CORROSION INHIBITION OF MOLYBDATE AND NITRITE FOR CARBON STEEL CORROSION IN PROCESS COOLING WATER

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Abstract

Process cooling water systems require effective chemical treatment to protect steel pipelines against corrosion attack. In this work, experiments were conducted to study the inhibition effect of molybdate and nitrite on the corrosion of carbon steel in the presence of open recirculating flow condition. Carbon steel grade 1018 was used as specimens by way of immersion test in a Simulated Cooling Water (SCW) solution, within a rotating cage and mini flow circuit experiments. Corrosion rates were measured by weight loss method after immersion for 72 hours. Results showed that the combined inhibitor treatment of molybdate and nitrite showed a synergistic effect in reducing the corrosion rate to less than 0.01 mm/y with the inhibition efficiency of 99.6%. The rotating cage results showed good correlation with mini flow circuit results. Surface morphology showed that inhibited steel was protected by oxide film but still suffered some pitting.

Keywords: Cooling water, Corrosion inhibitor, Molybdate, Nitrite, Process.

1. Introduction

Process cooling water system is an integral component in plant industries to remove heat from the heat-generating devices such as stage heaters, economizers and heat exchangers via recirculating water lines. Majority of the industrial production processes requires a recirculating cooling water system to operate efficiently [1]. The pipeline integrity of the cooling water system is one of the critical issues as the cooling water may contain aggressive ions that could lead to generalized or localized corrosion attack to the system [2]. In an open cooling water system, the return water is in direct contact with the atmosphere as it recirculates across the cooling tower structures. An open cooling system typically recirculates water in the loop for a number of cycles before it is partially replenished with fresh make-up water supply [3]. However, the water composition may significantly vary from the original intake water since the corrosion products, silts and organic matters are not removed but continue to build up and recirculate in the loop. This greatly affects the water hardness, pH, chemistry, fouling and scaling potential [4]. In addition, the oxygen ingress or water contamination may introduce dissolved oxygen or aggressive reducible ions that could increase the corrosiveness of the cooling fluid and drive up to any anodic reactions on the steel surfaces. The very trace of oxygen in water may cause a localized attack of aqueous corrosion [5].

Revie and Uhlig [6] mentioned that corrosion is a major issue as its consequences could lead to loss of integrity, process contamination, reduced system performance, increased maintenance cost or unscheduled shutdown. In order to ensure continuous plant operation, the cooling water system requires comprehensive chemical treatment program, which involves the proper selection of corrosion inhibitors and adjustment of water chemistry [7]. Corrosion inhibitors can be classified in terms of its mechanism as anodic, cathodic, film-forming or scavenging [8]. Anodic inhibitors are commonly used in cooling water systems. They are considered as passivation that could cause a positive potential shift in the anodic direction once the passive oxide film is formed on the metal surface. Anodic inhibitors can be divided into oxidizing and non-oxidizing anions. Oxidizing anions such as chromate, nitrite can passivate metal in the absence of oxygen, while non-oxidizing anions or weak oxidizers such as molybdate, phosphate require dissolved oxygen or other oxidizers to passivate the metal surface [2, 9, 10].

Chromate-based inhibitors have been used extensively in cooling water systems in the past; however, the concerns over its toxicity and wastewater disposal regulations have mandated to cease the use of using chromate-based inhibitors [10]. This has prompted the use of alternative inhibitors that are environmental friendly [11, 12]. Molybdate-based inhibitors are non-toxic but are not as effective as chromate-based inhibitors in a deaerated recirculating water system. Since molybdate is a weak oxidizer, the inhibitory action requires dissolved oxygen or other oxidizing agents such as nitrite, gluconate ions to form a protective oxide film [2, 13, 14]. In neutral to alkaline aqueous media, the presence of dissolved oxygen converts the unstable Fe (II) molybdate complex to a more stable Fe (III) molybdate complex that can passivate the metal surface [15, 16]. Ali et al. [15] proposed that molybdate ions were found to inhibit steels in neutral or basic aqueous media while nitrite ions were effective inhibitors in a slightly acidic solution. They were often injected together for a synergistic inhibitory effect, in which, the combined effect is greater than the sum of individual effects. Mohammadi et al. [2], Zhang et al. [12] and Ou et al. [13]

reported that the synergistic action of molybdate with other oxidizers such as chromate, nitrite, nitroethane and gluconate. The presence of aggressive chloride and sulfate ions in the cooling water could interfere with the adsorption of molybdate ions on the metal surface, hence higher molybdate concentrations were needed to ensure adequate protection [10]. Any injection of inhibitors below the required dosage may cause incomplete coverage of passivating film on the metal surface, leaving uninhibited areas prone to localized corrosion or pitting. Other researchers have studied the use of environmental-friendly inorganic-based inhibitors used in cooling water systems [11, 16, 17].

Operational parameters such as water chemistry, inhibitor concentration, water circulation velocity, temperature pose a considerable influence on the inhibitor efficiency in cooling water system. Most literature has focused on the experiments in static cooling water media with different corrosion inhibitor types, concentrations and solution pH [2, 10, 15].

According to Saremi et al. [18], few researchers had investigated the inhibitory efficacy of molybdate under circulating flow conditions. They reported an increase in inhibition efficiency with increased velocity. The decrease in corrosion rate can be attributed to passive layer formation because of the ease of passivating ions and dissolved oxygen to absorb on the metal surface in which, a porous, semi-protective layer was formed at under slow-flowing conditions [18, 19]. Other researchers reported a secondary reduction in the inhibitor efficiencies at higher rotation rate in the cooling water system due to enhanced wall shear stress [20]. Wehlman et al. [21] used both rotating cage and flow circuit to study the corrosiveness of inhibited water in long-term tests.

Most researchers have employed electrochemical techniques for the performance evaluation of anodic inhibitors, mostly in static condition. The present work aimed to study the effect of flow effect and the synergistic inhibitive action of molybdate and nitrite ions in simulated cooling water (SCW) using the rotating cage and mini flow loop set up.

2. Methods

2.1. Materials

Carbon steel grade C1018 was used as the test specimens with the chemical composition shown in Table 1. Saremi et al. [18] explained that simulated Cooling Water (SCW) was prepared as the test solution with its chemical composition listed in Table 2. All salts used are analytical grade. The specimens were machined into thin rectangular strips of dimensions $7.5 \times 1.0 \times 0.15$ cm and polished up to 600 grit with silicon carbide sandpaper.

Polished specimens were rinsed with deionised water followed by ethanol (reagent grade) and then dried with an air blower. They were installed as weight loss coupons in a rotating cage and mini flow circuit. The specimens were immersed in pH 8.0 test solution for 72 hours at 30 °C. The corrosion rate was measured by using a weight-loss method as per ASTM G31 [22]. Two levels of flow circulation were tested to simulate the low and high flow velocities: 0.3 m/s and 1.2 m/s. Two types of anodic corrosion inhibitors (CI): sodium molybdate and sodium nitrite salts were used. The synergistic effect when combining these two salts together was also tested.

Table 1. Chemical composition of C1018 steel.

Species	C	Mn	P (max)	S (max)	Fe
Composition (%)	0.18	0.75	0.04	0.05	Balance

Table 2. Chemical composition of simulated cooling water [18].

Species	Na^+	Ca^{2+}	Cl^-	SO_4^{2-}
Concentration (mg/L)	119	100	180	200
Species	HCO_3^-	CO_3^{2-}	Alkalinity as $CaCO_3$	Total hardness as $CaCO_3$
Concentration (mg/L)	35	15	44	250

2.2. Rotating cage experiment

A custom-made rotating cage was designed and machined from nylon material. The cage can be used to hold the corrosion coupons and simulate the stirring flow condition in a 1-litre beaker. The rotating cage has a dimension of 6.8 cm in diameter and 7.5 cm in height, almost similar in design to ASTM G184 [23]. Two opposite facing slots (1.0 × 0.15 cm) were machined at the outer edge of the cage to serve as the holders for two corrosion coupons. The cage assembly was attached to a stirring shaft driven by a motor as shown in Fig. 1. The speed controller can regulate the rotational speed. Two levels of rotational speed were selected to simulate the low flow (95 rpm) and high flow (382 rpm) conditions, equivalent to the tangential velocity of 0.3 m/s and 1.2 m/s, respectively. Corrosion experiments were conducted by rotating the cage with coupons in the SCW solution over for 72 hours at ambient 28°C and pH8. Following the immersion corrosion test in ASTM G31 Standard [22], the corrosion rates (CR) can be calculated from the accumulated mass removal of the coupons during the exposure period as below:
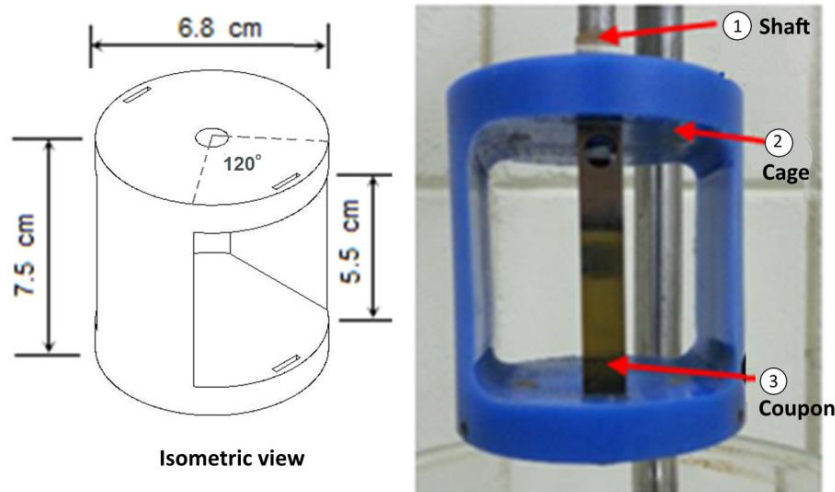
$$CR = \frac{KW}{ATD} \tag{1}$$

Fig. 1. Isometric view (left) and the nylon-made rotating cage with coupon installed (right).

2.3. Mini flow circuit experiment

A custom-built flow circuit was designed and fabricated as per ASTM D2688 [24] to simulate the dynamic flow in an open recirculating cooling circuit. The test setup consists of 15 mm diameter, 1.16 m long class-B PVC pipe as flow circuit, solution tank, water pump (75 W) and two corrosion coupons completed with mounting plugs, as shown in Fig. 2.

Two levels of flow velocities can be regulated by a ball valve to simulate low flow (0.25 m^3/hr) and high flow rates (1.0 m^3/hr), corresponding to a mean velocity (U_{mean}) of 0.3 m/s and 1.2 m/s in the flow circuit as measured by a variable-area flowmeter. Corrosion experiments were conducted by recirculating SCW solution in the flow circuit mounted with two corrosion coupons for 72 hours at ambient temperature 28°C and pH8.
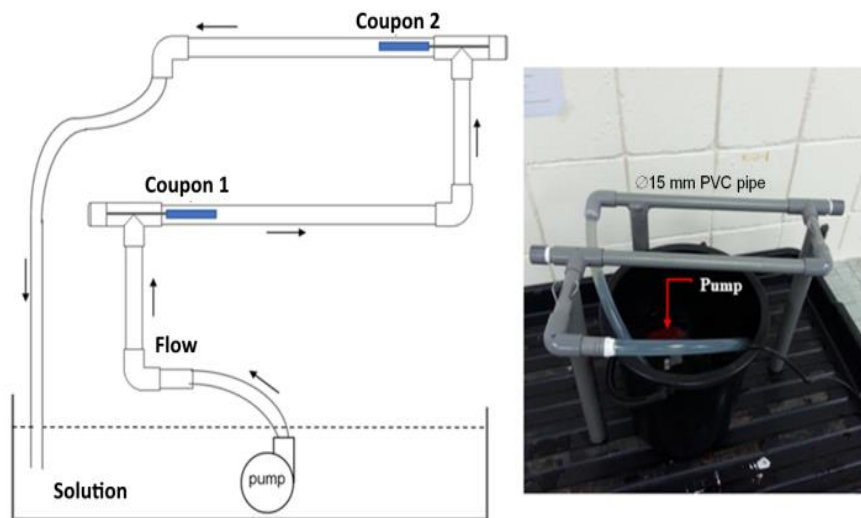

**Fig. 2. Schematic view (left) and experimental
setup (right) of recirculating flow circuit.**

2.4. Test matrix

The test matrix for this work is shown in Table 3. Two types of CI were studied: sodium molybdate and sodium nitrite. The chemicals used are an analytical grade (HmbG brand), specified as $Na_2MoO_4 \cdot 2H_2O$ and $NaNO_2$.

The chosen test parameters were CI types, concentration, flow velocity and test set up. Three different CI concentrations were selected: 400 ppm of sodium molybdate (M400), 400 ppm of sodium nitrite (N400) and the combined pair: 200 ppm sodium molybdate and 200 ppm sodium nitrite (M200-N200).

Prior to the start of the experiment, the CI was added and mixed to the SCW. Two levels of velocities: 0.3 m/s and 1.2 m/s were selected to simulate low and normal operating flow conditions. Blank solution without CI treatment was included as a control.

Table 3. Test matrix.

Parameter	Value
Coupon	C1018 steel coupon ($7.5 \times 1.0 \times 0.15$ cm)
pH	8.0
Temperature (ºC)	$28° \pm 1°$
Test duration (hr)	72
Test solution	SCW solution (refer Table 1)
CI type	M400, N400, M200-N200
CI concentration (ppm)	200, 400
Test set up	Rotary cage, mini flow circuit
Flow velocity (m/s)	0.3, 1.2

3. Results and Discussion

3.1. Rotating cage experiments

In a rotating cage (RC) experiment, the corrosion rates between different flow velocities and inhibitors are compared in Fig. 3. For low flow in uninhibited SCW, the corrosion rate was moderate around 0.44 mm/y but the corrosion became aggravated once the flow increased to 1.2 m/s. This can be explained by the increased rate of mass transport brought by the turbulent flow. In flowing condition, the high mass transfer rate increased the chances of dissolved oxygen to absorb on the steel surface and accelerate the corrosion process [25]. For inhibited SCW case, the CI treatment (M400, N400, M200-N200) successfully decreased the corrosion rate below the acceptance criteria for both levels of flow velocities, indicating molybdate and nitrite were effective at the present test conditions. The inhibition efficiency (%) is calculated from the ratio of the difference in corrosion rates with CI (CR_i) and without CI (CR_0), as given below:

$$\text{Inhibition Efficiency}, \% = \frac{CR_0 - CR_i}{CR_0} \times 100 \qquad (2)$$

The inhibition efficiencies for the rotating cage specimens with different inhibitor treatments and flow velocities are shown in Table 4, with the combined action of M200-N200 reporting the highest efficiency.
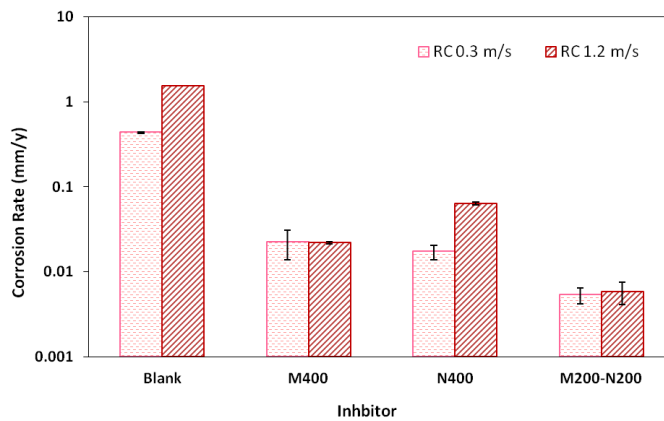

**Fig. 3. Comparison of rotating cage (RC)
results at mean velocity of 0.3 m/s and 1.2 m/s.**

Table 4. Inhibition efficiency (%) for rotating cage experiments.

CI Type	U_{mean} = 0.3 m/s Inhibition efficiency (%)	U_{mean} = 1.2 m/s Inhibition efficiency (%)
M400	94.9	98.6
N400	96.0	95.9
M200-N200	98.8	99.6

Test results showed that the inhibition efficiency increased with the combined inhibitor treatment of M200-N200, indicating synergistic behaviour between the two inhibitors. Molybdate is considered as a weak oxidizer, hence the addition of oxidizing agents such as nitrite helped to improve the inhibition efficiency at reduced concentration [2]. The synergistic pair: molybdate and nitrite provided the necessary oxidizing environment for the inhibitor to adsorb on the metal surface and form an oxide barrier that passivates the metal from further corrosion. Regarding the flow effect, the corrosion rates for steel in inhibited SCW were comparable in both levels of flow velocity, indicating the effective formation of the protective barrier under the flowing media. The corrosion rates were reduced to below 0.1 mm/y and were not flow sensitive. It is believed that the concentration of inhibitor was adequate to react with dissolved oxygen forming protective oxide barrier in both flow conditions. Kolman and Taylor [25] reported that the increased flow would passivate the metal better than stagnant flow because of the increased mass transfer that brought more dissolved oxygen to react with the inhibitor on the metal surface. The pH was not significantly changed for all cases during the experiments. Based on the results of Kolman and Taylor [25] and Karim et al. [26], the neutral or slightly alkaline pH environment seemed to favour the inhibitor performance.

3.2. Mini flow loop experiment

In the recirculating flow loop (FL) experiments, corrosion rates by weight loss method are compared in a chart in Fig. 4. It is observed that the results portray almost a similar trend with the previous rotating cage experiments. For low flow (0.3 m/s) in uninhibited SCW, the corrosion rate was moderate but the value increased fourfold when the flow rose to 1.2 m/s. The increased mass transfer rate caused by turbulent flow contributed to increased corrosion rate. For SCW solution treated with inhibitors, corrosion rates were significantly reduced to values lower than 0.01 mm/y, indicating the inhibitor was effective to form a protective barrier on the metal surface at the present dosage in flowing media. In an aerated environment, molybdate/nitrite ions adsorb on the metal surface and react with oxygen to form a complex oxide film that is negatively charged. Such oxide film repels aggressive chloride ions and ensures the protectiveness of the surface barrier [27]. Similar to the rotating cage experiment, the combined treatment of molybdate and nitrite displayed a synergistic effect by reducing the corrosion rate to the lowest value with reduced concentration. The flow did not appear to affect the corrosion rates in inhibited SCW solution in both flow conditions, though metals tend to passivate better in flowing mediums [25]. Further, the critical velocity was not investigated wherein the protectiveness of the film might be possibly impaired by the high shearing flow. The pH measured after the test was around pH 7.2-7.5, which did not differ much from the starting pH value of 8.

The inhibition efficiencies for the mini flow loop experiments in uninhibited and inhibited SCW with different inhibitor treatments and flow velocities are displayed in Table 5. Similarly, the combined treatment of M200-N200 showed the highest percent of inhibition efficiency.

Table 5. Inhibition efficiency (%) for mini flow loop experiments.

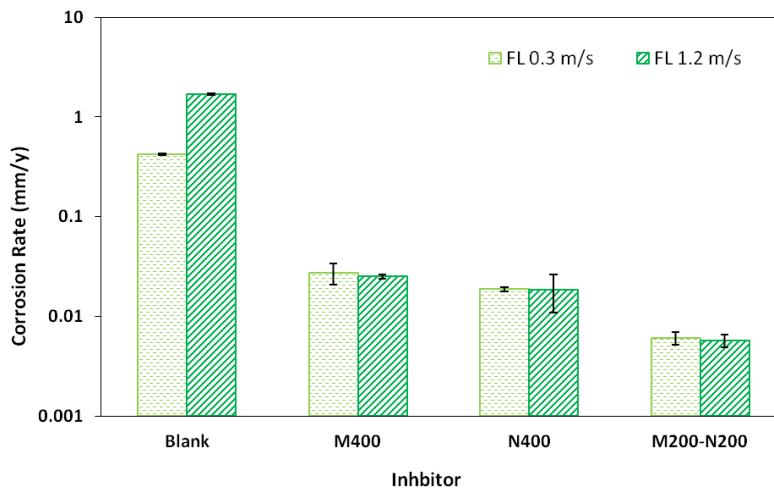| CI type	U_{mean} = 0.3 m/s	U_{mean} = 1.2 m/s
	Inhibition efficiency (%)	Inhibition efficiency (%)
Blank	-	-
M400	93.5	98.5
N400	95.6	98.9
M200-N200	98.6	99.7

**Fig. 4. Comparison of mini flow loop (FL)
results at mean velocity of 0.3 m/s and 1.2 m/s.**

3.3. Comparison between rotating cage and mini flow loop

Results comparing the rotating cage and mini flow loop test data are plotted in Fig. 5. As shown in the chart, the corrosion rates obtained from both testing are quite similar for all cases, with the uninhibited SCW solution having the highest corrosion rate and the inhibited SCW solution having low corrosion rates below the acceptance limit. Mustafa et al. [27] agreed in both testing, in which, reported the lowest corrosion rates and the highest inhibitor efficiency for the combined treatment of molybdate and nitrate salts.

The results from both testings were incomparable to each other, which showed a good relation between the two techniques. Rotating cage experiment is relatively straightforward and can be considered as fast beaker test while flow loop test is more elaborate and requires extensive setup [21]. However, more flow parameters should be tested out to validate the correlation between the two techniques.
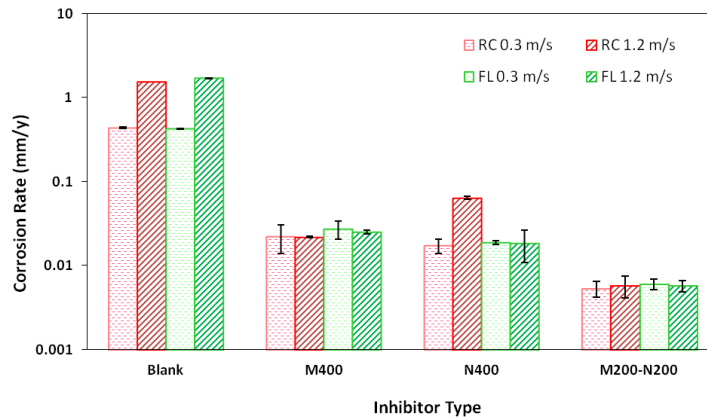
**Fig. 5. Comparison of rotating cage (RC) and mini flow
loop (FL) results at mean velocity of 0.3 m/s and 1.2 m/s.**

3.4. Visual inspection

Upon completion of the 72-hour test, all coupons were extracted from the flow loop
apparatus. Visual inspection and microscopy analysis were performed to examine
the exposed surfaces for any deposit of corrosion products or pitting. For the case
of uninhibited steel coupon, the shiny surfaces have turned dull and darkish colour
as can be seen in Fig. 6(a). The corroded surfaces of the coupon were uneven and
mostly covered with spotty rust products. Localized corrosion in the form of small
pits was found strewn randomly throughout the exposed surface. Pitting was more
difficult to detect visually since some pits were covered by the corrosion products.

The occurrence of pitting can be attributed to the corrosion attack at the weaker
sites of the oxide film that eventually led to localized film breakdown. For the case
of inhibited SCW treated with molybdate shown in Fig. 6(b), the extracted coupon
appeared to retain most of the shiny appearance with a minimal surface covered
with streaks of rusts. Upon inspection, small size pits can still be seen sparingly on
the surface. However, the coverage of the corroded area, pit size and pit number
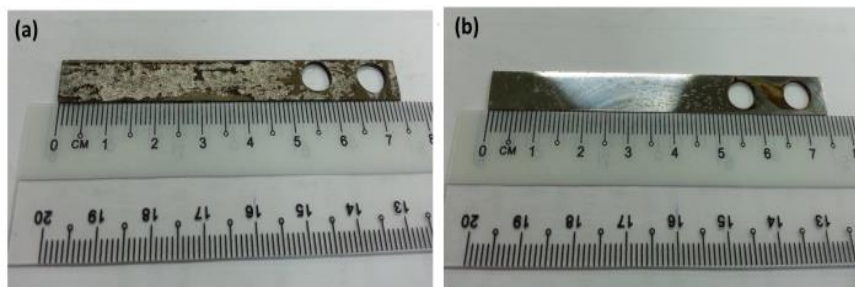decreased significantly as compared to the uninhibited coupons.

**Fig. 6. Coupons after 72-hour flow circuit tests in SCW
solution: (a) Without inhibitor, (b) With molybdate, M400.**

3.5. Surface microscopy

Surface morphologies of the steel coupons after 72-hour test in uninhibited and inhibited SCW solution are shown in Figs. 7 and 8, respectively. Images were taken using a stereoscopic microscope and the optical microscope, respectively. As shown in Fig. 7(a), untreated steel coupon is badly corroded and most areas are covered by significant scale products. The uniform corrosion rate by metal loss method was reported high.

On the contrary in Figs. 7(b) and (c), the steel coupons treated with inhibitors show relatively large surface free of scale products, but still randomly strewn with localized pitting. The surface smoothness of the coupon was not severely affected in inhibited case. The improvement in surface morphology in the presence of inhibitor can be attributed to the formation of a protective oxide barrier that impedes the corrosion process. The corrosion rates were reported low due to the protective barrier. However, the localized corrosion in the form of small pits can still be observed in all cases, indicating the susceptibility of the oxide film to the attack of aggressive chloride ions. Generally, the pits seen in untreated steel coupon were larger, deeper, and often covered by rusts as shown in Fig. 8(a). The close-up views of the pits for each inhibitor case are shown in Figs. 8(b) to (d). For the case of M400 and N400, the pits were often stained by rust product, showing a progressive breakdown of protective film initiated from the pit. For the combined inhibitor pair M200-N220, the exposed coupon surface appeared to be more protected as the pits were smaller, shallower and not stained by rust.
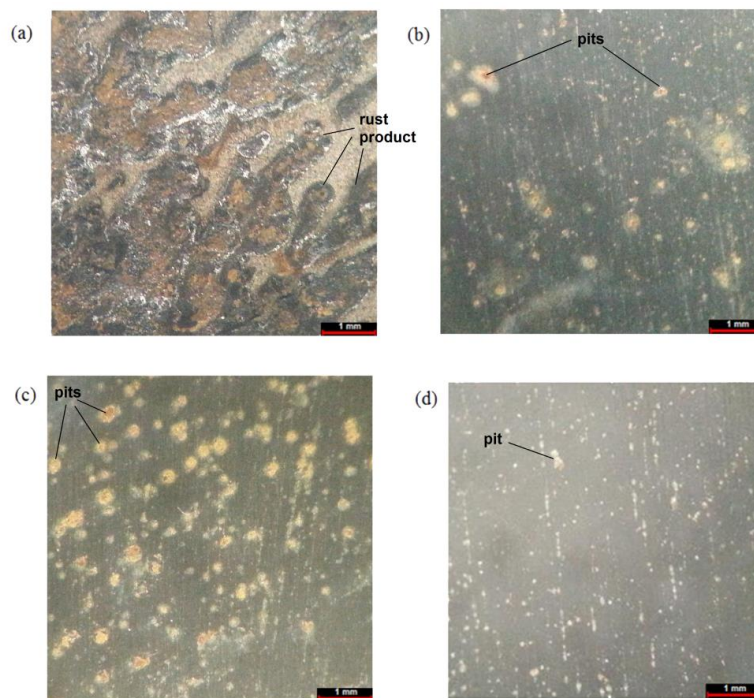

**Fig. 7. Stereoscopic micrographs (15X) after 72 h exposure to
SCW solution: (a) Without inhibitor, (b) With sodium molybdate M400,
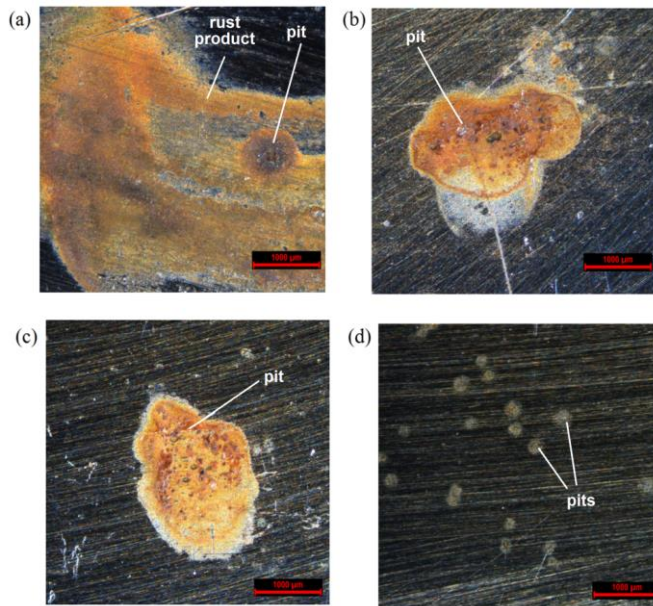(c) With sodium nitrite N400, (d) With combined pair M200-N200.**

Fig. 8. Optical micrographs (20X) after 72 h exposure to SCW solution:
(a) Without inhibitor, (b) With sodium molybdate M400,
(c) With sodium nitrite N400, (d) With combined sodium molybdate
and sodium nitrite, M200-N200.

This can be attributed by the repassivation of the pits via the synergistic interaction of the molybdate and nitrite ions [14]. Molybdate is a weak oxidizer and the addition of nitrite serves as the needed oxidizing species to chelate molybdate with the metal ions forming passive oxide film [2]. The interaction is synergistic in nature as the passivity of the oxide film proves to be more inert than molybdate or nitrite ions alone. The electrochemical results by Mohammadi et al. [2] further revealed that the combined CI shifted the corrosion potential of the steel specimen to more cathodic and simultaneously suppressed the corrosion current. The corrosion behaviour was in agreement with the mechanism of anodic inhibitor that displayed positive potential shift once the exposed metal surface is passivated by the oxide film. Though the uniform corrosion rate was reported low in inhibited SCW solution, the protectiveness of the barrier was challenged by pitting when promoted by chloride ions.

3. Conclusions

An experimental investigation has been made of the inhibitory effects of molybdate and nitrite salts used in the process cooling water system. Some concluding observations from the investigation are given below:

- Weight loss corrosion rate results using the rotating cage and mini flow circuit are comparable, showing that a rotating cage can be used as an effective fast beaker test for corrosion inhibitor screening.

- Both molybdate and nitrite were effective corrosion inhibitors in reducing the steel corrosion rates in SCW solution. The maximum inhibition efficiency was attained by using the combined pair of molybdate and nitrate salts.

- The elevated flow velocity in inhibited SCW solution did not affect the inhibition, as the corrosion rates remained low, showing effective adsorption of the inhibitor to form surface barrier film.

- Surface morphology showed that the steel specimens were protected from general corrosion in inhibited SCW. Localized pits were still observed but appeared to be less severe in the case of a combined pair of molybdate and nitrate salts.

Acknowledgement

Nomenclatures	
A	Exposed area (cm^2)
CR$_o$	Un-inhibited corrosion rate (mm/y)
CR$_i$	Inhibited corrosion rate (mm/y)
D	Metal density (g/cm^3)
K	Constant, 87.6
T	Exposure time (h)
U$_{mean}$	Mean velocity (m/s)
W	Metal mass loss (mg)
Abbreviations	
ASTM	American Society for Testing and Materials
CI	Corrosion Inhibitor
FL	Flow Loop
RC	Rotating Cage
SCW	Simulated Cooling Water

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