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Performance evaluation of Cu-Ni 90/10 alloyed structures exposed to various Seawater Compositions and their Remaining Service Life Estimation

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Abstract

The Cu-Ni 90/10 alloy is extensively used in seawater applications mainly because of its excellent heat transferability, resistance toward corrosion and marine fouling. The corrosion resistance of Cu-Ni 90/10 has been found to be far superior in open natural seawater, however, several premature failures have often been reported during their exposure in the pollutant-rich seawater typically found near harbours, jetties and coastlines. This paper investigates the corrosion behaviour of Cu-Ni 90/10 alloyed coupons exposed to natural seawater, and pollutant-rich harbour seawater in a submerged position. Moreover, this research also investigates the corrosion mechanism on marine heat exchanger tubes of material that failed prematurely while operating in similar seawater compositions. The field experimental results for short-term corrosion results from coupons, and the long-term corrosion results from heat exchanger tubes have been evaluated, to formulate a relationship and corrosion modelling.

Keywords: Cu-Ni 90/10 alloy; seawater compositions; natural seawater; polluted seawater; marine heat exchanger

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1. Introduction

In various offshore applications including shipping structures/equipment, cupronickel alloys (e.g., Cu-Ni 90/10) are used extensively for seawater piping, claddings on ships, and tubing in seawater-cooled heat exchangers, as well as desalination plants [1,2]. Their selection for marine utilities is mainly because of excellent heat transferability as well as superior resistance towards uniform/ localised corrosion and biofoulings particularly when exposed to natural seawaters [2–4]. Reviewed literature states that the corrosion reaction on Cu-Ni 90/10 alloys is highly dependent on the presence of chemical species and compounds in seawater, particularly the presence of sulphur-containing compounds, nutrients, and other detrimental compounds [5,6]. The water flow velocity, debris and large particulate-size silicon compounds in the surrounding medium may also damage the protective passivating films on Cu-Ni 90/10 alloyed metallic surfaces and may cause erosion-corrosion [7–9].

Contrary to the steels, the seawater temperature has not been considered influential corrosion accelerating factor in Cu-Ni based alloys [2,6,10]. Reviewed literature reveals that the corrosion rates in the Cu-Ni alloys rather tend to decrease with the rise in seawater temperatures beyond 27-30^{O}C, probably because of the rapid development of a stable and protective corrosion layer at higher seawater temperatures [11,12]. This protective film formation may take place within days at water temperatures around 27^{O}C [8]. Melchers [2] has reported that the Cu-Ni 90/10 alloy exhibits a higher level of longer-term corrosion when immersion seawater temperature ranges between 18^{O}C – 28^{O}C than at temperatures below and above this range. The formation of the protective surface layer and drop-off in instantaneous corrosion rates typically start with a delay at lower seawater temperatures, where the formation of a mature film may take up to 2 - 3 months, whereas at higher temperatures it may form with early few hours of exposure [2,13].

In unpolluted seawater exposures, the corrosion rates in copper and its alloys tend to reduce with an increase in the duration of immersion. The corrosion resistance of Cu-Ni alloys is thought to be associated with the protective capability of the corrosion product layers which are mainly comprised of copper oxides, nickel oxides, and iron oxides as minor constituents [2,12]. The presence of nickel or iron in the copper compound lattice has also been found to decrease its defect number and hence increase the passivating power of the corrosion layer. Some researchers disagreed with the concept of the insignificance of seawater temperature on the corrosion of Cu-Ni 90/10 alloy. In counterargument, some research studies have been reported showing an increase in the corrosion losses of Cu-Ni 90/10 alloys exposed to seawater temperatures between 20^{O}C and 80^{O}C [2,13–15].

In addition to the natural climatic factors, reviewed literature state that corrosion in Cu-Ni alloyed structures accelerates significantly with the additions of pollutant compounds such as sulphur containing compounds, and dissolved inorganic nitrogenous (DINs) compounds including nitrates, ammonia, etc. [2,5,6,16]. Typically, these detrimental compounds are added in the form of untreated domestic, agricultural, and industrial wastes, including those from offshore installations and transportation. These pollutants usually contain various harmful compounds which may accelerate the localized form of corrosion in Cu-Ni 90/10 alloys[5,17,18].

This paper investigates the corrosion behaviour of a Cu-Ni 90/10 alloy exposed to open natural seawater and pollutant-rich seawater (near coastal regions) in the Arabian Sea, by exposing experimental coupons for a short period of up to 60 days. In addition, prematurely failed Cu-Ni 90/10 tubes of a marine heat exchanger (of 1 mm thickness) that mostly operated in similar seawater compositions (of Arabian Sea in the Indian Ocean) were investigated for failure, and corrosion losses/maximum corrosion depths.

2. Experimental Procedure

In this paper, the uniform corrosion rates and losses on Cu-Ni 90/10 coupons were calculated after their exposure in the open natural seawater and polluted seawater sites off the eastern coast of Karachi-Pakistan (Arabian Sea). The standard average corrosion equations [19,20] were used to determine average corrosion rates/losses on coupons.

$$\text{CR } (\textit{mm/yr.}) = 87.6 \times (\text{W/DAT}) \quad (1)$$

$$\text{CL } (\textit{mm}) = \text{W/DA} \quad (2)$$

Where CR = corrosion rate and CL = corrosion loss; W = weight/mass loss in milligrams; D = metal density in grams/cm^3; A= area of a sample in cm^2; T= exposure time in hours

The metal surface was cleaned and prepared according to the ASTM standard [20]. The specimens at both locations were fully submerged in a shallow submerged zone throughout the experiment and all tide conditions. In case of leakage/failure of Cu-Ni 90/10 alloyed tubes, localized thickness losses were calculated using a dimensional metrology technique coupled with an optical microscope [21]. In this paper, localized thickness damage both on the waterside and refrigerant side of a failed tube of the heat exchanger has been calculated. During its service life cycle, the heat exchanger tubes were exposed to natural seawaters for the first few years, thereafter, they were frequently operated in the pollutant-rich seawater conditions of the Arabian Sea; until failure after 10 years of active service life.

The seawater samples from both site locations were frequently tested during the entire period of experimentation to acquire various physical, and chemical constituents, as shown in Table 1.

Table 1 Seawater specifications of experimental sites [22]

Parameters	Natural seawater	Polluted seawater
Avg. Temperature (^{O}C)	25-30	25-30
pH	7.5-8.2	6 – 6.9
DO (mg/l)	>3.5	0.63 ±0.39
EC (mS/m)	50	63 ± 4.8
Nitrates (mg/l)	<0.1	1.2 ± 0.3
Chloride (mg/l)	19,300 ± 500	23,000 ± 500
Sulphate (ppm)	1900	2922
Calcium (ppm)	106	68

The weight measurement of all specimens was carried out using an analytical weighing scale with an accuracy of micrograms. Coupons of Cu-Ni 90/10 alloy were recovered from either seawater site after every 15 days up to a maximum of 60 days. The specimens were chemically cleaned as per ASTM standards G1−03 for the removal of corrosion products/deposits; prior to corrosion loss measurements [22].

Corrosion experiments are sensitive to environmental variations; therefore, several uncertainties are associated with the entire process. Hence, in order to minimize variations in the climatic conditions, coupons exposed to seawater on either site were placed in very close proximity, and at the same depths (2 m). The seawater temperature variations at both sites were assumed to be the same during the entire experimental period. Moreover, homogeneity of seawater composition is assumed in each experimental site because of natural currents, tides and agitation. Table 2 shows the material compositions of coupons and tube.

Table 2 Elemental compositions (wt. %) of Cu-Ni alloyed coupons/tubes evaluated using EDS technique

Alloys	Cu	Ni	Fe	Mn	Al	Zn
Cu-Ni 90/10	R	12.3	1.5	0.94	-	0.3

3. Results and Discussion

The total uniform corrosion loss, corrosion rate and percent (%) mass loss on either side of Cu-Ni 90/10 coupons were calculated using standard weight loss method (using equations 1 and 2), as shown in Fig. 1, Fig. 2 and Fig. 3.

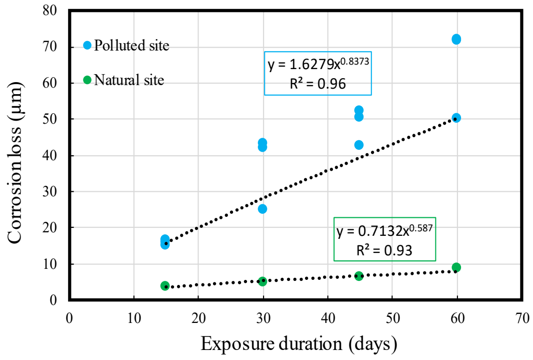

Fig. 1 Corrosion losses calculated on Cu-Ni 90/10 coupons exposed the polluted and natural seawater sites. trends lines have been added using power law model

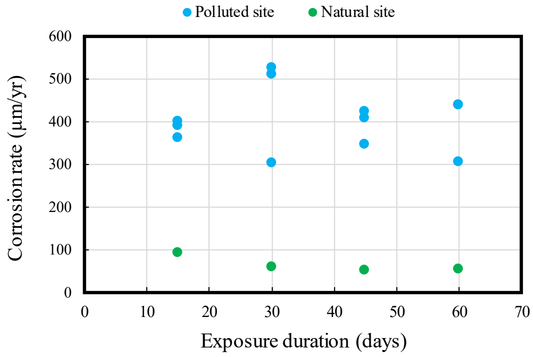

Fig. 2 Corrosion rates calculated on Cu-Ni 90/10 coupons exposed the polluted and natural seawater sites

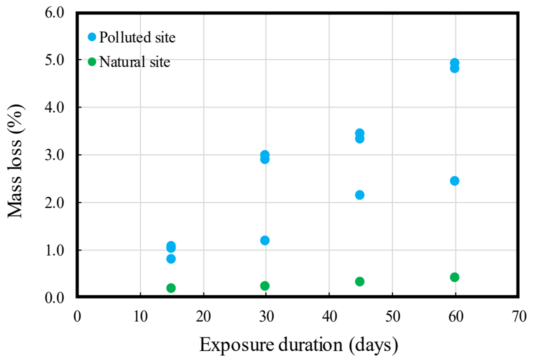

Fig. 3 Percent (%) mass loss calculated on Cu-Ni 90/10 alloyed coupons exposed the polluted and natural seawater sites

Uniform corrosion test results during these short-term exposures (Fig. 1, Fig. 2 and Fig. 3) show that the corrosion processes have taken place at an extremely high rate in the polluted seawaters rich in nitrates and sulphates, in addition to low pH levels, and lower dissolved oxygen content (Table 1). On the other hand, corrosion rates/losses on coupons exposed to natural seawater conditions were quite nominal and were found almost similar to that previously reported in research papers [6,18]. Using the corrosion trend of the power law model in Fig. 1, a corrosion loss prediction modelling for a duration of a maximum of up to 1000 exposure days has been formulated, and shown in Fig 4.

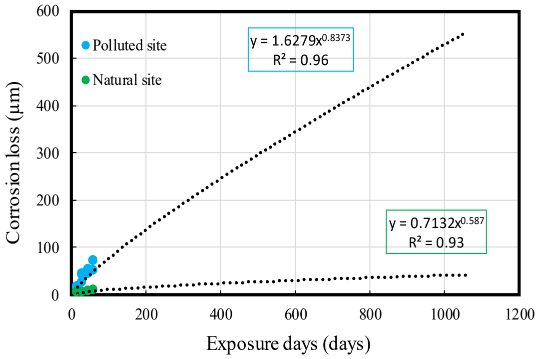

Fig 4 Predicted corrosion loss trend for a duration of up to a maximum of 1000 days

The predicted corrosion trend in Fig 4 shows that the uniform corrosion losses on coupons (both exposed sites) may reach as high as 500 µm within a span of just 1000 days. On the other hand, predicted corrosion losses in natural seawater were found to be very nominal (50 µm) in this duration of 1000 days. Similar corrosion trends with typical corrosion loss patterns were observed in research studies conducted previously.

Additionally, in this research, a marine heat exchanger having Cu-Ni 90/10 tubes was investigated for premature failure of tubes after operation of around 10 years mainly in a polluted seawater site. The tubes were extracted from the heat exchanger and several tube sections were examined under optical microscope; integrated with image analyser for measurement of corrosion depths using dimensional metrology approach. Fig. 5 shows the images of heat exchanger tube-sections possibly corroded from both seawater and dry refrigerant passageways.

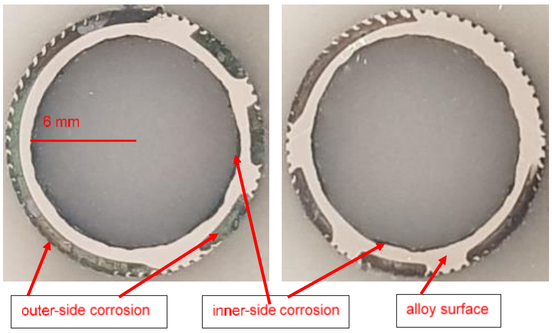

Fig. 5 Prepared cross-sections of the Cu-Ni 90/10 tubes exposed mostly in the polluted Arabian seawater (for an exposure period of around 10 years)

The cumulative probability (%) of corrosion damage depths on heat exchanger tubes (of 1 mm pre-corrosion thicknesses) is shown in Fig. 6.

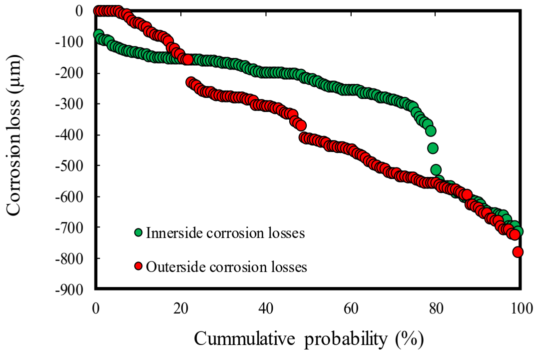

Fig. 6 Cumulative probability (%) of corrosion losses calculated with the DM-image analyzer technique on the inner side and outer side of heat exchanger tubes (Cu-Ni 90/10)

Again, these corrosion depths on the heat exchanger tube (in Fig. 6) were resulted in polluted seawater exposures, which subsequently lead to the failure of the tube (1 mm thick). These corrosion losses (Fig. 6) are significantly higher for Cu-Ni 90/10 material, in which annual average corrosion losses of around 10-50 µm/yr. have been reported in natural seawater exposures [2,5,12,23].

The corrosion losses observed in Fig. 6 are in addition to the five perforation/containment failures on heat exchanger tubes (of 1 mm thickness) indicate that the localized corrosion rate on the inner surfaces of the tubes has taken place at a rate of 100 µm/yr., which is significantly higher for Cu-Ni 90/10 material [6,8,23]. Although, the corrosion damage data (shown in Fig. 6) shows losses on the inner and outer side of the tube, however, in this study, possibility of corrosion losses on the refrigerant side (outer side of the tube) have not been assumed to be a reason for failure of the heat exchanger tube.

Comparison of uniform corrosion loss pattern observed on coupons exposed to the field corrosion tests (polluted site), and corrosion damage depths measured on failed tubes have shown many similarities. During the short-term exposure duration of up to a maximum of 60 days (Fig. 2), the total average corrosion rate (on all uncoated surfaces of coupons) of Cu-Ni 90/10 coupons has ranged between 300–500 µm/yr., which come out to be around 150–250 µm/yr. on either surface of the coupon. Cumulative corrosion depth data (Fig. 6), and maximum pit depths that lead to perforation of the heat exchanger tubes (corrosion assumed only of inner surfaces of the tube) of 1 mm thickness in a duration of approxaimately10 years. This implies that the average corrosion damage has proceeded at a rate of around 100 µm/yr. throughout the duration of 10 years. This corrosion rate (above 100 µm/yr. throughout service duration of 10 years) is extremely high for Cu-Ni 90/10 material exposed to seawater exposure conditions.

4. Conclusions

- This corrosion research showed that the rate of corrosion process in Cu-Ni 90/10 based coupons and heat exchangers and their estimated service life can be significantly influenced by variation in the chemical compositions of surrounding seawater medium.
- After a short-term exposure duration of up to a maximum of 60 days, approximately 3-4 times higher corrosion losses were observed on coupons surfaces exposed in pollutant-rich seawater site, than those on coupons exposed to natural seawater.
- The large presence of corrosion influencing chemical compounds in the harbor seawaters, in the form of dissolved nitrogenous compounds (nitrates), sulphur-containing compounds, as well as lower values of pH and DO because of added pollutants have possibly contributed towards accelerated corrosion rate/losses of Cu-Ni 90/10 coupons and tubes exposed to polluted seawater site. Whereas very nominal uniform corrosion losses/rates were observed on coupons exposed in natural seawater exposure conditions.
- Cumulative probability (%) of corrosion depth data measured on heat exchanger tube sections using dimension metrology approach have shown that the corrosion depths of up to a maximum of 700 µm were detected on the surfaces of tubes (carrying seawater) after 10 years of operation in polluted seawater site located in the Arabian Sea. These corrosion depths were in addition to the several tube perforations that led to the failure of heat exchanger.
- Corrosion losses/rates calculated on coupons exposed in polluted seawater were used to formulate a corrosion loss prediction model for an exposure duration of 1000 days, and loss results were compared with those observed on heat exchanger tubes after exposure duration of 10 years. Both corrosion loss data calculated on coupons and tubes in polluted seawater were considerably higher than those resulted in the coupons exposed in the natural seawater site.
- Hence, the observed corrosion loss data shows that the Cu-Ni 90/10 alloyed marine heat exchangers exposed directly in these polluted seawaters (without any water treatment or protective coatings) may not last till completion of the expected service life of up to 20 years.
- Extended part of this research in future works may include characterization of corrosion

products/deposits accumulated on coupons/tubes of Cu-Ni 90/10 alloy, exposed to the different seawater compositions and further experimental work for extended duration.

5. Contribution

Syed Ali Sarfraz conducted the experiments, Muntazir Abbas conducted dimensional metrology of tube samples and prepared initial paper draft, Shoaib carried out corrections, corrosion modelling and revision in the paper structure, whereas Farhan reviewed the paper.

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