

Early stages hydration of high initial strength Portland cement

Part I. thermogravimetric analysis on calcined mass basis

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Abstract Thermogravimetry (TG) and derivative thermogravimetry (DTG) were used to analyze the early stages of hydration of a high-initial strength and sulphate resistant Portland cement (HS SR PC) within the first 24 h of setting. The water/cement (W/C) mass ratios used to prepare the pastes were 0.35, 0.45, and 0.55. The hydration behavior of the pastes was analyzed through TG and DTG curves obtained after different hydration times on calcined cement mass basis to have a same composition basis to compare the data. The influence of the W/C ratio on the kinetics of the hydration process was done through the quantitative analysis of the combined water of the main hydration products formed in each case. TG and DTG curves data calculated on calcined mass basis of all the results were converted to initial cement mass basis to have an easier way to analyze the influence of the W/C ratio on the free and combined water of the different main hydrated phases. The gypsum content of the pastes was totally consumed in 8 h for all cases. A significant part of the hydration process occurs within the first 14 h of setting and at 24 h the highest hydration degree, indicated by the respective content of formed calcium hydroxide, occurs in the case of the highest initial water content of the paste.

Keywords HS SR cement · Early stage hydration · TG · DTG · Calcined mass basis

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Introduction

Thermogravimetric (TG) and derivative thermogravimetric (DTG) analysis have helped to understand and to study the behavior of cementitious materials during their hydration stages. Among these applications, there are: identification of the main different present phases [1–3] studies of the hydration degree [4–7], studies of the effects of different additives [4, 8–11], and the analysis of pozzolanic activities of mineral additives [2, 4, 8, 9, 12, 13].

When thermal analysis is performed without a previous drying step, distinct type of reactions may occur during the thermal decomposition of a cementitious paste: drying and dehydration steps, a dehydroxilation and a decarbonation. The first two steps include the loss of free water from the pores and from the water released from any C–S–H structured phase including tobermorite (Capillary, interstitial and physically combined water) [14, 15].

When thermal analysis is performed after an initial drying step at temperatures between 28 and 35 °C, the main decomposition steps of the hydrated phases are: dehydration of tobermorite (non necessarily in crystalline form) and Ettringite (50–200 °C); dehydration of the dihydrated calcium sulphate (110–145 °C); dehydration of calcium hydroxide (380–460 °C); decomposition of calcium carbonate (520–730 °C) [16, 17].

In this study, the evaluation of the influence of water/cement ratio in the kinetics of the hydration reactions was done by using TG and DTG analysis at different times during the first 24 h of setting, estimating the contents of free water, combined water released from Tobermorite and Ettringite phases, total combined water and portlandite, in the different water/cement ratio studied pastes.

Materials

For this study, a high-initial strength and sulphate resistant Portland cement (HS SR PC) [18] was used, which allows reaching high strengths still at the early hydration stages. The development of high initial strength is due to the use of a different proportion of limestone and clay in the production of the clinker than that used in usual Portland cement manufacture, as well as through a higher milling degree of the cement, in order to accelerate the reaction with the water, by the higher specific external area of the particles and consequently reaching a higher strength in a shorter time. This kind of cement may have a maximum of 5% of carbonates additions with aggregation of blast furnace slag or pozzolanic materials [19]. Its chemical composition is presented on the Table 1. The granulometric distribution curve of the HS SR PC, is presented in Fig. 1.

Table 1 Chemical composition of the cement

Compound	Content/%
CaO	66.92
SiO ₂	16.45
Al ₂ O ₃	5.00
SO ₃	4.44
Fe ₂ O ₃	3.30
TiO ₂	0.40
K ₂ O	0.35
MnO	0.28
SrO	0.25
ZnO	0.03
ZrO ₂	0.02
LOI	2.55

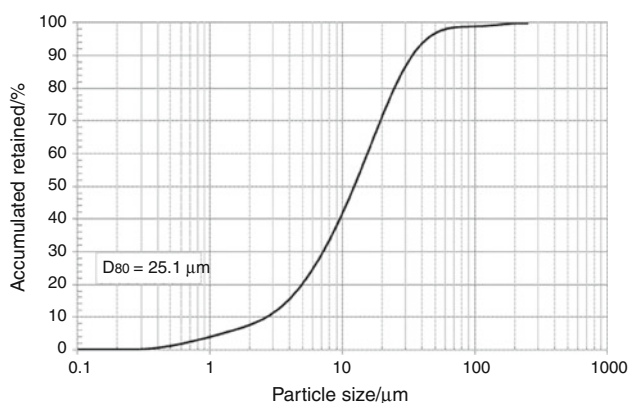


Fig. 1 Granulometric curve of the HS SR PC

Methods

Pastes with water/cement mass ratios (W/C) of 0.35, 0.45, and 0.55 were prepared. The cement was inserted in plastic bags previously containing the proper amount of deionized water with which homogenization was manually done for 1 min and after, the bag was tightly closed and maintained in a controlled temperature chamber at 30 °C. After that, a sample of about 10 mg, was collected for each analysis from respective stored bag at the established times of the experiments, which were of 1, 8, 14, and 24 h. To minimize the external environment influence, the time between collection and insertion of the sample in the thermal analysis pan was minimized. When the sample was gelly it was directly put into the pan. When it was solidified, a little amount was first collected and transferred into plastic bag, which was sealed, and then was manually milled. After that it was fastly transferred into the pan.

The thermal analyses were performed in a TA Instruments, SDT Q600 model TGA/DTA/DSC simultaneous apparatus at a heating rate of 10 °C min⁻¹, from 35 to 1,000 °C, by using 100 mL min⁻¹ of nitrogen flow. Before this, the samples were dried inside the equipment initially at 1 °C min⁻¹ from 30 to 35 °C, followed by an isothermal step at 35 °C for 1 h, to complete the drying in order to eliminate the residual non combined free water [16]. As during these drying steps the water/cement ratio is decreased significantly, which decreases the cement hydration rate, any possible little acceleration during drying was considered insignificant. The material of reference and sample pans was platinum.

Results and discussion

Figure 2 shows the TG and DTG curves of the HS SR PC.

In Fig. 2, the first mass loss step up to 150 °C refers to the gypsum dehydration. The second mass loss step from 350 to 450 °C is due to calcium hydroxide decomposition. From 450 to 700 °C occurs calcium carbonate decomposition.

Typical TG and DTG curve examples of the pastes prepared with W/C = 0.55, on respective sample initial mass basis, are presented, respectively, in Figs. 3 and 4.

We can see from Fig. 3 that after the drying step, performed at 35 °C, the free water content decreases with time, due to the progress of the hydration and paste setting process, being lower in the 24 h paste sample.

Considering the temperature ranges of the main decomposition steps [16], from Fig. 4, which shows the respective DTG curves and peaks, one can evaluate, with major resolution than from respective TG curves shown in Fig. 3, the behavior of the decomposition of the main

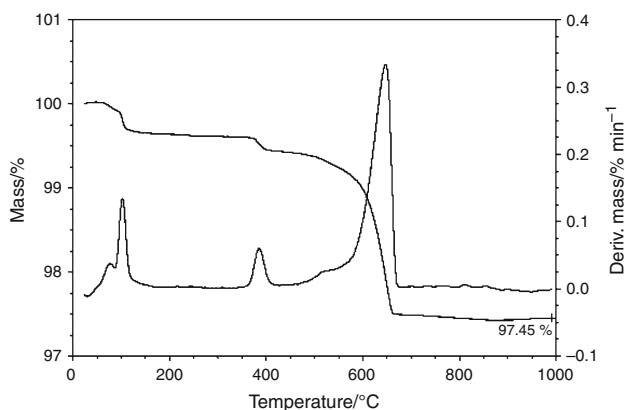


Fig. 2 TG and DTG curves of the HS SR PC

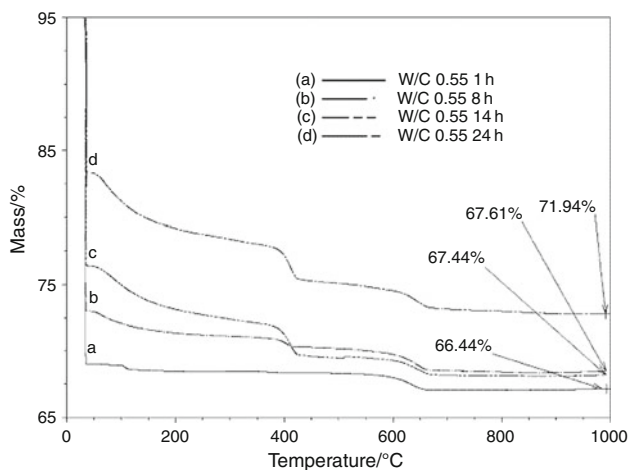


Fig. 3 TG curves of the pastes prepared with W/C 0.55 at 1, 8, 14, and 24 h of hydration on initial sample mass basis

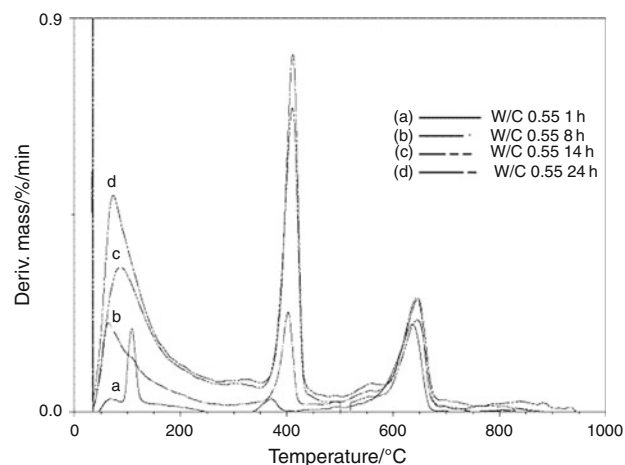


Fig. 4 DTG Curves of the paste with W/C 0.55 at 1, 8, 14, and 24 h on the sample initial mass basis

hydrated phases of each paste. It can be seen that the gypsum present in the anhydrous cement is totally consumed at 8 h of hydration.

It is also noticed from Fig. 2 that the anhydrous cement presents a little early hydration, maybe due to storage problems and great reactivity. From 8 to 24 h of hydration, the DTG peaks of combined water released from tobermorite and Ettringite phases, which occur between 50 and 200 °C, increase with hydration time. The same occurs with the combined water loss from the other hydrated phases until 370 °C. At this temperature the dehydroxylation of Ca(OH)₂ begins, which also increases with the hydration degree until 430 or 450 °C, respectively, for the 8 and 24 h cases.

It is seen a decrease of the Ca(OH)₂ content at 1 h, with respect to that of anhydrous cement, possibly due to some carbonation, which may have occurred during sampling at this reaction time, when it has a great reactivity.

From Fig. 2 mass loss that occurs and respective DTG peak at the decomposition temperature range of the calcium carbonate, which occurs after the dehydroxylation of calcium hydroxide extending up to 670 a 680 °C, we see that carbonate is initially present in the original cement, which was added during its manufacturing.

Comparing the DTG peaks of calcium carbonate decomposition of the pastes with that of original anhydrous cement, we can see a little decrease of peak height. Between 500 and 600 °C, a second little and broad peak appears before the higher original calcium carbonate decomposition DTG peak. This can be possibly due to a less crystallized carbonate phase formed during hydration [16].

The TG curves are, by default, shown on respective initial sample mass basis. As the initial masses of the pastes prepared with different W/C ratio have different chemical compositions, the direct comparison among respective TG or DTG curves on respective initial sample basis leads to an erroneous analysis, because the different percentual mass losses do not refer to a same composition.

However, the composition of the residual calcined products of all present cases is composed by the same oxides than the calcined mass of the anhydrous cement. Thus, to compare the analysis results on a same composition basis, to have correct comparisons, we have converted the TG and DTG data, which are given by the equipment software by default, on respective sample initial mass basis, first on calcined mass basis [12] by dividing all data by respective calcined mass:

$$M_{cb} = \frac{M_i}{M_c} \times 100$$

where M_{cb} is mass% at a temperature T on calcined mass basis, M_i is mass% at a temperature T on initial sample mass basis, and M_c is mass% of calcined sample on initial sample mass basis.

To have an easier and also same basis of comparison, the results obtained on calcined mass basis were transformed on initial cement mass basis, multiplying them by the original cement calcined mass percent:

$$M_{icb} = M_{cb} \frac{M_{cc}}{100}$$

Where M_{icb} is mass% at a temperature T on initial cement mass basis, M_{cc} is mass% of calcined cement on initial cement mass basis.

Thus, on initial cement mass basis, the TG and DTG curves for the paste with 0.55 W/C ratio are shown in Figs. 5 and 6 to exemplify these type of data basis change.

From Figs. 5 and 6, it can be seen that when the data are transformed on initial cement mass basis, it is possible to have a more correct comparison of the data. The curves tend to disperse when approaching to the lower

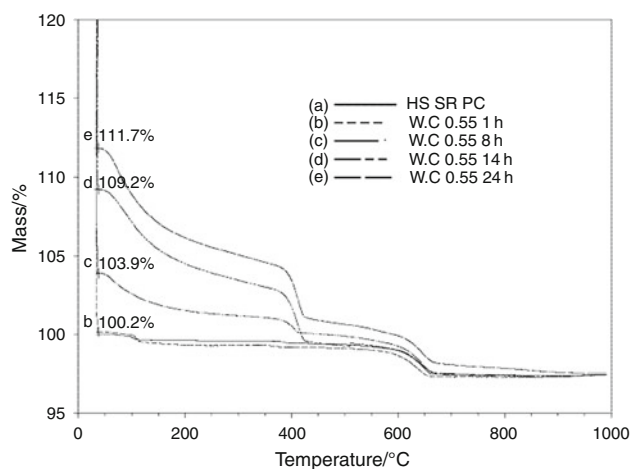


Fig. 5 TG Curves of the cement and the paste with W/C 0.55 at 1, 8, 14, and 24 h of hydration on cement initial mass basis

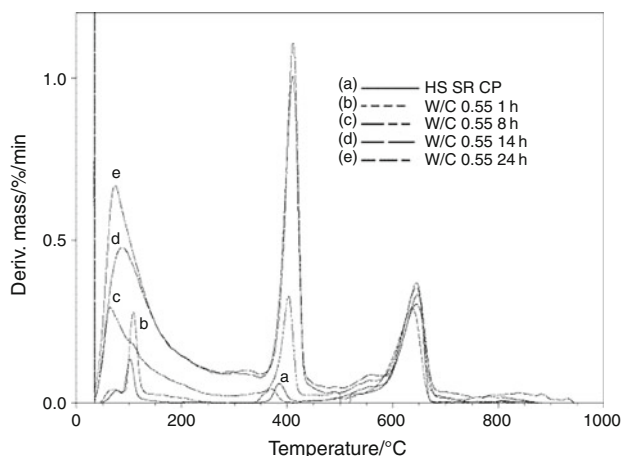


Fig. 6 DTG curves of the cement and the paste with W/C 0.55 at 1, 8, 14, and 24 h of hydration on the cement initial mass basis

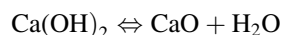
temperatures, showing the higher free water contents at the begging of respective cases, which are characterized by the initial mass loss during isothermal step of drying 35 °C. These curves confirm with more evidence, the increase of the $\text{Ca}(\text{OH})_2$ content with the increase of hydration time, because all have as reference, the same respective initial cement mass.

From the data on initial cement mass basis of each sample, the percentage of the following products can be calculated for each considered hydration time:

- The water released from gypsum decomposition between 90 and 140 °C (when respective DTG peak is apparent);



- The total combined water released during the products decomposition, including the water loss of dehydroxylation of the $\text{Ca}(\text{OH})_2$ between 50 and 450 °C;
- The water released from the Tobermorite and Ettringite decomposition between 50 and 200 °C;
- The water loss during the dehydroxylation of $\text{Ca}(\text{OH})_2$, between 380 and 450 °C according to the stoichiometry of the reaction:



(Theoretical mass loss = 24.32%);

The comparative histograms of the percentual contents of hydrations products, of the three samples referring to the three used W/C ratios (0.35, 0.45, 0.55) until 24 h, are shown from Figs. 7, 8, 9, and 10.

Figure 7, shows the behavior of the calcium hydroxide content evolution for the three W/C ratios. Until 1 h of hydration, the amount of $\text{Ca}(\text{OH})_2$ formed is small for the three pastes. At 8 h, the lower is the W/C ratio, the higher

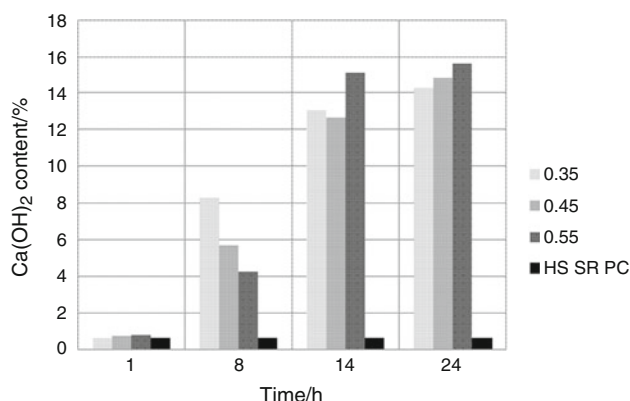


Fig. 7 $\text{Ca}(\text{OH})_2$ content on cement initial mass basis

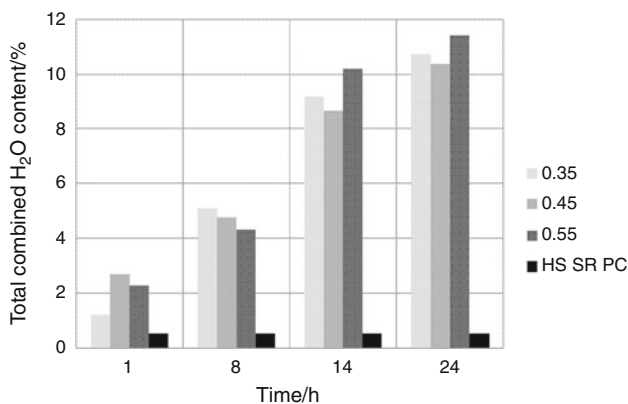


Fig. 8 Total combined water content on cement initial mass basis

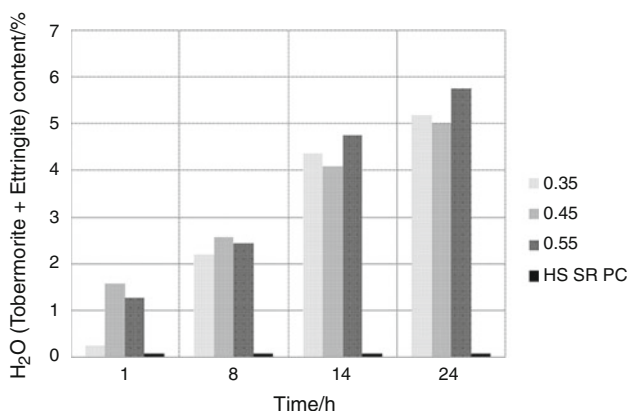


Fig. 9 Content of water released from tobermorite and Ettringite phases on cement initial mass basis

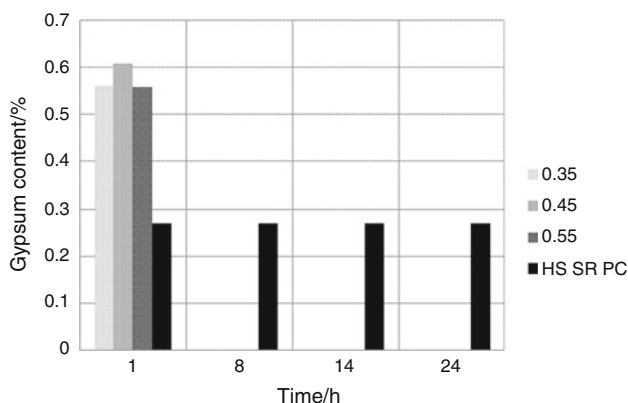


Fig. 10 Gypsum content on cement initial mass basis

is the formation of $\text{Ca}(\text{OH})_2$, but at 14 h, the sample with the highest W/C value (0.55) forms more $\text{Ca}(\text{OH})_2$ than the other ones. Owing to its highest free water content present at the first hours, the 0.55 W/C paste promotes the lowest increase of paste temperature, which decelerates the thermal-activation of the hydration reaction. This effect

disappears for hydration times higher than 14 h, due to the continuous consumption of more available free water for the hydration reactions in the operating conditions, forming more hydrated products than those formed in 0.35 and 0.45 W/C pastes.

This assumption is confirmed from Fig. 8, which shows that after 14 h of hydration, the sample with 0.55 W/C ratio presents more total combined water than the other cases, although at 8 h, the pastes with less humidity (0.35 and 0.45) present a higher cement hydration degree.

In the first hour, with more water available per cement mass, the pastes with 0.45 and 0.55 W/C ratios quickly form more initial hydration products than the 0.35 W/C paste. In the other hand, in the pastes with the highest W/C ratios, a decrease in the formation of hydration products occurs in the next hydration step until 8 h of hydration, caused also by the retarding effect caused by Ettringite formation during the first hour.

With a lower relative content of initial water the paste with 0.35 W/C ratio presents a lower content of formed hydration products at the end of 24 h period, with respect to respective initial cement mass. However, the amount of combined water in case of tobermorite + Ettringite phases and in case of total amount of combined water is lower for $\text{W/C} = 0.45$, because the influence of total water content of the different studied pastes, on the kinetics behavior of the hydration reactions, depends on the hydration time.

From Fig. 9 it can be seen that after 14 h of hydration, the sample with 0.55 W/C ratio, forms more tobermorite and Ettringite phases than the other cases. In the first hour, similarly to the total combined water content evolution, in the pastes with 0.45 and 0.55 W/C ratios, there is much more water released mainly from Ettringite phase than from 0.35 W/C paste. At 8 h of hydration a relative decrease occurs with respect to the water lost from tobermorite and Ettringite in the pastes with higher W/C ratio.

It must be noticed that in the first hour, the water released from Ettringite and tobermorite is mainly due to the dehydration of the former of this compounds, because during this period mostly Ettringite is formed. Between 1 and 8 h, induction period continues, when other hydration reactions slow down and then occurs the beginning of the acceleration period, where mainly are simultaneously formed tobermorite and calcium hydroxide and practically there is no Ettringite formation [20]. Thus, the difference between the sum of the water released from tobermorite and Ettringite phases at 8 and 1 h (Dif_{8-1}) is due practically to tobermorite dehydration. As the paste with $\text{W/C} = 0.35$ presents the lowest formation of Ettringite at 1 h and the highest value for Dif_{8-1} , this difference is due mainly to a higher tobermorite formation, which explains the higher simultaneous formation of calcium hydroxide at 8 h.

From Fig. 10 it is seen that at 1 h there is much more gypsum present than in the unhydrated cement which enhances Ettringite formation. This fact is due to the rehydration of the of anhydrous calcium sulfate, which is formed during milling step to simultaneously mix and mill the clinker with the gypsum and calcium carbonate added as aggregates [16] of the manufactured cement. After 8 h of hydration, the samples lose all the gypsum present in the beginning stages, which is consumed in the formation of Ettringite.

Conclusions

- The water/cement ratio plays a definite role in the kinetics of the cement hydration reaction kinetics and consequently in the formation of the hydration products.
- Thermogravimetric and derivative thermogravimetric analysis allow one to quantify the hydrated products and to evaluate the influence of the W/C ratio in the reactions that occur in the first 24 h of Portland cement hydration.
- Changing TG and DTG data to initial cement mass basis, based on the fact that the calcined compositions of all pastes and that of the calcined anhydrous cement are equal, more accurate values of the different phase contents can be estimated to study the effect of the W/C ratio on the cement hydration kinetics.
- From the analysis of the contents of the main formed products on cement initial mass basis of each paste as a function of the hydration time, the pastes with 0.55 W/C ratio, form in the first 24 h more hydrated products than the other 0.35 and 0.45 W/C cases.
- The influence of total water content of the different studied pastes, on the kinetics behavior of the hydration reaction, depends on the hydration time.
- Between 1 and 8 h, where there is more available water and the pastes are more diluted, the amount of cement controls the kinetics of hydration reactions and, in this case, the higher available free water promotes a higher cooling effect on the temperature of the paste, decreasing the thermal activation of the hydration reactions. Thus, during this period, the paste with 0.55 W/C ratio, forms less total combined water than in the other lower W/C cases.
- As free water is more consumed, for hydration times equal or higher than 14 h of hydration, which correspond to the accelerating and post-accelerating cement hydration stages, the available free water controls the hydration process and there is a higher formation of hydrated products. Thus, the paste prepared with $W/C = 0.55$ presents more hydrated products and total combined water than the pastes with $W/C = 0.35$ and 0.45.

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