



# RELIABILITY EVALUATION OF EMBEDDABLE REFERENCE ELECTRODES FOR USE IN REINFORCED CEMENT CONCRETE

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It is now fairly well established that the steel reinforcement bars (rebars) embedded in reinforced concrete bridges and structures can undergo electrochemical corrosion under aggressive marine and or industrial environments and suffer premature deterioration. More recently, quite a number of electrochemical techniques have been adopted for monitoring the corrosion of embedded steel reinforcement. Apart from monitoring corrosion, control of reinforcement corrosion has assumed considerable significance and cathodic protection of reinforced concrete bridges and structures is rapidly gaining ground as a foolproof technology. In all these cases accurate measurement of rebar potential is an essential requirement. Experiences have shown that surface mounted reference electrodes may often lead to misleading data and embedded reference electrodes close to embedded steel reinforcement may avoid unpredictable ohmic resistance in concrete and give reliable data on the electrochemical behaviour. Scanning of the available literature on embeddable reference electrodes reveals that in depth investigation on the reliability of such electrodes has not been attempted. In this investigation, performance of different types of embeddable reference electrodes viz (i) Graphite (Gr) (ii) lead (Pb) (iii) Titanium based electrode (TSIA) (iv) Hydroxyl ion reversible electrode (HRE) has been studied for their stability and reliability in three media viz (a) Aqueous solution (b) Sand mixed with alkaline solution (c) Concrete. Comparison has been made with respect to a standard saturated calomel electrode. It is shown that the hydroxyl ion reversible electrode performs satisfactorily and hence can be considered as a candidate embeddable reference electrode.

**Keywords:** Embeddable reference electrode, concrete, reliability, stability, polarized potential, decay Potential.

## INTRODUCTION

Steel reinforcements embedded in reinforced or pre-stressed concrete bridges and structures need continuous monitoring because of their susceptibility to corrosion. Since corrosion process is electrochemical in nature, various electrochemical techniques are being adopted to monitor reinforcement corrosion. More recently, cathodic protection of reinforced concrete structures is gaining ground as a foolproof technique of controlling reinforcement corrosion. In all these cases continuous monitoring of the half-cell potentials of embedded steel becomes a must. Such a situation calls for a stable and rugged reference electrode, which can be permanently embedded in concrete as close as possible to the embedded steel so as to generate reliable data.

Locke and Dehghanian [1] used Mo/ MoO<sub>2</sub> reference electrodes and found that the potentials of the electrodes in concrete containing 0.1 to 0.2%

of Cl were within a standard deviation of 10 mV whereas the potentials differed by 30 to 40 mV in 0.5% Cl. Manning and Schell [2] on the other hand observed that molybdenum electrodes can produce erratic signals and become unstable at lower temperatures say 278 K. Dehghanian *et al.* [3] have found that Hg/HgO reference electrode can remain stable and give reproducible readings. However, Gurusamy and Geoghegan [4] have reported that Hg/HgO system produced erratic potentials within six months of embedment in concrete. Schell and Manning [5] have examined five different types of reference electrodes and according to them, carbon and lead appeared stable in all normal temperatures and humidities. Mo/ MoO<sub>3</sub> and Ag/AgCl cells did not appear to offer any specific advantages and became unstable under cold temperatures.

Schell [6] and Padhmanaban [7] have advocated the use of Ag/AgCl system with proper manufacturing procedure. Gurusamy and

Geoghagan [4] have also evaluated the long term performance of Ag/AgCl cells in chloride contaminated and chloride uncontaminated concrete up to a period of 4.5 years and reported a mean potential difference of 30 to 35 mV with respect to SCE in 3%  $\text{CaCl}_2$  contaminated concrete. According to Ansuini and Dimond [8] Ag/AgCl electrodes are photosensitive. Oskar Klinghoffer *et al.* [9] have developed a system based on  $\text{MnO}_2$  and evaluated its long-term performance.

Ives and Janz [10] have described the construction and working of different reference electrode systems. The following drawbacks have been identified.

- i) Calomel electrodes and other mercury-mercurous electrodes are formed from mercury and hence any leakage may lead to pollution hazard. Further use of aqueous solutions either potassium chloride or other salts require careful maintenance as well as careful handling.
- ii) The process of making silver-silver halide electrodes is quite tedious as it involves either electrodeposition or thermal decomposition. It is rather difficult to achieve stability, sensitivity and reproducibility.
- iii) The process of making metal-metal oxide electrode is also laborious as it involves using powered metal - powered oxide in admixture. Sometimes aerial oxidation is employed but it will have only a very small electrochemical capacity. Anodic oxidation is also a difficult process.
- iv) In the case of Silver-Silver oxide electrode, it is rather difficult to secure adequate reproducibility. Electrode potentials tend to be rather erratic.
- v) The major draw back for metal-metal oxide electrodes is that nobility of metal and stability of oxide do not run together. Hardness and polymorphism obstruct the attainment of reproducible standard states.

It is also worthwhile to point out that ASTM C 876 specifies the use of  $\text{Cu}/\text{CuSO}_4$  as reference electrode for measurement of rebar potential in concrete [11]. The drawback of such surface mounted electrode is that the seepage of copper sulphate solution would contaminate the concrete and the copper ions would influence the steel

behaviour. Further surface mounted electrodes subjected to ultraviolet radiation effect which lead to erroneous data [12]. IR drop within concrete cover will also lead to erroneous interpretation.

It can be clearly seen from the foregoing that there is an utmost need to develop and evaluate the performance of reliable and maintenance-free systems for use in concrete. Such embeddable electrodes should have the following features.

- i) It should be rugged and maintenance free.
- ii) It should have desirable micro reversibility and low temperature coefficient.
- iii) It should have negligible liquid junction potential.
- iv) It should have adequate stability and reliability when compared to a standard reference electrode such as SCE.
- v) It should be capable of being embedded under any orientation.
- vi) It should not lead to undesirable contamination of surrounding concrete.

Keeping the above desirable features in view, for candidate systems VIZ lead; (Pb) graphite (G), Titanium Substrate Insoluble Electrode (TSIA) and Hydroxyl ion Reversible Electrode (HRE) were investigated for their stability and reliability. Saturated calomel electrode was taken as a reference system; it was found that the Hydroxyl ion Reversible Electrode could be considered as a promising embeddable reference electrode system for monitoring the health condition of reinforced concrete bridges and structures.

## EXPERIMENTAL

### Tests in aqueous media

The following three media were used as test solutions

- a) Passive medium: 0.04 N-NaOH solution.
- b) Active medium : deionised water containing 1500 ppm chloride.
- c) Passive-Active medium 0.04N-NaOH containing 1250 ppm of chloride.

### Stability test

The stability of different embeddable electrodes was assessed with reference to a saturated calomel electrode. The particular embedded reference electrode as well as the saturated calomel electrode were simultaneously kept immersed in 60 ml of test solution. An inter electrode spacing of 2.5 mm was maintained in all experiments. Potential of the embeddable electrode was monitored with respect to the calomel electrode over a period of 120 minutes using a high impedance multimeter.

### Reliability test

A 6 mm dia 50 mm long mild steel specimen with 50 mm long stem was mechanically polished on an emery wheel, buffed and then degreased with trichloroethylene. Stem portions as well as bottom end were masked with lacquer exposing only the circumferential portion of the specimen. After lacquering and drying, circumferential portion was slightly buffed and degreased. The mild steel specimens as well as the particular reference electrode were simultaneously kept immersed in 60 ml of test solution. An inter electrode spacing of 2.5 mm was maintained in all the experiments. Potential of the mild steel was monitored over a period of 120 minutes using a high impedance multimeter.

### Tests in sand medium

#### Polarization behaviour in sand medium mixed with 0.04 N-NaOH solution.

Washed and dried river sand was mixed with 0.04 N-NaOH solution so as to make a workable mixture. This semi-solid mixture was packed tightly in a non-metallic container of size 20 x 20 x 10 cm. Two numbers of cold twisted mild steel reinforcements (8 mm dia 10 cm long) were derusted and degreased. Electrical leads were taken from one end. The reinforcement rods were embedded at a depth of 8 cm from the top surface. The horizontal spacing between the rods was maintained at 8 cm. A saturated calomel electrode as well as the test reference electrode was surface mounted at the same location with a spacing of 2 cm.

The open circuit potential of the embedded steel rebars (which were externally short circuited) was monitored over a period of 60 minutes. Subsequently a pure magnesium anode of size 5 x 3 cm was placed on the top surface and externally short circuited with the rebar terminals. The potential of the rebars got shifted in the cathodic direction and this polarized potential was monitored over a period of 240 minutes. Subsequently the anode terminal was disconnected from rebar terminal and the decay in potential was recorded over a period of 60 minutes.

### Tests in concrete medium

A rectangular concrete prism of size 20 x 10 x 10 cm was cast with a derusted and degreased mild steel reinforcement of size 8 mm dia, 10.5 cm long embedded with a clear cover of 6 cm from the top surface. Electrical lead was taken from one end of the same reinforcement before embedment. A saturated calomel electrode as well as a hydroxyl ion reference electrode was surface mounted at the same location with a spacing of 2 cm.

The open circuit potential of the embedded steel rebar was monitored over a period of 60 minutes. Subsequently a pure magnesium anode of size 5 x 3 cm was placed on the top surface and externally short circuited with the rebar terminals. The potential of the rebar got shifted in the cathodic direction and this polarized potential was monitored over a period of 240 minutes. Subsequently the anode terminal was disconnected from rebar terminal and the decay in potential was recorded over a period of 60 minutes.

#### Long term performance of embedded electrodes

A mild steel reinforcement specimen of size 8 mm dia 10.5 cm long was embedded in a concrete prism of size 20 x 10 x 10 cm with a clear cover of 6 cm from the top surface. A hydroxyl ion reversible electrode (HRE) of size of 0.5 cm dia and 4 cm long was simultaneously embedded along with mild steel reinforcement of inter electrode spacing of 0.5 cm. Leads were taken from the steel specimen as well as HRE. The concrete prism was cured for 28 days in tap water

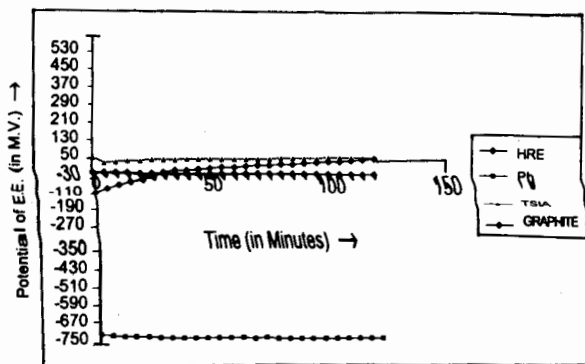


Fig. 1: Potential time behaviour of embeddable electrodes in 0.04 N NaOH medium (stability test)

and then exposed to ambient condition over a period of 3 years.

After three years of exposure, the open circuit potential of mild steel was measured with respect to HRE for a period of 60 minutes. Then a pure magnesium anode of size 5 x 3 cm was placed at the top surface of the prism and externally short circuited with rebar terminals. The potential of the steel got shifted in the cathodic direction. The polarized potential of the mild steel with respect to HRE was monitored over a period of 240 minutes subsequently the anode terminal was disconnected from rebar terminal and the decay in potential was recorded over a period of 60 minutes.

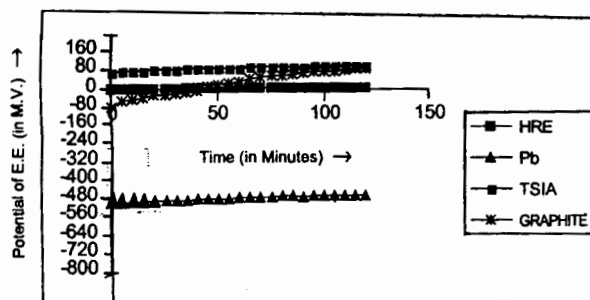


Fig. 2: Potential time behaviour of embeddable electrodes in 1500 ppm of chloride medium (stability test)

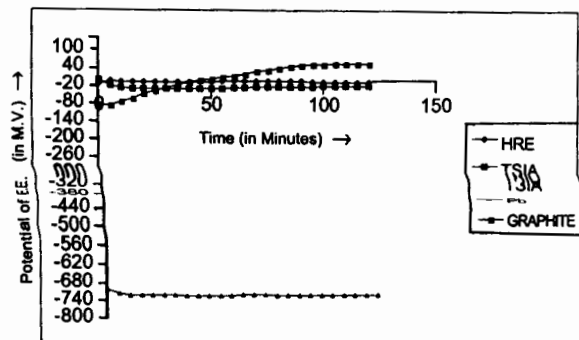


Fig. 3: Potential time behaviour of embeddable electrodes in 0.04 N NaOH containing 1250 ppm chloride medium (stability test)

## RESULTS AND DISCUSSION

### Stability test

Potential time behaviour of different embeddable electrodes with reference to saturated calomel electrode is shown in Figs. 1-3. As can be seen from Fig. 1, in the passive alkaline medium (0.04 N-NaOH), the hydroxyl ion reversible electrode is the most stable electrode. Next to that titanium based metal oxide appears to be stable. Lead electrode takes about 60 minutes to attain stability. Graphite is quite unstable.

It can be seen from Fig. 2 that in an active medium of 1500 ppm chloride solution, graphite again shows unstable behaviour. The other three electrodes show stable potentials right from the beginning. However hydroxyl ion reversible electrode appears to be maintaining better stability.

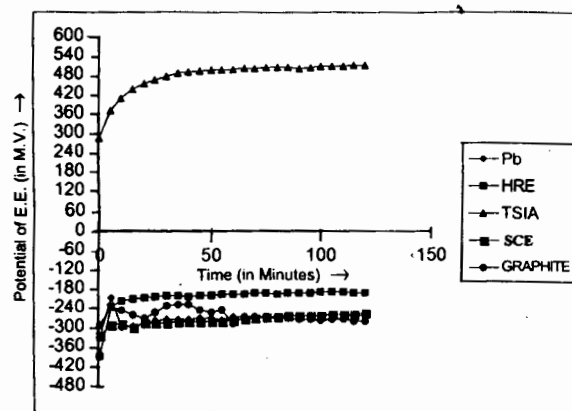


Fig. 4: Potential time behaviour of embeddable electrodes in 0.04 N NaOH medium (reliability test)

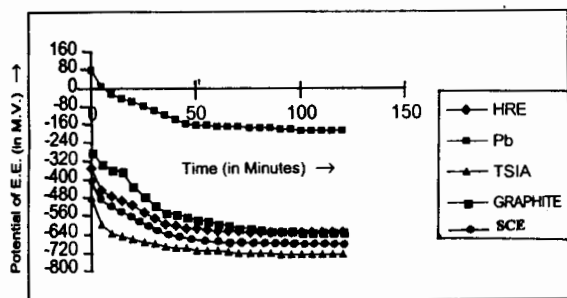


Fig. 5: Potential time behaviour of embeddable electrodes in 1500 ppm of chloride medium (reliability test)

Fig. 3 shows that in passive-active medium also, graphite shows quite unstable potential while the other three electrodes show more or less stable potential. Here again, Hydroxyl ion reversible electrode appears to be the most stable electrode maintaining stable potential right from the beginning.

#### Reliability test

The comparative potential time behaviour of a mild steel test specimen with respect to different reference electrodes is depicted in Figs. 4-6.

Fig. 4 shows the potential time behaviour of mild steel in a passive alkaline medium of 0.04 N-NaOH. As anticipated, the potential shifts in the nobler direction by a value of 60 mV with respect to standard saturated calomel electrode. Similar shift of 60 to 70 mV is observed in the case of TSIA. In the case of hydroxyl ion

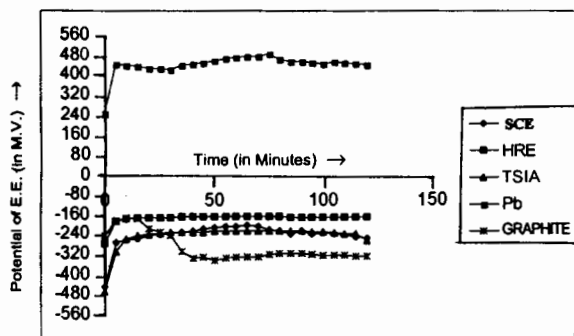


Fig. 6: Potential time behaviour of embeddable electrodes in 0.04 N NaOH containing 1250 ppm chloride medium (reliability test)

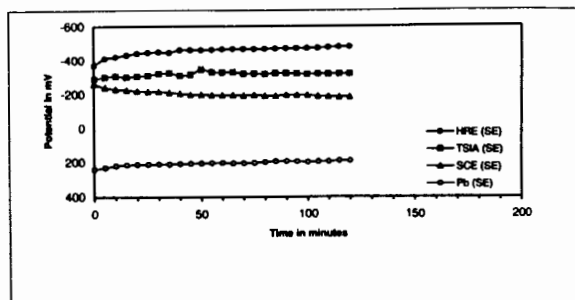


Fig. 7: Potential time behaviour of MS wrt HRE (SE), TSIA (SE), Pb (SE) AND SCE (SE) in sand mixed with 0.04 N NaOH

reversible electrode, the potential shift is exactly 60 mV. In case of graphite electrode, potential oscillates in the positive direction though the shift is 60 mV. On the other hand, lead electrode shows a shift of 180 mV in the positive direction making it unreliable.

Fig. 5 shows the potential time behaviour of mild steel in an active chloride medium (1500 ppm chloride solution). As anticipated potential moves in the negative direction. In all the cases the negative shift in the case of calomel electrode is 240 mV. Similar shift is observed in the case of TSIA and lead electrodes. Shift is slightly higher i.e. 260 mV in the case of hydroxyl ion reversible electrode. On the other hand, a much higher shift in potential i.e. 320 mV is observed in the case of graphite electrode making it unreliable.

Fig. 6 shows potential time behaviour of mild steel in a passive active medium (0.04 N-NaOH containing 1250 ppm chloride). In the case of calomel electrode, the potential of mild steel initially shifts in the positive direction by 100 mV

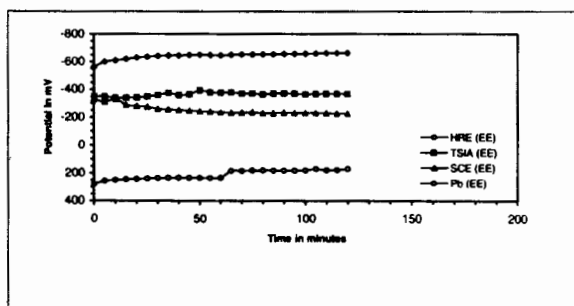


Fig. 8: Potential time behaviour of MS wrt HRE (EE), TSIA (EE), Pb (EE) AND SCE (EE) in sand mixed with 0.04 N NaOH

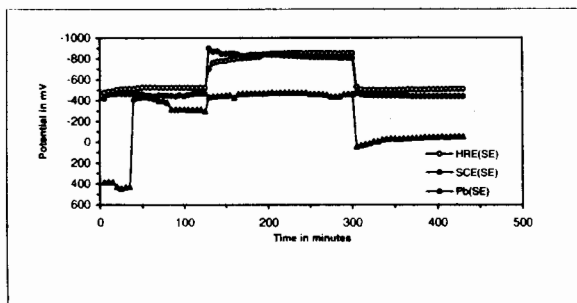


Fig. 9: Polarization time behaviour of MS wrt HRE (SE), SCE (SE), Pb (SE) in sand mixed with 0.04 N NaOH

and then shifts in the negative direction by 80 mV. In the case of hydroxyl ion reversible electrode, the potential initially shifts in the positive direction by 120 mV and then shifts in the negative direction by 110 mV. In the case of TSIA also, the positive shift is 120 mV and the negative shift is 110 mV. Thus both the electrodes have identical shifts. In the case of graphite, positive shift is 80 mV and the negative shift is 70 mV. However there is some oscillation.

In the case of lead, the potential immediately shifts in the positive direction by 210 mV and then remains more or less constant thus making it unreliable.

### Tests in sand medium

#### Potential - time behaviour in sand medium mixed with 0.04 N-NaOH

Fig. 7 depicts the potential time behaviour of mild steel specimen with respect to different electrodes mounted at the surface. It shows that all the four

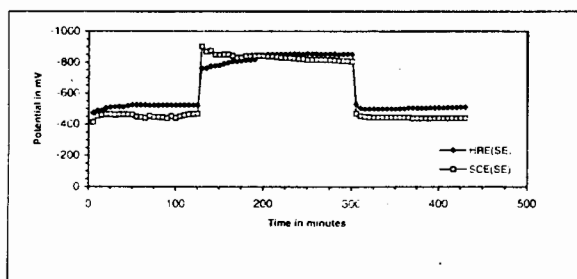


Fig. 10: Comparative potential time behaviour of MS wrt HRE (SE), SCE (SE) surface mounted in concrete prism

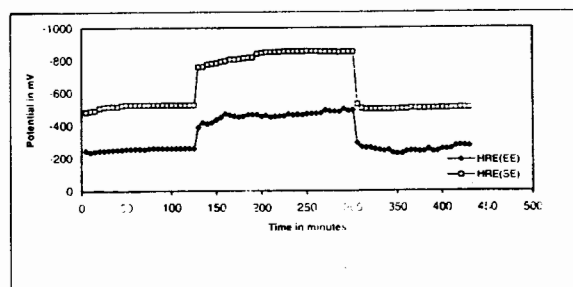


Fig. 11: Long term performance of embedded HRE (EE) - comparative behaviour at the end of three years

electrodes VIZ saturated calomel electrode, hydroxyl ion reversible electrode, TSIA & lead exhibits more or less similar behaviour.

Fig. 8 depicts the potential time behaviour of mild steel specimen with respect to different electrodes embedded at the same location nearer to mild steel specimens. Again it can be seen that all the four electrode exhibits more or less similar behaviour.

However it was observed that TSIA was showing oscillating signals and it was undergoing coating degradation under the alkaline environmental condition.

Further studies were therefore carried out with SCE, HRE and Pb electrodes.

#### Polarization behaviour in sand medium mixed with 0.04 N-NaOH

Fig. 9 depicts the polarization behaviour of mild steel specimen embedded in sand medium with respect to SCE, HRE and Pb electrodes. It can be seen that the behaviour of mild steel with respect to HRE is akin to that with respect to SCE. On the other hand, the polarization behaviour of steel with respect to lead is quite different indicating its unreliable behaviour under polarized condition.

In further studies, polarization behaviour of mild steel embedded in concrete was compared with respect to SCE and HRE.

### Tests in concrete medium

Fig. 10 depicts the comparative behaviour of the saturated calomel electrode and the hydroxyl ion

reversible electrode. It can be seen that the difference in potential values remains more or less constant under the three conditions VIZ open circuit potential, polarized and decay potential. Further it can be observed that the two curves more or less super pose on one another indicating that the electrodes have the same potential response.

### Long term performance of embedded HRE

Fig. 11 depicts the polarization behaviour of mild steel embedded in concrete. It can be seen from Fig. 11 that even after three years of embedment in concrete HRE exhibits reliable response with respect to the shifts in potential values. The shifts are identical for both the surface mounted HRE (SE) and embedded HRE (EE) under the three conditions VIZ open circuit potential, polarized potential and decay potential.

Among the four reference electrodes compared with SCE, graphite electrode was found to be quite unstable and unreliable even in studies, carried out in aqueous solution. This might perhaps be due to the impurities present in the graphite specimen. Even though TSIA as reference electrode was found to be stable & reliable in aqueous solution, its long term utility becomes questionable when embedded in concrete due to coating degradation in alkaline environment. Though the potential time behaviour of steel under un polarized condition, was found similar with respect to different reference electrodes studied, under polarized condition, the behaviour becomes unpredictable particularly when Pb was studied. The behaviour of hydroxyl ion reversible electrode was akin to that of saturated calomel electrode perhaps because mercury was the common reference metal employed in both the cases

### CONCLUSIONS

Reliability of any candidates embeddable reference electrodes should be tested and compared with saturated calomel electrode under identical

polarized condition. Shifts in potential values should remain more or less constant under the three conditions VIZ open circuit potential, polarized potential and decay potential.

Hydroxyl ion reversible electrode is a reliable candidate embeddable reference electrode as proven by its long-term performance when embedded in concrete.

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