THE EFFECT OF METAKAOLIN ON INTERNAL SULPHATE ATTACK OF THE HEAT-CURED MORTARS

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Delayed ettringite formation (DEF) is a type of internal sulphate attack caused by heat-induced decomposition and/or prevention of normal ettringite formed during the initial hydration of cement at elevated temperature (above about 70°C) and its re-crystallization in the hardened matrix. DEF is a physico-chemical phenomenon inducing an expansion of the cement paste that could lead to cracking of concrete. In this paper, the effect of metakaolin on DEF of the heat-cured mortars was investigated. To fulfil the aim of this study, a portion of cement was replaced by metakaolin, with three different dosages (10, 20 and 30%). The mortars were heat-cured at early-age, and the tests of expansion, strength, dynamic elastic modulus and thermogravimetric analysis were carried on these mortars a period of 650 days. Additionally, scanning electron microscopy (SEM) observations were realized. The test results obtained highlighted the mitigation effects of metakaolin on DEF.

Keywords: *Metakaolin, Delayed ettringite formation (DEF), heat-cured mortar, expansion, concrete*

1. Introduction

Delayed ettringite formation is a type of internal sulphate attack caused by heat-induced decomposition and/or prevention of normal ettringite formed during the initial hydration of cement at elevated temperature (above about 70°C) and its re-crystallization in the hardened matrix [1-3]. DEF is a physico-chemical phenomenon inducing an expansion of the cement paste that could lead to cracking of cementitious materials. These cracks result in a decrease of the mechanical performances and durability parameters of the material. Highlighted in the middle of 1980s, this pathology exists in most parts of the world and has become one of a major problem for the durability of concrete structures and precast concrete elements, causing significant and costly damages.

The use of pozzolanic and slag admixtures in partial substitution of cement may be an efficient way to prevent concrete from DEF [4-7]. Indeed, Ramlochan et al. [4-5] showed that the efficacy of a particular pozzolan or slag in controlling expansion may depend on its Al_2O_3 content. Metakaolin, which contains a high amount of reactive Al_2O_3, was the most effective at controlling expansion at relatively low cement replacement levels. Slag and fly ash, which are also sources of Al_2O_3, were also effective at suppressing expansion at higher replacement levels. Whereas at the conventional replacement levels used in concrete (i.e., 8%), silica fume was not effective at controlling long-term expansion related to DEF when heat cured at high temperatures. However, the onset of expansion may only be delayed as a result of the lower permeability of the silica fume mortars. The most recently, according to data recorded on 500 days specimens, Nguyen et al. have studied the effect of natural pozzolan and fly ash on DEF [6,7]. They showed that the fineness of the natural pozzolan significantly affects the kinetics of expansion due to DEF: the use of finely natural pozzolan in partial replacement of cement can reduce or even eliminate the expansion of the DEF. In contrast, the substitution of cement for coarse natural pozzolan is not only ineffective, but also accelerates the expansion phenomenon. According to these authors, the fineness of the pozzolan, which determines the microstructure of the mortar material, indirectly influences the formation of ettringite delayed [6]. For fly ash, the substitutions greater than or equal to 20% by mass of Class F fly ash for cement in mortar is effective to inhibit even eliminate the expansion related to the long-term DEF [7].

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Table 1

Chemical and mineralogical composition of cement used, % in weight

Chemical composition									Composition (Bogue)			
CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	SO_3	L.O.I	C_3S	C_2S	C_3A	C_4AF
64.2	19.5	5.20	2.3	0.90	0.07	1.07	3.5	2.40	64.2	19.5	5.20	2.3

Table 2

Chemical composition and pozzolanic index of metakaolin used, % in weight

Chemical composition, % in weight							Pozzolanic index
CaO + MgO	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	Na_2O+ K_2O	L.O.I	Chapelle test (mg $Ca(OH)_2$/g)
0.30	55.0	40.0	1.4	1.5	0.8	1.00	1100

Table 3

Mix-design for mortar specimens (g)

Reference	Components				
	Cement	Metakaolin	Sand	Na_2SO_4	Water
Ref	450	0	1350	13.95	252
MK10	405	45	1350	13.95	252
MK20	360	90	1350	13.95	252
MK30	315	135	1350	13.95	252

The objective of this paper was to characterize the influence of metakaolin with the occurrence of delayed ettringite formation using the mechanical and microstructural experimental study in a period of 650 days. Additionally, the storage conditions after heat treatment affect considerably to DEF because of the leaching of alkali hydroxide into the surrounding storage solution [8]. In most of previous DEF researches, the heat-cured mortars were stored in water or lime-saturated water whereas in this work, the mortars were storaged in deionised water that was regularly renewed.

2. Experimental Study

2.1. Materials

Ordinary Portland cement, CEM I 52.5 N CE CP2 NF was supplied from Couvrot plant (France). A summary of its chemical and mineralogical composition is presented in Table 1. Its density and Blaine fineness were 3090 kg/m^3 and 400 m^2/kg, respectively; In order to enhance the internal sulphate resistance of mortars, the ARGICAL-M 1000 metakaolin (MK) used was a commercially available grade made from IMERYS (France). Its chemical composition and pozzolanic index are given in Table 2. Its density and BET fineness were 2400 kg/m^3 and 17 m^2/kg, respectively; French siliceous sand with a particle size of 0-2 mm and density of 2600 kg/m^3 is used to make the standardized mortars. This sand meets standard NF EN 196-1 [9] and is classified as non-reactive with respect to alkali silica reaction (standard NF-P 18-590 [10]). Siliceous sand was chosen because it leads to faster expansion than limestone sand [11].

2.2. Preparation, casting and curing of specimens

The mortar specimens were prepared according to NF EN 196-1 standards [9], with three different metakaolin dosages (10, 20 and 30%). Considering the binder content as the sum of cement and metakaolin dosages, each mortar was mixed with a binder-to-sand weight ratio (B/S) of 1/3 and the water-to-binder weight ratio (W/B) of 0.56 were maintained. The mixture composition is presented in Table 3. In order to accelerate and amplify the appearance of expansion, 3.1% (by weight of binder) of sodium sulphate (Na_2SO_4) were added to the mortars [6,7,12,13]. It was dissolved in the mixing water before introduction in the mixer bowl.

Mortars were cast under the form of 40 × 40 × 160 mm prisms in steel moulds, equipped with brass studs to measure the specimen expansion. The moulds were thus readily covered with a plastic plate to prevent evaporation and the mortars were submitted to a four-stage heat treatment. They were initially cured for 2 h at 20°C, the temperature was then increased to 80°C at a rate of 30°C per hour, the temperature was maintained at 80°C for 10 h, and finally decreased during 11 h to reach 20°C. This heat treatment is representative of treatments used in some precast industries [6,7].

The specimens were then removed from the moulds and stored in closed tanks containing deionised water at 20°C. In order to accelerate the expansion appearance of DEF, the bath water was regularly renewed during the whole period test [6-7]. It was changed weekly up to 8 weeks, every two weeks up to 24 weeks and every four weeks until the end of the test period.

2.3. Testing methods

The length measurement was performed in the air with an extensometer with a resolution of ± 1μm. The first measurements were carried out 25 h after the casting. For each mortar mix-design, the expansion value was obtained from the average of three different specimens. These specimens were then used to determine the dynamic Young's modulus (E_{dyn}) and the compressive strength (R_c) of each mortar. E_{dyn} was measured via non-destructive impulse excitation tests using a Grindosonic® apparatus. The compressive strength was determined on pieces of half prisms (European standard NF EN 196-1).

The solids fractions of the Ref, MK10, MK20 and MK30 mortars were crushed and then used for thermogravimetric analysis (TGA). TGA was carried out on METTLER TOLEDO TGA/DSC 1 in atmosphere at heating rise rate of 5°C/min, from ambient temperature to 600°C, the mass of the sample is about 20 mg. The TGA data was used to calculate the derivative thermogravimetric analysis (DTG).

The polished samples prepared from the mortar prisms at different testing ages were examined by scanning electron microscopy (SEM) to identify whether the ettringite phase formed in the samples due to internal sulphate reaction and follow the microstructural changes by expansion due to delayed ettringite formation, the SEM used for observations is a ZEISS ЄVO®40 equipped with a Back-scattered Electron (BSE) detector. The microscopic examinations were carried out on polished sections on mortar specimens. The specimens were coated with a gold deposit for observations using the SEM in High-Vacuum (HV) mode.

3. Results and analysis

3.1. Expansion

The expansion of Ref, MK10, MK20 and MK30 mortars for a period of 650 days are showed in Fig. 1, the expansion limit (0.04%) specified by LCPC [14] has been added in this Figure. These curves present in tree distinct expansion behaviors: Ref mortars exhibited the significant expansions, the plateau expansions of the Ref mortar was 1.74; MK10 mortars began to show signs of a slow indeed, after 650 days, its expansion was almost 0.5% however, this is not the ultimate expansion value. Otherwise, the expansion onset was significantly delayed (about 365 days) and the expansive rate was slightly less compared to Ref mortar; Whereas, the MK20 and MK30 mortars did not expand appreciably (i.e., ~0.005%) after 650 days. It is attributed to water absorption during immersion [7]. Our results demonstrate that the mortar containing 10% by mass replacement of cement by metakaolin does not have the inhibitive capacity of long-term expansion due to DEF, whereas, a replacement rate is greater than 20% it allows to mitigate or even eliminate in long-term expansion.

3.2. Evolution of compressive strength, dynamic elastic modulus and porosity

The results of compressive strength and the dynamic elastic modulus of the studied mortars are presented in Fig. 2 and Fig. 3, respectively. These results show that:

At the age of 29 days, the metakaolin substitution (MK10, MK20 and MK30) causes a decrease gradually in compressive strengths as the amount of metakaolin replacement increases compared to the reference mortar (Ref). On the other hand, with the mortars such as MK20 and MK30 which were not yet expanded present the improvements in both compressive strength and dynamic elastic modulus over time. This can be explained by the reason of combination of the cement hydration process and the effect of pozzolanic reactions.

In the case of Ref and MK10 mortars affected by delayed ettringite formation, they were seen that the expansion kinetics is directly correlated to changes in mechanical resistance of the dynamic modulus. Indeed, they showed that firstly, the compressive strength and the dynamic modulus improve slowly (effects of normal development of cement hydration), after that they decrease slightly which corresponds to induction

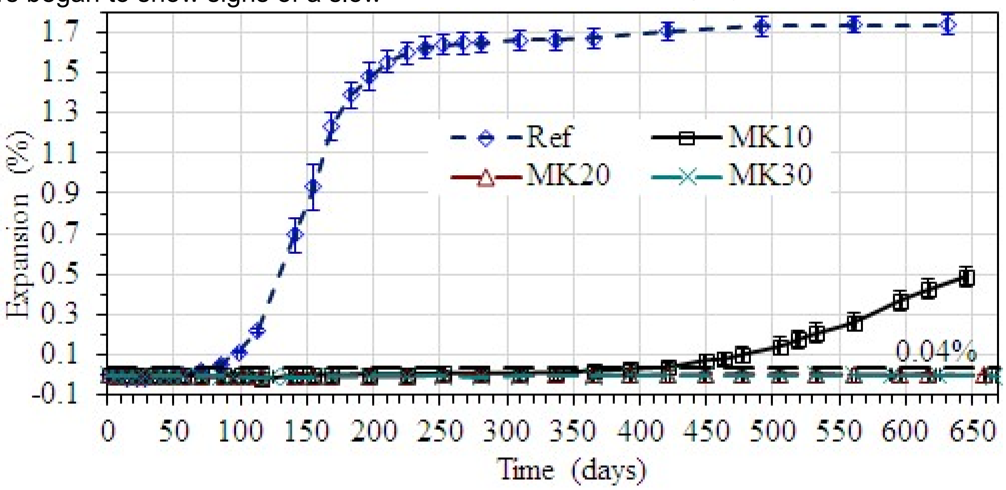


Fig. 1 - Expansion of reference sample and samples prepared with different dosages of metakaolin versus time.

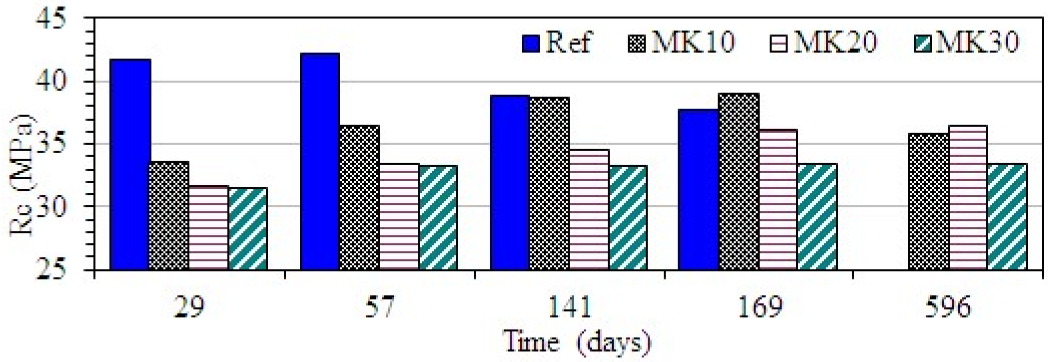


Fig. 2 - Compressive strength of reference sample and samples prepared with different dosages of metakaolin versus time.

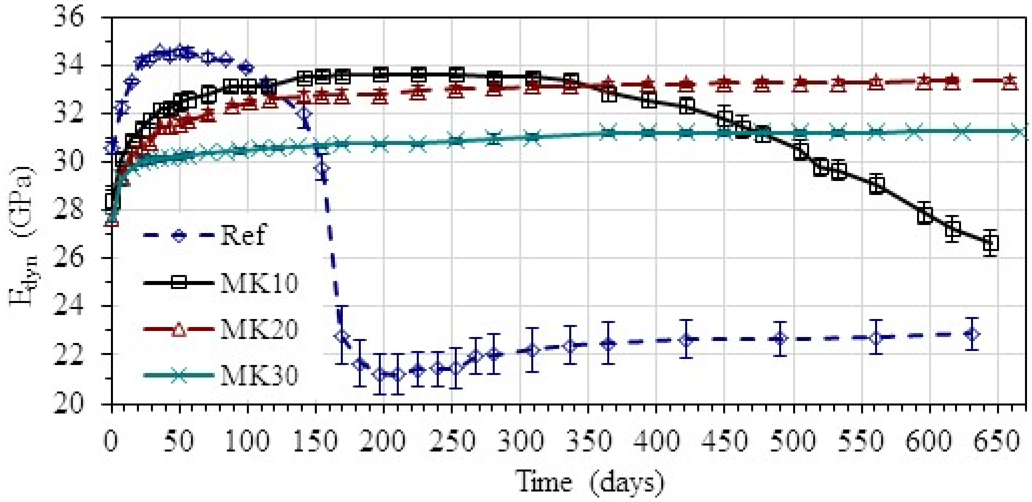


Fig. 3 - Dynamic Young's modulus of reference sample and samples prepared with different dosages of metakaolin versus time.

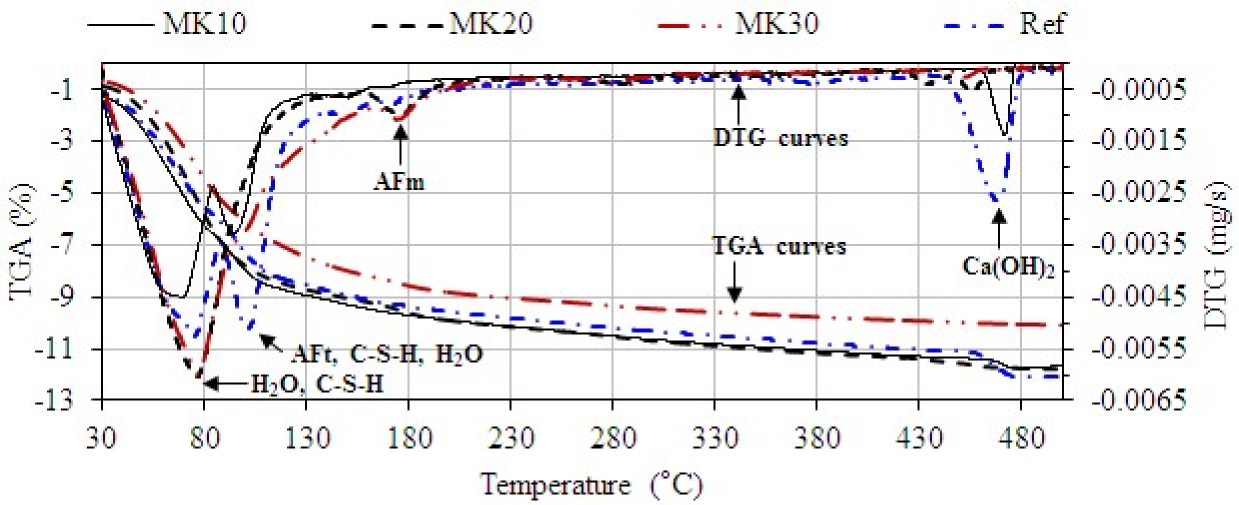


Fig. 4 - TGA and DTG results reference sample (at the age of 169 days) and samples prepared with different dosages of metakaolin (at the age of 596 days).

stage of the DEF mechanism, followed by a considerable diminution in compressive strength and a chute in dynamic elastic modulus which corresponds to acceleration phase of the DEF mechanism.

3.3. Thermogravimetric analysis

The data generated by Thermalgravimetric Analysis (TGA) and Derivative Thermalgravimetric (DTG) analysis on samples of Ref (at 169 days) and MK10, MK 20, MK30 (at 596 days) are presented in Fig. 4. Results of DTG analysis showed the presence of two distinct groups:

For samples of MK20 and MK30 at the age of 596 days (null expansions), it can be seen that their DTG curves exhibit clearly three distinct peaks in the temperature range 30-500°C: the first peak at about 80°C by the simultaneous evaporation of free water and chemically bound water within C-S-H gels; the second peak at approximately 175°C that corresponds to the dehydration of the hydrated calcium monosulfoaluminate (AFm), which was initially formed and embedded in the C-S-H gels during the heat treatment of the mortar, as already shown by Taylor et al. [1] and Tosun et al. [15]. This is in good agreement with the results of previous research works [7,16,17]; the third peak at around 470°C, which corresponds to the dehydroxylation of the portlandite.

Concerning samples of Ref (169 days, expansion at 1.23%) and MK10 (596 days, expansion at 0.37%) whose expansions are considerable, it is detected that the disappearance of the second peak at approximately 175°C which might be attributed to the conversion of AFm to calcium trisulfoaluminate (AFt). And the appearance of a new peak at roughly 105°C due to the simultaneous evaporation of AFt phase, free water, and chemically bound water within C-S-H gels.

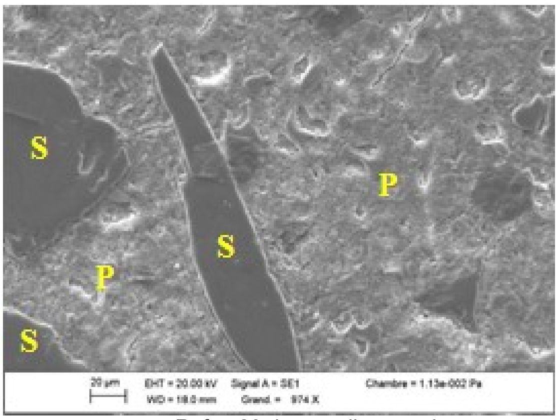
Comparison in two groups of DTG-curve mentioned above, it can be deduced that the peak observed at roughly 105°C on the DTG-curves of high expansion mortars (Ref at 169 days and MK10 at 596 days) is dictated primarily by the evaporation of water from the AFt phase. On other hand, Fig. 4 also shown the portlandite content decreases with the increase of metakaolin replacement level, even the portlandite contents were almost zero for MK20 and MK30, this is proven by the slope of TGA-curves and the valley area of DTG-curves in the range 450-480°C, these values close to zero for MK20 and MK30. This is due to the combination of the effect of portlandite consumption by the pozzolanic reactions between the amorphous silica of the metakaolin and the calcium hydroxide produced by the cement hydration reactions and the decrease in cement content (cement replacement by metakaolin).

3.4. Microstructural observations by SEM

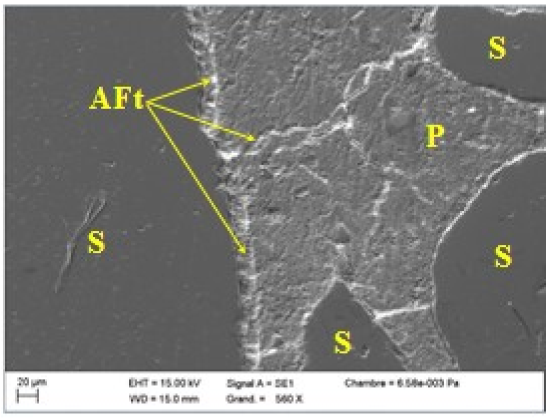
The SEM images obtained with back-scattered electron (BSE) on polished surfaces of mortars carried out at the age of 29 days, 169 days and 596 days are shown in Fig. 5. Similar to the DTG results, the BSE images characterized in two distinct groups:

For samples of Ref and MK10 (at 29 days), MK20 and MK30 (at 596 days) which did not show any expansion (Fig. 1) are presented in the Fig. 5a, 5c, 5e and 5f, respectively. These BSE micrographs showed a few micro-cracks that cross the cement paste and paste-sand interfaces, but did not find any trace of ettringite at the paste-sand rims. Thus, it can be concluded that the micro-cracks are caused by the sample preparation; and these samples did not undergo the delayed ettringite formation.

Fig. 5b and 5d correspond to the BSE images of Ref (at 169 day) and MK10 (at 596 days) which exhibited significant expansions (Fig. 1). The images showed clearly that many supplementary cracks appeared simultaneously in the cement paste and paste-sand interfaces, and the width of the rim cracks in these Figures is about 20 µm. It can be found clearly that these rim cracks were filled by ettringite and other cracks are still empty. These results confirmed that the cause of expansion due to the delayed ettringite formation and contributed to explain about the decrease in mechanical performances for mortars which have been subjected to the delayed ettringite formation.

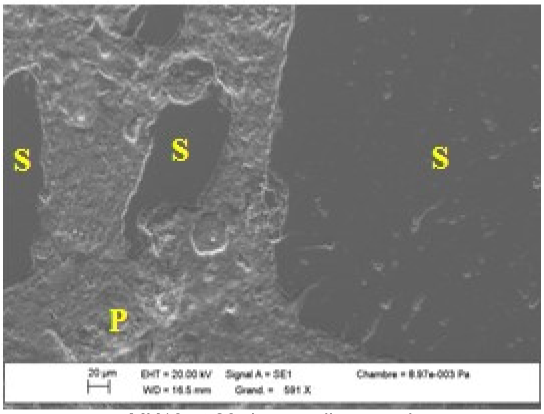


a. Ref at 29 days, null expansion

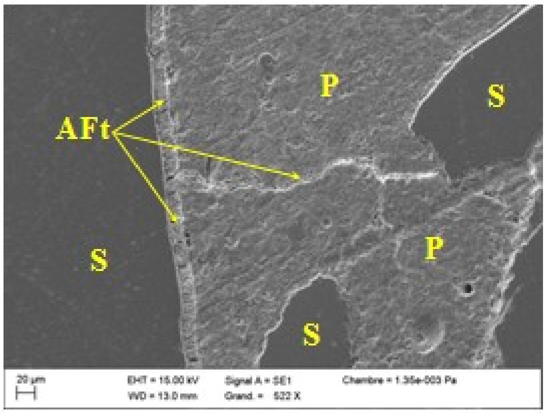


b. Ref at 169 days, expansion at 1.23%

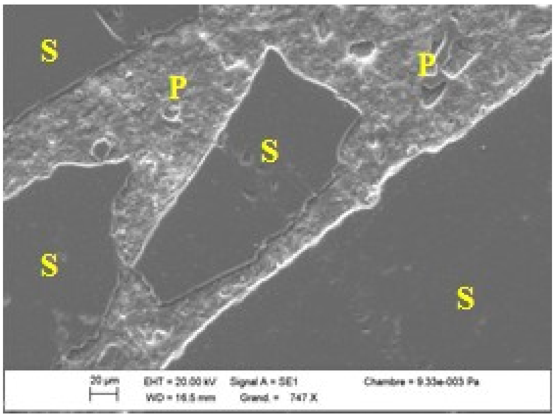
Figure 5 continues on next page



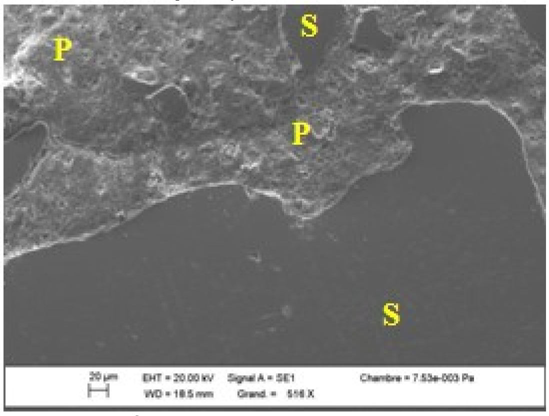
c. MK10 at 29 days, null expansion



d. MK10 at 596 days, expansion at 0.37%



e. MK20 at 596 days, null expansion



f. MK30 at 596 days, null expansion

Fig. 5. - BSE micrographs of reference sample and samples prepared with different contents of metakaolin (S: Sand, P: Paste, AFt: Ettringite).

4. Discussion of effect of metakaolin on DEF

The above experimental results indicated that the use of metakaolin in partial replacement of cement can inhibit or even eliminate the expansion due to DEF. This positive effect is considered as a combination of several factors:

The high pozzolanic index of metakaolin (Chapelle test of 1100 mg $Ca(OH)_2$/g) results the ability of portlandite consumption by the pozzolanic reactions is well. This leads to a reduction of the pH of the pore solution. Consequently, it causes a decrease of the concentration of SO_4^{2-} ions in the pore solution. It leads to limitation of the absorption of sulphates by C-S-H gels during heat treatment. Therefore, it reduces the expansion potential of the DEF. On the other hand, Min and Mingshu [18] also showed that if the $Ca(OH)_2$ concentration is low then the $Al(OH)^{4+}$ ions could migrate more freely and delayed ettringite could precipitate randomly in the pore solution without generating expansion.

The Al_2O_3 content of metakaolin is much larger than that of the cement (Table 1 and 2). Therefore, the partial replacement of cement by cement leads to a reduction in the SO_3/Al_2O_3 ratio and this will lead to a reduction of the expansion potential of the DEF [1,19]. The obtained results are generally in agreement with the results of Ramlochan et al. [4] who shown that the effectiveness of pozzolans or slag to control DEF expansion is related to their Al_2O_3 content. In addition, Ramlochan and et al [5] explained that an increase in Al_2O_3 rate leads to greater precipitation of monosulphate and would cause a decrease in the sulphate concentration in the pore solution. It leads to less adsorption of sulphate by the C-S-H gels and reduction in the expansion potential of the DEF.

Finally, it can be seen that the use of metakaolin in partial replacement of cement contribute to reduce the sulphate content in the cement-metakaolin binder (dilution effect). It leads to reduce the expansion potential of the delayed ettringite formation.

5. Conclusions

In this study, multiple techniques include expansion measurements, compressive tests, scanning electron microscopy, thermo-gravimetric analysis and ultrasonic measurements were used to investigate the mechanical properties and microstructure of the effect of metakaolin on

Delayed Ettringite Formation (DEF) of heat-cured mortars. Based on the finding of this experimental study, the following conclusions can be drawn:

1. The expansion development of delayed ettringite formation of the mortar is clearly correlated with the compressive strength, dynamic elastic modulus and microstructure.
2. The use of sufficient quantity of metakaolin enables to control expansion of the DEF: the incorporation of 10% of metakaolin in the mortar by mass replacement of cement was not sufficient to eliminate the long term expansion due to DEF. Nevertheless the expansion onset was significantly delayed. A higher replacement level, equal to 20%, may eliminate the long-term expansion due to DEF and improve mechanical properties.
3. This positive effect of metakaolin used in this research to control expansion of the delayed ettringite formation is considered as a combination of the portlandite consumption by the pozzolanic reactions, the Al_2O_3 high content and the dilution effect.

Acknowledgements

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