Study of efflorescences forming process on cementitious materials

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Efflorescence is a white deposit of calcium carbonate on surface of cementitious materials. It appears under specific climatic conditions. Beside the aesthetical problem, an important economical problem exists, especially for colored materials. Indeed, this phenomenon is a cause of reject of those products by customers. The aims of the study are the understanding of the mechanisms and the identification of the main parameters which control efflorescences formation.

A procedure was performed to produce primary efflorescences under laboratory conditions. This test consisted in applying controlled temperature and relative humidity to samples in a climatic chamber. A uniform white deposit could be obtained. Thus, the intensity of efflorescences was measured with a spectrocolorimeter: clarity has been linked with efflorescence intensity.

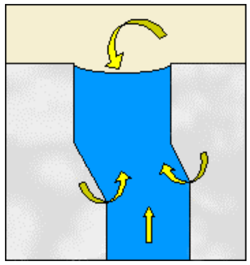
The formation of the efflorescences, for a given water to cement ratio, seems to be strongly depend on the degree of hydration before the efflorescence test and the relative humidity during the procedure.

1. Introduction

Cementitious constructions are submitted to natural conditions of temperature and relative humidity. Some of these climatic conditions are in favor of efflorescence phenomenon. Efflorescence is a white deposit of $CaCO_3$ at the surface of cementitious materials. This white deposit on dark constructions can be a cause of reject of product by customers and become a huge economical problem. So understand the mechanisms and identiy of the main parameters which control efflorescences formation, is the first step for reducing the formation of efflorescences.

Two kinds of efflorescences can be noticed, primary and secondary. The distinction comes from the point in time at which the precipitation of $CaCO_3$ occurs in relation to the curing process [1].
Primary efflorescence occurs during the curing process. Calcium ions from cement phases and carbonate ions from carbon dioxide of air, dissolve in the interstitial solution. Excess water in the cementitious matrix diffuses to

the surface with Ca^{2+} ions (Fig. 1.a), when water evaporates, the concentration Ca^{2+} and CO_3^{2-} increase and reach the saturation limit of $CaCO_3$. Then $CaCO_3$ precipitates. (Fig. 1.b).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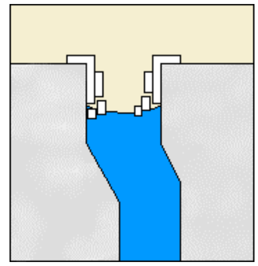
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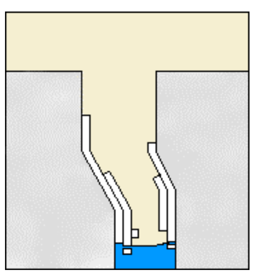
Fig. 1: Mechanism of appearance of efflorescences [2].

Secondary efflorescences whi ch occur in cured concretes, are not the subject of this program and will not be more detailed in this article.

The main parameters identified that influence primary efflorescence on cement are [3]:
- capillarity and permeability,
- ionic concentration in pores,
- climatic conditions (temperature and relative humidity) (Fig. 2).

Concerning the climatic conditions, it is known that for a fast drying (wind, sunshine) precipitation of $CaCO_3$ occurs in pores (Fig. 2.a), while for a longer drying (rainy weather, low temperature) the precipitation occurs on the surface of sample (Fig. 2.b) [3].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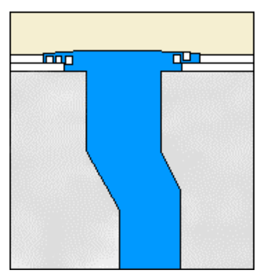
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Fig. 2: Efflorescences: influence of climatic conditions.

In order to study the efflorescences forming process, a procedure was performed to produce primary efflorescences under laboratory conditions. In the literature data [4,5] three types of tests exist in order to accelerate the formation of efflorescence: wicking test, percolating test and wet/dry test. This latest type of test is said to be not efficient, but this work shows that under particular conditions this test can form primary efflorescences.

The procedure performed in this work, consists in applying controlled temperature and relative humidity, to samples in a climatic chamber. The aim is to reproduce the favorable natural climatic conditions.

2. Material and method

2.1 Materials and sample preparation

The investigate cement was a grey Portland cement CPA CEM I 52.5, according to the NF EN 197-1. The cement paste was flowed in moulds of cubic shape ($2.10^{-6} m^3$) with a water-to-cement ratio (W/C) of 0.4.

The hydration period before demoulding the sample is called curing period. During the curing period, samples were stored under water-vapor-saturated atmosphere (100% of relative humidity).

2.2 Efflorescence test

According to literature data, a layer of water and a sufficient duration time are necessary to the formation of efflorescence on concrete [3]. Indeed, the water film allows ions to be propagated on the surface of sample.
The test developed, simulates these climatic conditions and it allows producing efflorescences in a reproducible way (Fig. 3).

Fig. 3: Efflorescences obtained after the efflorescence test.

This test can be divided into two parts:
- curing period
- demoulding and put into the climatic chamber:
    - stage of saturation of water (high relative humidity)
    - drying by decrease in the relative humidity.

The temperature of the climatic chamber is kept constant during the test.

2.3 Measurement of the intensity of efflorescence on cement: spectrocolorimetry

To validate the test, variations in the intensity of efflorescence have to be quantified. As efflorescence is a white deposit on the grey surface of cement, the clarity of the surface's samples varies: there is a correlation between intensity of efflorescences and the clarity of the cement. It's why the intensity of efflorescence is measured with a spectrocolorimeter. This apparatus gives, in the L*.a*.b* coordinates, the numerical color of a surface. L* corresponds to clarity and goes from 0 for black to 100 for white. a* and b* corresponds to chromaticity. Only L* is studied in this work. Indeed, few variation in a* and b* was noticed with grey cement. Each measure was conducted in triplicate. As the clarity of the cement could vary with different duration of hydration or different W/C ratio, we chose to study the difference of clarity between a sample reference and a sample after the efflorescence test. The reference was kept under nitrogen and water-vapor-saturated so that no $CaCO_3$ could be formed.

2.4 Mercury porosimetry

The intrusion porosimetry deals with analysing the penetration of a liquid in the porosity of the specimen material studied, via the intrusion at various pressures of the mercury. As pressure increases, mercury moves into the sample pores. Intrusion of different size pores occurs at different pressures. The greater pressure, the smallest is the pore diameter into which the mercury can be forced. The pore diameters are calculated, assuming that the pores have a cylindrical shape, with the pressure at which mercury is intruded. Therefore, it is possible to obtain the total porosity and bulk, as well as the apparent density.

As cement paste pores are not of cylindrical shape, the diameter calculated is the diameter of entry of mercury in the pore. This implies to be careful in interpretations of the pore diameter distribution.

3. Results and discussion

The influence of various parameters was studied. Firstly the parameters concerning the test were studied in order to confirm the literature data and to optimize the test. Then, a parameter of the cement (water-to-cement ratio) was considered to better understand the formation of efflorescences.

3.1 Influence of the atmosphere during the curing period

The influence of the type of atmosphere during the curing period before the test was studied by using three atmospheres: nitrogen and water-vapor-saturated, air and water-vapor-saturated, air. The intensity of the efflorescences on the sample of cement was measured with a spectrocolorimeter (Fig. 4). It was measured on reference (hydrated cement) and after the efflorescence test.

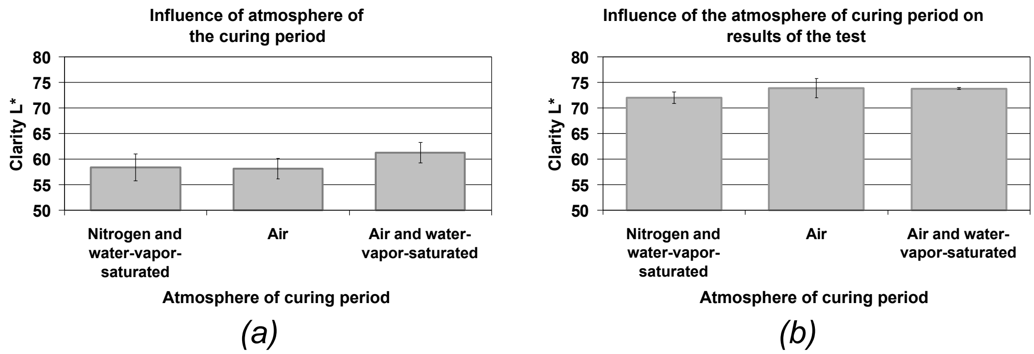


Fig. 4: Influence of the atmosphere of the curing period before the test.

It could be notice that there were few influences of the atmosphere on the clarity of a reference and on a sample after the test.
The atmosphere chosen was then nitrogen and water-vapor-saturated which permits to avoid carbonation.

3.2 Influence of the degree of hydration of the cement

The influence of the duration of the hydration preceding the test was studied from 4 to 16 h (Fig. 5). Up to 8 h of hydration efflorescences are perceptible and constant. Beyond, there was a drop in the difference of clarity. That implies that the duration of hydration is an influent parameter for the intensity of primary efflorescences. Indeed, during hydration two of the main factors controlling efflorescences varied: the composition of the pore solution and the porosity. There was a critical degree of hydration that started to reduce efflorescences.

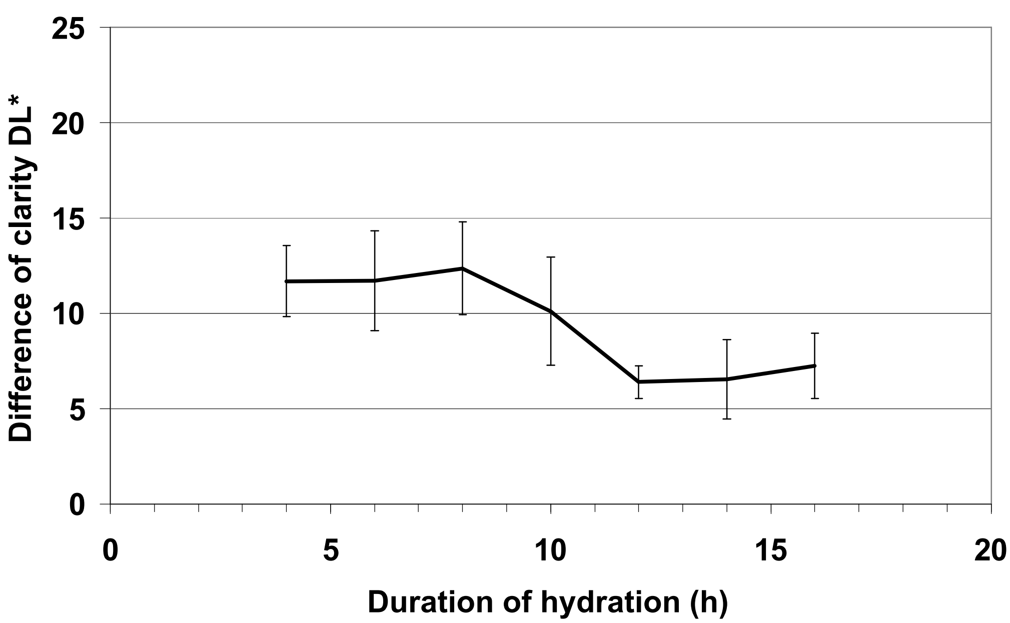


Fig. 5: Influence of the duration of hydration before the test.

3.3 Influence of temperature

The influence of the temperature was studied in the range of 7-30°C (Fig. 6). We could notice a max imum for temperature between 11-16°C. For higher temperature there was less efflorescences. This result is in accordance with empirical data: maximum efflorescences is observed on cementitious construction for fall and spring weather.

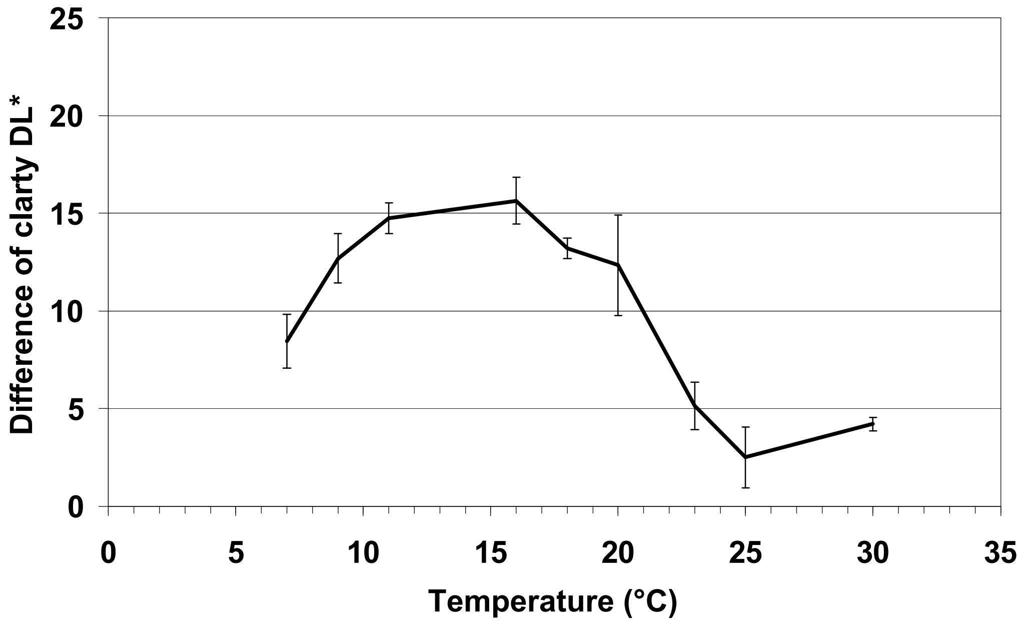
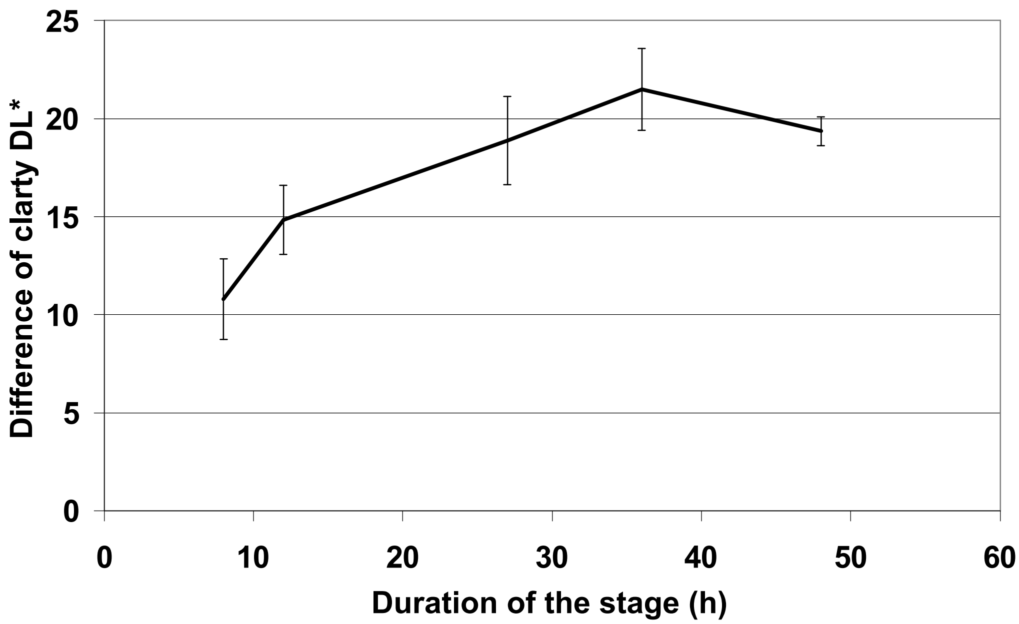


Fig. 6: Influence of the temperature.

3.4 Influence of the relative humidity (RH) in the climatic chamber

- Length of the stage: it was observed that a minimal duration of 12 hours was necessary. Beyond this duration of stage, the intensity of efflorescences is constant (Fig. 7.a).
- Value of the RH on the stage: It must be maximum (very near to 100 %) so that the water film can spread ions on surface, leaving uniform efflorescences. For a lower level (90 %) efflorescences have a lower intensity: slow drying made the face of evaporation to remain at the mouth of pores, causing a calcium carbonate deposit on this level, witch is probably responsible of this lightning.
- Duration of drying: The duration of drying was tested between 5 and 16 h (duration and value of RH on the stage: 100 % HR – 24 h) (Fig. 7.b). For this range, efflorescences are obtained. A long drying makes possible for the face of evaporation to remain on surface a long time involving the saturation in ions of water film.



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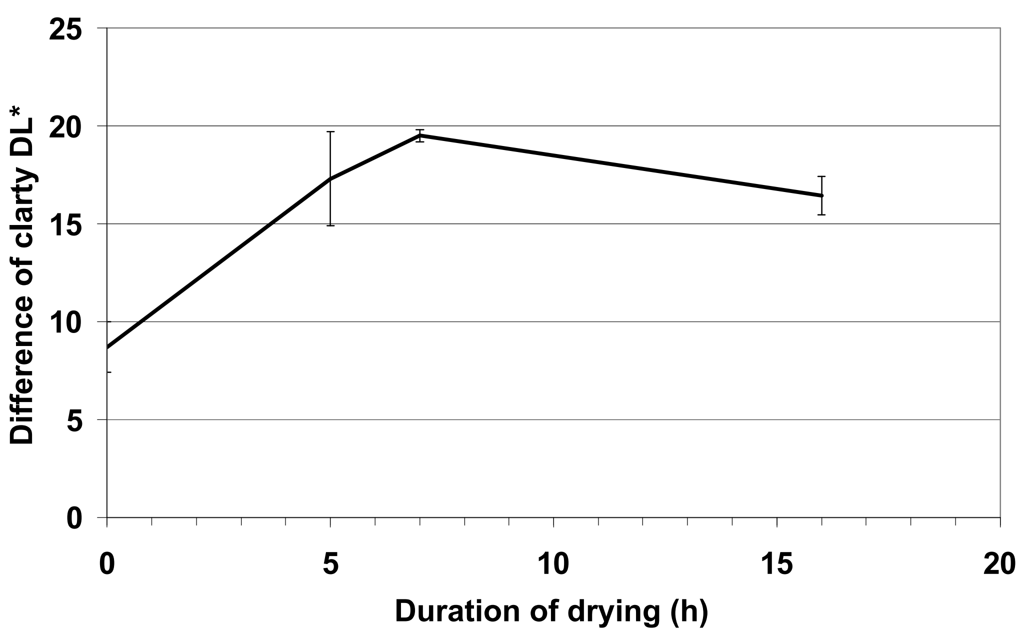

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Fig. 7: Influence of climatic conditions.

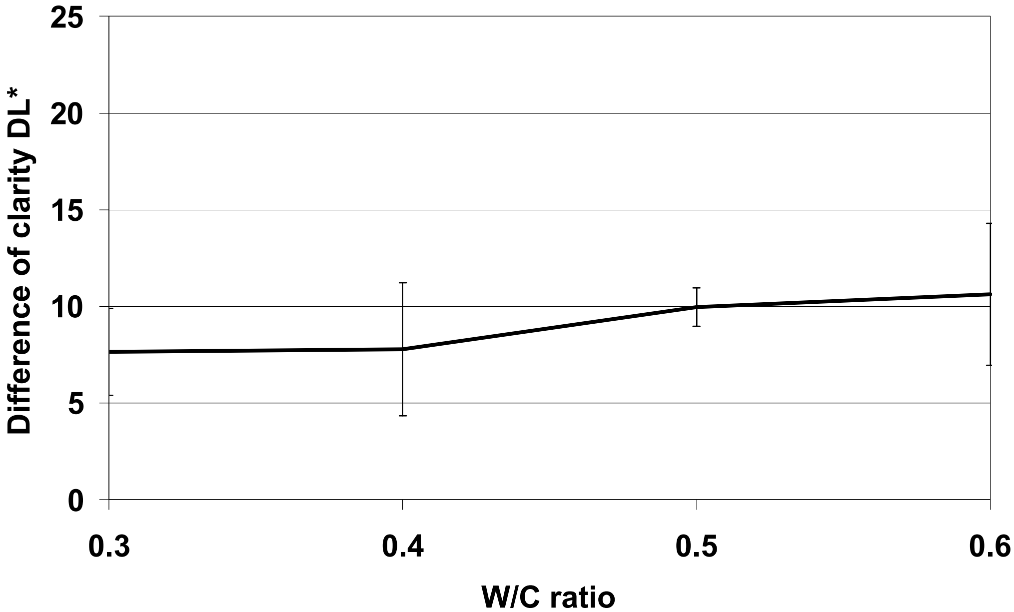
Then, it is possible to simulate, with variations of relative humidity, the natural climatic conditions that influence efflorescence:

- fast drying of sample: the carbonation takes place inside pores and not induces any efflorescence.
- rainy weather: the carbonation is at the mouth of the pores,
- fresh weather with formation of a water film on the surface of the sample: in these case the sample surface is entirely covered by efflorescences.

Then, the third condition was used for the next part of this study.

3.5 Influence of W/C

The difference of clarity between the reference and the samples after the efflorescence test is studied (Fig. 8.a).



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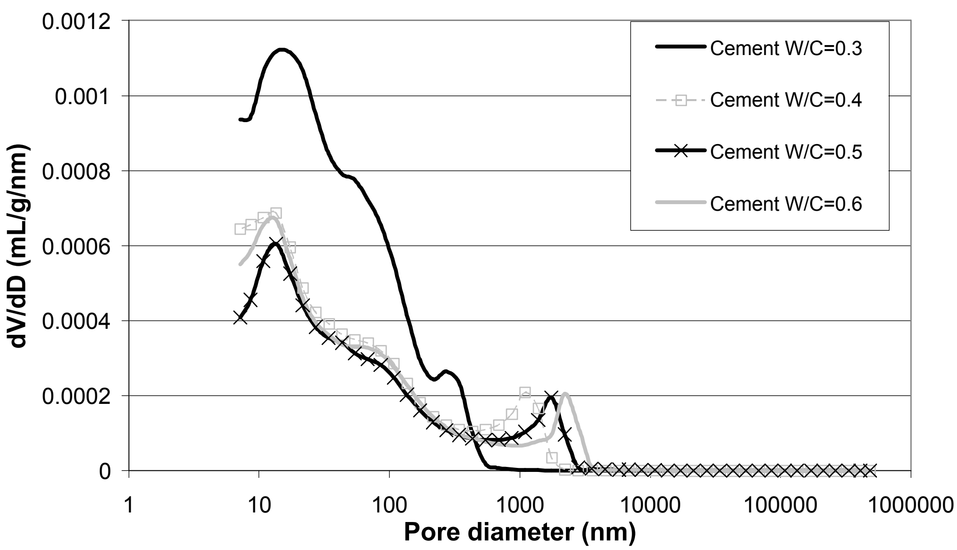

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Fig. 8: Influence of W/C on efflorescence (a) and on porosity (b).

We can observe that there was a slight increase in the clarity with the W/C ratio.

By porosimetry, for each ratio, two populations of pore diameters were revealed (Fig. 8.b). One was around 1 µm and the other one was under 0.1 µm. The porous distribution of a cement paste presents on one hand, inter residual grain pores which are commonly named capillary pores and on the other hand, a porosity relative to hydrates (in particular CSH) which size is around 10-20 µm [6]. Both families can be identified: the first one can be the capillary pores and the second one is relative to hydrates. The size of pores is in accordance with the literature data. We noticed that there was a decrease in the size of the pore of the first family with the decrease in W/C. This result is in accordance with the decrease in efflorescences, because capillary pores that permit to transport ions are reduced.

4. Conclusion

In this work, several parameters that could influence the formation of efflorescence on cementitious construction have been studied.

A test of wet/dry has been established and optimized for the formation of efflorescence and show that a maximum of humidity around the sample is a primordial factor. Moreover, the variation of intensity of efflorescence was digitized and quantified by spectrocolorimeter. The difference of clarity has been linked with variation of efflorescence intensity.

It was find out that the formation of the efflorescences, for a given water-to-cement ratio, seems to be strongly influenced by the degree of hydration before the test and the relative humidity during the procedure.

By studying impact of W/C on the intensity of efflorescences the correlation between efflorescences and porosity was highlighted.

5. References

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