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Engineering Properties and Microstructural Performance of Low Energy Super-Sulfated Cement Using Industrial Waste Anhydrite

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Abstract. This study aims at proposing the mix proportions of low energy super-sulfated cement (SSC) concrete from industrial waste anhydrite from circulating fluidized bed combustion (CFBC) fly ash (CFA) as an alternative sulfate activator of ground granulated blast furnace slag (GGBFS/slag). The optimized mix proportion of the SSC was carried out by using mixture of different amounts of CFA in range of 25－45 wt.% and various quantities of ordinary Portland cement (OPC) in range of 0－10 wt.% to trigger the hydration of slag. Experimental results showed that with the expected slump at values of 190－220 mm, the 28-day compressive strengths of the concrete with low energy SSC reached 43.69 MPa which can be feasibly applied for widely advanced construction materials. The OPC in range of 3－5 wt.% and 25 wt.% of CFA were considered as the optimum ingredients of the activator and was suggested to be used for fabricating the low energy SSC concrete with the good performance on compressive strength, dynamic Young’s modulus, UPV measurement, and stabilized change of length. The OPC additive up to 10 wt.% was encouraged to be used for producing the SSC concrete with significant reduction on creep.

1 Introduction

The ordinary Portland cement (OPC) has become one of the primary construction materials because of its lower energy consumption than those of others such as aluminum and steel. However, the cement industry has been remarked as an intensive consumer of natural raw materials, fossil fuels, energy, and a major source of multiple pollutants [1]. Indeed, during the manufacturing process of OPC cement, a great deal of amounts of lime stone, quartz, and clay are fed as the raw materials. As such, the OPC manufacture significantly causes the serious damage of natural resources, particularly the surface of the earth. During the past decades, super-sulfated cement (SSC), which is fabricated mostly without OPC, has become one of the promising candidates of alternative ordinary Portland cement and has been the research interest because of the lowered energy consumption and superior durability in terms of resistances to chemical attacks [2]. Indeed, the SSC has been commercially manufactured in Europe and India to reduce the impacts from OPC manufacture on high consumption of natural material and energy and air pollution caused by carbon dioxide emissions. In general, the SSC is comprised by mixture of 80-85% ground granulated blast furnace slag, 10-15% sulfate activator (anhydrite/gypsum) and low amount of OPC (normally 5%) [3-5]. Recently, to produce the SSC with lowered cost, the utilization of industrial waste gypsum such as flue gas desulfurization (FGD) gypsum was proposed to be used as sulfate activator instead of using commercial gypsum [6, 7]. In addition, the industrial waste anhydrite included in circulating fluidized bed combustion (CFBC) fly ash was also used as alternative sulfate activator in low energy SSC [8, 9]. However, the studies focusing on using the combination of CFBC fly ash and OPC as the activator for low energy SSC has not been found. Therefore, this study proposes a new way for manufacturing low energy SSC by using the CFBC fly ash totally replacing for commercial gypsum and small amount of OPC as the activator of slag. The proposed concrete with low energy SSC, in this study, plays an important role in enriching the categories of green cement mostly qualifying for the requirements from the development of sustainability.

2 Experimental program

2.1 Materials and mix proportions low energy SSC

The commercial Type I Portland cement in accordance to ASTM C150 and CFBC fly ash (CFA) were used as the alkali and sulfate activators, respectively. Ground granulated blast furnace slag (GGBFS) and CFBC fly ash

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(CFA) were used as the primary powder. The chemical and mineral compositions of raw materials were shown in Table 1 and Fig. 1, respectively. Crushed natural stone with maximum size of 20 mm and river sand with fineness modulus (FM) of 2.9 were used as coarse and fine aggregates, respectively. The specific gravities of sand and crushed stone are 2.65 and 2.67, and water absorptions are 0.8% and 1.0%, respectively. Both sand and crushed stone were carefully washed to ensure good binding in concrete mixtures.

Table 1. Physical properties and chemical compositions of three industrial solid by-products.

	Slag (GGBFS)	CFBC fly ash (CFA)
Specific gravity	2.90	2.70
Blaine fineness, cm^2/g	6000.00	3000.00
SiO_2, wt.%	34.90	5.22
Al_2O_3, wt.%	13.53	2.21
Fe_2O_3, wt.%	0.52	0.58
CaO, wt.%	41.47	56.80
MgO, wt.%	7.18	2.06
SO_3, wt.%	1.74	32.40

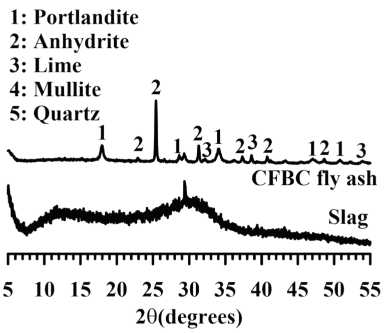


Figure 1. XRD patterns of two solid wastes.

In this study, the effects of ingredients on performance of low energy SSC concretes were estimated based on the various percentage of alkali (OPC) and sulfate (CFA) activators as replacements for the main powder (i.e., slag). Accordingly, three values of 25, 35, and 45 wt.% of CFA and four values of 0, 3, 5, and 10 wt.% of OPC as partial replacement for GGBFS were used to produce SFC-SSC. The water to binder ratio (W/B) of the low energy SSC concrete was fixed at 0.4. The volume of paste and weight ratio of sand to mixture of sand and stone were fixed at 37% and 0.41, respectively. To control the workability of fresh concretes with the slump value in range of 190－225 mm, Type G superplasticizer (SP) was used. The mix proportions of SFC-SSC concretes are shown in Table 2.

2.2 Specimen preparation and test methods

The property of fresh low energy SSC concrete was adjusted by using slump test by adapting ASTM C143. The cylindrical specimens of the concretes with diameter of 100 mm and length of 200 mm were cast for the tests of compressive strength in accordance to ASTM C39, dynamic modulus standardized by ASTM C215, ultrasonic pulse velocity (UPV) suggested by ASTM C597, and creep behavior in accordance with ASTM C512. After 24 hours of curing in the molds at room temperature of 25±2 ^{o}C, all specimens were removed and cured in the room temperature of 25±2 oC and 50 % RH. For the shrinkage/expansion test, the SFC-SCC concrete prisms with dimensions of 75×75×285 mm were cast. The specimens were demolded after 24 h of casting and followed the same curing regimes to the cylindrical specimens. The test would be stopped as the changes of shrinkage/expansion of the bars were no longer significant at all the curing regimes. In this work, the shrinkage/expansion of specimens was monitored until 60 days. The procedure of the length change of concretes was followed ASTM C596. For microstructural examination, the mortar collected from fractured concrete was soaked in to the alcohol for at least 7 days in advance and tested by using scanning electron microscopy (SEM) and X-Ray diffraction (XRD).

Table 2. Mix proportions of the low energy SSC (kg/m^3).

Mixture	Slag	OPC	CFA	FA	CA	W
S75-C0-CF25	350	0	117	688	990	184
S72-C3-CF25	336	14	117	688	990	185
S70-C5-CF25	327	23	117	688	990	185
S65-C10-CF25	304	47	117	688	990	185
S62-C3-CF35	289	14	163	688	990	184
S52-C3-CF45	241	14	209	688	990	183

Note: OCP: Ordinary Portland cement; CFA: CFBC fly ash; FA: Fine aggregate; CA: Coarse aggregate; W: Tap water; Superplasticizer (SP) was fixed at 2.1 kg/m^3.

3 Results and discussions

3.1. Fresh properties

The fresh properties of the resulting low energy SSC concretes were shown in Table 3. According to the table, the effects of both CFA and OPC as partial replacements of slag on the workability of the fresh low energy SSC concretes were insensitive because Table 2 shows that the expected slump values of the fresh SSC concretes were approached by using the equivalent amount of SP value. On the other hand, the increases of either OPC or CFA replacing for slag led to the decrease in both the initial and final setting time of the resulting low energy SSC concretes, which obviously implies that the hydration rate of the SSC binder was accelerated with the increase of the activators.

Table 3. Fresh properties of the low energy SSC

Mixture	Setting time (min)	Slump (mm)
	Initial :Final	
S75-C0-CF25	825 : 990	190
S72-C3-CF25	860 : 1006	225

S70-C5-CF25	837 : 987	225
S65-C10-CF25	797 : 944	220
S62-C3-CF35	799 : 963	220
S52-C3-CF45	746 : 887	190

3.2 Compressive strength

The compressive strengths of SSC concretes are shown in Fig. 2. Accordingly, the compressive strengths of the concretes specimens increased with the increase of curing ages. To produce the low energy SSC concretes with the expected compressive strength, a range of 3－5 wt.% of OPC accompanying with 25 wt.% of CFA was the optimum value of the activator. According to Fig. 2(a), the increase of OPC from 0 to 5 wt.% significantly increase the compressive strength of the hardened SSC concretes at all ages of curing. Such result could be due to the accelerated hydration of slag with the increase of OPC addition. On the other hand, Fig. 2(b) showed that the increase of CFA beyond 25 wt.% led to the significant decrease in compressive strength of the SSC concrete irrespective of ages of curing. The reason could be resulted from the destroyed structure of the SSC concrete with the excessive addition of anhydrite (i.e. from CFA) which causes the expansion of the hardened concrete specimens induced by the generation of gypsum and ettringite (AFt).

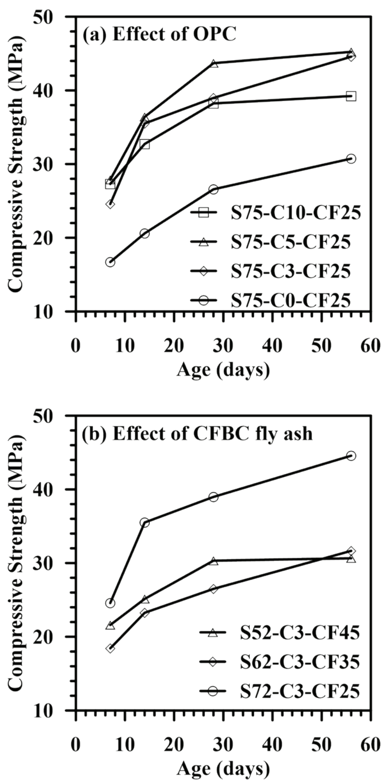


Figure 2. Compressive strength of low energy SSC concretes.

3.3 Dynamic Young's modulus

The dynamic Young's moduli of SSC concretes were conducted and the results were shown in Fig. 3. According to the figure, the dynamic Young's moduli of the concretes specimens increased with the increased ages of curing due to the increase of compressive strength with the days. In this study, the result of dynamic Young's moduli of the SSC concretes matched with the observation from the compressive strength results. As such, OPC amount in range of 3－5 wt.% and CFA with 25 wt.% was the optimum quantities of the activators because their additions led to the hardened concrete samples with the improved dynamic Young's moduli accompanying with the increased compressive strengths as aforementioned.

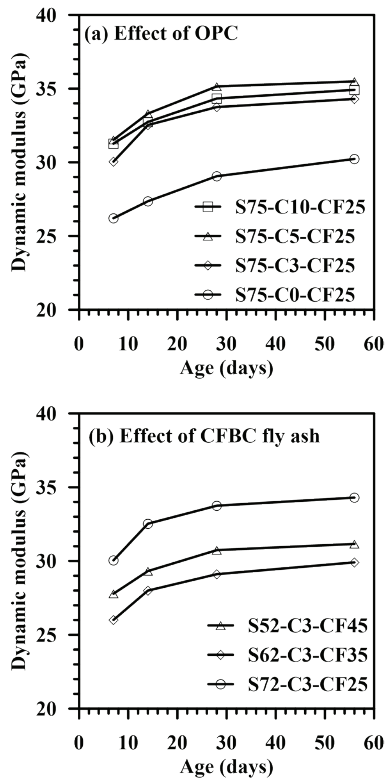
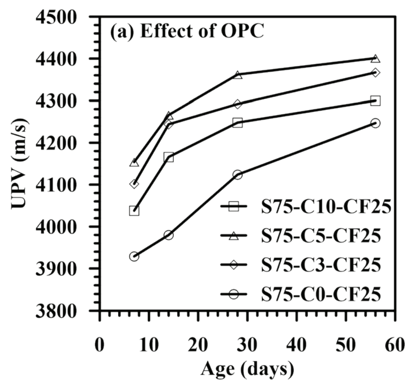


Figure 3. Dynamic modulus of low energy SSC concretes.



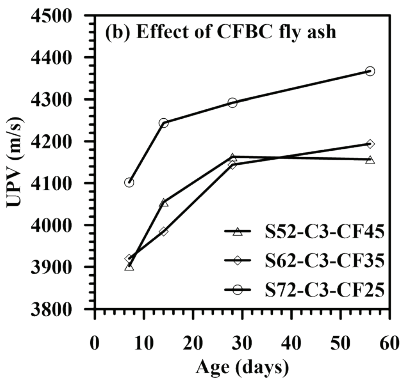


Figure 4. UPV measurements of low energy SSC concretes.

3.4 Ultrasonic pulse velocity (UPV)

The UPV measurements of the hardened SSC concretes as shown in Fig. 4 apparently proved for the observed results from the strength and modulus of the hardened concrete specimens. Generally, the detected UPV values of the hardened SSC concretes increased proportionally with the increase of ages of curing because of the increased compressive strengths of the samples. As can be seen in Fig. 4(a), the increase of OPC in range of 0－5 wt.% significantly increased the UPV value of the hardened concrete samples due to the more condensed structure of the binder system resulted from the accelerated hydration process of slag with the increase of OPC addition. On contrary, the damaged interior microstructures of the hardened concrete samples were obviously observed with excessive addition of CFA because of the remarkable reduction of UPV measurements (Fig. 4(b)).

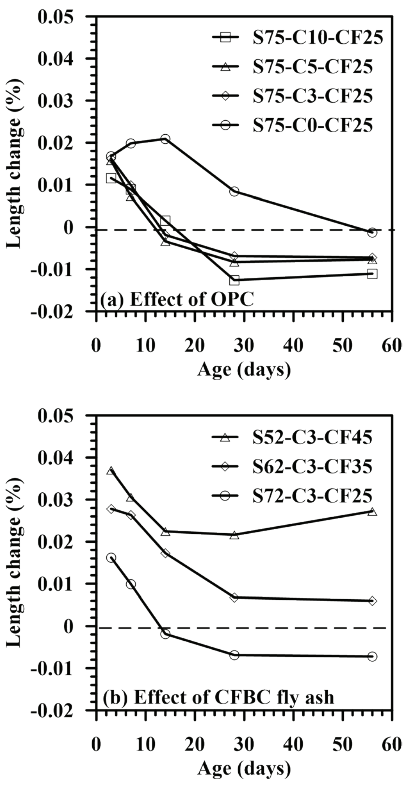


Figure 5. Shrinkage/Expansion of low energy SSC concretes.

3.5 Shrinkage/Expansion

The shrinkage/expansion values of the hardened SSC concretes as shown in Fig. 5 was also the valuable evidence supporting for the engineering performance of the concrete specimens. It was obvious to point out from the figure that both OPC and CFA additions had the distinguishing influence on shrinkage/expansion of the hardened SSC concretes. From Fig. 5(a), the addition of OPC increased the shrinkage of the hardened SSC concretes due to the reduction of AFt crystals induced by the reduction of alumina supplied from slag. However, the increase of the CFA led to the hardened SSC concretes with the significant increase in expansion possibly caused by the increases of AFt precipitation and delayed generated gypsum. As such, the addition of CFA further from 25 wt.% caused the impact of structure of the hardened SSC concrete and led to the concrete specimens with the reduction on both engineering indicators such as compressive strength, dynamic Young's modulus and UPV measurement.

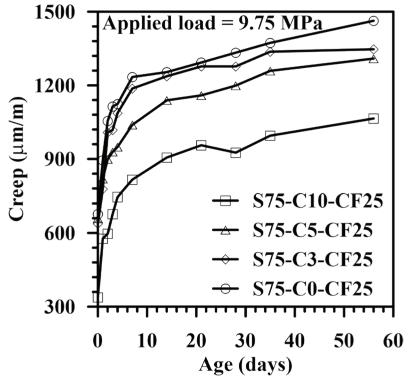
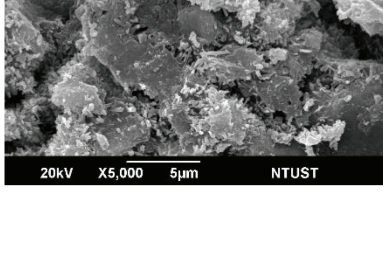


Figure 6. Creep behavior of low energy SSC concretes.

3.6 Creep behavior

The creep values of SSC concretes are shown in Fig. 6. Accordingly, the creep values of the concretes specimens increased with the increase of curing ages. For fabricating the low energy SSC concretes with the reduced creep, the addition of OPC up to 10 wt.% as replacement for slag was encouraged. Such result apparently implies that the cementing system of the SSC binder was strengthened with the addition of OPC. In this study, however, the influence of the CFA addition on creep behavior of the hardened SSC concretes was not conducted.



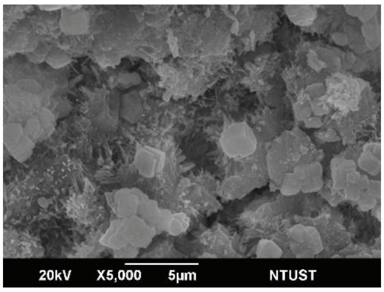


Figure 7. SEM image of low energy SSC concrete with S70-C5-CF25 mix at 28 days (top) and 56 days (bottom) of curing.

3.7 Microstructural examination

The hydration products of the hardened mortar collected from the fractured pieces of the low energy SSC with S70-C5-CF25 mix were conducted as shown in SEM image (Fig. 7). Accordingly, the hydration products of the hardened low energy SSC mainly included rod-like crystal of ettringite (AFt) blending with amorphous gels of C-S-H/C-A-S-H. From Fig. 7, presence of gypsum was also obviously detected. Such result could be resulted from the hydration of remaining anhydrite from CFBC fly ash with free water. The XRD patterns of the powder hydrated mortar with S70-C5-CF25 mix significantly clarified the observation from SEM images. Indeed, the peaks indicating the precipitations of AFt and gypsum were apparently detected from the figure. Because the C-S-H/C-A-S-H gels are amorphous, their presence was not obviously observed from XRD pattern. In this study, the peaks revealing for the presences of quartz and calcite was due to the presence of fine aggregate and unavoidable carbonation of the sample, respectively.

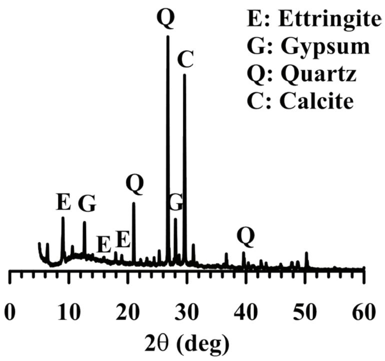


Figure 8. XRD patterns of low energy SSC concrete with S70-C5-CF25 mix at ages of 28 days.

4 Conclusions

The new manufacture of low energy super-sulfated cement (SSC) by using industrial waste anhydrite from circulating fluidized bed combustion (CFBC) fly ash (CFA) has been proposed for the future cement/concrete industries reaching the requirements for sustainable construction materials. The activator combining 3 − 5 wt.% of OPC with 25 wt.% of CFA was suggested to be used for manufacturing the SSC concrete with the expected compressive strength, dynamic Young ' s modulus, UPV measurement, and stabilized change of length. The 28-day compressive strengths of the low energy SSC concrete reached value of 43.69 MPa which possible applied for advanced construction materials. The SSC concrete with optimized ingredients illustrated the dynamic Young's modulus higher than 35 GPa at ages of 28 days. The observed UPV measurement of the SSC concrete was much higher than 4000 m/s which apparently implying the concrete with high quality. The addition of OPC was encouraged to be used for producing the SSC concrete with stabilized length change and significant reduction on creep. The excessive addition of CFA was avoided to assure the resulting concrete with eliminated impact on engineering performance induced by expansion phenomenon. In this study, the OPC addition of up to 10 wt.% replacing for slag led to the hardened SSC concrete with creep value 27.5% less than that of the SSC concrete samples without addition of OPC. Microstructure examination showed that the hydration products mainly included ettringite (Aft), C-S-H/C-A-S-H gels, and gypsum.

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