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A THERMOMETRIC STUDY OF THE KINETICS OF ACID DISSOLUTION OF FOUR COPPER ALLOYS USED IN DESALINATION PLANTS

RASHEED A. ARAIN and A.M. SHAMS EL DIN

Material Testing Laboratory, Water and Electricity Department, P.O. Box 219, Abu Dhabi (United Arab Emirates)

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ABSTRACT

The dissolution of four copper alloys, commonly used in desalination plants, in HNO_3 solutions of varying concentrations is studied by the thermometric technique. The difference between the initial and maximum temperature, ΔT, varies with the molarity of the acid according to $\Delta T = a(M - M^0)$, where a is a constant and M^0 is the concentration below which no detectable rise in temperature is recorded. High values of M^0 indicate better resistance to acid attack.

The reaction number (RN) varies with the molar concentration of the acid as: $\mathrm{RN} = AM^n$, with A and n depending on the nature of the alloy. One and the same value of n is, however, obtained when the effective acid concentration $(M - M^0)$ is considered. This shows that all four alloys dissolve following the same mechanism. Plots of log RN vs. $1/T_m$, where T_m, the maximum temperature (K), is linear, allowing the calculation of the activation energies of dissolution.

Additions of Cl^-, HSO_4^- and $H_2PO_4^-$ ions to copper alloys dissolving in nitric acid solutions lower their RN values. This inhibiting effect is attributed to the specific adsorption of the ions and their displacing NO_2 molecules from the surface, which causes the interruption of the autocatalytic cycle of dissolution in HNO_3. The uptake of the ions follows a Freundlich adsorption isotherm.

The applicability of the thermometric technique in evaluating corrosion problems in desalination plants is further exemplifed by studying the action of Stannine LTP on the dissolution curves of the four alloys in HNO_3. This compound is used as inhibitor in the acid-cleaning of distillers. In all cases a decrease in RN is recorded, due to the adsorption of the additive on the metal surfaces.

INTRODUCTION

Copper-base alloys exhibit good resistance to corrosion by sea water at normal and elevated temperatures [1]. This, together with the fact that most copper alloys are galvanically compatible among themselves and to normal stainless steels accounts for their wide use in the construction of components exposed to sea water in desalination plants. Much has been published on the corrosion behaviour of the various copper alloys under actual working conditions, and it is beyond the scope of the present paper to review this work. Comparatively little has been done, however, in the direction of comparing the corrosion characteristics of technically important alloys. The general conclusion reached at from these studies is that simple bronzes (Cu–Sn alloys) are better than simple brasses (Cu–Zn alloys); and that the cupro-nickels are superior to both [1].

The resistance to corrosion of the cupro-nickels increases hand in hand with the nickel content of the material, and their excellence is only surpassed by that of the nickel–copper alloys. However, because of cost considerations, the use of these last materials is restricted to conditions where other alloys would fail.

It appeared therefore, of interest to compare the corrosion behaviour of some copper alloys commonly used in desalination plants, under one and the same test condition. For a number of reasons the thermometric method of corrosion testing [2] was chosen for this purpose. First, it is a simple accelerated test, which relates the heat evolved during the dissolution of a metal in an aggresive medium to the stability of the metal as well as to the corrosivity of the electrolyte. Second, the thermometric behaviour of the single metals Cu [3], Al [4,5], Zn [6], Sn [7], Fe [8] and Ni [9] is well established. A recent review on the subject [10] reveals that the method has been employed to the study of only one binary alloy system, viz. the α- and β-brasses [11]. In the present study, work on the thermometric behaviour of alloys is extended to cover the following four copper-base alloys employed in the Umm Al Nar Desalination Plant (Abu Dhabi, UAE).

(a) Aluminium brass (AlBs), used as material for condenser tubes in the heat rejection section of the MSF distillers (composition: Cu, 76; Zn, 22; Al, 2; As, 0.03% as inhibitor for dezincification).

(b) Aluminium bronze (AlBz), used in the construction of water boxes (composition: Cu, 81; Al, 9.2; Ni, 4.4; Fe, 4; Mn, 1.4%).

(c) 90/10 Copper–nickel (90/10 Cu–Ni), employed as material for the tube plates (composition: Cu, 87.5; Ni, 10; Fe, 2;, Mn, 0.5%).

(d) 70/30 Copper–nickel (70/30 Cu–Ni), employed as material for condenser tubes in the heat gain section of the distillers (composition: Cu, 67; Ni, 29; Fe, 1.8; Mn, 1.8%).

Because the rate of dissolution of the alloys in HCl and H_2SO_4 is too low to be followed by the thermometric technique, the corrosion behaviour of the materials was examined in HNO_3 solutions of varying concentrations. The effect of the Cl^-, HSO_4^- and $H_2PO_4^-$ ions on the dissolution reaction was studied in some detail. Further, experiments were conducted to establish the effect of Stannine LTP(R), an inhibitor added during the acid wash of the distillers. No work on the four alloys from the present standpoint has previously been published.

EXPERIMENTAL

The arrangement for tracing a thermometric corrosion curve has been described before [4]. Experiments were carried out on test pieces measuring 4.0 × 1.5 cm. The specimens were first abraded with emery paper of increasing fineness, degreased with cotton wool soaked with acetone, washed with running demineralized water, and then dried between filter papers. Each experiment was carried out on a newly polished specimen and with 10 ml of the test solution.

AnalaR grade HNO_3 (BDH, England), and doubly distilled water were used in the preparation of the test solutions, and their molarities were determined by titration against carbonate-free, standard NaOH.

The reaction number (RN) [2] is defined as

$$RN = \frac{T_m - T_i}{t}$$

where T_m and T_i are the maximum and initial temperatures, respectively, and t is the time (min) taken to reach T_m. The initial temperature was always 28°C.

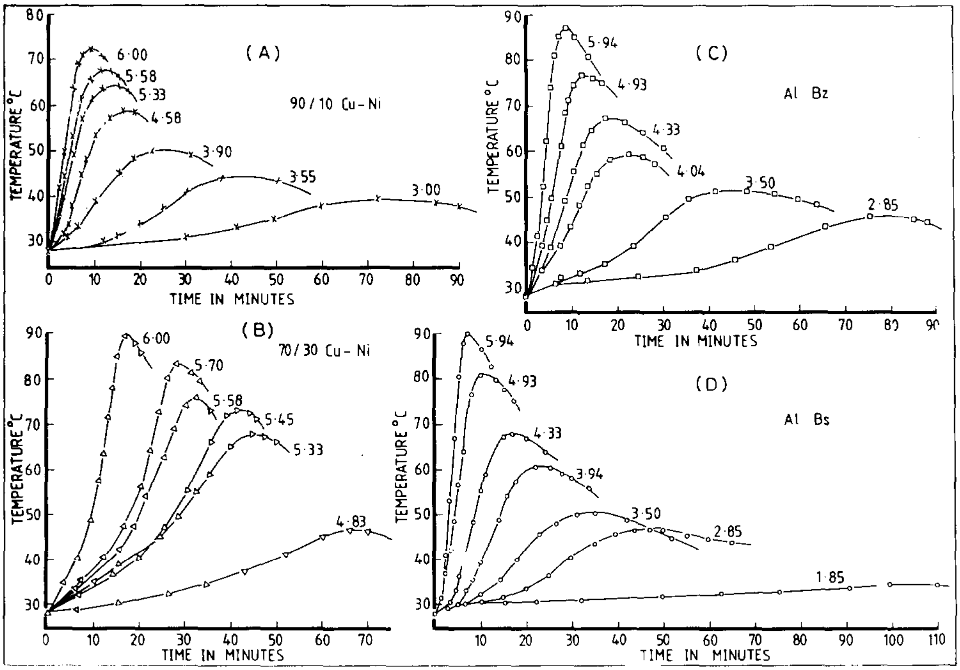

Fig. 1. Temperature–time curves for the reaction of (A) 90/10 Cu–Ni, (B) 70/30 Cu–Ni, (C) AlBz and (D) AlBs, with HNO_3 of different concentrations. Numbers on curves refer to acid molarity.

RESULTS AND DISCUSSION

The curves of Fig. 1 represent the variation of the temperature of the system with time when test pieces of the four copper alloys are made to react with 10 ml of HNO_3 solutions of varying concentrations. Overall, the behaviour of the four materials is identical. Below a certain acid concentration, the rate of attack on the metal pieces is too small to allow the recording of any measurable heat. As the concentration of the aggressive medium is increased, the temperature of the system rises, first slowly and then more rapidly, to reach a maximum temperature, T_m. As is seen from the curves of Fig. 1, T_m increases and the time, t, to reach it decreases, as the concentration, C, of the acid is raised.

From the curves of Fig. 2A it is evident that the elevation in temperature,

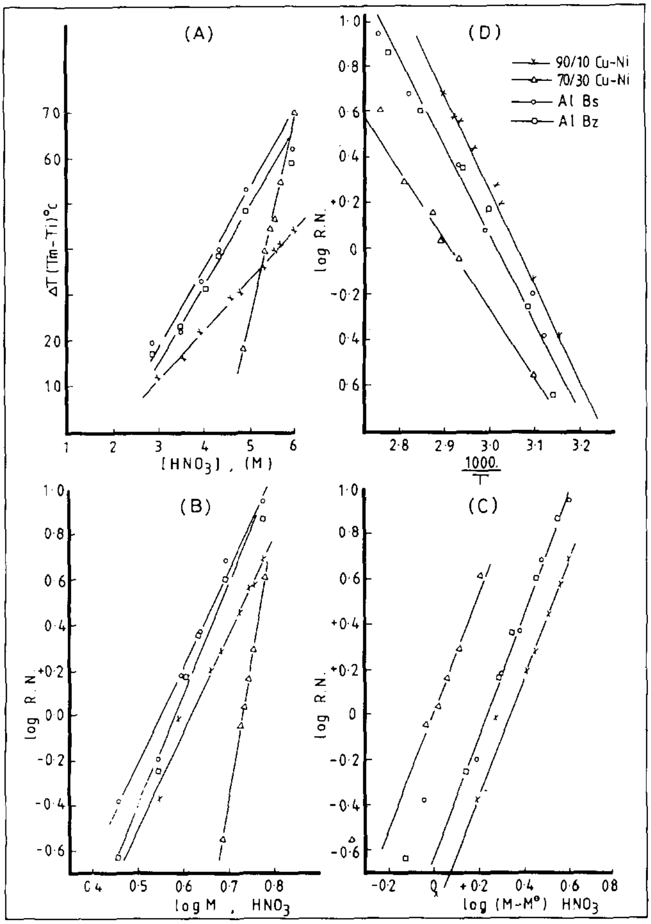

Fig. 2. (A) Variation of ΔT of the four Cu alloys with the molarity of HNO_3. (B) Variation of log RN of the four Cu alloys with log M HNO_3. (C) Variation of log RN of the four Cu alloys with log $(M - M^0)$ HNO_3. (D) log RN vs. $1/T_{abs}$ plots for Cu alloys.

$\Delta T(T_m - T_i)$, changes linearly with the acid molarity, M. However, the lines do not pass through the origin. The experimental results satisfy the relationship

$$\Delta T = a(M - M^0) \tag{1}$$

where M^0 is the acid concentration below which no rise in temperature is recorded. This parameter is a measure of the ability of the metallic alloy to withstand the corrosivity of the medium. The higher the value of M^0, the more corrosion-resistant the alloy will be. The values of M^0 for the four alloys tested are: AlBs, 1.95; AlBz, 2.10; 90/10 Cu–Ni, 2.00; 70/30 Cu–Ni, 4.40 M. The high value for 70/30 Cu–Ni is indicative of its good resistance to acid attack.

The term a in eqn. (1) is the rate of temperature rise/mole acid, in solutions of $M > M^0$. A large a value denotes a vigorous reaction, and hence a higher rate of attack. It is interesting to observe that, although the 70/30 Cu–Ni possesses the highest M^0 value, it also exhibits the highest a value (40°C mol^{-1}). This compares to 9.3°C mol^{-1} for the 90/10 Cu–Ni, and to 16.5°C mol^{-1} for both AlBs and AlBz.

The kinetics of dissolution of metals in corroding solutions using the thermometric technique are commonly expressed in terms of log RN/log M graphs [3,11,12]. In Fig. 2B, curves are given for the four alloys examined. These are invariably straight lines satisfying the general relationship

$$\text{RN} = AM^n \tag{2}$$

where A and n are constants. A is the theoretical RN value that would be measured in a 1 M solution of the aggressive medium. On the other hand, n is assumed to reflect on the mechanism of metal dissolution since it depends on the nature of the aggressive solution [12]. This, however, is not the case in the present study, where the same corrodant is used throughout. The variation of n among the various alloys examined is traced to the fact that the values of M considered are not actually the concentrations producing the measured reaction numbers. If plots are made between log RN and log$(M - M^0)$, the almost parallel straight lines of Fig. 2C are obtained. The exponent n is the same for all four materials (2.52). RN is therefore related to the effective acid concentration according to

$$\text{RN} = A(M - M^0)^n \tag{3}$$

The constancy of the exponent n under these conditions indicates that all four materials dissolve by the same mechanism. Since the four alloys are single phased, it is reasonble to conclude that they dissolve homogeneously. This conclusion was substantiated by the results of experiments in which the initial temperature, T_i, as well as the solution volume/specimen area were varied [11]. In neither of these experiments was a break in the temperature/time curve noted, indicative of preferential dissolution [11].

Comparison of the curves of Fig. 2B and C allows some interesting conclusions to be drawn. First, the line for the 70/30 alloy shifted its position from extreme right in Fig. 2B to extreme left in Fig. 2C. The outcome of this shift is that this particular alloy appears as if it were the easiest to corrode. This is, however, not the case. The shift in curve position results from the fact that both M and M^0 are comparable in magnitude, and that the net of their subtraction is correspondingly small.

Accordingly, when assessing corrodability from thermometric data, the values of a, M^0 and RN must be considered together. It is of interest to note here that expressions similar to eqns. (2) and (3), where rates of corrosion are substituted for RN, are frequently reported in the literature, when describing the dependence of metal corrosion on corrodant concentration [13,14].

The lines for AlBs and AlBz are close to one another in Fig. 2B and are practically superimposed in Fig. 2C, a fact which suggests that the corrosion behaviour of the two materials is very much the same. In fact, experience from the field of desalination lends strong support to this conclusion. In Abu Dhabi, the two materials have been used side by side in I-III MSF distiller units of the Umm Al Nar East Station for the past few years. Aluminium brass is used as material for the condenser tubes, whereas the water boxes are made of aluminium bronze. Both materials are galvanically compatible, and resist erosion corrosion and chloride attack to the same extent.

The position of the 90/10 alloy is of particular interest. Its A value places it first in terms of resistance to acid attack. On the other hand, its M^0 value is comparable to that of AlBs and AlBz. Its position on the log RN/log($M - M^0$) graph, however, tells that it surpasses these last alloys in withstanding the attacking action of HNO_3. All these features put the 90/10 alloy second to the 70/30 alloy as a corrosion resistant material.

The fact that the reaction numbers, RN, represent actual rates of dissolution can be gleaned from a consideration of the energetics of corrosion. It is well established that at constant concentration of reactants, the corrosion rate of a metal, r, follows an Arrhenius-type relationship [15,16] viz

$$r = B \exp(-\Delta H/RT) \tag{4}$$

where B is the pre-exponential constant, and ΔH is the activation energy of the corrosion reaction. A similar expression relates the corrosion current density to the temperature, namely

$$I_{\text{corr}} = B' \exp(-\Delta H/RT) \tag{5}$$

The term R in eqns. (4) and (5) is the universal gas constant. In determining the activation energies of corrosion reactions, the rates of dissolution, r, or the corrosion current densities, I_{corr}, are determined at a number of increasing temperatures, and eqns. (4) or (5) are applied. In thermometric experiments, on the other hand, the heat released during dissolution will correspondingly increase the rate, which in turn will produce more heat. When the temperature reaches its maximum value, T_m, the highest rate of corrosion is attained. In the experiments of Fig. 1 thermometric curves are given having different T_m values resulting from changes in the acid concentration. Apparently different rates of dissolution are operative at the maxima of these curves. That this is the case, and that RN values are good measures of these rates is substantiated by plotting log RN vs. I/T, represented by the lines of Fig. 2D for the four alloys.

The experimental results satisfy the Arrhenius relationship, and from the slopes of the lines the corresponding ΔH values are computed (90/10 Cu–Ni, 8.24; 70/30 Cu–Ni, 6.02 kcal mol^{-1}). On the other hand, an identical Arrhenius relationship describes the behaviour of AlBs and AlBz. Their corresponding ΔH value is 7.60 kcal mol^{-1}. All four values are comparable to those commonly encountered when pure metals freely dissolve in acids [15–18]. It is of interest to note that although 70/30 Cu–Ni proved to be least susceptible to attack by HNO_3 amongst the four alloys tested, it is the one with the smallest activation energy.

Although conclusions drawn from the thermometric behaviour of the four copper alloys in HNO_3 solutions might not directly correspond to their behaviour in desalination plants, the technique appears to be quite useful in studying and elucidating certain aspects of their corrosion under practical conditions. Thus, for example, it is well known that copper alloys greatly resist the destructive action of the chloride ion when present in high concentrations. This conclusion is simply and easily substantiated by the thermometric technique.

Experiments were carried out with the four test materials in 5.7 M HNO_3, to which increasing concentrations of NaCl were added. In all cases, the additive brought about a marked decrease in RN, whose magnitude depended on the Cl^- content of the solution. In the case of 90/10, 70/30 and AlBs alloys the reduction in RN was mainly the results of a decrease in T_m, whilst the time, t, to reach it was little affected. An example of this behaviour is represented by the curves of Fig. 3A for the 90/10 copper–nickel alloy. Aluminium bronze behaved in a similar manner in the presence of low Cl^- concentrations. Higher additions, however, caused the development of an induction period, during which the temperature slowly rose. The length of the induction period varies hand in hand with the additive content. The behaviour of AlBz is depicted by the curves of Fig. 3B.

As is readily seen from the curves of Fig. 4A,1, the RN value of the four alloys decreases linearly with the increase in the molar concentration of NaCl. Except for AlBs, the linearity extends to Cl^--free solutions, a fact which suggests the continuous covering of the metal surface with Cl^- ions (see below). Assuming, reasonably, proportionality between RN and the amount of anion adsorbed on the surface, it is concluded that adsorption follows a Freundlich isotherm. In Fig. 4A,2 the effect of the chloride ion is

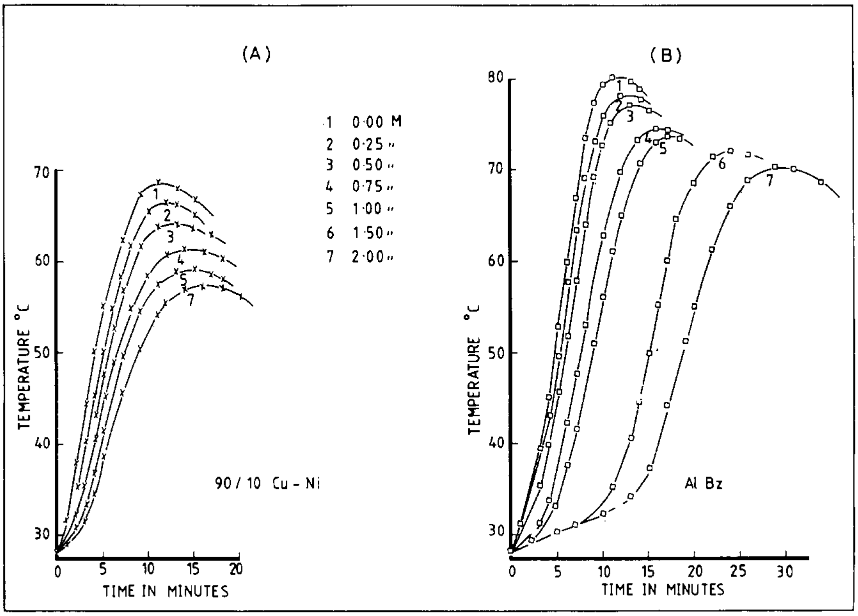

Fig. 3. Effect of NaCl additions on the thermometric behaviour of (A) 90/10 Cu–Ni and (B) AlBz in 5.7 M HNO_3.

represented in the more conventional manner, viz. as percentage inhibition, namely

$$\frac{(RN)_{add} - (RN)_{free}}{(RN)_{free}} \times 100 \qquad (6)$$

With all four test materials the relation is linear and passes through the origin. The difference in the slopes of the various lines is a measure of the affinity of the different metal surfaces to specifically adsorb the Cl^--ion. As is seen, this increases in the succession: AlBs < 70/30 Cu–Ni < AlBz < 90/10 Cu–Ni.

One of the main problems of sea-water desalination by thermal processes is that of alkaline scale formation in the heat exchange tubes. Various techniques are known for scale abatement and control, the most common of which is the acid treatment of make-up water [19], whereby sufficient acid is added to the feed water to lower its pH value to about 4.0.

Because of economic considerations, most pH-control systems use H_2SO_4. Construction material consdierations usually favour the use of acid containing more than 96 wt% H_2SO_4, since more dilute solutions are highly corrosive [19]. It was interesting to establish whether these conclusions could be substantiated by the results of the thermometric measurements of the present investigation. Experiments were conducted with the four alloys in 5.7 M HNO_3 to which increasing amounts of Na_2SO_4 were added. Since the

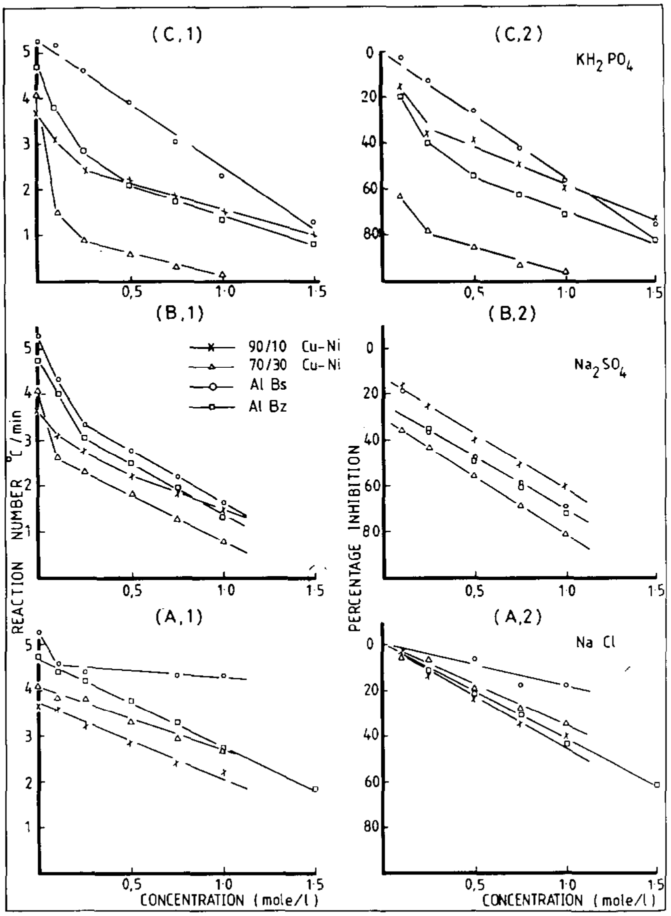

Fig. 4. Effect of addition of (A) NaCl (B) Na_2SO_4 and (C) KH_2PO_4 on the RN values (curves 1) and percentage inhibition (curves 2) of the four copper alloys in 5.7 M HNO_3.

ground solution is highly acidic and fully ionized, the use of the salt is justified in representing the behaviour expected from H_2SO_4 additions.

The dissolution of the four copper alloys in HNO_3 was inhibited by introducing Na_2SO_4 into the reaction medium. Overall, the four alloys behaved similarly. Small salt additions reduced RN mainly by extending the time, t, to reach T_m, whilst large amounts also affected the maximum temperature. The effect of Na_2SO_4 concentration on the RN values of the alloys is represented by the curves of Fig. 4B,1. Above ca. 0.25 M Na_2SO_4, RN and hence the rate of attack by H_2SO_4, decreases with increase in concentration. Further, the initial, non-linear portions of the curves at $C \leq 0.25$ indicate that the first small additions of HSO_4^- are effective in retarding attack more than later larger additions. The corresponding curves of Fig. 4B,2 show that the percentage inhibition of attack varies linearly with the Na_2SO_4 content of the solution. Two interesting features can be recognised from the same figure. First, all lines have practically the same slope. This indicates that not only does the uptake of HSO_4^- on the alloy surface follow the same adsorption isotherms, but also that the same coefficient of adsorption governs in every case. As is the case with Cl^-, the adsorption of HSO_4^- on the alloy surface appears to follow a Freundlich adsorption isotherm.

The second feature of interest is that, in contrast to the case of NaCl, the lines of Fig. 4B,2 do not converge to the origin. As has been stated above, the first small additions of HSO_4^- appear to be strongly specifically adsorbed on the surface and produce an initial marked reduction in the corrosion rate of the particular alloy. From the curves of Fig. 4B,2, it is concluded that the strength of specific adsorption of the HSO_4^- ion increases in the order 90/10 Cu–Ni < AlBs, AlBz < 70/30 Cu–Ni.

Threshold treatment is another successful technique for the inhibition of scale formation in condensers [20]. It involves the use of certain chemical agents (usually polyelectrolytes), in concentrations far below the stoichiometric levels of the scale-forming cations in water. Among the compounds successfully employed for scale control is sodium metaphosphate. In some of the MSF cells, particularly those operating at high temperatures, part of the anti-scalant will undergo partial hydrolysis to produce ortho-phosphate. This prompted us to examine in some detail the effect of KH_2PO_4 on the thermometric behaviour of the copper alloys.

The salt was found to exert strong inhibition to the dissolution reaction. The decrease in RN was caused by the simultaneous lowering of T_m and the increase in t. The thermometric curves of Fig. 5A represent the behaviour of AlBs dissolving in 5.7 M HNO_3, in the presence of increasing amounts of KH_2PO_4. Similar curves were obtained with AlBz and with the 90/10 Cu–Ni alloys. The additive had a more pronounced effect on the dissolution of 70/30 Cu–Ni, as is readily seen from the corresponding curves of Fig. 5B.

Here, although T_m values were comparable to those measured for the other alloys, considerably longer times were taken to attain them. The outcome of this strong inhibition of the dissolution of this last alloy is the rapid, non-linear decay of this RN vs. C curve, as compared to those of the other three materials (Fig. 4C,1). With AlBz and the 90/10 Cu–Ni alloy the corresponding curves are linear above ca. $C = 0.5$ M KH_2PO_4. With AlBs, on the other hand, a straight-line relationship covers the entire concentration range examined. The disparity in behaviour of the four test materials towards $H_2PO_4^-$ can readily be understood in the light of corresponding differences in the free energies of adsorption of the anion on their surface [21]. The same conclusion can be reached from a consideration of the percentage inhibition vs. concentration curves of Fig. 4C,2. The linear curves are obtained with AlBs and the 90/10 Cu–Ni alloy; the latter line does not, however, pass through the origin. On the other hand, the curves for AlBz and the 70/30 Cu–Ni alloy are non-linear at their initial stages. On these two

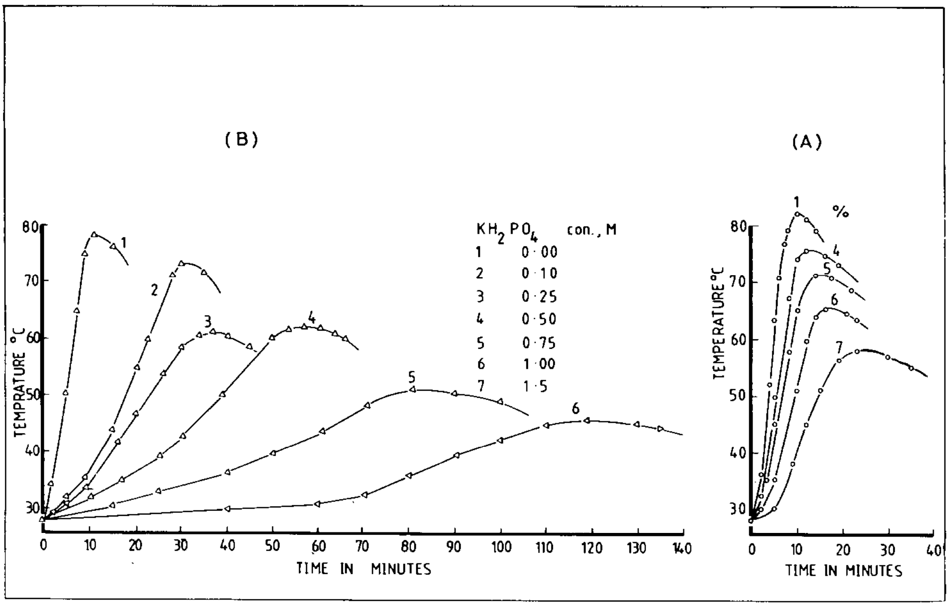

Fig. 5. Effect of concentration of KH_2PO_4 on the thermometric dissolution curves of (A) AlBz and (B) 70/30 Cu–Ni in 5.7 M HNO_3.

materials the $H_2PO_4^-$ ions are strongly adsorbed from dilute solutions and their uptake apparently follows an isotherm different from that governing more concentrated media.

The finding that the Cl^-, HSO_4^- and $H_2PO_4^-$ ions inhibit the dissolution of the four copper alloys examined, despite their known corrosition promotion character [22], is of particular interest. The retardation effect of these ions can be readily understood when one takes into consideration the fact that metal dissolution in HNO_3 is not a simple H_2-displacement reaction, as is the case with other strong mineral acids. The high dissolution rates of metals in nitric acid are the result of the occurrence of an autocatalytic process involving the partial reduction of the nitrate ion to NO_2 [23].

This latter is assumed to adsorb on the metal surface, and accept an electron to yield NO_2^-: $NO_2 + e^- = NO_2^-$. With abundance of H^+ ions in solution, undissociated HNO_2 is produced, which instantaneously reacts with HNO_3 to produce two molecules of NO_2.

$$H^+ + NO_2^- = HNO_2$$

$$HNO_2 + HNO_3 = 2\ NO_2 + H_2O \qquad (7)$$

This last reaction is a chain propagation reaction since two molecules of NO_2 are produced from the disappearance of one molecule.

In the presence of foreign anions in solution, competition for adsorption sites on the metal surface will occur between the foreign anions and NO_2. The larger the difference in the free energies of adsorption of the two species in favour of the anion, the more they will displace NO_2 from the surface. Since anions do not act as electron acceptors as do NO_2 molecules, a decrease in the dissolution rate of the metal will be recorded. As is evident from the curves of Fig. 4, all three anions tested lower the RN value of the alloys and, hence, compete for adsorption sites. The adsorption of anions on the alloy surface depends on anion type and concentration. At the same concentration, adsorbability increases in the order: $Cl^- < HSO_4^- < H_2PO_4^-$, which is the same as that for pure copper [3]. On the other hand, with the same anion in solution, the extent of dissolution retardation depends on the type of alloy used. As is seen, the adsorption of both the HSO_4^- and $H_2PO_4^-$ ions on the 70/30 Cu–Ni exceeds that on the other three materials.

It is to be noted, however that the adsorbability of the Cl^- ion on the same surface is not particularly high, and it is preceded by AlBz and the 90/10 Cu–Ni. Despite the disparities in their extent of adsorption, all three anions are taken up on the various surfaces according to the same absorption isotherm.

Calculations for the activation energies of dissolution of the four alloys in the presence of increasing concentrations of Cl^-, HSO_4^- and $H_2PO_4^-$ were carried out in a manner similar to that given above for pure HNO_3. Plots of log RN vs. $1/T_{abs}$ were linear in all cases, with a slight scatter of points around the curves. This scatter is to be expected since the energetics of dissolution would vary with the concentration of the anions added. The results of these computations are included in Table 1 together with the values for 5.7 M HNO_3 devoid of foreign salts.

Inspection of the data of Table 1 reveals two distinct types of behaviour. One is represented by 90/10 Cu–Ni, and by AlBs in all solutions, as well as AlBz in the presence of HSO_4^- and $H_2PO_4^-$. Here, the activation energy of dissolution is either equal to or lower than that calculated for the pure acid. Since in all cases a lowering in the dissolution rate is recorded, one can safely conclude that the anions concerned do not interfere with the energetics of

TABLE 1

Free energies of dissolution of copper alloys in 5.7 M HNO_3, containing different anions

Alloy	Activation energy (kcal/mol^{-1}) in the presence of:			
	No additive	Cl^-	HSO_4^-	$H_2PO_4^-$
90/10 Cu–Ni	8.24	6.14	8.12	6.63
70/30 Cu–Ni	6.02	7.32	8.71	7.92
AlBs	7.60	(4.65)	5.74	6.34
AlBz	7.60	13.66	7.72	4.92

dissolution, but inhibit by way of blocking the surface to the NO_2 molecules, and thus interrupting the autocatalytic chain reaction.

The second type of behaviour, exemplified by 70/30 Cu–Ni in the presence of three test anions, and also by AlBz in Cl^--containing media, is distinguished by the fact that the activation energies of dissolution are appreciably higher than those in the pure acid. Here, it is assumed that the additives, beside competing for adsorption sites, interfere with the dissolution proper, probably through raising their ionization potentials by altering the structure of the double layer. Support for this idea must, however, be obtained from other more elaborate techniques.

The thermometric technique of corrosion testing [24] still offers one greatly appreciated advantage, namely, that of evaluating corrosion inhibitors. Much work has been published in this direction [4,25–28], and the following example, taken from actual practice in desalination plants, helps to illustrate this idea.

In the Umm Al Nar Desalination complex the distillers are regularly subjected to an acid wash to remove alkaline scale formed inside the heat exchangers. Acid washing is carried out using 5% HCl solution to which Stannine LTP(R) is added as inhibitor. This additive is an ICI product, based on dibutyl-thiourea.

To show that Stannine actually possesses inhibiting properties, its effect in small concentrations on the thermometric curves of the four copper alloys in 6 M HNO_3 was examined. The results are given by the curves of Fig. 6. The additive brings about a noticeable lowering of the maximum temperature, as well as an elongation in the time to reach it. Both effects cause a reduction in RN. Plots of the RN as function of additive concentration (not shown) are linear above ca. 0.25% Stannine. It is thus concluded that the additive adsorbs on the alloys surface according to a Freundlich isotherm. The slopes of these curves increase in the order: AlBz, 70/30 Cu–Ni < AlBs, 90/10 Cu–Ni. The additive does not adsorb equally on all surfaces and, hence, dissolution retardation by the same inhibitor concentration varies from case to case.

It might appear from the curves of Fig. 6 that corrosion inhibition by Stannine is not particularly high. One must not forget, however, that the experiments were carried out in a highly aggressive medium. In practice, however, acid wash of distillers is carried out with ca. 0.01 M HCl (pH 2) which is intrinsically less corrosive. In practice, a 2% solution of Stannine is commonly used in the wash solution, which ensures a very low rate of attack.

An extended account of the reaction between Stannine LTP and concentrated acids will be published elsewhere. We would like to mention, however, that all experiments with this compound were carried out in a well-ventilated fuming cupboard. The reaction between the additive and concentrated HNO_3, even in the absence of alloys, is extremely vigorous and produces harmful gases.

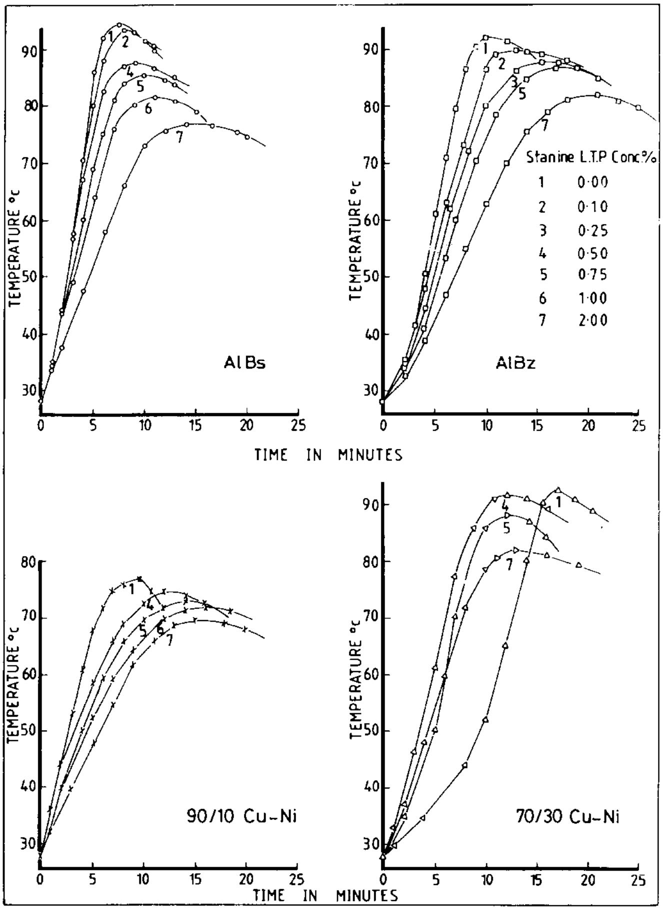

Fig. 6. Effect of additions of Stannine LTP on the thermometric curves of copper alloys in 6 M HNO_3.

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