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Study of Polyaniline/Silicon Dioxide Based Coating on Carbon Steel in Artificial Geothermal Brine

Gabriela Aristia, Le Quynh Hoa, Ralph Bäßler

Bundesanstalt für Materialforschung und -prüfung (BAM)

Unter den Eichen 87, 12205 Berlin, Germany

gabriela.aristia@bam.de, le.quynh-hoa@bam.de, ralph.baessler@bam.de

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ABSTRACT

Geothermal brines are corrosive in nature because of their salt contents and high temperatures. Therefore, they pose a major challenge to geothermal power-plants, which are mostly built of low alloyed steels, e.g., carbon steel. Carbon steel is susceptible to uniform and localized corrosion when exposed to geothermal brines having acidic-saline properties. To overcome this limitation, geothermal power plants should be built by either high alloyed materials or by integrating protection systems on carbon steel, such as coatings and inhibitors. We studied a coating system containing polyaniline/silicon dioxide basing on locally available resources that provides protection against corrosion of carbon steel and enhance the thermal resistance in geothermal environments. Here, exposure and electrochemical tests of coated carbon steels were performed in an artificial geothermal brine. The solution had a pH of 4, with the composition of 1,500 mg/L of chlorides, which is based on the chemical analysis of geothermal brine found in Sibayak, Indonesia. All exposure tests were conducted using autoclaves at 150 °C with a total pressure of 1 MPa, which was performed for up to six months to evaluate the durability of the coating system. Post-experimental analyses were performed by assessing the surface of specimens using optical and electron microscopes. On the other hand, electrochemical tests were performed for seven days at 25 °C and 150 °C to investigate the kinetics of electrochemical reactions by measuring open circuit potential and electrochemical impedance spectra. Experimental results showed the corrosion resistance of PANI/SiO_2 composite coatings, where polyaniline and SiO_2 play their roles as stabilizers.

1. INTRODUCTION

Geothermal energy is a clean and renewable energy that can be applied to reduce the consumption of fossil fuel (Stober and Bucher, 2013). In terms of installed power generation capacity from geothermal resources, Indonesia was reported to be the second largest producer in the world reaching 1,924.5 MW by the end of 2018 (Richter, 2018). This achievement is however still accounting for only 11 % of the existing preserved energy in the country, with a possibility of further foreseeable developments in the future. Most of geothermal wells in Indonesia are located close to volcanic regions. Among them there are geothermal wells in Sibayak (North Sumatera, Indonesia), located around young stratovolcanoes which are operating with temperatures up to 310 °C at the bottom of the well (Hochstein and Sudarman, 2015, Atmojo et al., 2000).

To produce geothermal energy, the hot geothermal fluid is extracted from a geothermal well. This process requires a suitable and reliable infrastructure which is built of different materials, e.g. carbon steel, stainless steel, and titanium. One major problem which encounters in building the geothermal power plant is corrosion due to the interaction between materials and the geothermal brines. In general, geothermal brines might contain a wide variety of salts with varying pH values depending on the location of the well. The unique physicochemical characteristics of a geothermal brine leads to different corrosivity levels of brine, which then constrain the choice of suitable materials (Nogara and Zarrouk, 2018). In order to overcome this challenge, geothermal power plants either use high alloyed materials, such as Ni-based alloy or titanium (Iberl et al., 2015), or use corrosion protection strategies on carbon steel, such as coatings and inhibitors (Reeber, 1980, Sugama et al., 2000). Carbon steel is widely used for infrastructural parts of geothermal powerplants, such as pipelines and heat exchangers, because it has a low production cost compared to other materials. Carbon steel is however susceptible to uniform and pitting corrosion when exposed to the geothermal brine, especially in the acidic-saline brine (Keserović and Bäßler, 2015), which necessitate either the use of expensive high-alloyed materials or the development of a cost efficient coating system to protect carbon steel in such environment.

Among all the available coating, organic coating is the most practical and versatile option, which also offers a reasonable cost (Munger and Vincent, 2014). Intrinsically conducting polymer (ICP) is often used as a pigment in coating systems to provide anticorrosion properties, because of its interesting reduction-oxidation properties (Wallace et al., 2008, Inzelt, 2012). In the investigated system, polyaniline as one of the ICPs was applied by dispersing the particles in a non-conducting polymeric matrix. Polyaniline has three different oxidation states, i.e. leucoemeraldine (fully reduced), emeraldine (half oxidized), and pernigraniline (fully oxidized). In this research, polyaniline particles have been synthesized chemically in phosphoric acid medium, because phosphate has the lowest risk to induce corrosion on carbon steel compared to other anions from inorganic acids, such as chloride and sulphate. In addition, silicon dioxide particles are also utilized to improve the thermal stability of the coatings. Here, the silicon dioxide is originated from the natural sand in Indonesia, which offer an advantage of a more affordable material processing cost, given that the raw material is available locally and close to the geothermal site. In this study, the role of polyaniline and silicon dioxide, as an individual component in the coating, on the improvement of coating's corrosion properties was observed. Therefore, the corrosion study was performed on the binary polyaniline and silicon dioxide composite coating to apply the advantages of each individual component.

2. METHODOLOGY

2.1 Materials

2.1.1 Carbon Steel

The uncoated carbon steel specimens used in this study were made of carbon steel St37 (German name), or also known as S 235 JR (European name), which were tested along with the coatings as control experiments. The specimens were prepared using two different dimensions depending on the testing methods. For the exposure test, carbon steel specimens have a dimension of 50 mm × 20 mm × 4 mm with a 5 mm hole to arrange the specimens in the autoclave. All the specimen surfaces were ground using 320-grit silicon carbide abrasive paper. The specimens were then cleaned using bi-distilled water and acetone. Whereas for the electrochemical test, the specimens have a dimension of 20 mm × 15 mm × 4 mm and were prepared using the same steps as for exposure tests, then additionally spot welded to a Ni-Cr based rod with a diameter of 2 mm to be mounted in the autoclave.

2.1.2 Coatings

In this experiment, commercial marine coating from PT. Bintang Energi in Indonesia was used, which is an alkyd-based marine coating, containing $CaCO_3$. The formulation of the investigated coatings was 10 g of the total mixture of binder and pigments which were then dissolved in 5 ml methyl iso butyl ketone (MIBK), using an orbital shaker with 225 rpm for 30 minutes. Pigments consisting of 2 wt% of PANI and 15 wt% of SiO_2 were added to the binder and solvent. This coating formulation is then mentioned as PANI/SiO_2. Coatings were applied on the surface of carbon steel that were ground up to 320-grit SiC paper by gravity feed double action air brush BELKITS, with the standard needle and nozzle diameter of 0.25 - 0.3 mm. The air brush was used with air pressure of 2.5 bar. The specimens were then left in the dust free area until they became dry. The synthesis of silicon dioxide and polyaniline pigments is described in previous papers (Aristia et al., 2015, Aristia et al., 2019).

2.2 Experimental Condition

Exposure and electrochemical tests were performed in the artificial geothermal solution, simulating the geothermal brine found in Sibayak, Indonesia (Atmojo et al., 2000, Keserović and Bäßler, 2015). The solution was prepared in the laboratory at room temperature, with pH 4 and a chemical composition as presented in Table 1.

Table 1. Chemical composition of artificial geothermal water based on the geothermal brine of Sibayak, Indonesia

Cond.	Cl^-	SO_4^{2-}	HCO_3^-	Ca^{2+}	K^+	Na^+
mg/L	1,500	20	15	200	250	600

Experiments were performed in autoclaves at 150 °C with a total pressure of 1 MPa, which was achieved by purging Ar with an initial partial pressure of 500 kPa at room temperature. Solution was purged by Ar for 30 minutes prior to the experiment.

2.3 Exposure Test

Three specimens were arranged in a glass vessel and immersed in the artificial geothermal water. The glass vessel was then put inside the autoclave and kept undisturbed in the climate chamber for 7 days. To investigate the durability of coatings, a long-term exposure test of polyaniline/SiO_2 based coating was performed using the same procedure as the 7-day exposure test, with exposure time of 28 days and 168 days. All experiments were performed continuously without changing the solution to avoid oxygen intrusion in the autoclave. Post-experimental analyses were conducted by assessing the surface of specimens using optical and electron microscopes. The cross section of specimens was also analyzed using Scanning Electron Microscope (SEM) to determine the particle distribution of the coatings before and after exposed to the geothermal solution. Cross section was made by embedding the specimen in epoxy resin, cutting, and polishing. Further analysis of coating materials was performed by Fourier Transform Infrared (FTIR) to identify the functional groups of the coatings before and after exposed to the geothermal solution. FTIR was performed using Thermofischer FTIR Nicolet 6700 instrument. The technique used in the experiment was Attenuated Total Reflectance (ATR), applied with the infrared range of 4000 - 750 cm^{-1}, using an average of 32 scans and a resolution of 4 cm^{-1}.

2.4 Electrochemical Test

Electrochemical measurements were conducted at 25 °C with ambient pressure and at 150 °C with 1 MPa using a three-electrode system using a potentiostat Gamry Reference 600. The system consists of specimens (carbon steel or coated carbon steel) as a working electrode, Ti/TiO_2 net counter electrode, and Ag/AgCl in 3 M KCl-saturated solution as reference electrode. The surface area of the working electrode was 8 cm^2. At 25 °C, experiments were performed in a glass vessel, whereas at 150 °C the experiments were performed in an autoclave equipped with a heating plate.

Open circuit potential (OCP), or also known as free corrosion potential (E_{corr}), was continuously recorded for 150 hours. Interruptions by electrochemical impedance spectroscopy (EIS) were made within the first 12 hours with an interval of 2 hours, and after every 24 hours. The electrochemical impedance spectra were obtained by applying AC potential of 10 mV around E_{corr}, with the frequency range of 10^5 - 10^{-2} Hz with the recorded data of 10 points per decade. The electrochemical measurement was analyzed using Gamry Echem Analyst Software. For analysis purpose, the impedance data is reported by plotting Z_{max} with respect to time, where Z_{max} is the total impedance value at the lowest frequency, i.e., 10^{-2} Hz.

3. RESULTS AND DISCUSSION

3.1. Selection of coating types

Corrosion rate determination was performed on carbon steel, which revealed that after exposed in the deaerated artificial geothermal water for 28 days carbon steel has a corrosion rate of 0.01 mm/year. This corrosion rate can be considered negligible and has a value much lower than the corrosion rate threshold for geothermal application which is set to 0.3 mm/year, considering the usage of 20 years (Bäßler et al., 2015). The optical microscopic image of carbon steel surface after exposure is presented in Figure 1. The carbon steel cross-section however shows that there is localized corrosion on carbon steel, which entails a protection strategy to prevent corrosion.

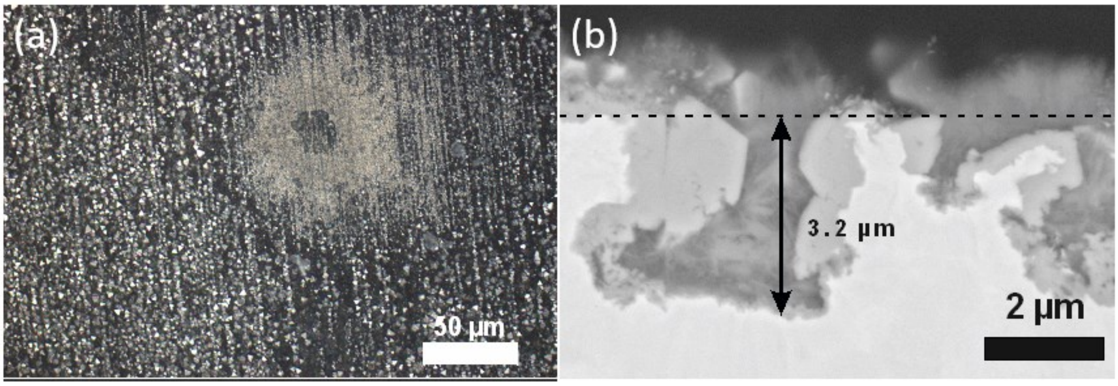

Figure 1. Carbon steel specimen after 28 days exposure in artificial geothermal water (a) surface (b) cross section

To utilize the locally available resources, commercial marine coating from Indonesia which based on alkyd with the addition of $CaCO_3$ was used as the polymeric matrix. A screening basing on surface structure of different coatings types were performed after exposing different specimens to the artificial geothermal water at 150 °C. Coating (a) is the unmodified alkyd coating, coating (b) is SiO_2 modified alkyd coating, coating (c) is the PANI modified alkyd coating, and coating (d) is the PANI/SiO_2 modified alkyd coating. Along with the PANI/SiO_2 composite coating, individual parts of coatings were tested in the artificial geothermal water for seven days to identify the role of each component of the coating to their properties. The visual appearance and optical microscopic images of coated specimens before and after exposed to the artificial geothermal water are presented in Figure 2. After being exposed to the artificial geothermal water for seven days, visual appearance and optical microscopic images show that the specimens of unmodified alkyd-based coating (a) underwent a severe discoloration right after 7 days. When SiO_2 is added to the alkyd coating, a discoloration is also observed at 7 days, albeit with lower degree, which became more severe after 28 days of exposure (Fig. 2b). With the addition of PANI to the alkyd coating, a similar discoloration was observed after 7 days and remained the same after 28 days (Fig. 2c). In contrast to the single component modified alkyd coating and the unmodified one, the binary PANI/SiO_2 modified alkyd coating (d) has an almost unchanged color after being exposed for 7 and 28 days in the artificial geothermal water. Based on this result the PANI/SiO_2 modified coating is used for further tests.

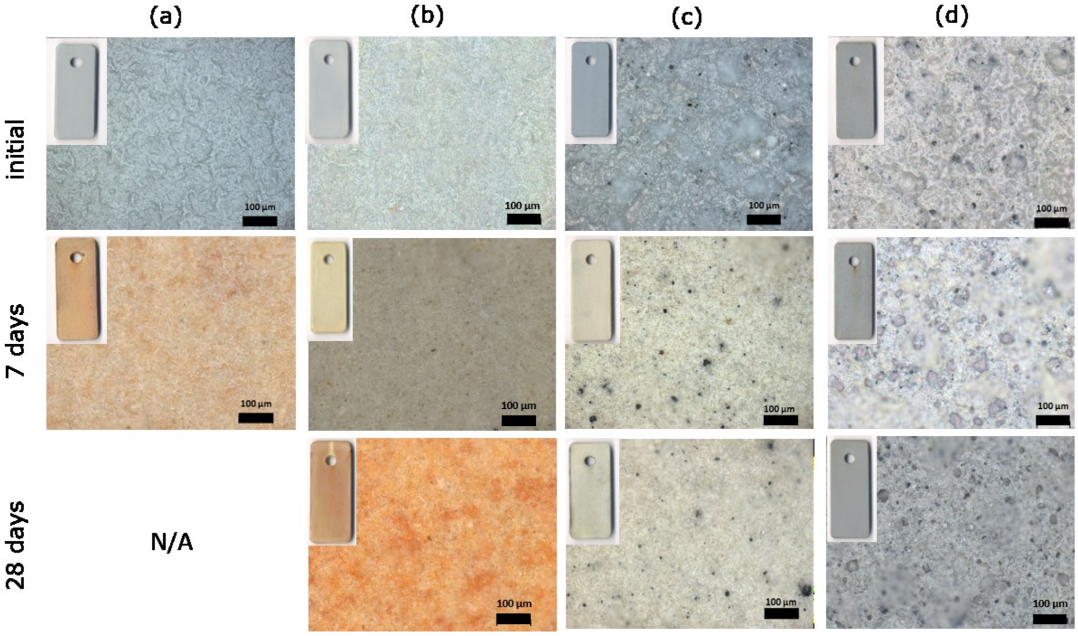

Figure 2. Visual appearance and optical microscope images of coated specimens in initial condition (upper), after 7 days (middle) and 28 days (bottom) exposure. The tested coatings consist of (a) binder (b) binder + 15 wt% SiO_2 (c) binder + 2 wt% PANI (d) binder + 15 wt% SiO_2 + 2 wt% PANI

Coating degradation processes can be identified by the presence of blisters and swelling, indicating ion incorporation within coatings, intrinsic defect formation, and the propagation of corrosion underneath the coating. Blisters, as also visible in the binder specimen after exposed to the artificial geothermal water, can generally occur in this system due to the reaction between H^+ from the artificial geothermal water with the $CaCO_3$ within the coatings. For all coatings, the pH of the artificial geothermal water changed before and after the exposure test from 4 to 6.5, indicating the initial reaction of coatings with H^+ until the medium is neutral.

3.2. Electrochemical Tests at Different Temperatures

Electrochemical tests were performed by monitoring the E_{corr} of carbon steel and coated carbon steel at 25 and 150 °C. Experiments were performed at 25 °C to investigate the E_{corr} of carbon steel and the coated carbon steel in the deaerated artificial geothermal water without any additional influencing factor, such as temperature. When in contact with the artificial geothermal water, carbon steel is actively corroding with a potential of -730 mV at 25 °C. PANI/SiO_2 coated carbon steel had an E_{corr} of about -500 mV at the beginning of the experiment, which then decreased until about -730 mV after 24 hours in the artificial geothermal water. There is no significant difference of potential between the coated and uncoated carbon steel after 24 hours, indicating that the electrolyte might be absorbed through the PANI/SiO_2 coated carbon steel within the first day, resulting in a contribution of potential which is almost similar to that of carbon steel. However, there is no corrosion observed on the PANI/SiO_2 coated carbon steel after the test.

At 150 °C, carbon steel potential increased from -730 mV to 100 mV within 24 hours. An increase of temperature promotes an oxidation of metal ions from Fe^{2+} to Fe^{3+} which contributes to a more positive potential. In addition, at higher temperature there is a faster nucleation and growth of iron oxides, leading to a formation of an iron oxide layer adjacent to the carbon steel substrate (Cornell and Schwertmann, 1996). Corrosion products might then accumulate and provide a coverage on the surface (Fig. 1b) which influence the E_{corr} of carbon steel. The E_{corr} data of coated carbon steel show the same pattern, where the increase of E_{corr} was also observed, albeit faster and remained lower than that of carbon steel, which was at about -500 mV. Although at room temperature, there is no significant difference of E_{corr}, which might be associated with the possible absorption of electrolyte through the coating, E_{corr} of PANI/SiO_2 coated carbon steel was much lower at higher temperature, indicating that the coating was able to impede the oxidation of Fe^{2+} at a higher temperature and protect the carbon steel from corrosion.

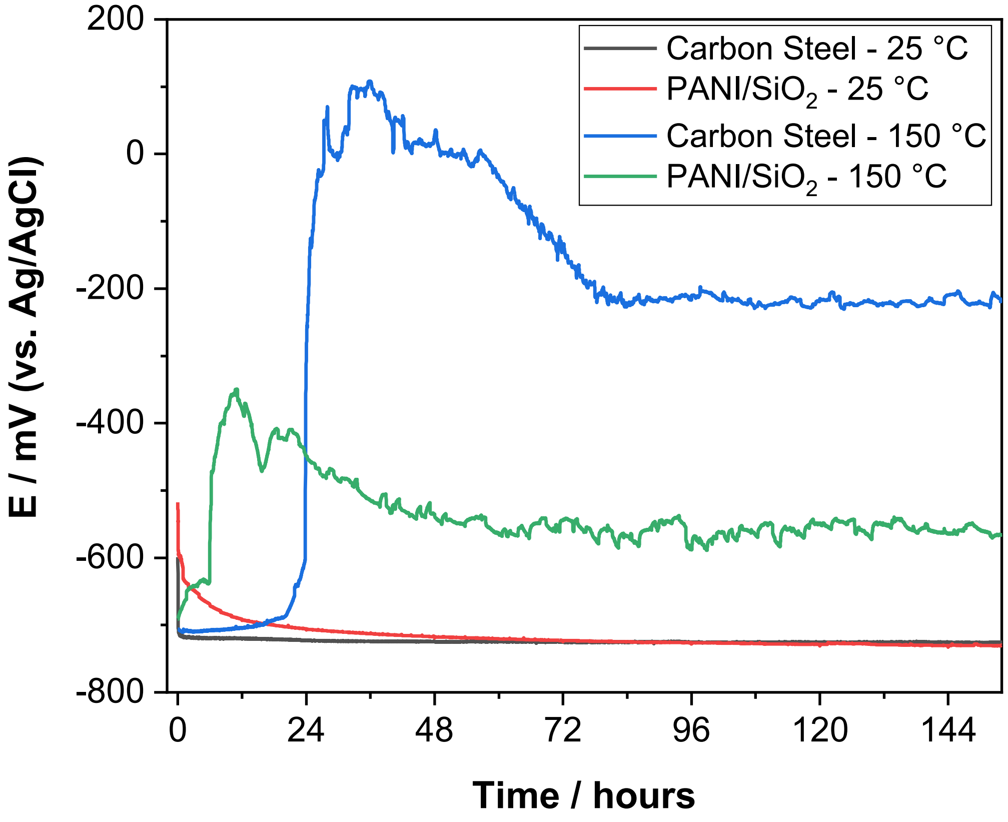

Figure 3. E_{corr} of PANI/SiO_2 coated carbon steel compared to carbon steel in deaerated artificial geothermal water at 25 °C and 150 °C.

Electrochemical impedance spectroscopy is a tool to measure the change in capacitive and resistive behavior of coatings, due to the changes in the coating properties which might be caused by the water uptake, incorporation of ionic species in the medium, micro cracks, and micro pores. The impedance data of specimens at the lowest frequency correspond to the interface between the coating and metal, where the corrosion resistance can be extracted. Figure 4 shows that the total impedance value of coated carbon steel decreases significantly in the first 24 hours when exposed to the artificial geothermal water at 25 °C. At 150 °C, the impedance of coated carbon steel remains stable between 500 - 5000 Ω.

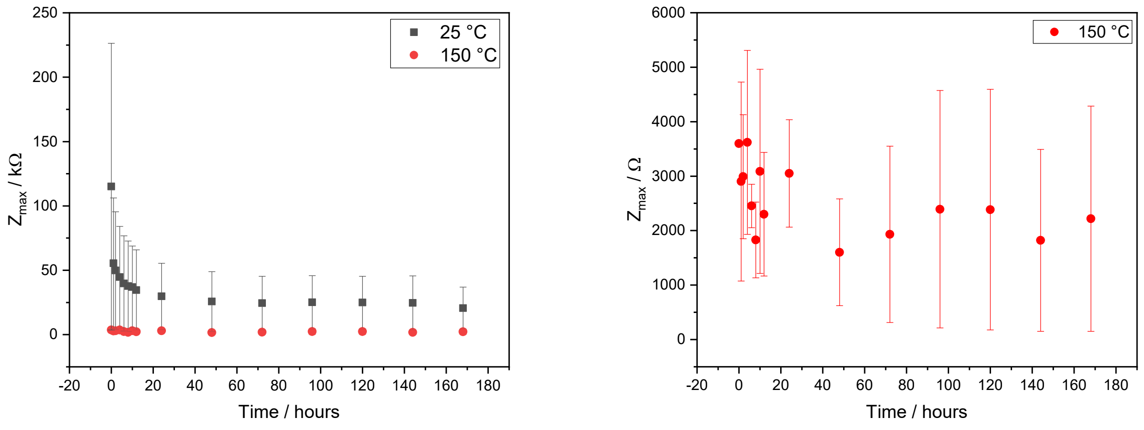

Figure 4. Z_{max} or $|Z|_{0.01Hz}$ of PANI/SiO_2 modified coating on carbon steel in deaerated artificial geothermal water at 25 °C and 150 °C (left), a magnification of EIS at 150 °C (right), error bar is a standard deviation from 2 experiments.

3.3. Durability of Coating

According to the screening experiments, coatings containing polyaniline and silicon dioxide show the best performance. A longer exposure test was performed for up to 6 months and the mass loss of coated specimens are presented in Table 1. There is no significant loss of materials with the maximum mass loss of 22 ± 2 mg after 6 months exposure to the artificial geothermal water.

Table 1. Mass loss of coated carbon steel with respect to time

Time (day)	**Mass loss (g)**			
	Sample 1	**Sample 2**	**Sample 3**	**Average**
7	0.020	0.019	0.022	0,020 ± 0,002
28	0.014	0.011	0.011	0,012 ± 0,002
168	0.021	0.024	0.022	0,022 ± 0,002

The visual appearance and microscopic images of tested specimens showed that there is no significant damage on the surface of coated carbon steel after exposed to the artificial geothermal water at 150 °C for up to 6 months, as shown in Figure 5. A further analysis using FTIR was performed to identify the change in the functional groups of the coatings by comparing the spectra of specimens before and after exposure. Although the specimens showed that there is no significant change by visual inspection, there are several changes in the IR absorption peaks, indicating a degradation in the molecular level. For example, C=O stretching of ester at 1725 cm^{-1} decreased significantly and disappeared after seven days of exposure. In addition, O-H stretching was still identified at around 2922 cm^{-1} after 6 months, although the absorption decreased significantly after only seven days. The same behavior was observed for the peak of C-H stretching and C=O stretching at 2850 cm^{-1} and 1795 cm^{-1}, respectively. For these peaks, the significant change was observed between 7-day and 28-day exposure. These changes of absorption peaks show that the polymeric matrix, which is based on alkyd coating was slowly degraded. The inorganic part of the coatings, which consisted of pigments, however remained intact within the coatings, indicated by the IR absorption peaks as presented in Figure 5 and Table 2. The polyaniline pigments were also intact, indicated by the dark particles dispersed on the surface, as observed in the optical microscopic images.

Table 2. FTIR Assignment of coated specimens (Stuart, 2004, Reig et al., 2002, Smith, 2018)

Assignment	**Reference**	**initial**	**7 days**	**1 month**	**6 months**
(C-H) CH_2 asymmetric stretch	2926 ± 10	2923	2916	2922	2927
(C-H) CH_2 symmetric stretch	2855 ± 10	2850	2850	2852	-
C=O stretching	1810 - 1640	1795	1792	1793	-
Aromatic C=O stretching	1730 - 1705	1731	-	-	-
$CaCO_3$	1420	1417	1410	1406	1410
-O-Si-O-	1070	1091	1022	1009	1020
$CaCO_3$	875	875	872	872	872
Symmetric SiO_2 bending	779	779	771	777	775

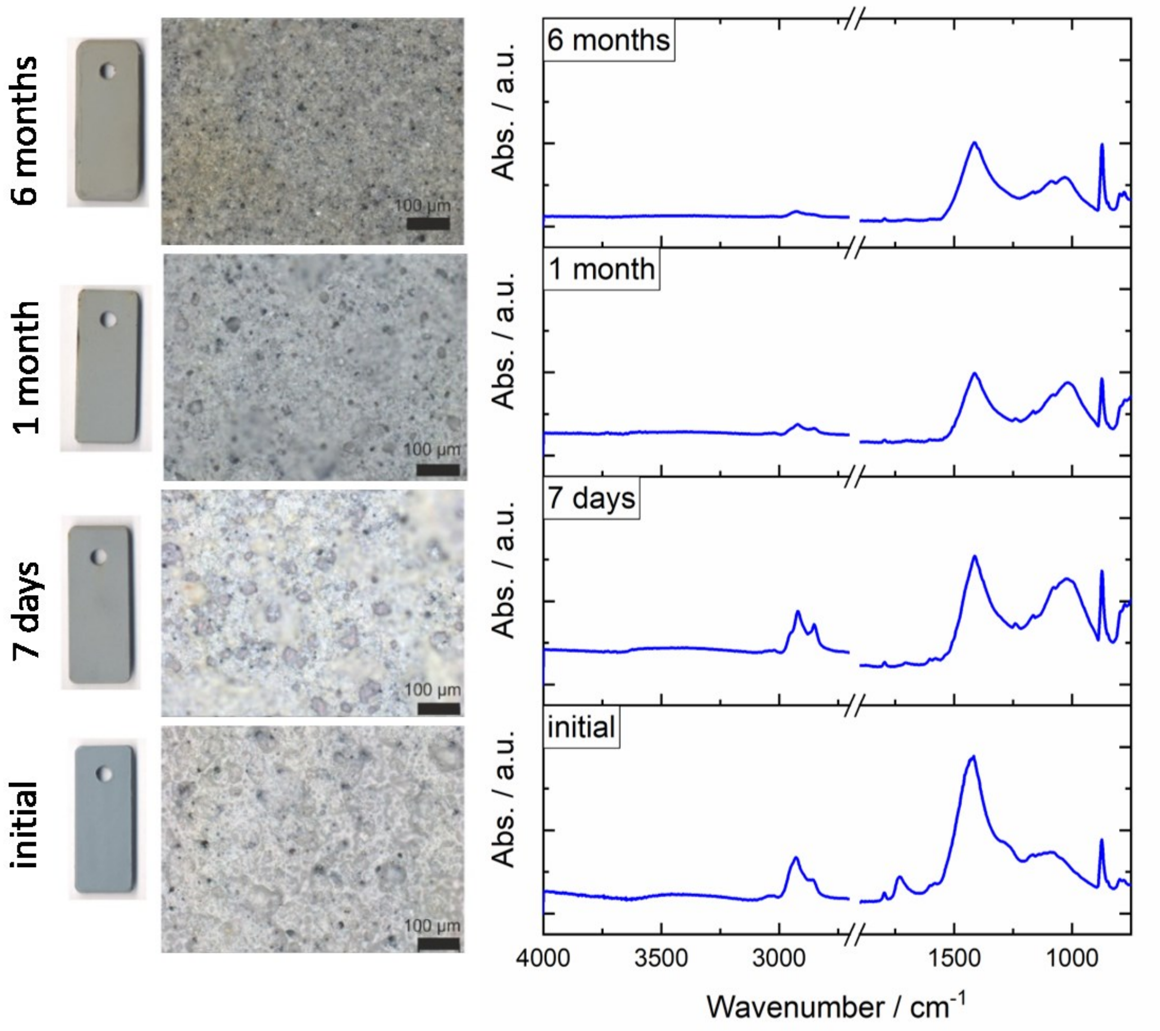

Figure 5. FTIR spectra evolution of coated carbon steel after up to 6 months exposure in deaerated geothermal solution

4. CONCLUSION

By using the available resources in Indonesia, such as silicon dioxide and marine coating base, the PANI/SiO_2 modified alkyd coating was able to protect carbon steel in a deaerated artificial geothermal water. The screening of coatings shows that the modification by adding individual pigment was not sufficient to protect carbon steel even during a short-term exposure, indicated by the discoloration after only seven days of exposure. Electrochemical tests indicated that there was no significant change in the E_{corr} between the coated and uncoated carbon steel at room temperature. At 150 °C, the coated carbon steel has a lower potential than that of carbon steel, indicating that the coating is protecting carbon steel cathodically or slowing down the corrosion reaction. Finally, a long-term exposure test confirmed that the PANI/SiO_2 modified coating successfully protects the carbon steel in the Sibayak artificial geothermal water up to 150 °C for 6 months.

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