

## **The hydration mechanism and hydrothermally hardened specimens made of autoclaved OPC– GGBFS – GS blends**

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### **Abstract:**

Different autoclaved specimens were prepared using ordinary Portland cement (OPC) and ordinary Portland cement– ground granulated blast-furnace slag (OPC-GGBFS) with the presence and absence of sand. All autoclaved specimens were prepared by the hydrothermal curing at a pressure of 8 atm. of saturated steam for different autoclaving ages of 0.5, 2, 6, 12 and 24 hours. The Kinetics of hydration process were studied via determination of chemically combined water and free lime contents at the different autoclaved ages up to 24 hours. The specimens made of OPC and OPC-GGBFS-GS blends were found to have higher strength values at almost all autoclaving ages. This attributed to the formation calcium of silicate hydrates (CSH) and calcium hydroxide (CH) hydrates, as the main hydration products, which possess a stronger hydraulic character with higher compressive strength. The hydrothermally hardened OPC-GGBFS pastes were found to have weaker strength, which could be due to the formation of calcium aluminosilicate hydrates ( $C_3ASH_4$ ).

**Key Words:** Ordinary Portland cement (OPC), Ground sand (GS), Ground granulated blast-furnace slag (GGBFS).

## 1. Introduction:

Extensive studies were reported on the hydration mechanism of hydrothermally hardened slag-alite ( $C_3S$ ) pastes. A mechanism of the hydrothermal process involving  $C_3S$  and slag grains was postulated on the basis of the results <sup>[1]</sup>. Early strength development claimed to be mainly as a result of  $C_3S$  hydration, whereas the later strength was attributed to the hydration products of the granulated blast-furnace slag.

Abd-El-Wahed et al. <sup>[2]</sup> investigated the effect of quartz on the hydration characteristics of hydrothermally hardened granulated slag- $C_3S$  pastes by studying the compressive strengths of the hardened product, determination of free lime and combined water contents.

High slag cement (HSC) and high slag cement (HSC) - ground sand (GS) specimens were hydrothermally treated at pressures of 8 atm. of saturated steam for different autoclaving ages. Compressive strength tests were done on the hydrothermally hardened specimens. Then hydration kinetics, phase composition and microstructure of the formed hydrates were studied using the ground dried samples. The results of compressive strength could be related to the phase composition and microstructure of the formed hydration products <sup>[3-5]</sup>. The hydration of Portland cement pastes containing three types of mineral additive; fly ash, ground-granulated slag, and silica fume using differential thermal analysis, thermogravimetric analysis (DTA/TGA) and isothermal calorimetry were investigated by Pane and Hansen <sup>[6-7]</sup>. Calcium silicate hydrates was formed at elevated temperature and pressure. At 180°C, the initially formed amorphous calcium silicate gel [C-S-

H] was transformed to a well-defined crystalline phases. The stability of which is primarily dependent on the C/S ratio in the CaO-SiO<sub>2</sub>-H<sub>2</sub>O system and the hydrothermal conditions. Hillebrandite [C<sub>2</sub>SH], a-dicalcium silicate hydrate [□-C<sub>2</sub>SH] and h-tricalcium silicate [h-C<sub>6</sub>S<sub>2</sub>H<sub>3</sub>] were predominantly the stable phases in the lime-rich part of the CaO-SiO<sub>2</sub>-H<sub>2</sub>O system and were typically associated with high permeability and compressive strength retrogression. The coexistent stably in aqueous solution with silica in the silica-rich part of the CaOSiO<sub>2</sub>-H<sub>2</sub>O system of Gyrolite [C<sub>2</sub>S<sub>3</sub>H~<sub>2</sub>], tobermorite [C<sub>5</sub>S<sub>6</sub>H<sub>5</sub>], truscottite [C<sub>7</sub>S<sub>12</sub>H~<sub>3</sub>] and xonotlite [C<sub>6</sub>S<sub>6</sub>H] have all been reported [8].

Several studies reported the test methods for assessing pozzolanic activity. There are two methods, direct and indirect methods. The direct method monitors the presence of Ca(OH)<sub>2</sub> and its subsequent reduction in abundance with time as the pozzolanic reaction proceeds, using analytical methods such as X-ray diffraction (XRD), thermo-gravimetric analysis (TGA) or classical chemical titration. The more commonly used method is the direct method which involves chemical titration to determine the dissolved Ca<sup>2+</sup> and OH<sup>-</sup> concentrations in a solution containing CEM-I and the test pozzolana. [9].

The objective of the present study is to study the main hydration characteristics of autoclaved building products derived from ordinary Portland cement (OPC) ground granulated blast furnace slag (GGBFS) and ground sand (GS). The values of chemically combined water, free lime, and compressive strength of hardened cement specimens were measured as a

function of curing time up to 24-hours. To follow up the hydration rate of the prepared samples, some selected hardened samples were investigated using the XRD and SEM techniques.

## 2. Experimental

### 2.1. Materials:

Ordinary Portland cement (OPC) with a Blaine surface area of 2932 cm<sup>2</sup>/g and ground granulated blast-furnace slag (GGBFS) (a by-product of big iron manufacture) were supplied from, Libya Zletin Cement Company. The ground sand (GS) used in this study was obtained by grinding of local sand to a Blaine area of 3450 cm<sup>2</sup>/g.

### 2. 2 Preparation of the hardened cement pastes:

Dry mixtures were prepared from Portland cement (OPC), ground granulated blast-furnace slag (GGBFS) and ground sand (GS). The percentage composition of OPC-GGBFS-GS dry mixtures are given in Table (1). Each dry mixture was first mixed using ethanol for 2 hours to obtain a homogeneous mixture. The mixture was then heated at 90°C for 3 hours to evaporate ethanol, and then was kept in air tight containers.

**Table (1):** Percentage composition of OPC – GGBFS - GS dry mixtures

Mix	Composition (Wt., %)		
	OPC	GGBFS	GS
M0	100	-	-
MI	50	50	-
MII	50	25	25
MIII	40	30	30
MIV	50	20	30

### 2.3 Curing and Stopping of Hydration

Various cement pastes were prepared by mixing the dry solid mixture with water using the water/cement (W/C) ratio of 0.28 by weight. The cement pastes were moulded in a cylindrical specimens having 2 cm diameter and about 2 cm height under hydraulic pressure of 50 kg/cm<sup>2</sup>. After curing at 100 % relative humidity for one day then dried at 80°C overnight and kept in a desiccator until the desired time of autoclaving was reached. The specimens of each mixture were cured under hydrothermal conditions in an autoclave at a pressure of 8 atm of saturated steam for 0.5, 2, 6, 12, and 24 hours. At the end of autoclaving process, the specimens were removed and a fraction of hardened specimen was first grounded and the hydration reaction of the hardened cement pastes was stopped using methanol-acetone mixture

(1:1 by volume) according to the method reported in earlier studies <sup>[10]</sup>. The specimen was then then dried at 80<sup>0</sup>C for 24 hours to remove the free water and kept in a desiccator.

### **3. Methods of Physicochemical Measurements:**

#### **3.1. Compressive strength determination:**

After each autoclaving time the compressive strength test was performed on the hardened cement pastes using three cylindrical specimens for each autoclaving time and the average value was recorded as Kg/cm<sup>2</sup>. This test was performed using a Ton industric machine (West Germany) for maximum load of 60 tons.

#### **3.2. Kinetics of hydration:**

The kinetic of hydration process was studied via determination of non-evaporable (chemically-combined) water (W<sub>n</sub>, %) and free lime (CaO, %) contents for the hardened specimens at different autoclaving time.

##### **3.2.1. Determination of chemically combined water content (W<sub>n</sub>, %)**

The chemically combined water content (W<sub>n</sub>, %) is used as an indication for the degree of cement hydration. W<sub>n</sub> is that portion retained in the sample after the free water is removed. The W<sub>n</sub>, % is considered as the percent of ignition loss of the dried sample (on the ignited weight basis). Approximately 2 grams of the pre-dried sample were ignited for one hour at 1000<sup>0</sup>C in an adjustable muffle furnace, cooled in a desiccator and then weighted. The

chemically-combined water content (i.e., the amount of water retained after drying) was calculated as  $W_n$  (%) using the following equation:

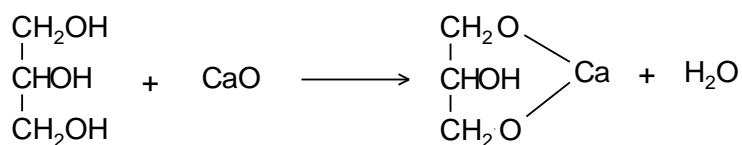
$$W_n (\%) = [(W_1 - W_2) / W_2] \times 100$$

Where,  $W_1$ : is the weight of the dried sample before ignition (g) and  $W_2$ : is the ignited weight of sample (g).

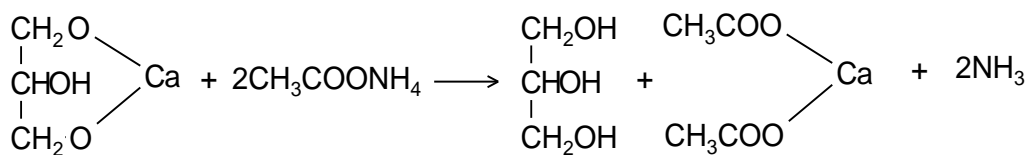
The results of  $W_n$ , % were corrected for the water of free lime present in each sample following the method reported by Didamony et al.,<sup>[11]</sup>.

### 3.2.2 Determination of the free lime content (CaO, %):

The free lime content of each hydrated cement paste was estimated by the following method; the sample (0.5 g) was poured in 40 ml of a glycerol-ethanol mixture (1:5 v/v), together with a small amount of anhydrous  $BaCl_2$  (0.5g) as a catalyst, and phenolphthalein as an indicator. This mixture was kept in a conical flask, fitted with an air reflux, and heated on a hot plate for 30 minutes (the color becomes pink). The contents of the flask were titrated with a standardized alcoholic ammonium acetate solution until the pink color just disappeared. If the pink color reappears, the titration was completed with ammonium acetate solution until no further appearance of pink color<sup>[12]</sup>. In the solution, where only calcium glycerate would be present, free CaO will reacts with glycerol and consequently would not present in solution. The reactions are as follows:



Then:



The free lime percentage was calculated as follow :

$$\text{CaO, \%} = [(W1 \times V) / W] \times 100,$$

Where, W = original weight, W1 = weight of CaO equivalent to the amount of the added alcoholic ammonium acetate, and V = volume of ammonium acetate per milliliter.

### 3.3 Phase composition and microstructure :

The phase composition of the formed hydrates was identified using X-ray diffraction (XRD) analysis. The morphology and microstructure of the hydrated phases were identified using scanning electron microscopy (SEM).

#### 3.3.1. X-ray diffraction analysis (XRD):

X-ray diffraction technique were carried on some selected hydrated and dried cement pastes. The sample was ground in an agate mortar as gently as possible to 10 – 15 μm. It was then packed into the specimen holder, which



was a metal plate 1mm. thick, and having a rectangular hole larger than the area irradiated by the X-ray beam and backed by a glass plate. It was finally pressed using a glass microscope slide. A stabilized X-ray generator (Bruker), equipped with D8 Advance Cu K $\alpha$  target with secondary nano chromator and fitted with a copper target X-ray tube, and Geiger Muller tube was used. The setting used were tube run at 30 KV, 15 mA divergence, receiving and scatter slides, 1,1 cm and 1, respectively, and chart speed 100 c.p.s.

### **3.3.2. Scanning electron microscopy (SEM):**

A JSM-5410 Scanning electron microscope (SEM), was used to study the morphology and microstructure of some selected cement pastes. Freshly fractured specimens were coated with a thin film of gold under vacuum evaporator with cathode rays.

## **3. Results and discussion**

### **3.1. Compressive strength:**

The results of compressive strength for the autoclaving mixes (mixes MII- MIV) made from 50/25/25, 40/30/30 and 50/20/30 of OPC/GBFS/GS, are given in Table (2). The same trend of increasing the compressive strength values with increasing the autoclaving ages up to 24 hours as in mixes M0 and MI was observed. However, the compressive strength of these mixes showed a notable higher values as compared to the mix MI and comparable values to those of mix M0 during nearly all ages of autoclaving. This improvement in the compressive strength of values for these mixes as

compared to mix MI is mainly attributed to the pozzolanic interaction between lime liberated from the hydration of the ordinary Portland cement with silica present in slag and sand. This led to the formation of additional amounts of nearly amorphous and ill-crystallized forms of calcium silicate hydrates (CSH) possessing a relatively high hydraulic characters.

**Table 2 . Compressive strength values (kg/cm<sup>2</sup>) versus autoclaving age of the hardened pastes of mixes M0, MI, MII, MIII and MIV.**

Autoclaving age (h)	Mixes				
	M0	MI	II	MIII	MIV
0.5	532.74	367.07	432.09	458.03	445.03
2	581.47	451.53	552.23	526.24	522.99
6	636.69	464.52	646.43	675.67	604.20
12	766.62	510.00	695.16	730.89	698.40
24	782.87	513.25	786.11	841.34	792.60

### 3.2. Hydration Kinetics:

The kinetics of hydration of each mixture was studied by determining the non-evaporable (chemically-combined) water (W<sub>n</sub>, %) and the free lime contents (CaO, %) in the autoclaved specimens at various age of autoclaving.

### 3.2.1. The non-evaporable (chemically- combined) water content

The results of non-evaporable water content of the neat OPC (mix M0), showed a relatively high value during early age of autoclaving (0.5 h), followed by a slight gradual increase up to the final ages of autoclaving (24 hours). These findings were attributed to the progress of hydration of OPC. The initial high combined water value after 0.5h. of autoclaving indicates a fast rate of hydration reaction. Results of the chemically-combined water obtained from the autoclaved specimens (mix MI: 50% OPC + 50% GGBFS), also showed the same trend as the case for mix M0, but with a notable lower values while. The lower combined water values obtained from mix MI can be explained in terms of formation of a lower amounts of hydration products, as a results of replacing 50% OPC by GGBFS. The result of chemically-combined water for the autoclaved mixes (mixes MII-MIV) made from 50/25/25, 40/30/30 and 50/20/30 (OPC/GBFS/GS, respectively) are given in Table (3). The chemically-combined water contents showed the same trend with autoclaving age as in mix M0, but with including the lower values during all ages of autoclaving. Such results are opposite to the compressive strength results and can be attributed to the nature of the hydration products formed from the interaction between lime liberated from hydration of ordinary Portland cement and silica present in slag and sand. The resulted calcium silicate hydrates have an ill crystallized character with high binding properties. This could explain the increase in the compressive strength values, the low water contents, and therefore, the low  $W_n$ -values.

**Table 3. Chemically-combined water content (W<sub>n</sub>, %) versus autoclaving age of the hardened pastes of mixes M0, MI, MII, MIII and MIV.**

Autoclaving age (h)	Mixes				
	M0	MI	II	MIII	MIV
0.5	8.990	4.565	4.889	4.949	4.310
2	10.230	6.328	5.000	5.093	4.830
6	10.922	6.899	5.787	6.042	5.090
12	11.397	6.279	6.241	6.399	5.640
24	11.997	8.123	6.694	7.230	6.900

### 3.2.2. The free lime contents:

The result of the free lime contents of mix M0 shows a continuous slight increase with the increase of the of autoclaving age, up to the final age (24 hours). This could be attributed to the hydration of Portland cement and formation of calcium hydroxide (CH). But the results of the free lime of mix MI, shows a very lower values from the early age of autoclaving, followed by continuous decrease up to the final age (24 hours), Table (4).

The free lime contents values for the mixes MII-MIV are given in Table (4). The values of the free CaO % showed the same trend as in case of mix MI but with notable lower values during all ages of autoclaving . This decrease in the free lime values is attributed to the presence of sand as a partial replacement of OPC with slag. So the lime liberated from the

Portland cement hydration is consumed via pozzolanic reaction with silica present in both sand and slag to form more calcium silicate hydrates.

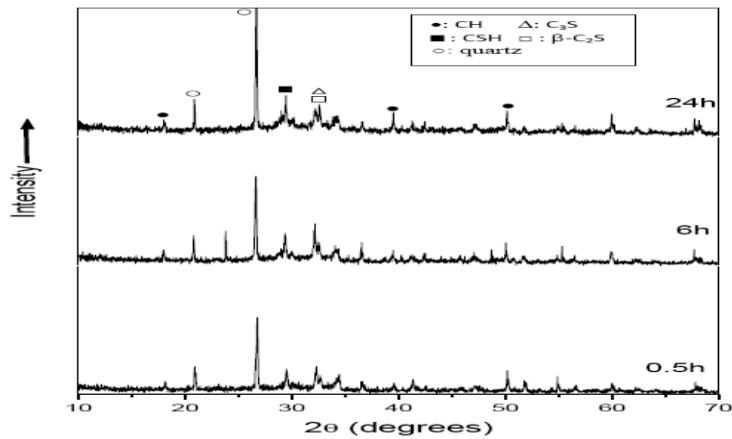
**Table 4 . Lime content (CaO, %) versus autoclaving age of the hardened pastes of mixes M0, MI, MII, MIII and MIV.**

Autoclaving age (h)	Mixes				
	M0	MI	II	MIII	MIV
0.5	3.18	0.91	0.76	0.57	0.71
2	3.95	0.71	0.67	0.50	0.54
6	4.24	0.60	0.53	0.19	0.28
12	4.60	0.58	0.50	0.13	0.20
24	4.67	0.51	0.36	0.04	0.19

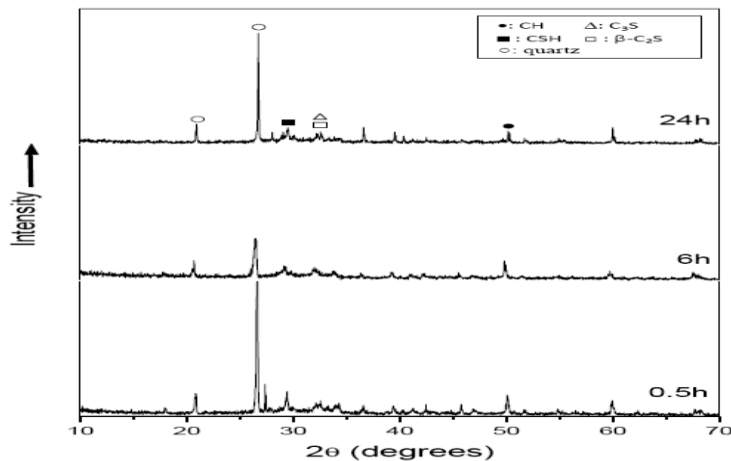
### 3.3.3 X-ray diffraction (XRD) analysis

The results of Figs.(1-3) showed that the intensities of the peaks characterizing  $C_3S$  and  $\beta-C_2S$  (the anhydrous constituents of ordering Portland cement) and quartz, decrease with increasing age of hydration. Meanwhile, the intensities of the peaks characterizing the hydration products, namely calcium silicate hydrates (CSH) and (CASH) increase with increasing time of autoclaving. It was also observed that as the percentage replacement of ordering Portland cement with slag and/or sand increases, the intensity of the main (CH) peaks will also increase, especially after 24 hours of autoclaving. This decrease in the main peaks characteristics for (CH) is accompanied with a marked increase in the intensity of the main peak

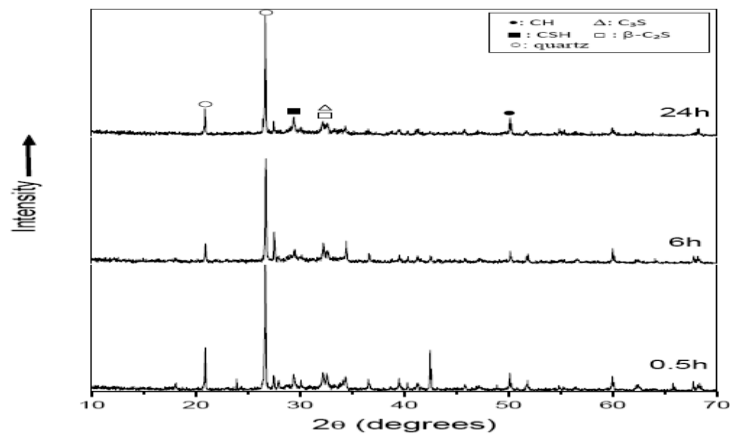
characteristic for calcium silicate hydrates (CSH), which attributed to the formation of additional amounts of calcium silicate hydrates as a result of the pozzolanic reaction.



**Figure (1):** XRD patterns of autoclaved specimens made from 50 % OPC, 25% GGBFS and 25% GS (mixMII).



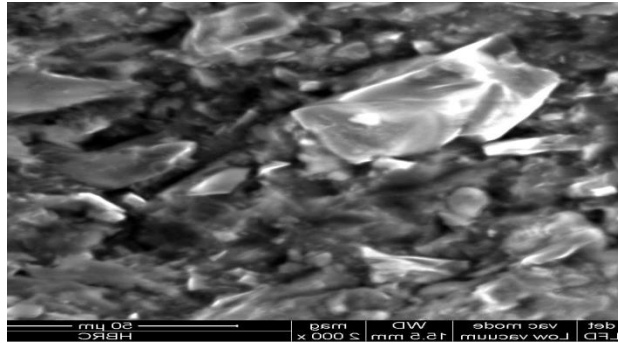
**Figure (2):** XRD patterns of autoclaved specimens made from 40% OPC, 30% GGBFS and 30% GS (mix MIII).



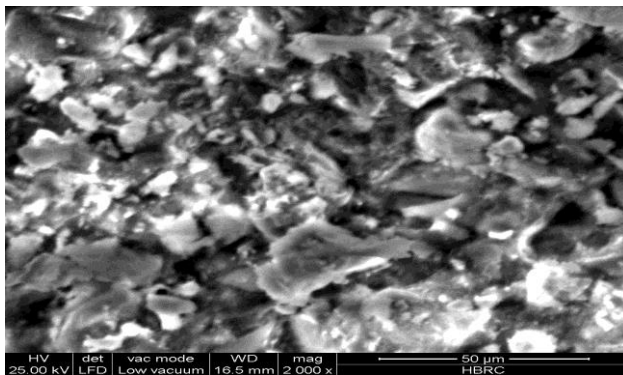
**Figure (3):** XRD patterns of autoclaved specimens made from 50% OPC, 20% GGBFS and 30% GS (mix MIV) .

### 3.3.4 Scanning electron microscopy (SEM):

The microstructure of the autoclaved specimens made from 40/30/30 of OPC/GBFS/GS (mix MIII ), after 0.5, 6 and 24 hours of autoclaving are given in Figs. (4-6). The SEM micrograph indicated the formation of the same hydration products as in the case of neat OPC (mix M0), with a notable more dense microstructure, especially at later ages of autoclaving (24 hours). Also the crystals of calcium hydroxide (CH) and porosity appeared in paste made of neat OPC (mix M0) are relatively disappeared in these pastes, as a result of its consumption in pozzolanic reaction with silica present in slag and/or sand.

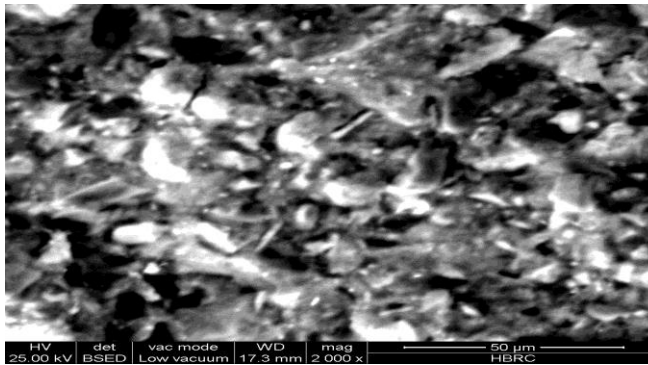


**Figure (4):** SEM micrograph for the autoclaved specimens made from 40% OPC, 30% GGBFS and 30% GS (mix MIII) after 0.5 hours.



**Figure (5):** SEM micrograph for the autoclaved specimens made from 40% OPC, 30% GGBFS and 30% GS (mix MIII) after 6 hours.





**Figure (6):** SEM micrograph for the autoclaved specimens made from 40% OPC, 30% GGBFS and 30% GS (mix MIII) after 24 hours.

#### 4. Conclusion

The present method of autoclaving is fast, very simple, and time consuming method comparing with the previously reported methods in this area. The study showed the direct dependence of the compressive strength of the resulted species with the autoclaved ages in all hardened specimens made of autoclaved OPC–GGBFS–GS blends (mixes MII, MIII and MIV), which was due to the formation of calcium silicate hydrates at all ages of autoclaving. The highest compressive strength values were achieved by the autoclaved specimens of OPC:GGBFS:GS with the relation of 4:3:3, respectively.

The hydration kinetics calculated for the resulted species obtained from the non–evaporable water ( $W_n, \%$ ) and free lime ( $CaO, \%$ ) were found in agreement with that of compressive strength development of the autoclaved pastes. A very low values following by a decreasing in the free lime contents obtained for the autoclaved pastes made of OPC-GGBFS-GS blends (mixes

MI-MIV) was also achieved. The study on the non-evaporable water and the free lime contents in the autoclaved specimens at various age of autoclaving also concluded that the main hydrothermal reaction products were formed all mixes (Mo, MII, MIII, MIV).

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