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1. Introduction

The utilization of alkali activated materials (AAMs) as substitute to ordinary Portland cement has attracted great attention in recent years. This type of material generally exhibits better performances such as mechanical properties, durability, thermal properties and lower environmental impacts when compared to ordinary Portland cement. They can be classified into two types according to the calcium content in the raw materials. One is the high calcium system, having a C-A-S-H type gel as the main reaction product [1]. The other is the low calcium system, having N-A-S-H type gels with three-dimensional network as the major reaction product [2]. Recently, growing attention is paid to blended alkaline systems that are produced by mixing calcium enriched precursors with aluminosilicates due to several modified properties such as setting times, workability, shrinkage, mechanical properties and durability [3]. The reaction products in the blended system are stable coexisted C-A-S-H and N-A-S-H type gels with a higher degree of cross-linking [4]. The recent progresses in understanding the blended system and those modified properties indicate a promising future for the application of alkali activated materials.

On the other hand, limestone powder has been widely utilized in Portland cement system for the purpose of energy saving and carbon reduction. It has also been known to improve the workability and strength, to accelerate the hydration of C_3S , to partly participate in the formation of C-S-H gels and to interact with aluminate phases to form monocarboaluminate [5]. Meanwhile, attention has also been paid to apply this more sustainable material in alkali activated systems. Moseson et al. [6] incorporated limestone powder into sodium carbonate activated slag, the reported maximum limestone content was up to 68 wt.% while the mechanical properties were comparable to Portland cement. Yip et al. [7] studied the effect of calcite on silicate activated metakaolin, showing that a calcite content of less than 20% benefits the compressive strength. Cwirzen et al. [8] investigated the effect of limestone on sodium hydroxide activated metakaolin, reporting that limestone slightly promotes the dissolution of metakaolin. As can be noticed, the previous studies showed the superiority of limestone powder addition with regard to mechanical properties in alkali activated low calcium systems. However, there are limited mechanism studies concerning the role of limestone powder in the blended alkaline system, where large amounts of reactive calcium, silica and alumina units are present simultaneously, hydrated gels of different types are coexistent, and the synthesizing parameters and curing conditions exhibit a more sensitive influence on the final performances.

The purpose of this study is to understand the influence of limestone powder on early age reaction kinetics, mechanical properties and reaction products of alkali activated slag-fly ash blends. The micro scale analyses are carried out by using isothermal calorimetry, thermogravimetry (TG), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The potential physical and/or chemical effects of limestone on the blended alkaline system are discussed.

2. Experiment

2.1 Materials

The solid materials used in this study were ground granulated blast furnace slag, class F fly ash and limestone powder. Their chemical compositions are shown in Table 1. The median

particle size (d50) is 12.43 μm for slag, 22.06 μm for fly ash and 10.12 μm for limestone powder. The activator used was a mixture of sodium hydroxide pellets (analytical level) and sodium silicate solution (27.69% SiO_2 , 8.39% Na_2O and 63.92% H_2O by mass). The desired activator modulus (M_s , $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio) was achieved by adding different amount of sodium hydroxide pellets into the sodium silicate solution. The mixed activator solution was cooled down to room temperature prior to further use. Distilled water was added in order to reach the desired water/binder ratios.

Table 1: Major chemical compositions of raw materials

Oxides (wt.%)	Fly ash	Slag	Limestone
SiO_2	54.6	34.4	0.84
Al_2O_3	24.4	13.3	0.24
CaO	4.44	37.4	53.96
MgO	1.43	9.89	1.01
Fe_2O_3	7.2	0.47	0.32
Na_2O	0.73	0.34	0.21
K_2O	1.75	0.47	0.34
SO_3	0.46	1.23	-
LOI	2.80	1.65	43.01

2.2 Sample preparation

The used activator has an equivalent sodium oxide (Na_2O) content of 5.7% by mass of the solid material and an activator modulus (M_s) of 1.4 for all mixes. Three levels of slag content (60, 50 and 40 wt.%) and limestone additions from 0% to 30% by mass were used. The water/binder ratio was kept constant at 0.35. All samples were prepared in a laboratory mixer; the solid raw materials were added into the mixer followed by the activating solution. The mixtures were mixed at a slow speed for 30 s, then rested for 30 s before another 120 s at a medium speed. The fresh pastes were poured into plastic molds of 40 x 40 x 160 mm^3 with a plastic film on the top surface for 24 h; finally all specimens were demolded and cured at a temperature of 20 $^\circ\text{C}$ and a relative humidity of 95% until the testing ages.

2.3 Testing methods

The reaction kinetics was studied by an isothermal calorimeter. The solid raw materials were firstly mixed with the activating solution externally for about 1 min with vibration, then the mixed paste was injected into an ampoule and loaded into the calorimeter. All measurements were conducted for 72 h under a constant temperature of 20 $^\circ\text{C}$. The compressive strength tests were carried out according to EN 196-1. Cube samples with a size of 40 x 40 x 40 mm^3 were prepared and tested at the ages of 7 and 28 days, respectively. The TG analysis was conducted in a STA 449 F1 instrument, powder samples after 28 days of curing were heated up to 1000 $^\circ\text{C}$ at a speed of 10 $^\circ\text{C}/\text{min}$ with nitrogen as the carrier gas. The FTIR analysis was performed in a Varian 3100 instrument with the wavenumbers ranging from 4000 to 650 cm^{-1} at a resolution of 1 cm^{-1} . The XRD analysis was carried out with a step size of 0.02 $^\circ$ and a 2 θ range from 10 $^\circ$ to 80 $^\circ$.

3. Results and discussion

3.1 Reaction kinetics

The normalized heat flows of alkali activated slag-fly ash-limestone blends (with 60% slag) within the first 72 hours are shown in Figure 1a. The presented calorimetric curves are in

accordance with the previous studies on silicate activated slag or its mixtures [9,10], which show four typical reaction stages including initial dissolution, induction, acceleration and stable period. The acceleration peak is located at around 16 hours after mixing, which is assigned to the massive formation of reaction products from dissolved Ca, Si and Al units. It can be noticed that as the limestone content increases, the heat evolution peak slightly shifts to earlier locations with higher intensities. It indicates that the reaction process is slightly accelerated in the presence of limestone powder. This is in agreement with the previous researches in Portland cement hydration [11]. The incorporation of limestone powder brings more fine particles in the system, which provides additional nucleation sites for the formation of reaction products, then as a result the reaction process is accelerated. Figure 1b illustrates the heat evolution curves of samples with a slag content of 40% and limestone additions up to 30%. Both the induction and acceleration stages are significantly retarded when compared to the mixes containing 60% slag. Those changes demonstrate the remarkable effects of the slag content on the early age reaction. Under alkali activation, the breakdown of a calcium enriched structure is easier than Si and Al dominated ones such as fly ash. Thus a higher slag content will lead to a larger amount of available Si, Al and Ca units in solution, and consequently a more intense dissolution and reaction process. An evident promotion in induction and acceleration stage due to the increase of limestone powder content is also observed. But compared to the significant changes caused by slag, the effect of limestone powder on the early age hydration is at a relatively minor scale.

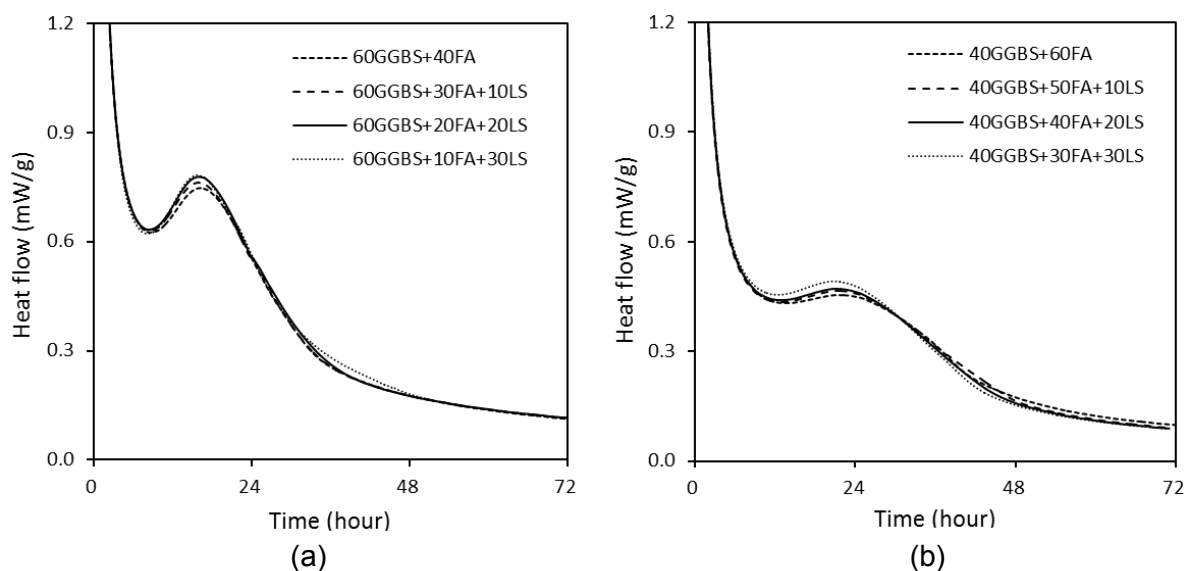


Figure 1: Normalized heat flow of AA slag-fly ash-limestone with 60% (a) and 40% (b) Slag

3.2 FTIR and XRD analysis

Figure 2 shows the infrared spectra of the unreacted slag, fly ash and slag-fly ash-limestone blends after alkali activation. The main vibration band is at around 900 cm^{-1} for slag and about 1020 cm^{-1} for fly ash, which are associated with the asymmetric stretching vibration of terminal Si-O and bridge Si-O-T bonds, respectively [12,13]. The difference in the main absorption band illustrates the different glassy networks of the raw materials. The absorption bands located at around 1080 , and 600 to 800 cm^{-1} in fly ash indicates the presence of quartz and mullite. After alkali activation, all mixes show OH groups at 1640 cm^{-1} and around 3350 cm^{-1} , demonstrating the presence of chemically bound water within the reaction products. The absorption bands at around 1420 , 870 and 710 cm^{-1} correspond to the vibrations of O-C-O in carbonates. The main absorption band of the reaction products is located at around 950 cm^{-1} in all mixes, which is assigned to the asymmetric stretching vibration of Si-O terminal (non-bridging) bonds, indicating that the main reaction product in is

a chain structured C-A-S-H type gel. The Si-O bond in unreacted slag is around 900 cm^{-1} ; the shifting of this band to higher wavenumbers implies the formation of a higher polymerized Si-O network. Concerning the fly ash, the main absorption bands shifts from 1020 cm^{-1} to lower numbers after activation, indicating that the high crosslinking networks with bridging Si-O bonds are not formed in this study. It can be seen that as the limestone content increases, the intensity of the absorption bands that represent carbonates increase significantly; while compared to the changes in O-C-O groups, no remarkable change is observed in the absorption bands (both location and intensity) of bound water and terminal Si-O.

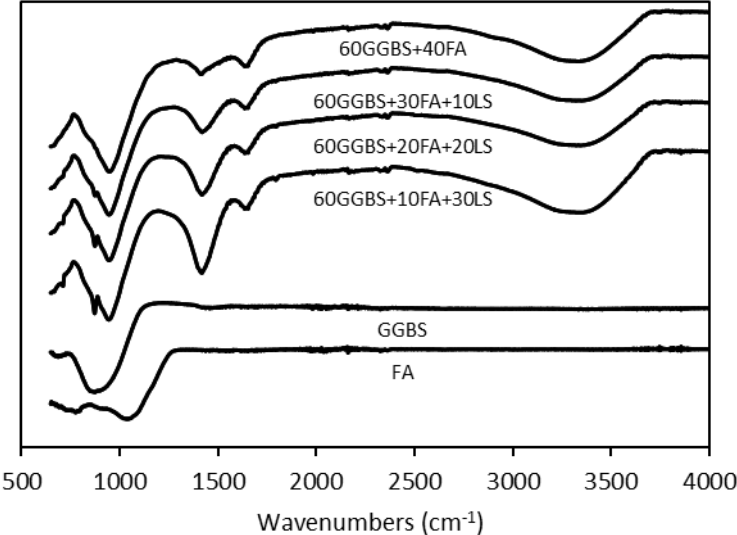


Figure 2: FTIR spectra of slag, fly ash and AA slag-fly ash-limestone

The XRD patterns of unreacted slag, fly ash are shown in Figure 3, as well as the samples with a slag content of 60% and limestone additions from 0 to 30%. It can be seen that the original slag is mainly amorphous without significant crystalline phases, and shows a peak hump between 25 and 35° due to the amorphous components; while the unreacted fly ash contains crystalline phases such as quartz (SiO_2), mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), maghemite and hematite (Fe_2O_3) with a broad amorphous hump between 15 and 30° .

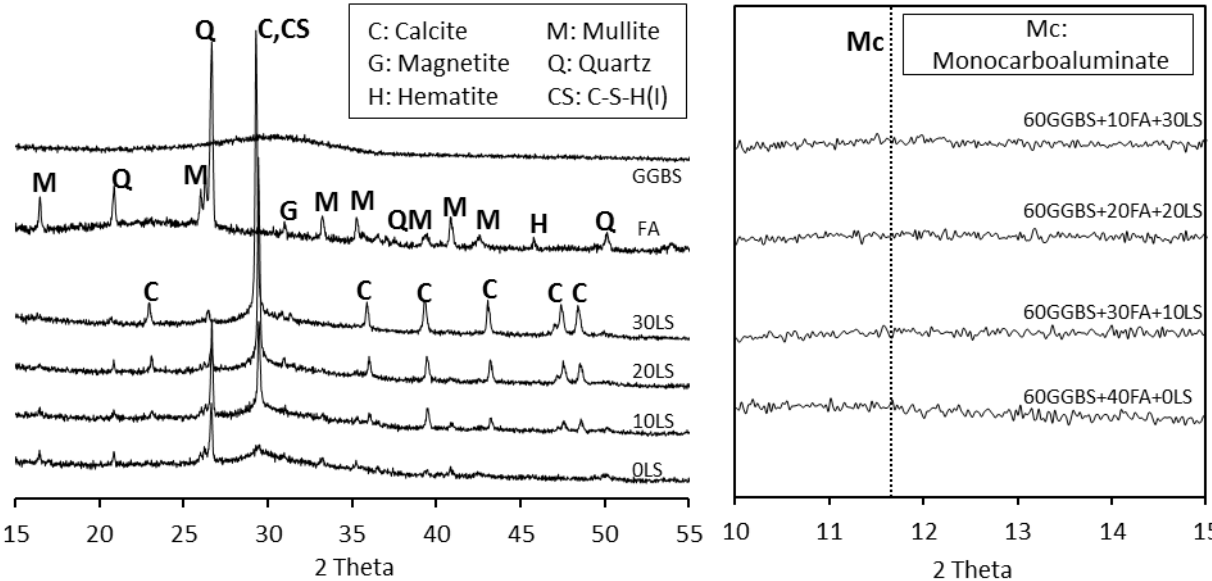


Figure 3: XRD patterns of slag, fly ash and AA slag-fly ash-limestone

After activation, the characteristic peaks of quartz, mullite and maghemite/hematite from fly ash remain existing. The incorporation of limestone leads to the presence of calcite peaks. The intensity changes of those crystalline peaks in the reaction products are due to the different relative content of fly ash and limestone in each mixes. All samples show a main reaction product at around 29.5° , which is identified as a poorly crystallized C-(A)-S-H gel. In addition, the previous studies concluded that the presence of limestone powder would lead to the formation of monocarboaluminate in both Portland cement and alkali activated system, especially in high aluminate conditions [5,8]. Thus an XRD observation that focused on low angles was conducted and the result is shown in Figure 3 on the left. The characteristic peak of monocarboaluminate, which is usually shown at around 11.7° [14], is not observed in this study. Thus it can be concluded that no evident chemical reaction took place between the limestone powder and the aluminate units in this case, or the chemical reactions involving the limestone powder did not result in the formation of additional crystalline phases.

3.3 TG analysis

The thermogravimetry results of samples with a slag content of 60% and limestone additions up to 30% are presented in Figure 4. All samples exhibit a remarkable mass loss before around 110°C , which is assigned to the loss of physically bound water within the paste. Specimens without limestone show an evaporable water content of 16.1%, which is slightly lower than the ones with limestone addition. Afterwards, all samples show a negligible mass loss between 105 and 180°C , followed by a gradual decrease in mass until heated to around 600°C . After around 600°C , mixes without limestone powder show a stable curve with slight mass loss until 1000°C , and no other abrupt mass losses are observed between 105 and 1000°C . It reveals that the reaction products are mainly amorphous gels with bound water. When the limestone powder is incorporated, samples show a remarkable mass loss between 600 and 800°C , which is mainly caused by the decomposition of the carbonates.

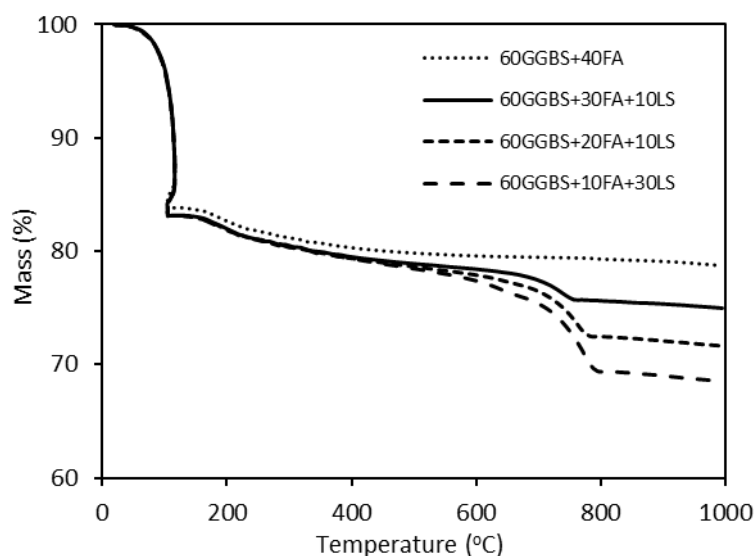


Figure 4: TG analysis of AA slag-fly ash-limestone

Based on the understandings above, a calculation on the physically and chemically bound water contents was carried out. The physically bound water content was calculated as the mass loss before 105°C ; the chemically bound water content in each mix is calculated by the mass loss between 105°C and 1000°C with the exclusion of the mass loss due to the incorporated limestone. The calculated total mass includes the alkali activator and solid raw materials. The results are presented in Table 2, as can be seen that the addition of limestone powder leads to a slight increase in the total chemical water content. Thus it is possible that

the additional nucleation sites that are provided by the fine limestone particles promote the formation of hydrated gels and refine the pore structures, then result in a slightly increased physically and chemically bound water contents; or a slight but non-ignorable amount of Ca^{2+} is released from the fine limestone particles under alkali activation, then participates in the reaction process and leads to a slight increase in the bound water content.

Table 2: Calculation of bound water content (wt.%).

	60GGBS 40FA 0LS	60GGBS 30FA 10LS	60GGBS 20FA 20LS	60GGBS 10FA 30LS
Mass loss between 105 °C -1000 °C	5.09	8.11	11.46	14.53
Limestone powder incorporated	0	6.70	13.38	20.07
Mass loss of limestone powder	0	2.88	5.75	8.64
Chemical bound water	5.09	5.23	5.71	5.89
Physical bound water	16.1	16.9	16.9	16.9

3.4 Compressive strength

The 7 and 28 day compressive strength of alkali activated slag-fly ash-limestone pastes are shown in Figures 5. For samples with constant slag content, both the 7 and 28 days compressive strength are increased when increasing the limestone powder content. Similar results are also found in samples with other slag contents and the highest strength is all shown in samples with the 30% limestone addition. The addition of limestone powder will lead to a higher content of fine particles within the paste, which could work as micro aggregates and reduce the total porosity, then result in an increment of strength.

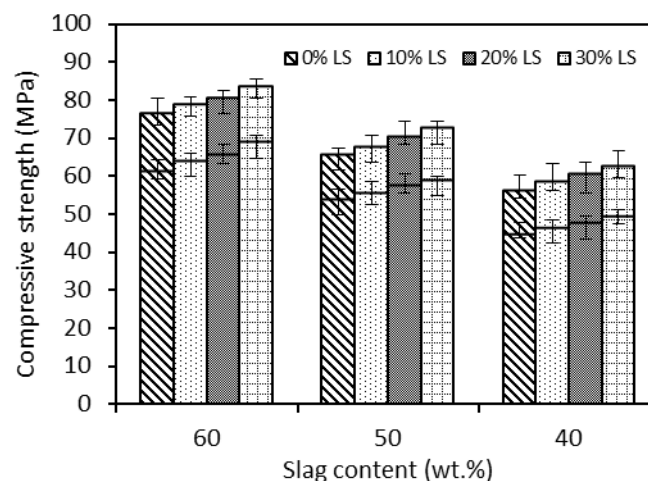


Figure 5: Compressive strength of AA slag-fly ash-limestone pastes

It can be obviously seen that for a constant limestone replacement, higher compressive strengths are achieved in samples with higher slag contents at both 7 and 28 days. The significant influence of the slag content on mechanical strength was also reported in previous studies [15,16]. This should be attributed to the considerably higher reactivity of slag than the rest components under ambient temperature. It can be noted that based on a constant slag content, mixes with different limestone contents show a similar rate of strength development

between the 7 and 28 days. Considering that the increased limestone content is at the expense of fly ash content in this case, it also demonstrates the low reactivity of fly ash until the age of 28 days under ambient curing condition; or the dissolved Si and Al units from fly ash exhibits much less influence than the Ca from slag on strength in this case.

3.5 The role of limestone powder in blended alkali systems

As commonly known, limestone powder exhibits both physical and chemical effects on Portland cement system, which can be briefly summarized as follows: lowering the water demand of cement paste; accelerating the hydration process; reacting with aluminate phases to form monocarboaluminate [17] and affecting the strength. While in alkali activated system, according to the investigations in this paper, the physical effect of limestone powder on blended alkaline system is also obvious. However, the chemical effects of limestone powder in blended alkali system are different from that in Portland cement system. It has been known that the presence of limestone in calcium and high aluminates conditions modifies the Portland cement system following the mechanism expressed as:



where: A=Al₂O₃, CH=Ca(OH)₂, H=H₂O, CC=CaCO₃.

This process increases the total volume of the solid phases and results in the increment of compressive strength in Portland cement system. The occurrence of this reaction is highly dependent on the Al and Ca supply. While in the case of alkali activated slag-fly ash-limestone blends, all the required elements for the reaction above are available but the formation of C₄ACH₁₁ is not observed. One possible explanation is that the dissolved Ca, Si, Al units from the slag and fly ash prefer the formation of more stable structure of C-(A)-S-H type gels, when the formation of C-(A)-S-H gel is saturated, the remaining units may react with limestone powder to form C₄ACH₁₁. However, it seems that the remaining do not meet the requirements of the equation above; a possible reason is the absence of calcium: the C-S-H gels in alkali activated system show a Ca/Si of around 1.0-1.2 and the Ca/Si (molar ratio) in the raw slag is 1.17. While the total Ca/Si in the system would be lower than 0.85 (in samples with 60% slag) when calculating the silicate from the activator, this value would be even lower when considering the silicate from fly ash. Thus no sufficient calcium will remain after the formation of C-(A)-S-H gels. Besides, it should be noted that the dissolution of Ca²⁺ from calcium carbonates in alkali activated system was actually confirmed by [8]; also the satisfying surface binding between the limestone powder and alkali activated materials was suggested in the previous study [7]. Thus the slightly increased bound water content together with the continuously increased compressive strength could be regarded as an indication that the limestone powder may not only work as a non-reactive filler, the release of Ca²⁺ from limestone powder and its topography characters may also make small but non-negligible contributions to the strength development and pore structure refinement by providing extra surface binding within particles.

4. Conclusions

This paper investigates the effects of the raw material composition on the reaction kinetics, gel characters and compressive strength of room temperature cured alkali activated slag-fly ash-limestone blends. The results show that the additional nucleation sites provided by limestone powder slightly accelerate the induction and acceleration stage of reaction. The gel character analyses conducted by FTIR, XRD and TG show that the reaction products are governed by the chain structured C-(A)-S-H type gels. The presence of limestone powder does not lead to the formation of new phases but slightly increases both the physically and chemically bound water content. Higher compressive strengths were observed in samples with a higher slag content; while for a constant slag content, the compressive strength increases with an increasing limestone powder content. The limestone powder shows mainly

physical with slight but non-ignorable chemical modifications of alkali activated slag-fly ash blends. It is suggested that the absence of monocarboaluminate is due to the insufficient supply of additional calcium in this case; and the small amount of the released Ca^{2+} from the limestone together with its filler effect result in the pore refinement and strength increment.

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