

Synergistic Effect of Some Inorganic Corrosion Inhibitors for Carbon Steel in Cooling Water

Mudhaffar Y. Hussein, Haider J. Mohammed , Alaa A. Nagy

Abstract

The current approach to cooling water treatment is to use a multi – component inhibitors. Cooling water formulations containing mixtures of inhibitors usually offer better and increased protection to ferrous metals than similar concentrations of either of the individual components. Such mixtures are synergistic in their action .But; the synergistic effects between nitrites, molybdates and inorganic phosphate were not investigated until recently. A weight loss technique was used to investigate such mixture and to optimize the concentrations of the components in the blend. Consequently; an efficient and effective blend was developed as a corrosion inhibitor for carbon steel in aerated Al–Daura refinery re-circulating cooling water in the pH range 6.75 to 7.25. The preferred concentrations of components in the multi- component inhibitor blend (as ppm) were: (SN + SM): SHMP = 800: 20 with SN: SM weight ratio =3:2. The reduction in corrosion rate was 97.6 % .

تأثير اضافة خليط متجانس من مثبطات التآكل اللاعضوية على الفولاذ الكربوني في ابراج التبريد

مظفر يعقوب حسين/جامعة ميسان، حيدر جاسم محمد/وزارة الصناعة والمعادن، ألاء عبدالزهرة ناجي/وزارة الصناعة
والمعادن

الخلاصة

السياق الحالي في معاملة مياه التبريد هو باستخدام مثبطات متعددة العناصر. خليط مثبط التآكل هذا يمنح وقاية أحسن وأكثر للمعادن الحديدية مما يمنحه أي من عناصر الخليط لوحده وبنفس تركيز الخليط . هذه التراكيب متداخلة في عملها ، ولكن لم يتم دراسة التأثيرات المتداخلة مابين النيتريتات والموليبيدات والفوسفات المتعددة الغير عضوية إلا في الفترة الاخيره . تم استخدام طريقة فقدان الوزن لدراسة هذا الخليط وإيجاد التركيز الأمثل لعناصره. وبناء عليه تم تطوير خليط مثبط تآكل كفوء وفعال للحد من تآكل الفولاذ ألكاربوني في مياه تبريد مصفى الدورة في مدى حامضية 6.75-7.25. إن افضل تركيز لعناصر خليط مثبط التآكل (جزء بالمليون) هو : (نترت الصوديوم +موليبيدات الصوديوم) : فوسفات الصوديوم السداسية = 800 : 20، وان النسبة الوزنية لنترت الصوديوم إلى موليبيدات الصوديوم تساوي 3:2. تم تقليل معدل التآكل بنسبة 97.6 % باستخدام هذا الخليط .

INTRODUCTION

Industrial cooling has become more of a problem during the past decades. Water is the most commonly used cooling fluid [1]. It removes unwanted heat from heat transfer surfaces in condensers and coolers. A cooling tower is a heat rejection device, which extract waste heat to the atmosphere through the cooling of a water stream to a lower temperature. The type of heat rejection in a cooling tower is termed "evaporative" in that it allows a small portion of the water being cooled to evaporate into a moving air stream to provide significant cooling to the rest of that water stream [2]. Make-up water must be added continuously to compensate for evaporation [3]. As evaporation occurs, the concentration of salts in the water will increase, hence, corrosion increases. Water is a corrosive media to most alloys and contributes to the build-up of insulating deposits through water-formed and water-borne foulants. Therefore, industry is confronted with the problem of saving cooling water as well as improving water quality. These two goals, saving and quality improvement can be reached only by adequate water treatment. Within the scope of this treatment, the inhibition of corrosion and scale deposition takes a key position [4]. Corrosion can be minimized by the addition of corrosion inhibitor. The current approach to cooling water treatment is to use multi-component inhibitors. Cooling water formulations containing mixtures of inhibitors usually offer better and increased protection to ferrous metals than similar concentrations of either of the individual components. Such mixtures are synergistic in their action [1,5-13]. But, the synergistic effects between nitrites, molybdates and inorganic phosphate were investigated by several previous authors [11, 13]. Sodium nitrite (SN) is classified as an oxidizing anodic inhibitor [5]. It can be effectively used for corrosion control of

carbon steel in water when the weight ratio of SN: total aggressive ions (Cl^- or $\text{Cl}^- + \text{SO}_4^{2-}$) equals one or less [5-7,9-12,14-16]. The protective oxide film formed on the treated metal surface with nitrite consists

mainly of $\text{Fe}_3\text{O}_4 + \text{Fe}_2\text{O}_3$ [17,18], which was confirmed by Tal et al. [10]. Sodium Molybdate (SM) is added, firstly, to inhibit both pitting and differential aeration attack [19] and secondly, to reduce the nitrite level. It is a non oxidizing anodic inhibitor and requires a suitable oxidizing agent, such as oxygen, to augment the inhibition and to impart a protective film. Sodium salts of the poly-phosphates {sodium hexa metaphosphate, SHMP, $(\text{NaPO}_3)_6$ } are normally used for corrosion control as well as for calcium carbonate scale control [4]. High levels of phosphates can create deposition problems (reduce the efficiency of process equipment and result in localized crevice corrosion) and can also act as nutrients for algae growth. Hence, phosphates alone are not recommended [20]. Phosphate concentration could be drastically reduced by blending it with SN [8]. Normal concentrations in re-circulating waters are 15-20ppm, and the pH should be maintained in the range of 6.5-7.5 if steel and copper alloys are both part of the system metallurgy [6].

Al-Borno et al. [8] reported that the corrosion inhibition was enhanced when some of SN was replaced with SM in the multi-component inhibitor blend. The best results were obtained at a ratio of SN:SM: poly-phosphate:ortho-phosphate equals to 3:2:1:1. Furthermore, Tal et al. [11] investigated the corrosion inhibition of carbon steel in simulated Azzarqa / Jordan Refinery re-circulating cooling water (containing total aggressive ions, i.e., $\text{Cl}^- + \text{SO}_4^{2-}$ equals 1150ppm) using a multi-component inhibitor system comprising SN, SM and SHMP. Optimum total concentration of SN and SM was obtained, i.e., 1200ppm, using a weight loss technique

at a ratio of SN: SM=3:2. The SHMP concentration was kept at 20ppm. The corrosion rate at a ratio of (SN+SM): total aggressive ions =1 was at minimum and almost nil. Using a potentiostatic technique and the above said inhibitors concentrations, the metal was characterized by an active-passive transition, a behavior that differs from that and not observed in an uninhibited solution.

Moreover, Hasen [11] studied the corrosion inhibition of carbon steel in neutral aerated water containing 600ppm Cl⁻ using a multi-component inhibitor blend of SN, SM and SHMP at a ratio of SN:SM:SHMP equals 3:2:1. The metal was also characterized by an active-passive transition a behavior that was not pronounced under static conditions which was also observed by Tal et al. [10]. Finally, AL-Qasem et al. [13] studied the corrosion inhibition of carbon steel in neutral aerated water containing 1200 ppm Cl⁻ using a multi-component inhibitor blend of SN, SM and SHMP at a ratio of SN: SM equal 3:2 and 20ppm of SHMP at pH values of 7.5 and 8.5. They found that the corrosion rate is independent of the pH of the solution. Other Workers [7, 9, 12] used SN and SHMP alone to inhibit the corrosion of carbon steel in water containing 600ppm Cl⁻. The metal was not characterized by an active-passive transition as in the presence of SM. The purpose of the present work is to develop a synergistic inorganic blend containing SN, SM and SHMP to inhibit the corrosion of carbon steel in aerated Al-Daura refinery re-circulating cooling water in the pH range 6.75- 7.25. A weight loss technique was employed to optimize the concentrations of the components in the inhibitor blend

EXPERIMENTAL WORK

The experimental work involved immersion tests the aim of which was to optimize the concentrations of the inhibitors SN, SM and SHMP in the blend to inhibit corrosion of

carbon steel in Al-Daura refinery re-circulating cooling water at 303 and 323 K bulk temperatures. Test coupons with dimensions of 50mm*25mm*1.5mm were cut from carbon steel sheet having the chemical composition (by X-Ray equipment) shown in Table1 [Central Organization for Standardization and Quality Control, Jadiryah, Baghdad-Iraq].

Table 1

Composition of carbon steel (wt %)

C	Mn	Si	Ni	S	Cr	Fe
0.13	0.371	0.044	0.031	0.017	0.0033	remainder

They were annealed, grinded to 1000 grit, washed with running tap water followed by distilled water and finally with acetone and dried with clean tissue paper. Then, they were kept in a desiccator over a silica gel. Tests were conducted in one liter glass flask containing 700ml of stagnant aerated Al-Daura refinery re-circulating cooling water with and without the different inhibitors blend mixtures. Table2 shows the composition of the cooling water [Private Communication with Al-Daura refinery, (2009)].

Table 2

Composition of Al-Daura refinery re-circulating

pH	Cl ⁻	SO ₄ ²⁻	TDS	TH(CaCO ₃)	Mg ²⁺	Ca ²⁺	HCO ₃ ⁻
8.4	600	200	1550	900	300	700	300

cooling water ppm

Test solutions were prepared from distilled water and Analar chemicals. Different concentrations of SN+SM (400, 600 and 800ppm) having SN:SM=3:2 [8,10,11,13] and 20ppm of SHMP [10,13] were used in the test solutions. The final

electrolyte pH was maintained in the range (6.75-7.25) [6].

Test coupons were weighed before immersion in the test solution. At the end of two – day immersion test the coupons were cleaned by 40% HCl then washed with running tap water followed by distilled water and finally with acetone and dried with clean tissue paper and reweighed. A total of five immersions (5*48 h) were made for each specimen using fresh solutions. Weight lost in each case was found and the total weight lost was used for the determination of corrosion rate [21]. The immersion tests were according to ASTM standard [22].

RESULTS AND DISCUSSION

The most convenient way of expressing corrosion rate is mils penetration per year (mpy) and calculated by using the following formula [21]:

$$\text{mpy} = \frac{534W}{ADT} \dots\dots\dots(1)$$

Where: W=weight loss,mg

D=density, g/cm³=7.87 for carbon steel

A=area of specimen, in²

T=exposure time, h

Using experimental data shown in Annexes 1 and 2 and Equation 1, the results of immersion tests with and without different concentrations of mixed inhibitor blend at temperatures of 303 and 323 K are shown in Table 3.

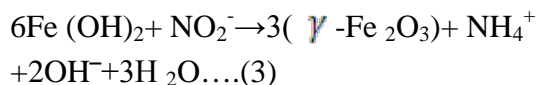
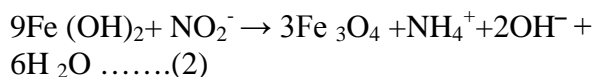
Table 3.

The corrosion rate with and without different concentrations of inhibitor blend at temperatures of 303 and 323K, mpy

(SN+SM)+SH MP, ppm(SN:SM=3:2)	0	400+20	600+20	800+20
Corrosion rate at 303K, mpy	8.697	5.16	0.8	0.249
Visual observation	Corroded coupon, red water and uniform corrosion	Corroded coupon, slightly yellow water and pitting observed	Fairly clean coupon and water and no pitting observed	Very clean coupon and water
Corrosion rate at 323K, mpy	14.596	9.612	0.98	0.344
Visual observation	Corroded coupon, red water and uniform corrosion	Corroded coupon, yellow water and pitting observed	Corroded coupon, slightly yellow water and little pitting observed.	Clean coupon and water

Table 3 shows that the corrosion rate decreases as the SN+SM concentration increases at both experimental temperatures, i.e., 303 and 323K. It reaches a minimum value at 800 ppm SN+SM concentration, i.e., below 1 mpy. A Corrosion inhibition program producing such low corrosion rate can be considered as an excellent one [17]. Several workers [11, 12, 14] reported that the corrosion rate was at minimum and almost nil when the ratio of SN+SM: total aggressive ions (Cl⁻ + SO₄²⁻) equals 1. In this work the ratio equals 1 (see Tables 2 and 3). Therefore, the present work is in agreement with the previous findings [11, 12, and 14]. Table 3 also shows that at inhibitor blend concentration less than 800+20 ppm, pitting was observed on the metal surface, especially, at higher temperature, i.e., 323K.

The corrosion attack, in the form of pitting was very pronounced at inhibitor blend concentration less than 600+20. However, in uninhibited solution the metal surface had suffered uniform corrosion only. On the other hand, at 800+20 inhibitor concentration, corrosion had almost ceased and pitting was completely arrested. This may be due to the synergistic effects of SN, SM and SHMP. It was stated previously that the protective oxide film formed on the treated metal surface with nitrite consists mainly of $\text{Fe}_3\text{O}_4 + \gamma\text{Fe}_2\text{O}_3$ [11, 18, and 19]. It is formed through the adsorption of nitrite ion followed by an oxidation step. The overall reaction is one or both of the following [25]:



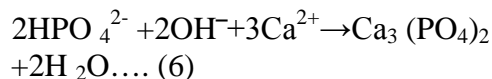
Joseph [26] suggested that in an aerated electrolyte, ammonium ions are oxidized by oxygen with regeneration of nitrite ions according to the equation:



Hence, adsorbed nitrite ions catalyze, as they were, the oxidation of divalent iron to trivalent iron by oxygen, while they themselves are regenerated. When SM is added, in presence of nitrite, ferric molybdate is formed which is both insoluble and protective in neutral water [7].

Rozenfeld [6] reported that SHMP has a property of forming soluble complexes with Ca^{2+} ion and other ions of metals. This prevents the formation of carbonate deposits of calcium and iron that interfere with heat transfer. Hence, SHMP was considered as the most effective compound for the prevention of scale formation.

Rozenfeld [6] further stated that, even in the presence of oxygen and Ca^{2+} ions, polyphosphates do not act directly as inhibitors, and the protective properties are manifested only by the product of SHMP hydrolysis (HPO_4^{2-}) which together with the hydroxyl ions, appearing on the electrode surface upon reduction of oxygen (see Eq.5), promote the deposition of calcium phosphate on metal according to Eq.6.



The scale forming tendency of $\text{Ca}_3(\text{PO}_4)_2$ is a complex function of pH, calcium hardness, PO_4^{3-} concentration, ionic strength and temperature [6]. The PO_4^{3-} ions produced fill in the voids in the oxide film of $\gamma\text{-Fe}_2\text{O}_3$ in parallel with MoO_4^{2-} and accelerate film growth, i.e., formation of $\text{Ca}_3(\text{PO}_4)_2$. These plugs prevent any further diffusion of Fe^{2+} from the metal surface. Therefore, the anodic dissolution will be drastically reduced [11]. Moreover, Table3 shows that the corrosion rate increases with temperature. This is to be expected as temperature increases the rate of almost all chemical reactions and the iron dissolution and oxygen reduction on the metal surface are temperature dependent [10,11,17,23].

The reduction percentages of the corrosion rates, for inhibitor blend concentration (SN+SM) +SHMP= 600+20 and 800+20, were calculated (using Eq.7) at 303 and 323K and are shown in Table 4:

$$\% \text{ reduction} = \left(1 - \frac{C_{in}}{C_{un}}\right) * 100 \dots \dots \dots (7)$$

Where:

C_{in}= corrosion rate in inhibited solution

C_{un}= corrosion rate in un inhibited solution

Table4

Percentage of corrosion rate reduction

(SN+SM)+SHMP,ppm	600+20	800+20
303K	90.8	97.1
323K	93.3	97.6

Table 4 shows that higher percent reduction of corrosion rate at a higher temperature, i.e., 323K. Temperature increases the hydrolysis of SHMP to HPO_4^{2-} and, hence, accelerates the deposition of calcium phosphate on the metal surface according to Eq.6. Therefore, corrosion of the metal is drastically reduced [11] as discussed above.

Table 4 also shows that high % reduction of corrosion rates, i.e., 90.8 and 93.3 at temperatures of 303 and 323 K respectively for inhibitor concentration = 600+20 ppm. But, pitting was observed on the coupon surface for this concentration at 323K. In drastically this temperature may be considered as an average temperature at the metal /

cooling water interface in water coolers tubes. Therefore, for corrosion inhibition of carbon steel in aerated Al- Daura refinery re-circulating cooling water, the synergistic multi- component inhibitor blend containing SN, SM and SHMP added as weight ratio (SN+SM): SHMP = 800:20, with SN: SM weight ratio = 3:2 is an efficient and effective corrosion inhibitor. The % reduction of corrosion rates at 303 and 323 K are 97.1 and 97.6 respectively.

CONCLUSIONS

A synergistic multi- component inhibitor formulation containing SN, SM and SHMP was developed. The inhibitor blend is very efficient and effective as a corrosion inhibitor for carbon steel in aerated Al-Daura refinery re- circulating cooling water in the pH range 6.75 to 7.25. The preferred concentration of components in the inhibitor blend (as ppm) are: (SN+SM): SHMP = 800:20, with SN: SM weight ratio = 3:2 and the corrosion rate reduction is 97.6%. At weight ratio of the inhibitor blend to the total aggressive ions =1, corrosion had almost ceased and pitting was completely arrested.

Annex1 Weight loss data with and without different concentrations of inhibitor blend at 303 and 323K, mg

(SN+SM) + SHMP, ppm	Temperature K									
	303					323				
	Time,h									
	48	96	144	192	240	48	96	144	192	240
0	12.0	32.5	63.5	99.5	141.5	35.3	76.9	121.9	170.9	222.9
400+20	11.3	23.0	35.1	55.3	77.3	24.8	52.6	82.1	113.3	146.8
600+20	1.6	3.8	6.2	9.0	12.0	1.9	4.4	7.4	11.0	15.0
800+20	0.7	1.5	2.3	3.0	3.7	0.9	1.8	2.9	4.1	5.3

Annex 2 Test specimens surface area,cm²

Temperature,K	(SN+SM)+SHMP,ppm			
	0	400+20	600+20	800+20
303	28.75	26.48	27.25	26.24
323	26.99	26.99	26.99	27.25

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