

## Studying The Effect of Copper And Zinc Ions on The Corrosion Rate of Carbon Steel

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Received on:26/7/2009

Accepted on:3/12/2009

### Abstract

An experimental work was performed to study the effect of Zn, Cu ions on the corrosion rate of carbon steel in distilled and tap water solution containing, 25 & 50 ppm concentration of Zn, Cu ions at pH range 4, 6 & 8 in distilled water and at pH8 in tap water at room temperature under both static for 10 weeks and 1, 2, 6 & 12 hours with dynamic conditions. The obtained results showed that the corrosion rate was increased in the presence of 50 ppm of Cu ions in tap water (2.326 mpy) after 10 weeks, under static conditions, whereas under dynamic conditions, it was reached (10.511 mpy), the presence of fine suspended solid particles in the solutions may also cause an increase in corrosion rate due to their movement over the carbon steel surface. In contrast, the presence Zn ions in solution as sacrificial anode, therefore, the corrosion rate was 2.24 times less than that in presence of Cu ions, at the same conditions. In distilled water, the corrosion rates were decreasing slightly with adding Zinc and copper ions comparing to absence of metals ions in solution except at pH4 in the presence 50ppm of Cu ions may be accounted due to the increasing in the conductivity of the solution, under static conditions. At 25ppm of Zn ions lowering in corrosion rate may be explained that the Zn ions were protected carbon steel surface by sacrificial. In the absence of Zn, Cu ions were also carried out.

**Keywords:** Carbon steel, Cu\Zn ions, tap \ distilled water

### دراسة تأثير ايونات النحاس والزنك على تأكل الفولاذ الكربوني

#### الخلاصة

تم في هذا البحث دراسة تأثير ايونات النحاس والزنك على معدل تأكل الصلب الكربوني بالماء المقطر وماء الحنفية الحاوي على تركيز (25, 50) ppm من ايونات النحاس والزنك عند حامضية 4, 6 & 8 للماء المقطر و 8 لماء الحنفية بدرجة حرارة الغرفة ولمدة 10 اسابيع بدون تحريك في حين تم حساب معدل التأكل في حالة التحريك للاوقات 1 و 2 و 6 و 12 ساعة. اظهرت النتائج ان معدل التأكل ازداد بوجود 50ppm من ايونات النحاس لماء الحنفية حيث وصل (2.326 mpy) بعد 10 اسابيع للظروف الساكنة في حين وصل معدل التأكل في حالة التحريك الى (10.511 mpy), ويعزى سبب ذلك الى وجود المواد الصلبة العالقة بماء الحنفية والتي تتحرك بسهولة فوق سطح المعدن. وعلى العكس, وبما ان الزنك يعتبر قطب مضحي للصلب الكربوني لذلك فان معدل التأكل قل ب (2.24) مرة من وجود ايون النحاس عند نفس الظروف. اما في حالة الماء المقطر فان معدل التأكل قل بشكل طفيف عند اضافة ايونات النحاس والزنك مقارنة بمعدل التأكل عن المحاليل عديمة الايونات عدا النسب العالية من ايونات النحاس عند حامضية (pH4) بدون تحريك والتي من الممكن ان تعمل على زيادة التوصيلية للمحلول, اما في حالة 25ppm لايونات الزنك فقد انخفض معدل التأكل بأسلوب التضحية وكذلك تم حساب معدل التأكل بغياب ايونات الزنك والنحاس.

## Introduction

In power plants, several major components such as steam generator tubes, boilers, steam/water pipe lines, water box of condensers and the other auxiliary components like bolts, nuts, screws fasteners and supporting assemblies are commonly fabricated from plain carbon steels, as well as low and high alloy steels. Corrosion of carbon steel in seawater is controlled by the availability of oxygen to the metal surface. Thus, under static conditions, carbon steel corrodes at between 100 and 200 mm/year, reflecting the oxygen level and temperature variations in different locations. As velocity causes a mass flow of oxygen to the surface, corrosion is very dependent on flow rate and can increase by a factor of 100 in moving from static or zero velocity to velocity as high as 40 m/s. Galvanizing confers only limited benefit under flow conditions, as corrosion of zinc also increases with velocity. For the thickness normally used in seawater piping, it will extend the life of the pipe for about 6 months. Plain carbon steels, low and high alloy steels, martensitic and ferrite stainless steels are some examples of steels that are generally used in power plants for fabrication of various components such as steam generators, condensers, water heaters, bolts, nuts and fasteners. During their service life, these steels

pick up metal ions from the surrounding environment, which migrates in to the matrix and causes damage [1]. The deposition of carryover heavy metals/oxides on steel components in desalination or power plants is a common problem and reported by many authors. The deposits may initiate localized attack in the form of pitting or crevice corrosion. The pits act as initiators of stress corrosion in the form of stress corrosion cracking, corrosion fatigue or intergranular corrosion and result in the failure of components [2]. The mechanism of corrosion resistance for stainless steels differs from that of carbon steels and alloy steels. For the carbon and alloy steels the formation of a barrier of a true oxide separates the metal from the surrounding atmosphere [3]. The degree of protection afforded by the oxide is a function of the thickness of the oxide layer, the continuity of the oxide layer, the coherence and adhesion of the oxide layer to the metal, and the diffusivities of oxygen in the oxide [4]. Velocity is the most important single factor influencing corrosion in seawater systems. The velocity chosen controls the dimensions of many components, such as piping and valves. Velocity also influences the corrosion behavior of the materials. When the corrosion rate is subjected to mass transfer control; flow velocity at the metal surface becomes the rate-

determining factor. This is also true with active-passive alloys, where flow, and thereby the ample supply of oxygen to the metal surface, provides the oxygen necessary to maintain the metal in the passive state. However, in the case of zero or low flow, special precautions have to be taken. Low flow may also result in the settling of deposits from the water, with the possible consequence of local corrosion cells being set up, possibly leading to localized corrosion attack [5]. High flow rates can also have detrimental effects in some cases. They can increase the rate of various corrosion processes and lead to erosion corrosion, impingement attack, enhanced graphite corrosion, etc. Uneven flow over an alloy surface can be undesirable when it leads to differential aeration effects. In considering velocity, it is important to note that local velocities may vary considerably from velocity [6]. Contact with heavy metal ions such as copper is another cause which has been attributed to pitting of steels. A number of cases have been reported regarding the copper induced pitting corrosion of iron and galvanized pipes and tanks in recirculating hot water system [7].

The deposits in the desalination plants and accelerate the corrosion of steel due to high Cu/Fe local cell action [8]. In desalination plant, green deposits of copper rich oxide

were found, on removing the deposits, deep pits were observed. The pitting was attributed to carryover copper from the heat exchanger by the distillate [9]. 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. 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. Copper is different from most other metals in that combines corrosion resistance with high electrical and heat conductivity, formability, machinability, and strength when alloyed, except for high temperatures. Whereas Zinc is not a corrosion resistance metal, but it is utilized as a sacrificial metals for cathodic protection of steel. Its chief use is in galvanized (zinc-coated) steel for piping, fencing, nails, etc. it is also utilized in the form of bars or slabs as anodes to protect ship hull, pipelines, and other structures. In the electrochemical series of elements, copper is near the noble end and will not normally displace hydrogen, even from acid solutions. Indeed, if hydrogen is bubbled through a solution of copper salts, copper is slowly deposited (more rapidly if the

process is carried out under pressure) [10].

As copper is not an inherently reactive element, it is not surprising that the rate of corrosion, even if unhindered by films of insoluble corrosion products, is usually low. Nevertheless, although the breakdown of a protective oxide film on copper is not likely to lead to such rapid attack as with a more reactive metal such as, say, aluminum, in practice the good behavior of copper (and more particularly of some of its alloys) often depends to a considerable extent on the maintenance of a protective film of oxide or other insoluble corrosion product [11].

The passage of a natural water through a pipe may modify the composition of the water and hence its corrosive properties. Consumption of constituents which in the circumstances may be corrosion inducing- e.g. oxygen or carbon dioxide, may reduce the water's corrosive properties. Dissolution of a metal into water may, on the other hand, make it more corrosive. An example of this is the attack of some waters on copper and the subsequent increased pitting corrosion of less noble metal such as iron, galvanized Steel and aluminum. It has been suggested that this enhanced pitting is caused by the redeposit ion of minute quantities of copper on the less noble metal thus setting up numerous bimetallic corrosion cells. Failure of the metal can be the most important effect of corrosive water, but other effects may arise from small concentrations of metallic ion

produced by corrosion [12]. Anees U. studied the effect of 1&100 ppm of Cu & Zn ions on the corrosion behavior of steels was founded no effect of metal ions on the corrosion rate of 316L in presence 1&100ppm concentration in either seawater or distillate water under static and dynamic conditions at room temperatures whereas the effect of metal ions on the corrosion rate of carbon steel was quite pronounced. It was reached (27.527mpy) for 1 month, under dynamic conditions, in presence 100ppm of Cu ions in seawater [13].

### Experimental work

#### 1- Materials

- Carbon steel.
- Copper and zinc concentration 25, 50 ppm.
- Distilled and tap water.
- Dilute HCl and NaOH solutions, WECO WEST GERMANY.

#### 2- Equipments

- Sensitive balance with three digits sensitivity, (type: BBB -600, England, 0.0001)
- Stirrer, AC-DC motor.
- Pyrex beakers, 1000ml

### Experimental setup

Commercial grade carbon steel was used for the tests; Table 1 show that the composition of carbon steel elements (state company of geological survey and mining). Specimens were machined from carbon steel alloy. Specimens were machined from carbon steel of dimension 3 X 2 X 0.2 cm and 0.2

cm diameter with a central hole to hold the specimen which it immersed in container with stirrer of 1000rpm, as shown in figure 1. The specimens were machined and grinded and polished sequentially with silicon carbide paper of grades 600grit then washed, and dried up. After taking the initial weight and dimension, carbon steel was hanged in the solution containing a varying concentration of metal ions 25 and 50 ppm of Cu and Zn by adding  $\text{CuSO}_4$  and  $\text{ZnSO}_4$  respectively, with nylon thread. In absence of heavy metal ions were also carried out. The solutions were made up with distillate and tap water, the compositions of tap water in Baghdad city in table 2(the directorate of water Baghdad).The pH of solution was adjusted to different ranges value from pH 4 to pH 8 by adding dilute HCL and NaOH solutions for distilled water whereas the tap water at pH8 was maintained. The immersion tests were carried out under both static and dynamic conditions, the test runs were of 1-10 weeks under static conditions whereas under dynamic conditions the runs were 1, 2, 6, 12 hours. After completion of the immersion test, the specimens were taking out. For preparing, cleaning from any localized attack. Corrosion rates were calculated according to the following correlation. [10]

$$\text{CORROSION RATE (mpy)} = \frac{534 W}{ADt}$$

### Where:

W: weight loss (mg)

D: density of specimen material  
( $\text{g/cm}^3$ )

A: area ( $\text{inch}^2$ )

t: time of exposure (hr)

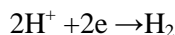
### **Results & Discussions**

The effect of Cu, Zn ions concentrations on corrosion rate of carbon steel at different pH values in both distilled and tap water under static for 10 weeks and 1, 2, 6 & 12 hours for dynamic conditions were studied at room temperature as shown in tables (3-6).

At higher Zn ions the observed increase in corrosion rate may be accounted due to the increase in the conductivity of the solution. Since Zn is anodic to carbon steel, the observed decrease in corrosion rate of carbon steel that due to get reduced and deposited on the carbon surface in distilled water, the corrosion rate of carbon steel under both static and dynamic.

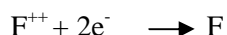
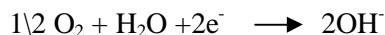
In near natural pH range ( $5 < \text{pH} < 9$ ), pH no more plays role in corrosion and any change in the corrosion behavior of carbon steel may be expected to be brought about by presence Zn ions in the solution. In addition that, under dynamic conditions the agitation of solution may also affect the corrosion rate, whereas the corrosion rate was increased at pH4 due to absence of a stable protective film and the solution made more acid also the corrosion rate was activation –controlled, the

$H^+$  was consumed by this reaction on carbon steel surface.



The results from immersion tests show very little changes in the corrosion rate of carbon steel at 6 & 8 pH values in this range at distilled water, while the corrosion rate was increased slightly in tap water under static conditions, the presence of metal ions in the solution were no played a significant role in the corrosion behavior. Under dynamic conditions, the presence of metal ions, agitation of solution and presence of solids in the solution also affect the corrosion rate.

In presence of higher concentrations of Cu ions, the corrosion rate of carbon steel was increased since two cathodic reactions occurrence as follows:



The initial corrosion rate of carbon steel in presence of metal ions is increased. After reduction of the metal ions the resulting metal gets deposited over the carbon steel surface. Whereas a lowering in corrosion rate may be explained on the basis of formation of a stable protective film over the carbon steel surface by deposited metal as follows:



The results from immersion tests show a decrease in the corrosion rate of carbon steel at pH8 in distilled water, while the corrosion rate was increased slightly in tap water at higher concentration of 50 ppm Cu, ions, the presence of fine suspended solid particles in the tap water may cause an increase in corrosion rate due to their movement over the carbon steel surface as shown in figure 2.

Figure 3 shows that the presence of Zn ions in distilled water influences on corrosion behavior of carbon steel greatly than that of Cu ions at pH 4. Higher deposit over carbon steel surface of 50ppm of Zn may be accounted due to the increase in the conductivity of the solution, while at lower concentration of Zn ions the corrosion rate was decreased due to the presence of Zn which was anodic to carbon steel. Since the deposited Cu protected the steel cathodically (reduction of  $O_2$ , evolution of  $H_2$ , deposited metal) a lowering in corrosion rate was observed, while at lower concentration of Cu ions the observed increase in corrosion rate was due to absence of a stable protective film on the carbon steel surface.

Under dynamic conditions, the effect of Cu ions on the carbon steel were greater than the effect of Zn ions at lower concentration (25ppm) in distilled water due to absence of a stable protective film also, since Zn was anodic to carbon steel therefore, corrosion rate was decreased as shown in figure 4.

In tap water, the results in figure 5 indicated increasing in the corrosion rate in presence of 50ppm Cu ions were due to erosive action of fine suspended solid particles on the barrier film whereas, in presence of Zn ions lowering in corrosion rate may be explained that oxidation of Zn ions and protected a metal by sacrificial

### Conclusions

1. In distilled water, Zn ions have no effect except at higher concentration on corrosion rate of carbon steel under static conditions.
2. At higher concentration of Cu ions, the corrosion rate of carbon steel was decreased in distilled water, whereas in tap water, it was limited under static conditions.
3. Under dynamic conditions, the presence of Cu ions in solution influences the corrosion behavior of carbon steel differently than of Zn in distilled and tap water.
4. The results from immersion test in the pH range 4 – 8 show limited effect of Cu, Zn ions on corrosion rate of carbon steel in distilled and tap water under static conditions.
5. At higher concentration of Cu in tap water, under dynamic conditions, effectively increases the corrosion rate of carbon steel which was reached (10.511mpy) after immersion for 12 hours.

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**Table (1) composition of carbon steel.**

STEEL	% COMPOSITION OF ELEMENTS									
	C	Si	Mn	P	S	Ti	Ni	Mo	Cu	Fe
Carbon Steel	0.12	1.21	1.29	0.01	0.022	0.069	0.37	-	0.061	96.827

**Table (2) properties of tap water for Baghdad city.**

PH	Turbidity	Alkalinity (M)	T.D.S ppm	Temp. C	Hardness ppm	Ca ppm	Mg ppm	Cl ppm	Fe ppm	Al ppm	SO <sub>4</sub> ppm	Na ppm	F ppm	SiO <sub>2</sub> ppm
8	10	125	1500	13-14	500	290	145	81	0.3	0.2	320	200	0.5-1.4	2.3

**Table (3) Effect Of Cu On The Corrosion Rate Of Carbon Steel At Different Ph Under Static Conditions**

Aqueous test medium	PH	ion concentration (ppm)	CORROSION RATE (MPY)									
			1 WEEK	2 WEEK	3 WEEK	4 WEEK	5 WEEK	6 WEEK	7 WEEK	8 WEEK	9 WEEK	10 WEEK
distilled water	4	0	1.221	1.462	1.882	1.916	1.945	1.998	2.011	2.038	2.037	2.037
	4	25	1.778	1.792	1.812	1.833	1.855	1.842	1.831	1.802	1.788	1.772
	4	50	0.211	0.231	0.248	0.263	0.257	0.243	0.231	0.222	0.203	0.192
	6	25	0.743	0.763	0.788	0.819	0.842	0.883	0.922	0.943	0.966	0.992
	6	50	0.231	0.259	0.284	0.292	0.311	0.339	0.355	0.377	0.432	0.477
	8	25	0.433	0.703	0.724	0.779	0.798	0.822	0.848	0.877	0.889	0.916
tap water	8	50	0.516	0.554	0.622	0.677	0.692	0.733	0.772	0.797	0.831	0.858
	8	25	1.893	1.908	1.923	1.951	1.972	1.996	2.035	2.082	2.131	2.162
	8	50	2.188	2.198	2.209	2.222	2.222	2.222	2.222	2.222	2.311	2.326



**Table (4) Effect of Cu on The Corrosion Rate of Carbon Steel At Different Ph Under Dynamic Conditions**

Aqueous test medium	pH	ion conc. (ppm)	CORROSION RATE (MPY)			
			1 HOUR	2 HOURS	6 HOURS	12 HOURS
distilled water	4	0	0.247	0.432	1.152	3.423
	4	25	1.551	2.011	4.331	6.776
	4	50	0.119	0.175	0.211	0.297
	6	25	1.1231	2.451	3.161	5.092
	6	50	0.021	0.046	0.069	0.091
	8	25	1.011	2.821	3.811	6.471
	8	50	0.011	0.033	0.062	0.073
tap water	8	25	0.987	2.778	5.239	8.451
	8	50	2.317	4.224	8.121	10.511

**Table (5) Effect of Zn ion on the corrosion rate of carbon steel at different PH under static conditions**

Aqueous test medium	pH	ion conc. (ppm)	CORROSION (MPY)									
			1 week	2 week	3 week	4 week	5 week	6 week	7 week	8 week	9 week	10 week
distilled water	4	25	1.887	1.893	1.911	1.923	1.936	1.949	1.941	1.932	1.921	1.902
	4	50	3.912	3.924	3.933	3.947	3.942	3.933	3.927	3.911	3.901	3.889
	6	25	1.445	1.461	1.475	1.491	1.522	1.511	1.501	1.491	1.488	1.481
	6	50	1.798	1.809	1.811	1.831	1.839	1.833	1.825	1.817	1.801	1.792
	8	25	0.988	0.997	1.012	1.43	1.062	1.083	1.092	1.102	1.112	1.12
	8	50	1.201	1.214	1.221	1.231	1.245	1.241	1.238	1.23	1.221	1.214
tap water	8	25	1.201	1.212	1.229	1.241	1.252	1.263	1.277	1.285	1.294	1.307
	8	50	2.009	2.019	2.033	2.047	2.051	2.055	2.051	2.044	2.039	2.031

**Table (6) Effect of Zn ion on the corrosion rate of carbon steel at different pH under dynamic conditions**

Aqueous test medium	pH	ion concentration ppm	CORROSION RATE (MPY)			
			1 HOUR	2 HOURS	6 HOURS	12 HOURS
distilled water	4	0	0.247	0.432	1.152	3.423
	4	25	0.241	0.273	0.292	0.322
	4	50	0.202	0.397	0.538	0.837
	6	25	0.167	0.189	0.219	0.283
	6	50	0.093	0.099	0.111	0.132
	8	25	0.151	0.177	0.198	0.231
	8	50	0.048	0.062	0.095	0.117

tap water	8	25	1.013	2.082	3.162	5.476
	8	50	1.166	2.121	2.632	4.676

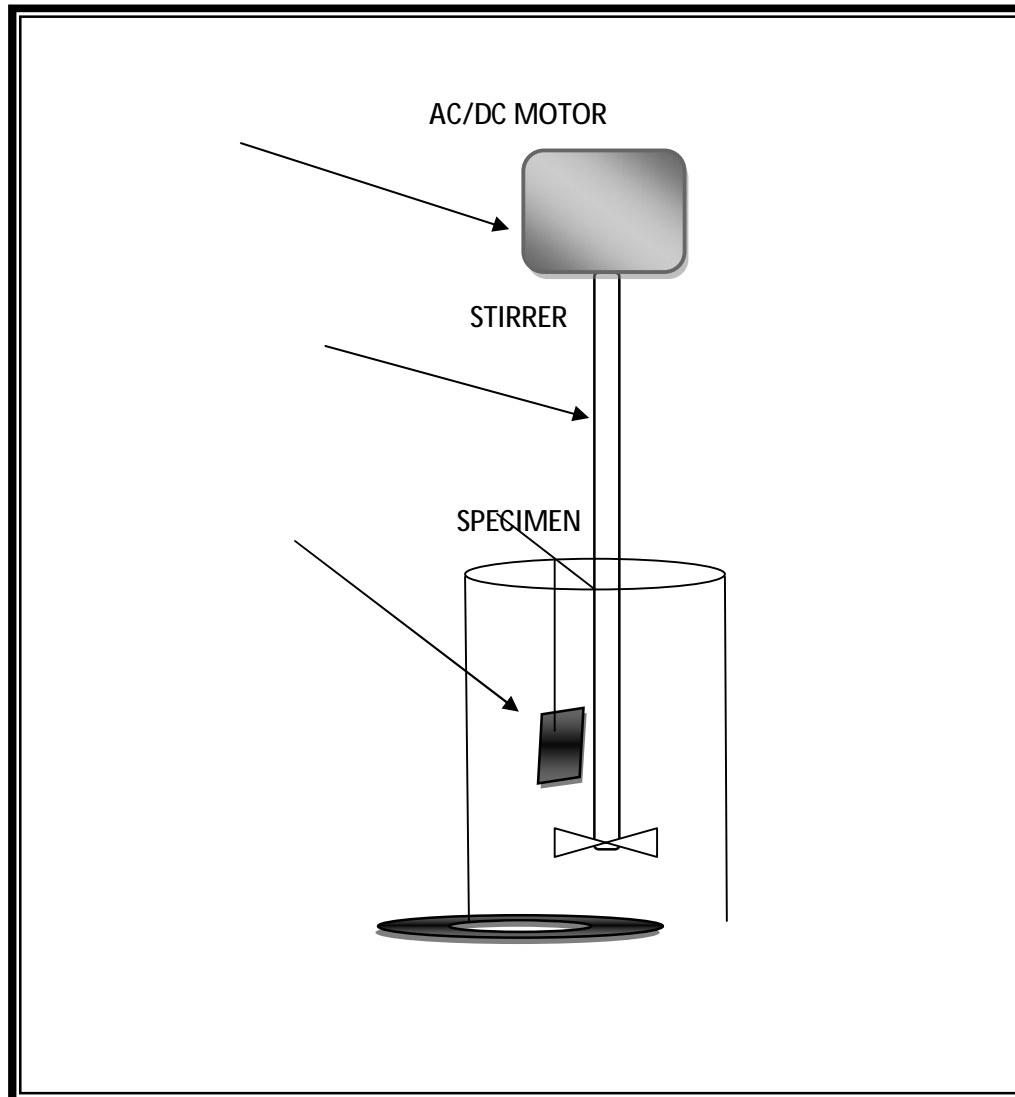


Figure (1) A schematic diagram of the experimental setup

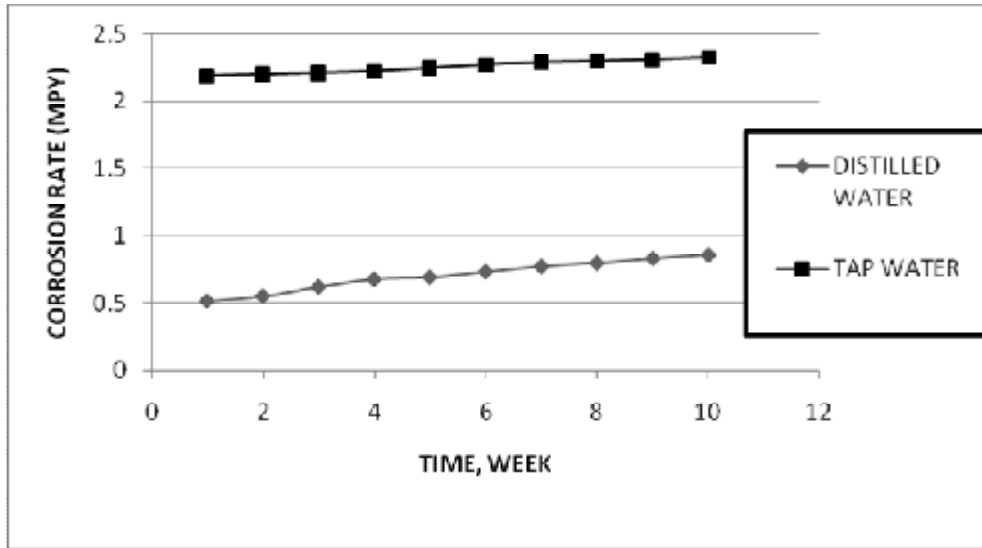


Figure (2) Effect of 50 ppm Cu on the corrosion rate of carbon steel at pH 8 in distilled and tap water under static conditions.

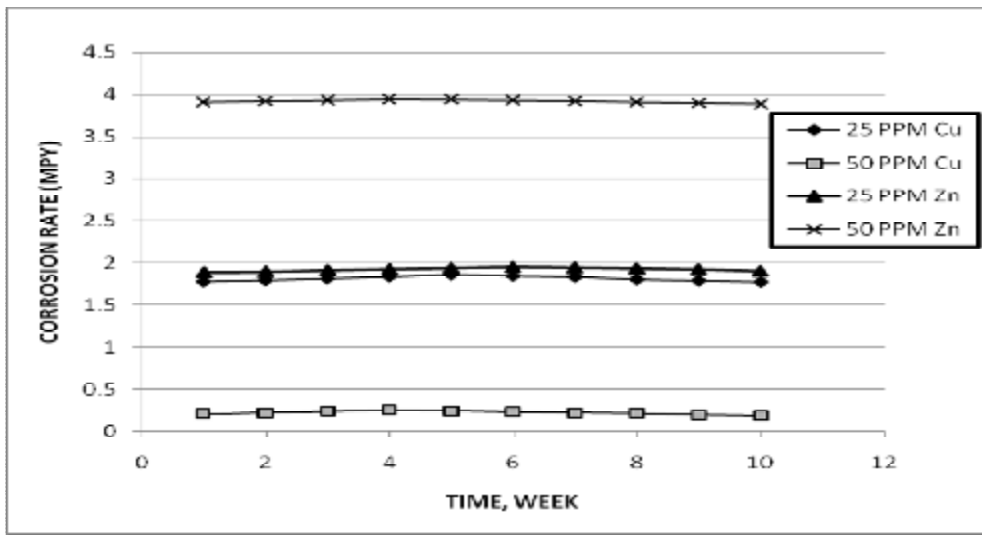


Figure (3) Effect of Cu & Zn ions on the corrosion rate of carbon steel at pH 4 under static conditions.

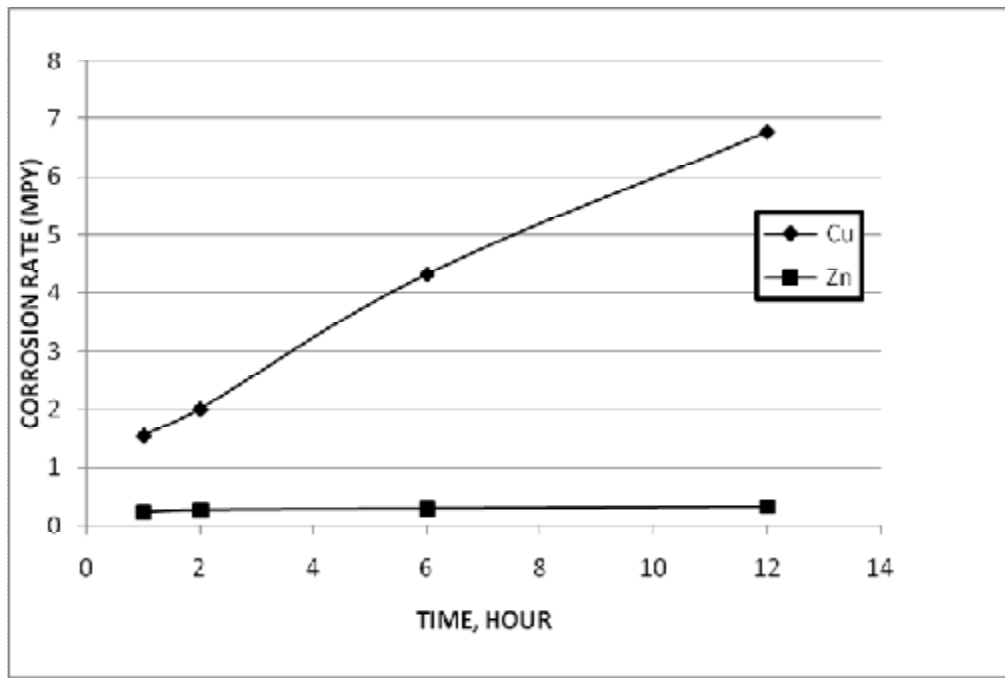


Figure (4) Effect of 25 ppm Zn, Cu ions on corrosion rate of Carbon steel at pH 4 in distilled water under dynamic conditions

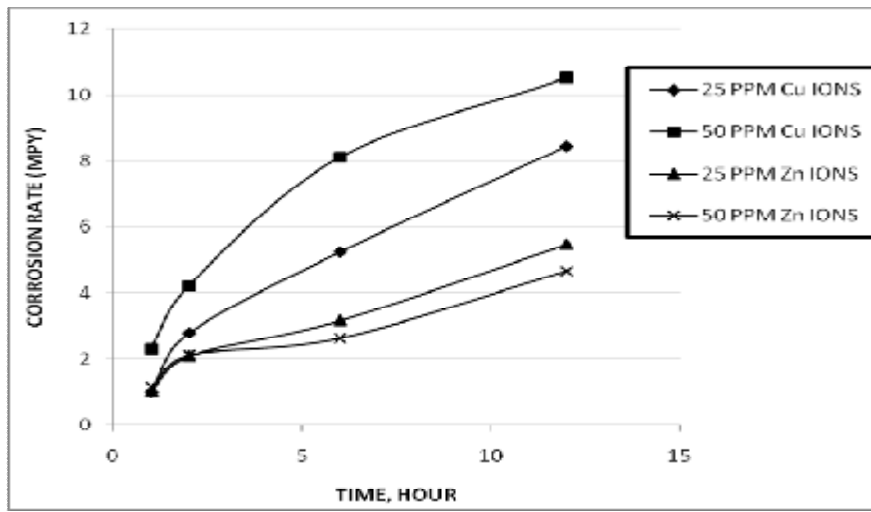


Figure (5) effect of 25, 50 ppm Zn, Cu ions on corrosion rate of carbon steel in tap water under dynamic conditions.