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Research paper

Mineralogical study of granite waste in a pozzolan/$Ca(OH)_2$ system: Influence of the activation process

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ABSTRACT

Despite the technological improvements introduced in the production of ornamental granite, sludge is inevitably generated in end product cutting and polishing. The present study constitutes the first attempt to scientifically analyse granite sludge, focusing in particular on its characterisation and pozzolanic activity and the morphological and microstructural changes taking place in both thermally activated waste and in the pozzolan/$Ca(OH)_2$ system in the first 360 days of reaction. The possible valorisation of this waste as a component of more eco-friendly cements is assessed with a view to furthering the circular economy. The findings show that thermal activation has no beneficial effect on sludge pozzolanicity, which at later ages was similar to the activity observed in other additions such as copper and manganese silicate slag but lower than in silica fume, fly ash and fired clay materials. The granite waste/$Ca(OH)_2$ system microstructure, in turn, contains C-S-H gels characterised by a low (0.6–1.0) Ca/Si ratio.

1. Introduction

The natural stone industry engages in quarrying and dressing the rock found on the Earth's crust. The end product of this industry, essential to the economy of many developed countries, is used in the construction industry, funeral art and sculpture, interior and exterior decorating and for a variety of artistic purposes.

Spain ranked seventh in natural stone output and sixth in export volume worldwide in 2014 (Piedra Cluster, 2014).

In 2013, 17.2% of all the ornamental stone produced nationwide was granite, the third ranking material after limestone and ornamental slate, which accounted for 42.5 and 17.9%, respectively (Secretaria de Estado de Energía, 2013). Two types of waste are inevitably generated by the ornamental stone industry: a) solid waste during rock quarrying and hewing; and b) sludge during dressing (granite cutting and polishing), consisting in a mix of water and fine particles (Galetakis and Soultana, 2016).

In today's context of sustainability, this granite sludge constitutes a serious problem for producers, given: i) the huge volume generated (0.1 m^3/t processed rock); ii) the need to find suitable places for its temporary stockpiling and subsequent evacuation (Marmol et al., 2010); the economic and environmental (CO_2 emissions) cost of shipping it to sanitary landfills; i*v*) the adverse effects of uncontrolled dumping on water quality and plant life photosynthesis; and v) the risk for human health posed by the suspension of small particles in the air (Torres et al., 2009).

Over the last 10 years a number of authors have attempted to explore the viability of valorising this granite waste by using it in construction, in light of the industry's capacity to absorb large volumes of waste in a wide range of products. Much of the research conducted has focused on the applicability of such waste in the manufacture of fired clay products such as vitrified tile, pavers and roof tiles (Hojamberdiev et al., 2011, Acchar et al., 2006, Ayangade et al., 2004, Simakin et al., 2001, Segadães et al., 2005). The authors have consistently reported that the partial replacement of clay with sludge yields high performing, visibly attractive products.

More recently, studies have been run on the use of granite waste as a partial replacement for fines (Ilangovana et al., 2008, Vijayalakshmi et al., 2013, Safiuddin et al., 2007) or cement (Li et al., 2013, Bacarji et al., 2013) in the manufacture of cement-based materials or as a pigment in new mortar design (Marmol et al., 2010). All reports concur that concrete made with fines and cement replacement ratios of under 15 and 5 wt%, respectively, meet mechanical strength and durability standards. Nonetheless, the present scientific gap around the possible applicability of sludge as an active addition in the design of new more eco-friendly cements calls for further research to foster what has come to be known as the circular economy.

The research community has deployed a good deal of effort in developing new industrial additions (Sáez del Bosque et al., 2013, Sáez del Bosque et al., 2014a, Sáez del Bosque et al., 2014b) and valorising clay-

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Table 1
XRF-determined chemical composition of granite industry waste.

Majority components (wt%)											
SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	SO_3	P_2O_5	TiO_2	MnO	LOI[a]
69.64	15.00	2.52	1.60	2.36	3.59	4.04	–	0.17	0.51	0.04	0.52

Trace elements (ppm)											
Zr	Y	Sr	Cu	Ni	Co	Ba	Cr	V	Zn	Pb	Cl
21	–	27	19	9	8	–	37	1	195	22	91,804

[a] LOI: loss ignition at 1000 °C.

based (Medina et al., 2013, Medina et al., 2016b, Medina et al., 2016a), agri-forest (Frías et al., 2011, Nakanishi et al., 2014) and other industrial (Frías et al., 2012, Frías et al., 2008) by-products as partial replacements for clinker to reduce the energy, CO_2 emissions and natural raw material consumption inherent in cement manufacture.

This study explored the effect of calcination temperature on granite sludge composition, structure, pozzolanicity and mineralogy, and identifies the hydrated phases in the granite waste/$Ca(OH)_2$ system and their fluctuations. To that end, the waste was studied using X-ray diffraction, infrared spectroscopy, differential thermal and thermogravimetric analysis and scanning electron microscopy.

2. Experimental

2.1. Materials

The granite waste used in this study was the dust generated during cutting for use as ornamental stone. This type of ornamental stone is quarried and cut in open pits, primarily with diamond wire saws, to obtain blocks of a size appropriate for processing and shipping. The cutting water is carried off to ponds where large volumes of a solid waste characterised by a very small particle size settle. This was the waste subsequently collected and shipped to the laboratory. Prior to testing, it was heated in a laboratory kiln for 24 h at 100 °C to a constant weight to eliminate the moisture.

The calcium hydroxide used was an extra pure Ph Eur, USP, BP chemical reagent.

2.2. Material characterisation

The 1, 7, 14, 28, 90, 180 and 360 day pozzolanicity of granite waste was found using a chemical procedure described by Medina et al. (Medina et al., 2016a) in a previous paper. The solid residue was analysed with XRF, XRD, FTIR, DTA/TG, and SEM.

X-ray fluorescence (XRF) was used to determine the chemical composition of the granite waste, analysing pressed powder samples on a Bruker S8 TIGER XRD spectrometer and processing the data with SPECTRAplus QUANT EXPRESS software.

The mineralogical composition of the both waste and the waste/calcium hydroxide system was found with X-ray diffraction (XRD) techniques. A CuKα ($\lambda = 1.54$ Å) Bruker D8 Advance diffractometer equipped with a Lynxeye detector, in turn fitted with a 3 mm antiscatter slit and a (0.5%) Ni K-beta filter was used for the readings, performed at 2θ diffraction angles of 5° to 60°.

For the FTIR analyses 1 mg of sample was pressed into 300 mg KBr pellets scanned on a Nicolet 6700FT-IR spectrometer over a range of 4000 cm^{-1} to 400 cm^{-1}.

A TA Instrument SDTQ600 thermal analyser was used for the DTA, TG and DTG analyses, conducted in a dynamic N_2 atmosphere, heating the samples from 20 °C to 1000 °C at a rate of 10 °C/min.

Carbon-coated samples, secured with a two-sided graphite adhesive to a metallic holder, were prepared for scanning electron microscope (SEM) analyses to enhance conductivity and thereby ensure that all the relevant signals would be detected.

In SEM analysis, the samples were secured to a metallic holder with a two-sided graphic adhesive after carbon coating the surface to ensure conductivity and detection of all the signals sought.

A Sympatec Helos 12LA laser granulometer was used to determine the particle distribution of the materials.

3. Results and discussion

3.1. Granite industry waste characterisation

The granite industry waste contained 69.6 wt% SiO_2, 15.0 wt% Al_2O_3 and other oxides with contents ranging from 1.5 to 4.0 wt% (see Table 1). The most abundant trace elements were Cl and Zn. The reactive silica content, found as specified in Spanish standard UNE 80225 (Spanish Committee for Standardization, 2012), amounted to 22.4 wt%, a value slightly lower than the 25 wt% threshold that

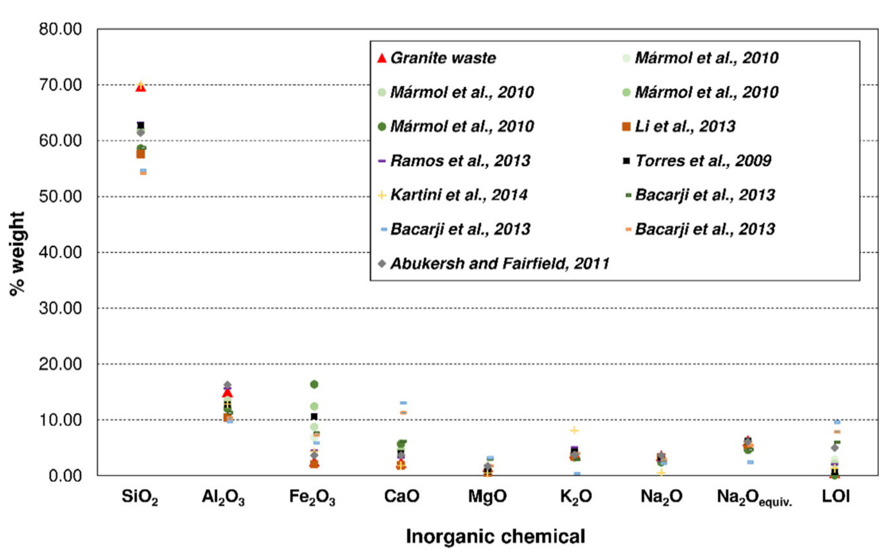

Fig. 1. Chemical composition of the different granites wastes.

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