The Effect of Chloride, Sulfate, and Nitrate Anions for Pitting Corrosion Behavior on ASTM A36 Steel in Atmospheric Environment

Sri Hastuty[1], Judha Purbolaksono[2], Rifki Yusup[3], Rahmat Fajtra[4]

{sri.hastuty@universitaspertamina.ac.id[1], yudha.purbolaksono@universitaspertamina.ac.id[2]
rifki.yusup@outlook.com[3], rfatjra@gmail.com[4]}

Pertamina University, Jakarta, Indonesia[1,2,3,4]

Abstract. The purpose of this research was to study the pitting corrosion initiation mechanism in different solutions containing chloride, sulfate and nitrate on steel in atmospheric environment. The research used experimental methods with ASTM A36 steel as the workpiece and digital microscopes to observe the corrosion that occurs by varied volumes of droplet solution (10 to 50 μL) on the surface of the workpiece. Afterwards, the critical time for pitting to initiate and the number of pitting were measured as parameters of corrosion resistance of steel in atmospheric. This research also shows that the anion of chloride is has the fastest in terms of initiating the pitting corrosion than the anion of sulfate and nitrate.

Keywords: Pitting Corrosion, ASTM A36 Steel, Anion, Atmospheric Environment, Solutions, Critical Time**.**

1 Introduction

Carbon steel is often used in building structures, bridges, car bodies, and much more [1]. This is because carbonsteel has advantages in high strength and high ductility also relatively cheap despite the low level of corrosion resistance. Carbon steel is a type of material that includes consisting of iron and carbon (Fe and C), where iron is the main element or basic element of steel while carbon is the supporting element or alloying element. Carbonsteel itself has a value of carbon content in iron which varies from 0.2% to 2.14% [2]. In addition to these two elements, other elements could be added (alloying), depending on how the desired material property of the steelitself, such as Phosphorus (P), Silicon (Si), Manganese (Mn), Sulfur (S), and other elements depends on the desired steel material properties [3].

Low carbon steel is a type of steel that has a very small carbon content in iron that is less than 0.3%. This contentwill give more strength and the ductility of the material property itself. But these material properties could be directly affected by air friction, raindrops, and other external

ICONIC-RS 2022, March 31-April 01, DKI Jakarta, Indonesia

DOI 10.4108/eai.31-3-2022.2320677

conditions because the usage of this material is commonly for external use [2]. These will make the material easily corrode, be more brittle and weaker due to wear resistance [1].

Corrosion could occur because the metal or steel surfaces that are placed in an atmospheric environment are exposed or exposed to droplets. The droplets of water could instantly react with the metal surfaces in an atmospheric environment because have a lot of contaminants or impurities [4]. The atmospheric environment usually contains various kinds of pollutants from suspended dust particles or salt particles from the sea that couldbe carried by the wind for long distances [5]. Atmospheric air conditions also contain harmful gases, like SO2, NO_x, H_2S, chloride, sulfate, nitrate ion, and many more that could lead to the corrosion of metals [4] [6].

Because the level of humidity in different places is diverse, if a place has high relative humidity which means thevalue of RH is more than 60%, it will support the formation of a layer of water in the air and could trigger the condensation process and forms a droplet. These water droplets contain harmful gases that could be stuck to themetal surfaces [6] [7]. Metals that are exposed to dew drops for a certain time could experience the electrochemical reaction which causes the corrosion problem, like atmospheric or pitting corrosion on the exposed surface [4].

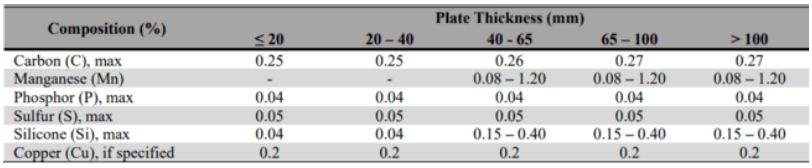
Pitting corrosion is a type of corrosion that attacks the surface of the material. Pitting corrosion can be characterized by the presence of small holes on the surface of the material. The spread of pitting corrosion throughout the surface of the material is relatively slow [8]. This is because pitting corrosion only attacks at one point which usually occurs due to the presence of impurity droplets, but the effect will continue until the corroded part forms a hole that slowly deepens [9]. Pitting corrosion most easily attacks metal materials that can form a passive layer such as stainless steel or aluminum, but it is possible that pitting corrosion can attack materials suchas steel, especially low carbon steel because carbon steel itself has a relatively low corrosion resistance comparedto other materials [10].

This research aims to study the behavior and mechanism of a droplet that contains chloride, sulfate, and nitrate contaminants against the pitting corrosion resistance of low carbon steel.

2 Materials and Methods

The specimen that is used in this research is carbon steel with Low Carbon Steel type ASTM A36 which has the composition shown on **Table 1**. The specimens were allowed to react with droplets of chloride, sulfate, and nitrate solutions in 1 M concentration in the atmospheric environment (±27ºC) until the droplets were at equilibrium conditions.

Table 1. Chemical composition ASTM A36 steel [11].



Composition (%)	Plate Thickness (mm)				
	≤ 20	20 – 40	40 - 65	65 – 100	> 100
Carbon (C), max	0.25	0.25	0.26	0.27	0.27
Manganese (Mn)	-	-	0.08 – 1.20	0.08 – 1.20	0.08 – 1.20
Phosphor (P), max	0.04	0.04	0.04	0.04	0.04
Sulfur (S), max	0.05	0.05	0.05	0.05	0.05
Silicone (Si), max	0.04	0.04	0.15 – 0.40	0.15 – 0.40	0.15 – 0.40
Copper (Cu), if specified	0.2	0.2	0.2	0.2	0.2

The ion of chloride, sulfate, and nitrate is contained in a 1 M solution of NaCl, Na2SO4, and NaNO3 respectivelythat should make first from the powder salts forms the Equation (1) [12].

$$M = \frac{\text{mass of solute}}{M_r \text{ of solute}} \times \frac{1000}{\text{Volume of Solution (mL)}} \qquad (1)$$

2.1 Experimental Setup

This research is carried out with at least 9 specimens for each solution. All specimens (ASTM A36 Carbon Steel – 5 mm thickness) were cut with 30×30 mm in dimension and were polished using Silicone Carbide (SiC) paper with the polishing machine (Forcipol 2V Grinding-Polishing, Metkon). The polishing activities are done in two stages, where first polished gradually with SiC paper grade 120–600 and distilled water as cooler. Then used grade800–2000 paper with alcohol 70% as cooler. After the specimen has been polished, each specimen is characterizedby an optical microscope (Carl Zeiss Microscopy Gmbhm ZEISS Primotech MAT) first with 200× magnificationfor observation (metallography) before the corrosion experiment started.

2.2 Experiment

The experiment started by dripping the solution with various volume of solution on each specimen using a micrometer pipette. This test was placed in an atmospheric environment for 60 minutes. Observations were made using a USB Digital Microscope with 1600× magnification to find out how the mechanism and how quickly the anions initiate the pitting corrosion on the ASTM A36 steel surface. The critical time is obtained by testing 3 times for each droplet of Volume Variation (10 μL, 20 μL, and 50 μL). Then the metallography characterization was carried out again to evaluate further corrosion damage on the surface of specimens.

3 Results and Discussion

3.1 NaCl Solution

Figure 1 shows that the larger the volume of a droplet, the more time it takes to initiate pitting corrosion. This could happen because the large volume is directly proportional to the thickness of the droplet. Thus, the oxygen content in the droplets with a larger volume is less than the oxygen content in the droplets with a smaller volume.With a limited amount of oxygen, the reaction that occurs between the droplet and the steel is also limited.

The reaction that occurs between the droplets and metal surfaces is [13]:

$\text{Fe (s)} \rightarrow \text{Fe}^{2+}\text{ (aq)} + 2\text{e}^-$ (oxidation)
$\text{O}_2\text{ (g)} + 2\text{H}_2\text{O (aq)} + 4\text{e}^- \rightarrow 4\text{OH}^-\text{ (aq)}$ (reduction)
$\text{Fe (s)} + 2\text{NaCl (aq)} + 2\text{H}_2\text{O (1)} \rightarrow \text{H}_2\text{ (g)} + \text{FeCl}_2\text{ (aq)} + 2\text{NaOH (aq)}$
$\text{Fe}^{2+}\text{ (aq)} + 4\text{OH}^- \rightarrow \text{Fe(OH)}_2\text{ (s)}$

$2Fe(OH)_2 (s) + O_2 (g) \rightarrow Fe_2O_2 \cdot nH_2O$ (rust / corrosion product)

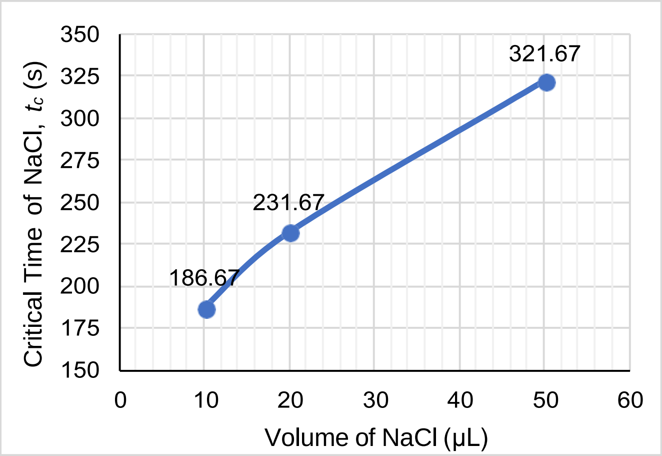


Fig. 1. The relation of volume of NaCl droplets and critical time to initiate the pitting corrosion initiation time.

Figure 2 shows the results of observations made on the surface of ASTM A36 steel with 1 M NaCl volume 10 µL droplets using a USB Digital Microscope. Furthermore, **Figure 3 and 4** also show the results of droplets volume 20µL and 50µL respectively.

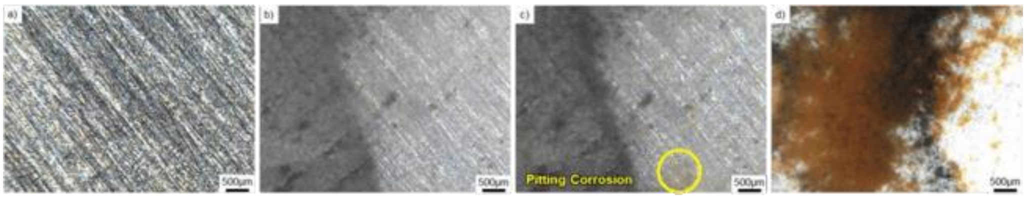


Fig. 2. Observation of Pitting Corrosion Under 10 µL Droplets NaCl Solutions at (a) the Beginning; (b) 60 Seconds Before the Corrosion Initiate; (c) Pitting Corrosion Occurs; and (d) 60 Minutes After the Observation.

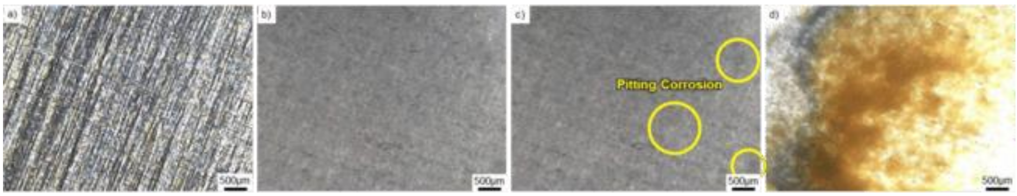


Fig. 3. Observation of Pitting Corrosion Under 20 µL Droplets NaCl Solutions at (a) The Beginning; (b) 60 Seconds Before the Corrosion Initiate; (c) Pitting Corrosion Occurs; and (d) 60 Minutes After the Observation.

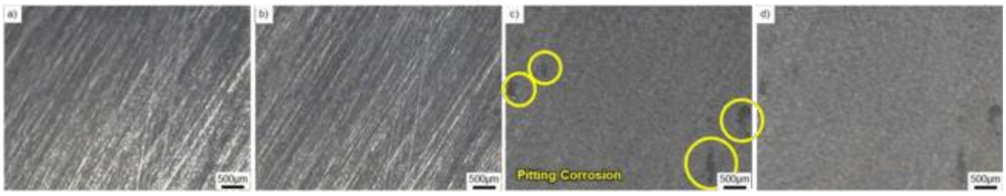


Fig. 4. Observation of Pitting Corrosion Under 50 μL Droplets NaCl Solutions at (a) the Beginning; (b) 60 Seconds Before the Corrosion Initiate; (c) Pitting Corrosion Occurs; and (d) 60 Minutes After the Observation.

The different volumes of NaCl droplets produce the critical time of corrosion initiation is varied, but still in the insignificant time range. Droplets with 10 μL volume were the fastest in initiating corrosion in all samples compared to droplets with other volumes. However, droplets with a volume of 50 μL initiated the most pits compared to droplets with other volumes when they first succeeded to initiated the corrosion on the surface of ASTM A36 steel.

3.2 Na_2SO_4 Solution

Figure 5 shows that Na_2SO_4 solution can initiate pitting corrosion on the surface of ASTM A36 steel in all samples even though not as fast as NaCl solution droplets.

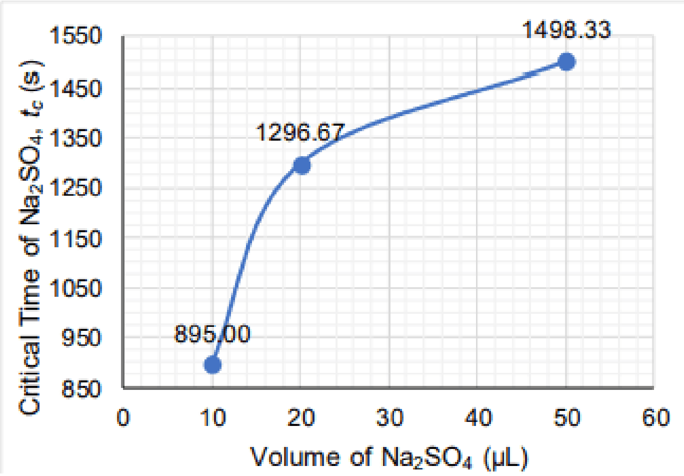


Fig. 5. The relation of volume of Na2SO4 droplets and critical time to initiate the pitting corrosion initiation time.

The reaction that occurs between the droplets and metal surfaces is [14]:

$$\begin{aligned}
&\mathrm{Fe\ (s) \rightarrow Fe^{2+}\ (aq) + 2e^{-}} && \text{(oxidation)}\\
&\mathrm{O_2\ (g) + 2H_2O\ (aq) + 4e^{-} \rightarrow 4OH^{-}\ (aq)} && \text{(reduction)}\\
&\mathrm{Na_2SO_4\ (aq) \rightarrow Na^{+}\ (aq) + SO_4^{2-}\ (aq)} && \text{(hydrolyzed)}\\
&\mathrm{Fe^{2+}\ (aq) + SO_4^{2-}\ (aq) \rightarrow FeSO_4\ (aq)} &&\\
&\mathrm{Na^{+}\ (aq) + OH^{-}\ (aq) \rightarrow NaOH\ (aq)} &&\\
&\mathrm{FeSO_4\ (aq) + 2NaOH\ (aq) \rightarrow Fe(OH)_2\ (s) + Na_2SO_4(aq)} &&\\
&\mathrm{2Fe(OH)_2\ (s) + O_2\ (g) \rightarrow Fe_2O_3{\cdot}nH_2O} && \text{(rust / corrosion product)}
\end{aligned}$$

Figure 6–8 shows the results of observations made on the surface of ASTM A36 steel with 1M Na_2SO_4 volume 10 µL, 20 µL, and 50 µL droplets using a USB Digital Microscope respectively.

Droplets of Na_2SO_4 solution with a volume of 50 µL crystallized within 60 minutes. This is due to the low relative humidity and high temperature during testing. This causes the solution droplets on the steel surface to be desiccated and evaporate until they become crystal. Thus, the corrosion process stops on the steel surface with 50µl volume Na_2SO_4 droplets after more than 60 minutes because there is no more solution on the steel surface. After all, the result of critical time is not much different from the NaCl solution. The 10 µL droplet is still the fastest to cause pitting corrosion on the surface of ASTM A36 steel.

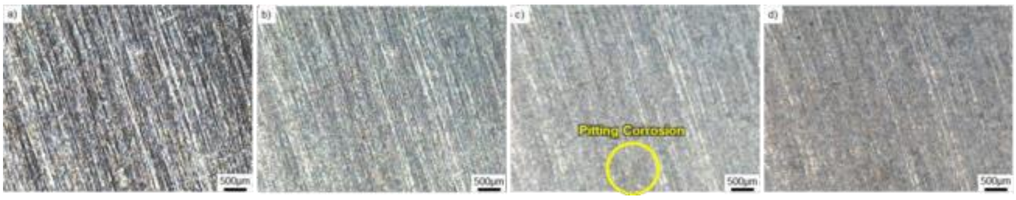


Fig. 6. Observation of Pitting Corrosion Under 10 µL Droplets Na_2SO_4 Solutions at (a) the Beginning; (b) 60 Seconds Before the Corrosion Initiate; (c) Pitting Corrosion Occurs; and (d) 60 Minutes After the Observation.

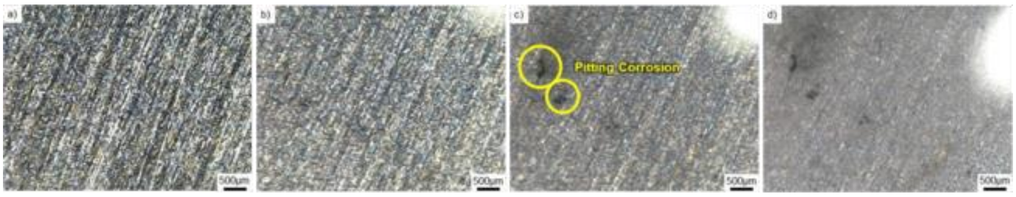


Fig. 7. Observation of Pitting Corrosion Under 20 µL Droplets Na_2SO_4 Solutions at (a) the Beginning; (b) 60 Seconds Before the Corrosion Initiate; (c) Pitting Corrosion Occurs; and (d) 60 Minutes After the Observation.

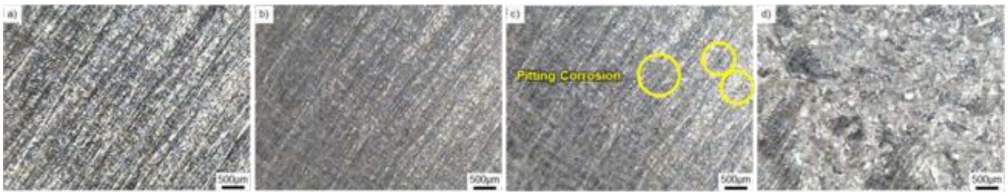


Fig. 8. Observation of Pitting Corrosion Under 50 μL Droplets Na_2SO_4 Solutions at (a) the Beginning; (b) 60 Seconds Before the Corrosion Initiate; (c) Pitting Corrosion Occurs; and (d) 60 Minutes After the Observation.

3.3 $NaNO_3$ Solution

Figure 9 showed that $NaNO_3$ solution droplets were very slow in initiating pitting corrosion on the surface of ASTM A36 steel compared to NaCl and Na_2SO_4 solutions. This is evidenced by the absence of pitting corrosion initiation in the 50 μL droplets volume as long as 60 minutes of observation.

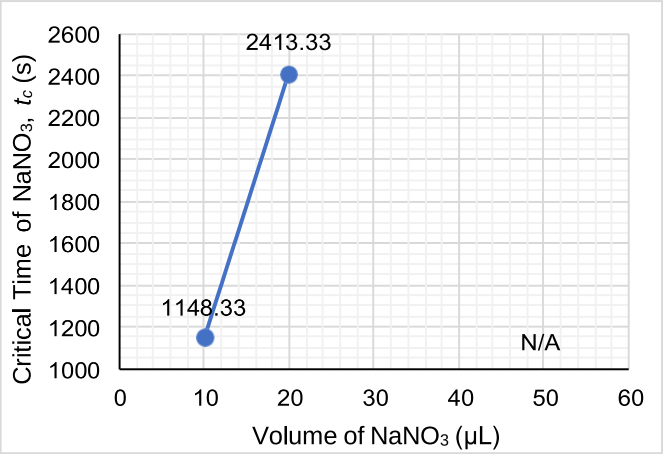


Fig. 9. The relation of volume of NaNO3 droplets and critical time to initiate the pitting corrosion initiation time (No corrosion has detected after 60 mins observation in 50 μL experiment).

The reaction that occurs between the droplets and metal surfaces is [15]:

$Fe\ (s) \rightarrow Fe^{2+}\ (aq) + 2e^-$ (oxidation)

$O_2\ (g) + 2H_2O\ (aq) + 4e^- \rightarrow 4OH^-\ (aq)$ (reduction)

$NaNO_3\ (aq) \rightarrow Na^+\ (aq) + NO_3^-\ (aq)$ (hydrolyzed)

$Fe^{2+}\ (aq) + 2NO_3^-\ (aq) \rightarrow Fe\ (NO_3)_2\ (aq)$

$Na^+ (aq) + OH^- (aq) \rightarrow NaOH (aq)$
$Fe(NO_3)_2 (aq) + 2NaOH (aq) \rightarrow Fe(OH)_2 (s) + 2NaNO_3(aq)$
$2Fe(OH)_2 (s) + O_2 (g) \rightarrow Fe_2O_3 \cdot nH_2O$ (rust/corrosion product)

Like behavior in NaCl and Na_2SO_4 solution, **Figure 10–12** show the results of observations made on the surface of ASTM A36 steel with 1 M $NaNO_3$ volume 10 μL, 20 μL, and 50 μL droplets respectively using a USB Digital Microscope.

Droplets of $NaNO_3$ with 50μL volume after reacting for 60 minutes did not show any changes. The absence of holes or pits and the absence of a red-brown pattern indicate that on the steel surface with the solution droplets, pitting corrosion does not occur or is not initiated.

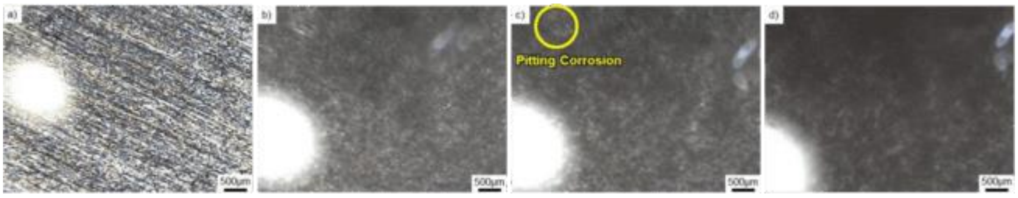


Fig. 10. Observation of Pitting Corrosion Under 10 μL Droplets $NaNO_3$ Solutions at (a) the Beginning; (b) 60 Seconds Before the Corrosion Initiate; (c) Pitting Corrosion Occurs; and (d) 60 Minutes After the Observation.

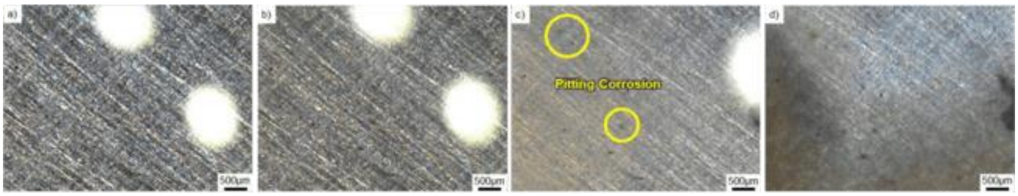


Fig. 11. Observation of Pitting Corrosion Under 20 μL Droplets $NaNO_3$ Solutions at (a) the Beginning; (b) 60 Seconds Before the Corrosion Initiate; (c) Pitting Corrosion Occurs; and (d) 60 Minutes After the Observation.

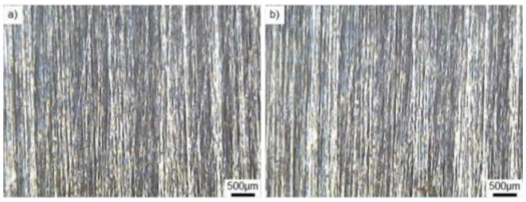


Fig. 12. Observation of Pitting Corrosion Under 50 μL Droplets $NaNO_3$ Solutions at (a) the Beginning; and (d) 60 Minutes After the Observation.

3.4 Droplets Behavior

The droplet behavior in each solution with different droplet volumes did not have a significant difference. The difference that occurs is that droplets with a smaller volume in each solution have a shorter corrosion initiation time compared to droplets with a larger volume. This happens because of the difference in the concentration of O_2 in the droplets with large and small volumes, causing differences in the required corrosion initiation time needed [16].

With the difference in oxygen concentration in the three types of droplets with different volumes, the rates of oxidation and reduction reactions are also different. This causes the droplets with a larger volume to have a greater difference in O_2 concentration than the smaller droplets with the mechanism of corrosion of this experiment shown in **Figure 13**. Thus, the rate of oxidation and reduction reactions to initiate further reactions in forming corrosion products is slower in droplets with larger volumes [16].

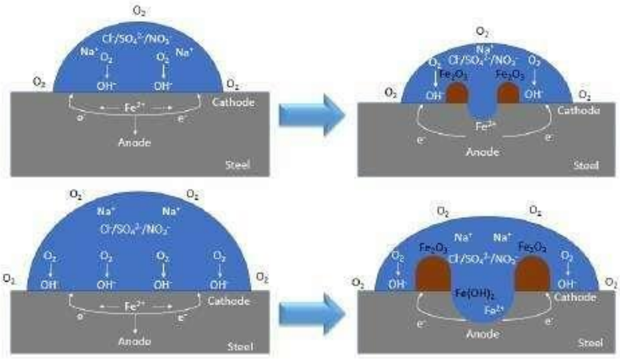


Fig. 13. Droplets Behavior with Different Volume to Initiate Corrosion at the Steel Surface.

1) *NaCl Droplets*

- Droplet Volume of 10 µL

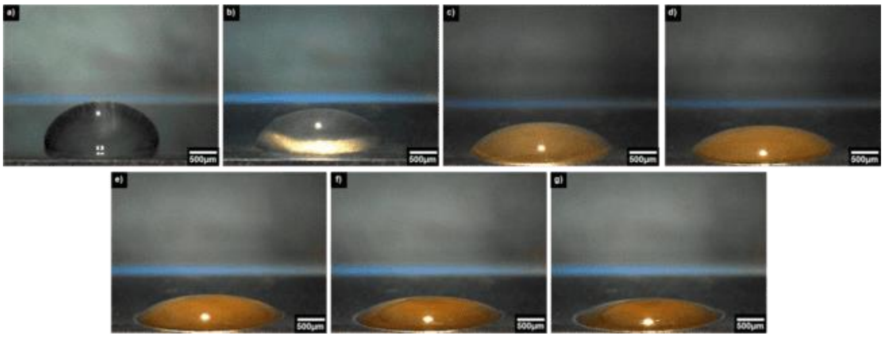


Fig. 14. Observation of 10 µL NaCl Droplet at: a) the Beginning; b) 10 mins; c) 20 mins; d) 30 mins; e) 40 mins; f) 50 mins; and g) 60 mins.

- Droplet Volume of 20 μL

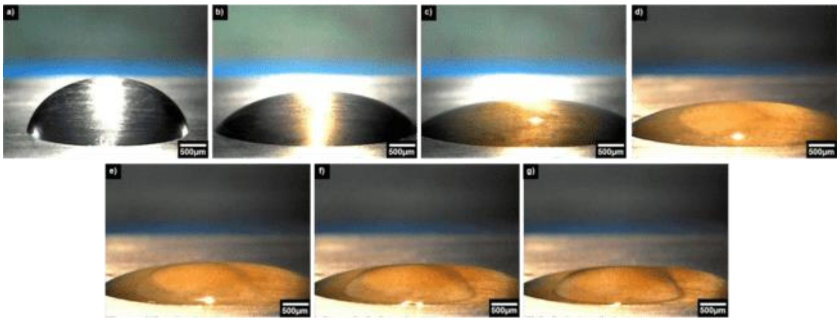


Fig. 15. Observation of 20 μL NaCl Droplet at: a) the Beginning; b) 10 mins; c) 20 mins; d) 30 mins; e) 40 mins; f) 50 mins; and g) 60 mins.

- Droplet Volume of 50 μL

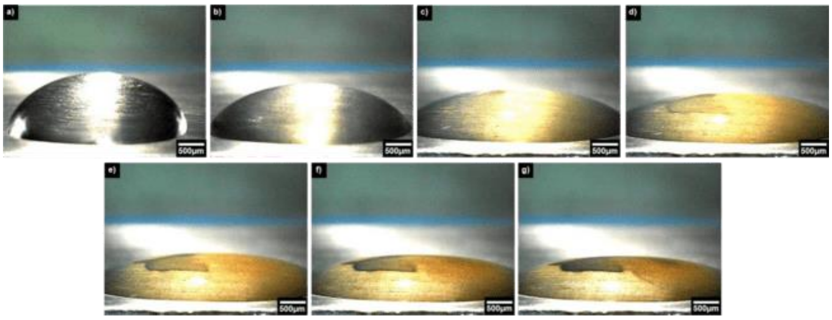


Fig. 16. Observation of 50 μL NaCl Droplet at: a) the Beginning; b) 10 mins; c) 20 mins; d) 30 mins; e) 40 mins; f) 50 mins; and g) 60 mins.

2) *Na_2SO_4 Droplets*

- Droplet Volume of 10 μL

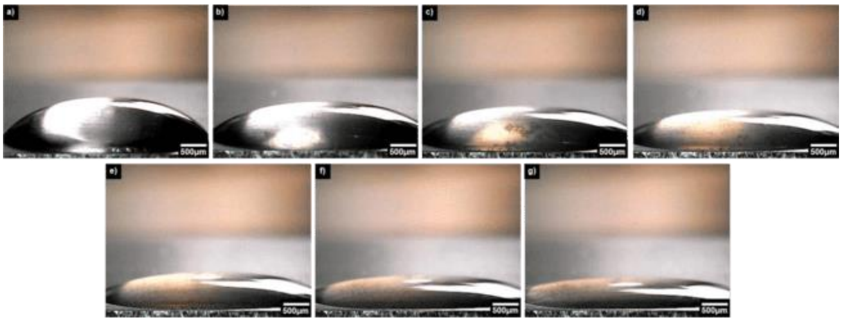


Fig. 17. Observation of 10 μL Na2SO4 Droplet at: a) the Beginning; b) 10 mins; c) 20 mins; d) 30 mins; e) 40 mins; f) 50 mins; and g) 60 mins.

- Droplet Volume of 20 µL

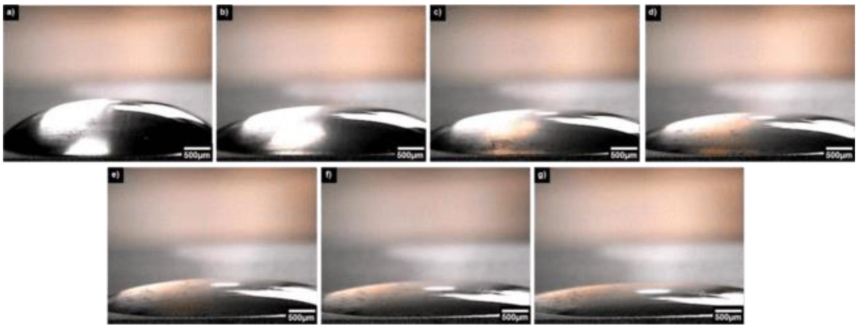


Fig. 18. Observation of 20 µL Na_2SO_4 Droplet at: a) the Beginning; b) 10 mins; c) 20 mins; d) 30 mins; e) 40 mins; f) 50 mins; and g) 60 mins.

- Droplet Volume of 50 µL

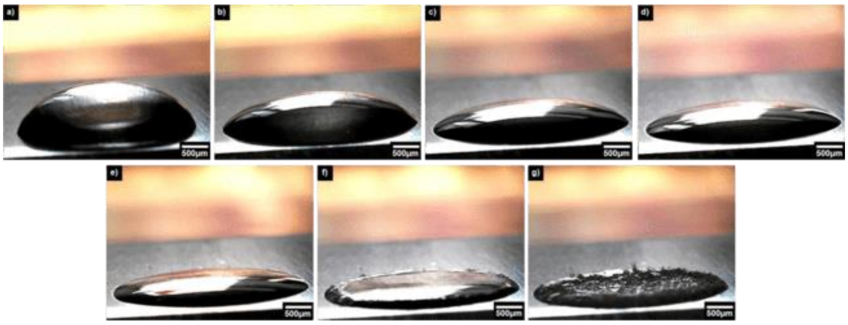


Fig. 19. Observation of 50 µL Na_2SO_4 Droplet at: a) the Beginning; b) 10 mins; c) 20 mins; d) 30 mins; e) 40 mins; f) 50 mins; and g) 60 mins.

3) *$NaNO_3$ Droplets*

- Droplet volume of 10 µL

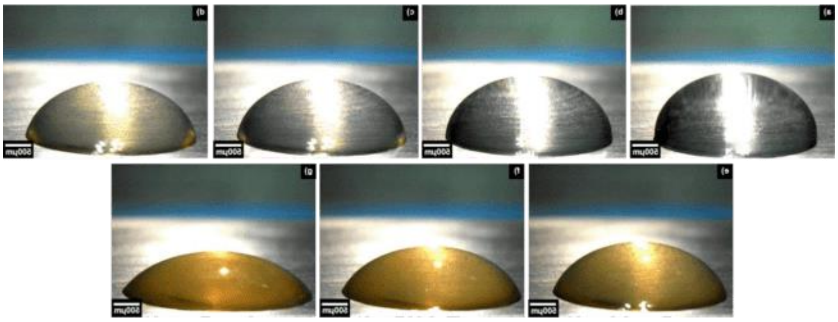


Fig. 20. Observation of 10 µL $NaNO_3$ Droplet at: a) the Beginning; b) 10

mins; c) 20 mins; d) 30 mins; e) 40 mins; f) 50 mins; and g) 60 mins.

- Droplet volume of 20 μL

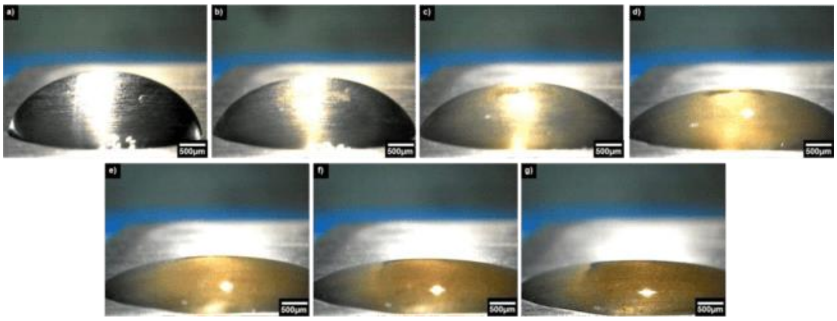


Fig. 21. Observation of 20 μL $NaNO_3$ Droplet at: a) the Beginning; b) 10 mins; c) 20 mins; d) 30 mins; e) 40 mins; f) 50 mins; and g) 60 mins.

- Droplet volume of 50 μL

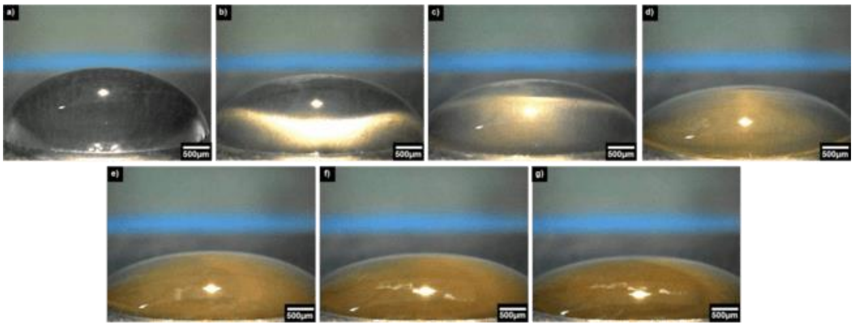


Fig. 22. Observation of 50 μL $NaNO_3$ Droplet at: a) the Beginning; b) 10 mins; c) 20 mins; d) 30 mins; e) 40 mins; f) 50 mins; and g) 60 mins.

4 Disclaimer

A corrosion product or rust can be identified using an optical microscope with a certain magnification if it hasthe following signs [17] [18]:

- The red-brown pattern on the metal surface.
- Has a different level of elevation with the surface around the hole or basin.
- In the area around the hole or basin, there is a red-brown pattern.

In this research, what can be obtained using only a USB Digital Microscope with 50–1600× magnification is a red-brown color pattern on the metal surface or test specimen. By maintaining the scope of the test from the beginning until the end of the observation, the USB Digital

Microscope cannot pay attention to a large area of steel which also reacts with droplets of a solution. Thus, the corrosion initiation time for each solution at differentdroplet volumes was taken while still fulfilling the requirements for the presence of a red-brown color pattern onthe metal surface. However, only in the specified test scope.

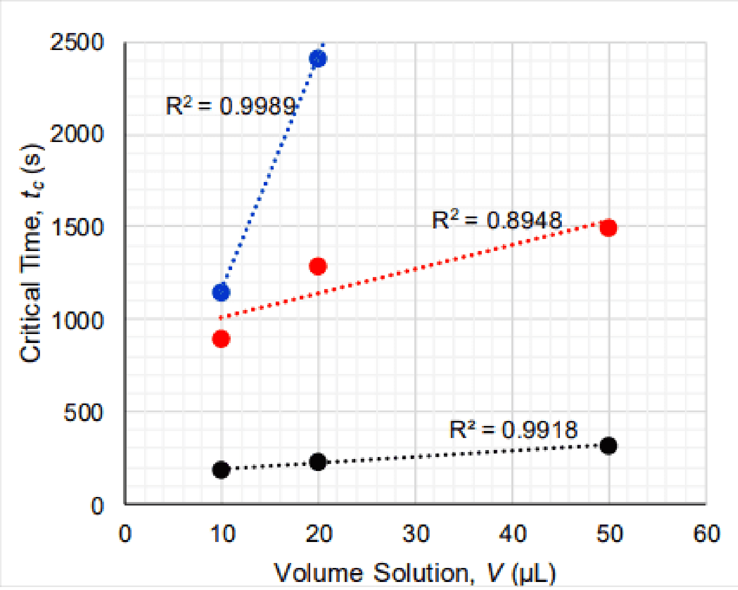


Fig. 23. The R^2 trendline of each NaCl solution critical time.

The determination of the critical time is taken from the tests that have been carried out on each droplet volume in3 different samples for each solution. Then, the corrosion initiation time of each sample is averaged and becomes the critical time which is the data result of this research. The uniformity of each critical time in each solution is maintained above 85%. Therefore, the test on a sample will be repeated if one of the samples has a different uniformity causing the trendline of the R^2 value to be lower than the predetermined number.

5 Conclusion

From the text above it could conclude that the effect of chloride, sulfate, and nitrate anions for pitting corrosionbehavior on ASTM A36 steel in the atmospheric environment as below:

1) Pitting corrosion could occur at the surface of ASTM A36 steel if it reacts directly with chloride, sulfateand nitrate solutions in an atmospheric environment. NaCl solution is the fastest in terms of initiating pitting corrosion on the ASTM A36 steel surface compared to Na_2SO_4 and $NaNO_3$ solutions.

2) Droplet volume affects the time required for the solution to initiate pitting corrosion on the steel surface,where the smaller size of the droplet will be faster to initiate the corrosion happen.

References

[1] Afandi YK, Arief IS, Amiadji A. analisa laju korosi pada pelat baja karbon dengan variasi ketebalan coating. Jurnal Teknik ITS. 2014;4(1).

[2] Podany P, Balcar M. Properties of low carbon steel with various microalloying additions after particular thermomechanical processing. Material Science and Technology. 2011:735-742.

[3] Illescas S, Fernandez J, Lorenzo JA, Soto MS. Study of the mechanical properties of low carbon content HSLA steels. Revista de Metalurgia. 2009;45(6):424-431.

[4] Roberge, R. Pierre. Handbook of Corrosion Engineer. New York: The McGraw-Hill; 2000.

[5] Jones, Denny A, Principles and Prevention of Corrosion, New York: Macmillan Publishing Company; 1992.

[6] Nasoetion R. Pemetaan tingkat korosifitas di Daerah DKI Jakarta. Majalah Metalurgi V. 2012:151-163.

[7] Adamson KG, Tawin DS. Corrosion, Volume I, Metal/Environment Reactions. In: Shreir LL, Jarman RA, Burnstein GT, editors. London: Butterworth-Heinemann; 1994.

[8] Trethewey KR, Chamberlain J. Korosi Untuk Mahasiswa Sains dan Rekayasa. Jakarta: Gramedia Pustaka; 1991.

[9] Kalpakjian S, Schmid SR. Manufacturing Engineering and Technology. 7th Edition. Sinagpire: Pearson; 2014.

[10] Pattireuw KJ, Rauf FA, Lumintang R. Analisis laju korosi pada baja karbon menggunakan air laut H2SO4. Jurnal Poros Teknik Mesin UNSRAT. 2013;2(1).

[11] ASTM International. Standard Specification for Carbon Structural Steel Designation: A 36/A 36/M- 05 [Internet]. ASTM International; 2005. Available from: https://www.academia.edu/33654528/Designation_A_36_A_36M_05_Standard_Specification_for_Carbon_Structural_Steel_1

[12] Raviola A, Farre AS, Schroh NT. Students understanding of molar concentration. Chemistry Education Research and Practice. 2021;22:486-497.

[13] Bouboukas G, Baunand A, Renon H. Oxidation of Fe (II) by oxygen in concentrated NaCl Solutions: Prediction of stirred gas-liquid reactor performance from homogeneous kinetic data. Hydrometallurgy. 1987;19:25-35.

[14] Mobin M, Hasan SK. Chemical interaction of Ferric Oxide with Sodium Sulfate at high temperature relevant to hot Corrosion. Journal of Materials and Environmental Science. 2012;3(1):109-116.

[15] Lohrengel MM, Kluppel I, Rosenkranz C, Bettermann H, Schultze JW. Microscopic investigations of electrochemical machining of Fe in NaNO3. Electrochimica Acta. 2003;48:3203-3211.

[16] Vasilenko GV. The effect of oxygen concentration on the corrosion of heat supply networks and heat exchangers. Thermal Engineering. 2007;54:156-158.

[17] Endo K, Suzuki M, Ohno H. Corrosion characteristic of ferric and austenitic stainless steels for dental magnetic attachment. Dental Material Journal. 2000;19:34-49.

[18] Xia HD, Song SZ, Behnamian. Detection of corrosion degradation using electrochemical noise (EN): Review of signal processing methods for identifying corrosion form. Corrosion Engineering, Science and Technology: The International Journal of Corrosion Processes and Corrosion Control. 2016;527-544.