Portugaliae Electrochimica Acta 21 (2003) 99-116

PORTUGALIAE
ELECTROCHIMICA
ACTA

Evaluation of Chromate as Dezincification Inhibitor for α-brass (Cu/Zn : 64/36) in 3% Chloride Buffer Solutions

H. H. Rehan[*], **N.A. Al-Moubarak, H.A. Al-Rafai**

Chemistry Department, College of Education for Girls,
Malaz, Riyadh 11417, P.O. Box 27104, Kingdom of Saudi Arabia

Received 20 September 2002; accepted in revised form 5 December 2002

Abstract

The inhibition behavior of chromate ions towards corrosion and dezincification of α-brass (Cu/Zn: 64/36) in acetate buffer solutions (pH 2.4, 7.0 and 8.5) containing 3% sodium chloride was studied. Weight loss and solution analysis were used for a long period (four weeks) and electrochemical polarization for a short period (one hour). Chromate accelerated corrosion and dezincification at pH 2.4 by acting as depolarizer but chromate suppressed efficiently the corrosion and dezincification at pH 8.5. At pH 7.0 the corrosion and dezincification suppressed in the presence of chromate but the inhibition action started to deteriorate at chromate concentration less than 0.005 mol/L. The inhibition effect is attributed to adsorption of chromate ions on the corroding surface and improvement of the passivity. Chromate led to an increase in the concentration of copper species in solution due to the formation of the more soluble $CuCrO_4$ than Cu_2O, which contributed to the apparent suppression of dezincification.

Keywords: α-brass, corrosion inhibition, dezincification, chromate.

Introduction

Dezincification, the selective dissolution of zinc from brasses, in chloride containing environments such as see waters, is receiving attention [1,2-7]. Models for dezincification of brasses in chloride environments have been proposed and tested due to the technical importance of these environments [1,5,6-12]. Cuprous chloride complex ions, especially $CuCl_2^-$, seem to be

---

[*] Corresponding author: on leave from Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt. E-mail address: hyman_rehan@yahoo.com.

important in the dezincification, though their mechanistic role in promotion of dezincification is a matter of controversy so far. Cuprous chloride complex ion $CuCl_2^-$ was assumed to accelerate the dezincification of brass in hydrochloric acid via catalyzing the dissolution of copper into cupric species, which consequently deposited on the expense of zinc dissolution [5]. Disproportion of Cu(I) species into Cu and Cu^{2+} was suggested as a probable process for dezincification [2,7,8] in chloride solutions, though the detailed study due to Newman et al. [1,13] dismissed Cu(I) disproportion. Suppression of dezincification via small addition of other elements such as arsenic is suggested [1,13,14]. Although the inhibition action of organic inhibitors such as azoles and triazoles towards the corrosion of brasses has been intensively studied [15-18], few studies were directed to study the suppression of dezincification by using corrosion inhibitors [19-21]. Chromate is known as a corrosion inhibitor and passivator for some metals and alloys, including iron, steel, copper and copper alloys [22]. The effect of chromate on the dezincification of brasses, however, seems to have no attention so far.

In the present study the corrosion and dezincification of α-brass (Cu/Zn : 64/36) in 3% sodium chloride buffer solutions at pH 2.4, 7.0 and 8.5 in the absence and presence of chromate (10^{-5}-10^{-2} mol/L) were studied.

Experimental

Specifications of the commercial α-brass alloy used were as follows: Cu% 64.03, Zn% 36.06, Pb% 0.003, Fe% 0.007 and Ni% 0.02. Specimens (2×3 cm^2) for weight loss and solution analysis were cut from 1.0 mm thick sheets and the disc electrodes for electrochemical tests were manufactured from cylindrical rods of a diameter 0.6 cm. The specimens and electrodes were mechanically polished with successively finer grades of emery papers down to grade 4/0, followed by a wet soft tissue, degreased in acetone, washed with doubly distilled water and immediately immersed in the test solution. The solutions were prepared from analytical grade glacial acetic acid, sodium acetate, sodium chloride, potassium chloride (BDH, England) and doubly distilled water. The buffer acetate solutions were prepared by mixing the appropriate volumes of 1 molar acetic acid and 1 molar sodium acetate, and the exact pH was checked by a digital pH-meter. All experiments were carried out in naturally aerated stagnant solutions at controlled temperature of 26 ± 0.2 °C. The corrosion potential and polarization experiments were made and analyzed on the electrochemical system ACM 4 (ACM Instruments, Cumbria, UK). A three-electrode electrolytic cell housing a platinum sheet ($2 \times 3\ cm^2$) as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode, beside the α-brass electrode as the working electrode, was employed. All potentials are given relative to SCE. Tafel plots were recorded, within the potential range ± 250 mV vs. the steady corrosion potential, E_{corr}, after one hour of immersion of the electrode in the test solution.

In weight loss tests, the specimen was first weighted and then immersed vertically and completely in a 100 mL-beaker containing 70 mL of the corrosive solution. After the specified period (1, 2, 3 or 4 weeks), the specimen was removed, washed with doubly distilled water, dried with a jet of hot air and re-weighed. A 5-mL sample of the corrosive solution was taken for analysis of copper and zinc species by atomic absorption. The percentage of inhibition due to chromate was calculated from the relation:

$$I\,\% = \{ 1 - (R_{in} / R_o) \} \times 100 \qquad (1)$$

where R_o and R_{in} are the corrosion rates in the absence and the presence of chromate ion, respectively.

Results and Discussion

Weight loss

Figs 1-3 show the variation of weight loss with corrosion time in the absence and the presence of different concentrations of chromate ion in 3% chloride buffer solutions at pH 2.4, 7.0 and 8.5. It is clear that chromate promoted corrosion at pH 2.4 (Fig.1). The corrosion acceleration increased as chromate concentration increased, though weight loss data showed that the acceleration effect at 0.01 M was lower than at 0.005 M. An explanation for that discontinuity will be given later. On the contrary, chromate inhibits the corrosion at pH 8.5 (Fig. 2) and the inhibition percentage, I%, mostly increased as chromate concentration increased (Fig. 4). The I% values after one hour were calculated from the polarization tests as will be seen later. In neutral chloride buffer solutions (pH 7.0) chromate acted as a good inhibitor for corrosion and dezincification at concentrations ≥ 0.005 M, while deterioration in the inhibition effect was observed at lower concentrations. At $[CrO_4^{2-}]$ = 0.0001 M, chromate acted as a corrosion accelerator and at $[CrO_4^{2-}]$ = 0.001 M, the inhibition action became a promotion action after three weeks (Fig. 2). The results indicate that chromate should be used cautiously as corrosion inhibitor in neutral chloride media for brasses and sufficient chromate concentration should be maintained. In marine waters (essentially non-buffer solutions), the deterioration of the inhibition may start earlier and monitoring and controlling the chromate concentration is strongly recommended.

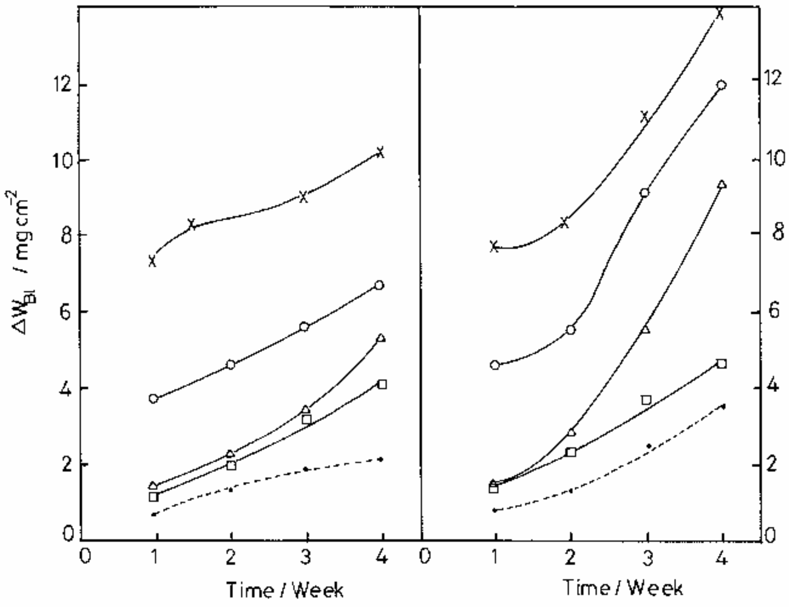

Figure 1. Variation of weight loss for α-brass (Cu/Zn: 64/36) with time in the presence of chromate ion in 3 % chloride buffer solutions at pH 2.4. Chromate ion concentrations were: □) 0.1 mM, Δ) 1.0 mM, ×) 5.0 mM and O) 10 mM. The dashed line refers to the losses in the absence of chromate ion.

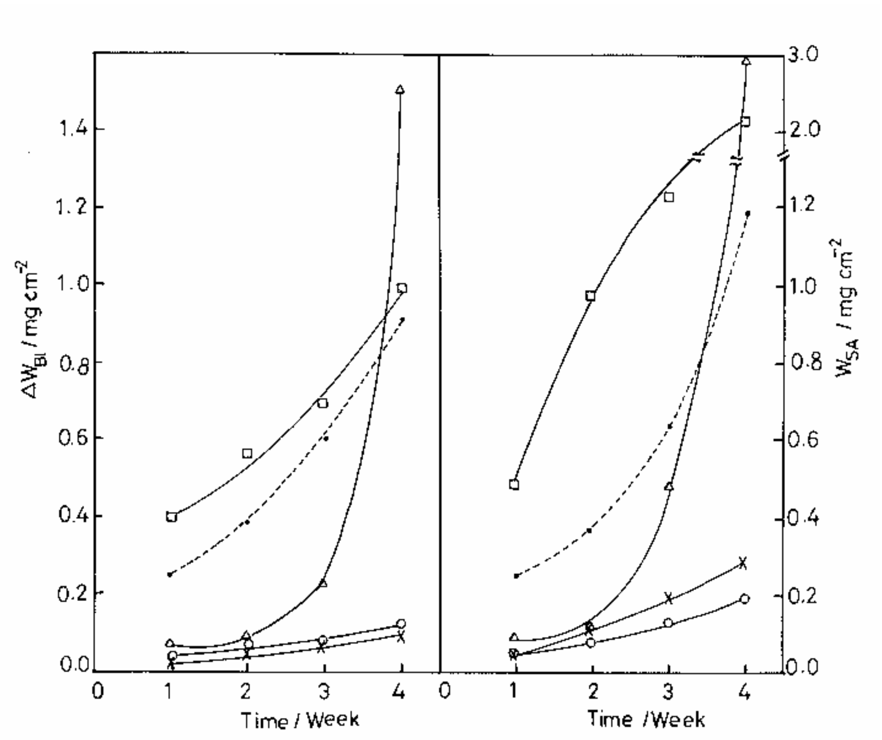

Figure 2. Variation of weight loss for α-brass (Cu/Zn: 64/36) with time in the presence of chromate ion in 3 % chloride buffer solutions at pH 7.0. Chromate ion concentrations were: □) 0.1 mM, Δ) 1.0 mM, ×) 5.0 mM and O) 10 mM. The dashed line refers to the losses in the absence of chromate ion.

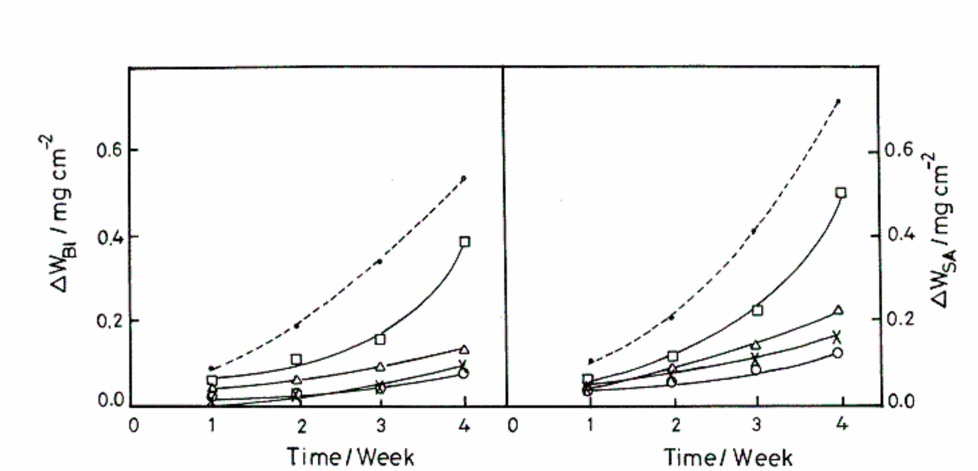

Figure 3. Variation of weight loss for α-brass (Cu/Zn: 64/36) with time in the presence of chromate ion in 3 % chloride buffer solutions at pH 8.5. Chromate ion concentrations were: □) 0.1 mM, Δ) 1.0 mM, ×) 5.0 mM and O) 10 mM. The dashed line refers to the losses in the absence of chromate ion.

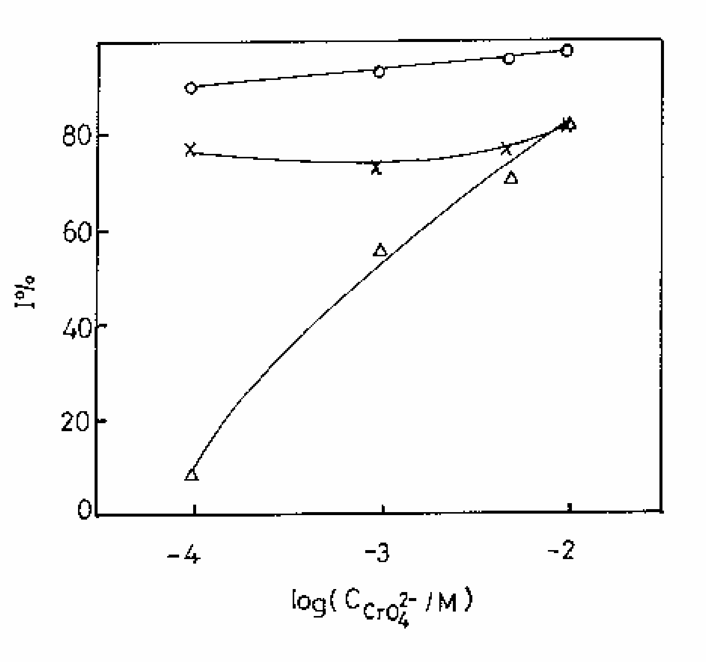

Figure 4. Dependence of the corrosion inhibition percentage, I%, on logarithm of chromate ion concentration for α-brass (Cu/Zn: 64/36) in 3% chloride buffer solutions at pH 8.5. Corrosion times were: Δ) 1 hour, ×) 1 week and O) 4 weeks.

The weight loss determined by balance, ΔW_{Bl} (mg cm^{-2}), was always lower than that determined by solution analysis for copper and zinc in solution, ΔW_{SA} (mg cm^{-2}). This indicates the formation and precipitation of some sparingly soluble corrosion products on the corroding alloy surface. The corrosion bath was clear and no precipitate on the bottom of the test beaker was observed. The difference (ΔW_{SA} - ΔW_{Bl}) measures the weight gain due to elements taken from solution to form insoluble corrosion products (essentially oxygen and hydrogen). The increase in (ΔW_{SA} - ΔW_{Bl}) with time indicated the thickening of the corrosion product layer. With the proper conversion factor, f, the real corrosion rate, R, can be calculated as follows:

$$R = \{\Delta W_{SA} + (\Delta W_{SA} - \Delta W_{Bl}) \times f\} / \text{time} \quad (2)$$

In NaCl solutions, the insoluble corrosion products are assumed to be Cu_2O and ZnO, beside the re-deposited copper, in proportions depending on pH, alloy composition and electrode potential, as reported in previous studies using X-ray photo-electron and Auger electron spectroscopy (XPS and AES) [2,3,7]. For simplicity, $Cu_2O.H_2O$ was taken as the formula of the insoluble corrosion products and hence, f = 63.5/17 = 3.7. The corrosion rates given in Table 1 were calculated according to equation (2) with f = 3.7, except in the presence of chromate at pH 7.0 and 8.5. In the latter solutions, f = 1.9 was used because the surface appearance after corrosion indicated the formation of dark precipitate on the surface due to the formation of CuO instead of Cu_2O. The R values in Table 1 do not reflect a systematic variation with time but the inhibition or the acceleration action of chromate could easily be distinguished. It is interesting to see from Table 1 that R increases with chromate ion concentration at pH 2.4 and the discontinuity at $[CrO_4^{2-}]$ = 5 mM disappeared (Fig. 1).

Table l. Corrosion rate, R, for α-brass (Cu/Zn: 64/36) in 3% chloride buffer solutions containing different chromate ion concentrations at different pH.

pH	$[CrO_4^{2-}]$/mM	R* / $\mu g\ cm^{-2}\ h^{-1}$			
		1 week	2 weeks	3 weeks	4 weeks
2.4	0.0	3.9	3.8	7.0	11.5
	0.1	12.2	10.1	10.1	9.6
	1.0	13.1	14.7	24.7	20.1
	5.0	42.3	21.0	37.4	27.8
	10.0	50.0	26.3	43.6	46.3
7.0	0.0	1.7	1.1	1.4	2.4
	0.1	7.7	4.7	4.6	6.6
	1.0	0.6	0.4	2.0	1.5
	5.0	0.7	0.6	0.9	1.0
	10.0	0.6	0.3	0.5	0.6
8.5	0.0	2.2	4.1	3.9	11.3
	0.1	0.5	0.3	0.6	1.1
	1.0	0.6	0.4	0.5	0.6
	5.0	0.5	0.3	0.3	0.4
	10.0	0.4	0.4	0.4	0.2

*) R values were calculated from equation (1) using f = 3.7 in the absence of chromate and in acidic chromate solutions and f = 1.9 in neutral and alkaline chromate solutions.

Dezincification trend

Dezincification of brasses is estimated usually via a dezincification factor, Z_f, defined as [23]:

$$Z_f = (W_{Zn} / W_{Cu})_{solution} / (W_{Zn} / W_{Cu})_{alloy} \qquad (3)$$

Eq. (3) does not take into consideration the contribution of the insoluble corrosion products and Z_f determined in this way should be interpreted cautiously. Figs. 5-7 show the dependence of Z_f on corrosion time in the absence and presence of chromate at different pH.

Although the Z_f behavior at pH 2.4 was complicated, chromate tended to promote the dezincification (Fig. 5). The opposite behavior occurred at pH 8.5, where chromate acted as a strong dezincification inhibitor ($Z_f \sim 1$), especially at concentrations ≥ 0.0001 M (Fig.8). At pH 7.0, chromate acted also as effective inhibitor for dezincification at concentrations ≥ 0.005 M but serious deterioration occurred at lower concentrations (Fig.6).

Visual inspection of the alloy surface after a month of corrosion showed the following observations:

- In acid chloride solutions without and with chromate ion, the surface was covered by a red to brown layer, due to the deposition of copper oxide (the main insoluble corrosion product) and redeposition of copper (during dezincification [1,2,5,7,13]).
- In alkaline solutions containing chromate ion, the surface appeared yellow as before corrosion (no dezincification) while in chromate-free solutions, red spots (copper) with dark brown layer (copper oxide) were detected.
- At pH 7.0, the surface appeared yellow in the presence of chromate ion at concentrations ≥ 0.005 M. In chromate-free solutions and at lower chromate concentrations, red zones with dark brown zones appeared.

It is interesting to compare the concentrations of copper and zinc species in solution in the presence and absence of chromate ion at different pH (Figs. 8-10). The effect of chromate at pH 2.4 is opposite to that at pH 8.5 (*cf*. Figs. 8-10). Dezincification in acid chloride solutions is accompanied by a low concentration of copper species in solution. It is assumed that $CuCl_2^-$ complex ion is the predominant copper species in acid chloride solution [1,5,13] and undergoes reduction and deposition as copper via disproportionation reaction [2,7,24] and/or electro-reduction [5]. Chromate did not affect significantly the concentration of copper species in solution but increased significantly the concentration of zinc species in solution, as can be seen in Fig. 8. Since chromate

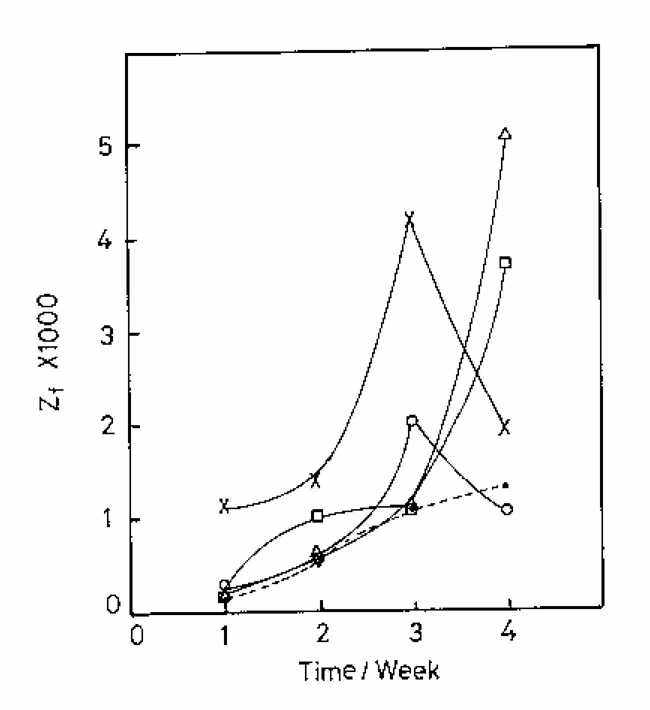

Figure 5. Variation of the dezincification factor, Z_f, for α-brass (Cu/Zn: 64/36) with time in the presence of chromate ion in 3 % chloride buffer solutions at pH 2.4. Chromate ion concentrations were: □) 0.1 mM, Δ) 1.0 mM, ×) 5.0 mM and O) 10 mM. The dashed line refers to Z_f in the absence of chromate ion.

promoted the corrosion in acid chloride solutions, one can infer that both copper and zinc in alloy dissolve simultaneously. Therefore copper species are reduced so rapidly that the concentration of copper species in solution was always low. At pH 8.5, the presence of chromate ion led to an increase in the concentration of copper species as well as a substantial decrease in the concentration of zinc species in solution (Fig. 10). The decrease in zinc species concentration is consistent with the inhibition effect of chromate at pH 8.5. On the other hand, increasing the copper species concentration is the key for the apparent retardation of dezincification in the presence of chromate. It is assumed that the promotion of copper concentration is achieved via formation of $CuCrO_4$, which is more soluble than CuO ($K_{sp} = 2.2 \times 10^{-20}$ [25]).

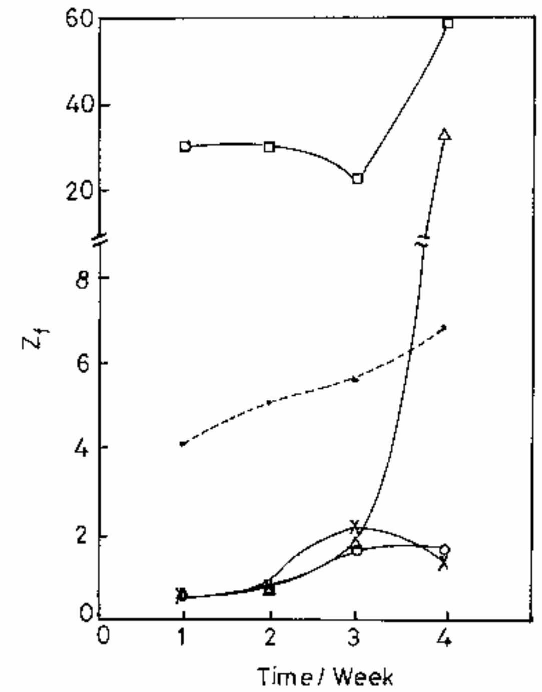

Figure 6. Variation of the dezincification factor, Z_f, for α-brass (Cu/Zn: 64/36) with time in the presence of chromate ion in 3% chloride buffer solutions at pH 7.0. Chromate ion concentrations were: □) 0.1 mM, Δ) 1.0 mM, ×) 5.0 mM and O) 10 mM. The dashed line refers to Z_f in the absence of chromate ion.

Depending on chromate concentration, $CuCrO_4$ ($K_{sp} = 3.6 \times 10^{-6}$ [25]) can yield a copper concentration in the order of 100 ppm (solubility), which is higher than the reported copper concentration at pH 8.5 (Fig. 10). The behavior at pH 7.5 is intermediate between those observed at pH 2.4 and 8.5, though it is closer to the alkaline case. At this pH copper concentration in chromate-free solutions was the highest and tended to decrease in the presence of chromate (copper concentration at $[CrO_4^{2-}] = 0.001$ M after three weeks is exception as can be seen in Fig. 9). It is assumed that the predominant copper species is Cu(II) which is difficult to be reduced on the corroding surface in contrast to Cu(I) which is predominant at pH 2.4 and easy to be reduced. Thus, the apparent inhibition of dezincification of chromate in neutral and alkaline chloride solutions is the result of two effects; efficient retardation of zinc dissolution and much less efficient retardation of copper dissolution due to the formation of Cu(II) instead of Cu(I).

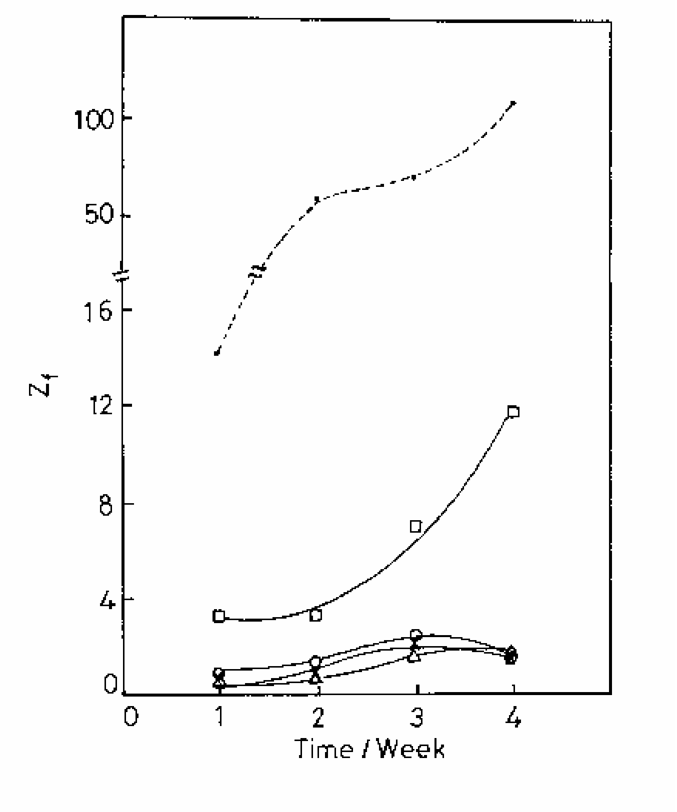

Figure 7. Variation of the dezincification factor, Z_f, for α-brass (Cu/Zn: 64/36) with time in the presence of chromate ion in 3 % chloride buffer solutions at pH 8.5. Chromate ion concentrations were: □) 0.1 mM, Δ) 1.0 mM, ×) 5.0 mM and O) 10 mM. The dashed line refers to Z_f in the absence of chromate ion.

Electrochemical measurements

The dependence of the quasi-steady corrosion potential, E_{corr}, on chromate concentration at different pH is shown in Fig. 11. Generally E_{corr} shifted to more positive potentials in the presence of chromate and increased linearly with logarithm of chromate concentration. The values of the slope $dE_{corr}/d\log [CrO_4^{2-}]$ were 54, 12 and 21 mV at pH 2.4, 7.0 and 8.5, respectively. E_{corr} is a mixed potential, which reflects the competition of various electrochemical processes, such as zinc and copper dissolution, formation of insoluble corrosion products, O_2 and H^+ ion reduction and chromate reduction. Chemisorption of chromate ions is expected to affect E_{corr} too. The nature of Cr(VI) species is controlled by the equilibrium:

$$Cr_2O_7^{2-} + H_2O \leftrightarrow 2CrO_4^{2-} + 2H^+ \quad (4)$$

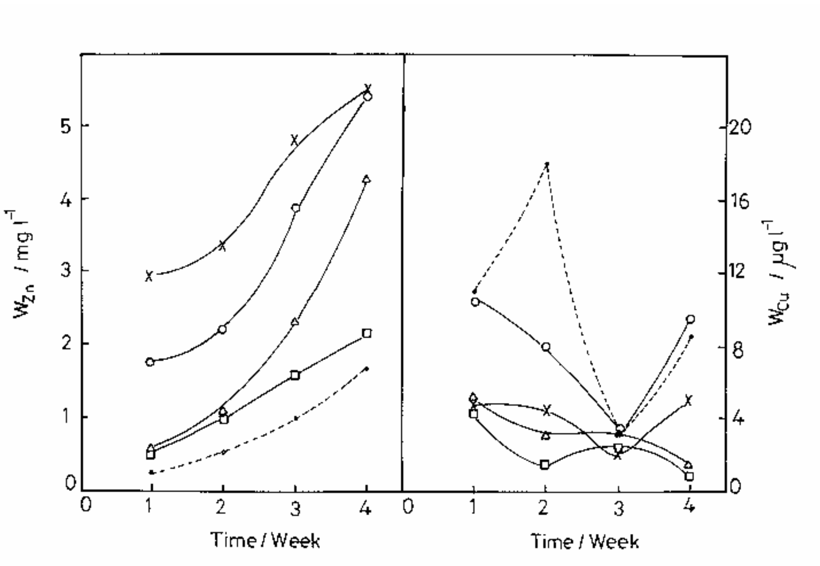

Figure 8. Variation of the concentrations of copper and zinc species in solution for α-brass (Cu/Zn: 64/36) with time in the presence of chromate ion in 3 % chloride buffer solutions at pH 2.4. Chromate ion concentrations were: □) 0.1 mM, Δ) 1.0 mM, ×) 5.0 mM and O) 10 mM. The dashed lines refer to the concentrations of copper and zinc species in solution in the absence of chromate ion.

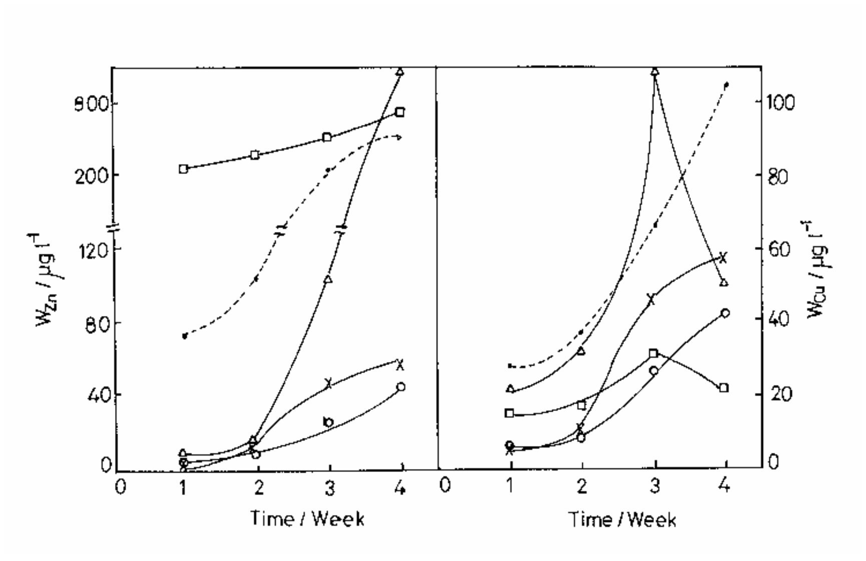

Figure 9. Variation of the concentrations of copper and zinc species in solution for α-brass (Cu/Zn: 64/36) with time in the presence of chromate ion in 3 % chloride buffer solutions at pH 7.0. Chromate ion concentrations were: □) 0.1 mM, Δ) 1.0 mM, ×) 5.0 mM and O) 10 mM. The dashed lines refer to the concentrations of copper and zinc species in solution in the absence of chromate ion.

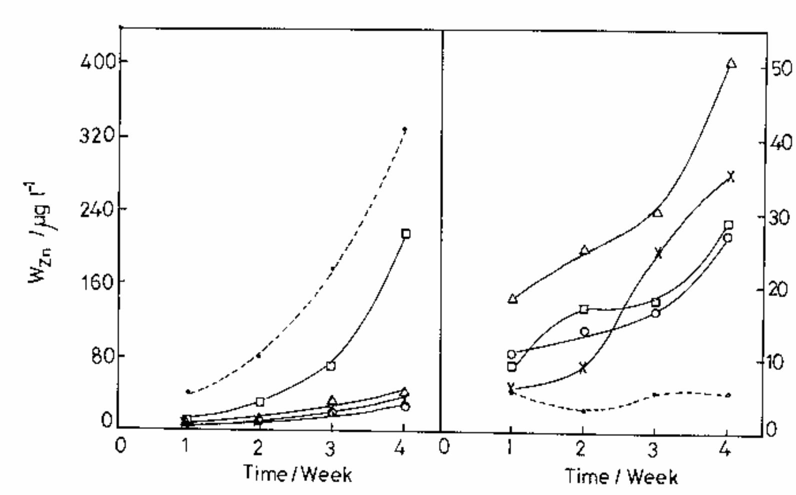

Figure 10. Variation of the concentrations of copper and zinc species in solution for α-brass (Cu/Zn: 64/36) with time in the presence of chromate ion in 3% chloride buffer solutions at pH 8.5. Chromate ion concentrations were: □) 0.1 mM, Δ) 1.0 mM, ×) 5.0 mM and O) 10 mM. The dashed lines refer to the concentrations of copper and zinc species in solution in the absence of chromate ion.

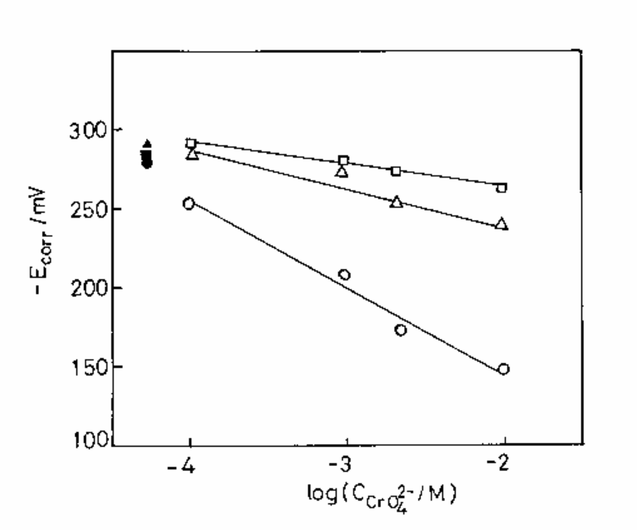

Figure 11. Dependence of the quasi-steady corrosion potential, E_{corr}, for α-brass (Cu/Zn: 64/36) on logarithm of chromate ion concentration in 3 % chloride buffer solutions at different pH : O) 2.4, □) 7.0 and Δ) 8.5. Solid symbols refer to E_{corr} in the absence of chromate ions.

The equilibrium constant, K, for the above equilibrium at 25 °C was calculated from the standard free energies of formation in aqueous solutions [25]; $K=3.2\times10^{-15}$. Accordingly, the added chromate ions exist predominantly at pH 2.4 as dichromate ions and can be reduced as follows:

$$Cr_2O_7^{2-} + 14H^+ + 6\ e \rightarrow 2Cr^{3+} + 7\ H_2O \quad ; \quad E^o = 1.18\ V \qquad (5)$$

The electrode potential for the above process is much higher than E_{corr} values (Table 2) and $Cr_2O_7^{2-}$ is expected to act as a cathodic depolarizer, in agreement with the experimental results. At constant Cr^{3+} ion concentration, a Nernstian slope of 20 mV with respect to chromate concentration should be expected. The predicted slope is substantially lower than the experimentally recorded slope (54 mV). The acceleration effect of chromate towards metal dissolution seems to contribute to the experimental slope via increasing the concentrations of Zn^{2+} and Cu^{2+} ions. At pH 7.0 and 8.5, chromate ion predominates and behaves as an inhibitor for corrosion. The recorded anodic E_{corr} shift of the passivation properties of the insoluble corrosion products. Both ways lead to diminishing the effective anodic area on the corroding surface [26].

Table 2. Corrosion potential, E_{corr}, corrosion current, i_{corr}, and corrosion rate, R, for α-brass (Cu/Zn: 64/36) in 3% chloride buffer solutions containing different chromate ion concentrations at different pH.

pH	$[CrO_4^{2-}]$ / mM	E_{corr} / mV	i_{corr} / µA cm^{-2}	R* / µg cm^{-2} h^{-1}
2.4	0.0	-280	7.2	8.6
	0.1	-255	18.8	22.6
	1.0	-221	51.5	61.8
	5.0	-172	142.9	171.5
	10.0	-151	326.5	391.8
7.0	0.0	-286	5.1	6.1
	0.1	-283	3.6	4.3
	1.0	-281	1.0	1.2
	5.0	-274	1.4	1.7
	10.0	-263	1.2	1.4
8.5	0.0	-290	2.8	3.4
	0.1	-280	2.6	3.1
	1.0	-278	1.2	1.4
	5.0	-252	0.8	1.0
	10.0	-243	0.5	0.6

*) The R values were calculated from the corresponding i_{corr} values.

The corrosion current, i_{corr}, given in Table 2 was determined after one-hour immersion from the polarization curves (Tafel plots). The i_{corr} values indicated that after one hour, chromate promoted corrosion in acid chloride solutions and retarded corrosion in neutral and alkaline chloride solutions, in agreement with the weight loss results after 1-4 weeks. The equivalent corrosion rate after one hour was calculated from i_{corr} by assuming that the number of electrons involved, n = 2 and the average atomic weight (Cu, Zn) = 64.5 (Table 1). Generally, R values after one hour were higher than those determined after 1-4 week(s), probably due to the partial blocking of the corroding surface by the deposited insoluble corrosion products (*cf.* Tables 1 and 2).

Electrochemical interpretation of chromate ion action

The role of chromate on the corrosion behavior of α-brass (Cu/Zn: 64/36) in chloride buffer solutions at pH 2.4, 7.0 and 8.5 can be explained adequately in terms of the partial anodic and cathodic polarization curves of the corrosion process. Following the schematic illustration of the partial anodic and cathodic polarization curves (Evans' diagrams) shown in Fig. 12, it is clear that chromate in acid chloride solutions (pH 2.4) affects the cathodic polarization curves (Part a) because it acts as a depolarizer, beside O_2 and H^+ ions. The cathodic polarization curves intersect with the active metal dissolution part of the anodic curve. The order of the cathodic curves is controlled by the E_{corr} value (Table 2). Thus, i_{corr} is expected to increase with increasing chromate ion concentration.

In alkaline chloride solutions (pH 8.5), chromate does not act as a depolarizer to any measurable extent and consequently has no effect on the cathodic curves. Alternatively, chromate affects the passivity region of the anodic polarization curve via improving the passivation properties, i.e. decreasing the passive current, and/or chemisorption of chromate species (Part b). In this case, the cathodic curve intersects with different anodic curves (different chromate concentrations) in the passivity region. As chromate concentration increases, E_{corr} increases and i_{corr} decreases. The order of anodic curves is controlled by E_{corr} value.

In neutral chloride solutions (pH 7.0) and after 1-4 weeks, chromate showed inhibition effect at concentrations ≥ 0.005 M and acceleration at lower concentrations. After one hour, electrochemical data indicated that chromate acted as inhibitor at all concentrations (Table 2). Chromate is assumed to affect the passivity region in the anodic curves at higher concentration ≥ 0.005 M regardless of corrosion period, where the cathodic and anodic curves intersect in the passivity region as in alkaline chloride solutions. At lower concentrations

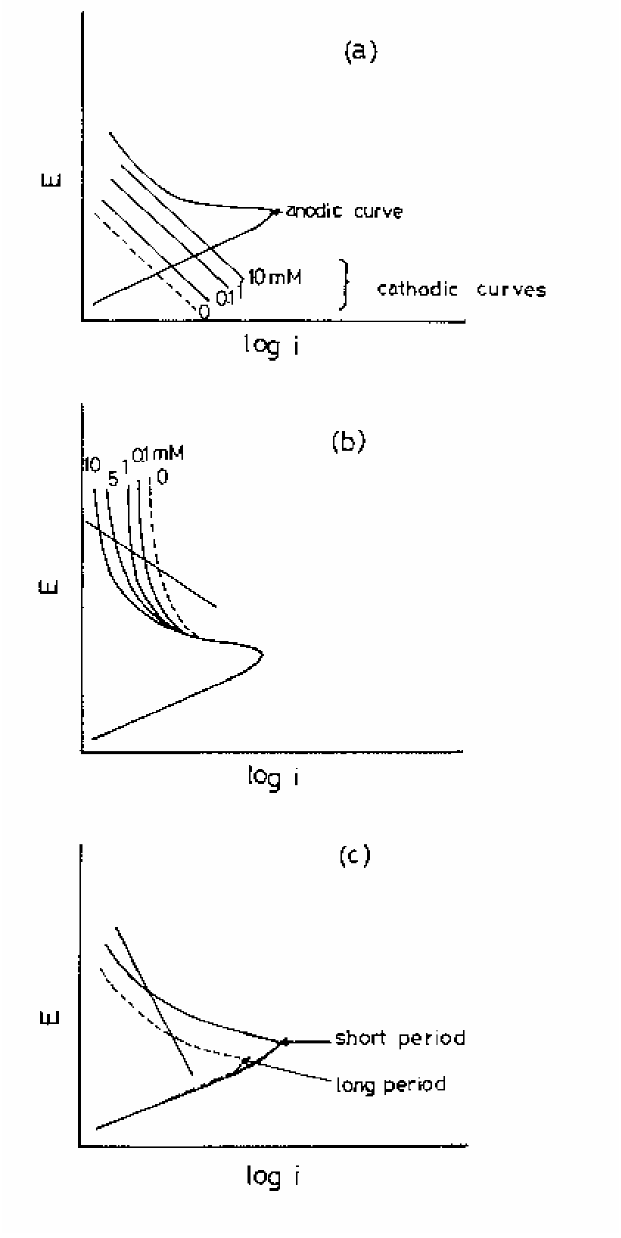

Figure 12. Schematic illustration of the partial anodic and cathodic polarization curves (Evans' diagrams) for α-brass (Cu/Zn: 64/36) in 3% chloride buffer solutions containing different chromate ion concentrations at different pH : a) 2.4, b) 7.0 and c) 8.5.

< 0.005 M, time has a significant effect on the corrosion trend. It is assumed that the corrosion is controlled by the active-passive transition region. The shape of the anodic polarization curve, especially the active-passive transition region, changes as corrosion time increases, due to promotion of passivity (Part c). The intersection of the anodic and cathodic curves lead to higher i_{corr} values at longer times, as recorded at 0.0001 M and 0.001 M after 3 weeks. Thus, sufficient chromate concentration should be used and maintained to insure that the partial anodic and cathodic curves of corrosion intersect in the passivity region. Monitoring pH is vital also, since corrosion in practical chloride environments (essentially non-buffer) leads to a decrease in pH and consequently the inhibition effect of chromate may deteriorate seriously or even corrosion acceleration happens.

Conclusion

Chromate accelerated corrosion and dezincification of α-brass (Cu/Zn: 64/36) in acid chloride buffer solutions by acting as a depolarizer. In slightly alkaline chloride buffer solutions, chromate suppressed strongly corrosion and dezincification by acting as an anodic inhibitor. Chromate can be used also in neutral chloride solutions at concentrations > 0.005 M but at lower concentrations deterioration in inhibition effect or even acceleration should be expected. The behavior of chromate can be explained adequately in terms of its effect on the partial anodic and cathodic polarization curves involved in the corrosion process.

References

1. R.C. Newman, T. Shahrabi, K. Sieradzki, *Corros. Sci*. 28 (1988) 873.
2. T.M.H. Saber, A.A. Warraky, *Desalination* 93 (1993) 473.
3. J. Morales, P. Esparza, G.T. Fernandez, S. Gonzalez, J.E. Garcia, J. Caceras, R.C. Salvarezza, A.J. Arvia, *Corros. Sci*. 37 (1995) 231.
4. J. Morales, G.T. Fernandez, S. Gonzalez, P. Esparza, R.C. Salvarezza, A.J. Arvia, *Corros. Sci*. 40 (1998) 177.

5. L. Burzynska, A. Maraszewska, Z. Zembura, *Corros. Sci*. 38 (1996) 337.
6. J.Y. Zou, D.H. Wang, W.C. Qiu, *Electrochim. Acta* 42 (1997) 1733.
7. A.A. El Warraky, *Br. Corros. J.* 32 (1997) 57.
8. G.V. Korshin, J.F. Ferguson, A.N. Lancaster, *Corros. Sci*. 42 (2000) 53.
9. G.T. Burstein, G. Gao, *J. Electrochem. Soc*. 141 (1994) 921.
10. S. Kohler, *Werkstoffe und Korrosion* 47 (1996) 65.
11. E.A. Ashour, B.G. Atyea, *Corros. Sci.* 37 (1995) 371.
12. W. Schwenk, *Werkstoffe und Korrosion* 47 (1996) 78.
13. R.C. Newman, T. Shahrabi, *Corrosion* 49 (1993) 60.
14. T. Shahrabi, R.C. Newman, K. Sieradzki, *J. Electrochem. Soc*. 140 (1993) 348.
15. H.C. Shih, R.J. Tzou, *Corros. Sci*. 35 (1993) 479.
16. H.H. Rehan, *Mat. –wiss. u. Werkstofftech*. 24 (1993) 304.
17. A.G. Gad-Allah, W.A. Badawy, H.H. Rehan, M.M. Abou-Romia, *J. Appl. Electrochem*. 19 (1989) 928.
18. L. Tommesani, G. Brunoro, A. Frignani, C. Monticelli, M. DalColle, *Corros. Sci*. 39 (1997) 1221.
19. S. Sayed, E.A. Ashour, B.G. Atyea, *ibid.* 36 (1994) 221.
20. V. Otieno-Alego, G.A. Hope, T. Notoya, D.P. Schweinsberg, *ibid.* 38 (1996) 213.
21. M.A. Quraishi, I.H. Farooqi, P.A. Saini, *Br. Corros. J.* 35 (2000) 78.
22. M.G. Fontana, *Corrosion Engineering*, 3rd ed, McGraw-Hill, New York, 1987, pp. 284-289.
23. T.K.G. Namboodhori, R.S. Chaudhary, B. Prakash, M.K. Agrawal, *Corros. Sci*. 22 (1982) 1037.
24. V.F. Lucey, *Br. Corros. J.* 1 (1965) 9, 53.
25. J.A. Dean, *Lange's Handbook of Chemistry*, 14th ed, McGraw-Hill, New York, 1992, Part 8.
26. A.G. Gad-Allah, H.A. Abd El-Rahman, *Corrosion* 43 (1987) 698.