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THE INFLUENCE OF THE ADDED AMOUNT OF GYPSUM ON THE PORTLAND CEMENT HYDRATION HEAT

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ABSTRACT

Gypsum is added to the Portland cement clinker in the amount of 3 to 5% in the grinding phase as the binding rate regulator. When it comes to the hydration of cement, if sufficient amount of gypsum is added, fast cementation will not occur because gypsum by its presence reduces the solubility of tricalcium aluminate and thus slows down rapid reaction with water. In this way the undisturbed hydration process of tricalcium silicate and dicalcium silicate is enabled, which are the bearers of cement hydraulics. The hydration process of cement minerals is exothermic. The heat of hydration is not released at once, but gradually over a long period of time. Large amounts of heat, which is released during hydration, causes certain stresses and formation of voids and cracks in cement composite leading to reduced structural durability. In this paper is examined the influence of the added amount of gypsum on the standard consistency, initial setting time and final setting time, and the heat of hydration during the first 7 days of cement hydration.

1. INTRODUCTION

Portland cement is the leading cement binder which is produced by thermal treatment of proper raw material mixture at a sintering temperature, at which a basic cement minerals are created (tricalcium silicate, dicalcium silicate, tricalcium aluminate, and tetracalcium-alumino-ferrite). Based on various studies, it has been concluded that tricalcium aluminate (C_3A) is the carrier of the cement fast-bonding phenomenon because it very quickly hydrates, immediately after the addition of water, which results in cement fast binding. The most effective way to slow down the initial setting time is to add gypsum (gypsum stone $CaSO_4 \cdot 2H_2O$) which, by its presence, reduces the solubility of tricalcium aluminate and thus the rate of its hydration, followed by the formation of calcium aluminate hydrate crystals [1].

By mixing cement with water, a hydration reaction occurs between the cement constituents with water. The hydration of the industrially obtained Portland cement sometimes occurs differently in relation to the hydration of certain clinker minerals. The individual constituent hydration reactions influence on each other, and as a result of that a new chemical balance in the liquid phase is established, all of which significantly influence the formation of hydration products [2].

During the hydration, a certain amount of heat is released because the exothermic type of reactions. The total heat of the cement hydration is equal to the sum of the heat that develops during the hydration of certain clinker minerals. The hydration heat is not released at once, but gradually over a long period of time and it is the most important tool in cement chemistry. Large amount of the heat released during the hydration causes certain stresses and formation of cracks in the cement composite, which leads to a reduction in the durability of the structure. The controlled hydration heat that can be adjusted by the cement mineral composition affects the formation of the hydration products and the cement paste density. Too low hydration heat results in very slow formation of hydration products [3].

In ordinary construction work, the released heat during the cement hydration is not a problem for which special attention should be paid, because this heat is lost by evaporation into the atmosphere. However, in the construction of large-scale concrete structures, such as for example hydro-dams, the amount of the heat developed in such a large mass can be remarkably high, especially due to the low thermal conductivity of the concrete that prevents heat release from the inside of the concrete mass to the surface or atmosphere. This leads to the high temperatures in the concrete mass which can reach values above 60 °C and which can become the cause of various destructions that can occur in even concrete mass that still has not been hardened. Such high temperatures cause a sudden drying of the concrete mass that is in the hydration phase, resulting in the loss of water needed to hydrate the cement hydraulic components. If the hydration process has been completed, the high temperature on which the large concrete mass is heated leads to sudden drying and shrinking of the monolithic concrete mass, which results in the formation of the various cracks in the concrete itself. This opens the entrance for possible penetration of corrosive water, thus destroying the whole structure even further.

Therefore, for building concrete constructions of large masses, it is crucial to know the cement characteristics in terms of the hydration heat and the heat that these cements develop in the process of their hydration. The incorporation of the cement with unknown thermal properties can lead to the demolition of the entire building, due to the disturbed compactness of concrete under the influence of high heating of concrete masses and resulting cavities, cracks, as well as the penetration of corrosive waters [4].

2. EXPERIMENTAL PART

For the preparation of cement samples, a cement clinker, produced in the Kakanj Cement Factory, and gypsum stone from Bistrica near Gornji Vakuf, were used. X-ray fluorescence analysis (XRF) was used for chemical analysis of raw materials. Preparation and testing of samples was done at the Kakanj Cement Factory. Samples with a specific surface area of 3000 cm^2/g and 5000 cm^2/g were prepared by grinding the cement clinker and gypsum using a laboratory ball mill. Since the specific surface areas were predetermined, during grinding after certain time intervals a specific surface area was checked (Blaine), until the desired specific surface area was reached. It is very difficult to obtain a precisely defined specific surface area of all samples, but it was trying to make this difference between individual samples as small as possible.

In order to determine the specific surface area of the samples, it is necessary to previously determine the specific mass of the sample. The specific mass is determined by the pycnometer method. Determination of the specific surface area was done using the Blaine's apparatus [5].

The standard consistency and the initial setting time and final setting time of cement were determined according to the standard BAS EN 196-3 using Vicat apparatus [5].

The heat of cement hydration is determined according to the standard BAS EN 196-8, which describes the dissolution method for determining the heat of cement hydration using a calorimeter for dissolution (Fig. 1). The hydration heat was determined after 7 days of hydration, and is expressed in Joules per gram of cement. The method consists of measuring the dissolution heat in a mixture of acids of unhydrated cement and cement hydrated under conditions prescribed by standard for a period of 7 days [5].

Figure 1. Calorimeter [5]

3. RESULTS AND DISCUSSION

Table 1 shows the composition of the tested cement samples, their designation according to standard BAS-EN 197-1, specific masses and specific surface areas.

Table 1. Composition of tested cement samples [5]

Cement designation according to standard BAS-EN 197-1	Mass content, (%)		Specific mass (g/cm^3)	Specific surface area (cm^2/g)
	Clinker	Gypsum		
CEM I	97	3	3.13	3070
CEM I	96	4	3.12	2970
CEM I	95	5	3.12	3010
CEM I	97	3	3.13	5070
CEM I	96	4	3.12	5060
CEM I	95	5	3.12	5120

Table 2 shows the results of the X-ray fluorescence analysis (XRF) of the raw materials used for the preparation of cement samples.

Table 2. The results of the X-ray fluorescence analysis (XRF) of the raw materials [5]

Raw material	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	SO_3 (%)	Na_2O (%)	K_2O (%)	Sum (%)
Clinker	20.35	6.72	3.74	64.80	1.00	1.07	0.08	0.45	98.21
Gypsum	4.53	1.66	1.20	31.40	2.60	38.45			79.84

Based on Table 2, it can be concluded that the used cement clinker (Cement Factory Kakanj) fully satisfies the standards [1] that prescribe the content of oxides of CaO (58-67%), SiO_2 (16-26%), Al_2O_3 (4-8%) and Fe_2O_3 (2-5%) for Portland cement clinkers.

The gypsum has the highest content of CaO and SO_3, but it can be noticed that the sum of the present compounds in gypsum is 79.84%. The reason for this is water, which is present in the gypsum, but was not determined by this analysis.

Table 3 and Figure 2 shows the results of testing the standard consistency of the cement samples.

Table 3. Standard consistency of cement samples [5]

Mass content of gypsum (%)	Standard consistency (%) (Specific surface area 3000 cm^2/g)	Standard consistency (%) (Specific surface area 5000 cm^2/g)
3	25.0	26.8
4	24.6	27,0
5	24.3	27,2

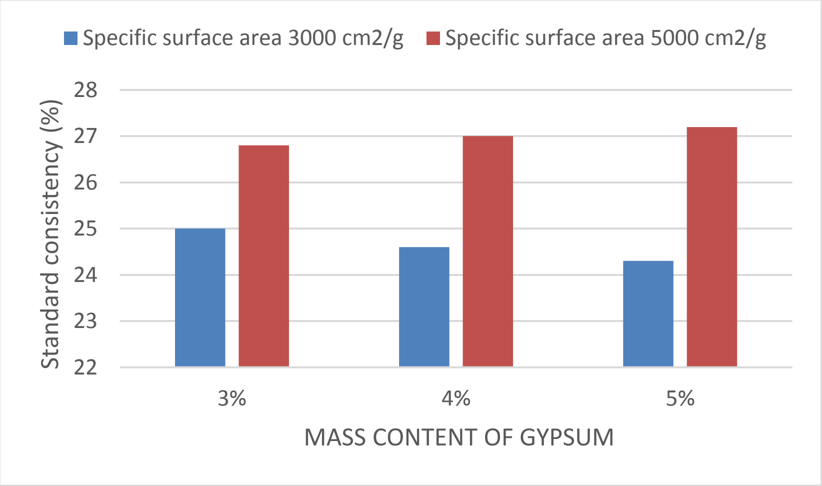


Figure 2. Standard consistency of cement samples [5]

From the diagram shown in Figure 2 it can be seen that the theoretical assertion is confirmed, on the basis of which the standard consistency of cement increases with the increase in the cement fineness, that is, with the increase of the specific surface area, for the same chemical composition of cement.

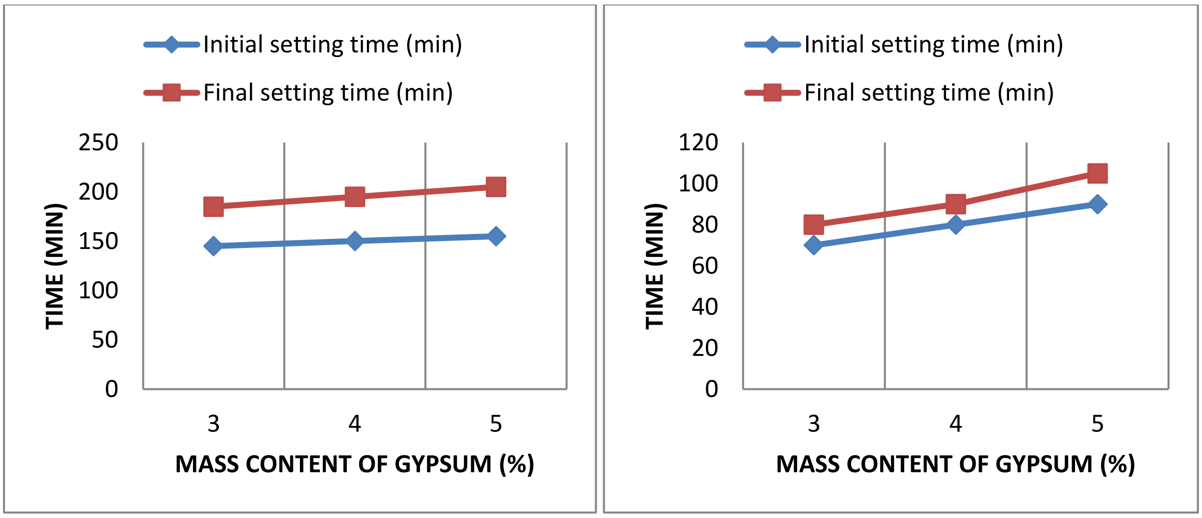
The standard consistency of the samples increases with the increase in the mass content of gypsum for a specific surface area of 5000 cm^2/g, while for a specific surface area of 3000 cm^2/g the standard consistency decreases with the increase in the mass content of the gypsum, which represents a certain deviation.

Table 4 and Figure 3 shows the results of testing the inital setting time and final setting time of cement samples.

Table 4. The initial setting time and final setting time of cement samples [5]

Mass content of gypsum (%)	Specific surface area 3000 cm^2/g		Specific surface area 5000 cm^2/g	
	Initial setting time (min)	Final setting time (min)	Initial setting time (min)	Final setting time (min)
3	145	185	70	80
4	150	195	80	95
5	155	205	90	105

Standard BAS EN 197-1 has prescribed that the initial setting time of cement should not be shorter than 60 minutes (except for high strength cements of 52.5 N and 52.5 R grades, for which the initial setting time should not be shorter than 45 minutes). Based on Table 4, it can be seen that all samples satisfy this standard with respect to the initial setting time of cement.



a) *b)*

Figure 3. The reliability of the initial setting time and final setting time of cement from gypsum content:
a) Specific surface area 3000 cm^2/g; b) Specific surface area 5000 cm^2/g [5]

From the diagrams shown in Figure 3 it can be seen that the initial setting time and final setting time of cement extend with the increase in the gypsum content. Precisely because of this effect gypsum is used as a binding agent. It can also be seen that the initial setting time and final setting time of cement is significantly shortened with the increase in specific surface area of cement when compared samples with the same chemical composition.

Table 5 and Figures 4 and 5 show the results of testing the heat of cement hydration

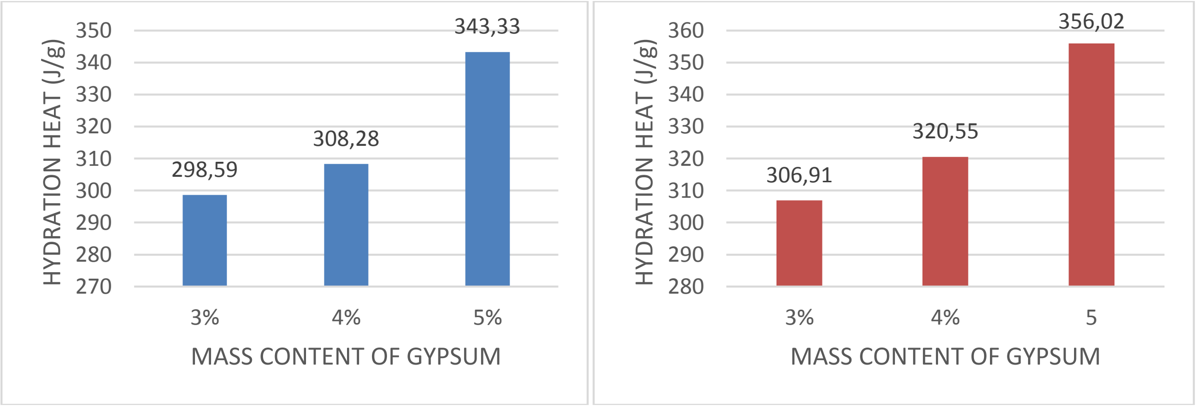
Table 5. The heat of cement hydration [5]

Mass content of gypsum (%)	Hydration heat (J/g) (Specific surface area 3000 cm^2/g)	Hydration heat (J/g) (Specific surface area 5000 cm^2/g)
3	298.590	306.910
4	308.280	320.550
5	343.330	356.020

Low-heat hydration cements, according to the standard BAS EN 197-1, are cements whose the hydration heat is less than 270 J/g and their mark is LH (low heat), while cements of very low heat of hydration, according to this standard, are cements whose the hydration heat is less than 220 J/g of and their mark is VLH (very low heat) [6].

From Table 5 it can be seen that the hydration heat for all tested samples is greater than 270 J/g, which means that with the use of only gypsum as an additive, low and very low hydration heat cements can not be produced.

Figures 4 and 5 show the reliability diagram of cement hydration heat from gypsum content for samples with specific surface area of 3000 cm^2/g and 5000 cm^2/g, and according to Figure 4, the hydration heat increases with increasing gypsum content, and according to Figure 5 samples with a specific surface area of 5000 cm^2/g have a higher hydration heat when compared with samples with a specific surface area of 3000 cm^2/g with the same gypsum content.



a) *b)*

Figure 4. The reliability of cement hydration heat from gypsum content:
a) Specific surface area 3000 cm^2/g; b) Specific surface area 5000 cm^2/g [5]

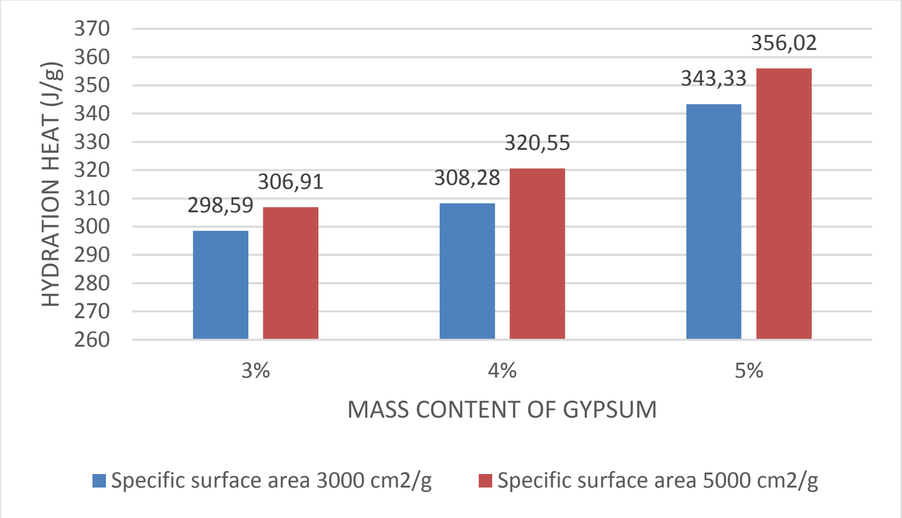


Figure 5. The reliability of cement hydration heat from gypsum content and specific surface area of cement [5]

4. CONCLUSION

Based on the testing of raw materials, it can be concluded that cement clinker from Cement Factory Kakanj fully satisfies the standards that prescribe the content of oxides of CaO, SiO_2, Al_2O_3 and Fe_2O_3 for Portland cement clinkers (these oxides form basic minerals of clinker: tricalcium silicate, dicalcium silicate, tricalcium aluminate, and tetracalcium-alumino-ferrite). The standard consistency of cement increases with the increase in the cement fineness for the same chemical composition of cement. The standard consistency of the samples increases with the increase in the mass content of gypsum for a specific surface area of 5000 cm^2/g, while for a specific surface area of 3000 cm^2/g the standard consistency decreases with the increase in the mass content of the gypsum, which represents a certain deviation. All tested samples satisfy standard BAS EN 197-1 with respect to the initial setting time of cement. The initial setting time and final setting time of cement is extend with the increase in the gypsum content, and it is significantly shortened with the increase in specific surface area of cement when compared samples with the same chemical composition, due to the larger active surface and therefore the faster chemical reaction. The hydration heat of cement grows with the increase of the specific surface area of cement and with the increase of the gypsum content. Using only gypsum as an additive, low and very low hydration heat cements can not be produced, and additives such as fly ash and granulated blast furnace slag should be used for these purposes.

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