Modification of Gunung Kidul Natural Zeolite and Its Application in the Corrosion Rate Reduction of Steel Plates in Acid Media

Mohammad Abdul Khafid¹, Aditya Pandu Wicaksono¹, Firstyananda Wahyu Andita², and Asifa Ihya Nurdina³

¹Department of Environmental Engineering, Faculty of Mineral Technology, Universitas Pembangunan Nasional Veteran Yogyakarta, DI. Yogyakarta, Indonesia
²Department of Chemical Engineering, Faculty of Industrial Engineering, Universitas Pembangunan Nasional Veteran Yogyakarta, DI Yogyakarta, Indonesia

*Corresponding author: abdulkhafid925@gmail.com

Abstract. The use of metals in the industry plays a very important role, where nearly 90% of industrial equipment comes from metallic materials. Corrosion is an electrochemical process between metals with its environment that can damage the metal quality. Gunung Kidul natural zeolite can be modified into a mixture of alkyd paint as a coating material to reduce the corrosion rate of steel plates effectively. In this research, the zeolite was activated by NaOH 1 N for 120 minutes. The zeolite was characterised using Surface Area Analyzer (SAA) and nitrogen adsorption analysis to investigate the surface area of zeolite by Brunauer-Emmet-Teller (BET) modelling. The lining was done by coating the steel plates by alkyd-zeolite paints and inserted into a 100 mL H₂SO₄ 1N, 2N, and 3N for 20 days. The results of this study showed that the corrosion rate of steel plate was 0.1374 miles/year (uncoated), 0.0407 miles/year (coated by alkyd paint), and 0.0095 miles/year (coated by alkyd paint-zeolite). Using activated zeolite as a mixture of alkyd paint is environmentally friendly and effective in lowering the corrosion rate of mild steel plates.

1. Introduction
The use of metal materials for industrial and infrastructure activities plays a very important role because metals are raw materials in infrastructure development, as well as in equipment for everyday needs. Some of the technical properties are owned by metals such as tensile strength, resistant to temperature, electrical and thermal conductivity [1]. However, steel is easily corroded and causes damage to material. Corrosion is a process of material destruction in the reaction to the chemical and electrochemical environment. Therefore, their resistance all depend on the corrosion resistance [2]. Degradation of steel or metal strength due to corrosion often occurs in the construction of concrete structures. Generally, the corrosion occurs to construction in areas with the condition of sour sulphate land such as swamp areas that are still affected by the tide of sea or coastal areas [3]. For an example of iron metal corrosion in moist air, the reaction process is as follows:

\[
\begin{align*}
\text{Anode} & : \ 2\text{Fe}(s) \rightarrow 2\text{Fe}^{2+}(aq) + 4e \\
\text{Cathode} & : \ O_2(g) + 4\text{H}^+(aq) + 4e \rightarrow 2\text{H}_2\text{O}(l) \\
\text{Redox} & : \ 2\text{Fe}(s) + O_2(g) + 4\text{H}^+(aq) \rightarrow 2\text{Fe}^{2+} + 2\text{H}_2\text{O}(l)
\end{align*}
\]
The methods of controlling corrosion in metals are metal coating, cathode protection, and addition. One of the common methods of repair to control corrosion is coating. There are two coating materials, namely liquid coating and concrete coating. The liquid coating is plating on the surface of the steel with chemicals, thus the steel can be protected from corrosion [4]. However, the use of these chemical compounds is expensive and quite dangerous for human beings and the environment. Hence, it needs environmentally friendly raw materials from natural resources that can lower the corrosion rate of steel plate. One of the quality compounds to reduce the corrosion rate of steel plate is zeolite [5].

Zeolite natural resources can be obtained in Indonesia, especially in West Java (District Bayah and Cipatuja), Central Java (District Wonosari, Gunung Kidul Regency, Yogyakarta), and East Java (Pacitan Regency) which has a zeolite reserve of more than two hundred million tonnes [6]. Zeolite is a mineral containing silicate aluminium compounds with the condition of a three-dementing skeleton structure formed by the tetrahedral composition of the \( \text{AlO}_4^{-}\) and the \( \text{SiO}_4^{+}\). Zeolite’s pores are filled by metal ions, dominated by alkali and alkali earth metals (Na, Ca, K, Mg, and Fe), and water molecules that can move freely in the cavity [7,8]. Zeolite appears as a corrosion-resistant material with porous and crystal coatings with uniform cross-section of 0.3 nm to 1.2 nm. Zeolite can be utilized as a catalyst and adsorbent in petrochemical and petroleum refining processes. Low silica zeolite has been used for many years as a hydrophilic coating material and antimicrobial for the industrial needs [8]. The process of cation and mixing exchange of alloyd paint, the permissible of zeolite solids are made homogeneous first through the process of physics with the grinding. Alkyd is a paint with a polyester base with a composition of ethane glycol, flax oil, and phthalate anhydride [9]. This paint dries through oxidative polymerization of oil so that it has a high oil content.

The process of enhancing the diffusion of reactants on catalysts and the additional mesoporous system is required in crystal micro pores. Thus, it is expected that molecules that have large size can enter into the pore system, to be processed and leave the pores system back [10]. The process of natural zeolite activation can be done chemically through addition of alkaline substance (NaOH), which aims to clean the surface of the zeolite pores, eliminating metal oxide as an impurity, and rearranging the location of atoms that can interchangeable. The activation of zeolite causes the occurrence of ion which causes increased surface area of zeolite due to impurities elimination that cover the pores of the zeolite. Increased surface area is expected to increase the ability of zeolite in the absorption process [11]. Zeolite is a very useful catalyst that demonstrates some important qualities that are better compared to amorphous catalysts. The amorphous catalysts are almost always made in powder form to provide a large surface area so that the number of catalytic sides is greater. The existence of the cavity in zeolite provides a very wide internal surface area so that it can hold 100 times more molecules than the amorphous catalysts with the same amount [12].

This research aims to determine the effect of activated zeolite addition in alkyd paint as a coating material on steel plates and study the corrosion rate of the plate in acid media. The corrosion rate MPY (miles per year) on the steel plate is calculated and discussed. The result is also compared with some samples to get optimum conditions of the coating process and corrosion rate.

2. Methods

2.1. Raw Material and Instrumentation
In this research, natural zeolite was obtained from Wonosari, Gunung Kidul Regency, Yogyakarta, Indonesia which has been separated through the 80-mesh sieve. The instruments used in this study were pH-meters (HI 9126), a Nabertherm oven, digital analytical balances (Matrix type Esj 210-4B), 80-mesh sieve, magnetic stirrer, desiccator, stopwatch, and Surface Area Analyzer (SAA) Quadrasorb Station 2 version 7.01. The chemicals used were \( \text{H}_2\text{SO}_4\), NaOH, alkyd paint, steel plates, and oil thinner.
2.2. Zeolite Activation
Firstly, zeolite was cleaned from other inorganic substances (Na, K, Ca, Mg and Fe), then grinded to obtain finer zeolite powder. Next, the zeolite powder was passed on an 80-mesh. The powder passed the sieve was used in the next step. The activation process was done by soaking 250 grams of zeolite in a NaOH 1 N for 2 hours at room temperature. The zeolite was then washed using distilled water until the color of the solution changes to almost clear. After that, the zeolite was filtered off, dried at room temperature, and then heated in the oven at 180°C until a constant mass was gained [13].

2.3. Zeolite Characterization
To determine the surface area of zeolite, Surface Analyzer (SAA) with Quadrasorb Station 2 version 7.01 was used. Firstly, the gas-absorbed (degassing) gases was removed by heating in a vacuum condition at 300 °C for 6 hours. Phase analysis of the isothermal adsorption was carried out on two samples (activated and inactivated zeolites) using nitrogen gas for 5 hours and an outgases temperature of 300 °C. Based on a partial pressure nitrogen, the adsorption test was done in the P/Po range of 0.01 – 0.30. The surface area of the activated zeolite was analysed by Brunauer-Emmet-Teller (BET) modelling [14].

2.4. Corrosion Testing
The steel plate was firstly weighted, then it was immersed in alkyd paint (four samples). Next, zeolite (50, 60, and 70 grams) was mixed with the paint alkyd and stirred until homogenous. Thus, there are five plate samples with different sample conditions: steel plate that was uncoated, steel plate that was coated with alkyd paint, and steel plates that were coated with alkyd paints + zeolite (50, 60, 70 grams). The five samples of steel plates were immersed in the 100 mL H₂SO₄ (1N, 2N, 3N) for 20 days. Data collection of each sample was collected three times. After the immersion, the samples were dried first and then weighed to determine the mass reduction of steel plates (every 5 day to up to 20 days). Steel plate mass reduction results were used to calculate the rate of corrosion. The corrosion rate was evaluated using the method of weight loss of steel plate as shown in Equation (2), in which W is the difference in metal weight or weight loss (g), D is density (g/cm³), A is the surface area of rusty metal (inch²) and T is corrosion time (Hour) [15].

\[ \text{M.P.Y} = \frac{(534.W)}{(D.A.T)} \]  
\[ (2) \]

3. Result and Discussion

3.1. SAA Results (Surface Area Analyzer)
To determine the surface area of zeolite specifically, a Surface Area Analyzer (SAA) with Branauer-Emmett-Teller (BET) modelling was applied. This method was done by using adsorption of N₂ gas to determine the surface area, the pores volume, and the pores diameter of a zeolite. This technique was done by measuring the amount of gas that was given by a solid in the gas pressure variation in an
isotherm state. The zeolite isotherm adsorption profile, treated with alkaline treatment and before alkaline treatment, is shown in Figure 1, respectively.

Based on Figure 1, the amount of nitrogen adsorption volumes on the activated and inactivated zeolite are considerably fluctuated and the relative pressure (P/PO), which tends to be low with the vulnerable value, is slowly increases in the middle and rapidly rises again at the pressure (P/PO) value of 0.01-0.30. The first increment process is caused by an adsorbed gas molecules interacting with an area that is energized on the surface of the solids. The filling of nitrogen gas had been formed into monolayer coating. The result of the isotherm data of these two samples is the type 1 isotherm, which is a type of physio-sorption of gas in the microporous solids and isothermal chemical adsorption.

Figure 1. Graph of isotherm adsorption, a) activated zeolite and b) un-activated zeolite.
BET test results indicate that the inactivated zeolite has relatively different pore volume and pressure than that of the activated zeolite. Figures 2 shows that the activated zeolite has a greater pressure with fewer pore volumes than that of inactivated zeolite. The result of calculation by BET method resulting in surface area values of 235.484 m$^2$/g (activated zeolite) and 68.279 m$^2$/g (inactivated zeolite). Activated zeolite has a larger surface area compared to the inactivated zeolite. This is due to the physical–chemical process of cation exchange and eliminating impurities, both organic and inorganic in the Gunung Kidul natural zeolite, resulting in pores enlargement and expanding surfaces. The internal surface area of zeolite can reach tens even hundreds of times greater than the surface of the exterior. This large surface area is very beneficial to the utilization of zeolite either as an adsorbent or as a heterogeneous catalyst. This result also support the fact that the alkaline treatment of Gunung Kidul natural zeolite can increase the surface area of zeolite which eventually increasing the capacity of ion exchanges and the absorption of zeolite [16].

**Figure 2.** Graph multi-point BET plots, a) activated zeolite and b) inactivated zeolite.

3.2. Results of Corrosion rate testing
The results of the corrosion rate calculation using equations (2) for all samples shows varying results. The uncoated sample indicate that on the day five of corrosion test in H$_2$SO$_4$ 3N, the corrosion rate of 0.1784 miles/years reaches the highest. Then it went much higher on day twenty with a value of 0.2082 miles/year. In general, there is a periodic decline every five days of calculation regarding the corrosion
rate. The value of the corrosion rate is influenced by the condition of the steel plate media, the acid media increases the corrosion rates. Meanwhile, the corrosion rates on the steel plate coated with alkyd paint in H₂SO₄ 3N shows a smaller value of 0.0645 miles/years. This is due to the presence of a coating of alkyd paint resin as a corrosion inhibitor that has protection or barrier properties. The corrosion rate results of uncoated and coated steel plates are shown in Figure 3.

![Figure 3](image)

**Figure 3.** Graph of corrosion rate on steel plates a) uncoated and b) coated of alkyd paint.

| Day | Corrosion Rate (Uncoated) | Corrosion Rate (MPY) | Corrosion Rate (MPY) |
|-----|---------------------------|----------------------|----------------------|
|     | 1N                        | 2N                   | 3N                   | 1N | 2N | 3N |
| 5   | 0.0938                    | 0.1531               | 0.1784               | 0.0138 | 0.0121 | 0.0265 |
| 10  | 0.0289                    | 0.0063               | 0.0234               | 0.0182 | 0.0124 | 0.0351 |
| 15  | 0.0118                    | 0.0026               | 0.0040               | 0.0055 | 0.0047 | 0.0026 |
| 20  | 0.0029                    | 0.0016               | 0.0024               | 0.0032 | 0.0026 | 0.0002 |

The corrosion rate shows smaller value for steel plates coated by alkyd + zeolite. The steel plate in H₂SO₄ 1N shows the lowest corrosion rate of 0.0086 miles/year with addition of 70 g zeolite, whereas steel plate in H₂SO₄ 2N shows the lowest corrosion rate of 0.0011 miles/year with addition of 60 g zeolite. The lowest corrosion rate in a higher acidity environment (H₂SO₄ 3N) is 0.0018 miles/year, obtained by addition of 70 g zeolite. These results indicated that the optimum inhibition can be achieved in the immersion period from day 1 to day 10 using a combination of alkyd paint and zeolite powder of 60 - 70 grams. Mass loss suggests that the bonding between the zeolite and alkyd paints can prevent direct contact with the corrosive environment (H₂SO₄), thus the steel plate can have more resistance to corrosion [17].

Based on Figure 4, the effect of activated zeolite addition against inhibitors efficiency in the corrosive medium is noticeable from reduction in corrosion rate occurred in day 5. The efficiency percentage of was increased by almost 90% by addition of 70 g zeolite. However, in the addition of 50 g zeolites, the efficiency value tends to decrease. The corrosion test was done three times to minimize data errors and get an overall average value of each sample tested for obtaining valid data. The effect of corrosion rate decreasing for steel plates is significantly influenced by voids and cracks in the protective coating of
zeolite [18]. The process of zeolite activation aims to minimize the presence of impurities and form a better homogeneous and compact layer, which is a way to obtain an efficient and effective corrosion-resistant coating, structures, and the morphology of the Gunung Kidul natural zeolite. The process of zeolite activation has the ability in formation of zeolite coating and the growth of zeolite crystal. The results show that the large surface area of zeolite causes smaller zeolite size, hence it becomes more homogeneous. This eventually affects the increased barrier layer to corrosion. The rate of corrosion in the medium with the addition of activated zeolite as a whole tends to be slower, this is due to zeolite and cation exchanger capability. The H$_2$SO$_4$ solution is a powerful cation exchange, in which Na$^+$ cation in zeolite can be replaced by the H$^+$ [19].

![Graph of corrosion rate on steel plates](image)

**Figure 4.** Graph of corrosion rate on steel plates in a) H$_2$SO$_4$ 1N, b) H$_2$SO$_4$ 2N, and c) H$_2$SO$_4$ 3N.

### 4. Conclusion

The modification of Gunung Kidul natural zeolite by NaOH can be applied as a corrosion inhibitor. Through a surface area analysis with BET modelling, the zeolite has a surface area value of 235.484 m$^2$/g (activated zeolite) and 68.279 m$^2$/g (inactivated zeolite). The mixture of 70 g zeolite with 150 mL alkyd paints in 20-day immersion of 100 mL H$_2$SO$_4$ (1N, 2N, 3N) produces the suitable composition in lowering the corrosion rate with a total value of 0.0086 miles/year, 0.0285 miles/year, and 0.0511 miles/year, respectively.
Acknowledgments
This research was supported by the Chemical Engineering Laboratory, Faculty of Industrial Engineering and Geotechnical Environmental Laboratory, Department of Environmental Faculty of Mineral Technology, Universitas Pembangunan Nasional “Veteran” Yogyakarta.

References
[1] McCafferty E 2010 Introduction to Corrosion Science (New York: Springer Science+Business Media) p 13
[2] Jones D A 1996 Principles and Prevention of Corrosion Second Edition (United State of America: Prentice Hall Inc) p 6
[3] Shukla H S, Halder N and Udaybhanu G 2012 E-Journal of Chemistry 9 149–60
[4] P Marcus and J Oudar 1995 Corrosion Mechanisms in Theory and Practice (New York: Marcel Dekker Inc) p 261-265
[5] Haryono G, Sugiaroto B, Farid H, and Tanoto Y 2010 Proc. Seminar Nasional Teknik Kimia “Kejuangaan” 5 maret 2010 (Yogyakarta) Vol 1 (Yogyakarta: Teknik Kimia, Universitas Pembangunan Nasional “Veteran” Yogyakarta)
[6] Schneider K 1974 Use of Local Minerals in the Treatment of Radioactive Waste Technical Report Series No 136 (Vienna: IAEA) p 11-13
[7] Arryanto Y, and Amini S, and Lu MGQ 2002 J. Zeolit Indones (Journal Indones. Zeolites) Chapter 1 pp 1–4.
[8] Breck D W 1974 Zeolite Molecular Sieves Structure Chemistry and Use (New York: John Wiley and Sons Inc) p 25
[9] Anton J Hartomo 1992 Paint Coating on Metals (Bandung: Ganesa) p 30
[10] Othmer K 1981 Encyclopedia of Chemical Technology (3th ed) vol 15 (New York: John Wiley and Sons Inc)
[11] Trisunaryanti W, Triyono, Rizki C, Saptoadi H, Zainal Z A, Syamsiro M, Yoshikawa K 2013 IOSR Journal of Applied Chemistry 3 29–34
[12] Smith J V 1988 Chemical Reviews 88 149–82
[13] Rosyid M, Nawangsih E and Dewita 2012 Proc. Seminar Penelitian dan Pengelolaan Perangkat Nuklir ISSN 1410-8178
[14] Wei Z, Xia T, Liu M, Cao Q, Xu Y, Zhu K and Zhu X 2015 Frontiers of Chemical Science and Engineering 9 450–60
[15] S K Chowdhary 2001 J. Of Metallurgy and material science 43 265
[16] Muhriz M A, Subagio and Pradoyo 2011 J. Sains dan Matematika 19 11-17
[17] Ertan A and Çakıcıoğlu-Özkan F 2005 Adsorption 11 151–6
[18] Mitr A, Wang Z, Cao T, Wang H, Huang L and Yan Y 2002 Journal of The Electrochemical Society 149
[19] Dyer A 1988 An Introduction to Zeolite Molecular Sieves (Chichester: John Wiley and Sons Ltd)