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Dissolution of Brass 70/30 (Cu/Zn) and its inhibition during the acid wash in distillers

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The corrosion behaviour of brass 70Cu/30Zn in deaerated solutions of pure dilute HCl and acidified 4% NaCl of pH 1.8–2 was studied at different temperatures between 25 and 60 °C by the weight loss method. The curves representing the variation of loss in weight with time indicate that there is an induction period followed by a linear relation. Analysis of the solution by the atomic absorption technique and investigation of the surface by scanning electron microscopy indicate that the linear relation begins at a critical value of copper-ion concentration of the corrodent due to autocatalysis. The addition of different concentrations of $CuCl_2$ eliminates the induction period and increases the corrosion rate. The effect of the addition of different concentrations of 2-methyl benzimidazole (MBIA) and Armohib 28 inhibitors on the dissolution of the alloy in both media was tested at 60 °C. MBIA has no effect in the case of acidified 4% NaCl, but with pure dilute HCl the inhibition efficiency in the presence of 300 p.p.m. MBIA amounted to 84.6%. On the other hand, the inhibition efficiency reached 93.4% and 94.6% in the presence of 10 p.p.m. Armohib 28 inhibitor in pure dilute HCl and acidified 4% NaCl, respectively.

1. Introduction

Copper-based alloys are an obvious choice for tubing in surface condensers because they have high thermal conductivity, good corrosion resistance in most environments, and satisfactory mechanical properties for most requirements. α-brass is often used as heat-exchanger material in distillers operating on sea-water. One of the major problems generally encountered during the operation of the heat exchanger is the formation of alkaline scales inside the condenser tubes. These scales are removed through subjecting the heat-exchanger cycle to an acid wash.

To prevent acid attack on the brass [1] and of the carbon steel components [2, 3] of the distillers, pickling inhibitors are usually added to the acidified sea-water. Several corrosion inhibitors are reported in the literature [3–8]. For example, dibutylthiourea (DBTU), marketed under the trade name of Stannine LTP, was subjected to a study by Saber *et al.* [9] to evaluate its role in the corrosion inhibition of Cu/30Ni and carbon steel. The inhibitor proved to be highly efficient as an inhibitor for corrosion during acid wash at 60 °C for the carbon-steel components, while it was not so for the cupro-nickels. Similarly, the inhibition of α-brass (70Cu/30Zn) was studied [10] during acid cleaning using DBTU and benzotriazole (BTA). It was reported that BTA is more highly efficient than DBTU because the latter is decomposed at 60 °C on the brass surface.

The aim of the present work was to study the mechanism of dissolution of α-brass (70Cu/30Zn) in deaerated solution of both pure HCl and acidified 4% NaCl of pH (1.8–2) in the temperature range 25–60 °C. The study also covered the evaluation of 2-methyl benzimidazole (MBIA) and the commercial inhibitor marketed under the trade name Armohib 28, as corrosion inhibitors for brass during an acid wash at 60 °C.

2. Experimental procedure

The corrosion rate (CR) of α-brass was determined by the weight loss method as milligrams per square centimetre per hour. The brass test coupons were in the form of rectangles of sides 1 cm × 4 cm × 0.3 cm thick. Each coupon carried a hole from which it was hung in the solution by glass hooks. Before use, the brass test coupons were pretreated following the standard procedures already described [11] in which each experiment started with a brass surface free from oxides. The corrosion cell and the other experimental details were essentially the same as described elsewhere [9, 10].

Each experiment was performed using 500 ml of deaerated 10^{-2} M HCl solution of pH 1.8–2.0 stirred by a magnetic stirrer. These solutions were made in doubly distilled water as well as in 4% NaCl as a substitute for sea-water.

Deaeration was made by bubbling pure nitrogen gas for 1 h and then the system was closed. When the brass coupons were withdrawn from the solution for weighing (i.e. the system is opened) deaeration was made for 15 min each time.

The corrosion rates were determined over several temperature settings of 25, 30, 40, 50 and 60 °C.

During the course of the dissolution experiments, small portions of the test solution were withdrawn and analysed for their copper and zinc content using a Perkin–Elmer type 2380 Atomic Absorption Spectrophotometer. The changes occurring on the sample surface were followed by scanning electron microscopy (Jeol, JSM T-20 Japan, accelerating voltage 19 kV, magnification ×35–×10 000).

The effect of $CuCl_2$ additions on the dissolution mechanism was measured at 25 and 60 °C in different concentrations. On the other hand, the effect of both MBIA and Armohib 28 inhibitors on the corrosion rate were determined only at 60 °C, which is the normal condition in practical applications. MBIA was used in concentrations of 100, 200 and 300 while the Armohib 28 content in solution was 10, 50, 100 and 300 p.p.m.

During measurement, which was extended to 700 h, the pH of the acid solution was kept constant through dropwise addition of 1 M HCl.

3. Results and discussion

3.1. Dependence of corrosion rate on temperature

The curves of Fig. 1 represent the variation of the weight loss with time of α-brass immersed in pure HCl and in acidified 4% NaCl solutions of pH 1.8–2.0 at temperatures varying between 25 and 60 °C. The curves show two distinct segments; the first represents an induction period in which a very low dissolution rate is recorded, indicating the resistance of the alloy to attack by the dilute acid. The second showed an increased linear slope revealing further dissolution of the alloy which increases with rising temperature.

It can be seen from the results that the higher the temperature the shorter is the induction period recorded. However, in case of acidified 4% NaCl, they are considerably shorter than those recorded in pure HCl solutions. Following the induction periods, the corrosion rates increase linearly with temperature rise, revealing that the dissolution of the alloy is activation controlled. Table I summarizes the corrosion rates and induction periods at different temperatures for the two media concerned. A plot of the logarithm of the corrosion rate as a function of reciprocal of absolute temperature is shown in Fig. 2 for pure HCl and acidified 4% NaCl. From the straight lines obtained, the apparent activation energy for the alloy dissolution process can be calculated, and was found to be 126 $kJ\,mol^{-1}$ in pure HCl and the two segments displayed in acidified 4% NaCl gave 92.6 and 53.1 $kJ\,mol^{-1}$ at 20–40 and 40–60 °C, respectively. These values of activation energy are not due to the dissolution reaction alone, because that of the complementary cathodic reaction is also incorporated. As the temperature is raised, the overvoltage associated with one (or more) of the various electrochemical reactions is greatly reduced or totally eliminated in addition to the increase of surface area at a given temperature. This interpretation is similar to that mentioned in the case of Cu/Ni [9] and Cu/Zn [12]. The increase in temperature also affects the dissolution of copper as $CuCl_2^-$, as will be discussed later. This explanation is supported by the corrosion rate results determined by weight loss (Table I), which are higher in the case of acidified 4% NaCl than in pure HCl, and confirmed by solution analysis of both copper and zinc.

3.2. Corrosion dependence on, cupric ion concentration

The effect of the addition of different concentrations of $CuCl_2$ solution on the variation of loss in weight with time was studied for both the electrolytes. A similar behaviour was seen at 25 and 60 °C. The data are summarized in Table II; Fig. 3 is given as an example at 60 °C.

These data indicate that:

1. the induction periods were eliminated and the linear relation started from the moment of immersion;
2. with increasing time another linear segment appeared after 4–5 h, as shown in Fig. 3;
3. the corrosion rate in the case of acidified 4% NaCl is higher than the corresponding value in pure HCl at the same temperature;
4. by increasing the temperature from 25 °C to 60 °C the corrosion rate is increased through the two segments;
5. the corrosion rate in all cases is increased as the concentration of $CuCl_2$ increased.

On the other hand, it was found that addition of different concentrations of $ZnCl_2$ does not affect the corrosion rate.

To discuss the above results we consider the following anodic reactions:

$$Cu = Cu^+ + e \quad (1)$$

$$Cu^+ + Cl^- = CuCl \quad (2)$$

$$CuCl + Cl^- = CuCl_2^- \quad (3)$$

$$2CuCl = Cu + CuCl_2 \quad (4)$$

$$CuCl_2 + Zn = ZnCl_2 + Cu \quad (5)$$

The availability of Cu^+ ions for the formation of cuprous compounds is possible due to their rapid formation as the intermediate species in the dissolution reaction [13] followed by the rate-controlling oxidation of Cu^+ to Cu^{2+}. As the medium has a high chloride content, any produced Cu^+ would be stabilized through the formation of CuCl precipitate (Reaction 2) and $CuCl_2^-$ soluble complex (Reaction 3) and the disproportionation reaction [14] appears unlikely to occur (Reaction 4).

During the induction period, the amount of Cu^{2+} produced (Reaction 4) takes some time to go to the solution due to its deposition through a galvanic reaction of Reaction 5. After prolonged immersion time, the amount of Cu^{2+} ions produced seems to be enough not only for precipitation as metallic copper (Reaction 5) but also to go to solution. Then it is increased with increasing immersion time until it reaches a value which is sufficient to start the linear rising segments of the curve.

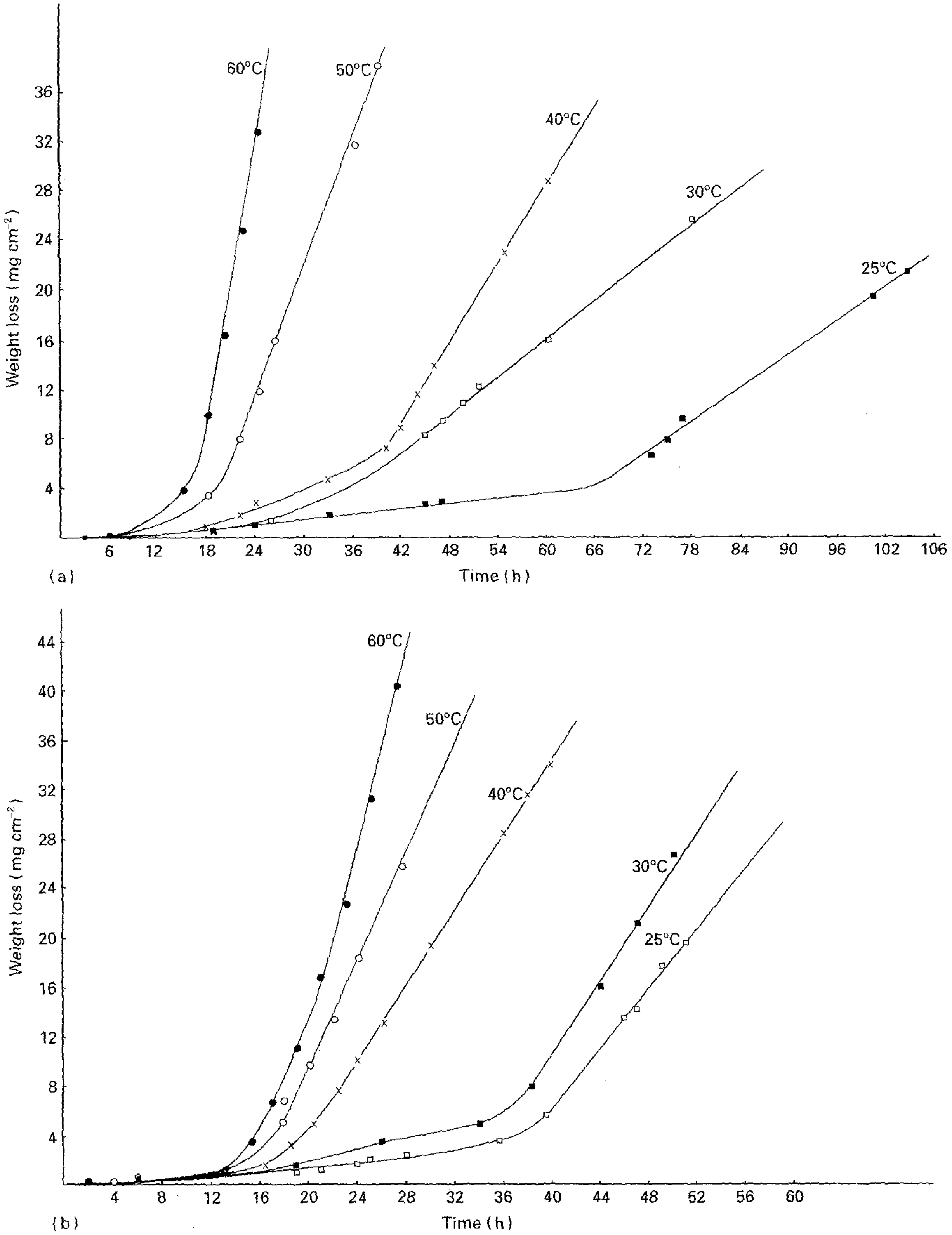

Figure 1 Weight loss–time curves of α-brass in acid solutions at pH 1.8–2.0 at different temperatures: (a) pure HCl, (b) acidified 4% NaCl.

This is supported by solution analysis for both copper and zinc using atomic absorption spectrophotometry which indicates that, through the induction period, the ratio of Zn/Cu in solution is higher than that of the alloy ratio indicating the onset of dezincification. During the linear relation, solution analysis proved that the alloy dissolves in such a way that the zinc/copper ratio in solution approximates that of the alloy. Along this linear relation the concentration of both copper and zinc increased continuously with time, and the rate of corrosion increased as in the case of addition of different concentrations of $CuCl_2$.

In Fig. 4 each point on curves b and d was made with the same coupon but in new solutions at 25 °C (i.e. a fresh solution was used before the start of the

TABLE I Corrosion rate and induction period length of α-brass in pure HCl and acidified 4% NaCl solutions of pH 1.8–2.0 at different temperatures

Temperature (°C)	Corrosion rate ($mg\,cm^{-2}h^{-1}$)		Induction period length (h)	
	Pure HCl	Acidified 4% NaCl	Pure HCl	Acidified 4% NaCl
25	0.44	1.0	67.0	38
30	0.50	1.4	42.0	36
40	1.06	1.6	39.0	20
50	1.77	2.3	21.0	18
60	3.77	4.3	17.5	16

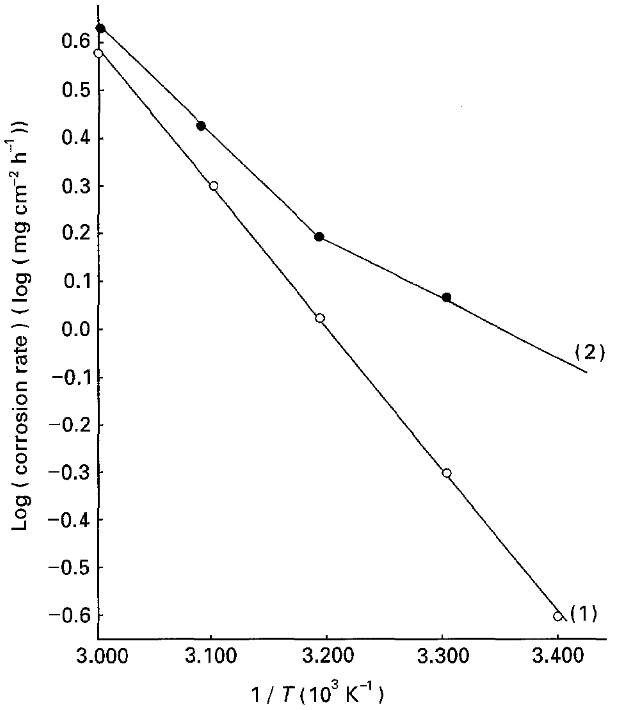

Figure 2 Log corrosion rate versus reciprocal of absolute temperatures for α-brass in (1) pure HCl, and (2) acidified 4% NaCl.

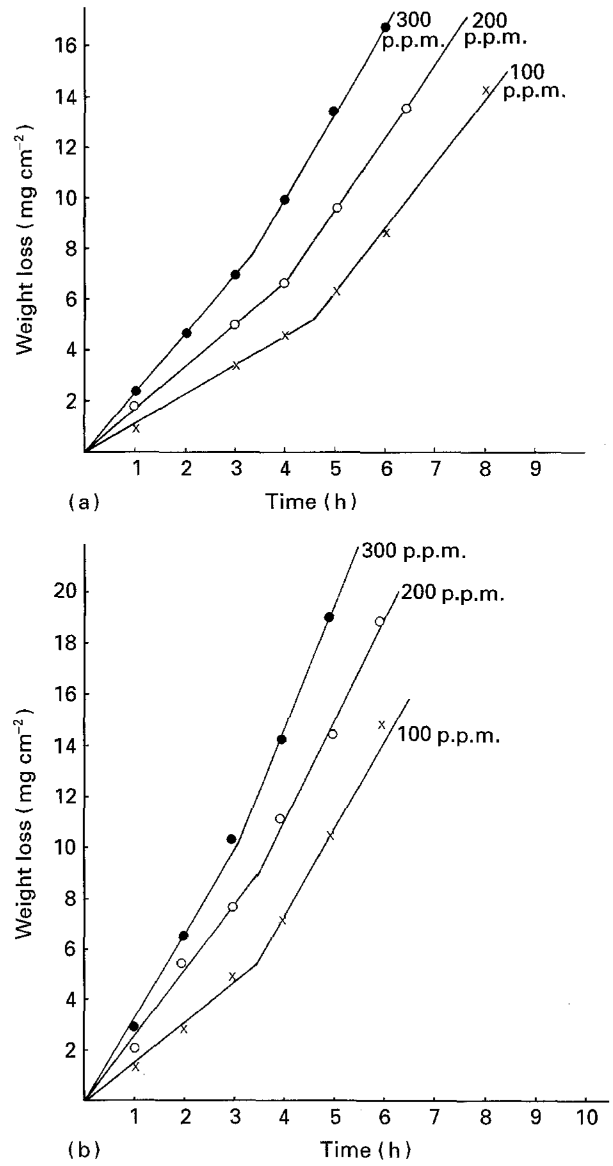

Figure 3 Weight loss–time curves of α-brass in acid solutions of pH 1.8–2.0 at 60 °C in the presence of different additions of $CuCl_2$: (a) pure HCl, (b) acidified 4% NaCl.

linear rising segments after ca. 17 h from the beginning). These curves show that by changing the solutions the induction periods were extended because the Cu^{2+} produced by Reaction 4 was insufficient to start the linear rising segments. Fig. 4 curves a and c show the above experiments but in the same solution for comparison. It is also seen from the curves that the presence of 4% NaCl increases the rate of dissolution, as in Reaction 3.

TABLE II Corrosion rate of α-brass in pure HCl and acidified 4% NaCl solutions of pH 1.8–2.0 in the presence of different concentrations of $CuCl_2$ at 25 and 60 °C

$CuCl_2$ conc. (p.p.m.)	Corrosion rate ($mg\,cm^{-2}h^{-1}$)							
	Pure HCl				Acidified 4% NaCl			
	25 °C		60 °C		25 °C		60 °C	
	1st segment	2nd segment	1st segment	2nd segment	1st segment	2nd segment	1st segment	2nd segment
100	0.35	0.6	1.16	2.5	0.40	0.6	1.50	3.4
200	0.55	0.9	1.66	2.9	0.65	1.3	2.48	3.9
300	0.62	1.1	2.32	3.3	1.00	1.7	3.20	4.8
400	0.92	1.4	–	–	1.54	1.9	–	–
500	0.92	1.4	–	–	1.80	2.4	–	–
600	0.95	1.5	–	–	2.12	2.95	–	–

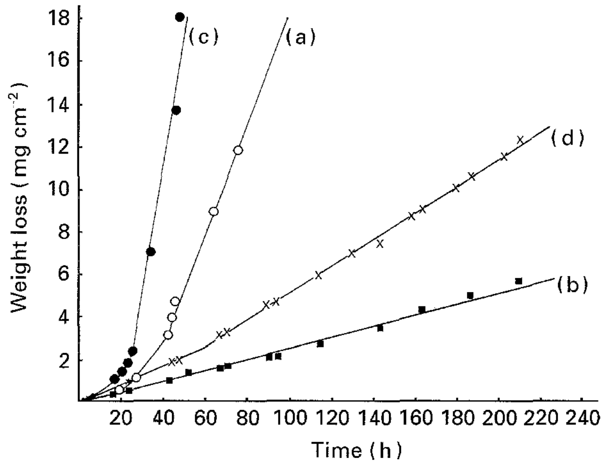

Figure 4 Weight loss–time curves of α-brass immersed in acid solutions at pH 1.8–2.0 at 25 °C. (a) and (b) Pure HCl without and with change solutions, respectively. (c) and (d) Acidified 4% NaCl without and with change solution, respectively.

These results can further be confirmed by immersion of brass coupon in solutions for 20 and 26 h at 60 °C (i.e. during the linear rising segments of Fig. 1) and after that only the brass coupon was changed (i.e. a new coupon). Fig. 5 indicates that the induction period is eliminated and that a linear relation appears from the first moment followed by another one with a higher slope (higher corrosion rate) as in the case of addition of different concentrations of $CuCl_2$.

Further insight into the dissolution mechanism could be gained using the SEM technique. Surface examination of the brass specimens equilibrated at 60 °C for 1, 7, 16 and 26 h in pure HCl and acidified 4% NaCl of pH 1.8–2 are shown in Fig. 6.

The scanning electron micrographs of Fig. 6a–d indicate that after 1 h, which is very near to the blank sample, the surface shows fine attack beside the corrosion product. On increasing the time of equilibration to 7 h (also within the induction period region), the surface shows that the attack increased with time and also the corrosion product increased until a critical point was reached between the induction period and the linear rising segments (16 h). Examination of the corroded surface immersed for 16 h shows severe attack and dense corrosion products. After 26 h immersion (in the linear rising segments of Fig. 1a) the surface shows more severe attack and grains demonstration (etching).

Fig. 6e–h show scanning electron micrographs of the surface of samples immersed in acidified 4% NaCl (pH 2) for the same periods 1, 7, 16 and 26 h. It can be seen that the same trend is obtained as in the case of pure HCl but the presence of 4% NaCl increased the attack on the surface at the corresponding period specially at 16 and 26 h (see Fig. 6e–h). The severity of attack becomes maximum and the grain size becomes much clearer than in the case of pure HCl. This indicates that, as mentioned before, the presence of 4% NaCl increased the rate of dissolution of Cu as $CuCl_2^-$, in addition to the dissolution through the disproportionation reaction as in Reactions 3 and 4.

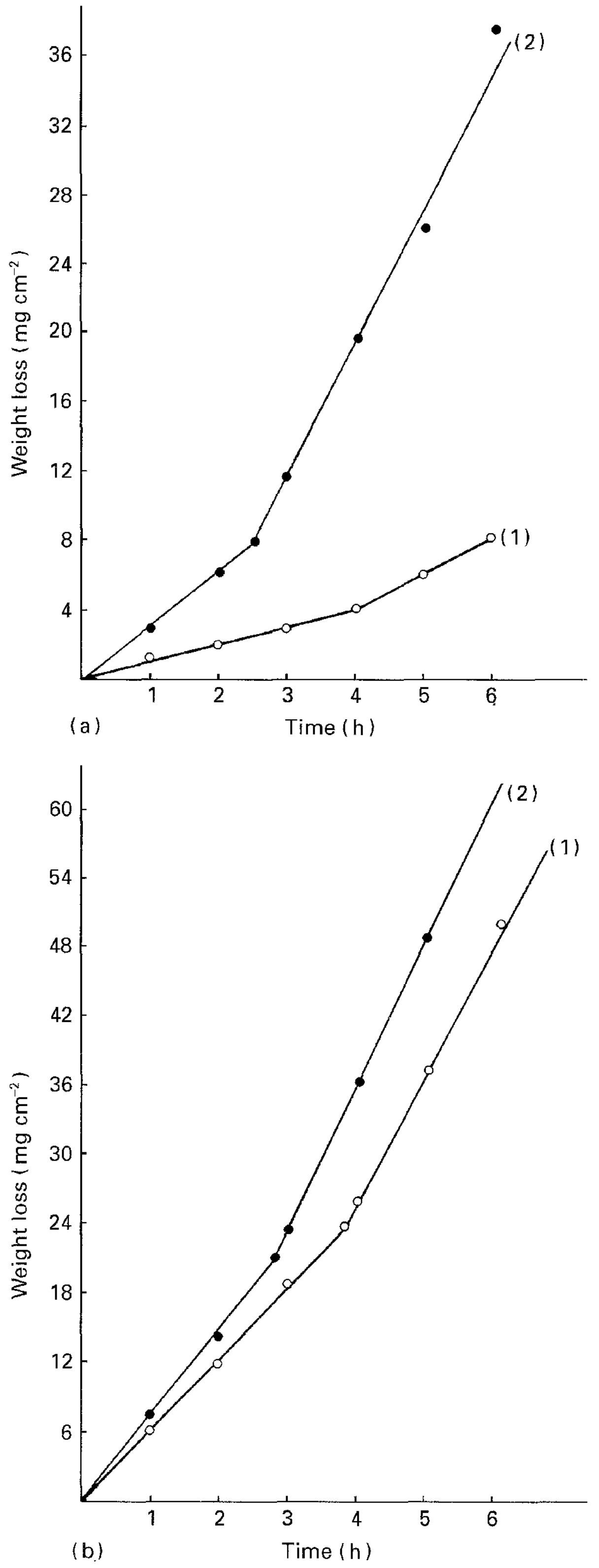

Figure 5 Weight loss–time curves of α-brass in acid solutions of pH 1.8–2.0 at 60 °C. A new sample was immersed in the same solution which contains dissolved product of the first sample, for different times. (a) Pure HCl, (b) acidified 4% NaCl. (1) New sample after 20 h. (2) New sample after 26 h.

On the other hand, no corrosion product was observed on the surface in the presence of 4% NaCl at 16 and 26 h, as shown in the case of the corresponding pure acid. This indicates that the formation of CuCl and its dissolution occurs at a higher rate and the

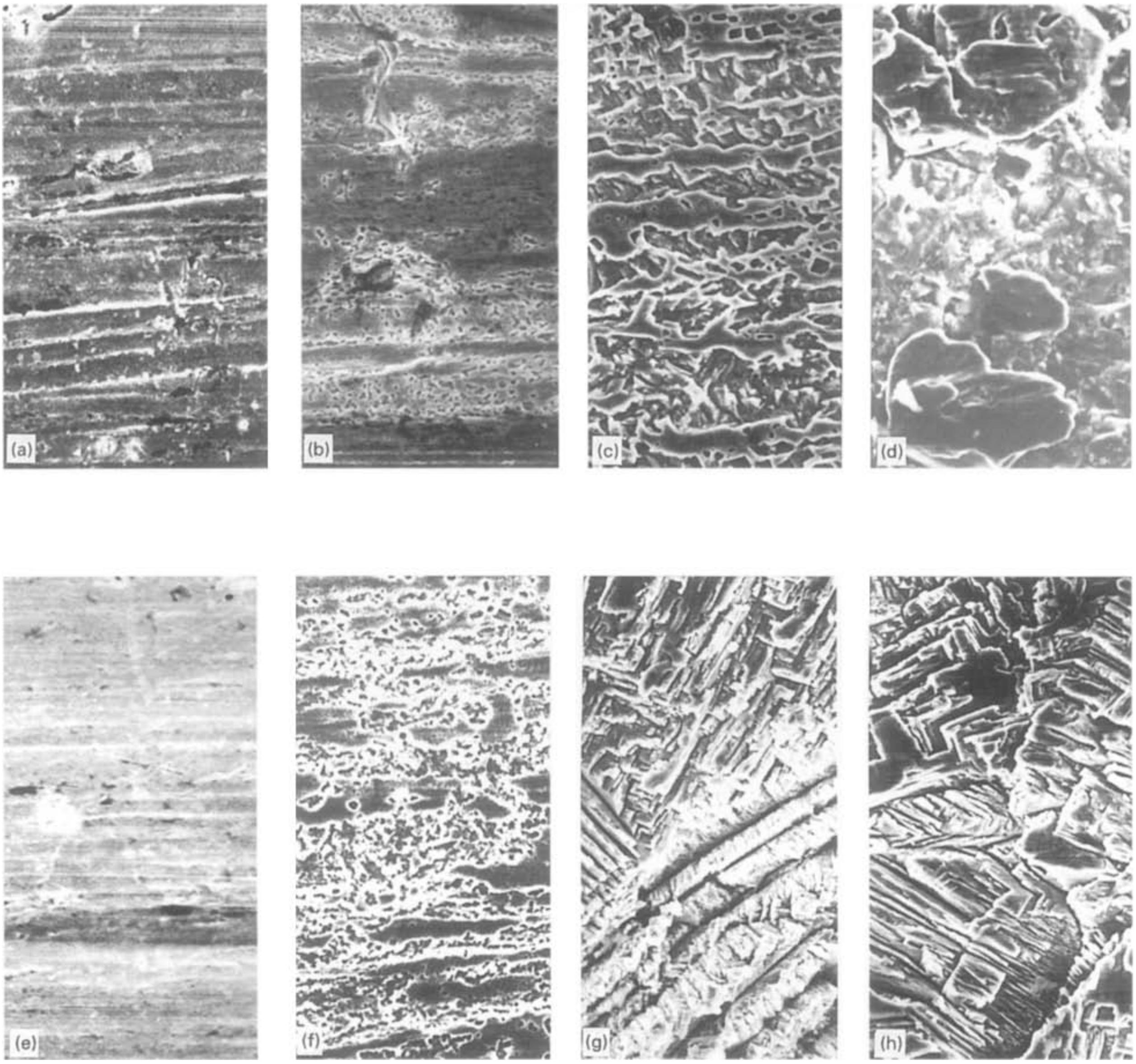

Figure 6 Scanning electron micrographs showing the surface of α-brass in acid solutions of pH 1.8–2.0 at 60 °C for different times: (a, e) 1 h, (b, f) 7 h, (c, g) 16 h, (d, h) 28 h. (a–d) Pure HCl, (e–h) acidified 4%NaCl. × 1000.

surface area exposed to the solution is greater than that in the case of pure acid.

Fig. 7a and b show scanning electron micrographs of the corroded brass surfaces immersed for 6 h after the 26 h experiment (i.e. the sample was replaced by another one after 26 h in the same solution). As shown from the corresponding weight loss–time measurements for pure HCl and acidified 4% NaCl, Fig. 5a and b curves 2, it is found that a severe attack occurred on the surface after this short period (6 h) (see Fig. 7a and b). This predicts an increased attack, more than in the case of 26 h immersion as shown in Fig. 6. It is indicated that, as mentioned before, when the concentration of Cu^{2+} increased in solution the corrosion rate increased due to autocatalysis through the disproportionation reaction, and not in the dissolution reaction as for $CuCl_2$ alone, but also acts in the formation of a CuCl film (i.e the rate of forward and backward reaction of Reaction 4 is increased).

A plot of the logarithm of weight loss as a function of time (Fig. 5) gives a straight line relation which is similar to that obtained by Kagetsu and Graydon [12] as a result of plotting the logarithm of cupric ion concentration against time. These results confirm the dependence of the dissolution of brass on Cu^{2+} due to autocatalysis.

The effect of MBIA and Armohib 28 on the dissolution of α-brass in pure HCl and acidified 4% NaCl was examined at 60 °C, which is the temperature commonly adopted during the acid cleaning of the distillers. The measurements were carried out in the usual manner in which the test coupons were exposed to the acid solution containing a definite inhibitor concentration. At increasing time intervals the specimens were withdrawn, washed, dried, weighed and reintroduced into the same solution for subsequent evaluation.

Fig. 8 shows the effect of increasing MBIA concentration on the dissolution of brass in pure HCl. The

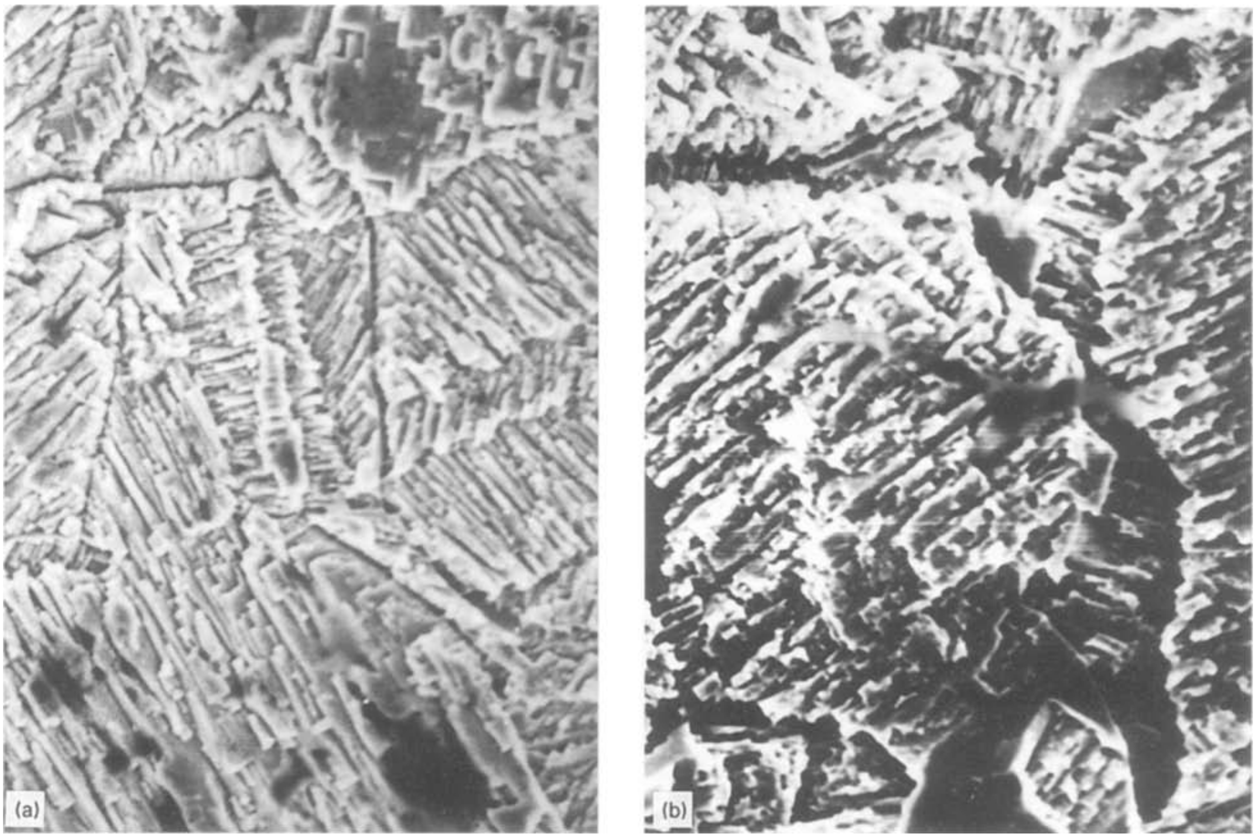

Figure 7 Scanning electron micrographs showing the surface of α-brass immersed for 6 h in the same solution which contained a dissolved product of the first sample, for 26 h in acid solutions of pH 1.8–2.0 at 60 °C. (a) Pure HCl, (b) acidified 4% NaCl.

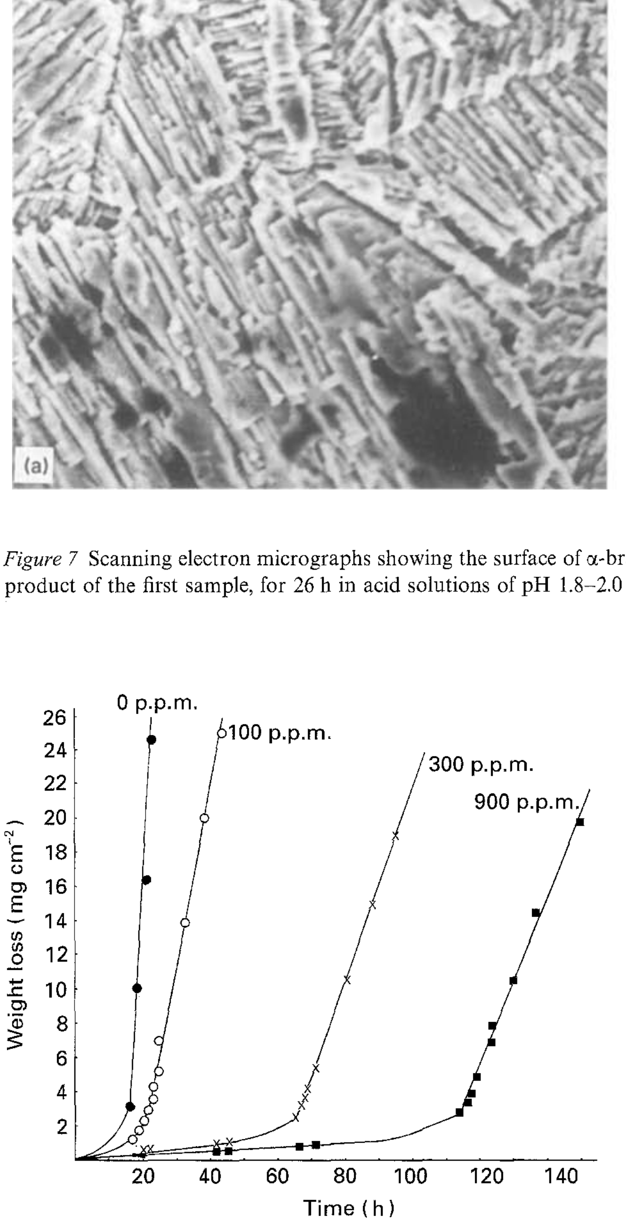

Figure 8 Weight loss–time curves of α-brass at 60 °C in the presence of different additions of MBIA in pure HCl of pH 1.8–2.0.

curve for 0 p.p.m. represents the inhibitor-free solution. Observation of the curves of this figure reveals that MBIA causes an extension of the induction period which increases with increase of its concentration. At the same time the corrosion rate decreases with the additive content, as shown in Table III. The inhibition efficiency is a function of its concentration, as represented in Table IV. By increasing the concentration from 300 p.p.m. to 900 p.p.m. the induction period increases fom 65 h to 120 h but a slight increase of the inhibition efficiency is recorded from 84.6% to 87.5%. On the other hand, MBIA does not affect the dissolution of brass in acidified 4% NaCl.

The effect of Armohib 28 (a commercial inhibitor) on the dissolution of brass alloy in the two test media was examined at 60 °C. The concentration of the inhibitor added varied between 10 and 300 p.p.m. The results are shown in Fig. 9, together with that of inhibitor-free solutions (curve 0 p.p.m.). As is evident from the curves, Armohib 28 retards the dissolution of brass and the induction period increases with increase of its concentration in the solution. In some cases the induction period is extended for the total experimental time (700 h). The inhibition efficiency was above 93% in the presence of a very small concentration of the additive (10 p.p.m.) as shown in Table IV. By increasing the concentration of the inhibitor to above 50 p.p.m., the dissolution of the alloy is almost completely stopped and the inhibition efficiency amounts to above 98%, Table IV.

The dependence of the total dissolution rate on the inhibitor concentration in the case of both inhibitors (Figs 8 and 9), resembles a typical adsorption isotherm, which suggests that inhibition of the process occurs due to simple molecular adsorption [15]. MBIA, can affect the overall dissolution rate due to its adsorption at the interface. This type of adsorption effectively hinders the adsorption of anions in the case of pure dilute HCl, but in the case of HCl-acidified 4% NaCl, MBIA is not effective, because its adsorption at

TABLE III Corrosion rate and induction period length of α-brass in pure HCl and acidified 4% NaCl solutions of pH 1.8–2.0 at 60 °C in the presence of Armohib 28 and MBIA

Inhibitor concentration (p.p.m.)	Armohib 28		MBIA		Induction period length (h)			
					Armohib 28		MBIA	
	HCl	HCl + NaCl	HCl	HCl + NaCl	HCl	HCl + NaCl	HCl	HCl + NaCl
0	3.77	4.3	3.77	4.3	17.5	16	17.5	16
10	0.25	0.23	–	–	350	70	–	–
50	0.055	0.19	–	–	440	110	–	–
100	0.025	0.08	1.01	–	700	140	22.5	–
300	0.017	0.06	0.58	Not affected	700	160	65	Not affected
900	–	–	0.47		–	–	120	

TABLE IV Per cent inhibition efficiency of Armohib 28 and MBIA on the corrosion rate (CR) of α-brass in pure HCl and acidified 4% NaCl solutions of pH 1.8–2.0 at 60 °C

$$\% \text{ inhibition efficiency} = \frac{\mathrm{CR}_{\mathrm{Inh.\ free}} - \mathrm{CR}_{\mathrm{inh}}}{\mathrm{CR}_{\mathrm{Inh.\ free}}} \times 100$$

Inhibitor conc. (p.p.m.)	Armohib 28		MBIA	
	HCl	HCl + NaCl	HCl	HCl + NaCl
10	93.4	94.65	–	–
50	98.5	95.6	–	–
100	99.3	98	73.2	0
300	99.5	98.5	84.6	0
900	–	–	87.5	0

the interface is negligible and cannot affect the overall dissolution rate.

On the other hand, the addition of Armohib 28 for both the electrolytes indicates that its adsorption acion is higher than in the case of MBIA, which prevents the adsorption of anions and stops the dissolution of the brass in both the media almost completely.

4. Conclusions

1. The dissolution of α-brass in pure HCl solutions and in acidified 4% NaCl of pH 1.8–2.0 in the temperature range 25–60 °C was characterized by an initial induction period which diminished with rise in temperature. The induction period was then followed by

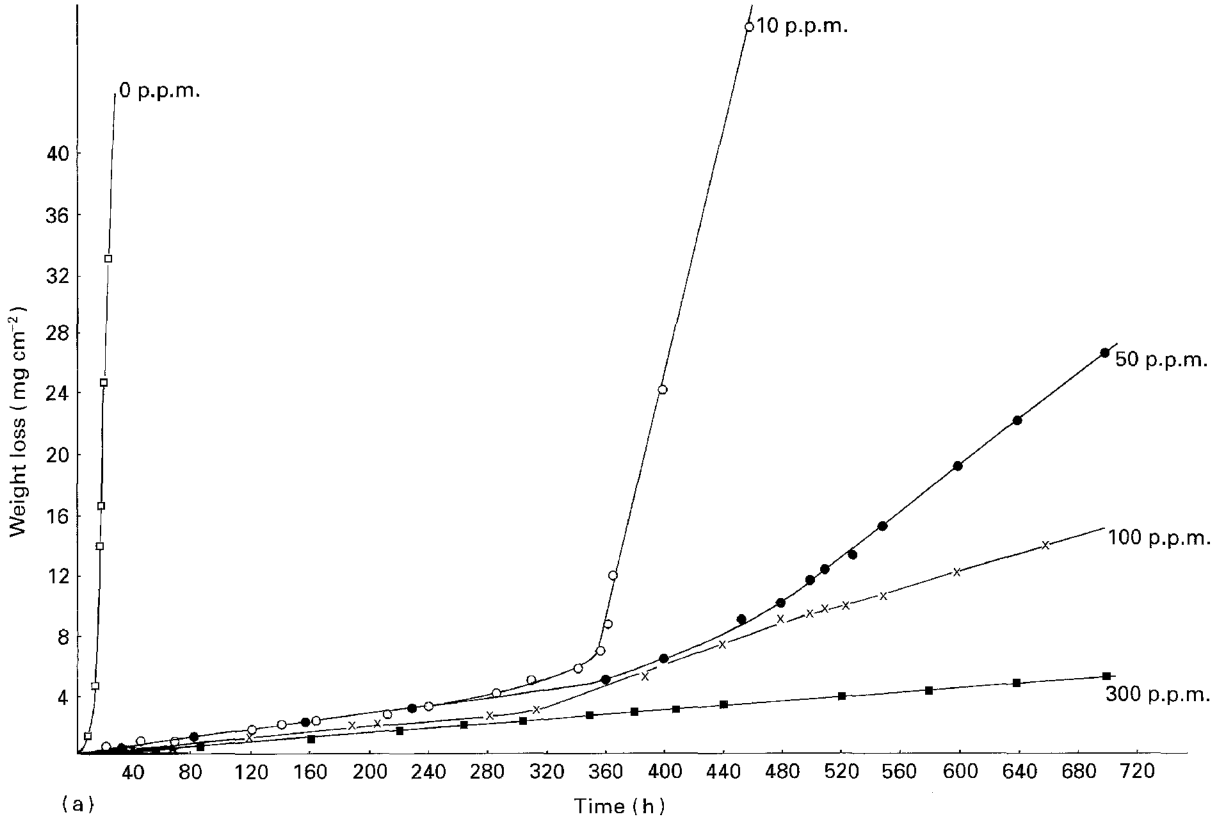

Figure 9 Weight loss–time curves of α-brass at 60 °C in the presence of different additions of Armohib 28. pH 1.8–2.0. (a) Pure HCl, (b) acidified 4% NaCl.

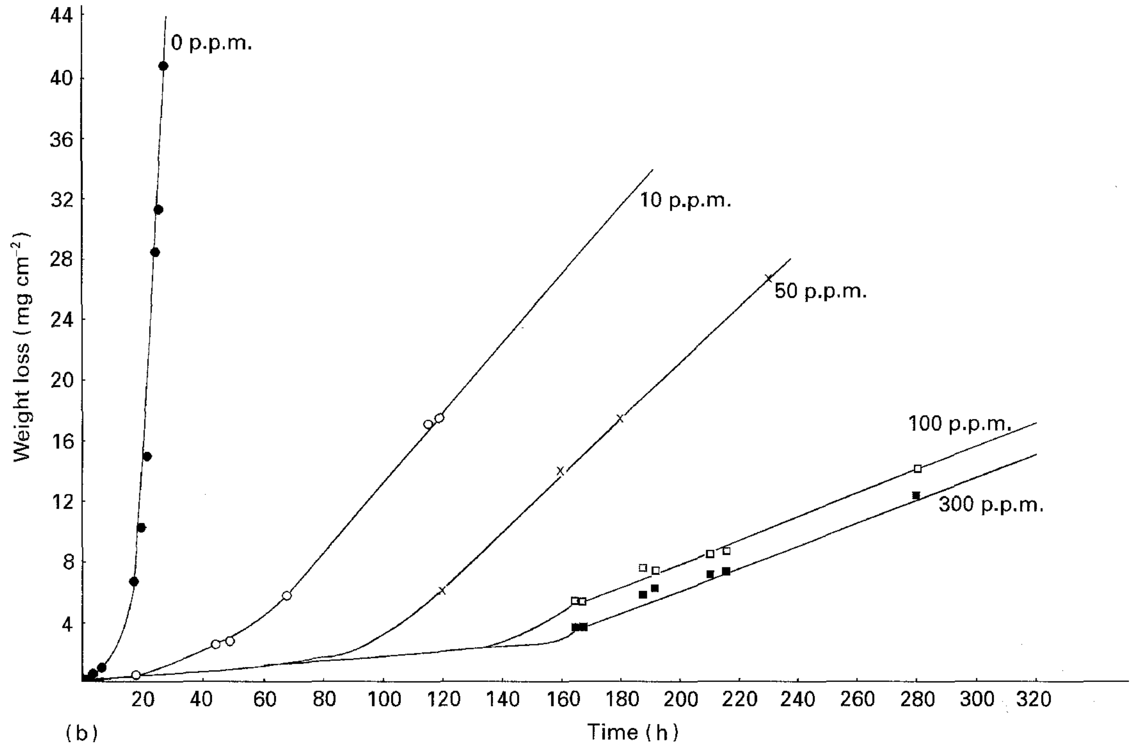

Figure 9 Continued.

a stage where the loss in weight increased linearly with immersion time, allowing the estimation of corrosion rates which increased with rise in temperature.

2. Examination of the corroded surfaces showed that the attack occurred from the moment of immersion.

3. Solution analysis indicated that through the induction period a slow dissolution favours dezincification, while along the linear relation the fast dissolution favours simultaneous corrosion.

4. The linear relation started at a limited value of copper concentration of the corrodent, due to the autocatalytic effect on the formation and dissolution of cuprous chloride.

5. The higher inhibition efficiency of Armohib 28 than MBIA inhibitor was attributed to the formation of a highly protective adsorbed layer which completely stopped the adsorption of anions on the brass surface.

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