Study of the Protective Capacity of Cements Regarding Corrosion of Reinforcements under Joint Action of CO₂ and Chloride Ions

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Abstract: To examine the protection against reinforcement corrosion due to the combined action of CO₂ and chlorides, experimental results of the evaluation of a study with three types of cement are presented. The study was performed observing the behavior of reinforcements which were put in samples submitted to accelerated carbonatation tests and accelerated tests under the effect of chlorides. For the evaluation, intensity corrosion measurements were used using the Pr (polarization resistance) technique, employing these measures as a deterioration indicator. Three types of cement available in the national market were used. The obtained results enabled the classification of the used cements, comparing their profile behaviors in the conditions of the proposed tests.

Key words: Carbonation, chlorides, corrosion, reinforced concrete, polarization resistance.

1. Introduction

Reinforced concrete structures subjected to reinforcement corrosion by carbonation of concrete or chloride contamination decrease their service life time. The study of reinforcement corrosion is important due to the high number of affected structures, with negative consequences for stability, functionality and structure aesthetics.

The reinforced concrete structures are stable when there are thermodynamic conditions which ensure that they work in the passivity zone of Pourbaix diagram [1]. The high alkalinity of fresh concrete, with pH higher than 12.6, is guaranteed by the ions from the present alkaline compounds: Na⁺, K⁺, Ca²⁺ and OH⁻. However, this equilibrium situation can be changed when the Cl⁻/OH⁻ ratio reaches values higher than 0.6 [2] due to the penetration or addition of chlorides or the pH reduction of the aqueous phase to values of about 9, after penetration of CO₂ [3]. When this equilibrium ceases, the phenomenon of reinforcement depassivation occurs.

After this depassivation, which determines the end of the initiation period [4], corrosion can occur in a general way in the case of the carbonation of concrete, or in a localized and timely manner in the case of the presence of chloride ions. In the propagation period, the manifestation of the corrosion in the form of fissures, coating displacement, stains, reduction of reinforcement section and loss of adhesion can be observed.

The type of cement influences the speed of carbonation as long as the alkaline reserve is a function of the chemical composition of cement and the additions. The carbonation is generally faster in the case of cements with additions [5].

The water/cement ratio is an important factor that can be used to limit the speed of carbonation. Usually, the reduction of water/cement ratio reduces the depth of carbonation [6]. This happens because the reduction in surface porosity of the concrete restricts the entrance of carbon dioxide. The reduction of the
water/cement ratio means an alteration in the capillary pores in a range from 0.05 \( \mu \text{m} \) to about 3 \( \mu \text{m} \), which are the ones that mostly influence the permeability to concretes and mortar [7].

The cement chemical composition has a great influence in the penetration of chlorides in order of the combination of these chlorides and C\(_3\)A e C\(_4\)AF forming the chloroaluminates, which reduces the penetration flow. According to Ref. [8], more C\(_3\)A the cement contains, more time will be necessary for the reinforcement corrosion to initiate.

Refs. [9, 10] are unanimous in affirming that the blast furnace slag, used as mineral addition, significantly reduces the diffusion coefficient of chlorides, either by the physical effect of addition (changes in porosity), or by the increased capacity of chloride fixation. Comparing several cements as to the development of corrosion by chlorides, Al-Amoudi et al. [11] concluded that the cements with addition of slag and silica fume have superior performance (having the cement with addition of slag corrosion intensity 10 times lower than the concrete without slag at the end of trials). Bauer [12], however, reported that the addition of slag to the cement, in the case of chloride entry, has a beneficial effect to the chloride binding capacity for a water/cement ratio below 0.5.

The water/cement ratio also controls the penetration of chloride ions due to its influence on porosity, form, volume and distribution of pore sizes, as mentioned earlier. The rate of chloride diffusion increases by 4 to 5 times with an increase in the water/cement ratio from 0.4 to 0.6, as verified by Page and Short [9].

Alonso and Andrade [13], working with chlorides added to concrete, examined that the simultaneous presence of chlorides and carbonation has an additional effect on the speed rate of corrosion on the reinforcement of mortars and results in higher values than in case separate acting. They also found that the type of cement causes a great difference in the corrosion rate in the presence of CaCl\(_2\) added to the mixture. According to Ref. [14], in partially carbonated concretes, the entrance of chlorides can be accelerated up to 100%.

The mentioned considerations illustrate the complex issue of the development of corrosion in the case of cements with additions. On one side, there is a positive behavior towards the action of chlorides with good performance, and on the other hand, there are negative aspects regarding the higher speed and depth of the carbonation front.

In this paper, part of a wider work that is still in development, the behavior of some national cements is presented in relation to the protection against corrosion of reinforcements, with different water/cement ratios when carbonation and chlorides are acting. In order to study the phenomenon, the electrochemical technique of Pr (polarization resistance) was used. This allows to determine the intensity of reinforcement corrosion by using sensors embedded in the samples. The samples were submitted to accelerated carbonation assays later chloride penetration with moistening and drying cycles.

2. Materials and Method

2.1 Materials

2.1.1 Portland Cements

Portland cement composed with filler (CPII F-32), blast furnace Portland cement (CPIII 32), Portland cement of high initial resistance to sulfates with silica fume (CPV-ARI-RS-MS) were used.

2.1.2 Aggregate

The sand was brought from Corumbá natural river.

The chemical, physical and mechanical characteristics of the studied cements are presented in another paper where its behaviors regarding the penetration of CO\(_2\) and chlorides were studied in more details.

2.1.3 Mixing Water

The used water was derived from the supply network of the sanitation company.

The result of the chemical analysis of the mixing water to determine the chloride content was about
87.5 mg/L, remaining within the maximum limit standard of 1,000 mg/L [15].

There was no analysis of the water for determination of sulfates.

2.2 Method

2.2.1 Quantity of Test Samples

Mortar samples with the following dosages were prepared:

- The workability of the samples, obtained by the flow table test, was in the range of 260 mm to 320 mm;
- The samples had the dimensions of 60 × 80 mm, with two bars with 5 mm diameter, 100 mm length and 10 mm covering, as shown in Fig. 1. All samples are slightly larger than those used in other studies [13, 16]. For each material, two samples with a water/cement ratio of 0.4 and two others, with a water/cement ratio of 0.7 were confectioned, maintaining the same workability, as shown in Table 1. All specimens had the same conditions in the fresh state, which means they were made within the same range of workability: 260 mm to 320 mm, through the consistency test of mortar [17]. The curing time was 7 days in a moist chamber;
- The exposure area of the bars was limited by adhesive tape, placed on the extremities of the bars, setting an area of around 7.7 cm².

2.2.2 Test Procedures

After curing, the samples remained in the laboratory environment for 15 days and were arranged afterwards in the carbonation chamber to start the process of accelerated carbonation in a sealed chamber. So there was no CO₂ output except for the exit orifice and its relative humidity was maintained at around 65%. The test procedure consists in the intermittent application of CO₂ in the carbonation chamber, which lasted for 8 min. In the development of the assays, the flows were established in intervals of 30 min until the depassivation of every reinforcement. After that, the flows were performed every three days. The frequency of the measurement of electrochemical variables was initially every 30 min, followed by a daily reading when there were three flows.

Shortly after the accelerated carbonation test, the samples were subjected to cycles of drying and partial immersion in a 5% NaCl solution. The semi-cycles are characterized according to Table 2.

The drying condition consists in disposing the samples in a ventilated greenhouse and keeping the temperature of 50 °C. In the condition of partial immersion, the solution level in the container at a position that corresponds to half the height of the exposure area of the bar was maintained. Thus, there is absorption by capillarity and once the saturation occurs, there is a diffusion process. The frequency of readings was at the end of each semi-cycle.

The variables measured throughout the test for carbonation as well as chlorides are the same, as shown in Table 2:

| Table 1 | Summary of the prepared samples. |
|----------------------------------|
| Cement  | Water/cement ratio | Ratio   |
| CPII-F 32 | 0.4 | 1:1.5 |
| CPII-F 32 | 0.7 | 1:3   |
| CPIII 32  | 0.4 | 1:1.5 |
| CPIII 32  | 0.7 | 1:3   |
| CPV-ARI-RS-MS | 0.4 | 1:1.5 |
| CPV-ARI-RS-MS | 0.7 | 1:3   |

| Table 2 | Summary of the prepared samples. |
|-----------------|-----------------|----------|
| Semi-cycle     | Condition        | Duration |
| Drying         | Greenhouse       | 5 days   |
| Partial immersion | Partially submerge | 2 days   |
• intensity of corrosion ($i_{corr}$);
• potential of corrosion ($E_{corr}$);
• ohmic resistance ($R_{ohm}$);
• mass variation ($M v$).
In this work, only the readings of $i_{corr}$ are presented.

2.2.3 Electrochemical Measurements
For the measurements of electrochemical variables, a potentiostat with ohmic drop compensation linked to a data input system, voltmeters with the sensitivity of a 10th of mV, reference electrode (saturated calomel electrode, to measure corrosion potential) and a stainless steel counter—electrode placed externally to the sample were all used.

The instantaneous corrosion intensity $i_{corr}$ was determined using the following expression proposed by Stern & Geary:

$$i_{corr} = \frac{B}{ARp}$$

(1)
where, $B$ is a constant that depends on the Tafel’s anodic and cathodic tangents which vary according to the type of steel, and with the environment in which it is subjected; $A$ is the area of exposure. Andrade and González [18] found that, for reinforcements embedded in concrete, values of $B$ are between 26 mV and 52 mV; The value for $R_p$ was obtained through some data input by means of a software program that directly computes the tangent of the curve under variation of the potential in relation to the variation of the current. The ohmic resistance of the system was determined by ohmic drop compensation through the potentiostat, at the time of the $R_p$ reading.

3. Results

Fig. 2 presents the evolution of the corrosion intensity of the reinforcements embedded in mortars with a water/cement factor of 0.4 during carbonation. It can be observed that the initiation phase (period of time from the beginning of the assay in which $i_{corr}$ surpasses the range of 0.1–0.2 $\mu$A/cm$^2$) from the series regarding the cement CPV-ARI-RS-MS is significantly inferior than the series regarding the cement CPIII 32. During the assay, it reaches levels of $i_{corr}$ just slightly inferior than CPV-ARI-RS-MS. The CPII-F 32 cement is the one that presents the highest initiation period.

Fig. 3 shows the evolution of the corrosion intensity of the bars embedded in mortars with a water/cement ratio of 0.7, evidencing a similar behavior than the samples with a water/cement factor of 0.4. The values

![Fig. 2](image)  Intensity of corrosion with a water/cement ratio of 0.4 during carbonation.
of $i_{corr}$ for the reinforcements of the samples made with cement CPV-ARI-RS-MS are greater than twice the values shown by the samples executed with CPIII 32. The samples produced with CPII-F 32 showed a higher protection capacity, as long as the period of the beginning of the reinforcements depassivation is greater and the corrosion intensity values of the bars are approximately 25% less than the values presented by those protected by other cements. This is a negative evidence of the silica fume and slag additions to the carbonation process. Using a water/cement ratio of 0.7, it can be verified that the initiation phase is reduced and the development of more intensive corrosion is observed. The values of $i_{corr}$ reach much higher levels comparing with the values obtained from the samples with a water/cement ratio of 0.4.

The evolutions of corrosion intensity for the water/cement ratios of 0.4 and 0.7, respectively, are shown in Figs. 4 and 5. The samples are cured for 7 days and subjected to cyclic testing by the effect of chlorides, after carbonation.

Once the values of $i_{corr}$ are obtained at the end of the drying stage and at the end of the partial immersion stage, it is observed that there is an amplitude of variation between the respective values due to the nature of the accelerated corrosion assay, this amplitude significantly increases with the elevation of the water/cement ratio.

The reinforcements of the samples made with cement CPIII 32 with a water/cement ratio of 0.4, reached up to three times the values measured in the samples from cement CPV-ARI-RS-MS, whose $i_{corr}$ did not exceed 1.8 $\mu$A. It is reported that the initiation phase was much greater for the CPII-F32 cement series in relation to other cements, although during the test, it reached a value of $i_{corr}$ which is greater than CPV-ARI-RS-MS (Fig. 4).

Fig. 5 shows the evolution of $i_{corr}$ for the reinforcements protected by mortars with water/cement ratio of 0.7. It is observed that the reinforcements embedded in mortars of the three types of cements already exceeded the range of 0.1–0.2 $\mu$A/cm² in the first cycle, in a situation much worse than the samples performed with a lower water/cement relation. This leads to a reduction of its useful life. It is verified that the values of $i_{corr}$ at the end of the test, for the CPV-ARI-RS-MS cement series, were higher than the values obtained for the other cements, showing an
inferior behavior when the water/cement ratio was 0.4.

In accordance with the results from other studies [6, 12, 19], the cements with additions, provide an inferior initiation phase when exposed to the environment contaminated with CO₂. This effect is noted with higher intensity for a more elevated water/cement ratio and can probably be explained by the reduction in alkalinity in the aqueous phase, but also by the decreased availability of alkalinity to maintain pH at levels that do not allow the reinforcement’s depassivation. The results also evidence the influence of the porosity in the initiation period, because the increase in the water/cement ratio significantly diminishes the moment of depassivation of the three studied cements.

However, the carbonated reinforcements really deteriorate when they are in contact with moisture, which supports the acceleration process of
reinforcement corrosion, corresponding to the propagation period from the model of Tuutti [4]. The improved performance of the samples produced with CPII-F 32 cement, with both water/cement ratios of 0.4 and 0.7, presents lower values of corrosion intensity when placed in a partially submerged condition. This can be explained by the lower porosity of the cement in comparison to cements containing additions, probably due to its lower absorption capacity [12].

The behavior of the carbonated samples, when submitted to cycles of drying and moistening in a solution of sodium chloride at 5%, is similar to that obtained by Dhir et al. [14] where concretes with the addition of fly ash had increased their diffusion coefficients by approximately 100% in relation to the concrete without additions. In the present work, the highest corrosion intensities occur at reinforcements embedded in samples performed with cements containing additions of silica fume and slag. This phenomenon can be explained by a lower alkalinity in the aqueous phase and by a lower chloride binding capacity since, as verified by Ref. [13], the products resulting from the combination of chlorine are more stable in saturated solutions of Ca(OH)₂. The CPII-F 32 cement which supposedly has higher alkalinity is the one which presented lower corrosion intensity values.

It is noteworthy to mention that similar samples, made with the same cements and same water/cement ratios but not carbonated, showed much lower corrosion intensities when subjected to the same conditions of cycles in a chloride solution with the same concentration [20].

It should be highlighted that porosity also influences these results because the water/cement ratio reduces capillary absorption and decreases the corrosion intensity values, especially for cements that does not contain additions of slag or silica fume.

Although the currently available data are not sufficient to explain the phenomena observed here, the results enable the report of practical observations regarding reinforced concrete structures. With the development of cement technology, which provided several alternative products with different physical and chemical characteristics, it is possible to obtain concrete with a much higher resistance with more elevated water/cement ratios and consequently reduce the consumption of cement. Considering that the usual reinforced concrete structures are dimensioned with compressive strength $f_{ck}$ between 18 MPa and 20 MPa and the water/cement relations that reach these resistances are in the range from 0.6 to 0.7, it is possible to suppose that the useful life of constructions decreases. This can be verified in the large number of buildings, which are being repaired. In order to minimize this aspect, an effort from the professionals involved in structural design and execution of constructions is necessary to increase the $f_{ck}$ of concrete structures, taking into account the useful life and maintenance of structures.

4. Conclusions

From this work, it can be emphasized that:

- The studied cements with additions have an inferior performance regarding carbonation;
- The efficiency of the additions used in commercial cements as a reduction factor of ion chloride penetration is reduced when the concrete is carbonated;
- The reduction of the water/cement ratio improves the performance of the three used cements even if they are carbonated;
- With the used polarization resistance technique, it is possible to classify the three cements studied in decreasing order of performance in carbonated and contaminated environments with chlorides: CPII-F 32 > CPIII 32 > CPV-ARI-RS-MS.

References

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