

CORROSION RATE OF COPPER AND IRON IN SEAWATER BASED ON RESISTANCE MEASUREMENT

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Received: November 15, 2001 ; Accepted December 3, 2001

ABSTRACT

Copper and iron metal wire corrosion in artificial sea water have been investigated in three corrosion systems, in the (i) closed bath, (ii) opened or air exposed bath, and (iii) aerated bath. The aim of our investigation is to determine the effect of oxygen contained in the air to the metals' corrosivity. Artificial sea water was prepared by dissolving 173.59 g sodium chloride and 4.91 g potassium chloride in 7.00 kg of water at 23°C. The corrosion experiment was carried out under the constant temperature of 32°C. Decrease of metal masses during corrosion was monitored by measuring the metal resistance change. Our experiment provided the corrosion rate in $\text{g}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ as 4.01×10^{-7} (in closed bath), 4.01×10^{-6} (in opened bath) and 9.43×10^{-6} (in aerated bath) of copper metal, and 2.12×10^{-6} (in closed bath), 5.99×10^{-6} (in opened bath), and 1.07×10^{-5} (in aerated bath) of iron metal. Experimental results show that air oxygen give strong effect on the corrosion of copper and iron metal.

Key words: Corrosion rate, copper, iron, seawater, resistance measurement

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INTRODUCTION

Corrosivity of metals used as construction materials are of important consideration for marine constructions planning (Tretheway and Chamberlain, 1991). Corrosion at marine areas occurs as a consequence of metals contact with seawater (Whitfield and Jagner, 1981 and Chang, 1991) blown by the wind that will cling to the metal surfaces. Fine sprinkling of seawater containing chloride is very corrosive to the metals. The corrosion is more rapid if the metals are dipped in seawater. Metals such as copper and iron, which are important for modern man's life tend to corrode. Corrosion of the metals as a result of fine sprinkling of seawater cause permanent reduction in the metal quality, which is not only materially disadvantageous, but could

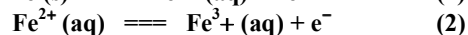
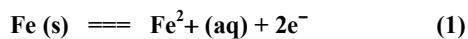
also create conditions which might cause disasters. Based on the above facts, we have conducted corrosion test of copper and iron. The corrosion experiment was carried out in aqueous medium containing primarily sodium chloride. This paper reports the results of our experiment.

The corrosion of metals can occur due to metal interaction with non-inert environment. Seawater media and oxygen-rich moist atmosphere are the non-inert environment example for iron and copper. Actually, based on standard oxidation potential data (Skoog, 1985), iron and copper can not corrode in water media only (1997). Experimental results reported by deMeo (1997) showed these facts. Iron and copper corrosion can occur as a result of oxidation in acidic media under the presence of oxygen and

carbon dioxide (Chang, 1991). In addition, copper and iron corrosion will occur at moist open atmosphere.

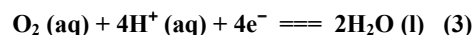
Corrosion has been studied according to various methods (Green, 1993). The simple but elegant experimental model of copper corrosion at different aqueous acetic acid systems has been demonstrated by deMeo (1997). The corrosion experiment of copper and iron was carried out in the (1) reactive system, an acidic solution system aerated by atmosphere or oxygen, (2) inert system, an acidic solution system aerated by separated nitrogen or carbondioxide, and (3) other inert system, atmosphere-aerated of water. However, he reported merely whether or not the copper corrosion take place . Therefore, de-Meo provided only limited qualitative information. The copper corrosion experiment at different situation was based only on a simple visual observation, although it reasonably represented the effort to estimate the metal corrosiveness/corrosivity. In his experiment, deMeo had not provided the corrosion rate information as quantitative explanation. In our work, iron and copper corrosion rate was measured to provide quantitative information. The aim of this research is to prove the effect of oxygen to copper and iron corrosion in seawater. Corrosion of metal specimen was carried out in (1) close system, (2) open systems exposed to the atmosphere and (3) aerated with wind flow. The corrosion rate is expressed through the change of mass per area of metal wire surface for a certain time scale and was observed by measurement of resistance changes using a digital multi- meter.

Corrosion of iron exposed to moist environment can be described with a reaction model (Chang, 1991) as follows : a part of metal surface acts as an anode and due to moist environment, oxidation reaction will occur

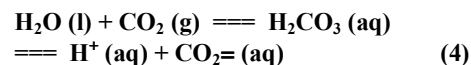


Electrons produced in oxidation (1) flow to the other surface through metal phase. On the surface, acting as a cathode, electrons reduce

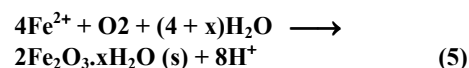
dissolved oxygen in the water with the following reaction



The H+ ion comes from carbonic acid ionization as a product of water and atmospheric carbon dioxide.



Both anodes of Fe²⁺ and Fe³⁺ migrate through aqueous phase adhering to metal surface to the part of water phase surface with the cathode surface. Fe²⁺ at that surface will be further oxidized by oxygen producing iron corrosion.



Copper corrosion is expected to follow the same process as the above with iron. Equation (3), (4) and (5) give a description that the presence of dissolved oxygen and carbon dioxide in water adhering to metal surfaces is a prerequisite for the corrosion process occurring at the metal surfaces . It is reasonable to expect, of course, that in this research, the corrosion medium was aerated in an open atmosphere instead of with oxygen from a gas tube.

Metal Mass Reduction Rate

As the effect of corrosion process, the metal weight will be reduced. The rate of mass reduction,

$$\frac{dm}{A \cdot dt}$$

is an easy measurable metal corrosivity. If the metal is a rod form of length L and diameter d, then the mass reduction can also be measured with the diameter reduction, since the metal has a resistance of R depending on its property and geometry (Barrow, 1988)

$$R = \rho_R \frac{L}{\pi d^2/4} \quad (6)$$

where ρ_R is metal resistivity. The diameter change, therefore can be measured as resistance changes. Singh and co-workers (1995) used Eqn. (6) as a starting point to estimate

the corrosion rate of copper wire by plotting the resistance changes against corrosion times. Singh et.al. define the corrosion rate v_c as the amount of metal wire specimen mass change per metal surface area per corrosion time

$$v_c = \Delta m / A t \quad (7)$$

where $\Delta m = m_0 - m_t$, t is corrosion time measured at initial corrosion through metal resistance measuring, A is surface area of the metal wire, m_0 is initial metal wire masses, and m_t metal masses measured at time t . The changes of metal wire mass relates to the changes of its diameter, with the equation of

$$\Delta m = \rho_D V_0 - V_t = \pi \rho D L (d_0^2 - d_t^2) / 4 \quad (8)$$

where ρ_D is metal density. Either equation (6) or (8) consists of variable wire diameter d . Therefore, both equations can be combined to solve equation (7).

MATERIALS AND METHOD

The experiment conducted required the seawater model, aerator pump, and digital multi-meters. Corrosion experiments was performed under 3 types of conditions, namely (1) corrosion in closed system, (2) corrosion in open atmosphere and (3) corrosion in the aerated system with the air flow rate of ± 25.0 mL per minute using aerator pump. Chemicals used are of technical aquadest, sodium chloride and potassium chloride with p.a. reagent grade as well as copper and iron wires. The corrosion cell was constructed from a 3.0 l plastic cup, thermostat, fishery aerator, self-made thermostat, battery equipped with voltage stabilizer, and digital multi-testers.

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Corroding specimen was prepared from spiral form of long wire, so that resistance changes could be monitored well, with significant changes. The resistance R was not measured directly, but through potential (E) and current (i) measuring. Measured parameter was rate of corrosion v_c estimated from slope of curve $R^{-1/2}$ versus corrosion time. Resistance, R , was measured from constant current and potential every 10 days.

The corrosion cell was filled with seawater model as corrosion media. Either tip of copper or iron wire dipped in the solution was connected to a 12-volt battery coupled with 2 multi-meters. One multi-meter was connected to the battery in serial mode and the other was connected in parallel mode.

Preparation of Corrosion Media

Seawater model was made from solutions of 173.59 g of sodium chloride anhydrous and 4.91 g of potassium chloride anhydrous soaked into 7.00 kg of aquadest at 23 $^{\circ}C$. (Whitfield & Jagner, 1981) The mixture was stirred with magnetic stirrer until both salts were dissolved completely with temperature kept constant using ice-salt water bath. The simulated sea-water was frozen in a refrigerator before being used.

Preparation of the Metals

Either copper or iron metal was in the form of a wire with a diameter of 0.2 mm, cut into 2.0 m lengths. The wires were cleaned by scraping the surface carefully with a fine abrasive paper. Then the wires were anodized for 30 minutes in nitric acid of 0.001 M with a 10 mA current. The wires were then dried using paper tissue after being cleaned with aquadest, then spirally rolled.

Experiment of Corrosion

The two new cleaned rolling wires were then dipped separately in 2.5 l of the seawater contained in plastic buckets of 3.0 l capacity.

Both tips of the wire were connected to a 12-volt battery . The current was kept constant at 50 mA. One multi-meter was connected serially and another in parallel to a current monitor for the former and a voltage meter for the latter.

The experiment was conducted for 100 days, with the time interval of current and voltage measurements of 10 days (at 4.00 pm). The recently collected data were voltages (volt) and time of corrosion since the corrosion started until the measurement conducted (days). The environmental temperature was kept constant at 32 °C using a thermostat bath while the corrosion experiment proceeded.

The experiment was carried out in the same way for iron wire, but the current was kept constant at 5.0 mA.

RESULTS AND DISCUSSION

The solution of the model equations (7) and (8) gives relationship between estimated quantity $vC = \Delta m/At$ and measured parameters directly from experiment, i.e. corrosion time and resistivity every observation of R_t

$$V_C$$

Table 1. Corrosion rate in $g.cm^{-2}.s^{-1}$

Specimen	System	-slope $\Omega^{1/2}.s^{-1}$	$vC = \Delta m/At$ ($g.cm^{-2}.s^{-1}$)
Copper	Cu _{CL}	4.30×10^{-6}	4.01×10^{-7}
	Cu _{OP}	4.30×10^{-5}	4.01×10^{-6}
	Cu _{AE}	1.01×10^{-4}	9.43×10^{-6}
Iron	Fe _{CL}	1.32×10^{-5}	2.12×10^{-6}
	Fe _{OP}	3.74×10^{-5}	5.99×10^{-6}
	Fe _{AE}	6.70×10^{-5}	1.07×10^{-5}

Table 2. Regression equation of rate of corrosion

Specimen	System	Regression Equation	r^2
Copper	Cu _{CL}	$Rt^{-1/2} = 0.0926 + 4.30 \times 10^{-6}.t$	0.7586
	Cu _{OP}	$Rt^{-1/2} = 0.0920 + 4.30 \times 10^{-5}.t$	0.9754
	Cu _{AE}	$Rt^{-1/2} = 0.0931 + 1.01 \times 10^{-4}.t$	0.9841

$$R_t^{-1/2} = R_0^{-1/2} - \frac{vC}{\rho_D(\rho_R L/\pi)^{1/2}} t \quad (9)$$

The linear curve as a plotting of $1/\sqrt{R_t}$ or $Rt^{-1/2}$ versus t gave the slope $vC/\rho_D(\rho_R L/\pi)^{1/2}$ that can be used to compute vC .

$$V_C = \{ \rho_D(\rho_R L/\pi)^{1/2} \} \times (-\text{slope}) \quad (10)$$

The value of $\rho_D(\rho_R L/\pi)^{1/2}$ for copper and iron wires of 2.0 meter in length, gave values of 9.3340×10^{-2} and 1.6026×10^{-1} , respectively, in $g.\Omega^{1/2}.cm^{-2}$.

Corrosion rate of copper and iron proceed into three ways, that are in closed and open system bath as well as aerated system as expressed in Table 1. In addition to the corrosion rate data presented in (4), Table 1 also contained negative value of the slope $vC/\rho_D(\rho_R L/\pi)^{1/2}$ (column 3) used to calculate the corrosion rate, vC . The value of the slope was found from linear regression equation shown at Table 2 column 3. Value of $\rho_D(\rho_R L/\pi)^{1/2}$ (in $g.\Omega^{1/2}.cm^{-2}$) for $L = 2$ m equals to 9.3340×10^{-2} for copper and 1.6026×10^{-1} for iron respectively.

Iron	Fe _{CL}	$Rt^{-1/2} = 0.0385 + 1.32 \times 10^{-5} \cdot t$	0.9660
	Fe _{OP}	$Rt^{-1/2} = 0.0386 + 3.74 \times 10^{-5} \cdot t$	0.9930
	Fe _{AE}	$Rt^{-1/2} = 0.0387 + 6.70 \times 10^{-5} \cdot t$	0.9879

Corrosion of Copper Specimen

The trend of $Rt^{-1/2}$ value change that described the corrosion rate of copper metal was expressed in Figure 1. It was shown that the values got higher for each of the slopes which represented the parameters of copper rate corrosion in open, closed, aerated system from 4.30×10^{-6} , 4.30×10^{-5} , and $1.01 \times 10^{-4} \Omega^{1/2} \cdot s^{-1}$. The corrosion rate of the copper specimen in the closed system, as presented in the Table 1, is $4.01 \times 10^{-7} \text{ g} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$. Experiment results expressed in Figure 1 show that the corrosion of copper specimen proceeded considerably slower without air. However, the corrosion rate of copper specimen was increased sharply to $4.01 \times 10^{-6} \text{ g} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$, or ten times that of the former whenever it proceeded in the open system, or in the free at-

mosphere. The corrosion even occurred faster when the corrosion was aerated with atmosphere air becoming $9.43 \times 10^{-6} \text{ g} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$, or 2.5 times faster than in air media only. This meant that there was more dissolved oxygen available in water when aerated system was used than in the air-exposure one.

Copper metal corrosivity of the above facts corresponded with a qualitative description demonstrated by deMeo (1997). The sharpness of corrosion rate increase in open system indicated that there was influence of oxygen in the air as described at Reaction (3). It could also be possible that carbon dioxide in the air together with oxygen gave a very high effect, as represented in Reaction (4) and (3).

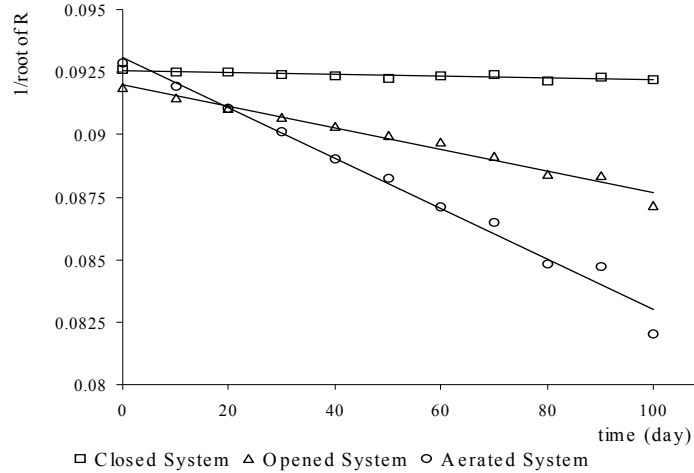


Figure 1. The $Rt^{-1/2}$ value trend of copper wire as function of time

Corrosion of Iron Specimen

The trend of $Rt^{-1/2}$ value change that described the corrosion rate of iron metal was expressed in Figure 2. As the copper specimen showed, the values got higher for each of

the slopes that represented the parameters of copper rate corrosion in open, closed, aerated system from 1.32×10^{-5} , 3.74×10^{-5} , and $6.70 \times 10^{-5} \Omega^{1/2} \cdot s^{-1}$. The values meant that the corrosion rate for iron was increased respectively. As presented in Table 1, the corrosion

of iron specimen in closed bath was $2.12 \times 10^{-6} \text{ g.cm}^{-2} \text{ s}^{-1}$. Iron corrosion proceeded faster than that of copper. But when the corrosion proceeded in the open system, in free atmosphere, the corrosion rate of iron specimen was increased sharply to $5.99 \times 10^{-6} \text{ g.cm}^{-2} \text{ s}^{-1}$, three times that of the former. The corrosion even occurred faster when the corrosion was aerated with atmospheric air changed to $1.07 \times 10^{-5} \text{ g.cm}^{-2} \text{ s}^{-1}$, and came close to two times faster than in air media. This meant that more dissolved oxygen and air is available in water when the aerated system was used compared to air-exposure only. The increase of iron corrosion, in comparison, was not so rapid as copper.

The iron metal corrosivity response was quite similar to copper, either from ex-

periment and qualitative description reported by deMeo (1997). The sharpness of the corrosion rate increase in open system indicated that there was an effect of oxygen in the air for both copper and iron. It would also be possible that carbon dioxide in the air together with oxygen provided a very high influence to iron corrosion. The slowness of the corrosion of the copper specimen, relative to iron, was probably due to the lower oxidation potential of copper compared to iron.

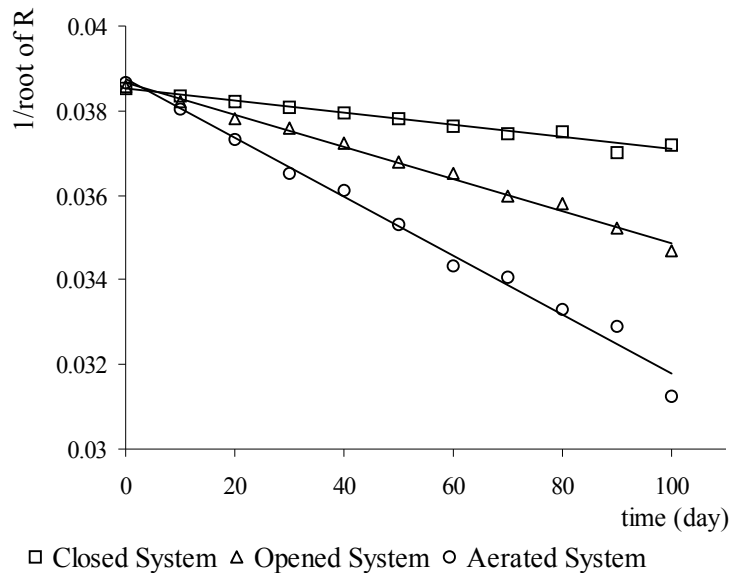
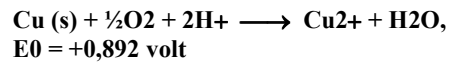
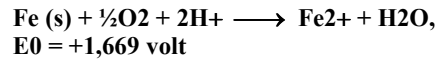


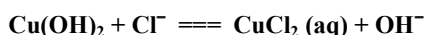
Figure 2. The $Rt^{-1/2}$ value trend of iron wire as function of time.

In responding to metals reactivities, Jensen (2000) expressed that active metals likely magnesium (Mg) will not react merely by dipping it in water, but only occurred in chloride salt solution. Similarly, iron and copper metals were notably less active than magnesium, and will not react with water and

cause corrosion, if they are only dipped in water. For copper, this corresponds to what deMeo expressed (1997). So in my experiments, copper corrosion occurred in sodium chloride solution as the main component of seawater without the influence of air, although the corrosion rate was not so signifi-

cant. In the mean time the dipping of the two metals in only water gave no reaction, even after 15 days, as demonstrated by deMeo. Iron showed a higher oxidation rate than copper in the same media.

According to Jensen (2000), iron and copper metals dipped in water will form slightly water-dissolved hydroxides of iron and copper. Consequently, the hydroxides can cover the surfaces of the metals and will inhibit further corrosion process, and will finally reduce the corrosion rate. The presence of chloride ions, therefore, copper and iron ions (their hydroxides) will exchange their hydroxides with chlorides, producing easily dissolving copper and iron chlorides corresponding to the equilibrium



The corrosion rate of copper and iron in chloride salt solution, by uncovering the surface hydroxides metal film, will be higher with significant increase of quantity.

It is clear, after all, that sodium chloride salt contributed greatly to the corrosion rate of copper and iron. Copper and iron contacts with salty environment due to the above facts, should be avoided assuring the corrosion of the metals. The application of resistance measurement method for the determination of copper and iron corrosivities can be developed for the metal wire specimen rate reactions in the acid, base or other sodium chloride salt solutions and this will make it more attractive and easy for kinetic reaction experiments. It was not done to obtain the results of the qualitative and quantitative experiments on copper and iron corrosion in water, but rather, it should be done in order to obtain comparison data for experimental validity.

CONCLUSION

Corrosion of copper wire takes place at the rate of $4.01 \times 10^{-7} \text{ g cm}^{-2} \text{ s}^{-1}$ (in closed bath),

$4.01 \times 10^{-6} \text{ g cm}^{-2} \text{ s}^{-1}$ (in open bath) and $9.43 \times 10^{-6} \text{ g cm}^{-2} \text{ s}^{-1}$ (in aerated bath). Iron wire was corroded with the rate of $2.12 \times 10^{-6} \text{ g cm}^{-2} \text{ s}^{-1}$ (in closed bath), $5.99 \times 10^{-6} \text{ g cm}^{-2} \text{ s}^{-1}$ (in open bath) and $1.07 \times 10^{-5} \text{ g cm}^{-2} \text{ s}^{-1}$ (in aerated bath). The facts show that either oxygen or carbon contained in the aerating air speed up the corrosion rates of copper as well as iron. Copper and iron metal corrosion was relatively more difficult to occur in salty media only with no oxygen than in other medium. It was found experimentally that iron shows a higher corrosivity than copper.

ACKNOWLEDGEMENT

This research was funded by DIK-RUTIN of Diponegoro University, under contract number 106/J07 11/PL/2001, April 9, 2001. We gratefully acknowledge the help provided by LEMLIT-UNDIP and FMIPA-UNDIP in the form of a generous financial support.

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