

## Electrochemical Studies on the Corrosion Behavior of Carbon Steel in Presence of Cu and Ni

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### Abstract

The work presented in this paper deals with the investigations on the effect of Cu and Ni on the corrosion behavior of carbon steel under different experimental conditions. Electrochemical techniques like potentiodynamic polarization, linear polarization resistance and AC impedance have been used to investigate the effect of Cu and Ni on the corrosion behavior of carbon steel. The important experimental conditions which include the nature of aqueous medium, metal ion concentration and pH have been taken into account.

The instantaneous corrosion parameters as computed by potentiodynamic polarization, linear polarization resistance and AC impedance show an increase in corrosion rates of carbon steel with increasing Cu and Ni concentrations. However, the corrosion parameter as computed by AC impedance for an extended period of one month follows an interesting trend. The presence of Cu and Ni in the aqueous medium produces almost identical effect on the corrosion behavior of carbon steel. The microscopic examination of the test samples, under controlled laboratory conditions, did not show the evidence of localized attack on carbon steel in presence of different concentrations of Cu and Ni.

**Keywords:** carbon steel, effect of Cu and Ni, potentiodynamic polarization, linear polarization resistance, AC impedance.

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### Introduction

The corrosion failure of components or material is the major cause of concern to the engineers in desalination and power plants. Among the various types of corrosion failures, general and pitting corrosion are more common modes of failures [1]. If dissolved oxygen and pH are under control, general corrosion is the predominant mode of attack on conventional construction materials such as

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carbon steel. Pitting, the most detrimental form of attack, accounts for at least 90% of metal damage [2].

Though there are several causes of pitting, the contact with heavy metal ions such as copper is another cause which has been attributed to pitting of steels [3]. This aspect has been given little attention and is least understood yet has great relevance to seawater desalination and power plants [4]. A number of cases have been reported regarding the copper induced pitting corrosion of iron and galvanized pipes and tanks in re-circulating hot water system [5-8]. A copper concentration of 0.1 mg/L was found to be sufficient to cause accelerated attack.

In multistage flash (MSF) desalination plants, as a result of condenser tube corrosion, the re-circulating brine has high copper content. This can deposit in the flash chambers and accelerate the corrosion of steel due to high Cu/Fe local cell action [9]. The frequent deposition of copper oxide in the distillate system has been reported in the MSF desalination plants of Abu Dhabi [10]. The presence of high concentration of copper in the distillate was due to the deterioration of protective copper oxide during the start up following outage.

In steam turbines, the deposits along the steam path resulting from boiler carryover are most problematic. These deposits are detrimental to efficiency, and can have a drastic effect on turbine reliability because of increased thrust loading and possibility of stress corrosion cracking of steam path components from high levels of salts/metal oxide carryover. A study of the corrosion related problems in steam generating equipment indicates that while 26% of the failures are attributed to pitting, 57% are caused by the deposition blades [11]. These deposits are formed from high dissolved and suspended solid carry over of steam. The present investigation deals with the effect of Cu and Ni on the corrosion behavior of carbon steel under different experimental conditions. The important experimental conditions which include the nature of aqueous medium, metal ion concentration and pH have been taken into account. Electrochemical techniques like potentiodynamic polarization, linear polarization resistance and AC impedance have been employed to study the effect of Cu and Ni on the corrosion behavior of steel. The results of the study shall provide important information about the role of Cu and Ni carryover on the failure of desalination and power plant components.

## **Experimental**

### ***Preparation of specimens***

Circular specimens with 1.5 cm diameter were punched from 3 mm thick carbon steel sheet. A nichrome wire was soldered to one face of the specimens for the electrical connection and the specimens were then mounted in epoxy resin to provide crevice free mount. The exposed circular face was ground to 180 grit SiC paper. The ground specimens were washed, degreased and dried up. The composition of steel as analyzed by optical emission spectrometer is given in Table 1.

**Table 1.** Composition of carbon steel as analyzed by optical emission spectrometer.

% Composition of elements									
C	Si	Mn	P	S	Cr	Ni	Mo	Cu	Fe
0.138	0.0167	1.30	0.0091	0.0064	0.0143	0.0115	-	0.0601	98.3112

**Preparation of test solutions**

The test solutions were made up with distilled water and filtered raw seawater. The composition of Arabian Gulf seawater is given in Table 2 [12]. The solutions containing 100 ppm, 1 ppm and 50 ppb of Cu and Ni, respectively, were prepared in distilled water and filtered raw seawater using Analar grade BDH chemicals. The pH of the solutions was adjusted using appropriate chemicals. For the test solutions made up with distilled water a pH of 6.5 was maintained, whereas for the test solutions made up with seawater a pH of 8.5 was maintained.

**Table 2.** Average seawater composition of the Arabian Gulf at Al-Jubail [12].

Constituents	Seawater
<b>Cations (ppm)</b>	
Sodium	13,440
Potassium	483
Calcium	508
Magnesium	1618
<b>Anions (ppm)</b>	
Chloride	24,090
Sulfate	3,384
Bicarbonate	130
Bromide	83
Fluoride	1
<b>Other parameters</b>	
Conductivity ( $\mu\text{S}/\text{cm}$ )	62,800
pH	8.1
Dissolved oxygen (ppm)	7
Carbon dioxide (ppm)	2.1
Total suspended solids (ppm)	20
Total dissolved solids (ppm)	43,800
Temperature range ( $^{\circ}\text{C}$ )	18-33

**Electrochemical tests**

The electrochemical tests like potentiodynamic polarization, polarization resistance measurements and electrochemical impedance were carried out to investigate the effect of Cu and Ni on the corrosion behavior of carbon steel. The electrochemical tests were carried out on Solartron AC Impedance System which comprised of 1250 B frequency response analyzer with blank front panel and 1287 electrochemical interface unit. The experiments were carried out using a corrosion cell from EG & G model K0047 with saturated calomel electrode (SCE) as reference and graphite rod as counter electrode.

#### *Potentiodynamic polarization measurements*

Potentiodynamic polarization measurements were carried out using a scan rate of 0.166 mV/s commencing at a potential above 250 mV more active than stable open circuit potential. To observe the effect of a particular metal ion in a given medium, potentiodynamic curves were obtained using the same specimen under similar experimental condition except a periodic change in metal ion concentration. However, before starting the polarization scan at each concentration, the specimen was stabilized for about 1 hour for attaining a steady state which was shown by a constant potential.

#### *Polarization resistance measurements*

Polarization resistance measurements were conducted at a scan rate of 0.166 mV/s with starting and final potential corresponding to -15 mV to + 15 mV vs. open circuit potential, respectively. The maximum current range was 0.1  $\mu$ A. All the measurements were completed on the same day with the same specimen. However, metal ion concentration was periodically changed and before starting the measurements at each concentration, the specimen was left for about 1 hr for attaining a steady state which was indicated by a constant potential.

#### *AC impedance measurements*

The electrochemical impedance measurements were performed under potentiostatic conditions at the free corrosion potential. Amplitude sine wave signal was 10 mV over the frequency range of 1 KHz to 1 mHz with five points per decade. All the ac impedance measurements were performed before polarization resistance measurements. However, before each measurement the specimen was left to attain a constant potential.

### **Results**

#### *Potentiodynamic polarization measurements*

The values of corrosion current,  $I_{\text{corr}}$  in presence of 0, 50 ppb, 1 ppm and 100 ppm of Cu and Ni, as computed from potentiodynamic curves, are given in Table 3. In general, though there is no significant effect of the presence of 50 ppb and 1 ppm of metal ions on the  $I_{\text{corr}}$  values, the presence of 100 ppm of metal ions in both distilled water and seawater has pronounced effect on the  $I_{\text{corr}}$  values. In presence of 100 ppm of Cu and Ni an increase in  $I_{\text{corr}}$  values is observed.

#### *Polarization resistance measurements*

The polarization resistance measurements were carried out on carbon steel immersed in distilled water and seawater containing 0, 50 ppb, 1 ppm and 100 ppm of Cu and Ni, respectively. Table 4 lists the polarization resistance values,  $R_p$  computed from linear polarization plots. The results from the polarization measurements show a lowering in  $R_p$  values with increasing Cu and Ni concentration in both distilled water and seawater.

**Table 3.** Effect of Cu and Ni on  $I_{\text{corr}}$ , as computed by potentiodynamic polarization curves, of carbon steel under different experimental conditions at room temperature.

Aqueous medium	Metal ion concentration (ppm)	pH	$I_{\text{Corr}}$ (A/cm <sup>2</sup> )	
			Cu	Ni
Distilled water	Nil	6.5	$6.788 \times 10^{-6}$	$5.585 \times 10^{-6}$
"	0.05	"	$7.371 \times 10^{-6}$	$7.390 \times 10^{-6}$
"	1	"	$8.528 \times 10^{-6}$	$9.333 \times 10^{-6}$
"	100	"	$2.046 \times 10^{-5}$	$2.817 \times 10^{-4}$
Seawater	Nil	8.5	$7.003 \times 10^{-6}$	$5.901 \times 10^{-6}$
"	0.05	"	$8.360 \times 10^{-6}$	$6.274 \times 10^{-6}$
"	1	"	$8.529 \times 10^{-6}$	$8.204 \times 10^{-6}$
"	100	"	$4.891 \times 10^{-5}$	$9.427 \times 10^{-6}$

**AC impedance studies**

The effect of Cu and Ni on the corrosion behavior of carbon steel in distilled water and seawater was studied by electrochemical impedance spectroscopy (EIS). The technique is unique as it allows the quantitative study of corrosion behavior of low corroding systems which is not entirely possible by conventional dc techniques. Parameters such as solution resistance,  $R_s$ , polarization resistance,  $R_p$  and interfacial capacitance,  $C$  evaluated from EIS proved to be useful in studying corrosion kinetics and associated interfacial phenomenon.

**Table 4.** Effect of Cu and Ni on the polarization resistance,  $R_p$  (as computed by linear polarization resistance) of carbon steel under different experimental conditions at room temperature.

Aqueous medium	pH	Metal ion concentration (ppm)	$R_p$ (ohm-cm <sup>2</sup> )	
			Cu	Ni
Distilled water	6.5	Nil	$3.14 \times 10^4$	$7.46 \times 10^4$
"	"	0.05	$2.57 \times 10^4$	$2.79 \times 10^4$
"	"	1	7012	$1.09 \times 10^4$
"	"	100	666	1141
Seawater	8.5	Nil	$4.17 \times 10^4$	$5.84 \times 10^4$
"	"	0.05	$4.08 \times 10^4$	$5.08 \times 10^4$
"	"	1	$1.91 \times 10^4$	$2.04 \times 10^4$
"	"	100	780	881

Nyquist curves were obtained to study the effect of Cu and Ni on the corrosion behavior of carbon steel. Nyquist plot is obtained by plotting the imaginary impedance ( $Z''$ ) against real impedance ( $Z'$ ) at each excitation frequency. At high frequency, the impedance is almost entirely created by solution resistance ( $R_p + R_s$ ). The  $R_p$  (inversely proportional to the corrosion rate of exposed metal surface) is the difference between low frequency limit and high frequency limit. Nyquist plots for carbon steel in distilled water and seawater containing varying concentration of Cu and Ni were obtained and the values of  $R_p$  computed from these plots are listed in Table 5. Though a well defined semicircle characteristic

of Nyquist plot lacked, the computed values of  $R_p$  show a decreasing trend with increasing Cu and Ni concentration. The result is in conformity with the values of  $R_p$  obtained from dc experiment (linear polarization resistance measurements). To observe the effect of metal ion concentration with time, the ac impedance measurement of carbon steel in distilled water containing 100 ppm Cu was extended for 1 month. The computed values of  $R_p$  at different time interval are listed in Table 6. The values of  $R_p$  appear to increase with increasing exposure period attaining a maximum after a period of 14 days; this is followed by a decrease in  $R_p$  values with increasing exposure period. The cycles of increasing and decreasing values of  $R_p$  are invariably observed during the period extending 1 month.

**Table 5.** Effect of Cu and Ni on the polarization resistance,  $R_p$  (as computed by AC impedance) of carbon steel under different experimental conditions at room temperature.

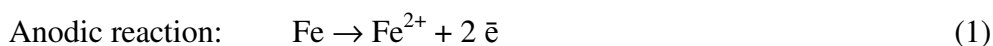
Aqueous medium	pH	Metal ion concentration (ppm)	$R_p$ (ohm-cm <sup>2</sup> )	
			Cu	Ni
Distilled water	6.5	Nil	4641	6014
"	"	0.05	2895	5305
"	"	1	2462	2999
"	"	100	285	602
Seawater	8.5	Nil	4741	4460
"	"	0.05	4557	4286
"	"	1	2191	3532
"	"	100	328	410

**Table 6.** The effect of Cu on the polarization resistance,  $R_p$  (as computed by ac impedance) of carbon steel with time, in distilled water with a metal ion concentration of 100 ppm.

Time (days)	$R_p$ (ohm-cm <sup>2</sup> )	Time (days)	$R_p$ (ohm-cm <sup>2</sup> )
1	8230	16	31027
2	7473	17	9766
3	6543	18	8456
4	4477	19	7865
5	7562	20	2579
6	10467	21	5541
7	12542	22	9843
8	12978	23	36429
9	14971	24	23419
10	21883	25	17890
11	43678	26	16789
12	80567	27	15265
13	78890	28	10638
14	84134	29	49667
15	38111	30	2222

## Discussion

The effect of Cu and Ni on the corrosion behavior of carbon steel in distilled water and seawater at pH 6.5 and 8.5, respectively, was studied at room temperature using electrochemical techniques. Carbon steel shows a complex dependence of corrosion rate on pH. In near neutral pH range ( $5 < \text{pH} < 9$ ), pH no more plays a direct role in corrosion [13]. The major reaction governing corrosion in most practical application in this pH range is the reduction of oxygen present in the solution. Therefore, under static conditions, the pH range under study is not expected to play a significant role in corrosion and any change in the corrosion behavior of steel may be expected to be brought about by presence of metal ions in the solution. In case of carbon steel, in presence of dissolved oxygen, the corrosion process is controlled by cathodic diffusion. In presence of dissolved oxygen and Cu or Ni the anodic and cathodic reactions may be written as follows:



Cathodic reaction: (Cathodic reactions in pH range of 6.5 to 8.5 are reduction of  $\text{O}_2$  and the Cu or Ni ions)



Since during metallic corrosion, the total rate of oxidation equals to total rates of reduction, the dissolution rate of carbon steel equals to the reduction rates of  $\text{O}_2$  and metal ions and hence the initial corrosion rate of carbon steel in presence of metal ions is expected to increase. After reduction of the metal ions the resulting metal gets deposited over the steel surface and forms a barrier which is likely to protect the steel from further corrosion. The extent of protection offered to the carbon steel shall depend upon the concentration of metal ion in the aqueous solution, the ability of the deposited metal to form a stable protective barrier and nature of protection offered to steel surface. The deposited Cu and Ni protect the steel cathodically. In aqueous medium containing high concentration of Cu and Ni a stable protective barrier is more likely to be formed and hence a lowering in corrosion rate is expected.

The corrosion parameters computed from potentiodynamic and linear polarization resistance measurements show an increase in  $I_{\text{corr}}$  and lowering in  $R_p$  values, respectively, with increasing Cu and Ni concentrations, indicating an increase in corrosion rate of carbon steel with increasing metal ion concentration in the aqueous medium. The parameters measured by the above techniques are instantaneous and the increase in instantaneous corrosion rate with increasing metal ions concentration is expected and can be explained on the basis of occurrence of two cathodic reactions (Equations 2 and 3). The effect of Cu and Ni on the corrosion behavior of carbon steel is almost identical. The trend of variation in the values of  $R_p$  as computed from ac impedance studies is also in

conformity with the trend in the values of  $R_p$  computed from linear polarization resistance measurements.

The corrosion parameter,  $R_p$  as computed by ac impedance for an extended period of 1 month shows an interesting trend on the corrosion behavior of carbon steel. The values of  $R_p$  appear to increase with increasing exposure period attaining a maximum after a period of 14 days; this is followed by a decrease in  $R_p$  values with increasing exposure period. The cycles of increasing and decreasing values of  $R_p$  are invariably observed during the period extending 1 month. An increase in the  $R_p$  values in presence of 100 ppm Cu is indicative of the formation of a protective barrier by the deposited Cu, thus causing a lowering in the corrosion rate of carbon steel. A decrease in  $R_p$  values indicates the breakdown or disruption of the protective barrier leading to an increase in the corrosion rate. The cycles of increase and decrease in the values of  $R_p$  in presence of 100 ppm Cu are indicative of the formation of protective barrier by the deposited metal, disruption of the coating and reformation of the protective coating. This lowering in the corrosion rate of carbon steel in presence of higher concentration of Cu finds support from a recent study where the results of immersion tests have shown a decrease in the corrosion rate of carbon steel in distilled water containing higher concentration of Cu and Ni [14].

### Conclusions

1. The instantaneous corrosion parameters computed by both dc and ac methods show an increase in corrosion rate of carbon steel with increasing Cu and Ni concentration in the aqueous medium.
2. The corrosion parameter measured by ac impedance after an extended period of time shows a decrease in corrosion rate of carbon steel at higher concentration of Cu.
3. The observed decrease in the corrosion rate of carbon steel in presence of higher concentration of Cu is due to the formation of a protective barrier by the deposited metal.
4. The presence of Cu and Ni in the aqueous medium produces almost similar effect on the corrosion behavior of carbon steel.
5. The microscopic examination of the test samples, under controlled laboratory conditions, did not show the evidence of localized attack on carbon steel in presence of different concentration of Cu and Ni.

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