

THE CHANGE OF pH UNDER A PAINT FILM DUE TO CATHODIC PROTECTION*

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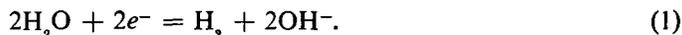
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Abstract—The diffusion of OH⁻-ions and H₂ formed during cathodic protection through a paint film is studied. The diffusion equation is solved for non-stationary conditions and from this the steady state is also derived. It is shown that under usual operating conditions of cathodic protection of ships the stationary state is reached in about 15 days. The danger of paint deterioration through high alkalinity and blistering is found to increase with current density and paint film thickness and with decreasing diffusion coefficient in the paint. For practical calculations a better knowledge of diffusion coefficients in paints is needed.

INTRODUCTION

IN ORDER to preserve the almost perfect smoothness of the submerged part of a ship's hull and its paint system, an impressed current protection system is used on many ships. However, occasionally unexpected disbonding or blistering of the paint-coat is observed. To find an explanation for this phenomenon the situation at the steel-paintcoat-water interface has to be studied in detail.

When paint has been submerged in water for some time it will be penetrated by water. It will then conduct a current and ions can pass through the film by diffusion as was shown for example by Brasher *et al.*^{1,2} Part of the current used for the cathodic protection will thus pass through the paint film. At the surface of the metal a cathodic reaction takes place, which in neutral solution may be written:



The hydroxyl ions and the hydrogen diffuse outwards through the film to the surrounding solution, as long as its solubility has not been surpassed. The hydroxyl-ion concentration and thus the pH will increase at the steel-paint interface, which might cause deterioration of the paint. If the hydrogen solubility is surpassed this may lead to blistering.

Most previous studies of the interaction between paint films and cathodic protection have been limited to phenomenological considerations (see, e.g.³⁻⁷). Engell and Forchhammer⁸ calculated the change in pH at a metal surface due to cathodic protection, but did not consider the influence of the paint-film on the diffusion processes.

*Manuscript received 24 January 1975.

In this paper the diffusion through a paint film during cathodic protection is analysed and the concentration changes at the steel-paint interface are calculated.

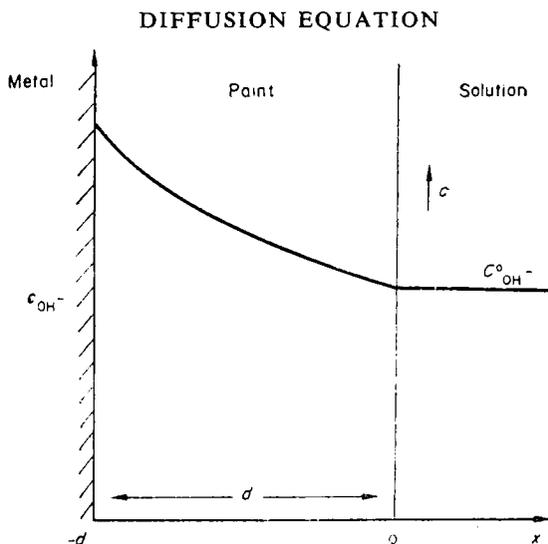


FIG. 1. Schematic cross-section through paint film with hydroxyl-ion concentration and geometry indicated.

In Fig. 1 a schematic cross-section of the system under consideration is given. The thickness of the paint film is d , the concentrations in the solution are supposed to be uniform (C^0) up to the paint-solution interface which is situated at $x = 0$.

The diffusion through the paint film of a component i is governed by Fick's second law:

$$\frac{\partial^2 C_i}{\partial x^2} - \frac{1}{D_i} \frac{\partial C_i}{\partial t} = 0, \quad (2)$$

with C_i = concentration of component i , D_i = diffusion coefficient of i . When a current I passes through the film Fick's first law gives the boundary condition:

$$\left(\frac{\partial C_i}{\partial x} \right)_{x=-d} = - \frac{I \nu_i}{n F D_i}, \quad (3)$$

where, when a cathodic current is taken positive, the stoichiometric coefficient ν_i is positive for substances produced by that reaction. F is the Faraday and n is the number of electrons consumed in the reaction. For reaction (1) we thus have: $\nu_{H_2} = 1$, $\nu_{OH^-} = 2$, $n = 2$.

From the assumption of uniform concentration C_i^0 in the solution we have as the second boundary condition:

$$C_i(x = 0) = C_i^0 \text{ for all } t. \quad (4)$$

Finally, when we take the current to be switched on at $t = 0$, we have as initial condition:

$$C_i(\text{all } x) = C_i^\circ \text{ for } t < 0, \quad (5)$$

In order to bring the set of equations (2)–(5) in a more convenient form we introduce the relative concentration u_i as:

$$u_i = \frac{C_i - C_i^\circ}{C_i}. \quad (6)$$

Then the equations (2)–(5) become:

$$\frac{\partial^2 u_i}{\partial x^2} - \frac{1}{D_i} \frac{\partial u_i}{\partial t} = 0, \quad (2a)$$

$$\left(\frac{\partial u_i}{\partial x} \right)_{x=-d} = - \frac{I_{v_i}}{nFD_i C_i^\circ} = -A_i \quad (3a)$$

$$u_i(x = 0) = 0 \text{ all } t, \quad (4a)$$

$$u_i(\text{all } x) = 0 \text{ } t < 0. \quad (5a)$$

SOLUTION OF DIFFUSION EQUATION

A convenient way to solve the set of equations (2a)–(5a) is by means of the Laplace-transformation.^{9,10} We denote the Laplace-transform of a function u by \bar{u} and use $\mathcal{L}(u)$ as a symbolic notation for the Laplace-transformation of the function u . We can then write:

$$\mathcal{L}(u) = \bar{u} = \int_0^\infty e^{-pt} u(x, t) dt. \quad (7)$$

Applying this to equation (2a) and using the initial condition (5a) gives the ordinary differential equation

$$\frac{d^2 \bar{u}_i}{dx^2} - \frac{p}{D_i} \bar{u}_i = 0, \quad (8)$$

with as boundary conditions obtained from equations (3a) and (4a):

$$\left(\frac{d\bar{u}_i}{dx} \right)_{x=-d} = - \frac{A_i}{p}, \quad (9)$$

$$\bar{u}_i = 0 \quad x = 0. \quad (10)$$

The general solution of equation (8) is

$$\bar{u}_i = Pe^{x\sqrt{p/D_i}} + Qe^{-x\sqrt{p/D}} \tag{11}$$

From equation (10) we obtain

$$P + Q = 0 \tag{12}$$

and from (9)

$$\sqrt{\frac{p}{D_i}} \left(Pe^{-d\sqrt{p/D_i}} - Qe^{d\sqrt{p/D_i}} \right) = -\frac{A_i}{p} \tag{13}$$

Solving P and Q from equations (12, 13) and substituting into equation (11) gives after some rearrangement:

$$\bar{u}_i = -\frac{A_i D_i}{p^{3/2}} \cdot \frac{\text{Sinh } x\sqrt{p/D}}{\cosh d\sqrt{p/D_i}} \tag{14}$$

This is not a transform occurring in the standard tables of transforms which means that the general inversion theorem would have to be used.

However, it is easily seen that:

$$\frac{D_i^{1/2}}{p^{3/2}} \cdot \frac{\sinh x\sqrt{p/D_i}}{\cosh d\sqrt{p/D_i}} = \int_0^x \frac{\cosh z\sqrt{p/D_i}}{p \cosh d\sqrt{p/D_i}} dz \tag{15}$$

We have in general [see, e.g.(11)]

$$\mathcal{L}^{-1} \int_0^x f(p,z) dz = \int_0^x \mathcal{L}^{-1} f(p, z) dz, \tag{16}$$

where \mathcal{L}^{-1} denotes the inverse Laplace transformation. For the integrand in equation (15) the inverse transform is given by Carslaw and Jaeger¹² to be

$$1 + \sum_{n=0}^{\infty} \frac{4(-1)^{n+1}}{\pi(2n+1)} e^{-D_i(2n+1)2\pi 2i/4d^2} \cdot \cos \frac{(2n+1)\pi z}{2d} \tag{17}$$

From equations (14-17) we then obtain:

$$u_i = -A_i x - A_i \sum_{n=0}^{\infty} \frac{8d(-1)^{n+1}}{\pi^2(2n+1)^2} e^{-D_i(2n+1)2\pi 2i/4d^2} \cdot \sin \frac{(2n+1)\pi x}{2d} \tag{18}$$

Substituting u_i from equation (6), A_i from equation (3a) and putting $x = -d$, we find for the concentration of component i at the steel-paint interface:

$$C_i = C_i^\circ + \frac{Iv_i d}{nFD_i} \left[1 - \sum_{n=0}^{\infty} \frac{8}{\pi^2 (2n+1)^2} e^{-D_i (2n+1)^2 \pi^2 t / 4d^2} \right]. \quad (19)$$

DISCUSSION

From equation (19) we see that when $t \rightarrow \infty$ a stationary state will be reached with

$$C_i(t \rightarrow \infty) = C_i^\circ + \frac{Iv_i d}{nFD_i}. \quad (20)^*$$

For practical purposes, i.e. with a deviation smaller than 1%, we can consider this stationary state to be reached when the exponent in equation (19) for $n = 0$ is larger than 5, thus:

$$\frac{D_i \pi^2 t}{4d^2} > 5. \quad (21)$$

When $D_i \approx 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ (which is of the order of magnitude of the diffusion coefficient of chloride ions in an epoxy-type paint¹⁴) and $d = 250 \mu = 2.5 \times 10^{-2} \text{ cm}$ this gives for the time necessary to reach the stationary state

$$t > 12.6 \times 10^5 \text{ s} \approx 15 \text{ d}. \quad (22)$$

This time is short enough for the stationary state to be reached well within the usual lifetime of stationary structures protected by cathodic protection. Ships making long voyages of, e.g. several weeks, such as tankers, also reach the stationary state within the time of one voyage. For ships making short voyages of, e.g. 6–8 days with cathodic protection shut off when the ship is in the harbour, the time of one voyage is not sufficient to reach the stationary state. After 6 d, under the condition given above, the first term in the series of equation (19) is about 0.14. As the time during which the cathodic protection is not applied will in general time be much shorter than the time of a voyage this means that the concentrations will not return completely to the initial values. This means that on subsequent voyages the concentrations start at values already higher than C_i° meaning that after some time the stationary concentration will still be reached, as shown schematically in Fig. 2.

This means that equation (20) can be used to obtain an estimate of the concentration of component i reached during cathodic protection. Using $I = 1 \text{ mA.m}^{-2} = 10^{-7} \text{ A.cm}^{-2}$ and taking the same values of D_i and d as used above this gives for the hydroxyl-ion concentration:

$$C_{\text{OH}^-} = C_{\text{OH}^-}^\circ + 2.5 \times 10^{-5} \text{ mole.cm}^{-3}. \quad (23)$$

*This result could of course also have been derived by an argument similar to that used in deriving the limiting current in concentration polarization using the Nernst diffusion layer¹³. However, in that way no information is obtained about the behaviour of the system as a function of time.

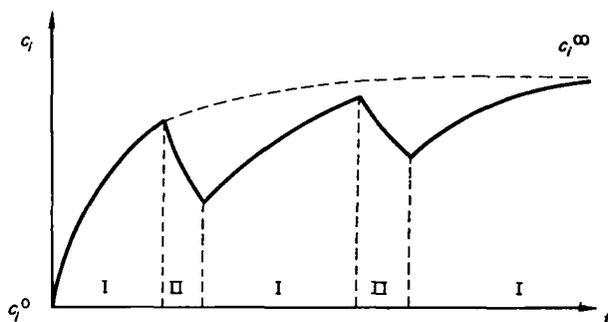


FIG. 2. Concentration of component is shown schematically as a function of time with alternate periods with (I) and without (II) cathodic protection.

Because the initial concentration $C_{\text{OH}^-}^0 \approx 10^{-10}$ to 10^{-11} mole.cm⁻³ this can be neglected with respect to the concentration change. Converting to mole.l⁻¹ and taking logarithms then gives under these circumstances:

$$\text{pH} (t \rightarrow \infty) \approx 12.4. \quad (24)$$

The current density used to obtain this value is typical of that used initially in cathodic protection of ships. Under certain circumstances this has to be increased to 30–35 mA m⁻² towards the end of the life-time of the coating. However, most of this extra current will be necessary to protect the steel at those spots where the paint has been damaged or destroyed. On the still covered portion of the steel the local current density will probably stay close to the initial value.

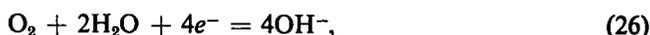
The value of the pH as given by equation (24) is dangerously close to the value of 13 which is often taken to be the pH at which excessive deterioration of paint occurs. Irregular current distribution caused for example by local differences in film thickness (which may easily be 25% of the average), local differences in pigment content causing differences in D_i and in resistivity or by unequal distances to the protective anodes, may easily give rise to local pH values which exceed the average one of 12.4, thus leading to local destruction of the paint film.

For the hydrogen concentration we obtain from equation (20) in a similar way:

$$C_{\text{H}_2} = 1.25 \times 10^{-5} \text{ mole.cm}^{-3}, \quad (25)$$

where it is assumed that $D_{\text{OH}^-} \approx D_{\text{H}_2}$. The effect of H₂ concentration is somewhat more difficult to judge. The solubility of H₂ in water at 10°C is 0.02 Ncm³H₂/gH₂O, i.e. about 10⁻⁵ mole.cm⁻³.¹⁶ This might lead to the conclusion that blistering could already result under these circumstances. However, no account has been taken of the solubility of H₂ in the paint film itself, which will certainly be of the same order of magnitude as that in water. Secondly the diffusion coefficient of H₂ in water is about four times as high as that of most ions.¹⁷ Both effects would lead to a lower C_{H₂} at the paint-steel interface and thus to a decreased danger of blistering.

Engell and Forchhammer⁸ based their calculation upon the cathodic reaction



instead of reaction (1) as used here. Using equation (20) with $v_{\text{O}_2} = -1$ and $D_{\text{O}_2} \approx 10^{-9} \text{ cm}^2 \cdot \text{s}^{-1}$ we obtain an estimate for the limiting current density of reaction (26) by putting $C_{\text{O}_2} = 0$. This gives

$$I_i = \frac{C_{\text{O}_2}^{\circ} n F D_{\text{O}_2}}{v_{\text{O}_2} d} \approx 4.5 \times 10^{-9} \text{ A} \cdot \text{cm}^{-2} = 4.5 \times 10^{-2} \text{ mA} \cdot \text{m}^{-2}. \quad (27)$$

As this is less than 5% of the externally applied current density the use of reaction (1) only in our calculations seems completely justified.

CONCLUSIONS

The most important conclusions to be drawn from equation (20) are that the dangers of high pH and H_2 -evolution both increase with increased current density and with increased thickness of the paint film. The first of these conclusions is in accordance with experience which has shown that overprotection leads to more extensive damage to paint films. The second point is perhaps somewhat unexpected and certainly runs counter to the usual practice of making the total thickness of the paint film as large as possible.

In order to apply equation (20) to practical cases the most important parameter to be determined is D_i , since only very scanty data are available at this moment.

Acknowledgements—The authors wish to thank Prof. R. Nottrot who checked the mathematical derivations. Thanks are also due to the Board of Directors of Rhine-Schelde-Verolme Engineers and Shipbuilders N.V. for permission to publish this paper.

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