Pergamon

Cement and Concrete Research 29 (1999) 873–883

CEMENT AND CONCRETE RESEARCH

A rapid cyclic voltammetric method for studying cement factors affecting the corrosion of reinforced concrete

Frank R. Foulkes [a],*, Patrick McGrath [b]

[a]Department of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College Street, Toronto, Ontario M5S 3E5, Canada
[b]Department of Civil Engineering, University of Toronto, Toronto, Ontario M5S 1A4, Canada

Manuscript received 1 January 1995; accepted manuscript 25 February 1999

Abstract

A rapid cyclic voltammetric method for studying the influence of cement factors on the corrosion of embedded iron and steel in hardened cement paste is described. The technique employs a "cement electrode" consisting of an iron or steel wire embedded in a miniature cylinder of hardened cement paste. The rapid cyclic voltammetric method is fast, reproducible, and provides information on the corrosiveness of the pore solution environment surrounding the embedded metal. The usefulness of the method is demonstrated by showing how it can be used to evaluate the threshold chloride content of hardened ordinary portland cement paste at which corrosion begins and by using it to evaluate the relative efficacy of several admixed corrosion inhibitors. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Pore solution; Corrosion; Electrochemical properties; Chloride; Corrosion inhibitors

The extent of steel corrosion in concrete can be measured by a multitude of test methods, such as potential measurements, weight loss measurements, cyclic voltammetry, linear polarization, and electrochemical impedance spectroscopy (EIS). While some methods (e.g., linear polarization and weight loss) give an indication of the rate and extent of corrosion, others (such as cyclic voltammetry and EIS) generally are considered to be better suited for determining the nature of the passive layer and the mechanisms of depassivation [1].

Over the past 10 years we have been developing a rapid cyclic voltammetric (RCV) method for studying the influence of various cement factors on the corrosion of iron and steel in cement [2–5]. Basically, the method consists of axially embedding a thin iron wire into a miniature cylinder of wet ordinary portland cement (OPC) paste having a water to cement (w/c) ratio of 0.45 (any other value also can be chosen) [see Fig. 1*(A)*]. After curing the specimen for 28 d at 100% relative humidity, it is immersed at 25°C for 24 h in saturated $Ca(OH)_2$ solution containing NaCl of varying concentrations to introduce chloride into the cement matrix. Following this immersion, cyclic voltammograms are obtained using the chloride-contaminated specimen as the working electrode in a potentiodynamic measuring system incorporating a potentiostat equipped with ohmic (iR) compensation and a saturated calomel reference electrode (SCE) (all potentials are reported as V vs. SCE). The voltammetric data typically are obtained between voltage limits of -1.4 V and $+0.4$ V at a linear sweep rate of 50 mV s^{-1}. Steady state voltammograms are observed after about 200 cycles.

Because of the high electrical resistivity of OPC, the voltammetric data obtained using cement-coated iron electrodes contain large iR components, which severely skew the diagnostic shapes of the resulting voltammograms, rendering even qualitative analysis very difficult. For example, the resistance of an OPC electrode with a 28-day cure is in the order of 950 Ω; at a typical voltammetric current of 0.5 mA this results in an iR drop of 0.48 V. This problem becomes even more serious as the sweep rate is increased because the current densities tend to increase with increasing sweep rate. For this reason, a key component of the measuring system is a potentiostat that is capable of providing iR compensation. Until about 10 years ago such equipment was not widely available commercially, precluding the use of rapid scan cyclic voltammetry for the study the electrochemical behavior of metals embedded in cured cement paste.

The following advantages of this technique for studying various aspects of the corrosion of iron and steel reinforcement in concrete can be cited:

1. Realistic pore solution environment: Since the RCV method uses metal that is embedded in actual cured

---

* Corresponding author. Tel.: 416 978 6432; Fax: 416 978 8605; E-mail: foulkes@chem-eng.utoronto.ca.

Present address of P. McGrath: James Neill and Associates, Ltd., North Vancouver, British Columbia V7K 2N1, Canada.

PII: S0008-8846(99)00056-3

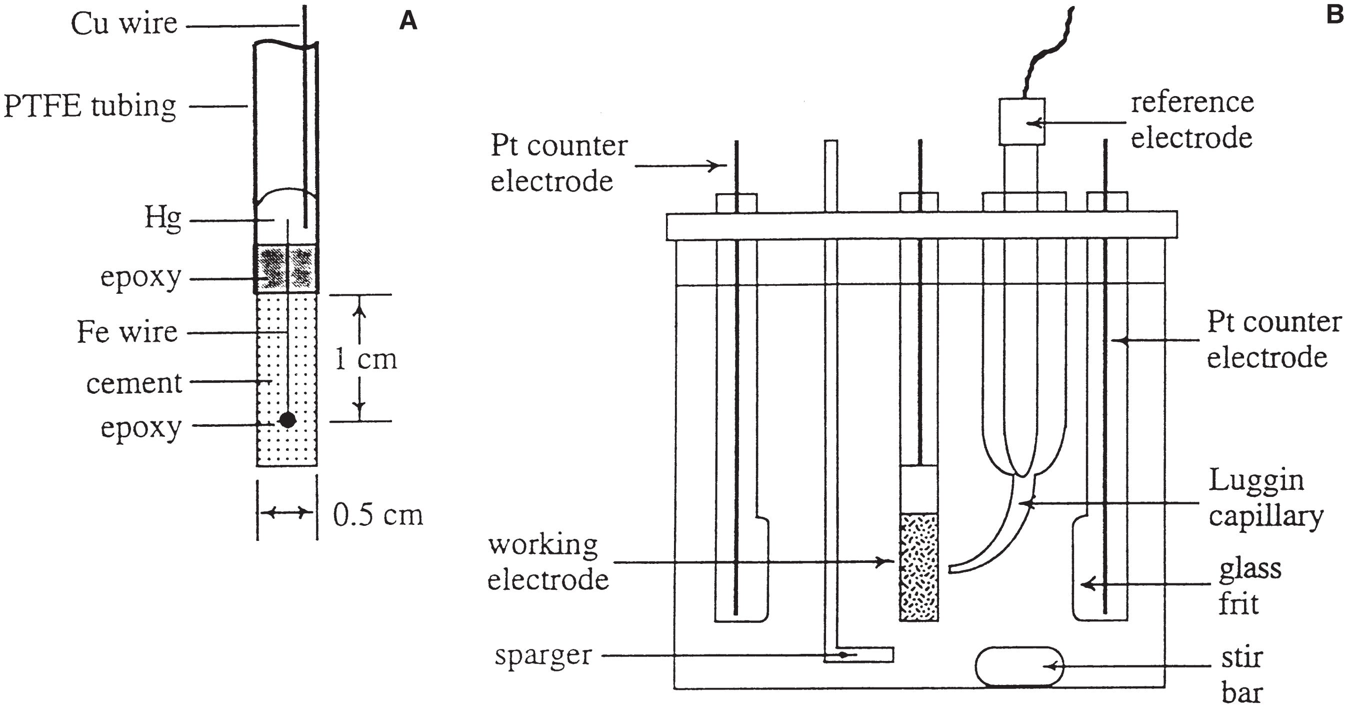

Fig. 1. *(A)* Details of cement-coated electrode. *(B)* Details of experimental cell.

cement paste, the pore solution environment contacting the embedded metal is essentially the same as that found in a corroding reinforced concrete structure. This is in contrast to those commonly used voltammetric techniques that involve the use of iron or steel immersed in simulated cement pore solutions; these latter solutions not only are oversimplified chemically, but also do not have the same mass transport characteristics found in a porous medium such as cured cement paste or concrete. Accordingly, conclusions drawn from experiments using simulated pore solution can be misleading if extended to cured OPC. For example, the corrosion resistance of iron in cured OPC paste has been found to be greater than in aqueous 0.1 M KOH or 0.1 M NaOH solution, but less than in saturated $Ca(OH)_2$ solution [2]. The enhanced passivity in cured cement paste compared with that in KOH or NaOH solution appears to be due to the $Ca(OH)_2$ in the cement pore solution. There is some evidence that this may give rise to the deposition of a calcium-iron containing protective layer of a compound such as calcium ferrate ($CaFe_2O_4$) [2].

2. Reproducibility: ASTM specification A706-76 permits a wide range of compositions for reinforcing steel. The consistent use of pure iron wire electrodes helps to impart reproducibility to the RCV method, enabling the results to be attributed to cement factors, rather than to metallurgical variations in the embedded metal. Fortunately, the voltammetric behaviour of iron wire has been shown to be similar to that of reinforcing steel, both with and without the addition of corrosion inhibitor or NaCl [3]. Of more importance than minor metallurgical factors, however, is the problem of poor reproducibility that can occur in corrosion studies that are carried out using large, reinforced concrete specimens. This lack of reproducibility, discussed in greater detail below, largely can be attributed to the dependence of the corrosion process on heterogeneities and other local environmental conditions in the concrete specimens. The use of miniature cement-covered iron electrodes in which the surface of the embedded iron wire is voltammetrically cycled to a steady state condition yields inherently more reproducible results, which can be duplicated from laboratory to laboratory and from worker to worker. Depending on the skill of the experimenter, we have found that, in general, from three to seven replicate runs must be made to obtain useful mean values.
3. Speed: Once the cement electrode has been prepared and cured, the voltammetric data can be obtained quite quickly: At a voltage sweep rate of 50 mV s^{-1} one complete voltammetric cycle requires 72 s; thus a 10-cycle and a 200-cycle experiment require a running time of 12 min and 4 h, respectively.

The purpose of this paper is to introduce the RCV method by showing how it can be used to yield information on the corrosivity of the pore solution environment in cured OPC paste that contains chloride. After first discussing the rationale for the RCV method we shall illustrate its application by means of several example studies.

1. Description of standard voltammogram

Throughout the course of repeated anodic and cathodic cycling there is a gradual buildup of a hydroxy-oxide film on the surface of the embedded iron electrode. Although there is still considerable debate on all the details of this film, it is probably composed of two distinct layers: an outer, relatively thick, porous hydrous layer containing iron mostly in the Fe(III) state, and an inner, relatively thin, compact layer consisting of iron mostly in the Fe(II) state. The compact inner oxide layer is believed to act as a barrier, protecting the iron substrate; whereas the outer layer, because of its high porosity, does not confer protection [6–8]. Fig. 2 shows a typical voltammogram obtained after 200 cycles using the RCV method as outlined above, with OPC paste in the absence of chloride. The current densities have been calculated by dividing the total current by the initial geometrical surface area of the iron wire exposed to the cement (~0.08 cm^2). For the purpose of expediently demonstrating the salient features of the RCV method, all the voltammetric data presented in this report were obtained using cement paste electrodes having only 3-day cures. In general, a 28-day cure is recommended, although our experience has shown that the trends are not significantly affected using the shorter curing times.

Four anodic peaks (peaks 1, 2, 3, and 3a) and three cathodic peaks (peaks 4a, 4, and 5) can be identified. The processes occurring on the surface of the iron that correspond to these various peaks have been the object of considerable study, but still have not been unequivocally identified [2–14].

Although it is not the purpose of this report to present a detailed discussion of the various electrochemical mechanisms of iron corrosion, nevertheless a brief description of the main features of the voltammogram shown in Fig. 2 will aid in understanding the basis behind the application of the RCV method. Peak 0 corresponds to hydrogen evolution; if the electrode is held at this potential long enough, the inner oxide layer eventually will be electrochemically reduced to yield a bare iron surface exposed to the cement pore solution. Peaks 1 and 2 have been attributed to the formation of a film of $Fe(OH)_2$ and/or FeO on the previously reduced iron surface. Peak 3 is believed to correspond to an Fe(II) → Fe(III) transition as ferrous iron of the inner layer is converted to ferric iron in the interfacial region between the inner (compact) layer and the outer (porous) layer. This transition reaction is probably a reversible reaction that is controlled by the diffusion of OH^- ions within the outer oxide layer [8]. Peak 3a has been attributed to an oxidation reaction within the compact oxide layer, probably involving the formation of Fe_2O_3, Fe_3O_4, or FeOOH [6,7]. Peaks 4 and 4a are considered to be the reverse (reduction) reactions corresponding to the anodic reactions at peaks 3 and 3a, respectively. Peak 5 has been attributed either to the corresponding reduction reaction of the $Fe(OH)_2$ film formed at peaks 1 and 2 or to some other reduction reaction at the inner oxide layer.

At this point we wish to anticipate the objection that the relatively reproducible oxide film that is developed on the surface of iron wire using the RCV method is undoubtedly different from any of the “natural” films that may develop

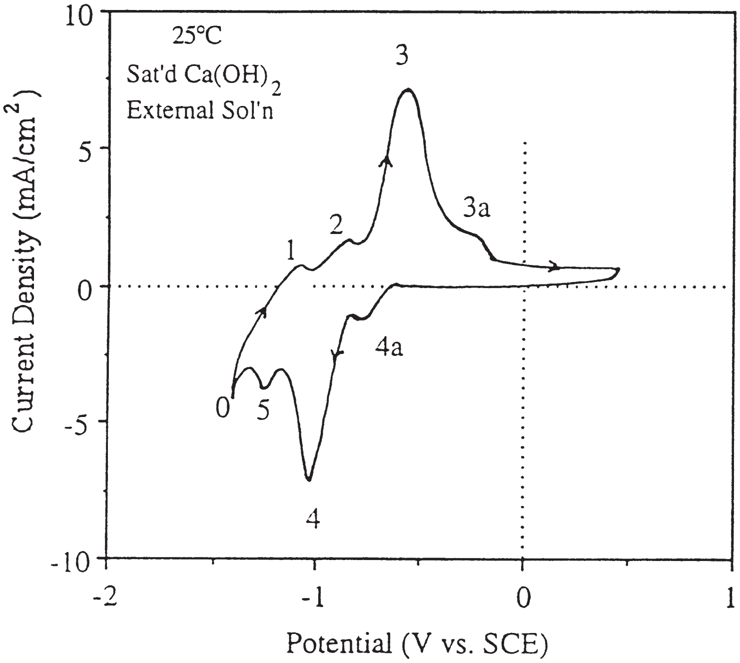

Fig. 2. Standard steady state voltammogram for cement-covered electrode.

in situ within a corroding reinforced concrete structure. As we explain below, this fact is an asset, not a liability.

With extensive potential cycling peaks 3 and 4 generally become larger, while peaks 1, 2, 3a, and 4a tend to remain relatively invariant, eventually becoming hidden by the growth of peaks 3 and 4. Peak 5 also tends to remain unaffected by the growth of peaks 3 and 4. The peak current densities associated with peaks 3 and 4 normally approach constant values after 170–190 cycles. These observed constant values indicate that repeated cycling leads to the net formation of a reproducible steady state oxide on the iron surface. This steady state can be attributed to a gradual thickening of the outer hydrous oxide layer that results from its slightly incomplete reduction during each previous cathodic half cycle. A limiting thickness develops for the outer oxide layer because its growth is gradually slowed down by the increasing difficulty of transferring water and OH^- ions through it to the interface between it and the inner oxide layer, where the formation of additional Fe(III) oxide occurs [6,7]. At the maximum current of peak 3 the rate of formation of Fe(III) compounds becomes so great that a condition of local saturation develops, resulting in the onset of the precipitation of electrically highly resistive compounds that passivate the iron surface, resulting in a sudden drop in the anodic current density (i.e., a sudden drop in the rate of iron corrosion).

The ensuing plateau of low current density—the so-called "passive region"—at potentials more positive than the potential at peak 3 is indicative of the degree of impermeability of the film on the iron surface. (A true passive current density is usually orders of magnitude lower than the current density at the preceding peak. In the case of iron in cement the reduction in current density is not so great. However, for want of a better term, we shall refer to this region of reduced corrosion current as the "passive region.") We have found that the value of the current density at 0 V (designated by the nomenclature "i_{0V}") is representative of the current density in the passive region, and is a good indicator of the extent of protection conferred by the oxide film. Thus, for a given oxide film, the greater the value of i_{0V}, the more corrosive is the pore solution environment that surrounds the embedded iron. This single fact is the basis of the RCV method, and is what makes it a rapid, reproducible way to study various cement factors that affect the corrosion of reinforced concrete exposed to chloride environments.

2. Why does the RCV method yield reproducible results?

A criticism sometimes encountered in connection with the use of the RCV method is that the type of oxide film formed on the metal surface is not the same as that formed in situ on the surface of an embedded rebar in a freely corroding reinforced concrete structure; it follows, therefore, that the information obtained through the use of the RCV method has no relevance to "real" structures in "real" situations. This criticism arises from a fundamental misconception about the purpose of the RCV method.

As can be attested by those who have employed any of the so-called "traditional" laboratory techniques such as long-term immersion tests or salt-spray or ponding tests to study the corrosion of embedded steel in salt-contaminated concrete, one of the major difficulties in this endeavor is the notorious irreproducibility of the results. Sometimes a reinforced concrete slab immersed in salt water will start showing signs of significant corrosion after a few months, whereas another seemingly identical specimen under seemingly identical conditions may still be corrosion-free after two years. And, of course, the irreproducibility is much worse under the uncontrolled conditions encountered in actual field structures.

When discussing the corrosion of a reinforced concrete structure there are two aspects that should be considered: The first is the "time to corrosion," which is the length of time required before the reinforcing steel actually begins to corrode. The second factor is the "rate of corrosion," which is the rate at which the metal deterioration proceeds once the corrosion actually has started. Obviously, even an extremely high rate of corrosion is not a problem if the time to corrosion is several hundred years. Similarly, a time to corrosion of even a few months does not matter if the rate of corrosion is extremely small once corrosion has begun. The failure of some workers to clearly distinguish between these two stages of the corrosion process has led to erroneous conclusions.

The time to corrosion is determined by a number of factors. In addition to the obvious influence of things such as heterogeneities or microcracks in the concrete and its porosity, the time to corrosion also is affected by the corrosivity of the pore solution environment contacting the embedded metal surface and by the state of the metal surface itself at the time of embedment. Such initial surface factors include the smoothness or degree of roughness of the metal surface, its cleanliness (freedom from oil, grease, dirt, chemicals, etc.), the presence of any preexisting surface micro-oxides and their morphologies, the presence of gross mill scale, especially its adherence and uniformity, and, finally, the actual composition of the metal alloy itself. If the steel is protected by a coating such as a fusion bonded epoxy, then the presence of pinholes or damage to the coating also can be significant factors affecting the ultimate performance of the steel.

The rate of corrosion, on the other hand, is strongly affected by the corrosivity of the pore solution environment surrounding the metal; this in turn is determined largely by the presence of dissolved corrosive chemical species such as chlorides, the concentration of the hydroxyl ion, the availability of dissolved oxygen, and the presence and concentration of corrosion inhibitors.

In general, once corrosion actually has initiated, providing there is a sufficient oxygen transport rate to the metal surface to sustain the corrosion process, the specific details of the oxide film no longer exert much influence on the corrosion rate. In other words, all "protective" oxide films, regardless of their composition and structure, will fail in a sufficiently corrosive pore solution environment (i.e., one containing a sufficiently high ratio of Cl^- ions to OH^- ions).

To summarize: The variability encountered in the corrosion behavior of reinforced concrete depends on: (a) the structure, composition, and homogeneity of the concrete; (b) the surface state of the embedded metal (especially its initial state at the time of placement); (c) the long term availability of dissolved oxygen at the surface of the embedded metal; and (d) the intrinsic corrosivity of the pore solution environment in contact with the metal.

With regard to the RCV method, it is not important (at least not in the way suggested above) that the oxide film developed on the metal surface during the application of the method differs from the natural oxide film that develops in situ on the surface of a rebar in a "real" structure. Indeed, this difference in the film is precisely the strength of the RCV method, because the RCV film is quite reproducible, whereas the "natural" film is subject to so many vagaries that it often renders the results of corrosion studies so scattered as to be useless. For example, in the study of the efficacy of certain classes of corrosion inhibitors, the wide variations often encountered in factors (a), (b), and (c) above often completely mask the effects of factor (d)—the corrosivity of the inhibitor-containing pore solution environment—which, in this case, is the factor of most interest.

In other words, it is neither claimed nor intended that the RCV method reproduces the same type of oxide film that is encountered on the surface of a freely corroding rebar embedded in concrete. The RCV method is not intended as a method for studying the mechanisms of oxide film formation and breakdown (although it is capable of providing much useful information in this area). Rather, the RCV method provides a reproducible way of quickly studying the inherent corrosivity of the pore solution environment surrounding the embedded metal. It is the corrosivity of the pore solution environment, not the ever-changing nature of the "natural" oxide film, that is important to the long term stability of a metal embedded in cured concrete or cement paste.

The RCV method, through the use of miniaturized specimens made from cured cement paste, makes it possible to achieve a highly reproducible medium so that variations in factor (a) are minimized. By voltammetrically cycling the cement electrode until more or less steady electrochemical behavior is attained, factor (b) is made reproducible. By operating under deoxygenated conditions, variations in factor (c) are eliminated. The net result is that factor (d), the inherent nature of the pore solution environment, is reproducibly isolated and rendered amenable to study.

A further bonus is that, compared with some traditional corrosion testing methods, the RCV method is fast, yielding results in from 4 to 30 days total time, depending on the curing time given the specimens. (As mentioned above, the actual voltammetric testing itself takes only from 12 min to 4 h to complete). To illustrate this feature, we draw attention to a recent study by Hope et al [15] to evaluate the potential usefulness of four commercial corrosion inhibitors. Hope and his coworkers employed ASTM Test Method G-109 in which the effectiveness of an admixed inhibitor is evaluated from the length of time required to initiate corrosion of a piece of reinforcing steel that is part of a macro cell configuration, the macro cell assembly being embedded in a concrete specimen that is subjected to alternate ponding in a 3% by weight NaCl solution and drying in the air. They found that, although their control samples without inhibitor had started to corrode after about 287 days, even after a total testing period of 511 days none of the inhibited concrete specimens had started to corrode. Thus, while concluding that all the inhibitors seemed to work, even after 1.4 years of testing they still were unable to achieve their original objective of determining which inhibitor worked best. The same authors also employed an immersion test using mortar "lollipops" partially immersed in a 3.5% by weight NaCl solution. The results of their lollipop tests did, in fact, enable a ranking of the four inhibitors; but, even after 640 days, some of the samples still had not started to corrode. Using the RCV method, we were able to rank the same four inhibitors in just 29 days of experimentation. (The detailed results of this study are presented in our next paper.)

3. Experimental details

3.1. Apparatus

Voltammograms were obtained using a PAR Model 273 Potentiostat (EG&G Instruments, Princeton Applied Research, Oak Ridge, TN, USA) fitted with current interrupt and positive feedback iR compensation. The cell, shown in Fig. 1*(B)*, consisted of a cell body (containing approximately 200 mL of electrolyte) fitted with a lid. The working electrode was a cement-coated iron wire [c.f. Fig. 1*(A)*]. Four platinum wire counter-electrodes were held in fritted glass compartments, which were placed in an equidistant configuration around the centrally located working electrode to provide uniform radial current distribution along the length of the working electrode.

Electrical contact with the saturated calomel reference electrode was maintained via a luggin capillary shield. The cell was maintained at 25.0 ± 0.2°C using a recirculating water bath.

Chloride determinations were carried out using static mercury drop polarography. Loss on ignition was determined using either a muffle furnace or a thermogravimetric analyzer.

3.2. 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. As indicated in Fig. 1, the iron wire was sealed with epoxy into a length of 0.5-cm diameter PTFE tubing. To minimize end effects, the tip of each piece of wire was masked with a drop of epoxy, leaving a length of about 1 cm exposed to the cement, and having a nominal exposed surface area of about 0.08 cm^2. The roughness factor for the iron wire used has been determined to be in the range 1.01–1.06 [9]. After 200 cycles it can be assumed that an initial roughness factor of this small magnitude can be ignored. Accordingly, the current densities are calculated using the initial geometrical surface area of the iron wire exposed to the cement paste. After permitting the epoxy to cure for 24 h, the surface of the iron wire was mechanically polished with 0.3 μm alumina, rinsed with deionized water, and blotted dry with tissue. Next a PTFE form, of 0.5-cm inside diameter and 1.5-cm length, was placed around the iron wire and was filled with cement paste having a w/c ratio of 0.45. The electrode was placed in a 100% relative humidity hydrostat at 25°C and allowed to set overnight, after which the form was carefully removed, the electrode put back into the hydrostat, and permitted to continue curing for a total of 3 days at 100% relative humidity. It was found that w/c ratios of 0.45 and curing times of 3 days gave reproducible results for the purposes of the present study. Depending on the factors being investigated, longer curing times may be advisable. The effects of curing time and w/c ratio are discussed in more detail in another work [2]. A new electrode was used for each experiment.

The standard 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. Cement pastes were made using de-ionized water.

3.3. Procedures

For investigating the effects of externally derived Cl^- ions, electrode specimens, prepared as described above, were immersed for 24 h at 25°C in aqueous saturated $Ca(OH)_2$ electrolyte to which NaCl had been added. The NaCl concentrations investigated were 0.00, 0.10, 0.20, and 0.40 M. Immediately following immersion for 24 h in the NaCl soaking solution, the electrodes were transferred to the saturated $Ca(OH)_2$ electrolyte in the cell, and cyclic voltammograms were obtained using the RCV method. For most experiments, three or more replicate electrodes were used for each NaCl concentration investigated.

For the experiments used to evaluate corrosion inhibitors [3], each corrosion inhibitor was dissolved in the cement mix water and introduced into the cement as an admixture. The inhibitors were added by weight, as a percentage of the dry cement in the cement mix.

The four platinum wire counter-electrodes and the saturated calomel reference electrode were placed in the cell, the cell electrolyte was sparged with presaturated nitrogen for at least 30 min, and then blanketed with nitrogen gas. Electrical connections were made with the potentiostat, and the working electrode potential continuously cycled from -1.4 V to $+0.4$ V at 50 mV s^{-1} with current interrupt iR compensation (4 ms sampling intervals). Owing to limitations of the equipment, a sweep rate of 50 mV s^{-1} corresponds to the maximum value for which current interrupt iR compensation can be used with confidence. At higher sweep rates a positive feedback mode of iR compensation must be used, which is less reliable. The potential of the working electrode was cycled continuously for 200 cycles, and cyclic voltammograms recorded for the first eleven cycles, and every tenth cycle thereafter up to cycle number 201. The i at 0 V for the 200th cycle was taken as a measure of pore solution corrosivity. In more recent work we have found that, providing extra care is taken to prevent segregation of the cement paste during the initial 24 h of curing time, the value of the current at zero volts for the tenth cycle yields reliable results. This has reduced the RCV time from 4 h to 12 min.

For each NaCl concentration investigated, total chloride determinations were made for at least three replicate specimens of cured OPC paste. In order to express the chloride contents on a dry cement basis, ignition losses at 1000°C were measured using either a muffle furnace or a DuPont Model 951 Thermogravimetric Analyzer (Wilmington, DE, USA). When the muffle furnace was used, the sample was heated at about 1000°C for 18 h. For thermogravimetric analysis a small portion (usually less than 50 mg) of the sample was heated from room temperature to 1025°C at a ramp rate of 25°C min^{-1}.

The total chloride content of each cured cement electrode was determined using a leaching procedure similar to that reported by Berman [16]. However, instead of titration with standardized silver nitrate solution, it was found to be more convenient to determine the Cl^- ion concentration using either differential pulse polarography or cathodic stripping [17,18]. Thus, each cement sample (usually less than 0.5 g) was dried at 105°C for at least 24 h and weighed using a weighing bottle. Then it was transferred into a beaker, 10 mL of deionized water (~20 MΩ cm at 25°C) added, and the mixture stirred for 3 min. Next, about 1 mL of concentrated nitric acid per g of dried sample was added to the mixture and large fragments of the sample were broken up with a stirring rod. 50 mL of hot water then was added and the mixture was gently heated on a hot plate until the solution reached its boiling point. The mixture was allowed to boil for 60 s, after which it was removed from the hot plate and filtered through two layers of medium porosity filter paper into a second beaker. The residue in the first beaker was transferred onto the filter paper and washed 3–4 times with hot deionized water. After the filtrate had cooled to room temperature, it was transferred into a 100-mL volumetric flask and the volume brought to the mark with deionized water. An aliquot (usually less than 10 mL) of the diluted filtrate then was transferred into a 50-mL volumetric flask and the volume increased to the mark with 0.1000 M nitric acid.

The chloride ion concentration in the 50-mL volumetric flask was determined using either differential pulse polarography [17] or cathodic stripping [18]. The data were collected and analyzed using a PAR (Princeton Applied Research) Model 384 Polarographic Analyzer, a PAR Model 303 SMDE (Static Mercury Drop Electrode), a PAR Model G0193 jacketed cell, a PAR Model RE0082 X-Y plotter, a PAR Model K0065 bridge tube, a PAR Model K0077 saturated calomel reference electrode, and a Julabo Type C-58 (Julabo Labortechnik GMBH, Seelbach, Germany) constant temperature bath. For differential pulse polarography, the supporting electrolyte in the SMDE cell was 0.100 M nitric acid; for cathodic stripping, the supporting electrolyte was 50% by volume 0.100 M nitric acid and 50% by volume acetonitrile-190. In all cases the saturated calomel reference electrode was isolated from the SMDE cell with a bridge tube to prevent chloride contamination from the saturated calomel reference electrode.

4. Results and discussion

4.1. Effects of NaCl intrusion from external soaking solutions

Fig. 3 shows the typical progress of i_{0V} with potential cycling for a standard electrode previously immersed for 24 h in saturated $Ca(OH)_2$ solution with no NaCl present. The value of i_{0V} is observed to approach a constant value by the 200th cycle. In the present case, the average value of i_{0V} for the 200th cycle for five replicate electrodes was 0.7 mA cm^{-2}, with a standard deviation of 0.2 mA cm^{-2}. As a rule of thumb, we have found that any value of i_{0V} equal to or less than about 1 mA cm^{-2} corresponds to a stable passive film on the surface of the embedded iron wire and, therefore, to a noncorrosive pore solution environment. As variations will be encountered depending on the type and condition of the cement used, the quality of the electronic equipment, the skill of the worker, etc., the choice of 1 mA cm^{-2} as the baseline value of i_{0V} that denotes a noncorrosive pore solution is somewhat arbitrary. Accordingly, it is advisable that each laboratory establish its own value of i_{0V}.

Fig. 4 shows the voltammograms obtained by repeating the above experiments with varying concentrations of NaCl present in the external $Ca(OH)_2$ solution. Significant depassivation of the embedded iron is readily observed with 24-h exposure to as little as 0.1 M NaCl in the external solution. Exposure to 0.4 M NaCl results in extensive depassivation, the voltammogram being extremely distorted with very large currents flowing throughout, especially in the normally passive "plateau" region at potentials anodic to peak 3. The rapid increases in i_{0V} in the specimens exposed to NaCl can be attributed to a chloride-induced iron dissolution reaction, which probably is initiated by Cl^- ions adsorbing onto small patches of bare iron which likely exist as flaws in the inner oxide film [14]. At sufficiently anodic potentials, an iron chloride complex is believed to form, which then separates quickly from the electrode surface and de-

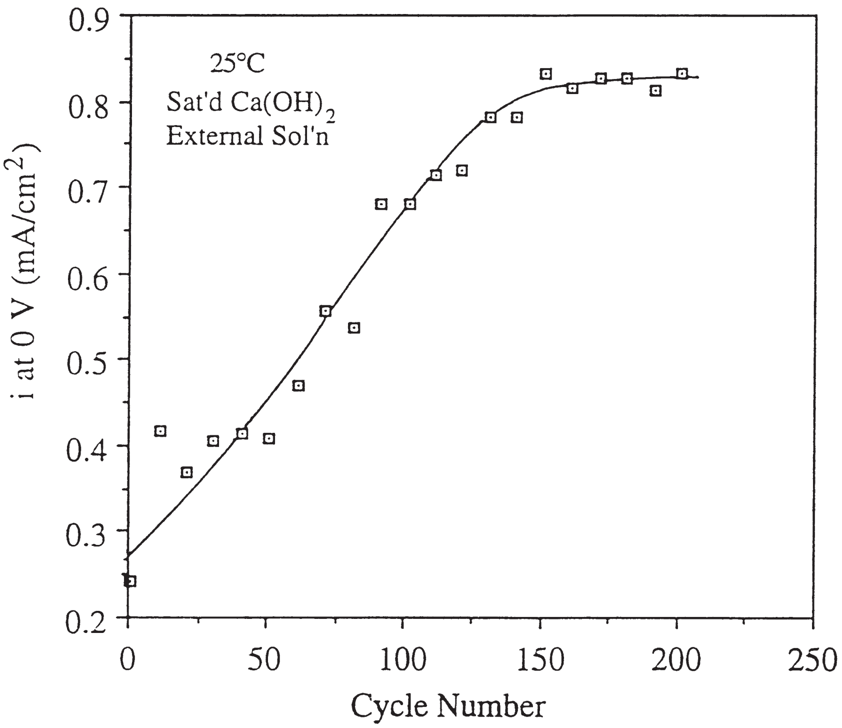

Fig. 3. Effect of cycling on i_{0V}.

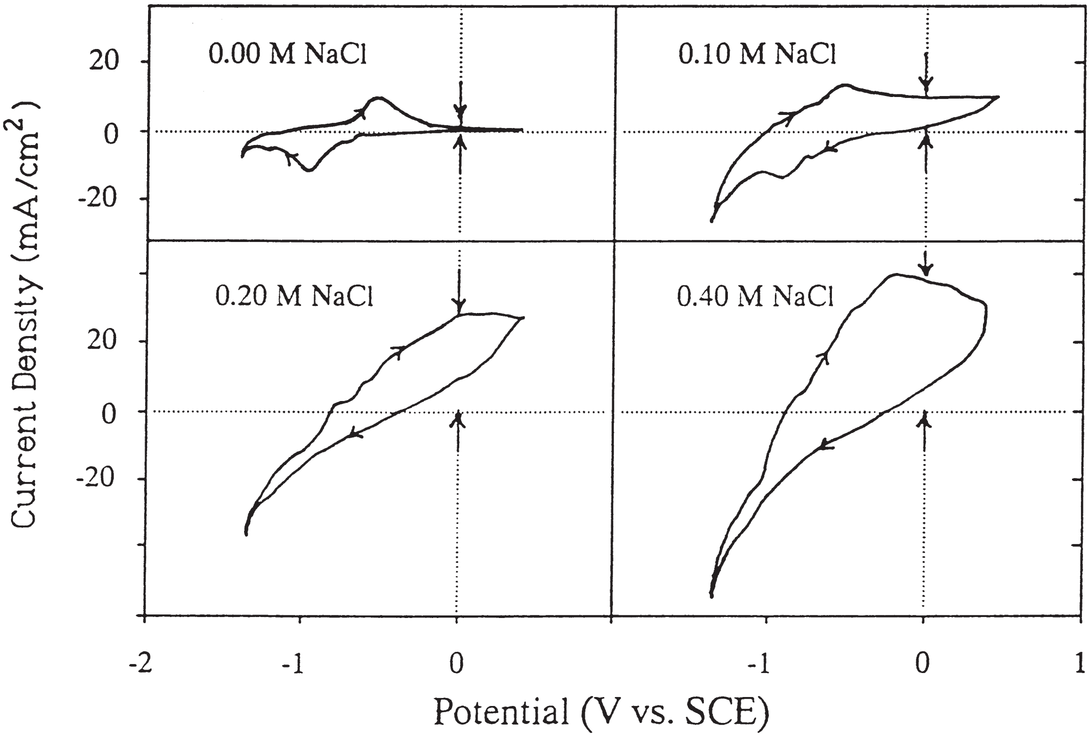

Fig. 4. Effect of addition of NaCl to external saturated $Ca(OH)_2$ solution. (Arrows indicate how the magnitude of i_{0V} varies with the concentration of NaCl in the external soaking solution.)

composes into iron ions and chloride ions, exposing the underlying iron substrate to further attack. At these anodic potentials there will be a competition between OH^- ions and Cl^- ions for adsorption onto reduced iron sites. When the concentration of the Cl^- ions in the pore solution is significantly greater than that of the OH^- ions and there is no inhibitor present, chloride tends to adsorb preferentially, leading to complexation and iron dissolution (corrosion); conversely, when the concentration of the OH^- ions is significantly greater than that of the Cl^- ions, hydroxyl tends to adsorb preferentially, repairing the partly reduced inner oxide film at potentials anodic to peak 3 (i.e., peak 3a) and leading to passive voltammetric behavior (noncorrosion) [6,7]. Fig. 4 indicates that relatively stable voltammograms can be obtained even in the presence of NaCl, providing the NaCl concentration in the external solution is not too much greater than about 0.4 M. The voltammograms shown in Fig. 4 are reasonably reproducible.

In a separate series of experiments, cement electrodes were exposed to chloride in the same manner as above and analyzed for total chloride content. The results of these analyses as well as the i_{0V} values from the corresponding voltammetric experiments are summarized in Table 1. Fig. 5 shows that as the NaCl concentration in the external solution is increased, there is a well-defined corresponding increase in the value of i_{0V}. Similarly, Fig. 6 shows that there is also a well-defined relationship between the NaCl concentration in the external solution and the total chloride content of the cement electrode at the end of each experiment.

4.2. Chloride content of cement for initiation of iron corrosion

The data in Table 1 show that immersion for 24 h in an external saturated $Ca(OH)_2$ solution containing 0.10 M NaCl results in iron depassivation ($i_{0V} > 1$ mA cm^{-2}), whereas immersion in 0.05 M NaCl does not ($i_{0V} \sim 1$ mA cm^{-2}). From the accompanying data on the chloride contents of the cement cylinders it can be seen that corrosion is initiated when the total chloride content of the cylinders is about 2.7 mg Cl/g cement. Numerical solution of the mathematical diffusion equations for these cylinders (to be published in a subsequent paper) indicates that the chloride con-

Table 1
i_{0V} and chloride content in cement electrodes vs. NaCl concentration in external soaking solution[a]

NaCl (mol/L)	i_{ov} (mA/cm^2)	N[b]	s[c]	Chloride content (mg Cl/g dry cement)	N[b]	s[d]
0	0.7	5	0.2	0.24	4	0.021
0.05	1.1	1	–	1.5[e]	–	–
0.10	5.8	3	4.2	2.71	3	0.45
0.20	24.7	3	4.0	4.64	3	0.21
0.40	38.2	3	3.5	6.45	3	0.16

[a] 24-h immersion at 25°C in saturated aqueous $Ca(OH)_2$ solution containing NaCl.

[b] Number of replicate experiments/determinations.

[c] Standard deviation, mA/cm^2.

[d] Standard deviation, mg Cl/g dry cement.

[e] Interpolated value.

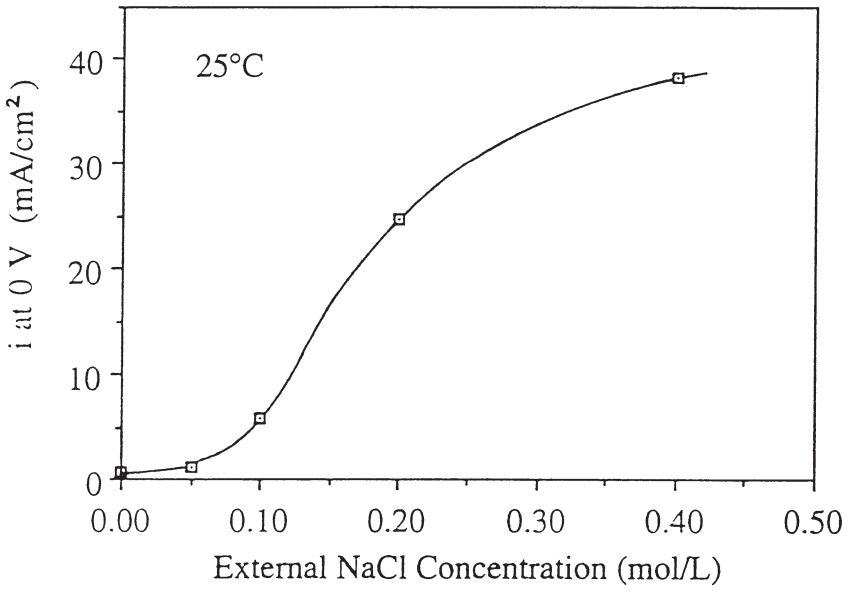

Fig. 5. Steady state i_{0V} after immersion for 24 h in external NaCl solution.

tent of the cement near the surface of the wire can be expected to be about 51% of the overall values reported in Table 1. Accordingly, it can be concluded that the corrosion of iron embedded in hardened OPC starts to occur when the total chloride content at the level of the iron is of the order of 1.4 mg Cl/g cement. This threshold limit can be compared with values reported in the literature. It is close, for example, to the FHWA limits of 1.5 to 3 mg Cl/g cement [19]. Conversely, the RILEM recommended value of 4 mg Cl/g cement [20] is somewhat higher than our data suggest, while the value of 2 mg Cl/mg cement reported by the ACI [21] is close to that indicated by the RCV method. Of course, a single corrosion threshold value cannot be specified because of its dependency on many variables. Rosenberg et al., for example, have reported that factors such as the proportions of the mix, the type and specific surface area of the cement used, the w/c ratio, the sulfate content, curing conditions, degree of carbonation, temperature, and relative humidity all are important [22]. In spite of this, the RCV method yields a threshold corrosion value for Cl content that is in good agreement with values suggested by other workers.

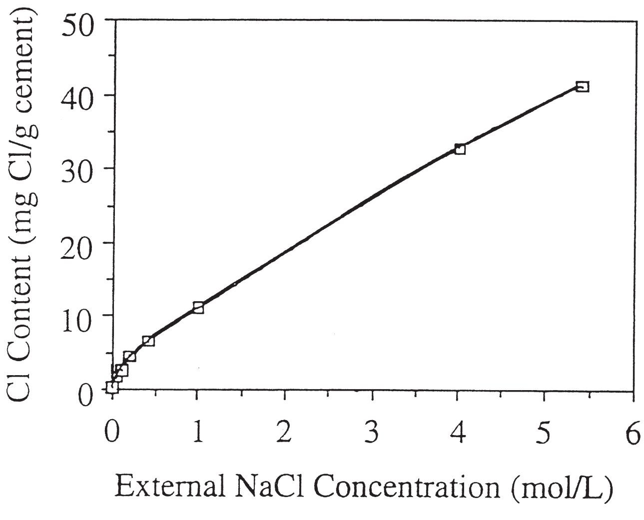

Fig. 6. Chloride content of cement cylinders after immersion for 24 hours in external NaCl solution.

4.3. Evaluation of several established corrosion inhibitors

The admixing of corrosion inhibitors with concrete mixes has been used to prevent, or at least to delay, the onset of corrosion of reinforcing steel [23–37]. Nitrites (both calcium nitrite and sodium nitrite) are the most widely studied inhibitors [23–26,28,31–37]. Potassium chromate and sodium benzoate, although not very practical, also have been reported to be effective in reducing the chloride-induced corrosion of steel in concrete [24,32]. In addition, numerous proprietary corrosion inhibitors are coming on to the market.

In order to illustrate the application of the RCV method to the study of corrosion inhibition in cement exposed to NaCl, a series of experiments was carried out in which standard cement electrodes were prepared with the above corrosion inhibitors added to the mix water. The inhibitor addition levels were all comparable (0.09–0.11 moles per kg of dry cement mix), except for 1.0% sodium nitrite, which represents a molar addition level of about 0.15 moles per kg of dry cement mix. The results are summarized in Table 2, which shows the effects of the admixed chemicals on i_{0V} for 24-h exposure to several external NaCl concentrations. This table clearly shows the potential usefulness of the RCV method for the evaluation of corrosion inhibitors. The attack by chloride on the passive film is marked by sharp increases in the values of i_{0V}. The function of the inhibitors is to main-

Table 2
Effect of admixed corrosion inhibitors on i_{0V} (mA/cm^2) for various NaCl concentrations in external soaking solution[a]

	NaCl (mol/L)								
Inhibitor[b]	0	0.05	0.10	0.20	0.40	0.60	0.80	1.6	1.8
No inhibitor	**0.9**	**1.1**	4.3	17[d]	28[d]				
1.7% K_2CrO_4	**0.7**	**0.7**	**0.7**	1.8	2.9	8.0[d]			
1.6% NaBnz[c]	**0.8**	**0.9**	**0.9**	**1.1**	7.9[d]				
0.6% $NaNO_2$	**0.9**	**0.9**	**0.9**	**0.95**	**1.1**	12[d]			
1.0% $NaNO_2$	**0.9**						**0.9**	**0.9**	22[d]

Numbers in boldface indicate low current densities as opposed to those of high current densities.

[a] Saturated aqueous $Ca(OH)_2$ solution containing NaCl. All data are at 25°C.

[b] All admixture concentrations are expressed as weight percents with respect to the weight of dry cement in the mix.

[c] Sodium benzoate.

[d] These values are less well defined.

tain the oxide films in a condition similar to that observed without NaCl (first column in Table 2). Table 2 clearly demonstrates regions of low-current densities (less than about 1 mA cm^{-2}), which are indicative of the presence of stable passive films (noncorrosive environment), and regions of high-current densities ($>$1 mA cm^{-2}), which are indicative of disruption of the films by chloride (corrosive environment). Of the three corrosion inhibitors studied, it is obvious that sodium nitrite is by far the most effective. At admixed levels of 1.0%, no depassivation is observed with this inhibitor, even after exposure to concentrations of external NaCl solution as high as 1.6 M.

4.4. Use of the RCV method to screen potential corrosion inhibitors

Although not used as corrosion inhibitors, sodium acetate, CMA (calcium magnesium acetate) [38,39], and urea [30–42] have been widely discussed as deicing chemicals that are noncorrosive alternatives to road salt. It also has been suggested that mixtures of CMA and NaCl might be less corrosive deicers than NaCl alone [39]. Possibly these deicing chemicals, if added to the cement mix water, also might exert some corrosion inhibiting effects. Accordingly, the RCV method was applied to standard electrodes containing sodium acetate, urea, and CMA to determine if these compounds had corrosion-inhibiting properties.

The results, presented in Table 3, indicate that up to external NaCl concentrations of about 0.2 M NaCl the current densities in the normally passive region at 0 V are somewhat lowered by the admixing of sodium acetate and urea, although significant depassivation does still occur at this level of NaCl, even when these chemicals are admixed at relatively high concentrations (0.23 moles per kg of cement mix). Similarly, the current densities at 0 V for 0.9% CMA also are slightly lower than those observed with no admixture, but are higher than those for admixed sodium acetate or urea, possibly because of a lowering of the pH in the cement pore solution caused by the presence of the magnesium ion ($Mg^{++} + 2OH^- \rightarrow Mg(OH)_2$). However, the voltammetric data indicate that acetate and urea are only marginally effective, if effective at all, as corrosion inhibitors for reinforcing steel in cement, and it is not recommended that NaCl be mixed with acetate deicing salts or urea.

The above results illustrate how the RCV method is useful for the preliminary screening of new corrosion inhibitors or for the evaluation of known corrosion inhibitors in new cement blends. Until the RCV method has undergone more extensive testing, however, it must be emphasized that the results reported above should be used only as a guide to the relative performance of corrosion inhibitors and, whenever possible, should be verified by comparison with longer term field data.

5. Concluding remarks

In this paper we have introduced the RCV method as a fast, effective, means of studying various aspects of the corrosion of iron and steel in salt-contaminated cement. We have shown that the value of i_{0V} is a useful criterion for distinguishing corrosive pore solutions ($i_{0V} > 1$ mA cm^{-2})

Table 3
Effect of admixed acetate and urea on i_{0V} (mA/cm^2) for various NaCl concentrations in external soaking solution[a]

	NaCl (mol/L)				
Admixed chemical[b]	0	0.05	0.10	0.20	0.40
None	**0.9**	**1.1**	4.3	17[e]	28[e]
0.95% NaAc[c]	**0.9**	**1.1**	1.4	5.3	12[e]
1.9% NaAc	**0.9**	**0.9**	1.4	3.1	12[e]
0.7% Urea	**0.9**	**1.1**	2.1	4.8	12[e]
1.4% Urea	**0.9**	**1.0**	1.8	3.0	12[e]
0.9% CMA[d]	**0.9**	1.3	1.6	13[e]	25[e]

Numbers in boldface indicate low current densities as opposed to those of high current densities.

[a] Saturated aqueous $Ca(OH)_2$ solution containing NaCl. All data are at 25°C.

[b] All admixture concentrations are expressed as weight percents with respect to the weight of dry cement in the mix. 0.95% by wt. sodium acetate and 0.7% by wt. urea are comparable to 0.6% sodium nitrite on a molar basis.

[c] Sodium acetate.

[d] Calcium magnesium acetate. CMA consisted of a 3:7 molar mix of calcium acetate and magnesium acetate, representing 0.08 moles acetate per kg of cement mix.

[e] These values are less well defined.

from noncorrosive pore solutions ($i_{0V} < 1$ mA cm^{-2}), and that the RCV method predicts corrosion threshold chloride contents in OPC that are consistent with values reported using other methods. Furthermore, by using the RCV method in conjunction with a number of well-known corrosion inhibitors (sodium nitrite, potassium chromate, sodium benzoate) and noncorrosive deicing chemicals (urea, sodium acetate, and calcium magnesium acetate) we have demonstrated how it also is well suited for evaluating the corrosion inhibition of iron and steel embedded in cement.

Acknowledgments

The authors gratefully acknowledge financial support for this research from the Natural Sciences and Engineering Research Council of Canada. We also wish to thank Dr. James T. Hinatsu and Ms. W.M. Ushirode, formerly of the Department of Chemical Engineering and Applied Chemistry, University of Toronto, for performing much of the experimental work; Prof. W.F. Graydon, for his many valuable insights; and Dr. J.W. Graydon for his help with scanning electron microscopy and energy dispersive spectrometry studies.

References

[1] S.G. Ehrlich, A.M. Rosenberg, Methods of steel corrosion control and measurement in concrete, in: Materials Science of Concrete II, J. Skalny, S. Mindess (eds.), The American Ceramic Society, Inc., Westerville, 1991, pp. 201–219.

[2] J.T. Hinatsu, W.F. Graydon, F.R. Foulkes, J Appl Electrochem 19 (1988) 868.

[3] J.T. Hinatsu, W.F. Graydon, F.R. Foulkes, J Appl Electrochem 20 (1990) 841.

[4] J.T. Hinatsu, W.F. Graydon, F.R. Foulkes, J Appl Electrochem 21 (1991) 425.

[5] W.M. Ushirode, J.T. Hinatsu, F.R. Foulkes, J Appl Electrochem 22 (1992) 224.

[6] L.D. Burke, O.J. Murphy, J Electroanal Chem 109 (1980) 379.

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

[8] M.L. Mateo, T. Fernandez Otero, D.J. Schiffrin, J Appl Electrochem 20 (1990) 26.

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

[10] J.O. Zerbino, J.R. Vilche, A.J. Arvia, J Appl Electrochem 11 (1981) 703.

[11] O.A. Albani, J.O. Zerbino, J.R. Vilche, A.J. Arvia, Electrochim Acta 31 (1986) 1403.

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

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

[14] O.A. Albani, L.M. Gassa, J.O. Zerbino, J.R. Vilche, A.J. Arvia, Electrochim Acta 35 (1990) 1437.

[15] B.B. Hope, C.M. Hansson, S.M. Trépaniér, L. Mammoliti, Corrosion Inhibitors for Concrete, report prepared for the Ontario Ministry of Transportation, 1995.

[16] H.A. Berman, J of Mater 7 (1972) 330.

[17] Anonymous, EG+G Princeton Applied Research, Application Note C-1, 1980.

[18] Anonymous, EG+G Princeton Applied Research, Application Note PB-2, 1980.

[19] C.E. Locke, Proceedings of 8th International Congress on Metallic Corrosion, National Research Council (Canada), Toronto, 1984, pp. 225–228.

[20] P. Schiessl, R. Bakker, Measures of protection, in: P. Schiessl (Ed)., Corrosion of Steel in Concrete, Chapman and Hall, New York, 1988, pp. 70–78.

[21] ACI Committee 201, Guide to Durable Concrete (ACI 201.2R77), American Concrete Institute, Detroit, 1977 (reaffirmed 1982).

[22] A. Rosenberg, C.M. Hansson, C. Andrade, Mechanism of corrosion of steel in concrete, in: Materials Science of Concrete I, J.P. Skalny (ed.), The American Ceramic Society Inc., Westerville, 1989, pp. 285–313.

[23] C. Andrade, C. Alonso, J.A. Gonzalez, Cem Concr Aggreg 8 (1986) 110.

[24] V.K. Gouda, G.E. Monfroe, J Res Dev Labs Portld Cem Assoc 7 (1965) 24.

[25] A.M. Rosenberg, J.M. Gaidis, T.G. Kossivas, R.W. Previte, Chloride Corrosion of Steel in Concrete, ASTM STP 629, ASTM, Philadelphia, 1977, p. 89.

[26] R.J. Craig, L.E. Wood, High Res Rec 328 (1970) 77.

[27] V.K Gouda, Br Corros J 5 (1970) 198.

[28] N.S. Berke, P. Stark, Concr Int Des Constr 7 (1985) 42.

[29] C.E. Locke, O. Rincon, Corrosion of Metals in Concrete, NACE, Houston, 1988, p. 99.

[30] D.F. Griffen, Corrosion of Metals in Concrete, ACI SP 49-8, ACI, Detroit, 1975, p. 95.

[31] V. Ratinov, S. Yenisherlova, R. Zagirova, Durability of Concrete, preliminary report, D-135, Prague, 1969.

[32] V.K Gouda, W.Y Halaka, Br Corros J 5 (1970) 204.

[33] J.T. Lundquist, A.M. Rosenberg, J.M. Gaidis, Mater Perform 18 (1979) 36.

[34] A.M. Rosenberg, J.M. Gaidis, Mater Perform 18 (1979) 45.

[35] J.M. Gaidis, A.M. Rosenberg, Cem Concr Aggreg 9 (1987) 30.

[36] Y.P. Virmani, K.C. Clear, T.J. Pasko, FHWA Report No. FHWA/RD-83/012, FWHA, Washington, DC, 1983.

[37] N.S. Berke, Mater Perform 28 (1989) 41.

[38] C.E. Locke, K.J. Kennelley, M.D. Boren, V. Luster, Transp Res Rec 1113 (1987) 30.

[39] R.L. McCrum, Mater Perform 28 (1989) 24.

[40] C.N. Hansen, U.S. patent no. 4 698 173, 1987.

[41] R. Vogel, Ger Offen DE 3 434 (1986) 953.

[42] J. Pelikan, J. Vosta, J. Mostecky, M. Smrz, J. Lohnisky, Czechoslovakian patent no. 184 118, 1980.