Behavior of Phosphate Inhibitor on Pitting Corrosion
Resistance of Cr-Mo Steel

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Abstract. Trisodium phosphate (TSP) and disodium phosphate (DSP) inhibitors are widely used in industrial area, for example in boiler and condenser system. Their primary uses as scaling inhibitor through anodic and cathodic reaction. Therefore, concentration of TSP and DSP is a dominant factor to intended service; it could be advantage if the concentration is proportional, or on the contrary, destructive if the concentration is not proportional because it will drive localized corrosion on tube boiler made from Cr-Mo steel. In this research, type of localized corrosion will be focused on pitting corrosion. To gain maximum protection effect of TSP and DSP inhibitors, which is also for controlling corrosion as destructive process, optimum concentration of inhibitor was determined. To investigate the effect of concentration variation of TSP and DSP on pitting resistance Cr-Mo steel and optimum concentration of TSP and DSP as inhibitor, pitting corrosion tendency by using cyclic polarization was measured. The result was TSP and DSP retarded pitting corrosion by adsorbed on Cr-Mo steel surface. It was also found that inhibitor optimum concentration range is between 20.000 ppm TSP + 1.000 ppm DSP. 100.000 ppm TSP + 1.000 ppm DSP (10%V), which pH optimum range is between 11 to 12.

1. Introduction
Corrosion is an event of metal destruction caused by the interaction between metal or metal alloy with its environment [1-5]. Corrosion process cannot be prevented because it is a natural process that cannot be avoided. In the steam generation system, the equipment that is often subjected to corrosion is the condenser and boiler. Both are a very important part in the continuity of the process. Steam production, which is the main component of the process supporting utility, takes place in the boiler so that interference in this section will affect the overall course of the process.

Corrosion in the condenser and boiler is generally caused by the reaction between the pipe surface made of steel and boiler water or condensate water, one of which often occurs is pitting corrosion. This corrosion is specifically caused by the amount of oxygen in the boiler water is in enough quantities, deposits attached to the surface of the pipe, and the use of inhibitor concentrations that are less precise. This reaction takes place through the mechanism of electrochemical reactions that commonly occur in metals.
Condensate water that has passed through a process of water containing silica (SiO$_2$) and ions, both relatively have small cations and anions. However, if this condensate water after being processed into steam then used to drive the turbine which requires very good boiler water quality requirements, then the level of silica must be minimized. While dissolved ions have the potential to react to particulates which can form deposits on the surface of the pipe, which in turn can be a barrier to heat exchange thereby reducing the boiler's ability. Worse consequences can lead to under deposit corrosion, caustic corrosion, and other differential aeration cells. If this crust is carried over to the next process equipment, it will cause new problems in the process equipment.

Therefore, to minimize the levels of silica and ions, especially Na$^+$, Mg$^{2+}$, Ca$^{2+}$ in boiler water, Trisodium Phosphate (TSP) and Disodium Phosphate (DSP) inhibitors are used. However, if the use of this inhibitor concentration is not appropriate and disproportionate, it will encourage corrosion of steel process equipment.

2. Experimental Procedure

The research methodology used was field observations, experimental methods, and literature studies conducted in the Materials Engineering laboratory and ITB Chemical Electrochemical Laboratory. The three methods are used to obtain quantitative and qualitative data. The experimental method is detailed as follows:

Measurement of Cr-Mo steel pitting corrosion with various concentrations of Trisodium Phosphate and Disodium Phosphate inhibitors, using cyclic polarization methods. Observation of forms of pitting corrosion attack using optical microscopy and Scanning Electron Microscopy (SEM). Analysis of corrosion products using X-Ray Diffractometric (XRD).

3. Results and Discussion

Loops generated from cyclic polarization testing are mapped in one abscissa and ordinate, then the open or closed loop is determined and then the loop area is calculated for each concentration of TSP inhibitor. It aims to determine the tendency of pitting corrosion at various TSP concentrations in general.

Figure 1 is a plot of curves produced by cyclic polarization at various TSP concentrations. From this figure, it is known that the tendency of pitting corrosion formation on Cr-Mo steel due to TSP inhibitor concentration is inappropriate or the tendency of protection given by TSP to pitting corrosion due to its proper concentration [6-7]. To analyze the tendency, two data are used, regarding the interpretation of cyclic polarization data, which consists of open or open loop analysis and the resulting loop area, so in general Fig. 1 informs that 20,000 ppm TSP + 1,000 ppm DSP (20% V) is the smallest TSP concentration capable of providing enough inhibitory protective effects to protect metals from pitting corrosion. This is evident by the closed loop and the small loop area so that this concentration is then called safe concentration. At higher concentrations of safe concentration all loops produced are closed and the area of the loop is not much different from the safe concentration. At 4,000 ppm TSP + 1,000 ppm DSP with 0.1% V (boiler concentration) it is relatively more susceptible to pitting corrosion as indicated by open loops and loop area larger than safe concentration.

The following is the table that composes the types of loops produced from cyclic polarization and pH. pH is an important data to determine the condition of the test solution when TSP is the cause of pitting corrosion or as a protective against pitting corrosion. From Fig. 1, it is known that the safe concentration and concentration of the boiler, the two concentrations will be the main point in determining the optimum TSP inhibitor concentration.
Figure 1. Cyclic Polarization in the various concentration of TSP

Figure 2 shows the effect of TSP on pH. The pH fraction volume of 20% TSP increases significantly from blank solution to a concentration of 20,000 ppm TSP + 1,000 ppm DSP which is from 7 to 11.5 where pH 11.5 is a pH of safe concentration (including the pH range conducive to optimum phosphate) Then, the addition of an inhibitor of up to 100,000 ppm TSP + 1,000 ppm DSP does not increase the pH, because the TSP and DSP inhibitor pairs produce a maximum pH of 12. While the pH achieved by the 0.1% volume fraction does not increase significantly, it can be seen from the pH price indicated by blank solution up to 100,000 ppm TSP + 1,000 ppm DSP only has a price of 7 to 7.5, and pH at the concentration of boiler 7. This is caused by the level of TSP dissolved to produce OH\textsuperscript{-} ions which are unable to increase pH.

In Figure 3a above we can see that the pit population is relatively dense, but based on cyclic polarization curve data, this metal is able to passivate its surface so that attack of pitting corrosion can be stopped. Based on the results of measurements using the Tafel method to provide corrosion rate of low carbon steel in DM aqua of 1,843.10-6mm / year and corrosion potential of -0.592V / SCE. Based
on the Pourbaix program, at a potential value of -0.592V the iron is in the stability area of Fe (OH)₂ [7]. Thus, it is estimated that the electrochemical reaction that occurs due to soft steel in contact with water containing dissolved oxygen is:

\[
\begin{align*}
\text{Fe} & \rightarrow \text{Fe}^{2+} + 2e \\
\text{O}_2 + 2\text{H}_2\text{O} + 4e & \rightarrow 4\text{OH}^- \\
\text{Fe}^{2+} + 4\text{OH}^- & \rightarrow 2\text{Fe}({\text{OH}})_2
\end{align*}
\]

From the pictures above it can be explained that figure 3b to 3i (except 3g and 3i) have pitting formed from the results of cyclic polarization. This pitting occurs because TSP and DSP inhibitors that are supposed to protect by forming a protective thin film on the metal surface cannot properly cover. This is caused by the amount of phosphate ions that are too small so that only anodic reactions can take place, the reaction that should occur next is a cathodic reaction that cannot occur. While figures 3g and 3i TSP and DSP have formed a protective film layer Fe₃(PO₄)₂ on the metal surface.

Figure 3. The macro structure of phosphate inhibitors on the occurrence of corrosion
4. Conclusion

The behavior of phosphate inhibitors on the tube boiler made of Cr-Mo steel was investigated. Based on the observations and results, the following conclusions can be drawn as the optimum pH range in order to avoid pitting corrosion is at 11 to 12 where phosphate can perfectly finish the Cr-Mo steel surface. Also, as the optimum concentration of inhibitor mixture to prevent pitting corrosion is 20,000 ppm TSP + 1,000 ppm DSP with a volume fraction of 10% V which has a price of pH 11.

Moreover, Concentration of boilers (4,000 ppm TSP + 1,000 ppm DSP - 0.1% V) is a concentration that is susceptible to causing pitting corrosion due to the pH of solution 7. The composition of protective thin films resulting from trisodium phosphate inhibition is Fe₃(PO₄)₂ and the Fe (PO₃)₃ corrosion product composition, Iron Phosphate.

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