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ANALYSIS OF CORROSION RATE OF ASTM A 387 GRADE 12 AND A 283 GRADE FOR SULFURIC ACID TANK MATERIAL

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Abstract

Corrosion is a process of degradation metal quality which is very detrimental in the industry. Especially in an industries related to utilization of acidic liquids such assulfuric acid, hydrochloric acid, etc. If corrosion rate of carbon steel can be estimated, the prediction of remaining life of carbon steel, and the preventive method of corrosion would be more appropriate. This will reduce technical, economic and aesthetic losses. The aims of this study was to determine corrosion rate of carbon steel in sulfuric acid. This study used ASTM A 387 Grade 12 and ASTM A 283 Grade A carbon steel type fortank material, where one material is represented by 5 specimen. The corrosion rate of Specimens were measured by the weight loss method for 31 days. The 5 specimens were divided into 3 regions where specimens no.1 and 2 were immersed in sulfuric acid, specimens no.3 were in the middle area or zone level (partially immersed), and specimens no.4 and 5 were not immersed in sulfuric acid. The highest corrosion rate occurred on specimen No.3 with maximum corrosion rate was 0,097 mm/y for ASTM A 387 Gr 12 and 0,096 mm/y untuk material ASTM A 283 Gr A. The results of corrosion rate on ASTM A 387 Grade 12 material are lower than corrosion rate of ASTM A 283 Grade A material. This is caused by presence of Mo and Cr alloy elements in ASTM A 387 Grade 12.

Keywords: ASTM A 283 GRADE A, ASTM A 387 GRADE 12, Corrosion, sulfuric acid

1. Introduction

Corrosion was form of metal deterioration due to electrochemical reactions with environment. Generally, corrosion was direct contacted with air and often referred to as atmospheric corrosion[1]. Close on all corrosion was caused by the atmospheric environment. Corrosion could also be caused by corrosive environments, where corrosion was affect by the presence of electrolytes. One of the compounds that have strong electrolytes was sulfuric acid [1]. In addition, rate of corrosion was determine by factors such as temperature, humidity and chemical content on air. [2].

Steel was one type of metal that was widely used in industry both as part in machines, concrete foundations, oil pipes, water tanks, oil tanks, chemical tanks, gas pipes in industry and others. This was because steel has material properties that were strength, toughness, durability, , easy to engineer by alloying elements and mirksotstructures treatment, and easy to manufacture.

Corrosion come about all metals such as steel, especially direct contact with corrosive air and fluids. In order to increase corrosion resistance of steel, alloying proseses and microstructure treatmens is needed [3]. Corrosive environment would affect mechanical properties of steel. Where material failure due to corrosion undergo microstructural changes such aspinhole, blowhole, , pitting, brittle crack, even rupture and fracture. Each year, about 13% of new steel were used to replace corrosive steel [4].

The aim of this study is to better understand the corrosion rate of carbon steel A 387 Grade 12 and A 283 Grade A on sufuric acid tank to liquid sulfide leveling. If the corrosion rate could be estimated, then the remaining life of steel carbon can be prediction, the process, and the preventive of corrosion would be more appropriate. It could decrease technical damage, economic loss, and the aesthetic factor.

2. Literature Review

A. Corrosion and Effects of Sulfur (Sulfide)

Corrosion is a process of material degradation and decrease quality of a material due the effect of chemical and electrochemical reactions with environmental conditions[5]. Corrosion is a phenomenon of material decay effect of environmental reactions that not support chemically, this phenomenon will produce new compounds. The corrosion product is a reddish-brown (scale) solid which is brittle and porous. The rate of corrosion depends on temperature, concentration, mass of metal, environmental, and mechanical factors such as stress.

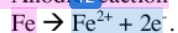
Corrosion occurs when all components of an electrochemical cell such as anode, cathode, electrolyte and electrical circuit (surface contact) are available, but corrosion will not occur if one of these components is not available.

Corrosion is referred as the reverse process of metal refining or extraction. Generally, metals exist in nature in the form of compounds, such as oxides, sulfides, carbonates, and silicates. Factors such as temperature, humidity and chemical content in air determine the corrosion rate [6]. Unfavorable environment such as low pH levels, amounts of elemental free chlorides, sulfates and other environmental factors also determine the corrosion rate.

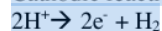
The rate of metal corrodes is influenced by: (a) Environmental conditions or media. The environment which object will be created and used is a factor in process of corrosion speed. (b) Construction materials. The material is chosen or used for construction also significantly affects corrosion rate, therefore it must choose the type of material to reduce impact of corrosion. (c) Form of construction, unsymmetrical shape or presence of gaps in construction also cause corrosion. For example, during the rainy season, the water will stagnate until enters the construction gap, causing metal to corrode.

Sulfuric acid is an aggressive fluid and has strong electrolyte levels. When sulfuric acid was diluted by contact with carbon steel, an immediate attack on the metal occurs with the formation of hydrogen gas and ferrous ions, as shown in the reactions (1) and (2) [7].

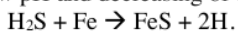
(a) Anodic reaction



(b) Cathodic reaction



The corrosion rate of carbon steels in sulfuric acid dependent strongly on chemical composition steels, in specially the carbon content [8]. The choice of material for liquid sulfur applications is important to consider, since resistance of material to hydrogen sulfide (H_2S). Failure of materials exposed to fluid is an embrittlement caused from hydrogen (hydrogen embrittlement) which is commonly known as Hydrogen Induce Cracking (HIC) or Sulfide Stress Cracking (SSC) happens if stresses exist in material application. The factors of material failure due to H_2S is the presence of high H_2S concentrations, presence of CO_2 and O_2 gas with low pH and decreasing of temperature ($<95^\circ\text{C}$) [5]. Hydrogen sulfide corrosion reaction on steel is:



Hydrogen sulfide (H_2S), besides providing element of sulfur ions (S^{2-}), it also produces hydrogen ions (H^+). This condition will affect another aggression on the steel, where Hydrogen will react with carbide in steel (Fe_3C) to form methane, resulting in decarburization, voids and surface blisters [9]. Hydrogen diffusion in steel will be speed up (increase) by Hydrogen sulfide (H_2S), then anion S_2^- will inhibit recombination reaction and cause H atomic activity to increase. The hydrogen atoms were formed from corrosion reaction process have a small diameter material. Hence, it will induced into the lattice microstructure which decrease the mechanical properties of steel as it become more brittle [5].

The effects of water and hydrogen sulfide will cause sour corrosion. Effect of water will make the hydrogen sulfide be ionized and has more corrosive properties. If applied to a high level of stress, it will appearance of SCC. The presence of water in liquid sulfur tank in chemical industry comes from condensation of water because of difference in temperature, where the temperature $<115^\circ\text{C}$ cause sulfur to freeze on surface of plate wall, while temperature of frozen sulfur was $<100^\circ\text{C}$. The combination of water condensation and effect of sulfuric acid can cause corrosion in tank.

B. Corrosion Rate

Corrosion rate is a rate of decline propagation in material quality with time. The rate of deterioration or corrosion can be determined by monitoring. Corrosion monitoring aims to determine the corrosion rate, so it can predict when and how long this structure can withstand corrosion aggression. Corrosion monitoring techniques can be divided into several methods such as weight loss and electrochemical methods.

Weight loss method is calculation of corrosion rate by measuring the underweight due to the corrosion. The principle of this method is to calculate the amount of material lost or weight loss after immersion testing in corrosive liquids. The advantage of this weight loss method is that we can immediately determine the corrosion rate when it is measured. The corrosion rate equation can be shown in the following equation [10]:

$$\text{Corrosion Rate} = (K \times W) / (A \times T \times D) \quad (1)$$

Where:

- K** : Constant
- T** : Time of exposure
- A** : Soaked surface area (Cm²)
- W** : Weight loss (Gram)
- D** : Density (ρ) gr/cm³

C. Steel

Steel is an alloy of iron and carbon which concentration is greater than other alloyed elements. There are thousands of alloys that have a composition or heat treatment. Generally, steel is clarified based on carbon content such as low carbon, medium carbon, and high carbon types. Plain carbon steels contain only the inherent elements like Mn, S, Si, P and carbon, while steel alloys were more specific with added alloy elements [11]. Carbon steels were generally classified as shown below:

- **Low Carbon Steels**

Low carbon steels are steels with main content of iron and carbon with carbon composition less than 0.25% carbon. Yield strength for low-carbon steel is ranging between 180 and 260 MPa, and high-strength low-carbon steels with range between 290 and 552 MPa. This indicates an increase in yield strength values around one and a half to two times, and ductility of about 225 % ksi (kilo square inch) is 1000 lb / in² or 5 ksi = 1000 psi[11].

- **Medium Carbon Steels**

Medium carbon steels have carbon content around 0.25% to 0.6% by weight. Medium carbon steel is stronger than low carbon steel but lower mechanical properties of ductility and toughness. Medium carbon steel generally used for rail wheels and track, gears, crankshafts, other engine components, and high strength structural components for combination of high strength wear-resistance[11].

- **High Carbon Steels**

High carbon steels have a carbon content of 0.6% to 1.4% by weight partly as hardest, strongest, but least ductile steel material. Usually used in hardened and tempered conditions, high carbon steel is also used specifically for wear-resistant conditions and is able to maintain sharp cutting edges[11].

The selection of steel material for sulfuric acid tanks in chemical industry must be resistance to sulfide corrosion, high temperature resistance and high pressure resistance. Type of steel usually used is alloy steel (low alloy steel). In this study, we want to test the materials commonly used in tanks. The type of material used were ASTM A 387 Grade 12 and A 283 Grade A.

The chemical composition of this material can be shown in the following table 1 and 2:

Table 1. The chemical composition of ASTM A387 GR 12

| Class | C | Mn | P | S |
|--------------------|-------------|-------------|-------------|-------------|
| ASTM A387 GR 12 | 0,05 - 0,17 | 0,40 - 0,65 | 0,025 | 0,025 |
| | Mo | V | Si | Cr |
| | 0,45 - 0,60 | - | 0,15 - 0,40 | 1,00 - 1,50 |

Table 2. The chemical composition of ASTM A283 GR A

| Class | C | Mn | P | S | Si | Cu |
|-------------------|------|-----|-----|-------|-------|------|
| ASTM A283 GR A | 0,14 | 0,4 | 0,9 | 0,035 | 0,040 | 0,20 |

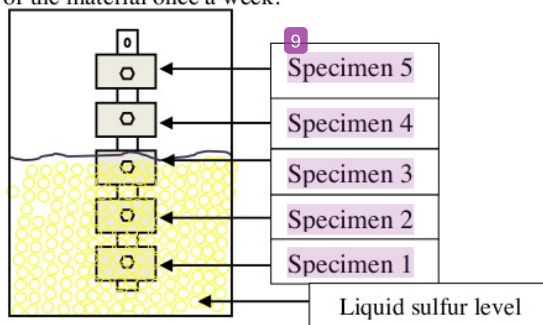
Tables 1 and 2 shows difference in alloy elements between two materials, where ASTM A387 Grade 12 contains Molybdenum (Mo) and Chromium(Cr), will increasing of corrosion resistance in material. While ASTM A283 Grade A does not have these alloys.

3. Methods

Test specimen in this research are 5 pieces of carbon steel ASTM A387 Grade 12 and ASTM A283 Grade A with 70 mm length, 50 mm width, and 6 mm thickness.

**Figure 1.** Test Specimen

This study process is divided into three areas, i.e.: vapor area (not immersed in liquid sulfur), level area (surface area of liquid sulfur), and submerged area of liquid sulfur. This process is carried out for 31 days, while weighing the weight of the material once a week.

**Gambar 1.** Condition of specimen during test process

4. Results and Discussion

8

A. Weight Loss Test

The weight loss method is a method that can be used to obtain corrosion rate. The principle of weight loss method is to calculate the amount of weight loss after the immersion test according to ASTM G 31-72 standard. By calculating initial metal mass while putting it in corrosive environment. After that, we need to recalculate metal mass after cleaning it from formed corrosion, and metal mass is expressed as the final mass. The results of weight loss test are as follows:

Table 3. ASTM A387 Grade 12 weight loss data

| Specimen Number | Initial Weight | Day 7 | Day16 | Day 23 | Day 31 |
|-----------------|----------------|---------|---------|---------|---------|
| 1 | 209,697 | 209,667 | 209,657 | 209,455 | 209,296 |
| 2 | 210,152 | 210,143 | 210,133 | 210,120 | 209,992 |
| 3 | 210,015 | 210,011 | 210,003 | 209,667 | 209,466 |
| 4 | 211,730 | 211,723 | 211,715 | 211,623 | 211,598 |
| 5 | 213,618 | 213,609 | 213,603 | 213,600 | 213,469 |

Tabel 4. ASTM A 283 Grade A weight loss data

| Specimen Number | Initial Weight | Day 7 | Day16 | Day 23 | Day 31 |
|-----------------|----------------|---------|---------|---------|---------|
| 1 | 212,537 | 212,525 | 212,412 | 212,218 | 212,049 |
| 2 | 215,614 | 215,603 | 215,330 | 215,323 | 215,087 |
| 3 | 214,610 | 214,600 | 214,423 | 214,219 | 214,067 |
| 4 | 210,773 | 210,755 | 210,673 | 210,668 | 210,655 |
| 5 | 214,979 | 214,959 | 214,933 | 214,930 | 214,876 |

Tables 3 and 4 shows weight loss test results for 31 days. From tables 1 and 2, the highest weight loss results were found in specimen No.3 (area level zone), both in ASTM A387 Grade 12 and ASTM A283 Grade A material.

The highest corrosion rate was specimen No.3 (level zone area). This occurred because carbon steel specimen No.3 in zone level area was exposed to hydrogen sulfide gas, it will produce a hydrogen sulfide corrosion reaction on iron. After iron specimen was exposed to hydrogen sulfide (H₂S) gas, iron specimen was in contact with oxygen which will make the corrosion faster.

B. Corrosion Rate

The corrosion rate can be calculated from carbon steel which has been tested to weigh loss in sulfuric acid . Corrosion rate calculation of specimens on ASTM A 387 Grade 12 and ASTM A 283 Grade A shown in table below:

Table 5. ASTM A387 Grade 12 corrosion rate data

| Specimen Number | Day 7 | Day16 | Day 23 | Day 31 | Day 7 | Unit |
|-----------------|-------|-------|--------|--------|-------|--------|
| 1 | 0,024 | 0,003 | 0,048 | 0,028 | 0,071 | mm / y |
| 2 | 0,007 | 0,003 | 0,003 | 0,023 | 0,028 | mm / y |
| 3 | 0,003 | 0,003 | 0,080 | 0,036 | 0,097 | mm / y |
| 4 | 0,006 | 0,003 | 0,022 | 0,004 | 0,023 | mm / y |
| 5 | 0,007 | 0,002 | 0,001 | 0,023 | 0,026 | mm / y |

Table 6. ASTM A283 Grade A corrosion rate data

| NO. SPESIMEN | Day 7 | Day16 | Day 23 | Day 31 | Day 7 | Unit |
|--------------|-------|-------|--------|--------|-------|--------|
| 1 | 0,009 | 0,039 | 0,046 | 0,030 | 0,086 | mm / y |
| 2 | 0,009 | 0,094 | 0,002 | 0,042 | 0,093 | mm / y |
| 3 | 0,008 | 0,061 | 0,049 | 0,027 | 0,096 | mm / y |
| 4 | 0,014 | 0,028 | 0,001 | 0,002 | 0,020 | mm / y |

| | | | | | | |
|---|-------|-------|-------|-------|-------|--------|
| 5 | 0,016 | 0,009 | 0,001 | 0,010 | 0,018 | mm / y |
|---|-------|-------|-------|-------|-------|--------|

Tables 5 and 6 shows the highest corrosion rates occurred in specimen No. 3, both ASTM A387 Grade12 and ASTM A283 Grade A. Value of corrosion rate would show different value when calculated because on the 7th, 16th day, and 31th day specimens with corrosion were put back to be investigated.

From the results of the calculation of weight loss and corrosion rate, it could be known that the material corrosion rate data of ASTM A387 Grade 12 and ASTM A283 Grade A by used linear regression to determine corrosion rate for one year (365 days). Results of calculating corrosion rate with linear regression can be seen as follows:

Table 7. Corrosion rate in 1 year for ASTM A387 Grade 12 material

| Specimen Number | Y Value | Corrosion rate for 1 year (mg/cm ²) |
|-----------------|------------------------------|---|
| 1 | 0.1940343460x - 1.6231943355 | 69,2 |
| 2 | 0.0692526547x - 0.6814548361 | 24.6 |
| 3 | 0.2904879888x - 2.8875098973 | 103.1 |
| 4 | 0.0688643398x - 0.5525342759 | 24.6 |
| 5 | 0.0628596649x - 0.6442902550 | 22.6 |

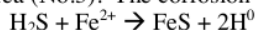
Tabel 8 Corrosion rate in 1 year for ASTM A 283 Grade A material pit

| Specimen Number | Y Value | Corrosion rate for 1 year (mg/cm ²) p |
|-----------------|------------------------------|---|
| 1 | 0.2415887195x - 1.8543743204 | 86.3 |
| 2 | 0.2358587064x - 1.2434791503 | 84.8 |
| 3 | 0.2695947507x - 1.8395804683 | 96.6 |
| 4 | 0.0467777437x + 0.1095995242 | 17.2 |
| 5 | 0.0378654422x - 0.0831751660 | 13.7 |

Tables 7 and 8 shows the highest corrosion rate for one year was No. 3 specimen (zone level area).

C. Sulfide Corrosion and the Effect of Alloy Element

The increased corrosion rate due to exposure to hydrogen sulfide (H₂S) gas in tank develop in zone level area (No.3). The corrosion reaction that occurs was:



Hydrogen sulfide gas (H₂S) will react with iron material and establish iron sulfide (FeS) compounds with characteristics of iron surface being peeled off and pit. This corrosion process could occur hydrogen induce cracking (HIC) and sulfide stress cracking (SSC). Mechanism of corrosion come out due to formation of hydrogen atoms on steel surface and adsorbed on surface, the adsorbed H atoms will diffuse into steel substrate. The accumulation of trapped hydrogen atoms creates voids or inclusions will establish increase internal pressure and triggered crack initiation and propagation. In presence of sulfide, H atoms will diffuse into the steel rather than forming H₂ on the surface. This condition will generate embrittlement and will cause high corrosion to tank structure. Excess H₂S gas will make acid to accelerate the rate of corrosion on steel carbon[5].

This study concluded that ASTM A387 Grade 12 tank material has a high corrosion resistance compared to ASTM A283. This was effected by the presence of Mo and Cr content in ASTM A387 Grade 12 material. The effect of Mo alloy elements in alloy steel could increase tensile strength at high temperatures, hot temperatures resistance, reduce susceptibility to embrittlement temper (400-450°C) and increase hardness of steel. While the effect of element Cr on alloy made corrosion and oxidation resistance, increase hardness, increase strength at high temperatures and increase resistance to abrasion effects.

5. Conclusions and Recommendations

A. Conclusions

Based on the study and analysis of data obtained from test, the conclusions obtained were:

1. Corrosion or weight loss occurs at all zone level of the test of ASTM A 387 Grade 12 and ASTM A 283 Grade A materials. The results of corrosion rate on ASTM A 387 Grade 12 material are lower than corrosion rate of ASTM A 283 Grade A material. This is caused by presence of Mo and Cr alloy elements in ASTM A 387 Grade 12.
2. The area with highest corrosion rate is in zone level area where the area was occupied by specimen no.3 with a maximum corrosion rate of ASTM A 387 Grade 12 was 0.097 mm / y with corrosion rate for one year was 103.1 mg / cm² and 0.096 mm / y with corrosion rate for one year was for ASTM A 283 Grade A. This occurred because carbon steel specimen No.3 in zone level area was exposed to hydrogen sulfide gas, it will produce a hydrogen sulfide corrosion reaction on iron. After iron specimen was exposed to hydrogen sulfide (H₂S) gas, iron specimen was in contact with oxygen which will make the corrosion faster.

B. Recommendations

1. It is necessary to do further research on microstructure of two tank materials to see to what extent sulfide corrosion damages these two materials.
2. Conducted research to see effectiveness of using corrosion inhibitors to slow down the corrosion rate of both tank materials without changing tanks and stopping the production process in the industry.

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