Pergamon

Cement and Concrete Research 31 (2001) 1207–1211

CEMENT AND CONCRETE RESEARCH

Sources of error in using silver/silver chloride electrodes to monitor chloride activity in concrete

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Received 3 January 2001; accepted 10 May 2001

Abstract

The silver/silver chloride electrode is discussed as a chloride-monitoring device in concrete rather than as a reference electrode. The effects of temperature, bromide ions, and applied potential fields on the reliability and accuracy of these electrodes are evaluated. The effect of temperature is assessed using a novel mathematical approach and the other two effects are examined experimentally. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Temperature; Corrosion; Chloride; Concrete; Bromide

1. Introduction

Durability is increasingly considered as one of the most desirable properties of concrete. Among the harmful substances carried into reinforced concrete by groundwater, seawater, or runoff water, none is potentially more damaging than chloride, which destroys the passivity of steel in alkaline environments leading to corrosion of the reinforcement. In concretes that are likely to carbonate rapidly, i.e., those subject to high temperatures or cyclic wetting and drying, the presence of chloride is even more serious. A simple, reliable, in situ method of determining chloride concentration is sought.

Silver/silver chloride electrodes are stable, easily prepared, and have long been used in electrochemistry. They have been shown to be capable of determining chloride activity in simulated cement pore solution [1] and in pressure-extracted cement pore water [2]. As reference electrodes, they are in commercial use for concrete [3], but this paper discusses their use as chloride ion concentration monitors. This is not necessarily the total chloride content as some may be chemically or physically bound by the cement hydrates.

In this use for silver/silver chloride electrodes, we have considered the effect of temperature, the effect of bromide ions, and the effect of applied potential fields. Temperature effects have been calculated. The two others have been investigated experimentally. Measurements were made in chloride solutions to which bromide was added over a range of concentrations including that found in seawater. The effect of potential fields was measured on the electrodes cast in concrete blocks.

Corrosion of steel in concrete creates potential field gradients through the material. These field gradients may cause an error in the measured potentials of the electrodes. In addition, it may be necessary to use the electrodes in the presence of an applied potential field, for example, in cathodic protection, chloride extraction, or realkalisation. It was therefore necessary to investigate the response of the silver/silver chloride electrodes in the presence of an applied electric field and the rationale for the field gradient experiment is based on the following argument. Two identical reference electrodes placed in the same electrolyte will register zero potential difference between them. If one electrode is an ion selective electrode, then the potential difference will be a function of the activity of that particular ion. In our case, we are following the change in chloride ion activity with a silver/silver chloride system. If two identical reference electrodes are placed in the same electrolyte when a field gradient is present in the electro-

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PII: S0008-8846(01)00544-0

lyte, there will be a difference in potential between the two and the magnitude of this will be a measure of the field gradient. If we attempt to use an ion selective electrode in an electrolyte that contains a field gradient, any variation in potential between it and a reference electrode could be caused either by changes in ionic activity or the presence of a field gradient. Ion activity and field gradient need to be independently assessed.

2. Temperature effects

2.1. Background

The silver/silver chloride electrode consists of a thin layer of silver chloride (on silver wire) in contact with a solution and following the chemical equation:

$$\mathrm{Ag} + \mathrm{Cl}^- \leftrightarrow \mathrm{AgCl} + \mathrm{e}^-$$

It is essentially a silver electrode in which the activity of silver cations is controlled by the solubility product K_s of AgCl and by the chloride ion activity a_{Cl^-} [4]. In sufficiently dilute solutions activity equates with concentration.

At temperature T the measured potential E is given by the Nernst equation (Eq. (1)):

$$E = E^0_{\mathrm{Ag/AgCl}} - \frac{\mathrm{R}T}{F} \ln a_{\mathrm{Cl}^-} \tag{1}$$

where the standard electrode potential of the Ag/AgCl electrode $E^0_{\mathrm{Ag/AgCl}}$ is given by (Eq. (2)):

$$E^0_{\mathrm{Ag/AgCl}} = E^0_{\mathrm{Ag^+/Ag}} + \frac{\mathrm{R}T}{F} \ln \mathrm{K_s} \tag{2}$$

and the other symbols have their usual meaning. At 25°C the value of $E^0_{\mathrm{Ag/AgCl}}$ is 0.22233 V [4].

Values of K_s in the range of 5–100°C are available [5]. Hence, the effect of temperature on $E^0_{\mathrm{Ag/AgCl}}$ can be calculated and over this temperature range is + 20.8 mV. Between 5°C and 50°C, a range of more practical significance for concrete, the effect is to raise $E^0_{\mathrm{Ag/AgCl}}$ by 19.2 mV.

2.2. Theory

If the potential is measured versus a silver/silver chloride electrode in contact with chloride solution of activity a'_{Cl^-} as reference, then the term $E^0{}_{\mathrm{Ag/AgCl}}$ is eliminated and the measured potential E_{meas} is given by (Eq. (3)):

$$E_{\mathrm{meas}} = \frac{\mathrm{R}T}{F} (\ln a'_{\mathrm{Cl}^-} - \ln a_{\mathrm{Cl}^-}) \tag{3}$$

hence,

$$\ln a_{\mathrm{Cl}^-} = \ln a'_{\mathrm{Cl}^-} - \frac{\mathrm{F}E_{\mathrm{meas}}}{\mathrm{R}T} \tag{4}$$

Eq. (4) allows a chloride activity to be calculated if temperature T and electrode potential are measured accurately and if the chloride activity of the reference electrode is known. The effect of a temperature difference, δT, between the electrodes on chloride activity (and hence on concentration) derived from Eq. (4) can be calculated.

Using the subscript "assumed" for the calculated concentration and "true" for the value in the concrete pore solution gives (Eq. (5)):

$$\ln a_{\mathrm{Cl}^-\ \mathrm{true}} - \ln a_{\mathrm{Cl}^-\ \mathrm{assumed}} = \frac{\mathrm{F}E_{\mathrm{meas}}}{\mathrm{R}(T + \delta T)} + \frac{\mathrm{F}E_{\mathrm{meas}}}{\mathrm{R}T} \tag{5}$$

hence,

$$\ln\left(\frac{a_{\mathrm{Cl}^-\ \mathrm{true}}}{a_{\mathrm{Cl}^-\ \mathrm{assumed}}}\right) = \frac{\mathrm{F}E_{\mathrm{meas}}}{R}\left(\frac{\delta T}{T^2 + T\delta T}\right) \tag{6}$$

Eq. (6) provides a useful basis to evaluate temperature difference effects. With a typical value of E_{meas} of 200 mV, a value of T of 293 K and δT of 50 K, the true/assumed ratio becomes 3.18. For δT of 20, 10, and 5 K the value decreases to 1.66, 1.30, and 1.14, respectively, showing the decreasing effect on the accuracy of chloride determination as the temperature difference becomes smaller. If silver/silver chloride electrodes were in use to monitor chloride concentration, the position in the concrete structure and the possible temperature difference from a reference electrode might have to be considered.

3. Experimental methods

Electrodes used in this work were manufactured in accordance with the method outlined by Ives and Janz [6] in which 99.99% pure silver wire is anodised galvanostatically in hydrochloric acid. The normal anodising conditions were a current density of 0.4 mA cm^{-2} for 30 min. Electrodes were kept in chloride solution (35 g dm^{-3} of sodium chloride) out of direct sunlight until required. Prior to use the potentials of all electrodes were measured against a standard calomel reference electrode.

3.1. Bromide ion effect and electrode preparation

3.1.1. Addition of bromide

To investigate the effect of bromide, 0.2 M potassium bromide solution was added in 1 cm^3 amounts to a silver/silver chloride electrode immersed in 500 cm^3 of sodium chloride solution of concentration 5, 15, 25, and 35 g dm^{-3}. The molar ratio of chloride/bromide thus changed over a range of 215 to 1505. The potential of the silver/silver chloride electrode was recorded at each addition against a saturated calomel electrode (SCE) in conjunction with an ammonium nitrate agar-agar salt bridge after each addition. Finally, the potentials of the electrodes used were recorded in saturated potassium chloride.

3.1.2. Time effect

Any effect of time of exposure to bromide was determined by measuring the potential of silver/silver chloride electrodes (prepared and stored by the usual method) placed in a solution containing both halides.

Electrodes were placed in a solution containing 65 mg dm^{-3} of bromide and 35 g dm^{-3} of sodium chloride; a similar concentration to seawater. The potential of an electrode versus a standard calomel electrode was measured at 2.5, 5, 7.5, 10, and 15 min, then it was replaced in the storage solution.

3.1.3. Electrode effect

The same bromide/chloride solution was used to investigate any effect of electrode preparation on the bromide response, but this time the electrodes were left in the solution for a few seconds only, sufficient to take the reading of electrical potential. Silver/silver chloride electrodes were manufactured at 0.2, 0.6, 1.0, 1.2, 1.4, and 2.0 mA cm^{-2} current densities for 30 min and at the normal 0.4 mA cm^{-2} for 0.5, 1, 1.5, and 2.0 h. The electrodes were stored in the usual way.

3.2. Applied potential fields

The concrete mix proportions were 1:1.5:3.5 of ordinary Portland cement/crushed limestone aggregate/building sand and the mix had a water/cement ratio of 0.55. Blocks were cast in 100 × 100 × 50 mm moulds and tamped by hand. Near the centre of each block, a Luggin probe and a silver/silver chloride electrode had been positioned. After 24 h, the blocks were demoulded and cured under polythene sheeting for 3 days. Four blocks were cast in which the distance between the probe and the electrode was 0, 5, 10, and 15 mm, respectively.

To measure the potential of an unpolarised electrode, we need the electrode in question, a working electrode and a reference electrode in the same electrolyte connected through a suitable voltmeter. Provided the impedance of the voltmeter is very high, negligible current will flow and a true potential will be measured.

If the electrode of interest is also polarised with a suitable counter electrode, then there will be a potential gradient (an *iR* drop) between the working and counter electrode, which will behave like a nonlinear potentiometer. For the reference electrode placed anywhere but exactly at the electrode surface, some fraction of the *iR* drop will be included in the measurement potential [7].

A fine capillary tube is used, which extends from the reference electrode and allows the reference electrode to be placed very close to the working electrode to largely eliminate this *iR* drop. The tube is known as a Luggin–Haber capillary or Luggin probe for short. As stated earlier, since the reference circuit passes no current, there can be no *iR* drop in this reference circuit.

Electrical potential fields were applied to the blocks using the arrangement of external platinised titanium counter electrodes as shown in Fig. 1, although large and small electrodes were not used together.

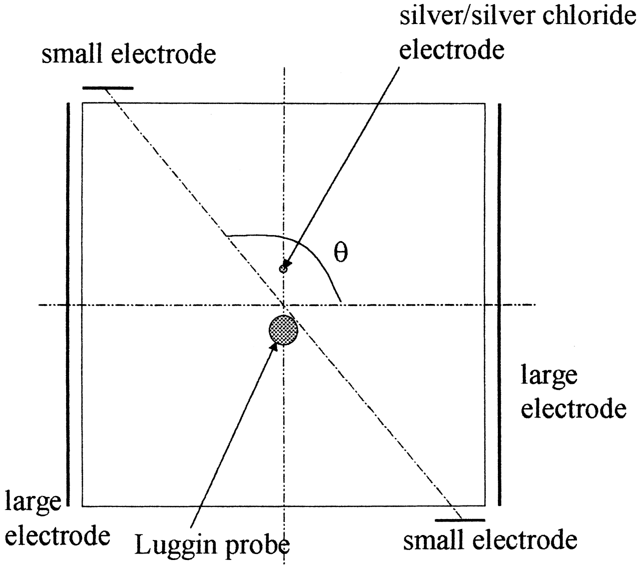

Fig. 1. Position of electrodes in and around the concrete blocks. Distance between the Luggin probe and the silver/silver chloride electrode was 0, 5, 10, and 15 mm.

Large platinised titanium electrodes were placed on 100 × 50 mm opposite faces of the blocks covering the entire area and firmly held in place. An alternating voltage of 150 mV (RMS) at a frequency of 50 Hz was passed between the electrodes. A storage oscilloscope recorded the peak amplitude of signals and any phase difference between the Luggin probe and the silver/silver chloride electrode.

The measurements were repeated with direct current and the resistivity of the concrete calculated from both AC and DC measurements.

The same blocks were used in direct current galvanostatic polarisation. The large electrodes were removed and small platinised titanium electrodes (12.5 × 75 mm) were placed as shown in Fig. 1 and polarised to 0.3 mA in 0.05-mA steps. The change in potential difference between the Luggin probe and the silver/silver chloride electrode at each step was monitored using a high impedance voltmeter in conjunction with a digital voltmeter. The platinised titanium electrodes were then moved around the surface of the block in fixed increments but keeping them on opposite faces so that angle ϑ varied from 0° to 180°. Again, any change in potential was recorded.

4. Results and discussion

4.1. Temperature effects

The effect of temperature on the solubility product term in the electrochemical equations over the range of usual climatic variation has been calculated as an increase of 19 mV to the electrode reading. This could be compensated for in practice.

The effect of a temperature difference between the reference electrode and concentration monitoring electrode can also be evaluated. Fig. 2 shows the temperature function considered plotted against the temperature difference between the reference and monitoring electrodes for a practical temperature range. The effect is greater at low temperatures.

4.2. Effect of bromide ion

The potential of the silver/silver chloride electrode will be affected by impurities that either form stable complex ions with silver or form compounds less soluble than silver chloride. Many silver salts have very low solubilities [8], but it is likely that only bromide or iodide, present in seawater, would be of practical importance for concrete.

In seawater, typical concentrations of bromide and chloride ions are 65 mg dm^{-3} and 19 g dm^{-3}, respectively [9]; that is a molar concentration of about 0.8×10^{-3} of bromide and 0.5 of chloride. Small amounts of bromide are known to exert a large effect on the potential of the silver/silver chloride electrode. Pinching and Bates [10] found an increase of 0.1 to 0.2 mV for each 0.01 mol% of bromide, that potential drifted for 24 to 48 h and was sometimes reversible.

Fig. 3 shows the change in potential of silver/silver chloride electrodes as bromide is added. The effect of bromide even at low concentrations was to decrease the measured potential difference. Further additions had little effect and were not permanent. When returned to chloride solution, electrode potentials regained their original values.

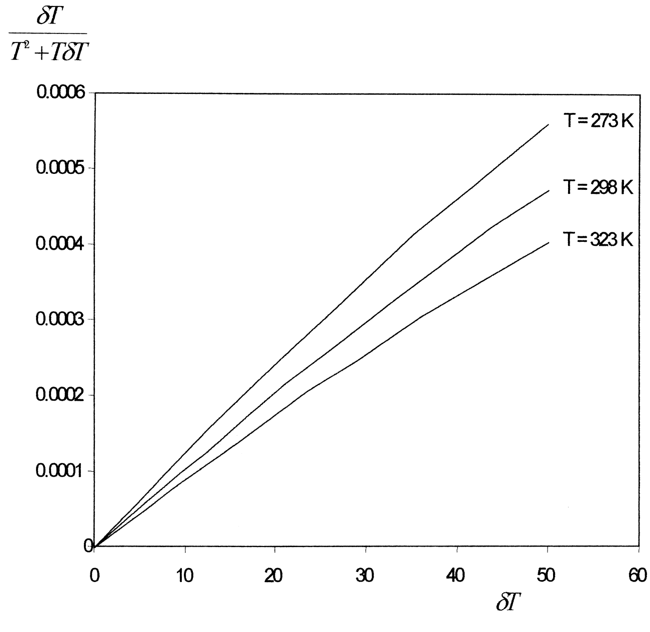

Fig. 2. Variation of the temperature function (in Kelvin) with the temperature difference δT between the two electrodes.

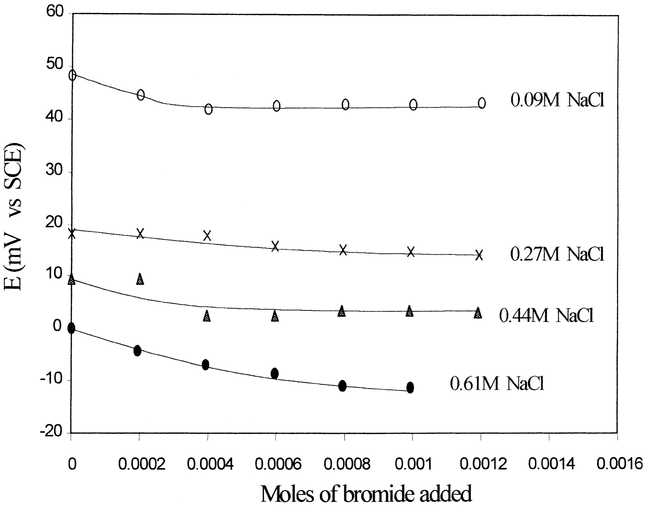

Fig. 3. Change in potential E of Ag/AgCl electrode versus an SCE on addition of bromide solution. Molarities refer to the initial concentrations of the sodium chloride. Each data set is the mean of three.

Time spent in bromide solution over the 15 min investigated had no effect on the potential decrease observed (8.5 ± 0.2 mV).

Similarly, there was no effect on potential change for the electrodes prepared at different anodising times. Table 1 shows the effect of current density used in preparing the electrodes on the bromide potential shifts. There is no significant effect in value except at the lowest current density of 0.2 mA cm^{-2}, suggesting a minimum is needed for an adequate and uniform silver chloride layer.

From the above it can be seen that the presence of bromide ion around a silver/silver chloride electrode causes the potential to become more negative, thus leading to an overestimation of the chloride ion activity. Chloride monitoring in reinforced concrete structures would be used to provide information regarding corrosion problems and an overestimation, while not desirable, could lead to the premature application of remedial measures. The nature of chloride diffusion through concrete is typically characterised by a chloride front. After the chloride reaches a certain depth into the cement, for laboratory samples at least, it is only a short period of time before that depth is saturated. In practice, the presence of cracks and the heterogeneity of concrete mean that chloride ingress is more complex. The ionic mobility of

Table 1
Potential difference ΔE between Ag/AgCl electrodes, prepared at different current densities, and SCE

Current density (mA cm^{-2})	ΔE (mV)
0.2	7.0
0.4	5.2
0.6	5.1
1.0	5.2
1.2	4.7
1.4	5.1
2.0	5.3

Table 2
Resistance and resistivity of the concrete blocks

	Resistance (Ω)	Area/path (m)	Resistivity (Ω/m)
AC at 50 Hz			
Block 1	28	–	–
Block 2	118	1	118
Block 3	220	0.5	110
Block 4	300	0.33	100
DC			
Block 1	4	–	–
Block 2	71	1	71
Block 3	113	0.5	56
Block 4	149	0.33	50

bromide ion in solution is similar to that of chloride ion so it would be expected that the ratio of bromide to chloride remains reasonably constant throughout the life of a structure. The electrodes would still be of use as an indication of the relative position of chloride through the concrete and a simple addition of a constant value to the potentials measured as a correction for the bromide effect could be made.

4.3. Electrical measurements

Values of resistivity of the concrete were calculated from the current provided by the titanium counter electrodes, the emf measured between the Luggin probe and silver/silver chloride electrode and the dimensions of the sample blocks. The value of the potential of the silver/silver chloride electrode versus a standard is accurately known. For all four samples, the area of concrete involved was 50 × 100 mm, but the path length between the inserted electrodes varied. The resistivity calculated is thus that of the volume of concrete between the two electrodes. Results are shown in Table 2.

The AC values are consistent and of similar magnitude to those reported for moist concrete of similar composition and treatment [11]. Although at 50 Hz no significant difference between AC and DC resistivity is expected, the DC values are lower and less consistent. Moist concrete behaves as an electrolyte with the current carried by ions in the evaporable water and with the aggregate offering an extremely high resistance. DC provides more disruption in terms of ionic migration, but it gives a more realistic simulation of cathodic protection.

In all the AC measurements, no phase shift was recorded between the applied field and the measured potentials between Luggin probe and silver/silver chloride electrode, suggesting that no capacitive effects occurred on the surface of the electrodes, and therefore no stray current passed through the electrodes so they were not reanodising. However, the small electrode measurements did indicate a resistance between the reference electrode and the silver/silver chloride electrode independent of distance. This could be due to the use of agar, which can dry out and shrink, in the Luggin probe.

5. Conclusions

Several external factors could affect the use of silver/silver chloride electrodes in monitoring chloride concentration in concrete.

Temperature difference between measurement and reference electrode could lead to errors but, in principle, could be estimated.

In seawater, the presence of bromide will give an overestimate of chloride concentration.

The application of a potential field across a Luggin probe and silver/silver chloride electrode arrangement causes a shift in potential measured between the two but has no permanent effect on the electrodes. The magnitude of the potential shift is dependent on the magnitude of the applied current that passes in line with the Luggin probe/electrode arrangement and the resistance between the two.

References

[1] C.P. Atkins, J.D. Scantlebury, J. Corros. Sci. Eng., http://www.cp.UMIST.ac.uk, 1995 (paper 2) vol. 1, pp. 1–5.

[2] C.P. Atkins, J.D. Scantlebury, P.J. Nedwell, S.P. Blatch, Monitoring chloride concentrations in hardened cement pastes using ion selective electrodes, Cem. Concr. Res. 26 (2) (1996) 319–324.

[3] Current practice sheet no. 120, Concrete 34 (7) (2000) 43–45.

[4] L.L. Shrier, Corrosion vol. 1, second ed., Butterworths, London, 1979.

[5] CRC Handbook of Chemistry and Physics, fifty-eighth ed., CRC Press, Florida, USA, 1978, p. B-254.

[6] D.J.G. Ives, G.J. Janz, Reference Electrode Theory and Practice, Academic Press, New York, 1961.

[7] A.J. Bard, L.R. Faulkner, Electrochemical Methods, Wiley, New York, 1980, p. 24.

[8] R.C. Weast, M.J. Astle, Handbook of Chemistry and Physics, sixty-first ed., CRC Press, Florida, USA, 1981.

[9] A.A. Fincham, Basic Marine Biology, Cambridge Univ. Press, Cambridge, England, 1984.

[10] G.D. Pinching, R.G. Bates, Purification of sodium chloride and potassium chloride for use in electrochemical work, and the determination of small amounts of bromide, J. Res. Natl. Bur. Stand. 37 (1946) 311–319.

[11] A.M. Neville, Properties of Concrete, fourth ed., Longman, Harlow, England, 1995, p. 346.