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Influence of Mineral Admixtures on Essential Properties of Ternary Cement Blends

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Abstract: Two $CaCO_3$-based materials (limestone and clamshells) and steel slag were used as mineral admixtures in cement to produce ternary blends and their influences on hydration and portlandite formation were analyzed. Additionally, mechanical properties were determined. These properties were determined using X-ray diffraction and scanning electron microscopic/energy dispersive X-ray analytical techniques as well as applying methods specified by EN (European Standards) and ASTM (American Standards for Testing and Materials). The portlandite ($Ca(OH)_2$) content was considerably reduced from 36.9% of reference cement to between 13.79% and 15.5%. With the water demand and setting times of the cements containing up to 10%, admixtures did not change significantly. The mechanical tests results showed that ternary blends produced 2-day strengths higher than that specified by EN 197-1 and that blends containing up to 20% admixtures can be used to produce both Class 32.5N and 42.5N cements.

Key words: Limestone, clamshells, steel slag, ternary cement, portlandite, compressive strength.

1. Introduction

Portland cement production has traditionally involved calcination of limestone and siliceous clay to produce clinker, which is then intergrounded with 3%-5% gypsum. However, current trends in cement production involve the addition of 5% to 70% mineral admixtures in order to improve the technical properties and durability of cement especially in tropical humid zones and acidic medium.

The presence of admixtures like fly ash, limestone, slag and pozzolana in Portland cement influences the rate and degree of cement hydration as well as the phase composition of hydrated cement paste. Their addition influences reactivity and may increase the hydration rate of clinker minerals and also improve the workability of cement, lower the heat of hydration and energy cost among others [1-3]. Admixture integration in cement could produce higher early strength due to the filler effect of admixtures as a result of the increased surface area that leads to an initial accelerating effect on cement hydration and, in some instances, increases the resistance of the blended cement to acidic water attack [3-6]. Addition of $CaCO_3$-based materials and slags reduces amount of clinker in cement, thus mitigating the effect of carbon gases emission during cement production.

Secondly, the utilization of otherwise waste steel slag would prevent potential environmental pollution which may result from leaching of deleterious compounds into the soil.

Several works by researchers have shown that $CaCO_3$ powder chemically interact with the aluminate phases in cement to stabilize a carboaluminate phase at the expense of monosulfoaluminate during hydration of cement [2-5].

There is also a positive effect of limestone on the setting time and water demand of cement [3, 7]. Composition of steel slag makes it a good partial substitute in Portland cement but has the disadvantage

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of longer setting time and lower early strength, which is attributable to the slow growth of calcium silicate hydrates gel when compared with ordinary Portland cement [6, 7]. However, these are compensated by the addition of other admixtures and usage of high-strength cement or high quality clinker with higher fineness.

Most steel slag used by Tsakiridis et al. [8] and Kourounis [9] contains high CaO content ranging from 35% to 56% with high calcium silicates, which are very essential for cement hydration and strength development. Also, limestones of high CaO content, above 47%, are usually employed for clinker or cement replacement [3, 4]. However, steel slag containing very low Ca mineral phases content and limestone with relatively low CaO content are used in this study. This paper presents the influence of limestone, clamshells and steel slag on cement hydration, precipitation of portlandite ($Ca(OH)_2$) in ternary cement blends. Their physical and mechanical properties were determined.

2. Materials and Methods

All the materials were obtained in Ghana, namely, OPC (CEM I Class 42.5N Portland cement) from Ghacem, a cement producing company, steel slag (S), a waste product obtained from Wahome Steel Company Ltd in Tema, limestone (L) used for cement production in Ghana and clamshells (Sh), obtained along the banks of the Volta River. The clamshells, steel slag and limestone were separately crushed and milled in a pulveriser, and then passed through a 75 µm BS (British Standard) sieve.

The milled and sieved mineral admixtures (limestone, clamshells and steel slag) were blended with the OPC using various mix designs as shown in Table 1. The chemical composition of samples was determined by XRF (X-ray fluorescence) analysis using Spectro X-LAB 2000 equipment. The blended cement samples were used to produce cement pastes, mortar and concrete samples respectively for the study.

The standard consistency, setting times and soundness of the cement pastes were obtained using standard methods specified by EN (European Standards) 196 [10], whilst the water permeability of the concrete samples was determined using ASTM (American Standards for Testing and Materials) C 642 [11]. The morphology of the hydrated cement samples was investigated by means of SEM (scanning electron microscopy) using Zeiss SEM analyser. The cement hydrates were characterized by XRD (X-ray diffraction) with a Philips PW 1830 X-ray diffractometer. The compressive strengths of the cement mortar cubes and concrete cubes were tested at 3, 7, 28, 90 and 365 days according to EN specifications [12]. The various mix designs employed in the moulding of mortar and concrete specimens for the compressive strength tests are given in Table 2. The mixes were used to achieve compressive strengths between 32.5 MPa and 42.5 MPa for the mortar cubes, and 20 MPa for the concrete specimen at 28 days.

3. Results and Discussion

3.1 Chemical and Mineralogical Compositions of Samples

As shown in Table 3, the main components of limestone are CaO (42%), SiO_2 (17.3%) and Fe_2O_3 (4.5%), whilst clam shells have 52.4% CaO. Steel slag

Table 1 Mix designs of blended cements.

Sample	Composition by mass (%)			
	OPC	Limestone	Clam shells	Steel slag
OPC	100	-	-	-
5L5S	90	5	-	5
5Sh5S	90	-	5	5
10L5S	85	10	-	5
10Sh5S	85	10	-	10
10L10S	80	10	-	10
10Sh10S	80	-	10	10

Table 2 Mortar and concrete mix design details.

Cubes	Mix proportion by mass			*w/c*
	Cement		Crushed aggregate	
	Blend	Sand		
Mortar	1	3	-	0.5
Concrete	1	2	4	0.55

Table 3 Chemical analysis of materials.

Oxides	OPC	Limestone	Steel slag	Clam shells
SiO_2	18.80	17.27	21.31	2.10
Al_2O_3	3.57	0.03	7.50	0.25
Fe_2O_3	4.36	4.58	31.52	0.50
MgO	1.89	0.05	7.61	0.60
CaO	57.04	41.97	12.44	52.41
LOI	3.60	31.00	7.50	41.07

is mainly composed of Fe_2O_3 (31.5%), SiO_2 (21.3%) and Cao (12.4%).

Fig. 1 indicates the presence of crystalline calcium silicates (C_2S) in steel slag as well as portlandite, calcite, quartz and olivine group. Limestone and clam shells consist mainly of calcite ($CaCO_3$). These minerals are essential for cement reactions and hydration [5]. The diffraction graphs of the cement samples (Fig. 2) show a reduction of portlandite (lower peaks) and increase in C_3S (higher peaks) in the ternary blends. Using Bishop's [13] equation, the portlandite content of 5L5S and 10L5S was 15.5% and 13.7%, respectively, compared to 36.9% of OPC. Reduction of $Ca(OH)_2$ in cement product reduces the susceptibility of the blended cement to acidic attack in higher water demand [14].

The micrographs (Fig. 3) from the SEM analysis indicated clearly that the pores of the blended cement were reduced as a result of addition of admixtures.

3.2 Physical and Mechanical Properties of Cement Samples

The physical and mechanical properties of the cement samples are presented in Table 4. The results of the permeability tests showed clearly that addition of the admixtures reduced the porosity of the cement by at least 3.0% and as much as 12.5%. This agrees with the assertion that admixtures fill the pores of cement products making it less porous [4, 5, 14]. The water demand did not change significantly for both binary and ternary blends containing up to 10% admixture content. However, samples containing 15% or more admixtures recorded values above 30% and this is due to the fact that increase in the amount of admixtures involves an increase in the effective water cement ratio resulting in higher water demand.

The setting times of cements with up to 10% admixture content were lower than reference cement. This was because the admixtures provided additional surface area, which accelerated hydration and provided interaction between tricalcium silicate (C_3S) and the admixtures [2, 4]. Increasing the amount of admixtures to 15% and above prolonged the setting times of the blended cements due to the decrease of C_3A content of cement. Nevertheless, the initial and final setting times

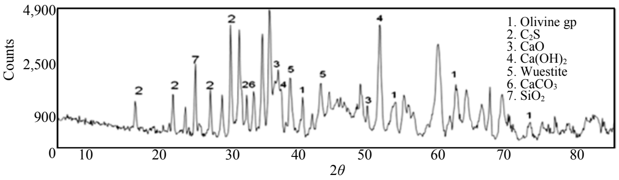


Fig. 1 X-ray diffraction graph of steel slag.

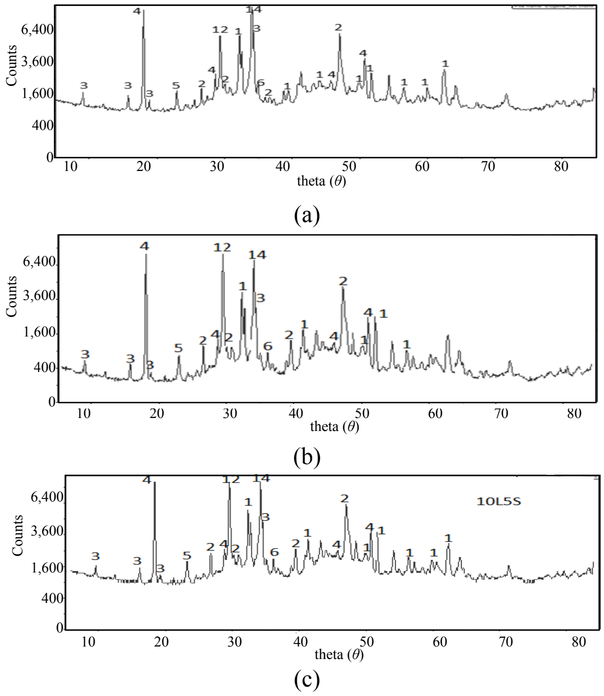
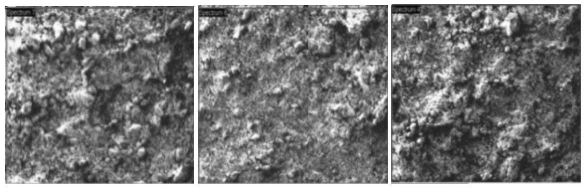


Fig. 2 X-ray diffraction graphs of OPC and blended cements at 28 days (1—C_3S; 2—C_2S; 3—ettringite; 4—$Ca(OH)_2$; 5—C_3A; 6—Quartz).



(a) (b) (c)

Fig. 3 Microstructure of: (a) OPC; (b) 5L5S; (c) 5Sh5S.

Table 4 Mechanical properties of cement samples.

Sample	Water permeability (%)	Water demand (%)	Setting time (min)		Compressive strength (MPa) Days			
			Initial	Final	2	7	28	90
OPC	4.42	26.0	120	210	22.6	31.7	43.2	43.5
5Sh5S	4.12	25.6	106	162	16.5	24.3	41.0	41.4
5L5S	4.22	26.2	106	159	19.5	23.5	40.9	42.2
10Sh5S	3.96	31.8	165	245	14.6	20.3	40.5	40.8
10L5S	4.21	31.2	162	234	14.2	20.8	39.2	39.0
10L10S	4.25	30.6	163	242	13.9	18.3	37.5	40.1
10Sh10S	4.31	31.5	162	241	13.4	16.9	39.1	40.4

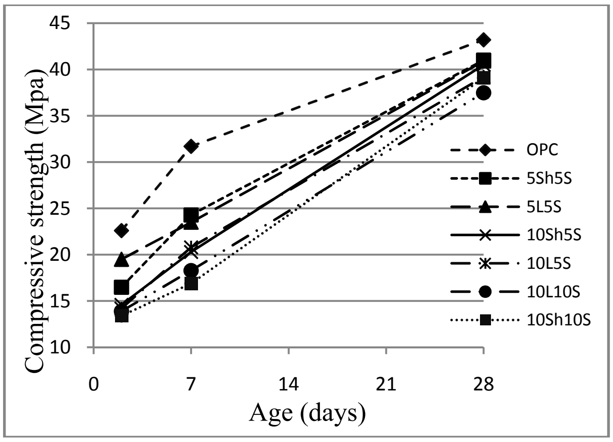


Fig. 4 Strength development of cement samples.

Table 5 Properties of concrete samples.

Sample	Slump (mm)	Compressive strength (MPa)
OPC	75	25.4
5Sh5S	74	24.0
5L5S	77	24.3
10L5S	76	22.6
5L10S	75	21.7
10L10S	77	21.2
10Sh10S	76	21.4

obtained for all cement blends were more than 75 min and less than 10 h, respectively, as stipulated by EN 197-1 [15].

Generally, the 2-day and 7-day compressive strengths of all the blended cement mortars (Fig. 4) were higher than the standard minimum value of 10 MPa and 16 MPa, respectively, stipulated by EN standards [15]. At 28 days, samples with 10% admixture content recorded strengths between 40.9 MPa and 43.0 MPa and those with 15% to 20% admixture content produced between 37.5 MPa and 40.5 MPa. These strengths ranged between 86.5% and 99.5% of the reference cement, more than 75% stipulated by ASTM C 618 [16]. The strengths with 20% replacement were always lower and this is attributed to the filler effect which was surpassed by the dilution effect and reduction of active clinker minerals needed to obtain early high strength. It was observed that strengths obtained from samples containing 10% of both slag and limestone (10L10S) ranged between 87% and 91.5% of the control as compared to 75% and 80% obtained by Korounis [9] and Altun [17].

The 28-day compressive strengths of the concrete samples obtained were higher than the targeted value of 20 MPa and the slump values showed the blended samples were more workable than the OPC (Table 5) . These results compared favourably with the ASTM [16] specification, which stipulates minimum 28-day strength of 75% of the reference.

4. Conclusions

The study has shown that the presence of a combination of limestone/clam shells and steel slag filler provided unique cement qualities such as low $Ca(OH)_2$ content, enhanced ettringite formation and improved impermeability of concrete. The blended cement produced higher early strengths specified by EN 197-1 and ternary cement blends containing up to 10% and 20% of both limestone/clamshells and steel slag satisfy specifications of Class 42.5 and 32.5N cements, respectively. Increasing the admixture content from binary to ternary blend improved the resistance to sulphate and seawater attack.

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