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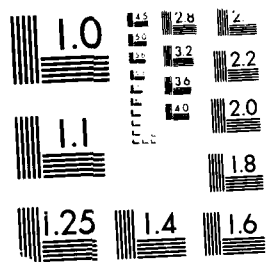
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**Variability with surface condition of  
potentials measured on reinforced  
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C C Naish and R F A Carney

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VARIABILITY WITH SURFACE CONDITION OF POTENTIALS  
MEASURED ON REINFORCED CONCRETE STRUCTURES

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ABSTRACT

This paper presents some observations on the variability of measurements obtained during a "potential mapping" survey of a concrete structure. The results are discussed in terms of Evan's diagrams and conclusions drawn on the cause of the effects observed.

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### Introduction

This paper presents some observations on the variability of measurements obtained during a "potential mapping" survey of a concrete wall. Very large discrepancies were observed during trials of a new potential logging instrument based on a portable micro-computer (Epson HX-20). The brief series of measurements reported here were carried out to find the cause of these discrepancies. The results are discussed in terms of Evans's diagrams and conclusions drawn on the cause of the effects observed.

### Experimental

The criteria used to determine the state of reinforcing steel in concrete by "potential mapping" are the value and distribution of the apparent half cell potential of the steel as measured on the surface of the concrete. These measurements are normally made by connecting the steel to the +ve side of a high impedance DVM, and the -ve side to a saturated calomel electrode which is in contact with the concrete surface via a suitable conducting electrolyte solution and a porous wooden plug (Figure 1).

In the tests described here, measurements were made on a grid pattern over one wall of a small exposed reinforced concrete structure. At each point on the grid the surface of the concrete was chipped away to remove the cement rich layer and any carbonated concrete. This was done before the first measurements, and all subsequent measurements were made at these points without further chipping or abrasion. Before each measurement the grid point was wetted by painting it with 0.1M NaOH solution and contact to the half cell was made by placing the wooden plug on the prepared surface. Wetting and measurements were done in blocks of ten, and good stable readings were obtained in this way.

The microcomputer system (Thompson Electrochem Ltd.) comprised an HX-20 Epson microcomputer linked to a high impedance ( $> 10^9 \Omega$ ) analogue voltage measuring circuit via an PS-232 interface. The complete system was battery powered from a 12V 1.8 Amp-hour sealed lead acid battery.

Initial readings were taken one afternoon immediately after heavy rain. The following day when weather conditions were dry, sunny and with a strong wind, potential measurements on a block of 10 points using a Fluke 806A multimeter in its high impedance mode ( $10^{10}\Omega$ ) were found to be much less negative than those obtained the previous day. This same block was then re-measured using the micro-computer system and this sequence (multimeter/micro-computer) was repeated several times at intervals of several minutes (see results) with the grid point being re-wetted with 0.1M NaOH as they appeared to dry out. A further series of readings was taken using the multimeter on the following morning after overnight rain.

### Results

Results are presented in Table 1 and in Figures 2 and 3. It is clear that the results obtained after heavy rain were much more electronegative, particularly the first results which were taken shortly after driving rain had thoroughly wetted the wall. With one exception (point 6/18) the results taken on the 'dry' wall showed a progressively more negative half cell potential with time. On further examination point 6/18 was found to be contaminated by a waxy substance which probably accounts for its anomalous behaviour. Similar results, exhibiting a movement to lower potentials on wetting, have been noted both in laboratory<sup>(1)</sup> and field<sup>(2)</sup> experiments by other workers.

### Discussion

The steady trends with time of readings from alternate instruments mean that these differences cannot be accounted for by instrument variations. However, it is hardly possible that the true half cell potential of the steel beneath at least 40mm of concrete could change so dramatically in so short a time and it is concluded the change in apparent half cell potential at the surface of the concrete must be due to changes in the resistivity of the outer few mm of concrete.

We believe the potential changes observed above can be explained by the following analysis, which is general in applicability, and that they have considerable consequences in the application of the potential rapping technique and its use to define degrees of corrosion attack.

The following analysis will use potential-current curves (Evans' diagrams) to illustrate the behaviour of steel in concrete, and a brief introduction to this approach may be appropriate. First let us examine some simpler hypothetical situations. Consider a steel electrode in concrete with equal, distinct anodic and cathodic areas, these areas having respective potentials  $E_a$  and  $E_c$  relative to some reference electrode ( $E_c$  would be positive of  $E_a$  in formal convention). If the concrete had infinite electrical resistance a diagram such as Figure 4 would apply. (The potentials could not actually be measured because of the insulating concrete.) If the resistance of the electrolytic medium becomes finite then a current flows from the cathode to the anode with the reinforcement bar completing the electrical circuit. As in any galvanic cell, (e.g. a battery) when a current flows, polarization occurs; the potentials of the anode and cathode move towards one another relative to their open-circuit (zero current) values.

For the case of equal area electrodes with negligible electrolyte (solution) resistance the polarization is governed by the kinetics of the charge-transfer reactions across the electrochemical interface (the solution-metal boundary), and these polarization characteristics (I-V curves or Tafel slopes) are plotted on an Evans diagram in Figure 5. This diagram indicates a corrosion potential,  $E_{corr}$  and a corrosion current,  $i_{corr}$  defined by the point at which the curves meet. The potential in such a situation can be measured by connecting a high-impedance digital voltmeter between a reference electrode in the solution and the metal reinforcement bar. The current cannot be directly measured as the anode and cathode cannot be separated. However, should it be possible to localize them and place a zero-resistance ammeter between them then the current observed would be  $i_{corr}$ .

To discuss the behaviour of steel in concrete, two changes must be made to the above. The first is the form of the cathodic polarization characteristic (Tafel relationship) and the second is to take account of the large, but finite resistance of concrete.

Any electrochemical oxidation (anodic) reaction e.g. iron dissolution:



must be balanced by a reduction (cathodic) reaction, otherwise a charge build-up would occur and any reaction would stop. In the case of steel corroding in concrete this reaction is nearly always oxygen reduction:



Hence overall:



Reaction (2) is kinetically slow (it has a small exchange current) and is limited, not by the rate of charge transfer across the interface but by the rate at which dissolved oxygen gas diffuses to the interface (it is a diffusion limited reaction). Such a cathodic reaction has a polarization characteristic that tends towards a maximum current which is almost potential independent, leading to large polarizations at quite small current levels. By contrast polarization of the anodic reaction is extremely small for the same currents.

The resistance of the concrete further limits the current which can flow between the anode and the cathode, which is reduced from  $i_{\text{corr}}$  to  $i'_{\text{corr}}$  by introducing an 'iR drop' (according to Ohm's law =  $V = i_{\text{corr}} R$ ), see Figure 6.

It can be seen from Figure 6 we no longer have a single value of  $E_{\text{corr}}$ . Some of the potential between the anode and cathode is being dropped by the current flow through the concrete. If the concrete is of uniform resistivity then the potential dropped can be related to the distance moved along the surface; the concrete surface can be treated as a potentiometer and various voltages tapped-off at distances along its surface. This is the basis of potential mapping: The potential variations

seen at the surface are caused by the flow of the corrosion current through the concrete and are hence a function of its resistance. Near to the cathode a cathodic, positive potential will be observed, whilst near to the anode, the potential will be an anodic, negative potential, but it is important to note that the potentials are a property of the current flow in the concrete and are not the actual potentials of the anode and cathode.

It is possible to explain the movements in potential with wetting and drying cycles using the Evans diagram approach in terms of changes in the surface resistivity of the concrete when it is wet or dry. The current-voltage flux lines along a two-dimensional section of reinforcement are shown in Figure 7. This assumes constant concrete resistivity. If the surface is wetted it becomes of a lower resistance, relatively more current flows through the surface layer, and the current flux (and hence potential gradients) are altered. The situation is illustrated in Figure 8, which shows that movements in the potentials measured along the concrete surface (potentiometer), because of the nature of the two polarization characteristics, is almost totally in a negative direction. Hence when the surface is wetted the current moves from  $i_{\text{corr}}$  to  $i'_{\text{corr}}$  and the points being measured move by  $\Delta E_c$  and  $\Delta E_a$  where  $\Delta E_c \gg \Delta E_a$ .

Furthermore, an important implication of the above analysis is that the actual rate of corrosion, indicated by  $i_{\text{corr}}$  and  $i'_{\text{corr}}$ , is indeed increased when the concrete surface is wetted and that significant changes can occur on a very short timescale. This, of course, also implies that misleading information can be obtained if potentials are measured on surfaces pre-treated by wetting and emphasises the need to carry out potential mapping surveys under typical environmental and surface conditions if they were to reflect the true state of reinforcement corrosion. Wetting and drying cycles can well be appreciated to be the worst situation for concrete reinforcement corrosion: near-surface wetting quickly decreases the effective concrete resistance, allowing  $i_{\text{corr}}$  to increase without effectively restricting the oxygen flow (as would be the case for a water saturated concrete). The oxygen flow will be restricted after some delay but the onset of a drying cycle will most likely pre-empt this and rapidly replenish the oxygen.

### Conclusions

These results and the following discussion reinforce the opinion that the resistivity of the concrete and its variation with depth beneath the surface must be taken into account if surface potential values are to be properly evaluated and conclusions drawn from them. Work towards this end is presently in progress at Harwell.

### Acknowledgement

The authors would like to acknowledge useful discussions with N.J.M. Wilkins. This work was funded by BNFL.

### References

1. Hope, B.B., Ip, A.K. and Manning, D.G., Cement and Concrete Research, 15, pp 525-534 (1985).
2. P. Vassie (Personal Communication).

Table 1 Potential-Time Variations

Instrument used, date and time												
Grid No	Epson		Fluke		Epson		Fluke		Epson		Fluke	
	DAY 1 1500 hrs	DAY 2 1356 hrs	DAY 2 1401 hrs	DAY 2 1405 hrs	DAY 2 1418 hrs	DAY 2 1430 hrs	DAY 2 1433 hrs	DAY 3 1030 hrs	DAY 2 1433 hrs	DAY 2 1430 hrs	DAY 2 1433 hrs	DAY 3 1030 hrs
6/16	-133	33	-12	-46	-69	-71	-74	-109	-74	-71	-74	-109
6/17	-155	-14	-39	-68	-89	-95	-99	-120	-99	-95	-99	-120
6/18	-161	-125	-130	-129	-131	-130	-131	-115	-131	-130	-131	-115
6/19	-224	-112	-137	-151	-171	-173	-176	-183	-176	-173	-176	-183
6/20	-228	-146	-144	-166	-171	-181	-182	-197	-182	-181	-182	-197
7/16	-118	45	0	-29	-45	-50	-56	-99	-56	-50	-56	-99
7/17	-139	-6	-57	-78	-89	-93	-97	-122	-97	-93	-97	-122
7/18	-165	-91	-110	-116	-136	-131	-135	-138	-135	-131	-135	-138
7/19	-222	-131	-150	-158	-176	-183	-180	-192	-180	-183	-180	-192
7/20	-200	-111	-109	-120	-132	-147	-151	-178	-151	-147	-151	-178

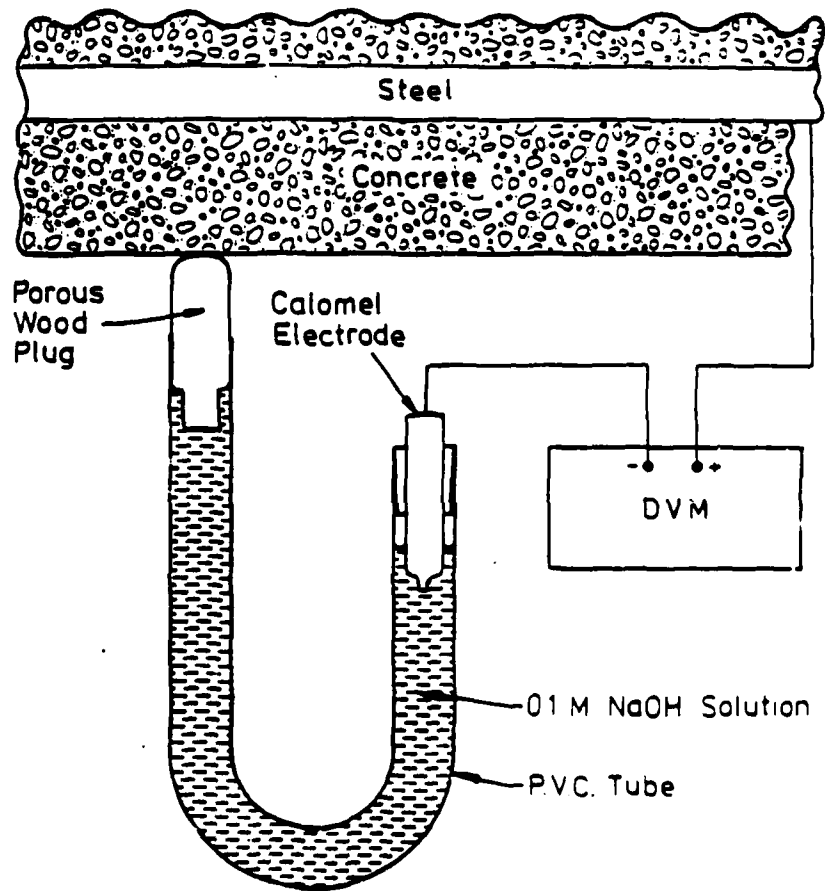


FIG.1 EQUIPMENT USED TO MEASURE APPARENT HALF-CELL POTENTIALS AT THE SURFACE OF REINFORCED CONCRETE.

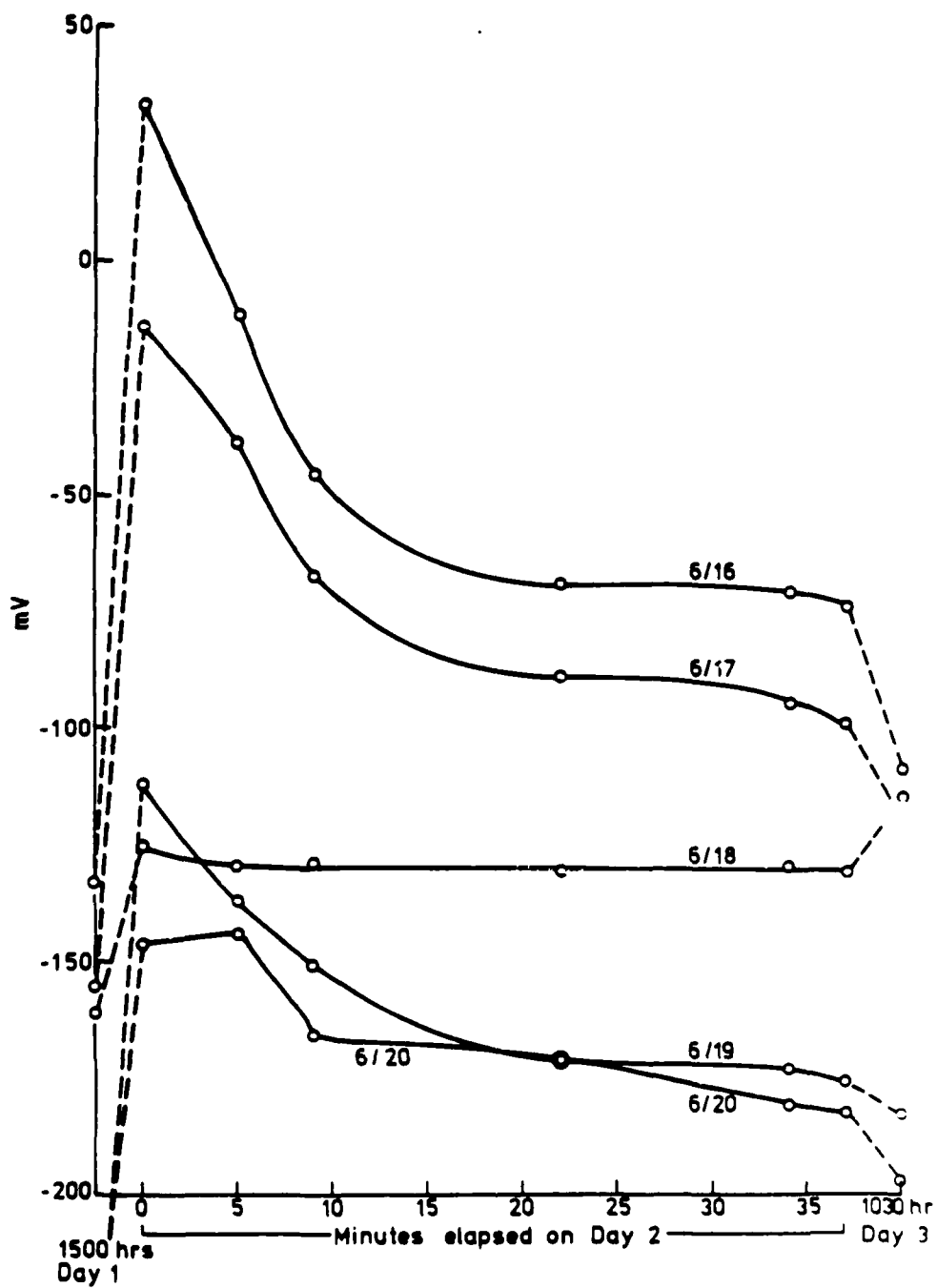


FIG. 2. POTENTIAL-TIME VARIATION  
(MAPPING GRID ROW 6 POINTS 16-20)

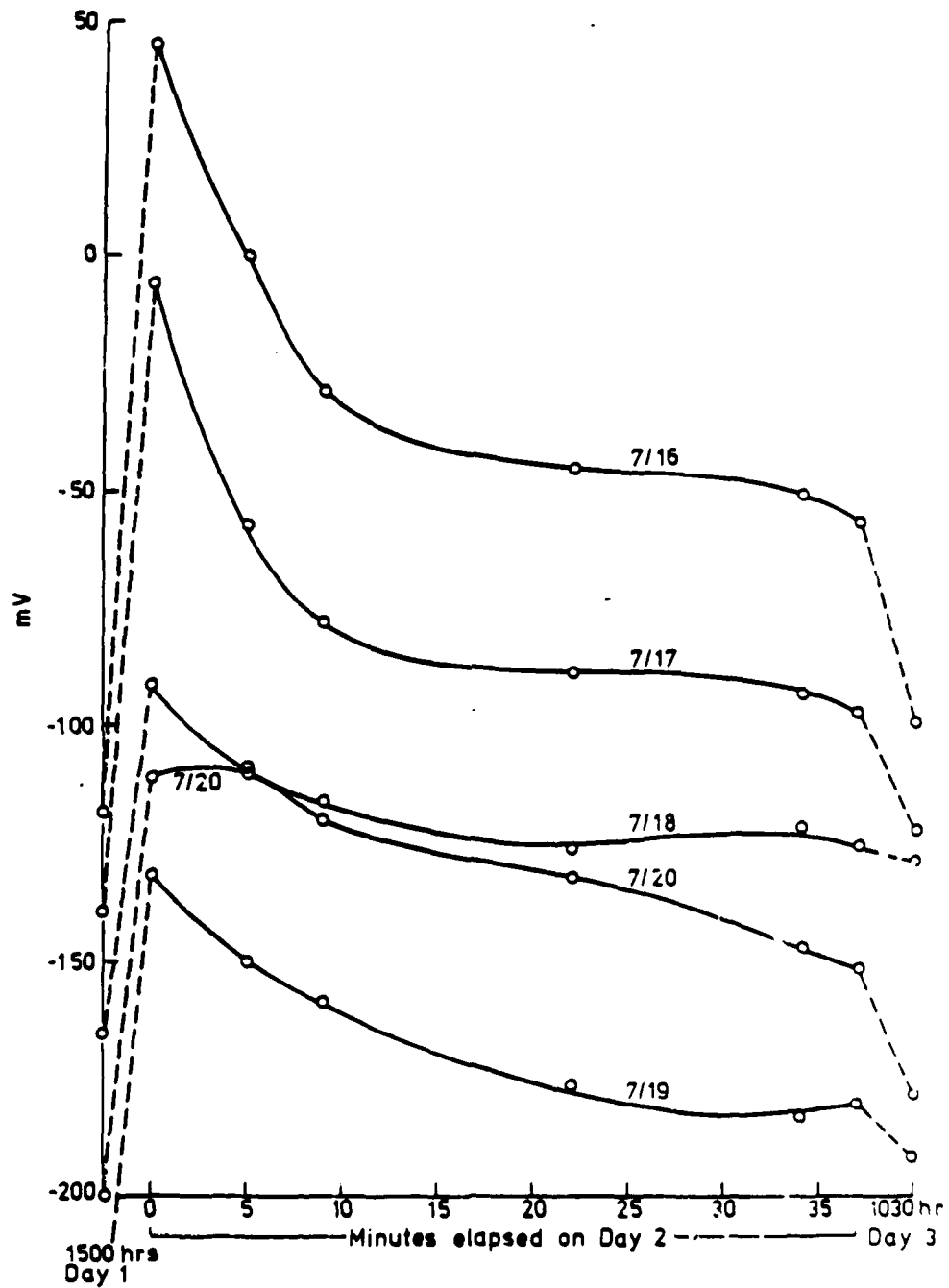


FIG. 3. POTENTIAL - TIME VARIATION  
(MAPPING GRID ROW 7 POINTS 16 - 20)

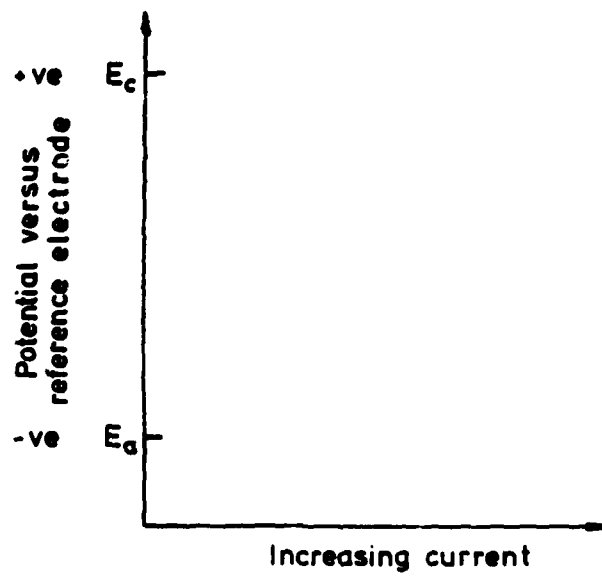


FIG.4. EVAN'S DIAGRAM REPRESENTATION OF ANODE AND CATHODE OPEN CIRCUIT POTENTIALS

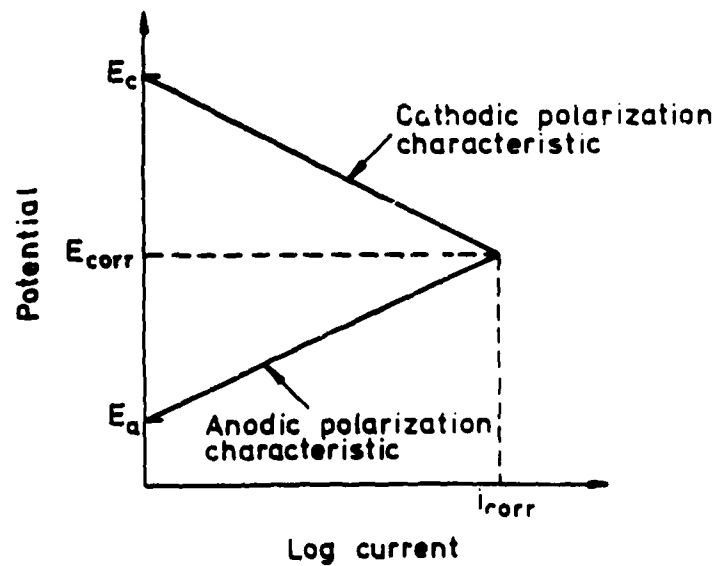


FIG.5. EVAN'S DIAGRAM FOR SYSTEM WITH SIMILAR ANODE AND CATHODE POLARIZATION CHARACTERISTICS

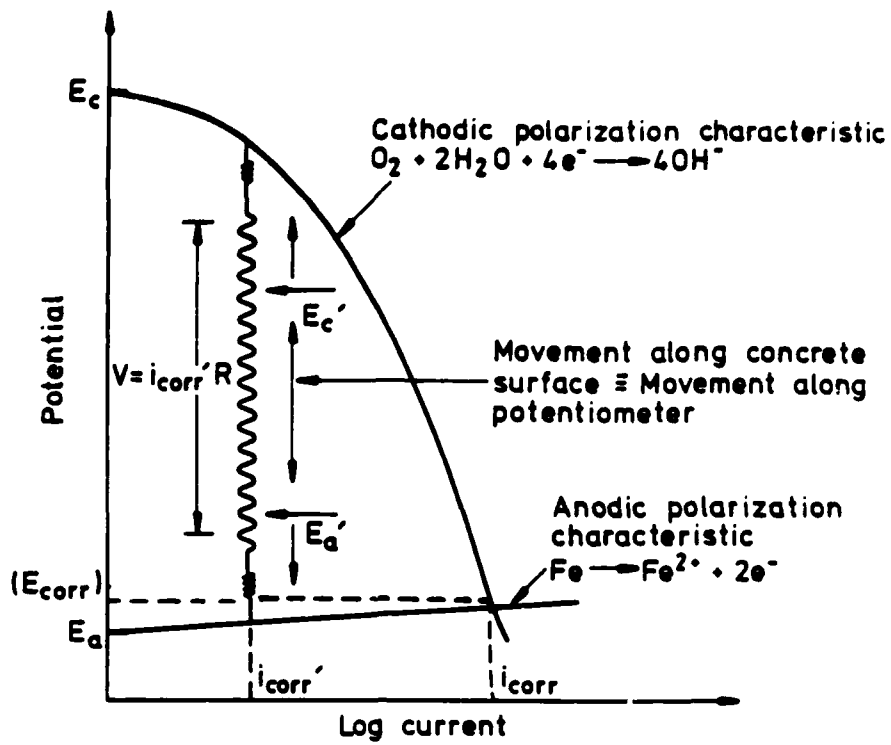


FIG.6. EVAN'S DIAGRAM FOR CORRODING STEEL IN CONCRETE

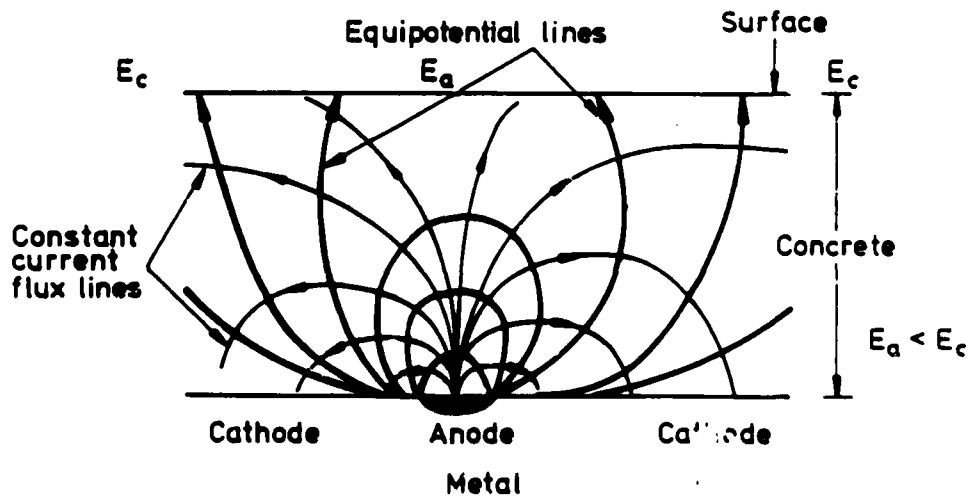


FIG.7. CURRENT AND POTENTIAL DISTRIBUTION IN CONCRETE NEAR ANODIC CORROSION SITE

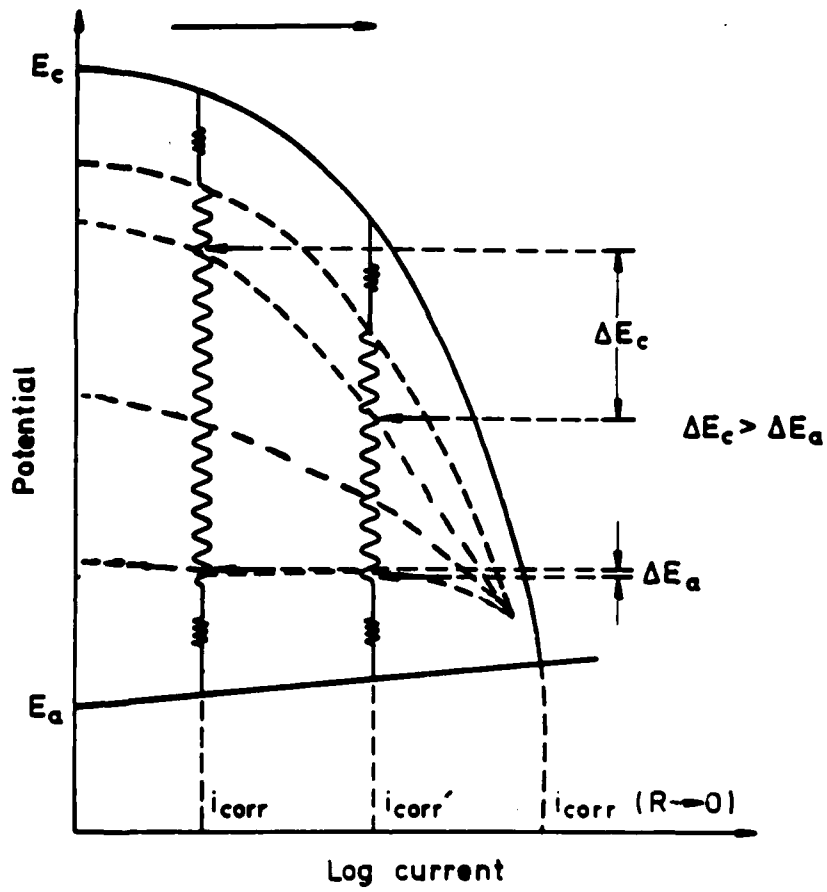


FIG.8.EFFECT OF SURFACE WETTING ON MEASURED POTENTIALS  
 EFFECT OF WETTING :  $i_{corr} \rightarrow i_{corr}'$

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