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Effects of Particle Size Distribution of Binders on the Performance of Slag-Limestone Ternary Cement

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Abstract**—**Using supplementary cementitious materials, such as ground granulated blast-furnace slag (GGBFS) and limestone to replace Portland cement (PC) is a promising method to reduce the carbon emissions from cement production. To efficiently use GGBFS and limestone, it is necessary to carefully select the particle size distribution (PSD) of the binders. This study investigated the effects of the PSD of binders on the performance of slag-limestone ternary cement. Based on the PSD parameters of the binders, three types of ternary cements with a similar overall PSD were designed, i.e., No.1 fine GGBFS, medium PC, and coarse limestone; No.2 fine limestone, medium PC, and coarse GGBFS; No.3. fine PC, medium GGBFS, and coarse limestone. The binder contents in the ternary cements were 50% PC, 40% slag, and 10% limestone. The mortar performance of the three ternary cements was investigated in terms of flow table value, strength at 28 days, carbonation resistance and non-steady state chloride migration resistance at 28 days. Results show that ternary cement with fine limestone (No.2) has the weakest performance among the three ternary cements. Ternary cements with fine slag (No.1) show an overall comparable performance to ternary cement with fine PC (No.3). Moreover, the chloride migration coefficient of ternary cements with fine slag (No.1) is significantly lower than the other two ternary cements.

Keywords**—**Limestone, particle size distribution, slag, ternary cement.

I. Introduction

CEMENT is the most widely used construction material on a global scale. The production of the major cement component, Portland clinker, is accompanied by high CO_2 emissions. To reduce the environmental impact, supplementary cementitious materials (SCMs), such as GGBFS and limestone have been successfully used in the past as cement replacing material [1], [2].

Researches showed that the synergetic use of GGBFS and limestone to partially replace PC has the potential to lead to a better performance of the mortar/concrete than binary cement with one SCM at the same replacement level [3]-[5]. To efficiently use SCMs and PC in blended cement, it is necessary to carefully select the PSD of each binder [6], [7]. References [8]-[10] show that in ternary cement, the high reactivity SCM (e.g. GGBFS and high-calcium fly ash), PC, and low reactivity SCM (e.g. limestone and low-calcium fly ash) are arranged into fine (< 8 μm), middle (8-32 μm), and coarse fractions (> 32 μm), respectively, in which high reactivity SCM contributes to the strength development more efficiently and low reactivity SCM mainly plays a filler effect. The strength and hydration development of obtained ternary cement is comparable to PC with a Blaine specific surface area of 350–360 m^2/kg, even for SCM replacement higher than 50 wt.%.

In this paper, the factual PSD effects of each binder on the performance of slag-limestone ternary cement were investigated. Based on the PSD parameters of binders, three ternary cements with a similar overall PSD were obtained i.e., (1) fine GGBFS, medium PC, and coarse limestone; (2) fine limestone, medium PC, and coarse GGBFS; (3) fine PC, medium GGBFS, and coarse limestone. The binder contents in the ternary cements were 50 wt.% PC, 40 wt.% GGBFS, and 10 wt.% limestone The mortar performance of three ternary cements was investigated in terms of flow table value, strength at 28 days, carbonation resistance and non-steady state chloride migration resistance at 28 days.

II. Materials and Methods

A. Materials

The Portland clinker, gypsum, and granulated blast-furnace slag were crushed and ground by a Jaw crusher and Pulverisette Planetary Mill (classic line 6, FRITSCH), respectively, to obtain different PSDs. The PC was prepared by grinding a mixture of 95 wt.% clinker and 5 wt.% gypsum. The two limestone powders with different PSDs were obtained from sieving (and grinding) an original limestone powder. The coarse fraction was the powder over 63 μm, the finer fraction was obtained by further grinding the residue. The PSDs of all binders named by their D50 values are measured by a laser diffraction machine (Analysette 22, dry dispersing unit, FRITSCH), as shown in Fig. 1. The chemical and mineralogical compositions of the clinker and GGBFS are listed in Tables I and II.

B. Preparation of Ternary Cement with Slag and Limestone

Ternary cement was prepared by manually mixing PC, GGBFS, and limestone homogenously at the mix proportion of 50 wt.% PC, 40 wt.% GGBFS, and 10 wt.% limestone. Based on the PSD parameters of binders, three ternary cements with a similar overall PSD were obtained i.e., (1) fine GGBFS, medium PC, and coarse limestone; (2) fine limestone, medium PC, and coarse GGBFS; (3) fine PC, medium GGBFS, and coarse limestone, as shown in Figs. 2 (a)-(c). Meanwhile, the three types of ternary cement are designed to have a similar total PSD curve to study the factual effects of binders' fineness, as shown in Fig. 2 (d). The physical parameters of ternary cements are listed in Table III.

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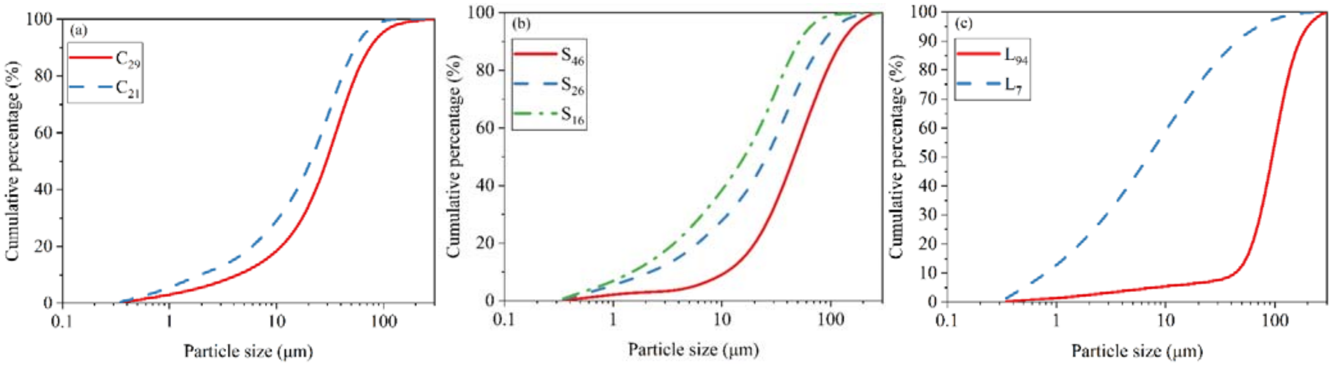

Fig. 1 PSD of PC, GGBFS, limestone: (a) PC (abbreviated as C), (b) GGBFS (abbreviated as S), (c) limestone (abbreviated as L) The PSDs of all binders are named by their D50 value

TABLE I
CHEMICAL COMPOSITION OF CLINKER AND GGBFS (WT.%)

Material	Chemical composition														
	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	P_2O_5	MnO	TiO_2	Na_2O	ZnO	SrO	Cl	BaO
Clinker	68.4	19.5	3.57	2.84	1.78	1.54	1.06	0.43	-	0.23	0.16	0.13	0.11	0.11	-
GGBFS	43.6	35.4	9.73	0.33	6.67	2.33	0.67	-	0.27	0.57	0.24	-	-	-	0.14

TABLE II
MINERALOGICAL COMPOSITION OF THE CLINKER (WT.%)

C_3S	C_2S	C_3A	C_4AF	Mayenite	Dolomite	Periclase	Quartz	Aphthitalite
65.84	15.61	3.74	8.98	2.52	1.16	0.71	0.92	0.52

TABLE III
PHYSICAL PARAMETERS OF TERNARY CEMENTS

Ternary cement	D10 (μm)	D50 (μm)	D90 (μm)
$C_{29}S_{16}L_{94}$	2.6	26.7	88.9
$C_{21}S_{46}L_7$	2.6	27.7	89.0
$C_{21}S_{26}L_{94}$	2.3	25.1	89.1

III. TEST METHODS

Mortars were prepared at a water-to-binder ratio of 0.5 and a sand-to-binder ratio of 3.0. The particle size of river sand ranged from 0 mm to 5 mm and its loose bulk density was 1650 kg/m^3. Fresh mortar, prepared according to NBN EN 196-1, was cast into 40 mm × 40 mm × 160 mm molds and covered with a plastic foil in the laboratory environment at 20 ± 1 °C for 24 h. Then the prisms were demolded and cured in a water tank at 20 ± 1 °C until testing.

A. Workability

The flow table test was performed on the mortars according to NBN EN 1015-3. Each test was conducted three independent times.

B. Compressive Strength

The flexural and compressive strength tests of mortars were conducted at 28 days according to NBN EN 196-1. Three mortar prisms were loaded in a 3-point bending test at a loading rate of 0.05 ± 0.01 kN/s until fracture to measure the flexural strength. Then the obtained six prism halves were used to measure the compressive strength. The loading rate is 2.4 ± 0.2 kN/s until fracture.

C. Carbonation Test

The carbonation test of mortars was based on NBN EN 13295. After 1 day in the mold and 27 days in the water tank at 20 ± 1 °C, the specimens were pre-conditioned in a climate chamber at 20 ± 1 °C and a relative humidity (R.H.) of 60 ± 10% until constant weight (mass loss < 0.2 wt. % in 24 hours). The carbonation test was conducted at 1.0% CO_2 concentration, 20 ± 1 °C, and a R.H. of 60 ± 10%. At the time of testing, the carbonation depth was determined by spraying phenolphthalein solution on a fresh split.

D. Non-Steady Chloride Migration Test

The non-steady chloride migration test was performed according to NT build 492. Fresh mortars were cast into ø 100 mm × 200 mm cylindrical molds and cured in the laboratory at 20 ± 1 °C for 24 h. After demolding, the specimens were cured in a water tank at 20 ± 1 °C until test ages of 28 days. Before the chloride migration test, specimens were clipped off 20 mm edges and then sawn into three slices with a size of ø 100 mm × 50 mm. The surface closest to the center was exposed to the catholyte. A 0.3 N NaOH and a 2 N NaCl were used as the anolyte and catholyte solutions, respectively.

An analysis of variance (ANOVA) test was conducted to analyze the test data by SPSS version 26.0 for Windows (SPSS Inc., Chicago, IL, USA). A value of $P < 0.05$ was considered significant.

IV. RESULTS AND DISCUSSION

The flow table values of mortars with ternary cements are shown in Fig. 3. There is an insignificant difference in flow table value between $C_{29}S_{16}L_{94}$ and $C_{21}S_{46}L_7$ (P = 0.47). The $C_{21}S_{26}L_{94}$ exhibits the highest flow table value.

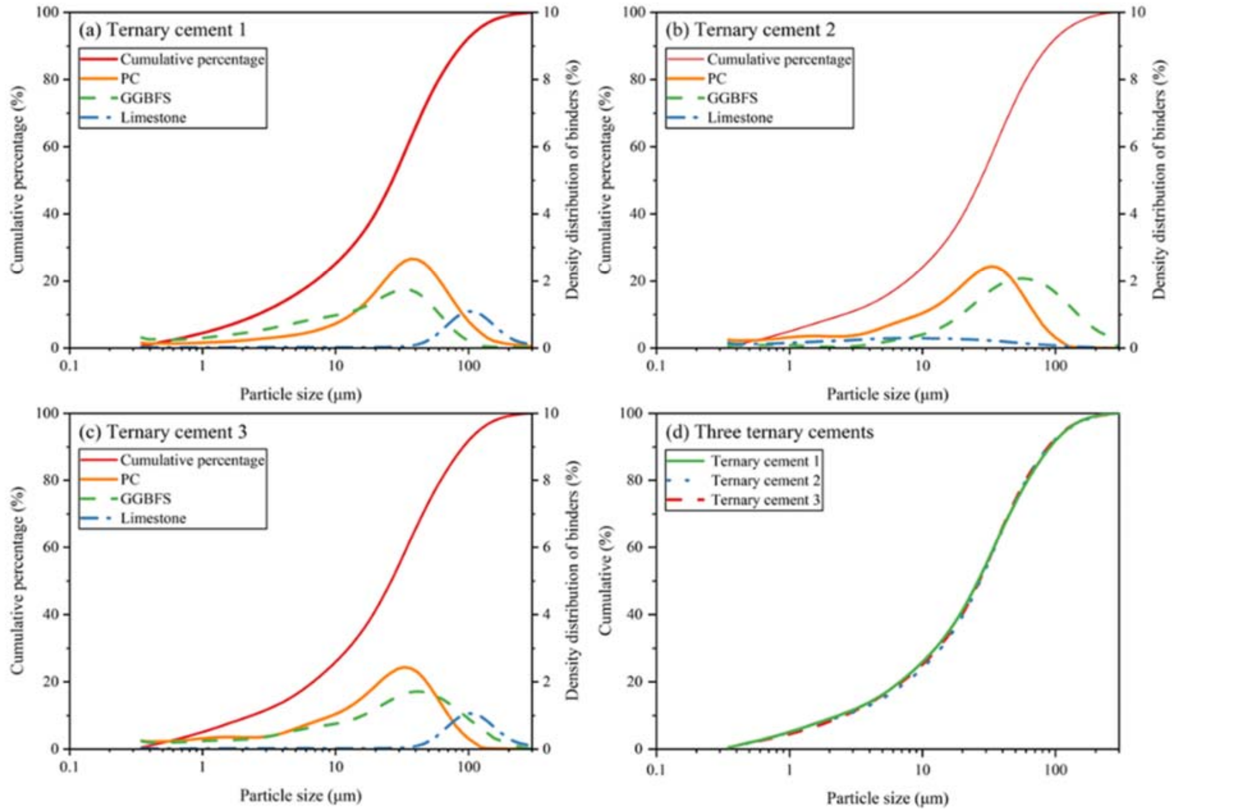

Fig. 2 The combination of PSDs of binders: (a) fine GGBFS, medium PC, and coarse limestone ($C_{29}S_{16}L_{94}$); (b) fine limestone, medium PC, and coarse GGBFS ($C_{21}S_{46}L_7$); (c) fine PC, medium GGBFS, and coarse limestone ($C_{21}S_{26}L_{94}$); (d) the overall PSDs of three ternary cements

The flexural strength and compressive strength of mortars with ternary cements at 28 days are shown in Table IV. The $C_{29}S_{16}L_{94}$ shows an insignificant difference in the flexural strength to the other two ternary cements (P > 0.05). The $C_{21}S_{26}L_{94}$ shows the highest mean value while $C_{21}S_{46}L_7$ shows the lowest value at 28 days. For compressive strength at 28 days, $C_{21}S_{46}L_7$ shows the lowest mean value while an insignificant difference is observed between $C_{29}S_{16}L_{94}$ and $C_{21}S_{26}L_{94}$ (P = 0.98).

For the carbonation depth of mortars, a fitting equation is used to represent the relation between carbonation depth and the time, as (1):

$$Carbonation\ Depth\ D\ (mm)\ = k\sqrt{t} \qquad (1)$$

where k is the carbonation coefficient and t is the exposure time. The carbonation depth of mortars is increased with the increase in k value. The $C_{21}S_{46}L_7$ with fine limestone, medium PC and coarse GGBFS has the highest k value, indicating the highest carbonation depth. With the same limestone powder, the $C_{29}S_{16}L_{94}$ with fine GGBFS and medium PC shows a similar carbonation depth to $C_{21}S_{26}L_{94}$ with fine PC and medium GGBFS.

The non-steady state chloride migration coefficients of mortars with ternary cements at 28 days are shown in Table V. The chloride ingress is increased with the increase of chloride migration coefficient. Although $C_{21}S_{46}L_7$ and $C_{21}S_{26}L_{94}$ have a finer PC than $C_{29}S_{16}L_{94}$, $C_{29}S_{16}L_{94}$ shows the lowest chloride migration coefficient at 28 days due to the fine GGBFS. The $C_{21}S_{46}L_7$ shows the highest chloride migration coefficient among the three ternary cements.

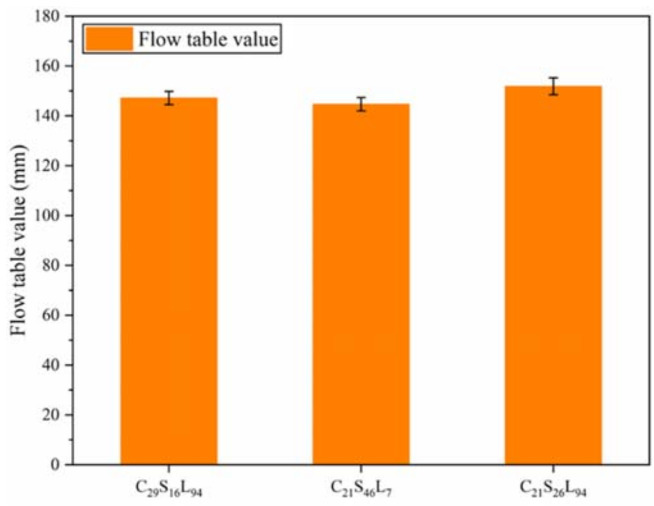

Fig. 3 Flow table value of mortars with ternary cements

TABLE IV
FLEXURAL AND COMPRESSIVE STRENGTH AT 28 DAYS

Ternary cement	Flexural strength (MPa)		Compressive strength (MPa)	
	Strength	Standard deviation	Strength	Standard deviation
$C_{29}S_{16}L_{94}$	6.7	0.14	26.1	1.5
$C_{21}S_{46}L_{7}$	6.1	0.42	20.6	1.0
$C_{21}S_{26}L_{94}$	7.3	0.37	26.3	1.0

TABLE V
CARBONATION PARAMETER AND NON-STEADY CHLORIDE MIGRATION COEFFICIENT AT 28 DAYS

Ternary cement	Carbonation depth	Non-steady chloride migration at 28 days	
	Coefficient (k)	Coefficient ($10^{-12}m^2/s$)	Standard deviation
$C_{29}S_{16}L_{94}$	0.99	7.23	0.41
$C_{21}S_{46}L_{7}$	1.20	11.13	0.36
$C_{21}S_{26}L_{94}$	0.99	9.97	0.36

V. CONCLUSION

This study provides insights into factual effects of PSD of binders on the performance of ternary cement with GGBFS and limestone. Using the test results of ternary cement with fine PC, medium GGBFS, and coarse limestone ($C_{21}S_{26}L_{94}$) as the reference value, an overview, in which mortar performances of the three ternary cements with a similar PSD are compared, is shown in Fig. 4. The $C_{29}S_{16}L_{94}$ with fine GGBFS, medium PC, and coarse limestone shows an overall better performance regarding the considered properties. Further research on microstructure and long-term performance is needed to confirm this work.

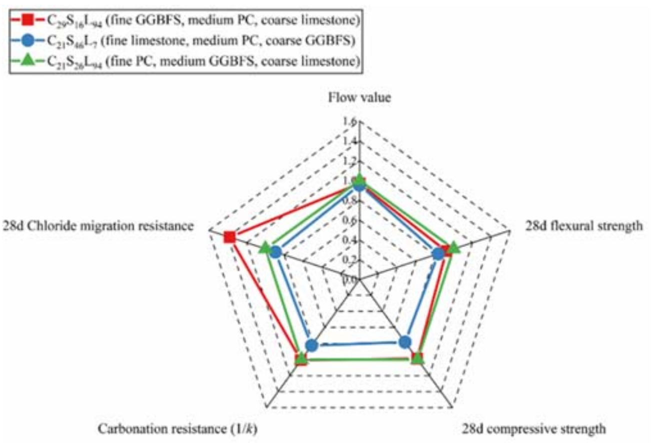

Fig. 4 Summary of mortar performances

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