

Physicochemical and Mineralogical Analysis of Steel-Slag Blended Cements

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ABSTRACT

The dominant role of ordinary Portland cement is slowly decreasing in the construction industry in favor of substituted or composite cements. This is due to the added advantage or benefits of blended cements such as durability, cost and environmental friendliness. Steel slag, an industrial waste in the manufacture of steel and a major mineral admixture in Europe is not well utilized in Ghana because no extensive scientific research has been conducted into its alternate use. Meanwhile an estimated 5,000 tons of steel slag is dumped as waste every year for the past 20 years and it is gradually becoming an environmental challenge. This work has studied the alternate use of steel slag from Wahome Steel Works, a steel manufacturing company in Ghana, as a mineral admixture in Portland cement for construction applications. The physical properties of the slag such as specific gravity, Blaine indices and particle size distribution were studied. The chemical and mineralogical (XRF, XRD and SEM) analysis revealed that the slag is chemically suitable and contained the relevant minerals and phases. The slag-cement mixture required less water to form a workable paste and increased in setting time as slag content increased in the mix. The results also revealed that, water permeability decreased with increasing slag content. The slag-cement mix recorded lower compressive strengths at early ages but appreciated in strength at later ages, recording strength of 48.9 MPa at 30% replacement.

Keywords - Portland cement, steel slag, specific gravity, mineralogical, Blaine indices, permeability

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I. INTRODUCTION

Portland cement, already being a very expensive material in Ghana constitutes a substantial part of the total construction cost of any project and the situation has been further aggravated by the energy and environmental challenges which comes with the manufacture of Portland cement. The dominant role of pure Portland cement is slowly decreasing in the construction industry in favor of substituted or composite cements. This is due to the added advantage or benefits composite cements come with such as durability, cost and environmental friendliness. Composite cements afford the engineer the opportunity to alter the properties of the cement to suit a specific job description. It is therefore of current importance that Ghana explores and develops other cementitious materials cheaper than Portland cement such as calcined clay pozzolan, steel slag, rice husk ash, fly ash etc. The only cementitious material that has been thoroughly investigated in Ghana is calcined clay pozzolan. Work done with clay pozzolans in Ghana indicates that by replacing approximately 30% by mass of ordinary Portland cement with calcined clay pozzolan with intimate mixing, results in Portland pozzolan cement (PPC)

which exhibits compressive strength values good for both load-bearing and non load-bearing structural applications [1]. For this reason, calcined clay pozzolan has been adopted and is being massively utilized by builders in Ghana for all forms of construction works. However, the utilization of steel slag in Portland cement remains unknown in the Ghanaian built environment unlike in developed countries.

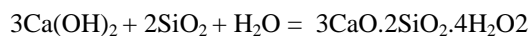
Steel slag (SS) is an industrial waste resulting from the steel-refining process in a conversion furnace. An estimated 50 million tons of steel slag is produced worldwide annually with nearly 12 million tons being produced in Europe [2]. Owing to the intensive research work in the past 30 years, about 60% of the steel slag is currently used in fields of technological application. The remaining 35% of these slags is still dumped as waste [3].

In Ghana, steel slag is produced by four main steel companies; namely, Western Casting and Forming Company, Wahome Steel Works, Tema Steel Works and Ferro Fabric Co. Ltd., all based in Tema. An estimated 5,000 tons of slag has been dumped as waste every year for the past 20 years [4]. The chemical composition of a typical steel slag

consists mainly of calcium oxide, iron oxide, silica, and aluminium oxide, which constitute more than 70% of the material. The common mineral compositions of steel slag, among others, include C_3S , C_2S , $CuAF$, C_2F , RO phase (a solid solution of MgO , FeO , and MnO), olivine and free lime [3]. Steel Slag could be classified into four groups such as the olivine group, merwinite group ($A = 1.4-6$), dicalcium silicate group ($A=1.6-2.4$), and tricalcium silicate group ($A = 2.4$); where A (Alkalinity) is calculated as:

$$A = \frac{CaO + MgO + Al_2O_3}{SiO_2} \cdot 1$$

The presence of C_3S , C_2S , C_4AF and C_2F generates the cementitious properties of steel slag. However, the C_3S content in steel slag is much lower than in Portland cement. Slag cement also contains amorphous silica (S) which reacts with calcium hydroxide (CH) to form additional C-S-H thereby improving strength (Eqn. 2).



Slag cement is not only pozzolanic but is also hydraulic, meaning the slag cement will hydrate when mixed with water [5].

II. MATERIALS AND METHODS

2.1 Materials

The steel slag used for this study was obtained from Wahome Steel Works, Ghana, ordinary Portland cement (OPC) of class 42.5N manufactured by Ghacem company limited, Ghana was also used. The OPC satisfied EN 197-1 [6] standard. Ordinary pit sand was used to prepare the mortar mixes and satisfied the BS 4550: Part 6 [7] requirements. The sand was sieved passing through 0.85mm test sieve and retained on 0.60mm test sieve. De-ionized water was used as the mixing water to prepare all mortar specimens.

2.2 Methods of preparation

The steel slag was crushed using a laboratory type hammer mill and milled in a laboratory type ball mill to fineness. The milled slag samples were sieved through a 75 μ m standard sieve and the percentage passing was intimately mixed with OPC to produce slag cement with varying slag content of 5%, 10%, 15%, 20%, 25% and 30%. The particle size distribution of the sand and slag were determined by the hydrometer method of sedimentation as specified by BS 1377 [8]. The specific gravity of the OPC and slag were also determined according to BS 1377 [8]. The chemical compositions of the materials were determined by X-ray Fluorescence (XRF) using a SpectroXlab 2000 spectrophotometer. The mineralogical properties of raw and blended cements

were determined using a PHILIPS PW 1830 X-ray diffractometer. Water demand, setting times and soundness were determined according to EN 196-3 [9]. 70 mm \times 70 mm mortar cubes were molded according to procedures outlined by EN 196-1 [10] and cured in a moisture cabinet. The specimens were tested after 2, 7, and 28 days. A water permeability study was conducted using methods prescribed by ASTM C642-06 [11].

III. RESULTS AND DISCUSSION

3.1 Physical properties

Some physical properties of the OPC, steel slag and blended cements are shown in Table 1. The particle size distribution of the steel slag and sieved sand are also shown in Figure 1. The specific gravity of the reference cement was 3.26 and that of steel slag was 2.85. Specific gravity of blended cement however decreased with increasing steel slag content.

Table 1: Physical properties of raw materials

Property	OPC	Raw materials						
		Steel slag	5%	10%	15%	20%	25%	30%
Specific gravity	3.16	2.85	3.14	3.11	2.88	2.75	2.7	2.58
Blaine fineness, m^2/kg	388	387	382	370	368	364	355	350

The particle size distribution curve of the sieved sand shows that the sand was mostly coarse, 95% of it within the 0.5mm and 2mm range. In addition, it did not contain any fines ($< 75\mu$ m). The steel slag was also very fine with 85% finer than 10 μ m.

3.2 Chemical properties

The chemical compositions of slag and the reference cement as determined by X-Ray fluorescence (XRF) are shown in Table 2. The sum of the CaO and SiO_2 content of the OPC amounted to 78.5% which satisfies the standard limit according to EN 197-1 [6]. Chemically, the OPC could be considered as good cement. Also, the analysis showed that the slag contained 35.8% Fe_2O_3 , 19.51% SiO_2 and 12.89% CaO . The SiO_2 content and the corresponding loss on ignition of the slag passed the requirements specified by the EN 197-1 [6]. The sum of SiO_2 , Fe_2O_3 and Al_2O_3 content in the slag exceeded the minimum value of 70% required by ASTM C 618 [12]. The Na_2O_{eq} ($N_2O + 0.682 K_2O$) of the steel slag was 0.7% which is higher than the minimum 0.6% per ASTM C150 [13] and when added to cement could lead to alkali silica reaction (ASR).

3.3 Mineralogical properties

The XRD analysis of steel slag is shown in Fig. 2. The main minerals present in steel slag were wustite, belite, calcite, SiO₂, Portlandite, and olivine gp. The XRD patterns of the hydrated samples of the reference cement and OPC containing 10%, 20% and 30% steel slag are also presented in Figures 3(a), 3(b), and 3(c). They show reduced peaks for Ca(OH)₂ compared to the reference cement. The intensity of the Ca(OH)₂ peaks decreased as steel slag content increased whereas C₃S peaks were intensified with steel slag increase indicating more dense structure [14].

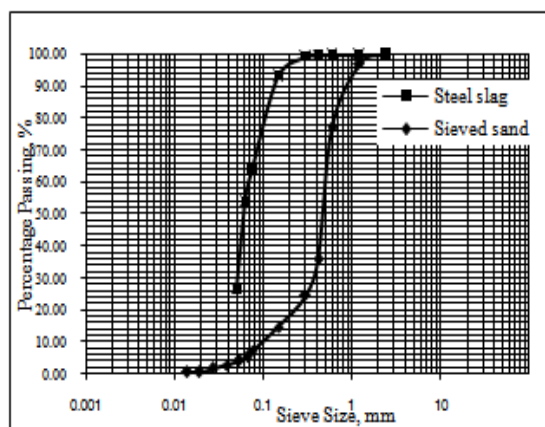


Fig. 1: Particle size distribution of steel slag and sieved sand

Table 2: Chemical composition of raw materials

Materials	Constituents, %										
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	MnO	TiO ₂	SO ₃	Na ₂ O	P ₂ O ₅	K ₂ O
OPC	18.9	3.57	3.36	59.6	1.89	0.14	0.14	4.93	4.7	0.22	2.12
Steel slag	19.51	2.12	35.8	12.89	6.54	4.37	0.63	0.26	0.62	0.31	0.12

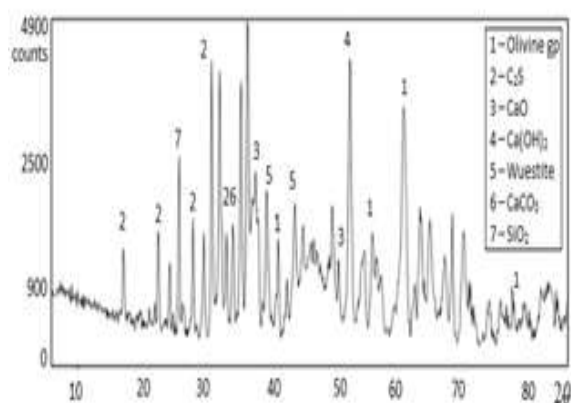
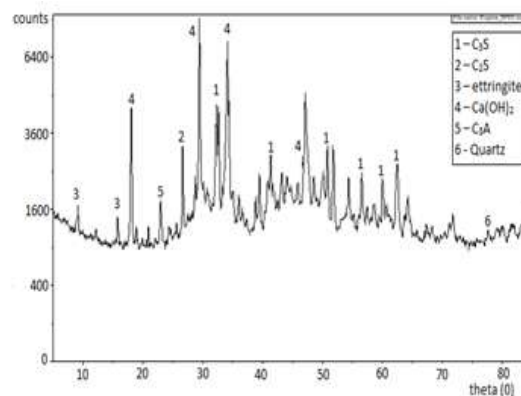
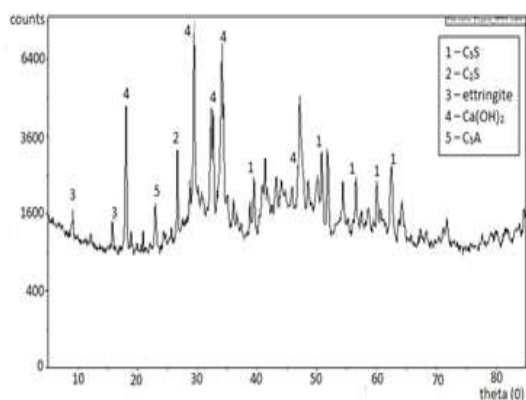


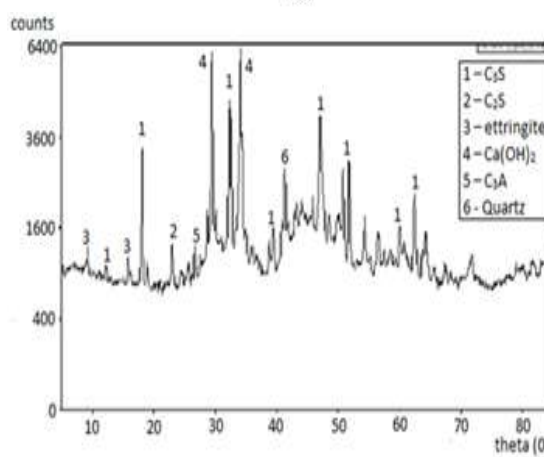
Fig. 2: XRD graph of steel slag



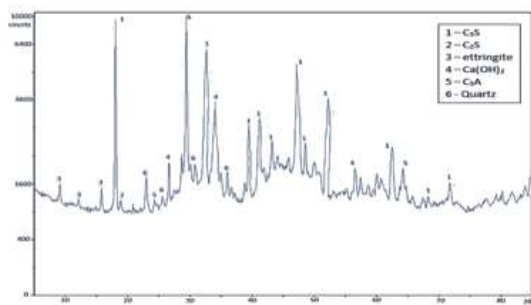
(b)



(a)



(c)



(d)

Fig. 3: XRD graph of (a) OPC, (b) 10% steel slag (c) 20% steel slag (d) 30% steel slag cement hydrated for 28 days.

3.4 Engineering properties

From the results in Table 3, the reference cement recorded the highest water demand (28.5%). Generally, the slag cement pastes required less water to form a workable paste compared to the reference cement, reducing as the slag content was increased. The substitution of a minimum steel slag content of 5% reduced water demand by 11.6% and up to 22.8% as slag content increased to 30%. This trend could be attributed to delayed hydration of slag, due to its mineralogical composition. The slag reduces ettringite formation because it is less reactive than the replaced cement and thus improving workability [15,

16]. The soundness test in Table 3 showed the reference cement expanded more than the blended cements. Figure 4 shows that increasing the slag content increases the setting times of the cement pastes. This is due to dilution effect on the cement which affects cement hydration [16]. However, the setting times obtained satisfied the recommended EN 196-3 [9] standards.

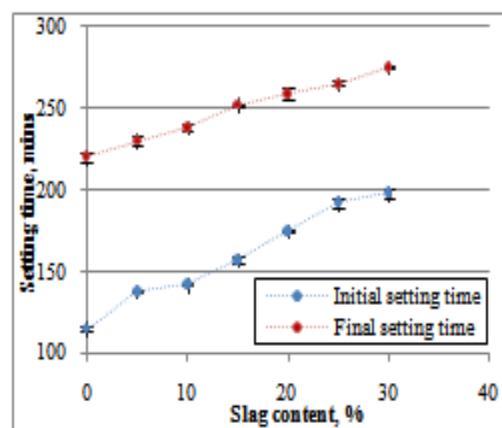


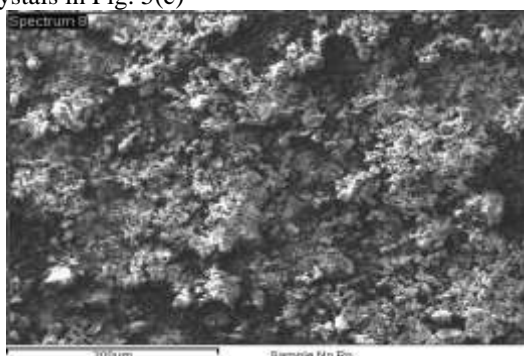
Fig. 4: Setting time of steel slag blended cements

Table 3: Some physical properties of OPC and blended steel slag cements

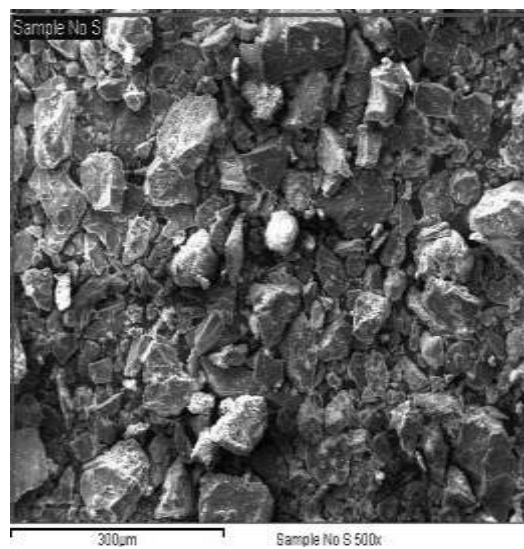
Property	OPC	5%	10%	15%	20%	25%	30%
Expansion, mm	1.04	1.02	0.89	0.83	0.87	0.95	1.02
Standard consistency, %	28.5	25.2	24	23.6	23.2	22.4	22

3.5 Microscopic analysis

The micrographs of the SEM analysis performed on both the raw and hydrated cement samples at 28 days are shown in Fig. 5. The SEM micrographs indicated clearly that the pores of the blended cement were reduced as a result of addition of the steel slag. Fig. 5 (d) confirms the formation of angular alite (C_3S) and round belite (C_2S) crystals in place of the abundant cauliflower-like Portlandite crystals in Fig. 5(c)



(a)



(b)

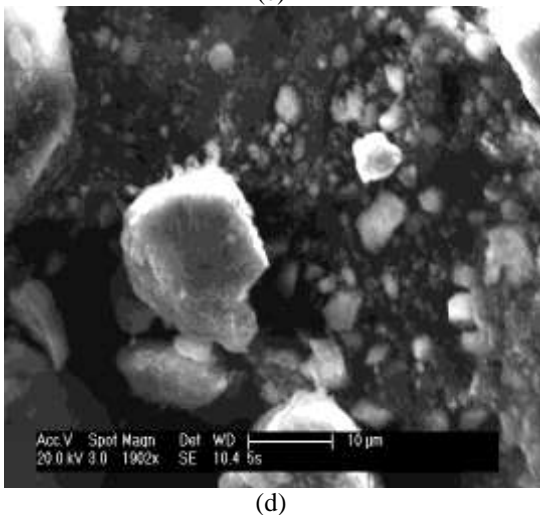
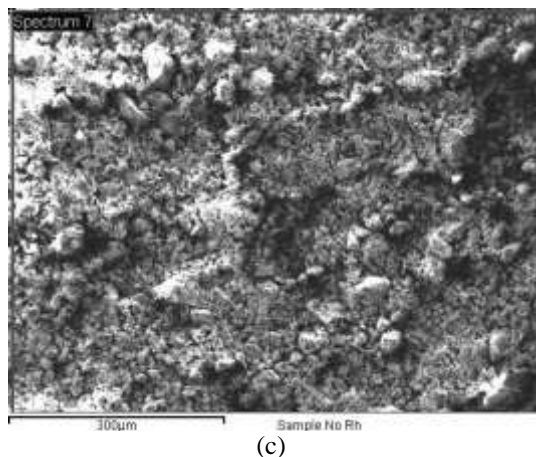


Fig. 5: Microstructure of (a) OPC (b) Steel slag (c) Hydrated OPC (d) Hydrated 5% slag cement

3.6 Mechanical properties

Figure 6 shows the compressive strength development of slag cements in relation to the cement replacement levels. The results indicate that slag cements develop lower strength at 2 and 7 days, compared to the reference cement. The higher the slag content, the lower the strength at early ages. This trend however changed when the curing period was extended to 28 days. The incorporation of 5% slag could not have any appreciable effect on the compressive strength at 28 days. When slag content increased to 30%, compressive strength increased by 9.6%. The results in Figure 6 confirm that all the blended cements satisfied the EN 197-1 [6] minimum strength requirement of 42.5 MPa. This is because the reactivity of the slag is slow and depends on the calcium hydroxide availability; the strength gain takes longer time with slag content [17].

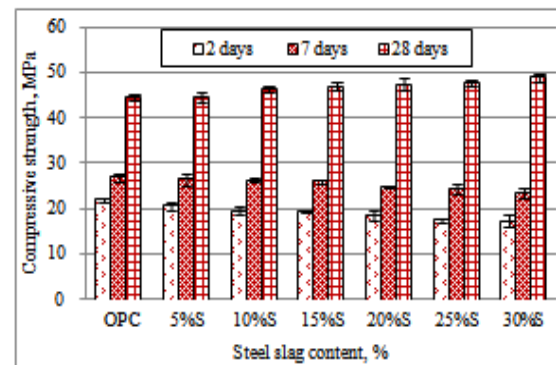


Fig. 6: Compressive strength of steel slag blended cements

IV. CONCLUSIONS

The chemical analysis of the steel slag as determined by X-ray fluorescence showed the presence of relevant minerals such as SiO_2 , Al_2O_3 and Fe_2O_3 . The sum of the compositions of these minerals exceeded the minimum 70% for natural pozzolans but must be interpreted with caution. Thus the reactive silica must be determined to confirm pozzolanicity or otherwise. The Na_2O eq (0.7%) for the slag was higher than the maximum permissible limit of 0.6% and suggests that when added to cement could lead to alkali silica reactivity with reactive aggregates.

X-ray diffraction analysis of the slag blended cements showed significant reductions in $\text{Ca}(\text{OH})_2$ and increasing C_3S with increasing slag content. SEM micrographs confirmed the formation of alite and belite crystals and indicated clearly that the pores of the blended cement were reduced as a result of addition of the steel slag.

Steel slag blended cements studied had lower permeability, demanded less water and was more sound than the reference cement. However, the blended cements showed longer setting times as compared to the reference cement.

Steel slag cements developed lower strength, at early ages but increased in strength at later ages. Blended steel slag cements studied satisfied the requirements of the strength Class 42.5. With the addition of 30% steel slag, compressive strength increased by 9.6%.

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