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EMBEDDABLE Ag/AgCl SENSORS FOR IN-SITU MONITORING CHLORIDE CONTENTS IN CONCRETE

Miguel A. Climent-Llorca *, Estanislao Viqueira-Pérez * and
Mª Mar López-Atalaya **
* Dep. Ingeniería de la Construcción, Obras Públicas e Infraestructura Urbana,
Universidad de Alicante, Ap. 99, 03080 Alicante (España)
** Instituto Técnico de la Construcción, Avda. de Elche 164, 03008 Alicante (España)

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ABSTRACT

The possibility of using Ag/AgCl wire electrodes as in-situ sensors of chloride concentration in concrete was studied by embedding them in a series of mortar specimens with different admixed NaCl contents. They show a sensitive potentiometric response to overall Cl^- concentrations. The stability of the potential readings depends on the Cl^- concentration and allows these electrodes to be used as Cl^- content sensors in short-term tests.

Introduction

In-situ monitoring of chloride (Cl^-) concentrations in concrete would be highly desirable in a number of fields related with the corrosion of reinforcement and its prevention: early detection of risk of corrosion in existing structures, modelization studies of the processes of Cl^- ingress into concrete, testing on the effectiveness of coatings as Cl^- barriers, etc.

The most interesting characteristics of such in-situ Cl^- concentration sensors would be: non-destructive character of the testing procedure allowing to follow the variation of chloride content with time, high sensitivity, wide operative concentration range (including the appropriate Cl^- threshold content for corrosion of reinforcement), low detection limit and long-term stability of the response.

Silver chloride coated silver wires (Ag/AgCl) are electrodes of the "kind" (1) that give potentiometric response to variations in the activity of Ag^+ or Cl^- ions in solution and that, in principle, could be embedded in concrete due to their mechanical stability.

Very little is known about the performance and stability of Ag/AgCl electrodes in contact with such an alkaline medium as the inner concrete pore solution, although Ag/AgCl elements surrounded by a mortar rich in chloride have been used as reference electrodes embedded in concrete, showing a stable potential in a 4½ year service period (2).

In this paper we have studied the potentiometric responses of Ag/AgCl electrodes embedded in Portland cement mortars with different Cl^- contents and their variations with time.

Experimental

Preparation of the Ag/AgCl Electrodes. Silver wires (99,99% purity), 0.5 mm in diameter and 4 cm in length, were subjected to the following program (1): they were cleaned for 6 hours in concentrated NH_4OH (PA quality) and immersed in distilled water overnight; a length of 3 cm of each one was anodized in 0.1M HCl (PA) for 30 minutes at a current density of 0.4 mA/cm^2; they were immersed in distilled water for 24 hours and finally the non-anodized zones were protected with Teflon® tape.

Calibration of the Electrodes in Solution. The potentiometric response of the Ag/AgCl electrodes to Cl^- concentrations in solution was checked by measuring their potential against a saturated Hg_2SO_4 reference electrode in a saturated $Ca(OH)_2$ solution to which measured amounts of a 1M NaCl solution were added.

Preparation of the Mortar Specimens. The mortar specimens (4 × 4 × 16) were obtained by mixing distilled water, a Spanish ordinary Portland cement (I-45 type) and a calcareous sand with maximum size of 2 mm, in the mass proportions 270:450:1350. The Cl^- contents of the cement and the sand were 0.019 and 0.005% respectively. NaCl (PA) was incorporated to the mixes so as to get a series of specimens with the following chloride contents: 0.04, 0.1, 0.2, 0.4, 0.8 and 1.6% relative to cement weight, that is 100 to 4000 ppm of Cl^- in the mortar series. A control specimen without admixed NaCl was also prepared. The cement content and the water/cement ratio were kept constant for the whole series.

After mixing and compacting, the active zones of the Ag/AgCl electrodes were embedded into the mortar specimens at approximately 2 cm from the 4 × 4 face and centered in the width of the 4 × 16 one.

Potential Measurements. The potentials of the Ag/AgCl electrodes were measured periodically, with a Crison 2002 mVmeter, against a saturated Hg_2SO_4 reference electrode but all results were converted to the SCE scale. The reference electrode contacted the mortar specimen through a piece of filter paper impregnated with 1M KNO_3 (PA) solution on the nearest 4 × 4 face. The potentials were recorded after 2 and 3 minutes from the contact in order to check their stability. The values reported in FIG.1 correspond to the 3 minutes readings.

Results and Discusion

FIG.1 shows the evolution with time of the potentials of the Ag/AgCl electrodes embedded in mortar specimens with different admixed chloride contents. Lines **A** and **B** in FIG.1, which correspond to data taken at 8 and 41 days after preparing the specimens, show a potentiometric response that allow the discrimination of total Cl^- concentrations with a good sensitivity. A fitting by linear regression of all data in either curve **A** or **B** gives a slope of approximately 85 mV/decade.

Since these electrodes, in principle, must be sensible to free Cl^- concentrations in pore solution, a calibration of their potentiometric response has been carried out in a $Ca(OH)_2$ saturated solution trying to simulate the inner electrolytic medium of concrete (FIG.2). A clear nernstian relationship, with an approximate slope of 60 mV/decade, is observed between potential and

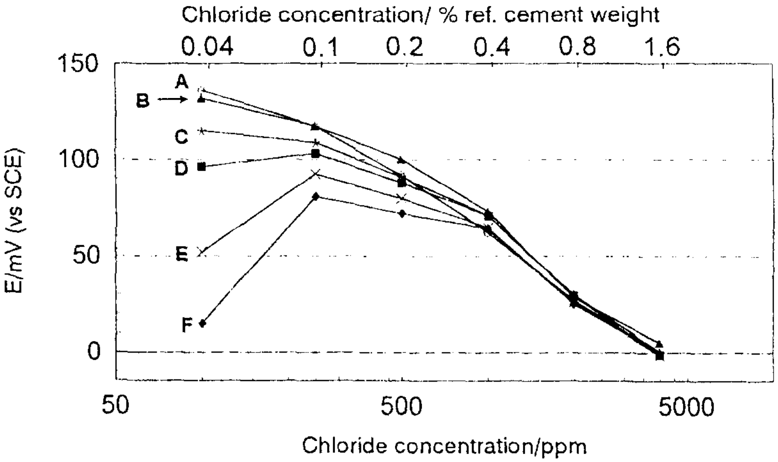

FIG. 1.

Evolution with time of the potentials of the Ag/AgCl electrodes embedded in mortar specimens with different total chloride concentrations as ppm of Cl$^-$ in mortar or % relative to cement weight. Times from mixing (days): **A**:8; **B**:41; **C**:85; **D**:99; **E**:116; **F**:137.

Cl$^-$ concentration in solution with a slight deviation from linearity at low Cl$^-$ contents. By comparing the potentials of Ag/AgCl electrodes embedded (lines **A** and **B** in FIG.1) and in solution (FIG.2) the free Cl$^-$ concentrations in the mortar specimens would range from 5×10^{-3} to 0.7M. These values are consistent with the Cl$^-$ contents found by Haque and Kayyali (3) in the expressed pore solutions from a series of Portland cement concrete specimens with similar total Cl$^-$ contents.

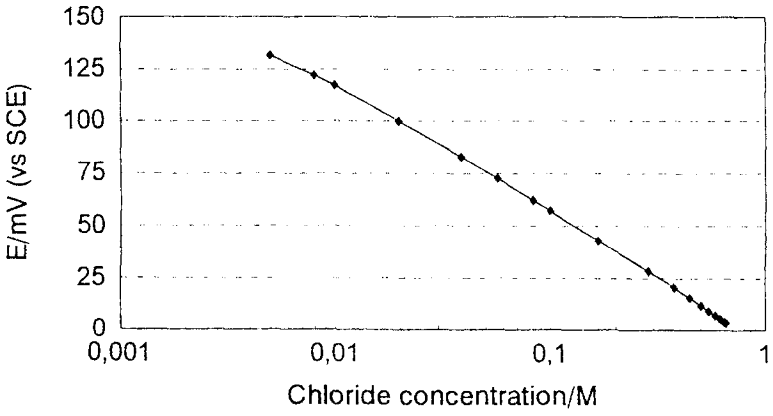

FIG. 2.

Potentiometric response of an Ag/AgCl electrode in a saturated $Ca(OH)_2$ solution with increasing concentrations of Cl$^-$.

Lines A and B in FIG.1 show a more negative slope at high than at low chloride contents. This observation is paralleled by the existence of two branches of different slope in the relationships between free and total (admixed) Cl^- concentrations in concrete: the free chloride content increases more rapidly at high than at low total Cl^- concentration (3). This fact may be interpreted as due to the progressive exhausting of the chloride binding capacity when the amount of admixed Cl^- is increased.

The response of the Ag/AgCl electrodes against total chloride concentrations changes only slightly during the first 85 days of the test (lines **A**, **B** and **C** in FIG.1) except for the specimens with the lowest Cl^- contents. For these last the potentials gradually decrease, for instance the electrode in the 0.04% chloride specimen (refered to cement weight) reaches a difference of 20 mV between the readings at 8 and 85 days. This trend is becoming more marked for testing periods longer than 85 days when a branch with positive slope appears for low concentration specimens. These facts indicate an estimated stability of the potentiometric responses of approximately 3 months, especially for the study of cases not requiring high sensitivity at low total Cl^- concentrations. On the other hand the potentials measured in the specimens with chloride concentrations higher than 0.4% are stable during a testing period of 4½ months in good agreement with results obtained by Gurusamy and Geoghegan (2). This fact points out to an important influence of the Cl^- concentration over the stability of the readings taken with the embedded Ag/AgCl electrodes. The evolution of the potential of the Ag/AgCl wire embedded in the control specimen (without admixed NaCl) is similar to the trend shown by the electrodes in low Cl^- content mortars (FIG.3).

The concentration of free Cl^- in the inner electrolyte of the mortars may have changed during the testing period both by binding with the mineral phases of cement and by changes in the humidity of the specimens due to its progressive drying. Nevertheless none of these effects may explain fully the shifts of potentials shown by the embedded Ag/AgCl wires since the combination of Cl^- should lead to a lowering of the free Cl^- content and then to an increase in potential instead of a decrease. It is also difficult to explain why only the electrodes embedded

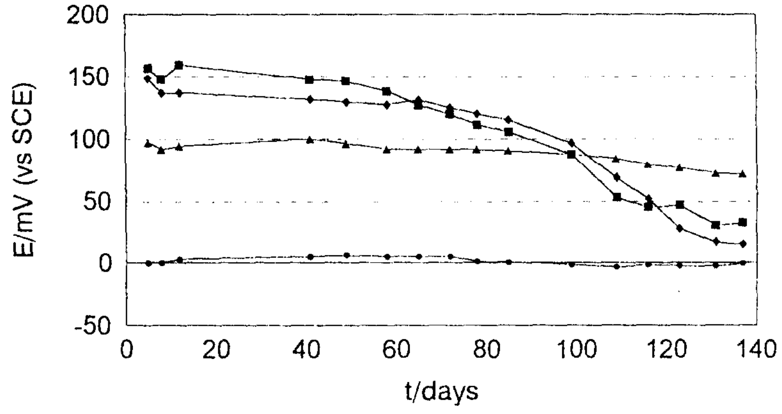

FIG. 3.

Variation of the potential of the Ag/AgCl electrode embedded in the control specimen (without NaCl) (■), compared with the mortars containing (◆):0.04; (▲):0.2 and (●):1.6% Cl^-.

in mortars with low chloride content shift their potential. It seems that a minimum Cl^- concentration is required for the potential readings to remain stable. The effect of the humidity over the long term stability of the potentials of these embeddable sensors is currently under research. While finishing this work Elsener et al. (4) have reported the application of embedded Ag/AgCl electrodes to the detection of Cl^- uptake by concrete.

Conclusions

Embedded Ag/AgCl electrodes show a sensitive potentiometric response to overall Cl^- contents in mortar specimens. The potential readings for specimens with chloride concentrations higher than 0.4% refered to cement weight are stable for periods of at least 4½ months, while the potentials for specimens with lower Cl^- concentrations show a progressive decrease. So Ag/AgCl electrodes may be used as in-situ sensors for monitoring total Cl^- concentration in short-term (less than 3 months) tests in our experimental conditions, especially for the study of cases not requiring high sensitivity at low total chloride contents. For longer-term tests the potential readings may lead to ambiguous results.

The Cl^- concentration in the mortar specimens plays an important role on the stability of the potentiometric response of the embedded Ag/AgCl electrodes. The origin of this influence is not yet known.

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