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Reuse of waste sandstone sludge via alkali activation in matrices of fly ash and metakaolin

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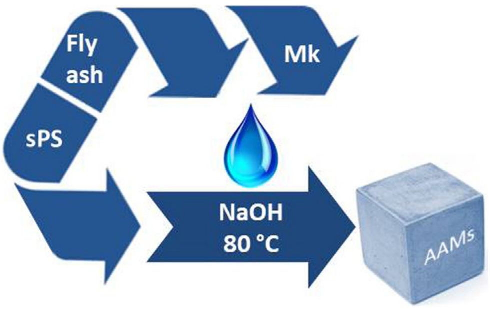
HIGHLIGHTS

- Sludge from cutting of Pietra Serena can be turned into secondary raw material via alkaline activation.
- Waste stone sludge can be used in blends to design new cements.
- Binary mixtures of waste sludge with class F fly ashes produce materials with high mechanical strength.
- Pietra Serena-based alkaline cement resembles the original stone and can be used for restoration purposes.

GRAPHICAL ABSTRACT



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ABSTRACT

This work aims at investigating the possibility of reusing sludge from sandstone sawing in alkaline cements. In particular, the behaviour towards alkali activation process of Pietra Serena sludge (sPS), either alone or in binary mixtures with class F fly ashes and metakaolin, was evaluated. The binders were synthesised with 8 M and 12 M NaOH solutions and cured at 85 °C for 5 or 20 h. Mechanical strength was determined after one day and the reaction products were characterized by XPRD, FTIR and SEM/EDX. Also colorimetry tests were performed. The alkali activation of sPS gives a material with limited amount of amorphous gel, in which unreacted particles can be still recognized, and showing a compressive strength of 3.6(2) MPa. The use of fly ashes and metakaolin in different proportions enhances mechanical strength up to 36(2) MPa. In these blends, the sludge acts basically like a filler. However, calcium carbonates present on the sludge partially dissolve and react in the alkaline mixture favouring the formation of some local high-calcium, high Si/Al ratio (C-A-S-H-type gel) areas co-existing with N-A-S-H-type gel.

1. Introduction

Pietra Serena is a bluish-gray sandstone mainly quarried in the district of Firenzuola (Appenine, North East of Florence, Italy), which belongs to the Marnoso-Arenacea formation [1–3]. The proximity of the quarries to Tuscan cities and towns have made Pietra Serena one of the most mined and used stones of the Italian architecture from Renaissance until nowadays [4]. A problem related to its cultivation, and generally common to all stone processing, is the production of waste materials, such as the sludge or slurry obtained by the cutting of stone blocks. While the coarser fractions of quarrying wastes can be reused in construction industries [5,6], sludge has low commercial value and needs precise requirements for its suitable disposal. Furthermore, appropriate

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disposal sites must be found. Reuse, rather than disposal, would be the ideal solution. Within this purpose, one possibility might be the use of these materials for designing cements and mortars for seals, replacements and replicas.

Suitability of alkaline activation process applied to waste stone sludge is here addressed aimed at evaluating the possibility of designing materials for replacements and replicas, with features as similar as possible to Pietra Serena stone in texture and colour, compatible with the original stone, and showing good workability, low shrinkage, high durability and resistance to environmental pollutants.

Many studies on alkali activated materials (AAMs) as alternatives to traditional construction materials, such as mortars or Ordinary Portland Cement (OPC), have been performed with a view towards reducing the CO_2 footprint [7,8] and improving their durability, especially in acidic and sulphate environments, as well as in other aggressive media, such as seawater [9]. Furthermore, growing interest for the themes of sustainability and reuse of waste materials has been observed. In fact, wastes derived by various human activities, until now under-utilized or simply dismissed, start to be valorised by the alkaline activation [10,11].

The synthesis of AAMs require the use of two main compounds: an alkaline activator, generally in aqueous solution, and a precursor sufficiently rich in reactive silica and alumina, mainly available as amorphous phase [12]. Among the calcined clays, metakaolin represents one of the most studied precursors, due to its high reactivity and the good properties in terms of resistance and durability of the final products [13–17]. Among the industrial by-products, largely used are the blast furnace slags from iron-making processes, and the fly ashes (FA) from coal combustion power plant. In literature, many studies can be found on their characterization and on the performances of pastes, mortars and concrete [18–22]. Slags and/or fly ashes can be further combined with secondary raw materials to maximise the conversion of wastes into novel resources [23–25].

Studies concerning the identification of other potential secondary raw precursors in the synthesis of AAMs have been recently collected in thorough reviews [26,27]. Works on the use of waste stone sludge and reservoir sludge as raw materials are reported [28,29]. Few researches have instead explored sandstone rocks as precursors in the alkaline activation process, achieving encouraging results by transforming the product of soil erosions into resource to produce cementitious materials binders [30,31].

In this paper, the opportunity to reuse the waste sludge derived from the production of Pietra Serena sandstone in the synthesis of AAMs has been tested for the first time. A synergic use with a fly ash (FA) class F and a high-quality metakaolin is also proposed with the aim to produce novel construction materials.

2. Materials and methods

2.1. Selection and characterization of the starting materials

2.1.1. FA and Sl-K kaolin

The FA from a thermo-electric power plant located in Andorra (Teruel-Spain) and classified as Class F in the ASTM C 618 normative on “Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete” were used. Powders were used after milling in a ball miller for 1 h at 32 rpm in order to increase their reactivity [32–35].

The kaolin, labelled Sl-K, was provided by Sibelco Italia S.p.A. and derives from the Seilitz kaolin deposits (Germany). More information about its characterization and uses is reported in prior researches [17,36]. Sl-K was submitted to thermal treatment at 800 °C for 2 h to obtain the reactive metakaolin (hereafter labelled Sl-MK).

2.1.2. Pietra Serena sludge

Sludge deriving from cultivation of Pietra Serena (hereafter labelled sPS) were provided by Pietra Serena Group s.r.l. of Firenzuola (Italy) and used after drying at 100 °C for 24 h in oven. Pietra Serena sandstone comes from a quarry in the Firenzuola district and can be classified as a feldspathic litharenite. The petrographic description, carried out by Pietra Serena Group s.r.l. company on the basis of UNI-EN 12407:2007 “Natural Stone Test Methods – Petrographic Examination” indicated a dominant silicoclastic component, constituted by quartz, feldspars (K-feldspar and plagioclase), phyllosilicates (biotite, chlorite and muscovite), accessory minerals and a carbonatic component (clasts and cement).

The chemical compositions of sPS and of the other starting materials were determined by X-ray fluorescence (XRF) using a PHILIPS PW1004 X-ray spectrometer and are reported in Table 1. Loss on ignition (L.o.I.), determined by mass loss up to 1000 °C, is also reported in table.

The particle size distribution of the starting materials was analysed by laser granulometry using a laser diffractometer SYMPATEC with a measuring range of 0.05–875 μm and is shown in Fig. 1. A unimodal distribution is observed for all materials with the particle size distribution ranging between 0.3 μm and 90 μm for sPS, from 0.3 μm to 45 μm for Sl-MK and between 0.25 μm and 65 μm for FA.

2.2. Sample preparation and characterization

Raw materials (sPS, FA and Sl-MK) and binary binders obtained by mixing sPS with FA and Sl-MK in different weight ratios were alkali activated with sodium hydroxide solutions. An 8 M NaOH solution was used for sPS_100 and FA-based blends and a higher alkalinity (12 M) for MK-based blends. Details of all samples prepared are reported in Table 2. Pellets of sodium hydroxide, supplied by Sigma-Aldrich Co. (purity of 99 wt%), were used to prepare the solutions. The pastes were mixed for 3 min by using a mechanical mixer before being poured in 1 × 1 × 6 cm^3 prismatic steel moulds and compacted by mechanical vibrations for 60 s to remove the entrained air. For each formulation, the liquid/solid weight ratio was chosen in order to guarantee workability of the slurry and to pour it in the moulds. All samples were cured at 85 °C in sealed vessels to ensure 100% Relative Humidity (R.H.); MK-based blends were cured for 5 h, whereas sPS_100 and FA-based blends for 20 h, according with the literature [18,37,38]. At the end of the curing, specimens were demoulded. At one day, the specimens were tested for bending and compressive strength (six specimens for bending and twelve for compressive strength). Flexural strength was determined via three-point bending failure tests conducted on a Netzsch 401–2 (Selb, Germany) constant

Table 1
Chemical composition (XRF) of Pietra Serena waste stone sludge (sPS), fly ash (FA) and kaolin (Sl-K).

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	Other	L.o.I.[a]
sPS	43.50	8.28	2.44	19.53	4.19	0.18	1.46	1.74	0.42	0.25	18
FA	39.03	27.06	19.50	6.40	1.04	1.76	0.16	1.41	0.96	0.85	1.82
Sl-K	67.00	31.50	0.32	0.12	0.23	/	/	0.35	0.24	/	10

[a] L.o.I.: weight loss after calcination at 1000 C for one hour.