

Dissolution of Copper by Oxidation Agents in Acid Chloride Solution

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Investigations have been made on the dissolution of copper by cupric, ferric, and permanganate ions in unstirred acid chloride solutions. Except at relatively low chloride concentrations, where precipitation of cuprous chloride on the metal surface complicates the matter, the corrosion rate is determined by the limiting reduction rate of the oxidation agent and the corrosion potential (E_c) varies with this rate (i_c) and the chloride concentration (Cl) according to:

$$d E_c/d \ln i_c = RT/F \text{ at constant (Cl)}$$

$$d E_c/d \ln (\text{Cl}) = nRT/F \text{ at constant } i_c$$

where n is 2 at chloride concentrations below about 1 M and 3 at higher concentrations. This is independent of the oxidation agent applied, whereas the actual values of the corrosion potential at given corrosion rates and chloride concentrations to some extent depend on the properties of the oxidation agent. All results are well accounted for by a mixed potential treatment of the red/ox and $\text{Cu}/\text{CuCl}_n^{(n-1)-}$ electrode, regarding the former to operate at its cathodic limiting current and the latter to exhibit pure concentration polarization.

1.0 INTRODUCTION

Following previous work¹ on the behaviour of the copper/cuprous electrode under galvanostatic conditions in non-oxidizing acid chloride solutions, studies have been made on the dissolution of this metal by cupric, ferric, and permanganate ions in otherwise the same type of solutions. This work is a continuation of analogous studies on copper in acid sulphate solutions² and on iron in acid solutions³ and is aiming at contributing to the elucidation of metal dissolution reactions and their possible interactions with cathodic reduction reactions simultaneously occurring at the same metal surface.

Much data are available on the rate of dissolution of copper in chloride solutions of oxidation agents. A comprehensive study has recently been made by Ferrari⁴, who also gives an excellent survey of the literature on the subject. However, it does not seem to be much data on the correlation between the dissolution rate and the mixed potential of copper in such solutions, data which are necessary for the evaluation aimed at in the present work.

2.0 EXPERIMENTAL

The experimental work consists in determinations of the dissolution rate (corrosion rate) and the mixed potential (corrosion potential) of copper in unstirred solutions of cupric chloride (0.005 to 0.1 M), ferric chloride (0.005 to 0.3 M), and potassium permanganate (0.001 to 0.03 M), respectively, in 0.1 N sulphuric acid + potassium chloride to various total chloride concentrations (0.1–3 M) at 20°C (room thermostated to $\pm 0.5^\circ\text{C}$).

The solutions were prepared from A.R. quality acid and salts in water distilled from a "pure" fresh water and the experiments were performed with the solutions exposed to air. The high purity copper sheets used, were of the same type and were given the same pretreatment as previously described².

The rate measurements were performed partly by the continuous quartz helix technique previously described², and partly by determining the weight change of copper sheets over given experimental periods (mostly from 1 to 3 hours). Sheets of 14 cm² geometrical surface area were used in these experiments and each of them were exposed to 600 ml test solution.

The potential measurements were carried out as previously described² (sheets of 2 cm² geometrical surface area in 100 ml test solution). The saturated calomel electrode used has been ascribed the potential⁵ 0.245 V on the normal hydrogen scale (NHS) at 20°C. No attempts have been made to correct for the (possibly negligible⁶) liquid junction potentials between the test solutions and the saturated potassium chloride solution.

3.0 RESULTS

The rate curves obtained were mostly linear and the potential-time curves usually showed very nearly time independent stationary potentials (as in Figs. 3 and 4 of Ref.²) except at the higher ox-ion concentrations in the solutions of low chloride content. This deviating behaviour, which was strongest in the cupric chloride solutions, was found to be accompanied by a precipitation of cuprous chloride on the copper surface. In some cases, this precipitation even resulted in a weight gain instead of a weight loss of the copper sheets. More detailed investigations are now being made on this matter, which will be more thoroughly discussed in a separate paper, whereby we here mainly will deal with the dissolution occurring under entirely active conditions.

In Figs. 1–3, values obtained for the dissolution rate and the mixed potential of copper at various ox-ion (Cu^{++} , Fe^{+++} , and MnO_4^- , respectively) and chloride ion concentrations are presented in the form of Tafel diagram plots. The dissolution rate is there expressed in A/cm², the current density values having been calculated from the weight loss data on the basis of the dissolution being solely to the monovalent state¹. Solid curves are drawn through points applying to given total chloride ion concentrations, and dashed curves through points applying to given ox-ion concentrations. Except for the above mentioned deviations in the upper part of these diagrams (see especially Fig. 1), it is obvious that these curves essentially represent Tafel lines for the anodic dissolution reaction and limiting current curves for the cathodic ox-ion reduction, respectively.

The anodic Tafel lines in Figs. 1–3 have all been drawn with a slope of

$$b_a = 2.303 RT/F \quad (1)$$

i.e. 58 mV per logarithmic unit in dissolution rate at 20°C. This is the same as

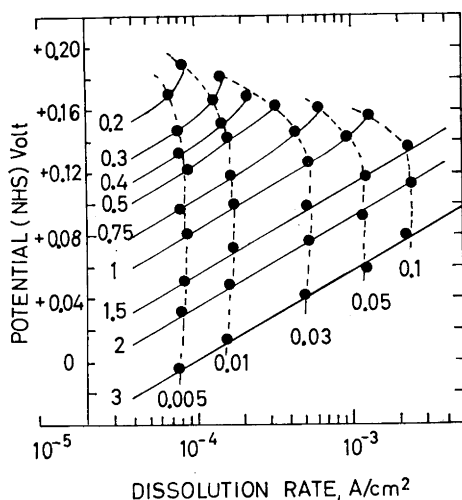


Fig. 1. Dissolution rate and corrosion potential of copper in unstirred 0.1 N sulphuric acid solutions of cupric sulphate (0.005–0.1 M) and potassium chloride (0.2–3 M) at 20°C.

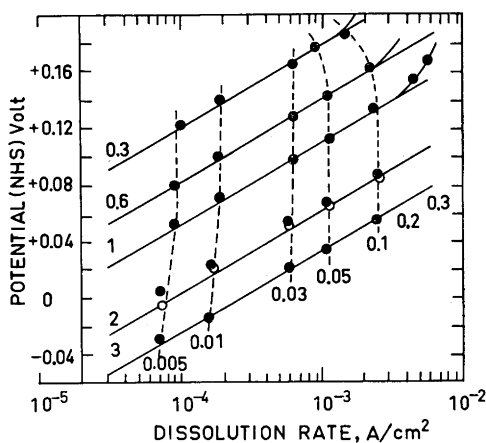


Fig. 2. Dissolution rate and corrosion potential of copper in unstirred 0.1 N sulphuric acid solutions of ferric chloride and potassium chloride at various ferric ion (0.005–0.3 M) and chloride ion (0.3–3 M) concentrations. 20°C.

has previously been found for the anodic dissolution of copper in chloride solutions by amperostatically applied currents¹.

From the position of the anodic Tafel lines it is further seen that the rate of the anodic dissolution reaction at given potentials distinctly increases with increasing chloride ion concentration. This effect of the chloride ions is more explicitly shown in Fig. 4, where the rate of the anodic dissolution reaction at the potential of the standard hydrogen electrode is plotted as function of the chloride ion molality in solutions of any of the three oxidation agents applied. The straight lines drawn in this diagram correspond to a parabolic and a cubic relationship:

$$i_a = k_p(\text{Cl}^-)^2 \exp(FV/RT) \quad (2)$$

$$i_a = k_c(\text{Cl}^-)^3 \exp(FV/RT) \quad (3)$$

at low and high chloride concentrations, respectively. This is analogous to what has previously been obtained from experiments with amperostatically applied currents¹. In (2) and (3), regard is also made of (1).

The results in Fig. 4 further clearly show that the rate of the anodic dissolution reaction is not only a function of the chloride concentration and the electrode potential, but that it to some extent also depends on how the electrode potential is obtained. Thus, at equal chloride ion concentrations and potentials, the rate is slightly higher in the permanganate solutions and appreciably lower in the cupric solutions than in the ferric solutions, in which it is nearly

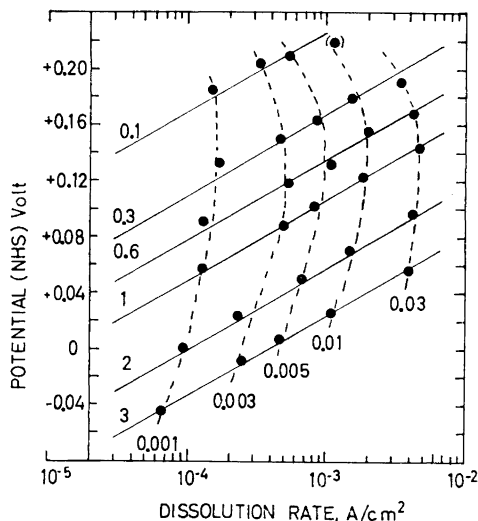


Fig. 3. Dissolution rate and corrosion potential of copper in unstirred 0.1 N sulphuric acid solutions of potassium permanganate (0.001–0.03 M) and potassium chloride (0.1–3 M) at 20°C.

equal to what is found for the pure anodic dissolution by applied current in non-oxidizing chloride solutions¹. This is quantitatively expressed by the values given in Table 1 for the anodic rate constants k_p and k_c defined by (2) and (3). These data refer to *concentration* values (molality) and not activity values for the chloride ions, and to hydrogen scale values for the potential.

Table 1. Values of the anodic rate constants k_p and k_c under various conditions at 20°C (in $\mu\text{A}/\text{cm}^2$).

Condition	Mixed potentials			Pure dissolution potentials (Ref. ¹)
	Cu ⁺⁺	Fe ⁺⁺⁺	MnO ₄ ⁻	
k_p	2.5	10	13	9.9
k_c	3.4	10	13	9.9

The limiting rate of the various cathodic reduction reactions, as given by the dashed curves in Figs. 1–3, shows a tendency to decrease with increasing chloride ion concentration. This tendency is weak for the cupric and the ferric reduction (Figs. 1–2), but appreciable for the permanganate reduction (Fig. 3). From the same diagrams is further seen that the limiting rates are nearly proportional to the ox-ion concentration. This is more explicitly shown in Fig. 5, where the maximum dissolution rate at various ox-ion concentrations is plotted *versus* the ox-ion concentration. The straight lines drawn there correspond to the following relationships:

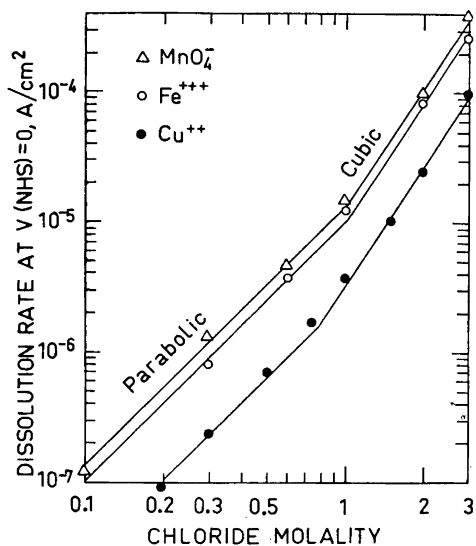


Fig. 4. Effect of the chloride ion concentration and various balancing cathodic reduction reactions on the rate (at given potential) of the simultaneous anodic dissolution reaction of copper.

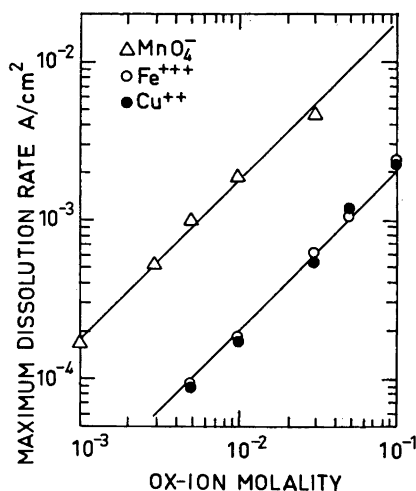


Fig. 5. Maximum dissolution rate of copper by various oxidation agents as function of their concentration in the applied unstirred solutions. (Equivalent to the limiting reduction rate of the oxidation agents).

$$i_{\text{lim}} = 0.020 \cdot 1 \cdot (\text{Cu}^{++}) \text{ A/cm}^2 \quad (4)$$

$$i_{\text{lim}} = 0.020 \cdot 1 \cdot (\text{Fe}^{+++}) \text{ A/cm}^2 \quad (5)$$

$$i_{\text{lim}} = 0.036 \cdot 5 \cdot (\text{MnO}_4^-) \text{ A/cm}^2 \quad (6)$$

for the three cathodic reduction processes under the present conditions. Quite similar equations are also valid at various constant chloride concentrations. The first numerical factor in these equations, especially the one in (6), varies somewhat with the chloride ion concentration, however. It is further possible that the results would be better represented by functions having an ox-ion concentration exponent slightly higher than 1 (see Fig. 5).

The results in (4)–(6) are of the right type and magnitude for limiting diffusion currents in unstirred solutions. For such cases, Kortüm and Bockris⁷ give as an average at 25°C:

$$i_{\text{lim}} = 0.025 \cdot n \cdot c \text{ A/cm}^2 \quad (7)$$

based on an average diffusion coefficient of $1.3 \cdot 10^{-5}$ cm²/sec for the reacting species. The above results may thus be explained simply by assuming other values for the actual diffusion coefficients. On the basis of what is known about diffusion of electrolytes^{8–10}, it is not surprising that the permanganate diffusion is appreciably faster than the cupric and the ferric diffusion, and that the

latter two are mutually equal. It is namely likely that FeCl^{++} is the main ferric species present in these relatively strong chloride solutions¹¹. The present results in ferric chloride solutions and the previous results in ferric sulphate solutions² further show that the limiting rate of the ferric reduction is almost twice as high in the former as in the latter case (0.020 : 0.011). There does not seem to be any direct diffusion data available for checking this relationship. However, in dilute solutions at 25°C, magnesium chloride and magnesium sulphate have diffusion coefficients⁸⁻¹⁰ of 1.2 and $0.7 \cdot 10^{-5}$ cm²/sec, respectively. The ratio between these values is not far from that indicated above for the corresponding ferric compounds.

4.0 DISCUSSION

The correlating rate and potential measurements made in the present work, reveal cathodic limiting curves for the reduction of the oxidation agents applied and anodic polarization curves for the dissolution of copper under the applied conditions.

The cathodic limiting curves obtained clearly show that the rate of dissolution of copper by permanganate, ferric, and cupric ions in unstirred chloride solutions of sufficiently high chloride content is controlled by the diffusion of the oxidation agent from the solution to the metal surface. This is in accordance with what is to be expected (at least for the permanganate and the ferric solutions) from previous results on metal dissolution processes of this type in general (recently reviewed by Hoar¹²) and on copper in ferric sulphate solutions in particular².

The anodic polarization curves obtained show exactly the same Tafel slope and the same type of chloride dependence as previously found for the anodic dissolution of copper by applied currents in unstirred, non-oxidizing chloride solutions¹. Together with the values obtained for the anodic rate constants k_p and k_c (see Table 1), this strongly supports the previous conclusion that the complex copper/cuprous-chloride electrode exhibits pure concentration polarization in unstirred solutions. On this basis, it is further easily understandable why the above mentioned rate constants are appreciably lower in the cupric solutions than in the other oxidizing and corresponding non-oxidizing solutions. This may simply be due to the extra amount of cuprous species produced and chloride ions consumed (by complex formation) at the copper surface by the cupric reduction. At given dissolution rates, this reduction reaction should namely be expected to make the potential determining activity relationship $(\text{CuCl}_n^{(n-1)-})/(\text{Cl}^-)^n$ at the copper surface more than twice as high as in the case of pure anodic dissolution in non-oxidizing solutions, and thereby to lower the anodic rate constant by the same factor. The values of 3 to 4 obtained for this factor (see Table 1) do therefore not seem unreasonable, and it seems logical that this factor should be slightly higher for the parabolic (low chloride concentrations) than for the cubic (high chloride concentrations) rate constant. The slightly higher value found for these rate constants by the permanganate reaction than by applied current, may similarly be due to the concentration polarization being lowered by a possible homogeneous reaction of cuprous chloride complexes with permanganate ions in the diffusion layer.

As a conclusion, it may thus merely be said that all the observations made in the present work on the dissolution of copper by oxidation agents in unstirred acid chloride solutions, are well accounted for by regarding it a mixed $\text{Cu}_n\text{Cl}^-/\text{CuCl}_n^{(n-1)-}$ ($n = 2$ above and 3 below chloride concentrations of about 1 M) and red/ox electrode, the latter operating at its cathodic limiting current and the former exhibiting pure concentration polarization. In cases like this, both the corrosion rate and the corrosion potential are independent of the exact mechanism of the electrode reactions occurring, and can therefore reveal neither their kinetics nor their possible interaction at the metal surface.

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