The effect of Lead (Pb) Hot dipping on seawater corrosion rate in ASTM A36 Steel

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Abstract. Corrosion attacks are a scourge on offshore industrial structures. The hot dipping method is a common method used in protecting submerged material from corrosion attacks. The main objective of this study was to investigate the effect of variations in hot dipping time in Lead (Pb) on corrosion attack by performing corrosion rate test, weight loss measurement, microstructure analysis and fatigue test. The results revealed that the longer the hot dipping was carried out there was a decrease in the value of corrosion rate and weight loss of ASTM A36.

1. Introduction
In designing a structure, it is very important to ensure of safety and risk management that is strongly influenced by many factors. In offshore construction, corrosion and material selection are two of many of the main factors that need to be considered [1]. Corrosion in submerged structures causes considerable cost losses due to structural failure [2] that reported as the most common forms of failure which is threatening the performance of infrastructure both on land and offshore [3]. The structural failure caused by corrosion also has an impact on environmental pollution [4]. Seawater contains variety of factors that influence the corrosion of metal construction such as salinity, temperature, pH, flow, oxygen solubility, hydrostatic pressure, pollution and organic compounds [5]. This factor makes the structure submerged in seawater can be degraded resulting in failure [6].

ASTM A36 is a structural steel that is quite flexible to use in various structural applications. This material has good ductility, strength and toughness characteristics. This material is included in the structural class in the American Society of Testing Materials as the most commercialized material in the world because of its use in the automotive industry, offshore oil mining and others [7]. The submerged material is susceptible to degradation and failure faster than atmospheric corrosion [8,9].

The hot dipping method is an effort to protect submerged material from corrosion due to the sea environment. The protection mechanism is to isolate components from direct exposure of seawater using other materials with lower melting point to prevent tearing of the steel [10]. Hot dipping process could be conducted on various types of low carbon steel with various mechanical properties, the disadvantage of this process is the possibility of a slight decrease in steel ductility caused by precipitation of carbon steel due to the age hardening process [11]. The material coating process with hot dipping basically does not have a big effect on the strength value of the main metal, but this process is very influential on the service life of the steel. It will affect the reduction in costs required for maintenance and replacement of damaged materials due to corrosion attacks [12]. Lead (Pb) has characteristics that are quite appropriate as a coating material in the Hot Dipping process. The main properties of this material are good corrosion
resistance, ductile, low melting point, flexible, relatively high density, and good electrochemical properties which make this material used in many various industrial fields [13].

The main objective of the present work is to investigate the influence of Lead (Pb) Hot dipping to the corrosion rate of ASTM A36 steel. In this respect, Hot dipping process was conducted by using different time variations. The results of this study are possible to determine significant differences in weight loss and failure behavior of ASTM A36 Steel that was submerged in seawater.

2. Experimental Details

2.1. Pre-treatment of ASTM A 36 Steel
ASTM A36 was prepared in three conditions those are Non-hot dip, hot-dip in lead 1 minutes, and hot-dip in lead 2 minutes. The Specimens preparation begins with cutting process according to testing standard to be performed. Specimens preparation were done by grinding, degreasing by immersing the specimen into a NaOH solution with a concentration of 5-10% for 10 minutes, Pickling process by immersing the specimens into 15% HCl for 5 minutes then cleaned with distilled water, and the last part is fluxing process by immersing the specimen into ammonium chloride solution which aims to cover the specimen thus preventing oxidation by the air. The Specimens drying process was conducted by using room temperature for 15 minutes.

2.2. Hot Dip in Lead
The hot dipping process is carried out where ASTM A36 specimens are coated with lead scrap etalase liquid which has been melted at 427 ℃. The smelting process is carried out by using a gravity casting furnace in 2-time variables, 1 minute and 2 minutes. The cooling process was conducted by dipping the specimens into normal water (quenching process) to get rapid Colling rates. The last step is to cut the uneven parts after the Hot dipping process by using hand grinding.

2.3. Chemical Composition Analysis
Chemical composition analysis was conducted thru two stages of testing. Lead and Steel chemical composition analysis carried out by using Bruker handheld XRF analyzer, and Chemical composition of Corrosive media (seawater) was conducted by water content analysis tool.

2.4. Thickness Test
Thickness test carried out by Ultrasonic Thickness Meter which The testing procedure refers to the ASME 5 standard.

2.5. Corrosion Test
Corrosion testing was done by the total immersion method. The specimen was dipped in seawater as a corrosive medium. Observations were conducted to see the phenomenon of corrosion rate and weight loss of specimens. Calculation of corrosion rate is carried out by the following formula:

\[ CR (\text{mpy}) = \frac{(K \times \Delta W)}{(A \times T \times D)} \] (1)

where \( CR = \text{Corrosion rate} \); \( K = \text{Constant Factor} \); \( W = \text{Weight loss in gram} \); \( A = \text{Surface area in cm}^2 \); \( T = \text{Exposure time in Hour} \); \( D = \text{Density in (gram/cm}^3\).\)

2.6. Microstructure Analysis
Microstructure observations were carried out with preparation stages based on metallographic observation standards, that are cutting, mounting, sanding by using sandpaper with 60 to 8000 grits, metal polishing using TiO₂, etching process was conducted by using a mixture of HNO₃ 3ml + Alcohol 97ml to steel and using HF 1ml + HCl 1.5ml + HNO₃ 2.5 ml + Aquades 95ml to lead. Metallographic observations were carried out using a light optical microscope.
2.7. Fatigue Test
Fatigue test was conducted to determine the limits of material fatigue resistance. In this study, the test was carried out on three specimen conditions, which are non-hot dip, hot-dip in lead 1 minutes, and hot-dip in lead 2 minutes. Each condition is only carried out only in 1 (one) level of load, that is 1⁰. This test was carried out by using Torsee's Torsion Repeated and Bending Fatigue Machine which the standard of testing is based on JIS Z 2273.

2.8. Fractography Failure Analysis
Fractography observation was carried out by using Scanning electron Microscope (SEM) type FEI inspect S50 based on ASM Handbook Vol. 12 about Fractography. This observation is aims to see the fracture phenomena on the surface of fatigue specimens that already tested.

3. Result and Discussions

3.1. Chemical Composition Analysis
ASTM A36 were tested for chemical composition analysis by using Bruker handheld XRF analyzer and the result are shown in Table 1 below. Based on the data, the steel that used in this study is low alloy steel with the element of carbon content (C) of 0.25%. This material is often used in bridge construction, buildings, welded constructions and submerged structures.

| Table 1. Main chemical compositions of ASTM A36 (wt%) |  |
|-----------------------------------------------------|--|
| Element | Percentage |  |
| Carbon   | 0,25       |  |
| Silicon  | 0,28       |  |
| Manganese| 1,02       |  |
| Phosphorus| 0,04      |  |
| Sulphur  | 0,05       |  |
| Copper   | 0,2        |  |
| Iron     | Remainder  |  |

| Table 2. Main chemical compositions of Lead (wt%) |  |
|-------------------------------------------------|--|
| Element  | Percentage |  |
| Stibium  | 1,22       |  |
| Stannum  | 0,57       |  |
| Iron     | 0,42       |  |
| Lead     | Remainder  |  |

The results of chemical composition analysis of lead are shown in Table 2 above. The data concluded that material used in hot dipping process in this research was classified as lead because the Pb element content is greater than Sn. The Pb element is contained 97.79%, while the Sn element contained only 0.57%.
Table 3. Main chemical compositions of Corrosive media

| pH  | SO₄  | Cl   | Ca   | Mg   | Na   |
|-----|------|------|------|------|------|
| 7.4 | 438.2| 16908| 187.6| 542.8| 8680 |

The chemical composition of corrosive media was obtained as shown in Table 3 above. Corrosive media that used in this research is sea water from Bangka Island. Although all sea water on the earth is corrosive, the degradation reaction that occur in metal structures is vary greatly depending on geographical location, which has the different contents of Cl, SO₄, HCO₃, CO₃, CO₂, O₂, Temperature and PH [14].

3.2. Thickness Test

![Figure 1. Lead Layer Thickness](image1)

![Figure 2. The Decrease of Steel thickness after corrosive process](image2)

Investigation results of thickness measurement are presented in Figure 1. Based on the data below, specimens with 2 minutes hot dipping in lead had the highest thickness and were significant when compared to specimens with 1 minutes hot dipping in lead. This result confirms that the longer the
immersion takes place, the thicker the layer will be [15]. The experiments shown in figure 2 show that specimens without hot dipping experienced the highest thickness reduction with very significant differences compared to the specimens that had been done hot dipping in lead. Hot dip in lead 2 minutes shows a lower range of thickness reduction compared to 1-minute hot dipping specimens. This proves that in several experiments carried out, the longer hot dipping process, the decrease of steel thickness due to corrosion will be lower.

3.3. Corrosion Analysis
Corrosion test was carried out using total immersion method, the working principle of this method is to immerse all parts of the specimen into the prepared corrosive media of seawater. The material immersed in a corrosive solution for 10 days or for 240 hours in each variable based on time length of hot dipping process.

| Condition                        | Corrosion rate (mpy) |
|----------------------------------|----------------------|
| Non-Hot Dipping (1)              | 72.04                |
| Non-Hot Dipping (2)              | 76.76                |
| Non-Hot Dipping (3)              | 76.03                |
| Non-Hot Dipping (4)              | 66.81                |
| Non-Hot Dipping (5)              | 57.70                |
| Hot Dip in Lead 1 Minute (1)     | 15.36                |
| Hot Dip in Lead 1 Minute (2)     | 16.79                |
| Hot Dip in Lead 1 Minute (3)     | 13.84                |
| Hot Dip in Lead 1 Minute (4)     | 19.79                |
| Hot Dip in Lead 1 Minute (5)     | 21.21                |
| Hot Dip in Lead 2 Minutes (1)    | 13.80                |
| Hot Dip in Lead 2 Minutes (2)    | 10.01                |
| Hot Dip in Lead 2 Minutes (3)    | 12.04                |
| Hot Dip in Lead 2 Minutes (4)    | 13.73                |
| Hot Dip in Lead 2 Minutes (5)    | 14.35                |

Table 4 and Figure 3 show the comparison of the corrosion rates that occurred in the three conditions. Non-hot dipping specimens have a very high corrosion rate when compared with hot dip in lead for 1 minute and 2 minutes specimens. Corrosion rates can also be affected by hydrogen solubility, salinity and seawater conductivity used as corrosive media. The absence of protection on the specimen’s surface caused direct contact between corrosive media with steel. It makes corrosion growth occur rapidly. The specimens of Hot dip in lead 2 minutes have the lowest value of the corrosion rate it proves that the hot dipping time is inversely proportional to the corrosion rate, that is the longer hot dipping takes time, the corrosion rate will be smaller.

Table 5 shows the results of weight loss of specimens non-hot dipping and with hot dipping in leads for 1 minute and 2 minutes. specimens non-hot dipping indicated the higher weight loss compared to specimens that hot dipping in lead. The phenomenon is related to the surface of specimens that are not protected from corrosion attacks which initiating direct contact between metal and aggressive media [16]. This behavior also proves that the longer the hot dipping process is carried out, the lower the reduction caused by corrosion attacks can be minimized.
From the data above, the corrosion rate is directly related to weight loss. Where the higher corrosion rate occurred, the higher weight loss of the specimens. Non-hot dipping specimens have the highest average weight loss and corrosion rate values that are 0.6289 gram and 69.86 mph. Very significant compared to the value of hot dipping in lead specimens. Specimens of hot dip in lead 1 minute has an average weight loss and corrosion rate that 0.164 grams and 17.39 mph. the lowest average value of weight loss and corrosion rate owned by hot dip in lead 2 minutes specimens, the value of weight loss and corrosion rate are only 0.1242 grams and 12.786 mpy. This result confirms that specimens with longest hot dipping time has the best corrosion resistance. This result confirms that the longest specimen with heat immersion in tin has the best corrosion resistance. The layer on the steel surface provides a barrier and protection effect that protects the steel surface from the corrosive environment, where the lead functions as a sacrificial material in a wet environment [17,18].

3.4. Microstructure analysis
Figure 4. Micro structure ASTM A36 non-hot dipping with 100x magnification (a) Non-etching (b) with etching

Figure 5. Micro structure ASTM A36 hot dipping in lead 1 minute with 100x magnification (a) Non-etching (b) intermetallic layer
**Figure 6.** Micro structure ASTM A36 hot dipping in lead 2 minute with 100x magnification (a) Non-etching (b) intermetallic layer

Figures 4a, 5a, and 6a show the results of micro-observations of specimens from the three test conditions without etching. It was seen that the surface of the non-hot dipping specimens had more impurities than the specimens with hot dipping. The longer the hot dipping the smoother the steel surface will be. While in figure 4b shows the spread of ferrite / pearlite on the surface of the specimen. Figure 5b and figure 6b show the intermetallic layer where in the hot dipping in lead 2 minutes has a thicker layer and produces a smoother steel surface due to total protection by the lead layer.

3.5. *Age of fracture analysis using fatigue test*

Age of fracture was carried out using a fatigue test with only 1 (one) loading level with 5x each performed, so it does not produce-N Curve. The comparison of age of fracture of three conditions is shown in Figure 7 below.

**Figure 7.** Comparison of age fracture analysis

As reported in the literature, fatigue strength of hot dipping specimens has higher value than non-hot dipping specimen [19]. The difference in the strength of fatigue on hot dip in 1-minute leads and hot dip in lead 2 minutes is not too significant, it is because the surface of the specimen is not as smooth as the non-hot specimens which are due to the hot dipping process. Surface smoothing and surface measurements are needed to measure the smoothness of the surface of the specimen so that premature failure does not occur.

3.6. *Fractography Analysis*
Figure 8. non-hot dipping fractography (a) enlargement I (b) enlargement II

Figure 9. hot dip in lead 1 minute fractography (a) enlargement I (b) enlargement II

Figure 10. hot dip in lead 2 minutes fractography (a) enlargement I (b) enlargement II
Fractographic observations were carried out to analyze fracture phenomena that occurred in specimens after fatigue testing. Fractographic observations are shown in figures 8 to 10 as above. Based on Figure 10 it can be seen that the striation line is not too clear with the flat shape of the fracture area, it indicates that fracture occurs without any metal power to resist the given load back and forth. This can occur because of the corrosion on the surface as an initial crack gets promote premature failure in the specimen. In hot dip in lead 1 minute specimens, crack propagation seems more clearly, this can be observed with the angles produced on the fracture surface, where the fatigue machine used is a torsional machine that is resulting fracture in a 45° angle. In the the longest hot dipping time hot dip in lead 2 minutes, the fracture pattern is transgranular. This indicates that the strength of grain is quite strong.

4. Conclusion

Another section of your paper. Based on the observations, the longer hot dipping time will affect to the decrease in corrosion rate and weight loss. The lead layer on the steel surface is useful as a protector that isolates steel from corrosion attacks, so it has a better fatigue toughness value compared to material without hot dipping.

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