

## SOME STUDIES ON CORROSION, PASSIVITY, INHIBITION AND IMMUNITY

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The variation of corrosion parameters with changes in anode and cathode area ratios, as also the rate equation for polarisation resistance for different metals have been dealt with.

Mechanism of dissolution of metals has been studied by various techniques such as potential step method. Kinetic criteria of cathodic protection to provide immunity has been discussed briefly.

The development of phosphating processes based on anodic treatment and development of inhibitive primers are also dealt with. Other aspects like examination of the tolerable limits of the chloride ion in inhibitive mixtures, adsorption of inhibitors by tensammetric measurements are also discussed.

**Keywords :** Corrosion; Inhibition; Passivity; Immunity

### CHANGE IN CORROSION POTENTIAL OF ALUMINIUM BY CHEMICAL SURFACE TREATMENTS

SURFACE treatments such as MBV, Pylumin, Arlok, EW processes reduced the corrosion of aluminium in NaCl solution though the potential became more negative (Rajagopalan, 1959). This was understood by the application of the theory of reaction rates to the coupled reactions responsible for corrosion.

Rajagopalan and Doss (1957) showed that the open circuit potential of a corroding metal could be given by the equation

$$\phi = \frac{RT}{F(1 + \alpha_c - \alpha_a)} \ln \frac{K_1 A_c}{K_2 A_a} \cdot C_0$$

where  $K_1$ ,  $K_2$  are terms which include the standard rate constants at equilibrium potentials for the reduction and oxidation reactions,  $C_0$  is the concentration of the reducible species,  $A_c$  and  $A_a$  are the areas on which the two types of reactions take place,  $\alpha_c$  and  $\alpha_a$  are the transfer coefficients of the electrode reactions and the metal solution potential. Assuming  $K_1$ ,  $K_2$  and  $C_0$  to be constant for the reason that reactions are unaltered the change in corrosion potential was understood in terms of the change in the area ratio if  $A_0$  was reduced. Fig. 1 presents the potential-time curves for aluminium treated by different pre-treatment processes and Fig. 2 presents the polarisation curves for one of them. The increased cathodic polarisation confirmed the decrease in cathodic area for treated aluminium.

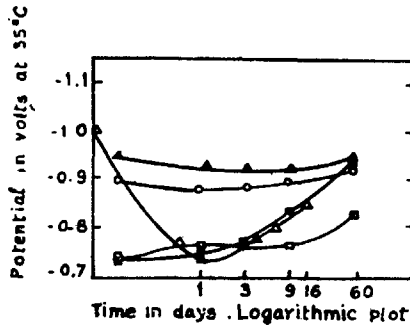


FIG. 1. Potential time curves of aluminium treated by different pretreatment processes

- Untreated Aluminium
- EW Process
- ▲—▲ Alok Process
- Pylumin Process
- △—△ MBV Process.

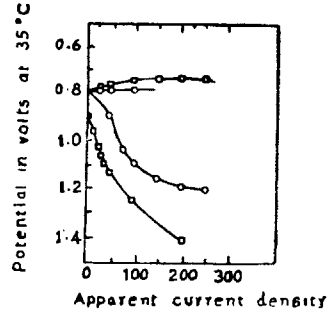


FIG. 2. Polarisation curves of treated and untreated aluminium

- Cathodic
  - Anodic - Untreated
  - Cathodic
  - Anodic - MBV treated
- Potentials were measured against SCE; Current Density in  $\mu\text{Amp}/\text{cm}^2$ .

Rajagopalan and Rangarajan (1961) plotted corrosion potential, corrosion current and polarisation against  $A_c/A_a$  and showed that corrosion potential remained fairly constant and corrosion current reached a maximum when the ratio was unity and the same degree of polarisation could be obtained at two different areas ratios (Figs. 3a, & 3b).

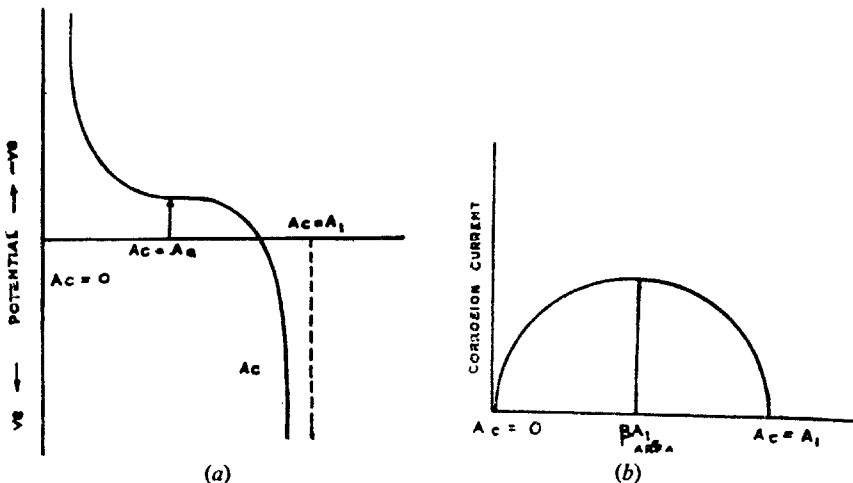


FIG. 3. (a) & (b) Effect of area ratios on corrosion potential and corrosion current.

#### RATE EQUATIONS FOR LINEAR POLARISATION

Following the work by Stern and Geary (1957), Rajagopalan and Rangarajan (1972) considered five models of corrosion processes and derived the rate equations for

polarisation resistance close to the corrosion potential for each of these models (Table I) and showed that the model of the corrosion process had to be identified to use the appropriate relationship.

TABLE I  
Main features of different models

Model	Net rate of reaction (cathodic +ve) $\Delta i = f(x)$ $x = F\phi/RT$	$x_c = F\phi_{corr}/RT$ Solution of $f(x) = 0$	$(\delta \Delta i / \delta x)_{\Delta i \rightarrow 0}$ Linear Polarisation
1	2	3	4
(A)	$i_{ck} \exp(\alpha_{ck}x) - i_{am} \exp(-\alpha_a x)$	$x_c = \frac{[\ln i_{am}/i_{ck}]}{(\alpha_{ck} + \alpha_a)}$	$(\alpha_{ck} + \alpha_a) i_{corr}$
(B)	$i_{cd} - i_{am} \exp(-\alpha_a x)$	$x_c = \frac{[\ln i_{am}/i_{cd}]}{\alpha_a}$	$\alpha_a \cdot i_{corr}$
(C)	$i_{ck} \exp(\alpha_{ck}x) + i_d - i_{am} \exp(-\alpha_a x)$	Solve for : $i_{zm} \exp(-\alpha_a x_i) - i_{ck}(\alpha_{ck} \cdot x_c) = i_d$	$(\alpha_{ck} + \alpha_a) i_{corr} - \alpha_{ck} i$
(D)	(a) $i_{cd} + i_{om}(x - x_m)$	$x_c = x_m - i_{cd}/i_{om}$	$i_{om}$
(D)	(b) $i_{ck} \exp(\alpha_{ck}x) + i_{om}(x - x_m)$	Solve for : $x_c \exp(x_c) = Z$ $Z = \alpha_{ck} \cdot i_{ck} \exp(\alpha_{ck} \cdot x_m) i_{om}$	$i_{om} + \alpha_{ck} i_{corr}$
Activation	$i_{ck} = n_1 F A_c C_{01} k_{s1} \exp(-\alpha_{ck} \phi^0 F/RT)$		
Diffusion	$i_{cd} = n_2 F A_c D_0 C_{0,2} / \delta$		
Dissolution	$i_{am} = n F A_a C_r k_{s2} \exp(\alpha_a \phi_m F/RT)$		
	$i_{om} = \text{Exchange Current density for metal reaction} \times A_a$		
	$x_m = F\phi_m/RT$		

### MEASUREMENT OF INSTANTANEOUS RATES OF CORROSION

A new method of study of the kinetics and mechanism of corrosion of metals was put forward. By potential step and current step methods transients were obtained which when extrapolated to  $t = 0$ , gave the instantaneous values free of the effects of concentration profiles established by superimposition of various overvoltages (Fig. 4). These could be substituted in the appropriate rate equations to get instantaneous rates of corrosion. These could also be used to find out Tafel slopes and reaction orders free of diffusion effects. Thus both kinetics and mechanism of corrosion could be elucidated.

The method used to bring out the enormous variation in corrosion current within the first 30 min in the case of iron in  $H_2SO_4$  and HCl solutions (Fig. 5).

### MECHANISM OF CORROSION

Using both steady state measurements and instantaneous measurements mentioned above, the mechanism of corrosion of zinc in concentrated sodium hydroxide solutions was elucidated (Muralidharan & Rajagopalan, 1978a, b). The steady

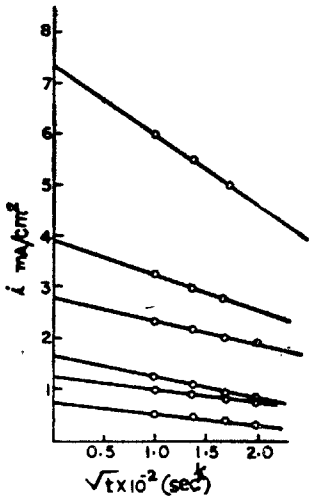


FIG. 4. Plot of  $i$  vs.  $\sqrt{t}$  for Zinc in Sodium hydroxide solution for determining the instantaneous corrosion rate.

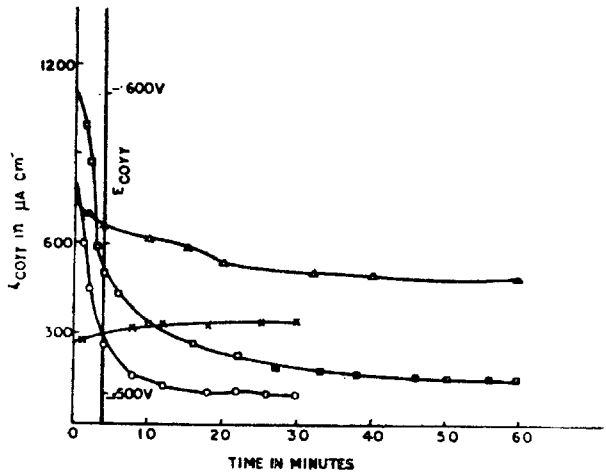


FIG. 5. Variation of corrosion current and corrosion potential of iron in acid solutions.  
 □—□ Corrosion Current, Fe in 1N HCl  
 ○—○ " " " Fe in 1N H<sub>2</sub>SO<sub>4</sub>  
 ×—× Corrosion Potential, Fe in 1N H<sub>2</sub>SO<sub>4</sub>  
 △—△ " " " Fe in 1N HCl

state measurements showed agreement with the Bockris mechanism for the formation of zincate ions in which the rate determining step was the second electron transfer and the dependence of  $E_{\text{corr}}$  and  $i_{\text{corr}}$  on solution parameters could be explained if redeposition of zincate was taken into account. However, the results for the instantaneous measurements could be best explained only by using Ferr and Hampson mechanism in which the first electron transfer was the slow step and the dependence of  $i_{\text{corr}}$  on solution parameters agreed with the relationship obtained if redeposition of zincate was not taken into account (Table II). The rate determining

TABLE II

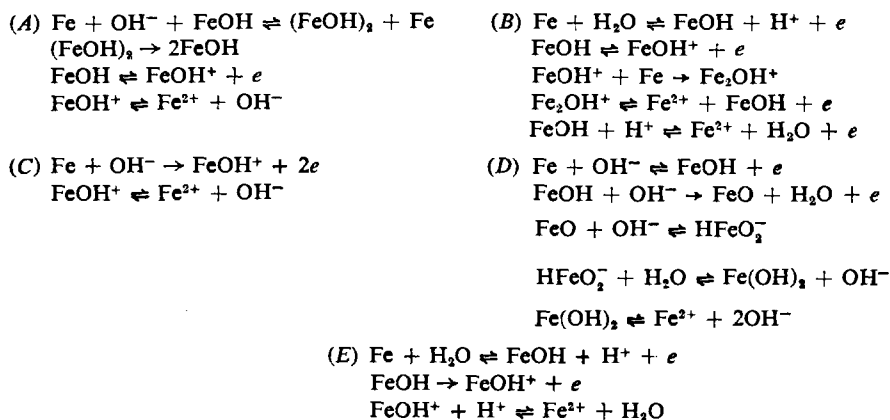
*Different schemes proposed for dissolution/deposition of zinc*

(1) $\text{Zn}_{\text{ad}} + 2\text{OH}^- \rightarrow \text{Zn}(\text{OH})_2 + 2e$ $\text{Zn}(\text{OH})_2 + 2\text{OH}^- \rightleftharpoons \text{Zn}(\text{OH})_4^{2-}$	(2) $\text{Zn}_{\text{ad}} + \text{OH}^- \rightarrow \text{Zn}(\text{OH})_{\text{ad}} + e$ $\text{Zn}(\text{OH})_{\text{ad}} + \text{OH}^- \rightleftharpoons \text{Zn}(\text{OH})_2 + e$ $\text{Zn}(\text{OH})_2 + 2\text{OH}^- \rightleftharpoons \text{Zn}(\text{OH})_4^{2-}$
(3) $\text{Zn} + \text{OH}^- \rightleftharpoons \text{ZnOH}^-_{\text{ad}}$ $\text{ZnOH}^-_{\text{ad}} \rightarrow \text{ZnOH}_{\text{ad}} + e$ $\text{ZnOH}_{\text{ad}} + \text{OH}^- \rightleftharpoons \text{Zn}(\text{OH})_2 + e$ $\text{Zn}(\text{OH})_2 + 2\text{OH}^- \rightleftharpoons \text{Zn}(\text{OH})_4^{2-}$	(4) $\text{Zn} + \text{OH}^- \rightleftharpoons \text{Zn}(\text{OH}) + e$ $\text{Zn}(\text{OH}) + \text{OH}^- \rightleftharpoons \text{Zn}(\text{OH})_2^-$ $\text{Zn}(\text{OH})_2^- + \text{OH}^- \rightarrow \text{Zn}(\text{OH})_3^- + e$ $\text{Zn}(\text{OH})_3^- + \text{OH}^- \rightleftharpoons \text{Zn}(\text{OH})_4^{2-}$

step of the cathodic hydrogen evolution reaction was found to be as proposed by Kabanov. The study of the mechanism of corrosion of pure iron in phosphoric acid solutions (Muralidharan & Rajagopalan, 1978*a, b*) showed that it was the same as that of sulphuric acid (Bockris *et al.*, 1961) (*see* Table III) and the difference in behaviour arose from the slow coverage of the surface by adsorption of phosphate ions.

TABLE III

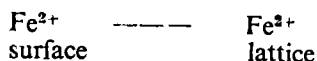
*Five possible mechanisms for the dissolution and deposition of iron*



#### ANODIC PHOSPHATING

A new method of phosphating involving only the use of sodium phosphate solution in the place of those containing zinc or manganese phosphate solutions was developed. In this method, phosphating was done by passing a current with the object to be phosphated as anode or by maintaining a passivation potential on the object to be phosphated (Rajagopalan *et al.*, 1972 & 1973). Unlike chemical phosphating this could be carried out at room temperature (Fig. 6).

By potential step method, it was shown that three distinct current peaks (Fig. 7) were observed in  $\text{Na}_2\text{HPO}_4$  solutions in the *pH* range three to five (Muralidharan & Rajagopalan, 1978*a, b*). The peaks were identified as due to the two dimensional growth of phosphate film on steel. The dependence of growth rate constant on potential, *pH*,  $\text{Fe}^{2+}$  ions and phosphate ions concentration showed that the rate determining step in the formation of the film is



By using the Hackerman square wave techniques (Brod & Hackerman, 1957) the electrical capacity of iron/phosphate solution interface was measured at different potentials and compared with anodic behaviour as obtained from *E-i* relationships (Fig. 8). It was concluded that adsorption of phosphate ion preceded passivation.

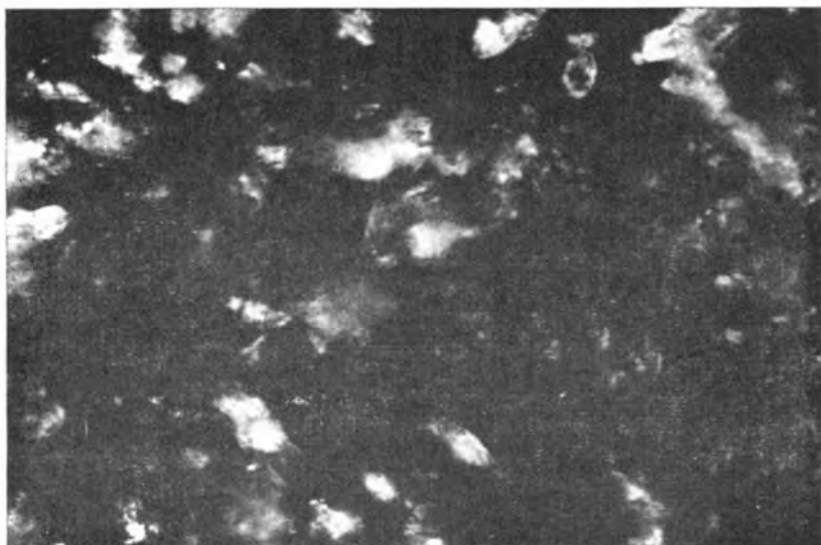


FIG. 6. Photomicrograph of anodically phosphated steel at  $4\text{mA}/\text{cm}^2$  for 15 minutes.

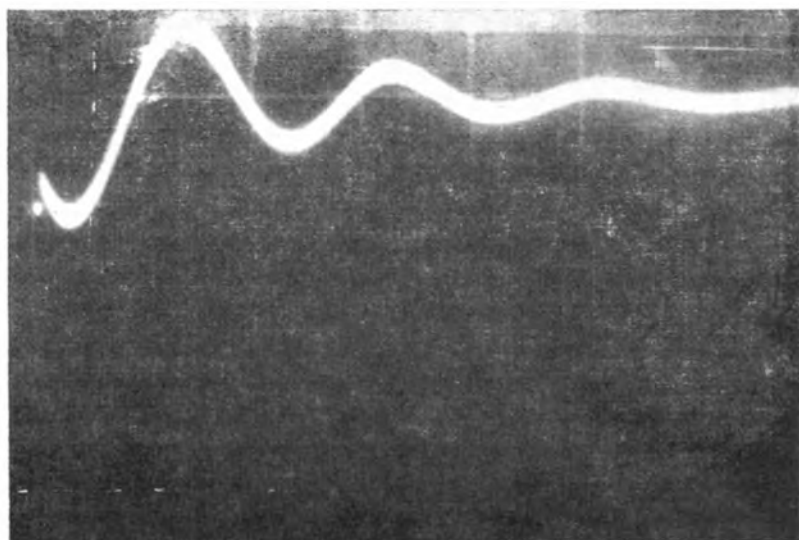


FIG. 7.  $i-t$  transient for steel in 0.135M Phosphate at pH 2.9

x axis 1cm = 0.1m. sec.

y axis 1cm = 0.2mA

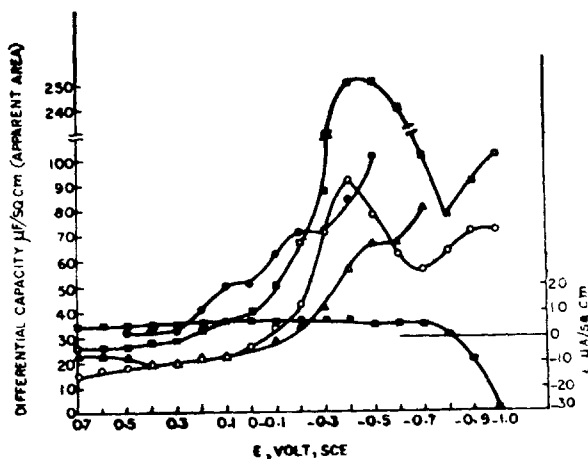


FIG. 8.  $E$  vs. differential capacity for inhibitor solution. (Potentiostatic  $E$  vs.  $i$  curve for 0.1M  $\text{Na}_2\text{HPO}_4$  (■) is also given)

○—○ 0.1M  $\text{Na}_2\text{HPO}_4$       □—□ 0.1M  $\text{Na}_2\text{B}_4\text{O}_7$   
 △—△ 0.1M  $\text{K}_2\text{CrO}_4$       ●—● 0.1M  $\text{NaOH}$

#### ACTIVATION OF PASSIVATED STEEL

Potentiostatic study of the behaviour of steel in inhibitor solutions containing oxygen showed that the breakdown of passivity took place at specific potentials and the peak potentials in galvanostatic studies coincided with these. The breakthrough potential could be related to the concentration of inhibitor and chloride ion concentration by the equation

$$E_b = A + BP_{\text{Cl}^-} - CP_I$$

where  $P_{\text{Cl}^-}$  refers to the negative logarithm of chloride ion concentration and  $P_I$  refers to the negative logarithms of inhibitor ion concentration.

Breakthrough potential and passivation current, provide yet another method of distinguishing the effectiveness of inhibitive anions. An inhibitive mixture based on phosphate and borate which gave the highest breakthrough potential at lowest passivation current was formulated for use in cooling systems.

Constant current measurements (Rajagopalan *et al.*, 1970) indicated that the inhibitive anions seemed to fall into three categories viz., (a) those which cannot re-passivate pits once formed at breakthrough potential e.g., hydroxide, chromate, (b) those which re-passivate all the pits when the potential fell below the breakthrough potential e.g., phosphate, borate and (c) those which help in the growth of a film subsequent to pitting at or above the breakthrough potential e.g., benzoate, nitrite, tungstate, molybdate and hence give rise to a constant potential (Fig. 9).

Constant potential measurements (Rajagopalan & Venkatachari, 1975) showed three distinct types (a) increase of current with time e.g., chromate, borate, hydroxyl, phosphate, (b) constant current with time e.g., nitrite, benzoate and (c) decrease of current with time e.g., molybdate and tungstate (Fig. 10).

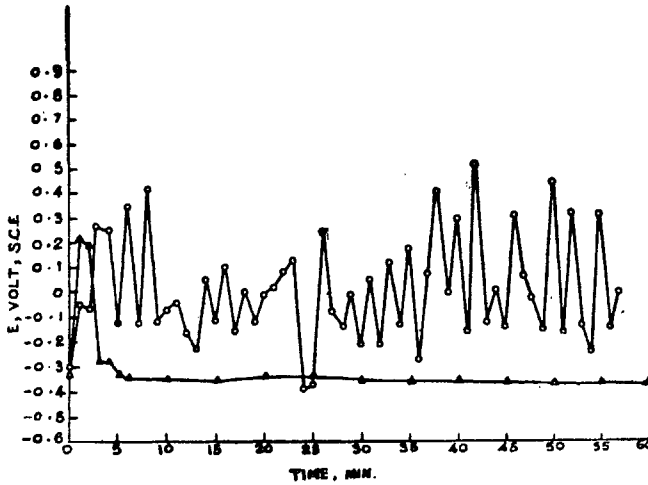


FIG. 9. Galvanostatic  $E$  vs.  $t$  curve for 0.1M Inhibitive solutions containing 0.05M NaCl

○—○ 0.1M  $\text{Na}_2\text{HPO}_4$  + 0.05M NaCl

△—△ 0.1M  $\text{Na}_2\text{CrO}_4$  + 0.05M NaCl

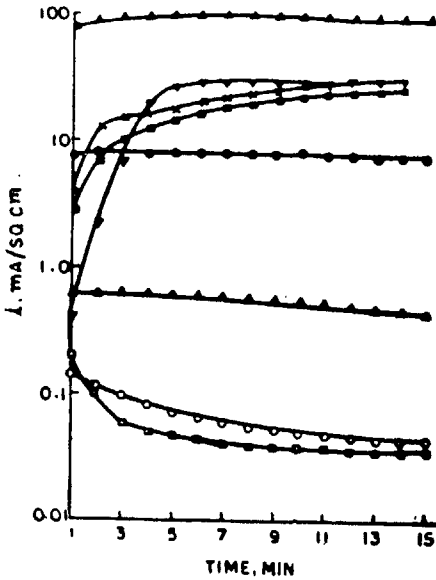


FIG. 10.  $i$  vs.  $t$  at 50mV above breakthrough potential in 0.1M Inhibitor solution containing 0.1M NaCl.

▲—▲  $\text{Na}_2\text{HPO}_4$     ▽—▽ NaOH  
 ×—×  $\text{Na}_2\text{CrO}_4$     ○—○  $\text{Na}_2\text{WO}_4$   
 □—□  $\text{Na}_2\text{MoO}_4$     △—△  $\text{C}_6\text{H}_5\text{COONa}$   
 ●—●  $\text{NaNO}_2$     ■—■  $\text{Na}_2\text{B}_4\text{O}_7$

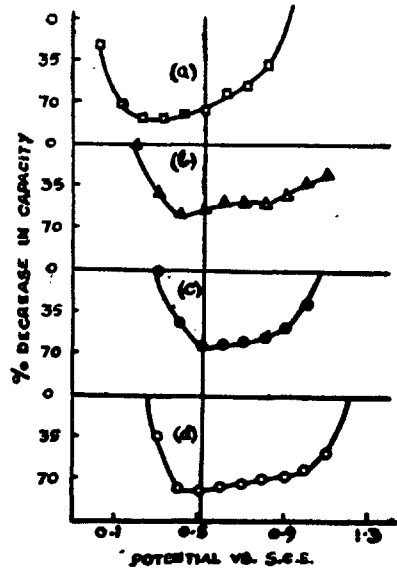


FIG. 11. Percentage decrease in capacity by inhibitor at different potentials.

(a) Cyclohexylamine

(b) Morpholine

(c) *p*-Toluidine

(d) Naphthylamine



## APPLICATION OF TENSAMMETRY TO CORROSION INHIBITION

Tensammetry was applied to find out the potential range over which adsorption takes place on metal surfaces as represented by mercury. By this method, it was shown that meta-dinitrobenzene was not adsorbed on mercury but naphthol is adsorbed over a wide range of potentials (Fig. 11). Both act as vapour phase inhibitors (Rajagopalan *et al.*, 1959).

## TOLERABLE LIMIT OF CHLORIDE IN CONCRETE

In a solution of sodium or calcium hydroxide the potential of steel jumped to the potential of oxygen evolution on application of a small anodic current (Rajagopalan & Venu, 1968; and Rajagopalan *et al.*, 1969). When chloride was present, the jump does not take place at high chloride concentration. At intermediate concentrations, the jump took place but fell back after a time. When the current required for potential to jump was plotted against chloride ion concentration an S type curve was obtained which divided NaOH-NaCl solutions into two types those which require very large current and those which require very small current to jump the potential of  $O_2$  evolution (Fig. 12). The transition point corresponded to a current of  $290\mu\text{Amp}/\text{cm}^2$  using this current, the tolerable limit for chloride for this concentration of NaOH were found out. This showed that only 100ppm  $Cl^-$  was tolerated by cement extract before it became corrosive. The rest potentials in these solutions were next measured with respect to time and maximum potentials reached were taken and impressed upon the system by means of a potentiostat. It was shown that 1000ppm of  $Cl^-$  could be tolerated by cement extract. It was concluded that the application of external current modified the tolerable limit. The tolerable limit from the potentiostatic method agreed with that given by linear polarisation measurements (Rajagopalan *et al.*, 1975). Based on this, an inhibitor solution to be added to cement which could raise the tolerable limit to such a high value that the environment

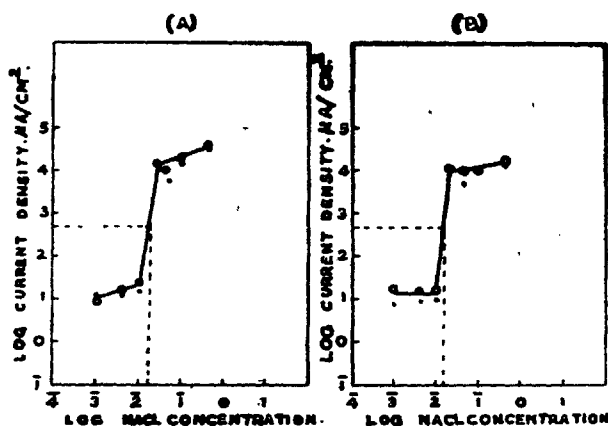


FIG. 12. Applied current density vs. Sodium chloride concentration (A) Immediately after immersion of specimen to get +0.3V (SCE) (●—●) and +0.6V (SCE) (○—○) (B) 48hr after immersion in solution to get +0.3V and +0.6V (SCE)

would remain inhibitive in spite of the maximum availability of chloride in concrete under natural conditions was developed. The protection treatment for steel reinforcement based on this has been adopted on a large scale in the country in the construction of bridges and buildings.

#### PREVENTION OF TARNISHING OF COPPER AND BRASS

When copper or brass was made anode in an alkaline solution of MBT, a protective film was formed which prevented tarnishing of copper and brass in sulphide solutions or SO<sub>2</sub> atmosphere (Rajagopalan & Aravamudhan, 1968).

#### CATHODIC PROTECTION

Kinetic criteria of cathodic protection to provide immunity were put forward (Rajagopalan, 1961). Two well-defined situations were considered where the reducible species is in abundant supply and only activation controlled cathodic reaction has to be considered where the rate of diffusion of reducible species controls the cathodic reaction during cathodic protection. The kinetic equations derived are

$$\eta = \beta_z \ln i_{\text{corr}}/i_x - \beta'_a \ln C/i_0 \quad \dots(1)$$

where  $\beta_z$  and  $\beta'_a$  are the slopes of the cathodic and anodic reactions,  $i_0$  is the exchange current density for anodic reaction,  $i_{\text{corr}}$  is corrosion current and  $C$  is the permissible corrosion current.

$$\eta = \frac{RT}{ZF} \ln C/i_L \quad \dots(2)$$

where  $i_L$  is the limiting current.

The Hull cell was applied to test equation (1) in relation to the cathodic protection of steel in sulphuric acid (Rajagopalan & Ramachandra Row, 1960) where it was found that in the presence of inhibitors the current required for cathodic protection was reduced and the protection potential changed although the corrosion potential was only slightly altered.

When cathodic protection is used to prevent pitting corrosion it may be sufficient to cathodically polarise to a value close to the Flade potential in which case

$$i_{\text{appl}} = i_{\text{passive}} \cdot 10 \frac{(E_{\text{passive}} - E_{\text{Flade}})}{\beta_c}$$

#### INHIBITIVE PRIMERS

A study made elsewhere of the known chromate pigments showed that only zinc chromate, barium chromate and calcium chromate give sufficient chromate ion in solution to inhibit in distilled water (>14mg/100ml). These were incorporated in different vehicles. It was found that zinc chromate gave sufficient chromate ion in solution only in two vehicles, modified phenolic stand oil and epoxy

ester. Barium chromate and calcium chromate gave sufficient chromate ion in other vehicles such as alkyd linseed oil. Two types of inhibitive primers were then developed zinc chromate on epoxy ester and calcium chromate iron oxide in epoxy ester. Both give for better performance than the one containing zinc chromate and red oxide.

#### ACKNOWLEDGEMENT

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#### Discussion

L. I. KRISHTALIK (*Institute of Electrochemistry, Academy of Sciences of USSR, Moscow*):

1. What is the reason for different r.d.s. for Zn-dissolution under steady and transient conditions ?
2. What are the arguments in favour of the mechanism of H<sub>2</sub> evolution via Na<sup>+</sup> discharge ?

K. S. RAJAGOPALAN (*Central Electrochemical Research Institute, Karaikudi*): 1. I do not think the rate determining step changes. In steady state measurements, the rate determining factor is really the slow diffusion of zincate away from the surface. The diagnostic data consequently

seem to indicate that the second electron transfer is the r.d.s. But if we eliminate the redeposition of zincate in the measurement by using the transient techniques the slow step is found to be the first electron transfer which follows ad-atom or ad-ion diffusion. 2. Three mechanistic schemes have been considered including hydrogen evolution *via*  $\text{Na}^+$  discharge, cathodic transfer coefficient reaction, reaction order of one for  $\text{Na}^+$ , reaction order of 0 for  $\text{OH}^-$  in steady state and transient measurements show best agreement with the Kabanov mechanism of hydrogen evolution *via*  $\text{Na}^+$  discharge.

HIRA LAL (*Indian Institute of Technology, Bombay*) : The potential corresponding to complete protection should not be dependent on the presence or otherwise of the inhibitor in the solution. Has some other criterion been used to define the protection potential ?

K. S. RAJAGOPALAN : In the ultimate, the equilibrium potential of the anodic reaction is the potential at which there is no net dissolution current and hence complete cathodic protection. But it would not be realistic from the point of view of practical use of cathodic protection. We used highly polished plates in the Hull Cell study and the dividing line was identified easily for the loss of polish and etching. The current corresponding to such a dividing line could also be considered as cathodic protection current from a practical point of view. The potential corresponding to this current is affected by the inhibitor as anodic polarisation of the metal is affected by the inhibitor. Hence, we get a protection potential which is removed from the so called equilibrium potential by several tens of milli volts depending upon the system and such a protection potential could be affected by inhibitor.

C. P. DE (*Naval Chemical & Metallurgical Laboratory, Bombay*) : 1. Were the thickness of the paint films for various types of compositions comparable ? 2. The compositions based on vinyl resins are known to be very resistant to permeability to moisture and ionic uptake making them corrosion resistant coatings. Such compositions have not been included in the present programme of work. Can the author give reasons for it ?

K. S. RAJAGOPALAN : While it is not possible to get identical thicknesses of the different films, we could get comparable thicknesses say  $75 \pm 10$  microns. These comparable thicknesses were taken for the study. Initially we have studied the varnishes earlier used by us in our field exposures on protective schemes i.e., epoxy ester, phenolic stand oil, epoxy polyamide chlorinated rubber. But we will extend to other durable varnishes also like vinyl, polyurethane etc.