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TITLE

CORROSION PROBLEMS WITH COPPER-NICKEL COMPONENTS IN SEA WATER SYSTEMS

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CORROSION PROBLEMS WITH COPPER-NICKEL COMPONENTS IN SEA WATER SYSTEMS

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ABSTRACT

Recent changes in construction techniques and operational practice have resulted in a number of failures of copper-nickel components in sea water systems. These failures include erosion corrosion of welded 90/10 copper-nickel pipe, erosion corrosion of 90/10 copper-nickel heat exchanger tubes, "hot-spot" corrosion of 70/30 copper-nickel tubes and denickelification of 70/30 copper-nickel tubes. Case histories describing examples of each of these problems are presented. Factors contributing to these failures, such as welds protruding into the flow stream, tight bends, contamination by marine organisms, unusual flow patterns and exposure to sulfide-polluted, stagnant sea water, are discussed. Methods to prevent or reduce the future occurrence of these problems are also presented.

Keywords: corrosion, sea water, copper-nickel alloys, erosion, impingement, denickelification, sulfide-induced corrosion.

INTRODUCTION

Several significant changes in fabrication technology and operational use of sea water systems have recently been introduced during the construction, modernization and maintenance of Canadian naval vessels. These changes include the use of welded copper-nickel piping, modular construction and the supply of "water on demand" instead of continuous flow. While these changes provide some notable benefits, they have also contributed to a number of rapid failures of copper-nickel components in sea water. In this paper, a brief history of the experience with copper-nickel alloys prior to these changes will be provided. This will be followed by several recent case histories involving erosion corrosion and denickelification. Methods to prevent the future occurrence of these problems will also be discussed.

HISTORICAL PERFORMANCE OF COPPER-NICKEL ALLOYS

Sea water systems using 90/10 copper nickel (UNS C70600) piping have provided many years of reliable service in surface ships operated by the Canadian Forces. Very few failures of this piping have been brought to the attention of either of the Dockyard Laboratories (this one in Esquimalt, BC or the other in Halifax, NS). Most of these failures have involved erosion corrosion caused by unintentional obstructions at flanges or by modifications to the piping systems to accommodate new equipment or operational procedures. An example of the latter involves a blackwater piping system that had been in service since 1964. The 90/10 copper nickel pipe shown in Figure 1 perforated in 1992 as a result of erosion corrosion near the exit of the small discharge pipe from one of the crew's heads. The system had originally been designed for sea water-flushed overboard discharge. However, in 1985, the blackwater system was adapted to accommodate vacuum collection into a holding tank. The changes in velocities and composition of the effluent resulting from this conversion caused erosion corrosion of the original copper nickel collection pipes.

Heat exchangers using sea water as a coolant have been used extensively in ships of the Canadian Forces. In the past, most of these heat exchangers have been fabricated with 90/10 copper nickel tubes and Naval brass (UNS C46400) tube plates. These systems have provided excellent service as long as the alloys have been protected against corrosion by the use of sacrificial steel anodes. When these anodes have not been properly utilized, failure of the 90/10 tubes and erosion corrosion of the Naval brass tube plates has occurred (Figure 2).

The performance of copper nickel alloys in sea water continues to be the subject of a substantial amount of research. For example, at CORROSION/97, three of the papers presented at the Symposium on Marine Corrosion were specifically devoted to these alloys[1-3]. This research is driven, in part, by efforts to understand the differences in the relative behavior of 90/10 and 70/30 (UNS C71500) copper-nickel alloys in different environments. There is, for example, general agreement that sulfides liberated from decaying organic matter can cause accelerated corrosion of both alloys. However, in one study, Popplewell[4] determined that 70/30 was substantially more susceptible to localized corrosion in flowing sea water than 90/10, whereas Todhunter[5] reported that tubes made of 70/30 had a lower incidence of failure in sulfide polluted Los Angeles harbor water than those made of 90/10. Gudas and Hack[6] found that 70/30 and 90/10 were both susceptible to sulfide-induced pitting, but higher sulfide concentrations were required to trigger the attack of 70/30. Our own work in flowing sea water suggested that these contradictory reports in the literature could be related to the nature of the corrosion product films that had developed on the components in question and that these films were very dependent on the sea water chemistry and the length of exposure[7].

EROSION CORROSION OF COPPER-NICKEL SEA WATER PIPING

The extensive use of welded copper-nickel sea water piping has recently been introduced. Welded systems offered the advantage of reducing the cost and weight of flanged elbows and cast T fittings. A reduction in the number of flanged joints also allowed pipe runs to be situated closer together, thereby saving space. Furthermore, welded systems held the promise of removing some of the shock resistance problems associated with the brazed joints that had previously been used. Finally, the use of welded systems was intended to reduce the problems with leaks that were associated with brazed joints and bolted connections.

A section of piping which increased the diameter of a sea water system from 150 mm to 200 mm is shown in Figure 3. The pipe developed a leak in this transition section just downstream from a circumferential weld. Depending on the rate of flow through the pipe, the change in diameter alone could create enough turbulence to cause erosion. However, a cross-section of the transition piece revealed that the circumferential weld protruded into the flow stream and contributed to the erosion corrosion (Figure 4). The eroded section of piping was also found to have an iron content of 1.11% (Table 1). Although this iron content was within the required specification for the 90/10 copper nickel piping (United States Department of Defense specification MIL-S-16420 alloy C70600 Class 200), a content of at least 1.4% is recommended for sea water service[8]. The importance of iron additions in improving resistance to flowing sea water has been known for many years. For example, in 1972, Pearson[9] published a review which included references to comprehensive studies of copper-nickel alloys that were conducted in the early 1950's[10-12].

This piping system was also found to contain a number of seamed elbows with a very tight radius of curvature (Figure 5). The welds in these elbows which ran parallel to the direction of flow had been carefully ground out, but the circumferential welds, which connected the elbows to the rest of the piping system, protruded into the flow stream (Figure 6). The resulting turbulence gave rise to erosion corrosion (Figure 7) similar to that observed in the transition section. Also like the transition section, the material in the bend had a lower iron content (1.10%) than that recommended for sea water service. The turbulence cause by the tight radius led to impingement attack in the classic "horse walking upstream" pattern[13] (Figure 8). Prevention of the corrosion problems observed in the bends could be achieved by tighter quality control of the welding, by using an alloy with a higher iron content and by using bends with larger radii. LaQue[14] has recommended bends with a minimum radius of three pipe diameters. This is the minimum radius specified in the piping standard that is normally applicable to Canadian naval vessels. However, in a few cases, exemptions were granted in order to solve some pipe routing problems. Similarly, the welding specification allowed a maximum root concavity of 1.5 mm. This specification could be achieved during the fabrication of individual modules but proved difficult to meet in some of the field welds that tied the modules together. These welds were located in areas that made electrode manipulation awkward and efficient argon purging difficult, with excessive weld penetration as a result. In the future, the selection of locations for field tie-ins should be made with accessibility for welding and the sea water flow conditions in mind.

In an effort to reduce staffing requirements, remotely operated flow control systems have been incorporated into new or updated sea water systems. Complicated arrangements of cross-over pipes and valves, intended to provide redundant flow paths to important pieces of equipment, have also been utilized. These factors have led to some unusual flow conditions within the piping systems. For example, a section of firemain failed in a cross-over pipe that was nominally upstream from a butterfly valve. The erosion corrosion was very localized (Figure 9), suggesting that the valve had been left slightly open, creating an eddy in the "upstream" pipe.

Table 1. Chemical Composition of Transition Section (weight percent)

Element	Cu	Ni	Fe	Pb	Zn	Mn	Al	Si
Percent	rem	9.58	1.11	0.03	0.02	0.34	<0.01	0.04

EROSION CORROSION OF COPPER-NICKEL HEAT EXCHANGERS

The redundant sea water flow paths mentioned earlier, along with a new philosophy of supplying water on demand, have given rise to another problem that had only been observed on a few isolated occasions in the past. The gentle flow of sea water in some pipe runs has provided an ideal environment for the attachment of marine organisms. As a result, these pipes have become heavily fouled (Figure 10). For a number of reasons, including visits to fresh water ports, the colonies can die off. When this happens, particularly in the case of hydroid colonies, parts of the colonies break off in chunks and become lodged in the orifices in the tube plates of heat exchangers. Figure 11 shows the extent of the blockage that occurred on the supply side of a heat exchanger just three months after it had been completely cleaned. The mass of dead hydroids provides an ideal home for other organisms and thriving colonies of mussels and barnacles have been observed (Figure 12).

With so many tubes blocked, the flow through the remaining tubes occurred at a higher velocity than that assumed in the original design. As a result, erosion corrosion of the tube ends has occurred (Figure 13). The altered flow patterns have also caused erosion of the divider plate (Figure 14). The installation of sacrificial steel anodes in the end bells would increase the resistance to erosion corrosion. Ship staff and the Fleet Maintenance Facilities have been installing these anodes as opportunities arise. While anodes will help to reduce the extent of erosion corrosion, elimination of the problem will require removal of the marine growth throughout the ship. Under current operating conditions, this will be very difficult to achieve.

DENICKELIFICATION OF 70/30 COPPER-NICKEL TUBES

Several 70/30 copper-nickel tubes in a sea water-cooled heat exchanger for engine oil were found to have perforated near a baffle plate. Splitting these tubes lengthwise revealed that the perforations had resulted from deep pits (Figure 15) which had been initiated on the sea water side of the tubes. When the tube wall became thin enough due to this corrosion, the oil (under pressure) ruptured the tubes inward. Other tubes that were removed at random from this heat exchanger were also found to be pitted, with most of the damage concentrated in areas corresponding to the locations of the baffle plates.

This heat exchanger was mounted on the engine block, with one of the support angles quite close to the baffle plate that was near to the perforated tubes. When the engine was shut down, the pump which delivered sea water to the heat exchanger was shut off as well, leaving quiescent sea water inside the tubes. Furthermore, an oil circulation pump was then turned on, which kept hot oil flowing through the heat exchanger and thereby maintained a high temperature for the sea water trapped in the tubes for an extended period of time after the engine was shut off. These conditions gave rise to a particularly severe form of denickelification, known as "hot-spot" corrosion. "Hot-spot" corrosion has been reproduced in the laboratory[15-16] but reports of in-service problems seem to be quite rare, as the general industry approach seems to be to avoid the conditions known to cause this form of corrosion[17]. The laboratory investigations indicated that "hot-spot" corrosion occurred at temperatures between 90° and 170°C and that the corrosion was intensified in the presence of sulfides.

As noted earlier, some sea water supply lines are heavily fouled, so the presence of sulfides from decaying marine organisms in the sea water trapped in the heat exchanger during shut-downs is very likely. The temperature of the sea water will remain within the studied region for some time after the

engine is shut down. Finally, the proximity of the baffle plate to the engine mount could lead to localized conductive transfer of engine heat.

A number of steps can be taken to prevent future "hot-spot" corrosion in this system. The simplest, and most effective, action is to keep sea water flowing through the heat exchanger at all times. Ideally, when not in use for extended periods of time, the heat exchangers should be drained, flushed and ventilated. Sacrificial steel anodes should also be installed in the end bells and replaced as required. Although these anodes only provide cathodic protection within a few tube diameters, the ferrous ions that they release have been shown to be beneficial to the development and maintenance of protective films throughout the tubes[7]. The heat exchangers should also be relocated to alleviate any problems with the residual heat.

The precise mechanism of denickelification is still a matter of some controversy. However, the end result is a pit with associated deposits of copper. Some of this copper can be found in locations downstream from the original pit (Figure 16). Denickelification has also been observed under conditions that are less severe than those known to cause "hot-spot" corrosion. For example, a leak developed in a hydraulic oil cooler after it had been in operation for 15 months. Examination of the failed 70/30 copper-nickel tube (Figure 17) revealed a deep pit that had been initiated on the sea water side. There were several other pits containing deposits of copper. The hydraulic oil normally bypasses this cooler until the oil reaches a temperature of 30°C, so the temperature of the oil entering the cooler is normally between 30°and 40°C. If the temperature reaches 65°C, an alarm is activated. Sea water flows constantly through the cooler while the ship is at sea, but flow to the cooler is shut down while the ship is in port, leaving the cooler full of stagnant sea water. Because this tube had been cleaned prior to delivery to the Dockyard Laboratory, it was not possible to determine the exact sequence of events that led to the perforation. Almost certainly, the pit was initiated during a shut-down period as a result of contact with sulfide-polluted, stagnant sea water. It could not be determined whether the ensuing corrosion occurred only during shut-downs or also continued under a deposit which shielded the pit from flowing sea water while the ship was at sea.

A final example indicates the role that operational practice can have on the corrosion of 70/30 copper-nickel tubes. A tube from an air cooler perforated as a result of pitting that had been initiated on the sea water side (Figure 18). Discussions with crew members on different ships revealed that there was no set routine for the operation of this cooler. Some ships closed the valves to the coolers during periods of inactivity while others left them open, thereby allowing the sea water to flow through them continuously. These coolers were also not fitted with sacrificial steel anodes. To date, those ships which maintained continuous flow have not reported any problems with these coolers. The manual supplied by the manufacturer for this cooler recommends that it be completely drained and vented when not in use. Although this would be an acceptable alternate to the installation of anodes and maintenance of continuous flow, this recommendation appears to have been overlooked in the overall design of the ship, as provisions for easy draining and venting do not exist.

SUMMARY

The case histories of several failures involving copper-nickel sea water piping or heat exchangers were presented. These failures were attributed to problems with construction techniques and operational practices that have recently been introduced. The erosion corrosion that has been observed in the welded 90/10 copper-nickel piping system was caused by circumferential welds that protruded into the flow

stream, by bends that were tighter than the recommended minimum of three pipe diameters or by unusual flow patterns near cross-over valves. A new philosophy involving redundant pipe runs which supply water on demand, instead of the continuous flow used previously, has led to the creation of an ideal environment for the attachment of marine organisms. Masses of dead organisms have become trapped at the entrances to heat exchangers, providing a base for subsequent generations and altering the flow patterns in the heat exchangers. This has led to erosion corrosion of the tube plates. Sacrificial steel anodes should be installed in all heat exchangers to reduce the extent of corrosion. Removal of the existing biological contamination will be difficult but, if successful, subsequent fouling can be substantially reduced by maintaining flow rates that are sufficiently high to prevent the initial attachment of marine organisms.

One heat exchanger was located and operated in such a manner that its 70/30 copper-nickel tubes suffered a particularly severe form of denickelification known as "hot-spot" corrosion. This problem could be prevented by maintaining a continuous flow of sea water, installing anodes and relocating the unit. Denickelification was also observed in 70/30 tubes under less severe conditions. In these cases it had been initiated during periods of exposure to sulfide-polluted sea water during shut-downs. Prevention of biological contamination and maintenance of continuous flow of sea water would reduce or eliminate these corrosion problems as well.

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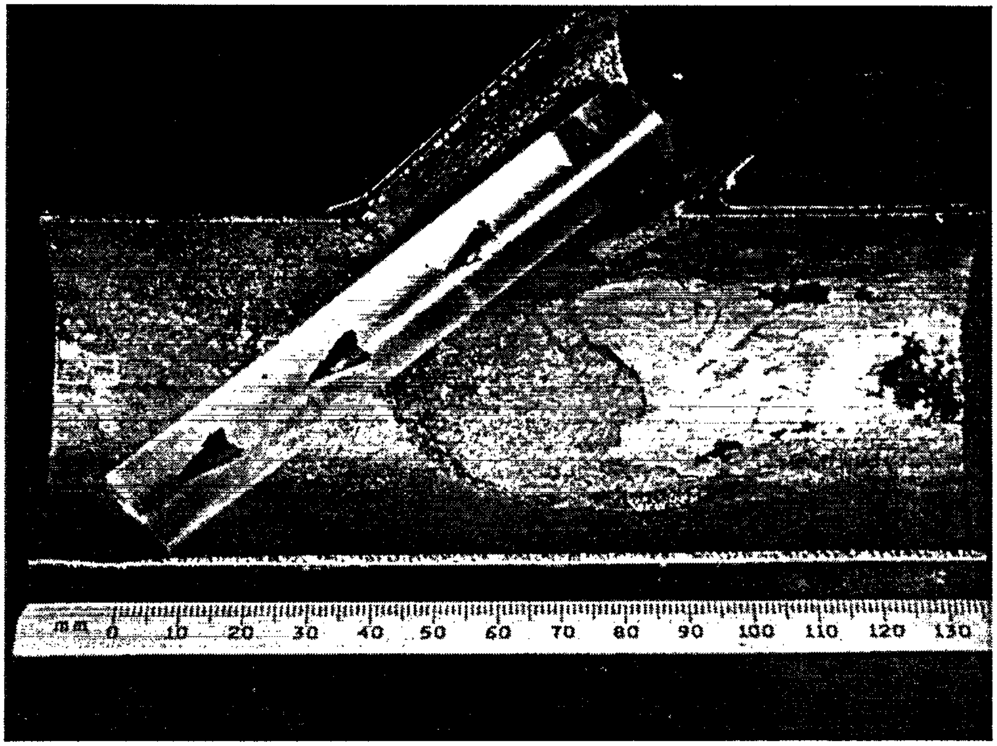

Figure 1. Erosion corrosion of 90/10 Cu-Ni pipe in a blackwater system.

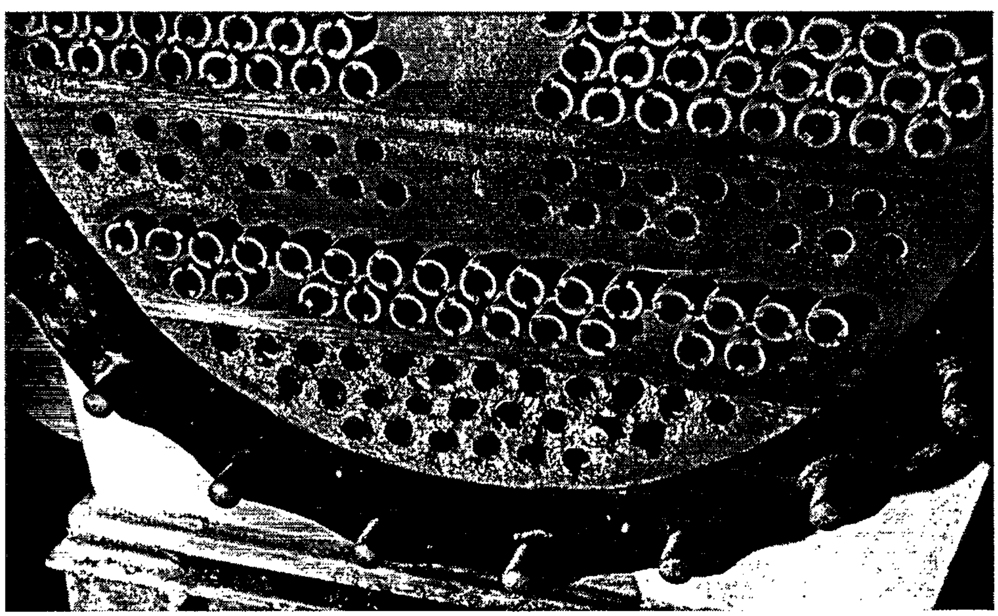

Figure 2. Erosion corrosion of 90/10 Cu-Ni tubes and Naval brass tube plate (assisted by dezincification of the tube plate).

Figure 3. Transition section of 90/10 Cu-Ni pipe that increases the diameter of the pipe run from 150 mm to 200 mm.

Figure 4. Cross-section of transition piece showing erosion corrosion downstream from a circumferential weld.

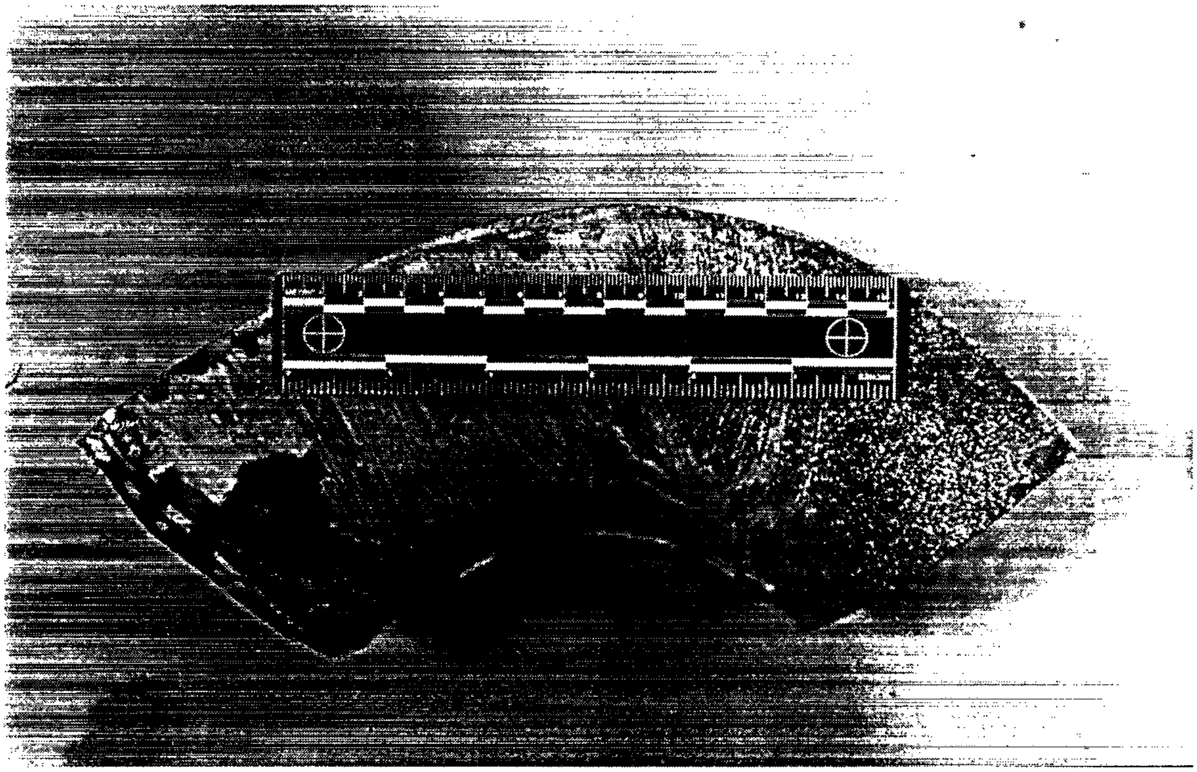

Figure 5. Seamed elbow with tight radius of curvature. This elbow was bisected in the direction of flow prior to this photograph.

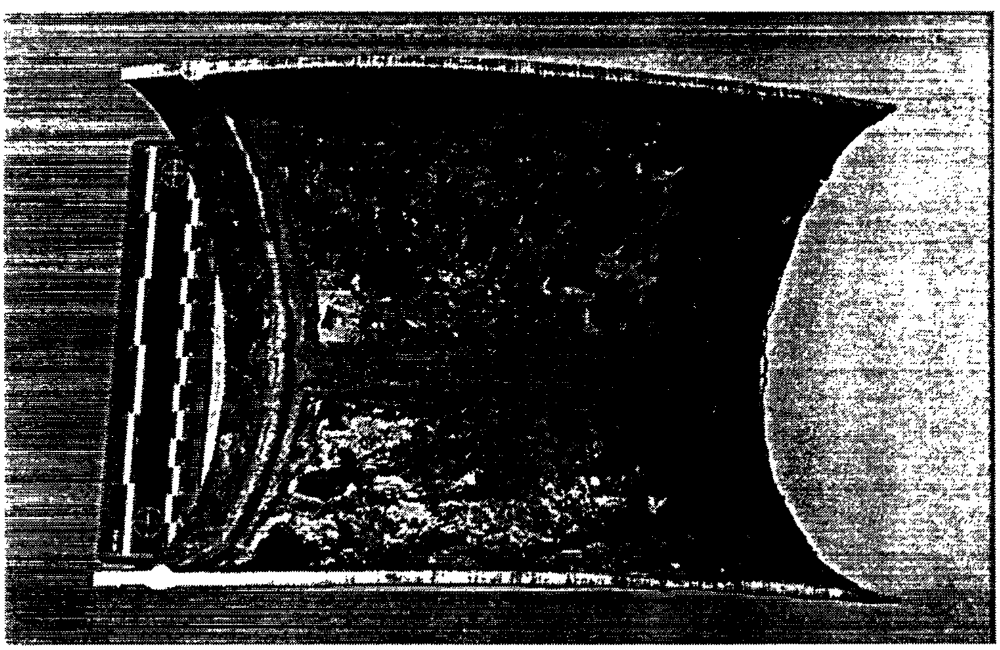

Figure 6. Seamed elbow with weld in direction of flow ground out. Circumferential weld protrudes into flow stream.

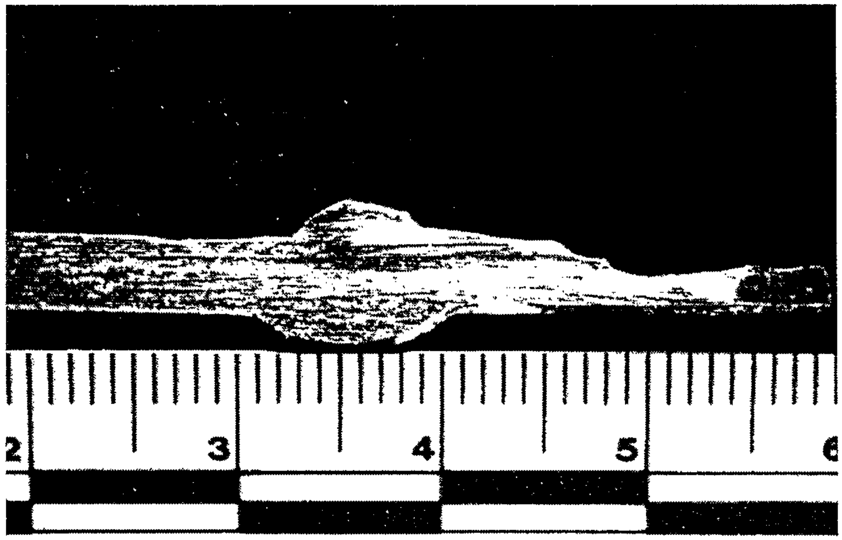

Figure 7. Cross-section showing erosion corrosion downstream from a weld.

Figure 8. Horseshoe pattern typical of impingement corrosion in a tight bend.

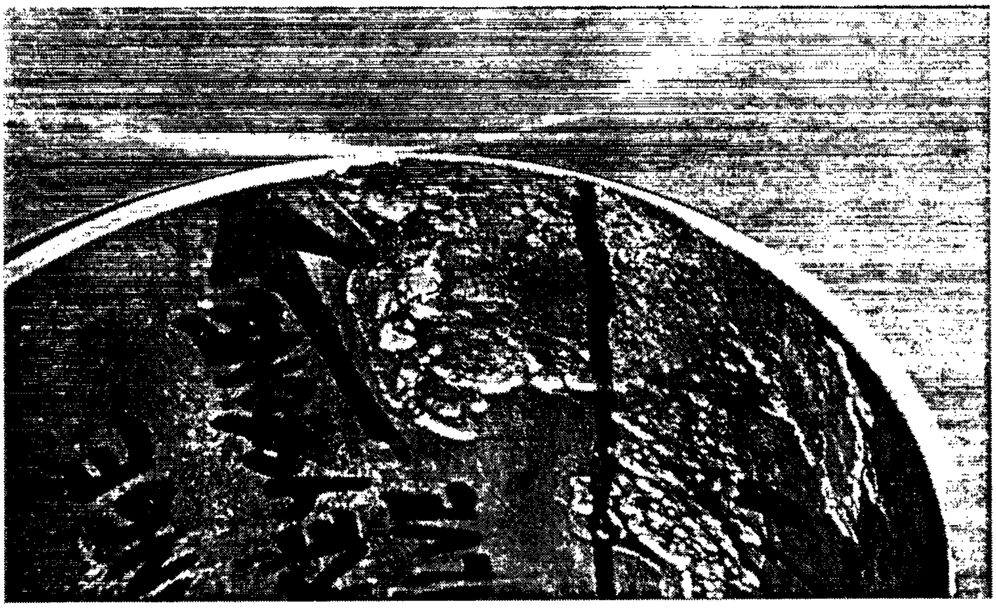

Figure 9. Erosion corrosion near a cross-over valve.

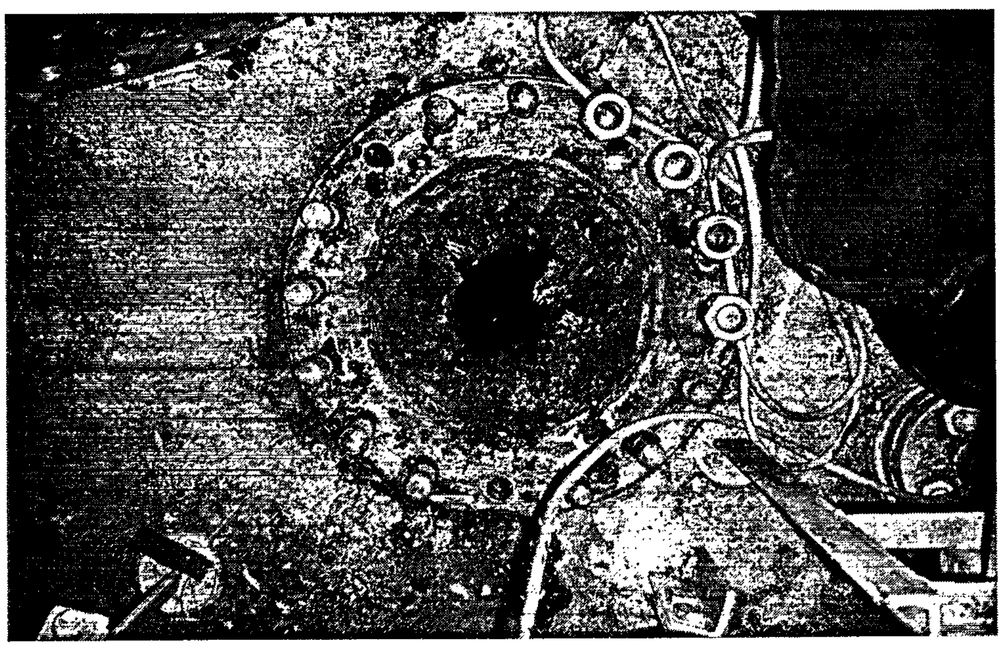

Figure 10. Firemain fouled with marine organisms.

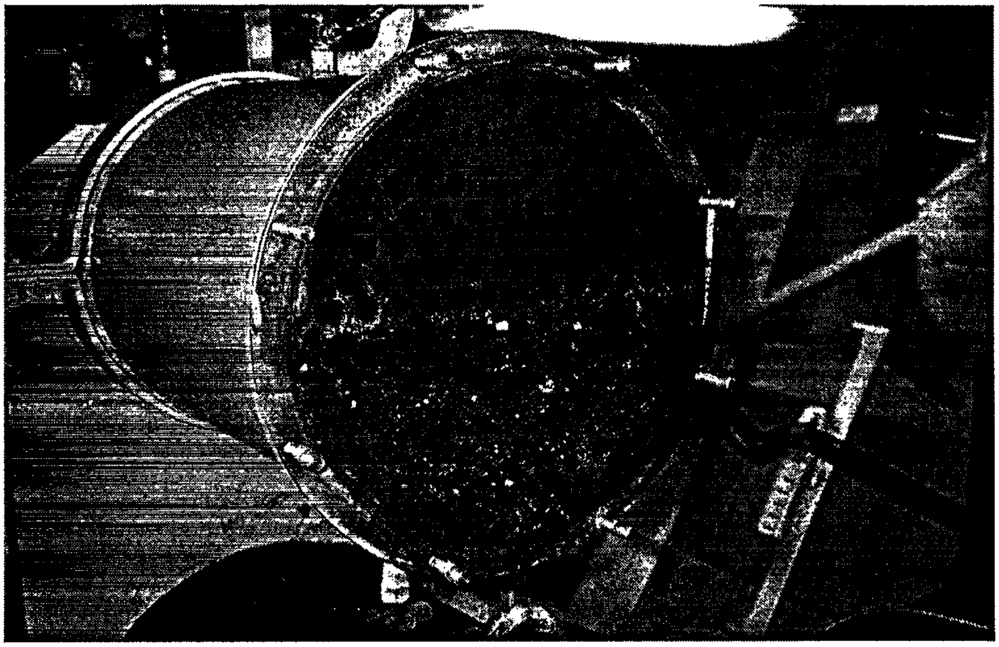

Figure 11. Extent of blockage in a chiller 3 months after cleaning.

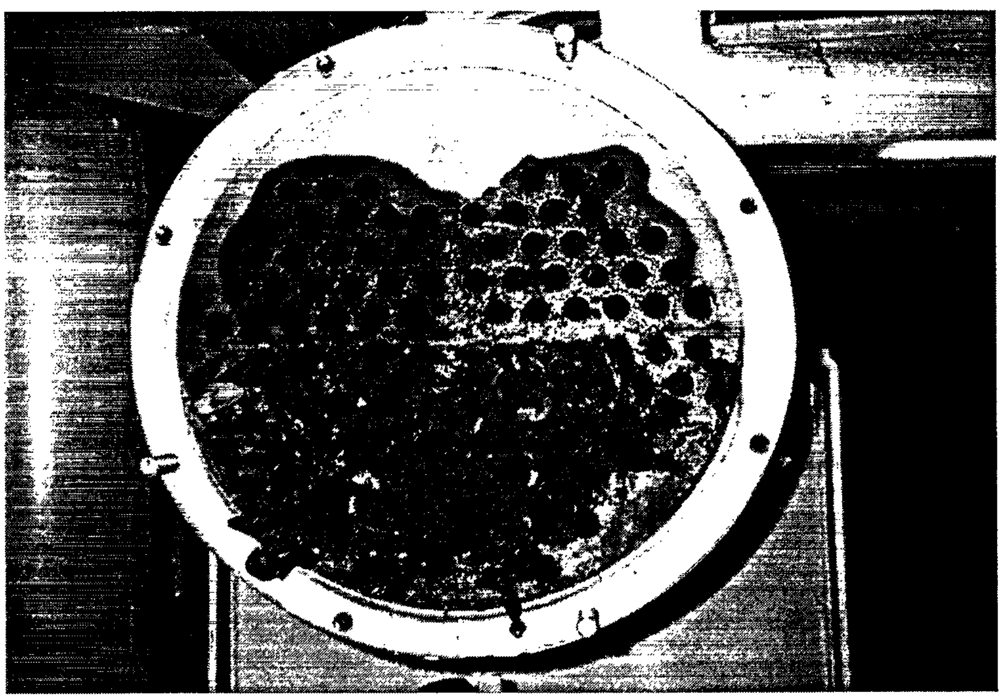

Figure 12. Mussels and other marine organisms blocking a chiller that had been in service without cleaning longer than the chiller shown in Figure 11.

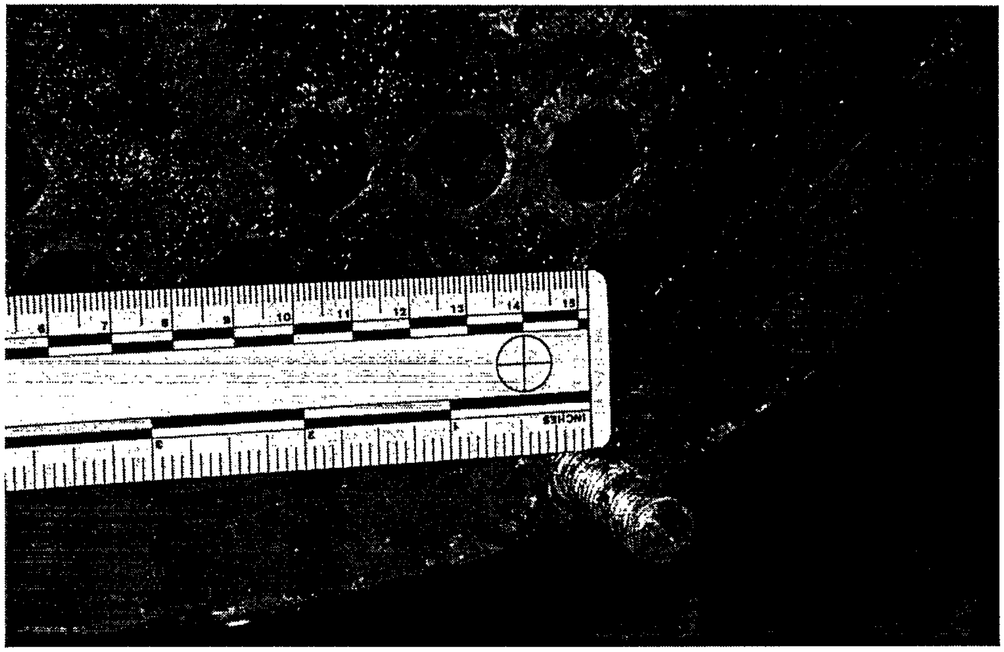

Figure 13. Erosion corrosion of 90/10 Cu-Ni tube ends resulting from blockage.

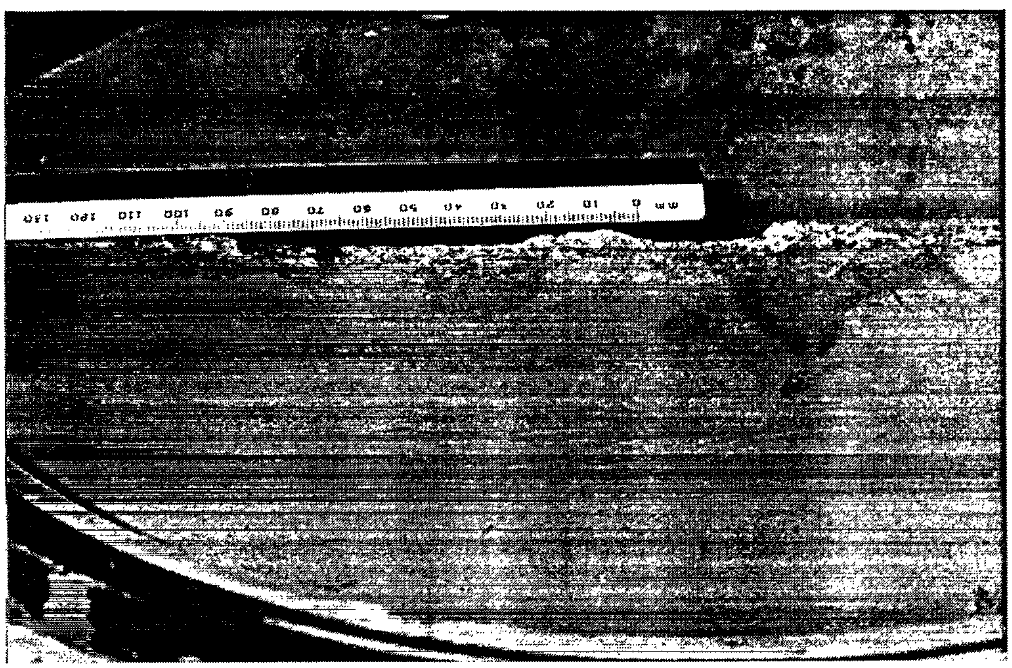

Figure 14. Erosion corrosion of divider plate resulting from blockage.

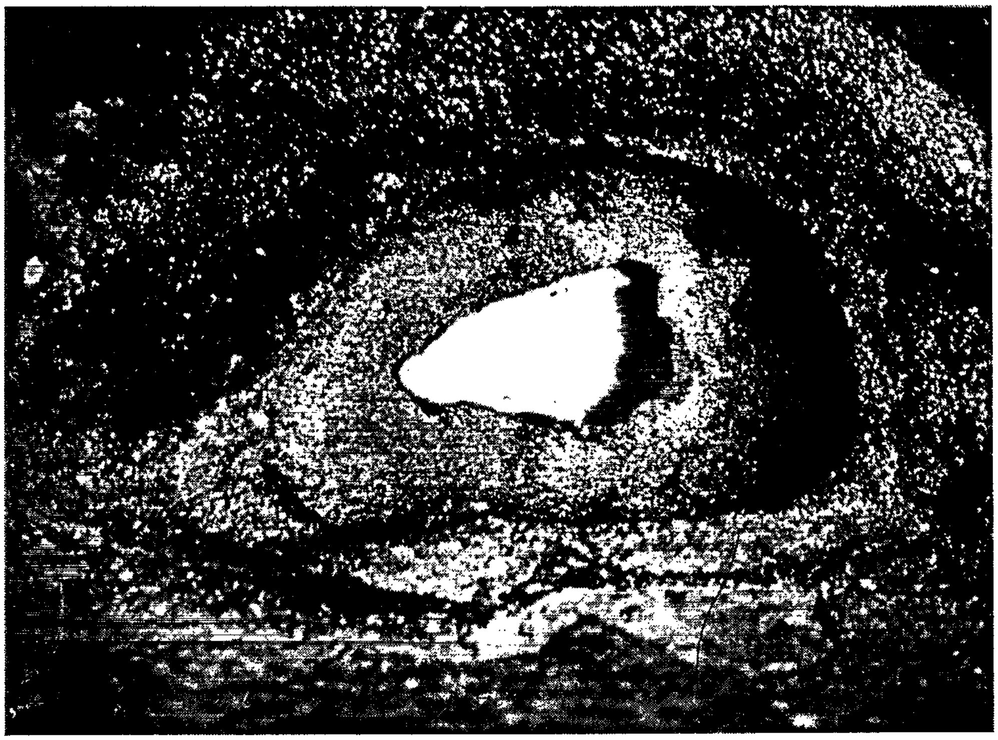

Figure 15. Pit initiated on sea water side of 70/30 Cu-Ni tube. 18x.

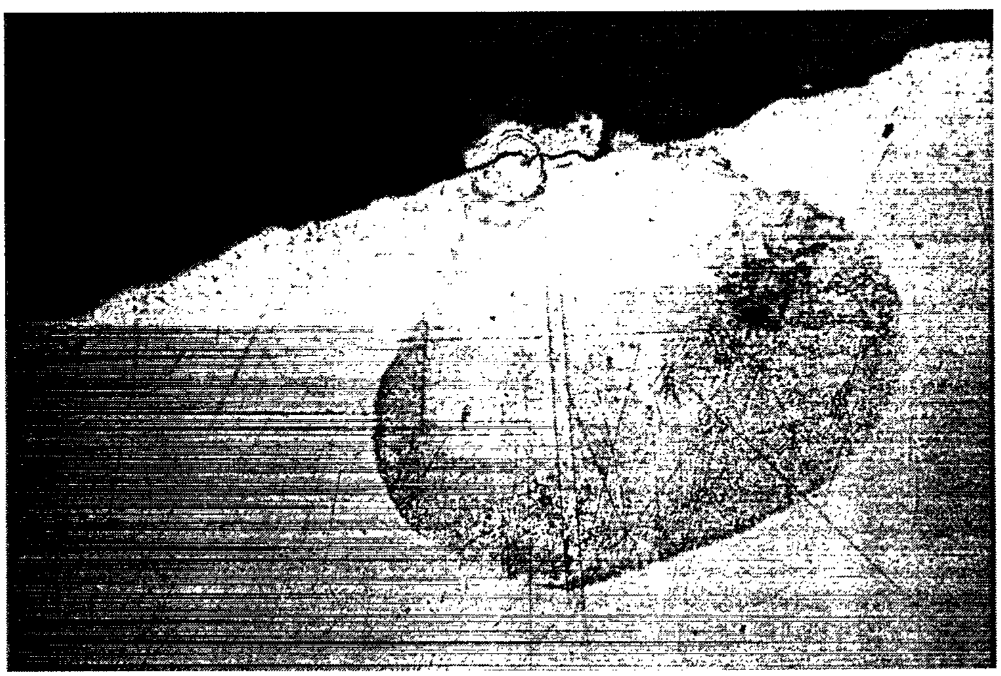

Figure 16. Copper particle downstream from a pit. An alcohol stain is also visible. 450x.

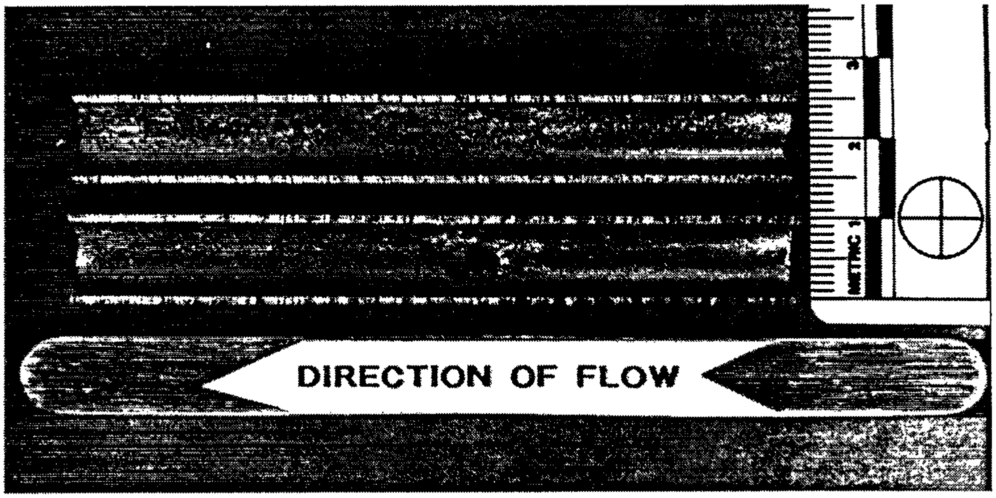

Figure 17. Pit initiated on the sea water side of a 70/30 tube in a hydraulic oil cooler.

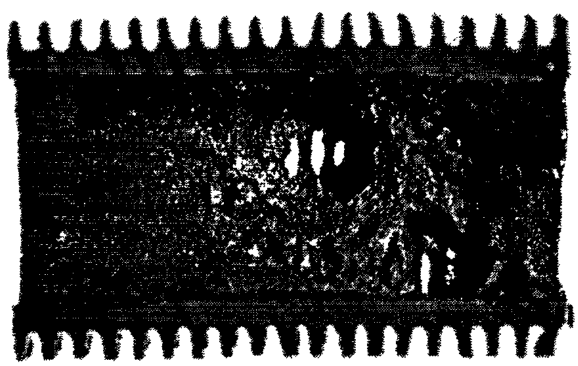

Figure 18. Pits initiated on the sea water side of a 70/30 tube in an air cooler.

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