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25 YEARS EXPERIENCE WITH SEA-WATER-COOLED HEAT-TRANSFER EQUIPMENT IN THE SHELL FLEETS

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25 Years Experience with Sea-water-cooled Heat-transfer Equipment in the Shell Fleets

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SYNOPSIS

A review has been made of the experience gained over 25 years of operations of sea-water-cooled heat-transfer equipment in a large modern fleet. The state-of-the-art in the 1960s is presented and the problems encountered with vessels built during that decade are discussed together with the need for changes in the selection of materials of construction. During the 1970s the changes suggested were implemented and some premature failures of a type not previously experienced were encountered. Work was then carried out to develop an understanding of the cause of such failures. This involved laboratory testing under realistic heat-exchanger conditions using natural sea water as the cooling medium and numerous ships trials. The results of this work are presented, together with the rationale for further changes which were made in the specifications of materials used in the construction of heat exchangers. The changes recommended were incorporated into vessels built in the late 1970s and subsequent experience with these systems is reported. It is concluded that the materials used during the construction of these systems are such that with existing designs, vessels entering service can expect to operate trouble-free throughout their useful lives. Some of the methods used to prevent fouling in sea-water circulating systems are considered and the performances of selected systems are discussed in detail. The limitations of materials currently being used are detailed and the possibility of using alternative higher-performance materials in systems of advanced design is mentioned.

INTRODUCTION

In the early 1960s the incidence of failures in the sea-water-cooled heat-transfer equipment on newly built vessels was first highlighted by the occurrence of tube perforations which necessitated stops at sea. The sea-water systems on these vessels were in general non-ferrous with pumps made from gunmetal and piping from aluminium brass, with rubber-lined waterboxes and heat-exchanger tubes of aluminium brass. Additionally the newly built tankers were larger *D Class* (56 000 dwt) and required bigger engines, which in turn meant larger condenser units with increased flow-through rates of cooling seawater.

The failures took the form of pitting and eventually perforation at the inlets of aluminium brass (BS 378 alloy no. CZ 110) tubes. An investigation showed that the perforations, which could occur in as little as six months, were all associated with tube end impingement attack. Figure 1 shows the inlet end of a condenser tube which has been pitted by impingement attack. This form of damage was difficult to understand because the literature suggested that it was a suitable material for use with water speeds of up to 8 ft/s and the sea-water cooling system was designed such that speeds of 6 ft/s would not be exceeded.

SERVICE EXPERIENCE WITH ALUMINIUM BRASS

The influence of size and flow-through rates of cooling waters was highlighted by the vessels *Zaphon* and *Zenatia*. The *Zaphon* was originally commissioned in April 1957 and sailed between then and 1966 with no heat-exchanger problems being reported. In December 1966 the vessel was 'jumboised', after which numerous main condenser tube failures occurred resulting in it being retubed in September 1967 with aluminium brass

(BS 378 alloy no. CZ 110) tubes. Fresh failures were reported in the new tubes in March 1968 and between then and August 1968 over 100 tubes were plugged. A detailed examination carried out in August 1968 showed that the tubes and the Naval brass tube plate had been severely damaged by impingement attack. The damage was associated with turbulence at the inlet end of the tubes and the degree of turbulence was associated with:

- The speed of flow of cooling water through the tubes.
- The size and layout of the waterbox.
- The configuration and diameter of the cooling-water inlet piping adjacent to the waterbox.

Note that before jumboising neither vessel had suffered condenser-tube failures. As the design of the condensers had not been changed when the ships were jumboised we believe it correct to assume that the speed and probably turbulence of the cooling water through the tubes had been increased. This increase in the speed/turbulence of the cooling water would achieve greater operating efficiency of the condenser but had resulted in impingement damage to the condenser tubes. A further investigation showed that the condenser on the *Zenatia* had also been retubed but apparently had a longer life since retubing than the condenser tubes on the *Zaphon*. This increase in life was attributed to the use of metal inserts. However, the inserts were only a temporary palliative, increasing the thickness of the tube inlets but not reducing the amount of damage. It was the increase in thickness of the tube inlets with metal inserts which accounted for any increase in the life of the tubes.

We believe that the depth of the waterbox was insufficient and the design of the cooling-water inlet would certainly have promoted turbulence. Before jumboising, when the cooling water speeds were lower, it is probable that design factors were not critical. However, at higher water speeds these factors would have increasing importance and while the design water speed (6 ft/s) may not have been excessive the increased turbulence could have been decisive. The turbulence in the condenser on the *Zaphon* must have been very high. Slight impingement damage was found to have occurred at the outlet end of the tubes. This occurs under conditions of high turbulence.

Damage continued to be reported with the *N Class* vessels (110 000 dwt) but came to a climax with the *M Class* vessels (250 000 dwt). A typical example of the performance of the aluminium brass alloy in this class of vessel is obtained by considering the *Mitra*. This vessel was commissioned in February 1969 and the main condenser was a single pass unit which operated from a scoop. It contained 6000 tubes and iron anodes were fitted onto the cast-iron door of the rubber-lined waterbox.

Several failures which could be attributed to impingement attack occurred during the vessel's first year of service. In January 1970 attempts were made to alleviate the damage by fitting plastic inserts into the tube inlets. Failures, which necessitated stops at sea, continued to occur intermittently and by June 1970 16 tubes had been plugged off, 11 in the lower half and 5 in the top half of the condenser. The failures had occurred in a random manner.

When the *Mitra* was docked during June 1970 an examination was made of the condenser and it was concluded that the majority of the tubes had suffered inlet attack extending beyond the first 6 in of th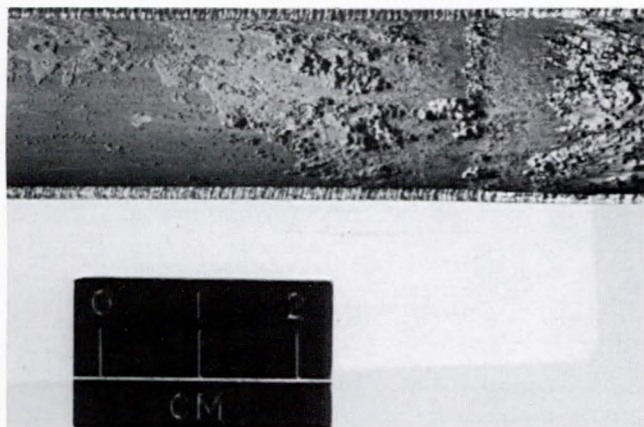e tubes. The inserts that had been fitted were of insufficient length to protect the tubes from all damage. Additionally the soft iron anodes fitted into the waterbox had corroded away, but neither the cathodic protection this would have afforded nor the liberated iron salts had prevented the impingement attack. Urgent remedial action was now required to ensure that further similar failures did not occur.

It was agreed that two courses of action should be considered:
1. Provide a source of iron salts in the cooling water and promote the formation of protective films rich in iron oxide on the surface of the aluminium brass.
2. Re-tube the heat exchangers with a more suitable material.

Ferrous sulphate treatment

Until the 1960s the sea water in a vessel's cooling system had been in contact with numerous sources of iron salts from corroding cast iron or steel valves, pipelines, waterboxes etc. The iron-containing corrosion salts from these components and the additional benefits of the cathodic protection they afforded undoubtedly contributed to the protection of copper alloy heat-exchanger tubes especially in the most vulnerable tube end areas. It is probable that iron salts in the cooling water promote the formation of protective films, rich in iron oxides, on the surfaces of the copper alloys and thus reduce the damage caused by impingement. In all the investigated cases of premature failure it was observed that few sources of iron salts were available to assist in the formation of protective films, either because the ferrous components had been coated with plastics or elastomers or they had been replaced by non-ferrous alloys.

Great interest was aroused by a paper by Bostwick[1] which referred to the power-plant condensers of the City of Jacksonville, USA, where rapid failures caused by impingement attack were occurring in aluminium brass tubes with average water speeds of 2 m/s. The cooling water from the St John river had one-half to three-quarters the salinity of normal strength sea water. When ferrous sulphate was added to the cooling water failures, which had been occurring almost daily, ceased immediately. Only small quantities of ferrous sulphate were needed to produce this startling improvement in performance, with 1 ppm of iron (about 5 ppm of hydrated ferrous sulphate) being added for about 1 h per day, or for 30 min twice a day.

While iron injection can readily be applied to shore-based installations, we believed that difficulties could arise on ships. For a system to be suitable for marine use it must be simple to operate and require little maintenance. The programme of operation must not be too involved and must conform with normal engine-room routines. A variety of ferrous sulphate injection systems have been devised by ships' engineers. In some vessels solid ferrous sulphate was added directly to the cooling water through the sawdust injector but the time the crystals take to dissolve was probably too long for such a method to be effective. In another system a ferrous sulphate solution was injected into the cooling water using compressed air.

These systems, although generally beneficial, were unreliable and control of addition rates was difficult. They also relied on existing inlet points, which were not usually in the best positions to provide maximum coverage of all the tubes.

Nevertheless we felt that there was ample evidence from shore installations to suggest that efficient ferrous sulphate injection systems could provide very high levels of protection for aluminium brass tubes. We therefore designed and built a reliable ferrous sulphate injection system for use on ships. It was decided at an early stage that the design should satisfy the following requirements:
1. Injection to be by gravity feed to reduce costs and increase reliability by eliminating the use of pumps and compressed air. This necessitated the main head being sufficient to

FIG. 1: View of the inlet end of an aluminium brass tube pitted by impingement attack

overcome the pressure expected in the inlet of the main condenser.

2. Non-corrodable materials to be used because of the corrosive nature of the ferrous sulphate solution.

3. Mixing tank to be capable of holding sufficient solution to treat all injection points in one mixing.

4. Protection to be provided for the main condenser, auxiliary condenser, lubricating-oil cooler and salt-water services.

5. Inlet points to be robust and compatible with the materials of the system to be treated.

6. Injection of the solution to be controlled to give the calculated concentration of ferrous sulphate in the areas to be protected.

7. Provision to be made for separate injection at all inlet points.

8. System to have the minimum of controls, require minimal supervision and be completely flexible so that it could be easily accommodated in the many different engine-room designs and layouts.

A unit was designed consisting of the following basic components:

- A 250 gallon low-density polythene mixing tank.
- A mixer–agitator.
- Nylon-braided PVC tubing.
- A distribution manifold machined from nylon and fitted with four HSB (high styrene–butadiene) membrane valves.
- Injection probes machined from nylon with clamps of 90:10 copper nickel and retaining bosses of aluminium brass.

The prototype ferrous sulphate injection unit was built and tested at Thornton Research Centre prior to being fitted into the *Mitra* in June 1970. On the final trip before the system was fitted the ship had lost some 12 days due to condenser-tube failures. During the dry-docking it was found that many of the tubes were in an unsatisfactory condition and the decision was taken to re-tube the whole condenser. Unfortunately because of unforeseen difficulties only 2000 of the 6000 tubes were replaced.

The ferrous sulphate system was fitted during the docking and the general layout shown in Fig. 2 was adhered too. A site for the tank mixer was found in the engineers' store-room situated at main deck level. The tank was firmly fixed in position by welding brackets from the main frame to the bulkhead. A water supply was coupled in from the fresh-water supply and a platform and steps constructed to allow easy filling of the tank.

The nylon-reinforced PVC main delivery line was fed to the engine room and clamped to the main bulkhead wherever possible and carried on pipe trays where no fixed supports were available. The control manifold was bolted to a main stanchion approximately mid-way between the four injection points.

The injector probes were argon-arc welded into position at points where maximum mixing could take place. The main-condenser injector was positioned on the outside of the bend of the main inlet to the waterbox. The lubricating-oil cooler inlet was also positioned on the outside of the bend in the inlet pipe but the injector to the auxiliary system had to be fitted into the main body of the pump because of lack of space elsewhere. Two injectors were fitted into the salt-water services inlets fed by a single pipe so the system could be treated whichever of the two valves was operated. The injector points were sited immediately behind the two valves on the shipboard side.

The condenser was brought into service and a suggested programme, Appendix I, of treatment based on the recommendations of leading condenser manufacturers and other users was followed. The recommended routine treatment programme (Appendix II) was then commenced. The crew found the injection unit easy to operate and reported no operational difficulties.

As soon as the unit became operational tube failures ceased and the success of the treatment was such that units were quickly installed on all *D, N* and *M Class* vessels. Waterside

corrosion problems appeared to vanish overnight although the exact mechanism by which this protection was achieved was not fully understood.

North and Pryor[2] have suggested that the film deposited on copper by cathodic treatment in a fresh 0.5 mol/l NaCl solution containing a small additon of ferrous sulphate is primarily lepidocrocite together with some cuprous oxide as a minor constituent. They concluded that the lepidocrocite was acting as a 'classic cathodic inhibitor and in accordance with the classification of Evans,[3] it must be regarded as a "safe" inhibitor'. Inhibitors of this type rely upon the general coverage of the metal surface rather than the de-activating of active anodic sites and should provide substantial protection in terms of reduction of pitting corrosion, general corrosion, corrosion–erosion and crevice corrosion.

Later, Gasparini et al.[4] placed a new interpretation on the phenomenon of the protective film based on the application of the concept of zeta potentials of extended metal surfaces and suspended particles. They proposed that the copper alloy condenser tubes are coated with a film of Cu_2O and that negatively charged particles of lepidocrocite are deposited over the Cu_2O film. The electric field associated with the Cu_2O film, which has a positive zeta potential, extends into the bulk of the solution at the operating flow rates, attracting the lepidocrocite particles and causing those that reach the surface to adhere to it. The existence of a spontaneous cathode (positive zeta potential) associated with the Cu_2O film further favours the deposition of negative lepidocrocite particles.

If this interpretation is correct then it is difficult to understand how the active anodic regions (bare metal) can be coated with a protective lepidocrocite film. This theory also assumes that all copper and copper-based alloys are normally coated with Cu_2O. In such circumstances it is difficult to explain why different copper-based alloys have different critical flow rates above which they experience corrosion–erosion damage in flowing sea water. It is more probable that the various alloys are coated with different complex oxides. Thus the surface layers on aluminium brass tubes are probably rich in aluminium whereas those on the iron-containing copper nickel alloys may be rich in iron.

We examined samples of the deposits present on tubes taken from numerous Shell tankers using X-ray diffraction and electron microprobe techniques. This work showed that deposits of lepidocrocite $[\gamma\text{-}FeO(OH)]$ were often present but so were compounds of the pyroaurite type. This latter
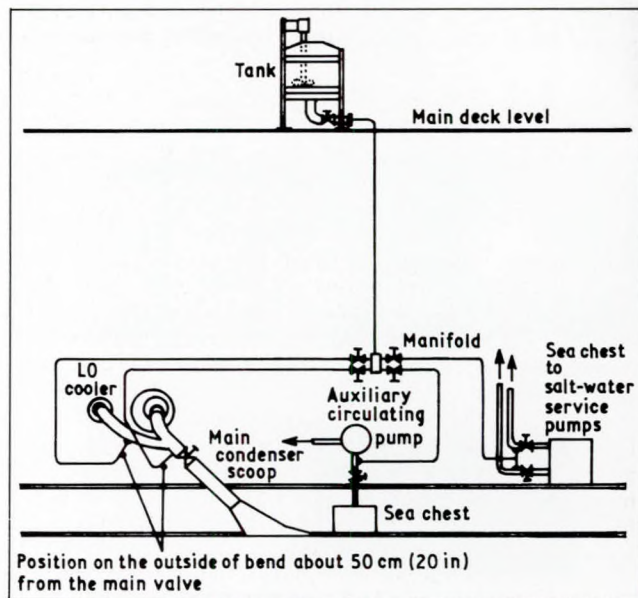

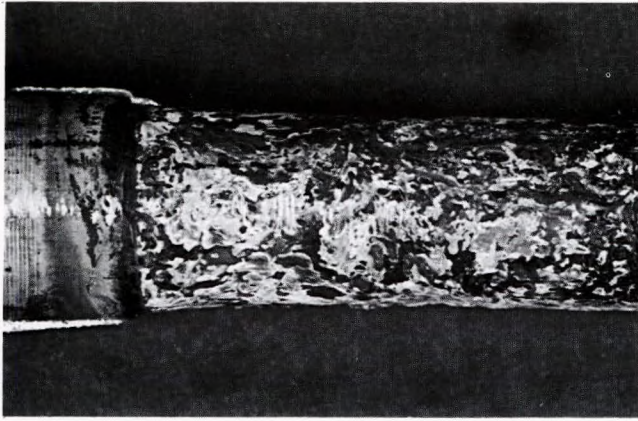**FIG. 2: General layout of the ferrous sulphate injection system**

FIG. 3: Section of a condenser tube taken from near a support plate showing the tube to be severely corroded by ammonia
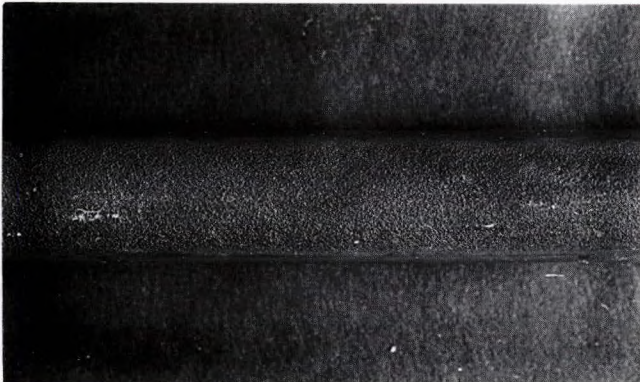

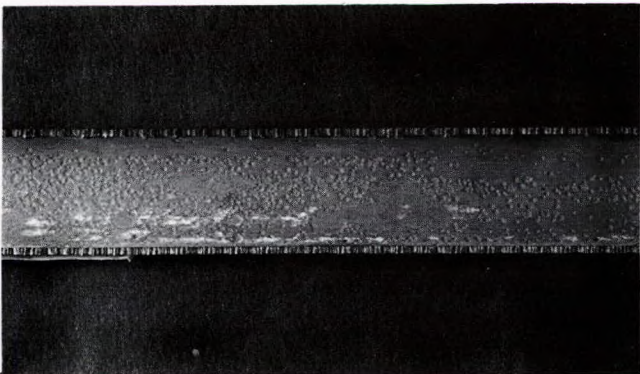FIG. 4: Section of a tube damaged by steam impingement

FIG. 5: Pitting corrosion associated with the presence of harmful cathodic films on the tube surface

material was layered, the inner deposit often being of $Mg_6Al_2CO_3(OH)_{16}\cdot4H_2O$ (hydrotalcite). Above this layer was deposited a similar brown compound with some of the Al^{3+} being substituted by Fe^{3+}. These layers were often contaminated by each other and extraneous materials such as sand and calcite.

These findings were in agreement with the later work of Epler and Castle,[5] who found that condenser tubes in seaside power stations become coated with an inner layer of hydrotalcite-type mixed Al, Mg, Zn hydroxide and an outer layer of FeO(OH). They concluded that the hydrotalcite layer had a buffering capacity that allowed it to respond to changes in local pH by release or absorption of magnesium ions. This capacity could be altered by repeated drying out or if ferrous sulphate injection is carried out and the outer iron-rich layer

controls the diffusion of ions into or away from the hydrotalcite/solution interface.

Steamside problems

Once the life expectancy of the aluminium brass tubes had been increased to exceed 5 years, other forms of attack, this time on the steamside, became apparent.

Hydrazine

One type of damage was associated with the use of an excess of hydrazine, an oxygen scavenger which decomposes to produce ammonia. The damage was particularly severe on tubes either in or adjacent to the air-extraction section and adjacent to support plates. Figure 3 shows an example of this type of damage on a tube taken from the *Latona*. On this vessel over 2000 tubes had to be replaced. A report by a condenser manufacturer[6] outlines methods of alleviating the damage and concludes that the primary remedy is to control closely the excess of hydrazine in the feed water. Shipboard efforts to reduce the hydrazine reserve within the boilers have been successful in reducing the incidence of failures but have not entirely prevented them.

Steam impingement

Another type of damage that occurred was associated with steam impingement. The tubes affected by this form of attack were usually those in the way of the steam inlet ducts. Figure 4 shows a tube taken from the top row near the entry from the LP turbine on the *Medora* and typifies this form of attack. It can be seen that the aluminium brass tube surface has been roughened where the steam has impinged. Damage of this type did not present a major operational problem for the fleets.

INITIAL SERVICE EXPERIENCE WITH 70:30 COPPER NICKEL

In view of the fact that when the *L Class* vessels were to be ordered and the effectiveness of the ferrous sulphate systems had not yet been established, a decision was made to have these vessels tubed with an impoved alloy. Following an extensive literature review and discussions with many manufacturers it was agreed that the most suitable material would be the alloy BS 2871 Part 3 CN 108. This material, a 66 copper, 30 nickel, 2 iron, 2 manganese alloy, was believed to be very resistant to steamside corrosion and able to tolerate coolingwater speeds of up to about 12 ft/s.

In an attempt to obtain some in-service experience with the alloy an opportunity was taken to re-tube the main condenser of the *Diala* with this alloy tube in September 1971. Prior to this, numerous leakages had occurred in the aluminium brass tubes. After a year in service the tubes in this condenser were examined and found to be in excellent condition. A decision was then made to use tubes of this alloy in future vessels. To date, no tube failures have occurred on this vessel and a recent eddy-current survey indicated that the condenser is still in excellent condition.

Cathodic films

One of the first vessels to be fitted with the CN 108 tubes was the *Latia*, which entered service in 1974. During its maiden voyage 69 tubes were perforated and had to be plugged. It was later established[7] that these failures were attributable to the presence of carbon and manganous oxide films on the tubes' surfaces. These films were highly cathodic, and at defects in them the exposed underlying anodic tube material corroded in the flowing sea water.

An example of the pitting corrosion that occurred is shown in Fig. 5. These harmful films had formed during the manufacturing process and it seemed probable that tubes in other

vessels may have been supplied in a similar condition and could therefore be prone to corrosion. The next *L Class* vessel was already under construction in the yard and tubes had been fitted into the main condenser. It therefore became essential to develop a simple test that could be used to establish the cleanliness of the tubes and if necessary develop an in situ cleaning technique for the tubes.

Method of detection of harmful films

Assessment of the extent of carbon contamination of the inner surface of copper tubes had been carried out successfully for many years using the carbon black (CB) method quoted by Cornwell et al.[8] Unfortunately this method was not applicable to either copper alloys or complex deposits of carbon and manganous oxide, and another technique had to be developed. The principle of the method was to determine the corrosion (rest) potential of the tube bore in the 'as-received' condition relative to the corrosion potential of freshly abraded tube alloy. This is an indication of the 'nobility' of the films on the bore surface. A positive value indicates that the tube bore is noble (cathodic) relative to the clean alloy and the larger this value then the greater is the risk that the tube will suffer pitting in service. A difference of <70 mV has been used as a criterion for the acceptance of new tubes.

Cornwell et al.,[8] working with copper tubes in cold fresh water, were able to relate the surface potential of a tube contaminated with carbon deposits to the onset of pitting and showed that corrosion occurred if potential differences of >70 mV were measured. Whilst the corrosion characteristics of copper and copper nickel alloy are different, it is not unreasonable to suggest that cathodic films would behave similarly on both materials. Details of the methods used to determine the corrosion potential of new tubes are given in Appendix III.

Using this test procedure it was shown that the tubes fitted into the next vessel to be commissioned were also coated with harmful films. It was agreed that these films must be removed. Acid foam cleaning was used and continued until the tubes were found to be clean using our test criteria of 70 mV. The presence of harmful films on tubes had highlighted a serious problem and we were interested in establishing how many suppliers were providing tubes in this condition.

Tubes representative of those supplied by four European manufacturers were examined and it was found that those from three manufacturers were coated with harmful films rich in carbon and manganous oxide. Portions of the tubes from the various manufacturers were immersed in static synthetic sea water and after three weeks pitting was observed on the tubes coated with highly cathodic films. Some of these tubes were fitted into a ship's condenser during a partial re-tubing. Two years later they were removed and upon examination were found to be heavily pitted. Further work showed that most manufacturers were able to remove the surface films using blast cleaning; however, considerable expertise was required or the quality of cleaning was very variable.

One manufacturer demonstrated that chemical cleaning could be undertaken successfully. However, it is recommended that whatever the cleaning procedure used, potential-difference measurements should be carried out on representative samples at least until the credibility of the manufacturer has been established.

All future CN 108 alloy tubes were purchased to a specification which called for the manufacturers to issue test certificates showing that each batch of tubes supplied were free of harmful films.

THE PRE-COMMISSIONING OF 70:30 COPPER NICKEL

Having purchased tubes that are free from harmful films it is essential to ensure that this good condition is maintained during the initial contact with sea water. For ships' condensers this occurs during pre-commissioning operations prior to the first sea trials when the cooling-water system and the main condenser are filled with water. Since at that time the vessel is moored in a fitting-out basin, dock water tends to be used, by tradition and common practice, and this water could remain stagnant in the cooling system for long periods before the acceptance trials. A careful study of the published literature revealed that no systematic study of the effects of pre-commissioning on tubes had been undertaken although various authorities had made recommendations relating to specific procedures.

The Royal Navy advocate the use of an inhibitor, sodium dimethyl dithiocarbamate, for pre-commissioning and re-dosing, although this treatment is expensive and requires the services of a chemist to administer. Stal Laval have recommended that a 3 wt% solution of aerated sodium chloride in condensate water be circulated through the system during the period of rotor alignment up to the sea trials. Others have suggested that ferrous sulphate should be added to the circulating water to assist in the formation of good protective films.

Whilst these recommendations are made, no comparisons have been made between them and they do not all appear to be based on a sound technical understanding of the problem. In view of this, a programme of research was initiated to determine the optimum pre-commissioning procedures and form the basis of recommendations for the treatment of tubes by manufacturers, shipyards and during the initial periods at sea.

Experimental

Our work was divided into two main areas aimed at:
- Determining the effect that pre-commissioning treatments have on the corrosion of condenser tubes. These tests were carried out by applying the appropriate chemical as necessary to tubes and then exposing these to stagnant waters so as to simulate the period that a vessel could be in the fitting-out basin.
- Determining the corrosion characteristics of tubes exposed to selected pre-commissioning procedures when initially exposed to service conditions. These tests were carried out using a condenser test rig sited on a dockside at Birkenhead.

Procedures

The possible procedures that have been examined were:
1. Exposure to stagnant dockwater for up to two months. This has been common practice in shipyards over many years.
2. Exposure to a solution of sodium chloride (3 wt%) in de-ionized water circulated in a closed circuit. This procedure is similar to that recommended by a major turbine manufacturer.
3. Exposure to a static solution in fresh water of sodium dimethyl dithiocarbamate (SDD) at a concentration of 0.05 wt% for 24 h prior to introducing dockwater. This is a procedure recommended by the Ministry of Defence,[9] who state that a daily monitoring of the corrosion rate is necessary once the tubes are exposed to sea water. If the corrosion rate rises to a specified value then it is recommended that a further application of SDD be made.
4. Treatment by a ferrous sulphate (5 ppm) solution in fresh water for 24 h. This was followed by a daily dosage of ferrous sulphate (10 wt%) solution for 1 h per day at a flow rate sufficient to give 5 ppm ferrous sulphate in the flowing sea water. This treatment continued for the first month in the test condenser and was followed by the same dosage twice a week thereafter. We have previously used this treatment for aluminium brass alloy tubes with some considerable success.
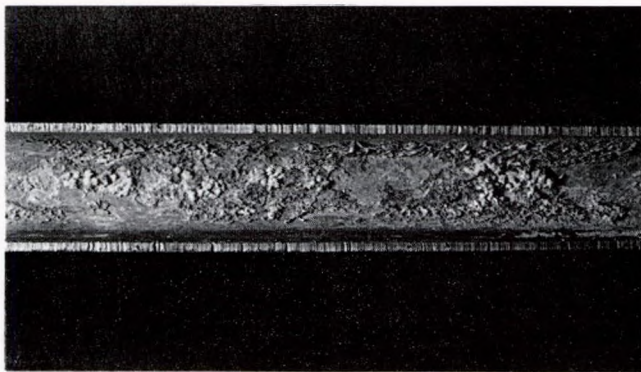5. Circulation of 300 ppm ferrous sulphate in fresh water for

FIG. 6: Corrosion damage in the top of a tube taken from a main condenser

two weeks. This was followed by a test in the condenser rig during which ferrous sulphate solution was injected for 1 h per day to give a concentration of 5 ppm in the sea water.

6. Aerated steam treatment at 100 °C for 72 h, which was found to be beneficial during research work in the USA.[10] This work had shown that treatment resulted in a five-to-ten-fold reduction in the rate of corrosion of copper nickel alloy tubes on exposure to sea water for 8 h compared with an untreated tube of the same alloy.

7. Exposure to potable water, either under aerated flowing conditions for 2 weeks or stagnant for 8 weeks. The water used in these tests had a pH of 7.5, contained 88 mg/l of chloride ions and had a total hardness of 130 mg/l (as $CaCO_3$).

8. Exposure to stagnant distilled water for 8 weeks.

9. 'Incralac' treatment.* The use of this material as a coating for condenser tubes under total immersion conditions had been suggested by Castle et al.[11] who tested a number of organic coatings and found Incralac to be the most promising.

The tests were carried out either in 150 mm long tubes or in a rig which is a model condenser. In this rig service conditions are simulated by condensing steam on the outer surfaces of three tubes (each 19 mm in diameter and 880 mm in length, made up into a tube bundle by expansion into 90:10 copper nickel alloy tube plates), cooled by a once-through flow of natural sea water. The rig was used to simulate the initial exposure of tubes which had been pre-commissioned using the procedures described. Hence the effects of these pre-commissioning procedures on the early corrosion performances of CN 108 tubes could be assessed under realistic but controlled conditions.

During the tests the rig was operated at a flow rate of 80 l/min through three tubes (equivalent to a water speed of 2 m/s in each tube), with a boiler temperature rise of 1 °C between the inlet and outlet. Corrosion potentials of the inner surfaces of the tube, relative to a saturated calomel reference electrode (SCE), were monitored daily for the majority of the tests.

The experimental details of this programme are given elsewhere,[7] but the conclusions of this work included the following:

● Stagnant waters, particularly polluted dockwater, should not be allowed to come into contact with CN 108 alloy tubes.

● Clean, aerated, flowing, potable water, distilled water, sodium chloride (3 wt%) solution or sea water are acceptable for pre-commissioning CN 108 alloy tubes.

● SDD treatment can be very effective in combating corrosion but its use involves careful monitoring to ensure success and

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* Incralac is an acrylic resin containing benztriazole to inhibit copper corrosion. It has been developed by International Copper Research Association (INCRA) for the prevention of tarnishing of copper and copper alloys exposed to the atmosphere.

other simpler, cheaper and more reliable methods have been found.

● Pre-commissioning with ferrous sulphate of CN 108 alloy tubes is of no value under the conditions tested.

● Steam treatment does not prevent pitting by stagnant dock water.

● Treatment with Incralac may be beneficial under some conditions but more work is needed to assess the effects of high temperatures, fouling and erosion.

Recommendations

As a result of this work it was agreed that all future vessels would be pre-commissioned using the following guidelines:

1. Tubes should preferably remain free of water until the vessel enters service.

2. If it is necessary to fill tubes with water for non-operational purposes, eg turbine alignment, then fresh potable water should be used. The potable water should preferably be circulated with the outlet water from the condenser dropping through air into the pump suction tank to promote aeration. To avoid excessive iron ion contamination (if steel circulation lines are used), pipework should be coated or non-metallic.

3. For equipment requiring dock-water cooling during the commissioning period, it is recommended that (a) dock water, once introduced, be maintained at operational flow rates and (b) if it is necessary to stop the dock-water flow, the tubes should be refilled and drained at least twice with fresh potable water to remove all deposits, weed etc., finally being drained and maintained dry.

The main consideration during this pre-service period is that sea water is never allowed to remain stagnant in the copper alloy tubes.

It was interesting to note that the tubes exposed to stagnant sea water become coated with cuprous sulphide (Cu_2S) and that on subsequent exposure to aerated sea water severe corrosion occurs as the copper sulphide becomes unstable. Clean sea water could be regarded as polluted sea water after about 24 h of stagnation since in that time all living matter will die and sulphides will form in the water.

INFLUENCE OF LOW WATER VELOCITIES ON THE CORROSION OF COPPER NICKEL

During the late 1970s a few tube perforations were reported on vessels fitted with CN 108 alloy tubes. In general the performance of this alloy was very satisfactory, although the few failures that did occur caused concern as the reasons were not easily discernible. The failures had occurred in luboil coolers and main condensers and the damage was most severe at the slightly hotter sea-water outlet end and only the top portions of the tubes were corroded. An example of a corroded tube of this type is shown in Fig. 6. Whilst it was initially suggested that the damage may have been of the 'hot-spot' type, in these instances the tube-wall temperature was about 60 °C and much lower than that previously associated with this form of corrosion. According to the literature,[12–14] a characteristic feature of hot-spot corrosion is that de-alloying of the tube material usually occurs leaving metallic copper deposits in the corrosion pits. In these instances little evidence of de-alloying was apparent.

'Hot-spot' corrosion is believed to occur under service conditions where the tubes are exposed to localised high temperatures above 80 °C. For example, it has been reported that local hot-spots formed where steam impinged directly onto the outer surface of a tube.[12] Various mechanisms have been proposed for hot-spot corrosion[12–15] but none of these seemed to explain fully the failures observed on the vessels. In order to gain a fuller understanding of the corrosion of CN 108 alloy tubes the model heat-exchanger rig was again used. In this

series of tests the influence of sea-water velocity and steam temperature on the corrosion characteristics of the alloy were examined.

It was found that the sea-water velocity and tube-wall temperature were critical factors in determining the mechanism and rate of corrosion. The in-service failures could readily be reproduced in the test rig when the sea-water velocity fell to below 0.14 m/s. We believe that at these low water speeds pockets of air formed in the tops of the tubes and shielded them from the cooling water. Under these conditions localized high temperatures could occur in the moist chloride-containing air pockets and rapid corrosion would then take place. An example of the damage produced in the condenser test rig under low flow conditions is shown in Fig. 7. Further testing showed that the 90:10 copper nickel alloy and aluminium brass were also prone to this form of corrosion under similar conditions.

It was concluded that CN 108 tubes can operate satisfactorily at a sea-water velocity of between about 0.25 and 4 m/s and at a steam temperature of less than 62 °C provided there is no fouling, thick scales or entrapped air present.

CURRENT SERVICE EXPERIENCE WITH 70:30 COPPER NICKEL

No steamside corrosion problems have been reported with the CN 108 alloy although in the 1970s this alloy was fitted into two *B Class* (500 000 dwt), 15 *L Class* (300 000 dwt) and five *G Class* (75 000 m³ liquified natural gas) vessels. Tube inspections have been carried out at regular intervals since they entered service and records kept of the incidence of tube failures. This work is summarized in Table I, which lists the numbers of tubes plugged during the service lives of these vessels.

Each *L* and *G Class* vessel has approximately 7000 tubes fitted and each *B Class* vessel has 14 000 tubes fitted. We believe that this survey illustrates how successful the decision to use this alloy has been. If we exclude the *Latia*, since we know that this vessel was fitted with tubes that did not meet our requirements, only 149 tubes of the 161 000 fitted have been plugged. Many vessels have now been in service for 10 years or longer and to date experienced no heat-exchanger problems. From this we can only conclude that the copper nickel alloy CN 108 is very suitable for service on vessels providing it is purchased free of all harmful films, pre-commissioned correctly and operated with water speeds above 0.25 m/s and below 4 m/s.

SERVICE EXPERIENCE WITH TITANIUM

In the late 1970s there was also considerable interest in the possible use of titanium as a heat-exchanger material, particularly for plate heat-exchanger applications where other materials had been shown to be very prone to impingement attack. In these applications aluminium brass and the copper nickel alloys were found to have very short service lives before perforation occurred. However, when titanium was used as the plate material failures associated with impingement attack ceased and problems of any type became extremely rare.

One such failure did occur on a plate from a fresh-water cooler on the *Lepeta*. This failure occurred on a plate with four blind corner discs that was positioned next to the steel end plate remote from the water inlet and outlet. The failed plate, which is shown in Fig. 8, had a roughly circular hole about 90 mm in diameter in it and the area around this hole was covered with rust.

At first glance it was not easy to account for the hole since titanium is not prone to corrosion in sea water under the prevailing operating conditions. However, a close examination showed the damage to have been caused by fretting of the titanium which had been in contact with the steel end plate. This could only have occurred if the titanium had been distorted and tests were carried out to establish at what water pressure we could expect this distortion to occur. This was done by taking an undamaged corner, clamping it between steel flanges and applying a hydrostatic pressure to the water side.

By progressively increasing and releasing this pressure in small steps of about 0.3 bar (5 psig) a stress/strain curve for the corner was determined. This showed that at a pressure of about 3 bar the blind corner disc had a permanent deflection sufficient to allow the titanium to have contact with the steel backing plate. The vibration on the vessel would then be sufficient to initiate fretting corrosion of the titanium in a roughly circular manner. Once fretting had occurred thinning soon followed and when a hole was worn through sea water would penetrate to the steel backing plate causing it to rust.

It is more difficult to postulate the next step since in a galvanic couple between steel and titanium we could expect the corrosion of the steel to increase and the titanium not to corrode. However, since fretting debris and rust had embedded into the naturally protective titanium oxide film it was possible for the titanium to corrode, since the oxide film would not be able to reform completely at damaged regions. This could allow corrosion of a very active exposed metal to occur.

Whilst the latter work is a little speculative there is no doubt that the distortion followed by fretting were the causes of the damage and we did not believe that a total of three plate failures of this type merited further work.

Apart from test purposes, titanium tubes have not been used on any Shell vessels built to date, although the power-generating and offshore industries have used such tubes with considerable success, but not entirely without problems.

PREVENTION OF FOULING

Over the last 25 years various measures have been taken to combat the problem of marine fouling in heat exchangers, including careful screening of sea inlets to prevent larger objects being drawn into systems and the injection of toxins, chlorine and hypochlorite to produce a hostile environment to either discourage fouling settlement and growth or remove existing fouling.

In the 1960s toxins were widely used but their popularity and use has decreased for various reasons, including the problems associated with handling, supply, storage, toxicity to humans, injection-equipment requirements and environmental considerations. Concern also existed over their addition to sea water which was to be evaporated for drinking water.

Shipboard experience also indicated that these materials were only successful in preventing fouling when used at high dosages with accompanying high costs. This finding is in
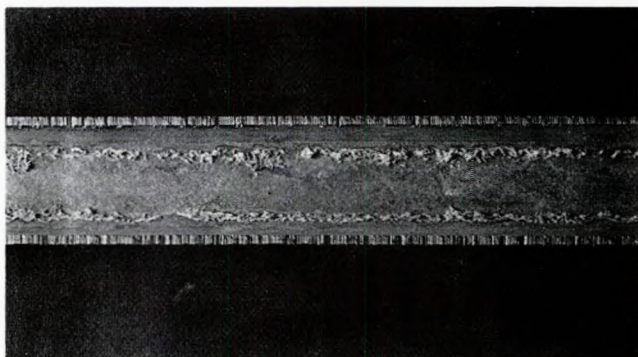

FIG. 7: **Example of the corrosion that occurred in the top of a condenser tube when the cooling-water flow rate was low**
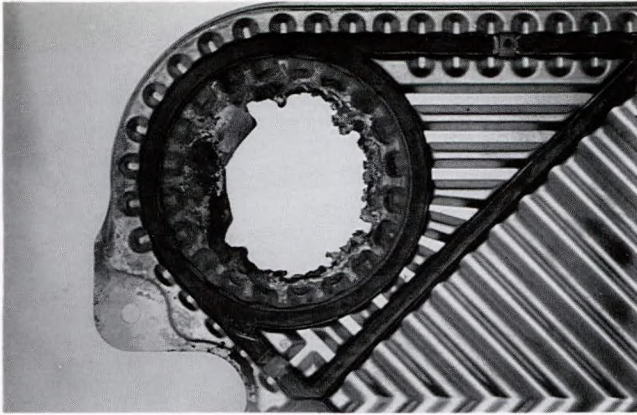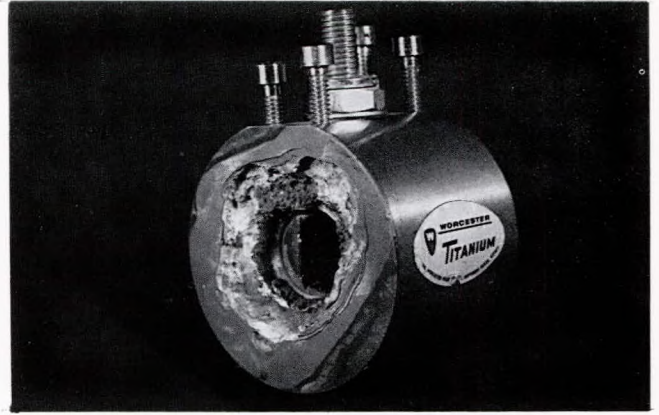
FIG. 8: Failed titanium plate from the *Lepeta*

FIG. 9: Corroded titanium valve

general agreement with that of Trotman[16] and is discussed in more detail in a paper by Grim.[17]

During the 1970s electrochlorination units were fitted into most vessels in the Shell Fleets and various problems became apparent including platinum loss from electrodes, flow switch malfunctions, cell and pipework leakage, cell blockage by calcereous deposits and complicated interactions of each of these. Platinum loss was experienced to a greater or lesser degree with several systems and was the subject of investigation for a considerable period. The platinum loss was promoted by increased anode potentials, which under operating conditions were influenced by sea-water salinity and temperature.

To prevent excessive platinum loss some cells were fitted with a thermostat that operated and reduced anode current densities, and hence anode voltages, when sea water at less than 10 °C passed through the chlorination unit. Equipment does exist which it is claimed does not have a sea-water temperature limitation; here voltage is prevented from rising above a certain level by electrical circuit design and again the result is reduced anode current and hence reduced chlorine production. Other units were protected by a manufacturer's

warning that they should not be operated in sea waters below 10 to 14 °C.

Cell manufacturers sometimes claimed that this reduction in cell output was not detrimental to fouling control in that less chlorine was needed in cold water. This was not entirely correct, and additionally it must be remembered that actual water temperatures within hot condensers are sufficiently elevated to enhance fouling growth, which will require chlorine for control and which may not be available under cell low-temperature current-density control. These temperature constraints applied to electrochlorination units are undesirable and must be taken into account by ships trading in colder waters. An alternative utilized in some vessels was to use a warmed water supply to chlorinators, ie a supply tapped downstream of a condenser, to avoid subjecting cells to cold water conditions and accompanying problems.

In general, few electrical difficulties have been experienced with electrochlorinators, problems in the main having been a consequence of cell leakage. Several instances of anode insulation failure have occurred and the result of one such failure is indicated in Fig. 9. Here, catastrophic corrosion occurred to a titanium valve situated at a main-condenser chlorine injection

TABLE I: Performance of copper nickel alloy tubes to BS 2871 Part 3 CN 108 in the main condensers of *L, G* and *B Class* vessels

Vessel	Date entered service	Reported tube failures and comments		Vessel	Date entered service	Reported tube failures and comments	
Latirus	January 1974	April 1979	29 tubes plugged	*Liparus*	June 1975	June 1979	1 tube plugged
		November 1982	1 tube plugged			Vessel laid up December 1983	
		February 1983	1 tube plugged	*Limnea*	July 1975	No tube leakages prior to vessel	
		Vessel left service April 1984			Laid up	being laid up in December 1983	
Lagena	May 1974	August 1979	4 tubes plugged		July 1975–		
		October 1979	43 tubes plugged		April 1976		
		January 1980	2 tubes plugged	*Labiosa*	July 1975	August 1977	1 tube plugged
		March 1981	6 tubes plugged			Vessel left service May 1981	
		Vessel left service February 1984		*Lampas*	November 1975	April 1981	1 tube plugged
Liotina	August 1974	No tube leakages				October 1982	4 tubes plugged
Latia	August 1974	September 1974	69 tubes plugged			Vessel laid up December 1983	
		August 1976	1968 tubes replaced	*Lottia*	December 1975	March 1981	2 tubes plugged
		August 1976–				December 1981	1 tube plugged
		May 1981	18 tubes plugged			November 1982	1 tube plugged
		May 1981–		*Lepeta*	July 1976	December 1981	3 tubes plugged
		December 1983	No tube leakages	*Leonia*	December 1976	March 1982	1 tube plugged
		Vessel left service December 1983		*Lima*	June 1977	No tube leakages	
Limatula	December 1974	April 1980	14 tubes plugged			Vessel became floating storage	
	Laid up	September 1980	13 tubes plugged			December 1984	
	December 1974–	October 1980	8 tubes plugged				
	February 1977	Vessel left service October 1981		*Gari*	December 1973	No tube leakages	
Linga	March 1975	No tube leakages		*Gastrana*	June 1974	December 1975	3 tubes plugged
	Laid up			*Geomitra*	March 1975	June 1982	1 tube plugged
	March 1975–			*Gouldia*	July 1975	No tube leakages	
	August 1976	Vessel left service August 1981		*Genota*	December 1975	No tube leakages	
Lepton	April 1975	November 1982	6 tubes plugged				
	Laid up	January 1983	2 tubes plugged	*Batillus*	July 1976	No tube leakages	
	April 1975–	July 1983	1 tube plugged			Vessel laid up August 1983	
	September 1977	Vessel left service May 1985		*Bellamya*	December 1976	No tube leakages	
						Vessel laid up January 1984	

point, following its polarization by a cell anode. The result is clearly evident.

From the experience we have gathered we believe that an electrochlorination system capable of producing a feed-water concentration of 0.5 ppm of free chlorine will maintain sea-water cooling systems free of fouling. In practice, this usually produces a chlorine residual at main-condenser outlets of about 0.1 ppm. During deep-sea operation such levels of chlorine injection may be limited to 4 h per day whilst continuous additions are affected for 12 h prior to entering harbour and maintained until 12 h out of inshore waters.

The success of the electrochlorination is illustrated in Fig. 10, which shows the main-condenser inlet on the *Limnea*. On this vessel the chlorination system had operated as it was designed to. Figure 11 shows the main condenser of the *Latia*, which was heavily fouled following a failure of the electro-chlorination cells.

FUTURE DEVELOPMENTS

We believe that the current requirements of the oil shipping industry are readily met by the copper nickel alloy CN 108, but if in the future it became desirable to have compact, light-weight units that would have sea water flowing through them at high speeds then alternative materials would have to be considered. Titanium is one such material. Others, such as the recently developed stainless steels, appear from the literature[18-20] to have excellent resistance to pitting and crevice corrosion in salt water. It is unfortunate that most of the testing of these alloys appears to have been carried out in filtered sea water and little work has been undertaken to assess their performance under more realistic conditions. However, we anticipate that this will be rectified in the near future when results relating to the performance of some of these materials on offshore platforms in the North Sea become available. Additionally we are currently undertaking an evaluation exercise to establish better the limitations of these materials in sea water.

Before concluding we point out that whilst in this paper we have only considered heat exchangers, this is for reasons of brevity as we do not believe that they should be considered in isolation. The heat exchangers are only part of the sea-water handling system and therefore must be compatible with it to ensure reliability of the whole.

ACKNOWLEDGEMENTS

FIG. 10:   Main-condenser inlet of the *Limnea* free of fouling

FIG. 11:   Main-condenser inlet of the *Latia* heavily fouled following failure of the electrochlorination cells

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APPENDIX I

Suggested programme of treatment for aluminium brass tubed condensers

Treatment for new or re-tubed condenser

A new or re-tubed condenser should first be filled with a solution of 5 ppm ferrous sulphate in fresh water. This solution should be circulated in the unit for at least 8 h although 24 h would be preferable. The procedure outlined below should then be carried out.

Routine treatment for a condenser

The recommended ferrous sulphate addition to the cooling water is about 5 ppm hydrated ferrous sulphate (giving 1 ppm iron) for about 1 h every 24 h or 30 min every 12 h. This concentration is equivalent to 5 kg hydrated ferrous sulphate to each 100 m^3 of water (or 0.5 lb to each 10 000 gal). It is therefore necessary to calculate the daily ferrous sulphate dose. For an *M Class* tanker with a main condenser throughput of 7500 m^3/h of sea water, about 40 kg of ferrous sulphate would have to be added uniformly over a period of 1 h. The throughput figure for the auxiliary condenser is given as around 2×200 m^3/h, while those of the luboil cooler and the sea-water service are about 300 and 220 m^3/h, respectively, and proportional additions would have to be made to these systems.

On board vessels storage space for the ferrous sulphate crystals may be limited and manpower may not be available to carry out the ideal daily dosage. Experience has indicated that it may not be necessary to carry out the dosages as frequently once the protective film has been formed. It is therefore suggested that as an alternative the following is adhered to:
1. Initial treatment for new or re-tubed condenser as previously recommended.
2. Daily dosage of ferrous sulphate as about 5 ppm hydrated ferrous sulphate for 1 h every 24 h for 1 month; followed by a twice weekly dosage at the same rate.
3. A daily dosage should be administered 3 days prior to a vessel entering or leaving port and during berthing if the berthing period is greater than 48 h.

APPENDIX II

Operating instructions for the ferrous sulphate injection system

A 10% solution of ferrous sulphate is prepared by running 100 gal of fresh water into the tank. The stirrer motor is started and 50 kg of ferrous sulphate crystals (one sack) can be added slowly through the top opening and the lid replaced. The mixture should be stirred for at least 1 h before use to ensure the complete dissolution of the crystals and it must be ensured that all valves on the manifold are fully closed. The valve at the bottom of the tank can then be opened fully and the appropriate valve on the manifold opened to a predetermined setting to give the required feed rate. Up to 200 gal of 10% ferrous sulphate solution can be prepared at any one mixing using this ferrous sulphate injection unit.

Some caution should be exercised when handling ferrous sulphate crystals for while the crystals are not harmful they can contain a small amount of acid. If any spillage onto either skin or clothing occurs the contacted area should be carefully washed with fresh water.

APPENDIX III

Determination of corrosion potential of new tubes

The principle of the method is to compare the corrosion (rest) potential E_{corr}^a of freshly abraded tube alloy with the rest potential E_{corr}^t of the tube bore in the 'as-received' condition. The difference, $E_{corr}^t - E_{corr}^a$, is a measure of the 'nobility' of films on the tube bore surface. The more positive the difference, the more cathodic is the tube.

A clean, acceptable tube left in the atmosphere will develop an oxide film which itself can be up to +0.070 V cathodic measured in this way and our criterion for acceptance has been taken as $<+0.070$ V.

To enable the steady-stare potential to be reached quickly a dilute solution of potassium chloride (0.02 mol/l or approximately 1.5 g/l) has been used to fill the tube under test in conjunction with the robust silver, silver chloride reference electrode, also in 0.02 mol/l KCl, so avoiding liquid-junction potentials.

The tube should be degreased thoroughly by pulling a soft cloth, soaked in a petroleum spirit, through the tube and repeating this until the cloth is clean. The solvent is then allowed to evaporate. This degreasing may not be necessary but it is a precautionary operation that avoids floating, non-steady meter readings. In the laboratory or in a tube factory one end of the tube is plugged with a rubber stopper and, with the tube either vertical or inclined, it is filled with the potassium chloride solution. Without undue delay the reference electrode, removed from its safe-storage capsule, is carefully lowered into the tube to dip into the solution, so completing the circuit via a high-impedance millivolt meter, such as Fluke Model 8000A.

The connections to the meter are reference electrode to the ground (or black) terminal and tube/crocodile clip (kept dry) to the positive (red) terminal. It is important to prevent the solution wetting either the tube exterior/crocodile clip junction or a freshly cut end of the tube, since either possibility will result in false readings. The potential E_{corr}^t is noted 10 min after inserting the reference electrode.

To obtain the value for the freshly abraded tube alloy a piece of tube is stoppered as before with a rubber bung and the outer surface of the tube is abraded with silicon carbide paper under clean water to obtain a bright surface. This is rinsed first with clean water and then with the potassium chloride (KCl) solution (0.02 mol/l) before being immersed in fresh KCl solution into which the reference electrode is placed. A crocodile clip is attached to a dry portion of the tube and the potential E_{corr}^a noted after 10 min.

For CN 108 alloy repeated measurements of many tubes have shown that E_{corr}^a determined by this method is -0.230 ± 0.010 V, where $\Delta E = E_{corr}^t - (-0.230)$ V, eg for an acceptable tube E_{corr}^t may be found to be -0.180 V so that $\Delta E = -0.180 - (-0.230) = +0.050$ V, whereas for an unacceptable tube E_{corr}^t would be more positive than -0.160 V.

Discussion

J. L. SNOWDON: I would like to thank Messrs Shone and Grim for their most interesting paper and put the following questions and comments to them.

What is the probable effect on aluminium brass sea-water-cooled heat-exchange tubes if zinc corrosion plates or rods are fitted instead of iron or steel corrosion plates? In several occasions in the past zinc plates have been specified and sometimes they were fitted.

Have Messrs Shone and Grim ever used what I believe was a chlorinated rubber composition (known as DETEL and produced by Detel Products Ltd in about 1950) which was applied to the first 6 in of the sea-water inlet of aluminium brass tubes as corrosion/erosion protection? This product and method was first successfully used as a repair and protector in two steam reciprocating engine condensers which probably had naval gun metal tubes.

A large number of the tubes had pin holes of about 1½ mm diameter at the sea-water inlet end. The inlet ends of the tubes were cleaned using a ¾ in diameter wire brush attached to an electric drill. The composition was then applied by dipping a bottle brush into the tin of composition and then inserting it into the condenser tubes with a rotary motion. The repair lasted for about six years, until the ship was scrapped.

This method of protecting aluminium brass condenser tubes was also used successfully for at least 11 years in two turbine installations with water tube boilers, and for at least seven years on two other similar installations. Over these periods no trouble whatsoever was experienced with the condenser tubes but I then lost touch with the ships.

Whilst copper nickel tubes have been used very successfully, they are believed to be considerably more expensive than aluminium brass tubes. What is the relative cost of copper nickel tubes compared with aluminium brass tubes assuming each to be of the same tube thickness? I believe it is about 3:1.

Mention is made in the section headed 'Initial service experience with 70:30 copper nickel' to 'a recent eddy current survey'. Is this a modern method of detecting tube leakage in condenser tubes or does Shell still fill the steam side of the condenser with fresh water to which a fluorescent substance has been added and then shine ultraviolet light on the tube plate?

What was Shell's experience with heat-exchange systems as a whole, including sea-water-carrying pipes? Is there a case for using aluminium brass prefabricated bends, tees etc., up to about 9 in bore, and then using steel pipes (never less than 14 mm thick) for the remainder of larger-bore pipes? The steel pipe bore slowly wastes away providing a protective iron deposit on the aluminium brass surfaces.

Generally it has been found that a 14 mm thick steel pipe does not hole for about 12 years, and if it does it is easy to patch now that most owners provide gas and/or electric welding sets onboard ships.

With reference to the use of electrochlorination units, and some of the troubles experienced with them, has Shell ever considered the use of steam for heating the water in heat exchangers and their attendant sea-water pipes, which may be fouled up with marine growth? Steam injection has been used successfully in some badly fouled up systems.

It is believed that some of the failures of aluminium brass tubes could have been avoided if the operators of the plants had kept the rate of flow of the sea water through the tubes to the minimum required for the efficient operation of the machinery. For example, turbine plants should only pass the minimum amount of sea water through the condenser to obtain the designed vacuum and avoid over-cooling the condensate.

Surplus cooling water is bad thermodynamically and at low condensate temperatures oxygen is more readily absorbed. This can cause pitting on the water side of the boiler fire tubes,

leading to the use of hydrocene. This in turn will introduce ammonia, which may attack brass fittings.

In diesel installations, where many of the heat exchangers have aluminium brass tubes, the cooling systems should be designed and operated so that the fresh-water and lubricating-oil temperatures are maintained at the design limit by regulating the sea-water cooling flow and not by by-passing the heat exchanger on the fresh-water or lubricating-oil sides.

J. M. STITT (Chevron CTC): I was very impressed with the results obtained using the electrochlorination cells on the condenser of the *Limnea*, but I am surprised that the 'Elinca' system was not mentioned. This is a similar type of system and was recently fitted on a Chevron VLCC, giving 100% improvement over the ferrous sulphate results.

The system consists of pairs of probes fitted in the sea-water inlet pipes to the main condenser, with a potential difference of 0.6 V maintained between the two probes. Deposits from the probes combine with sea water to form a jelly-like substance which makes the condenser uninhabitable for marine organisms. This leads to a considerable increase in fuel economy and more efficient plant operation.

I. G. WEBSTER: I would like to ask Messrs Shone and Grim if the sea-water velocities of 0.25 and 4.0 m/s for satisfactory operation of the CN 108 tubes are the theoretical velocities, ie proportional to the total cross-sectional area of tubing and the pressure, or actual velocities, ie taking account of friction at the tube walls.

Dr W. E. HEATON (Central Electricity Generating Board): The corrosion problems of heat-exchanger plant described in this paper are broadly similar to those encountered in CEGB power plants where sea water or saline estuarine water is used as coolant. At present, this represents nearly half of the 55 000 MWe generating plant capacity of the CEGB and contamination of condensate by chloride represents a major potential hazard to the boiler plant at these locations.

Condenser leaks usually occur as a consequence of water-side corrosion of the condenser tube material in the form of pitting corrosion or impingement corrosion or a combination of both. It may be of interest to compare the strategies adopted to overcome this problem in our two industries.

The use of ferrous sulphate to form protective iron-rich films on aluminium brass, first described by Bostwick in 1961, was taken up with enthusiasm by the power industry throughout the world. In the UK, Lockhart described the successful use of the method to overcome the problems of impingement attack in the aluminium brass tubes of 120 MWe condensers,[1] but the success of the method has been variable.

It has been found that the fully filmed surface is cathodic to the bare metal and if the film is damaged, for example by the ingress of debris to form a lodged obstruction, the film may not re-form under highly turbulent active impingement conditions. Power station cooling-water systems operate under syphonic action, in which dissolved gases come out of solution because of the negative pressure conditions. The collapse of

Table DI: Specifications for boiler water purity

	Boiler class				
	60 bar	100 bar	160 bar coal-fired	160 bar oil-fired	AGR
Boiler water chloride (μg/kg as NaCl)	6000	6000	2000	500	2

these gas bubbles on the tube surfaces results in turbulence and impingement corrosion and is particularly severe and localized at a lodged obstruction or a pre-existing pit.

Where cooling waters contain a high proportion of silt, this may form a tightly adherent film on the tube surface. The iron-rich film cannot form beneath this, but might form on the non-silted areas. The pitting corrosion which may occur under the silt film will then proceed unabated, and may even be accelerated. The copper nickel material CN 108 has found wide application in the power industry, and although it has a higher resistance to impingement corrosion than aluminium brass, failures do occur.

The problem is highlighted by the current specifications for boiler water purity, where it is seen that for modern high-capacity and high-pressure plants chloride ingress is to be virtually eliminated (see Table DI).

The only material which has shown a very high resistance to abrasion damage from suspended solids and a total immunity to impingement, crevice and pitting corrosion in a wide variety of environmental and experimental conditons is titanium. Titanium has been installed, in trial batch quantities, at both sea-water and estuarine cooled CEGB condensers since 1959. Systematic NDT surveillance since then has shown that no deterioration has taken place.

The first complete condenser re-tube was carried out in 1972 and current CEGB policy is to specify titanium for the condensers and heat exchangers of all new plant where seawater or saline estuarine water is to be used as coolant.[2] The current standard is for seam-welded 0.7 mm wall thickness, 25.4 mm o.d. tube in titanium grade 2 for both new condenser construction and condenser re-tubing. Over six million metres of titanium condenser tubing is now installed in CEGB plant.

The tube-plate materials vary; in the majority of re-tubed condensers the original naval brass (CZ 112) tube-plates have been retained and have been given high-grade protective coatings. In certain new plant, aluminium bronze alloy 'D' (CA 106) has been used. Aluminium bronze alloy 'E' (CA 105) has been used in certain auxiliary coolers.

In CEGB South Eastern Region, a total of 65 163 GWh of power was generated in 1984–85; of this, 48 723 GWh (74.77%) was generated from plant tubed with titanium.

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D. HONOUR (BP Shipping Ltd): I found that reading this paper was like looking through an old photograph album. Memories of headaches and heartaches of the late 60s and early 70s came flooding back as I read of the same problems we faced and of the almost identical remedies adopted.

One of the most important aspects of learned Institutes must surely be to chronicle the lessons and the experiences of one generation for the benefit of those to come. I feel that this paper makes a great contribution to this dissemination of knowledge. I would now like to add to some of the points raised and perhaps show that although we may have overcome some of the problems, we may not have done it in the most efficient manner.

First of all, it should be pointed out that impingement attack on condenser tubes and tube-plates is not a phenomenon that suddenly appeared in recent years. Reference to a paper by Dr P. T. Gilbert[1] will show just how serious it was in the early part of this century and how the arsenic-inhibited aluminium brasses and the iron-modified copper nickels had been developed.

To quote from this paper: 'Thirty years ago condenser-tube failures were all too frequent an occurrence. Today it is confidently expected that condenser tubes will last for the whole life of the ship, and a premature failure is an unusual and notable event'.

What, we may ask, went wrong, for there were many 'unusual and notable events' in the 1970s, and they occurred with embarassing regularity! Was it perhaps that the designers hadn't really taken heed of Dr Gilbert's conclusions about designing to minimize turbulence and the introduction of free iron to promote good protective films? Or perhaps the ship operators were at fault for not checking that the basic tenets of good design were followed?

If we look dispassionately at the essential difference between the ships built in the 60s and 70s and those of Dr Gilbert's day, we see that, in general, we were dealing with higher-powered plant in which, for economic reasons, ratings, stresses and velocities were pushed to the limit. In addition, again for reasons of cost, material changes were being implemented. Thus water-boxes that promoted turbulence were accepted, and, to add to the problems, they were rubber-lined steel, thus removing a major source of free iron.

However, the first corrective measure to be taken included the design and provision of ferrous sulphate dosing systems. Messrs Shone and Grim haven't dwelt on the fact but this wasn't as straight forward as it might appear. Besides the ineffectiveness of this treatment when the ship's engineers tried to take short cuts (to minimize the time occupied in the mixing and dosing routines), there were major problems where sodium hypochlorite treatment was used.

BP Shipping had been convinced of the efficacy of this form of antifouling treatment since 1968, and when 'condenseritus' occurred in a big way there were those who claimed that the chlorine content was 'eating away at the tubes'. It is now known that the presence of the added hypochlorite can affect the ability of the ferrous sulphate to promote the formation of the protective film on the non-ferrous materials.

This led to guidelines being laid down on when ferrous sulphate dosing and hypochlorite treatment should be used. Also, it is now realized that the relatively high hypochlorite dose rates employed in the days of iron-rich sea-water systems cannot be tolerated today.

It was of course a natural reaction to look for alternative tube materials whilst, at the same time, trying to develop the ferrous sulphate dosing system. With hindsight, and bearing in mind the economic factors, would Messrs Shone and Grim feel confident in a system that employed aluminium brass tubes, ferrous sulphate dosing and sodium hypochlorite treatment today, always assuming of course that the plant was being operated at full power? Or would they support a contributor to Dr Gilbert's paper who suggested 'when in doubt use cupro-nickel'?

With regard to CN 108 alloy, the harmful carbon films found on tubes from certain manufacturers were also encountered by BP Shipping, and the material specifications were modified to ensure that this does not occur again. Could Messrs Shone and Grim expand on the need to ensure that water velocities above 0.25 m/s are maintained with this material. Economy steaming at very low speed encourages operators to run with scoop circulation as low down the range as possible, and tube failures have been attributed to 'deposit attack corrosion' where very low velocities were prevalent.

As must be appreciated, sea water corrosion is very close to my heart and I could go on. However, I will close by once again thanking Messrs Shone and Grim for a paper which will rank with that of Dr Gilbert as a major contribution to the subject.

1. P. T. Gilbert, 'The resistance to failure of condenser and heat exchanger tubes in marine service'. *Trans.I.Mar.E.*, Vol. 66, Paper 1 (1954).

Dr B. N. HALL (Ministry of Defence): In general, MoD experience would support that of Shell. Aluminium brass was used successfuly for well over 30 years before being replaced in the early 1960s by copper nickel iron alloys. The RN did not, however, share the merchant fleets' enthusiasm for tube

inserts or 'corrosion pieces' and did not appear to have such severe fouling problems, although this often reflects the temperatures of the sea in which the vessel was operating.

Titanium has been evaluated as an 'option' for use and developments in stainless steels have been watched with interest. A jaundiced view of stainless steels in chlorine environments was modified by the progress made in recent years in improving these materials but it is believed that there is still some way to go.

The difference between RN and merchant fleet experience was mainly in operating requirements and conditions. The paper had rightly pointed out that the system should be regarded as a whole and not as isolated components.

While the RN had no significant problems with tube materials, the cast items in the system could present problems. Gun metal, mentioned in the paper, while attractive for merchant use had drawbacks with regard to shock resistance which eliminated its use in most RN applications. Nickel aluminium bronze had been used for many years but corrosion problems and requirements for longer operating periods had lead to a demand for a better material. The 70:30 copper nickel alloy containing chromium, IN 768, is being evaluated and appears to offer considerable promise.

G. WILDSMITH (Yorkshire Imperial Alloys): This is a very helpful paper in that it records practical experience of using aluminium brass (CZ 110) and 70:30 copper nickel (CN 108) tubes in ships' heat exchangers and demonstrates what needs to be done to ensure satisfactory performance of such materials. It is particularly encouraging that detailed knowledge has been presented in a manner that will be of significant benefit to users of these materials in similar circumstances.

The work of Cornwell et al. is cited on page 6; it is suggested that the onset of pitting with copper tubes in cold fresh water occurred when the tube bore surface (contaminated with carbon) was more than 70 mV cathodic compared with freshly abraded metal. In fact, Cornwell et al. showed that the potential difference must exceed 100 mV before pitting occurred and that the pitting corrosion rate only became significant when the potential difference exceeded 170 mV.

Whilst cathodic films on copper alloy tubes in sea water are known to be detrimental, it does not follow that the same potential difference will be critical. Indeed, Messrs Shone and Grim chose a figure of 70 mV based on the extent to which an air-formed film is cathodic to bare metal. This figure may be rather low since experience suggests that copper alloy tubes in sea water are less susceptible to pitting under the influence of cathodic films than copper tubes in some fresh waters.

The BNF Metals Technology Centre has recently completed some preliminary work on the effect of residual manufacturing films on the performance of copper alloy heat-exchanger tubes in sea water, and it would be useful to have their comments on the choice of an appropriate potential difference.

Under the heading 'future developments', the recently developed super-stainless steels are mentioned. In considering such materials it is important to be aware that crevice corrosion could still be a problem in situations where chlorination is necessary. Fabrication of stainless steel is often more difficult than with copper alloy (particularly when compared with 90:10 copper nickel) and control of welding conditions is more critical.

Furthermore, the stainless steels are more expensive and do not possess the inherent resistance to marine fouling shown by 90:10 copper nickel. This paper demonstrates the long and successful use that can be obtained from copper alloys. Only time will tell whether super-stainless steels perform as satisfactorily or as cost effectively.

B. TODD (INCO Europe Ltd): Messrs Shone and Grim have provided a very valuable addition to our knowledge of marine heat-exchanger tube corrosion and I am sure this paper will be a source of reference for many years to come.

I am particularly interested in their work on cathodic films on the copper nickel iron manganese alloy. Although British tube manufacturers have for many years claimed that the carbonaceous films which can form during heat treatment are detrimental, this is the first authoritative and quantitative information I have seen on the subject. The simple electrochemical control test devised by Messrs Shone and Grim will be of great value in avoiding corrosion problems from this cause in the future.

There is also great emphasis these days on the commissioning treatments for new condensers. Several papers on this subject have recently appeared in the literature. The procedure recommended in this paper is about the simplest and least costly I have seen and I wonder if perhaps the aim is to avoid unsatisfactory treatments rather than apply some special procedure to give extra protection. Most condensers enter service with no special precautions and most operate satisfactorily. I would appreciate Messrs Shone's and Grim's comments on this.

On the subject of minimum water velocities, the figure of 0.14 m/s is low compared with many specifications which set a minimum of 1 m/s. I had always assumed that the latter was largely determined by the need to prevent silt etc. depositing from the sea water. At 0.14 m/s I would expect most entrained solids to deposit and I wonder if Messrs Shone and Grim could comment further on this. Do the limits they set apply only to failures in the top of the tube bundle or are they satisfied that these limits would avoid problems throughout the tube bundle? Although their limits of 0.25–4 m/s and less than 62 °C may be correct for marine heat exchangers, in other applications, such as desalination plants, these alloys work well at temperatures in excess of 100 °C, often with scales present. In this case, however, the sea water is de-aerated.

It is interesting to compare data from the desalination industry with those of Messrs Shone and Grim for the parts of the plant handling aerated sea water. A survey by the A. D. Little Corporation of 123 plants showed a failure rate of 0.05% for the CN 108 alloy. The data given in the paper work out at 0.09%. Allowing for the differences in the service lives of the two groups to which the data relate, the alloy gives remarkably consistent performance.

Any failures I have seen with this alloy in service have been caused by unusual factors such as high chlorination (16 ppm residual), deposits of sulphide-containing silt etc. I have never seen an impingement failure in clean sea water and would like to hear of Messrs Shone's and Grim's experience in this respect.

The use of high water speeds with this alloy may be possible. However, if very high water speeds are desired, then the stainless steels are excellent. Recent projects in the Norwegian offshore industry are using high alloy stainless-steel piping systems designed for 7 m/s, which was chosen as the best compromise between pipe size and pumping costs. For heat-exchanger applications the optimum velocity is likely to be below this, and I would like to ask Messrs Shone and Grim if they have decided on design velocities for their future heat exchangers.

D. A. HAWKER (Hamworthy Engineering Ltd): First I would like to thank Messrs Shone and Grim for their excellent paper. I am not a scientist but an engineer with knowledge of making sea-water pumps and seeing what happens to them in sea-water systems.

One of the reasons that sea-water systems get in a mess is because of entrained air. If I have any criticism of the paper it is that air does not get a mention until page 7. However, in its conclusion the paper recommends that sea-water systems be considered as a whole and with that I am in complete agreement.

Figure D1 shows an aluminium bronze impeller from a sea-water pump after 15 months service in a new ship (the first of a long series). The heat-exchanger tubes were in holes as
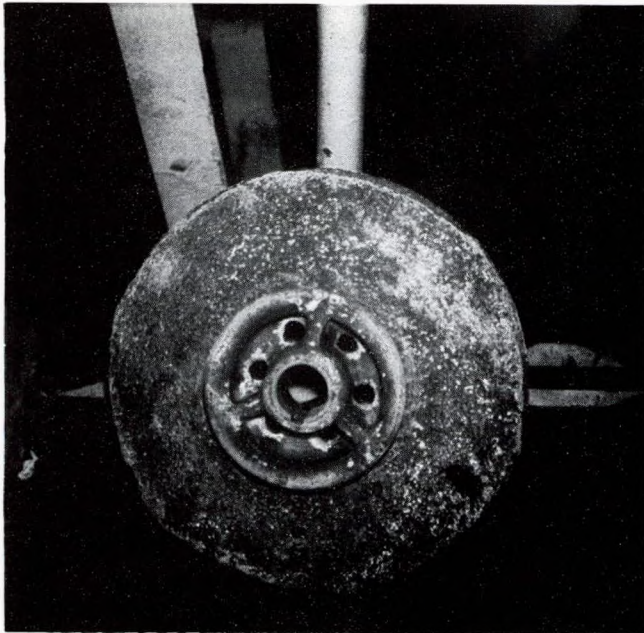
FIG. D1: Aluminium bronze impeller from a sea-water pump after 15 months service

were other bits and pieces of the system. I do not intend to go into details of what was done, but for the cost of a few dollars, mostly on steelwork, and attention to detail normal experience was re-established.

The complete line of ships is still in service with the same owner, although the problem with the first ship occurred in the 1970s. No change was made to the materials used for the sea-water pumps.

The most valuable collection of scientific and engineering knowledge that I am aware of on this subject is with the British Admiralty. My company has been making bits and pieces for the British Admiralty almost since hull materials changed form oak to steel. On the mechanical construction of pumps (and other things) we have contributed something, but on the choice of materials for sea-water pumps we have contributed nothing at all.

Now and then, despite the accumulated knowledge, there is a mini-disaster with a sea-water system, but because of the great attention to detail in the construction of the system it is normally relatively easy to identify what has gone wrong. In the case of the owner who had the impeller shown in Fig. D1, an advantage was that the ships had always been built locally and the equipment was from suppliers of longstanding repute. When there was a mini-disaster there were not too many variables: something had changed and it was identified and corrected.

Companies such as mine do their best to understand the needs of customers and are always very happy to discuss their problems with them. If customers are sure they know best and want expensive materials we are pleased to supply them, but it is sometimes amusing that, faced with a mini-disaster, some shipowners will clutch for materials which are more costly than those used in warship construction.

Finally, Fred Bown has asked me to say a word on stainless steel in sea-water systems. Various publications coming mainly, I think, from the Far East, advocate the use of stainless steel. Possibly experiments have been performed with machined samples of stainless steel in filtered flowing sea water. Messrs Shone and Grim emphasize the need to avoid stagnant polluted sea water, and I know that stainless steels can quickly disappear in such water.

The function of many of our warships was often to lie idle for long periods in very suspect water, after which England expects etc. I can only speculate that, at some time in the past,

some of them did not fulfil the expectations because the Navy will not permit the use of stainless steel in sea-water systems.

In commercial pumps stainless-steel shafts are common and, provided that reasonable precautions are taken in the fitting out basin, such shafts normally give acceptable performance at acceptable cost. Once a pit starts in stainless steel, things develop quickly. The ground surface of a shaft is one thing but a case surface is another and, as far as I am concerned, it is experimental.

D. J. ALLEN (GEC Power Transformers Ltd): I do not have wide experience of sea-water-cooled heat exchangers in marine equipment, but I am seeking information concerning the performance of copper nickel tubes in a harsh sea-water environment.

I am concerned that the installation I have in mind is one where active steps have been taken to eliminate contact between sea water and steel components. The steel pipes have been protected with rubber liners and the water boxes are made of fibreglass, effectively eliminating any protective films formed by iron salts. In addition, I believe that sulphide-containing salts are present in abundance as the equipment operates using warm harbour water.

The problems of corrosion have been described but no mention has been made of interactions between corrosion and other phenomena such as static mechanical stress or vibration. I would be most interested to know if Messrs Shone and Grim have any experience of such interaction effects, and whether the presence of mechanical stress would accelerate corrosion in copper nickel tubes.

Dr P. T. GILBERT (Metallurgical Consultant): This paper is a welcome addition to the literature on sea-water-cooled heat-exchange equipment and it is valuable to have specified the conditions under which aluminium brass and copper nickel condenser and heat-exchanger tubes have been used with conspicuous success in a large fleet of modern vessels.

I would like to comment on the section of the paper concerned with harmful films and on Appendix III. Reference is made to the work of Cornwell et al. on the behaviour of copper tubes in fresh water. This situation has important differences from that described by Messrs Shone and Grim for condenser tubes, namely:

1. For copper tubes in fresh water, initial readings show little variation, both freshly cleaned copper and carbon-contaminated surfaces showing potentials of around -0.05 V (SCE, saturated calomel electrode). Differences develop slowing over periods of some weeks or months, the potential of clean surfaces rising to only 0.0 or $+0.05$ V (SCE), whereas carbon-contaminated surfaces rise to over $+0.17$ V (SCE) in cases where severe pitting develops.

   Thus the cathodic films with which pitting is associated grow slowly in service and cannot be detected by potential measurements after short periods. By contrast, the harmful films found by Messrs Shone and Grim seem to pre-exist, being shown up by measurements after 10 min immersion.

2. When copper tubes pit, very high potentials are recorded, eg as much as $+0.25$ or even $+0.35$ V (SCE). The difference between these readings and those for freshly cleaned copper is therefore as much as 0.3–0.4 V.

   Little pitting occurs when this difference is less than about 0.22 V [ie below $+0.17$ V (SCE)] and none when it is less than 0.15 V [ie below $+0.10$ V (SCE)]. By contrast, Messrs Shone and Grim are speaking of much smaller differences, eg 0.05 V for 'good' tubes and 0.07 V for 'bad' tubes.

The following questions occur to me:
- To assist in comparisons with other work, what are the absolute values mesaured for the condenser tubes? Is the value of -0.23 ± 0.01 V for freshly abraded tubes, for instance, with respect to silver, silver chloride in 0.02 mol/KCl, or with respect to some other standard?

- What values were found for 'bad' tubes and how reproducible were the measurements? Were differences of much more than 0.07 V found in practice? Decisions about acceptability or otherwise would seem difficult to make at values of around 0.07 V when 'good' tubes are at 0.05 ± 0.01 V.
- Manganous oxide seems an unusual constituent of the harmful surface film, though MnO_2 would have been surprising. Could Messrs Shone and Grim please comment?

B. E. SHINN (Alfa-Laval): Referring to the illustration of the failed titanium plate (Fig. 8), while such failures are rare, plate heat-exchanger suppliers do not like any failures, and I would question the conclusions arrived at as to the cause in this case.

Figure D2 shows that the plate is contoured (profiled) so as to ensure sufficient stiffness of the 'blank' at the end of the water manifold which is supported by the pressure plate. The area of the 'torn' hole therefore had stiffening and support such that it can take a working pressure of 8.6 bar, although the paper refers to a permanent deflection at 3 bar.

Obviously there has been a problem, the cause of which I do not know, but I wonder if the unit was fully tightened.

Authors' reply _____

We thank Mr Snowdon for his questions and will answer them in the order in which they were asked.

The problems associated with the use of zinc corrosion plates have previously been discussed in an excellent paper by Gilbert,[1] who pointed out that their use could not be recommended since they can prevent the formation of protective films at tube inlets. Instead of protective films a cathodic deposit containing calcium carbonate may be produced. As long as the protector blocks continue to function this is unimportant. However, zinc blocks, although very active initially, soon become polarized and almost invariably cease to function after a short time. When this takes place rapid damage may occur at or near the tube inlets as the cathodic deposit is not protective.

When condensers enter service they should be fitted with soft-iron protector blocks which remain active until they have corroded away. The soft-iron anodes are advantageous in that they are able cathodically to protect the inlet ends of the tubes in their immediate vicinity and the iron corrosion salts they produce help to form protective films on the aluminium brass tubes.

With respect to the use of the chlorinated rubber composition DETEL, we have no knowledge of its use in the application described. Any simple coating which can be applied as a thin film to copper alloys and adheres well over a long period of time under conditions of severe turbulence would be very useful. However, we find it difficult to imagine any simple coating remaining intact for very long in the conditions that prevailed within our heat exchangers.

Mr Snowdon suggests that the relative cost of copper nickel tubes compared with aluminium brass is about 3:1. We think that this is unlikely and while the price of these alloys is variable, partly because of commerial interests, a recent paper by Canetta and Valota[2] states that the ratio is 1.68:1. They present this information as cost in US dollars per square metre of alloy and point out that the scrap value of the alloys should also be considered when cost comparisons are made.

The eddy current survey mentioned in the paper is a system that has been utilized since about 1935, although many updates have occurred with the equipment and techniques used. The system remains one of the most useful for assessing the condition of tubes prior to leakage occurring. It is not used to detect leakages; the preferred method for that is the one Mr Snowdon describes.
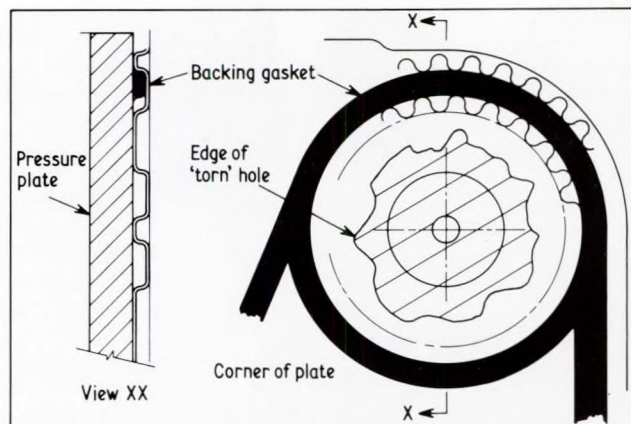

FIG. D2: Diagram of titanium plate, showing contouring

As we state in our paper, sea-water systems should be considered as a whole and we believe that if copper nickel heat-exchanger tubes are used then the piping should preferably also be of copper nickel with rubber-lined valves. We do not recommend the use of mixed metal systems because we wish to reduce maintenance to a minimum and accelerated corrosion always occurs at galvanic interfaces resulting in localized corrosion of the less noble material (steel).

One area where steel pipes could be used in aluminium brass systems is as 'waster' pieces. In such applications the iron corrosion products would help to form protective films on the rest of the system. However, replacement pieces should be available on the vessel and they should only be used in areas where replacement is possible without closing down essential parts of the system.

It is well established that steam injection can be used to clean badly fouled systems. However, we believe that it is essential to prevent the fouling occurring since damage is initiated with its onset. The electrochlorinators used on the Shell vessels prevent fouling from beginning.

The failures associated with the use of aluminium brass tubes were not related to bad operating practice. We believe that if the units were operated near their design maximums then the erosion limitations of aluminium brass would be exceeded.

1. P. T. Gilbert, 'The resistance to failure of condenser and heat exchanger tubes in marine service'. *Trans.I.Mar.E.*, Vol. 66, Paper 1 (1954).
2. V. Canetta and N. M. Valota, Quality Label Association Conference, Bahrain (Oct. 1985).

Mr Stitt quite correctly points out that we did not mention the 'Elinca' system which uses probes fitted into the sea-water inlet pipes to produce a jelly-like substance which makes the condenser uninhabitable for marine organisms. This was a deliberate omission since we have little experience with systems of this type.

We believe that the 'Elinca' system is similar to the 'Cathelco' system which was evaluated in 1977 by the British Ship Research Association for the Genreal Council of British Shipping. It was shown that by using this technique fouling could be prevented, but if for any reason the anodes bcame inoperative it was not possible to re-energize them and remove fouling. In this respect these systems are inferior to electrochlorinators. It is not surprising to find that the 'Elinca' system recently fitted to a VLCC was giving a 100% improvement over the ferrous sulphate treatment since the latter is not known to have any significant antifouling capabilities.

In reply to Mr Webster's question, the sea-water velocities mentioned in the paper are all actual measured values.

It is interesting to find that the corrosion problems we have

experienced are broadly similar to those encountered in CEGB power plant. Dr Heaton reports that the use of ferrous sulphate to overcome the problems of impingement attack met with variable results. This is not surprising if the ferrous sulphate was not added close to the tube inlets in the desired form. With some CEGB installations this was probably not possible and results would therefore be variable.

We disagree with Dr Heaton's comment that films formed by the addition of ferrous sulphate and then subsequently damaged cannot be reformed under highly turbulent active impingement conditions. From our experience this would appear to be very possible. On several vessels damage had occurred because there was insufficient iron present in the system to maintain good protective films on the tubes. However, by increasing the amount of iron available for the formation of protective films, ie adding ferrous sulphate, further damage was prevented and the films were repaired at these active sites. Perhaps at this stage we should remember that ferrous sulphate is only a convenient way of putting iron into the system and that the same effect can be achieved by allowing steel in the system to corrode.

On the subject of silt entrainment we have less experience because most of our vessels operate in deep waters. Our recommendation of minimum water velocities of 0.25 m/s should also ensure that silt settlement does not occur unless the silt burden in the cooling water is high and then a figure of 1.0 m/s, as suggested in some specifications, may be necessary.

We agree entirely with Dr Heaton when he says that titanium has an excellent resistance to most forms of attack and can readily understand why the CEGB have opted for this solution for many of their plants. However, extreme care has to be taken when selecting tube-plate materials that are compatible with this alloy. From our experience naval brass is totally unsuitable and we know of no high-grade protective coatings that can be applied with any confidence to ensure that the alloy is adequately protected. Both the aluminium bronze alloys D and E are very prone to corrosion when coupled to titanium and whilst maintenance of the tube-plates may be feasible on land-based installations, at sea tube-plate failure poses more problems.

The initial results of work we are currently undertaking on this subject suggest that suitable tube-plates should be made from either solid titanium or steel clad in titanium. Additionally the use of improved high alloy austenitic stainless steels of the SMO 254 type could be considered. Another possible problem area with titanium is on the steamside where failures associated with steam impingement have been observed.

As we have said in the paper, for service on vessels we believe the CN 108 alloy to be very suitable providing it is purchased free of all harmful films, precommissioned correctly and operated with reasonable water speeds.

Mr Honour's contribution enhances our paper in that it highlights the work of Dr Gilbert and points out how ships built in the 60s and 70s differed from those of previous eras. As pointed out, the design and provision of a reliable ferrous sulphate dosing system was not quite as straight forward as it may appear in the paper.

Problems did occur if chlorination and ferrous sulphate treatments were carried out simultaneously. It appeared that the chlorination nulified all of the advantages to be gained from using the ferrous sulphate. Fortunately this problem, once recognized, was easily overcome: the chlorination unit was used intermittently and well separated from the time of ferrous sulphate dosing.

When a choice has to be made between aluminium brass plus ferrous sulphate dosing and copper nickel we fully support the contributor to Dr Gilbert's paper who suggested 'when in doubt use cupro-nickel'. The reason for this is perhaps more one of economics and convenience than the technical merits of the materials, which would have similar corrosion characteristics. If a ferrous sulphate treatment is to be carried out successfully on tankers, then supplies of the material must be readily available worldwide, storage facilities must be available on the ship, and dosing must be carried out.

Ferrous sulphate crystals are prone to oxidize in moist air and then convert into basic ferric sulphate, which is less effective, therefore regular fresh supplies of the salt must be available. Additionally it must be added in the form of a freshly mixed 10% solution since the solution will odixize with storage. Caution must be exercised when handling ferrous sulphate crystals since the commercial-purity material contains acid. In general the ferrous sulphate storage area and equipment can soon become rusty and this necessitates frequent cleaning and painting. Whilst the ferrous sulphate dosage is simple to apply, it does take manpower and this is usually at a premium onboard ships. It is for these reasons, coupled with their excellent service record, that we would prefer to use the CN 108 alloy.

The subject of minimum water velocities was introduced in replying to Dr Heaton's questions and we can only reiterate that if low water speeds prevail then corrosion will occur in the tops of tubes where air pockets can form, and if silt settles out in the tubes then corrosion may occur in the bottoms of the tubes.

Dr Hall's useful contributions highlights some of the differences between the RN and merchant fleets and it is extremely interesting to note that the RN do not have such severe fouling problems.

In Mr Wildsmith's contribution he quite correctly questioned the need to specify that CN 108 alloy should be supplied free of films which make the bore more than 70 mV cathodic compared with freshly abraded metal. We accept that this value is a little conservative but see no reason to change it and increase the risk of failures since several European manufacturers of CN 108 tube have shown that this standard is readily attainable. If we reduced our standard to 100 mV it is probable that some pitting would occur, and although after a time this may become stifled we have not carried out sufficient work to be certain of this.

Mr Wildsmith points out that the pitting corrosion rate of copper in some fresh waters only becomes significant when the potential difference exceeds 170 mV. With the CN 108 alloy in natural and synthetic sea water, significant corrosion occurred when the potential difference was lower than this. Tubes from three suppliers were fitted into a ship's condenser during a partial retubing. Two years later they were removed and upon examination were found to be heavily pitted. Details of the potentials measured on the surface of the tube bore and coatings shown to be present are given in Table D2.

After 2 years these tubes were removed and an examination showed them to be heavily pitted. This work suggests that the guidelines set out by Cornwell et al. for copper in fresh water may not be applicable to CN 108 alloy. If our standards were lowered then it is feasible that some of these tubes could have been approved, particularly if the deposits were of variable quality as the potential measurements indicated they may have been (+100 to +170mV). We have not examined any tubes with potentials of between 70 and 100 mV and whilst it is feasible that the minimum acceptable potential could be raised

Table D2: Details of potentials and coatings

Manu-facturer	Analysis of surface film		Potential of surface film with respect to abraded metal
	X-ray diffraction	Electron probe microanalysis	
A	Manganous oxide	Manganese and carbon	+ 154 mV
B	Manganous oxide	Manganese and carbon	+ 164 mV
C	Manganous oxide	Manganese and carbon	+ 100 to + 170mV

to 100 mV we believe that considerable work would first have to be carried out to justify this small change.

Mr Wildsmith's comment that crevice corrosion is a problem with stainless steels is correct, although some of the newer alloys of the 254 SMO type appear to have overcome it. Under conditions of chlorination with residual chlorine levels of between 0.5 and 1.0 ppm crevice corrosion is not a problem with these alloys. In work we have recently completed we have shown that the rest potential of stainless steels in natural chlorinated sea water is about 2–300 mV lower than in unchlorinated sea water. This reduction in potential favours a lower probability for the initiation of crevice corrosion. We do not accept that the fabrication of stainless steel is more difficult than that of copper alloys; it is merely different, as are the welding procedures.

Stainless steels are certainly more expensive than copper alloys if identical shapes and forms are considered. However, one should never do this since the true value of stainless steels can only be achieved if systems are designed using the properties of these alloys. This can result in pipe sizes being significantly reduced (from say 20 to 14 in) because the stainless steels do not have practical erosion limitations. These alloys may also be stronger and therefore wall thicknesses can be reduced.

The cost of a system designed in stainless steel is very competitive with those in copper alloys and for applications where weight and space saving are important the stainless steels could be preferred. For marine application where weight and space are not at a premium, copper alloys are currently preferred. Additionally, copper alloys are available worldwide, as is shipyard expertise in their fabrication.

On the topic of the inherent resistance of 90:10 copper nickel to marine fouling there is little to say other than we regard it as being insignificant in a sea-water system. If it had any significant antifouling properties in practical sea-water systems then we can assure you that we would not waste money on the installation and maintenance of antifouling systems.

Mr Todd points out that many condensers enter service with no special precautions being taken to ensure that they operate satisfactorily. This is correct and we find it difficult to understand why more failures do not occur. Perhaps the answer is not so much related to science as book keeping and the fact that accurate records of heat-exchanger performance are not always kept.

We have previously mentioned the subject of minimum water velocities and explained that our work was designed to prevent damage in the tops of tubes. In deaerated sea water it is easy to understand that the temperature limits could be raised. Like Mr Todd we have never seen an impingement failure of tubes in clean sea water but have always assumed that that was because this alloy was used below its critical maximum velocity.

At this stage in our work it is far too early to define the design velocities for future heat exchangers in ships; however, in other areas such as offshore platforms the upper limits of either titanium or stainless steel are unlikely to be achieved because the cost of pumping would be too high.

We cannot agree with Mr Hawker's comment that 'sea-water systems get in a mess because of entrained air'. Over the years we have examined many sea-water systems on vessels both in our Fleets and those belonging to others and have never needed to evoke this as a cause of failure. All too often systems are constructed from either unsuitable materials or unsuitable combinations of materials. Pump failures, particularly with high-speed centrifugal pumps, occur because the properties of the materials of construction are inadequate.

Mr Allan introduced an aspect of heat-exchanger performance not covered in the paper, namely the influence of corrosion on either vibration or static mechanical stress. With the CN 108 alloy, even in highly stressed conditions in sea water, we have never seen evidence of stress corrosion cracking. If tubes are allowed to vibrate in sea water then corrosion fatigue occurs. Damage of this type is usually observed near baffle and tube plates, the exact form of the damage depending on the design of the unit.

Dr Gilbert's comments and questions help to remove any confusion that may exist on the subject of harmful films. As he points out, the work of Cornwell et al. was on copper tubes in fresh water and as such is different from our work. However, the concept they used of potential monitoring and critical pitting potentials is similar.

In their work the electrolyte was a poor conductor, namely fresh water, which explains why it took periods of weeks or months to detect the potential differences he mentions. In our test, potassium chloride was selected as the electrolyte because this allowed the steady-state potential to be measured after only 10 min. The absolute steady-state potential of the freshly abraded CN 108 tubes is as stated in the paper, -0.23 ± 0.01 V with respect to silver, silver chloride in 0.02 mol/l KCl.

From experience we have found that if the potential of the CN 108 tube is more positive than -0.13 V then significant pitting will occur and hence we suggest that such tubes may be defined as 'bad'. This value is 100 mV positive with respect to freshly abraded CN 108.

In our paper we recommend that differences greater than 70 mV should not be accepted. We do not know what would happen if tubes coated with films with potential differences of between 70 and 100 mV were exposed to sea water. However, since it has been found that manufacturers can readily clean tubes why should we risk purchasing tubes of dubious quality? Reproducibility of test results was excellent, but since the measured potential is dependent upon the carbon present on tube surfaces, which is not always present as a uniform coating, some scatter is inevitable. If carbon is present the measured potential is always greater than -0.13 V.

We agree that manganous oxide is an unusual constituent of the harmful surface film and certainly one that we did not anticipate. Unfortunately, we can offer no explanation for its presence, we merely report it.

As Mr Shinn points out, failures of titanium plate heat exchangers are rare. The failure mentioned in the paper was one of three that occurred on the same vessel. This vessel was prone to more vibration than others of this type and whilst we could discuss the tightening of the bolting in the unit and its influence on the failure for some considerable time, it would still not alter the conclusion: namely that the damage was caused by initiated fretting corrosion associated with the rubbing of the backing plate against the titanium. Since no other solution seems feasible we can find no reason to change the views expressed in the paper.