Living with the threat of microbiologically influenced corrosion in submarine seawater systems: The Royal Navy's perspective

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SYNOPSIS

Microbiologically Influenced Corrosion (MIC) has been recognised as a serious threat to both availability and safety in a number of industries for many decades, none more so than in the marine sector. The Royal Navy (RN) has suffered significant platform downtime in recent years as a result of MIC related defects in seawater cooled shell and tube heat exchangers, particularly in submarines. The move to titanium, one of the few metals that appears to be resilient to this form of corrosion, has been an obvious and very successful solution to problems with smaller, removable tube stacks within surface ship machinery. For in-service submarines, however, which extensively employ copper-nickel alloy tubing, such a retrofit option could not be considered for a variety of reasons. As such, the UK MOD has had to examine a number of strategies to allow the continued operation of submarine heat exchangers in microbially hostile waters whilst minimising the risk of MIC. Given the enormous financial and operational consequences of a further MIC event, extremely conservative short-term solutions have been adopted. These have included the complete exclusion of dockyard water from heat exchangers whilst in upkeep, using a combination of "sacrificial" interface coolers, closed loop circulating rigs or even total loss fresh water. Interim solutions still being developed include the identification and deployment of cooler conditioning chemicals to make the system alloys more tolerant to microbial attack. Finally, following an exhaustive series of laboratory scale microbiological experiments and corrosion replication trials, work is now in progress to evaluate a number of water treatment options, such that the risk of contaminating vulnerable submarine coolers with the bacteria cited in the MIC mechanism whilst in harbour can be minimised.

INTRODUCTION

Copper-nickel alloys have been employed in seawater cooled systems for over half a century. Although originally developed due to their resistance to corrosion, it was quickly established that copper alloys also exhibited excellent resilience to macrofouling, the size and extent of which could otherwise disable flow through a heat exchanger within a matter of weeks[1]. Increasing the nickel content improved the resistance of the alloy to impingement attack due to the shear stresses of the water flowing in the bore of the tube, allowing greater seawater speeds to be employed and in turn reducing the size of the cooler for a given heat transfer rate. These features have allowed copper-30%nickel alloys (here on referred to as 70:30) to capture and retain the vast majority of the submarine heat exchanger market.

Throughout this half-century period, it has been well established that the corrosion resistance offered by copper-nickel alloys relies on the formation of a thin, tightly adherent, cuprous oxide surface that forms naturally upon exposure to clean, oxygenated seawater, neither of which can be taken as given for the seawater in a typical upkeep dockyard. By their very nature, dockyards tend to be located in estuarine areas, or make use of non-tidal basins for the provision of graving docks and maintenance berths. The stagnant conditions that such basins inevitably encourage lead to a high oxygen demand, allowing anaerobic bacteria to thrive and for their metabolic by-products to accumulate. For vulnerable copper alloy tubing (either brand new or freshly cleaned and descaled), the most threatening of these by-products are sulphide ions produced by the group of sulphide generating bacteria. An oxide coating formed on the surface of tubing in the presence of sulphide contamination will be weak and brittle rendering it liable to greatly accelerated corrosion during subsequent service, even following return to nominally clean seawater. The process of ensuring that copper alloy receives an effective oxide coating prior to service is known as "conditioning".

Assuming the material has been adequately conditioned, corrosion rates for copper alloys can be as little as 0.02 mm/year [(2)]. Armed with the knowledge that conditioning is crucial, those authorities responsible for the refit and

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maintenance of UK submarines have, in the past, been successful in ensuring that heat exchangers meet their design life intent. In the current decade, however, a move to reduce the length of maintenance periods, together with pressures on resource and finance have slowly lead to the demise of the care and attention that was once afforded to these components. Whilst it is apparent that no formal conditioning procedure was ever strictly adhered to, it is clear from the literature that coolers were afforded some protection, largely on an ad-hoc basis. In some cases this was achieved by circulating clean seawater imported by barge through the new cooler, in other cases mains fresh water has been used. Regardless of how it was achieved, the conditioning process took time. For those looking to shorten the programme it was an inevitable target, and for submarines entering upkeep periods in 2005 and 2006, it was seen as a luxury which could easily be removed from the package. Such a decision meant submarine coolers would now experience their first seawater exposure with water from a non-tidal basin and as such become vulnerable to MIC attack. In the space of a year, the submarine flotilla lost a total of 8-months operational availability across 2 platforms as a result of rampant pitting corrosion[3]. The first pit to breach through a tube wall occurred after just 6-months of service, an overall corrosion rate of 2 mm/year (Fig 1).

Fig 1 View along bore of failed cooler tube (7/16 inch OD) showing through wall pit

This paper reviews the actions taken by the UK MOD in light of the lessons learnt from these MIC events, from the immediate response to exclude all suspect basin waters from vulnerable coolers and to re-educate the community on the importance of conditioning, through to the formulation of longer term solutions, including studies with chemical corrosion inhibitors and water treatment technologies.

BACKGROUND

Biofouling on the increase

The turn of the century saw the UK submarine force increasingly deployed to the littoral and to warmer and shallower waters, as opposed to their previous ‘cold war’ operating areas in the North Atlantic. This new environment, rich in marine life and organisms, led to vastly increased occurrences of cooler blockage by biofoul such as crustaceans and sea grass (Fig 2 & 3).

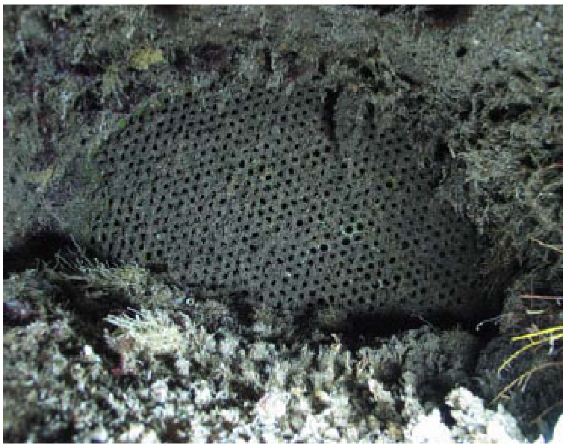

Fig 2 Severely fouled submarine cooler outlet header and tubeplate following deployment (tubeplate diameter 850mm)

Fig 3 As Fig 2 – detail on inlet tubeplate with only a small number of tube inlets clear

This was much to the surprise of the scientific community who have always considered copper based systems to be immune to macrofouling. The reality was, however, that submarines deployed on operations were suffering limitations to machinery, or worse, returning to port in order to strip heat exchangers such that tube blockages could be cleared. Reduction in heat exchange is not the only issue surrounding fouling, choked flow in blocked tubes will lead to higher seawater velocities in clear tubes, resulting in higher rates of erosion, stripping the oxide coating from the tube wall and rendering it vulnerable to pitting corrosion.

The process of dismantling a submarine cooler to facilitate mechanical cleaning is lengthy, expensive and extremely disruptive to adjacent equipment. Extensive system pressure testing is furthermore required following re-build. In 2004 therefore, the UK MOD conducted trials on a number of chemical descalers that would allow the non-intrusive clean of a cooler's internals by circulating a 'treatment' via the sea tubes. All such cleaners are based on a variation of a dilute hydrochloric acid and it was recognised that such cleaning would result in any pre-existing copper oxide coating (such as that formed through a conditioning process) being removed; this would therefore need to be re-established. The process proved to be extremely effective in restoring complete cooler cleanliness requiring just 24-hours rather than the previous 2-week strip, clean and re-builds (Fig 4).

Fig 4 View as Fig 2 following chemical clean and debris removal (tubeplate diameter 850mm)

Corrosion inhibitor trials

The success of chemical cleaning came with the caveat that the copper alloy must subsequently be re-conditioned. Such a caveat conflicted with the underlying drive to shorten maintenance programmes. In an attempt to harmonise this, the UK MOD embarked on a programme to assess the effectiveness of a corrosion inhibitor, which would allow coolers to be operated alongside without the need for prior conditioning. The first such inhibitor to be assessed was also asserted by the manufacturer to control macro (mussels, crustaceans etc.) and micro (slime, bacteria) fouling and to further inhibit scale formation. The product was offered as a "green" alternative to oxidising treatments of cooling water such as chlorination and is based on filming amine technology. Despite the application of this treatment some submarine coolers suffered from pitting failures (Fig 5 & 6). Metallurgical analyses of these failures have suggested MIC, in particular the presence of sulphide produced by Sulphate Reducing Bacteria (SRB) which have previously been reported as deleterious to copper-nickel alloys.

Fig 5 A pitted tube identified in a cooler using a shell side hydrostatic test and an endoscope

Given the failure of trials with inhibitors, it was clear that the role of the environment in the MIC mechanism and the copper alloy's response to it, needed to be fully understood before long term mitigations against this risk could be worked up. From November 2006, a moratorium was applied on all existing treatments. Chemical cleaning was brought under the sanction of the UK MOD for use only in exceptional circumstances and all vulnerable submarine coolers, whether newly re-tubed or recently cleaned, were subject to an exclusion policy such that only clean, aerated water would be passed through coolers when in harbour. The various methods used are discussed in more detail in the following paragraph.

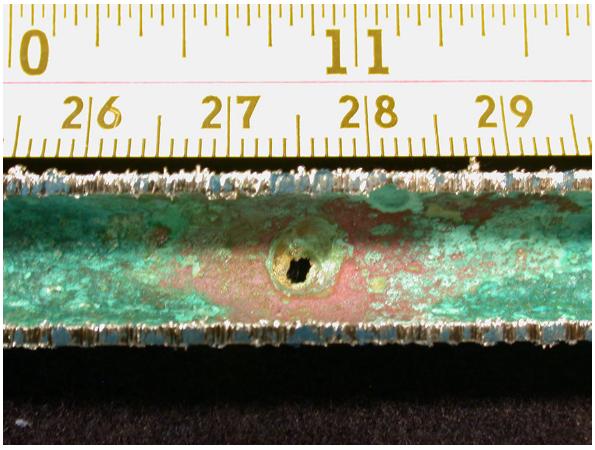

Fig 6 Defective 70:30 tube sectioned during metallurgical examination showing through wall pit with classic MIC morphology

IMMEDIATE MEASURES

Exclusion of dockyard water

Despite the UK MOD's attempts to tackle the issue, the RN submarine flotilla programme had been severely disrupted by MIC in 2006. For submarines entering dock for maintenance from the end of that year, the UK MOD equipment section ordered a "lockdown" from the as yet undefined threat. The waterfront authorities were instructed to exclude all local water from submarine coolers, using only clean, aerated sources for heat rejection purposes. This clearly presented a number of challenges, particularly when considering the diversity of berthing scenarios which included vessels both afloat and in dry dock. Until a more sustainable method of exclusion could be worked up and acquired, submarine coolers were supplied through docking bonnets with town main fresh water on a once through or "total loss" basis. With systems largely shut down, the required flow of fresh cooling water for heat rejection was significantly less than rated flow, keeping consumption to an absolute minimum. In the meantime, commercial heat exchangers were hired, whereby the cooling load was met by circulating fresh water through the seawater side of the cooler, with an intermediate heat exchange process occurring with the dockyard water in an "interface" or "sacrificial" cooler.

Optimal conditioning

It was further recognised that, in parallel with the process of heat rejection, the coolers would also need to be afforded an optimal conditioning regime and work was conducted to quickly ascertain whether any treatments or modifications should be made to the "interface" coolant to accelerate or assist the formation of a copper oxide coating. An intensive laboratory task investigated the use of the following cooling media[5]: full salinity clean seawater, flowing town main fresh water, fresh water with the addition of Sodium Dimethyl Dithiocarbamate (SDD – a treatment with reported biocidal and inhibitory properties) and ferrous ions added to fresh water. This work concluded that following 4-weeks of exposure, full salinity seawater, free of sulphide pollution, produced the most effective and efficient copper oxide coating. The next best option was simply town main fresh water, regularly aerated and periodically replenished. The use of SDD had clear benefits, but these were massively outweighed by the environmental and disposal regulations, which would discount its use in a short-term, "quick win" context.

As a result of these findings, the "interface" cooling rigs were deployed with a facility to monitor the oxygen content of the coolant, which could be replenished as required to maintain a saturated level. Such a finding is logical, since oxygen is consumed from the electrolyte in the formation of an oxide coating on copper.

INTERIM MEASURES

Strategy

The strategy to develop interim measures to combat MIC was based upon gaining a better understanding of the processes to achieve optimal conditioning and as such built on the scientific studies already undertaken. A clearer understanding of the threat posed by the environment was also necessary. In order to coordinate expertise in these diverse yet related disciplines, the UK MOD established a scientific advisory panel to address the issue. This was conducted in collaboration with the main submarine dockyard, bringing together microbiology experts from academia and corrosion engineers from defence and industry. This, combined with technical exchanges with other NATO navies, provided a forum from which a coordinated package of work could be developed to address the problem of MIC, with specific reference to copper-nickel alloys.

The work was conducted under two overarching strands. Firstly, the equipment: this would further investigate the optimal conditioning regime and treatments to combat the risk of MIC. Secondly, the environment: this strand would seek to assess water quality across UK dockyards in order to establish the extent of exposure to MIC risk. This would be conducted through a programme of water sampling and microbiological cultures taken from active coolers in submarines alongside.

The Equipment

At this time the majority of coolers requiring to be operated in potentially hostile dockyard waters were instead being serviced with fresh water circulating through an "interface" cooler. Having established this safe, albeit conservative position, the laboratory studies were extended to assess the corrosion performance of copper-nickel alloys following exposure to a wider range of conditioning media and under various environmental threat conditions, namely the level of sulphide pollution (Fig 7). Sulphide ions are known to be deleterious to the corrosion resistance of copper alloy surfaces. Indeed, in the 1970's, following several failures of copper alloy heat exchangers during build, the UK MOD established an additive (SDD)[6] which was designed to prevent the adverse effects of such sulphide exposures[7]. The application of SDD ceased shortly after inception due to environmental concerns regarding disposal of the solution.

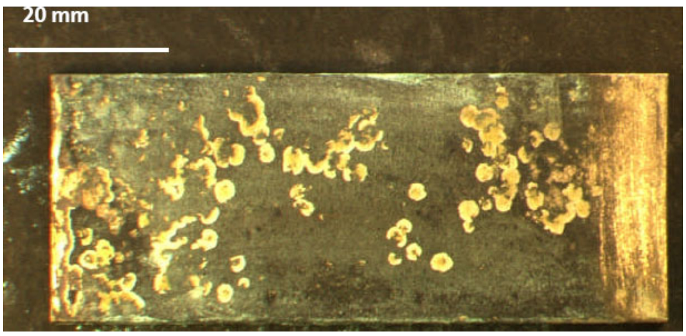

Fig 7 4-week clean seawater conditioned 70:30 following 1-week exposure to 25ppm sulphide pollution

The laboratory work was specified by the UK MOD scientific advisory panel and re-visited established treatments such as SDD and ferrous ions, but also examined some newer ones such as benzotriazole (BTA). The study used linear polarisation resistance and mass loss to determine the resilience of the oxide coating and its subsequent corrosion performance[8]. This study found that short-term (24 - 48 hour) conditioning with BTA and a ferrous ion treatment in 1.1% saline fresh water provided superior corrosion resistance when subsequently exposed to clean seawater when compared with conditioning in clean seawater alone. A surface conditioned in fresh water for 28-days was as effective as a seawater conditioned specimen when subsequently exposed, since the resistance of all the treatment films broadly converged after this period. Conditioning with SDD was not found to be particularly effective. The studies concluded that any exposure of conditioned 70:30 to strongly sulphide contaminated waters led to the rapid formation of copper-sulphide films and rapid corrosion. These films did not readily revert to a protective nature when subsequently exposed to clean, aerated waters, as has previously been suggested, persisting instead for at least 28-days. Dosing with ferrous ions was found to be extremely beneficial, particularly when the coupon was subsequently exposed to sulphide pollution. This confirmed the findings of previous studies into the performance of ferrous ions on copper-nickel alloy in polluted waters[9].

From these studies, it was evident that the policy of exclusion from dockyard water, with the attendant risk of contamination, was a sensible course of action to pursue in the interim. It was clear that exposure to sulphide pollution, whether background, or locally produced within coolers by sulphide generating bacteria, was not a tolerable option. Interface cooling rigs were therefore further developed, allowing the use of fresh water to be minimised. In parallel, procedures were developed to deploy a ferrous ion treatment method for vulnerable submarine coolers in harbour, with the first platform to receive this treatment planned for the end of 2007.

The Environment

Coordinated by the scientific advisory panel, and in parallel with laboratory investigations into copper alloy corrosion behaviour, a programme to assess the extent of the environmental risk to RN platforms was also instigated. Following a lengthy consultation with experts in the water industry and microbiologists, a seasonal programme of bulk water sampling and assessment was instigated. As an industry first, a new and much more sensitive technique for the measurement of viable bacteria, such as sulphate reducing bacteria (SRB), was developed and deployed in support of this work. In order to understand the relationship between local water quality and the bacterial cleanliness of the coolers, a programme of swabbing heat exchanger internals was undertaken. Once cultured, the results highlighted a large population of both anaerobic (such as SRB – Fig 8) and aerobic bacterium, most notably the *pseudomonad* genus, which secrete highly corrosive acid whilst metabolising organic matter[10].

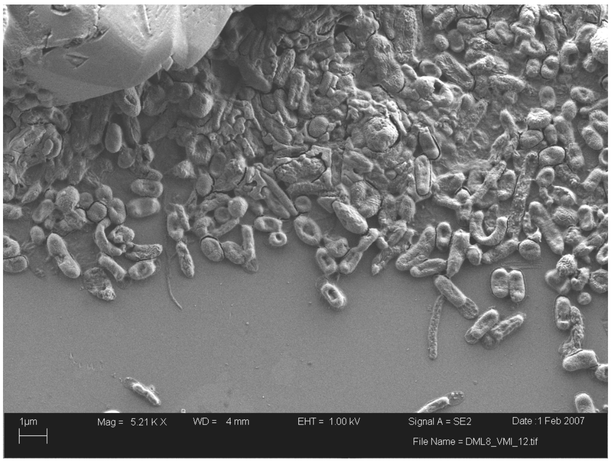

Fig 8 Microscopic image of bacterial population on a cooler swab – the curved rod shapes are "vibrio" anaerobes[10]

The population profile was the same across the submarine cooler fleet and didn't necessarily correlate with the bacterial count of the host dockyard water, with coolers operated in nominally clean and cold tidal waters exhibiting a similar degree of bacterial contamination as those largely operated in non-tidal basins or in warmer waters. Given that it has exclusively been coolers from the latter group that have experienced accelerated pitting failures, the presence of equally aggressive bacteria in coolers operated in colder and nominally cleaner climes, yet without the associated history of failure, was puzzling. To confirm that there were indeed no accelerated defects in these coolers, which might not yet have breached through wall, a series of inspections was conducted on sample tube lanes. Using an eddy current and visual process, there was no evidence of pitting in any tube, and measurements of general wall thinning were commensurate with normal corrosion rates.

Given that the same bacteria that have created such rampant pitting corrosion in warmer dockyards are not causing problems to copper-nickel in cooler waters, is the process strongly dependent on even relatively small differences in temperature? This work will continue into 2008 to attempt to establish which variables drive the MIC mechanism.

From these results, the following questions inevitably arose: How quickly does a biofilm take to form on a copper-nickel surface immersed in typical dockyard water? And assuming such water is host to the bacteria identified as aggressive and a proponent of the MIC mechanism, for how long can this exposure be tolerated before pitting is likely to begin? To answer this and also to assess whether a durable copper oxide coating was any defence against MIC, the UK MOD scientific panel established a series of laboratory experiments which would attempt to replicate the likely failure mechanism[10]. The experimental matrix employed 70:30 flat coupons, some of which had been conditioned in fresh water and some which were left "vulnerable". The coupons were immersed in stagnating water from a UK submarine dockyard. This water was also inoculated with bacteria originating from an in service cooler that had suffered an MIC event. After just 5-weeks immersion, the coupons exhibited an established biofilm which was clearly host to a diverse range of bacteria. The biofilm was then carefully removed to examine the alloy surface beneath it. Using an electron microscope, this revealed a number of embryonic pits a few microns wide, each displaying the beginnings of classical MIC morphology (Fig 9). This was true of the coupon surface both with and without an oxide coating. It has previously been suggested that such a coating may provide a measure of defence against this pitting mechanism, although the current work would tend to question this.

Now that the experimental feasibility of this ground breaking work has been demonstrated, it is the UK MOD's intention to develop it further before concluding. This will include employing a wider experimental matrix using coupons with a variety of conditioning histories and will allow judgement to be made as to how best to condition coolers in the future. The experiment will also seek to replicate more accurately the actual environment that the material would see in a naval cooler, such as circulating flow rather than stagnating. Additionally, an assessment will be made of the effectiveness of various water treatment options which may be capable of rendering the species cited in the MIC mechanism harmless. These treatments are discussed in detail in the following paragraphs.

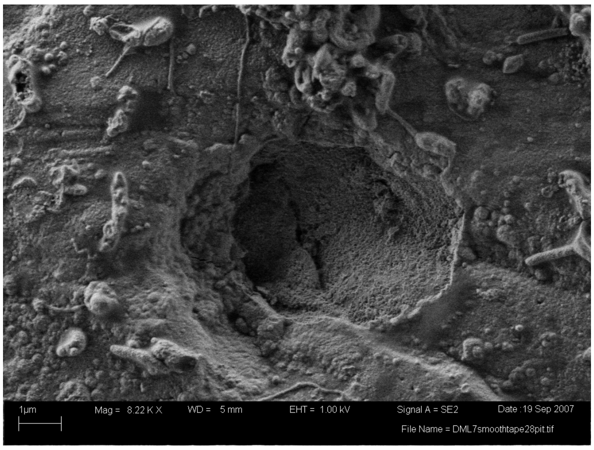

Fig 9 Embryonic MIC pit following 5-weeks exposure to inoculated dockyard water[10]

LONG TERM SOLUTIONS

Defence in depth

This paper has described the consortia of complex processes which are required for a successful MIC attack. It is clear that for this problem, one could either protect the cooler internals such that the material is sufficiently robust to withstand the mechanism, or one could treat the cause at root source, thus preventing contamination passing through the system from the outset. Given the consequences of a repeat, large scale MIC event in a submarine heat exchanger, it would be entirely appropriate to actually do both of these, providing defence in depth. This is exactly how the UK MOD intends to pursue this issue; the proposed methods of cooler protection and water treatment will be described in turn.

Cooler protection

Enhanced conditioning treatments have now been identified to give copper-nickel alloy the best possible start. These include ferrous ions, SDD and BTA. All have been shown to be effective, although the latter two are offered with considerable environmental constraints. Future work aims to understand the effectiveness of coatings conditioned using these treatments against the threat of MIC. In 2008, the UK MOD will be publishing a Defence Standard which will invoke the procedures and guidelines for the use of such treatments when fitting out or simply re-conditioning copper alloy seawater heat exchangers.

Water treatment

Given the conclusion from the scientific research and specifically the MIC replication experiments, the UK MOD scientific panel advised that water treatment technologies were likely to be a solution to the accelerated corrosion events which had occurred in 2006. Various technologies were identified mainly from the water industry and the marine sector, but some novel approaches were also considered from other sectors (Table I).

Table I Summary of water treatment technologies

Method	*Sterilising/Disinfecting Medium*	*On-line application?*	*Proven applications*	*Disadvantages*
Ozonolysis	Ozone	Possibly	Medical	Safety
Ultra Violet	UV	Yes	Medical	Fine filter
Titanium Dioxide Autocatalyst	Hydroxyl radicals	Yes	Ballast water treatment	Fine filter
Electrochlorination	Hypochlorite anions	Yes	Cooling water treatment	Chemical in cooler
Hypochlorous acid	Un-dissociated hypochlorous acid	No	Recent medical	Unproven, not on-line

Following a feasibility study, electrochlorination has been taken forward initially as a candidate technology and will be subject to a trial on a submarine in a UK dockyard. This technology is an already proven method of eliminating biofoul in marine systems, but has been further used to manage biofilm corrosion in the coastal power generation sectors[11]. This is achieved by a daily, short 'shock' dose treatment of chorine which detaches or kills the biofilm populace, taking with it the bacterial species resident within the slime. Overall, it is anticipated that the circulation of chlorine through the cooler will provide a level of cleanliness from bacterial colonisation that will minimise the risk of MIC. Additionally, free chlorine in the seawater will oxidise the attendant sulphide pollution, ensuring it cannot become deleterious to the formation of the crucial copper oxide coating. The proposed method will allow the hypochlorite to be injected into the inlet strainer from a commercial chlorination unit on the jetty, making the system non-intrusive to the submarine and allow uninterrupted heat rejection. The trial is due to commence in the second quarter of 2008.

Materials selection

MIC has not solely been an issue for the submarine community; it has previously been responsible for a particularly damaging defect sequence in marine gas turbine lubricating oil coolers. These coolers have suffered a number of MIC attacks leading to seawater contamination of the lubricating oil which circulates through the shell. With no warning to the operators, this dilution and salinisation of the oil would lead to rapid corrosion of the turbine bearings. Given that the cooler employs a tube stack which is only 1.1 m long, its inherently removable nature enabled a re-design to titanium to be easily adopted[12] (Fig 10).

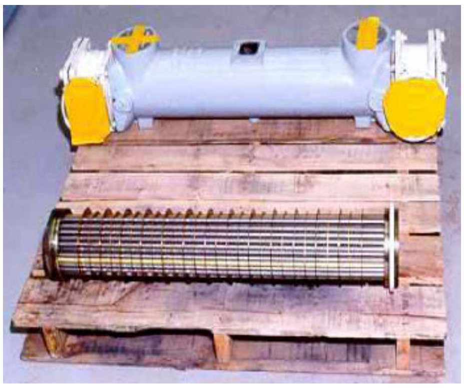

Fig 10 Gas turbine lube oil cooler shell with removable tube stack in foreground

Given the success of this implementation, the question was first raised of the submarine MIC issue: Why not use titanium? A surface ship cooler such as that shown in Fig 10 contains no more than 100 tubes, weighs less than 20 kg dry and can be typically removed from the ship by one man in a matter of hours. A submarine cooler on the other hand contains some 2,600 tubes and has an overall length of 5 m (Fig 11). The entire unit dry weighs 7,000 kg and can only be removed by cutting a hole in the submarine's pressure hull; the whole task would take as much as a year to complete. Even if this were done, the risk of accelerated galvanic or selective phase corrosion in the adjacent nickel-aluminium-bronze cast headers would be intolerable.

Fig 11   Eddy current inspection via a removed seawater header – there are 2,584 Cu-Ni tubes in this design

That said, the UK MOD is looking to employ novel materials in future submarine designs, including titanium and advanced nickel alloys. The requirement for this is not simply one of corrosion resistance, but it will certainly help in achieving this. The concern that titanium fouls more readily than copper is also recognised, although one might argue this fact given the experiences detailed in this paper. All shell and tube heat exchangers will be vulnerable at least to bio-debris such as macro fouling, since the cooler acts like a strainer to the contents of the handled seawater (Fig 12). There are mitigation strategies to reduce fouling of course, most notably the use of chlorination which has already been discussed as a method of treating the microbial content of the water.

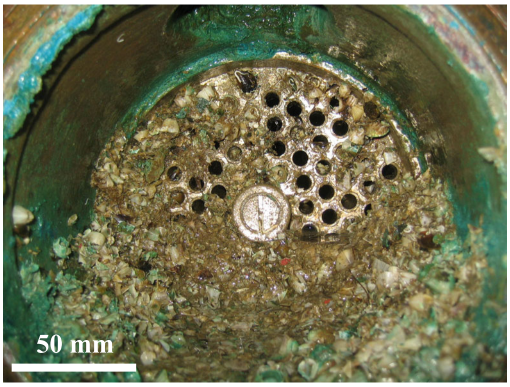

Fig 12   Macro fouling in a surface ship cooler employing titanium tubes

CONCLUSIONS

The RN has suffered significant platform unavailability due to MIC attacks in submarine seawater coolers this decade.

The bacteria cited in the MIC mechanism are ubiquitous across UK dockyards; however the instances of failure are not. What causes such bacteria to attack in some instances but not in others appears to be climate related.

Exposure of vulnerable copper alloy to sulphide pollution will lead to greatly reduced service life and susceptibility to MIC. Conditioning in clean water has previously been recognised as crucial for copper alloy, although reduced timescales for maintenance and upkeep packages this decade have led to the demise of this best practice. This resulted in some instances of coolers failing within as little as 6-months.

The modern operating profile of UK submarines has led to massively increased occurrences of biofouling, the like of which is unprecedented in copper systems. Chemical cleaning of coolers has been hugely successful in combating this, whilst recognising that heat exchangers will be left vulnerable by such a process unless subsequently re-conditioned.

Interim palliatives to eliminate the risk of MIC have included the complete exclusion of dockyard water as a cooling medium, in turn allowing the alloy an optimised conditioning process.

For future mitigation, ground breaking MIC replication experiments and studies into water treatment technologies would suggest that eliminating the bacterial content of the handled seawater will substantially reduce the risk of an attack. The first such treatment to be assessed for the RN will be electrochlorination, with a trial due to begin in spring 2008.

Finally, this work has proven that there is no single, complete solution to the problem of MIC. As long as we continue to use copper in the marine environment, the best form of defence is to understand the issue, and then do all that is possible to minimise the risk.

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