The Use of Geo-Nano TiO2/SiO2 Photocatalyst-Based Self-Cleaning Material as a Coating for Tanker Ship Deck Line Pipe Corrosion Prevention

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Abstract. The use of geo-nano TiO2/SiO2 self-cleaning material as a coating prototype for deck line pipe to stop corrosion on tanker ships was successfully studied in this study. The objective was to produce a synthetic material that would be able to clean itself and be applied to tanker ship deck line pipes. The self-cleaning materials were created by changing the amount of Nano TiO2/SiO2 added in three distinct compositions of a geopolymer composite based on metakaolin. Applying the geopolymer paste to the surface of stainless-steel pipes was part of the composition testing procedure. The sample was prepared for testing after the proper composition was determined. By calculating the sample's contact angle, the self-cleaning qualities were examined; the average result was 57.3. These findings suggest that the sample has self-cleaning qualities even though it is still hydrophilic, allowing liquids to moisten its surface. Field Emission Scanning Electron Microscopes—Energy Dispersive Spectroscopy (FESEM-EDS) and XRD were used to characterize the materials' microstructure and test for crystallinity. Tests were done on the samples both before and after they were submerged in seawater. A homogenous connection between the geopolymer paste and the nanoTiO2 and nanoSiO2 aggregates was demonstrated by the favorable results of the FESEM study. Following immersion in seawater, the sample's surface morphology showed evidence of peeling as a result of seawater damage. A new Cl peak was found in the XRD and EDS diffractogram analysis, which suggested that seawater (NaCl) and geopolymer were reacting. Furthermore, the soaked sample's EDS test revealed that the composite surface did not produce the corrosive FeCl2 crystal phase. This indicates that the production of corrosion material (FeCl2) on the surface of stainless steel may be inhibited by Nano TiO2, a photocatalytic anti-corrosion material.

Keywords: Corrosion, FESEM, Geopolymer, Nano TiO2/SiO2, Self-cleaning.

1 Introduction

Sea transportation is rapidly advancing, as seawater covers more than 70 percent of the Earth's surface (Saptoyo, 2021). The maritime sector serves as a crucial center for ship

R. Mahmud et al. (eds.), *Proceedings of the 3rd International Conference and Maritime Development (ICMaD 2024)*, Advances in Engineering Research 255,
https://doi.org/10.2991/978-94-6463-628-4_10

However, this activity is accompanied by various challenges and consequences, such as material wear, corrosion, and damage to the ship's structure. Corrosion, in particular, poses a significant threat, as it can lead to structural weakening that compromises the safety of the vessel and its crew.

Ship construction predominantly utilizes steel for the hull, walls, and piping systems (Bayuseno, 2009). Steel is inherently unstable and tends to react with its environment, forming stable oxide or carbonate compounds. As ships operate at sea, corrosion becomes an inevitable issue. The iron content in steel is particularly prone to oxidation when exposed to environmental elements, which can diminish material quality and shorten service life. A specific concern is the frequent mechanical damage to cargo hoses on vessels.

According to Bayuseno (2009), effective corrosion prevention can be achieved through the application of specialized anti-corrosion coatings. Numerous studies have focused on enhancing ship materials to combat corrosion. Modern ship construction involves coating various components, such as the hull, pipes, floors, and roofs, with special paints, lacquers, varnishes, and steel coatings. Research findings indicate that the corrosion rate of coated materials is significantly lower than that of uncoated materials. However, limitations still exist; for instance, the durability of paint is finite, necessitating periodic maintenance to ensure ongoing protection.

The demand for various structural and non-structural applications in industry is on the rise. Advanced materials are characterized by their lightweight nature, durability, fire and heat resistance, chemical resistance, saltwater durability, corrosion resistance, and ease of production. The development of these advanced materials has progressed to include intelligent or smart materials, which possess capabilities such as self-cleaning, self-healing, and self-sensing.

Typically, advanced materials are composite, comprising several base materials that exhibit different physical and chemical properties. Each composite material serves a specific purpose and possesses a range of functionalities that can be mechanical, optical, medical, electrical, magnetic, or energy-related. Materials like this are known as functional composites, namely materials that are the intersection of physics, chemistry, biology, materials science, and technology both in terms of engineering and application (Park et al., 2017; Yaumi et al., 2017).

Composite materials that have these properties are geopolymers. Na-Poly (siloxy-sialate) type geopolymers are produced from kaolin (metakaolin) base materials with high compressive strength, namely from 60 to 90 MPa after 28 days (Subaer & Riessen, 2017). Geopolymers are inorganic polymers synthesized from abundant, readily available, and cost-effective aluminosilicate minerals. They exhibit remarkable properties, including mechanical strength, heat and fire resistance, anti-biofilm characteristics, and environmental friendliness. Recently, geopolymer coatings have emerged as one of the most widely studied and adaptable coating systems designed to combat corrosion in low-carbon and structural steel (Singh Tomar et al., 2023). To improve the capabilities of geopolymers, aggregates in the form of nano TiO2 and nano SiO2 are added. Both materials have been recognized as one of the best materials as self-cleaning materials so that they can improve the capabilities of the material (Banerjee et al., 2015; Farahmandjou & Khalili, 2014; Padmanabhan & John, 2020;

Rosales et al., 2021; Sanalkumar & Yang, 2021). Previous studies have also revealed that TiO_2 has been proven to be an anti-biofouling material (de Oliveira et al., 2020) and anti-corrosion (Rosales et al., 2021), so it is very suitable for use in maritime applications.

2 Experimental

SiO_2 nanopowders (SiO_2 NPs) are obtained from burned silica glue, and TiO_2 NPs are obtained from precipitated TiO_2 powder. The self-cleaning materials of Geo-Nano TiO_2/SiO_2 were produced with a chemical reaction by alkaline solution. It was produced from metakaolin as raw materials and TiO_2/SiO_2 NPs as aggregate. Geopolymer paste were initially synthesized in 3 different compositions, keeping the mass of metakaolin constant with varying the mass of TiO_2 NPs, namely 0 g, 1 g, 2 g, and SiO_2 NPs constant with 0.1 g. The mixture of geopolymer samples was put in the molds and cured at 70oC for 2 hours. This process is repeated until the best composition is obtained. After the best composition is obtained, the geopolymer paste is applied as a coating material by painting it on stainless steel plates and pipes for testing.

The crystal structure and phase of the samples were measured using X-ray diffraction (XRD) with Cu Kα radiation in the range of 2θ 10o-70o. The XRD patterns were analyzed by using powder diffraction analysis (PDXL2) software. Field Emission Scanning Electron Microscopy (FESEM) thoroughly investigated the samples' surface morphology. Further comprehensive testing was carried out to determine the self-cleaning material properties of Geo-nano TiO_2/SiO_2, namely contact angle testing and immersion in seawater for 14 days.

3 Result And Discussion

There are two categories of basic principles of self-cleaning materials, namely, hydrophilic and hydrophobic properties (Sendner et al., 2009). The main principle of self-cleaning is to utilize the hydrophilic ability of TiO_2 to form a hydroxyl layer on the surface coated with a catalyst (Sari & Astuti, 2013). That way, the dirt that comes does not have direct contact or stick to the surface of the self-cleaning material. SiO_2 is hydrophobic and can also be used as a self-cleaning material. In recent years, the development of materials with coatings that function to clean themselves with anti-reflective, anti-fouling, and anti-fog properties has increased.

In this study, geopolymer pastes with varying compositions were applied to the surface of stainless steel plates to see the adhesion and rejection between the plate and the paste (Figure 1). After 24 hours, observations were made, and one of the best compositions was obtained by adding 1 g of nano TiO_2 and 0.1 g of nano SiO_2 (Table 1). The crystal structure and phase composition of the Geo-Nano TiO_2/SiO_2-based self-cleaning material can be determined using X-ray diffraction (XRD). The XRD results are in the form of a diffractogram (graph). Sharp peaks indicate the crystalline phase, while broad peaks indicate that the sample is in the amorphous phase. The XRD graph was analyzed using the Highscore Plus application to determine the phase composition of the sample. Figure 2 shows the diffractogram of metakaolin, nanoTiO2, and nanoSiO2, which are the basic materials used in this study. It can be seen from the graph that metakaolin and nanoSiO2 show an amorphous phase characterized by a lack of sharp peaks. In metakaolin, two peaks represent the Si and Al peaks, which are the dominant phases. This material is one of the base materials for making geopolymers. The nanoTiO2 graph shows sharp peaks, especially at an angle of 2θ 25.34°. That peak indicates that nanoTiO2 is in the crystalline phase.

Fig. 1. The coating process on stainless steel pipes as a prototype.

Table 1. Material composition for synthesizing self-cleaning of geo-nano TiO2/SiO2.

materials	mass (g)
Metakaolin	30
Sodium silikat	24
NaOH	3
H2O	9
Nano TiO2	1
Nano SiO2	0.1

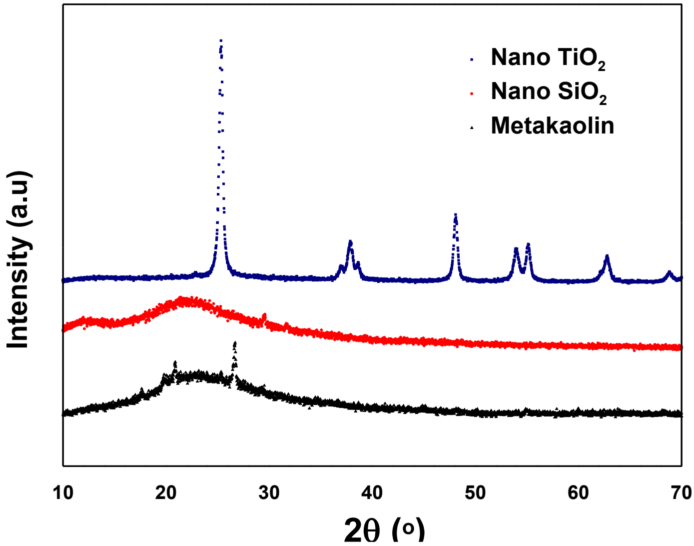

Fig. 2. XRD diffractogram of Metakaolin, nano TiO2, Nano SiO2

The samples were synthesized using the optimal composition for various tests, including saltwater resistance testing on uncoated and coated stainless steel using geoTiO2/SiO2. Data analysis was performed using the HighScore Plus application, yielding the composition distribution of both samples before and after immersion in seawater (Figure 3). The results are summarized in Tables 2 and 3.

XRD diffractogram analysis revealed a peak shift between the samples before and following seawater immersion. Specifically, for the sample after seawater immersion, new peaks appeared at angles of 2θ 19.84° and 38.66°. These peaks correspond to (Si5Cl12) and (SiCl4), indicating a reaction between the geopolymer material and seawater. The results were derived from qualitative analysis utilizing the Relative Intensity Ratio (RIR) method in the HighScore Plus application. Figure 3 provides a detailed comparison of the XRD diffractogram for the self-cleaning samples before and after a 14-day immersion in saltwater.

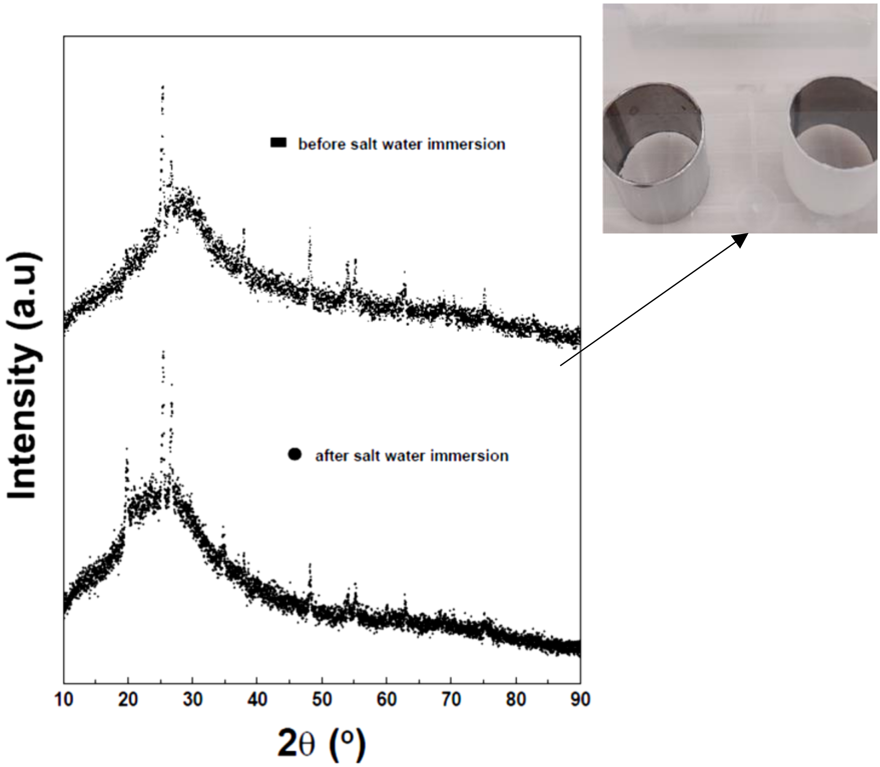

Fig. 3. XRD diffractogram of self-cleaning material before and after salt water immersion.

Table 2. Composition of self-cleaning material phase before salt water immersion.

Phase Name	Formula	Score
Silicon Oxide	$Si\ O_2$	10
Sodium Aluminum Silicate Hydrate	$Na_{88}\ Al_{88}\ Si_{104}\ O_{384}\ (H_2\ O)_{220}$	2
Quartz	$Si_{3.00}\ O_{6.00}$	1
Titanium Oxide	$Ti\ O_2$	60

Table 3. Composition of self-cleaning material phase after salt water immersion.

Phase Name	Formula	Score
SiO_2	$Si_{16.00}\ O_{32.00}$	7
Sodium Hydrogen Aluminum Silicate	$Na_{0.5}\ H_{0.5}\ (\ Al\ Si_2\ O_6\ )$	9
Quartz low	$Si_{6.00}\ O_{6.00}$	23
Titanium Oxide	TiO_2	53
(Si5 Cl12) (Si Cl4)	$Cl_{128.00}\ Si_{48.00}$	4

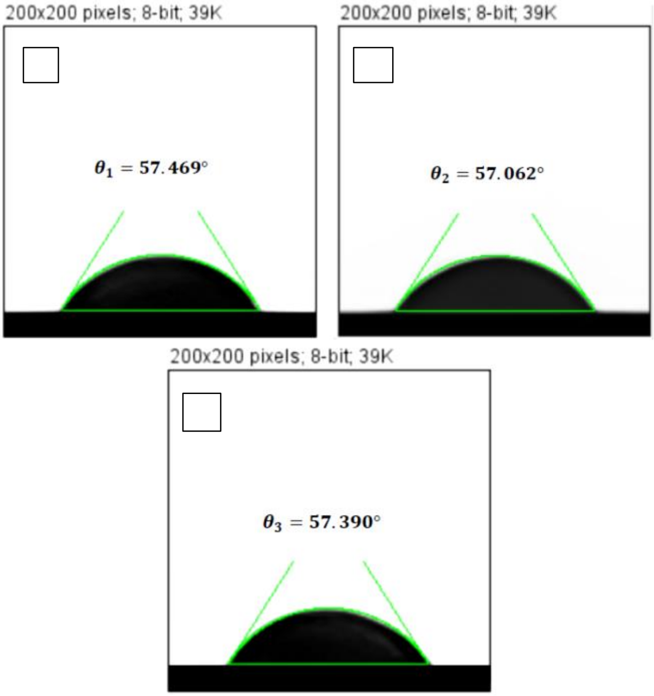

Fig. 4. The contact angle test results of self-cleaning of Geo-TiO2/SiO2 materials.

Table 4. Percentage of contact angle value of self-cleaning material.

θ	σ
57.469	0.162
57.062	0.245
57.390	0.083
θavg	**σmax**
57.307	0.245

Contact angle testing was conducted on samples with the same composition as those used in the seawater immersion tests. The purpose of measuring the contact angle is to assess the surface properties of the test material, determining whether it is hydrophobic or hydrophilic. The results of the contact angle test, along with the percentage of the contact angle values obtained in this study, are presented in Figure 4 and summarized in Table 4.

The contact angle tests yielded significant results. In all three tests, the contact angle values exceeded 57°. These findings indicate that the nano TiO2/SiO2 material falls within the category of hydrophilic self-cleaning materials. This classification is supported by previous research indicating that materials with a contact angle between 10° and 90° are considered hydrophilic self-cleaning materials (Padmanabhan & John, 2020; Banerjee et al., 2015). Therefore, this study demonstrates the capability of TiO2 as a hydrophilic self-cleaning material, while the addition of SiO2 serves as a filler to close the pores and enhance the contact angle of the geopolymer.

The morphology of the samples was analyzed using a Field Emission Scanning Electron Microscope (FE-SEM) tool. The FE-SEM image taken was a sample that had been immersed in salt water for 14 days. The images were analyzed at 2000x magnification using the BSE (Back Scattered Electron) sensor shown in Figure 5 and Figure 6. Figure 5 shows the microstructure of geo-nano TiO2/SiO2 without salt water immersion. The microstructure of TiO2/SiO2 nano-geopolymer shows that the geopolymer bond with TiO2 nano and SiO2 nano aggregates is well mixed and looks homogeneous. The FESEM image shows cracks on the surface of the sample. This is due to the effect of heating or curing the sample. Figure 6 shows the microstructure of TiO2/SiO2 nano-geopolymer that has been immersed in salt water for 14 days. It can be seen that the morphology of the sample shows peeling of material on the surface due to seawater attack. This shows good results, as evidenced by the sample's EDS and XRD analyses before and after seawater immersion.

The difference in weight percentage (wt%) composition of the samples before and after seawater immersion can be analyzed by examining the EDS graph. The post-immersion samples of geo-nano TiO2/SiO2 demonstrated successful binding of Cl from seawater, as evidenced by a Cl distribution of 0.8 wt% (Figures 7 and 8). In this study, nanoTiO2 not only serves as a self-cleaning material but also provides resistance against NaCl attacks from seawater.

EDS testing of samples soaked for 14 days revealed no presence of the corrosive FeCl2 crystal phase on the composite surface. These findings suggest that nanoTiO2 acts as an anti-corrosion photocatalytic material, effectively preventing the formation of corrosion products (FeCl2) on the stainless steel surface. The incorporation of nanoSiO2 is intended to enhance the hydrophobic properties of the material while serving as a filler, which helps inhibit seawater ingress into the geopolymer pores and increases the contact angle of the material. This enhancement contributes to the ability of geopolymer ceramics to reduce the rate of corrosion in tanker deck lines.

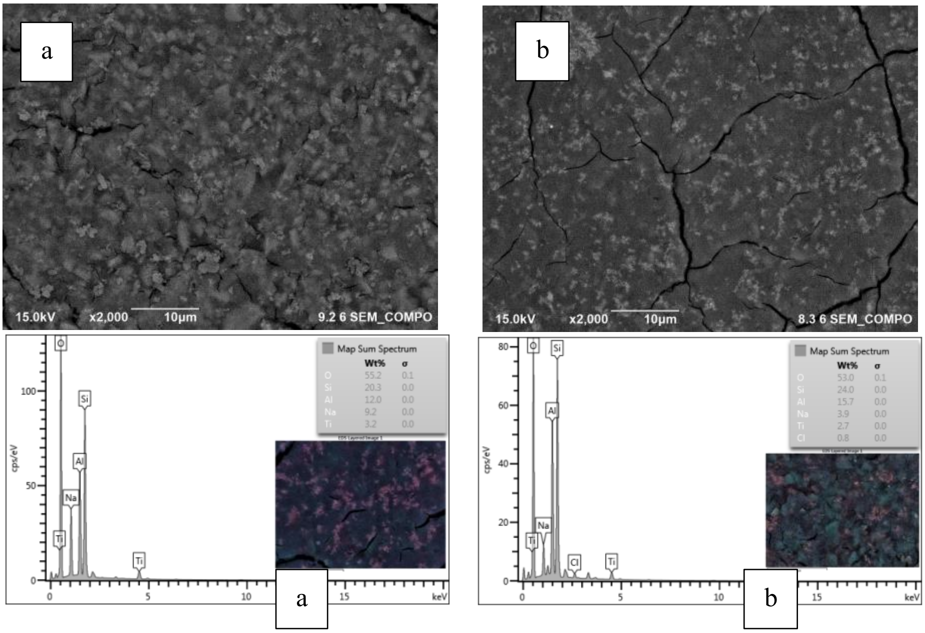

Fig. 5. EDS images of self-cleaning geo-nano TiO2/SiO2 before and after salt water immersion

4 Conclusion

Geopolymers are synthesized from metakaolin base materials activated by an alkali solution. The addition of 1 g of Nano TiO2 and 0.1 g of nano SiO2 into the geopolymer matrix was successfully carried out, leading to the formation of a geo-nano TiO2/SiO2. The structure of the geo-nano TiO2/SiO2 was obtained based on the results of X-ray diffraction (XRD) and Field Emission Scanning Electron Microscopes (FE-SEM) characterization that had been carried out. The results of the XRD characterization showed an amorphous phase with peaks indicating the presence of TiO2 and SiO2 with a crystalline phase in the geopolymer. The morphological structure of the geo-nano TiO2/SiO2 showed that the samples that had been immersed in seawater showed peeling due to NaCl attack; based on EDS analysis, it was obtained that the samples that had been immersed in seawater for 14 days bound the Cl element from the salt water. The absence of corrosive FeCl2 crystal phases on the composite surface indicates that Nano TiO2, as an anti-corrosion photocatalytic material, can prevent the formation of corrosion (FeCl2) on the stainless steel surface. Contact angle analysis was also conducted to identify whether the TiO2/SiO2 nano-geopolymer sample was hydrophobic or hydrophilic. Based on the tests carried out three times, the average contact angle value of the sample was at θavg 57.31 with σmax 0.24. These data indicate that the sample in this study has behaved as a self-cleaning hydrophilic material, showing great potential for future applications in materials science and engineering.

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