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Evaluation of inhibitors and biocides on the corrosion, scaling and biofouling control of carbon steel and copper–nickel alloys in a power plant cooling water system

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HIGHLIGHTS

• The components of a power plant cooling system, including tube sheet, water box, pipeline and condenser tubes were inspected.

• Despite attention to pretreatment, the condenser tubes, tube sheet and water box were covered with corrosion products and biofilm deposits.

• The results show that, using scaling inhibitor, corrosion inhibitor and biocide, corrosion rates and deposit weight of materials were decreased.

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1. Introduction

The recirculating cooling water systems are used to remove wasted heat to the environment. The power plant cooling system consists of the towers, circulation water pumps, pipelines and heat exchanger network. In cooling towers, heat of water is removed through evaporation and dissolved constituents of the recirculating water become concentrated. To excessive concentrations of the certain constituents, part of the recirculating water is removed as blow down. Therefore, make-up water must be added to the circulating water system in order to maintain an acceptable level of water salinity and or conductivity.

Three of the main problems of cooling water systems are corrosion, scaling and biofouling depending on raw water conditions, pretreatment,

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ABSTRACT

Corrosion, scaling and biofouling are three problems in the power plant cooling system. In this paper, the influence of inhibitors and biocides on control of these problems for mild steel and copper–nickel alloys in a power plant cooling water system was investigated. The results showed that alone sodium hypochlorite (NaClO) in the presence of 1-Hydroxyethylidene-1,1-Diphosphonate (HEDP), maleic anhydride homopolymer (HPMA), 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC) as scaling inhibitors, and ZnSO₄, 2-Mercaptobenzothiazole (MBT) as corrosion inhibitors was not effectively reduced corrosion, scaling and biofouling. In the presence of Alkyl Dimethyl Banzil Ammonium Chloride, one of the Quaternary Ammonium Compounds (QACs), the inhibition efficiency was increased. The effects of inhibitors on carbon steel copper–nickel were studied through electrochemical and weight loss measurement. © 2015 Elsevier B.V. All rights reserved.

chemical treatment of cooling water and concentration cycle. Raw water used in the recirculating system is usually provided from rivers and underground. The underground water is harder, contains more alkalinity and total dissolved solid (TDS) than the river water. However, the underground water is less turbid and less sensitive to microbiological contamination than surface water [1]. In general, pretreatment includes sedimentation, coagulation, water clarification, softening, pH adjustment (sulfuric acid addition) and chlorination [2,3]. As evaporation continues, the water becomes more concentrated than the original make-up water. The term cycles of concentration compares the level of TDSs of the recirculating cooling tower to the level of TDSs of the make-up water. Generally, corrosion, scaling and biofouling problems increase with increase of concentration cycles. These problems have a great economic impact, since they involve deterioration of metallic surface and loss of capacity of thermal exchange [4]. Therefore, water in cooling systems is usually chemically processed to avoid corrosion, formation of scaling and fouling. Many inhibitors and biocides have been used in cooling water systems in order to solve these problems [5]. It is common



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Table I				
Chemical composition	(average)	of make-up an	d recirculating	cooling water.

Parameter	Is	рН	M meq/l	TH meq/l	Ca ²⁺ meq/l	Cl- mg/l	Mg ²⁺ mg/l	Na+ mg/l	SO ₄ ²⁻ mg/l	Al ³⁺ mg/l	TDSmg/l	Cond. µs/cm
Make-up water	6.5	7.9	1.9	21	12.5	1125	104	600	700	0.07	2900	4800
Recirculating Water	6.2	7.8	3	27	17	1600	145	980	1200	0.1	4600	6500

to use scaling inhibitor like phosphates, polyphosphates, and organophosphonates, and corrosion inhibitors such as zinc sulphate and azoles. Generally, chlorine and or sodium hypochlorite are the most widely used as antifouling biocide in cooling systems [6–11]. Inhibitors and chlorine are added continuously, while non-oxidizing biocides such as QAC are usually added once a week [10].

Considering the fact that carbon steel and copper alloy are employed widely in pipelines and heat exchanger (condenser and cooler) tubes, corrosion, scaling and biofouling are usually studied on these alloys. The influence of biocides and inhibitors was studied in detail and many researchers evaluated the role of biocides in corrosion in the presence of inhibitors [10–17]. The purpose of the present investigation is to study the influence of a QAC biocide on the efficiency of corrosion and scaling inhibitors of carbon steel and copper–nickel in a power plant cooling system.

2. Experimental procedures

2.1. System description

Ramin Power Plant is located 20 km from the city of Ahwaz, Iran. The power plant consists of 6 units. Four units were designed and built with total capacity of 305 MW and two units were implemented with 315 MW. The recirculation water system consists of towers, circulating water pumps (CWPs), condensers and inter-connecting piping. Each condenser has a two-pass with 19,600 tubes (OD = 28 mm, thickness = 1 mm and 9 m long). The tube metal is 95Cu-4Ni-1Fe (copper-nickel). The tube sheets and water boxes are made from carbon steel which is coated with coal tar epoxy. Velocity through the tubes in condenser tubes is 2 m/s. The average temperature of water in tubes is 35 °C.

The source of make-up water for the cooling system is the Karun river. Water is pumped from the Karun river into the coagulation pools. Poly-aluminum chloride (PAC) is used as coagulants. Sulfuric

Table 2	
Chemical composition of copper-nickel specimen (wt.%).	

Zn	Pb	Sn	Mn	Fe	Ni	Si
0.03	0.01>	0.01>	0.65	1.41	6.09	0.005>
Cr	Al	S	Р	Ag	Со	Cu
Trace	Trace	None	0.15	Trace	0.01>	Base

ble	3
	ble

Chemical composition of carbon steel specimen (wt.%).

С	Si	Mn	Р	S	Cr	Ni	Мо	Cu
0.12	0.01	0.6	0.012	0.006	0.01	0.02	0.002	0.03
Ti	Со	Al	Sn	As	Sb	V	Zr	Fe
0.001	0.005	0.05	0.01	0.002	0.002	0.003	Trace	Base

acid is injected to control scaling. Microbiological fouling is to be controlled with chlorine or sodium hypochlorite. Average values of the chemical composition of make-up and recirculating water are shown in Table 1. The recirculating cooling water was designed for stability index (I_s) control with sulfuric acid. The condenser tubes, water box, tube sheet and pipeline are regularly inspected.

2.2. Metal coupon preparation

Chemical compositions of the carbon steel and copper–nickel specimens are shown in Tables 2 and 3, respectively. The specimens with dimensions of about $80 \times 13 \times 1$ mm were polished and used in the weight loss experiment and 2 cm² specimens were used for electrochemical studies.

2.3. Formulation of inhibitors and biocides

After evaluating the corrosion, scaling, biofouling, costs and environmental considerations of the inhibitors and biocides, it was decided to implement a formulation of chemicals for the aforesaid problems. HEDP, PBTC and HPMA as scaling inhibitors, MBT and ZnSO₄ as corrosion inhibitors for copper–nickel and carbon steel respectively and sodium hypochlorite as biocide were used. The scaling inhibitor was blended from HCl, HDEP, PBTC and HPMA according to Table 4. MBT and ZnSO₄–7H₂O powders were solved in 3% NaOH solution and water, respectively. The selection of this composition was based on scale and deposit analysis in condenser tubes. Results from experimental observation indicated that hypochlorite sodium is not effective on the control corrosion and scaling. Therefore, QAC (Alkyl Dimethyl Banzil Ammonium Chloride) was used as auxiliary biocide.

2.4. Electrochemical tests

Electrochemical polarization studies were carried out in 400 ml glass cell having three electrode system assembly. An Ag/AgCl electrode was used as a reference. The auxiliary electrode was a platinum rode. The working electrode was carbon steel or copper–nickel with surface of about 2 cm². Before each experiment, the working electrodes were polished, degreased and dried. Potentiodynamic measurements were carried out using an EG & G 263-A potentiostat. Polarization studies were carried out in recirculating water with various concentrations of the inhibitors. All electrochemical tests were performed in cooling water with conductivity of about 6500 (μ s/cm) under 35 °C. The evaluation of corrosion kinetic parameters was obtained using a fitting by Sten–Geary equation. The inhibition efficiency (E %) was evaluated from the measured corrosion rate (C.R) values using the relationship:

 $E \% = (C.R_{unhibited} - C.R_{hibited})/C.R_{unhibited} \times 100$

Table 4

Scaling and corrosion inhibitors formulation.

Scaling inhibitor	HEDP: $12 \text{ CC} + \text{PBTC}$: $12 \text{ CC} + \text{HPMA}$: $12 \text{ CC} + \text{ZnCl}_2$: 12 gr + HCl: $50 C + 55 CC + 0$
(dilli-scale)	12 gi + Hcl, 5-CC + 55 -CC + 120
Cu-Ni corrosion inhibitor	$MBT = 2 \text{ gr } MBT + 3 \text{ gr } NaOH + 95 \text{ CC } H_2O$
Carbon steel corrosion	$ZnSO_4 = 18 \text{ gr} + H_2O 82 \text{ CC}$
inhibitor	

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