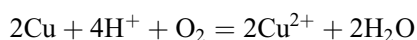


Study of film growth on copper in chromate solution by a radioactive tracer technique

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Pure copper (Cu), despite its deficiencies and poorer mechanical properties than its alloys, has some industrial applications. It possesses a high specific chemical stability in a number of corrosive media. Cu and its alloys find extensive use in heat exchangers, condenser tubes in water-cooling systems and marine equipment. In the electromotive series, the standard electrode potential of Cu in solutions of Cu^{2+} ions at unit activity is +0.34 V and in solutions of Cu^+ ions at unit activity is +0.52 V at 25 °C. Thus, Cu is noble with respect to a hydrogen electrode. Secondly, the formation of Cu^{2+} ions is thermodynamically favoured over the formation of Cu^+ ions. Under normal conditions, Cu cannot corrode by hydrogen depolarization. However, Cu can corrode electrochemically by cathode oxidation depolarization. Corroding Cu goes into solution as Cu^{2+} . The removal of these ions from the electrical double layer by stirring or by the addition of complexing agents such as KCN and NH_3 makes the potential of the Cu electrode much less noble. Cu has a very low tendency to become passive in aqueous solutions, and the lowest tendency to passivate in aerated 0.5 N NaCl [1]. Cu has a low rate of corrosion in low and medium concentrations of non-oxidizing acids (HCl, H_2SO_4 and acetic acid) in the absence of oxygen or other depolarizing agents. However, in the presence of oxidants such as HNO_3 , H_2O_2 , and bubbling oxygen or air through such solutions, the corrosion of Cu in aqueous solutions increases considerably, according to



Rapid corrosion of Cu in water was associated with destruction by various agencies of the protective Cu_2O film [2]. Where possible, corrosion control in Cu water-recirculating systems can be obtained by deaeration and by pH control [3]. Cu tubing for potable water corroded (i) under non-scale-forming water at low pH gives uniform attack and (ii) with a high CO_2 concentration in conjunction with dissolved O_2 produces pitting and early failure, without a significant amount of Cu going into solution [4].

Chromates are in a class of inhibitors called passivators and are widely used in industry as aqueous corrosion inhibitors. Chromates are widely used because of their versatility and favourable cost-effectiveness ratio for a variety of metals and alloys, over a large range of pH values in aqueous systems, in both the presence and the absence of air. Chromates slow down the corrosion of almost all

important metals, e.g., iron, aluminium, zinc and copper. They protect by the formation of an oxide film on the metallic surface [5–8] which grows logarithmically with time at 30 °C and inversely logarithmically at 40 and 50 °C [9, 10]. Chromates are a mixed inhibitor and affect both anodic and cathodic reactions.

The ability of pure Cu to enhance its corrosion resistance by the formation of oxide film is very insignificant. In the atmosphere, Cu forms a protective layer of $\text{CuCO}_3\text{-Cu(OH)}_2$ (malachite type). In aerated natural water, a protective film of porous oxide and cupric hydroxide forms on Cu, which appreciably retards the corrosion potential of Cu. Natural fresh water generally promotes the formation of protective coatings on Cu. It is, therefore, used ideally in water lines, tanks and heat exchangers. Other constituents present such as acids, metallic chlorides, ammonia and hydrogen sulphide may accelerate corrosion. Cu is effectively inhibited in 0.1 N $(\text{NH}_4)_2\text{CrO}_4$ solution at pH 1.6 [11]. The inhibition is obtained owing to the formation of a mixed cuprous chromic oxide with a lower chemical activity than Cu_2O [11].

The radioactive tracer technique is the most sensitive method so far to study the film formation and distribution of the constituents in an oxide film on the surface. It is, however, limited to systems where suitable radioactive isotopes are available.

The present investigation uses a mixture of radioactive and inactive sodium chromate for the study of film growth on Cu in aqueous solution at room temperature. The thickness of the protective chromatic film is measured as a function of time and the concentration of the solution. The open-circuit potential is measured continuously against a saturated calomel electrode to indicate the nature of the polarization responsible for the protection of Cu.

Cold-rolled commercial-purity copper specimens of size 1.5 cm × 1.5 cm were polished, degreased and pre-exposed to air for 35 min and fitted onto a glass holder for exposure. The specimens were sealed with wax on all sides except the front surface. In the earlier works [5, 12], the whole specimens were exposed in the solution and the film containing radioisotope formed on all available surfaces. This required a correction of 21% to be applied pertaining to the counts from the edges and the underneath of the specimens. This uncertainty was avoided by sealing the unwanted specimen surfaces with wax in the present work.

Radioactive ^{51}Cr in sodium chromate solution (15 cm^3) of specific activity 220 mCi mg^{-1} was obtained from Bhabha Atomic Research Centre, Trombay. The NaCl content was 0.91 mg ml^{-1} ; 500 cm^3 of dilute active solution was made. The standards were prepared by putting 0.05 cm^3 of dilute active solution (containing $0.1435\text{ }\mu\text{g}$ of active Na_2CrO_4 and $0.04545\text{ }\mu\text{g}$ of active ^{51}Cr) onto the sample, drying by infrared radiation. Two experimental solutions were prepared by mixing 15 cm^3 of dilute active solution (containing $43.04\text{ }\mu\text{g}$ of active Na_2CrO_4). The balance of the chromate was made up by inactive sodium chromate (9.95 cm^3 and 19.5 cm^3 , respectively, of 0.005 M inactive Na_2CrO_4 solution). This was done to adjust the desired activity for maximum sensitivity in counting in the modified radiotracer technique developed in the National Metallurgical Laboratory, Jamshedpur, India, and used currently [8, 9, 13]. 40 cm^3 of the experimental solution was used for each exposure. The counting for the standard as well as the exposed samples was done using a Geiger-Müller counter. The count rates were corrected for the background and the finite resolving time of the counting system. The corrected count rates were found to be proportional to the relative concentrations of active Cr. The inactive Cr content in the film deposited on the exposed surface was found from the proportional weight in the experimental chromatic solution.

The prepared specimens were immersed in the solutions saturated with purified nitrogen in the experimental set up fabricated in the National Metallurgical Laboratory (Fig. 1). Immersion times from 10 to 360 min were used at both compositions of the solution. The open-circuit potential of the specimens was measured constantly against the saturated calomel electrode using a Luggin capillary and a microvoltmeter. After immersion, the specimens were washed in distilled water and acetone, dried and subjected to counting. The pH of the solutions were measured before and after the exposures. The exposed specimens were examined optically for the presence or absence of corrosion.

The film thickness of the inhibitor (weight of Cr divided by the surface area) deposited on the Cu surface was found to increase logarithmically with increasing time of immersion, t_s , from 10 to 360 min at 30°C (Fig. 2). Optically clean and bright surfaces were obtained without any rust spots after immersion.

The film thickness on the Cu specimen was found to increase with increasing concentration of sodium chromate in the solution (Fig. 2).

The open-circuit potential of Cu against the saturated calomel electrode was found to be positive throughout the exposure, as expected (Fig. 3). The potential becomes more anodic (positive) initially on immersion up to 20 min, leading to anodic polarization. The potential later starts to decrease, leading to cathodic polarization up to 360 min. The higher-concentration solution generates higher potentials at all times.

The pH of the solutions measured before and after

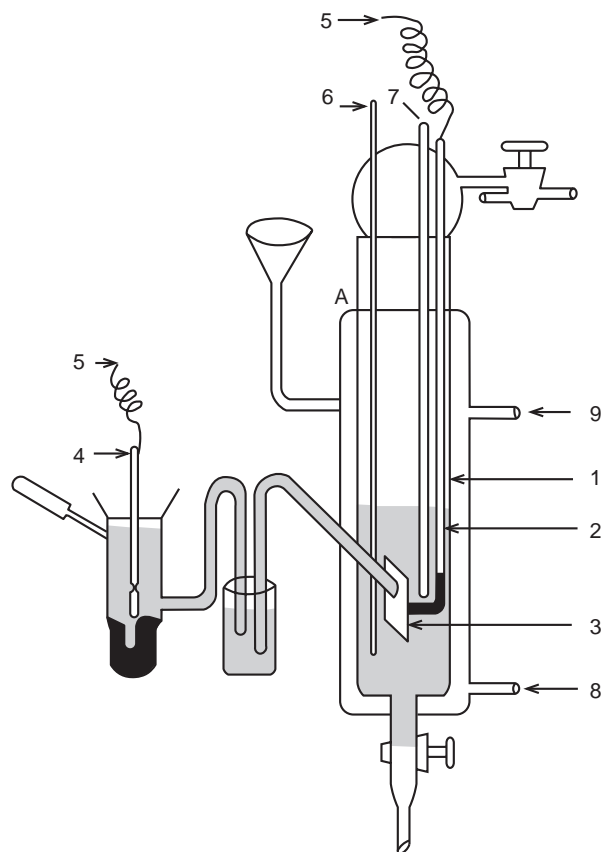


Figure 1 Experimental set-up for the measurement of the open-circuit potential and for immersion of the specimens. 1, Glass cylinder containing experimental solution; 2, specimen holder; 3, specimen fixed with wax to the specimen holder; 4, calomel electrode; 5, connection for a direct-current microvoltmeter; 6, glass tube for introducing N_2 ; 7, glass tube container for the thermometer; 8, hot-water entrance; 9, hot-water exit.

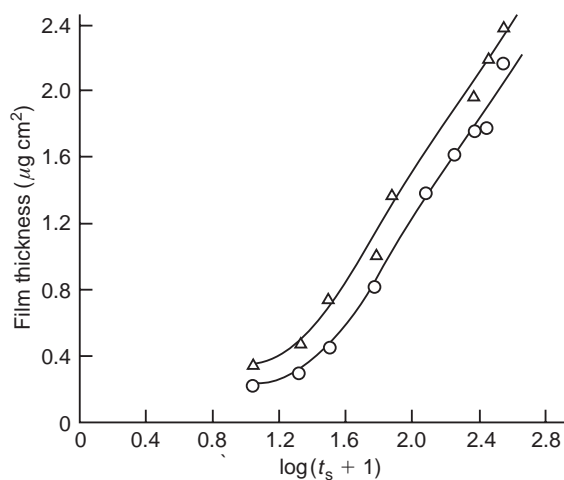


Figure 2 Cr pick-up by copper immersed in Na_2CrO_4 solutions at 30°C as a function of time t_s (min). (Δ), 0.025 M; (\circ), 0.00125 M.

immersions shows slight variations only, for both concentrations of the solution. For shorter times of up to 30 min, the pH decreases marginally but increases marginally for longer times of immersion (Tables I and II).

For a protective film, the rate of oxidation

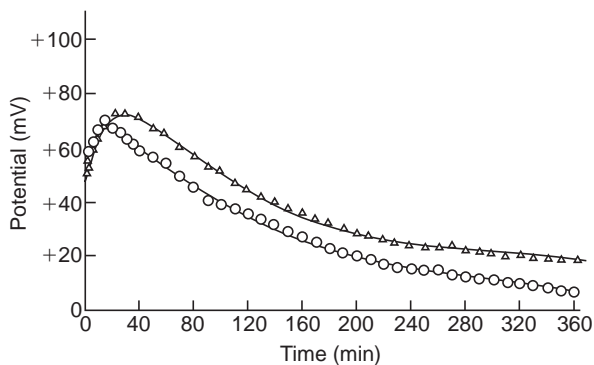


Figure 3 Change in open-circuit potential of copper with time in Na_2CrO_4 solutions saturated with N_2 at 30°C . (Δ), 0.0025 M; (\circ), 0.00125 M.

TABLE I pH of copper specimens exposed in 0.00125 M Na_2CrO_4 solutions

| Specimen number | Time of exposure (min) | pH before exposure | pH after exposure |
|-----------------|------------------------|--------------------|-------------------|
| 1 | 10 | 8.04 | 7.75 |
| 2 | 20 | 8.02 | 8.03 |
| 3 | 30 | 7.96 | 8.14 |
| 4 | 60 | 8.02 | 8.12 |
| 5 | 120 | 8.12 | 8.26 |
| 7 | 180 | 8.14 | 8.33 |
| 8 | 240 | 8.07 | 8.59 |
| 10 | 300 | 8.09 | 8.27 |
| 11 | 360 | 8.10 | 8.47 |

TABLE II pH of copper specimens immersed in 0.0025 M Na_2CrO_4 solutions

| Specimen number | Time of exposure (min) | pH before exposure | pH after exposure |
|-----------------|------------------------|--------------------|-------------------|
| 14 | 10 | 7.43 | 6.96 |
| 15 | 20 | 7.43 | 7.41 |
| 16 | 30 | 7.45 | 7.32 |
| 17 | 60 | 7.45 | 7.51 |
| 18 | 120 | 7.51 | 7.61 |
| 19 | 180 | 7.48 | 7.83 |
| 20 | 240 | 7.46 | 7.88 |
| 21 | 300 | 7.47 | 7.83 |
| 22 | 360 | 7.46 | 7.77 |

decreases as the thickness of the film increases. Film growth according to direct linear logarithmic laws, as follows, possesses the best protective properties:

$$\log m = k \log (t_s + 1)$$

where m is the amount of oxide formed and t_s is the time of immersion.

In these cases, the film growth falls off after some time, gradually coming to a complete stop. The protective film is found to form and grow logarithmically with time on Cu. This is in line with the results of corrosion inhibition of iron by chromates obtained earlier [5–10].

For Cu in aqueous solution, the protective film is known to be Cu_2O . The growth and repair of this film are promoted by some anodic inhibitors such as chromates. In the present case, the oxide film formed supposedly by the oxidation of Cu to Cu_2O , with coprecipitation of Cr_2O_3 . The latter forms as an integral and constant part of the growing film. It protects the Cu surface from corrosion. On the assumption that Cr is laid down as Cr_2O_3 and represents a constant and integral part of a growing oxide film (i.e., Cu to Cr ratio is constant), the units of micrograms per square centimetre can be converted to film thickness.

Immediately on immersion, an adsorbed layer containing Cr ions forms, followed by logarithmic growth of oxide film with an adsorbed film always present, as in the passivation of iron in chromatic solutions [14]. The downward displacements of the growth curves initially may indicate an adsorbed layer. The curve may meet the y axis (i.e., zero time of immersion) at a positive value, which may represent an adsorbed layer containing Cr. The kinetics of the film suggest that a very thin oxide film on the metal adsorbs on its surface atoms (or ions) of the oxidizing agent, e.g., oxygen or CrO_4^{2-} . The electrons pass through the film from the metal to the adsorbed surface layer by the tunnel effect. The direct logarithmic film grows by the movement of electrons or electron defects across the film which is postulated as the rate determining step, according to the Mott and the Hauffe–Ilshner [15] model.

The increase in the film thickness with increase in the concentration of sodium chromate solutions may be attributed to the continued film formation. The nobler potential (+18 mV) as observed for 0.0025 M Na_2CrO_4 (Fig. 3) supports the above arguments. This agrees with the earlier observation on mild steel passivation by chromate solution [9]. Also, the predominance of cathodic polarization is more marked in 0.00125 M Na_2CrO_4 solution. This may be attributed to more chances of formation of cracks or discontinuities of the passive film owing to the lower concentration of the inhibitor.

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References

1. N. D. TOMASHOV, "Theory of corrosion and protection of metals", (Macmillan, London, 1966) p. 487.
2. G. B. HATCH, *J. Amer. Water Works Assoc.* **53** (1961) 1417.
3. M. E. TESTER, US Atomic Energy Commission Report GAT-296 (1966) p. 14.
4. C. R. RAMBOW and R. S. HOLMGREN JR, *J. Amer. Water Works Assoc.* **58** (1966) 347.
5. D. M. BRASHER and A. G. KINGSBURY, *Trans. Faraday Soc.* **54** (1958) 1214.
6. O. KUBASCHEWSKI and D. M. BRASHER, *ibid.* **55** (1959) 1200.
7. D. M. BRASHER, D. REICHENBERG and A. D. MERCER, *Brit. Corros. J.* **3** (1968) 144.

8. K. D. MAJI, I. SINGH and R. KUMAR, *Trans. Indian Inst. Metals* **29** (1976) 374.
9. K. D. MAJI, A. BAHADUR and I. SINGH, in Proceedings of the Fifth European Symposium on Corrosion Inhibitors, Ferrara, 1980 (1980) p. 593.
10. A. BAHADUR, *Corros. Rev.* **10** (1992) 155.
11. K. F. LORKING, *Nature* **208** (1965) 778.
12. J. G. N. THOMAS, *Brit. Corros. J.* **5** (1970) 41.
13. A. BAHADUR, *Corros. Rev.* **7** (1987) 85.
14. D. M. BRASHER, A. H. KINGSBURY and A. D. MERCER, *Nature* **180** (1957) 27.
15. HAUFFE and ILSCHNER, *Z. Elektrochem* **58** (1954) 382.

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