



EMBEDDABLE REFERENCE ELECTRODES FOR USE IN CONCRETE

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ABSTRACT

The properties of commonly used electrodes used as embedded reference electrodes are reviewed.

A new improved type of electrode, the MnO_2 -electrode, shows a repeatable and stable behaviour.

By comparison, surface potential measurements can vary considerably with the age and surface condition of the concrete, the contact solution used and the time of contact.

Key-words: Concrete, potentials, reference electrodes.

1. INTRODUCTION

Measurements of the electrochemical potential of embedded steel in concrete are used in corrosion surveys (potential mapping), in the control of cathodic protection and sometimes for other purposes. Most often potentials are measured on the surface, using a portable reference electrode, e.g. in accordance with ASTM C876-80. There is also a need to make use of permanently embedded reference electrodes for the following reasons:

Continuous monitoring

Measurements in inaccessible parts of the structure

Minimizing of potential drops due to passage of current (IR-drops)

Avoidance of the variability of surface potential measurements.

Several types of electrodes have been proposed or used for embedding in concrete. For some applications electrodes with short-term stability over a few hours or days are all that is needed, e.g. in measurements of potential decay or recovery in connection with cathodic protection, and nearly any type of electrode will serve that purpose. But ideally the embedded electrode should have a stable "absolute" potential, unaffected by changes in the chemical environment in the concrete (pH, salt content, oxygen access etc) and by climatic changes (temperature, humidity).

In this paper it will be discussed, to which extent presently available types of electrodes can be expected to behave as "ideal" reference electrodes, and the development and testing of a new type of embeddable electrode will be described.

2. TYPES OF ELECTRODES

A reference electrode is a special form of halfcell. A halfcell consists of a piece of metal or carbon, both of which are electron conductors, surrounded by an electrolyte, which conducts electricity by the mobility of ions. The halfcell potential is a function of the electrochemical reactions, which may take place at the interface. The halfcell potential can only be measured relative to another halfcell in contact with the same electrolyte. The special about a reference electrode is that the electrochemical reactions at the metal/electrolyte interface are in equilibrium, which means that they are proceeding in both directions with no net chemical reaction, and the half-cell potential of the reference electrode is a reproducible and well-known function of the chemical environment. A corroding metal can therefore - by the above definition - never qualify as a true reference electrode, but the potential of the corroding metal should be measured against a reference electrode.

Most reference electrodes are double-junction electrodes. They have an inner electrolyte of constant composition, which determines the half-cell potential of the primary junction, and a secondary junction, formed by a diffusion barrier, which separates the inner electrolyte from the outer electrolyte.

Table 1 lists the most commonly used reference electrodes for surface potential measurements on concrete.

Table 1. Composition and potential of commonly used reference electrodes for surface potential measurements.

Electrode type	Inner electrolyte used	Potential in the hydrogen scale
Ag/AgCl	Saturated KCl	+205 mV
Calomel	Saturated KCl	+245 mV
Cu/CuSO ₄	Saturated CuSO ₄	+305 mV

Of the electrodes listed in table 1 only the Ag/AgCl electrode has been used - and used quite commonly - as an embedded electrode in concrete. The Cu/CuSO₄ electrode is often used as an

embedded electrode in soil, but it is definitely unsuitable in concrete because the copper sulphate will react with the alkaline pore solution and precipitate copper hydroxide in the pores of the diffusion barrier.

A number of single junction electrodes have been suggested and most of them used as embedded electrodes in concrete. A brief overview of their properties, based partly on electrochemical theoretical knowledge, partly on published reports on their behaviour /1/ /2/, can be given as follows:

Zinc This metal will sometimes corrode actively, sometimes behave almost passive in concrete. Not surprisingly the potential of this metal in concrete is reported to be unstable and erratic.

Lead Lead also corrodes in concrete, but only slowly, and a stable behaviour may be found over quite long periods. Some reporters have found "highly erratic" behaviour and advise against its use.

Carbon, Graphite, Stainless Steel, Platinized Titanium

These materials are either inert or covered with very stable oxides when embedded in concrete. The only equilibrium reaction, that may take place on their surface, is a reaction involving oxygen, which means that they function as Redox-electrodes. The potential of a redox electrode is a function of both pH (60 mV per pH-unit) and of the partial pressure of oxygen (15 mV per decade). They might be expected to show a reasonably stable behaviour, as long as the pH of the concrete is normal and the oxygen access is not severely limited. The platinized titanium will normally attain the highest potential among these types of electrodes and is closest to the oxygen equilibrium potential by virtue of its catalytically active surface.

Graphite or carbon electrodes are cheap, are often used in practice and have been reported stable. At the moment of writing, no reports are available on the performance of these electrodes under conditions of very low oxygen access, as may occur in fully immersed concrete and in the interior of concrete, where the reinforcement has been cathodically protected for long time.

Electrodes of platinized or otherwise activated titanium are also commercially available in packaged form, mounted in cementitious plugs of fixed composition.

Mo/MoO₃ This commonly mentioned electrode consists of a rod of molybdenum metal, covered with an artificially formed layer of molybdenum oxide. It is difficult to understand either the function or the use of this electrode. A look at the Pourbaix diagram for molyb-

denum will tell, that MoO_3 is unstable in an alkaline environment, and the unstability of its potential in concrete was mentioned when it was first published and has been echoed since.

Ag/AgCl A rod of silver covered with silverchloride will show a potential, which - in many media - will be a linear function of the concentration of chloride. When embedded in chloride-free concrete with its high pH it will become unstable and gradually convert into an silver/silveroxide electrode, which is a pH-dependent electrode. Nevertheless, also in the single junction version the Ag/AgCl electrode has been used commercially, delivered in precast plugs of a chloride-containing mortar. Naturally, its long-term behaviour must be affected by the gradual effusion of chloride into the surrounding concrete as by any subsequent ingress of chloride from the environment /3/.

3. DEVELOPMENT OF A MnO_2 ELECTRODE

In the course of a BRITE-Programme /4/ supported by the EEC, which Korrosionscentralen has carried through with 3 European partners, it has been our task to study and develop embeddable sensors for use in concrete. The development of a trustworthy "true reference electrode" was one of the first objectives.

A survey of the available or previously used electrodes concluded, that the double-junction Ag/AgCl electrode was the only "true" reference electrode, which had been used in concrete. Some users had reported trouble with this electrode, e.g. the development of very high circuit resistance, due to separation of either concrete from the membrane or separation of the internal gel from either the membrane or the electrode metal. Damage after frost had also been reported. It was also noted that this type of electrode had very large concentration gradients across the diffusion barrier (membrane). The choice of membrane material is always a compromise between the wish to have high diffusion resistance and the need to have some electrolytic conductance.

It was decided to find a double junction electrode, where the inner electrolyte could be of the same composition as the typical porewater in concrete, and a Manganese dioxide electrode was chosen. This electrode is extremely well known from its use in alkaline batteries, and in spite of a very complex structure and a complex electrochemical behaviour it can exhibit a nice, straight-line pH-dependent potential in an alkaline environment. A plug of cement paste was chosen for the diffusion barrier. The protruding end of this plug would bond well to the embedding concrete. The whole cell added no foreign or damaging elements to the concrete, and there would be no concentration gradients across the plug. The interior of the cell was constructed in such a way, that good electrolytic contact would be maintained, even if some drying-out might occur after several years.

This reference cell (Figure 1) has now been under test for more than 4 years, and some results are reported below. Several hundred electrodes are in actual use.

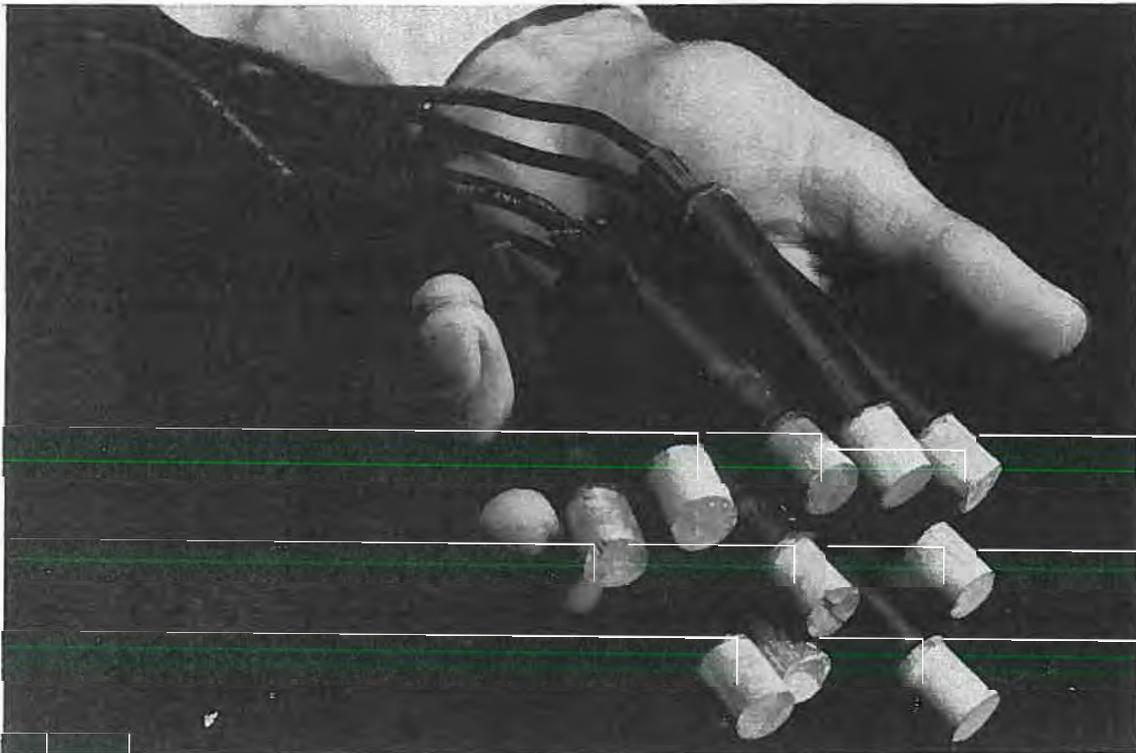


Figure 1. Photograph of MnO_2 embeddable reference electrode.

4. TEST RESULTS FOR MnO_2 EMBEDDABLE REFERENCE ELECTRODES

4.1. Calibration Against SCE

The potential of a MnO_2 electrode relative to the saturated calomel electrode varies with the composition of the common electrolyte.

In $Ca(OH)_2$ (pH = 12.5) nearly all electrodes have a potential of +160 mV \pm 10 mV. The change with temperature is negligible (0-40°C). In other electrolytes potentials are less stable and can vary from +120 mV (in 0.5 M NaOH) to +200 mV (in water).

4.2. Long Term Stability

Where two or more MnO_2 -electrodes are embedded together in the same block of mortar or concrete, they will usually agree among themselves within \pm 10 mV and stay in the same narrow scatterband, even after periods of drying out, freezing etc.

Figure 2 shows the potential of steel reinforcement measured against 6 reference electrodes in the same slab.

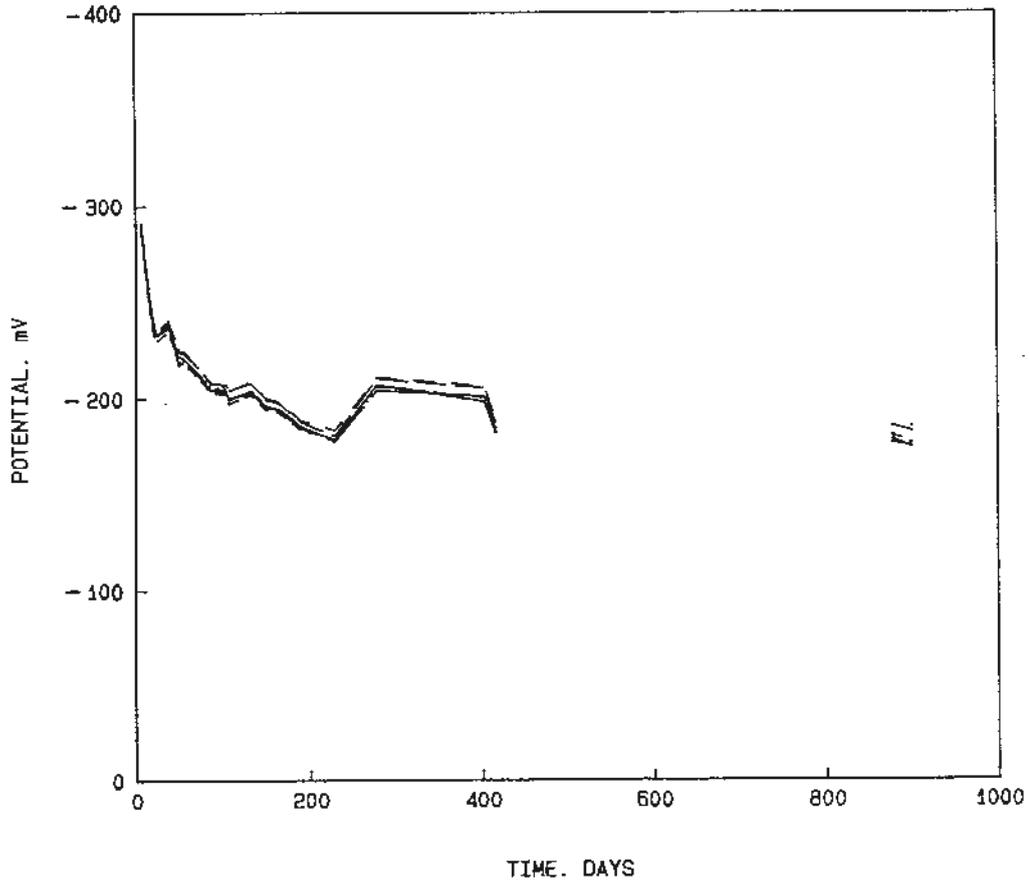


Figure 2. Potential of steel reinforcement in a block of concrete, measured against 6 MnO_2 -reference electrodes embedded in the block. Note the good agreement between the individual electrodes. No measurements were made between 410 and 880 days.

4.3. Comparison with Surface Mounted Electrodes

When embedded MnO_2 electrodes are "checked" against a surface mounted electrode over a period of time, it is common to see a fluctuation of the potential with time. This might be explained by junction potentials either across the plug/concrete interface, where porewater concentration gradients take a little time to level out, or at the concrete/moist pad interface. Other authors have noted the potential deviations from measurements on a carbonated and/or dry surface /5/.

The latter effect was investigated by using the slab from Figure 2 and measuring the now very stable potential of an embedded electrode against surface mounted electrodes. This was done in different ways:

- Using MnO_2 , SCE, and CSE ($Cu/CuSO_4$) electrodes.

- Using tapwater, 0.5 M NaOH and saturated KCl as the contact electrolyte.
- Using either the weathered (dry, carbonated) surface for contact or a freshly drilled hole.
- Time dependence was recorded over 5 minutes.

The results obtained are preliminary. Additional tests are planned and will be reported later. Some conclusions can be drawn already:

- o The difference between "surface" and "bottom" readings could be more than 200 mV, measured at 5 seconds, and diminished with time of wetting. Wetting with NaOH gave the smallest differences, but also a large time dependence for surface readings. Surface readings were always higher than bottom readings.
- o SCE and CSE readings differed by approx. 50-80 mV in reasonable agreement with the accepted difference in halfcell potentials.
- o The potential of the MnO_2 relative to the other two showed much larger variation with electrolyte and time, due to the use of a cementitious plug.
- o The potential of the embedded MnO_2 electrode relative to the surface-mounted electrode varied from -60 mV to +230 mV.
- o Wetting with KCl in the bottom position gave measurements which did not change with time.

The difference between measurements on old and new surfaces has been noted earlier /5/ /6/ and has been attributed to either carbonation (pH) or humidity changes. The answer is perhaps not yet clear, it is probably a combined action.

It is noteworthy, however, that the difference can be so great.

5. CONCLUSION

All potential measurements with surface-mounted electrodes suffer from a large and poorly controlled dependence on the age and surface condition of the concrete, the contact solution used and the time of contact.

This will seriously invalidate any reference to "absolute" values of surface potential as a decisive criteria for the corrosion state of embedded steel.

An embeddable MnO_2 reference electrode, which is designed to minimize junction potentials across its diffusion barrier, has been tested. A very repeatable performance over several years has been found.

6. REFERENCES

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