INFLUENCE OF THE MS-MODULUS ON THE EARLY AGE VOLUME CHANGE AND HEAT RELEASE OF SLAG AND FLY ASH PASTES ACTIVATED BY SODIUM HYDROXIDE AND SODIUM SILICATE

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Abstract

Blended pastes composed of slag and fly ash (ratio 50:50) are used with sodium hydroxide and sodium silicate as precursors. Each composition has the same solution to binder ratio (S/B) and the Ms-modulus varies between 1.04 and 1.58. All the experiments were conducted at a constant temperature of 20°C. The physical mechanisms related to the volume change in sealed condition are studied by means of repeated thermal variation using an adapted Autoshrink device, a new testing protocol and by means of isothermal calorimetry tests. From these tests, the autogenous strain, the coefficient of thermal expansion (CTE) and the heat release are determined. It is observed from the results, that an increase of the Ms-modulus causes a decrease of the autogenous shrinkage and the CTE. A linear relationship is observed between the autogenous shrinkage and the heat release by the binder. Thus, the development of the autogenous shrinkage seems to be mainly driven by one major mechanism in case of slag and fly ash paste activated by sodium hydroxide and sodium silicate.

Keywords: Alkali-activated materials, Ms-modulus, heat release, autogenous shrinkage, CTE

1. INTRODUCTION

Alkali-activated materials (AAM) are considered as a new alternative to Ordinary Portland cement, and are obtained by the reaction of calcium-silicates or alumino silicate-rich solid precursor with an alkaline solution. As a result of the chemical and microstructural properties of AAMs, they offer several potential advantages as compared to OPC. They are characterized by high strength development at early-age and an enhanced resistance to acid and sulphate attacks [1]. Despite these advantages, AAMs possess a crucial shortcoming, which is rapid hardening, resulting in very short setting times and large shrinkage deformations which can be up to seven times larger than that in OPC [2]. This induces a high risk of early-age cracking, which, in turn, endangers mechanical properties and durability performance [3,4].

The research of this paper is done in the context of the Interact project (INTERdisciplinary multiscale Assessment of a new generation of Concrete with alkali activated maTerials). The link of the website is https://interact.ulb.be/. Four universities (ULB, KULeuven, UGent, TU Wien) and one institution (VITO) are currently working on the subject of AAMs within the framework of this project. Each university/institution works on a precise field and the ULB mainly tackles the problem of the volume stability and mechanical behavior. The objective of this paper is to experimentally investigate the influence of the silica modulus (Ms) on the autogenous shrinkage, the coefficient of thermal expansion (CTE) and the heat release of AAMs pastes. This paper is divided in two parts. First, there is a description of the materials used, as well as the experimental methods. Secondly, the results will be presented. In the first place, there is an analysis of the heat release. After that, results of the autogenous shrinkage and the CTE will be analyzed.

2. MATERIALS AND METHODS

2.1 Materials and mixture proportions

This study considers pastes obtained by alkali-activation of fly ash and GGBFS. Two activators are considered: a sodium silicate solution (Na2O+ SiO2) and a sodium hydroxide solution 8M (NaOH). The sodium silicate solution is made with 18% in mass Na2O, 28.5% SiO2 and 53.5% H2O. The density is 1.37 g/mL. The silica modulus is the mass ratio between SiO2 and Na2O and will vary between 1.04 and 1.58.

4 different AAFS pastes were tested and were prepared according to the European Standard EN 196-1:2016 [5]. There is the same amount of fly ash and slags (50:50) and the 2 activators are used with deionized water. Compositions T1 to T4 have the same S/B (0.55) but Ms is changed between 1.04 and 1.58. Those compositions are presented in Table 1. All the tests are performed at an average temperature of 20°C.

Table 1: Mix proportion of the AAFS pastes

Mix	S/B	W/B	Ms	GGBFS (g)	FA (g)	Sodium silicate (g)	NaOH 8M (g)	H2O (g)
T1	0.55	0.45	1.04	50	50	22.9	11.1	21.5
T2		0.44	1.24			24.9	6.4	23.9
T3		0.42	1.44			26.5	2.5	25.9
T4		0.42	1.58			27.5	0.1	27.2

2.2 Experimental methods

Monitoring of the autogenous strain and the coefficient of thermal expansion

The original version of the auto-shrink device allows measuring the autogenous deformation as a function of time in an environment where the temperature remains constant. But this device was improved at the Université Libre de Bruxelles (ULB) in order to be able to apply controlled temperature variations to the samples [35]. These temperature changes allow determining the CTE by imposing a variation of -3°C to +3°C to the system. This change is produced by the thermal regulation system composed of a thermostatic bath and a convolution system as shown in Figure 1. The device is isolated from the environment by an insulated box in order to improve the thermal regulation. Hence, care is taken to the control of the temperature. In addition to all of this, the auto-shrink device contains 3 samples in the same test to ensure the repeatability of the results obtained [50, 51]. The picture from Figure 1 shows the auto-shrink device from the ULB. On this photo are present the different elements: the thermal regulator, 3 corrugated tubes, the insulator and the digital gauge.

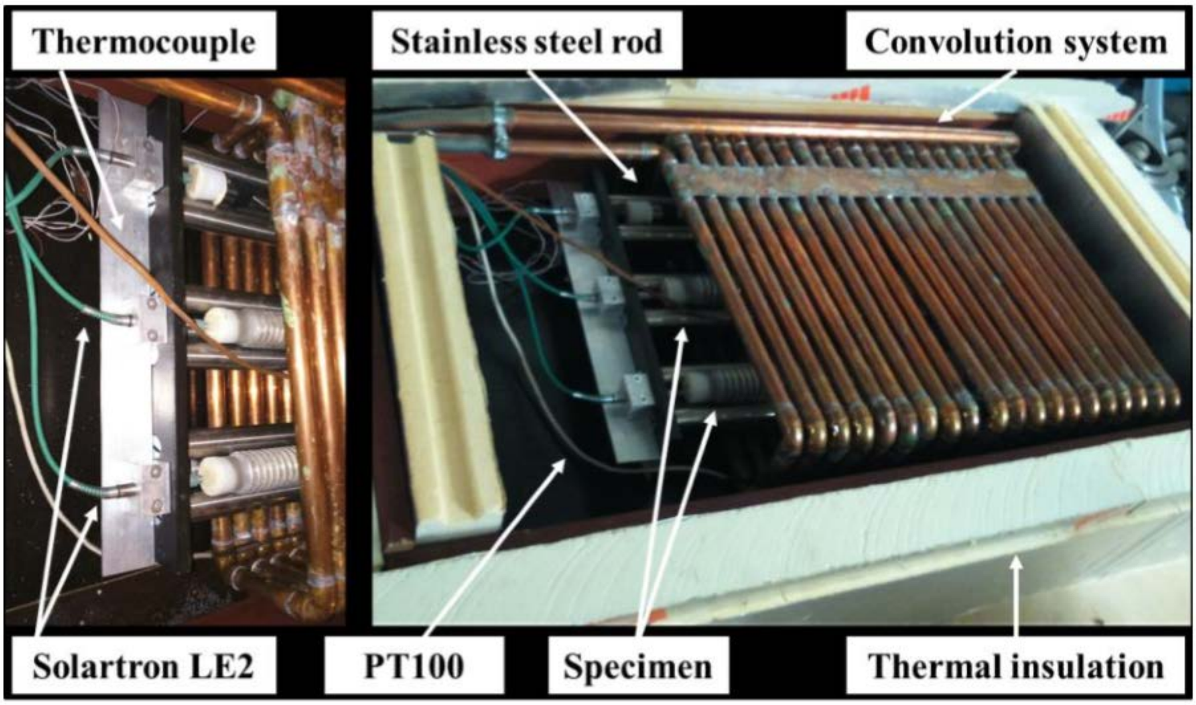

Figure 1: Adaptation of the Autoshrink device for the simultaneous determination of the CTE and the autogenous strain.

A complete and detailed presentation of the experimental setup, the test protocol and the data treatment can be found in [6,7].

Isothermal calorimetry

The heat release is determined with the TAM Air micro-calorimeter device [8]. This device is composed of 8 channels. Each channel is composed of two ampoules. One is filled with the paste (approximately 8g of paste), the other one is the reference filled with sand. For each test, it is necessary to use 2 channels in order to measure the heat release of 2 pastes for the repeatability of the results. The data acquisition consists of the heat release in function of the time. The test usually lasts 2 weeks because after that, the rate of heat flow is very low and the device is not accurate enough to monitor precisely the heat flow [7,8].

3. RESULTS AND DISCUSSION

3.1 Heat release

Figures 2 to 3 present the results of the different isothermal calorimetry tests. Results presented here correspond to the average of two tests. The heat flow is plotted in function of the equivalent age and 2 peaks are observed. The first one corresponds to the early dissolution of the FA and BFS. The second one corresponds to the acceleration of the formation of the reaction products, the C-N-A-S-H gels. The decrease between the two peaks is called "induction period" and is due to the fluid-solid transition time [9]. Globally, the Ms-modulus does not have a major influence on the heat release on long duration. At an equivalent age of 100h, the heat release is higher when the Ms-modulus is lower, but this tendency is not exactly the same later. The second peak of the heat flow is higher when the Ms-modulus is lower, and the induction period decreases.

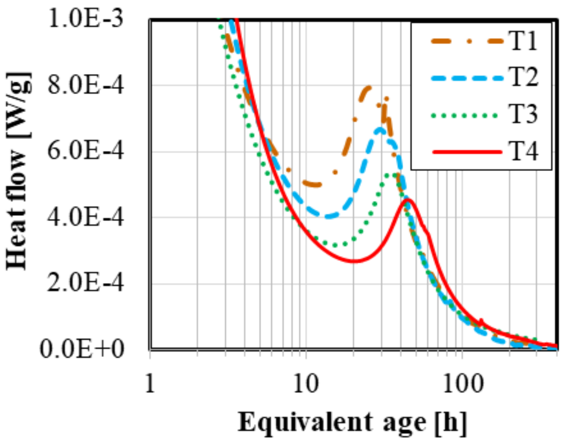

Figure 2: Heat flow

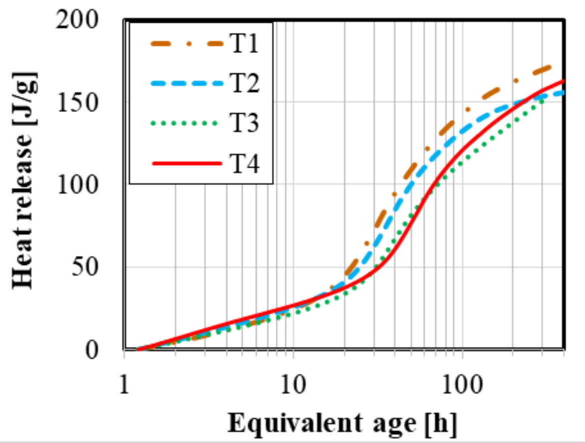

Figure 3: Heat release

3.2 Autogenous strain

Figure 4 shows the development of the autogenous shrinkage of AAFS pastes over a period of two weeks. Each results presented correspond to the average of two tests. Globally, the autogenous strain increases when the Ms-modulus decreases. A smaller Ms also means more NaOH in the composition. As for the results obtained with the heat release, this higher amount lead to a higher pH in the solution and may be at the source of the higher autogenous shrinkage. Similar trend was found by D. Kumarappa [10].

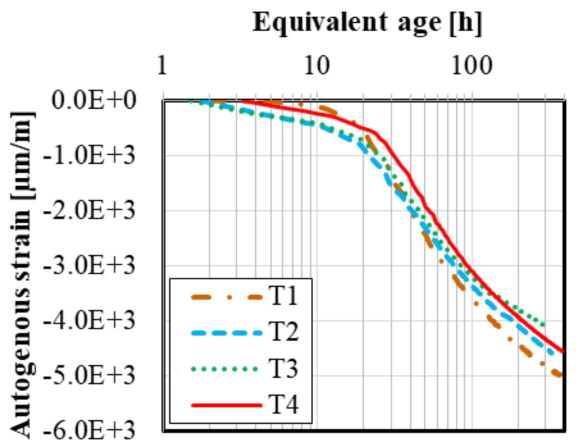

Figure 4: Autogenous shrinkage in function of the equivalent age

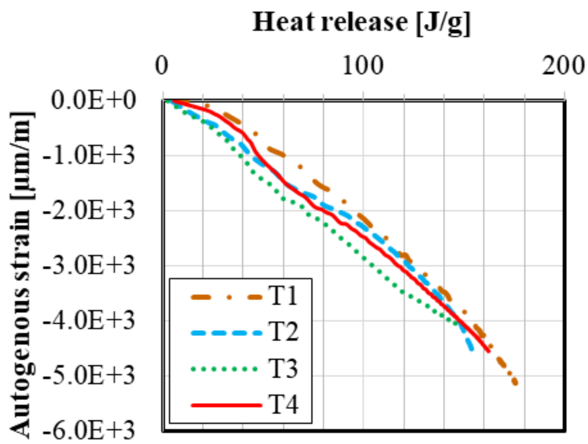

Figure 5: Autogenous shrinkage in function of the heat release

The development of the autogenous shrinkage is associated to the hydration process (formation of capillary pores) and thus the heat release [11]. Several mathematical expressions were developed in the literature to link both parameters. Power law and sinusoidal law were generally used [12]. In Figures 5, the development of the autogenous shrinkage is plotted according to the heat release. It is observed that the autogenous shrinkage evolved linearly according to the heat release. This suggests that there is one major reaction occurring and that induces autogenous deformations when slag and fly ash react with both NaOH and sodium silicate. The slope of this linear trend increases when the silica modulus decreases. The end is less linear. This is probably due to the precision of the isothermal calorimeter. The rate of heat flow is really low at the end of the test and the device will not monitor accurately this heat flow. When Ms is plotted in function of the slope (Figure 6), there is a parabola that is formed. This means that there is an optimum value of Ms to minimize the shrinkage.

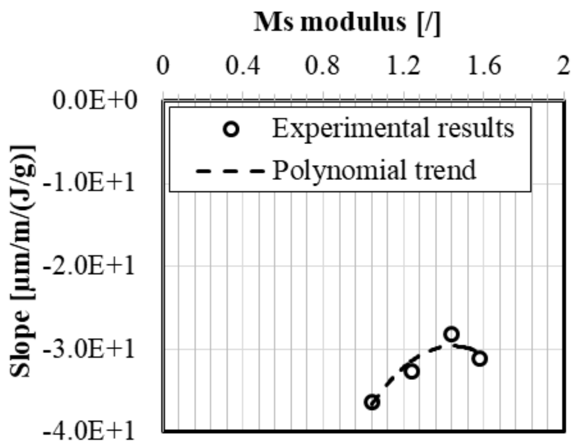

Figure 6: Ms in function of the slope of the linear relation observed in Figure 5 between the autogenous strain and the heat release

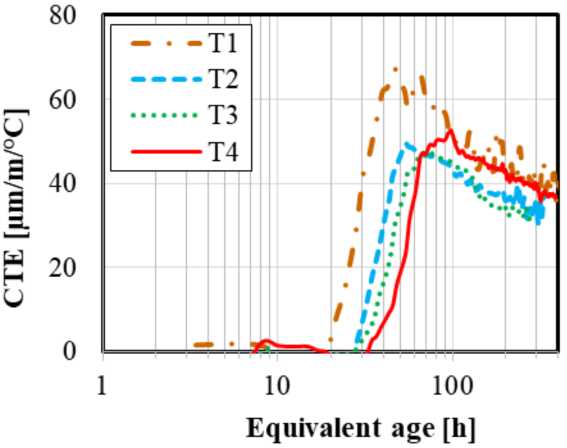

Figure 7: Coefficient of thermal expansion

3.3 Coefficient of thermal expansion

Figure 4 shows the development of the coefficient of thermal expansion of AAFS pastes over a period of two weeks. Each results presented correspond to the average of two tests. The development of the CTE and the magnitude of the CTE are both related to the Ms-modulus. For each composition, the evolution of the CTE can be divided in 3 stages. Firstly, the value of the CTE is very low during the first hours after setting (around 3µm/m/°C). Secondly, an increase of the CTE is observed till a maximum value between 50 and 65 µm/m/°C. This increase starts sooner for pastes with a lower Ms-modulus. This maximum value of the CTE is reached first for pastes with lower Ms-modulus at an equivalent age between 50 and 90 hours and is higher in case of low Ms-modulus. Thirdly, the CTE decreases till a value between 30 and 40 µm/m/°C at an age of 2 weeks. No specific trend is obtained between the Ms-modulus and the CTE reached at an equivalent age of 2 weeks. This can be explained by the fact that, when the Ms-modulus decreases, there is a small increase of the W/B ratio. Water has a CTE value higher than the one of solids. This means that when there is less water, the CTE is decreased. This can explain the fact that CTE of AAM pastes decreases as the W/B ratio decreases [13]. However, the E-modulus of the solid skeleton has also an influence on the CTE. In case of lower E-modulus, the pressure applied by the water for a temperature change causes higher volume change. Both properties should be considered simultaneously to interpret the results of the CTE obtained at later ages.

4. CONCLUSIONS

Based on the different experiments conducted in this paper, some conclusions can be drawn on the influence of the Ms-modulus on the early age volume change and heat release of slag and fly ash pastes activated by sodium hydroxide and sodium silicate.

The heat release increases when the Ms decreases. The study of the autogenous shrinkage highlighted the influence of the Ms-modulus. A higher Ms will decrease the autogenous shrinkage. It also confirmed the higher value for AAMs paste compared to OPC paste. And while plotting it in function of the cumulative heat release, a linear trend was discovered. This suggests that only one mechanism linked to the hydration is the main driver of the development of the autogenous shrinkage. The exact reason could not be identified and will have to be the object of further work where the chemical shrinkage will have to be characterized, as well as the evolution of the porosity (total quantity as well as pore distribution). Also the development of hydrates is also a data to be known. However, this information is not easy to determine, as a chemical shrinkage test cannot be carried out as for cement pastes, the pore size is so small compared to OPCs that it may not be possible to correctly determine the porosity distribution as well as the total pore quantity. A review and validation of a suitable method is therefore surely necessary.

The coefficient of thermal expansion was also studied and was found to be higher compared to an OPC paste. A smaller Ms increases the CTE at early age while at later ages no clear trend is observed between the magnitude of the CTE and the Ms-modulus.

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