

**THE CORROSION BEHAVIOUR OF STEEL IN
PHOSPHATE SOLUTIONS IN NEUTRAL AND ALKALINE MEDIA**

BY

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ABSTRACT

The potential of steel electrode in aqueous phosphate solutions was measured at 30°C as a function of both pH and electrolyte concentration. It is suggested that the metal behaves as phosphate electrode in the pH range 6.42-8.5 and at phosphate concentration higher than 0.1 M. At higher pH values the potential decreases with phosphate concentration up to a maximum value. This was attributed to the formation of a protective semiglassy interface. The potential increase on further increase of concentration; this might be due to the area of the metal.

INTRODUCTION

The action of phosphate anions especially in neutral and alkaline solutions on steel surface has long been explained on the basis of film formation theory [1]. It was found that the primary phosphate ions promoted the corrosion of steel [2-4]. It was however, pointed out that phosphate forms initially a sparingly soluble ferrous phosphate ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) which is converted into ferric

phosphate in the presence of air [5].

The effect of phosphate anions as corrosion inhibitors for steel in the presence of air [6] was taken to demonstrate that the reduction of the inhibitors is not a prerequisite for passivation, and that inhibition is mainly due to the reduction of oxygen in presence of these inhibitors. Phosphate considered as inhibitive ions affect the positive branch of the electrocapillary curve [7].

In this paper the investigation is extended to the neutral and alkaline phosphate solutions.

EXPERIMENTAL

The potential of the steel electrode was measured as a function of time within a period of 24 hours in aqueous phosphate solutions of concentration varying between 10^{-4} and 10.5 M. In order to prevent any variation in potential due to pH changes, the phosphate solutions were adjusted to definite pH values except in the case of tertiary phosphate solutions. The different series and the corresponding pH values are given in table 1. The electrode was prepared from low carbon steel rod of 6 mm diameter (0.05% C). The chemicals used were of analar grade.

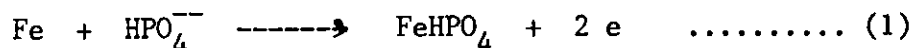
RESULTS AND DISCUSSION

The plot of the steady state potentials against the logarithm of the molar phosphate concentration for the first

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two series, pH 6.42 and pH 8.5 are shown in figure 1. For the first series the potential was kept constant up to $10^{-2}M$, above which a linear relation was observed with a slope of -60mV. For the second series the potential remained constant up to 0.06M and then a straight line having a slope of -67 mV was obtained.

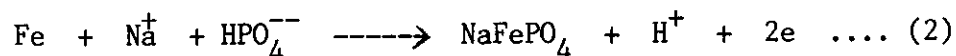
From the free energy data [8] the standard potential of $Fe/Fe(OH)_2$ at unite OH^- ion activity and at $30^\circ C$ was calculated as -0.819 V. Since the standard potential are little affected with temperature [9] this value was taken to represent the standard potential at $30^\circ C$. On increasing the phosphate concentration the metal phosphate becomes more stable than the hydroxide and the electrode behaves as a phosphate electrode. As thermal data for the different iron phosphate are not available, the elucidation of the electrode reaction was based on the slopes of the potential - log C relation only. The experimental slopes observed in primary - secondary phosphate solutions (-67mV) cannot be ascribed to a secondary phosphat film since the reaction ;



requires a slope of $-30 mV$. at $30^\circ C$. To account for the observed high slopes, it was suggested that the resisting product is sodium ferrous phosphate which forms on the electrode according to ;

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The electrode potential is given by :

$$E = E_o + \frac{RT}{2F} \ln \frac{[\text{H}^+]}{[\text{Na}^+][\text{HPO}_4^{--}]} \dots (3)$$

The concentration of Na^+ ion is proportional to that of H^+ ion hence, at constant pH value the equation reduces to;

$$E = E_o - \frac{2.303 RT}{F} \log[\text{HPO}_4^{--}] \dots (4)$$

indicating a slope of 60 mV at 30° C which is in good agreement with the observed values.

As evident from fig. 1, the potential - log C relation is shifted towards more negative values as the pH is increased. This agrees with equation (3). The theoretical pH effect deduced from this equation is expressed as:

$$(dE/dpH) (\text{HPO}_4^{--}) (\text{Na}^+) = - 30 \text{ mV} \dots (5)$$

Hence a change of 2.08 pH unite requires a shift in potential of 62.4 mV, which is fairly consistent with the observed shift in potential amounting to 70 mV.

The behaviour in alkaline solutions

Corrosion inhibition by phosphate ions:

Measurements in very diluted equimolar solutions of

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secondary-tertiary phosphates gave a potential of -0.50 V (fig. 2). Since the calculated potential for the $\text{Fe}/\text{Fe}(\text{OH})_2$ couple in these solutions (pH 10.96) is 0.638 V, the observed potential does not correspond to a hydroxide film. Moreover, the potential decreases with increasing the concentration till reaches -0.0435 V. in the 0.1 M solution and then increases sharply with further increase in concentration. Solutions of pure sodium tertiary phosphate exhibited a similar behaviour but the maximum potential amount to -0.325 V and correspond to the 0.01 M solution. These results indicate that although the electrode is covered with a certain phosphate, steel does not behave as a phosphate electrode at such high pH value. The increase of potential with phosphate concentration, indicate that phosphate ions exert an inhibiting effect on the corrosion of steel, as already was observed with lead [2], zinc [3] and tin [4].

Anodic polarization measurements in secondary- tertiary phosphate solutions showed that, up to 10^{-4} A/cm^2 , the observed potentials (although including resistance overpotential) are markedly smaller than those shown in fig. 2. It is therefore obvious that the freshly formed phosphate layer is not so inhibitive as the aged one persisting on a nonpolarised electrodes; a fact which means that the interface between the layer and solution acquires additional inhibitive properties with elapse of time. It is suggested that adsorption of phosphates ions in a certain orientation or in a

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certain condensed form is responsible for the formation of the inhibitive interface. This suggestion was used to explain similar behaviour in case of lead [2], tin [3] and zinc [4].

The increase of potential after reaching a minimum value is more sharp than expected if the metal behaves as a phosphate electrode. Hence the potentials are still mixed potentials rather than thermodynamic ones. Cathodic polarisation measurements in 0.1 - 0.05 M secondary - tertiary phosphate solutions revealed that, at a given current density the potential becomes more negative as the concentration is increased. Since the solutions have the same pH value, the shift of potential to the negative side is attributed to the decrease of the surface area of the cathode. This was taken to indicate that phosphate ions are adsorbed on the metal surface, with the result that the actual current density is larger than the apparent value. In dilute solutions, the concentration has no effect on the cathode potential. The increase of corrosion potential with concentration (fig. 2) can thus be attributed to adsorption of phosphate ions on the cathodic areas of the electrode surface.

The corrosion potentials were also measured in tertiary phosphate solutions in presence of 0.01 M and 0.5 M NaOH. The results are similar to those obtained in pure tertiary

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phosphate solutions, except that the minimum potentials are reached at higher phosphate concentrations (fig. 3). It is worthy to mention that in presence of 0.5 M NaOH zinc is not protected by PO_4^{-3} ions [3]. The present investigation shows that steel phosphate coating of valuable corrosion resisting properties in much alkaline solutions.

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Table I

The different series and the corresponding pH- value:

Series No.	Composition	pH
I	$\text{NaH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$	6.42
II	Na_2HPO_4 (in ammonium acetate buffer)	8.50
III	$\text{Na}_2\text{HPO}_4 + \text{Na}_3\text{PO}_4$	10.80
IV	Na_3PO_4	9.4-12.8
V	Na_3PO_4 (in 0.1 N NaOH)	11- 13
VI	Na_3PO_4 (in 0.5 N NaOH)	14

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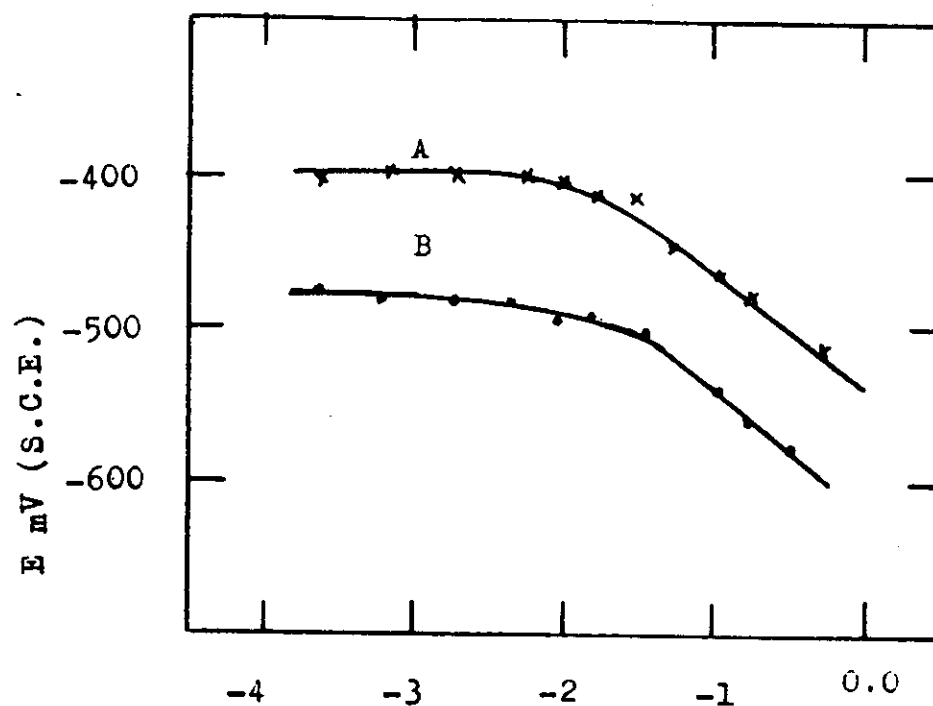
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Figure 1 : Potential of steel in : $\log C$

A- $\text{NaH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$.

B- Na_2HPO_4 in amm. acetate buffer.

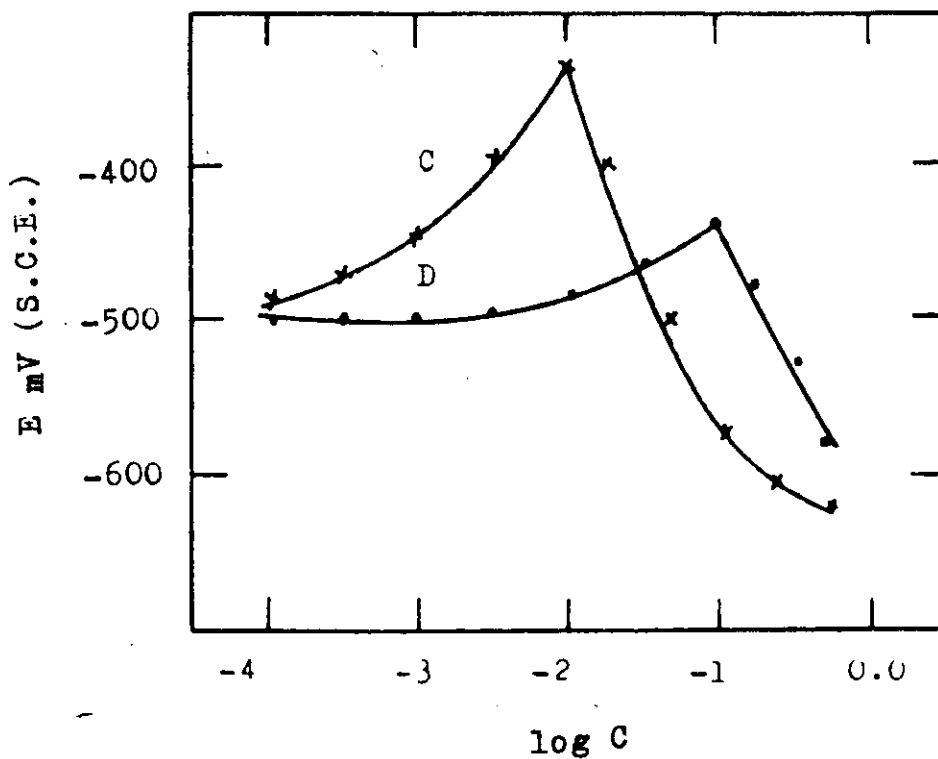


Figure 2 : Potential of steel in :

C- Na_3PO_4 solution.D- $\text{Na}_2\text{HPO}_4 + \text{Na}_3\text{PO}_4$.

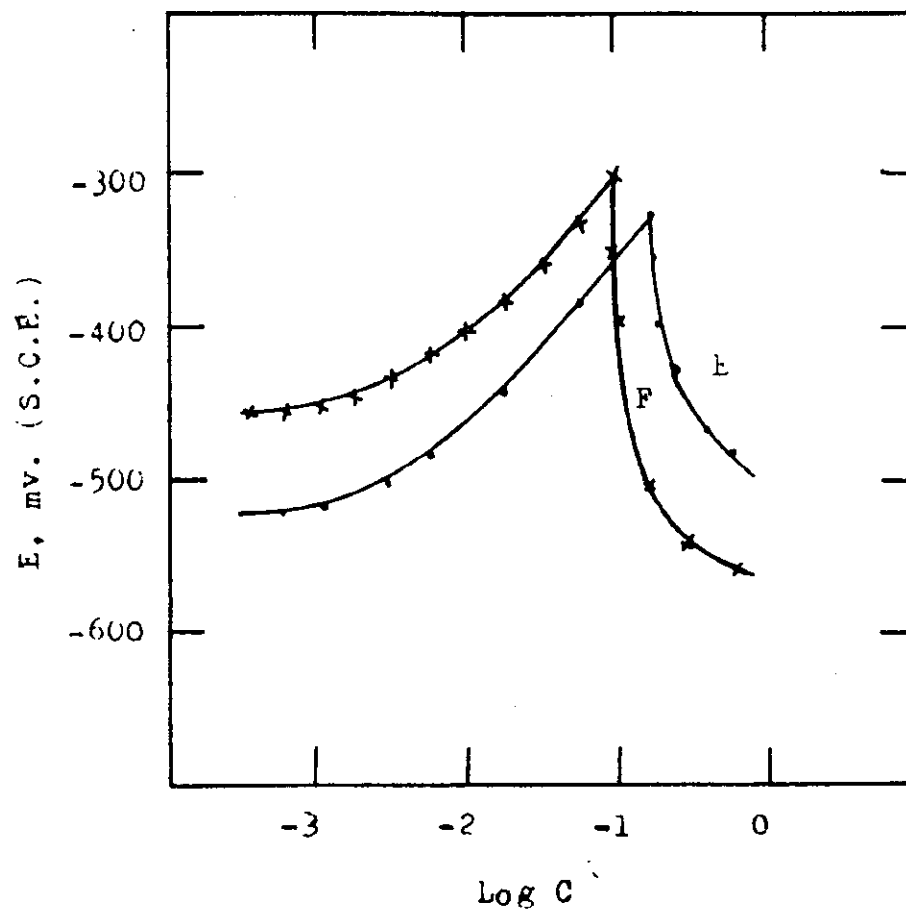


Figure 3, Potential of Steel in ;

E- Na_3PO_4 in 0.5 N NaOH,
 F- Na_3PO_4 in 0.01 N NaOH.

التصرف التآكل للصلب فى محاليل فوسفات متعادلة وقلوية

د. جمال كامل جمعة د. حسنى يوسف البرادعى د. سعد محمد عبد الوهاب
 تم قياس جهد قطب الصلب فى محلول مائى يحتوى على أيونات
 الفوسفات عند درجة ٣٠م وعلاقة هذا الجهد بالرقم الهيدروجينى والتركيز
 الالكترولىتى يعتقد أن الفلز يعمل كقطب فوسفات فى مدى رقم هيدروجينى
 ٦,٤ - ٨,٥ ويعمل كتركيز فوسفات فى تركيز أيون أعلى من ٠,١ مول أما
 عند أرقام هيدروجينية أعلى فأن الجهد يقل بزيادة تركيز أيون الفوسفات حتى
 قيمة دنيا ويمكن أرجاع ذلك الى تكوين طبقة حافظة شبة زجاجية وكنتيجة
 للوصول الى الحد الأدنى فان الجهد يزداد بزيادة التركيز ويمكن أرجاع ذلك
 الى الزيادة فى سطح الفلز .