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EVALUATION OF TECHNIQUES FOR INVESTIGATING THE
CORROSION OF STEEL IN CONCRETE

by

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ABSTRACT

Electrode potential, constant anodic current polarisation, and electrical resistance probe measurements have been employed to investigate the corrosion of mild steel in concrete and cement/water grouts. The usefulness of the data obtained is discussed and corrosion threshold sodium chloride concentrations reported. The influence of moisture content on the electrode potential measurements is examined and shown to be of critical significance. It is indicated that corrosion threshold data are dependent on exposure conditions and surface state of the steel and the difficulty in relating results in calcium hydroxide solutions and concrete is described.

1. INTRODUCTION

A considerable amount of work has been reported on the corrosion of the steel reinforcement in concrete and the influence of chloride ions on this corrosion. However there is little agreement in the literature for the value of chloride ion concentration above which corrosion is significant and there is no satisfactory method of measuring corrosion rates in concrete. The three methods which have been used to monitor corrosion of steel in concrete are:

- 1) visual examination and/or weight loss determination of reinforcement after derusting¹
- 2) potential measurements on the reinforcement vs a reference electrode²
- 3) electrochemical polarisation studies^{1,3}

All these methods have limitations namely:

- 1) Weight loss determination is a destructive test and the necessity to remove both concrete and rust from the steel introduces errors into the measurement.
- 2) Potential measurements can establish the thermodynamic feasibility of the corrosion reaction but give no reliable information concerning the corrosion rate.
- 3) Electrochemical polarisation studies give information about the stability of the passive film formed on steel in concrete, but no values of corrosion rate.

Experiments on the corrosion of mild steel in $\text{Ca}(\text{OH})_2/\text{NaCl}$ solutions⁴ are useful in studying the mechanism of the corrosion reaction but the results are of little value in forecasting the corrosion rate of steel in concrete; there is no known method of determining the chloride ion concentration in the pore water of concrete, and the transport of oxygen to the steel surface is a very different process in solutions and in concrete.

It was decided to investigate the corrosion of steel in concrete using three different methods which have previously been examined in $\text{Ca}(\text{OH})_2$ solutions.⁵

- a) electrode potential measurements
- b) constant anodic current polarisation measurements
- c) electrical resistance probe measurements.

This last method is new to concrete reinforcement studies⁶ and produces the results in the form of corrosion rates. It is based on the measurement of changes in electrical resistance which are proportional to the loss in metal due to corrosion, since the corrosion product, being non-metallic, has an electrical conductivity many orders of magnitude lower than the metal. In order to obtain sufficient sensitivity, the measurements are carried out using a metal specimen of small but precisely known cross sectional area and recording the resistance changes with a compensating AC bridge network. The influence of chloride content and moisture content on the corrosion of mild steel in concrete was investigated using methods a, b and c.

A significant amount of the vast literature on the corrosion of steel in concrete is in conflict or incomplete but a brief review of the literature relevant to this paper follows.

The relationship between the rate of corrosion of iron and the alkalinity and chloride content of the environment has not been completely elucidated although it has been suggested that there is a threshold sodium chloride concentration which must be exceeded before corrosion can occur⁴, indicating that at higher alkalinities more chloride can be tolerated. Chlorides present in concrete can result from a number of sources such as:

- 1) aggregates - from marine sources or thawed with de-icing salt
- 2) mixing water - marine water or normal water contaminated with salt
- 3) cement - some cements contain small quantities of chloride
- 4) CaCl_2 - used as an accelerator
- 5) de-icing salts and marine spray by penetration during the service life of the structure following concrete curing.

A substantial quantity of these salts are known to be present in an insoluble form⁷, possibly calcium chloro-aluminate, within the concrete. It should be noted that the soluble and insoluble chloride are in chemical equilibrium and if the soluble chloride is leached out, insoluble chloride will dissolve to maintain the equilibrium state.

It has been claimed⁸ that because the solubility of oxygen in sodium chloride solution is a maximum at about 3 per cent NaCl a maximum corrosion rate will occur at about this concentration. However, except in fully saturated concrete the oxygen diffuses through air filled pores up to the steel where it diffuses through a thin film of liquid. Hence the major difference is between oxygen transport through a fully saturated concrete and through a concrete specimen containing air filled pores.

The tricalcium aluminate, (C_3A), content of the cement influences the effect of chloride ions on the corrosion of steel in concrete⁷ as this is the cement component which is said to react with chlorides to form the insoluble calcium chloro-aluminate. This is not the only cement constituent which converts chloride ions into an insoluble form however, as cement containing no C_3A also reduced the free Cl^- concentration.

For corrosion to occur it is necessary:

- a) to have sufficient oxygen, water and chloride to break down the passive film on the iron
- and
- b) to have differences in electrode potentials along the steel reinforcement

These differences can arise from heterogeneities in the steel (eg sharp bends, welds), heterogeneities in the concrete or from differences in environmental exposure at different places on the structure. Normally all

three of these factors will be freely present and hence (a) is the critical requirement. The main differences in electrode potential result from differences in alkalinity, chloride concentration and oxygen concentration which can be caused by bleeding, segregation or cracking of the concrete. Generally a well prepared concrete will not have major faults, but by its very nature all concrete is heterogeneous, and variable to some degree.

Differences in chloride ion concentration resulting in potential differences may occur on bridge decks due to non uniform application of de-icing salt, or because the upper side of the reinforcing steel is exposed to a higher chloride concentration than the lower side or in the structural beams due to drainage through joints and cracks. This type of drainage can result in leaching of OH^- producing differences in alkalinity.

It is claimed that the corrosion rates of reinforcing steel and prestressing steel under similar conditions are almost indistinguishable⁷ and the application of stress has little influence on the corrosion rate⁹.

2. EXPERIMENTAL

2.1 Preparation of specimens

Lengths of 3mm diameter mild steel rod were embedded in concrete or grout cylinders of dimensions 80mm long x 40mm diameter. The rods had previously been degreased in trichloroethylene and abraded with 250 grade emery paper before masking the ends with a lacquer to a depth of 10mm from the concrete/air boundary to prevent possible short term carbonation effects.

The concrete and grout characteristics were as follows:

	Sand Laleham	Cement Normal Portland	Water Distilled
Concrete	3	1	0.45
Grout	0	1	0.40

The aggregate characteristics were as follows:-

Sand size	% by weight
5mm - 2.4mm	14
2.4mm - 1.2mm	21
1.2mm - 600 μ m	21
600 μ m - 300 μ m	28
300 μ m - 150 μ m	16

The sodium chloride additions were made to the mixing water and the mould was vibrated for 3 minutes after pouring and cured for seven days in a humid environment. The sodium chloride contents are expressed as a percentage by weight of the cement content of the concrete.

2.2 Potential measurements

Two reference electrodes were used for comparison, the saturated calomel electrode (SCE) and the saturated copper/copper sulphate electrode (Figures 1 and 2). The potential between the steel and the reference electrode was measured using a high impedance voltmeter, sufficient time being allowed to attain equilibrium.

The weight of the concrete/grout/steel samples was measured to ± 10 mg.

- after soaking in distilled water for 2 days, and surface drying
- periodically after natural drying in laboratory environment
- finally after drying in an oven at 105°C to constant weight.

2.3 Constant current polarisation measurements

The steel/concrete specimens were made the working electrode in a cell with a stainless steel counter electrode and a saturated calomel electrode as reference electrode in a separate compartment connected to the main cell by an agar bridge, prepared using potassium nitrate for the conducting species, with a luggin capillary (Figure 3). Constant anodic currents were applied using a potentiostat in the galvanostat mode and the resultant potential-time curves were plotted on a linear recorder. Tests were performed in the presence and absence of oxygen.

2.4 Corrosion rate measurements using resistance probes

Mild steel (EN2A) resistance probes 50 μ m thick were embedded in concrete and grout cylinders. After curing for 7 days in a moist atmosphere, measurements were commenced using a Magnachem CK3 corrosometer resistance bridge. The concrete and grout specimens were exposed in two distinct environments.

- a) the laboratory environment Temperature $23 \pm 3^{\circ}\text{C}$
Relative Humidity $30 \pm 10\%$

- b) partially submerged in water Temperature $23 \pm 3^{\circ}\text{C}$

3. RESULTS

3.1 Potential measurements

Potential-time curves for concrete containing a range of sodium chloride concentrations is shown in Figure 4. The empirical dividing line between corrosion and non-corrosion for mild steel in concrete occurs at about -0.3V vs the saturated copper/copper sulphate electrode¹⁰. On this basis at sodium chloride concentrations at or below 2.5 per cent corrosion does not occur after the initial few days of exposure in the laboratory environment. After longer exposure periods the potential of the 5 and 10 per cent samples increases predicting a cessation of corrosion.

Figure 5 shows a comparison of the potential-time curves obtained for 0.1 per cent NaCl in concrete using two different reference electrodes, the saturated calomel (SCE) and saturated copper/copper sulphate electrodes. It can be seen that at equilibrium the SCE is about 0.11V more positive than the copper/copper sulphate electrode and this is in good agreement with the standard difference of 0.09V showing that both these electrodes are suitable for monitoring potential measurements in concrete systems.

Figures 6, 7 and 8 show the influence of moisture content on the potential of mild steel in concrete and grout. It can be seen that a small change in moisture content can result in a large change in potential and consequently have a major influence on corrosion prediction. For example at high moisture contents all concrete specimens indicated corrosion while at low moisture contents only the 10 per cent NaCl sample indicated corrosion.

A similar pattern was observed with the grout samples. For the concrete samples the degree of saturation of the concrete over which the potential changes rapidly is in the narrow range 75-90 per cent of total saturation for all samples.

3.2 *Anodic polarisation measurements*

These curves shown in Figure 9 indicate that a sodium chloride concentrations of 1 per cent and less there is no corrosion.

3.3 *Resistance probe measurements*

Figure 10 shows that in a dry laboratory atmosphere, 30 per cent R.H., the corrosion of steel in concrete and grout does not occur to any significant extent until the sodium chloride concentration exceeds 2.5 per cent. When the specimens are partially submerged in water to simulate a splash zone significant corrosion occurs at much lower sodium chloride concentrations in the case of concrete at concentrations in excess of 0.1 per cent NaCl.

4. DISCUSSION

4.1 *Potential measurements*

Figures 4, 6, 7 and 8 illustrate the limitations and pitfalls which must be closely observed when making predictions about the corrosion of steel in concrete from electrode potential measurements.

i) over a critical range of moisture content values, 75-90 per cent total saturation, the electrode potential varies rapidly from values indicating corrosion to values indicating passivation. Consequently, when making a potential survey of a structure a single determination at a given point could give misleading results and it would be advisable to make surveys at suitable intervals over a period of about a year so that the effect of moisture content can be allowed for.

ii) the potential of steel in concrete which is submerged in saturated calcium hydroxide solution always gives a very low value indicative of corrosion irrespective of the sodium chloride content of the concrete (Figure 11). It is well known however, that steel embedded in good quality concrete containing no chloride ions and reinforced concrete submerged completely in sea water do not corrode to any significant extent in the first

instance. A passive film is formed on steel at the pH of concrete and secondly the oxygen for the cathodic corrosion process has to diffuse through an aqueous medium to the steel which is a very slow process due to the low solubility of oxygen in water and salt solutions. This illustrates a further limitation.

iii) electrode potential measurements indicate whether corrosion is thermodynamically feasible, but gives no information concerning corrosion rates.

It has been claimed that although the potential of the steel does not correspond with a rate of corrosion, with an increasing amount of corrosion the value of the potential decreases². In this way the potential has been related empirically to the cracking of concrete due to steel corrosion. However, it has been shown that a fully submerged reinforced concrete structure has very low potentials indicating the thermodynamic feasibility of corrosion, but very low corrosion rates owing to the slowness of the cathodic reaction. The empirical relationship between potential of steel and the concrete cracking is only useful providing all conditions can be accurately reproduced because the cracking of concrete resulting from steel corrosion is dependent on concrete strength, absorption, moisture content, stresses and depth of cover.

The threshold sodium chloride concentration making allowances for the above limitations appears to be about 2.5 per cent NaCl. At concentrations of 1 per cent and below corrosion seems unlikely while at concentrations above 5 per cent it seems almost certain except under very dry conditions. 2.5 per cent NaCl is a borderline case in which neither corrosion nor passivity is clearly indicated.

The saturated calomel and copper/copper sulphate electrodes both performed satisfactorily on concrete systems. The calomel is somewhat more accurate than the copper/copper sulphate but the latter is more robust and simple to prepare and consequently is to be preferred for site work¹¹. Calomel electrodes are contaminated by bromides and iodides and copper/copper sulphate electrodes by chlorides¹² so efforts should be made to avoid possible contamination. The electrolyte of the copper/copper sulphate

cell requires frequent replacement if a constant potential is to be maintained.

4.2 *Constant current polarisation measurements*

The results indicate a threshold sodium chloride concentration in the range 1.0-2.5 per cent. These results are in satisfactory agreement with those of Lewis³ who, using a similar method obtained a threshold concentration in the range 0.78-1.56 per cent CaCl_2 . Norwood¹³ using a potentiostatic polarisation technique obtained a threshold concentration in the range 1.5-3 per cent NaCl. The constant anodic current polarisation technique is much quicker than the potentiostatic polarisation technique and more clearly distinguishes the corroding from the passive condition although it does not give any information concerning the potential of passive film breakdown. Baumel¹⁴ using galvanokinetic polarisation measurements had predicted a threshold concentration in the range 0.9-1.7 per cent CaCl_2 and Kondo¹⁵ has reported a threshold concentration of 1 per cent CaCl_2 if stray currents are present resulting in electrolysis.

It should be noted that it is necessary to allow the steel/concrete sample to soak for 24 hours in the calcium hydroxide solution otherwise the rate of increase in potential with time will be very slow on application of the constant anodic current.

4.3 *Resistance probe measurements*

The threshold sodium chloride concentration based on corrosion rate measurements using the resistance probe technique indicates that in a laboratory atmosphere, the threshold range is 1-2.5 per cent NaCl for concrete and 2.5-5 per cent NaCl for cement/water grout. When the steel/concrete and steel/grout samples were partially submerged in water, the threshold concentrations were 0.1-1.0 per cent NaCl for concrete and 1-2.5 per cent for grout. The differences between concrete and grout could be due to the grout having a higher pH due to its higher cement content and when partially submerged in water it absorbed water up to the top of the sample while the concrete absorbed water to a level of about 5mm above the water line. These conditions probably represent the extreme cases of exposure, in the first case a very dry atmosphere ultimately giving a low water content and secondly, an environment with differential oxygen and moisture contents.

Consequently, it can be seen that environmental exposure conditions should not be under-estimated when attempting to establish a threshold sodium chloride level for corrosion. In freely exposed structures it is likely that the water content is higher than in the laboratory and varies from place to place on the structure resulting in differential oxygen and water corrosion cells.

The sodium chloride contents used in this paper are percentages by weight of the cement in the concrete and as such cannot be directly related to the sodium chloride concentrations in $\text{Ca}(\text{OH})_2$ solutions. The common practice in concrete technology of representing salt contents as a percentage of the cement content of the concrete could prove misleading as it is possible to have the same cement content per unit weight of concrete and consequently the same salt content but different aggregate and water contents per unit weight of concrete. It has also been reported that substantial amounts of chloride added to the mix are subsequently converted into an insoluble form, calcium chloroaluminate, thus causing a further complication.

Consider a 200g sample of concrete containing 50g cement and 20g of water and 1g NaCl (2 per cent by wt cement), assume 90% of NaCl is in an insoluble form⁷, therefore the resultant concentration of sodium chloride in pore water is 0.5 per cent, similar to the threshold sodium chloride content predicted by resistance probe and polarisation resistance methods in saturated calcium hydroxide solution⁵. In order to obtain a pore water sodium chloride concentration of 0.03 per cent predicted by electrode potential measurements in saturated calcium hydroxide 99.4 per cent of the sodium chloride would have to be converted to an insoluble form.

5. CONCLUSIONS

1. The resistance probe method is the most suitable way of determining corrosion rates of steel in concrete although it suffers from the limitation that where severe pitting occurs and the probe is non uniformly corroded, the resistance probe measurements will indicate a total loss of metal somewhat greater than has actually occurred. Hence this method cannot be used alone to evaluate corrosion of a severe pitting nature. In this respect the method is similar to the weight loss technique where a metal penetration

somewhat less than has actually occurred in a severe pitting situation is indicated.

2. Environmental factors, especially those influencing the moisture content of the concrete and causing differential oxygen contents must be considered when specifying threshold sodium chloride concentrations. The initial surface condition of the steel and pH of the concrete are also likely to have a significant influence.

3. Potential measurements recorded with due allowance for variations in moisture content can give information relating to the active or passive condition of the steel in concrete.

6. ACKNOWLEDGEMENTS

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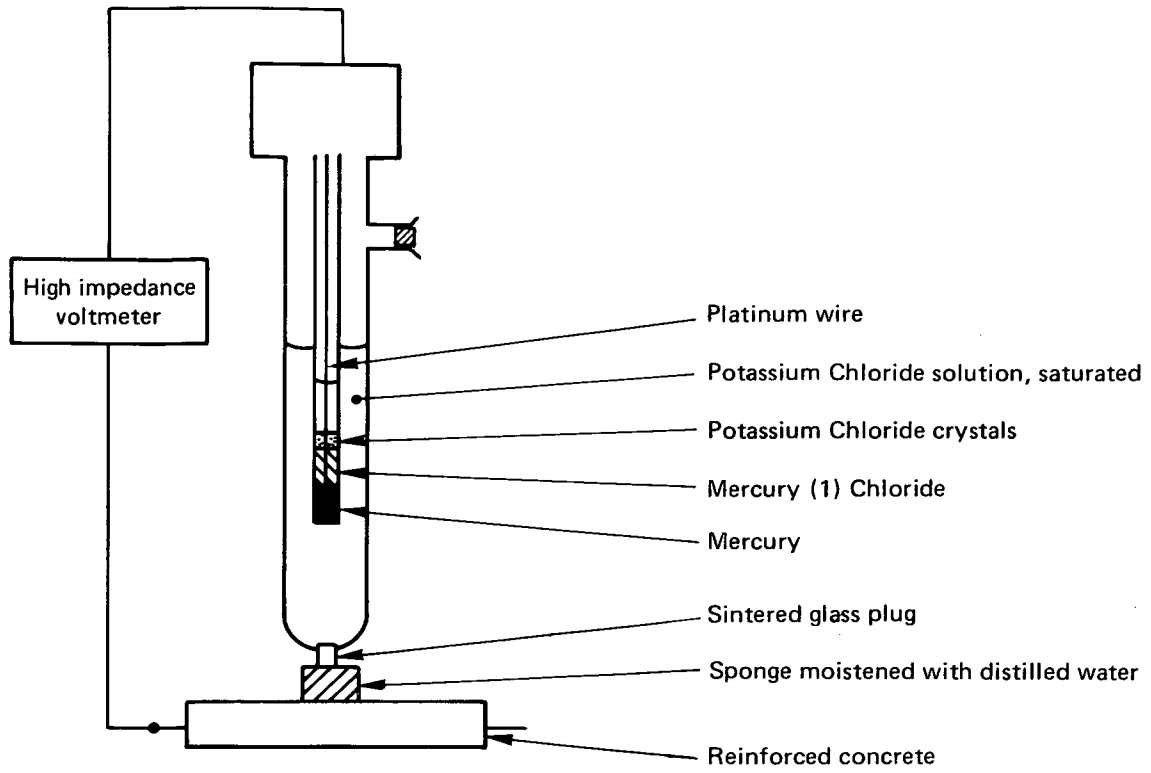


Fig. 1 THE SATURATED CALOMEL REFERENCE ELECTRODE MEASURING THE POTENTIAL OF REINFORCED CONCRETE

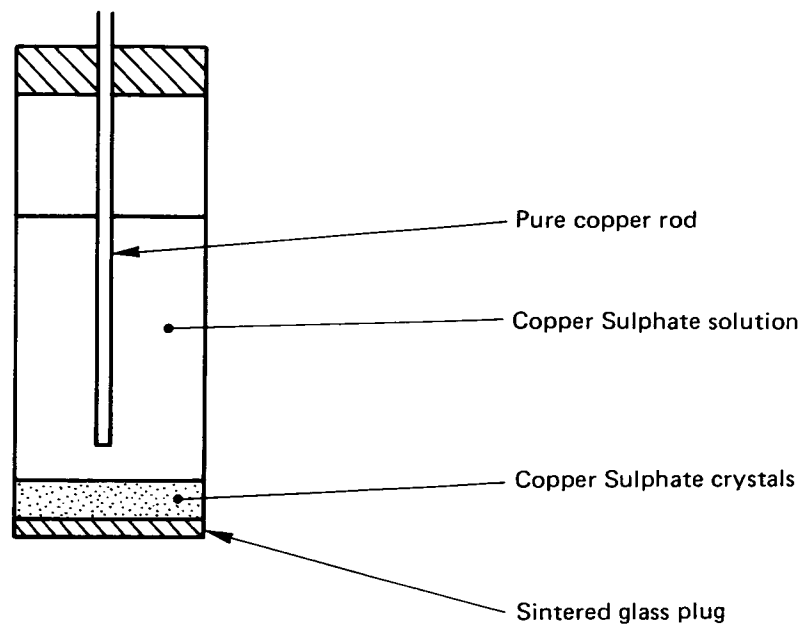


Fig. 2 THE COPPER/COPPER SULPHATE REFERENCE ELECTRODE

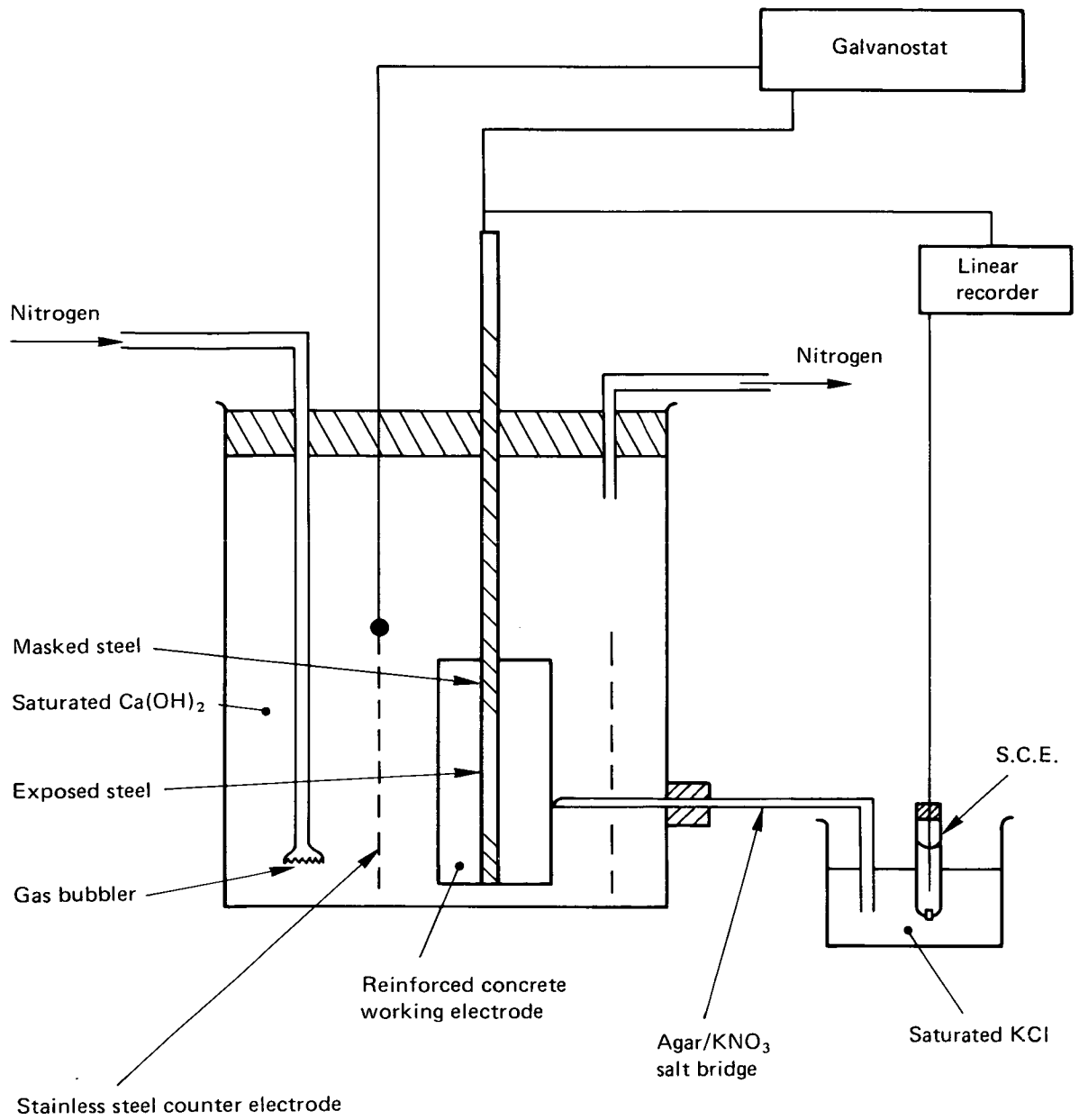


Fig. 3 ELECTROCHEMICAL CELL FOR CONSTANT ANODIC CURRENT POLARISATION STUDIES

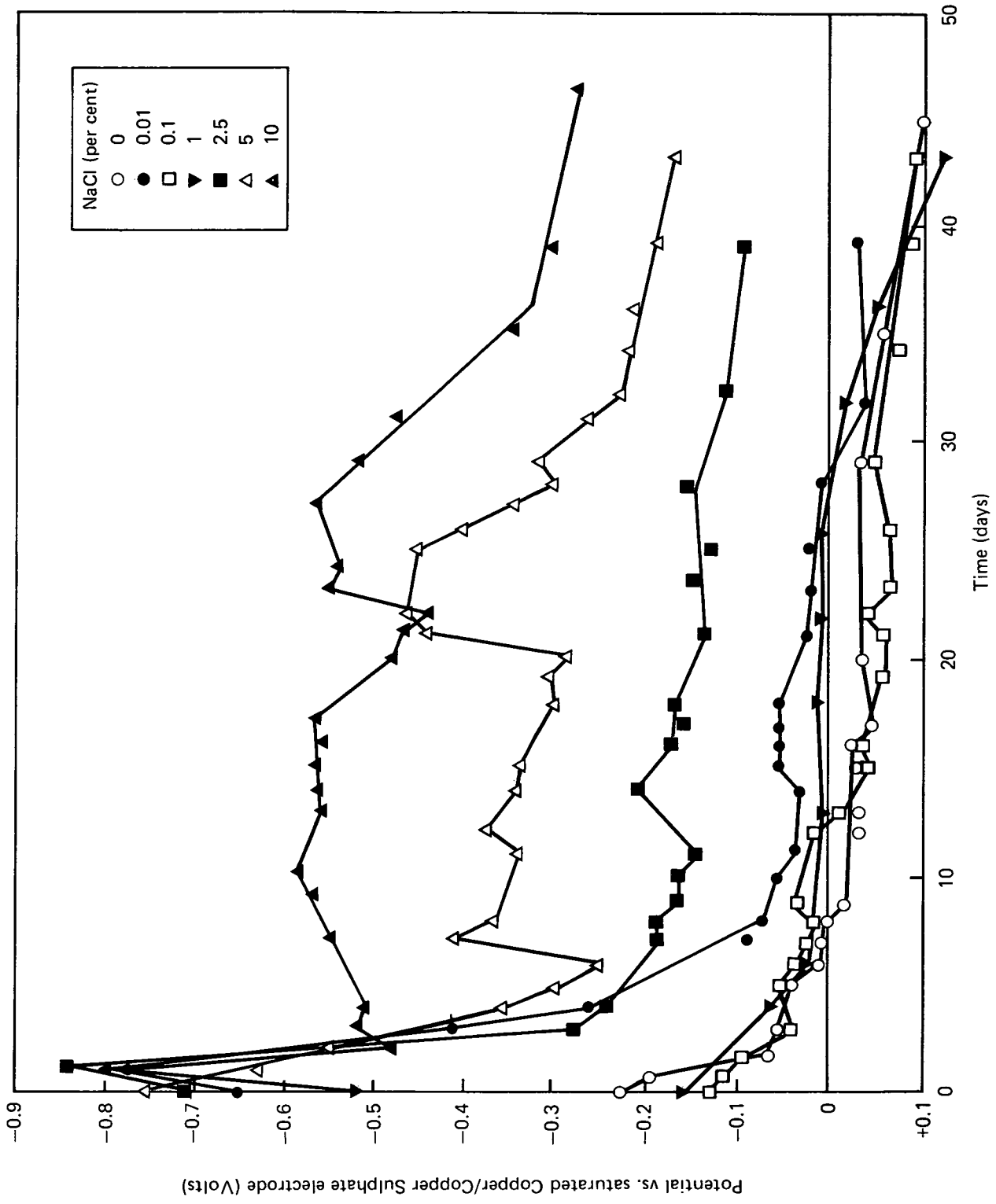


Fig. 4 POTENTIAL OF MILD STEEL IN CONCRETE CONTAINING NaCl ADDITIONS

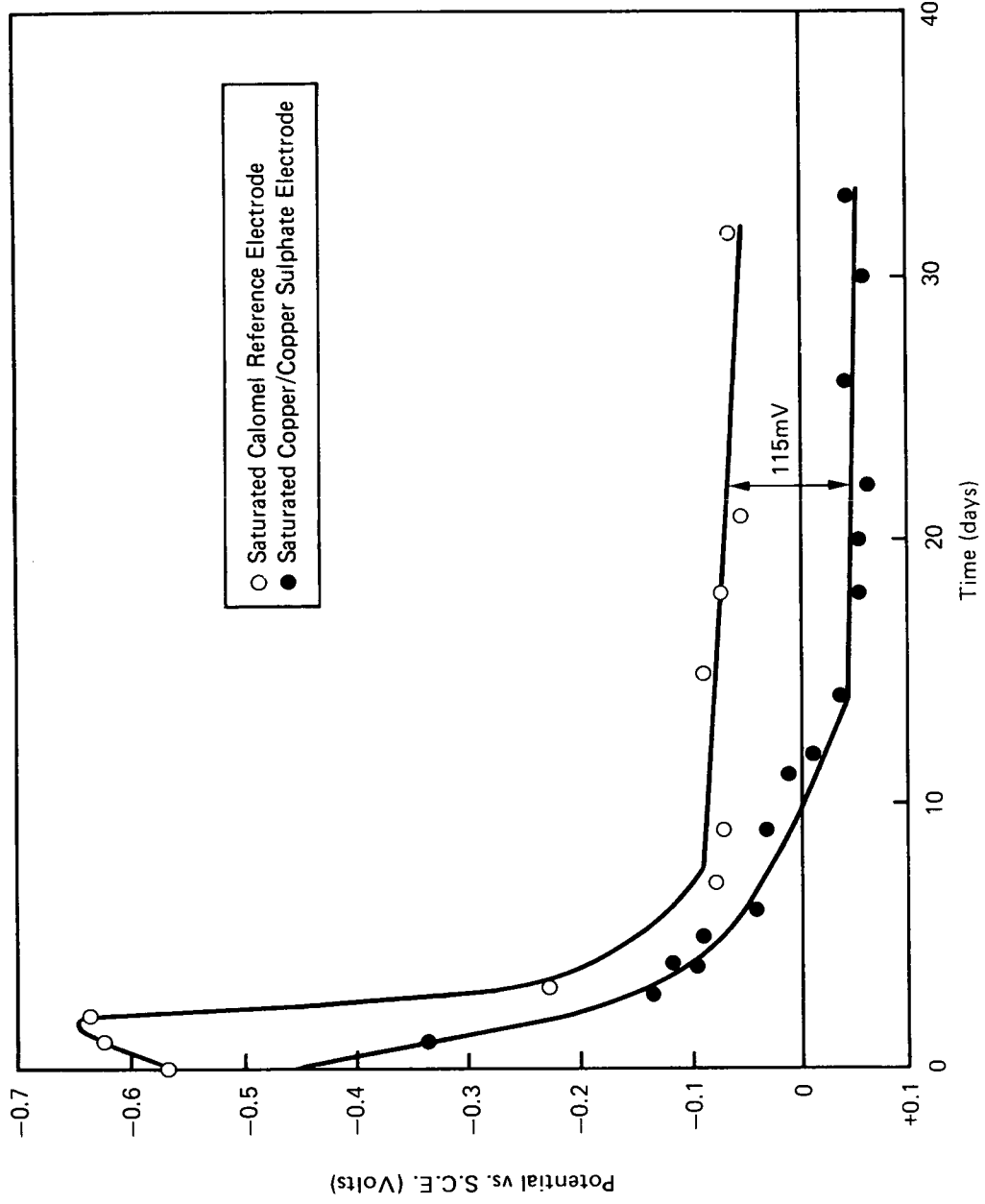


Fig.5 THE POTENTIAL OF MILD STEEL IN CONCRETE CONTAINING 0.1% NaCl MEASURED USING TWO DIFFERENT REFERENCE ELECTRODES

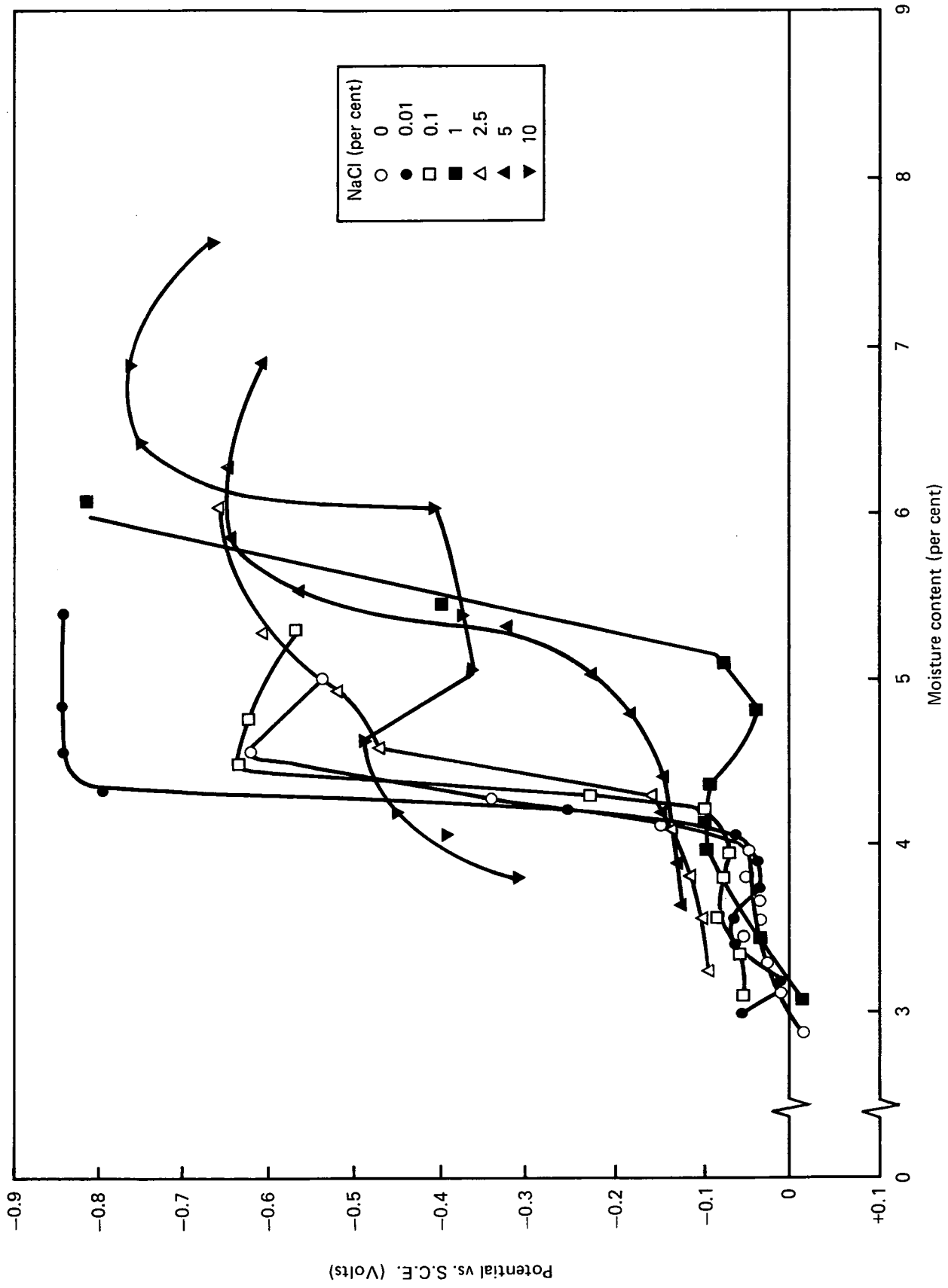


Fig. 6 THE EFFECT OF MOISTURE CONTENT ON THE POTENTIAL OF MILD STEEL IN CONCRETE

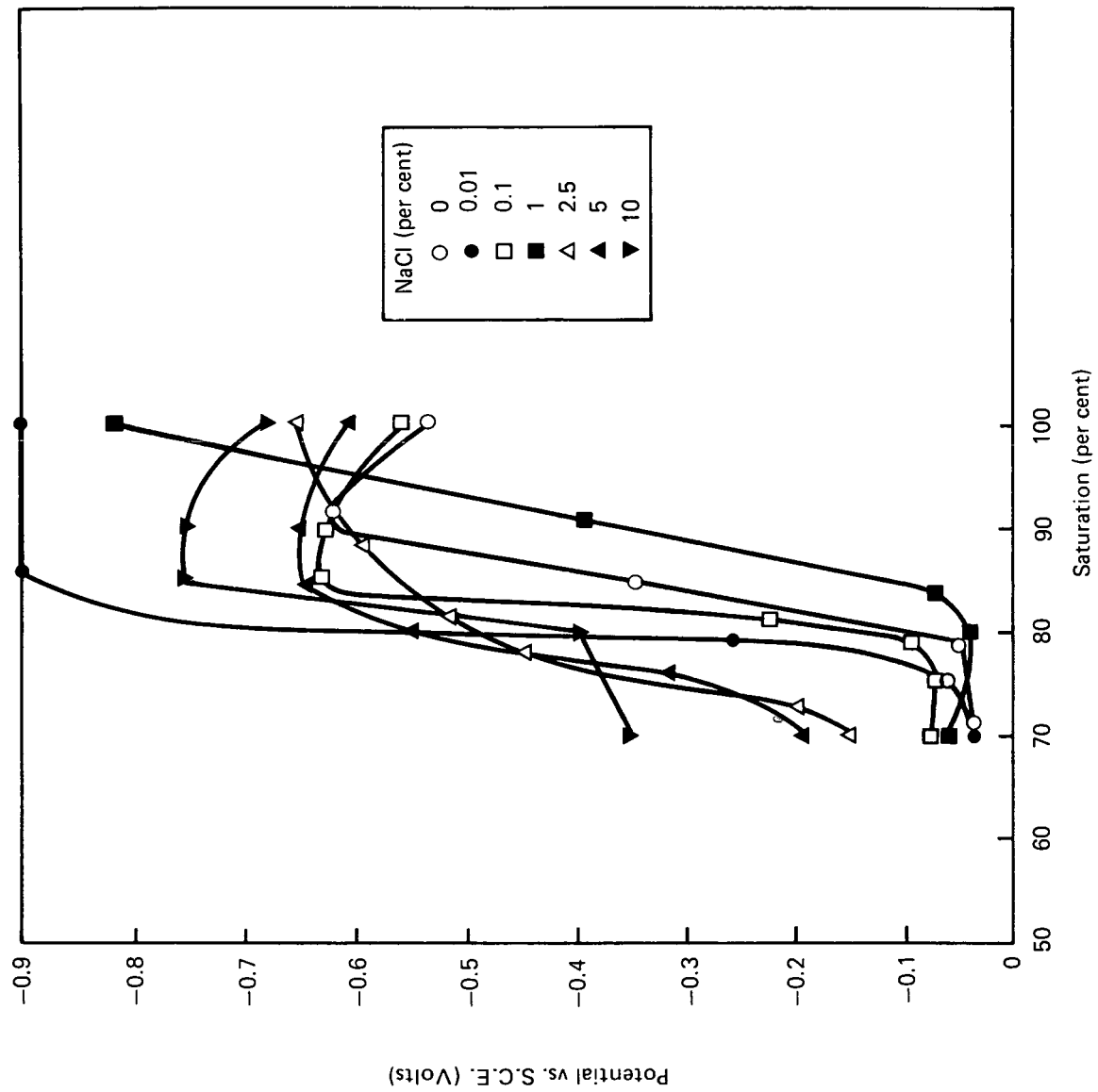


Fig. 7 THE POTENTIAL OF MILD STEEL IN CONCRETE AS A FUNCTION OF DEGREE OF SATURATION OF CONCRETE WITH WATER

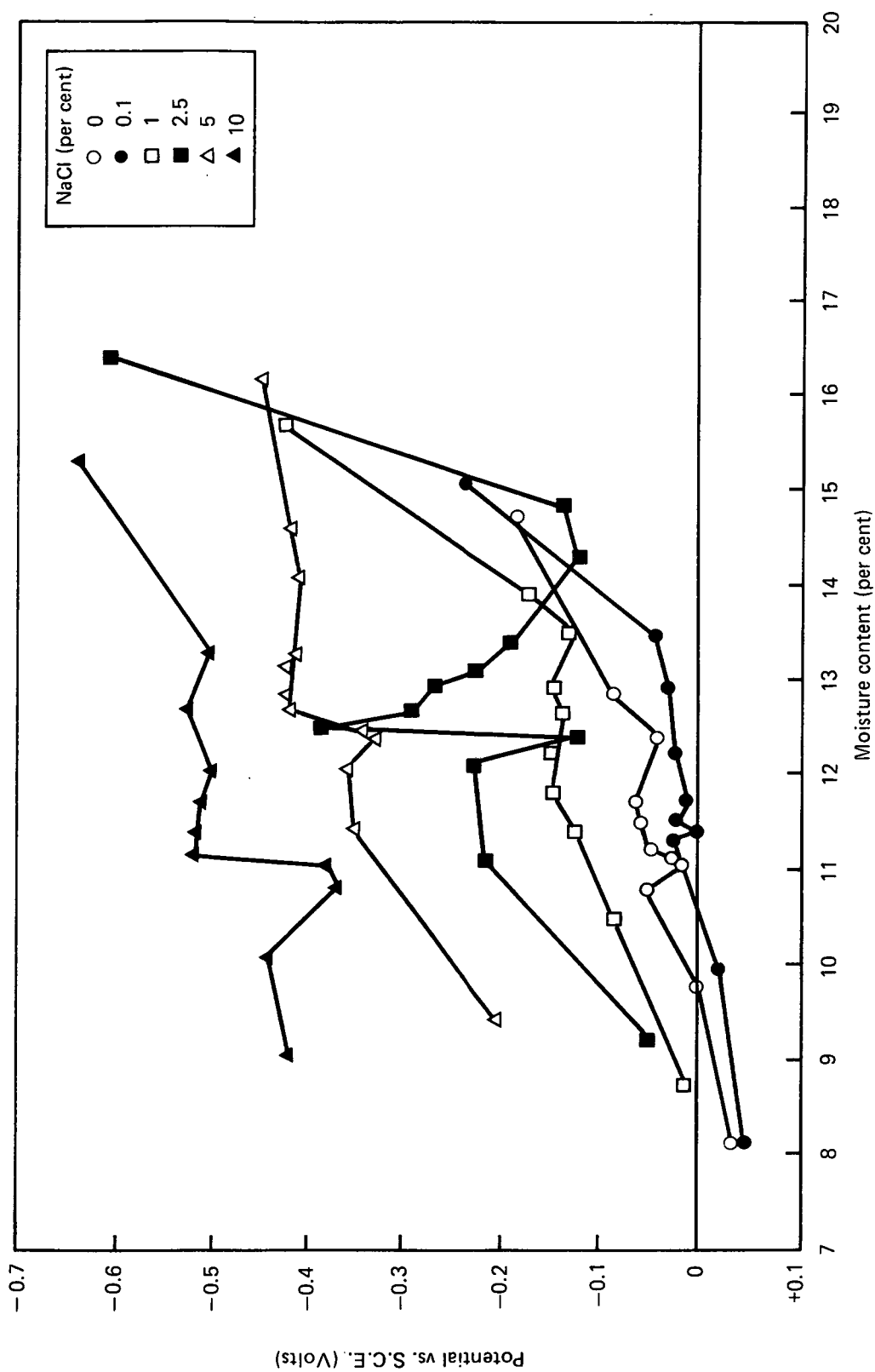


Fig. 8 THE EFFECT OF MOISTURE CONTENT ON THE POTENTIAL OF MILD STEEL IN A CEMENT/WATER GROUT

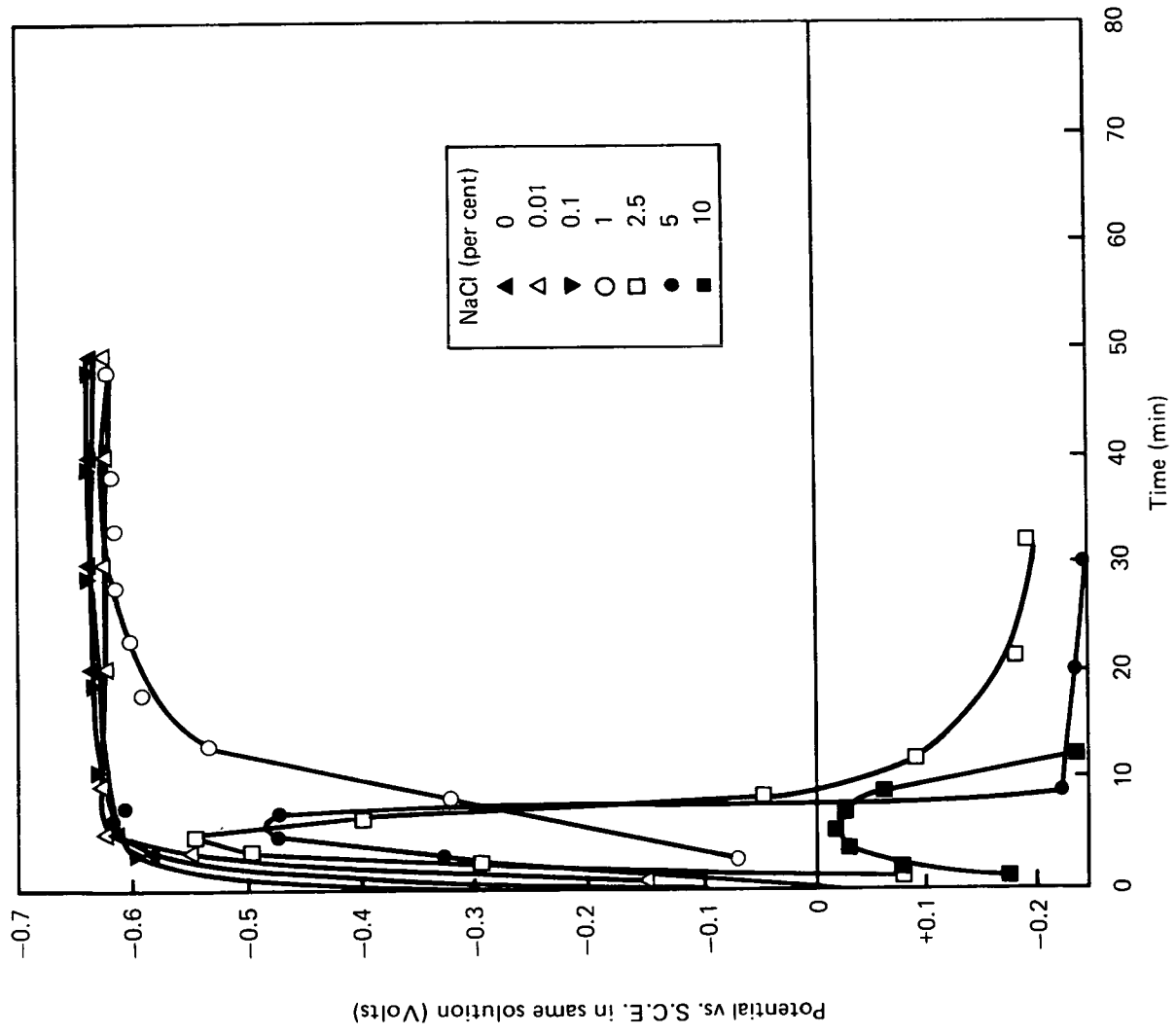


Fig. 9 CONSTANT CURRENT POLARISATION CURVES FOR MILD STEEL IN CONCRETE

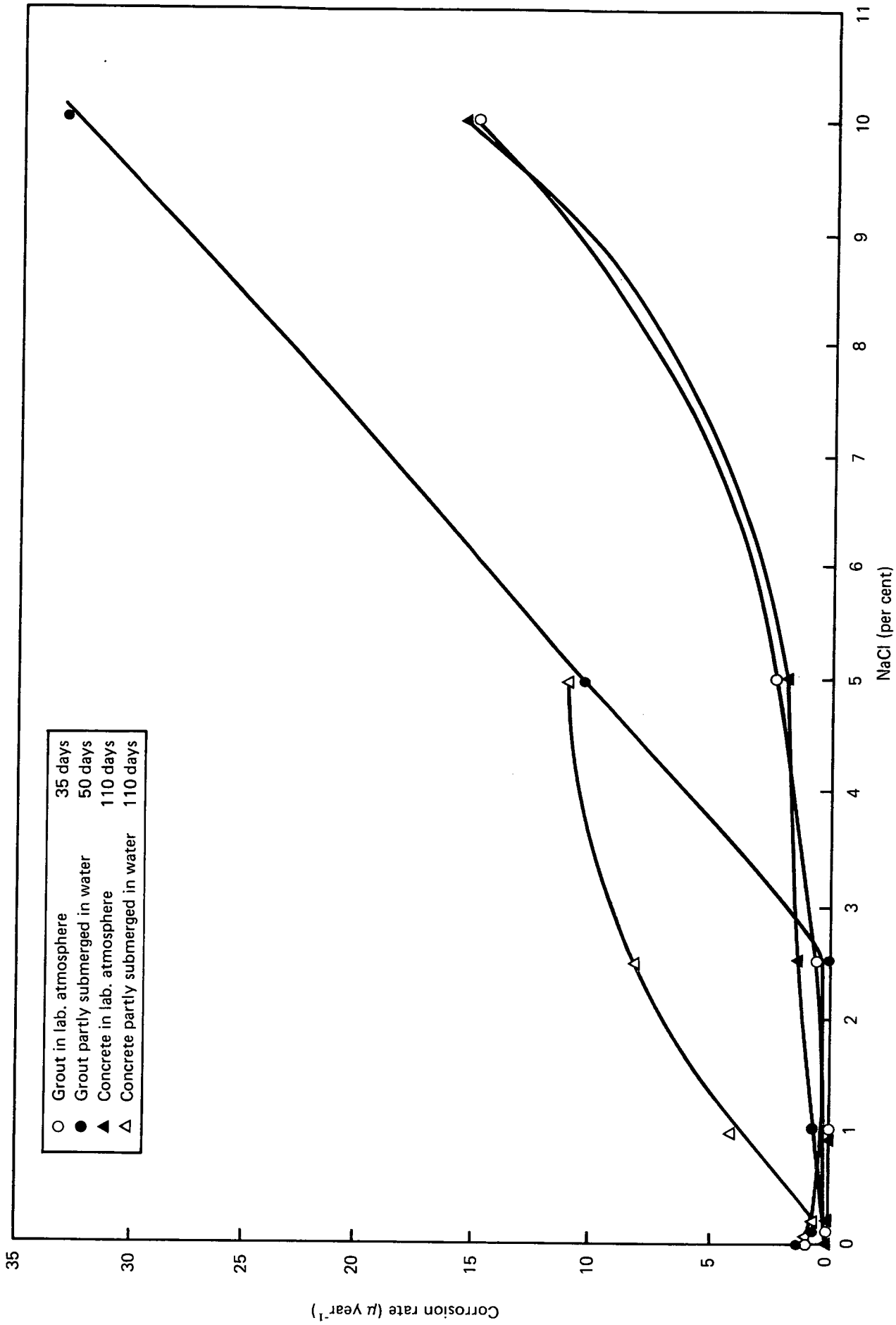


Fig. 10 THE EFFECT OF SODIUM CHLORIDE CONCENTRATION ON THE CORROSION RATE OF MILD STEEL IN CONCRETE AND GROUT

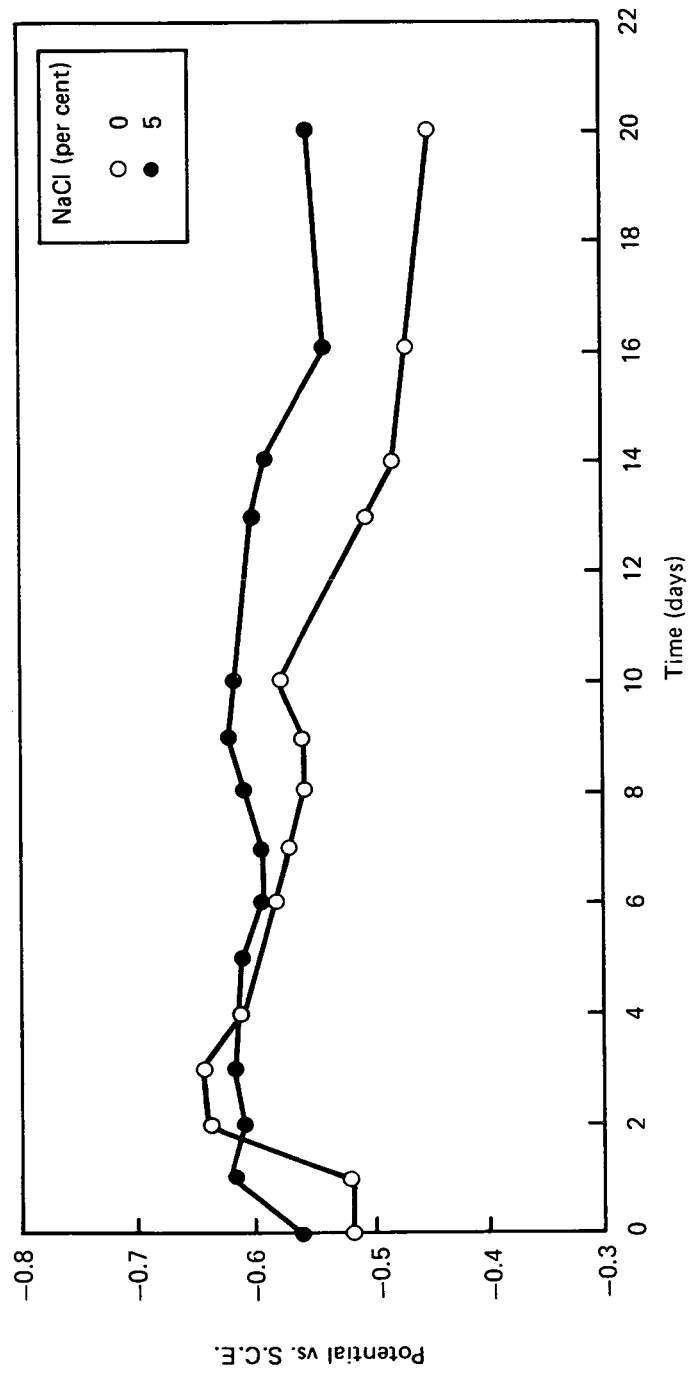


Fig. 11 POTENTIAL TIME CURVES FOR STEEL/CONCRETE SPECIMENS FULLY SUBMERGED IN SATURATED CALCIUM HYDROXIDE

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