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STUDY OF EFFLORESCENCE FORMING PROCESS ON CEMENTITIOUS MATERIALS

ETUDE DU PROCESSUS DE FORMATION DES EFFLORESCENCES SUR DES MATERIAUX CIMENTAIRES

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ABSTRACT – Efflorescence is a white deposit of calcium carbonate on the surface of cementitious materials. It appears under specific climatic conditions. Besides the aesthetic problems, an important economical problem also exists, especially for colored materials. Indeed, this phenomenon is a cause for rejection of products by customers. The aims of the study presented herein are to understand the mechanisms involved and identify the main parameters which control efflorescence formation. A procedure was previously performed to produce primary efflorescence in a climatic chamber. As pozzolans are frequently used in order to decrease the intensity of efflorescence, substitution of cement by different pozzolans was studied. This latest research allowed the Authors to underline which parameters were modified by the substitutions and to link decreases in the intensity of efflorescence with those modifications.

RÉSUMÉ – Les efflorescences forment un dépôt blanc de carbonate de calcium à la surface de matériaux cimentaires. Elles apparaissent pour des conditions climatiques spécifiques. Au delà du problème esthétique, un important problème économique intervient car ce phénomène peut être la cause du rejet d'un produit par les clients. Les objectifs de l'étude sont la compréhension des mécanismes et l'identification des paramètres principaux qui contrôlent la formation d'efflorescences. Au préalable, un test a été mis au point dans une chambre climatique pour reproduire des efflorescences. Comme les pouzzolanes sont souvent utilisées pour atténuer les efflorescences, la substitution du ciment par différentes pouzzolanes a été étudiée. Cette étude a permis d'identifier les paramètres affectés par ces substitutions et de relier ces modifications à l'atténuation des efflorescences.

1. Introduction

Cementitious constructions are subjected 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 on the surface of cementitious materials. This white deposit on dark constructions can be a cause of rejection of products by customers and thus sometimes becomes a significant economic problem. Understanding the mechanisms involved and identifying the main parameters which control efflorescence formation are the first steps for reducing the formation of efflorescence.

Two kinds of efflorescence can be noticed: primary and secondary. The distinction comes from at witch time in the curing process the precipitation of CaCO_3 occurs (Bolte and Dienemann, 2004). Secondary efflorescence which occurs in cured concretes, is not the subject of this program and is not detailed in this article. Primary efflorescence forms during the curing process. Calcium ions from cement phases and carbonate ions from carbon dioxide in air dissolve in the interstitial solution. Excess water in the cementitious matrix diffuses to the surface with Ca^{2+} (Figure 1.a). When water evaporates, the concentrations of Ca^{2+} and CO_3^{2-} increase and reach the saturation limit of CaCO_3 . Then CaCO_3 precipitates (Figure 1.b-d).

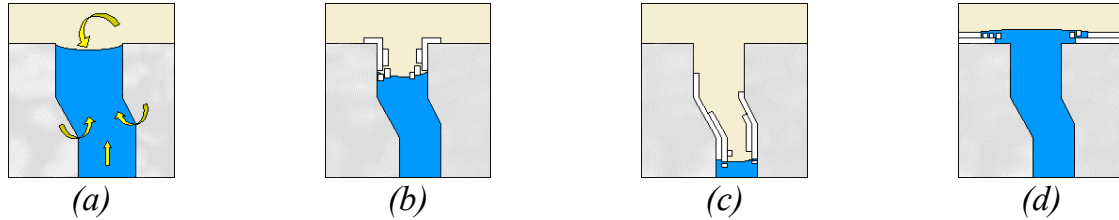


Figure 1. Mechanism of appearance of efflorescence (Dossier Ciment 5, 1995).

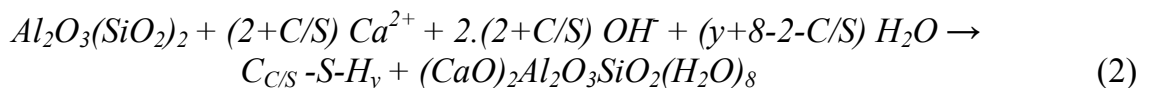
The main parameters identified that influence primary efflorescence on cement are (Dow and Glasser, 2003): capillarity and permeability, ionic concentration in pores and climatic conditions (temperature and relative humidity) (Figure 1.c-d).

Concerning the climatic conditions, it is known that for a fast drying (wind, sunshine) precipitation of CaCO_3 occurs on the inside of pores (Figure 1.c), while for a longer drying (rainy weather, low temperature) the precipitation occurs on the surface of sample (Figure 1.d) (Dow and Glasser, 2003). In order to study the efflorescence forming process, a procedure was performed to produce reproducible primary efflorescence under laboratory conditions in a climatic chamber.

Pozzolanic reactivity is known to decrease the intensity of efflorescence. Metakaolin is used in industry in substitution of cement for its beneficial action on efflorescence. This action is realized thanks to the pozzolanic reaction of metakaolin when it is mixed with cement. According to Garcia-Diaz, contact between metakaolin and basic solution supersaturated in calcium is necessary for the pozzolanic reaction (Garcia-Diaz, 1995). In this case, it was the process of the tricalcium silicate hydration, the majority compound of the anhydrous cement, which gave birth to this basic solution according to reaction (1).



Metakaolin ($\text{Al}_2\text{O}_3 \cdot (\text{SiO}_2)_2$), after the hydroxylic dissolution, reacts with Ca^{2+} and OH^- ions in the solution. The straetlingite ($(\text{CaO})_2 \text{Al}_2\text{O}_3 \text{SiO}_2 (\text{H}_2\text{O})_8$) and silico-calciques hydrated gels (C-S-H) form in detriment of portlandite ($\text{Ca}(\text{OH})_2$ hydrate of cement) according to reaction (2):



An acceleration of cement hydration is observed in case of a mixture of cement and pozzolans (Takemoto and Uchikawa, 1980).

2. Materials and method

2.1. Materials

The investigated cement was a grey Portland cement CPA CEM I 52.5, according to the NF EN 197-1 standard.

Three metakaolins (MK) were used. These differed by physical parameters such as BET surface, given in *Table I*, and particle size distribution, given in *Figure 2*.

Table I. BET surfaces of MK.

| Sample name | MK0 | MK1 | MK2 |
|---------------------------------|-----|-----|-----|
| BET surface (m ² /g) | 8 | 20 | 22 |

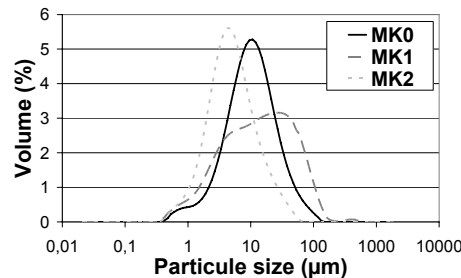


Figure 2. Particle size distribution of MK obtained by laser granulometry measurement.

Average diameters of the three MKs are specified in the *Table II*.

Table II. Average diameter of MK.

| Sample name | MK0 | MK1 | MK2 |
|---------------------|-----|------|-----|
| D _a (μm) | 10 | 13.6 | 4.7 |

Specific surface and particle size distribution are indicators of the reactivity of powder. Thus, we can firstly suppose that MK2 should have a higher reactivity than MK0 or MK1.

2.2. Sample preparation

Four types of cementitious paste were prepared and cast in moulds of cubic shape (2.10⁻⁶ m³) with a water-to-solid ratio (W/S) of 0.4. The first paste was a pure cement paste. The three others paste were mixes of cement and MK0, MK1 or MK2 in ratio of substitution of cement between 3 to 30 %.

The hydration period before demoulding the sample is called the curing period. During the curing period, samples were stored under nitrogen and in a water-vapor-saturated atmosphere (100% relative humidity) to avoid carbonation.

2.3. Efflorescence test

According to the literature in this area, a layer of water and a sufficient duration are necessary to the formation of efflorescence on concrete (Dow and Glasser, 2003). Indeed, the film water allows ions to be propagated on the surface of the samples.

The test developed simulated these climatic conditions and it allowed for producing efflorescence in a reproducible way. This test could be divided into two parts:

- Curing period
- Sample demoulding and placing into the climatic chamber:
 - Stage of saturation of water (100% of relative humidity)
 - Drying by decrease in the relative humidity (100% to 50%).

The temperature of the climatic chamber was kept constant during the test (16°C).

2.4. Measurement of the intensity of efflorescence on cement: Spectrocolorimetry

To validate and exploit the test, variations in the intensity of efflorescence had to be quantified. As efflorescence is a white deposit on the grey surface of cement, the clarity of the sample surface varied: there is a correlation between intensity of efflorescence and the clarity of the cement. This was why the intensity of efflorescence was 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^* correspond to chromaticity. Only L^* was studied in this work. Indeed, few variations in a^* and b^* were noticed with grey cement. Each measurement was conducted in triplicate. As the clarity of the cement could vary with introduction of MKs (nearly white powders), 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 at 16°C so that no CaCO_3 could be formed and interfere with the measurements.

2.5. Mercury porosimetry

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 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 mercury can be forced. Pore diameters are calculated with the pressure at which mercury is intruded, assuming that the pores have a cylindrical shape.

As the pores of cement paste are not of cylindrical shape, the diameter calculated is the diameter of entry of the mercury in the pore. This implies that one must be careful in interpreting the pore diameter distribution obtained by this method.

2.6. Electrical conductivity

Electrical conductivity measurements were performed in dilute suspensions with a water-to-solid ratio of 20 and 50. For experiments with cement, a water-to-cement ratio of 50 was used. Conductivity equipment consisted of a 25°C thermostated reactor, two stainless steel annular electrodes, and a conductimeter. The constant cell was first calibrated with a 0.1 M KCl solution. For experiments with cement, MK (0.1g), with a MK-to-cement ratio of 0.05, was mixed with 100 ml of deionized water (Millipore, mQ, USA). Then, after 30s, cement (2g) was introduced.

3. Results and discussion

Firstly the influence of MK on the intensity of efflorescence was considered. Then the pozzolanic reactivity of MK was studied, as well as the influence of MK on cement hydration and on porosity of cement past. Finally, links between the evolution of intensity of efflorescence and the parameters studied were highlighted.

3.1. Efflorescence test

After the efflorescence test, clarity of samples was measured. The evolution of the difference of clarity v.s. MK content in the cement is given in *Figure 3*.

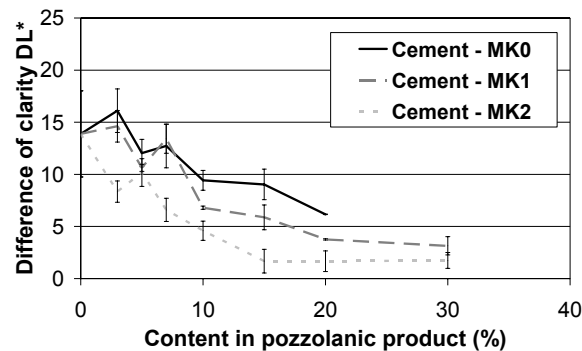


Figure 3. Influence of the MK content in cement on intensity of efflorescence.

We observed for low metakaolin content that there was an increase of efflorescence. Then for content over 10%, we noticed that MK2 is better for attenuation of efflorescence.

3.2. Pozzolanic reactivity of MK

MKs were introduced in a lime solution to evaluate their pozzolanic reactivity. The conductivity of the solution decreased, meaning that ions were more consumed than they were dissolved (*Figure 4*). MK2 showed a greater decrease of conductivity than other MKs. This order is kept for two various water-to-solid ratios (W/S) 20 and 50.

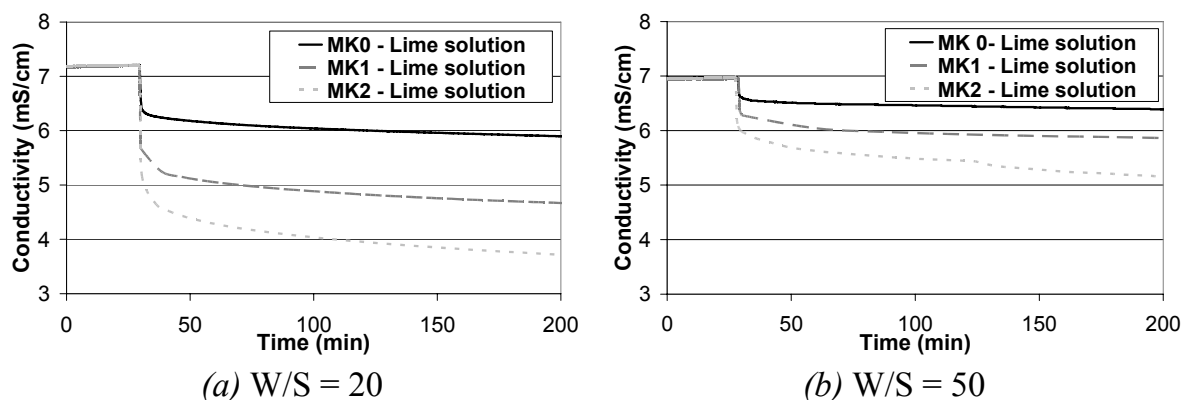


Figure 4. Evolution of conductivity of a lime solution in which MK was introduced.

The pozzolanic reaction (2) indicates that the decrease of conductivity should be due to calcium consumption. This hypothesis was verified by ionic chromatography measurements (*Figure 5*) in the lime solution where MKs were introduced with a water-to-solid ratio of 50.

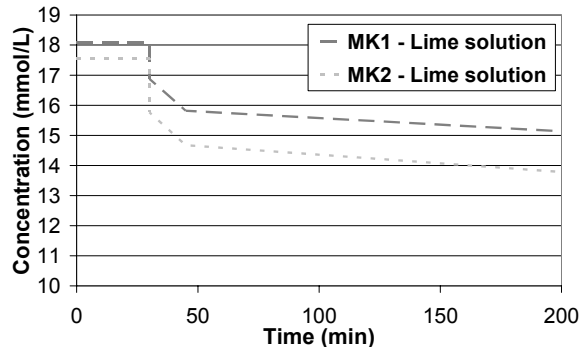


Figure 5. Evolution of calcium concentration.

It could be noticed that MK2 was more efficient in consuming Ca^{2+} and OH^- so MK2 had a pozzolanic reactivity higher than MK1 and MK0.

3.3. MK and cement

3.3.1. Influence on cement hydration

The influence of MK on cement hydration was studied by conductimetry. The precipitation of portlandite (CH) was taken as a benchmark to identify acceleration or delay in the cement hydration (*Figure 6*).

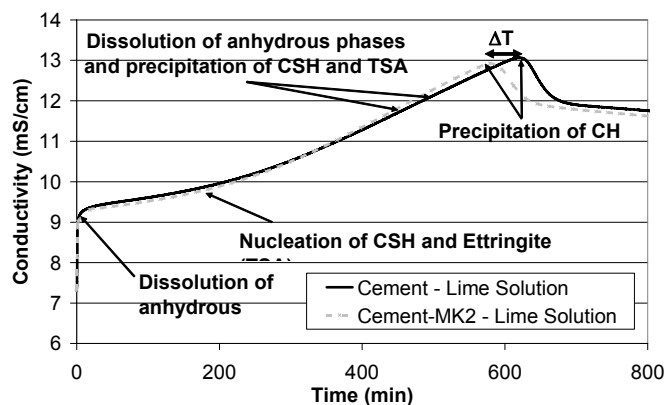


Figure 6. Influence of MK on cement hydration.

The time differences are given in *Table III*. Acceleration by MK was observed as it was expected from the literature (Takemoto and Uchikawa, 1980). We noticed that MK2 was the one that accelerated more the cement hydration.

Table III. Acceleration in time of hydration.

| Sample name | Cement - MK0 | Cement - MK1 | Cement - MK2 |
|------------------|--------------|--------------|--------------|
| ΔT (min) | 9 | 16 | 24 |

3.3.2. Influence on porosity of cement paste

For three rates (5, 10 and 20%) of substitution of cement by MK, we studied the modifications induced in the distribution of the pore size of the paste after 6 h of hydration. This time corresponds to the curing period before the efflorescence test.

By porosimetry, whatever the MK and the ratio, two groups of pore diameters were revealed (*Figure 7*). One was around 1 μm and the other one was under 0.1 μm . The porous distribution of a cement matrix presents inter residual grain pores which are commonly named capillary pores, for which the size is around 0.003-10 μm (Moon et al., 2006). Both families can be ascribed to capillary pores and their sizes are in accordance with the literature.

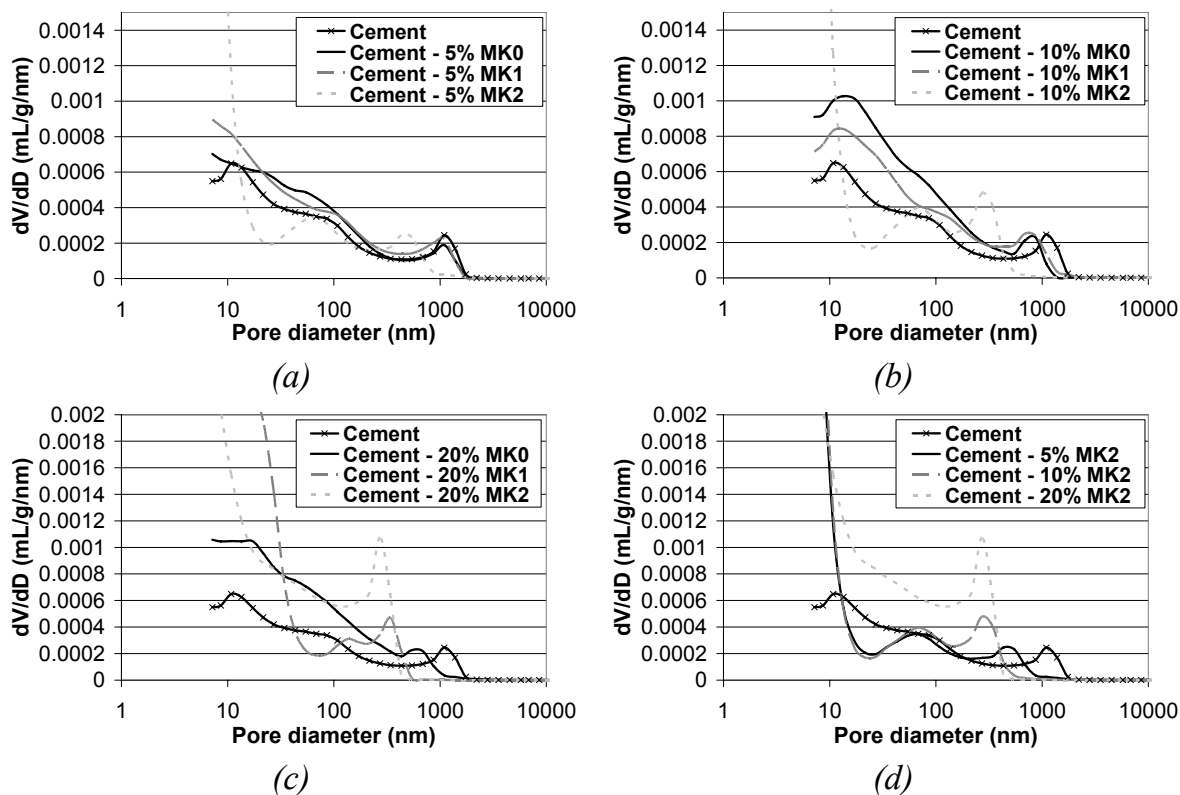


Figure 7. Influence of MK content on porosity.

We noticed that there was a decrease in the size of the pore of the first family with the increase of MK, in particular for MK2 (*Figure 7.d*). This result can be linked with the decrease in efflorescence, because capillary pores that permit the transport of ions are reduced.

3.4. Discussion

Thanks to the pozzolanic reactions, MKs consume calcium dissolved from anhydrous cement, leaving less calcium available for efflorescence formation. MK2 is the metakaolin which consumed more calcium. This fact can explain the acceleration of the precipitation of CH in this case. Acceleration of cement hydration explains that MKs reduce pore size entry, making transport of ions more difficult. MK2 reduced pore sizes more than MK1 and MK0.

Considering that MK2 reduced the efflorescence intensity by acting in a favorable way on two parameters, physical and chemical actions couldn't be distinguished.

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 for the formation of efflorescence, the variation of intensity of efflorescence was digitized and quantified by spectrophotometer.

It was determined that the formation of the efflorescence was reduced by substitution of cement by MK. Moreover, by studying the impact of substitution of cement by MK on the intensity of efflorescence, the correlation between efflorescence, calcium consumption, and porosity was highlighted. It was determined that a MK could be chosen by the way it consumes calcium and reduces pore size.

5. Acknowledgements

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