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Basalt waste added to Portland cement

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ABSTRACT. Portland cement is widely used as a building material and more than 4.3 billion tons were produced in 2014, with increasing environmental impacts by this industry, mainly through CO_2 emissions and consumption of non-removable raw materials. Several by-products have been used as raw materials or fuels to reduce environmental impacts. Basaltic waste collected by filters was employed as a mineral mixture to Portland cement and two fractions were tested. The compression strength of mortars was measured after 7 days and Scanning Electron Microscopy (SEM) and Electron Diffraction Scattering (EDS) were carried out on Portland cement paste with the basaltic residue. Gains in compression strength were observed for mixtures containing 2.5 wt.% of basaltic residue. Hydration products observed on surface of basaltic particles show the nucleation effect of mineral mixtures. Clinker substitution by mineral mixtures reduces CO_2 emission per ton of Portland cement.

Keywords: mineral admixture, particle size, microstructure, nucleation.

Adição de resíduo de basalto ao cimento Portland

RESUMO. O cimento Portland é amplamente utilizado como material de construção; mais de 4.3 bilhões de toneladas de cimento Portland foram produzidas em 2014, aumentando os impactos ambientais relacionados a esta indústria, principalmente a emissão de CO_2 e o consumo de matérias-primas não renováveis. Diversos resíduos têm sido empregados como matérias-primas ou combustíveis, a fim de reduzir estes impactos ambientais,. A resistência à compressão foi determinada aos sete dias, e a microstrutura da pasta foi analisada por meio de Microscopia Eletrônica de Varredura (MEV) e sonda de eléctrons retro-espalhados (EDS). Ganhos na resistência à compressão foram observados para composições contendo 2.5% de resíduo de basalto. Foram observados produtos de hidratação sobre a superfície das partículas de basalto, demonstrando o efeito de nucleação das adições minerais. A substituição do clínquer por adições minerais permite a redução na emissão de CO_2 por tonelada de cimento Portland.

Palavras-chave: adição mineral, tamanho da partícula, microestrutura, nucleação.

Introduction

Portland cement is widely used for building material and, according to Cembureau (2014), approximately 4.3 billion tons were processed in 2014. The 2014 Brazilian production reached 81 million tons of Portland cement. Several researches have been recently developed to reduce the environmental impacts of the cement industry, mainly by the co-processing of residues as raw materials (Schneider, Romer, & Bolio, 2011) or fuel (Cembereau, 2013). Currently, emission of particulated material has been restricted by environmental codes, resulting in residues collected by filters (Kim, Park, & Kim, 2013), which, in turn, are used as a mineral admixture to Portland cement (Hekal, Abo-El-Enein, El-Korashy, Megahed, & El-Sayed, 2013). However, several minerals, such as basalt and granite, do not have large scale industrial application and require environmental management.

Many studies have been developed for the proper disposal of these residues, such as raw material for clinker production (Andrade, 2010) or as mineral admixture to Portland cement (Uysal & Sumer, 2011). Hassan (2001) presents similar rates of compressive strength for clinkers obtained from basalt as raw material when compared to clinkers obtained from clay. Yen, Tsegn, and Lin (2011) published similar results for clinker produced from marble waste. Results published by Laibao, Zhang, Zhang, Zhiyoug, and Zhang (2013) have shown a loss of compressive strength for mixtures with basaltic waste as a mineral admixture (Figure 1). Unicik and Kmecova (2013) published similar results for mixtures containing 10, 20 and 30 wt.% of basaltic residue. Uysal and Yilmaz (2013) reported compression strength loss for all mineral admixtures when they compared mixtures containing 10, 20 and 30 wt.% of basalt, marble or calcium carbonate residues.

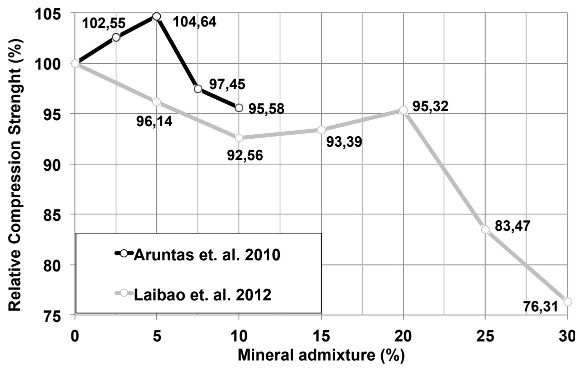

Figure 1. Effect of mineral admixture on compression strength.

Similar results were published by Vijayalakshimi, Sekar, and Ganeshm (2013) for mixtures containing 5, 10, 15 and 20 wt.% of granite waste. In the case of large amounts of mineral admixture, Jain (2012) presents a linear reduction in compression strength for mixtures containing 20, 40 and 60 wt.% of marble residue. Similar results were obtained by Vardhan, Goyal, Siddique, and Singh (2015) for formulations containing 10, 20, 30, 40, 50 wt.% of marble waste. In the case of mixtures with 34 wt.% of marble residue, Tennich, Kallel, and Ouezdoul (2015) presented a compression strength gain when compared to reference. Almeida, Branco, Brito, and Santos (2007) reported a gain on compression strength for mixtures containing 8 wt.% of marble residue for self-compact concretes with 0, 8, 15, 22, 27, 39, 56, 65 wt.% of marble waste.

In the case of mixtures containing 0, 5, 10 and 20 wt.% of granite and marble wastes, Bacarji, Toledo Filho, Koenders, and Figueiredo (2013) and Rodrigues, Brito, and Sardinha (2015) registered a similar value of compression strength for mixtures with 5 wt.% residue. For mixtures containing 0, 5, 7.5, 10, 15 wt.% of marble waste, Aliabdo, Elmoaty, Elmoaty and Auda (2014) demonstrated an improvement on compression strength for a formulation containing 10 wt.% residue. Similar rates of compression strength were achieved for mixtures containing 10 wt.% of marble residue, as published by Baeza, Payá, Galao, Saval, and Garcés (2014) and Corinaldesi, Moroconi, and Naik (2010). For a lower content of mineral admixture, Ergun (2011) presented a maximum compression strength for mixtures containing 7.5 wt.% of marble residue, whilst published results by Aruntas, Guru, Dayi, and Tekin (2010) indicated a maximum gain of compression strength for mixtures containing 5 wt.% of marble waste (Figure 1).

According to Aictin (2000), ultrafine particles act as natural nucleation sites for the formation of calcium hydroxide (CH). They are developed as small Portlandite crystals, or calcium silicate hydrate and calcium aluminate hydrate (CSH/CAH). Mass loss at a temperature between 100 and 200ºC does not constitute a considerable difference for mixtures with 7.5 and 15 wt.% of granite residue, when compared with reference (Aliabdo, Elmoaty, Elmoaty and Auda (2014). The peak intensity of calcium hydroxide (CH) measured by X-ray diffraction does not present a considerable difference in spite of smaller amounts of clinker in mixtures containing the mineral admixtures (Laibao, Zhang, Zhang, Zhiyoug, & Zhang, 2013; Aliabdo et al., 2014). Current study evaluates a Coarse Fraction (< 200 micrometers) and a Fine Fraction (50 micrometers) of basaltic residue, both obtained by sedimentation, as a mineral admixture to Portland cement.

Materials

Basalt residue collected by filters was separated by sedimentation into two fractions: Coarse Fraction (CF) and Fine Fraction (FF). Portland cement CPV and natural sand were used in current study, following Associação Brasileira de Normas Técnicas (ABNT, 1991; 2012), respectively. The chemical composition of basaltic fractions was determined by X-ray fluorescence, with P'ANalytical Axios Advanced X-ray spectrometer. The chemical composition of Portland cement CPV was provided by the manufacturer (Table 1).

Table 1. Chemical composition of raw materials.

Raw material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	L.I.	I.R.	SUM
Portland cement (PC)	19.06	4.03	2.65	60.06	5.16	2.82	2.89	0.65	93.78
Coarse Fraction (CF)	51.0	15.1	13.0	9.26	4.37	n.d.	1.27	0	94.00
Fine Fraction (FF)	51.8	16.3	11.3	8.80	3.71	n.d.	2.08	0	93.99

As may be seen in Figure 2, the particle size distribution of Coarse Fraction (CF), Fine Fraction (FF) and Portland cement (PC) was determined by laser granulometry with Malvern Metasizer 2000 granulometer. Figure 3 shows the diffractogram of Fine Fraction (FF). Data were measured with a Philips P'ANalytical X'Pert PRO MPD X-ray diffractometer (Cu 40 kV 30 mA Kα 2θ = 10 - 70° 0.1° s^{-1}). Figure 3 also displays the main mineral phases observed in basalt rocks: Albite ($NaAlSi_3O_8$), Anorthite ($CaAl_2Si_2O_8$), Augite (Na, Ca - Mg, Fe^{2+},Al, Fe^{3+}, Ti) [(Si, $Al)_2O_6$] and Labradorite (Ca, Na) [Al (Al, Si) Si_2O_8].

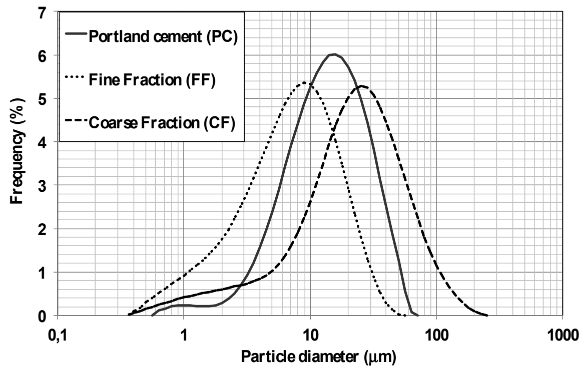

Figure 2. Particle size distribution of raw material.

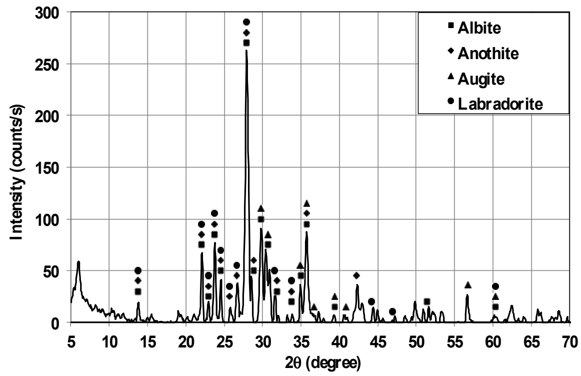

Figure 3. Basaltic Fine Fraction diffractogram.

Methods

Table 2 shows a list of all studied mixtures. The mortar's compression strength followed ABNT (1997), using three 5 x 10 cm cylindrical specimens, employing a water: (cement-mineral admixture), ratio 0.48; and a (cement-mineral admixture): sand at a proportion of 1:3. After one day of initial curing, the specimens underwent submerged curing at room temperature (20°C). Following ABNT (1991), compression strength of Portland Cement CPV was measured after 1, 3, 7 and 28 days. For comparative analysis, compression strength was measured after 7 days.

Table 2. Studied Mixtures.

Mixture	Portland Cement (PC)	Fine Fraction (FF)	Coarse Fraction (CF)
REF	100%	0	0
2.5 FF	97.5%	2.5%	0
5.0 FF	95.0%	5.0%	0
10 FF	90.0%	10%	0
15 FF	85.0%	15%	0
5 CF	95.0%	0	5.0%
10 CF	90.0%	0	10%
15 CF	85.0%	0	15%

Mortar samples were ground and sifted in a 200-mesh sieve (0.075 mm) and calcined at 950°C (American Society for Testing and Materials [ASTM], 2013). Water absorption of mortars was determined according to American Society for Testing and Materials (ASTM, 1972). The microstructural effect of basaltic powder was analyzed in pastes containing 15 wt.% of Fine Fraction (FF) with a Scanning Electron Microscope (SEM) Quanta 600 FEI-Philps. The paste samples were molded with the same water:(cement-mineral admixture) ratio, employing a silicone cylindrical mold, and subjected to submerged curing for 7 days at room temperature (20°C). Samples were dried and gold-coated.

Results and discussion

Figure 4 demonstrates the results of compression strength mortar samples. Reduction of compression strength occurs in mixtures containing Coarse Fraction (CF) due to increase in mineral admixture (Laibao et al., 2013; Unicik & Kmecova, 2013; Uysal & Yilmaz, 2013). In the case of samples containing 2.5 wt.% of Fine Fraction (FF), a gain in compression strength was observed and for mixtures with 5 wt.% of Fine Fraction (FF), a similar rate was obtained when compared to the reference mixture (Aruntas, Guru, Dayi, & Tekin, 2010). A subsequent reduction was verified for contents above 10 wt.% for a large quantity of Fine Fraction (FF). No considerable difference was reported with regard to compression strength for mixtures with large amounts of the two fractions.

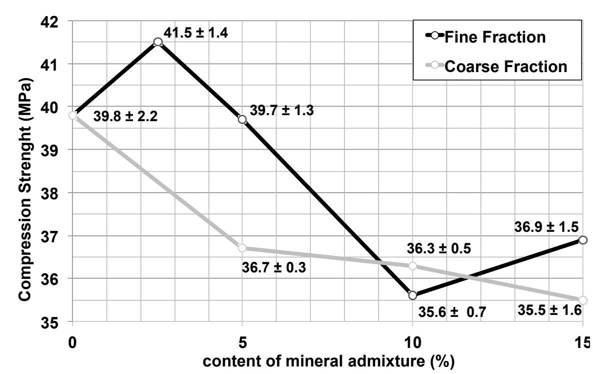

Figure 4. Effect of basaltic powder on compression strength.

When water absorption of samples, displayed in Table 3, is taken into account, a constant trend in open porosity is given for the two fractions analyzed. According to Taylor (1990), loss of mass occurred up to 300°C, which corresponded to the chemically bounded water from etringite (E), calcium silicate and aluminate hydrate silicate (CSH/CAH). Calcium hydroxide (CH) loses mass at temperatures ranging between 300 and 600 at 950°C, mass loss represents calcium carbonate ($CaCO_3$) from the reaction of calcium hydroxide (CH) with CO_2.

According to Almeida and Hollanda (2009), loss in ignition (L.I.) of basaltic samples is related to the intemperism level of materials, mainly the clay minerals such as kaolinite and montmorilonite, caused by alterations of feldspar and silicates in basaltic rocks. Initial L.I. of raw materials is subtracted Mass Loss at 950°C to estimate total hydration products of sample $E/CSH/CAH/CH/CaCO_3$, as Equation 1 shows. Table 3 presents calculated values.

$$E/CSH/CAH/CH/CaCO_3 = M.L.\ 950°C - [PC \times (L.I._{PC}) + FF \times (L.I._{FF}) + CF \times (L.I._{CF})] \quad (1)$$

where:
$E/CSH/CAH/CH/CaCO_3$ – total hydration products of Portland cement (wt.%);
M.L. 950°C – samples' mass loss at 950°C (%);
PC – content of Portland cement (wt.%);
$L.I._{PC}$ – Loss in Ignition of Portland cement (%);
CF – content of Coarse Fraction (wt.%);
$L.I._{CF}$ – Loss in Ignition of Coarse Fraction (%);
FF – content of Fine Fraction (wt.%);
$L.I._{FF}$ – Loss in Ignition of Fine Fraction (%).

Table 3. Water absorption and mass loss at 950°C.

Mixture	Water Absorption	M. Loss 950°C	(E/CSH/CAH/ CH/$CaCO_3$)	CO_2 Emission (kg ton^{-1})
REF	6.64%	13.70%	10.81%	849
2.5 FF	6.63%	20.47%	17.60%	827
5.0 FF	6.45%	17.60%	14.75%	806
10 FF	6.73%	18.27%	15.46%	764
15 FF	6.60%	15.76%	13.00%	721
5 CF	6.72%	19.31%	16.50%	806
10 CF	6.33%	17.32%	14.59%	764
15 CF	6.39%	18.37%	15.72%	721

Mixtures containing basalt have an increasing trend on total hydrated products ($E/CSH/CAH/CH/CaCO_3$) in spite of the reduction in total amount of Portland cement CPV. Results indicate that coarse and fine fractions may function as a nucleation point. A maximum rate was calculated for mixture with 2.5 wt.% of Fine Fraction (FF); a reduction was observed for contents bigger than this rate.

Further, 849 kg of CO_2 derived from limestone decomposition and burning of fossil fuels are obtained to produce one ton of clinker. The replacement of clinker by calcium carbonate, slag and pozzolans reduces total emission of CO_2 per ton of Portland cement (Cemberau, 2013). The chemical analysis of Portland cement CPV (Table 1) provides samples´ Lost Ignition which mainly represents gypsum and calcium carbonate. This value indicates a calcium carbonate content of approximately 5 wt.%, following ABNT (1991). Portland cement´s insoluble residue is due to the addition of pozzolans, also identified in the chemical composition (Table 1). Clinker content in the Portland cement CPV analyzed was fixed at 95 wt.%. Emission of CO_2 is estimated by Equation 2 (Table 3). In the case of mixtures containing 5 wt.% of Fine Fraction, there was a reduction in CO_2 emission without any decrease in its mechanical properties.

$$CO_{2\ Emission} = PC \times (C \times C_{CO2}) \quad (2)$$

where:
$CO_{2\ Emission}$ – CO_2 emission of Portland cement (kg ton^{-1});
PC - Portland cement content (%);
C - Clinker content (%)
C_{CO2} – emission of CO_2 per ton of clinker (1000 kg ton^{-1}).

Figure 5a shows the sample's micrography with 15 wt.% of Fine Fraction (FF), obtained by Scanning Electron Microscopy (SEM). One may observe a spherical particle of fly ash and a nucleation point on the surface.

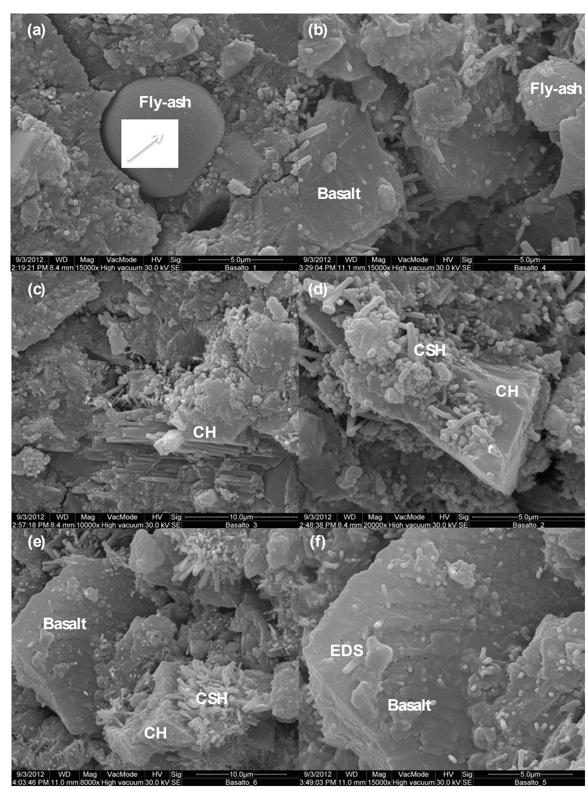

Figure 5. Micrographs (SEM) of mixture 15 Fine Fraction.

Figure 5b shows particles of fly ash and basalt, calcium silicate hydrates (CSH) and calcium hydroxide (CH) on particles' surface. Figure 5c and d present calcium hydroxide (CH) platelets (CH) and calcium silicate hydrates (CSH), whilst Figure 5e shows a basaltic particle and hydration products such as calcium silicate hydrates (CSH) and calcium hydroxide (CH). Figure 5f reveals small quantities of calcium silicate hydrates (CSH) on the particles' surface, indicating nucleation effect. A point on the basaltic particle was analyzed with a back-scattered electron probe (EDS) to identify the semi-quantitative chemical composition. Figure 6 shows the obtained spectrum, highlighting the predominance of Si peak when compared to Ca, Mg, Na, K peaks, consistent with basalt chemical composition (Table 1).

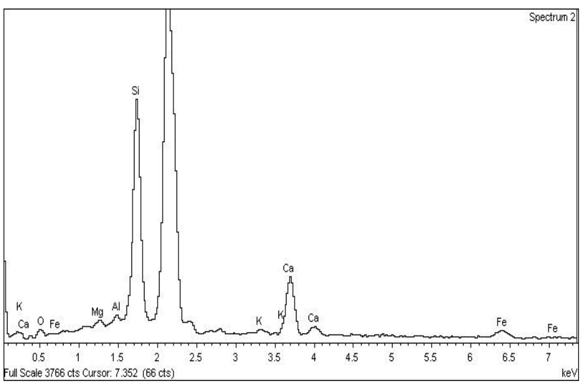

Figure 6. Spectrum of chemical analysis (EDS).

Conclusion

The mechanical performance of Portland cement is directly affected by basalt residue. A positive effect was observed for contents varying between 2.5 and 5 wt.% of Fine Fraction, although a negative effect was identified on compression strength for larger amounts of mineral admixture. Consequently, the distribution of particle size directly affects the mechanical performance of the mixtures under analysis.

The nucleation effect was also identified for all studied mixtures; content of mineral admixture and the particle size distribution were two main aspects related to total hydration products. MEV analysis visualizes the nucleation effect which occurs on the surface of basaltic particles. The replacement of clinker by basalt waste contributes towards the reduction of emission of greenhouse gases.

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