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Voltammetric behaviour of iron in cement. I. Development of a standard procedure for measuring voltammograms

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A reproducible procedure has been developed to study the cyclic voltammetry of iron electrodes embedded in cured Portland cement. It is recommended that such *in situ* measurements be used in preference to those in simulated pore solutions. This method, which should prove useful as a means of studying the corrosion of reinforced concrete, is described in detail. The usefulness of the method has been demonstrated by means of a series of brief preliminary studies. Specifically, studies on the effects of sweep rate, chloride additions, and the role of $Ca(OH)_2$ in the passivation of iron in alkaline solutions, were performed. The sweep rate behavior of the passivation peak in cement was consistent with that predicted by a pore diffusion model. As expected, the chloride additions were found to disrupt the passivity, as evidenced by a general increase in the voltammetric currents and the electrode resistance, as well as by the appearance of a new anodic peak in the normally passive potential regime. The results indicated that, although the reaction mechanism is similar in cement to that in aqueous alkaline solution, the passivity of iron is enhanced in cement, relative to that observed in aqueous KOH or NaOH solutions. This is shown to be related to the presence of $Ca(OH)_2$ in the cement pore solution.

1. Introduction

On account of the associated severe damage to concrete structures, the corrosion of reinforcing steel in concrete is a problem of great importance. Because of its high pH, concrete normally provides a passivating environment for iron and steel. However, the increased use of road salt, for which there still is no cost-effective alternative, has led to widespread corrosion of reinforcing steel and subsequent deterioration of the surrounding concrete. For example, the U.S. Federal Highway Administration has found more than 243 000 bridges in the United States to be structurally deficient as a result of iron corrosion [1]. The cost associated with this potentially hazardous deterioration was estimated to be $24 billion. Parking garages also have been badly affected. As a result, research into the electrochemical behavior of iron and steel in concrete structures currently is the focus of considerable effort and interest [1, 2].

Cyclic voltammetry has proven to be a useful technique for studying various aspects of the electrochemical behavior of iron and steel in alkaline solutions [3–18]. Since the pore solutions in cement and concrete are thought to consist mainly of aqueous KOH, NaOH and $Ca(OH)_2$ [19], it is possible that the many previous studies of the cyclic voltammetry of iron in these solutions could be useful as a basis for understanding the electrochemical corrosion behavior of steel reinforcement in poured concrete structures. However, it has not been established that the voltammetric behavior of steel is the same in cured concrete as it is in simple alkaline solutions. Accordingly, the focus of our present effort is to determine the electrochemical behavior of iron *in situ* in cured cement paste. However, since poor reproducibility is a well-recognized problem in investigating the electrochemical behavior of iron even in simple alkaline solutions [16, 17], our initial work has been towards establishing a reliable procedure for cyclic voltammetric measurements in the relatively complex medium of Portland cement. Thus, the primary objective of this first paper is to establish a method for such measurements that yields reasonably reproducible results, in order that differences in behavior caused by chlorides, corrosion inhibitors, or other factors can be noted with confidence. It is our hope that the procedures developed here will form the basis for a standard method which will facilitate the comparison of data from different laboratories.

2. Experimental details

2.1. *Apparatus*

The cyclic voltammetric experiments were conducted with a Princeton Applied Research (PAR) model 273

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potentiostat, which was equipped with current interrupt and positive feedback iR compensation. A PAR model 175 universal programmer was used to provide analog triangular potential waveforms, and the voltammograms were recorded on a PAR model RE0089 X-Y recorder.

The cell was essentially of conventional 'three-electrode' design. The cell body was made of Pyrex glass and held approximately 200 ml of electrolyte. The Teflon lid was fitted with a neoprene gasket. The working electrode was a cement-coated iron wire. The four platinum wire counter electrodes were held in fritted glass compartments, which were placed in an equidistant array around the centrally-located working electrode. Electrical contact with the saturated calomel reference electrode (sce) was maintained via a Luggin capillary. The cell was maintained at 25 ± 0.2° C by a re-circulating water bath.

2.2. *Electrodes*

The working electrodes were prepared from 99.999% iron wire (Johnson Matthey), of 0.25 mm diameter, with the following impurities in ppm: Si, 10; Mg, 3; Al, 2; Ca, 1; Ni, 1; and Cu, Mn and Ag, < 1. The electrode configuration is shown in Fig. 1. Pieces of the iron wire were sealed with epoxy into 0.5 cm diameter Teflon tubing. The end of each wire also was masked, leaving an exposed length of about 1 cm, or a nominal exposed surface area of about 0.08 cm^2. A mercury contact facilitated electrical connection to the iron wire. A new electrode was used for each experiment.

In the case of cement-coated electrodes, a plastic form, of 0.5 cm inside diameter and 1.5 cm length, was placed around the iron wire and filled with cement paste, which was allowed to set overnight. The form then was removed, and the resulting iron-reinforced cement cylinder was cured at 100% relative humidity. The relatively small electrode area and thin cement cover were used in order to maintain the iR drop at a value low enough to be handled by the model 273 potentiostat. The cement used was provided by Lake Ontario Cement Ltd and was classified as Portland type 10, meeting CSA standard CAN 3-A5-M83. The chemical analysis was given as 62.15% total CaO, 0.97% free CaO, 20.63% SiO_2, 5.92% Al_2O_3, 4.09% SO_3, 2.43% Fe_2O_3, 1.30% K_2O, 0.16% Na_2O and 2.18% MgO, with 0.65% loss on ignition and 0.20% insoluble residue. The cement pastes were prepared by weight, using de-ionized water of $\sim 20\,M\Omega\,cm$ resistivity.

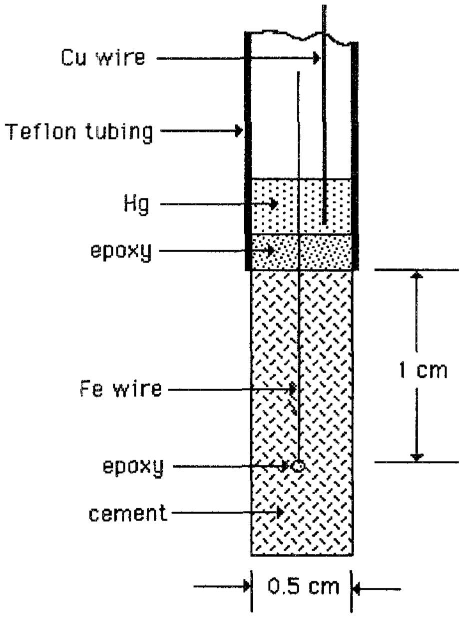

Fig. 1. Details of working electrode construction.

2.3. *Solutions*

All solutions were prepared from analytical grade chemicals (BDH) and de-ionized water, and were sparged with pre-saturated nitrogen (Canadian Oxygen Co., 'O_2-free') for at least 30 min prior to a run, and blanketed with nitrogen during a run. KOH and NaOH solutions were prepared from 2.0 M stock solutions, which were standardized periodically by titration against potassium hydrogen phthalate. The cell electrolyte for runs with cement-coated electrodes was saturated $Ca(OH)_2$, which was filtered prior to use. Measurements of pH were conducted using a Fisher combination pH electrode, calibrated using standard buffer solutions of pH 7.41 and 10.4.

2.4. *Procedure*

The potential generally was cycled between -1.4 and $+0.4$ V (all potentials are reported as volts versus sce); the former value was the initial potential, and the latter value was chosen so as to ensure exclusion of oxygen evolution. Current interrupt iR compensation was utilized throughout. A moderate sweep rate of 0.050 $V\,s^{-1}$ was generally used, since current interrupt iR compensation can be used with confidence at this sweep rate. The electrodes were cycled at least 201 times, the first five, seventh, eleventh, and every tenth cycle thereafter being recorded.

3. Results and discussion

3.1. *Typical voltammograms for iron in Portland cement*

Typical iR-compensated voltammograms for iron in cured Portland cement, 0.1 M KOH (pH = 12.9) and saturated $Ca(OH)_2$ (pH = 12.4) are shown in Figs 2, 3 and 4, respectively; similar, well-defined voltammograms were routinely reproduced. The voltammograms for 0.1 M KOH, shown in Fig. 3, are similar in appearance to those we obtained for iron in 1.0 M KOH, 0.1 M NaOH and 1.0 M NaOH (pH = 12.9–13.6), as well as to those reported by previous workers, with minor variations in peaks 1, 2 and 3a [3, 10–13, 15–18]. The voltammograms for saturated $Ca(OH)_2$ shown in Fig. 4 are similar to those reported for the same medium in [9]. The current densities at peaks 3

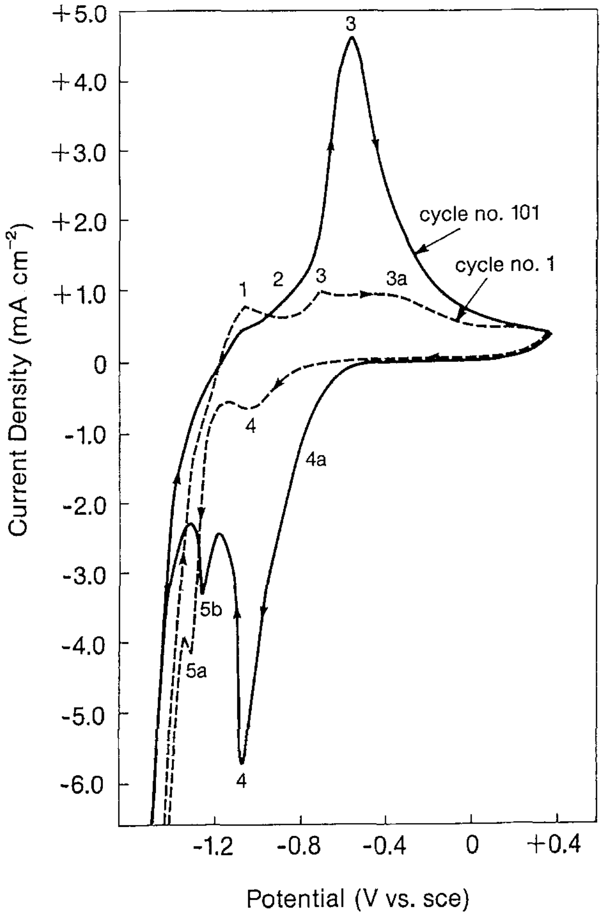

Fig. 2. Typical voltammograms for iron in Portland cement; cycles no. 1 and 101, W : C = 0.45, 3 day cure, 0.050 V s^{-1}, 25° C.

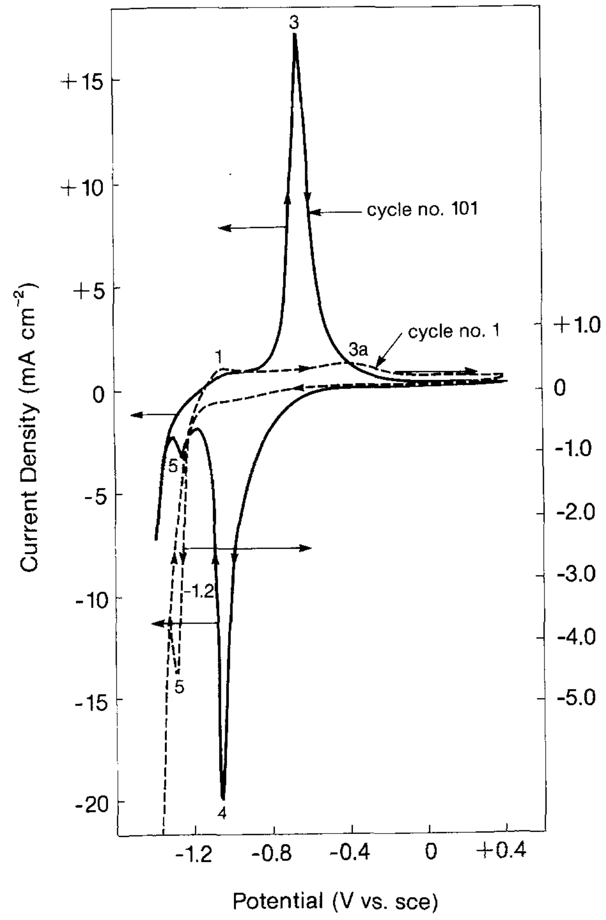

Fig. 3. Typical voltammograms for iron in 0.1 M KOH: cycles no. 1 and 101, 0.050 V s^{-1}, 25° C.

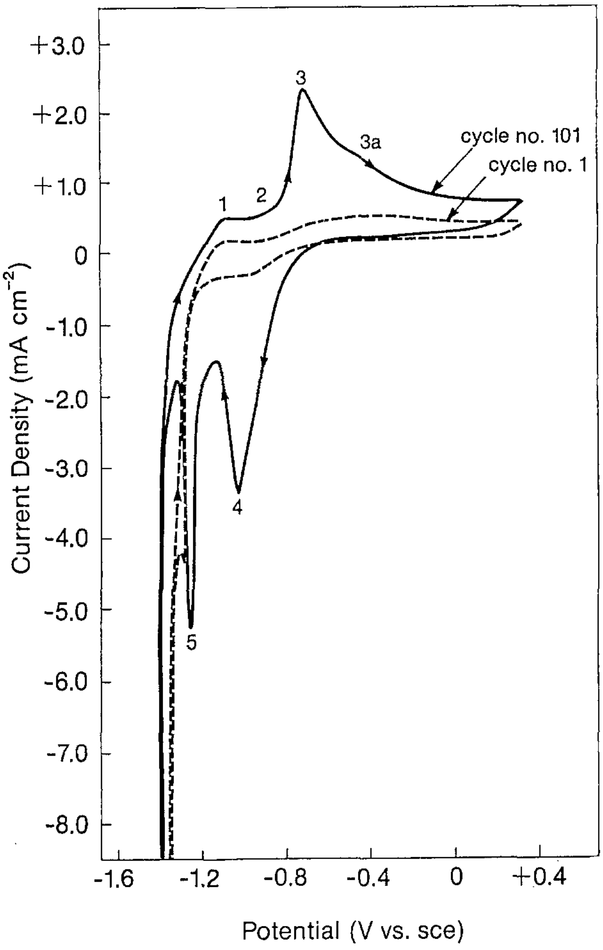

Fig. 4. Typical voltammograms for iron in saturated $Ca(OH)_2$, cycles no. 1 and 101, 0.050 V s^{-1}, 25° C.

and 4 in cement were about four times less than those in 0.1 M KOH or 0.1 M NaOH solutions after 100 cycles, but also were approximately double those in saturated $Ca(OH)_2$; consequently, we recommend that the *in situ* measurements with iron in cement described herein be used in preference to those in simulated pore solutions. On the other hand, as can be seen from Figs 2–4, the major features of the respective voltammograms are the same, and therefore it is likely that the general reaction mechanism in cement is similar to that in the alkaline solutions.

Four anodic peaks (peaks 1, 2, 3 and 3a) and three cathodic peaks (peaks 4, 5a and 5b) were observed over the course of 200 cycles. The electrochemical reactions corresponding to the various peaks in alkaline solutions have been discussed by several previous investigators [3–18], but have not been unequivocally identified. However, peaks 1 and 2 generally have been attributed to the formation of ferrous hydroxide. Peak 5 most often has been identified as the corresponding reduction peak, although it also has been said to be related to peak 3a. Peaks 3 and 3a have been assigned to ferrous–ferric transformations in a hydrous outer oxide layer, and in a relatively compact, anhydrous inner oxide layer, respectively. Peaks 3 and 4 likely are conjugated, as are peaks 3a and 4a (peak 4a generally is discernable only as a broadening of the anodic side of peak 4).

In the present study, anodic peaks 1 and 3a were relatively prominent at low cycle numbers, but became obscured upon repeated cycling by the growth of peaks 2 and 3, and were almost unobservable (except in saturated $Ca(OH)_2$) after about 50 cycles. The behavior of the large cathodic peak, peak 4, mirrored that of the large anodic peak, peak 3. In the case of cement-coated electrodes, interesting transient behavior was observed in the region of peak 5. For the first 5–10 cycles, peak 5 was observed as a distinct peak at about -1.26 V to -1.30 V (peak 5a). The peak then generally became indistinct, and shifted over the next 30 ~ 50 cycles to about -1.2 V whereupon it reappeared as the sharply-defined peak 5b. Peak 5b remained relatively invariant, both in magnitude and position thereafter. Somewhat analogous behavior, but with less extensive potential shifts, was observed in alkaline solutions. It is noteworthy that dual peaks, one in each of the above potential regimes, occasionally were observed during the transition from peak 5a to peak 5b. Two processes in the region of peak 5 also have been detected in an ellipsometric investigation of the passivation of iron in 0.05 M NaOH [20], and were ascribed to reduction of both the outer and inner oxide layers at peak 5b, followed by reduction of only the inner layer at peak 5a. Correspondingly, in the present study, the development of peak 5b parallelled the initial rapid growth of the outer oxide layer, and therefore is attributed to increasing amounts of ferrous hydroxide being formed in the outer layer at peak 4, and subsequently being reduced at peak 5b.

3.2. *Development of a standard procedure for cyclic voltammetry of iron in Portland cement*

3.2.1. Variation with cycle number of the peak current densities in cement. The progression of the peak current densities upon cycling was monitored in order to obtain an indication of the reproducibility, as well as of the approach to a steady state. The peak current densities for peaks 3 and 4 were used for this purpose. These peaks were used because they were the most prominent, and therefore the most amenable to quantitative analysis, and also because passivation of the iron occurs at peak 3. In all cases, the residual current levels after peak 3 and before peak 4 were utilized as base lines for the respective peaks, and the geometric iron surface area was used to convert the currents to current densities. The average curves for the progressions of the peak current densities (i_p) are shown in Fig. 5. These composite curves represent the averages for 30 runs with cement-coated iron electrodes, encompassing various curing times (3, 5, 10, 25 and 50 days) and water-to-cement (W:C) ratios (0.45 or 0.30). The approach to steady state is seen to be very similar for peaks 3 and 4. The peak current densities initially increased rapidly from very low values; however, the slopes of the curves decreased monotonically such that the peak current densities approached constant values after about 170–180 cycles. Similar behavior for iron in KOH and NaOH solutions was observed in the present study, and has also been reported [3, 7] and alluded to [10, 11, 16, 17] by previous investigators. This similarity between the results obtained in cement and KOH or NaOH solutions gives rise to added confidence in the validity of the voltammograms obtained with iron in cement. The observed approach to steady state can be attributed to the initiation and thickening of the outer hydrous oxide layer, which in turn results from the slightly incomplete reduction at peak 5 (and beyond) of the ferrous state of the outer layer (formed at peak 4) on each cycle. The steady state thickness of the outer layer is reached as a result of the increased inhibition of water and hydroxide ion transfer through that layer to the inner compact layer [7].

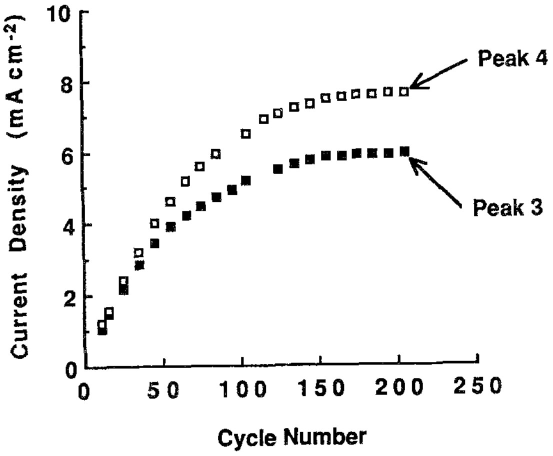

Fig. 5. Progression of peak currents for peaks 3 and 4; iron in cured Portland cement, $0.050\,V\,s^{-1}$, 25° C.

The orderly manner of the progression of the peak currents was routinely reproduced. However, the data for the 30 runs indicate that the variability in the magnitudes of the peak currents to be expected for a single run is fairly high, the average standard deviation for a single run being ±10%. Therefore, it is recommended that runs be performed in triplicate, in order to reduce the standard deviation by a factor of $\sqrt{3}$, to about ±6%.

3.2.2. Electrode pretreatment. Measures commonly suggested to improve the reproducibility of voltammetric measurements with iron in alkaline solutions are mechanically polishing the iron with SiC paper and/or alumina [3–7, 11–16, 18], and electropolishing the iron electrode by holding it in the hydrogen evolution region (e.g. -1.4 to -1.6 V) for 5–20 min [10–12, 15–17].

Mechanically polishing the iron with alumina (0.3 μm, Micro Metallurgical, Ltd), prior to immersion in the solution or to coating with cement, greatly improved the reproducibility. The average standard deviation for the peak currents at peaks 3 and 4 in saturated $Ca(OH)_2$ was reduced from ±52% for unpolished iron, to ±10% for mechanically polished iron electrodes; the corresponding average standard deviation for mechanically polished electrodes in cement also was ±10%. Accordingly, mechanical polishing of the iron is recommended.

Electropolishing the iron, either prior to cycling or after 100 cycles, affected only the first 10–20 subsequent cycles, and statistical analyses (standard 't' tests at the various cycle numbers [21]) indicated that there was no significant, lasting effect on the voltammograms, either in cement or in saturated $Ca(OH)_2$. These results indicate that electropolishing is unnecessary, if the electrode is to be repeatedly cycled prior to data acquisition. However, some hydrogen evolution during cycling is necessary in order to study the voltammetric features. Voltammograms for cement-coated iron, in which the cathodic sweep was cut off at -1.1 V, so as to exclude any possibility of hydrogen evolution, were severely truncated and quite unsatisfactory. (The equilibrium potential for hydrogen evolution was calculated as -1.1 V, by applying the Nernst equation to the reaction

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \qquad (1)$$

and assuming a pH of 13; the actual potential at which hydrogen evolution began was probably somewhat more negative, because of the overpotential of about 0.08 V [22].) The electrode remained essentially passive, and the voltammogram featureless, unless the sweeps were extended into the hydrogen evolution region. Consequently, extension of the potential cycling into the hydrogen evolution region (for example -1.4 V), but not holding of the electrode potential in the hydrogen evolution region, is recommended.

3.2.3. *Water to cement (W : C) ratio and curing time.*

The effects of varying the W : C ratio from 0.30 to 0.60 (using a constant curing time of 5 days), and the curing time from 1 to 50 days (using a constant W : C ratio of 0.45), were investigated. At least 4 runs were performed at each set of conditions. The peak currents for peaks 3 and 4 obtained at a relatively high W : C ratio of 0.60 were significantly lower (95% confidence) than those at W : C ratios of 0.30 or 0.45. Similarly, the peak currents obtained at a relatively short curing time of 1 day were significantly lower (99% confidence) than those at curing times of 3 days or more. However, there were no significant differences between the average peak currents obtained at W : C ratios of 0.30 or 0.45, or at curing times greater than 3 days. These results indicate that W : C ratios less equal or less than about 0.45 and curing times of at least 3 days are required in order to obtain representative data.

3.2.4. *iR compensation.*

Compensation of iR is very important because of the large resistance of the cement covering. Voltammograms for iron in cement, with and without iR compensation, are shown in Fig. 6. The peaks of the voltammogram taken without iR compensation are severely skewed and shifted, rendering even qualitative analysis very difficult. The current interrupt method of iR compensation, in which the iR drop is measured at very close intervals (4 ms), and then automatically compensated for, was utilized in the present study. However, this method was limited by the equipment to sweep rates less than, at most, about 0.5 V s^{-1}. At higher sweep rates, it is necessary to employ positive feedback iR compensation, in which a single, constant value of 'R' is used to provide the appropriate value of the iR drop.

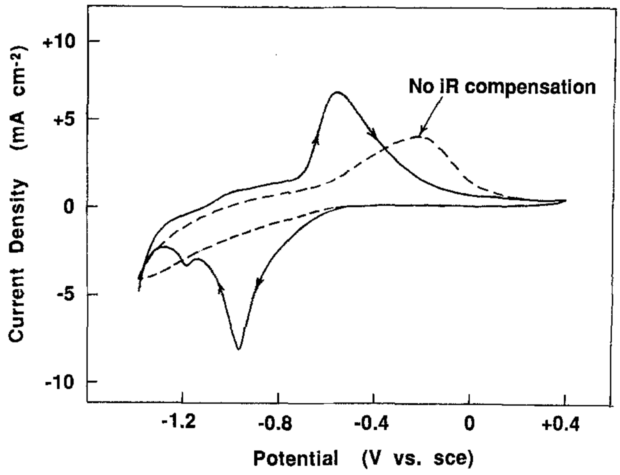

Fig. 6. Voltammograms for cement-coated iron, with and without iR compensation; W : C = 0.45, 25 day cure, 0.050 V s^{-1}, 25°C.

A plot of electrode resistance versus the cement-to-water ratio (Fig. 7) yields a straight line through the origin. These results imply that the resistance of the solution and the oxide film are negligible, as has been alluded to previously [17]. This was verified by runs with bare iron in alkaline solutions, in which the iR compensation had no discernable effect. Thus, practically all the resistance encountered resides in the cement, and consequently, the value of the electrode resistance remains essentially constant; this, in turn, implies that the positive feedback method can be used. However, the positive feedback method can compensate for only about 90% of the iR drop before stability of the response becomes a problem. The use of positive feedback iR compensation resulted in reasonably good reproduction of most of the voltammograms obtained with current interrupt iR compensation at

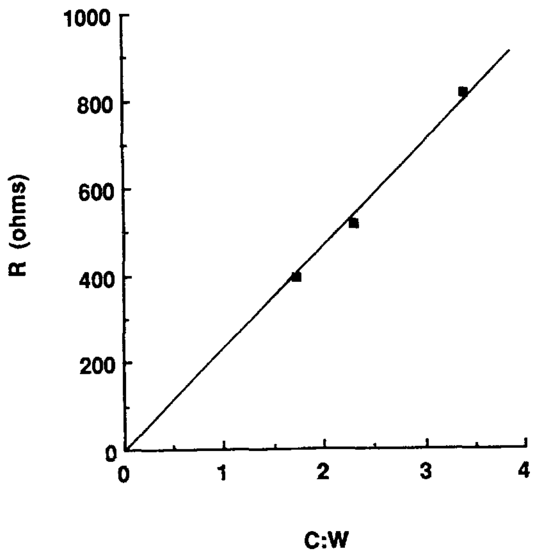

Fig. 7. Effect of cement-to-water ratio (C : W) on electrode resistance; 5 day cure, 0.050 V s^{-1}, 25°C.

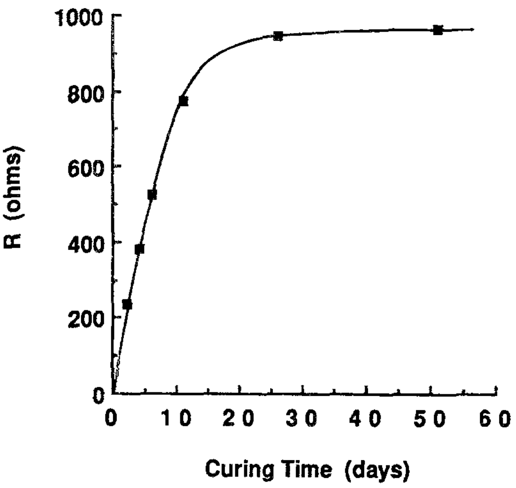

Fig. 8. Effect of curing time on electrode resistance; W : C = 0.45, 0.050 V s^{-1}, 25° C.

0.050 V s^{-1}. However, the significant residual iR drop that is necessarily present with the high-resistance, cement-coated electrodes was sufficient to cause small, but noticeable distortions at peaks 3 and 4. We therefore used the current interrupt method for the most accurate quantitative work, although the positive feedback iR compensation is sufficient for qualitative or semi-quantitative studies. In the present study, sweep rates were limited to less than about 0.2 V s^{-1}.

The variation of the electrode resistance with curing time is shown in Fig. 8. The electrode resistance initially increased rapidly with curing time, but approached a constant value at curing times greater than about 20 days. These data imply that the permeability of the cement decreases significantly over about the first 20 days of curing. However, we suggest that a relatively short curing time of 3 days be used, for the following reasons: first, there were no significant differences in the voltammetric results for curing times greater than about 3 days, which indicates that a 3 day cure is sufficient to allow representative voltammograms to be obtained over the course of at least 200 cycles. Furthermore, since the electrode resistance after a 3 day cure is relatively low (see Fig. 8), the iR compensation required and, accordingly, any possible accompanying deleterious effects, are minimized. The convenience afforded by a short curing time also is a significant advantage.

3.2.5. Proposed standard procedure. Based on the results discussed above, we recommend that a standard procedure for voltammetric measurements with iron in cured Portland cement should incorporate the following measures: (i) mechanical polishing of the iron prior to embedment in cement; (ii) extension of the potential sweeps into the hydrogen evolution region (for example -1.4 V), but not holding of the electrode potential in this region; (iii) the use of W : C ratios between about 0.30 and 0.45, and a curing time of 3 days; (iv) current interrupt iR compensation for all runs; (v) cycling of the electrode about 200 times at a sweep rate of 0.050 V s^{-1} prior to data acquisition; and, (vi) performance of runs in triplicate. We also recommend that such *in situ* measurements with iron in cement be used in preference to those in simulated pore solutions.

3.3. *Application of the standard procedure*

3.3.1. Enhancement of the passivation of iron in Portland cement versus KOH solutions. Significant (three to fourfold) enhancement of the passivation of iron in Portland cement, relative to that observed in 0.1 M KOH or NaOH, is indicated in Fig. 9 and by the different current density scales in Figs 2 and 3. Also, it is clear from Figs 2 and 4 that an even greater enhancement of the passivation process is obtained with iron in saturated $Ca(OH)_2$. These results indicate that the improved passivity in cement, as compared with that observed in KOH or NaOH solutions, is a consequence of the presence of $Ca(OH)_2$. In order to test this hypothesis, the voltammetric behavior of iron in 0.1 M KOH with various $Ca(OH)_2$ additions was investigated.

The voltammograms for iron in solutions of 0.1 M KOH and 0.1 M KOH + 0.3 mM $Ca(OH)_2$ are compared in Fig. 9 with that for cement-coated iron. The voltammogram for iron in 0.1 M KOH + 0.3 mM $Ca(OH)_2$ is strikingly similar to that for iron in cement. On the basis of this accurate simulation, it is proposed that the improved passivity of iron in cement, relative to that in KOH or NaOH solutions, is related to the presence of small amounts of $Ca(OH)_2$. The dependence of the peak current density for peak 3 on the $Ca(OH)_2$ concentration (in 0.1 M KOH and after 200 previous cycles) is shown in Fig. 10. The peak current densities drop by a factor of four, from about 25 mA cm^{-2} to about 6 mA cm^{-2}, over a range of $Ca(OH)_2$ concentrations from about 0.03 mM to 0.3 mM. It is apparent that the presence of very small amounts of $Ca(OH)_2$ is sufficient to significantly enhance the passivation. It also is clear that this enhancement effect is a critical phenomenon; that is,

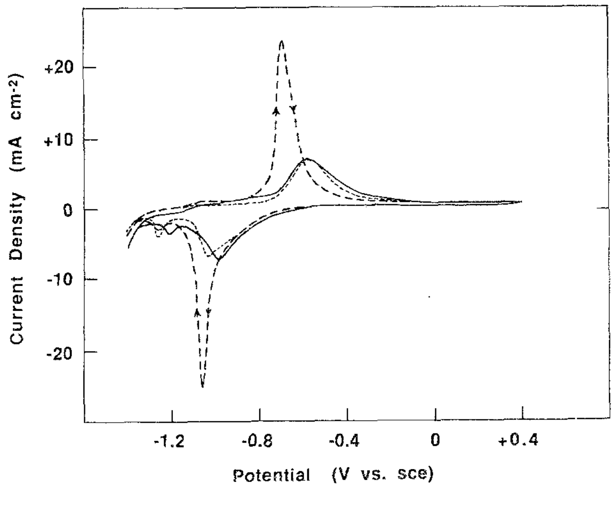

Fig. 9. Voltammograms for cement-coated iron (W : C = 0.45, 3 day cure), uncoated iron in 0.1 M KOH, and uncoated iron in 0.1 M KOH + 0.3 mM $Ca(OH)_2$; cycle no. 201, 0.050 V s^{-1}, 25° C. – – –, 0.1 M KOH; – – – – –, 0.1 M KOH + 0.3 mM $Ca(OH)_2$; ——, Cured Cement.

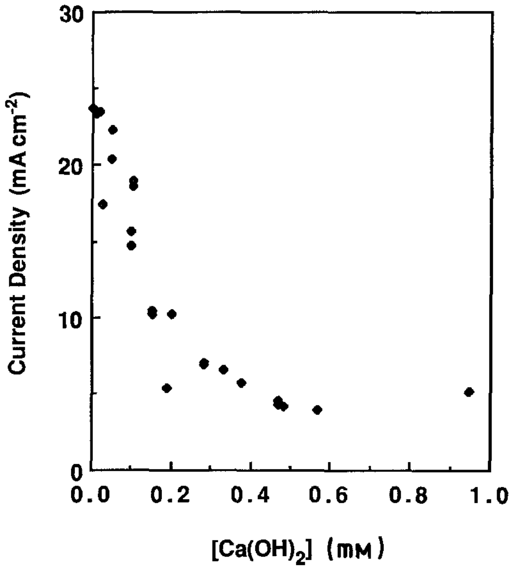

Fig. 10. Effect of $Ca(OH)_2$ additions on the peak current densities for Peak 3; cycle no. 201, 0.050 V s^{-1}, 25° C, 0.1 M KOH.

the effect occurs over an extremely small range of $Ca(OH)_2$ concentrations. However, because of erratic results at $Ca(OH)_2$ concentrations less than about 0.3 mM, the exact location of the critical concentration was difficult to determine. A similar critical effect for the passivity of carbon steel in $Ca(OH)_2$ solutions has been reported, the critical concentration being in the order of 1 mM [23].

A somewhat analogous enhancement of the passivity of iron in 0.1 M KOH was obtained simply by wrapping the iron electrode with glass wool (Corning 3950, composed of 8 μm Pyrex fibres), although the voltammograms were considerably distorted, especially in the region of peak 4. This suggests that the passivity enhancement effect primarily is a blocking or shielding effect, caused by precipitation of a calcium-containing species on the electrode surface. In this regard, crystals observed near the rebar-concrete interface in SEM micrographs have been considered to be $Ca(OH)_2$ [24, 25]. However, it is unlikely that precipitation of $Ca(OH)_2$ occurred from our KOH + $Ca(OH)_2$ solutions, since the critical $Ca(OH)_2$ concentration range for the enhancement of the passivity in 0.1 M KOH is much lower than the saturation concentration of about 2.0 mM (pH = 12.9, and $K_{sp} \sim 10^{-4.9}$ M^3 at an ionic strength of 0.1 M [26]). Furthermore, the pH near the electrode surface may well be lower than that measured in the bulk solution. It has been suggested that the enhanced passivity of iron in $Ca(OH)_2$ solutions may be caused by the precipitation of compounds of calcium and iron, identified only as 'complex' compounds [23]. Our SEM micrographs of the surface after 200 cycles in saturated $Ca(OH)_2$ (Fig. 11) show that the iron was covered by a thin crystalline coating. The X-ray spectrum of the extracted coating showed strong peaks for Ca and Fe only, the Fe-to-Ca ratio being approximately 2 : 1 (1.8 : 1), which indicates that the surface film is probably composed primarily of calcium ferrate ($CaFe_2O_4$). Similar, but not identical, Ca–Fe compounds were identified in recent work on the corrosion of steel in contact with gypsum in an alkaline medium [27]. However, SEM observations of the surfaces of iron electrodes that had been cycled in 0.1 M KOH or 0.1 M KOH + 0.3 mM $Ca(OH)_2$ indicated that the morphology of these surfaces was quite different from that shown in Fig. 11. Further investigation of these phenomena is currently being conducted and will be reported in a later paper.

3.3.2. Sweep rate study. The variation of the peak current density (i_p) and the peak potential (E_p) for peak 3 with sweep rate for cement-coated electrodes are shown in Figs 12 and 13, respectively. In all cases, the electrodes were cured for 3 days, and a W : C ratio of 0.45 was used. The data were obtained in the following manner. The electrode was first cycled 200 times at 0.050 V s^{-1}. Voltammograms then were recorded consecutively at the various sweep rates, in the following descending order: 0.200, 0.100, 0.050, 0.020, 0.010 and 0.005 V s^{-1}. The second cycle at each successive sweep rate was recorded. In the interest of accuracy, current interrupt iR compensation was used throughout; accordingly, the maximum sweep rate used was 0.200 V s^{-1}. The data shown in Figs 12 and 13 represent the average values from three different runs. The peak current densities and peak potentials were proportional to the square root of the sweep rate. Similar

Fig. 11. SEM Micrograph of electrode surface after 200 cycles in saturated $Ca(OH)_2$; 0.050 V s^{-1}, 25° C.

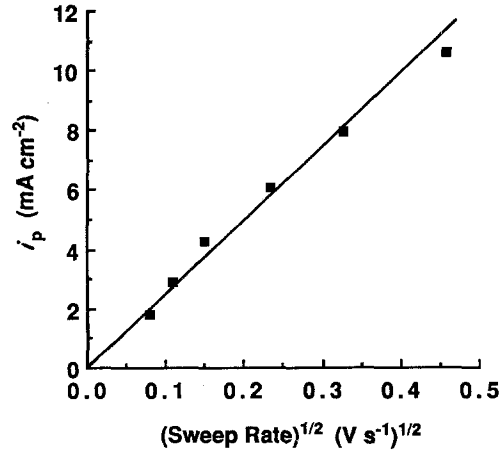

Fig. 12. Variation of peak current densities for peak 3 with sweep rate for cement-coated iron; W : C = 0.45, 3 day cure, 25° C.

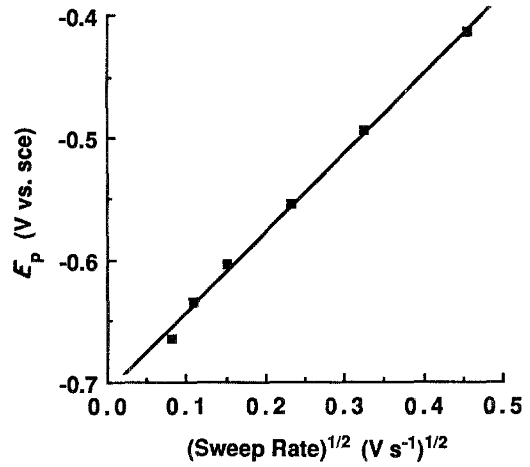

Fig. 13. Variation of peak potentials for peak 3 with sweep rate for cement-coated iron; W : C = 0.45, 3 day cure, 25° C.

results were obtained with electrodes that had been cured for 50 days, the peak current densities being almost identical to those shown in Fig. 12, although the corresponding peak potential plot had a somewhat lower slope than that shown in Fig. 13. These data are consistent with a pore resistance model, in which the oxide layer spreads over the electrode surface until only small pores remain; diffusion through the pores then controls the rate of layer formation. Sarasola *et al.* [3] recently used such a model to describe the behavior of peak 3 for iron in 0.1 M KOH at sweep rates of 0.003 to 0.200 V s^{-1}. This is further evidence that the voltammograms obtained using iron in solid Portland cement are reliable and sensitive electrochemical procedures, and that the reaction mechanism in cement is similar to that in KOH solutions.

3.3.3. Effect of chloride additions. Some preliminary runs were performed using cement-coated electrodes in saturated $Ca(OH)_2$ + 1 M NaCl (external chloride addition), as well as cement-coated electrodes in which 1 M NaCl was substituted for the water in the cement mix (internal chloride addition). For the runs with external chloride additions, the shapes of the voltammograms, the progression of the peak currents, and the electrode resistances were essentially the same as those for runs with no chloride additions. This clearly demonstrates that the external solution does not significantly penetrate the cement during the course of a 4–5 hour run. However, after 25–30 hours of immersion, there was evidence of significant chloride penetration in the form of a general increase in the currents and in the electrode resistance (the latter presumably indicating a large buildup of corrosion products), as well as the appearance of a new anodic peak in the normally passive potential regime, at about 0 V. Such seemingly rapid chloride penetration also has been detected by a.c. impedance studies [28]. These latter results obtained using external chloride additions are similar to those obtained using internal chloride additions, for which a typical voltammogram is shown in Fig. 14. Similar voltammograms have recently been reported for iron in solutions containing 0.04 M NaOH + 0.05 M NaCl [4]. A detailed investigation of the effects of chloride additions will be reported in a later paper.

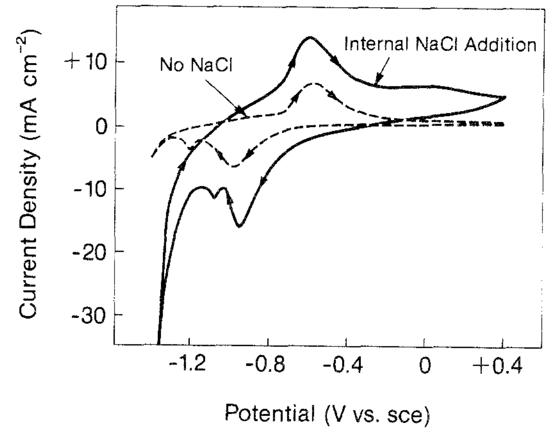

Fig. 14. Voltammogram for cement-coated Fe with internal NaCl addition; cycle no. 201, W : C = 0.45, 3 day cure, 0.050 V s^{-1}, 25°C.

4. Summary

A reproducible procedure has been developed to study the cyclic voltammetry of iron electrodes embedded in cured Portland cement. This procedure, which should prove useful as a means of studying the corrosion of reinforced concrete, incorporates the following measures: (i) mechanical polishing of the iron prior to embedment in cement; (ii) extension of the switching potential into the hydrogen evolution region (for example, − 1.4 V), but not holding the electrode potential in this region; (iii) the use of W : C ratios between about 0.30 and 0.45, and a curing time of 3 days; (iv) current interrupt iR compensation for all runs: (v) cycling of the electrode about 200 times at a sweep rate of 0.050 V s^{-1}, and (vi) performance of runs in triplicate. It is strongly recommended that such *in situ* measurements be used in preference to those in simulated pore solutions.

The usefulness of the method has been demonstrated by means of a series of brief preliminary studies. Specifically, studies on the effects of sweep rate, chloride additions, and the role of $Ca(OH)_2$ in the passivation of iron in alkaline solutions were performed. The sweep rate behavior of the passivation peak in cement was consistent with that predicted by a pore diffusion model. As expected, the chloride additions were found to disrupt the passivity, as evidenced by a general increase in the voltammetric currents and the electrode resistance, as well as by the appearance of a new anodic peak in the normally passive potential regime. The results indicated that, although the reaction mechanism is similar in cement to that in aqueous alkaline solution, the passivity of iron is enhanced in cement, relative to that observed in aqueous KOH or NaOH solutions. This is shown to be related to the presence of $Ca(OH)_2$ in the cement pore solution.

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References

[1] J. Tinnea, *Mater. Perform.* **26**(12) (1987) 9.

[2] 'Corrosion of Metals in Concrete,' NACE, Houston (1988).

[3] C. Sarasola, T. Fernandez and Y. Jimenez, *Electrochim. Acta* **33** (1988) 1295.

[4] S. Juanto, J. O. Zerbino, M. I. Miguez, J. R. Vilche and A. J. Arvia, *Electrochim. Acta* **32** (1987) 1743.

[5] R. C. Salvarezza, D. V. Vasquez Moll and A. J. Arvia, *Electrochim. Acta* **32** (1987) 1421.

[6] G. Paruthimal Kalaignan, V. S. Muralidharan and K. I. Vasu, *J. Appl. Electrochem.* **17** (1987) 1083.

[7] L. D. Burke and M. E. G. Lyons, *J. Electroanal. Chem.* **198** (1986) 347.

[8] M. E. Vela, J. R. Vilche and A. J. Arvia, *Electrochim. Acta* **31** (1986) 1633.

[9] O. A. Albani, J. O. Zerbino, J. R. Vilche and A. J. Ariva, *Electrochim. Acta* **31** (1986) 1403.

[10] M. Sheedy, M. A. Sc. Thesis, University of Toronto, 1985.

[11] A. Wieckowski and E. Ghali, *Electrochim. Acta* **30** (1985) 1423.

[12] V. S. Muralidharan and M. Veerashanmugamani, *J. Appl. Electrochem* **15** (1985) 675.

[13] J. Dunnwald and A. Otto, *Z. Anal Chem.* **319** (1984) 738.

[14] A. Wieckowski, E. Ghali and H. H. Le, *J. Electrochem. Soc.* **131** (1984) 2024.

[15] R. S. Schrebler Guzman, J. R. Vilche and A. J. Arvia, *J. Appl. Electrochem.* **11** (1981) 551.

[16] R. S. Schrebler Guzman, J. R. Vilche and A. J. Arvia, *Electrochim Acta* **24** (1979) 395.

[17] D. D. MacDonald and B. Roberts, *Electrochim Acta* **23** (1978) 781.

[18] D. Geana, A. A. El Miligy and W. J. Lorenz, *J. Appl. Electrochem* **4** (1974) 337.

[19] C. L. Page and K. W. J. Treadaway, *Nature*, **297** (1982) 109.

[20] Z. Q. Huang and J. L. Ord, *J. Electrochem Soc.* **132** (1985) 24.

[21] I. Miller and J. E. Freund, 'Probability and Statistics for Engineers,' Prentice-Hall Inc., Englewood Cliffs, NJ (1977).

[22] U. R. Evans, 'The Corrosion and Oxidation of Metals', Arnold Publishers Ltd, London (1960).

[23] A. P. Akol'zin, P. Ghosh and Yu. Ya. Kharitonov, *Zashch. Met.* **19** (1983) 302.

[24] T. Yonezawa, V. Ashworth and R. P. M. Procter, *Corrosion* **44** (1988) 489.

[25] C. L. Page, *Nature* **258** (1975) 514.

[26] A. Ringbom, 'Complexation in Analytical Chemistry,' Interscience Publishers, New York (1963).

[27] R. Schicht, *Sprechsaal* **113** (1980) 318.

[28] P. Lay, P. F. Lawrence, N. J. M. Wilkins and D. E. Williams, *J. Appl. Electrochem* **15** (1985) 337.