



Activation temperature-mediated mineralogical transformations in slate quarry sludge: Pozzolanic properties

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HIGHLIGHTS

- Slate sludge exhibits pozzolanic activity.
- Thermal activation improve slate sludge pozzolanicity.
- Slate sludge thermal activation barely affects the morphology of C-S-H gels formed.
- Slate sludge waste is apt for use as an addition in eco-efficient cements.

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ABSTRACT

Ornamental stone quarries generate huge volumes of waste. The valorisation of such waste as possible additions (supplementary cementitious materials) to cement would contribute to the implementation of circular economy criteria in the construction industry. The study reported here constitutes a first-time analysis of the pozzolanicity and morphological and microstructural changes induced in slate quarry sludge by thermal activation. The findings showed that thermal activation enhanced waste pozzolanicity, which at later ages was slightly higher than found in granite sludge and lower than in silica fume and fired clay-based materials. According to the Frattini test, the materials resulting from blending 20% or less of this waste cannot be regarded as CEM IV pozzolanic cements. A microstructural study revealed the surface formation of C-S-H gels in the slate sludge/Ca(OH)₂ system, which was more intense when the waste was activated. According to the statistical analysis performed, three factors -time, activation temperature and replacement ratio-, significantly affected slate sludge pozzolanicity.

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1. Introduction

The cement industry is characterised by high energy intensity, over-exploitation of natural resources and the emission of vast amounts of greenhouse gas (GHG), particularly CO₂. The carbon dioxide generated during fossil fuel-fired limestone calcination in pre-heaters and rotary kilns amounts to around 0.83 t per tonne of cement produced [1,2]. The cement industry has been pursuing a number of strategies to enhance its sustainability and lower CO₂ emissions: i) use of alternative fuels [3,4]; ii) more energy-efficient clinker production [5]; iii) introduction of alternative

calcium-rich raw materials that need not be decarbonated to manufacture clinker [6]; and iv) replacement of part of the cement or clinker with supplementary cementitious materials (SCMs). The fourth strategy is deemed to be the most effective in reducing the GHG emitted per tonne of cement, for in addition to being the phase of clinker manufacture that accounts for the highest fuel consumption [5], limestone calcination itself entails the emission of 0.5 t of CO₂ per tonne of CaO produced [7,8].

Supplementary cementitious materials can be grouped by type: i) industrial by-products such as fly ash, blast furnace slag and silica fume; ii) natural pozzolans; iii) burnt clays, regarded as artificial pozzolans, primarily metakaolin obtained by burning kaolinite or kaolinite-rich minerals; and iv) other artificial pozzolans sourced from mainly clay-based waste. The fourth group includes solid waste such as brick, wall and floor tile, sanitary ware waste, coal-mining waste, waste water treatment plant sludge, paper

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industry sludge, dam sediment and marble and granite quarry sludge.

The third and fourth groups (burnt clay and other artificial pozzolans) have been studied fairly intensively in recent years, primarily because clays are the basis for most of the materials involved. Clays contain a combination of minerals, usually phyllosilicates such as micas (muscovite or biotite), chlorite (clinochlore, chamosite), kaolinite (halloysite) and other scanty reactive phases such as quartz, feldspar and metallic oxides [9]. Under the right conditions, thermal activation induces a loss of crystallinity of the constituent minerals in clay, due primarily to dehydroxylation and the partial or total breakdown of the phyllosilicate lattice structure, resulting in silica- and alumina-high phases. Disorderly crystalline or completely amorphous, such silica and alumina phases are highly pozzolanic [9,10], i.e., they react with portlandite in the presence of water to form calcium silicate (C-S-H), calcium aluminosilicate (C-A-S-H) or calcium aluminate (C-A-H) hydrates. Such thermal activation, moreover, is less energy-intensive and emits less CO₂ than clinkerisation, for the temperatures required are lower (500 °C to 900 °C) and starting material decarbonation much more moderate.

In addition, the use of waste as SCMs is in line with sustainability policies aiming to change the (produce-consume-discard) linear economy model to a (produce-consume-recycle) circular model. That would reduce stockpiling and its associated costs while conserving non-renewable natural resources.

Not all SCMs call for thermal activation or grinding. Bricks [11], roof tiles [12,13] and sanitary ware [14] need only be ground for use with cement and granite quarry sludge [15] requires neither pre-treatment.

In a similar vein, slate quarry waste has been studied as a raw material in roof tile [16] and ceramic product [17] manufacture. This study explored the thermal activation of waste from the slate quarrying industry as a possible SCM in new cements, focusing on its pozzolanicity as determined chemically by the saturated lime and Frattini tests. The statistical significance of the effect of factors such as age, activation temperature and replacement ratio and their interactions were analysed with one- and multi-way analysis of variance (ANOVA).

2. Experimental procedure

2.1. Materials

The slate sludge used was generated during commercial ornamental stone quarrying and cutting. The waste was collected directly at the slate plant and dried in the laboratory at 100 °C for 24 h to eliminate any environmental moisture. The resulting powder had a BET (Brunauer, Emmet and Teller nitrogen adsorption isotherm) specific surface area of 4.43 m²/g. It was characterised by X-ray fluorescence (XRF), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and thermogravimetric (DTA), thermogravimetric (TG) and differential thermogravimetric (DTG) analysis.

The slate sludge was also thermally activated at 600 °C or 700 °C for 2 h and the resulting material was studied with XRD, FTIR and DTA/TG/DTG.

Both the activated and non-activated waste was tested for pozzolanicity with the Frattini and saturated lime tests.

2.2. Methodology and characterisation techniques

Two chemical methods, the Frattini and saturated lime tests, were applied to monitor pozzolanic activity. The former was performed as described in European standard EN 196-6 [18]. This test determines the pozzolanicity of a material by comparing the calcium ion concentration, expressed as the calcium oxide equivalent, present in 40 °C, 8 d and 15 d aqueous solutions containing the problem cement sample (here, 10% slate waste/90% OPC or 20% waste/80% OPC) to the standard (40 °C) calcium hydroxide solubility curve. The curve, which represents Ca(OH)₂ in ordinary Portland cement (OPC), plots OH⁻ concentration on the X-axis against Ca²⁺ concentration (expressed as CaO equivalent) on the y-axis, both in mmol/L. An addition is regarded as pozzolanic if it lies below the Ca(OH)₂ solubility curve, an indication that it absorbed part of the Ca²⁺ in the solution.

The saturated lime test explores the pozzolanicity of a system consisting in the addition and a saturated calcium hydroxide solution kept at 40 °C, as described in [14]. Here the solution was filtered at 3 d, 7 d, 28 d and 90 d and the filtrate analysed for Ca²⁺ ion concentration (expressed as calcium oxide or fixed lime). The results were expressed in % of the total CaO absorbed.

In this study, the 28 d filtrate was subsequently vacuum dried for DTA/TG/DTG and SEM/EDX analysis.

The XRD analyses were conducted on a Bruker D8 Advance X-ray powder diffractometer fitted with a 3-kW (CuKα1.2) copper anode and a wolfram cathode X-ray generator. The voltage generator tube typically operated at 40 kV and 30 mA. Readings were taken at 2θ diffraction angles ranging from 5° to 60°.

Differential thermal (DTA) and thermogravimetric analyses (TG) analyses were run in a dynamic nitrogen atmosphere on a TA Instruments analyser (SDT Q600) over a temperature range of 20 °C to 1000 °C, ramping at a rate of 10 °C/min.

Fourier transform infrared (FTIR) spectra were obtained on a Nicolet 6700FT-IR spectrometer over a range of 4000 cm⁻¹–400 cm⁻¹. Specimens were prepared by mixing 1 mg of sample with 300 mg of KBr.

The solids obtained from the saturated lime test were studied for microstructure under a scanning electron microscope to analyse the pozzolanic reaction products. 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.

2.3. Statistical analysis

One- and multi-way analyses of variance (ANOVA) were performed to assess the effect of three factors (temperature, age and replacement ratio) and their interactions on slate waste pozzolanicity. As the significance level defined in the statistical study was α = 0.05, factors with a lower p-value were determined to have a significant effect on the results obtained. IBM SPSS Statistics 2.0 software, version 22, was used for the statistical analyses.

3. Results and discussion

3.1. Characterisation of non-activated slate sludge

The chemical composition of the slate sludge is given in Table 1 and its mineralogical composition in Fig. 1. The predominant oxides, SiO₂ and Al₂O₃ (~78%) were present mineralogically in the form of quartz (SiO₂) and phyllosilicates such as muscovite (KAl₂(-AlSi₃O₁₀)(OH)₂). Fe₂O₃ and MgO were found in the chlorite group of phyllosilicates such as chamosite ((Fe₅Al)(AlSi₃)(OH)₈) and clinochlore ((AlSi₃)O₁₀(OH)₈). TiO₂ adopted the form of rutile and K₂O of muscovite and potassium feldspars.

The XRF findings showed that the slate analysed met the chemical requirements (SiO₂ + Al₂O₃ + Fe₂O₃ ≥ 70%; SO₃ ≤ 4%, LoI ≤ 10%) for artificial pozzolans specified in U.S. standard ASTM C 618 [19]. The data were also coincident with the range of values calculated for different types of slate (waste or otherwise) reported by other authors [16,20–25], with significant differences only in connection with the CaO content, as mirrored in the standard deviation (see Fig. 2).

The mineralogical composition found for the slate sludge was also consistent with published data [16,21–23,25–29], according to which slates essentially comprise: i) quartz; ii) micas, primarily muscovite and on occasion biotite; iii) chlorites, at times identified as clinochlore and chamosite; iv) (usually potassium) feldspars and in some cases plagioclase group minerals such as albite; v) clays, primarily illite; vi) titanium oxide minerals such as rutile and anatase. The presence of minerals such as tourmaline [16], calcite or dolomite has also been reported [23], albeit sporadically.

The FTIR spectrum for slate sludge is reproduced in Fig. 3. O–H bond stretching vibrations in the phyllosilicates in the 3700 cm⁻¹–3300 cm⁻¹ range were visible on the spectrum in the bands at 3627 cm⁻¹, 3431 cm⁻¹ and a shoulder at 3540 cm⁻¹. According to several authors [30,31], the first band was generated by the OH stretching vibrations in muscovite, the second by chlorite group minerals and the shoulder by both. Although interpreting the bands for the Si–O bonds is not straightforward due to the considerable variation in the number of Si replaced by Al in

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