B. Potentio dynamic polarization curves and steel corrosion

MRS. IR. W. L. SLUIJTER AND PROF. IR. P. C. KREIJGER

Summary

Potentio dynamic polarization curves were measured on mild steel in several aqueous solutions (acids, salts and bases), that are corrosive for steel in different degrees. The accent in the investigation was on a simulated concrete environment, viz. saturated lime water $(Ca(OH)_2)$ with or without concrete admixtures, specially Calcium chloride.

1 Introduction

For practical requirements it is frequently of great inportance to know whether a particular concrete environment around reinforcing steel or prestressing steel is corrosive to the steel or whether it will become corrosive in the long run and, if so, after what length of time, to what degree and in what form.

The most reliable answer to these questions is provided by carrying out exposure tests under conditions corresponding exactly to the environment under investigation. Such tests are time-consuming, usually taking some tens of years to carry out. For this reason tests of shorter duration are often performed, the results of which are extrapolated to longer periods of time. For example, the *corrosion rate* of steel can be investigated by determining the decrease in weight of the steel after a certain period of exposure, e.g., one year. This method suffers from some disadvantages, however, such as:

- in an environment with low corrosivity the exposure time has to be very long before a loss of metal can be measured with any accuracy; hence this method is often time-consuming;
- during the period of exposure no *changes* in corrosion rate with the passage of time are measured; only the overall loss at the end of the test is determined.

A rapid method of obtaining an insight into the corrosivity of a particular environment for steel at a given moment is based on the measurement of *potentio dynamic polarization curves*. Measuring such a curve takes only a short time (an hour at most). A further advantage is that any changes in corrosivity of the environment in course of time can be studied by performing a number of measurements spread out over the period of time concerned. Polarization curves are therefore very suitable for *comparative* tests.

The relationship between the corrosivity of an environment or the corrosion rate

and polarization curves will be explained below. The present article, however, is more concerned with the *qualitative* assessment of these curves than with the quantitative determination of corrosion current densities, since this latter aspect constitutes a whole subject in itself and is moreover not directly essential in the present context, because the shape and position of the curves already provide a reasonably good indication of the corrosiveness of the environment with regard to steel.

As we know, the corrosion of steel is an electrochemical process. The dissolution of steel can be represented by the following electrochemical reaction equation:

$$Fe \rightarrow Fe^{\circ\circ} + 2e \tag{1a}$$

or iron atom → iron ion + electrons
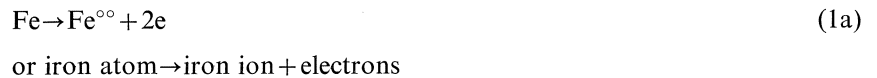
i.e., an iron atom at the surface of the steel in contact with an aqueous solution is transformed according to equation (1a) into a positively charged iron ion, which is absorbed into the aqueous solution (accompanied by the formation of rust, for example), and a negatively charged electron, which remain in the metal. The metallic iron is *oxidized*.

For reasons of electrical equilibrium it is necessary that, simultaneously with the accomplishment of reaction (1a), an electron passes *out of* the metal at some other point on the surface thereof. This does not occur by discharging of an iron ion from the solution – because iron has a reversible potential more active (negative) than hydrogen – but, in an acid environment, by discharging (*reduction*) of positive hydrogen ions in accordance with the electrochemical equation:

$$2H^{\circ} + 2e \rightarrow H_2 \tag{2a}$$

hydrogen ions + electrons → hydrogen gas
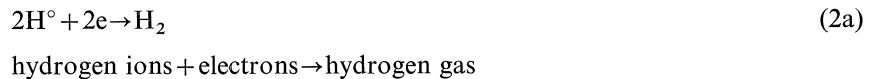
Thus, in this reaction, hydrogen gas is liberated simultaneously with the dissolving of the iron In an alkaline environment there occurs, instead, reduction of oxygen present in aqueous solution, in accordance with the electrochemical equation:

$$O_2 + 2H_2O + 4e \rightarrow 4OH' \tag{3}$$

oxygen + water + electrons → hydroxyl ions
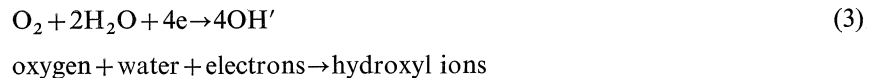
If substances such as chromate, nitrate, etc. are present, these can be reduced, just as oxygen is.

The oxidation reaction (1a) must always be coupled with a reduction reaction (2a) or (3) or a similar reduction reaction. This means that corrosion of steel is accompanied by the passage of electric current between the steel and the surrounding solution (or the concrete). This flow of current per unit time and per unit area (of steel surface) is therefore a measure of the rate at which corrosion takes place. To convert a gram

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atom of iron (55.85 g) into a gram ion of iron requires a charge of 2×96500 coulombs. A quantity of electricity of 1 ampere-day will dissolve 3.18 cm^3 of steel.

By measuring the corrosion current density it would therefore be possible to determine the corrosion rate at a particular instant. Actually, however, the flow of current is chaoticly distributed with regard to the position on the surface of the metal and with regard to time. It cannot be measured directly, but an indirect measurement is possible, for it is known from the literature how the corrosion current density can be determined under certain circumstances from the relationship between current and potential, e.g., by the method of linear-polarization or by Tafel extrapolation.

Applied-voltage polarization curves indicate the relationship which exists (or which may exist) between an artificially applied potential difference between a metal and an aqueous solution (including wet mortar or concrete) and the external current density needed to maintain this potential. As a rule a polarization curve is characteristic of the given combination of metal and environment.

A complete polarization curve comprises an actual cathodic curve and an actual anodic curve which cannot be measured separately and which, at zero external current density, merge into each other at the equilibrium or corrosion potential.

By *anode current direction* is understood the direction of the positive current I_a *from* the metal into the solution or into the concrete, the *anode reaction(s)* being the accompanying reaction(s). The anode current density is of major importance with regard to the dissolution of steel (anodic oxidation). The cathode current density I_k refers to the reverse direction of the positive current, i.e., from the solution (or the concrete) into the steel, the accompanying reactions being called the cathodic reactions.
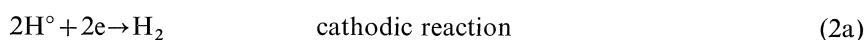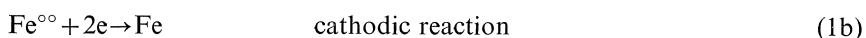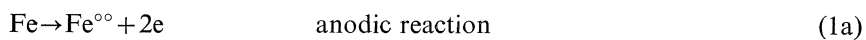
The shape and position of the polarization curves is brought about by the nature of the electrochemical anodic and cathodic reactions which can take place at a particular potential and by the rate at which these reactions can, once they occur, proceed at the surface of the steel.
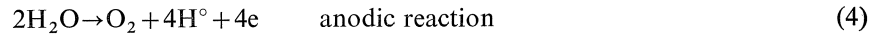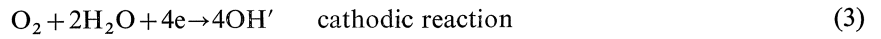
What reactions occur is determined by the magnitude of the applied potential, the acidity (pH), and the presence or absence of particular substances.

For example, hydrogen gas is evolved below a certain value of the pH, while oxygen gas can be evolved at an at least 1.2 volts higher potential. The explanatory comments on the Pourbaix diagram in the preceding article are relevant in the present context.

The rate at which the electrochemical reactions occur at a particular potential is determined by a variety of factors associated with activation polarization, the formation of surface films, etc.

Every electrochemical equilibrium reaction, e.g., any of the following:

$$Fe \rightarrow Fe^{\circ\circ} + 2e \qquad \text{anodic reaction} \qquad (1a)$$

$$Fe^{\circ\circ} + 2e \rightarrow Fe \qquad \text{cathodic reaction} \qquad (1b)$$

$$2H^{\circ} + 2e \rightarrow H_2 \qquad \text{cathodic reaction} \qquad (2a)$$

$$H_2 \rightarrow 2H^{\circ} + 2e \qquad \text{anodic reaction} \qquad (2b)$$

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$$O_2 + 2H_2O + 4e \rightarrow 4OH' \qquad \text{cathodic reaction} \qquad (3)$$

$$2H_2O \rightarrow O_2 + 4H° + 4e \qquad \text{anodic reaction} \qquad (4)$$

can theoretically be expressed in total an actual anodic or cathodic polarization curve. The applied-voltage curve ultimately measured is to be regarded as the resultant of the actual anodic and actual cathodic curves (Figs. B1a and B1b).

Fig. B1a presents, plotted to a linear scale, an example of a fictitious polarization curve (heavy line) which is the resultant of two separate actual curves (partly drawn as thin lines) which cannot be measured separately, however: the applied current is always measured as the resultant of an actual anodic and a cathodic current density.
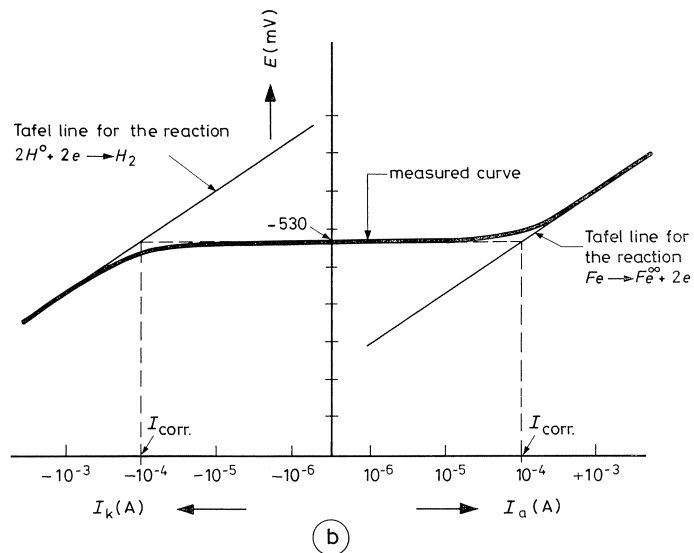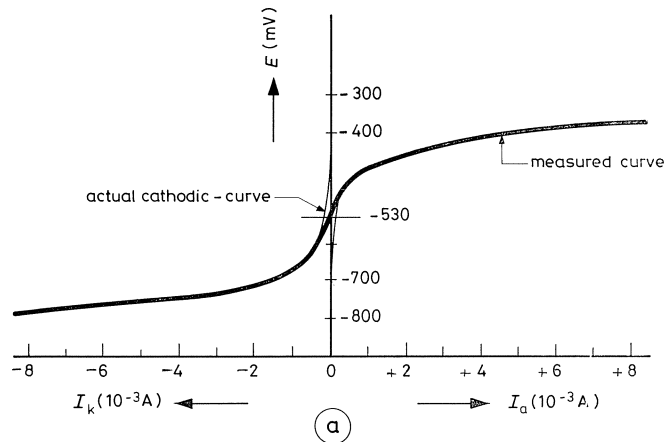

Fig. B1. Schematic representation of an applied-voltage polarization curve resulting from one actual anodic curve and one actual cathodic curve.

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The same polarization curve has been plotted to a semilogarithmic scale in *Fig. B1b*. This diagram also shows that the *corrosion current density* can be determined by extrapolation of one or both of the Tafel lines. This procedure will not be further considered here, however (the method is suitable for a highly acid environment).

If four equilibrium reactions are possible, the polarization or *E–I* curve is composed of eight separate (sub-)curves, namely, four cathodic and anodic curves, each of which may differ in position, slope and shape.

The reaction velocity associated with a particular reaction is manifested in a somewhat more complex manner in the slope of the polarization curve measured at the potential concerned. The greater the change in reaction velocity under the influence of a small shift in potential (ΔE) resulting in a relatively large change in current (ΔI), the smaller becomes the ratio $\Delta E/\Delta I$ and the less the polarization. A change in slope of the curve therefore frequently denotes a change in the reaction velocity concerned (e.g., due to the formation of a surface film or to lack of oxygen). Hence a good deal can already be inferred from any changes in the ratio $\Delta E/\Delta I$, as will be shown with reference to a number of examples relating to some characteristic environments.

It should be noted that shape and position are determined not only by the reaction mechanisms that may occur, but also to some extent by the measuring procedure employed. With reference to this consideration the procedure adopted in the IBBC-TNO investigations is illustrated in *Fig. B2*.

The desired potential difference between the metal and the aqueous solution or between the metal and the mortar or concrete, measured in relation to a saturated
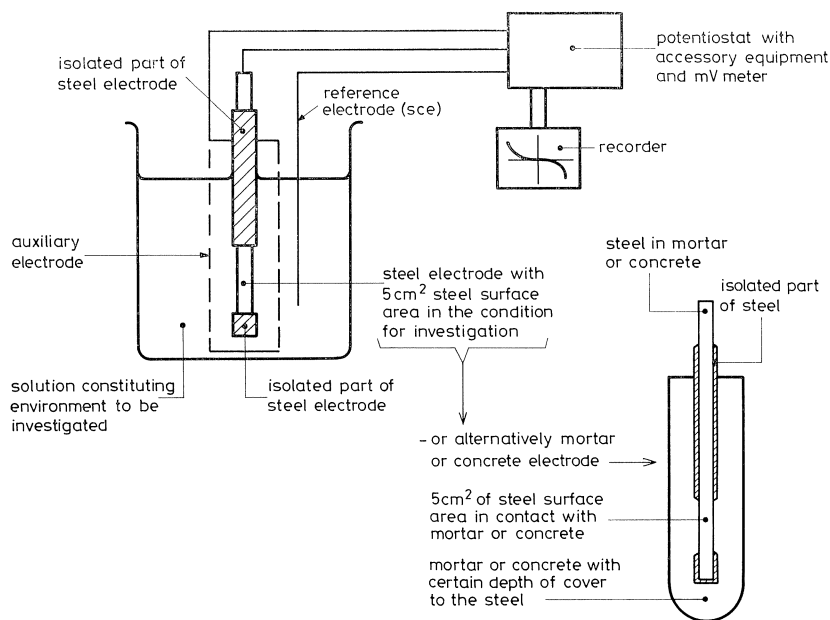

Fig. B2. Diagram of experimental procedure for determining the polarization curves discussed here.

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calomel electrode, is adjusted with the aid of a *potentiostat*. A cylindrical counter-electrode of platinum wire gauze surrounds the steel or mortar electrode to be measured and serves to make the passage of current possible. The potential is usually raised in the positive direction at a rate of 30 mV per minute, starting at a cathode current.

The potentiostat is connected to an *X–Y* recorder which plots the curves in graph form on a linear or a semi-logarithmic scale. The potential *E* of the measured steel electrode is indicated in volts on the vertical axis, while the applied anodic current density and the applied cathodic current density in amp./m^2 are indicated on the right and left of the horizontal axis respectively. The maximum current density is a few amp./m^2.

The composition of the tested mild steel without mill scale (expressed in % by weight) is as follows:

carbon	C 0.19
manganese	Mn 0.30
silicon	Si $\leqslant 0.02$
phosphorus	P 0.047
sulphur	S 0.034
copper	Cu 0.10

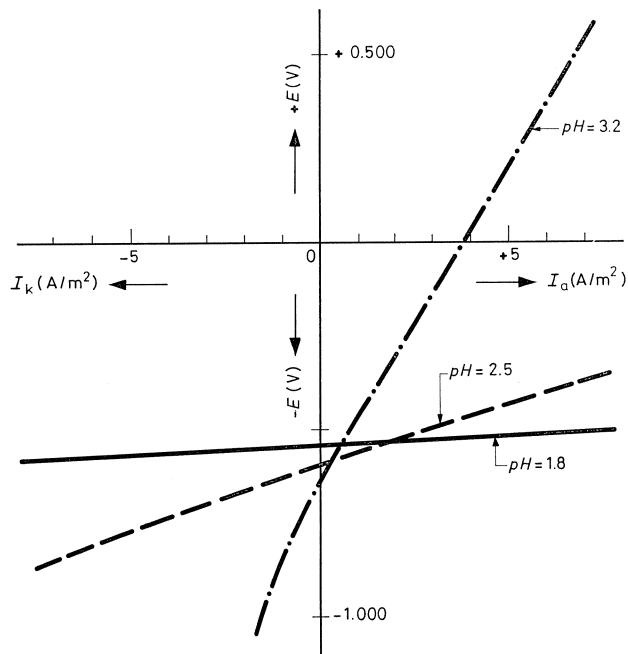The measuring area was always approximately 500 mm^2.

Fig. B3. *E–I* curves measured for mild steel in water containing SO$_2$ in different concentrations and with different values of pH.

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2 An acid environment

By way of examples of polarization curves measured in an acid environment three such curves are presented in *Fig. B3*. They were obtained from measurements performed in an aqueous solution of sulphur dioxide in three different concentrations and therefore with three different pH values.

It is known that steel is severely attacked by sulphur dioxide (SO_2). The high rate of corrosion at pH = 1.8 manifests itself in a very low degree of polarization ($\Delta E/\Delta I$ is very low). The effect of the increasing pH coupled with a higher electrolyte resistance finds expression in a higher degree of measured polarization. It is notable that two curves are (almost) straight lines with a low angle of slope, which is likewise indicative of a high degree of corrosion (high corrosion current density).

3 Neutral salt solutions

Characteristic of neutral salt solutions, such as a 1% solution of common salt, is that the *E–I* curves are not straight lines at low angles of slope, as in (strongly) acid solutions. See *Fig. B4*. The difference with regard to the curves obtained in an acid environment is not so much in the anodic part of the curve, but more particularly in the cathodic part. This is so because now no (rapid) reduction of hydrogen ions (H°) can take place in accordance with formula (2a), since the hydrogen ion concentration is too low for that (10^{-7} gram ion H°/litre approximately). The oxygen dissolved in the electrolyte is now reduced to hydroxyl ions (OH′) in accordance with reaction (3). The marked change of slope of the cathodic part of the curve can be explained as follows. With increasingly high cathodic current densities the consumption of oxygen
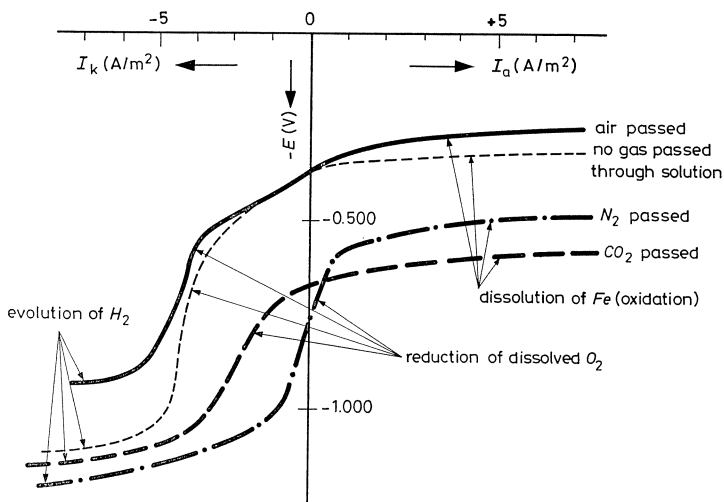

Fig. B4. *E–I* curves measured for mild steel in a 1% solution of common salt through which air, N_2 or CO_2 gas was passed.

greatly increases. Oxygen is, however, only to a limited extent soluble in water, with the result that the rate of supply of oxygen from the bulk mass of the electrolyte to the steel surface lags behind the rate of reaction (concentration polarization). The polarization ($\Delta E/\Delta I$) increases and may, at a given instant, become infinitely large for a higher value of the current density. The latter attains a limit, called the *limiting diffusion current density*. This situation continues until, with further lowering of the potential, the cathode current density again increases considerably because now a third reaction becomes possible, in which hydrogen gas is evolved according to the equation:

$$2H_2O + 2e \rightarrow 2OH' + H_2 \tag{5}$$

All this is shown in *Fig. B4*. In this example, the following were respectively passed through the 1% NaCl solution: air, nitrogen, carbon dioxide, and nothing. In the solution through which air was passed the diffusion current density is (approximately) greater than in the solutions with lower oxygen content through which nitrogen (N_2) and carbon dioxide gas (CO_2) were respectively passed.

The limiting oxygen diffusion current density determines the maximum corrosion current density. The more oxygen there is in the solution, the greater is this maximum current density. It is known that steel do not corrode in an oxygen-free environment, as is exemplified by reinforcement in concrete permanently submerged in sea-water. On the other hand, severe rusting of steel occurs on the borderline between water and air because here the rate of oxygen supply from the air is relatively high.

That the part played by oxygen in the corrosion process is dominant, while the nature of the neutral salt solution has much less, if any, effect, is apparent from *Fig. B5*, which shows two curves measured for mild steel in 1% solutions of sodium
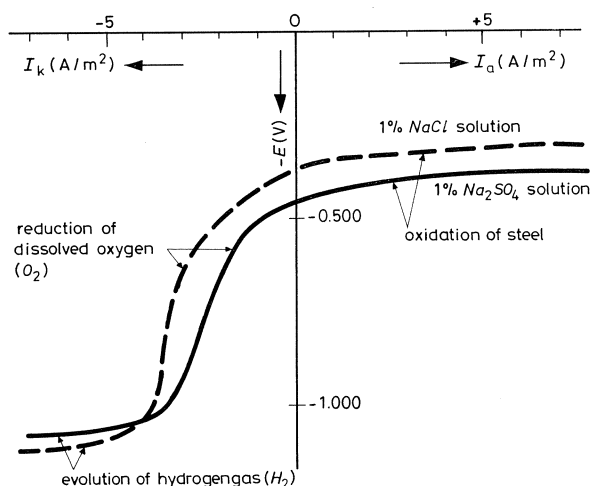

Fig. B5. *E–I* curves measured for mild steel in a 1% solution of NaCl and of Na₂SO₄ respectively.

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chloride (NaCl) and sodium sulphate (Na_2SO_4) respectively. In shape and position he two curves are very similar, almost identical. The NaCl solution may, however, have contained more oxygen than the Na_2SO_4 solution.

4 Saturated lime-water

An entirely different $E-I$ curve in terms of shape and position, as compared with the curves obtained in an acid or a neutral solution, is obtained in saturated lime-water, i.e., with an excess of solid lime $Ca(OH)_2$ on the bottom of the vessel.

Over a very wide range of potential, approximately 1.000 volt in *Fig. B6a*, the
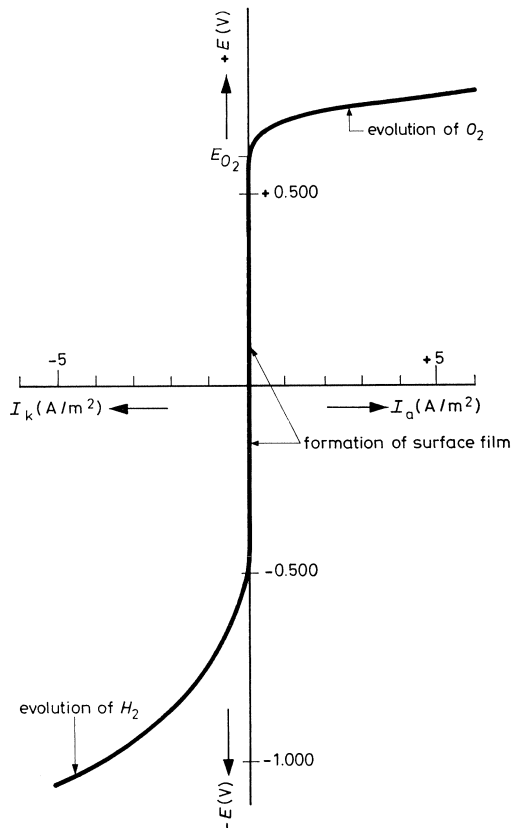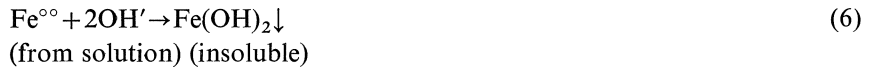

Fig. B6a. $E-I$ curve measured for mild steel in saturated lime-water.

current density is practically zero and the polarization $\Delta E/\Delta I$ is practically infinite. This is explained as follows.

The surface of the steel is covered by a passive film which is formed, for example, in accordance with the equation:

$$Fe \rightarrow Fe^{\circ\circ} + 2e \tag{1a}$$

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$$Fe^{\circ\circ} + 2OH' \rightarrow Fe(OH)_2\downarrow \qquad\qquad (6)$$
(from solution) (insoluble)

Only when the potential has risen so high that a different reaction can take place in accordance with:

$$2H_2O \rightarrow 4H^\circ + O_2 + 4e \qquad\qquad (4)$$
(water)   (oxygen)

in which oxygen gas is evolved, does the current density rapidly increase again and the polarization decrease. The potential above which this latter effect manifests itself is called the *oxygen evolution potential*, designated as E_{O_2}. It is a little above $+600$ mV (saturated calomel electrode).

Fig. B6b shows such a curve plotted on a semi-logarithmic scale. Among the advantages offered by this scale is that very low current densities which play an impor-
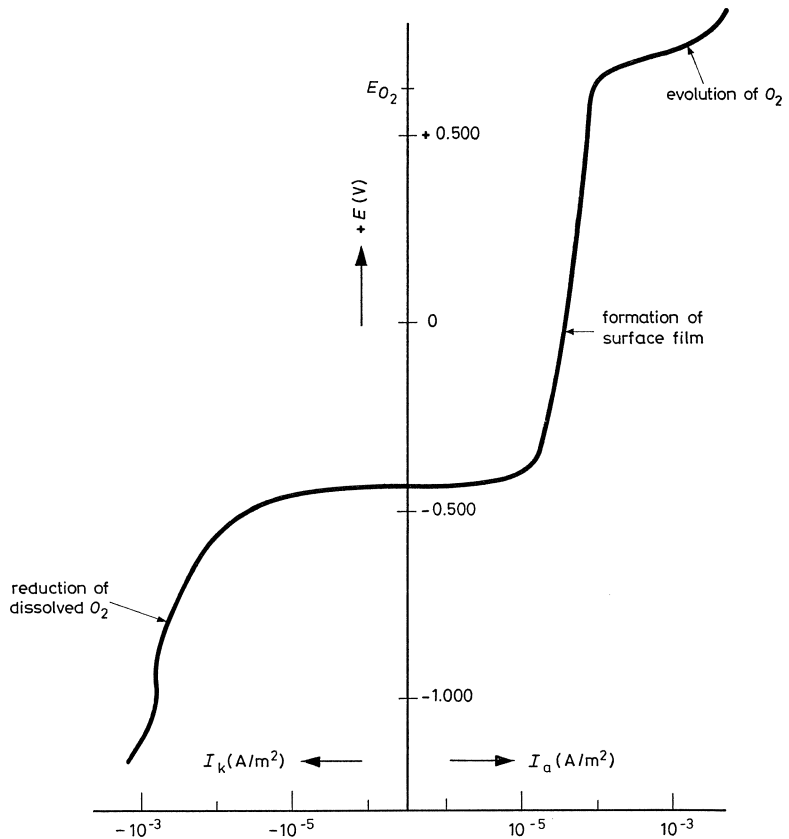

Fig. B6b. Polarization curve measured for mild steel in saturated lime-water, plotted on *semi-logarithmic* scale.

tant part in connection with passivity (formation of a surface film which seals off the metal from the solution or water in the mortar), can be suitably represented in such diagrams.

E–I curves measured for reinforcement embedded in concrete (chloride-free and alkaline) show considerable similarity with the curve plotted in Figs. B6a and B6b. Hence this curve is important as a basis for assessing the corrosion of reinforcement. Although the reaction (1a) is greatly retarded by the formation of a surface film in accordance with (6), evolution of oxygen above +600 mV takes place as indicated in reaction (4). This signifies that the surface film does not constitute any (major) obstacle to O_2 evolution. Hence it can be inferred that this layer is indeed electrically conductive (not for ions, but for electrons) and that O_2 evolution takes place largely at the interface of the oxide film and the electrolyte.

5   Saturated lime-water with calcium chloride

The influence of the presence of free chlorine ions (chloride) in saturated lime-water manifests itself in a decrease in the potential range in which the current density is practically zero. The presence of those ions is more particularly evidenced by the anode curve and hardly at all by the cathode curve. The reason for this is that the
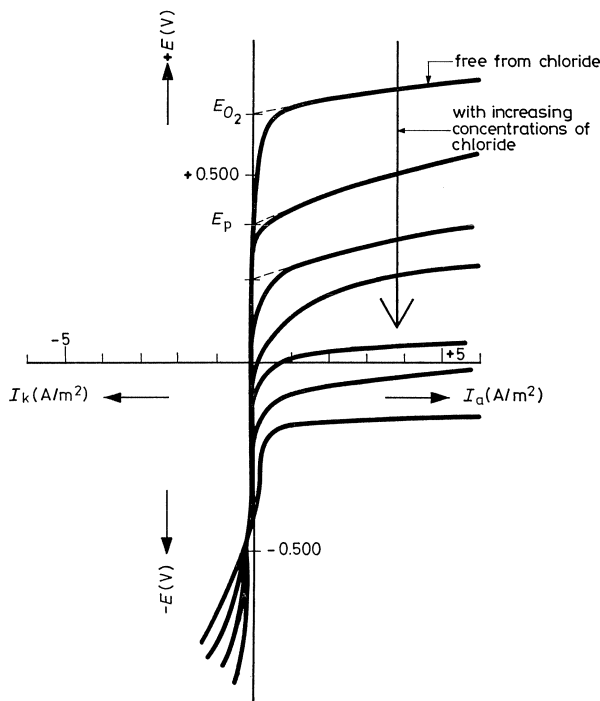

Fig. B7. E–I curves measured for steel in saturated lime-water with different chloride concentrations.

negatively charged chlorine ions from the solution are, during anodic polarization, as it were forced towards the surface of the metal.

When the potential rises from, say, -600 mV, passivation does indeed at first occur, but before the oxygen evolution potential ($+600$ mV) is reached the current density undergoes a considerable increase and $\Delta E/\Delta I$ decreases sharply. The passive film of iron (hydr)oxide is now as it were locally pierced by the highly active chlorine ions. Pitting occurs. The potential above which this takes place is sometimes referred to as the *pitting potential*, designated by E_p.

The effect of chloride, which manifests itself in the occurrence of a pitting potential below the oxygen evolution potential, is already apparent at a chloride concentration of only 0.017 gram ion of chlorine per litre of saturated lime-water or a 0.060% Cl' solution. The pitting potential is lower according as the chloride concentration is higher. The dependence of the pitting potential on increasing chloride concentration is illustrated qualitatively in *Fig. B7*.

No clear-cut relationship between the chloride concentration and the pitting potential was established, however: from a measured pitting potential it was not possible to determine the chloride concentration. This was because a wide range of scatter was found. In *Fig. B8* the results of 159 pitting potential measurements in saturated lime-water with varying calcium chloride concentrations have been plotted. The two solid lines connect the highest and the lowest values respectively, while the dotted line represents the average.
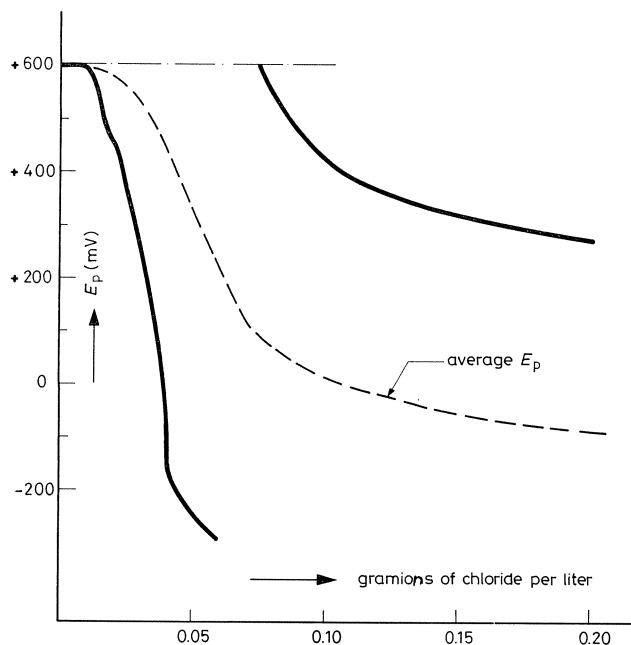

Fig. B8. Relationship between pitting potential of mild steel and the concentration of chloride in saturated lime-water.

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If this average line is plotted on a semi-logarithmic scale, a linear relationship (in the form of a band) between the pitting potential and the logarithm of the chloride concentration is obtained. The slope of this line corresponds to approximately 0.6–0.7 volt. Polster and Keucher [3] likewise found a linear relationship.

6 Saturated lime-water with concrete admixtures

Twenty concrete admixtures were studied in demineralized water as well as in saturated lime-water. These investigations related to the specified amounts and also to three fold increased amounts of admixture, based on a theoretical water/cement ratio of 0.50. The chloride content and the pH were also measured. Some of the admixtures were found to have an acid reaction; all of them were to be rated as free from chloride for practical purposes. The highest chlorine content (0.08% Cl) was found in the
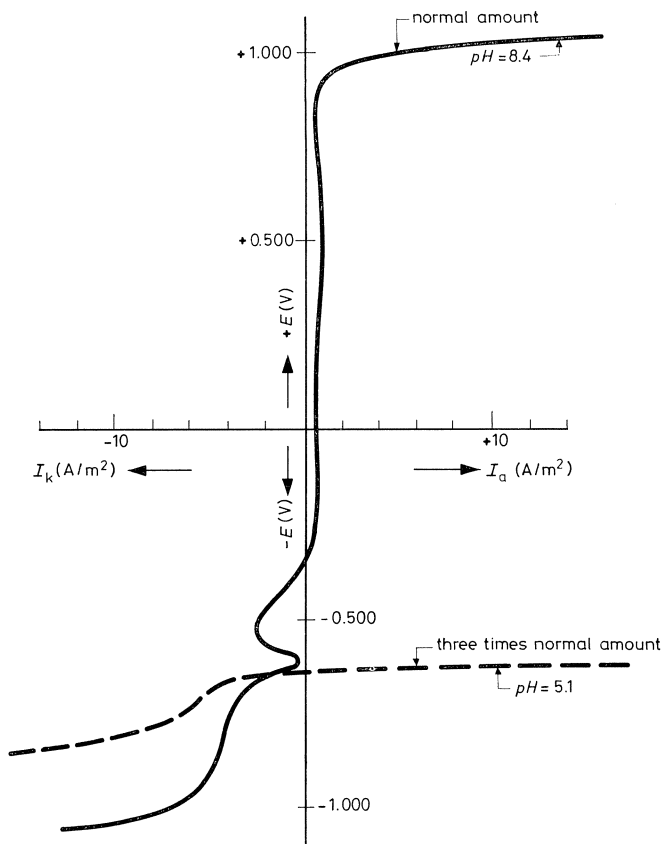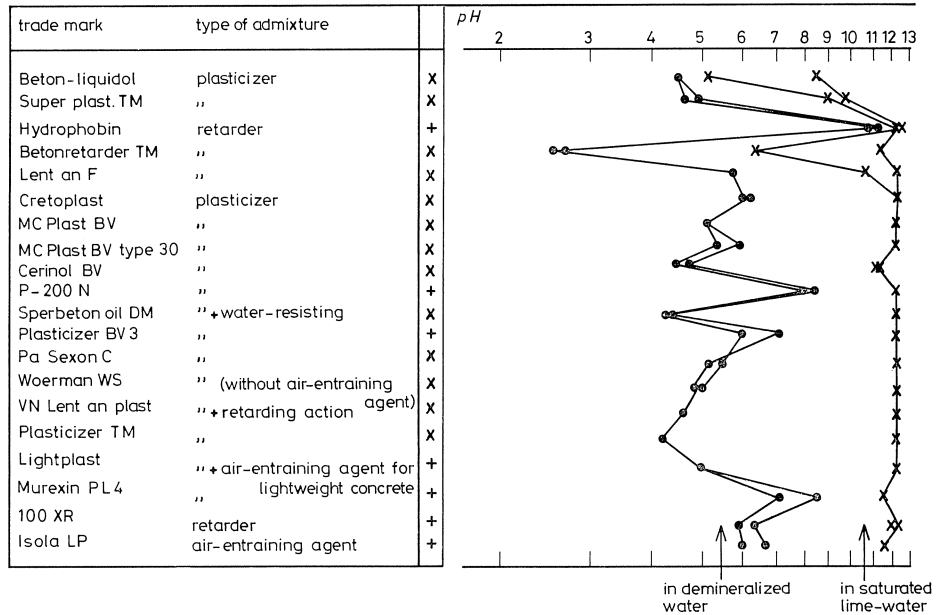

Fig. B9. *E–I* curves measured for mild steel in saturated lime-water with "Liquidol" (as formerly manufactured) in the normal specified amount and in three times that amount (assumed water/cement ratio = 0.50).

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trade mark	type of admixture		pH
Beton-liquidol	plasticizer	x	
Super plast. TM	,,	x	
Hydrophobin	retarder	+	
Betonretarder TM	,,	x	
Lent an F	,,	x	
Cretoplast	plasticizer	x	
MC Plast BV	,,	x	
MC Plast BV type 30	,,	x	
Cerinol BV	,,	x	
P-200 N	,,	+	
Sperbeton oil DM	,, +water-resisting	x	
Plasticizer BV 3	,,	+	
Pa Sexon C	,,	x	
Woerman WS	,, (without air-entraining agent)	x	
VN Lent an plast	,, +retarding action	x	
Plasticizer TM	,,	x	
Lightplast	,, +air-entraining agent for lightweight concrete	+	
Murexin PL 4	,,	+	
100 XR	retarder	+	
Isola LP	air-entraining agent	+	

in demineralized water   in saturated lime-water

admixture known commercially as "Hydrophobin", but this did not cause any change in the *E–I* curve for saturated lime-water.

The measured pH values of the various admixtures are listed in *Table B1*. Only for "Liquidol" was the threefold amount in lime-water found liable to cause corrosion, as indicated by the *E–I* curve in *Fig. B9*. In lime-water, ammonia was split off by the "Liquidol" investigated at the time. In mortar an excess of free lime is present, however, so that there is no reason to fear that corrosion will occur in mortar (or concrete).

7 Prestressing steel

The polarization curves appeared not to be suitable for the investigation of prestressing steel in concrete as regards its susceptibility to hydrogen embrittlement. For testing this susceptibility a method is deliberately used in which atomic hydrogen is discharged in accordance with:

$$H^\circ + e \rightarrow H \tag{2c}$$

The atomic hydrogen (H) then penetrates into the lattice of the metal. In an alkaline environment the reaction (2c), however, hardly occurs because of the low hydrogen ion concentration. Molecular hydrogen gas (H_2) is evolved. Probably (molecular) hydrogen gas is developed in sequent on a direct reaction between two water molecules, as follows,

$$2H_2O + 2e \rightarrow 2OH' + H_2 \tag{5}$$

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The molecular hydrogen cannot penetrate into the steel, so *this* hydrogen appears to be as yet of little interest as regards hydrogen embrittlement.

8 Conclusions

An insight into the electrochemical corrosion behaviour of metals in various environments can be obtained rapidly by the measurement of polarization curves.

For reinforcing steel (mild steel without mill scale) at first the effect of some model liquids with different corrosive actions on steel was investigated upon shape, slope and position of the polarization curve. After that polarization curves were used to study the influence of calciumchloride in lime-water.

When salt (e.g., chloride) is added to lime-water, even quite low concentrations (above 0.060% Cl') will disturb the passive layer formed by the lime-water.

The behaviour of 20 concrete admixtures which were investigated showed that these substances will not cause attack of the metal in a concrete environment, even though some of them react with the free lime: in relation to the small amount of admixture there is an excess of free lime in the concrete. However, when admixtures are stored in, for example, steel drums it may occur in some cases that such drums undergo corrosion.

With regard to reinforced concrete or prestressed concrete, for which the action of chloride is more particularly important, it is not sufficient to confine the investigations to model liquids, however. The much more complex behaviour of concrete itself will then have to be considered.

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