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Some Studies on the Corrosion of Copper and its Alloys in Calcium Hypochlorite

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Abstract : Corrosion behaviour of copper and eleven of its alloys has been studied in 20% calcium hypochlorite liquor containing 60% available chlorine at 35°C. Potential time curves, galvanostatic anodic and cathodic polarization behaviour and conventional weight loss data were utilised in the study. All the alloys studied were found to be self passivating under the experimental conditions used. The time taken for the formation of the protective film was less than an hour. The corrosion potentials of the alloys were in the range 0.650 to 0.680 V (vs SCE). Anodic polarization revealed that passivity broke down, leading to pitting in some alloys and general corrosion in certain other alloys. The latter behaviour was due to the formation of a soluble product. The Tafel slopes ranged from 0.120 to 0.254 mV in the transpassive region. Cathodic polarization curves exhibited two Tafel regions. Weight loss data under total immersion conditions indicate that nickel tin bronze (high nickel) is the most resistant. The corrosion rate of this alloy was three times higher under intermittent immersion conditions and eleven times higher under partial immersion conditions.

1. Introduction

Studies on the corrosion of copper and its alloys have been reviewed by Leidheiser.[7] Only a few workers have studied the corrosion of copper in bleaching liquor. Fitzerald Lee has reported the corrosion rates of six copper alloys in saturated $Ca(OCl)_2$ solution at 16°C.[6] Other workers have reported the corrosion of brass in NaOCl solution containing 9% available chlorine.[11] All these studies were based on weight loss data. No fundamental electrochemical studies of copper corrosion in hypochlorite has been reported.

This paper describes the study of the corrosion behaviour of copper and a number of its alloys in calcium hypochlorite liquor containing about 60% available chlorine (High Test Hypochlorite). Hypochlorite solutions are used for bleaching in the textile industries of Sri Lanka. Electrochemical and gravimetric methods were utilised in this study. The experimental work involved determination of the variation of open circuit electrode potential with time and the measurement of anodic and cathodic galvanostatic polarization data. In addition, weight loss data were also obtained.

2. Experimental

Only a brief outline of the experimental procedure is given below as full details have been given elsewhere.[1]

2.1 Materials and specimen preparation

The alloys were cast and analysed quantitatively by standard methods. The percentage composition of the alloys are reported in column 1 of Table 1. The surface was prepared by hand abrading with emery paper of successively finer grades from 120 to 500, then washing thoroughly with distilled water and finally by degreasing with acetone.

A concentrated solution (20%) of High Test Hypochlorite (DCM Chemicals New Delhi) in distilled water was used in all studies. This solution had a pH of 11.5 and an available chlorine content of 60.3%. All experiments were conducted at 35 ± 0.2°C.

2.2. Electrochemical studies

The polarization cell had two compartments separated by a sintered disc. The cell had a capacity of 100 ml. One compartment contained a cylindrical platinum counter electrode and the other contained the working electrode. The reference electrode (saturated calomel electrode) was kept in a cell of saturated KCl solution and connected to the working electrode compartment by a Luggin bridge designed after Greene.[4]

The working electrodes were cut from 0.86 cm diameter rods to 5 cm length. The working electrodes were mounted on a Teflon electrode holder so that only the polished surface (of area 0.586 cm^2) was exposed to the solution. The distance between the exposed electrode surface and the Luggin capillary tip was about 2 mm.

The variation of open circuit electrode potential with time was recorded, for about an hour after immersion, on a potentiometric recorder. The counter electrode was disconnected from the circuit during these measurements.

Galvanostatic polarization experiments were started after the electrode potential reached the steady state corrosion potential. Anodic polarization was first performed followed by cathodic polarization. Current densities ranging from 0.0025 to 15.5 mA cm^{-2} were applied. Potentials were measured five minutes after applying current.

TABLE 1. Corrosion Characteristics of Copper Base Alloys in Calcium Hypochlorite

Alloy	Corros Pot. (volts vs. SCE)	Tafel slope, b (volts per decade)	corros. current (mA per cm^2)	corros. rate (mm per year)
1. Copper	0.686	0.196	0.055	0.058
2. Silicon bronze (Si 1.5)	0.683	0.191	0.063	0.102
3. Silicon bronze (Si 3.0)	0.665	0.222	0.115	0.102
4. Brass (Zn 9.7)	0.688	0.251	0.123	0.284
5. Tin bronze (Sn 9.4)	0.650	0.168	0.148	0.130
6. Nickel tin bronze (Sn 5.8, Ni 2.1)	0.692	0.165	0.046	0.063
7. Nickel tin bronze (Sn 1.2 Ni 5.0)	0.648	0.161	0.239	0.038
8. Cupronickel (Ni 5.0, Fe 5.5)	0.655	0.195	0.380	0.185
9. Aluminium brass (Zn 17.7, Al 2.0)	0.650	0.254	0.234	0.358
10. High leaded tin bronze (Pb 14.8, Sn 5.9)	0.670	0.167	0.048	0.112
11. Gunmetal (Sn 8.4, Pb 3.8, Zn 3.1)	0.680	0.236	0.095	0.119
12. Leaded naval brass (Zn 36.7, Pb 2.1, Sn 1.9)	0.680	0.120	0.151	0.345

2.3. Gravimetric Methods

The cells used were cylindrical glass vessels 80 mm high and 40 mm diameter. A glass hook was fixed to the stopper to support the corrosion coupon. The spherical coupons had a diameter 12.5 mm and thickness 3 mm. A hole, 3 mm diameter, was drilled near the edge to support the specimen. The solutions were neither agitated nor aerated.

The corroded coupons were treated with 10% sulphuric acid to remove the corrosion products, then washed thoroughly with distilled water and finally rinsed with acetone. The coupons were then dried and weighed. An uncorroded specimen lost less than 0.0001 g during the above treatment.

All the twelve copper alloys studied were subjected to total immersion tests of 24 hour duration. On the basis of their corrosion rates the best alloy was selected to undergo the planned interval tests recommended by Wachter and Treseder[12] which provides an excellent procedure for evaluating the effect of time on the corrodibility of the metal and the corrosiveness of the environment. The maximum duration of these tests was 96 hours. The effect of changing the immersion conditions to partial and total immersion was also studied.

3. Results and Discussion

3.1. Potential-time curves

Typical potential-time curves are given in Figure 1 and the steady state corrosion potentials are given in column 2 of Table 1. The curves show that the electrode potentials of copper base alloys rise sharply to a noble steady state value of about 0.650 to 0.680 V (vs SCE). Such behaviour indicates the formation of a protective film on the metal surface. Consequently, here is a rare instance of copper exhibiting passivity. This may be due to the high oxidising power of the corrosive. The corrosion potentials recorded for copper in the present work are considerably higher than those reported in literature. The highest corrosion potential of copper, 0.45 V (vs SCE), was obtained in 0.05M chromic acid solution.[8]

The nature of the protective film formed is not certain. The colour of the film, which was brownish black, indicated that it is probably CuO. Potential-pH diagrams[10] and the recent work by Faita *et al.* who worked with aerated 0.5M NaCl solutions[3] indicate that the protective film is CuO. On the other hand, Hoar *et al.* have indicated that the black film covering brass in chloride solutions is Cu_2O.[5] North and Pryor support this view.[9] In the present work, polarization behaviour (see below) indicates the possibility that the film consists mainly of Cu_2O.

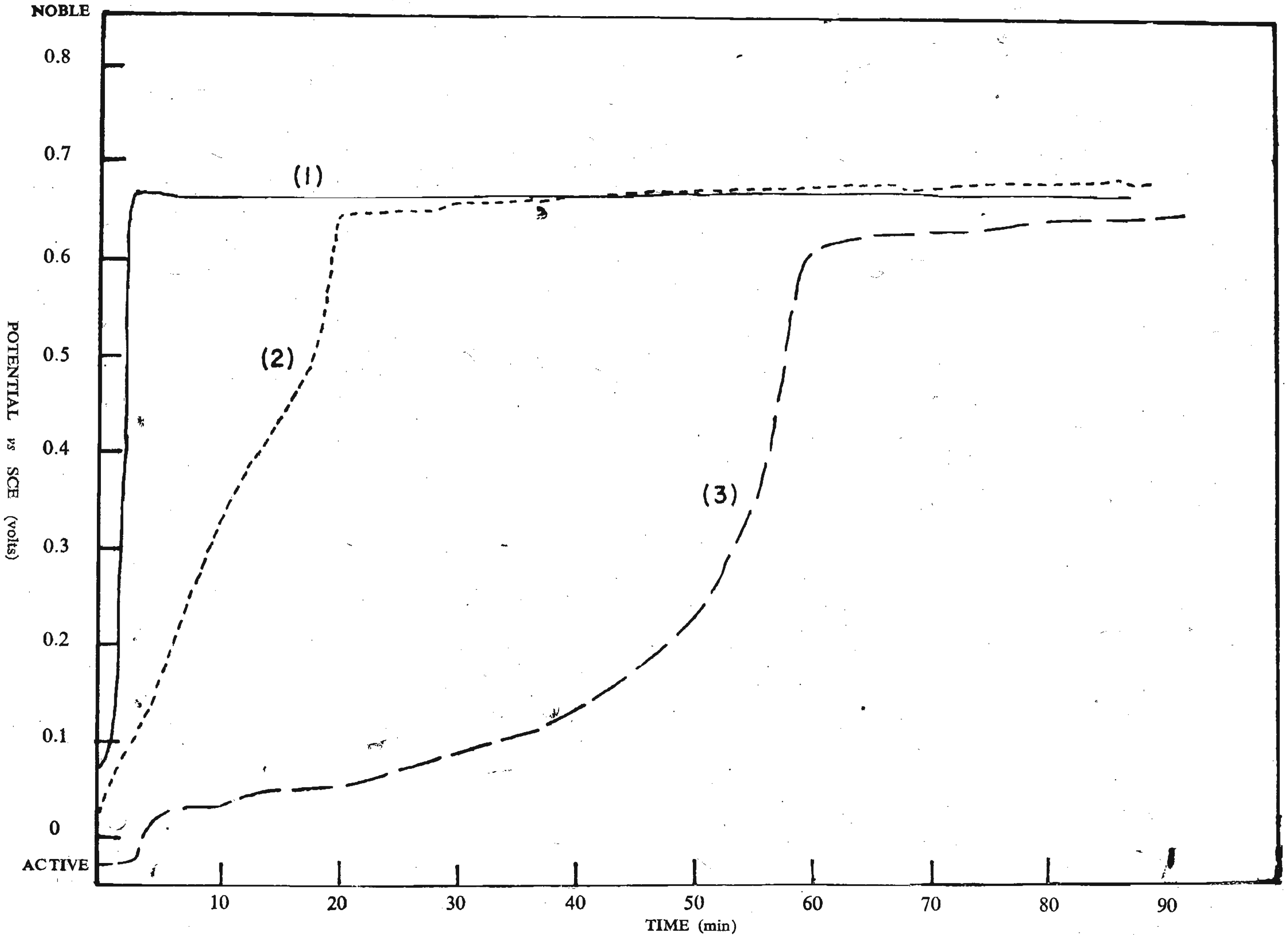

Figure 1. Potential—time curves

The time taken for the formation of the protective film varies with the alloy studied. Formation of the protective film was very rapid in the case of unalloyed copper, 90 : 10 brass, aluminium brass and the three nickel alloys. This behaviour is exemplified by the potential-time curve of nickel tin bronze-high tin (Curve 1). Film formation was slower with the addition of silicon (Curve 2, high silicon bronze) to copper and with all the three alloys containing lead. It seems that the addition of silicon and lead delays film formation while zinc, nickel, aluminium and iron have no effect on the rate of film formation. The longest time of one hour was observed with tin bronze (Curve 3).

3.2. Anodic polarization

Since copper appears to be self passivating in hypochlorite liquor, the anodic polarization curve is in the transpassive region. Typical anodic polarization curves are shown in Figures 2 and 3. The curves are seen to obey the Tafel equation

$$\eta = \frac{2.303\ RT}{\alpha\, nF} \log i_o + \frac{2.303\ RT}{\alpha\, nF} \log i \qquad (1)$$

at overvoltages greater than about 0.050V. In this equation η is the overvoltage, i the current density, i_0 the exchange current density, R the universal gas constant, T the absolute temperature, α the transfer coefficient, n the number of electrons involved in the process and F the Faraday constant. The Tafel slopes for the transpassive region obtained in the present work range from 0.120 to 0.254 V for the different alloys and are reported in column 3 of Table 1. Figure 2 shows the anodic behaviour of brass and nickel tin bronze (high Ni). The other alloys exhibit an intermediate behaviour with respect to their Tafel slopes.

The anodic curve was extrapolated to the corrosion potential to calculate the corrosion current density. Corrosion current density (i_{corr}) values so calculated are given in column 4 of Table 1. Figure 3 shows two extreme behaviour with respect to i_{corr}. The anodic curve of copper ($i_{corr} = 0.055$ mA cm^{-2}) and that of Cu.Ni.Fe alloy ($i_{corr} = 0.380$ mA cm^{-2}) are shown in the figure. The other alloys exhibit an intermediate behaviour.

A few alloys (leaded naval brass, high leaded tin bronze, tin bronze, low silicon bronze and unalloyed copper) exhibit a second Tafel region at higher current densities with slopes ranging from 0.058 to 0.118V (Figure 3). As the values of the Tafel slopes in this case is approximately half as that in the early transpassive region, it is probable that the second anodic reaction involves double the number of electrons as that in the first reaction (see Equation 1). Hence it is reasonable to assume that the first reaction involves an one electron transfer and the second reaction, a two electron transfer. Consequently, it follows that the simplest anodic reactions are the formation of cuprous and cupric ions,

$$Cu \longrightarrow Cu^{+} + e^{-} \qquad (2)$$

$$Cu \longrightarrow Cu^{2+} + 2\,e^{-} \qquad (3)$$

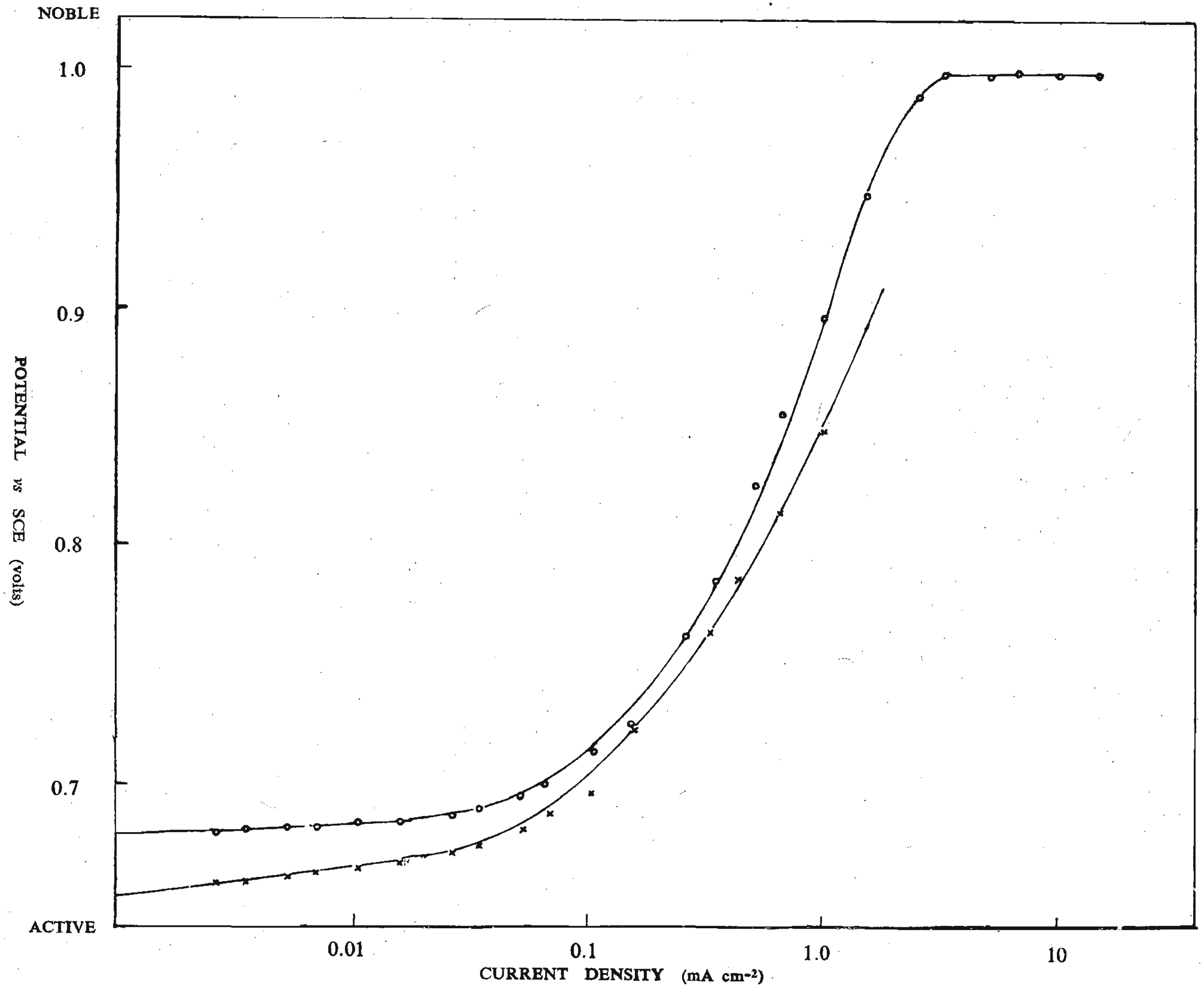

Figure 2. Anodic polarization curves
o-o-o-o brass
x-x-x-x nickel tin bronze (high Ni)

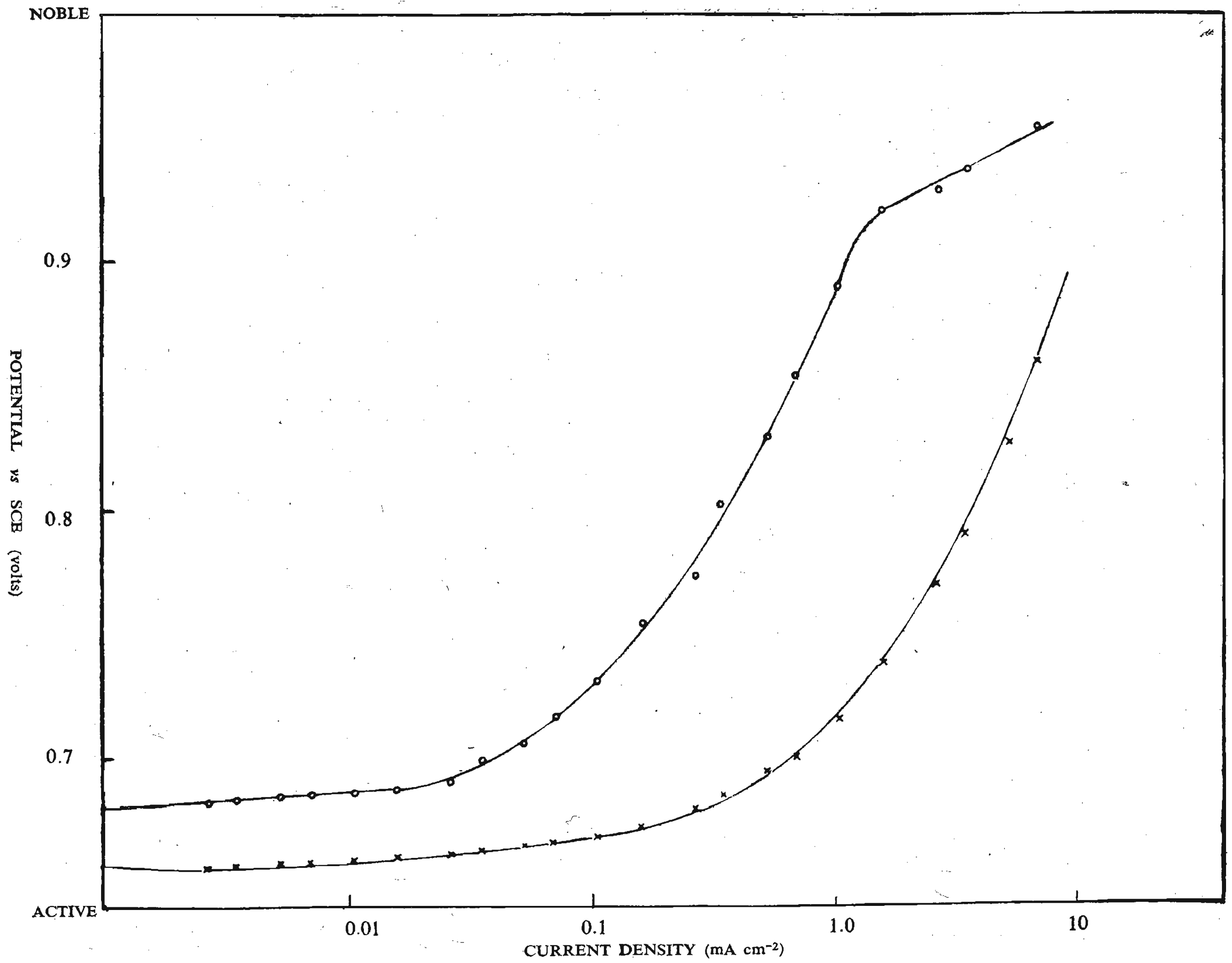

Figure 3. Anodic polarization curves
o-o-o-o copper
x-x-x-x Cu. Ni. Fe alloy

The Tafel slope values can be used to calculate the transfer coefficient for the two reactions (Equation 1). The transfer coefficient of the first reaction rnages from 0.24 to 0.51 and for the second reaction from 0.26 to 0.53. Myer[13] has indicated that low values for α experimentally obtained (as in the present work) indicate that the reaction process involves charge transfer through the film in addition to the usual charge transfer process at the interface.

The anodic polarization curve of gunmetal and brass exhibited a region of constant potential at high current densities (Figure 2). This can be interpreted as due to pitting. The breakdown potentials, E_b, for gunmetal and brass were 0.960 and 1.000 V respectively (vs SCE).

As for the nature of the corrosion product formed, reference has to be made to previous work. Many workers have indicated that the corrosion product covering copper in aerated, acid and alkaline solutions, is Cu_2O.[3,5,8,9] Hence, it is probable that the electrochemical reaction involving one-electron transfer leads to the formation of Cu_2O. Assuming that this reaction serves to plug any defects in the protective film, it can be said that the protective layer is likely to be made up of Cu_2O. The black colour of the protective layer observed also indicates this possibility as Hoar *et al.* have observed that the black layer covering brass in chloride solutions is Cu_2O.[5]

As for the two-electron reaction, the first impulse is to say that cupric oxide it formed. This is in agreement with the work of Faita *et al.*[3] who have shown that, at high potentials, the corrosion product covering copper in alkaline solutions is CuO. But in the present work a green product was observed in the vicinity of the electrodes. This leads to the assumption that CuO and $CuCl_2$ are formed initially and then the green complex CuO. $CuCl_2$, which is insoluble in water, is formed.

3.3 Cathodic polarization

Cathodic polarization behaviour of two alloys are shown in Figure 4. From the curves it can be noted that each alloy exhibits four regions. The first region is a slight curve where the overvoltage is not sufficient enough to produce polarization. The second region shows a sharp fall in potential indicating that the cathodic reaction is diffusion controlled. The third region is a Tafel slope showing that a second reduction reaction occurs in this region. The fourth region is again a steep fall in potential even beyond the range of the potentiometer (— 1.8 V vs SCE).

The first cathodic reaction is under diffusion control and obeys the equation

$$\eta_c = \frac{2.303\ RT}{nF} \log \frac{i_L - 1}{i_L} \qquad (4)$$

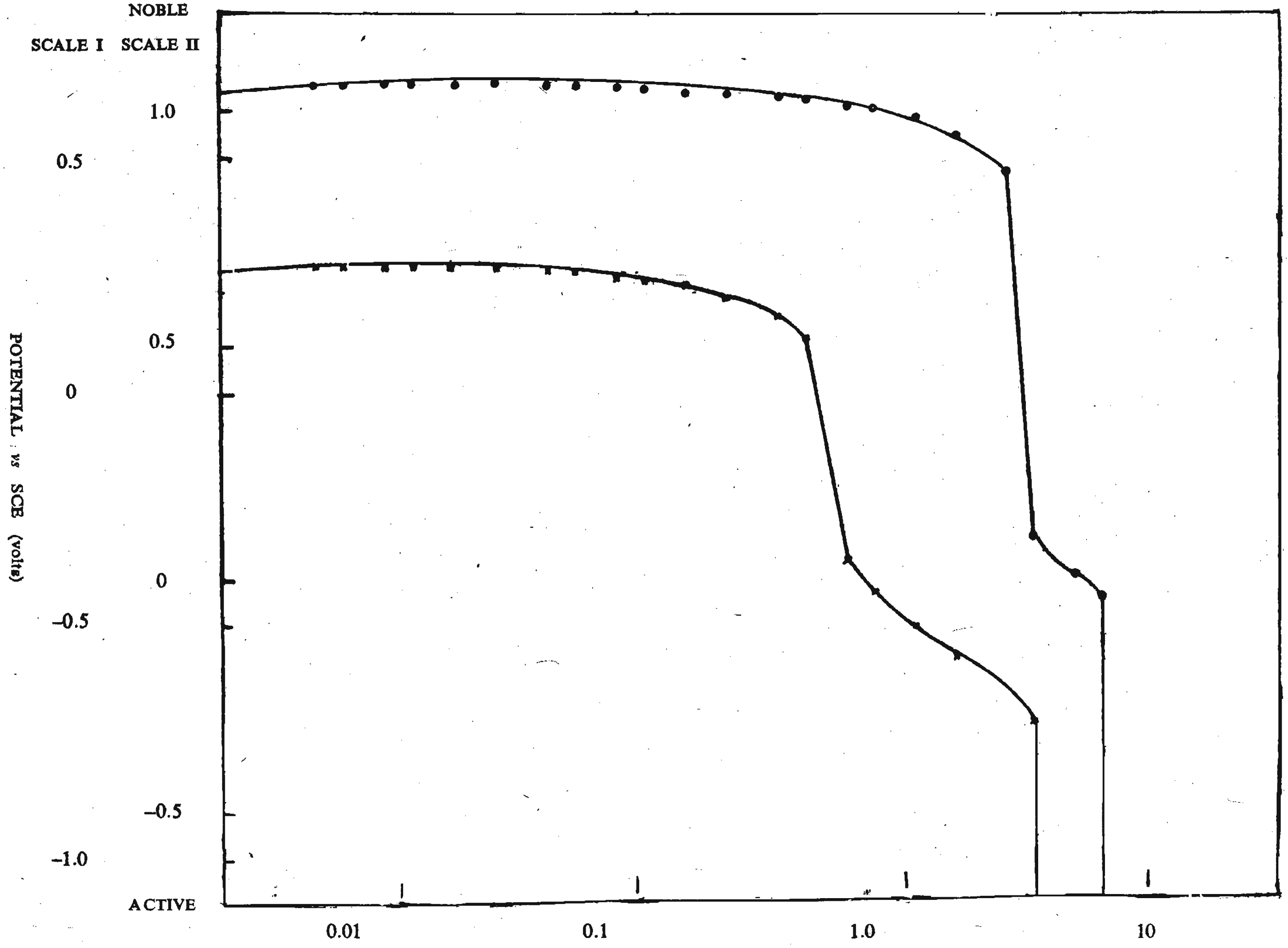

Figure 4. Cathodic polarization curves
scale I o-o-o-o tin bronze
scale II x-x-x-x High leaded tin bronze

where i_L is the limiting diffusion current density. When the applied current density approaches the limiting diffusion current density ($i \rightarrow i_L$) the overvoltage tends to infinity. That is, the potential falls sharply. In the present case, the limiting diffusion current density ranges from 0.34 to 3.4 mA cm^{-2}. Figure 4 shows the two extreme cases and the other alloys exhibit intermediate behaviour.

As for the nature of this reaction, it cannot be hydrogen evolution as the corrosion potential is very positive (around + 0.9V vs SHE) and hydrogen evolution occurs at negative potentials. Besides, gas evolution was not observed. This reaction cannot be the reduction of hypochlorite ion as the concentration of this ion in the solution is too high for diffusion control. Assuming the diffusion layer of thickness, δ, in an unstirred solution to be 0.05 cm and the diffusion coefficient, D, to be 8×10^{-6} $cm^2\ sec^{-1}$ the limiting diffusion current density has been calculated to be 62.5 mA cm^{-2} by using the equation

$$i_L = \frac{Dn\ F\ a}{\delta} \tag{5}$$

where a, the activity of the hypochlorite ion is 2.23 gm ions per litre and n the number of electrons involved in the reaction

$$ClO^- + 2\ H_2O + 2e^- \rightarrow Cl^- + 2\ OH^- \tag{6}$$

s 2. This value of 62.5 mA cm^{-2} is much higher than the experimentally obtained value of 0.34 to 3.4 mA cm^{-2}. Hence the first cathodic reaction is not the reduction of hypochlorite.

The only possibility, then, is that the first reaction is the oxygen reduction reaction, more so, as the solution was not deaerated.

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \tag{7}$$

The nature of the second cathodic reaction is not known.

3.4. Weight loss methods

The corrosion rate (in mm per year) for a duration of 24 hours is given in column 5 of Table 1. Of all the alloys tested, nickel tin bronze (high nickel) alloy is the most resistant. Pitting was not observed in any alloy. This may be because the test duration was very short.

The nickel-tin-bronze alloy (the most resistant alloy) was subjected to special tests. The planned interval tests showed that while the corrosiveness of the solution remained constant with time, the corrodibility of the alloy decreased with time. This can be explained as due to the formation of the protective film. Corrosion rate under intermittent immersion conditions was about thrice as fast compared with that under total immersion conditions for the same duration (0.102 vs 0.036 mm per year). The most severe corrosion was observed in partial immersion tests, where the corrosion loss was 4.42 mm per year compared to 0.30 mm per year in total immersion. This severity is probably due to the availability of atmospheric oxygen at the water line which acts as an efficient depolariser of the cathodic oxygen reduction reaction.

4. Conclusions

Copper and its alloys were found to be self passivating in strong calcium hypochlorite solution. The passivity broke down in some alloys leading to pitting. In certain other alloys there was a region of active dissolution after transpassivity. Of the remaining alloys, from corrosion current and weight loss data, the nickel tin bronze seem to be the most corrosion resistant. However, this alloy cannot be used under partial immersion conditions as corrosion is very severe. Corrosion under intermittent immersion conditions is only slightly more severe than under total immersion conditions and the nickel tin bronze alloy can be used.

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