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The influence of inhibitor Na₂CrO₄ and NaNO₃ on corrosion and micro structure on AISI 348 steel material

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Abstract. The influence of inhibitor Na_2CrO_4 and $NaNO_3$ on corrotion and microstructure on AISI 348 steel material have been carried out. A series of corrosion tests were conducted with polarization and potentiodynamic and microstructure resistance methods on AISI steel 348 for secondary cooling pipes at steam power plants. This research was carried out in demineralized water at room temperature (25°C) using Na₂CrO₄ and NaNO₃ inhibitors whose concentration varied between 0-150 ppm for corrosion rate inhibitors. Observations of microstructures were performed using optical microscopy and SEM. The corrosion test showed that in the NaNO₃ inhibitor solution, the highest corrosion rate was 0.05 mpy at 15 ppm and the lowest corrosion rate was 0.0058 mpy at 30 ppm, and the highest tail was 174.89 mV at 75 ppm and the lowest tail 103, 04 mV at concentration 0 ppm. While in Na₂CrO₄ inhibitor solution obtained the highest corrosion rate 0,0606 mpy at concentration 75 ppm and lowest corrosion rate 0,0197 mpy at concentration 15 ppm, and highest tail 264 mV at concentration 30 ppm and lowest tail -128 mV at concentration 75 ppm from Inhibitor Na₂CrO₄. The optimum concentration of NaNO₃ was 30 ppm with an efficiency of 72.1%, and the optimum concentration of Na₂CrO₄ was 150 ppm with an efficiency of 1.9%. The result of microstructure observation showed that on the surface of the sample was formed a protective film of oxide, and on corrosion of AISI 348 steel corrosion of well form.

1. Introduction

The secondary cooling tube located in the interior of the reactor building is austenic steel, while located on the outside of the reactor building is carbon steel [1,2]. The problems encountered in secondary cooling systems are corrosion, microorganisms and deposits. Corrosion should be watched and controlled, as it may result in decreased equipment efficiency, leakage in piping systems, explosions in high pressure process equipment that could cause loss of life or environmental pollution or even equipment malfunction. To counteract the above, it has been investigated by the addition of Nalco inhibitor products with urea and thiourea media to the behavior of carbon steel DIN ST 35.8 [3]. A corrosion inhibitor is a chemical which, when added in a small concentration to a corrosive environment, will be very effective in lowering corrosion rate, even inhibitors can slow down corrosion rates by increasing anodic or cathodic polarization, reducing displacement or diffusion of ions to metal surfaces, As well as enlarge the electrical resistance at the metal surface [4]. Corrosion control with inhibitors is a controlling process by slowing corrosion speed, since inhibitors can chemically react with metallic surfaces or environments around the

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metal to provide a certain level of protection against the metal. Use of inhibitors is said to be effective when it can protect metals from corrosion attack at low concentrations and does not cause deposits (crust) on metal surfaces.

The AISI 348 steel which is steel with a ferritic phase has a bcc crystal structure, containing 14-18% chromium with a carbon content of 0.1%. Ferritic steels are not resistant to reducing acids such as HCl, have very strong and hard strength properties, but their resistance to corrosion is reduced, and resistant to oxidation processes at high temperatures, since they have a melting point between 1427° C and 1510° C [5]. In this study used AISI 348 steel with the addition of inorganic inhibitor Na₂CrO₄ and NaNO₃ which concentration varied between 0-150 ppm, through polarization and potentiodynamic resistance method to know the rate of corrosion [9,10], as well as observation of microstructure before and after corrosion by using optical microscope and SEM . This research was conducted in DM water (demineralization) at room temperature (25 $^{\circ}$ C).

2. Research Methodology

2.1. Materials and Equipment

<u>Material</u>: the materials used in this experiment are steel plate AISI 348, which is made in the form of a circle of 15.0 mm in diameter, with the composition as written in Table 1.

Table 1. AISI-548 steel composition with AA spectrometer tool								
Name of element	C	Mn	Ni	Cr	Р	S	Fe	
Percentage (%)	0.039	0.84	8.0	18.0	0.07	0.002	73.12	

Table 1. AISI-348 steel composition with AA Spectrometer tool

The corrosion medium used was demineralized water with pH = 7.13 at room temperature (25 0 C), whereas the inhibitor used in this study was Sodium Chromate (Na₂CrO₄) and Merck's Sodium Nitrate (NaNO₃).

Equipment: The corrosion analyzers used in this study are as follows:

- M342, commonly referred to as "Softcorr Corrosion Measurement, Software" equipped with -M273 Potensiostat / Galvanostat made by EG & G Princeton, Applied Research Corporation Buehler Samplmet2 cutting machine, Struers Dap-V sanding machine,

-Analytical scales of Ohaus brand, and Corrosion cells equipped with saturated columnelled electrodes (EKJ), auxiliary electrodes and cup holders, SEM and EDXS.

2.2. Working procedure

- Sample preparation

Preparation of the sample is done by forming AISI-348 Steel according to ASTM 262 with diameter 15,0 mm as many as 60 pieces mµ. After that the specimens are polished by using a SiC sandpaper with fineness no.120, 600, 800, 1000, and 1500, and followed by washing according to ASTM G1-90 using hot alcohol to sample fat free. Ready-use sample storage is done in the desiccator.

– Preparation of the solution

For the corrosion test solution is divided into two types, namely the solution containing Sodium Chromate inhibitors (Na_2CrO_4) and Sodium Nitrate Inhibitors $(NaNO_3)$ with concentrations varying from 0-150 ppm.

- Corrosion Testing

First, the preparation of the potentiostat instrument and the preparation of the solution, after which the sample to be dissolved is placed on the trailer holder. Then the sample was

immersed into corrosion cells containing a solution or a corrosive medium of 600 ml. Inside corrosion cells, this sample will act as a working electrode. Thereafter, the auxiliary electrode and the comparative electrode (EKJ) are fed into the corrosion cell, for which the three electrodes are then connected to the potentiostat instrument. The tail measurements were then measured against the current density with a scan speed of 0.1 mV / s, to obtain the Tafel curve and the pacific curve to determine the characteristics of the sample passivation. From this measurement will also get the density of corrosion current (Ikor), corrosion potential (Tail), polarization resistance (Rp), and corrosion rate.

- Observation of microstructure

After corrosion testing, the surface of the sample was analyzed by using Scanning Electron Microscope (SEM-EDXS) to see the corrosion forms on the surface of each sample.

3. Results and discussion

3.1. Analysis of polarization resistance

Corrosion testing by using polarization resistance technique (Polarisation Resistance) is intended to see the resistance of the sample to oxidation when given the outside potential. Polarization resistance is a fast method for determining the corrosion rate without damaging the metal and the measurement results more accurately. The experimental results using the polarization resistance method are as shown in Table 2 and Table 3.

Cocentration (ppm)	Na ₂ CrO ₄					
	E _{kor} (<i>mV</i>)	i_{kor} ($\mu A/cm^2$)	Rp (K.ohm/cm ²)	Corrosion rate (<i>mpy</i>)		
0	103.04	0,08	273,78	0,0208		
15	40.45	0,08	289,04	0,0197		
30	264	0,1	207,11	0,0275		
75	-128.66	0,23	94	0,0606		
150	-89.12	0,08	279,36	0,0204		

Table 2. Corrosion test results in Na₂CrO₄ inhibitor solution

Tabel 3. Corrosion test results in NaNO₃ inhibitor solution

Cocentration (ppm)	NaNO ₃				
	E_{kor}	i_{kor}	Rp	Corrosion rate	
	(mv)	(µA/Cm)	(K.Onnucm)	(тру)	
0	103,04	0,08	273,78	0,0208	
15	105,78	0,19	113,95	0,05	
30	147,79	0,02	982,86	0,0058	
75	174,89	0,03	1087,56	0,0075	
150	108,52	0,03	789,25	0,0072	

The results in Tables 2 and 3 show that the value of free corrosion potential (Tails), the density of the corrosion current (kink), the polarization resistance (Rp) and the corrosion rate of each sample metal vary in each type and the concentration of inhibitor used. When the

metal is introduced into the solution there will be electrochemical reactions at the interface between the metal and the solution. This reaction produces an electrochemical potential called corrosion potential (Tails). This potential is determined by the amount of negative charge formed when the metal is introduced into the solution. At the tail, the oxidation rate is equal to the reduction rate so that the system is called equilibrium. The ired reduction stream, occurs in a reduction process. Aqueous corrosion current occurs by an oxidation process. On the Tail, I red = I x and I total – I red + I oks = 0.

The measured current on the instrument is the total current. If a potential that is not equal to the tail is given to a system there will be polarization resulting in a reduction reaction and oxidation, thus the I_{red} and I_{ox} on the tail can be determined. This potential can not be measured directly, but can only be compared with the potential of a known reference electrode.

3.2. Analysis of Corrosion rate

In accordance with the results of corrosion tests showed that the different in concentration of water-soluble inhibitors affect the size of the metal dissolution rate. At certain concentrations there is an indication of the addition of corrosion rate from the initial corrosion price before being given the inhibitor as shown in rate Fig. 1. Basically AISI-348 is a type of metal that is resistant to corrosion in the water environment because the chromium content present in AISI-348 can react in corrosive media to form chromium oxide membrane, but that does not mean it cannot be corroded. This can be seen from the very small corrosion rate when corrosion test on pure water media is 0.0208 mpy. The corrosion rate of corrosion test result with potentiostat as shown in Figure 1 obtained the largest and smallest corrosion rate for the sample which was dissolved in two different solutions ie NaNO₃ and Na₂CrO₄. For the sample which was dissolved in NaNO₃ solution obtained the highest corrosion rate of 0.05 mpy at a concentration of 15 ppm (2.4 times greater than corrosion without inhibitor) and the lowest corrosion rate of 0.0058 mpy at a concentration of 30 ppm. In Figure 2, the curve rises up to 15 ppm and falls after 15 ppm, this is because NaNO₃ is one of the inorganic inorganic metals inhibitors. In theory, if the addition of passive element is added in an insufficient quantity into a corrosive medium there will be an increase in corrosion rate because the process of pacification or decreasing corrosion rate can only be reduced if the added inhibitor has reached the minimum concentration to pacify the metal. What if the minimum concentration for passage is not reached then the protective layer formed cannot protect the entire surface of the sample so that the part having the oxide protective layer will be cathodic and the part that is not covered by the oxide protective film will be anodic, thus increasing the corrosion process in the sample. The decline in corrosion rate at concentrations above 30 ppm NaNO₃ because at that concentration has perfectly formed a protective film that is evenly distributed across the surface of the metal sample so as to cover the entire metal surface. While at concentrations below 30 ppm there is an increase in corrosion rate which is the result of not reaching a minimum concentration for inhibitors to inhibit the rate of corrosion, resulting in membranes formed only in certain parts of the metal surface to form anodic and cathodic parts in Metal surfaces as a larger corrosion trigger. The presence of sulfate elements that enter with the addition of NaNO₃ inhibitors also accelerate the destruction of the oxide protective membrane because the sulfate element is an active element in attacking the metal at concentrations below the minimum.



Figure 1. Graph of the relationship between corrosion rate and NaNO₃ concentration And Na₂CrO₄



Figure 2. Graph of the relationship between polarization resistance and NaNO₃ and Na₂CrO₄ concentrations

In accordance with its function Na₂CrO₄ is one inorganic inhibitor that is also a passive on metal, so that when added in an amount that has not met the minimum limit for the passage it will increase the rate of corrosion. Based on the theory can be explained that at the concentration of 15 ppm Na₂CrO₄ deviation from the price that should be. The occurrence of deviation at 15 ppm Na₂CrO₄ is possible due to the presence of active corrosion-causing elements that follow along with Na₂CrO₄ such as chloride (Cl) because the inhibitor of Na₂CrO₄ used contains a number of chloride elements which are inevitable so that at higher concentrations the chloride content will also Higher and will have a great effect on sample corrosion. The magnitude of the corrosion current density, as shown in Fig.2. According to the current-generated corrosion mechanism, when the resistance per unit area is large, the small unity current is small. Increasing the price of the polarization resistance on the sample surface causes the diffusion of the ions and electrons apart from the metal surface to decrease so that the resulting current is small and the corrosion rate will decrease vice versa in the sample having the price of the small polarization resistance having a large corrosion rate.

The decline in corrosion rate at concentration of 150 ppm Na_2CrO_4 because at this concentration formed a thin protective film that is evenly distributed across the surface of the metal sample so that the oxidation process becomes reduced. If the entire metal surface has

been covered by a protective layer then the metal is more cathodic and the corrosion rate will decrease.

3.3 Analysis of potentiodynamic

To determine the active-passive behavior of the sample was conducted corrosion test using potentiodynamic techniques. The results of the measurements are shown in the form of a cassette-like curve shown in Figures 3, and 4.





Figure 3 Active-passive curves at concentrations of 0 ppm, 15 ppm, 30 ppm, and 150 ppm Na₂CrO₄ inhibitors



The potentialododynamic curves for both Na₂CrO₄ and NaNO₃ inhibitors show different curve shapes. The difference in the curve's slope and the corrosion potential of the tail depends on the protective layer formed on the sample surface by both types of inhibitors. In a sample measurement of 0 ppm (without inhibitor), 2 passivations occur by the protective membrane formed on the metal surface where the second passive region has a greater potential range than the first passive region. The first passive potential occurs at a potential of +100 mV with a very small passive potential range so that it is only seen as a straight line on the curve. This instantaneous passage is characterized by a rapidly decreasing current density. This decrease in current density occurs due to the cessation of the corrosion process in the metal sample. The second passive potential of Epp occurs at + 1250 mV and is then followed by the formation of the transverse region. This second passage also does not last long because the formed membranes are also easily damaged by the potential changes that are given toward the positive potential. Overall it is seen that the sample has a high rate of passivity on the water medium. In the samples tested in a 0 ppm sodium chromate inhibitor solution, 15ppm, 30ppm, 75ppm and 150ppm of Na₂CrO₄ inhibitors as shown in Figures 3 was no passive region. This occurs because there is no perfect layer of protective oxide and evenly distributed on the metal surface, thus never reaching the passive potential of Epp, whereas at 15 ppm there is a passive region at +1230 mV potential. The 15 ppm passing on consentration indicates that at that concentration an oxide protective film covering the entire surface of the sample is capable of halting corrosion in the potential range from +1230 to +1350 mV, whereas at potentials above +1350 mV the protective film will break and the sample will recorrodate.

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In the sample tested in a solution of 0ppm sodium nitrate inhibitor, 15 ppm, 30 ppm 75 ppm and 150 ppm of NaNO₃ inhibitor as in Figures 4. The occurrence of passivity at these sodium nitrate concentrations resulting from the protective layer of oxide formed throughout the metal surface is able to isolate or protect the sample from its corrosive solution completely so that at +1250 mV potential the sample is cathodic and the corrosion process stops. The passive region formed at these sodium nitrate concentrations has the same passive potential value of + 1250 mV and has the same potential passive range

3.4. Analysis microstructure

For AISI 348 steel samples of Na₂CrO₄ inhibitor and AISI 348 solutions NaNO₃ inhibitor solution by Scanning Electron Microscope 500X and 1500X magnification is seen in Fig. 5a-5b, and composition unsure with EDXS.(Fig.5c)







Figure 5. Surface Morphology with SEM-EDXS, a). AISI 348 steel in Na₂CrO₄ solution (Magn.1500X), b). AISI348 steel in NaNO₃ solution (Magn.1500X)
c). EDS from AISI 348 steel in Na₂CrO₄ result of sample bulk of grey area dominated by Cr and Fe element beside oxygen, showing the possibility of chrome-oxide forming there is a possibility that chrome oxide or iron oxide are present on the spot.

The cracked region is an area of the oxide membrane that has begun to deteriorate due to a higher potential supply (see Figure 5a). Cracking can also occur by attack of chloride and sulfate ions. Around the cracked surface there has been corrosion characterized by a blackish color which means that corrosion processes have occurred when the protective membrane begins to crack or break. Areas with irregularly blackish colors are areas that have been

corroded because their protective oxidant membranes have been damaged (see Figure 5b). In this area the corrosion process is fast so that it will form a basin / overdraft. EDS pattern (Fig. 5c) on a selected bulk spot in this very small surface area part reveals the possibility of iron oxide (Fe₂O₃) and/or chrome oxide (Cr₂O₃) being present in the sample. Based on the microstructure investigation supplemented by EDS data it could be claimed that in AISI 348 steel, pitting/erosion corrosion have certainly occur.

4. Conclusion

The conclusions can be drawn from the results of the discussion and analysis conducted on the research data are as follows:

- The highest corrosion rate in NaNO₃ solution inhibitor was 0.05 mpy at 15 ppm concentration and the lowest corrosion rate was 0.0058 mpy at 30 ppm, whereas in the Na₂CrO₄ solution the highest corrosion rate was 0.0606 mpy at 75 ppm and The lowest of 0.0197 mpy at 15 ppm concentration.
- The optimum concentration of NaNO₃ was concentrated 30 ppm with the inhibition efficiency of 72,1% and the optimum concentration of Na₂CrO₄ at concentration 150 ppm with the efficiency of inhibition equal to 1,9%.
- From the active-passive curve of the potentiodynamic measurement, there is a passive region at +100 mV and + 1250 mV in a sample that is corroded in pure water media, +1230 mV in addition of 15 ppm Na₂CrO₄ and + 1250mV in addition of 15 ppm to 150 ppm NaNO₃. In general the rate of sample passing on pure water media with NaNO₃ addition is higher than that of Na₂CrO Na₂CrO₄ and without inhibitor.
- From the results of micro structural observations using SEM it is seen that all samples of corrosion test result have a corrosion attack well.

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