

Alkali-activated Carbonatite and Slag Composite Cementitious Materials

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Abstract: Alkali-activated carbonatite and slag cementitious material (AACSCM for short) with adequate strength and suitable setting time was prepared by activating ground low-grade carbonatite and ground granulated blast-furnace slag (GGBFS for short) with sodium silicate solution at room temperature. AACSCM behaves quick setting when a proper setting retarding technique is not applied. In this experiment, it was found that barium chloride had a satisfactory retarding effect on the setting of the material. Besides, the strengths of AACSCM mortars were also improved after the addition of barium chloride. The effect of preparation parameters, such as GGBFS addition, concentration and modulus n (mole ratio of SiO_2 to Na_2O) of sodium silicate solution on the strength of AACSCM was also investigated. There exists synergistic effect in the AACSCM system, i.e. ground carbonatite and granulated blast-furnace slag have a synergistic contribution to the strength gain of AACSCM.

Key words: alkali-activated cementitious material; carbonatite; granulated blast-furnace slag; setting; synergistic effect

1 Introduction

The production of Portland cement has resulted in serious impacts on energy, natural resource and environment. Therefore, producing cementitious materials with less energy consumption, less waste and pollution generation using industrial by-products and wastes has aroused worldwide concerns and interests[1]. Carbonatite, with CaO less than 45% and MgO of 6-20% by mass in composition, cannot be used both in metallurgy industry and cement production, practically being a natural rest-resource with large reservation in China. Granulated blast-furnace slag

(GBFS), a by-product, is produced during the production of pig-iron from iron ore. Carbonatite was used to prepare alkali-activated carbonatite cementitious material (AACCM)[2] and granulated blast-furnace slag for alkali-activated slag (AAS) cement[3-7]. The reaction degree of the starting components in AACCM and AAS is different: low at early age but increases slowly with time for AACCM and high at early age but ceases to increase later for AAS. Based on the difference in reaction process and performance complementarity of the two materials, a new type of material, called alkali-activated carbonatite-slag cementitious material (AACSCM) in which ground carbonatite served as dominative starting material, was developed in this study.

S.Y.Zhao and Q.J.Yu et al[8] found that with partial replacement of ground carbonatite with ground GBFS(GGBFS) in the preparation of AACCM, both the compressive strength and water impermeability of the material were much improved, but at the same time the setting time and fluidity of the material were greatly decreased. Evidently, developing an effective agent to retard the setting of the material is of significance to its application.

In this experiment, several setting retarding reagents often used in AAS[4,9-13] were used to retard the setting of AACSCM, but it was found they were ineffective or with a little effect. By trial and error, BaCl_2 was found effective. The strength property and the synergistic effect occurring in AACSCM system were investigated as well. The synergistic effect was studied by comparing mortar strength of the following three systems: (1) AACSCM; (2) AACSCM system but in which carbonatite was wholly replaced with the same volume of ground zirconite (inactive to alkalis); and (3) AACSCM system but in which GGBFS was substituted with the same volume of ground zirconite and microstructure observation.

2 Experimental

2.1 Raw Materials

Natural carbonatite, granulated blast-furnace slag from Shaoguan Iron and Steel Group Co. Ltd., zirconite from Shanghai, industrial grade solid sodium silicate with modulus n of 2.0 (molar ratio of SiO_2 to Na_2O) and chemically pure sodium hydroxide were used in the experiment. Carbonatite and granulated blast-furnace slag were finely ground before use. Chemical composition, particle size distribution and physical properties of raw materials used in the experiment are given in Table 1 and Table 2, respectively. Chemical reagents, $\text{Zn}(\text{NO}_3)_2$, H_3PO_4 , Sugar, $\text{Ca}(\text{NO}_3)_2$, $\text{Ca}(\text{OH})_2$, $\text{Pb}(\text{NO}_3)_2$, Malic acid, Na_3PO_4 , NaCl , $\text{Na}_2\text{B}_4\text{O}_7$ and BaCl_2 , used as setting retarder of AACSCM, were of analytically pure grade.

Sodium silicate solution was prepared by dissolving solid sodium silicate and sodium hydroxide in tap water to achieve required modulus and concentration.

Table 1 Chemical composition of pulverized raw materials used in the experiment(%)

Materials	Loss on ignition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O
Carbonatite	44.91	1.11	0.62	1.35	37.15	14.39	0.10	0.36
GGBFS	0.01	31.14	19.33	1.03	34.24	11.75	0.43	0.60

Table 2 Particle size distribution(%)and physical properties of pulverized raw materials

Materials	Particle size, μm							Blaine specific surface, $\text{m}^2 \cdot \text{kg}^{-1}$	Density, $\text{kg} \cdot \text{m}^{-3}$
	<2	2-5	5-10	10-15	15-20	20-30	30-60		
Carbonatite	19.45	21.82	18.98	13.39	8.45	10.74	7.17	520	2740
GGBFS	20.52	22.36	21.41	14.51	10.52	9.11	1.57	500	2920
Zirconite	19.17	20.15	18.59	12.06	9.36	10.28	10.39	470	4160

2.2 Specimen Preparation

The chemical reagents were weighed by the mass percentage of GGBFS and dissolved in tap water (except for Ca(OH)₂) prior to mixing, giving setting retarder solution.

The typical AACSCM pastes were prepared as following: GGBFS was mixed with setting retarder solution (tap water was used in control sample) in a planetary mixer for 4mins at a mass ratio of setting retarder solution to GGBFS of 0.5 at first, then sodium silicate solution and ground carbonatite were added and mixed for another 4mins. The w/c, i.e. the mixing solution (sodium silicate solution + setting retarder solution or tap water) to ground carbonatite and GGBFS was 0.8 by mass ratio. The paste was finally poured into GSM-III type mill for further grinding and homogenization.

In the preparation of the pastes for setting time test, the replacement ratio of ground carbonatite with GGBFS (denoted as M_s) was 30%, and the mixing solution used was with n of 1.6 and C_{ss} of 35%, where n denotes the mole ratio of SiO₂ to Na₂O (modulus), and C_{ss} the mass percentage of Na₂O and SiO₂ in the solution.

The mix proportions of the three comparable systems mentioned above are given in Table 3. One is CS system, i.e. AACSCM, consisted of ground

carbonatite, GGBFS and sodium silicate solution. The others are ZS system and CZ system, in ZS system finely pulverized zirconite was used to replace ground carbonatite and in CZ system GGBFS was replaced by pulverized zirconite by iso-volume. The preparation process of ZS system and CZ system are the same as that of CS system described above.

In the preparation of 40×40×160mm mortar prisms, the volume ratio of paste to ISO standard sand was fixed at 0.43. After casting and moist curing for 1 day, the prisms were demoulded and then cured at 20±1 °C and R.H. of 95%.

Table 3 Experimental scheme and proportions of materials

CS system				ZS system	CZ system
Serial number	Sodium silicate solution		GGBFS content, $M_s, \%$	Serial number	Serial number
	Modulus n	Concentration, $C_{ss}, \%$			
CS1	1.6	35	15	ZS1	CZ1
CS2	1.6	35	40	ZS2	CZ2
CS3	1.6	40	30	ZS3	CZ3
CS4	1.6	45	30	ZS4	CZ4
CS5	1.8	40	30	ZS5	CZ5
CS6	1.8	45	30	ZS6	CZ6

3 Results and Discussion

3.1 Influence of chemical reagents on the setting time of AACSCM

It has been reported that some chemical reagents such as NaCl, malic acid, $Zn(NO_3)_2$, $Pb(NO_3)_2$, phosphate, calcareous material, etc. can well retard the setting of Alkali-activated Slag (AAS) cementitious materials[4,9-13]. Therefore, the effect of the above reagents and a newly found setting retarder, $BaCl_2$, on AACSCM was studied.

Fig. 1 shows that the influence of chemical reagents on the setting time of AACSCM paste is varied with their kind and added amount. With adding $Ca(NO_3)_2$, $Ca(OH)_2$, malic acid and H_3PO_4 to AACSCM, its setting time is shortened in comparison to that of control sample, whereas it is extended when sugar, NaCl, $Na_2B_4O_7$ and $BaCl_2$ is added. $Pb(NO_3)_2$, $Zn(NO_3)_2$ and Na_3PO_4 have retarding effect when their addition is greater than 3.0% of GGBFS by mass, but the setting time is merely extended by 30mins. Of all

the chemical reagents investigated, BaCl_2 can markedly retard the setting of AACSCM paste, with 4.5% BaCl_2 addition the setting time is increased to 5.5h. Furthermore, it is proportional to the addition of BaCl_2 (Fig.2). Therefore, the setting time of AACSCM can be well adjusted by the addition of BaCl_2 . The retarding mechanism of BaCl_2 in this system was discussed in our previous reports[14].

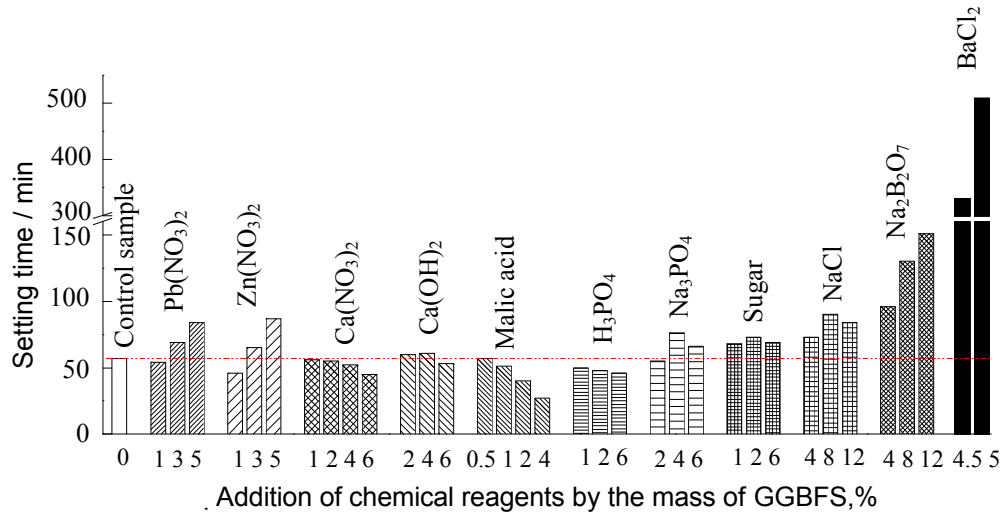


Fig.1. Effect of chemical reagents on the setting time of AACSCM

3.2 Strength development of AACSCM

3.2.1 With and without BaCl_2 addition

The compressive strength of AACSCM mortars with or without BaCl_2 addition are shown in Table 4. The results show that the compressive strengths of AACSCM mortars at different curing ages are all increased evidently after BaCl_2 addition. With BaCl_2 added, the setting time of AACSCM is increased and the fluidity of fresh AACSCM mortars is improved, resulting in forming a more compact structure after hardening.

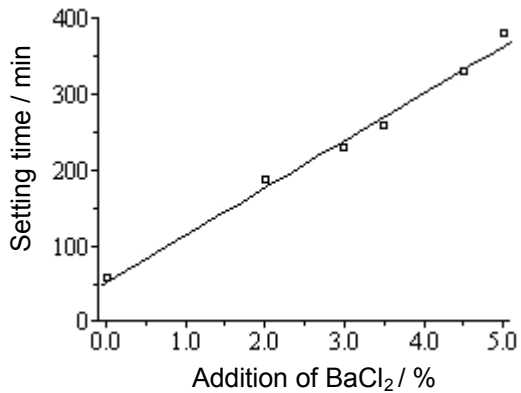


Fig.2. Retardation effect of BaCl_2 ($M_s=30\%$, $n=1.4$, $C_{ss}=40\%$)

Table 4 Effect of BaCl₂ on the compressive strength of AACSCM mortars

Modulus <i>n</i>	<i>C_{ss}</i> , %	<i>M_s</i> , %	Compressive strength, MPa					
			Without BaCl ₂			With 5% BaCl ₂ addition		
			3d	7d	28d	3d	7d	28d
1.4	35	15	5.6	7.7	9.9	9.4	11.0	12.5
1.4	35	30	13.8	15.2	20.1	21.1	28.3	34.0
1.4	40	15	6.9	8.3	11.1	10.1	12.0	13.4
1.4	40	30	16.7	18.4	23.6	25.8	32.3	36.9
1.6	35	30	16.0	16.3	24.4	17.2	18.7	22.5

3.2.2 Effect of preparation parameters

The relation between mixing proportion and compressive strength of AACSCM mortars are summarized in Table 5 from which it can be seen that when GGBFS replacement is between 30% and 50%, have high strength. For instance, with $n=1.4$, $C_{ss}=35\%$ and 30% GGBFS replacement of carbonatite, the 3d and 28d strength of AACSCM mortar specimens was around 30MPa and 60MPa, respectively, and when GGBFS replacement is increased to 50%, compressive strength at 3d and 28d reaches about 50MPa and 90MPa, which is in much excess of the compressive strength of pure AACCM specimens reported by S.H.Yin and Z.Y.Wen et al[2], also higher than those reported by A. R. Brough and A. Atkinson for sodium silicate-based alkali-activated slag mortar specimens, 44MPa at 3d and 78MPa at 28d[5].

From Table 5 it can be also found that: (1) strength of the tested specimens continues to increase during the tested ages; (2) at the same concentration of sodium silicate solution and with the same amount of GGBFS replacement, the mortar strength at ages up to 90 days are greatly influenced by the modulus of sodium silicate: the lower the modulus, the higher the strength gains; (3) for given modulus of sodium silicate solution and GGBFS replacement, the strength is increased with the concentration of sodium silicate solution; and (4) strength of the specimens with the same modulus and concentration of sodium silicate solution is enhanced with the increment of the replacement of ground carbonatite with GGBFS.

3.2.3 Synergistic effect occurring in AACSCM

The compressive strengths of CS_i , ZS_i , CZ_i and ZS_i+CZ_i $i=1-6$ at different ages are shown in Fig.3, from which it can be seen that for given preparation parameters, at early ages, e.g. 3d and 7d, there is no evident difference between CS_i and ZS_i+CZ_i . However, at late ages, e.g. 28d and

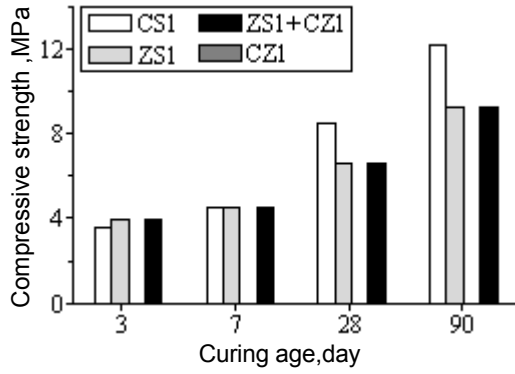
90d, the strength of CS system is much higher than that of the sum of ZS and CZ.

Table 5 Compressive strength of AACSCM

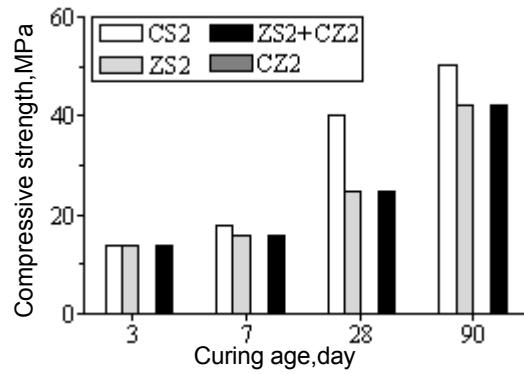
Sodium silicate solution		M_s , %	BaCl ₂ addition, %	Compressive strength, MPa			
Modulus n	C_{ss} , %			3d	7d	28d	90d
1.4	35	30	4.5	29.3	36.5	61.8	71.7
1.4	35	40	3.5	41.2	55.4	78.9	88.8
1.4	35	50	4.0	49.5	66.5	89.3	97.5
1.4	40	30	4.0	35.2	44.4	66.4	76.6
1.4	40	40	3.5	49.2	61.0	84.9	100.3
1.6	35	30	4.0	25.2	26.3	34.8	66.4
1.6	35	40	3.0	33.2	36.8	52.8	80.7
1.6	35	50	3.25	38.8	47.4	68.6	84.9
1.6	40	30	3.75	29.8	31.2	40.2	56.0
1.6	40	40	3.0	40.9	47.2	67.2	89.5
1.8	35	30	3.0	22.2	21.4	24.7	30.9
1.8	35	40	2.5	26.8	25.5	31.7	56.9
1.8	35	50	2.5	27.9	27.5	37.8	74.2
1.8	40	30	3.0	25.4	26.9	33.6	40.9
1.8	40	40	2.75	36.3	38.9	46.7	68.4

Zirconite can be considered to have little contribution to the strength gain of the material at room temperature because it is chemically inert when exposed to alkali. Due to the closeness of Blaine specific surface area and particle size distribution of the three materials used, the difference in physical filling effect among them is minor. So the reason for the superiority of the strength of CS system to others is likely attributed to the synergistic effect between GGBFS and ground carbonatite under the activation of sodium silicate solution.

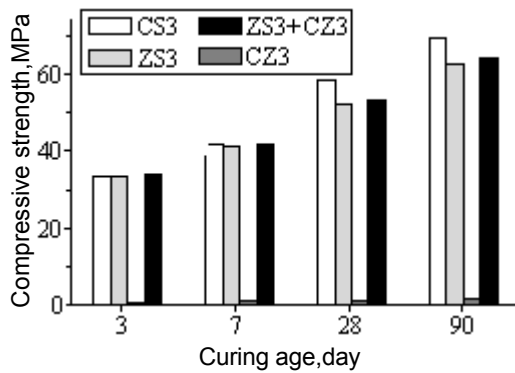
It is known that GGBFS is an active mineral admixture and a major constituent contributing to the strength development of AACSCM, which can also explain why the strengths of AACSCM is elevated considerably with the addition of GGBFS. But at late ages the contribution of GGBFS to strength development becomes weak. Some SEM images of hardened AACSCM mortars with different ages are given in Fig.4. It can be seen that at 3d the starting particles are about 3 μ m in size and become thinner and smaller with time. The mechanism for the formation of synergistic effect might be described as follows: carbonatite particles is gradually corroded in sodium silicate solution, releasing Ca²⁺ and Mg²⁺, which react with GGBFS



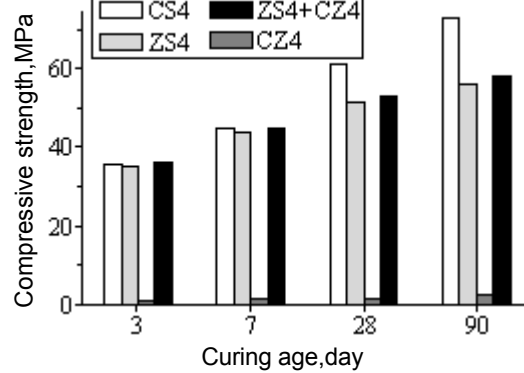
(a) Compressive strength of AACSCM with $n=1.6$, $C_{ss}=35\%$ and $M_s=15\%$



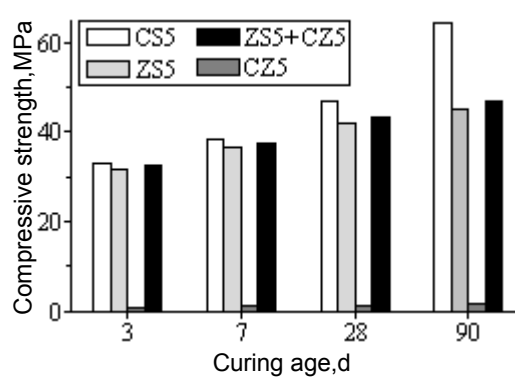
(b) Compressive strength of AACSCM with $n=1.6$, $C_{ss}=35\%$ and $M_s=40\%$



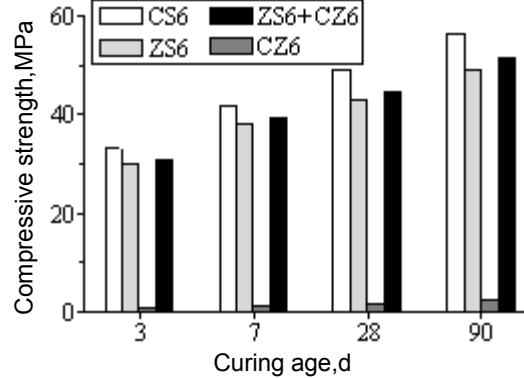
(c) Compressive strength of AACSCM with $n=1.6$, $C_{ss}=40\%$ and $M_s=30\%$



(d) Compressive strength of AACSCM with $n=1.6$, $C_{ss}=45\%$ and $M_s=30\%$



(e) Compressive strength of AACSCM with $n=1.8$, $C_{ss}=40\%$ and $M_s=30\%$



(f) Compressive strength of AACSCM with $n=1.8$, $C_{ss}=45\%$ and $M_s=30\%$

Fig.3 Comparison of the compressive strength of different systems and sodium silicate solution to form hydrated calcium silicate and hydrated

magnesia silicate. On another hand, the reaction promotes the corrosion and size minimization of carbonatite particles, leading them to become irregular and thin-sized at late stage of reaction. These minimized particles fill in the pores and make the hardened paste more compact, contributing to the strength increment in a large scale.

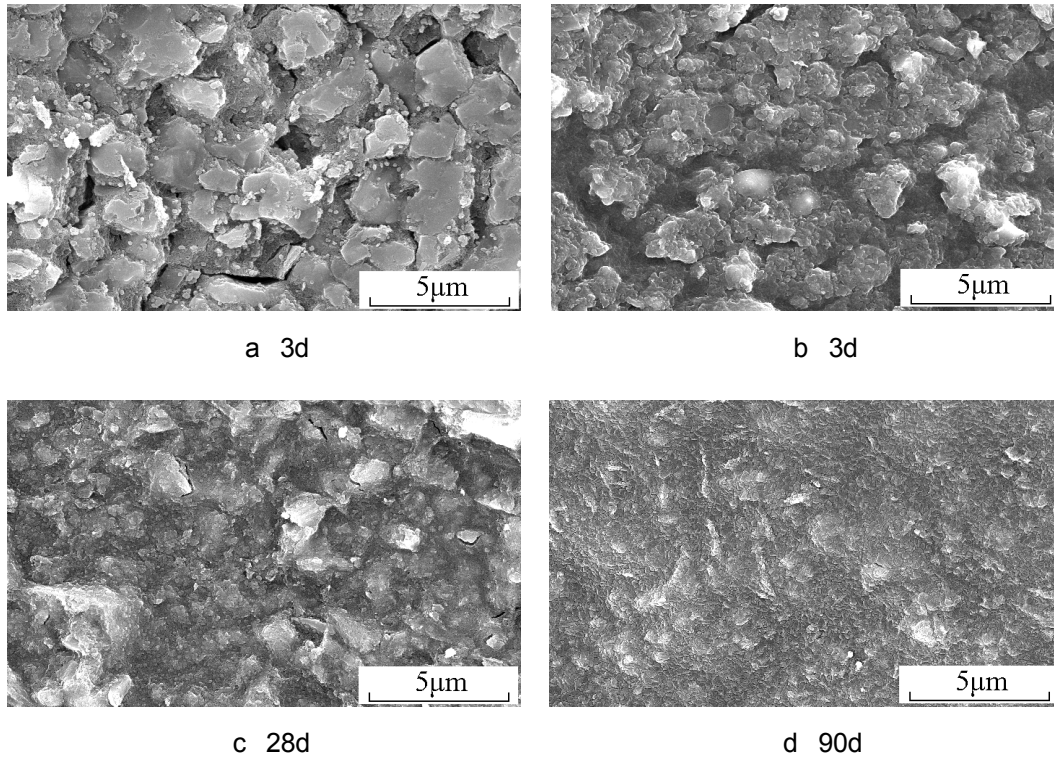


Fig.4 SEM images of AACSCM pastes ($n=1.6$, $C_{ss}=35\%$, $M_s=30\%$)

4 Conclusions

(1) Chemical reagent $BaCl_2$ can efficiently retard the setting of AACSCM paste and improve the strength of AACSCM mortars when the modulus, concentration of sodium silicate solution and the replacement of GGBFS are between 1.4-1.8, 30-50%, 15-50%, respectively.

(2) The strength of AACSCM mortars is improved with the increase of curing time, the replacement of ground carbonatite with GGBFS and the concentration of sodium silicate solution. But the increase of the modulus of sodium silicate solution is unfavorable to the strength gain of AACSCM.

(3) There does exist synergistic effect in AACSCM system, which improves the strength of AACSCM at late ages. The formation of the synergistic effect is attributed to: the corrosion effect of sodium silicate solution on carbonatite particles; reaction occurring among GGBFS, sodium silicate solution and Ca^{2+} , Mg^{2+} released from the corrosion of carbonatite particles promotes

the minimization of the size carbonatite particles, leading them to become irregular and thin-sized at late stages of reaction. These minimized particles fill in pores and make the hardened paste more compact, contributing to the strength gain in a large scale.

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