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Corrosion Control of *Kunifer-5* Seawater Piping Systems of Naval Ships by Cathodic Protection Technique

M. B. Deshmukh, P. V. Rodrigues & Iqbal Akhtar
Naval Chemical and Metallurgical Laboratory, Bombay-400023

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Abstract. The cause of premature corrosion of *Kunifer-5* (copper alloy containing *Ni* 5 per cent and *Fe* 1.35 per cent) pipes used in seawater piping systems on board ships for feeding seawater to various units has been discussed. It has been shown that the *Kunifer-5* alloys suffer from heavy corrosion-erosion attack at unavoidable bends and places where local seawater velocity exceeds the specified limit. The field observations as well as laboratory study have indicated that satisfactory protection of the pipes could be achieved by galvanic cathodic protection using aluminium alloy anodes.

1. Introduction

Corrosion in seawater systems on board ships is considered as a matter of material selection at the design and construction stage. Once the materials are selected and the system is installed, the corrosion control methods become mandatory to avoid any malfunctioning of the main engineering units. In the event of corrosion, the affected pipe section has to be plugged during operation and subsequently replaced by a fresh one. This involves undesirable shut down period at high costs. Replacement of the entire existing seawater system by new pipes of superior corrosion resistant material is impracticable and therefore protection measures have to be resorted. Such a situation was experienced in respect of some ships built abroad and commissioned in Indian tropical waters.

The seawater system in the present context may be categorised into following groups:

(i) Cooling seawater systems for heat exchangers, diesel engine etc.

(ii) System for feed water cooling, oil cooling etc.

(iii) Flooding and draining systems.

(iv) Seawater systems for holds and decks.

(v) Fire mains.

(vi) Miscellaneous branchings.

These systems incorporate many branches emerging from T and cross joints and are fabricated out of *Kunifer-5* (5% *Ni*, 1.35 % *Fe* and rest copper) pipes of dia. from 10 to 110 mm and wall thickness from 2 to 5 mm, because *Kunifer-5* alloy has resistance to corrosion/erosion in unpolluted seawater up to velocity of 2 m/sec, normally observed in service.

Kunifer alloys owe their corrosion resistance to the surface oxide films which are modified by nickel and iron. The ability of the alloy to withstand the dynamic condition of seawater has been found to be related to its refilming tendency which is adversely affected by certain pollutants as well as by turbulent flow exceeding 2 m/sec[1]. In the practical situation, localised corrosion is possibly initiated on the spots where film damage occurs[2]. Further propagation of corrosion requires to be controlled either by inhibitors or by cathodic protection. Efficacy of the inhibitors is doubtful because these are applicable to closed systems and also these may not be effective in presence of aggressive pollutants like sulphides. Further, the data on practical parameters of cathodic protection technique is also inadequate for non-ferrous alloys in contact with flowing seawater. Unlike the structural steels, the protective potentials of non-ferrous alloys have not been clearly defined. The work presented here is aimed at establishing the cause of premature corrosion of *kunifer* pipes and efficacy of cathodic protection technique using aluminium alloy anodes.

2. Field Investigation

The design and layout of the seawater system of the ship were studied with reference to drawings. Since it was not possible to inspect the sections of the system without seriously hampering normal operations of the ship, small sections of the failed seawater pipes were removed and examined in the laboratory.

It was observed that the failures were caused by numerous pit perforations and that the concerned sections either had bends or protrusions produced by brazed and misaligned flanged joints. The depth and density of pits had a striking correlation with the amount of protrusion, bend and pipe diameter. The observations in respect of two representative pipe sections are briefly summarised below:

Visual Examination : *Specimen No. 1*—This pipe was removed from a T section having a protrusion of about 2 to 5 mm of the brazed joint along the circumference (Fig. 1). The pipe had an external dia. 110 mm and wall thickness 2.5 mm. The deepest pit was 2.0 mm. The pipe gave a life of five years against the expected life of 15 years. Internal surface of the pipe exhibited numerous pits having a characteristic pattern producing elongated troughs following the direction of seawater flow. Figure 2 gives the dimensions of four troughs in terms of maximum length, width and depth. The internal surface of pipes did not have any deposit including corrosion product. No fouling organism was found in any of the tubes examined.

Specimen No. 2—This pipe was removed from a section with a bend. The pipe had an external dia. 35 mm, wall thickness 2 mm, and the maximum pit depth 1.50 mm. The pipe gave a life of five years againt expected life of 15 years. Internal surface of the pipe exhibited numerous pits. The pits had a characteristic circular pattern having

Figure 1. Seawater pipe of *Kunifer-5* alloy failed in service due to severe corrosion-erosion attack.

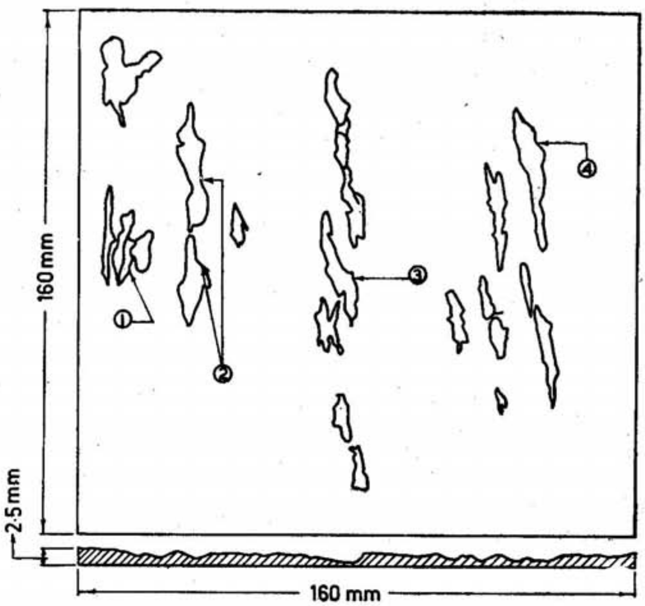

Figure 2. A sketch showing a pattern of corrosion-erosion observed on the failed *Kunifer-5* pipe 1.

a black corrosion product deposited over the pits. No fouling organism was found inside. The black deposit was found to be sulphide of copper.

Seawater Composition at Berthing Place—The seawater at the berthing place was analysed during low and high tides. The characteristics of seawater are given in Table 1.

Table 1. Characteristics of seawater at berthing place

	Salinity parts per thousand	*pH*	Dissolved oxygen ppm	Dissolved sulphides
Low tide	33.4	7.9	2.5	2 ppm
High tide	33.1	8.0	3.0	1.5 ppm
Ocean water	33.0	8.0	5.5	Nil

Operational Data—Maximum temperature of seawater was 45°C. Specific volumetric flow rates were recommended for pipes having different diameters. The volumetric flow rates on board ships were reduced by pressure reducing valves. The volumetric flow rates are converted into linear flow rates and are given in Table 2.

Table 2. Operational flow rates in failed pipes

Pipe dia. mm	Minimum vol. flow rate (m^3/hr)	Minimum linear velocity (m/sec.)	Maximum vol. flow rate (m^3/hr)	Maximum linear velocity (m/sec.)
110	55	1.60	110.0	3.216
35	6	1.73	10	3.2

Most of the seawater systems were reported to be silent during the berthing period. The berthing period may extend from few hours to several days.

Existing Protective Measures—The pipes were fitted with plug type and ring type zinc anodes. These anodes were intended to be replaced at quarterly interval. However, the zinc anodes, were found inactive primarily due to development of hard compact calcerous deposit (Fig. 3) over the surface.

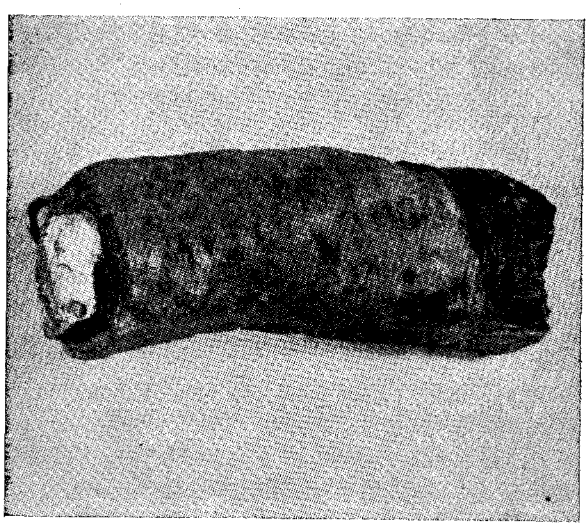

Figure 3. Used zinc anode showing heavy calcerous deposit.

Composition of Pipe Materials and Anodes—The seawater pipes were composed of 95/5 *Kunifer* alloys for all categories except those of the heat exchanger system. Pipes for heat exchanger system were of 90/10 *Kunifer*. The chemical analysis of the pipe material and zinc anodes is given in Table 3.

Table 3. Results of chemical analysis

Pipes	Elements %			
	Copper	Nickel	Iron	Manganese
No. 1	91.7	6.5	1.13	0.57
No. 2	92.2	6.2	1.06	0.50
Specified Limits (B. S. 2871-CN 101)	Remainder	5.0-6.0	1.05-1.35	0.3-0.8

Zinc anodes	Elements (parts per million)				
	Aluminium	Cadmium	Copper	Iron	Tin
Plug type anodes	Nil	Nil	500.0	500	300
Ring type anodes	Nil	Nil	34	56	Nil

3. Laboratory Study

The laboratory experiments were conducted to ascertain the electrochemical parameters affecting the corrosion of *Kunifer* alloy. The major parameters are the steady state potential under various seawater conditions and galvanostatic polarisation under static and dynamic conditions. The relevant parameters for galvanic anodes for cathodic protection are the driving potential, current efficiency and the consumption rate.

The steady state potentials for *Kunifer* and other copper base alloys normally used for valves and pipe fittings had been determined in clean unpolluted seawater and polluted seawater. Seawater in the harbour basins gets contaminated by sulphide produced by sulphate reducing bacteria. The polluted seawater medium was produced in the laboratory by innoculating the culture of sulphate reducing bacteria. Variation of steady state potentials with time are given in Fig. 4. The potential/time behaviour determined at 45°C is given in Fig. 5.

The polarisation of *Kunifer-5* specimens was studied using a rotating disc apparatus. Rectangular specimens (degreased and polished) 1 cm^2 in area were mounted on the circumferential area of a disc which was rotated in seawater medium. The rotational speed of the disc was 1000 rpm (equivalent linear velocity = 5.8 m/sec). The specimens were polarised by external current source up to -1410 mV versus saturated calomel electrode (SCE). The unpolarised specimens were also subjected to this dynamic test at the same rotational velocity. Results of this test are given in Table 4.

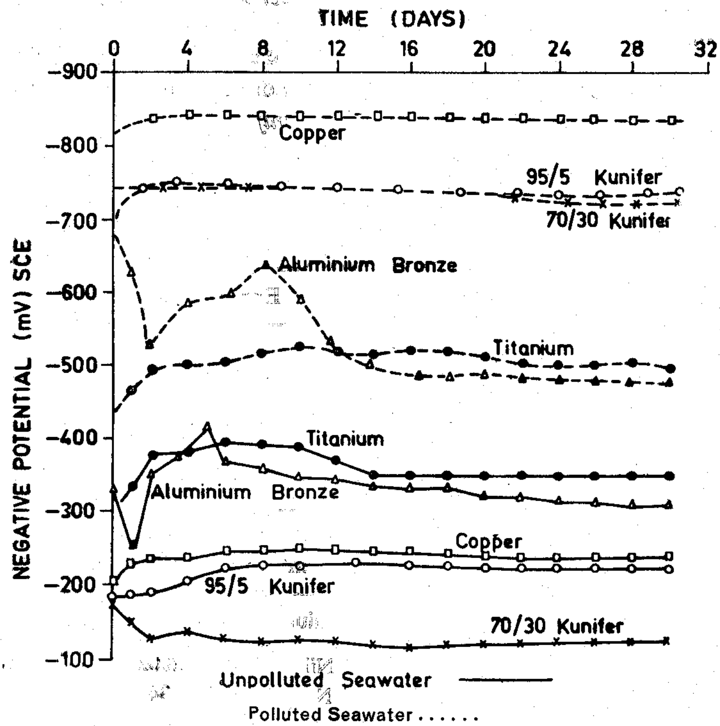

Figure 4. Potential/time decay behaviour of various copper alloys exposed to unpolluted and polluted seawater.

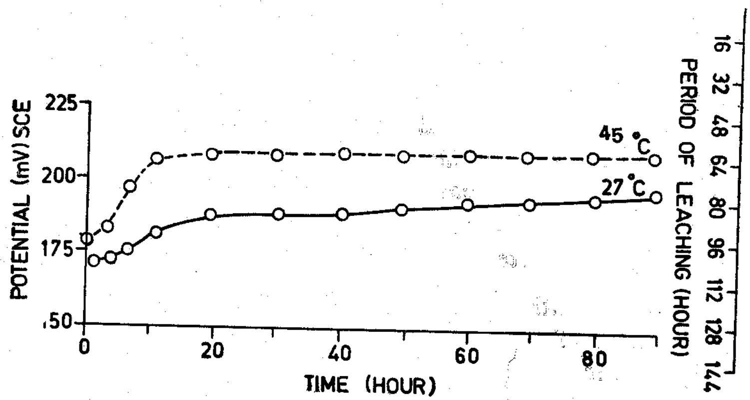

Figure 5. Potential time decay behaviour of *Kunifer-5* alloy in seawater at 27°C & 45°C.

Table 4. Cathodic polarisation data of *Kunifer-5* at 27°C and 1000 rpm in seawater (equivalent linear velocity = 5.8 m/sec)

Current density (mA/sq dm)	Potential *v*. SCE (− mV)
0	190
0.05	370
0.1	500
0.2	690
0.3	1200
0.4	1410

The specimen which was subjected to this dynamic test without application of external current was observed to develop fine pits (Fig. 6). Effird's[3] work on potential/*pH* diagram of 90/10 *Kunifer* shows that its immunity potential lies around —700 mV SCE. In the present laboratory experiment the *Kunjfer-5* specimen was held at —700 mV under intermittent dynamic condition for several days by application of current-density of 0.2 to 0.3 mA/sq dm. This specimen was found to be completely immune to corrosion.

In order to find out the distribution of potential along the length of the pipe, the potential was measured along the length of a 2-meter pipe polarised by external current source. The potential variations along the length of the tube and with time are shown in Fig. 7. The potential decreased linearly with distance and became uniform after about 5 days.

Figure 6. *Kunifer-5* specimen subjected to rotating disc test without application of external current.

Efficacy of Anode Materials for Cathodic Protection—The zinc anodes earlier used for protection, were found to be inefficient in providing the required amount of current. The anode properties viz. the current efficiency, driving potential against *Kunifer* as well as consumption rate were determined under stagnent conditions for the existing zinc anodes and aluminium anodes developed at Naval Chemical and Metallurgical Laboratory, Bombay. The current efficiency, driving potential and consumption rate were 57 per cent, 150 mV and 6.04 kgm/mA year respectively of zinc anodes as against 70 per cent, 230 mV and 4.46 kgm/mA year of aluminium anodes. The zinc anodes contained undesirable impurities of iron and copper which were detrimental for its electrochemical dissolution process. In view of the encouraging results in respect of aluminium anodes, Service trial was carried out for protection of already pitted *Kunifer* pipe section (Table 5).

Examination of internal surface of pipe receiving cathodic protection revealed that pitted surface developed a thin resistant film and aluminium anodes dissolved smoothly.

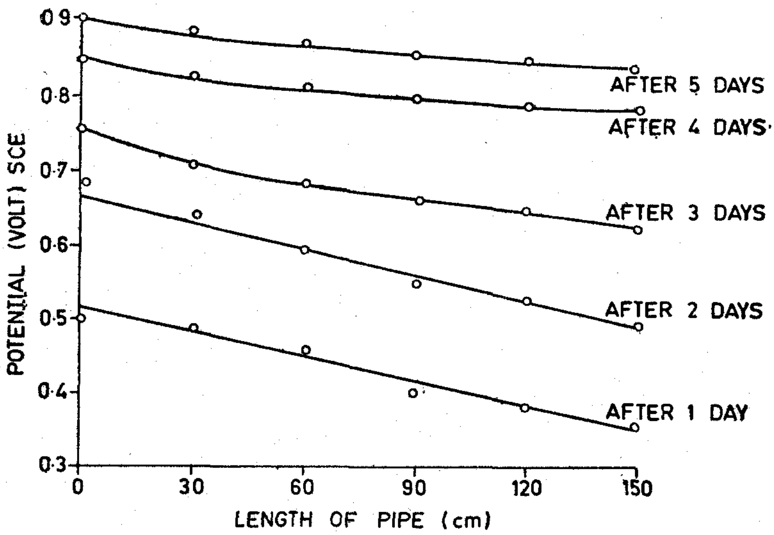

Figure 7. Variation of potential along the length of cathodically protected tube in stagnant seawater.

Table 5. Service trial data of aluminium alloy anodes (period 28 days)

Dia. of anode (mm)	Average pressure of seawater (kgm/sq cm)	Internal dia. of *Kunifer* tube (mm)	Temp. (°C)	Consumption of the anode during trial period (%)
30	7	150	26	18
32	7	150	26	15
32	7	150	26	15
30	7	150	26	18

4. Discussion

The cause for corrosion of *Kunifer-5* alloys as indicated by field observations, could be attributed to the severity of erosion in the wake of high velocity and turbulence coupled with aggressive attack of sulphide pollutants. Seawater velocities in pipe sections having different diameters under the identical volumetric flow rate, were liable to change and could exceed the design limit of 2 m/s in sections of smaller diameter. The velocity and consequent turbulence could reach alarming proportions at unavoidable bends and protrusions produced by brazed and misaligned flanged joints.

The elongated pattern of corrosion pits (Fig. 2) indicate conjoint attack of corrosion/erosion to which the *Kunifer-5* alloys are susceptible at velocities exceeding 2 m/s. Evidence of sulphide corrosion products deposited at pits (Fig. 3) and presence of sulphide pollutants in seawater at berthing place led us to believe that sulphide attack was also a contributory factor in accelerating pitting corrosion process. The propagation of pitting corrosion process proceeds without any interruption because of inadequate protection afforded by zinc anodes. Zinc anodes were found to contain deleterious elements in large proportions which made them inactive in Service condition.

Susceptibility of *Kunifer-5* alloys to corrosion/erosion attack at velocities exceeding 2 m/s is an established fact and does not need further elaboration. The existing problem was to control the pitting process by obtaining the immunity potential of the alloy. The immunity or protective potential value in respect of *Kunifer-5* alloys has not been determined in dynamic seawater medium so far. This value is more negative to the steady potential in respect of other alloys in a given environment. The steady state potential which is related to the structure of metal/electrolyte interface could be interpreted in terms of modification of surface state of the alloy. *Kunifer-5* alloy in seawater at 27°C and 45°C exhibited different steady state potentials. This difference was found to decrease with lapse of time. The negligible potential difference at the end of the experiment indicated that the surface films at these temperatures did not undergo any modification. Under polluted condition of seawater, *Kunifer-5* alloys as well as other copper base alloys exhibited less noble potentials (Fig. 4). The potential shift noted in the less noble direction could be attributed either to the incorporation of sulphide ions in the oxide scale or to the formation of mixed oxide and sulphide films. Such heterogeneity in the surface film produced regions of potentials differing by about 500 to 550 mV where film damage and consequent pit initiation was possible. The potential difference of 500 to 550 mV was large enough to drive the reactions of concentration and galvanic microcells that might be formed in the crevices and on the bared areas.

The corrosion reactions could be brought under control by polarising the corroding metal to protective potential. At this potential the protected alloy exhibits only cathodic reactions and anodic reactions are suppressed. Effird's[3] work on potential/*pH* diagram for *Kunifer-10* suggested that immunity potential for *Kunifer-5* may also be in the zone of —700 mV SCE. Cathodically unpolorised or unprotected *Kunifer-5* alloy under high velocity laboratory conditions was found to undergo pitting process. *Kunifer-5* alloy was polarisable by small amount of current densities under dynamic conditions. It was inferred from the polarisation data that 0.2 mA/sq dm cathodic current density was sufficient to protect the alloy and that the immunity potential lay between —600 and —700 mV SCE.

Aluminium alloy anodes developed at NCML were found to possess appreciable (70 per cent) current efficiency for protection of *Kunifer-5* pipes. Their electrochemical properties when coupled with *Kunifer* alloys were superior to zinc anodes earlier used. Polarisation data in Fig. 7 indicated that the potentials fall off linearly along the length. Taking this into consideration the aluminium anodes of proper size were installed at different lengths during the service trial. On the basis of 70 per cent anode efficiency, the cathodic protection system (Fig. 8) was so designed that the current density of 20 mA/sq m, to a rough approximation, could be distributed to pipes. The development of an adherent film over the pitted surface indicated that the aluminium anodes provided additional protection by inhibition mechanism. The cathodic currents from zinc anodes might interfere in the formation of this protective film.

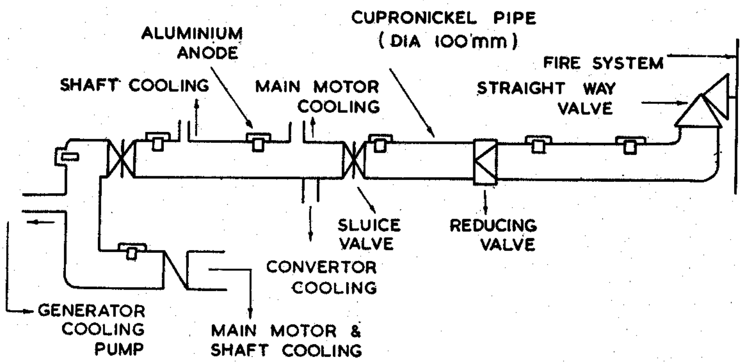

Figure 8. A schematic view of a small *Kunifer-5* pipe section fitted with aluminium alloy anodes.

The application of cathodic protection by means of proper design and distribution of aluminium alloy anodes, has been affording protection to *Kunifer-5* systems. At present, the dissolution of aluminium anodes, as periodically observed, has been taken as a criterion for effective protection.

5. Conclusion

Kunifer-5 alloys are susceptible to high velocity turbulent attack of seawater at bends and protrusions.

The corrosion of *Kunifer-5* alloys can be effectively controlled by cathodic protection using aluminium anodes.

Aluminium alloy anodes, unlike zinc anodes, do not form calcerous deposit and help towards the inhibition of the pitting process of *Kunifer* alloys in seawater.

References

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2. Ijsseling, F. P., *Corrosion Science*, **14** (1974), 97.
3. Effird, K. D., *Corrosion*, **31** (1975), 77.