(C) RESULTS

The curves of Figs. (2-10) represent the variation of the potential of the copper electrode with time in oxygen saturated solutions of Na_2CO_3, $NaHCO_3$, Na_2HPO_4, Na_2CrO_4, $Na_2B_4O_7$, Na_2WO_4, NaCl, NaBr and Na_2SO_4, respectively, of concentration varying between 10^{-6} – 1M.

In Fig. (11) the final steady-state potentials in the different electrolytes are plotted as a function of logarithm of the molar concentration of the different salts in solution.

The way of variation of the potential of the Cu electrode in solutions of 0.01 M of Na_2CO_3 and 0.1 M of Na_2CrO_4 and $Na_2B_4O_7$ containing increased concentrations of NaCl and NaBr was followed till new steady-state values were reached. These were represented, respectively, by the set of curves of Figs. (12-17), respectively.

In another set of experiments, the steady-state passivation potential of Cu electrode in solutions of Na_2CO_3, Na_2CrO_4 and $Na_2B_4O_7$ of varying concentrations was awaited for. When this was reached, a weighed quantity of the aggressive salt was added and a constant potential was again left to be attained. Then other quantities of the salt were introduced. After each addition, the electrode was left to aquire a steady-potential. The results of this set of measurements in solutions of Na_2CO_3, Na_2CrO_4 and $Na_2B_4O_7$ of varying concentrations to which NaCl and NaBr were added, are depicted by the curves of Figs. (18-23), respectively. These curves represent the variation of the steady-state potential with the total weight of the aggressive salt in solution.

Figures (24a,b) show the variation of the concentration of the inhibiting CO_3^{--} anion that can withstand a certain concentration of the aggressive, Cl^- and Br^- anions on a double logarithmic scale. Figs.(25,26) and Figs. (27, 28) show the same behaviour of Cl^- and Br^- in solutions of CrO_4^{--} and $B_4O_7^{--}$, respectively.

and Cl^- ions at a certain concentration which is anion dependent, the steady-state potential was reached from positive value or that after the potential is shifted quickly from negative direction to rather higher values which are less positive the higher the concentration of the solution.

It is clear from the curves of Figs. (2-10), that the anions of this group promote the corrosion of copper, and the extent of corrosion promotion increases with the salt concentration. However, the copper electrode develops different steady-state potentials in solutions of equimolar concentrations of the various anions, indicating the specific action of the anions. The steady-state potentials developed by the copper electrode in oxygen-saturated, 1×10^{-3}M, solutions of the different anions, relative to the saturated calomel electrode (S.C.E.), are as the following:

Anion	Steady-state potential
CO_3^{--}	-60 mV,
$B_4O_7^{--}$	-55 mV,
Br^-	-45 mV,
HPO_4^{--}	-35 mV,
HCO_3^-	-26 mV,
Cl^-	-19 mV,
CrO_4^{--}	0.0 mV,
SO_4^{--}	+ 5 mV,
WO_4^{--}	+ 7 mV.

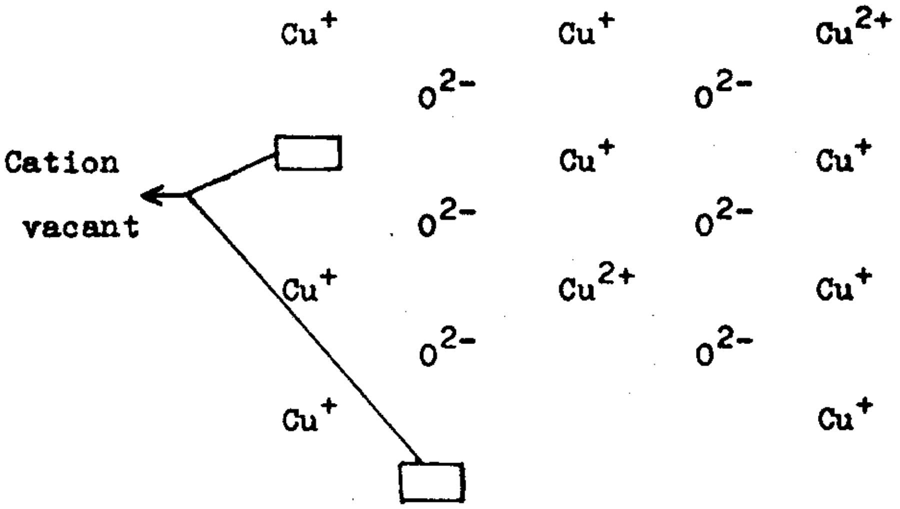
The corrosivity of these anions decreases in the same order.

Since practically all metals are covered with an air-formed pre-immersion oxide film, thus, the ennobling of the copper electrode potential when immersed in highly-oxygenated solutions of the various anions under test denotes that the pre-immersion oxide film, is not sufficient to impart passivity.(134,135) It is well stablished that, a large supply of oxygen actually reduces the corrosion rate due to restoring and thickening of the oxide film till passivity is reached. It can be concluded, therefore, that the cathodic reaction predominates over the anodic ones. This may occur through either an increase in the self polarization of the anodic areas or a decrease in the self polarization of the cathodic sites. In solutions exposed to a strong supply oxygen, the most common cathodic reaction is the reduction of oxygen to hydroxyl ions according to:

$$O_2 + 2\ H_2O \longrightarrow 4\ OH^- \quad \ldots\ldots\ldots \quad (7)$$

Under conditions of oxygenation and stirring, concentration polarization is unlikly to be the rate determining in the cathodic reduction of oxygen. The electrons necessary for the reduction process are furnished from the ionization of the copper atoms entering the oxide phase. This reaction takes place under the influence of an anodic current that polarizes the electrode and shifts its potential towards the positive direction. The structure and properties (such as conductivity, lattice structure) of the cuprous oxide formed on the copper electrode vary through the thickness of the layer. The amount of oxygen in the oxide is a maximum at the oxide/O_2 interface and decreases to minimum at the metal surface.

If, however, several oxides form on a metal, the oxide richest in oxygen will be the outermost one and the poorest in oxygen will be innermost. Many oxides have an internsic non-stiochiometric composition. For cuprous oxide, it is generally denoted as Cu_2O, yet chemical analysis indicates that a more accurate formula would be $Cu_{1.8}O$. Charge neutrality is maintained, since the oxide contains some cupric ions in the correct proportion. The structure of the oxide must accomodate the cupric ions by the creation of vacant cation sites, since two Cu^+ cations are electrically equivalent to one Cu^{2+} cation. For every Cu^{2+} cation present there must be one former Cu^+ cation site vacant. Since ionic conduction is a diffusion process and is dependent upon the existence of vacant sites, the more the cupric ions that are present in the oxide, the higher will be the ionic conductivity, which will be cationic in nature, i.e., based upon cation movement within the cation sublattic. The reaction: $Cu^{2+} + e \rightleftharpoons Cu^{+}$... (8) occurs very readily and in cuprous oxide, the presence of these two cations permits the easy passage of electrons. This oxide has too, therefore, high electronic conductivity. Since the oxide conductivity Ω is an important determinant in parabolic growth, cuprous oxide will grow more easily than the more stiochiometric oxide. The schematic arrangement of ions in the cuprous oxide structure is shown in the following figure:



The arrangement of ions in Cu_2O

The variation of the steady-state potential E with the logarithm of the molar concentration of the ions, log C, in solution is represented by Fig.(11). Invariably straight lines were obtained. The potential of a number of metals in aerated solutions of different anions changes with concentration according to Brasher's equation(136,137)

$$E_{st.} = a_1 - b_1 \text{ Log } C \quad \ldots\ldots \quad (9)$$

where a_1 and b_1 are constants. Similar behaviour was also reported for Fe, Zn, Cd, Pb.(138,137,132) With these last metals, active corrosion was operative, the intensity of which increases with the increase of the anion content of the solution.(137)

Within the concentration range studied (10^{-6} – 1 M) no ennobling of the electrode potential was recorded as the concentration was increased. It could be safety concluded that those anions behave uniformally, promoting corrosion of copper and the extent of corrosion promotion increases as the concentration of the solution was increased. The behaviour of the copper electrode in the sulphate anion solution is of interest. Below specific concentration the electrode develops steady-state potential which is concentration independent. In this case corrosion is assumed to occur at the same rate of film repair by the dissolved oxygen.(131) However, above this specific concentration, the steady-state potential starts changing into the active direction and corrosion becomes the predominate reaction. This phenomenon, to some extent, is observed in the case of chloride and bromide anions. However, at concentrations higher than 10^{-4}M Cl^- and 10^{-3}M Br^-, the potential starts to change sharply into the active direction. This may be attributed to the lack of dissolved oxygen in the solution, since the solubility of oxygen decreases with the increase of anion concentration (e.g.in NaCl solution).(97) The lines for CO_3^{--} and HCO_3^- are nearly parallel, having a slope of 37.5 mV/Log C unit, while for HPO_4^{--}, CrO_4^{--}, $B_4O_7^{--}$, WO_4^{--}, Cl^-, Br^- and SO_4^{--} the slopes are, respectively, 29.8, 21.6, 17.1, 25.8, 49, 59.2 and 18.1mV/Log C unit. These slopes were calculated using the least square method.(139)

The promotion of corrosion as marked by the decrease of the steady-state potentials with anion concentration could be attributed to an alter balance between anodic and cathodic areas set up by the competing action of the oxide film destruction by the anions, and oxide film repair by oxygen in solution.(137) Variation in the ratio of the anodic areas to that of the cathodic ones, is not, however, the sole factor which might cause the (negativation) shift of the steady-state potential toward negative values with concentration. Thus the rate of dissolution of copper

$$Cu \longrightarrow Cu^+ + \acute{e} \quad \ldots\ldots (10)$$

can be expressed in terms of the number of electrons n_1, the anodic area A_1, the rate constant K_1, the electrode potential E and the standard electrode potential E_1^o in the form.

$$i_a = n_1 A_1 K_1 F \exp\left(\alpha_1 n_1 (E-E_1^o)\ F/RT\right) \quad \ldots .(11)$$

where F, R, T are the Faraday of electricity, gas constant and absolute temperature, respectively. In the same manner, the rate of the cathodic reduction of oxygen can be given by the equation

$$i_c = n_2 A_2 K_2\ CF \exp\left(-(1-\alpha_2) n_2\ (E-E_2^o)\ F/RT\right) \ldots(12)$$

where C is the effective concentration of the depolarizer. At equilibrium the rate of anodic reaction equals that of cathodic one, and the potential of the electrode (E) becomes the steady-state potential ($E_{st.}$). This potential depends on the standard potentials of both the anodic and cathodic reactions, as well as on their transfer coefficient α_1 and α_2. It is assumed that these last terms are constants. Experimental results and theoretical consideration are, however, available which show that these may vary as the concentration of the electrochemically active species and the electric potential applied to the electrode are varied.(140) On the other hand; E_c is governed by the ratio of rate constants, as well as the balance between the cathodic and anodic areas. Noting that $(A_1 + A_2)$ equals the total area of the metal, it is clear that, the corrosion potential will shifts towards positive values if $A_2(K_2)$ increases and/or $A_1(K_1)$ decreases. Evidence that this occurs as a result of an altered balance between anodic and cathodic areas is only reasonable when it is proved that all the other parameters remain constant and unaltered.

2. AMOUNT OF THE AGGRESSIVE ANIONS THAT CAN BE TOLERATED BY CERTAIN PASSIVATORS:

The determination of the minimum concentration of a certain passivator that can withstand the corroding action of a particular aggressive anion is of great importance from the theoretical as well as the practical point of view.(141-144) This concentration was determined using various experimental techniques such as weight-loss and visual tests(144-147, 143) which are both time consuming. Another methods based on accelerated polarization techniques(148-150) were also applied. These last methods are, however, not representative to the natural corrosion conditions. A simple potentiometric method was established(141, 144) for the determination of the extent of resistance of passivity to corrosive ions in some systems. This method allows valuable conditions to be drawn regarding the way by which the potential of a previously passivated electrode changes upon the addition of aggressive ions to the medium.

Figures (12-14) and (15-17) represent the behaviour of copper electrode in solutions of 0.01 M CO_3^{--}, 0.1 M CrO_4^{--} and 0.1 M $B_4O_7^{--}$ containing increasing amounts of NaCl and NaBr, respectively, according to procedure A.

It is clear from the curves of Figs. (12 - 17) that, addition of a small amounts of Cl^- and Br^- ions to the passivating solution has a little or no effect on the steady-state potential reported in aggressive-free solutions.

These concentrations are assumed to have no influence on the dissolution kinetics of the passive film, already formed on the electrode surface.(151-153) When the concentration of the aggressive ions (Cl^- and Br^-) was further increased, a different state of affairs was soon reached, where, the potential of the electrode was changed into the negative direction, indicating the destruction of the protective film on the metal surface and the initiation of the localised type of attack, the extreme of which is pitting.

Figs. (12-17) reveal that Cl^- and Br^- ions do not attack the passive film directly upon the addition of the aggressive ion. A certain length of time elapses before the potential of the copper electrode changes from that measured in the Cl^- and Br^- free solutions. This time is identified as the induction period for pitting(148,154) corrosion to occur. It decreases with the increase of the concentration of the aggressive anions.(148,154) For relatively high concentrations of Cl^- and Br^-, the induction period is too short to be recorded.

In the presence of Cl^- and Br^- ions the copper electrode aquires a new steady-state potential. This potential becomes more negative the higher the aggressive ion content in solution. On the other hand, the potentials developed in equimolar solutions of Cl^- and Br^- ions depend on the type of the passivating ions, being more negative in the order $CO_3^{--} < CrO_4^{--} < B_4O_7^{--}$ (Figs. 12-17).

The curves of Figs. (18,19) show that the variation of the steady-state potential of the passive copper electrode with the amount of NaCl and NaBr added to solutions of Na_2CO_3 of concentration between 1×10^{-3} and 1×10^{-1}M, using procedure (B) of measurements. The curves of Figs. (20,21) represent the same behaviour obtained in solutions of Na_2CrO_4 in the presence of increasing amount of Cl^- and Br^- ions. While Figs.(22,23) illustrate the effect of the same aggressives in solutions of $Na_2B_4O_7$.

The curves of Figs. (18-23) are sigmoid in nature, showing the normal mode of potentiometric titration curves. Here, however, it seems that, the passivity caused by the inhibitor is titrated with the corrosive agent. Thus one may use these curves to determine the concentration of the passivator that can withstand a certain concentration of the aggressive ions.

In these Figs., there occurs a definite inflextion in the potential of the copper electrode when enough aggressive salts i.e. Cl^- and Br^- were added to the solution of the inhibiting anions, namely, carbonate, chromate and borate, respectively. This inflection signifies that the inhibiting film is being destroyed.

It is clearly noted that starting potentials, measured in aggressive-free media, are more negative the higher the concentration of the inhibitor in solution. The rate of potential change at the inflexion point of the curves is, however, inversely proportional to the same parameter. This is to be expected since it is easier to initiate pitting corrosion, the type of attack which occurs under these conditions,in dilute passivating solutions than in concentrated ones. From these figures, it appears that as the concentration of the inhibiting agent in solution is raised, more of the aggressive anion is needed to destroy the protective film on the metal surface and induce pitting corrosion.

It is to be noted that similar curves having the same features as those obtained here were reported by Shams El Din and Abd El Haleem(141) in the case of zinc and Abd El Haleem et.al.(155,144) in the case of low carbon steels.

From the curves of Figs. (18-23) it is also clear that there is no definite potential above which the metal withstands attack, and below which it undergoes pitting.(149,154) Accordingly the choice of such a potential, to be taken as a basis for comparison, is only arbitrary. Since the initial potential E_i of the copper electrode in the aggressive-free solutions is dependent on the ambient concentration of the inhibiting anions, it is assumed that pitting corrosion is operative to the same extent in all solutions when enough of the aggressive anion is present to displace the initial potential to the negative direction by a definite values(143) e.g. 0.0,20,40,60,80 and 100 mV.

Figures 24(a,b) represent the double logarithmic plots of the concentrations of aggressive ions Cl^- and Br^- and of the inhibiting anion CO_3^{--}. Figures (25, 26) and (27,28) show the behaviour of Cl^- and Br^- in solutions of CrO_4^{--} and $B_4O_7^{--}$, respectively. Invariably straight lines were obtained satisfying the relation

$$\text{Log } C_{inh.} = K_3 + n_3 \text{ Log } C_{agg.} \quad \ldots\ldots(13)$$

where "K_3" and "n_3" are constants.

The values of the exponent "n_3" are given in Table (1) for solutions of CO_3^{--}, CrO_4^{--} and $B_4O_7^{--}$, containing the aggressives Cl^- and Br^-.

Table (1)

Inhibitor / Aggressive	Carbonate	Chromate	Borate
Cl^-	0.29	0.27	0.90
Br^-	0.30	0.29	0.42

From Figs. (24-28) and the above table, the following conclusions could be drawn:

1. The value of "n_3" is dependent primarily on the type of the inhibitor. It is considerably higher, in borate