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Corrosion Behaviour of Lead in Salt Solutions

II. Lead - steel couple

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Galvanic currents flowing through electrically connected Pb and Fe sheets and the corresponding corrosion rates in $1-10^{-6}$ M NaCl, $0.1-10^{-6}$ M Na_2SO_4 and sea water and in cement extracts have been measured. In neutral solutions Pb is initially anodic to Fe and its corrosion rate is enhanced. Reversal of polarity takes place after 2-20 min according to the salt concentration, and the corrosion rate of Pb decreases markedly with time. After reversal Fe becomes anodically polarised so that its corrosion rate becomes much higher in the coupled than in the uncoupled state. The corrosion rate of coupled Pb in sea water becomes vanishingly small after one month. Coupling results in a great increase in the corrosion rate of Pb in cement extract, but Cl^- and SO_4^{2-} ions counteract this effect. The influence of salt concentration on the galvanic current and the role played by Cl^- and SO_4^{2-} ions have been interpreted in the light of the electrode behaviour of the separate metals.

Introduction

THE present study is a continuation of earlier work¹ designed to investigate the factors which may affect the corrosion of Pb shields of marine constructions. Part I deals with the corrosion of Pb in Na_2SO_4 and NaCl solutions covering a wide range of concentrations, in sea water and in cement extracts. The present work was initiated in order to assess the corrosion rate of Pb when it is coupled with Fe in the above solutions.

Experimental

The composition of the Pb was as described in Part I. The second metal, usually designated Fe in this paper, was mild steel containing 0.2% C, 0.035% P, 0.30% Mn and 0.035% S. The specimens had the dimensions $2 \times 2 \times 0.1$ cm. Each specimen had a protruding arm used for electrical connection. The distance between the two electrodes was always fixed at 2.5 cm. Prior to each experiment Pb and Fe were cleaned, fitted tightly in the cover of the cell, connected to the ammeter and then lowered into the solution. There was no time lag between contact with the solution and the flow of current.

In the weight-loss experiments arms from the Pb and Fe specimens, respectively, were joined by means of teflon nuts and bolts. Surface preparation and removal of the corrosion products were effected as described elsewhere.^{1,2} Solutions were made up from reagent grade salts and distilled water.

During potential measurements, the specimen was connected to a S.C.E. via a bridge carrying the same solution as in the electrode vessel. A Metrohm potentiometer type E-353 was used. The experiments were conducted at 25°C.

Results

Galvanic current-time curves

Figs 1 and 2 show current-time curves for a Pb-Fe couple immersed in chloride or sulphate solutions, in sea water or in cement extracts. The curves obtained in the sulphate or chloride solutions (or in sea water) show that the galvanic current diminishes rapidly, changes its sign after 1-20 mins, according to salt concentration, reaches a maximum negative value (the current is positive when Pb is the anode) and finally decreases, whereby a steady state is approached. The initial positive, and the steady-state currents are higher, and the time taken by the current to reverse its sign is less, the higher the concentration of the solution. In very dilute solutions (10^{-6} M), the current remains at very low negative values (sulphate) or does not reverse its sign and may even attain slightly more positive values than the initial one (chloride).

The galvanic currents obtained in the cement extracts (Fig. 2) maintain markedly high positive values throughout the experiment. The galvanic current in tap water extract is nearly double that in sea water extract.

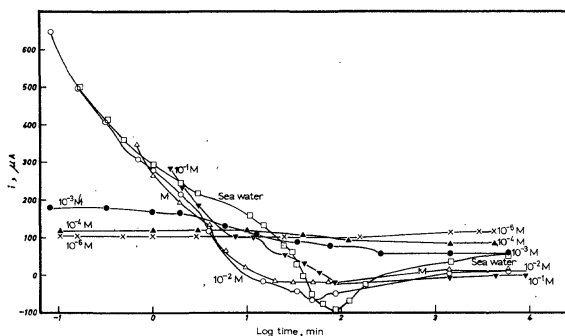


Fig. 1. Change of galvanic current with time for Pb-Fe couple in sodium chloride solutions and sea water

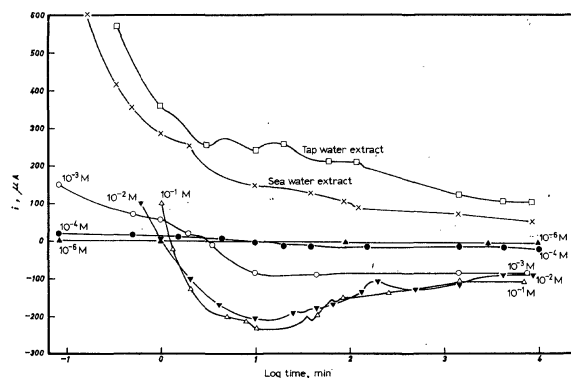


Fig. 2. Change of galvanic current with time for Pb-Fe couple in sodium sulphate solutions and cement extracts

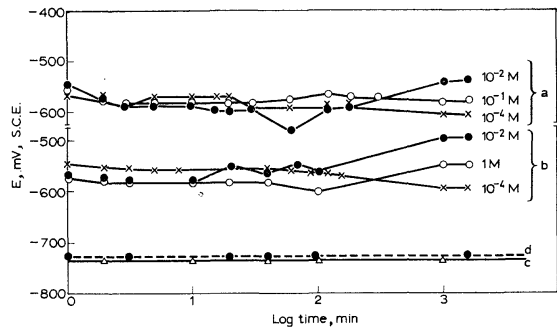


Fig. 3. Change of potential with time for Pb in (a) sodium chloride solutions, (b) sodium sulphate solutions, (c) tap water extract, (d) sea water extract

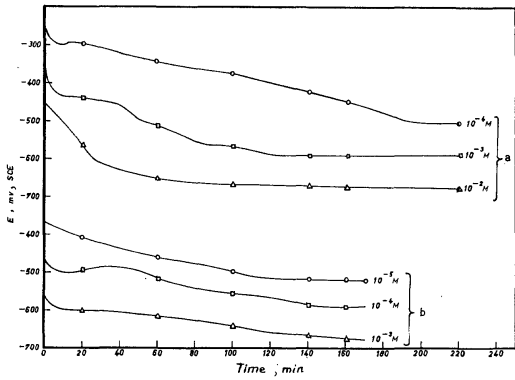


Fig. 5. Change of potential with time for Fe in (a) sodium chloride solutions, (b) sodium sulphate solutions

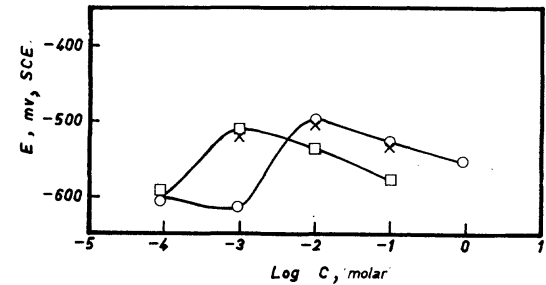


Fig. 4. Relation between steady-state potential of Pb and log salt concentration

□ Na₂SO₄ (24 h) × Na₂SO₄ (48 h) ○ NaCl (24 h)

Potential-time curves

Lead

Open-circuit potentials of Pb immersed in 1-10⁻⁴ M NaCl, 0.1-10⁻⁴ M Na₂SO₄, sea water or cement extracts were measured. Representative potential-time curves for NaCl and Na₂SO₄ and for cement extracts are shown in Fig. 3. From these measurements it was evident that the corrosion potential of Pb in 1-10⁻² M NaCl, in 0.1-10⁻³ M Na₂SO₄ and in sea water shifts with time toward more noble values. In the case of 0.1 M Na₂SO₄ the change of potential with time is relatively insignificant. In 10⁻³ and 10⁻⁴ M NaCl and in 10⁻⁴ M Na₂SO₄, on the other hand, the steady-state potentials are approached from less negative values. In Na₂SO₄ solutions the positive shift in potential is maintained if the measurements are continued for 3 days. This is not so in chloride solutions. In the cement extracts the potential of Pb remains constant throughout the experiments, at -725 mV in sea water extract, and at -740 mV in tap water extract.

Fig. 4 shows a semi-logarithmic plot of the steady-state potentials of Pb in solutions of NaCl (24 h) and Na₂SO₄ (24 and 48 h) vs concentration. Starting at 1 M (or 0.1 M) the potential shifts towards more noble values with decrease in concentration, reaches a maximum and then decreases with further dilution. Although this decrease takes place at a lower concentration for the sulphate than for the chloride solutions, the value attained in 10⁻⁴ M solution is almost the same for the two anions.

Steel

Potential-time curves (representative curves are shown in Fig. 5) show that steady-state corrosion potentials of Fe in NaCl, Na₂SO₄ or sea water are approached from less negative values. Fig. 6 shows that final steady-state potentials (values after 220 min) are related to molar concentration (up

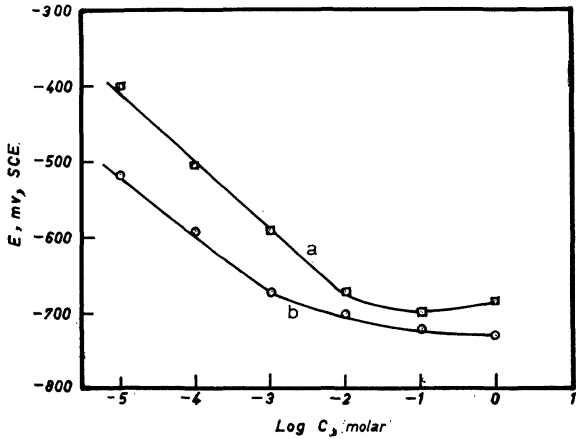


Fig. 6. Relation between steady-state potential of Fe and log salt concentration

□ NaCl ○ Na₂SO₄

to 10⁻² M) by an equation of the type
$$E = a - b \log C \quad (1)$$

where a is a constant depending on the type of anion and b has a value of ~ 80 mV in both solutions (up to 10⁻² M).

In sea water extract (Fig. 7) the potential increases with time till it reaches a certain value which remains constant for about 100 min; it then decreases with time approaching a less noble steady-state value. In tap water extract, on the other hand, steel shows a continuous drift in potential toward more noble values.

From the foregoing measurements it is evident that the potential-time curves obtained for Pb and Fe in chloride or sulphate solutions and in sea water intersect after about 10 min immersion. In cement extracts the curve for Pb lies at a much more active potential than that for Fe.

Weight-loss experiments

Electrically connected Pb and Fe were immersed in 10⁻¹, 10⁻³ or 10⁻⁵ M Na₂SO₄ or NaCl, in sea water and in cement extracts for periods of 6 or 30 days. The weight losses observed for both metals are given in Table I. The corresponding data obtained for the separate metals (from Part I¹) are given for comparison.

Lead

Based on the data shown in weight-loss columns 1 and 2 of Table I it may be stated that, in general, coupling with Fe

causes an initial increase in the corrosion rate of Pb in chloride and sulphate solutions. Weight-loss columns 3 and 4, on the other hand, show that the corrosion rate of the Pb electrode diminishes markedly with time. Comparison of the values in columns 2 and 4 reveals that the weight losses are (in most cases) less after 30 days than after 6 days. This will be commented on later. Columns 3 and 4 show that the steady-state corrosion rate (loss/30 days) of Pb in 10^{-1} , 10^{-3} and 10^{-5} M NaCl decreases by 50, 70 and 90% respectively if it is coupled with Fe. The corresponding decreases in the sulphate solutions amount to 83, 87 and 47% respectively.

Fig. 8 shows that the dependence of the corrosion rate of the coupled Pb electrode (after 6 days) on the Cl^- ion concentration may be expressed by the equation

$$W = a C^{-b} \quad (2)$$

where W is the corrosion rate ($\text{mg}/\text{dm}^2/\text{d}$), C the salt concentration (molar) and a and b are constants. The constant b has the value 0.24 (as compared with 0.32 for the separate Pb electrode; Part I¹).

A similar slope is obtained for $10^{-1} - 10^{-3}$ M Na_2SO_4 (curve b). The markedly higher values obtained for the 10^{-5} M solution are confirmed by the experiment conducted for 30 days (column 4).

As is the case with sulphate and chloride solutions, coupling causes an initial increase in the corrosion rate of Pb in sea water, but this rate decreases with time so that practically

no corrosion could be detected after 30 days. Table I shows also that coupling accelerates the corrosion of Pb in tap water extract and decelerates it in the sea water extract.

Steel

The results for Fe (weight-loss columns 5–8 in Table I) show that, except in the sea water extract, the corrosion rate of Fe increases appreciably if it is coupled with Pb. Thus in 10^{-1} , 10^{-3} and 10^{-5} M NaCl the corrosion rates of the coupled Fe are (from data for 30 days) 7, 5 and 8 times those of the uncoupled Fe, respectively. For the corresponding sulphate solutions the corrosion rates of coupled Fe are 7, 4 and 3 times those of the uncoupled Fe. It is also seen that the corrosion rates for coupled Fe generally increase with time (compare the weight losses observed after 6 days with those after 30 days).

The corrosion rates, W' and W , calculated from the galvanic current (steady-state values, after 48 h) and from the corresponding weight loss of Fe, respectively, are shown in

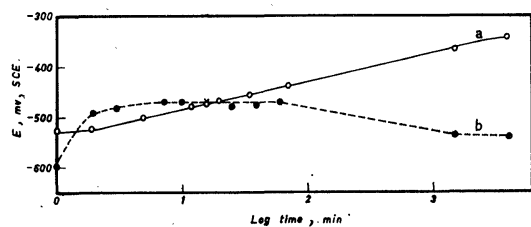


Fig. 7. Change of potential with time for Fe in cement extracts (a) tap water extract, (b) sea water extract

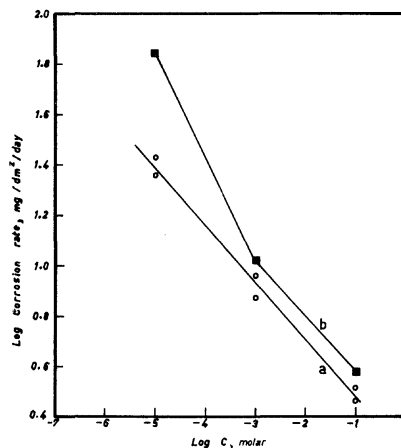


Fig. 8. Relation between corrosion rate of coupled Pb and log salt concentration (a) sodium chloride solutions (b) sodium sulphate solutions

TABLE I

Loss in weight of uncoupled and coupled Pb and Fe electrodes immersed in various solutions

Solution	Weight loss, mg/dm^2							
	Lead				Steel			
	6 days		30 days		6 days		30 days	
	u	c	u	c	u	c	u	c
10^{-1} M NaCl	11.64	20.0	58.2	18.75	57.0	250.0	285.0	1905
10^{-3} M NaCl	48.96	55.0	244.8	60.00	42.0	210.0	210.0	1125
10^{-5} M NaCl	227.10	165.0	1135.5	67.25	28.8	171.3	144.0	1092.5
10^{-1} M Na_2SO_4	27.42	22.5	137.1	23.50	80.4	432.5	402.0	2750
10^{-3} M Na_2SO_4	58.26	62.5	291.3	37.50	66.6	287.5	333.0	1250
10^{-5} M Na_2SO_4	137.40	420.0	687.0	362	52.8	142.5	264.0	763.7
Sea water	4.50	5.0	22.5	0.00	67.8	175.0	339.0	850
Cement extract (S.W.)	90.00	75.0	450.0	50.00	30.0	30.0	150.0	62.5
Cement extract (T.W.)	132.00	982.5	660.0	3750	0.0	6.5	0.0	31.2

u = uncoupled c = coupled S.W. = sea water T.W. = tap water

TABLE II

Corrosion rates of coupled iron (after 6 days), mg / dm² / day

Solution	Corrosion rate, mg/dm ² /day	
	W (from weight loss)	W' (from galvanic current)
10 ⁻¹ M NaCl	41.7	31.3
10 ⁻³ M NaCl	35.0	15.7
10 ⁻⁵ M NaCl	28.5	3.1
10 ⁻¹ M Na ₂ SO ₄	72.1	34.4
10 ⁻³ M Na ₂ SO ₄	47.9	26.6
10 ⁻⁵ M Na ₂ SO ₄	23.8	6.2

Table II. It is clear that W' is always less than W; nevertheless the same trend, that is, a decrease in corrosion rate with decrease in salt concentration, is evident from the two methods. The values obtained by the two methods are not far from each other for 10⁻¹ M NaCl, but the difference increases with dilution.

Discussion

The appearance of a maximum in the corrosion potential—concentration curves obtained for Pb in sulphate or chloride solutions down to a concentration of 10⁻⁴ M and the mode of change of potential with time are in line with the increase in its corrosion rate with dilution. Both trends suggest that Cl⁻ or SO₄²⁻ ions act as anodic inhibitors for Pb. The ratio anodic: cathodic areas on the metal surface will increase with decrease in salt concentration, the anodic and cathodic reactions being the anodic dissolution of Pb and the reduction of dissolved oxygen respectively. Our results agree with those reported by Brasher *et al.*³ regarding the attainment of an initial steady state and the further rise in potential above this steady-state value when the measurements are continued.

The progressive negative drift of potential of a steel electrode immersed in Na₂SO₄ or NaCl solutions is most probably caused by depolarisation of the anodic process due to adsorption of SO₄²⁻ or Cl⁻ ions on the anodic sites. Competition between these ions and the film-repairing OH⁻ ions (produced cathodically) may reveal itself as a break or even a plateau in the time-potential curves. The partial anodic and cathodic processes operating on the surface of Fe are the passage of Fe²⁺ ions into solution and the reduction of O₂ respectively. The dependence of the steady-state potential of Fe on the concentration of Cl⁻ or SO₄²⁻ ions is in line with the findings of Gouda & Sayed⁴ concerning the influence of anions on the corrosion of steel in neutral media.

When both metals are connected electrically in sulphate or chloride solutions, Pb is initially anodic to Fe. Pb will be polarised anodically and Fe cathodically.⁵⁻⁹ As a result, the corrosion of Pb will be enhanced. The data in columns 1 and 2 in Table I provide evidence for this assumption.

The continuous negative drift of the potential of Fe already mentioned, will lead to reversal of polarity. Consequently Pb will be polarised cathodically and the cathodic process may partially consist in the discharge of Pb²⁺ ions already formed before reversal of polarity. This possibility is supported by the markedly low weight loss estimated after 1 month. In fact a Pb deposit could be clearly distinguished on the electrode surface.

The inhibitive action of Cl⁻ and SO₄²⁻ ions on this anodic corrosion of coupled Pb in the initial stages manifests itself

in the mode of change of the corrosion rate with concentration (Fig. 8). The corrosion rate may still be governed (like that of uncoupled Pb) by the adsorption of these ions on the electrode surface. However, they are less effective than on the separate electrodes (compare the values of b in eqn (2)). In very dilute solutions (10⁻⁵ M) SO₄²⁻ ions afford but very slight protection.

Under the conditions in this work Fe will be (after reversal) anodically polarised so that its corrosion rate will be much higher in the coupled than in the uncoupled states. The weight-loss data obtained for Fe (Table I) reveal the dramatic increase in its corrosion rate by reason of coupling. They show also that the response of the corrosion rate to changes in anion concentration is greater than that found for the separate electrodes. This may be explained by assuming that the effective c.d. on the anodic areas is increased by coupling.

It is perhaps justifiable to suggest that the initial positive, the maximum negative and the steady-state galvanic currents depend on the conductivity of the solution and on the ratio of anodic to cathodic areas. This ratio will increase on Pb and decrease on Fe with decrease in concentration of the sulphate or chloride solutions. Consequently the corrosion potentials of the two metals approach one another with decrease in salt concentration. It is probable that the corrosion of each metal continues even after coupling, despite the fact that the corrosion rate of Pb will decrease and that of Fe will increase.⁷ It is unlikely that the resistance of the corrosive medium plays a substantial role when the corrosion couple consists of microcells on the same metal. However, when the two metals comprising the corrosion couple are situated opposite to one another, then the current path is affected and will depend in this case on the resistance of the medium. Tomashov⁶ discussed the contribution of the specific resistivity of the electrolyte to galvanic corrosion of a bimetallic couple (Fe-Cu). For instance, if the distance between the electrodes was 1 cm, the ohmic control amounted to 0.1, 9 and 19% for 0.5 M NaCl ($\rho = 25 \Omega \text{ cm}$), 0.01 M NaCl ($\rho = 1000 \Omega \text{ cm}$) and distilled water ($\rho = 8210 \Omega \text{ cm}$), respectively. The progressive deviation of W' from W with dilution can be thus understood.⁶

The passage of the negative galvanic current (Pb as cathode) through a maximum before it decreases to a quasi-stationary steady state may be associated with a decrease of the cathodic areas on Pb. This decrease could be brought about by the rapid accumulation of OH⁻ ions produced cathodically, i.e., the pH increases rapidly in the vicinity of the electrode. The potential will be shifted to less noble values. The maximum is, however, very pronounced in concentrated solutions (and in sea water), where the galvanic current is relatively high and diminishes with dilution. The other possibility, of competition between OH⁻ and Cl⁻ or SO₄²⁻ ions (OH⁻ ions migrating from the Pb cathode to the Fe anode) may be discounted by virtue of the constant, or even increasing, corrosion rate of Fe.

The experimental results obtained in sea water are readily explicable in the light of the above discussion. Thus the corrosion of Pb in sea water, already very small, may be stifled by coupling with Fe.

In the cement extract Pb will always be anodic to Fe. The anodic process at the Pb electrode, namely, the oxidation of Pb to PbO which in turn is attacked by the alkaline solution (producing HPbO₂⁻ ions¹⁰) is enhanced by coupling with Fe. The measured potential of Pb is only 15 to 30 mV more negative than the equilibrium value of the Pb/PbO system at the pH value of 12.1 prevailing in the cement extract. The higher corrosion rate of Pb in the coupled than in the separate conditions is to be expected. The presence of SO₄²⁻ and Cl⁻ ions (sea water extracts), however, leads to the diminution of

cathodic areas on Fe and hence to a lower potential difference between the two electrodes (compare the potential-time curves of Fe in the two cement extracts; Fig. 7). Moreover, the Cl^- and SO_4^{2-} ions migrating to the Pb anode may interfere with its anodic dissolution. Both effects lead to a markedly lower corrosion rate of coupled Pb in sea water extract than in tap water extract.

The rather unexpected corrosion rate of coupled Fe (as compared with uncoupled Fe) in cement extract made with tap water may be explained by supposing that coupled Fe is cathodically polarised so that its corrosion potential is brought below the Flade potential, i.e., it is depassivated by coupling. Coupling nevertheless markedly reduces the corrosion rate of Fe (in 30 day period) in cement extract prepared with sea water. This may be attributable to cathodic polarisation to near the protection value effected by coupling.

Conclusions

Coupling of lead with steel in neutral media results in a marked decrease in the corrosion rate of lead and an increase in the corrosion rate of steel. In alkaline solutions this coupling increases the corrosion rate of Pb. Cl^- and SO_4^{2-} ions however reduce the corrosion rate of coupled Pb in alkaline solutions.

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