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Corrosion of carbon steel after exposure in the river of Sukabumi, West Java

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Abstract. In this study, the corrosion behavior of carbon steel had been investigated in the river of Sukabumi Region, West Java. The corrosion rates of those steels were measured by weight-loss method after exposure for certain periods of time in various depth of water (0 meters and 1 meter). The surface morphology and the composition of their corrosion product were characterized using scanning electron microscopy (SEM), XRD (X-ray diffractometer) and energy dispersive spectroscopy (EDS). After exposure, the entire surface of carbon steel was covered by corrosion product in all depth of water. On the basis of results, the corrosion rate of those steels was 19.86 mpy for 0 meters of depth and 7.01 mpy for 1 meter of depth after exposure for 76 days, respectively, which means the no protective oxides on the surface of carbon steel at 0 meters.

1. Introduction

Carbon steel has been widely applied in different applications and the industry significantly increased its production in recent years. The mechanical properties of those alloys are excellent [1]. Recently, carbon steel is used in different engineering applications for the production of some automobile components, structural shapes and sheets that are used in pipelines, buildings, plants and bridges [2]. So, the evaluation of corrosion on carbon steel in natural water environments is very important for engineering constructions in bridges, as this phenomenon is responsible for costly social, economic and sometimes even human losses.

Corrosion is a serious problem to the long-term function and integrity of a steel bridge. Structural steel will corrode if left unprotected or inadequately protected from the natural environment. This corrosion can take the form of general uniform thickness loss or concentrated pitting depending on exposure to the environment. The engineer should view corrosion as a long term threat to the integrity of the bridge structure – a critical design consideration that must be addressed in a rational manner during the design process.

Several studies have been performed to determine the corrosion rate of carbon steel and those alloys [3-8]. The rate of corrosion of plain carbon steels is dependent on both the environmental conditions, structural and compositional properties of the steel [6]. Corrosion behavior of mild steel in seawater was



studied by Sundjono et al [7] who found that uniform corrosion occurred on the mild steel during the immersion test. The corrosion resistance of the steel decreased with increasing exposure time. Prifiharni et al [8] studied the corrosion performance of steel in seawater at Karangsong and Limbangan region and found that the surface of the steel was covered by oxide film and the main corrosion product of steel was Fe_3O_4 and $FeOOH$. In another study, the Corrosion behavior of carbon steel in river water was investigated by mass-loss method [4]. Corrosion rates of commercial mild steel have been determined in underground water samples using conventional gravimetric measurements [9]. The corrosion behavior of steel has a correlation with several factors such as the concentration of free chlorides, electrolytic conductivity, and total dissolved solids. The experimental of the corrosion behavior for mild steel in five different media show that corrosion of mild steel decreasing intensity in the order of 0.1M of hydrochloric acid, underground (soil), atmosphere, salt water and fresh water [10]. The corrosion rate of carbon steel in the natural water is generally lower than that in seawater. Although corrosion of carbon steel was studied in a variety of aqueous media ranging from natural water to artificially water, the result of their corrosion rates always different.

In this work, the primary objective of the present study is to determine corrosion rates of carbon steel in the river water with different of depth at Sukabumi and to study correlate the water quality parameters with corrosion rate of those steel samples. The corrosion rate of these samples was investigated by mass-loss methods. The differences between corrosion products formed of these samples after exposure are described.

2. Materials and Methods

2.1. Sample preparation

Commercial carbon steel was used in the present study. Specimens (dimensions 150 x 80 x 2 mm) of carbon steels was used. The chemical composition of the samples is presented in Table 1.

Table 1. Chemical composition (wt%) of mild steel used.

Elements	Carbon	Manganese	Silicon	Sulphur	Phosporus	Iron
Percentages	0.051	0.734	0.126	0.004	0.016	Balancing

The specimens were prepared, before and after the test, using procedures as described in ASTM G-1 and the procedures are briefly described here. The specimens were polished with fine quality silicon carbide (SiC) emery sheet (400 grits). After polishing, specimens were washed with distilled water, degreased by using acetone, ultrasonically cleaned for 2 min, dried and stored in desiccators before use.

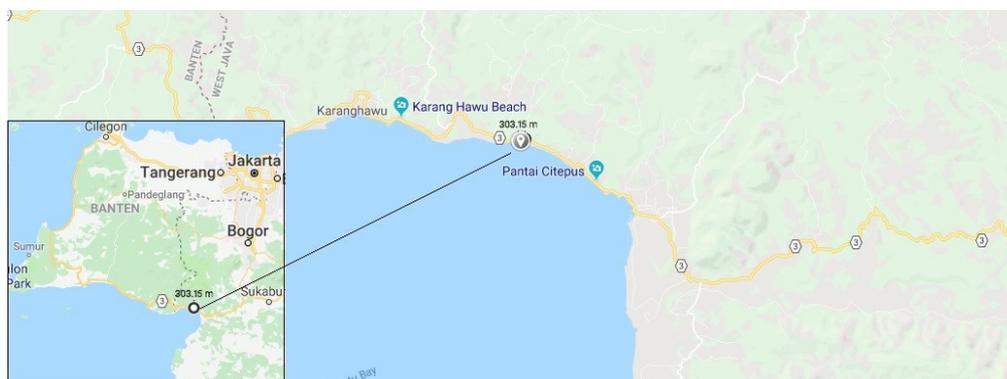


Figure 1. Map of site location for specimen testing.

The specimen testing locations in the river of Sukabumi ($6^{\circ}58'13.5''S$; $106^{\circ}31'28.6''E$ & -6.970427 ; 106.524611), 1.2 km from the shore south marine region of the district of Sukabumi, West Java -

Indonesia. The geographic site location of the experiment is shown in Figure 1. The specimens were installed exposed to the racks on PVC panels for a period of certain as shown in Figure 2.



Figure 2. The rack of specimen testing.

2.2. Weight loss analysis

Before the specimens were cleaned with the pickling solution, which contained hydrochloride acid and hexamethylenetetramine [11], they were weighed for initial weight by using an analytical balance (accuracy of 0.0001 g). After that, the specimens were immersed in the river at Sukabumi. After exposure, each specimen was taken out at a certain interval (27 and 76 days). Before weighing, the specimens were cleaned with distilled water and immersed in the pickling solution to remove the corrosion product. The specimens were washed with distilled water, dried and weighed in order to get the final weight. The method for the calculation of the corrosion rate is based on weight loss, as expressed in Eq. (1) as follows [7]:

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

Where:

W = weight loss in milligrams, D = metal density in g/cm³, A = area of the sample in cm², T = time of exposure of the metal sample in hours.

2.3. Water parameter analysis

The natural water quality parameters were measured using an HQ40d Advanced Portable Meter. This instrument is a handheld system for field measurement of dissolved oxygen (DO), salinity, conductivity, temperature, total dissolved solids (TDS), and pH. At the certain interval period immersion experiment, the parameters were measured.

2.4. Corrosion products analysis

The morphologies of corrosion products were observed by using a scanning electron microscope (SEM JEOL JSM-6390A) equipped with Energy Dispersive Spectrometer (EDS). The working distance is 10 mm and the accelerating voltage is 20 kV. The characterization of corrosion products was analyzed using X-ray diffractometer (Shimadzu XRD 7000).

3. Result and Discussion

3.1. Visual Inspection

The surface visual appearances of carbon steel specimens exposed in the river natural environment of Cidaho for 27 and 76 days are shown in Figure 3. Products of carbon steel in 1 meter of depth have more outer rust. In the surface zone (0 meters), the products are not protective and porous.

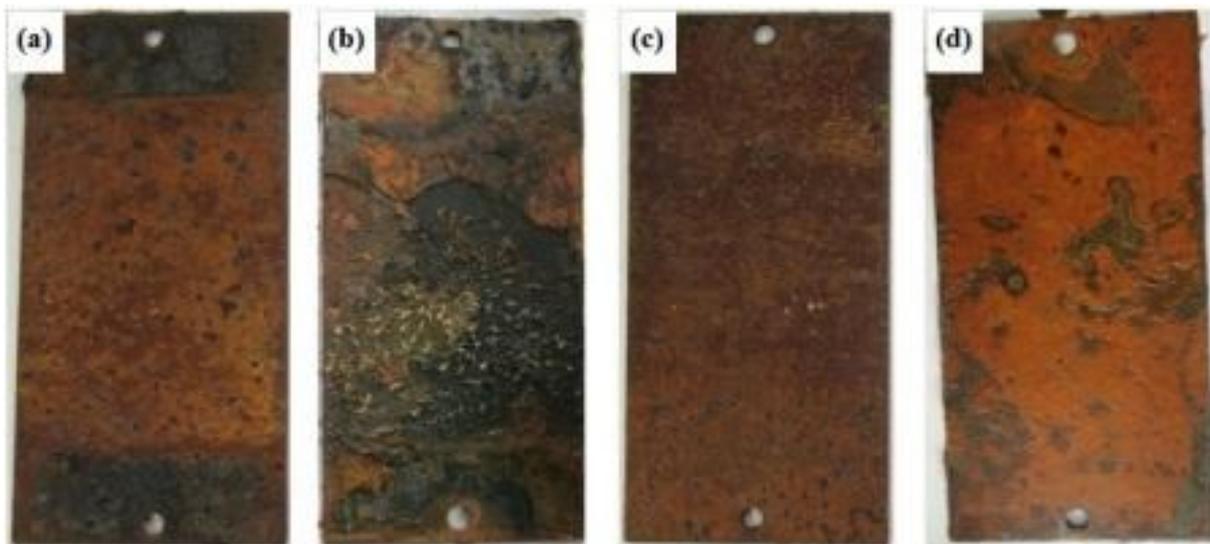


Figure 3. Visual images of specimens in river water for: (a) 0 meter, 27 days, (b) 1 meter, 27 days, (c) 0 meter, 76 days, (d) 1 meter, 76 days.

3.2. Weight Loss

Figure 4 shows the corrosion rates of the carbon steel used at site location exposure and under different exposure time. The results show that the carbon steel at the surface water level has the maximum corrosion rate whilst the carbon steel in 1-meter depth shows the lowest corrosion rate. The corrosion rates of the specimens at surface water are higher than the specimens at full immersion. This attack could be due to the formation of differential aeration of water (wet and dry phenomena). Due to low oxygen solubility in water, the oxygen concentration will be higher above the water surface [12].

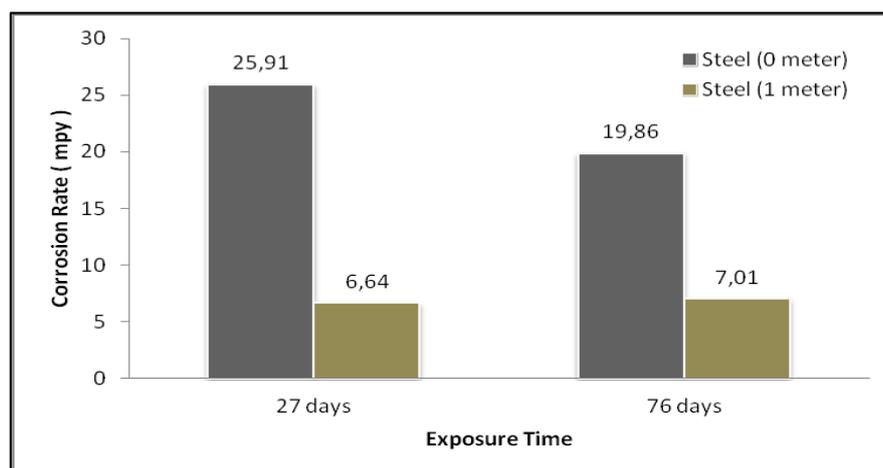


Figure 4. Correlation of corrosion rate to exposure time.

The corrosion rate from weight loss after 27 days corresponds with 25.91 mpy and 6.64 mpy for the 0 meters and 1 meter of depth, respectively. It is evident that the corrosion of specimens located in surface water zone is more serious than that of full immersion specimens, which can be explained by that the different content of oxygen[13]. Surface water zone (0 meters) also suffer dry-wet alternate and the oxygen is sufficient, which make it corrode more severe than immersion zone.

The wet-dry cycle accelerates these rusting process, especially precipitation and transformation with deprotonation and dehydration. The mechanism of the rust product in the wet-dry cycle is explained by Liu et al [12] and Stratmann et al [14] through 3 stages:

Stage 1: wetting of the dry surface

a corrosion cell starts where the anodic dissolution of iron is balanced by the cathodic reduction of Fe(III) in the rust layer:



During this stage, the cathodic O₂ reduction reaction is very slow compared to anodic iron dissolution. The metal dissolution rate is high, but the amount of dissolved iron is restricted to the amount of reducible FeOOH in the rust layer [14].

Stage 2: wet surface

Once the reducible FeOOH has been used up, the O₂ reduction reaction becomes the cathodic reaction:



The metal dissolution rate is determined by the diffusion limited current density of the O₂ reduction reaction on the pore surfaces. Because the pores in the rust layer are filled with electrolyte, the corrosion rate is quite slow during stage 2, as the diffusion rate is lower in the electrolyte than in the gas phase.

Stage 3: drying-out of the surface

During drying out, the rate of the diffusion limited O₂ reduction reaction is extremely fast due to thinning of the electrolyte film on the inner surface of the rust layer. Accordingly, the corrosion rate is very high, O₂ reduction again being the cathodic reaction.



In addition to this, O₂ can reoxidize the reduced Fe²⁺ formed in stage 1. As a consequence of the high corrosion rate, stage 3 seems to dominate the metal loss during the whole wet-dry cycle. That is, after each wet-dry cycle, so the FeOOH (rust) is increased. The rust itself took part in the corrosion processes and hence increased the corrosion rate of the wet-dry sample [12]

Also, from Figure 4. It is obvious that corrosion rates decrease with exposure time at 0 meters of depth. The decrease in corrosion rate of carbon steel with time could be attributed to the thickening of the passive film on the alloy surface. This result agrees with previous studies [15,16] on corrosion of steel after exposure in different natural environments. The reason for this phenomenon can be due to the corrosion product (rust product) builds upon the surface, therefore the diffusion rate of oxygen and other agents decreasing to the metal surface. This results in the slowing down of the kinetics of the cathodic reactions. Therefore, the increase in corrosion product thickness decreases the corrosion rate [8].

3.3. Effect of Water Parameter on Corrosion Rate

The resulting test of water quality parameters on the river – Sukabumi is clearly shown as summarized in Table 2. The results of water quality in Table 2, show that the water in this study is included in freshwater because content chlorides are less than 1000 ppm. the classification of water based on chloride content can be divided into freshwater containing less than 1000 ppm chlorides, brackish has

1000 to 25,000 ppm chlorides, sea water has between 2.5 and 3.5 percent sodium chloride, and salt water with a higher chloride concentration [17]. From a corrosion standpoint, a significant water component is dissolved oxygen (DO). Oxygen acts both as a cathodic depolarizer and as an oxidizer. As a cathodic depolarizer, DO can remove hydrogen from the cathode during electrochemical corrosion and accelerate the corrosion attack. As an oxidizer, DO can be reduced on the metallic surface and participate directly to the electrochemical processes [18].

The effect of DO on the corrosion of carbon steel at full immersion conditions is illustrated in Figure 5. The corrosion rate of carbon steel for 27 days was calculated to be 6.64 mpy with 4.95 mg/L of dissolved oxygen. It was significantly increased to 7.01 mpy with increasing 8.3 mg/L of dissolved oxygen at 76 days of exposure time. Similar results were observed for different carbon steel [10]. Corrosion rates for mild steel were increased to 72% by increasing DO concentration from 9 ± 0.5 mg/L to 2 ± 0.5 mg/L [13]. This result clearly expresses that DO significantly influence the corrosion properties of water rivers.

Table 2. Result of the water quality parameters.

Exposure Time	Temp. (°C)	pH	Salinity (ppt)	Conductivity ($\mu\text{s}/\text{cm}$)	DO (mg/L)	TDS (mg/L)
0	27.1	6.92	0.33	667	6.23	332
27	27.2	6.86	0.5	1018	4.95	500
76	25.5	7.61	0.03	61.5	8.3	28.8

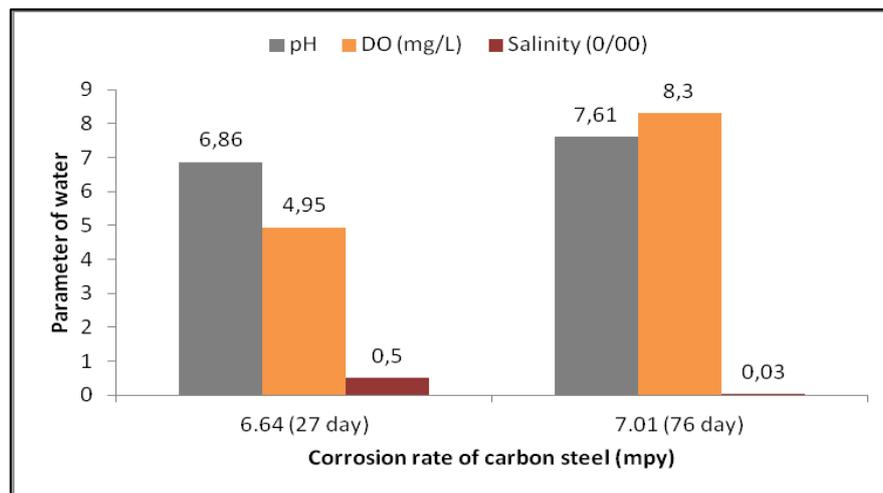


Figure 5. Corrosion rate as a function of the quality water and exposure time of carbon steel under the immersion test in 1 meter.

The temperature greatly influences the corrosion behavior of steels in water as has been indicated by the values of corrosion parameters from electrochemical studies [15]. In general, with the same exposure time, the severity of corrosion attack increases with increases in temperature. The value of temperature was not significant in this experiment as shown in Table 2. This result seems that the stability of the specimen is situated in the same corrosion area in the room temperature ($25.5 - 27.2$ °C). In this experiment, the pH level obtained was also almost the same as the temperature was not significant. The water conditions in the river of Sukabumi are categorized as fresh water because the pH levels are in the range of 5.8 and 8.5 [9].

Table 2 shows the value of chloride ion is very small. Salinity is evaluated by determination of the $[\text{Cl}^-]$ ion concentration in the water, which empirically states that salinity equals $1.80655 \times [\text{Cl}^-]$ [19].

It is known that an increase of salinity can increase corrosion risk. However, on the basis of the present results, the magnitude of salinity in the freshwater is very low at various exposure times. Therefore, the corrosion risk of the carbon steel in all the test solutions did not depend on the salinity.

3.4. Corrosion Products

SEM-EDS of corrosion products for carbon steel samples is shown in Figure 6 and Figure 7. The samples were exposed for 76 days in river water at Sukabumi. Differences in surface elevation are visible as the sample surface is not polished. The sample in this study shows some dark-brown corrosion product, or nodules, which are randomly arranged over the corroded surface, and also shows a separate layer on the surface (Figure 6). A sample in 0 meters of depth from surface water reveals a few of rust attached to the sample surface.

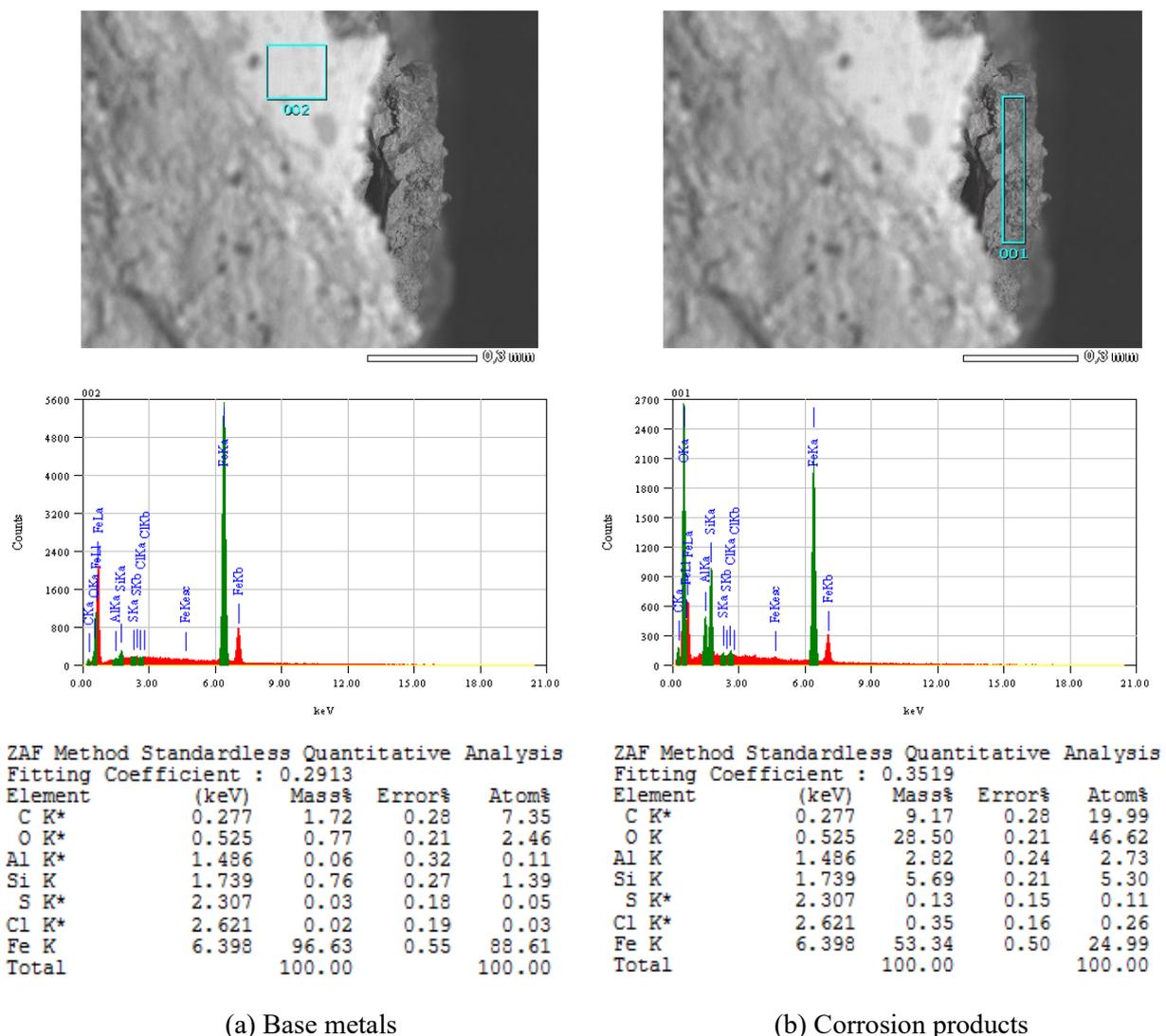


Figure 6. SEM-EDS for the morphology of carbon steel after exposure time 76 days in surface water (0 meters).

The SEM image of the carbon steel samples corroded in 1 meter of depth immersion shows corrosion product embedding on the surface which inhibits further corrosion of those sample in this environment. The sample in 1 meter of depth immersion shows the generation of large corrosion products which forced the layer apart sometime after the corrosion commenced (Figure 7). The

corrosion products might be basic iron oxides and iron carbonates under these conditions [4] because, in addition to oxides, river water contains carbonate salts [9]. Identification of the corrosion products would be confirmed by Energy Dispersive Spectrometer (EDS) analyses exactly over the products.

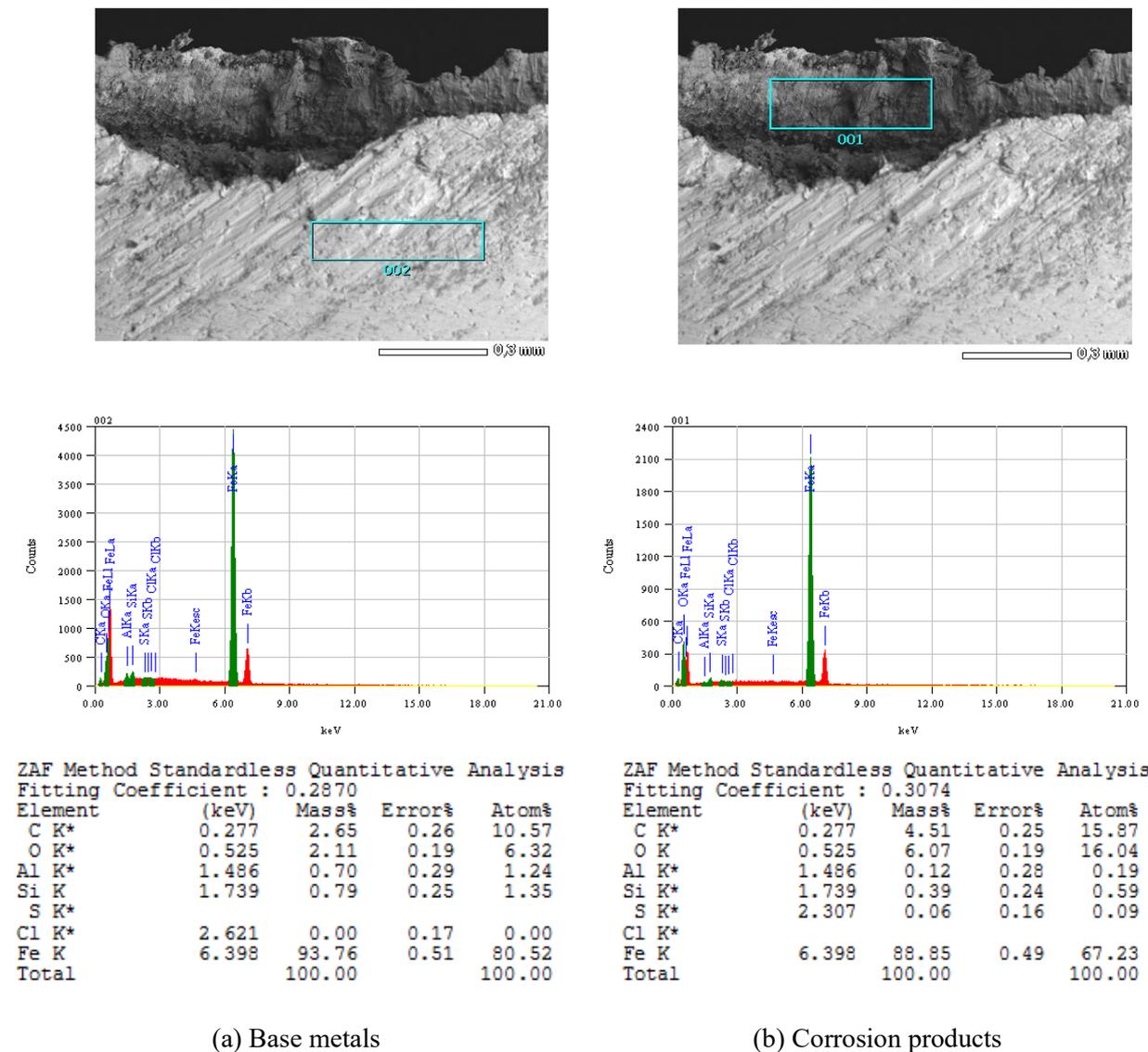


Figure 7. SEM-EDS for morphology of carbon steel after exposure time 76 days in depth water (1 meter).

Analysis of corrosion products on carbon steel specimens exposed to surface water (0 meters) from figure 6, revealed common features for the iron, carbon, oxygen, and chloride-containing corrosion products. whereas the results of EDS on corrosion products at a depth of 1 meter was not detected the chloride content as shown in Figure 7. It implies that the presence of chloride ions contributes to increasing the corrosion rate of carbon steel at 0 meters so that the corrosion rate at a depth of 0 meters is higher than 1 meter.

The analysis of corrosion products on carbon steel samples exposed to fresh water in the river shown in Figure 8. The result of the analysis by X-Ray diffractometer at Figure 8 shows that the

phases formed after certain exposure were iron hydroxide (FeOOH) and black iron oxide or magnetite (Fe₃O₄).

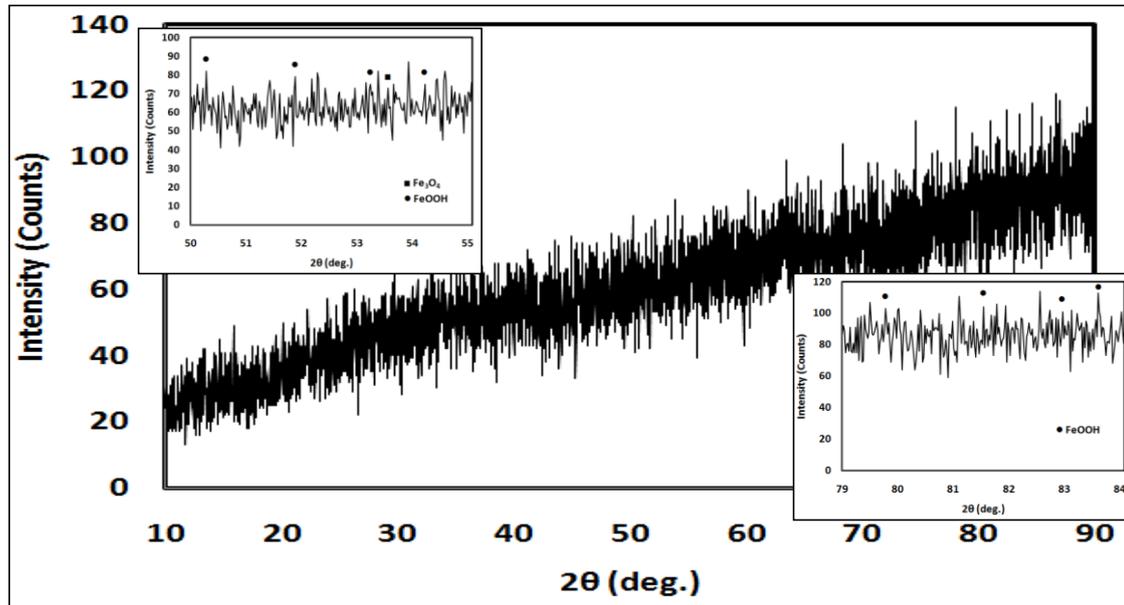


Figure 8. The result of XRD pattern of carbon steel after 76 days immersion in the river.

4. Conclusion

The corrosion of carbon steel was investigated in the river of Cidaho at Sukabumi – West Java. Weight loss analysis was conducted and the result shows that the corrosion rate increases with respect to the immersion period. On the basis of results, the corrosion rates of those steels were 19.86 mpy for 0 meters of depth and 7.01 mpy for 1 meter of depth after exposure for 76 days, respectively. These results indicate that corrosion rate of carbon steel at the wet-dry level more higher than that full-immersion. This results, of course, it still needs research and development or simulated under wet and dry cycles.

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