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Effect of South China Sea Water on Corrosion Behaviour of Copper Alloy and Mild Steel

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Abstract: The oxidation behaviour of copper alloy and mild steel were investigated in South China Seawater at temperatures around 50° C for a period of 10 h. A procedure was applied to measure the pH of the seawater at elevated temperature. The susceptibility to heavy internal oxidation increases with increasing time. A mechanism involving chloride and oxygen dissolution in the alloy matrix as well as internal oxidation, exhibits mass gains throughout the experiment. Immersed in South China Seawater, the alloy of incomplete recrytallisation showed thick, loose and porous films, of which the inner layer was metallic oxides/chlorides and the outer layer contained a great amount of seawater species, and of which the underlying substrate was found with severe inter-granular corrosion.

Overall, the South China Seawater species have a deleterious effect on the surface of the alloy and rapid degradation is noted. The scale morphologies were determined by Optical and Scanning Electron Microscopic techniques.

Key words: Metallic oxides, seawater, copper alloy, scale morphologies.

Introduction

The quality of near-shore waters in terms of physicochemical properties exhibits considerable variations depending upon the regional environmental conditions and human activities. The South China Seawater with varying degrees of pollution are regarded as a gradually increasing aggressiveness in the environment, aggravated by increase in flow rates and changes in the temperature and oxygen content of the water. A recent assessment of the quality of coastal water in southern part of Peninsular Malaysia has been reported (Yap et al., 2011). The effect of monsoon (Satpathy et al., 2011), wind direction (Kok et al., 2015) and location (coastal or offshore) (Akhir et al., 2014) on quality of water are demonstrated. Relatively high salinity values were observed during summer compared to pre and post monsoon periods (Satpathy et al., 2011). The salinity of South China Sea increases during northeast monsoonal wind, while it decreases during southwestern monsoonal wind due to cooler and warmer water respectively (Kok et al., 2015). Another study shows high temperature and low salinity near coastal areas as compared to offshore areas (Akhir et al., 2014).

Due to their good corrosion resistance, copper and copper alloys are used extensively in high-quality marine and industrial piping systems and also in marine, urban and industrial environments (Melchers, 2015). Also, mild steel and copper alloys are used in water treatment units, condensers, and heat exchangers, where fresh or salt water is used for cooling. Copper

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alloys resist many saline solutions, alkaline solutions, and organic chemicals. Also copper alloys have exhibited antimicrobial properties (Santo et al., 2011; Grassat et al., 2011; Sudha et al., 2012). However, copper is susceptible to more rapid attack in oxidizing acids, oxidizing heavy-metal salts, sulphur, ammonia (NH_3), and some sulphur and NH_3 compounds. Many components in valves, pumps, machineries as well as pipes and pipe fittings, are made from copper alloy or mild steel. Apart from the wide use of copper alloys or mild steel immersed in seawater, they are also used in industrial chemical and power generating plants, and buried in the earth for water distribution systems.

An extensive research related to marine corrosion was made over the last two decades to investigate the flow dependent corrosion behaviours of several tubing materials used in the manufacturing of heat exchangers for seawater applications which caused failures of the tubing materials (Al-Hashem et al., 1996; Macdonald et al., 1979; Badawy et al., 1999). Seawater contains dissolved air that enables some corrosion. The adsorption process depends on the electronic characteristic of the molecules (adsorbates), the chemical composition of the seawater, nature of the metal surface, temperature of the reaction and on the electrochemical potential at the metal-seawater interface (Gouda et al., 1988; Trabanell and Mansfeld, 1987; Laque, 1975; Amin et al., 2002). The influence of chloride salts, separately or in combination with transition metal sulphates, have been studied but not in so much detail (Amin, 1997; Malik, 1984; Amin and Ahmad, 1995). Several studies have been reported on corrosion of Cu-Ni alloys in seawater but limited results are reported on Cu-Zn alloys and mild steels. Marine corrosion has been investigated but most of the experiments are carried out in simulated seawater (Wang et al., 2012).

The aim of the present work was:

1. To analyze the quality of coastal waters of the South China Sea (SCS) at a few coastal locations of Peninsula Malaysia, which are used for human activities, and
2. To investigate the effect of the quality of water on the nature of corrosive deposits on the surface of the two alloys, Copper Alloy and Mild Steel (MS-1008) being the most common engineering materials used for the marine structures such as bridges, harbours, and wharfs.

Materials and Methods

On-shore Sampling Locations

The polluted South China Seawater in the tests was collected from three different locations of Pahang, Terengganu and Kelantan (Figure 1). The samples were analyzed for different parameters to ascertain the quality of seawater at the sea coasts of the Malaysian peninsula. The result is reported in Table 1.

Figure 1: Sampling sites for coastal water of Peninsular Malaysia.

Table 1: Characterization of South China Sea water at different coasts of Malaysia (N = 10)

Sampling points (on shore)/Variables	*Pahang Mean ± SD (range)*	*Terengganu Mean ± SD (range)*	*Kelantan Mean ± SD (range)*
Temperature (°C)	27.8±1.9 (25.0-29.0)	26.3±1.2 (25.0-29.0)	27.6±1.4 (26.0-29.9)
pH	7.55±0.07 (7.5-7.6)	7.2±0.08 (7.1-7.4)	7.4±0.10 (7.3-7.6)
Conductivity (µS/cm)	74.2×10^3	62.6×10^3	68.2×10^3
Turbidity (NTU)	0.66±0.2	0.56±0.2	0.56±0.2
Salinity (mg/l)	33.3±1.2 (33.0-33.6)	32.8±0.6 (32.0-33.4)	32.9±0.6 (32.0-33.6)
TDS (mg/l)	68.6	58.4	56.8
Hardness (TCH, mg/l)	609±45	474±32	532±39
DO (mg/l)	6.0	6.9	7.2
DOC (mg/l)	1.8-4.6	1.8-4.6	1.8-4.6
Ionic strength (µg/l)	Fe^{2+} $(0.97\pm0.15) \times 10^2$ Cu^{2+} (1.1±0.15), Zn^{2+} (0.4±0.15) Mn^{2+} (ND) SO_4^{2-} (16.8×10^6) Cl^- (2.6×10^6)	Fe^{2+} $(0.97\pm0.15) \times 10^2$ Cu^{2+} (1.1±0.15), Zn^{2+} (0.4±0.15) Mn^{2+} (ND) SO_4^{2-} (16.8×10^6) Cl^- (2.6×10^6)	Fe^{2+} $(0.97\pm0.15) \times 10^2$ Cu^{2+} (1.1±0.15), Zn^{2+} (0.4±0.15) Mn^{2+} (ND) SO_4^{2-} (16.8×10^6) Cl^- (2.6×10^6)

TCH = Total carbonate hardness; TDS = Total dissolved solids; DO = Dissolved Oxygen; DOC = Dissolved organic concentration

Instruments Used

The conductivity, pH and turbidity were measured with a conductivity meter (Orion, USA). The pH of the polluted seawater was monitored before the experiment and during the experiment. The concentration of each ion was analyzed by using an ion chromatographic analyzer (Dionex ICS-3000, USA). The organic matter concentration of each sample was analyzed in terms of dissolved organic concentration (DOC) by using a TOC-5000A analyzer (Shimadzu, Japan).

Alloy Samples Used

The present study has been carried out using C-2100 and MS-1008 alloys in plate which were obtained from Steel Co., Sweden. The composition of the alloys is reported in Table 2 (Alloy Guide, 2016; Olesen, 2000).

Corrosion Studies

The coupons of 2.0 × 1.5 × 0.2 cm were cut from the plate and wet-abraded on successive grades of 180, 320 and 500 SiC paper until a smooth surface was obtained. This was followed by washing with distilled water, degreasing by methanol and drying. Weighed test coupons were totally immersed in each of the samples of seawater, contained in 200 ml-beakers separately, and put into an oven which was maintained at 50°C. The mass change was recorded at 2 h intervals throughout the 10 h period of the study.

The investigation was based upon oxidation kinetics and morphologies of scale, and was characterized by Optical and Scanning Electron Microscopy techniques. The mounted coupons were abraded and polished by means of SiC paper and diamond pastes of various grades respectively. The seawater immersed polished coupons were subjected to gold plating in order to make the surface conducting and fill the pores for SEM examinations.

Results and Discussion

Water Quality

The physico-chemical parameters (Table 1) shows a slightly higher range (25-29°C) at Phang and Terengganue compared to Kelentan (26-29°C) but

Table 2. Typical composition of copper alloy (FCTC, 2016) and mild steel (Olesen et al., 2000)

Element (Wt.%)	*Cu*	*Zn*	*Fe*	*Mn*	*Al*	*C*	*F*	*S*	*Si*
Copper alloy (C 2100)	94-96	4-6	-	-	-	-	-	-	-
Mild steel (MS 1008)	-	-	99.633	0.244	0.031	0.05	0.015	0.013	0.014

these are regarded as lower ranges compared to the South Western Coastal Waters of Pennisular Malaysia (SWCWPM) (Yap et al., 2006) and River and Drainages Water of Peninsular Malaysia (RDWPM) (Yap et al., 2009). For all sites, the pH of the water is a little above neutral values (7.1-7.6) satisfying the Interim National Water Quality Standards (INWQS) for Malaysia (DOE, 2008). Thus, the coastal water at all places under study is suitable for bathing and water-sports activities (DOE, 2008). Salinity is an important factor which evaluates the quality of sea water needed for marine environment including the material structures. Our reported average value (33.0 mg/L) for salinity of water at all the three places is higher than the values (0.18-32.42 mg/L) reported earlier for south coastal water of Peninsular Malaysia (Yap et al., 2011) but almost the same as reported in a recent analysis on South China Sea (Akhir, 2014).

The conductivity value for water samples at three locations varies from 62.6×10^3 to 72.4×10^3 µS/cm. These are higher than the south coastal waters (368-49,452 µS/cm). Also the elevated values of conductivity is significant showing the presence of ionic components in water samples at three sites which could be attributed to the presence of different ions and reported higher TDS (56.8-68.6 mg/L) in Table 1 (Yap et al., 2011). As per Malaysian DOE scale the water quality is of class II category—for human use such as recreational but not for drinking. Higher DO values (6-7.2 mg/L), an indicator for O producing activity such as photosynthesis by aquatic plants, are reported in our study sites compared with lesser values in SWCWPM (Yap et al., 2006) and RDWPM (Yap et al., 2009).The lower turbidity values (0.56-0.66 NTU) at all the sites indicate that water does not contain clay, silt, planktons, micro-organisms, fine particles of inorganic or organic matter etc. (Yap et al., 2011).

The main corrosive ions in the South China Sea water were identified as chloride and sulphate. The co-existence of SO_2 and NaCl (NaCl + Na_2SO_3) initially increases the corrosion weight gains which show the industrial nature of coastal water (Chen et al., 2014). Industrial activity affects the surface water quality, thus resulting in low DO, and higher COD and BOD (Sujaul et al., 2013). But we find high values of DO, thus, no industrial activities in the vicinity are suggested, making seawater suitable for human use.

The results showed that the coastal zone conditions are very corrosive to cast iron, due to temperature and humidity variations as well as the high chloride and sulphate concentrations in the seawater as Saricimen et al. (2011) find similar results in the Arabian Sea waters.

Corrosion Studies

The corrosion rate of copper alloys increases with time during the initial exposure period at 50^{o}C. However, after 6 h onwards, the corrosion rate is observed to be decreasing with time in the case of different locations of seawater (Figure 2). This is due to the contamination of the seawater environment by corrosion deposits that weakened the water and reduced its chemical reactivity. This tends to stifle further increases in the amount of corrosion relative to time. It was expected that, during the time after the experimental period in this study, which is 10 h, the corrosion rate of C-2100 alloy coupons in Pahang Seawater will increase until the entire corrosion mechanism stops. Figure 3 (a, b and c) shows the photomicrographs of C-2100 alloy immersed in three places of South China Seawater at 50° C for 10 h. Pitting corrosion represents the most common form of corrosion product, particularly in solution containing chloride ions. Due to the presence of S, O and Cl, the white and yellowish green oxides of copper (possibly Cu_2O as inner, CuO as outer layer, CuCl and $Cu_2(OH)_3Cl$) (Horton et al., 2015) and oxide of zinc so formed adhere to the surface, showing porous and spalling in nature. In NaCl and Na_2S polluted environment, mixed oxides/hydroxides and Cu_2S were formed on the surface of the Cu-Zn as demonstrated in an earlier study (Awad et al., 2015). There is a correlation between the microstructure and the characteristics of the corrosion product films of copper alloy in South China Seawater. The increase of the immersion time in solution increases the thickness of corrosion films on the surface of alloy. The thickening of the corrosion film is by the diffusion of oxygen and resulting oxidation of copper and iron into metallic oxides.

The corrosion behaviour of MS-1008 in Seawater is studied, showing a significant difference between the types of seawater condition applied to the thickness of deposition on the alloys and the rate of corrosion. The weight gain in all three seawater conditions and the graphs of weight gain versus the period of immersion for 10 h is shown in Figure 4. The calcareous deposits found on the surface of MS-1008 alloy are thick, uniformly rough with bulk (Figure 5), suggesting the presence of Fe, O, S and Ca. This observation is in line with the earlier analysis by X-ray diffraction which shows presence of FeO(OH) and $CaSO_4$ as corrosion product (Sujaul et al., 2013). This type of deposition is called cathodic precipitation which increased the local pH and caused the dissolution of the Fe matrix and the initiation of pitting corrosion (MaCafferty,

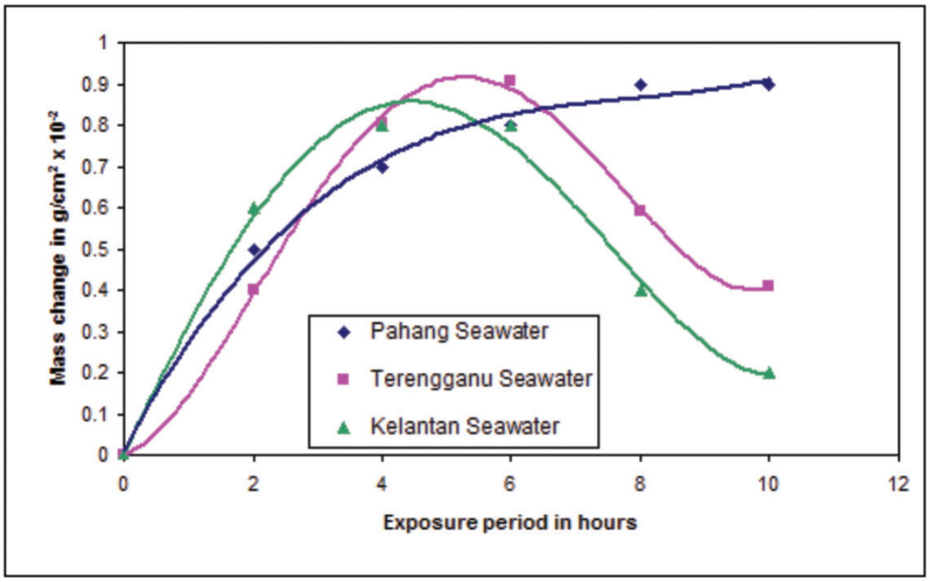
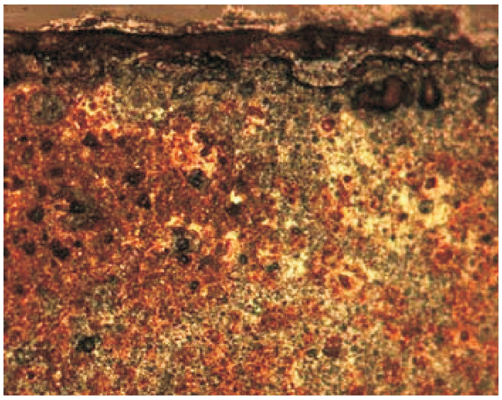
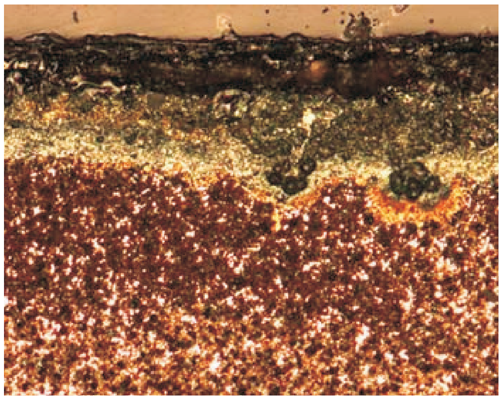


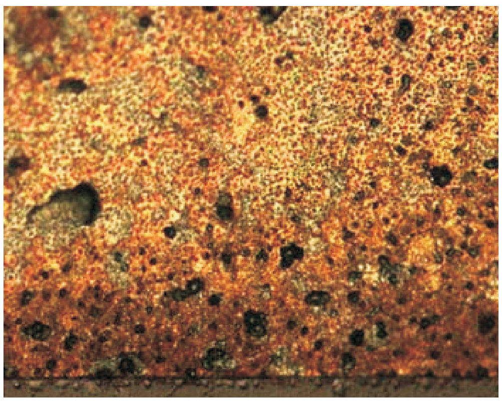
Figure 2: Variation of mass change with exposure time for C-2100 alloy immersed in Pahang, Terengganu and Kelantan Seawater at 50^o C for 10 h.



(a) Pahang



(b) Terengganu



(c) Kelantan

Figure 3 (a, b and c): Micrographs of C-2100 alloy surface immersed in Arabian Seawater at 50^o C for 10 h. (Magnification 100 X)

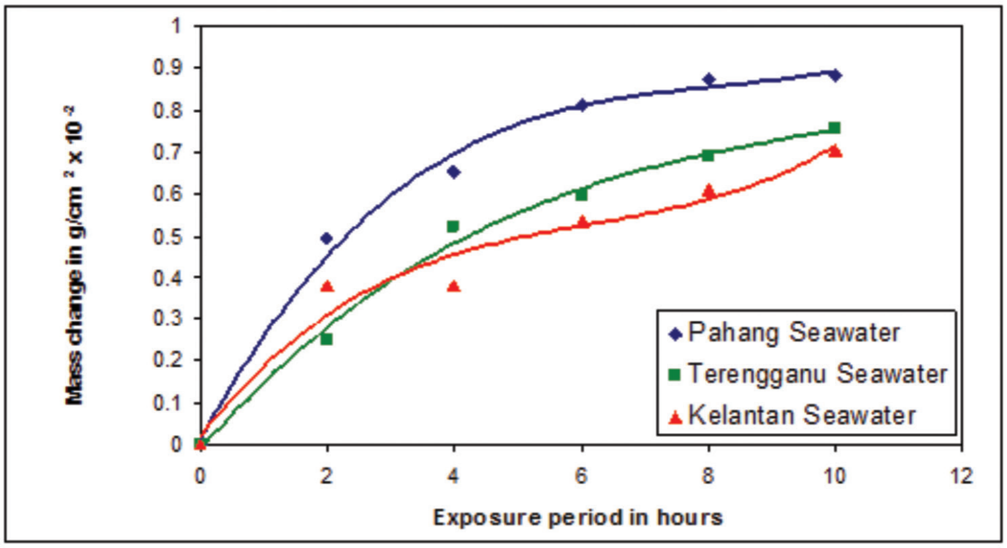
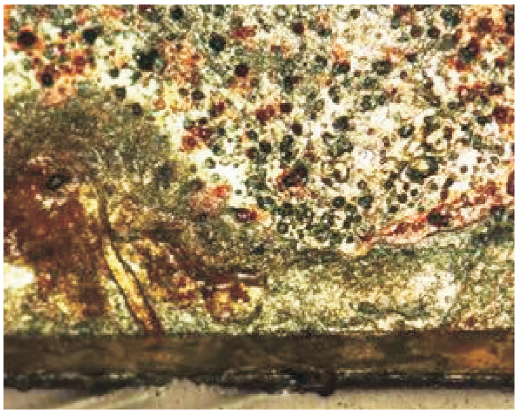
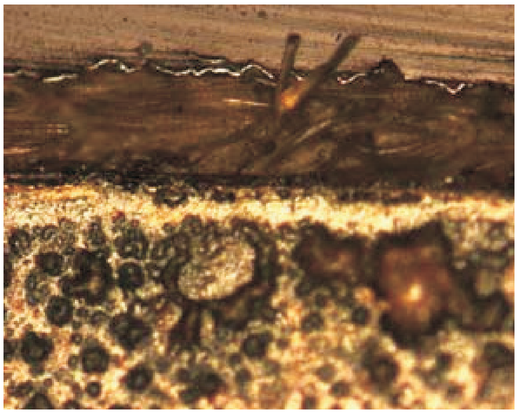


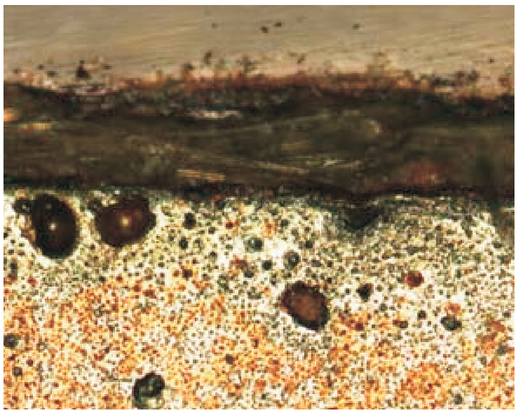
Figure 4: Variation of mass change with exposure time for MS-1008 alloy immersed in Pahang, Terengganu and Kelantan Seawater at 50^o C for 10 h.



(a) Pahang



(b) Terengganu



(c) Kelantan

Figure 5 (a, b and c): Micrographs of MS-1008 alloy surface in South China Seawater at 50° C for 10 h. (Magnification 100 X)

2003). A recent study shows the higher corrosion rate for mild steels in the presence of Na_2CO_3 solution as compared to NaCl + Na_2SO_4 (Ikechukwu et al., 2014). Thus, greater hardness value (TCH) which produces CO_3^{2-} might be affecting the corrosion rate in our studies (Table 1).

In general, the deleterious effect of seawater on the scales and rapid degradation of the alloy is noted. The corrosion rate in Pahang Seawater is higher than Terengganu and Kelantan seawater. The main factors that cause these distinct corrosion rates in those different seawater environments are salinity and the chlorination effect, as well as industrial polluted atmospheres and transition metal salts. The study proves that rates of metal corrosion correlate positively and significantly with South China Seawater. Further, extensive experimentations are planned for corrosion studies on a number of other alloys considering different factors such as time periods, effects of bio-films, salinity in seawater at different locations of the coasts of Malaysia.

Conclusion

The influence of Pahang, Terengganu and Kelantan Seawater on the corrosion of copper alloy and mild steel has been studied at 50°C for the period of 10 h. In the exposure to South China Seawater, the film deposited on the C-2100 and MS-1008 alloy coupons is thick, compact and exhibited voids and cracks due to bio-fouling and oily deposits. Corrosion of alloys in Kelantan Seawater is less than Pahang and Terengganu, exhibiting the thin, uniform and compact layer of scales. Terengganu seawater-induced corrosion is much higher, seems to be a result of industrial wastes and fluxing products. The pitting-type corrosion is commonly observed on both alloy scales.

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