



Study physico-chemical properties of blended cements containing fixed amount of silica fume, blast furnace slag, basalt and limestone, a comparative study



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HIGHLIGHTS

- Basalt can be added to cement without negative effect on the compressive strength.
- The pozzolanic activity of basalt lower than silica fume and blast furnace slag.
- Basalt can be used as a good filled-pozzolanic material.
- Basalt pastes have better physico-mechanical properties than limestone as filler.
- We found that basalt has obvious pozzolanic activities at later ages.

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ABSTRACT

The present study investigates the effect of substitution of Portland cement by 20% of basalt, as natural pozzolana, on the physico-chemical properties of blended cement in comparison to silica fume, granulated blast furnace slag and limestone. For this purpose, a reference sample and four cements containing up to 20% w/w of silica fume, granulated blast furnace slag, basalt and limestone were tested. Bulk density, compressive strength, total porosity and chemically combined water were determined up to 360 days. The hydration products were investigated with FT-IR and DSC. The results showed that basalt has lower pozzolanic activity at early ages than that of silica fume and slag but at later age increases. Whereas the basalt acts as filled materials at early ages and then its reactivity increase due to pozzolanic reaction. It is concluded that basalt has low pozzolanic activity and has a better filling effect on cement hydration with better physico-mechanical properties than other pozzolanic materials.

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1. Introduction

The Cement industry is one of the industries that produce large amount of carbon dioxide, the production of every 1 ton of Portland cement clinker is accompanied by emission approximately 1 ton of carbon dioxide. [1–3]. A pozzolana is a material, which is capable of reacting with lime, $\text{Ca}(\text{OH})_2$, in the presence of water at ordinary temperatures to form compounds have cementitious properties (as C–S–H gel) [4]. Nowadays, different types of mineral admixtures are added to Portland clinker during the milling process or directly to the cement. The pozzolanic materials used in the cement industry, including pozzolanic (natural pozzolana, low calcium fly ash, silica fume), autopozzolanic (high calcium fly ash and blast furnace

slag) and crystalline materials (as a filler) [5,6], some of which interact physically and/or chemically with Portland cement or its hydration products [7,8]. The performance of mineral admixtures in blended cements and concrete depends on some factors such as particle size distribution, specific surface area, chemical composition and crystallinity [4,9]. Mineral admixtures are widely used in concrete to improve the physical and chemical properties or to reduce the costs and saving of energy. The using of cement replacement materials may reduce the factors related to declining concrete durability or to improve its resistance against sulfate attack [10–14]. Also, mineral additions have improved the strength by filling of the pores and change its diameter and distribution [15]. One of the observed disadvantages of the used natural pozzolana in cement is decreasing the early strength. Natural pozzolana have been widely used in blended cement for many applications

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[16,17], Some of them are pyroclastic rocks that are containing siliceous, or siliceous and aluminous volcanic glass [18–20].

Basalt is one of igneous rock, which was formed during the cooling of magma in the old ages of the earth. Most of igneous minerals are present in active state and that are changed under environment conditions, physical or chemical weathering, into more stable clay minerals [21]. The effect of limestone powder, basalt powder and marble powder as mineral admixtures on the fresh and hardened properties of self compacting concrete was investigated [22]. The basalt as a mineral admixture was investigated, where the physical properties and chemical compositions were studied [23,24]. The effect of basaltic pumice on the mechanical and physical properties [25,26] and the seawater resistance of the concrete was studied [27]. Also, the deterioration effect of blended cement combinations with red brick dust (RBD) and ground basaltic pumice (GBP) was investigated [28]. Silica fume is produced from the manufacture of silicon element or its alloys. It has an important role in improving the physical and chemical properties of concrete, this is mainly due to it has high surface area and pozzolanic activity [29]. The slag is produced as by-product material from the manufacture of pig iron. Due to its pozzolanic nature, SG is used as a mineral admixture in concrete [30].

This study is aimed to investigate the influence of basalt at 20% on the physicochemical properties of cement pastes, in comparison with slag, silica fume, and limestone at the same proportions.

2. Experimental

2.1. Materials

The investigated materials were Ordinary Portland cement OPC provided by Tourah Cement Company, silica fume provided by ferrosilicon company nag hamady, blast furnace slag provided by Iron and steel company-El-Tibin, Egypt, basalt was obtained from El-wahate El-bahareua quarry, Egypt and limestone was provided from Samalout, ElMinia. Chemical compositions of the Portland cement (OPC), silica fume (SF), blast furnace slag (SG), limestone (LS) and basalt (BS) are given in Table 1.

By comparing the chemical compositions, it can be seen that the mass fractions of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ and CaO are 86.26% and 9.68% of basalt powder, 80.86% and 11.47% of slag, 94.6% and 0.2% for silica fume. This conforms well to the requirements (>70%) stated in ASTM C618-89 [31,32] for a natural pozzolana. The experimental results are listed in Table 2. Also, the basalt contains CaO , MgO and traces of SO_3 , Na_2O and K_2O . Chakchouk et al. [33] indicated that a total percentage of SiO_2 , Al_2O_3 , and Fe_2O_3 greater than 50% is sufficient to produce good pozzolanic material. X-ray diffraction (XRD) used for identification of mineralogical composition of basalt. The XRD patterns were recorded on (M/S. Shimadzu Instruments, Japan) diffractometer XRD 7000 with Ni filtered $\text{CuK}\alpha$ as a radiation source at 2θ scan speed of 4° min^{-1} . Fig. 1 shows that, the basalt composed of plagioclase (Labradorite) (3.20 Å and 3.17 Å) and cyclopyroxene (Augite) (2.98 Å and 2.93 Å). Thermal behavior of basalt was studied by a Perkin Elmer DTA7, Differential scanning calorimetry (DSC), with rate $20^\circ \text{C min}^{-1}$ alumina crucible, Fig. 2. It shows that, the basalt has a large low-temperature endothermic peak at about $75\text{--}150^\circ \text{C}$. This peak is due to loss of moisture in basalt. Also, shows the basalt does not have, thermally, unstable minerals [34]. Fig. 3 shows the FT-IR spectra of basalt. The spectrum of basalt shows the strong absorbance bands at 452, 538, 584, 772, 1,022, 3,410, and $3,764 \text{ cm}^{-1}$. The broad band centered at $1,022 \text{ cm}^{-1}$ is attributed to the asymmetric stretching frequency of Si-O-Si , the band at 776 cm^{-1} due to symmetric stretching of Si-O-Si and the band at 452 cm^{-1} is due to the bending frequency of Si-O-Si [34].

Table 1
Chemical composition of raw materials.

Raw materials	Chemical composition (%)									
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI*	Total
OPC	20.24	4.95	4.02	61.58	2.63	2.49	0.49	0.21	2.25	98.80
SF	93.00	00.40	1.20	0.20	1.20	0.30	0.10	1.10	1.75	99.25
SG	51.68	16.93	12.25	11.47	4.28	0.27	0.85	0.41	1.90	100.00
BS	59.37	15.39	11.40	9.68	1.87	0.06	0.24	0.40	1.50	99.91
LS	0.26	00.16	00.29	54.59	0.29	0.05	0.11	0.03	43.72	99.50

* LOI = loss on ignition.

2.2. Mixture proportions

The mixture proportion is shown in Table 3. Basalt, silica fume, slag and limestone were added as a partial replacement of cement at a level of 20% by weight. The ingredients of each mixture were mixed in an agate mortar to homogeneity. Cement pastes were prepared with a standard water-to-cement ratio [35]. A commercially available, Microwave oven was used to stopping the hydration of cement pastes [36].

2.3. Methods

2.3.1. Mechanical test

The cement pastes were molded into $2.54 \times 2.54 \times 2.54 \text{ cm}$ cubic steel molds, compacted through external vibration, then covered by plastic sheets on the molds to prevent moisture evaporation. The specimens were cured at 25°C and approximately at 100% relative humidity for 24 h, then de-molded and cured under water up to the time of testing. After 3, 7, 28, 90, 180 and 360 days curing, the compressive strength was conducted according to ASTM C349-08 [37]. Three samples of each batch were tested. The average value was served as the compressive strength. The compressive strength measurement was carried out using a manual compressive strength machine.

2.3.2. Total porosity

The bulk density (Bd) was carried out before the specimens subjected to the compressive strength determination. Bulk density was determined through weighing the samples of the hardened paste (suspended in water) and in air (saturated surface dry) according to Archimedes principle [38]. After the determination of bulk density and the total water (W_t) content of hardened cement pastes, the total porosity (ξ) of the hardened cement paste could be calculated as follows [38], $\xi = [(0.99 \times W_e \times \text{Bd}) / (1 - W_t)] \times 100$. Whereas, ξ = total porosity; Bd = bulk density; W_e = non-combined water (evaporable water).

2.3.3. Chemically combined water, (W_{ne})

The chemically combined water, (W_{ne}), was determined from the loss of hydrated samples at 1000°C , for 2 h, in a muffle furnace and cooled in a desiccator. The chemically combined water content is the percent of the loss in weight in respect of the ignited weight of cement paste [39].

2.3.4. Differential scanning calorimetry (DSC), A Fourier Transform (FT-IR)

Crushed samples from hardened pastes at given age (28d) were ground to powder to be used in thermal analysis (DSC) and FT-IR measurements. A Fourier Transform IR (FT-IR) spectrophotometer (Perkin Elmer 880) was used, within the range from 400 to 3500 cm^{-1} were obtained with the use of the KBr pellet technique (1:99) [40]. On the other hand, some samples were investigated using a differential scanning calorimetry (DSC) of the type a Perkin Elmer DTA7 with rate $20^\circ \text{C min}^{-1}$ alumina crucible.

3. Results and discussions

3.1. Chemically combined water

Non-evaporable water content (W_{ne}) can be used to determine the degree of hydration, but for cement pastes with pozzolana or filler materials, the following the degree of hydration from W_{ne} is difficult where overlaps between combined water associated with the reaction of the pozzolanic or filler materials from and that of cement hydration [41]. Fig. 4 shows the chemically combined water contents of OPC and blended cement pastes as a function of curing time up to 360 days. Generally, the combined water contents of all cement pastes increase with curing time up to

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