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ADVANCING GREEN CEMENT: REACTION KINETICS AND MECHANICAL PERFORMANCE OF CARBONATED WOLLASTONITE--LIMESTONE-GYPSUM BLENDED COMPOSITES FOR SUSTAINABLE CONSTRUCTION

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With the growing global demand for wollastonite, its potential as a supplementary cementitious material has been explored by inducing carbonation. This study investigates the impact of partially replacing cement with varying amounts of carbonated wollastonite (10–50 wt%) while maintaining a constant proportion of limestone (15 wt%) and gypsum (5 wt%). The developed mixes of blended Portland cement (PC) composites were evaluated for mechanical performance in terms of compressive and flexural strength. The results indicate that the mix containing 20 wt% wollastonite, along with 15 wt% limestone and 5 wt% gypsum, exhibited an approximately 30% higher compressive strength compared to conventional mortar, along with a significant increase of about 62% for the flexural strength. X-ray diffraction (XRD) analysis was performed to assess the phase composition, while thermogravimetric analysis (TGA) quantified the portlandite content and chemically bound water. Microstructural analysis further revealed the formation of the main hydration products such as ettringite, portlandite, and anhydrite enhanced structural integrity. The findings highlight the potential of carbonated wollastonite along with limestone and gypsum in enhancing the mechanical and microstructural properties of the cementitious composites. The mixes with 20 wt% wollastonite along with 15 wt% limestone and 5 wt% gypsum exhibited superior performance compared to other the mixes. However, excessive incorporation resulted in a weakened mechanical performance and microstructure. The findings demonstrate the potential for utilizing carbonated wollastonite in the development of eco-friendly binders, contributing to the reduction in the environmental impact caused by the construction industry.

Keywords: wollastonite; sustainability; cleaner environment; mechanical performance microstructure

INTRODUCTION

To reduce CO_2 emissions in the construction sector, alternative materials are being explored to partially replace cement in the production of concrete. Commonly used materials are industrial by-products such as silica fume, blast furnace slag, and fly ash [1-6]. Various sources have been explored the inclusion of alternative materials as a partial replacement for cement. Some mineral powders such as wollastonite powder have been studied for their partial replacement for cement in concrete and mortars [7-9]. Wollastonite is an inert material and generally considered as a microfibrous material. Its utilisation in concrete as partial replacement for cement is explored and experimental investigations have been carried out. Wollastonite is primarily composed of calcium silicate

(β-CaO-SiO2) and exhibits acicular morphology [10, 11]. This unique morphology makes it favourable to enhance the mechanical performance of composites. When such a material is used as a partial replacement for cement in concrete, it enhances the performance and cost-effectiveness of the concrete [12, 13]. In the study conducted by Kalla et al. [14], where the composite was formulated with the addition of fly ash and wollastonite, it was observed that a wollastonite content between 5 wt% and 15wt% offered favourable conditions for concrete densification, resulting in the enhancement of concrete durability. Mandrawalia et al. [15] investigated the effect of incorporating wollastonite and waste granite powder as partial replacement for cement on the concrete properties. When the blended concrete specimens were tested for compressive strength and abrasion resistance, increases of 5.7% and 10.2%, respectively were observed when compared to conventional concrete, in addition to considerably reducing the coefficient of capillary rise. Archez et al. [16] recorded a significant effect of wollastonite on improvement of the viscosity and mechanical properties of metakaolin-based polymers. Ren [17] investigated the influence of different proportions of metakaolin and WS mixture on concrete properties. The experimental results showed that within the designated range, the addition of 5 wt% wollastonite, 5 wt% zeolite, and 2 wt% short basalt fibers resulted in the highest compressive strength for metakaolin-based cementitious material. Ransinchung et al. [18] studied the effect of WS on the setting time of ordinary Portland cement (OPC) paste and mortar. They observed that the replacement of cement with wollastonite powder led to unexpected increases of 25% and 27.5% in the initial and final setting times, respectively, rather than the anticipated reduction. Additionally, their findings indicated that the utilization of a combination of microsilica and wollastonite as a cement substitute resulted in substantial enhancement of the compressive strength. Furthermore, finely ground wollastonite can strongly accelerate cement hydration due to the filler effect [19] while the phase itself is not reactive in alkaline conditions. As a consequence of its reactivity towards CO_2, wollastonite is discussed in the context of mineral carbonation as a suitable material for carbon capture and storage or use [20-21].

Although wollastonite has been studied for its feasibility to be incorporated as partial replacement for cement, studies are limited pertaining to carbonated wollastonite. In the present paper, an experimental investigation was carried out on carbonated wollastonite, limestone and gypsum blended cement composites. The effect of the alternate material incorporated as partial replacement for cement on the hydration activity and overall performance of the material is discussed. The novelty of the present work is that there is no literature available pertaining to the utilisation of carbonated wollastonite along with limestone and gypsum. This study gives an insight into the reaction kinetics of the developed carbonated wollastonite based blended concrete composites.

MATERIALS AND METHODS

Materials

OPC cement was utilised as the binding material. Wollastonite supplied by Wolkem India Ltd. was utilised as partial replacement for cement, along with limestone and gypsum. Standard sand conforming to ASTM C 778 was used as the fine aggregate in the study. A SP 430 was the admixture employed to attain good workability conditions. Six different mortar mixes were formulated in the study. The ratio of the binder to the fine aggregate considered in the study was 2.75 with a water cement ratio of 0.45. The content of limestone was kept constant at 15 wt% along with the gypsum at 5 wt%. The addition of wollastonite was varied from 0 to 50 wt%.

Mix proportion and sample preparation

Six mortar mixes were formulated by varying the wollastonite and cement content and by keeping the limestone and gypsum content constant at

15 and 5 wt%. The mixes were prepared in an automatic mortar mixer according to according to [24]. A flow table test was conducted according to ASTM C1437 to determine the dosage of superplasticiser to sustain the flow of the mixes. The prepared mixes were poured into moulds of 50 x 50 x 50 mm and 40 x 40 x 160 mm to determine the compressive strength as per [25] and flexural strength. The specimens were demoulded after 24 hours and immersed in water till the time of testing.

First, the cement, wollastonite along with the weighed quantities of limestone and gypsum were mixed together. Then the graded sand was added and mixed properly. Next the superplasticiser mixed in water was added. Afterwards the mixture was poured into the moulds. After 24 hours, the specimens were demoulded and cured for a period of 7 and 28 days. The mix proportions are presented in Table 1.

Paste samples were prepared for XRD and TGA testing. The samples were prepared by mixing the cement, wollastonite, limestone and gypsum in the stipulated proportions along with the water. These specimens were cured for 28 days and ground to powder using a mortar and pestle. The ground powder was used for XRD and TGA studies.

Experimental methods

The initial setting time for the formulated mixes was determined as per [26] with a modified Vicat needle apparatus. The flow table test was carried out to determine the workability of the mixes as per the procedure mentioned in [27]. The workability test was conducted for all the formulated mixes to determine the effect of replacing cement partially with the wollastonite, limestone and gypsum. The compressive strength test was conducted on the specimens cured at 7 and 28 days as per [28] applying a loading rate of 200–400 lb/s. Flexural strength tests were also conducted on specimens 40 x 40 x 160 mm at 7 and 28 days of curing.

The cast pastes were ground to powder for XRD and TGA testing to observe the peak intensities of the formed hydration products and to determine the portlandite and chemically bound water at 28 days of curing. XRD was conducted using PANalytical X'Pert Pro diffractometer. The samples were scanned between 10^0 and 90^0 (2 Θ) for 50 minutes. The hydration process of the hardened pastes was halted by immersing in an isopropanol solution, then ground for 20 minutes using a McCrone micronizing mill. The obtained peaks were analysed for the formed hydration products [22]. Thermogravimetric analyses were carried out on 50 mg of the ground powder of each sample. The samples were heated from 30°C to 1500°C under nitrogen maintaining a heating rate of 20 K/min utilising a Mettler-Toledo TGA 2 device. The bound water was calculated by taking the mass loss at 550°C and normalized to 100 g of unhydrated binder [23]. The characteristic mass loss (approximately between 400°C and 500°C) was taken as portlandite contents by tangential evaluation.

TABLE 1. **Mix compositions of blended cement composites**

MIX	Cement (kg/m^3)	Limestone (kg/m^3)	Gypsum (kg/m^3)	Wollastonite (kg/m^3)	Fine aggregate (kg/m^3)	Water (kg/m^3)
WL0	240			0	660	108
WL1	168	36	12	24	660	108
WL2	144	36	12	48	660	108
WL3	120	36	12	72	660	108
WL4	96	36	12	96	660	108
WL5	72	36	12	120	660	108

RESULTS AND DISCUSSION

Setting times

The results of the setting time are shown in Fig. 1. It was observed that the blended cement composites exhibited an increase in the setting times when compared to the conventional mix consisting of only cement. The initial setting time of the control mix was observed to be 156 minutes. For mortars where the cement is partially replaced with wollastonite, limestone and gypsum, the observed setting times increased. The initial setting times increased by 36, 55 and 63%, respectively, when compared to the control mix. The results conform to the research carried by Zhang et al. [29] where the setting times increased with the addition of wollastonite. The setting time is related to the degree of polymerization, which is influenced by the dissolution of calcium and silica [30]. Wollastonite, mainly composed of CaO and SiO_2, leads to an increase in the dissolution time in the system as its content increases, thus prolonging the reaction time.

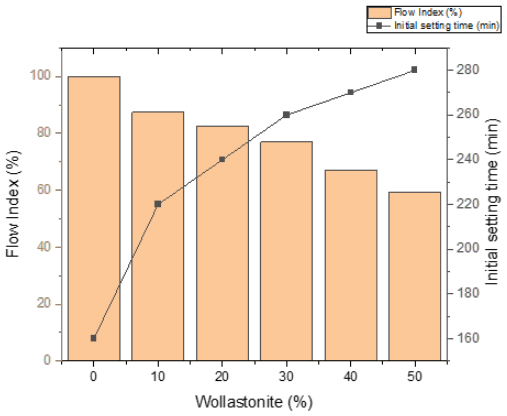

Fig. 1. Initial setting time and flow index with wollastonite percentage addition

Workability

The workability of the mortar mixes determined using the flow index values is presented in Fig. 1. The flow index value of the control sample was 128% (128 mm). The flow indices values presented in the figure are presented as the percentage of the flow value of the control mix. (i.e. 100% Ordknary Portland Cement). It was observed from the experimental work that with the partial replacement of cement with wollastonite, limestone and gypsum, the flow indices decreased. The values reduced from WL1 to WL6. This decrease can be attributed to the incorporation of the finer material such as wollastonite, limestone and gypsum as partial replacement for the cement. As the finer material possesses a high specific surface area, the amount of water required will be high to cover the surface of the binder particles. The results are consistent with the research carried out in [29], reporting that the higher friction might be caused by the wollastonite which has acicular morphology compared to the limestone and gypsum, resulted in a decrease in the flow index of the formulated mixes [31]. The required water to lubricate the mortar grew with the higher replacement levels due to the number of acicular wollastonite particles present in the mix, resulting in less fluidity.

Mechanical properties

Compressive strength

The compressive strength results at 7 and 28 days are presented in Fig. 2. The compressive strength for the control mix at 7 and 28 days is 17.1 and 28.86 MPa, respectively. There is an observed incremental trend from WL1 to WL2, which consists of cement replaced by 30 wt% and 40 wt% wollastonite. Mix WL2 attained a strength 38% higher than the control mix at 28 days of curing. The rise in the strength can be attributed to the densification of the matrix with the formation of the hydration products resulting from the reaction between amorphous silica and cement. When the wollastonite is subjected to carbonation, amorphous silica is formed in larger amounts, which have the potential to participate in cement hydration. The results are in consistent with the research carried out by Leeman et al. [32] who conducted the research on carbonated wollastonite and concluded that the amorphous SiO_2 of carbonated wollastonite participates in cement hydration resulting in a denser matrix, which increased the compressive strength of the system. For the other

mixes such as WL3, WL4 and WL5a decrease in strength was observed, which may be due to weakening of the bond between the materials and unavailability of water for sufficient hydration to take place.

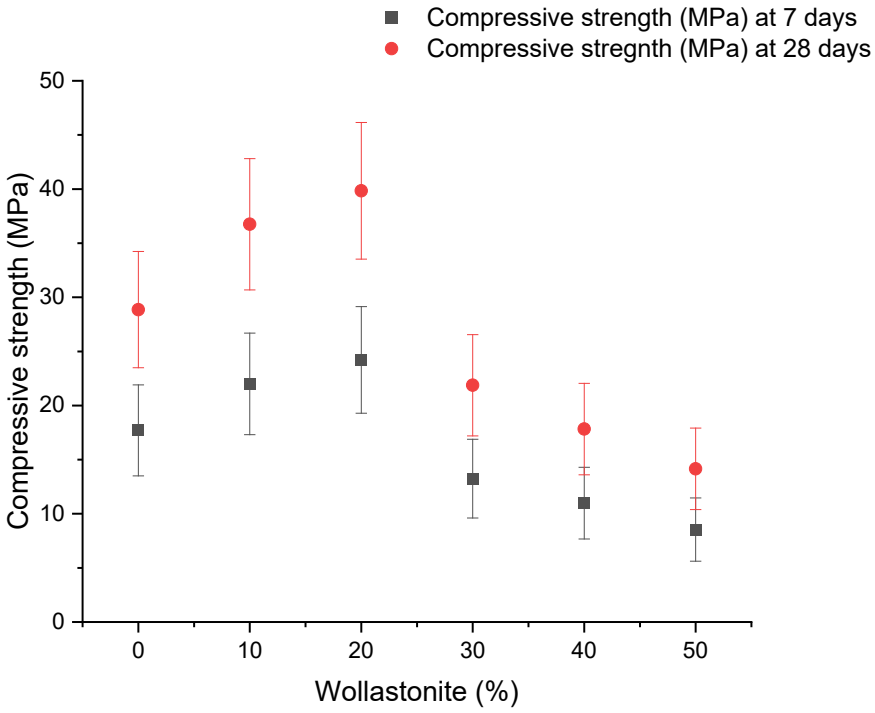

Fig. 2. Compressive strength at 7 and 28 days

Flexural S strength

The flexural strength for the mixes is presented in Fig. 3. It can be observed from the results that for mix WL2, the strength was about 62% higher than the control mix. The flexural strength exhibited by mix WL2 can be attributed to the densification of the matrix with the formation of the hydration products. When the wollastonite was subjected to carbonation, which is a naturally available calcium silicate mineral, it causes the formation of calcium carbonate and amorphous silica. With the incorporation of carbonated wollastonite as partial replacement for the cement the amorphous silica present participates in the hydration process, resulting in the formation of hydration products. This generates an increase in the strength along with the bridging of cracks by the unhydrated wollastonite particles. These results are in line with the investigations carried out by Leeman et al. [32], who concluded that the strength grows in the case of carbonated wollastonite blended cement composites, as amorphous silica is the critical element in the hydration, bringing about the formation of a dense structure. There was an observed rise in the strength up to the dosage of 20 wt% carbonated wollastonite along with 15 wt% limestone and 5 wt% gypsum. With the increasing content of the wollastonite, a decreasing trend was observed. The decline in the strength can be attributed to the poor bonding between the materials in the matrix, which results in the formation of pores, thereby reducing the strength of the matrix.

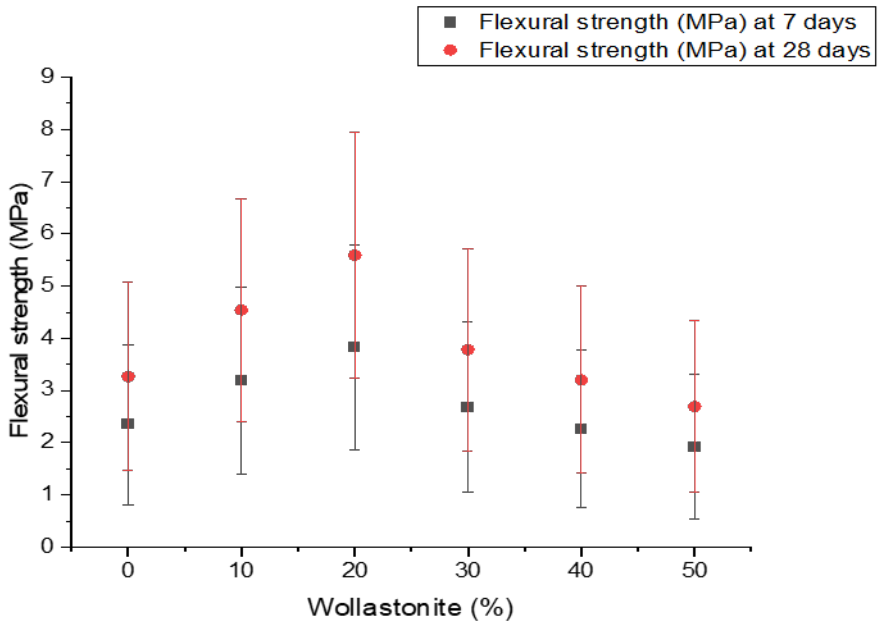

Fig. 3. Flexural strength at 7 and 28 days

Microstructural investigation

XRD

The XRD diffraction pattern for the wollastonite-limestone blended cement composites is presented in Fig. 4. The observed phases are ettringite, portlandite, anhydrite, alite and traces of gypsum. It can be observed that the hemicarbonates were dissolved to form monocarbonates. From the analysis, it can be concluded that carbonated wollastonite being a pozzolanic material and with its participation in the hydration process, leads to the formation of portlandite and ettringite, followed by other hydration products like anhydrite. From the XRD diffraction pattern, it can be seen that the with the increase in the addition of carbonated wollastonite, the amount of portlandite dwindled owing to the formation of hydration products, which is a result of the pozzolanic activity of the carbonated wollastonite. The results are in consistent with those of Winnefeld et al. [31], who observed the same trend of the formation of hydration products with the incorporation of carbonated wollastonite as partial replacement for the cement in the mortar. The XRD results are in line with the compressive strength and flexural strength of the carbonated wollastonite blended cement composites, thereby concluding the hydration reaction of the carbonated wollastonite, which is rich in amorphous silica and calcium carbonate.

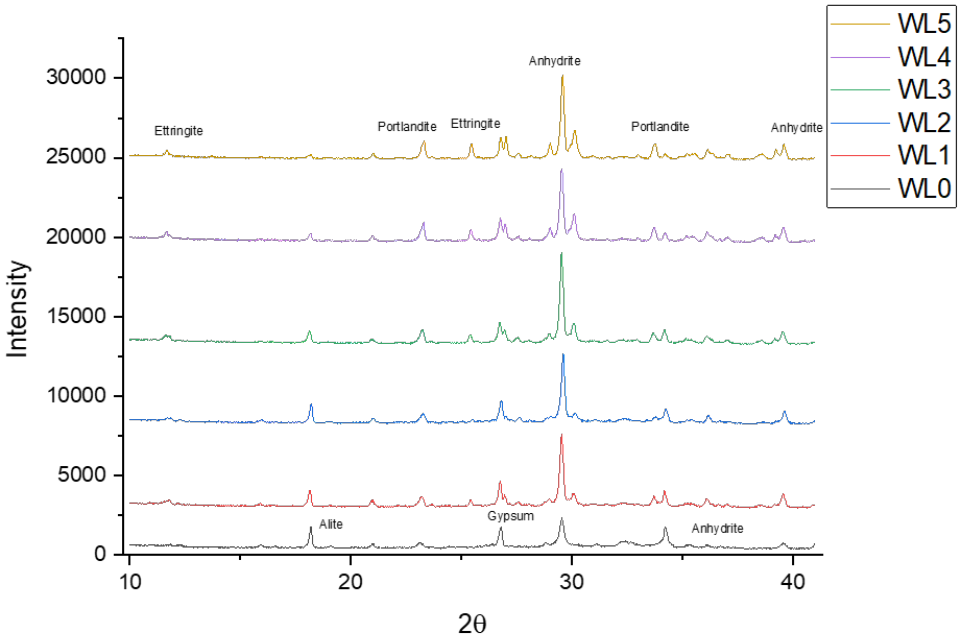

Fig. 4. XRD diffraction pattern for various mixes

Thermogravimetric analysis

Figs. 5 and 6 show the TGA and DTG curves for mixes WL0 to WL5. The presented TGA thermograms were analysed to quantify the portlandite and chemically bound water in the paste samples. The quantification of portlandite was done by integrating the DTG peak formed between 400-500°C. The chemically bound water contents were determined for the temperature between 150-990°C. The calculated portlandite content per gram of cement is presented in Table 2. There was an observed increment in the portlandite content up to Mix WL2, where the amount of replacement of cement is 40 wt% with 20 wt% wollastonite, 15 wt% limestone and 5 wt% gypsum. When the replacement of cement is increased beyond that, there is a drop in the quantity of portlandite. The increase in portlandite is a sign for the hydration reaction, which results in the formation of hydration compounds, thereby densifying the matrix of the paste.

In similar lines, the chemically bound water, which is a measure used to determine the degree of hydration, was also found to increase up to 40 wt% replacement of cement with 20 wt% wollastonite, 15 wt% limestone and 5 wt% gypsum. The chemically bound water per gram of cement content is presented in Table 2. Chemically bound water decreased with the increment in the replacement of cement. A significant effect was observed when cement was replaced with wollastonite by keeping limestone and gypsum as constant proportions. The contents of portlandite and chemically bound water grew up to the 20 % addition of wollastonite, above which there was a reduction and demonstrated their influence on the strength as well.

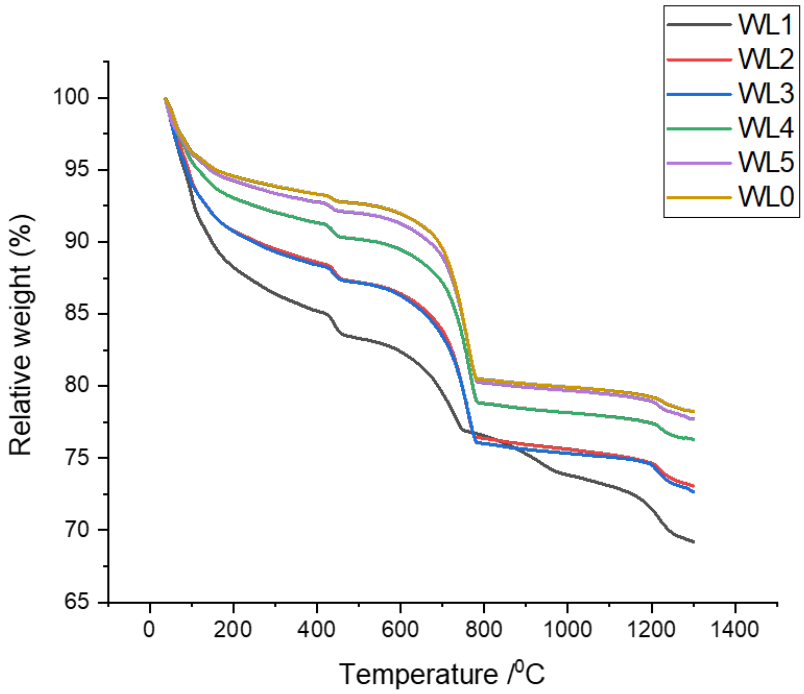

Fig. 5. TGA thermogram of wollastonite blended Portland Cement composites

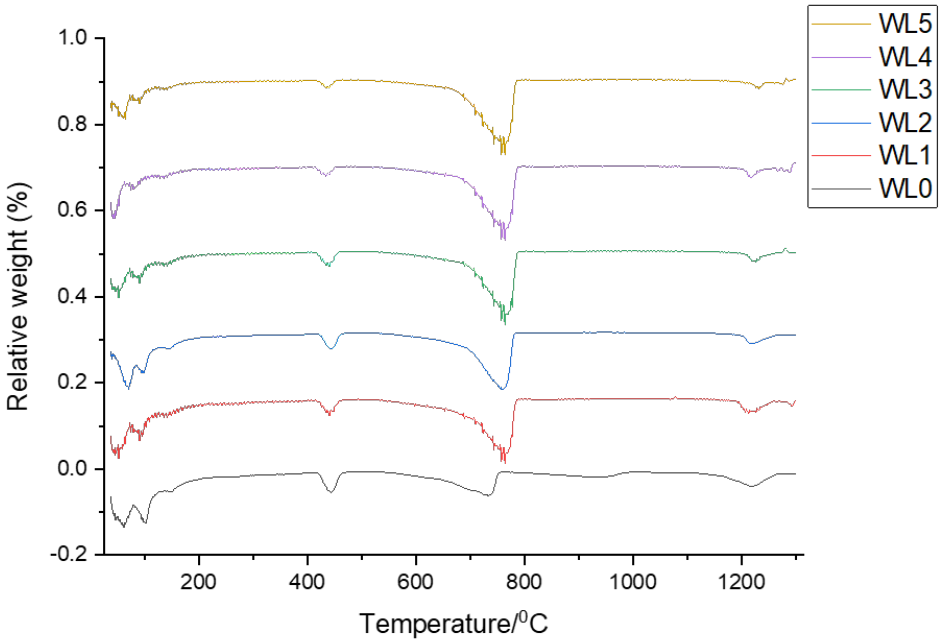

Fig. 6. DTG curves for the wollastonite blended Portland cement composites

TABLE 2. **Bound water and portlandite of wollastonite blended cement composites**

Mix	Chemically bound water (g/100 g of paste)	Portlandite (g/100 g of paste)
MWL0	18.04527	8.606844
MWL1	18.21811	6.357422
MWL2	18.81709	5.872443
MWL3	17.19017	5.351687
MWL4	16.32407	3.935844
MWL5	16.13016	3.460651

CONCLUSIONS

In the study, where cement was partially replaced with wollastonite, limestone and gypsum, it was observed that the replacement of cement with 20 wt% wollastonite along with 15 wt% limestone and 5 wt% gypsum proved to be the most advantageous mix. This mix designated as WL2 exhibited enhanced compressive and flexural strength. About 32% and 64% increases in the strength, respectively, in relation to the conventional mix, were observed at 28 days of curing. With the increase in the dosage of wollastonite, the flow index with respect to the conventional mix, declined owing to the fineness of the wollastonite, which results in the absorption of more water. This leads to a reduction in the workability of the formulated mixes as the wollastonite content was increased from 0 to 50%. The initial setting time was also observed to grow with the increasing replacement of cement with wollastonite from 0-50%. It was observed from the microstructural analysis that the increase in portlandite is a sign for the hydration reaction, which results in the formation of hydration compounds, thereby densifying the matrix of the paste, and in turn enhancing the strength of the composites.

Conflict of interest

The author declares that there is no conflict of interest.

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