

Development of a Blended Corrosion, Scale and Micro-Organism Inhibitor for Open Recirculating Cooling System

† Dong-Jin Choi¹, Seung-Jae You¹, Jung-Gu Kim¹, and Woo-Suk Hwang²

¹Department of Metallurgical Engineering, Sungkyunkwan University
300 Chunchun-Dong, Jangan-Gu, Suwon 440-746, Korea

²School of Materials Science and Engineering, Inha University
253, Yonghyun-Dong, Incheon, 402-751, Korea

This paper presents the results of a study that was undertaken to optimize the ratio of the components of a new multi-component inhibitor blend composed of orthophosphate/ phosphonates/ acrylate copolymer/ isothiazolone. The effects of newly developed inhibitor on carbon steel dissolution in synthetic cooling water were studied through weight loss tests, electrochemical tests, scale tests, and micro-organism tests. The obtained results were compared to blank (uninhibited specimen) and showed that developed inhibitor revealed very good corrosion, scale, and micro-organism inhibition simultaneously. All measurements indicated that the efficiency of the blended mixture exceeded 90 %. The inhibitive effects arose from formation of protective films which might contain calcium phosphate, calcium phosphonate, and iron oxide. The nature of protective films formed on the carbon steel was studied by scanning electron microscopy (SEM) and auger electron spectroscopy (AES). Inhibitor used in this study appeared to have better performance for scale inhibition due to their superior crystal modification effect and excellent calcium carbonate scale inhibition properties. The effect of inhibitor on microorganisms was evaluated through minimum inhibitory concentration (MIC) test. All kinds of micro-organisms used in this study were inhibited under 78ppm concentration of inhibitor.

Keywords : inhibitor, corrosion, scale, micro-organism, open recirculating cooling system

1. Introduction

Water, the most commonly used cooling fluid, removes unwanted heat from heat transfer surfaces. At the present time, some of demand for better utilization of the limited water supplies is due to growing population and increasing development. Because of this, open recirculating cooling water systems which reuse cooling water are frequently used at large utility central stations : at chemical, petrochemical, and petroleum-refining plants ; in steel and paper mills ; and at all types of processing plants.¹⁾ Open recirculating cooling water systems continuously reuse the water that passes through the heat transfer equipment. The only function performed by a cooling tower is cooling warm water. The cooling water circulates to operating units where it picks up heat while cooling or condensing process streams and the resulting warm water is returned

to the cooling tower.²⁾ If absolutely pure water was used for cooling water, the problems would not exist in cooling system. Unfortunately, waters contain dissolved and suspended solids, dissolved and suspended organic matter, and dissolved gas.³⁾ Finally, the open recirculating system, with its longer holding times and higher temperatures and dissolved solid concentrations, produces more severe corrosion, scaling, and microbiological organisms.⁴⁾

The objective of this study was to develop a new multi-component inhibitor for the inhibition of corrosion, scale and microorganism simultaneously. New multi-component inhibitor consisted of orthophosphate, phosphonate, acrylate copolymer and isothiazolone. A series of laboratory experiments was carried out in synthetic cooling water containing mixtures of orthophosphate, phosphonate, acrylate copolymer, and isothiazolone, from which the most promising mixture has been selected for more detailed investigation by corrosion, scale, and microorganism tests.

† Corresponding author: djchoi@skchemicals.com

2. Experimental

2.1 Formulation of inhibitor

In order to solve corrosion, scale, and microorganisms problems at the same time, a blended, environmental friendly new, inhibitor for cooling water systems has been developed. The inhibitor was blended from orthophosphate, HEDP, acrylate copolymer, and isothiazolone. Generally speaking, orthophosphate functions as a non-oxidizing inhibitor and stabilizer for new multi-component inhibitor. Also, HEDP functions as a corrosion and scale inhibitor. An additional role of the polymer in this blend is the control of scale. Isothiazolone is used as a biocide.

2.2 Weight loss tests

Tests were conducted in atmospheric pressure and one-liter glass beakers containing synthetic cooling water with and without inhibitor. The temperature and pH of the water were adjusted to $30 \pm 1^\circ\text{C}$ and 8.0 (within ± 0.1 pH unit) respectively. The solution flow rate over the specimens was 160rpm. Cooling water was collected on the representative sites where open recirculating systems were operated. Table 1 gives the chemical composition of the synthetic cooling water. Test specimens with dimensions 7.5 by 1.3 by 0.16 cm were cut from G10100 carbon steel. The chemical composition of G10100 is presented in Table 2.

Table 1. Chemical composition of the synthetic cooling water

Calcium Hardness (as CaCO_3)	M-Alkalinity (as CaCO_3)	Magnesium Hardness (as CaCO_3)	PH
200 ppm	200 ppm	40 ppm	8.0

Table 2. Chemical composition of G10100 (Wt. %)

Fe	C	Al	Mn	P	S	Si
Bal.	0.08-0.13	0.03	0.3-0.6	0.04 max.	0.05 max.	0.21

These were polished with silicon carbide paper to a 600 grit surface finish cleaned in detergent rinsed with acetone and weighed before immersion in the test solution. At the end of the immersion tests, the specimens were removed and cleaned for 10 min in the cleaning solution (500 ml HCl + 3.5 g hexamethylene tetramine and distilled water to make 1000 ml).⁵⁾ The specimens were then rinsed in distilled water, dried in an oven at 80°C for 30 min and reweighed to 10^{-4} g for the determination of corrosion rates.

2.3 Electrochemical tests

The specimens were in the form of cylinder with the

dimensions of 1.3 cm (length), 1.3 cm (diameter), 0.1 cm (thickness) and were prepared from G10100 carbon steel. Potentiodynamic polarization curves were generated using an EG&G 273A potentiostat. The electrochemical tests were carried out in a 1-L glass cell similar to that used elsewhere. The cell contained the working electrode, a glass capillary probe connected to a reference electrode, and two graphite rod counter electrodes. Before each test, the specimens were polished with silicon carbide paper to 600 grit, degreased in acetone, and washed in distilled water. It features a specimen mounted on a rotating holder so that the water flow rate over the steel surfaces could be maintained at a velocity of 160 rpm. All tests were performed at $30 \pm 1^\circ\text{C}$ and under ambient conditions. All tests were carried out at a scan rate of 0.17 mV/s after OCP. Electrode potential measurements were made with reference to a saturated calomel electrode (SCE). Polarization resistance tests were performed for 48 hours. The same specimen and cell as polarization test were used in this test.

2.4 Scale tests⁶⁾

Inhibitors were evaluated in flasks to which calcium and M-alkalinity were added. Test conditions were : with and without 100 ppm inhibitor ; 100, 200, 300 ppm calcium hardness (as CaCO_3) and M-alkalinity (as CaCO_3) ; 24 hours at 70°C . The flasks were incubated for twenty-four hours at the test temperature. After the incubation period, the flasks were removed from the heat source (an oven) and an aliquot was filtered through a $0.45\mu\text{m}$ membrane. The filtrate was titrated for calcium and Percent calcium carbonate inhibition was calculated from the following equation :

$$\% \text{ inhibition} = \frac{C_a}{C_b} \times 100$$

where :

$C_a = \text{Ca}^{2+}$ concentration after tests, $C_b = \text{Ca}^{2+}$ concentration before tests

2.5 Micro-organism tests (MIC experiments)⁷⁾

The biocide evaluation, controlling the specific growth of different micro-organism, was based on the minimal inhibitory concentration (MIC) technique. The inhibitor was tested on 4 species of bacterium and 4 species of fungus. A series of test tubes was prepared, all containing the same volumes of medium inoculated with the test bacteria and fungi to 10^5 CFU/ml (colony forming unit/ml). The efficacy of the inhibitor was tested ranging from 0 to 5,000 ppm concentration. Decreasing concentrations of

inhibitor were added to the tubes. Stepwise dilution by a factor of 2 was used. The samples containing inhibitor and cultures were then incubated at 30°C for 48 hours. The culture tubes which showed turbidity were considered positive and others were considered negative effect about microbial growth. The minimum inhibitory concentration of the inhibitor in a culture tube, containing specific bacteria or fungi which did not show any turbidity.

2.6 Surface analyses

Examination of the carbon steel after exposure to the water with and without inhibitor was carried out using optical microscopy and SEM. Elemental analyses for the exposed surfaces were determined by AES. A Perkin-Elmer PHI 600 AES/SAM electron spectrometer was used for measurements. Survey and high-resolution spectra were obtained with the energy analyzer operating in a constant analyzer transmission energy mode at pass energies of 100 and 25 eV, respectively. The pressure in the analyzer chamber was maintained at less than 10⁻⁹ Pa during the analysis. An argon ion gun with a voltage of 5 keV, was used for depth profiling studies. The sputter rate was approximately 180 Å/min.

3. Results and discussion

3.1 Weight-loss tests

Table 3 shows the corrosion rates of carbon steel. The results indicate that the corrosion rates were reduced to negligible values in synthetic cooling water with an inhibitor.

Table 3. Corrosion rates of carbon steel with and without inhibitors

	No-inhibitor	Inhibitor
Weight loss	231.4 mg	8.8 mg
Corrosion rate	38.72 mpy	1.47 mpy

The inhibition efficiency of corrosion of steel was calculated from following equation by using weight loss :

$$\eta (\%) = (W - W_{inhi}) / W \times 100 = 96.2 \%$$

where W and W_{inhi} are the values of weight loss of steel after immersion in solutions without and with inhibitor, respectively. The inhibitor showed high inhibition efficiency. Optical micrographs of the surfaces of the carbon steel coupon after the immersion tests are shown in Fig. 1. It can be seen that, without an inhibitor, the corrosion product formed is scaly, nodular, and porous. The inhibited

sample is covered by a coherent protective surface film. The inhibitor mechanism can be deduced from SEM morphological examination (Fig. 2). Addition of the blended mixture results in the formation of uniform, more

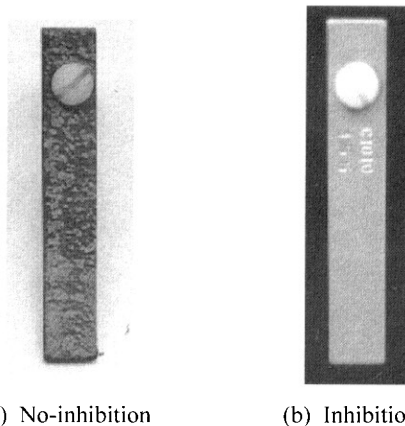
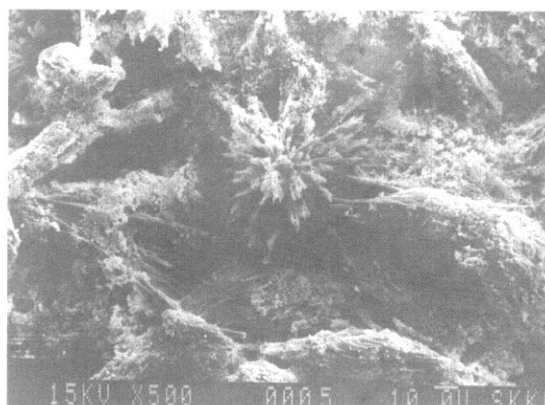
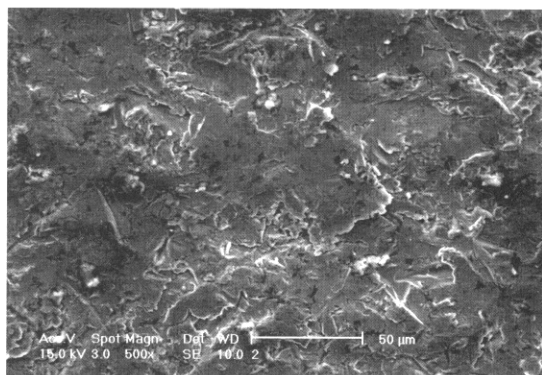


Fig. 1. Optical micrographs of carbon steel after testing



(a) No-inhibition



(b) Inhibition

Fig. 2. SEM micrographs of carbon steel after testing for 5 days

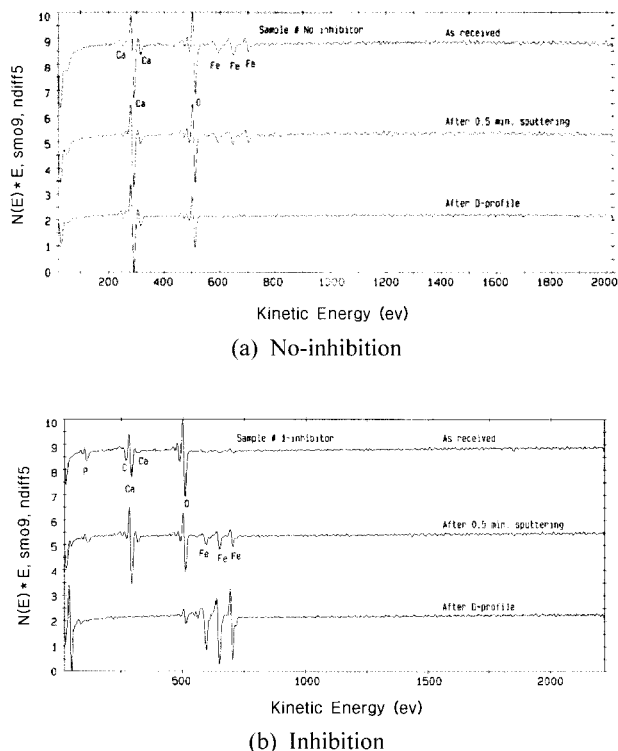


Fig. 3. AES analyses of carbon steel after testing

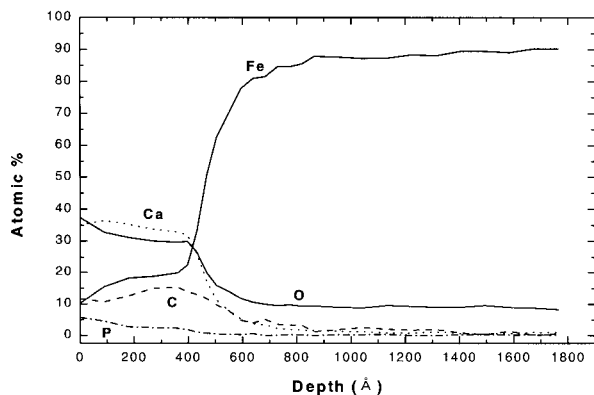


Fig. 4. Auger depth profiles of carbon steel with inhibitor

coherent inhibitor film, the protective nature of which is reflected in the corrosion rate measurements.

AES analyses of the specimen surfaces (Fig. 3) detected iron, calcium, and phosphorus after immersion in the solution containing the blended mixture, which might indicate the presence of calcium phosphate, calcium phosphonate and iron oxide.⁸⁾ Orthophosphate acts in two ways to inhibit corrosion in newly developed inhibitor. In the presence of oxygen, orthophosphate promotes formation of the gamma-Fe₂O₃ passive film on the steel surfaces. Also, to some extent, it forms calcium salts

which precipitate locally at high cathodic sites, stifling the cathodic reaction thereby decreasing the area of the metal available for metal dissolution. Finally orthophosphate functions as anodic and cathodic inhibitor forming bi-polar layer consisted of anion selective layer and cation selective layer. Namely, Fe(OH)₃/FeOOH combination film control anodic reaction and calcium salts which may contain calcium phosphate prevent cathodic reaction.⁹⁾⁻¹²⁾ On the one hand, calcium phosphonates suppresses the cathodic reaction as it prevents oxygen reduction. Also, phosphonates allow bicarbonate to function as a corrosion inhibitors, by forming Fe₃O₄-gamma Fe₂O₃ in the presence of oxygen.¹³⁾⁻¹⁴⁾ In view of this results so far achieved, a thin film containing calcium phosphate, calcium phosphonate and iron oxide prevents corrosion of carbon steel. The Auger depth profiles (Fig. 4) are in general agreement with the above mechanism.

3.2 Electrochemical tests

Potentiodynamic polarization curves for carbon steel electrodes immersed in synthetic cooling water with or without inhibitor, are shown in Fig. 5. The inhibited curve has a large anodic shift of ~150 mV compared to the uninhibited, indicating strong anodic inhibition. This shift is a result of the anodic inhibition effect of orthophosphate and HEDP.¹⁵⁾ Also, the cathodic regions show a decrease in the limiting current for oxygen reduction as a result of cathodic inhibition. This indicates that the blended mixture inhibits both the anodic and cathodic reactions. Corrosion rates were then calculated from I_{corr} values. Fig. 6 shows the electrochemical corrosion rates obtained in solution without and with inhibitor. The value of the corrosion rate of carbon steel in the presence of an inhibitor was much smaller than that in the absence of an inhibitor. Excellent corrosion rates were obtained with an

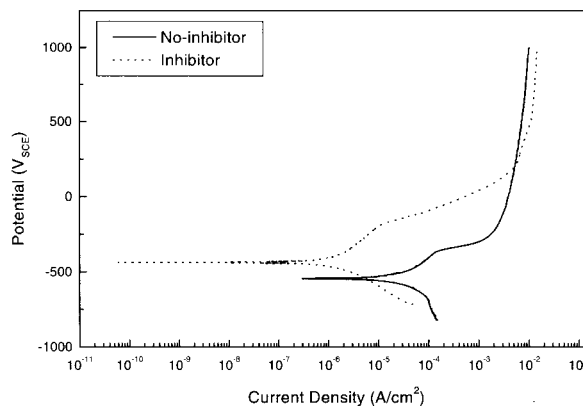


Fig. 5. Polarization curves of carbon steel with and without inhibitors.

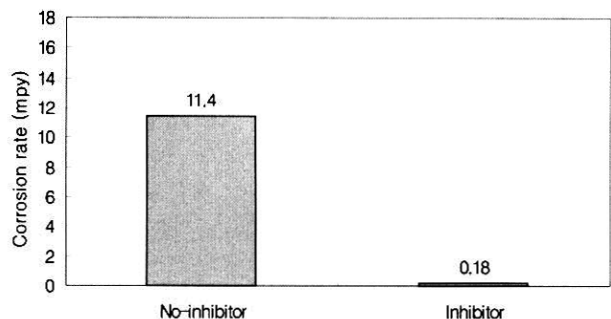


Fig. 6. Corrosion rates of carbon steel without and with inhibitors

inhibitor.

The inhibition efficiency of inhibitor for the corrosion carbon steel was calculated by using I_{corr} as follows :¹⁶⁾

$$\eta (\%) = [I_{corr} - I_{corr(inhi)}] / I_{corr} \times 100 = 98.4 \%$$

Where I_{corr} and $I_{corr(inhi)}$ are the corrosion current density values without and with inhibitor, respectively. The inhibition efficiency is very high. This result indicates that a blended inhibitor effectively inhibited the corrosion of carbon steel in the same as the results of weight loss tests. Polarization resistance method was used to identify the action of the inhibitor for 24 hours (Fig. 7). Polarization resistance of carbon steel in the inhibited solution was much higher than that for the inhibitor-free solution. The inhibition efficiency of corrosion of steel is calculated from the following equation by using the average polarization resistance :

$$\eta (\%) = [R_p^{-1} - R_{p(inhi)}^{-1}] / R_p^{-1} \times 100 = 96.9 \%$$

where R_p and $R_{p(inhi)}$ are the average polarization resistances without and with inhibitor, respectively. Also the inhibition efficiency is very good. It can be seen that inhibition efficiencies obtained from electrochemical tests and weight loss tests are in reasonably good agreement.

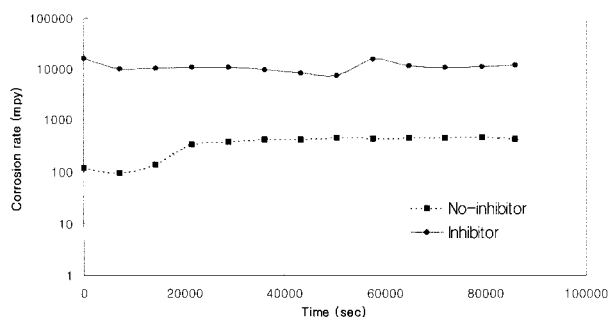


Fig. 7. Polarization resistances for carbon steel with and without inhibitors



(a) No-inhibition (b) Inhibition

Fig. 8. Optical micrographs of carbon steel after testing

Surface morphology of the carbon steel after the tests is shown in Fig. 8. It can be seen that the corrosion products were formed in inhibitor-free solution. On the other hand, the inhibited sample is covered by a coherent protective surface film.

3.3 Scale tests

The ability of blended inhibitor to inhibit calcium carbonate was compared with that of free-inhibitor in flask tests. The results are shown in Table 4 and Fig. 9.

Table 4. Inhibition efficiency of calcium carbonate scale

Ca-H / M-Alkalinity (as CaCO ₃)	100 ppm / 100ppm		200 ppm / 200ppm		300 ppm / 300ppm	
	Ca-H	Efficiency	Ca-H	Efficiency	Ca-H	Efficiency
No inhibition	90 ppm	90 %	125 ppm	62.5 %	98 ppm	32.6 %
Inhibition	100 ppm	100 %	200 ppm	98 %	300 ppm	95.3 %

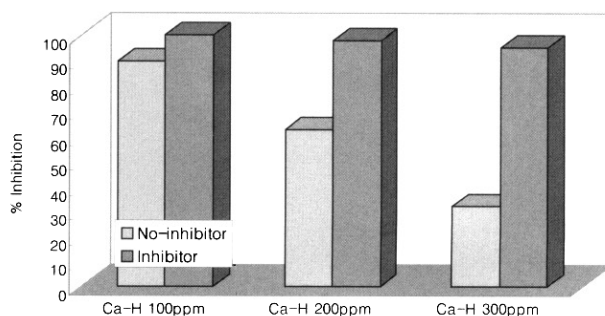


Fig. 9. Inhibition efficiency of calcium carbonate scale

In the case of free-inhibitor, percent calcium carbonate inhibition was reduced with increasing calcium concentration, whereas in the case of the inhibitor, percent calcium carbonate inhibition is observed to achieve >95% at all calcium concentration ranges. In the solution with the inhibitor, sufficient scale inhibition was obtained. It is due to the functions of phosphonates and the polymer. The phosphonates minimize the deposition of large amounts

of calcium carbonate.¹⁷⁾ A polymer can be adsorbed on foulant surfaces - imparting a like charge to them and thereby causing the particles to remain in suspension because of charge repulsion. Also, polymer can distort scale crystals by disrupting their lattice structure and normal growth patterns. The inclusion of a relatively large irregularly shaped polymer in the scale lattice tends to prevent the deposition of a dense uniformly structured crystalline mass on the metal surface.¹⁸⁾

3.4 Microorganism tests

The effects of inhibitor on microorganisms were evaluated as shown in Table 5. It indicated that all microorganisms were inhibited under 100 ppm concentration.

It is evident that the inhibitor of 100 ppm concentration can control the microorganisms. It is due to the functions of isothiazolone. Isothiazolone has been used for several years to kill microorganisms. The isothiazolone ring reacts with nucleophilic cell entities such as amino acids, proteins and enzymes, with the opening of the ring, thus exerting anti-microbial activity.¹⁹⁾

Table 5. Minimum inhibitory concentration of inhibitor on bacteria and fungus

Microorganisms		Concentration (ppm)	
		1 day	2 day
Bacteria	Escherichia coli	39	78
	Pseudomonas aeruginosa	39	39
	Micrococcus luteus	39	78
	Staphilococcus aureus	78	78
Fungi	Rhizopus oryzae	78	78
	Penicillium citrinum	9.8	19.5
	Aspergillus niger	39	78
	Trichoderma viridae	19.5	39

4. Conclusions

(1) The inhibitor appears to exhibit an anodic and cathodic inhibition. SEM and AES have shown that inhibition of corrosion is due to the formation of protective films on the metal surface.

(2) The inhibitor could minimize the deposit of large amounts of calcium carbonate scale.

(3) All kinds of microorganisms used in this study were

inhibited under 78 ppm

(4) No reference to the use of such a corrosion, scale, and microorganism inhibitor mixture has been found in open literature ; it is thus believed to represent a potential new blend suitable for treating cooling water systems.

References

1. S. D Strauss and P. R Puckorius, *Power*, **6**, 1 (1984).
2. P. R. Puckorius, B. Cunningham, "Cooling water technology advanced course", *International Water Conference*, Pittsburgh, (1997).
3. A. Cognetti, J. Parsons, M. Geraghty, and D. Vanderpool, "Opearation of cooling towers at high cycles of concentration : corrosion and scale control", *CORROSION/96*, Paper no. 575, Houston, TX:NACE, (1996).
4. G. Bohnsack, K. H. Lee, D. A. Johnson, and E. Buss, *Materials Performance* **25**, 32 (1986).
5. ASTM Designation G1, Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens.
6. NACE Standard TM0374-95, "Laboratory screening tests to determine the ability of scale inhibitors to prevent the precipitation of calcium sulfate and calcium carbonate from solution", Houston, TX:NACE, (1997).
7. S. P. Sharma, P. Sanyal, S. Chakraborty, and A. Kumar, *Fertiliser News*, **2**, 15 (1988).
8. J. Schreifels, P. Labine, "Auger depth profiles of corrosion inhibiting films formed under cooling water conditions", p.II-8-1, NACE, Houston (1993).
9. N. Sato, T. Noada, and K. Kudo, *Electrochemica Acta*, **19**, 471 (1974).
10. N. Sato, K. Kudo, and T. Noada, *Electrochemica Acta*, **16**, 1909 (1971).
11. N. Sato and K. Kudo, *Electrochemica Acta*, **16**, 447 (1971).
12. F. H. Al-Hajjar and W. T. Riad, *Br. Corrosion J.*, **25**, 119 (1990).
13. V. S. Sastri, "Corrosion Inhibitors", p.777 WILEY, New York 1998.
14. J. G. Knudsen, "Drew Principles of Industrial Water Treatment", p.61, Drew Korea Ltd , New Jersey (1988).
15. B. P. Boffardi, "Corrosion control of industrial cooling water systems", p.II-6-1, NACE, Houston (1993).
16. F. Bentiss, M. Traisnel, L. Gengembre, and M. Lagrenee, *Applied Surface Science*, **152**, 237 (1999).
17. T. Suzuki and T. Kawamura, "Corrosion and scale inhibitors for cooling water systems", p.II-10-1, NACE, Houston (1993), .
18. J. G. Knudsen, "Drew Principles of Industrial Water Treatment", p.79, Drew Korea Ltd, New Jersey (1988).
19. W. Paulus, *Microbicides for the Protection of Materials*, p.14, CHAPMAN & HALL, London, (1993).