Effect of Halogen Ions on The Corrosion of Brass In Na$_2$SO$_4$ Solution

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Abstract

This research involves study effect of halogen ions presence in 0.2M sodium sulphate on the corrosion of brass at room temperature (30°C). Three concentration of halogen ions (F⁻, Cl⁻, Br⁻, and I⁻) were used 0.1, 0.2, and 0.3 M. The different in corrosion parameters before and after added the halogen ions interpreted and discussed which involves corrosion potentials (E$_{corr}$), corrosion current densities (i$_{corr}$), and Tafel slops (b$_c$ & b$_a$) in addition to discuss the polarization curves.

Polarization resistances (R$_p$) and the change in free energy (ΔG) were calculated and interpreted, in addition to calculate the rate of corrosion (R$_{mpy}$).

The results of this work indicates that the presence of halogen ions in experimental solution increases the rate of corrosion, and the effect of halogen ions follows the sequence to increase the corrosion I > Cl⁻ > F⁻ > Br⁻.

Keywords: Corrosion of Brass, Effect of Halogen ions.

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تأثير أيونات الهالوجين على تأكل البراص في محلول كبريتات الصوديوم

الخلاصة

يتضمن هذا البحث دراسة تأثير وجود ايونات الهالوجين في محلول 0.2 مولاري كبريتات الصوديوم على تأكل البراص عند درجة حرارة الغرفة (30 °م). استخدمت ثلاثة تراكيز من ايونات الهالوجينات (ايونات الفلوريد والكلوريد والبروميد واليوديد) وكانت 0.1 و 0.2 و 0.3 مولاري. تم تفسير ومناقشة متغيرات التاكل المقاسة والتي تضمنت جهود التأكل وكثافات تيار التأكل وميول تافل الكاثودية والانودية بالاضافة الى مناقشة منحنيات الاستقطاب.

تم حساب قيم مقاومات الاستقطاب والتغير في الطاقة الحرة لكيبس وكذلك معدل ســـرعة التاكل بوحدة المل لكل سنة. وقد بينت النتائج ان اضافة ايونات الهالوجين تؤدي الى زيادة معـــدل التاكل والزيادة تتبع التسلسل التالي يوديد > كلوريد > فلوريد > بروميد.

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1- Introduction

Brass is alloy of copper, zinc, containing between about 10 and 45% Zn, but many other additions made, and the resulting alloys are the most complicated of all the copper-base series. Copper has high degree of resistance to atmospheric corrosion, the nature of the corrosion products formed on copper exposed to the atmosphere was exhaustively studies by Vernon and Whidbey[1]. In the early periods of exposure, the deposit contains sulphide, oxide and soot. By the action of sulphuric acid and by the oxidation of sulphide, copper sulphate is form, and this hydrolyses and forms a coherent and adherent basic copper sulphate. The approximates initially to CuSO$_4$.Cu(OH)$_2$, but gradually increases in basicity until after 70 years or so it becomes CuSO$_4$.3Cu(OH)$_2$.

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Eng. & Tech. Journal, Vol. 28, No.7, 2010

**Effect of Halogen Ions on The
Corrosion of Brass In Na$_2$SO$_4$ Solution**

Brass is the most numerous and the most widely used of the copper alloys because of their low cost, easy or inexpensive fabrication and machining, and relative resistance to aggressive environments. They are, however, generally inferior in strength to bronzes and must not be used in environments that cause dezincification. As a general rule, corrosion resistance decreases as zinc content increases. It is customary to distinguish between those alloys containing less than 15% zinc (better corrosion resistance) and those with higher amounts. The main problems with the higher zinc alloys are dezincification and stress corrosion cracking (SCC).

In dezincification, a porous layer of zinc-free material is form locally or in layers on the surface. Dezincification in the high-zinc alloys can occur in a wide variety of acid, neutral, and alkaline media [2].

Copper alloys are resistant to many, but not all, saline solutions, neutral or slightly alkaline solutions, except those containing ammonia, or amines in the presence of oxygen. Strong alkalis will dezincify susceptible brass and corrode copper alloys when strongly oxidizing contaminants, e.g., chlorates, are present. In strongly reducing conditions at temperatures from 290-400 ^{o}C copper alloys are often superior to stainless steels and other stainless alloys.

The standard potentials for the equilibria:

$$Cu^{2+} + 2e \leftrightarrow Cu$$
$$Cu^{+} + e \leftrightarrow Cu$$
$$Cu^{2+} + e \leftrightarrow Cu^{+}$$
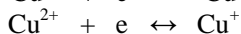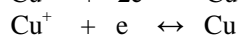
are +0.34V, +0.52V and +0.17V respectively.

Halogens have little action on copper at room temperature when dry, but are corrosive when wet. Hypochlorite solutions are corrosive. Attack can, however, occur if halogenated compounds hydrolyze in the presence of moisture to give traces of hydrochloric acid.

There are many studies for corrosion of brass in different media and by using different techniques. M.C. Bastos and co-workers studied the electrochemical behavior on the corrosion of brass in seawater under anaerobic conditions [3].

D. Örnek and co-workers studied the corrosion control using regenerative biofilms on brass in different media [4]. Khaled and co-workers studied the effect of Zn and Pb contents on the electrochemical behavior of brass alloys in chloride – free neutral sulphate solution [5].
Hintz and co-workers studied stress corrosion cracking of alph– beta brass in distilled water and sodium sulphate solutions [6]. Reinaldo and co-workers studied electrochemical behavior of Cu, Ni, and Cu55/Ni45 alloy in aqueous sodium acetate [7].

2- Experimental Part

The material used for this study was sheet of brass (70Cu/30Zn), which put in the holder to insulate all sides but one side with surface area 1cm^2. The open side polished manually to a mirror finish with abrasive papers used 200, 400, 600, and 1000 mesh grit and finally with cloths and alumina, rinsed in distilled water and stored in desiccators.

The basic solution was 0.2M Na$_2$SO$_4$ which prepare in distilled water. Study effect of halogen ions were performed by perpetration three different concentrations (0.1, 0.2, and 0.3M) of each NaF, NaCl, NaBr, and NaI.

Eng. & Tech. Journal, Vol. 28, No.7, 2010

**Effect of Halogen Ions on The
Corrosion of Brass In Na$_2$SO$_4$ Solution**

Polarization experiments were performed on WINKING M Lab Potentiostat from Bank-Elektronik with electrochemical standard cell with provision for working electrode (Brass), auxiliary electrode (Pt electrode), and a Luggin capillary for connection with an saturated calomel electrode (SCE) as reference electrode.

Electrochemical measurements were performed with a potentiostat at a scan rate 0.5mV.sec^{-1}.

Galvanostatic experiments were performed with the range of current density between -80 and +20 mA.

The main results obtained were expressed in terms of the corrosion potentials (E$_{corr}$) and corrosion current density (i$_{corr}$) in addition to measure the Tafel slops.

3- Results and Discussion
3-1 Polarization Behavior

Figure (1) shows the polarization behavior of brass in sodium sulphate with concentration of 0.2M, this behavior consist of two main regions were cathodic and anodic Tafel regions. At cathodic region, below section, reduction reactions can occur which involves reduction of hydrogen ions in addition to reduction of oxygen, while at anodic region, upper section; dissolution of brass can occurs which involves oxidation the copper and zinc metals to metal sulphate and produce two electrons. The Tafel region was very wide with low value of current density. The reactions can take place at electrodes were:

*Brass(70Cu-30Zn) + 2Na$_2$SO$_4$ → CuSO$_4$ +
ZnSO$_4$ + 4Na$^+$ + 4e   At anode
2H$^+$ + 2e → H$_2$ At cathode*
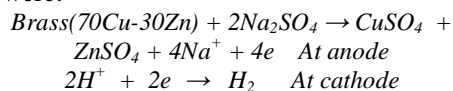
Figures (2) to (5) show the effect of halogen ions on the corrosion behavior of brass in 0.2M Na$_2$SO$_4$, this effect involves the shape of polarization curve, corrosion parameters and the nature of reactions and products of corrosion. The effect of halogen ions increases the corrosion behavior according to the following sequences:

*Increases of corrosion
in the presence of $I^- > Cl^- > F^- > Br^-$
halogen ions*

The effect of fluoride ions presented in sodium sulphate solution shows in Fig. (2), where the current density increases with decrease of fluoride ion concentration in solution, this noted through the narrow in the Tafel region of polarization curves. From the results of corrosion parameters, the presence of fluoride ions was less effective than iodide and chloride ions in the increasing of corrosion. The effect of fluoride ion action on the metal surface covered with an oxide film can differ from the action of other halogen ions.

The difference comes from the radius of F$^-$ which is smaller than that of O$_2$ (r=1.4^{o}A), therefore F$^-$ can replace O$_2$ in the oxide film. The radius of the ions increase in the same order as follows:

Halogen ions	*F$^-$*	*Cl$^-$*	*Br$^-$*	*I$^-$*
r (^{o}A)	*1.36*	*1.81*	*1.96*	*2.2*

Fig. (3) shows the effect of chloride ions in solution of sodium sulphate which show that the presence of 0.2M Cl$^-$ in solution gives more corrosive behavior for brass. Three main reasons for the specific effect of chloride ion appear to be, (a) Its ability to increase the activity of hydrogen ion in the pit electrolyte, (b) Its ability to form salt layer at low pH at the bottom of the pit, and (c) Ability to form complexes with cations and hydroxides[8].

Eng. & Tech. Journal, Vol. 28, No.7, 2010

**Effect of Halogen Ions on The
Corrosion of Brass In Na$_2$SO$_4$ Solution**

Fig. (4) shows the effect of presence bromide ions in sodium sulphate solution, this behavior was less effective on the corrosion of brass compared with other halogen ions and the little effect of Br$^-$ was indicated from the shape of polarization curves.

Finally, Fig. (5) indicates the effect of iodide ions which more corrosive than other halogen ions to increase rate of corrosion. This effect may be attribute to the complexes that form between the metals (Cu & Zn) and I$^-$ in the sodium sulphate solution. These complexes were stable and then the dissolution of metals increase and the increasing in the rate of corrosion. At first time the CuX$^+$ and ZnX$^+$ were formed and then converted to CuX$_2$ and ZnX$_2$ (X= F$^-$, Cl$^-$, Br$^-$, and I$^-$).

3-2 Corrosion Parameters

The presence of halogen ions in sodium sulphate solution shift the corrosion potentials (E$_{corr}$) either in the noble or in the active direction except addition the bromide ion was shift the corrosion potential only to the noble direction comparison with corrosion potential value of corrosion in sodium sulphate in the absence the halogen ions. The results of corrosion potentials were listed in the table (1).

When (E$_{corr}$) becomes more negative, the potential of the Galvanic cell becomes more positive and hence the Gibbs free energy change (ΔG) for the corrosion process becomes more negative. The corrosion reaction is then expected to be more spontaneous on pure thermodynamic ground and vice versa.

It is thus shown that (E$_{corr}$) value is a measure for the extent of the feasibility of the corrosion reaction on purely thermodynamic basis.

The change in free energy (ΔG) is a direct measure of the work capacity or maximum electric energy available from a system.

The free – energy change accompanying an electrochemical reaction can be calculated by the following equation [1]:

$$\Delta G = -nFE \quad \ldots\ldots(1)$$

where ΔG is the free – energy change, n is the number of electrons involved in the reaction, F is the Faraday constant (96484 C.mol^{-1}), and E is the corrosion potential and its sign is reversed prior to its use in equation (1) to represent the potential of the reversibly operating cell and not the applied potential from the potentiostat.

The values of calculated free – energy change were shown in Table (2), the negative sign of ΔG refers to spontaneous of corrosion process of brass in experimental solutions (0.2M Na$_2$SO$_4$) in absence and presence of halogen ions. The variation of ΔG for experimental solution in the absence and presence of halogen ions shows in Fig. (6).

The variation in the ΔG values comes from the variety in the corrosion potentials values. In general, there are two sources of energy to be considered in corrosion processes. The first is a driving force that determines whether corrosion will take place under certain conditions. If the free energy oxidation is less than zero, then oxidation will occur spontaneously, as in the metals in the alloys. The second source of energy occurs when positive and negative charges (metal ions and electrons, respectively) are separated from one another during corrosion. The ions are

Eng. & Tech. Journal, Vol. 28, No.7, 2010

**Effect of Halogen Ions on The
Corrosion of Brass In Na₂SO₄ Solution**

released to solution or go on to form an oxide or another compound, and the electrons are left behind in the metal undergo other electrochemical reactions, such as reduction of oxygen or hydrogen or hydrolysis of water.

This between the charges contributes to what is known as the electrical double layer and creates an electrical potential across the metal – solution interface (much like a capacitor), as expressed by equation (1).

The addition of halogen ions to the experimental solutions increases the current densities values (i_{corr}) and the increases were variable with variation of additive concentration.

The corrosion current density (i_{corr}) is a kinetic parameter and represents the rate of corrosion under specified equilibrium condition. Any factor that enhances the value of (i_{corr}) results in an enhanced value of the corrosion rate on pure kinetic ground.

The rate (R_{mpy}) of corrosion in a given environment is directly proportional with its corrosion current density (i_{corr}) in accordance with the relation:

$$R_{(mpy)} = 0.13 \times (e/r) \times i_{corr} \quad \ldots\ldots(2)$$

where (R_{mpy}) is the rate of corrosion in mil per year, (e) is the equivalent weight of the alloy and (ρ) is its density (8.53 gm/cm³). The values of rate were shown in table (2), these values indicates increase the rate corrosion of brass after addition of halogen ions to sodium sulphate solution.

The ratio (E_{corr}/i_{corr}) thus corresponds to the resistance of the metal/solution interface to charge-transfer reaction. It is also a measure of the resistance of the metal to corrosion in the solution in which the metal is immersed.

The polarization resistance (R_p) may be defined as [9, 10]:

$$R_p = \frac{dh}{di} = \frac{d(E - E_{corr})}{di} = \frac{E_{corr}}{i_{corr}} = \frac{RT}{Fi_o} \ldots(3)$$

Where E and E_{corr} are the applied and corrosion potential (Volt) respectively, i is the current density (A.cm⁻²).

i_o is the equilibrium exchange current density (A.cm⁻²). The reaction resistance (R_p), which mainly depends upon the equilibrium exchange current density (i_o) determines what may be termed the polarizability, i.e., what overpotential ($\eta = E - E_{corr}$) a particular current density needs or produces[11, 12].

The polarization resistance (R_p) was also determined in another way from Stern- Geary equation, where:

$$R_p = \left(\frac{dE}{di}\right)_{i=0} = \frac{b_a b_c}{2.303(b_a + b_c)i_{corr}} \ldots..(4)$$

where b_c and b_a are cathodic and anodic Tafel slop respectively. The values of R_p have been calculated from eq.(4), which are presented in table (2). The results of polarization resistance indicates the high resistance to corrosion in the absence halogen ions in sodium sulphate solution, and the lowest values of R_p in the presence of iodide ions in solution shows highest effect in direction of increase the corrosion of brass in experimental solutions.

4- Conclusions

From this study can be conclude that the iodide ions (I^-) have more effect than other halogen ions (F^-, Cl^-, and Br^-) in direction of increases the corrosion of

Eng. & Tech. Journal, Vol. 28, No.7, 2010

**Effect of Halogen Ions on The
Corrosion of Brass In Na$_2$SO$_4$ Solution**

brass in Na$_2$SO$_4$ solution. This effect can be show from the shape of polarization curves where the Tafel regions become more narrow when added the (I⁻) to solution, and this effect was enhanced from the values of corrosion current densities (i$_{corr}$) because of the stable complexes which formed between (I⁻) and (Cu^{2+} and Zn^{2+}) and increasing the dissolution of metals in brass.

The results of polarization resistance (R$_p$) were less in the presence of (I⁻) in solution, this is indicates that the (I⁻) more corrosive than other halogen ions for brass in sodium sulfate solution at room temperature (30^{0}C).

5- References

[1]-L. L. Sherir, "Corrosion", Metal/ Environment Reactions, second ed. vol.1, 1976.

[2]- Pierre R. Roberge, "Handbook of Corrosion Engineering", Mc Graw – Hill, 2000.

[3]- M. C. Bastos , L.F.A. Proença, M. M. M. Neto, I. T. E. Fonseca, *Journal of Solid State Electrochemistry*, Vol.12, No.2, February 2008, p.121–131.

[4]- D. Örnek, T. K. Wood, C. H. Hsu and F. Mansfeld, *Corrosion Science*, Vol.44, Issue 10, October 2002, p.2291-2302.

[5]- Hhaled M. Ismail, Rabab M. Elsherif, and Waheed A. Badawy, *Electrochimica Acta*, Vol.49, Issue 28, 1 November 2004, p.5151-5160.

[6]- Hintz M.B., Nettleton L.J., and Heldt L.A., *Metallurgical and Materials Transaction A*, Vol.16, No.5, May 1985, p.971-978.

[7]- Reinaldo S.G., Denise S.A., Alzira Maria, Marlise P.R., and Annelise M. Schmidt, *Materials Research*, Vol.4, No.2, 2001.

[8]- Scheib-Ratzar, J.H., Teller. G.H., *Corrosion Sci.*, Vol.13, 1973, P.11.

[9]- K. B. Oldham and F. Mansfeld, *Corrosion Sci.*, Vol.14, 1973, P.813.

[10]- M. Periassamy and P. R. Karishnaswamy, *J. Electronal Chem.*, Vol.61, 1975,P.349.

[11]- J. Janko Wisk and R. Juchniewicz, *Corrosion Sci.*, Vol.20, 1980, P.841.

[12]- I. Qamor and S. W. Hausion, *British Corrosion J.*, Vol.25, 1990, P.202.

Table (1) Corrosion parameters for polarization behavior of brass in 0.2 M sodium sulphate in the presence of halogen ions in solution at room temperature (30°C).

Medium (Molarity)	Corrosion potentials -E_{corr}(mV)	Corrosion current density i_{corr}(μA/cm^2)	Cathodic Tafel slop -b_c(mV/decade)	Anodic Tafel slop -b_a(mV/decade)
0.2Na₂SO₄ only	1336.7	197.18	322.5	1074.4
0.2Na₂SO₄ +0.1NaF	1316.5	451.06	188.8	1079.1
0.2Na₂SO₄ +0.2NaF	1397.3	277.12	257.2	1347.9
0.2Na₂SO₄ +0.3NaF	1290.0	261.06	175.9	1282.8
0.2Na₂SO₄+0.1NaCl	1256.9	408.09	243.8	1228.3
0.2Na₂SO₄+0.2NaCl	1370.9	514.15	272.1	1363.4
0.2Na₂SO₄+0.3NaCl	1398.9	270.43	236.1	903.50
0.2Na₂SO₄+0.1NaBr	1226.8	197.71	188.1	1217.7
0.2Na₂SO₄+0.2NaBr	1303.5	217.45	209.8	1095.9
0.2Na₂SO₄+0.3NaBr	1330.9	202.74	310.3	922.30
0.2Na₂SO₄ +0.1NaI	1242.7	1240.0	320.3	872.00
0.2Na₂SO₄ +0.2NaI	1291.9	1011.0	214.3	1416.1
0.2Na₂SO₄ +0.3NaI	1434.4	337.19	325.5	1195.4

Table (2) Change in free energy (ΔG) and Rate for polarization behavior of brass in 0.2 M sodium sulphate in the presence of halogen ions in solution at room temperature (30°C).

| Medium (Molarity)	Polarization resistance R_px10^{+3}(mΩ/cm^2)	ΔGx10^{+3} (Joul/mol)	R_{mpy} (mil/year)
0.2Na₂SO₄ only	0.546228	257.9403	96.29699
0.2Na₂SO₄ +0.1NaF	0.154686	254.0424	220.2846
0.2Na₂SO₄ +0.2NaF	0.338427	269.6342	135.3374
0.2Na₂SO₄ +0.3NaF	0.257291	248.9287	127.4941
0.2Na₂SO₄+0.1NaCl	0.216447	242.5415	199.2993
0.2Na₂SO₄+0.2NaCl	0.191566	264.5398	251.0959
0.2Na₂SO₄+0.3NaCl	0.300554	269.9429	132.0702
0.2Na₂SO₄+0.1NaBr	0.357835	236.7331	96.55583
0.2Na₂SO₄+0.2NaBr	0.351625	251.5338	206.1963
0.2Na₂SO₄+0.3NaBr	0.497277	256.8211	99.01234
0.2Na₂SO₄ +0.1NaI	0.082030	239.8013	605.5800
0.2Na₂SO₄ +0.2NaI	0.079942	249.2954	493.7431
0.2Na₂SO₄ +0.3NaI	0.329454	276.7933	164.6738
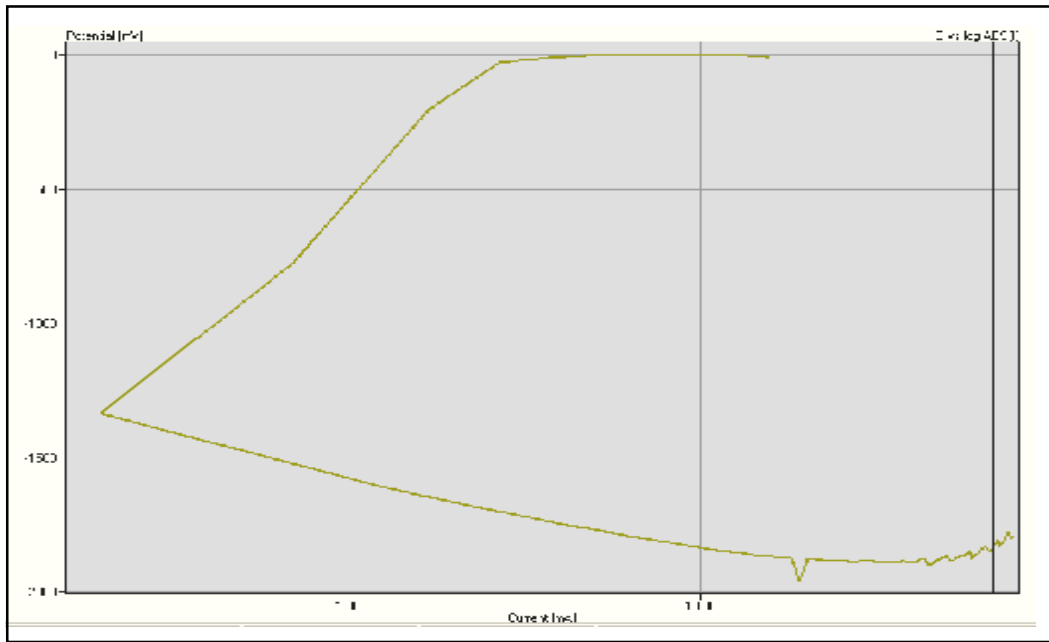
**Figure (1) Polarization behavior of brass in 0.2M Na$_2$SO$_4$ solution
in the absence of halogen ions at room temperature (30°C).**

(a) 0.2M Na$_2$SO$_4$+0.1M NaF
(b) 0.2M Na$_2$SO$_4$+0.2M NaF
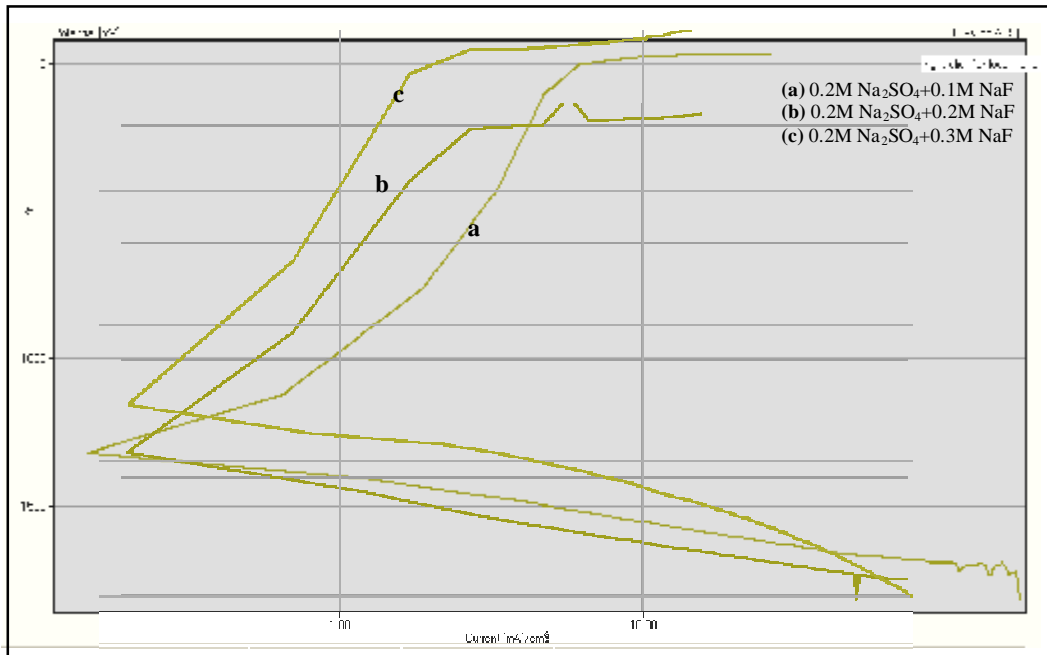**(c)** 0.2M Na$_2$SO$_4$+0.3M NaF

**Figure (2) Polarization behavior of brass in 0.2M Na$_2$SO$_4$ solution
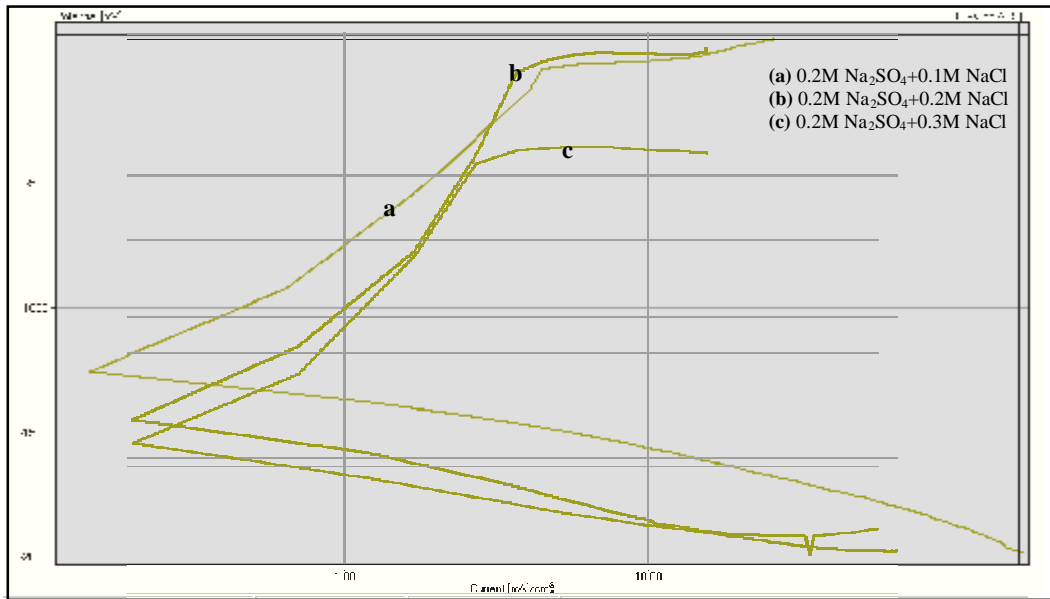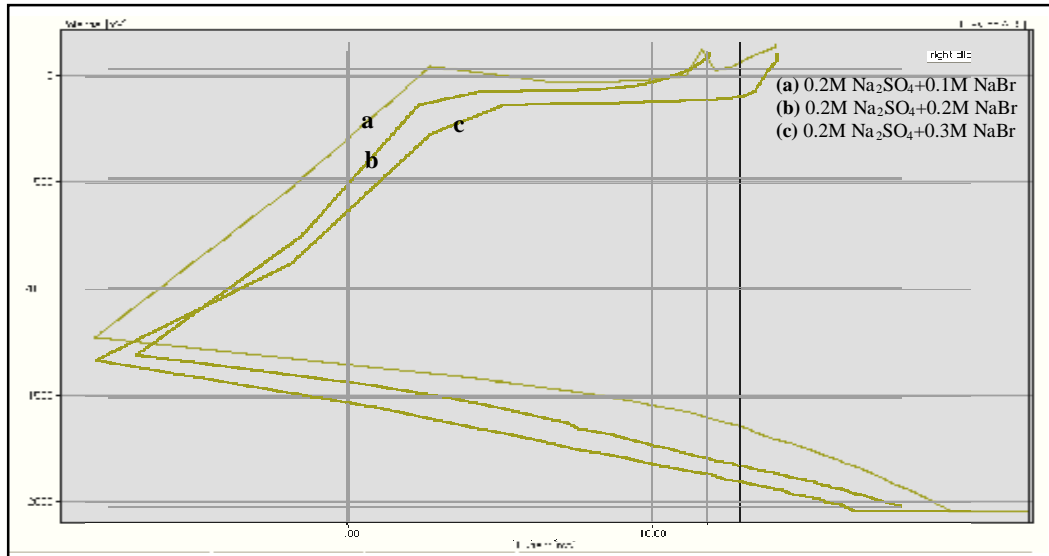in the presence of fluoride ions with three concentrations at room temperature (30°C).**

Eng. & Tech. Journal, Vol. 28, No.7, 2010

**Effect of Halogen Ions on The
Corrosion of Brass In Na$_2$SO$_4$ Solution**

**Figure (3) Polarization behavior of brass in 0.2M Na$_2$SO$_4$ solution
in the presence of chloride ions with three
concentrations at room temperature (30°C).**

**Figure (4) Polarization behavior of brass in 0.2M Na$_2$SO$_4$ solution
in the presence of bromide ions with three
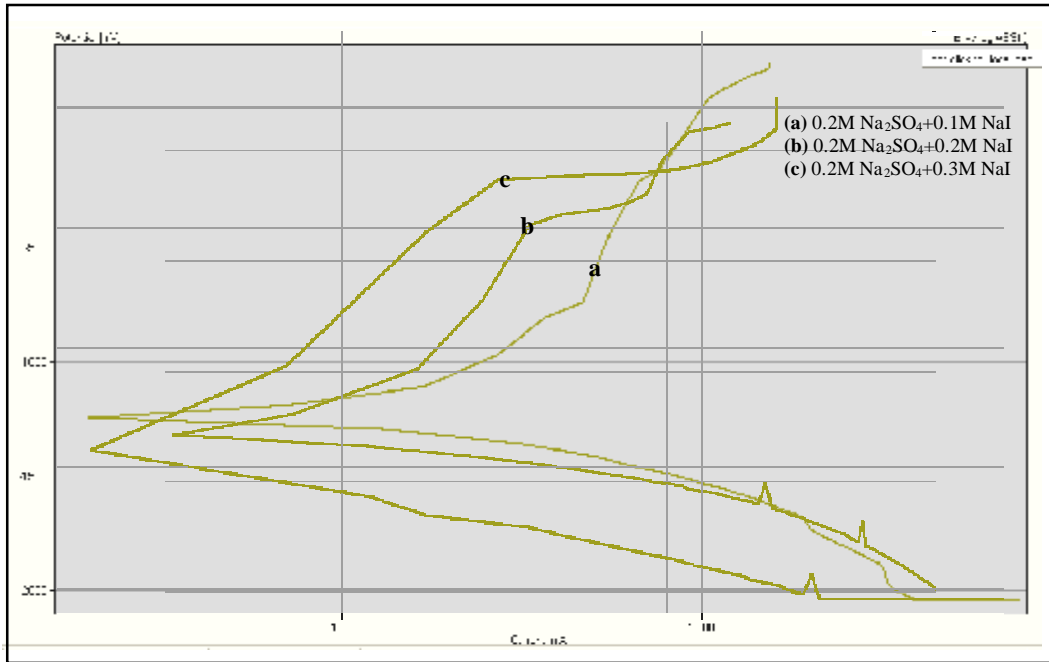concentrations at room temperature (30°C).**

Eng. & Tech. Journal, Vol. 28, No.7, 2010

**Effect of Halogen Ions on The
Corrosion of Brass In Na₂SO₄ Solution**

**Figure (5) Polarization behavior of brass in 0.2M Na₂SO₄ solution
in the presence of iodide ions with three
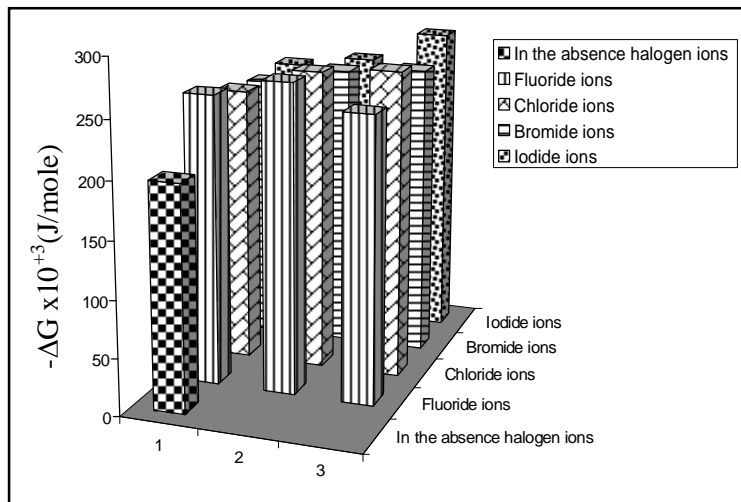concentrations at room temperature (30°C).**

**Figure (6) The variation of ΔG for the corrosion of brass in
0.2M Na₂SO₄ Solution in the absence and presence of halogen
ions with three concentrations (0.1, 0.2, and 0.3M)
at room temperature (30°C)**

1395