that there are in effect only two main boiler troubles produced by water conditions; these are deposition and corrosion. Even these are so closely bound together in their effects that one can hardly be considered without the other. For example corrosion in the feed system can cause deposition of corrosion products in the boiler which in turn can accelerate corrosion of the boiler metal. It is this interrelationship which probably turns a basically simple subject into the somewhat complex technology we have to live with today.

### SOURCE AND QUALITY OF FEED WATER FOR HIGH PRESSURE MARINE BOILERS

The basic reservoir of all water in the world is of course the sea, demonstrating by its salinity and other impurities the

fact that water is a universal solvent. In maritime practice we generally remove most of these impurities by distillation. However no evaporator produces a perfectly pure distillate due to entrainment of water droplets containing impurities from the concentrated sea water in the body of the evaporator. Since the distillate is in contact with air (especially oxygen and carbon dioxide from the decomposition of bicarbonates in sea water), these gases dissolve in the distillate and produce an acid feed water. This is the basis of troubles in our boiler plant.

Consideration of what happens in the evaporator is perhaps a logical starting point to see what goes on in a marine power plant and hence to determine what we do and why, to combat these problems.

A well designed modern evaporator will probably produce distillate with a total dissolved solids content of less than 1 ppm, but with a sufficient CO<sub>2</sub> content to give a pH value of about 5.4<sup>(1)</sup>. This is sufficient to initiate corrosion of copper or brass and ferrous metal.

These materials will be in contact with the distillate:

Copper: From the evaporator condenser;  
Iron: From service piping and storage tanks.

Can the problem be alleviated at this stage? The answer is that several things can be done. If the distillate is to be used as make-up only (and not for domestic supplies) we can raise the pH value with a volatile amine, which the authors will consider in greater detail later. We can consider the use of less corrodable materials, such as nickel alloys in place of aluminium brass. We can protect storage tanks with paints of which the epoxy resin type are extensively used for this purpose. Considerable care is however necessary in the application of these paints, both in the initial preparation and in the application. Unless this is done the life of the protective layer will be short and even minor imperfections can result in serious local attack taking place, perhaps even to the extent of making the "cure" worse than the sickness.

Corrosion in service tanks may also be controlled by the use of small doses of polyphosphate, of the order of 5 ppm, which act as film formers on the surface of ferrous metal. These materials are not toxic and hence the treatment may be used even if the distilled storage feeds into the domestic water system<sup>(2)</sup>.

A further method of alleviating the problem is to allow the distillate to condense at the highest practicable temperature by controlling the cooling water flow to the evaporator condenser. Since it is well known that the solubility of gases is reduced at higher temperature, the oxygen and CO<sub>2</sub> contents can be reduced by this method. However, the system is only of value if the distillate is used almost immediately as obviously storage for any length of time will obviate any advantages of this method of control.

Finally under this heading we should consider the use of ion-exchange treatment to demineralize the make-up supply completely. The process usually involves the use of a mixed bed plant employing anion and cation resins fitted into the make-up line. This will remove all heavy metals, such as calcium, and magnesium, which could be present in the event

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of evaporator carryover, or copper and iron contamination as described above. It will also remove CO<sub>2</sub> but not oxygen. Regeneration may be carried out on board using sulphuric or sulphamic acid, and caustic soda, or the exhausted resin may be changed for reactivated material and sent ashore for re-processing.

It is usual to incorporate recirculation with a plant of this type. The reasons are that, in the first place, if the demand is very small, small trickles may channel through the plant by the same route, resulting in local exhaustion of the resin material and hence lack of treatment. Secondly, the results of any subsequent contamination such as CO<sub>2</sub> or iron pick-up are again eliminated and the make-up maintained in a high state of purity.

### CORROSION IN MAIN FEED SYSTEM

Let us now turn our attention to what is undoubtedly the greatest single cause of feed contamination, and hence potentially of boiler tube failures, in the modern marine high pressure boiler plant, which is corrosion in the main feed system itself. If we take a total iron and copper content in the feed water on only 0.03 ppm, which is not unreasonable, it is a simple calculation to show that the potential amount of deposition in the boiler from this source alone is about 30 kg/year in the case of a VLCC with an evaporation rate of 113 400 kg (250 000 lb)/h. Fortunately the word "potential" is important because this would assume that all the contaminants settled on the heat transfer surfaces, which in practice is not the case.

It is, in fact, worth digressing slightly at this state to consider in greater detail just what this problem is and why it is only during recent years that we appear to have heard so much about it.

The reason is that we have in fact almost certainly always had this problem of corrosion in the feed system, but that in general the proportion which actually sticks to the boiler tubes depends on the metal temperature and rate of heat transfer. Thus whilst the problem was not entirely unknown in pre and immediately post-war ships, it descended on us in a big way in the new generation tankers which came around 1953 with operating pressure around 55 bar. At that time it was a particularly serious problem as, not only was it only partly understood, but the chemical tools which we now employ to combat these conditions simply did not exist.

To deal successfully with this type of problem, we must start at the very beginning of the life of the plant; that is, the building of the boiler system in the shipyard. Fortunately most boiler manufacturers and their sub-contractors are now alive to the need for "good housekeeping" in this matter and it is rare to see stacks of boiler tubes designated for use in new construction exposed to the weather. Nevertheless, the new shipowner would do well to ensure that for his money he gets tubes in the best possible state of cleanliness, as free as possible from mill scale and surface rust.

Despite such precautions it is unlikely that the new installation will be in a fit condition to be certain that the needs of modern steaming conditions can be met and pre-commissioning cleaning is essential. Here it must be stressed that very few yards have the detailed technical knowledge to ensure a thorough job and it is usually worth while either to pass this on to a specialized firm, or to ensure at least that the job is carried out under expert supervision. Broadly speaking the pre-cleaning should consist of:

- 1) alkaline soak/degreasing;
- 2) wash out;
- 3) acid clean to remove mill scale etc;
- 4) washout and neutralize;
- 5) passivation with hydrazine.

Having thus produced a magnetic layer, it is important to preserve it, as it is this which is the defensive barrier between the boiler water and the metal; indeed it has been said that a boiler is simply the supporting structure for a magnetite film. The essential factor here is that the boiler water must have an adequate pH value (free caustic present) and reducing conditions maintained. The latter implies good mechanical de-aeration and the maintenance of a reserve of reducing agent in the boiler water. In practice, this normally means

hydrazine in high pressure boilers and sodium sulphite in low pressure or auxiliary plant.

### HYDRAZINE AND EFFECTS OF AMMONIA ON FEED SYSTEM

As suggested above, probably the greatest source of trouble in high pressure marine boiler plant today is corrosion of the feed system, resulting in deposition of copper-iron scale in the boiler. The composition of this scale is surprisingly constant and consists normally of about 70 per cent of iron, 10 per cent copper, 10 per cent calcium with the remainder taken up with minor constituents which may be magnesium, zinc, sodium etc. On occasion, however, the zinc content can rise to as much as 50 per cent and this has been traced in particular instances to the employment of galvanized pipe in sections of the feed system. Whilst most authorities agree on the basic treatment to obviate this type of trouble, i.e. hydrazine and pH control, considerable controversy has been generated on two aspects of the problem. These are:

- a) where to put the hydrazine into the system;
- b) the effect of ammonia on the corrosion rate of copper components.

Dealing with the first of these, the evidence is probably that it does not make a great deal of difference in practical terms where hydrazine is put into the system. Some time has now elapsed since the suggestion that there were advantages in feeding into the cross-over between the H.P. and L.P. turbines under full power and after the de-aerator during manoeuvring. Many ships in fact adopted this suggestion but, on the other hand, many more did not and injected at all times after the de-aerator or de-aerator extraction pump. Since to date there has been no clear advantage or disadvantage of one system over the other, one feels justified in claiming little advantage for either scheme. However, it must be borne in mind that, in feeding into the de-aerator extraction pump discharge, the de-aerator is left free to do the job for which it was designed, i.e. to de-aerate, and furthermore a chemical or meter check for oxygen can be instituted to confirm its operation, without interruption of treatment, which is not the case if hydrazine is fed earlier in the cycle.

The question of the effect of ammonia is one which has caused considerable discussion. The ammonia results of course from breakdown of hydrazine in the boiler when an excess over the oxygen present in the feed is added, as in practice must be the case.

In most cases analysis of the feed in a typical marine feed system will show ammonia contents between 0.6 and 1.2 ppm. Fears have been expressed that ammonia contents at this level, in the presence of oxygen, could cause attack on copper.

In practice there seems to be very little evidence that this is the case and if serious copper corrosion is experienced, it can usually be traced to either low pH or excess oxygen. In fact, some electrical generating stations, both in the United States and United Kingdom, actually inject ammonia into the feed system to elevate the pH value, but this is invariably combined with careful monitoring of the oxygen levels.

The following figures were reported, following tests in an American industrial plant<sup>(3)</sup>:

pH	Ammonia (ppm)	Copper (ppm)
6.75	0.80	0.55
7.30	0.70	0.25
8.0	1.04	zero
8.7	1.76	zero
9.5	6.2	zero
9.5	9.1	zero
9.6	11.0	zero

These figures show that in this plant there was no copper pick-up, even with ammonia contents far greater than we would expect on any marine plant.

Where in practical terms does this leave us? It would appear that the basic requirements of the modern high pressure system are as follows:

1) A positive reserve of hydrazine in the boiler water at all times.

Provided that this is a true reserve, the exact limits are

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probably less important than the controversy about their values would suggest. However with the very low value of 0.01 ppm recommended by some authorities the margin of error is likely to prove to be too low to be practical. Further although the hydrazine test has been improved recently it is difficult to measure such low values with any degree of accuracy. It is important to remember that if the hydrazine reserve is lost at any time, then free oxygen can be present and the corrosion cycle may be initiated. In practice, a value of 0.1 ppm hydrazine is probably a minimum working figure.

The upper limit is less critical and must be fixed in part by the relatively high cost of hydrazine. However it must be borne in mind that the higher the hydrazine the higher the ammonia and, although we have shown that ammonia as such does not cause corrosion, if there is an interruption in the hydrazine feed, due, for example, to trouble with the feeding equipment, we may lose the hydrazine reserve in the boiler, whilst the ammonia, owing to its high solubility, remains in the system. Again, therefore, we could have free oxygen plus ammonia in the system. The authors' organization therefore favours an upper limit of 0.3 ppm hydrazine.

2) Control of the pH value of the feed water between 8.5 and 9.5 with a preferred value of 9.2 at which corrosion rates of iron and copper are at a minimum. This means that the range recommended for most ships will be 9.0 to 9.5. Using hydrazine alone it will normally be found that the value will settle down around 8.8. To achieve the recommended optimum we can increase the hydrazine dosing, but this has the disadvantages suggested above. The alternative, now widely adopted, is to use additional products for the sole purpose of raising the pH.

The most frequently employed product for this purpose is monocyclohexylamine which can be added at any point in the feed system, either continuously, or as a daily slug, since it distils off with the steam and recirculates continuously. In practice, a second product is often used in addition, known as morpholine. The reason for this is that cyclohexylamine is effective in raising the pH of cool condensate, whilst morpholine protects the plant in the area of the first formed condensate, i.e. in the area of the condenser immediately below the Wilson line.

3) Good mechanical de-aeration. Many modern ships are now fitted with efficient full-flow de-aerators which give excellent results under all conditions, including harbour service. They are in fact so efficient that they tend to be neglected and their operation taken for granted.

Since the end product is obviously the oxygen content of the effluent, this at least should be monitored regularly, preferably by an efficient oxygen meter supported by an occasional chemical check, say once a week. Should the efficiency fall off (i.e. an oxygen value above 0.03 ppm) the following should be checked:

- i) temperature/vacuum, which must correspond to boiling conditions;
- ii) spray nozzles — whether blocked, corroded, eroded, or simply adrift mechanically;
- iii) vent system operating correctly, free passage for non condensibles through vent condenser and ejector, if fitted.

Cases have been reported recently from one particular class of ship of severe corrosion in condenser tubes resulting in perforation. Investigation showed that make-up and under-aerated drains were admitted to the condenser and this was considered to be the cause of the trouble. The operators were advised to change the system so that the make-up was admitted to the de-aerator which could be achieved without a great deal of modification and it is anticipated that further trouble will not recur.

### TOTAL FEED FLOW FILTRATION

Before leaving this subject of iron and copper contamination, we might for a moment look at the special problems associated with tanker operation. The trouble lies in the large amount of ancillary plant, particularly the cargo discharge system, which lies idle for the length of a voyage. Calculations based on checks at sea indicated that the potential iron contamination of the boilers could amount to 50–75 kg every

1000 days, with about 80 per cent of this suspended. The corresponding figure for copper was 8–15 kg. At first sight these figures do not appear excessive, but two things must be borne in mind; firstly, although the contamination may not seem excessive on the average, in fact it occurs in short bursts, on each occasion over 24 hours or so. Consequently the boiler tubes are subjected to appreciable contaminating material during these periods. Secondly, it must be appreciated that whilst only a proportion of the iron entering a boiler actually sticks to the tubes as deposit, most of the copper does in fact remain on the boiler tubes.

Hence, in effect, copper concentrates up in the boiler relative to the iron. The position can be considerably improved by the installation of a 5 micron filter which will remove 80–90 per cent of the suspended matter. The replaceable cartridge type is the most convenient to deal with and it has been found that the most useful filter medium is cotton, as nylon seems to harden with age and temperature.

### CONTAMINATION FROM SEA WATER AND OIL

Having dealt at some length with contamination due to copper and iron, let us turn now to the other contaminants which are always with us, i.e. the natural contents of sea water and, occasionally, of shore waters. Here we are dealing with three sets of conditions; the "normal" one where we are faced with small quantities of the contaminants which cause no trouble; slight contamination which may only marginally affect plant operation, and gross contamination which is a serious condition. In the first instance we may be faced with contamination from evaporator carry-over, main or auxiliary condenser leakage, and more obscure happenings such as leakage from domestic calorifiers etc. The well known method of dealing with these is to precipitate calcium as the insoluble phosphate, magnesium as insoluble hydroxide and to eliminate them together with soluble salts, chlorides etc. by means of blow-down. However, again modern plant is frequently so efficient that it is its own enemy. Particularly if the make-up is ion-exchange treated, as outlined above, the contamination entering the boilers from this source is so slight that the routine chemical checks show that the chloride values are virtually not changing and hence the boilers are not blown down, as concentrations are well below the recommended maximum. But in fact suspended matter, sludge etc. is accumulating in the boilers daily and this must be eliminated, whatever the test results show. It is therefore advised that about two tonnes are blown out weekly however good the apparent condition of the water. Where slight, but heavier than normal, contamination occurs, which might be defined as chloride concentrations up to about double the normally recommended maximum value, the thing which must not be done is to inject large quantities of boiler treatment chemicals in the hope that they will neutralize the trouble. In fact anything which is done should be regarded as a temporary measure pending the locating of the source of the contamination and dealing with it. In the meantime the following steps should be taken:

- a) maintain phosphate and alkalinity reserves at not more than the minimum recommended values;
- b) blow as frequently as is practicable;
- c) reduce load on the boilers to a minimum; this may mean reducing the ship's speed if this is operationally feasible;
- d) add extra anti-foam, if available.

Dealing finally with the situation of gross contamination, with chloride levels many times the recommended maximum, we have a different situation in which we must abandon any ideas of keeping normal treatment going. We are in fact trying to buy time in an emergency situation. The only treatment which should be used is, again, anti-foam, if available, plus sufficient alkali to maintain minimal alkalinity values in the boiler water. Reduction in load will be virtually essential, whilst blow-down is of doubtful value. The reason for this statement is that under these conditions a chloride concentration of, say, 4000 ppm is little different from a value of, say, 5000 ppm and the additional load and heat loss in attempting to blow-down under these conditions, but, in practice, achieving very little, may be self-defeating. What

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must be done of course is to wash the boiler out completely as soon as possible.

One further form of contamination which sometimes afflicts us to a greater or lesser degree is that of oil. If of serious proportions, such as results from rupture of a fuel heater, little can be done except to call for the services of a specialist firm to clean out the plant as soon as possible. However, more often the problem takes the form of small amounts of emulsified oil in the feed, which accumulate in the boiler and may not be recognized until seen in the gauge glasses.

Treatment consists of the application of 350g of Epsom salts (if boiler is off load), 100g of Epsom salts if the boiler is on load, repeated every 24 hours, if necessary adding alkali about one hour afterwards to restore normal operating alkalinities.

Again additional anti-foam is useful if available. The boiler is then given flash blow-downs for 5–20 seconds at intervals to remove the precipitated sludge and oil.

The principle of the method is that a precipitate of magnesium hydroxide is formed in the boiler water which coagulates and precipitates the oil, which is subsequently removed as recommended above.

Although not strictly within the province of this paper, a further word of advice on oil contamination may not be misplaced, since one hears of the same story so frequently; this is that following severe contamination, the natural reaction is to empty the boiler completely as soon as possible. The effect of this of course is to distribute the oil in a uniform layer over all the tube surfaces in the boiler.

What should be done is to leave the boiler full but to overflow it through the steam drum manhole by feeding water lower down. By this method most of the oil which is floating on the water surface will be removed from the boiler into the bilges.

### ADDITIONAL CHEMICAL TREATMENTS

Let us finally consider how chemical products are helping in the task of maintaining modern steam plant in the best possible operating condition, it being of some interest to bear in mind that many of the products now in normal use and taken for granted did not exist commercially as little as fifteen years ago.

The paper has already dealt with the uses of hydrazine, cyclohexylamine, and morpholine. Hydrazine was first introduced about 1962, being in fact commercially produced for the space-rocket industry and it is interesting to note that the British shipping industry was amongst the first to appreciate the value of this material. Cyclohexylamine and morpholine were introduced about the same time.

The paper has mentioned anti-foams above. These are organic materials of two basic types known as polyoxides and polyamides introduced about 1940 mainly for the benefit of the railway locomotives. The exact mechanism of their function is not fully understood, but they appear to be materials which maintain a balance of hydrophilic and hydrophobic properties. In practice they promote the formation of large steam bubbles which burst cleanly and smoothly as opposed to the production of numerous small bubbles which encourage foam formation.

The value of these materials can be demonstrated by simple steam purity measurements. It has been found that the dissolved solids in a boiler water having only 10 ppm of anti-foam in the boiler water can be ten times higher than a boiler water without anti-foam, for a comparable level of steam purity.

A further range of products now in common use is known as polyelectrolytes. These are an interesting group of organic materials having long-chain molecules of which the properties can vary to an extraordinary degree according to the manufacturing process, the main variables being the length of the molecular chain and the electrical sign on the active groups. The practical effect is that they can act as either dispersants or coagulants according to the type of product. In the marine boiler plant field, we are mostly interested in the former where polyelectrolytes are of value for treatment of evaporators to produce sludges instead of scale, and to ensure free-flowing deposits in boilers which can be eliminated by blow-down.

In practice most chemical supply companies now incorporate anti-foams and polyelectrolytes in their treatment products to ensure that these materials are automatically added with the routine application of the feed water treatment.

Coming up to the edge of current research we have a further interesting range of products known generally as S.C.A. (scale control agents). These again are a range of organic materials which have the property of forming soluble complexes with the heavy metals, i.e. we can look forward to the virtual elimination of the headaches caused by scales consisting of calcium, magnesium, iron and copper etc. These are already being used successfully in a number of plants ashore and their possible application on the marine field is receiving consideration at the present time.

A further development is the adoption by some operators of a form of treatment known variously as co-ordinated phosphate, congruent phosphate, or zero-caustic treatment. It is not new, having been around and, in fact, used for twenty years or more. However, it has caused a considerable amount of both interest and controversy in the marine field.

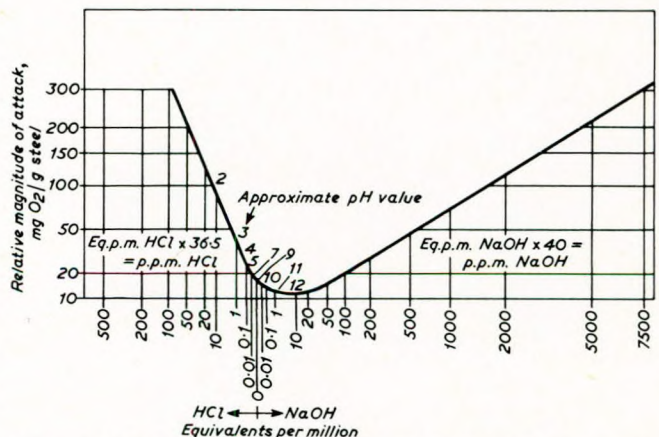
### LOW ALKALINITY BOILER WATER TREATMENT

So far a review of the water treatment as outlined in British Standards 1170 : 1968 has been undertaken and we now move on to the latest type of treatment to be applied to the marine industry and this can generally be classified as a low alkalinity boiler water treatment.

The low alkalinity boiler water treatment system, as exemplified by the co-ordinated phosphate-pH type of treatment, became popular in the United States in the early 1940's because they were faced with a popular trend towards higher steam generation pressures combined with higher heat transfer rates.

As the boiler pressures and the heat transfer rates increased, a serious problem arose due to caustic corrosion of boiler tubes. This caustic corrosion otherwise known as caustic gouging, ductile gouging, and crater corrosion, can only take place if, by some mechanism, caustic soda concentrates on the tube surface. The activity which appears to take place is to a large extent dependent upon the amount of deposit which is present on the tubes, be this deposit of magnetite, or of other products such as calcium products.

The most common is a build up of deposit, primarily of iron and copper corrosion products on the water wall. This causes the tube to become insulated with inherent loss of heat transfer and, subsequently, the metal below the deposit will become overheated, causing moisture below the deposit to flash evaporate, leaving the boiler water solids containing caustic soda behind in a highly concentrated form. In this connexion, concentrations in excess of possibly 10 000 ppm are not unknown. Caustic attack of the tube metal will result from this highly concentrated caustic soda solution (see Fig. 1).



Attack on powdered steel for 75 hours at 310°C and 98 bar by water of varying degrees of acidity and alkalinity

FIG. 1—Relative attack on steel at 310°C by Hydrochloric acid and sodium hydroxide

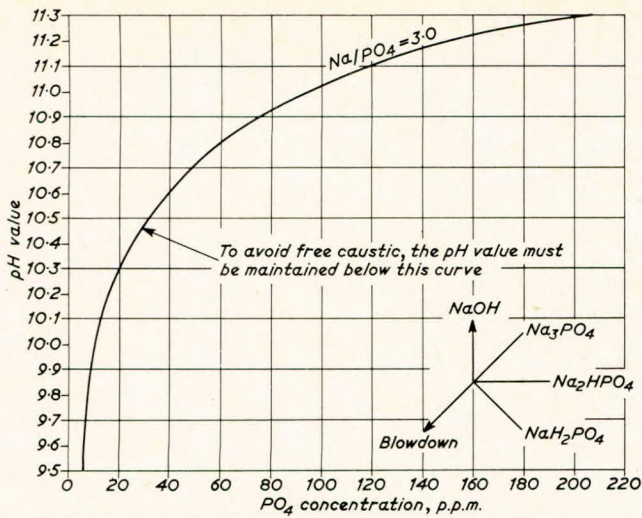


FIG. 2—Conventional co-ordinated phosphate curve

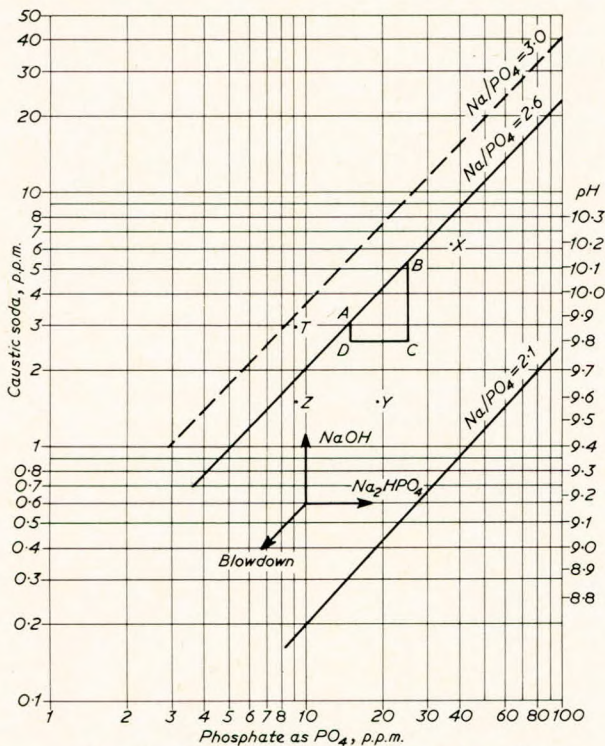


FIG. 4—Congruent phosphate control graph

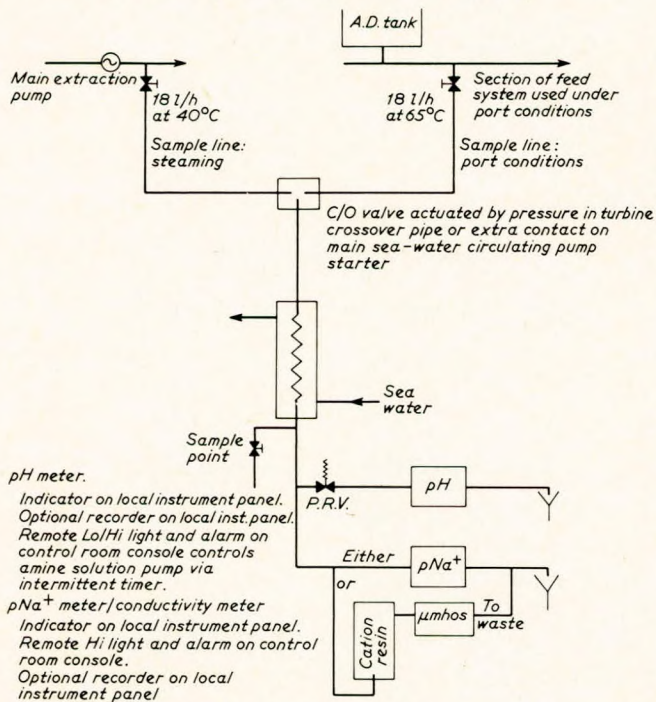


FIG. 6—Condensate sampling

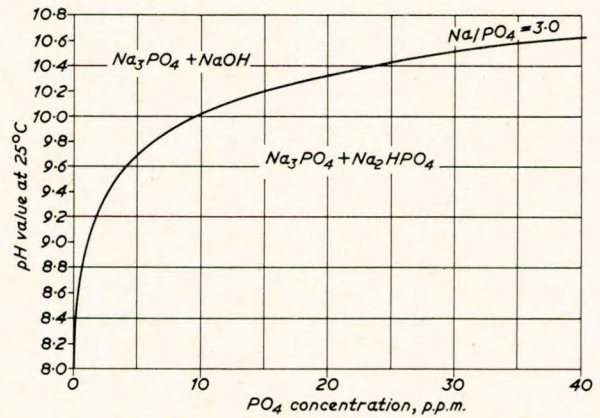


FIG. 3—Low level phosphate curve for use in high pressure boiler

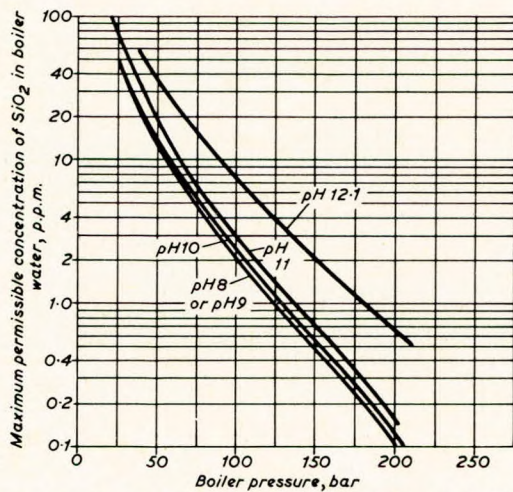


FIG. 5—Permissible concentration of silica in boiler water to prevent silica carry-over — Based on maximum of 0.02 ppm SiO<sub>2</sub> in steam: pH values are for boiler water cooled to 20°C

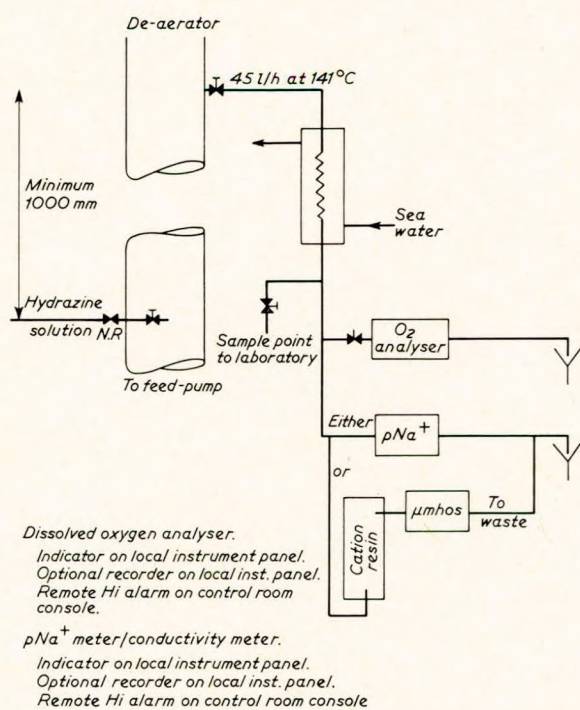


FIG. 7—Feed water sampling

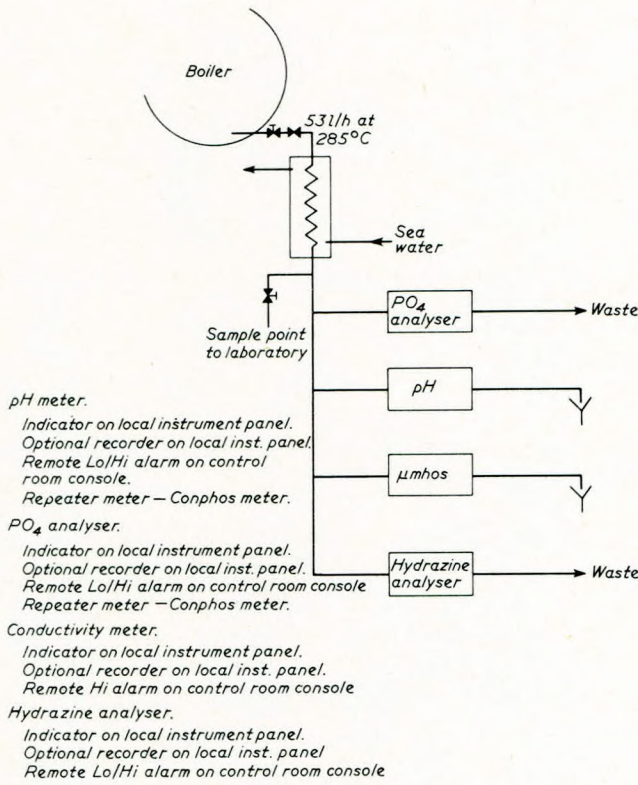


FIG. 8—Boiler water sampling

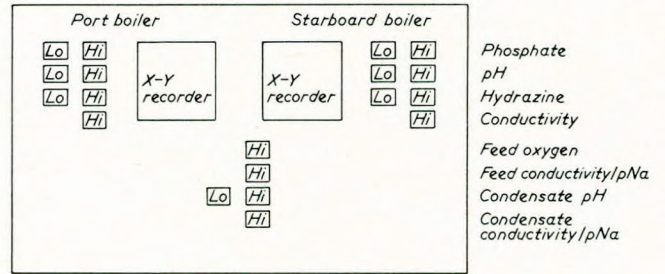
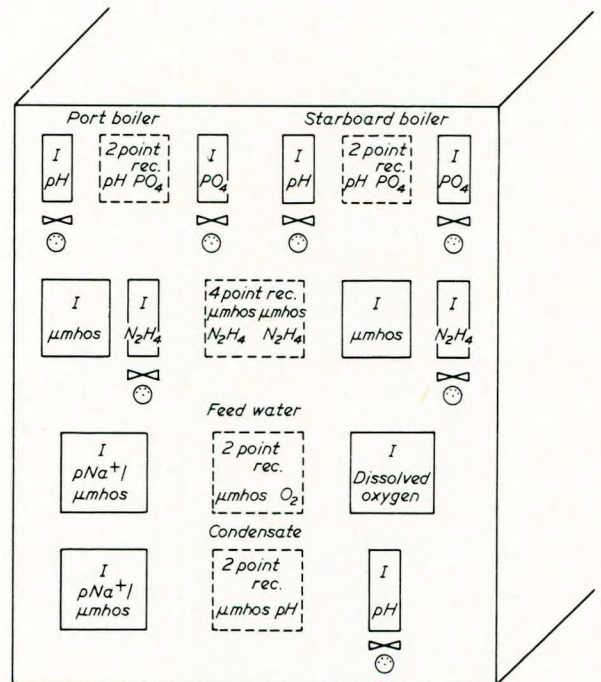


FIG. 10—Suggested layout of remote panel in control room

Tests	Local instrument panel	Remote on control room console
<b>Boiler water port</b>	Optional	Lamp indicators and alarms
pH	Indicator (meter) *	} X-Y recorder
Phosphate	Indicator *	
Hydrazine	Indicator *	
Conductivity	Indicator *	
<b>Boiler water starboard</b>	4 point recorder	} X-Y recorder
pH	Indicator *	
Phosphate	Indicator *	
Hydrazine	Indicator *	
Conductivity	Indicator *	Hi
<b>Feed water</b>		
Dissolved oxygen	Indicator	Hi
pNa <sup>+</sup> or conductivity after cation resin	Indicator	Hi
<b>Condensate</b>		
pH	Indicator *	Lo Hi
pNa <sup>+</sup> or conductivity after cation resin	Indicator	Hi

\* Auto/manual switch fitted to enable associated chemical pump to be controlled by hand

FIG. 9—Instrumentation and positioning



- ⊗ Change over from automatic to manual for parameter immediately above
- ⊙ Manual control potentiometer for parameter immediately above
- I Indicating meter
- [Rec.] Optional recorder with parameter

FIG. 11—Suggested layout of local instrumentation panel

Porous deposit such as is common in boilers having a low hardness feed water with respect to iron and copper, is particularly susceptible to caustic concentration within the deposit. The other mechanism for caustic build-up is the result of too high a heat input to a given tube surface area. This causes what is known as departure from nucleate boiling (DNB). Film boiling, steam blanketing, and water disengagements being other terms which are synonymous.

Because the trouble mentioned above is due to the caustic soda concentration within the boiler water, the obvious answer was to use a chemical treatment which did not permit any free sodium hydroxide alkalinity to be present in the boiler water which could conceivably concentrate on the tube walls. Hence the co-ordinated phosphate treatment was developed which increases the pH and gives some alkalinity buffering capacity to the boiler water without having free sodium hydroxide alkalinity present.<sup>(4)</sup> The co-ordinated phosphate-pH and its related treatments, such as the congruent phosphate treatment, did reduce the failure rate of the boiler tubes due to caustic attack; however, because of the very low buffering capacity of the boiler water with these treatments, the number of incidents of hydrogen attack caused by low boiler water pH has increased. In a paper by H. A. Klein<sup>(5)</sup> it was reported that in 1955 to 1960 there were 41 cases reported of ductile gouging (caustic attack) and in the same period 7 failures due to brittle corrosion type failure, whilst in the period 1966 to 1970 failures due to ductile gouging were 8 and those due to brittle corrosion failure were 21.

#### The Theory of Co-ordinated Phosphate-pH Treatment

The paper given as reference (4) forms an excellent basis for understanding the theory of co-ordinated phosphate treatment.

The treatment is based upon the fact that if one selects carefully the type of phosphate that is to be used as a boiler water treatment medium, then it is possible to select a mixture of phosphates, such as trisodium phosphate  $\text{Na}_3\text{PO}_4$  and disodium hydrogen phosphate  $\text{Na}_2\text{HPO}_4$ , in combination which will fulfil the requirements as laid down by Whirl and Purcell<sup>(4)</sup>; this is diagrammatically indicated in Fig. 2. With this graph it is mandatory to maintain the intersection point of the phosphate concentration and the pH value of the boiler water below the line on the graph to make certain that no free caustic soda remains in the boiler. At any point above the line on the graph, there will be free caustic soda in the boiler with the danger that should any of the conditions mentioned above be arrived at, caustic attack can become a reality. Fig. 3 shows an enlarged version of the area of the graph with which we shall become more familiar, namely that indicating low level co-ordinated phosphate curve for use in high pressure boilers. Here again the same area will be noticed as was referred to in Fig. 2. At pressures up to 103 bar g, it was recommended that the phosphate would lie within the range 15 to 25 ppm and the pH range from 9.8 to 10.2.

Fig. 4 indicates the chemical control vectors using the three phosphate compounds referred to plus caustic soda if necessary and the physical action of blow-down upon any point on the co-ordinated phosphate pH control curve. It is thus obvious that the intended control of this type of treatment could result in the use of a multiplicity of chemicals.

This curve, therefore, as produced by Whirl and Purcell, was a theoretical curve based upon the work done using stoichiometric quantities of trisodium phosphate  $\text{Na}_3\text{PO}_4$  and it was left to another set of workers namely Marcy and Halstead, who took the matter further and found that even if this curve, which represented a mol ratio of sodium to phosphate Na/PO<sub>4</sub> as 3.0 to 1, were adhered to, there was still a distinct possibility of producing some caustic soda within the boiler water and a possibility of the caustic attack should this caustic soda concentrate. On the basis of their work they concluded that the pH of a boiler water should be kept in a region below the curve for 2.8 to 1 or perhaps 2.6 to 1 mol ratio of sodium to phosphate and not the 3.0 to 1 composition as had been cited previously. It is control to this latter mol ratio sodium/phosphate of 2.6 to 1 that is referred to as the congruent phosphate treatment. If this is put into terms about which we are all familiar, it means that the phenolphthalein

alkalinity should never exceed 0.315 times the phosphate concentration of the boiler water expressed as ppm phosphate as such. Any boiler water which has a higher "P" that that cannot under any circumstances claim to be congruent phosphate treatment. Fig. 5 indicates the old accepted curve, i.e. 3.0 to 1 and the now accepted 2.6 to 1, and gives some indication of the area present where caustic soda could be a menace using the old method. Fig. 6 indicates the chemical vectors added to control completely this modern type of treatment. On the control graph will be seen an area delineated A B C D: any point plotted, i.e. pH versus ppm phosphates PO<sub>4</sub> must lie within this given area. For example let us suppose that a test shows that the boiler water parameters lie at point "X". All that is necessary to put the point within the prescribed area is to blow-down the boiler, testing of course at frequent intervals, until the situation is corrected. A sample which indicated a position "Y" would require the addition of 1.5 ppm of sodium hydroxide to correct conditions. A point "Z" provides a very interesting example of control technique. It is possible to correct conditions from point "Z" by two routes, one to add caustic initially and bring the pH up to 9.88, i.e. point "T", and from there to add 11 ppm phosphate which would be satisfactory. Unfortunately, however, point "T" lies above the Na/PO<sub>4</sub> line representing the 2.6 ratio and hence would have free caustic present if any of the concentration conditions existed within the boiler. It is obvious therefore that in order to correct condition from point "Z" there is only one way to proceed and that is to add the phosphate first, followed by the caustic soda.

So far an outline has been given of the methods for controlling and arriving at suitable parameters for the use of the congruent phosphate-pH boiler water treatment. There are however, three main snags to this treatment:

#### Point 1

As a reduction has been made in the amount of alkalinity present in the boiler water, i.e. the buffering effect has been reduced, it is mandatory that the quality of the feed water is extremely high, and this necessitates the use of cartridge type filters immediately prior to the de-aerator to make certain that excessive amounts of iron and copper do not enter the boiler as particulate matter, as otherwise this would permit concentration below a semi porous deposit.

#### Point 2

Because of the lower buffered effect of the boiler water, it is imperative that sea water leaks are reduced to an absolute minimum, or the standard of feed water monitoring is greatly improved.

#### Point 3

Fig. 5 will indicate that, for any given boiler pressure, a reduction in pH of the boiler water will reduce the maximum permissible concentration of silica ( $\text{SiO}_2$ ) in the boiler water that can be carried whilst still maintaining a given amount of  $\text{SiO}_2$  in the steam. This necessitates a strict control of silica concentration in the boiler water particularly at the start-up of a boiler from new. It is not felt however that, with a well run ship, the snags mentioned above are insurmountable particularly if attention is paid to the aspects of monitoring as will now be discussed.

#### Desirability of Total Automation of Boiler Chemical Treatment

It does appear to the authors that, whilst colossal strides have been made on the automation of other aspects of ship board work, little attention has been paid to the automation of the boiler chemical treatment aspect. It should be said immediately that one main problem has arisen with the old treatment to British Standards 1170:1968 and this is the measurement of alkalinity/pH. With treatment to that British Standard the pH of the boiler water usually settled at around 11.2 to 11.3 and at this elevated pH any glass electrodes used for the measurement of pH suffered from certain errors and a short life. If, however, we are prepared to look seriously at a co-ordinated phosphate-pH type of treatment with the advantages that we can derive from it, then total automation becomes a reality. The problem with glass electrodes and pH measurement are minimized at the lower pH and these

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measurements become infinitely more reliable. Because of the lack of buffering effect of the boiler water itself, we must upgrade however the instruments for detection of contamination and Fig. 6 shows what is considered to be the minimum for the sampling of any condensate system. Here an attempt has been made to differentiate between normal steaming conditions and port conditions, and indicating that pH measurement and pNa positive measurements or conductivity preceded by a cation resin column should be used (the latter will prevent any interference of the tests by neutralizing amine). Fig. 7 indicates the minimum requirements for the feed water sampling after the de-aerator at this point measuring dissolved oxygen as a check to de-aerator performance and once again pNa or conductivity preceded by a cation resin column.

Fig. 8 indicates that four parameters will require checking on the boiler system, namely phosphate and pH to determine the position on the congruent phosphate control graph of the boiler water at any moment in time, conductivity to determine the concentration of salts in the boiler water and hydrazine to be certain that one is running the boiler water under reducing conditions (hence removing any dissolved oxygen and maintaining a magnetite layer within the boiler).

At the present moment any engineer officer sitting in the central control room of a vessel has very little indication to acquaint him of the conditions that he is running in the boilers. It is suggested that if these ideas were put into practice, the engineer would have full control and full knowledge of the conditions in the boiler. It is entirely feasible to take the output from the phosphate analyser and the pH monitor and by means of an X - Y plotter to plot the exact position on a simulated congruent phosphate control graph, so that the engineer would know at all times that he was running with correct congruent phosphate conditions.

Once all the parameters mentioned have been displayed on the necessary panel, it is merely a matter of electronics to convert these "parameter" signals into signals that will

operate pumps which would inject the chemicals into the correct points in the steam water cycle. Obviously, any constraints necessary will have to be built into the electronics system such as that necessary to inject any phosphate treatment component into the boiler before the alkalinity component is added, but this is purely a matter of final design and timing.

It is therefore, felt that this approach to a modern vessel to give it a total automation system, for a system which has otherwise been neglected, is now entirely feasible and the authors would commend it as being worthy of further consideration.

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### ACKNOWLEDGMENTS

- Fig. 1: "Boiler Corrosion and Boiler Feed Water Treatment" by R. Hillier, *Trans.I.Mar.E.*, Vol. LXII, 1950, No. 1, p. 18.
- Fig. 5: "Industrial Water Treatment Practice" by Hamer, Thurston and Jackson, p. 441.

## Discussion

Mr. J. L. HUTCHINSON, opening the discussion said that he had five points to make and four questions.

Firstly, assuming that the single boiler of a modern VLCC could evaporate approximately 100 tonnes of water every hour, of which about 99 tonnes would be "recycled" condensate and only 1 tonne would be high quality "make-up water" distilled by the evaporator from sea water, it was apparent that a very slight contamination of the condensate would have much greater effect on the boiler water chemistry than a similar contamination of the evaporator distillate. In fact, carryover of sea water salts from the evaporator had not figured as a major problem area in the modern VLCC.

TABLE I—RESULTS OF RECENT CHEMICAL CLEANING PROCESSES COMPARED WITH ANALYSIS OF MONTHLY WATER SAMPLE

Iron removed	Average on monthly test results
1790 kg (3947 lb)	0.094 ppm iron
1179 kg (2600 lb)	0.073 ppm iron
862 kg (1900 lb)	0.061 ppm iron

Secondly, Table I showed the amount of iron oxide removed, by a chemical cleaning process, from three VLCC boilers. The right hand column showed the average results obtained from analysis of a composite sample of feed water collected from a daily water sample accumulated on board these same ships for one month periods. Although these figures confirmed the authors' conclusion that the major problem was iron and copper and gave some idea of its scale (no pun intended) they did not support the authors' view that iron would be removed from the boiler by blowdown.

It might well be that particular designs of boiler had a tendency for iron and copper to stick to the tubes. On one VLCC a series of water samples gathered over a five day period revealed considerable variations in total iron content in the boiler water, without any blowdown having taken place. Analysis of the results indicated that any dissolved or suspended iron which entered the boiler had deposited on the tubes in a matter of hours.

TABLE II—LEVELS OF IRON MEASURED IN FEED AND BOILER WATER

Measuring point	Iron content
Evaporator distillate	0.003 ppm
Storage tank	0.004 ppm
Condensate pump discharge	0.003 ppm
De-aerator storage tank	0.006 min. to 0.06 max. ppm
HP heater drains	0.11 min. to 0.48 max. ppm
Boiler drum	0.031 min. to 0.47 max. ppm

Table II showed typical iron levels measured at various points which were comparable with those given by Mr. P. B. Owen in his 1971 paper. It seemed probable that the major source of iron was the low pressure condensate drain system and the influx of iron into the main system was in the form of "slugs" when auxiliaries such as cargo pump turbines systems or low pressure drains systems were operated after being idle for part of the voyage.

Thirdly, Table III showed typical water analysis obtained in service.



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TABLE III—MARINE BOILER FEED WATER CONTAMINANTS

Water analysis	Evaporator Distillate	In ppm boiler feed	Boiler water
Chloride	0.08	0.17	7.8
Calcium	0.045	0.076	0.117
Sodium	0.48	0.027	0.064
Magnesium	0.03	0.027	0.031
Copper	0.3	0.015	0.011
Iron	0.007	0.007	0.019
Zinc	0.02	<0.005	0.043
pH	5.3	9.5	10.8

Hydrazine was used for oxygen scavenging and was generally injected after the de-aerator. Amines were used for pH control. Full flow feed filtration to 5  $\mu$  was used to remove suspended material. Despite these measures the composite sampling data still showed there was an ongoing problem with iron and copper. The trend appeared to show that a sample having a high iron content would have a high copper content. This could simply be due to sampling error but it might support the opinion that oxygen ingress into the condensate drain system was the major cause and not variations in pH value.

Fourthly, the point at which hydrazine should be injected into the system was still debatable. In the present economic climate many ships were operating at reduced speed, which had the effect of raising the temperature at the turbine cross-over pipe and might increase the rate of dissociation of hydrazine cross-over if injected at this point and hence led to a risk of attack by ammonia on the steam side of the condenser, especially where air leakage rates were high.

Finally, it did not appear to be generally appreciated that the points at which unde-aerated drains or make-up feed water entered the system were important and could affect the water treatment quality of the whole system. One occasionally encountered situations where the temporary "drag" lines which had been installed to enable drain pumps to be bypassed whilst being overhauled, had become the normal scheme and nobody on board was aware of the potential problems these arrangements could cause.

The questions Mr. Hutchinson would like to ask were:

1) Despite the use of all techniques and treatments described in the paper, the problem of iron and copper corrosion was still with us. The co-ordinated phosphate treatment scheme did not appear to be addressed to this problem. Would the authors care to say what should be done next?

2) In view of the statement about the fear of ammonia attack on copper in the presence of excess oxygen what should the marine engineer superintendent do when faced with a condenser system handling air in leakage of between 0.25 and 0.28 m<sup>3</sup>/min (9 and 10 ft<sup>3</sup>/min) resulting from a system design incorporating 508 mm (20 in) diameter gate valves for cargo pump turbine exhausts, turbo alternator exhausts and other auxiliary systems? These valves were extremely difficult to keep airtight even with water seal arrangements, and this problem was a fact of life on many ships. In such cases what level of hydrazine was recommended?

3) Where should the hydrazine and the amines be injected?

4) Would the authors care to comment on the view that the role of the water treating specialist should now be directed towards the design and treatment of the whole feed system, in particular the low pressure end, rather than with the boiler, which ultimately received the problem?

MR. M. B. LEVENS, said he would like to defend the principle of injecting hydrazine into the cross-over. The reason why the contributor's company changed to this was because it was found that by direct injection of hydrazine into

the cross-over less copper pick-up occurred in the feed water. The authors argued that it was better to ensure efficient working of the de-aerator by injecting into the discharge from this unit, but surely, as long as a hydrazine reserve in the boiler was maintained the removal of residual oxygen was assured. As to the pulsing mentioned by the authors this was not important because the hydrazine would be fully mixed in the feed water. Therefore there were really two points. There was no disadvantage in injecting into the cross-over whilst copper pick-up in the boiler was reduced by injecting into the cross-over.

Reference was made by the authors to the table in the paper showing measured ammonia levels against pH and copper pick-up in the condenser. This possibly supported the view held by the contributor: local injection of hydrazine, which broke down to ammonia, elevated the pH in the condenser thus preventing copper alloy corrosion — in the absence of air leaks.

The next point Mr. Levens wished to bring up was about the amount of copper found in boiler tube deposits. He and his company had found that it was generally higher than the authors suggested. It was always of the order of 25 to 40 per cent in the screen tube flame pass region and could be as high as 60 per cent. Reference was also made to severe steam side condenser tube corrosion. Mr. Levens thought the authors were probably referring to the AEG underslung design. His company had recently been investigating this type of attack in regard to other designs of condensers and found that it was not confined to this one design but was a general problem. Nor was it confined to condensers in which make-up feed was fed into the condenser by a drag line.

His company therefore believed they had quite a problem as far as both the deposition of copper in the boiler and the steam side corrosion of condenser tubes was concerned and believed they were helping to obviate the problem by injecting hydrazine into the cross-over directly.

MR. R. J. TOZER, M.I.Mar.E., thanked the authors for a most interesting paper, which had clarified some woolly areas in the feed water treatment, particularly if he could accept that provided oxygen free condensate was maintained, high ammonia contents would not produce the copper lined boilers with the inevitable disastrous results which he was sure had been the experience of many superintendent engineers.

The figures quoted by the authors indicated a zero copper content, even with figures of 11 ppm ammonia which would appear to dispel any fears in the theory that high ammonia content was dangerous.

Mr. Tozer asked at which point in the closed feed system were the ammonia readings taken, as he had personally recorded ammonia readings of 54 ppm at the air ejector drain of a marine system, while at the same time the main condensate from the condenser was recording only 40 ppm of ammonia. The indications being that concentrations of ammonia at 100 times, the main system quantities could be concentrated at the air ejector drains, this occurring at a point in the closed feed system where copper and air did exist in large quantities. It might well be that air ejector drains should be considered as a contamination area or the copper content designed out of this particular piece of equipment.

While he accepted the logic of the use of a secondary amine treatment such as monocyclohexylamine, it did, however, introduce an additional chemical and control. While the control advantage of the single amine treatment of hydrazine was that the pH meter indicated that complete de-oxygenation had been achieved, as it was only the excess hydrazine after complete oxygen scavenging which produced the ammonia and consequent alkali pH of the condensate.

The key objective of VLCC operators was to achieve trouble free continuous steaming, dry dock to dry dock, which could be in the order of 24 months, and his company looked to the effective chemical treatment of boiler water to help achieve this end.

It was important that parameters of control were laid down for the ship's staff guidance, not only of chemical levels of treatment but also forecasted levels of quantities used, as the contributor was firmly of the opinion that as much damage had been done by over dosing as under dosing (after

all, chemistry was a quantitative science).

In addition to the control by sea staff to within set limits there should be organized a system to control by exception any deviation from the desired values should be reported back immediately, if necessary by radio, and it was such times as these that chemical treatment specialists such as Mr. Powell and Mr. Withers were looked to for one of the most valued products their organization produced; after sales service.

It was only by strict control of treatment that avoidance of expensive post-mortems could be expected, which inevitably followed. (A dose and wait and see attitude.)

MR. E. F. BARTON said there were references to pH in different parts of the paper. Would the authors confirm that all such references were to the pH value of a cooled sample.

MR. D. ROBINSON asked whether either of the authors considered the possibilities that a major contribution to boiler corrosion could be caused by the activity of deposited copper and the iron mass of the boiler forming an electrolytic couple?

It might be possible for water at high pH and temperature to dissociate by electrolytic phenomena to form free hydroxyl ions, these capable of stripping iron away from boiler tubes forming a recognizable deposit of ferrous or ferric hydroxide.

As a chemist, some years ago, he did a series of experiments on the extraction of copper metal from a solution of its salt by its deposition on iron scrap.

Theoretically, copper should have deposited and replaced the iron on an equimolecular basis. This did not

appear to have happened. It was observed, however, that once a small deposit of copper plated onto the iron, a voluminous floc of ferrous hydroxide started to form along with a stream of hydrogen gas. Subsequent analysis of the floc revealed a copper to iron content of 1 to 5. Further investigation showed that the original liquor was depleted of copper and that the iron which had been stripped away was far in excess of the theoretical.

A theory developed at that time was that in the conditions which prevailed, a battery circuit must have been set up in which water was being electrolyzed and the hydroxyl ions were attacking the iron.

To avoid preprecipitation of the copper the pH was no higher than 6.0. After being in contact with the iron the copper appeared to be absorbed by the ferrous hydroxide floc.

Mr. Robinson continued by saying that as a further topic for discussion the authors had mentioned the use of ion-exchange resins for reducing salinity in condensate. Did they recognize the use of sulphite saturated anion resins which could strip dissolved oxygen from water? Alternatively, a ferrous hydroxide saturated resin had a remarkable affinity for the removal of oxygen. Was it not possible to use such a process in place of chemical addition such as hydrazine?

To eliminate the use of chemicals within the boiler could the authors foresee a use for an ion-exchange polishing unit to be situated either in the make-up line or the condensate return?

Mr. Robinson believed that this had been successfully used by the Central Electricity Generating Board. The process involved the use of replaceable high pressure units through which the condensate passed at up to ten times normal flow rate.

## Correspondence

MR. R. G. BODDIE, F.I.Mar.E., in his written correspondence, said that he was interested to hear during the discussion several contributors speak of their reluctance and fear about blowing a boiler down direct to sea in order to reduce the density. In the days when the majority of ships in the Royal Navy were operating on steam at 26 to 32 bar, it was common practice to have to blowdown the boilers and problems seldom, if ever, arose.

MR. W. J. MARTIN wrote that he regretted not pursuing Mr. C. Kameen's line of reasoning regarding the direct blowdown method of boilers *via* the open bottom blow, to regulate T.D.S., at the meeting.

He had had the good fortune to sail in T2 tankers where it was common practice to bleed off from the steam drum into an evaporator as a continuous blowdown, usually for two watches, rather than a short burst from the bottom blow which left everyone in rather a nervous condition.

This system was effective and saved water, which on the P.G. run was at a premium, and was carried out approximately every six to eight weeks. A check was kept to ensure the alkalinity, etc, was not reduced beyond the recommended limits.

He would like the authors' views on this.

MR. D. R. EVANS, F.I.Mar.E., wrote that he appreciated the authors giving an informative paper which highlighted some of the problems which could and did affect high pressure water tube boiler installations. Some conditions did affect lower pressure boiler installations also. The graphs of co-ordinated and congruent phosphate treatment helped to understand the philosophy behind this approach.

The paper did not delve too much into chemistry of water treatment, which was an advantage, as most of the operating engineers were not chemists and did not profess to be.

On the subject of feed water quality, Mr. Evans wrote that on many of the larger VLCC and container type vessels, ion-exchange equipment was fitted on discharge from evaporators, for instance. This "polishing" of the feed make-up could only be advantageous to boilers. An operational point

here was that while ion-exchange would remove CO<sub>2</sub>, all too often the water stayed too long in distilled water storage tanks, thus absorbing more CO<sub>2</sub> before passing into the system. Where distilled water storage tanks had not been coated, or where coatings had deteriorated, tests have shown quite high iron figures, higher in fact than the laid down maximum for feed water.

On feed system corrosion and pre-commission cleaning, he wrote that the desirability of an efficient pre-commission chemical cleaning programme should be appreciated by owners and shipbuilders alike. Emphasis was laid on corrosion in the main feed system, and rightly so. It was therefore worth repeating that a comprehensive pre-commission cleaning programme should include steam lines, feed lines, main condenser and certain auxiliary lines if thorough initial cleanliness was to be attained.

The figures quoted for iron and copper in boiler tube deposits were generally agreed with but this could vary considerably depending on operating conditions and where deposits were found.

He did not personally know of many cases where galvanized piping had been used in sections of a main feed system; it certainly should not be. Zinc being an amphoteric material, it could be removed from galvanizing at a wide pH range and this was obviously undesirable because of boiler deposits resulting.

On hydrazine and feed system ammonia. This question of ammonia levels in the presence of dissolved oxygen being undesirable. With this condition, copper or copper bearing alloys (condenser tubes etc) could be oxidized and in this form the ammonia could act as a chelant taking copper into solution. The statement was made that it made little difference where hydrazine was injected into the feed system. At least one well known turbine manufacturer favoured the HP/LP cross-over pipe position. The basic reason being that hydrazine as hydrazine would be available in initial condensate to absorb any dissolved oxygen entering the low pressure positions. Therefore elimination of one of the two necessary factors for copper pick up would considerably reduce the copper pick up itself.

It was agreed that operation of the de-aerator was often taken for granted and that such conditions mentioned could affect its efficiency and resultant effluent quality. Many de-aerators had orifice controlled vents to atmosphere which although not always convenient, was the best method for removal of undesirable ammonia from the system. Too often, de-aerator operation allowed vented gases to be returned and re-dissolved into the system.

On the theory of co-ordinated phosphate-pH treatment, the paper explained the desirable area under graph which it was beneficial to aim for.

Some water treatment companies still used the two forms of phosphate but it was doubtless easier for the controlling engineer to use  $\text{Na}_2\text{HPO}_4$  and  $\text{NaOH}$  independently. By this method and appropriate dosage, he could better control the desired vectors individually and thus easily attain the correct phosphate and caustic relationship mentioned in the graph.

Regarding point one in this section of the paper, Mr. Evans wrote that although percentage removal of particulate matter was earlier mentioned, the impression here was that cartridge type filters removed all troublesome material.

A great deal of iron and copper in solution could pass through a filter in time with general tendency for precipitation in alkaline boiler water, bearing in mind the solubility differences of iron and copper.

About point two, full flow ion-exchange plants had been considered to reduce or eliminate the effect of sea water contamination. Such plants although perhaps effective, would be extremely large and rather costly. Therefore make-up

polishing plants and faith in a tight condenser seemed the order of the day.

Mr. Evans wrote that the question of silica (point three) was an important one. Over concentration could give turbine blade deposit problems of tenacious glass-like nature and difficult to remove. A silica removal process was not usually included in a pre-commission cleaning programme and silica could leach out from welds, etc, for one to two years. In earlier days, sand filled bending of pipes also contributed.

In general, many desirable check tests have been heard, which were to be taken for various undesirable constituents. It was essential in a modern high pressure turbine installation for simple and accurate tests for ammonia, silica, pH, etc, to be carried out. All these things were important for long term system life and trouble free operation and these tests must be carried out on board as routine. Iron and copper determinations on board were difficult, therefore periodic tests for iron and copper on condensate samples gave a good indication of system corrosion rate, desirable maximum figures being 10 ppb (parts per billion) for iron and 5 ppb for copper.

The electronic, mechanical and general problems were appreciated and without doubt automation was now an accepted part of modern ships, except, as the authors stated, to the important sphere of boiler water and feed treatment. Long term reliability had been a problem on some pilot systems but also the owner was not always ready to spend thousands of pounds extra on a semi or fully automated system. Most necessary analysis could be done but accurate phosphate determination had hitherto been a problem.

## Authors' Reply

The authors thanked Mr. J. L. Hutchinson for his excellent and valuable contribution. To his first question, the authors replied that there was full realization that the problem of iron and copper deposition in boilers was still present, and, indeed, one of the principal objects of the paper was to clarify thoughts in this connexion.

The co-ordinated phosphate scheme of treatment was introduced into the field of marine practice on the claim that it would reduce "caustic gouging" of the boiler metal itself and was not claimed to have any effect on the parallel problem of attack on iron and copper in the feed system.

It was agreed that evidence to date suggested that there was no clear-cut advantage in the adoption of this process except possibly through the fact that the tighter limits for boiler water conditions led to a greater amount of blowing down which must obviously be useful in reducing the concentration of any contaminants present in the boiler.

This, therefore, was suggested as the first part of the answer: it should be carefully examined whether the small amount of blowdown normally given to high pressure marine boilers was sufficient to reduce iron and copper concentrations rather than in consideration of the more traditional role of chloride limitation.

Secondly it was suggested that the problem must be further reviewed from all angles — mechanical layout, choice of materials, as well as chemical aspects. The considerations might include examination of the method of returning drains from auxiliary systems into the plant, how far the installation of a low pressure system could relieve the problems of the main high pressure units, and whether the use of more sophisticated materials such as titanium could justify their initial cost. Bearing in mind the high cost of keeping a ship idle for repairs, the latter point might have more significance than was generally appreciated.

On the chemical side, suppliers were obviously continually working to improve their products and techniques and indeed many of the products which were quite unknown not so many years ago were now in normal use. Such products would include hydrazine, amines, polyelectrolytes and anti-foams.

Mr. Hutchinson's second question highlighted the fact that many of the problems were of a mechanical nature and the authors would suggest that initially they should be faced

as such. However, on the chemical side, it was generally accepted that corrosion of copper (not iron) by ammonia only occurred if oxygen was also present. The short answer was therefore that adequate hydrazine reserves must be maintained at all times. Practical values have been discussed and suggested in the paper.

If the value of the reserve was likely to be affected by widely varying oxygen content of the feed, which could be the case under the conditions described, the installation of a continuous hydrazine analyser would be of obvious value.

The third question had been discussed at some length in the paper and therefore would not be reviewed in detail here. In short, it would seem that since this controversy had been carried on for at least four years, if there was any clear-cut case for the injection into one point in the system as compared with another in terms of a marked and proved improvement in internal boiler conditions (which was the only final yardstick) it should by now have shown itself.

The authors were of the firm opinion that there was far too little co-operation between design staff and water treatment specialists at the important stage, i.e. when the layout was on the drawing board. As Mr. Hutchinson himself had pinpointed, problems were sometimes built into the design which might well be impossible to deal with once the vessel had entered service. It was agreed that the low pressure end contributed its quota of problems and this highlighted the view that the plant as a whole must be examined in this light.

The comment by Mr. M. B. Levens on the point of injection of hydrazine was, as indicated above, reviewed at some length in the original paper. The authors recognized that this was a controversial issue and attempted to give the pros and cons of both schools of thought and would again suggest that a clear pattern in terms of failure of boiler tubes had yet to emerge. If this was accepted, however, then one was led to question whether the main disadvantage of injection into the cross-over was justified, i.e. that a de-aerator was installed and operated at some expense and it was then nullified since all the de-aeration was left to hydrazine.

On the question of uneven injection rate, this referred to the normal practice of employing a single throw ram type pump for hydrazine injection and since it was understood that one of the reasons for selecting the cross-over as the injection point was to ensure adequate treatment of the first-formed

## Authors' Reply

condensate it seemed that one should also consider that injection at this point was into the steam flow and not the feed water. Therefore, the uneven dosing of the region in which it was hoped to introduce treatment seemed possible bearing in mind the much higher velocity of the steam flow compared with the feed water.

If this point was taken, of course, it would be possible to use a different type of chemical pump to provide a more even, or preferably, continuous flow.

It was agreed that different values for iron and copper were obtained from different ships which tended to highlight the complexity of the problems in this connexion and to confirm that design factors were as relevant as the purely chemical aspects involved.

The authors concurred that problems with corrosion/erosion of condenser tubes appeared to be widespread and that this appeared to be related to the current slow steaming rates of vessels. Comments did not, in fact, relate to one particular make of condenser.

In reply to the question raised by Mr. R. J. Tozer, the readings for ammonia concentration in the examples given were on cooled samples of the main feed flow. The authors agreed with Mr. Tozer's remarks on concentration of ammonia in the air ejectors and would comment that cases have been reported where a strong ammoniacal smell could be detected in the engine room near the ejectors.

The use of cyclohexylamine did, as Mr. Tozer stated, introduce a further chemical: it would be possible to rely on hydrazine alone to perform this duty by breakdown into ammonia and thus elevate the *pH*. However, it must be borne in mind that hydrazine was more expensive than C.H.A. and also that the introduction of large doses of ammonia into the system might have disadvantages if there was a sudden fall-off in de-aerator efficiency, in which circumstances oxygen and ammonia could be left in the system, resulting in copper corrosion.

For the above reason it was not correct to say that the *pH* value was an indication that complete de-oxygenation had been achieved since owing to the high solubility of ammonia a high *pH* value could remain even after the hydrazine reserve in the boiler might have been lost.

Mr. Tozer's comments on guidance of ship's staff were fully appreciated, for which reason the authors' organization had a comprehensive system of back-up service to ships in addition to the mere supply of chemicals. This was more important in the marine field than in shore practice since in the former, staff changes were more in evidence due to engineers being transferred from one ship to another or being away on leave. In cases of particular difficulty technical staff have sailed on ships, whilst attendance on trials was also useful in ensuring that all was well before a ship entered service. Finally it was not uncommon to have direct talks with chief engineers by radio, or by teleprint where appropriate.

The authors agreed with Mr. Tozer's comments concerning the excessive use of chemicals and possible damage which could result. The correct product at the correct dosage must be the maxim.

The authors replied to Mr. E. F. Barton by saying that *pH* values where stated were on normal cooled samples. It was recognized that these might differ from the values at source but the relative basis of comparison was reasonably constant.

Mr. D. Robinson's point concerning electrolytic couples would appear to have some theoretical basis since it was recognized that many conditions involving metals in contact with an ionized solution could give rise to differences of

potential, e.g. scaled and clean surfaces, slag inclusions, tool marks, etc. However, in the opinion of the authors this had not been shown to be of particular practical importance in relation to the problems under discussion.

The use of ion-exchange "polishing units" had been discussed in the paper. The authors were not aware of any ion-exchange process developed to date which could effectively remove oxygen from water.

In reply to Mr. R. G. Boddie's written contribution, the authors had already indicated that the question of the amount of blowdown normally given to marine boilers in service should receive urgent consideration particularly from the angle as to whether it should be increased. It could well be that on many vessels mechanical arrangements made this difficult in which case a review of this aspect was obviously indicated.

Mr. Powell was familiar with the system described by Mr. W. J. Martin for continuous blowdown back to the evaporators as used on T2 tankers and concurred that this was an excellent institution, and fully agreed with its value. Like the absence of refinements on modern cars which were standard some twenty years ago, it appeared to be a case where design had gone into reverse, and it was hoped that in line with increased attention to blowdown the question would receive attention in future ship designs.

Mr. D. R. Evans's comments on the role of CO<sub>2</sub> in the make-up feed tanks were appreciated. The problem could sometimes be partially dealt with by continuous recirculation through the ion-exchange unit. Protection of the storage tank surfaces was obviously important, as suggested by Mr. Evans.

The importance of pre-commission cleaning was fully agreed with. Too often this matter was left to people or organizations who were not fully appreciative of the factors involved. It was sometimes worthwhile to employ at least one specialist to oversee and advise on the details of the cleaning procedure. The question of the point of injection of hydrazine had been discussed at some length above but on the point that injection into the cross-over might remove oxygen it should perhaps be borne in mind that with good de-aeration and a reserve of hydrazine in the boiler water, oxygen levels in the steam should be very low.

On the question of operation of de-aerators the authors agreed with the importance of checking the function of the vent system and other parameters having a bearing on the functioning of the unit. Too often it was found that these were not fully understood by operating personnel.

It was not intended to imply that filters removed all troublesome material — only that anything which could be done to reduce contamination of the boiler must be advantageous.

It was not agreed that silica was normally an important factor in marine practice as sea water (the normal starting point for distilled make-up in modern plant) was relatively low in silica. Where problems were encountered it was usually in fairly new plants arising from the use of casting sand, shot blasting grits, etc. in the builder's yard.

The problem of deciding on a balance between what tests were necessary and possible on board, and avoiding overloading of ship's personnel was always difficult. Fortunately air mail services were reasonably rapid and results of check tests carried out at a shore establishment could be communicated back to operating personnel within a reasonable period. Many ships were in fact keeping a check on iron and copper using the Millipore filter technique, the small sample filter being mailed back to the central laboratory for evaluation.