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Recycling the product of thermal transformation of cement-asbestos for the preparation of calcium sulfoaluminate clinker

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HIGHLIGHTS

- An hazardous waste was successfully recycled as a secondary raw material.
- Innovative, novel binding materials, designed to reduce CO_2 emissions, were created.
- Phase compositions close to those of commercial analogues were reproduced.
- Effect of annealing temperature on clinker phase composition was investigated.
- Reduction of need for natural resources in cement manufacturing was demonstrated.

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ABSTRACT

According to recent resolutions of the European Parliament (2012/2065(INI)), the need for environmentally friendly alternative solutions to landfill disposal of hazardous wastes, such as asbestos-containing materials, prompts their recycling as secondary raw materials (*end of waste* concept). In this respect, for the first time, we report the recycling of the high temperature product of cement-asbestos, in the formulation of calcium sulfoaluminate cement clinkers (novel cementitious binders designed to reduce CO_2 emissions), as a continuation of a previous work on their systematic characterization. Up to 29 wt% of the secondary raw material was successfully introduced into the raw mix. Different clinker samples were obtained at 1250 °C and 1300 °C, reproducing the phase composition of industrial analogues. As an alternative source of Ca and Si, this secondary raw material allows for a reduction of the CO_2 emissions in cement production, mitigating the ecological impact of cement manufacturing, and reducing the need for natural resources.

1. Introduction

Prompted by the recent European Directives and reinforced by the latest resolution of the European Parliament (2012/2065(INI)), the need for a safe disposal and/or inertization of asbestos containing materials (ACMs) has become a priority of the environmental protection agenda. In this scenario, several industrial inertization processes involving thermal treatment, have been proposed (see for example Refs. [1–5]). Investigations on the transformation of cement-asbestos (CA) minerals during prolonged annealing in the temperature range 1200–1300 °C of sealed packages of CA slates, led to the development of an innovative process [5–8]. During thermal treatment, CA slates undergo a series of solid state reactions leading to total structural changes of the matrix and to the complete crystal chemical transformation of asbestos minerals as well [9]. The newly formed phases are mainly calcium–magnesium silicates, calcium silicates and aluminates in variable proportions, depending on the chemical composition of the corresponding pristine raw material [10].

A study conducted on 27 samples removed from the environment in different localities in Italy, allowed for the identification of three classes, possessing distinct mineralogical and chemical characteristics, for the product of thermal transformation [10]. To this end, the CaO/SiO_2 (C/S) molar ratio has been recognized as the major discriminating factor.

The economic sustainability of any process of this kind, bears also on the perspective of possible recycling opportunities for the end product. Encouraging results have been obtained testing this secondary raw material in specific applications, ranging from clay bricks, glasses, glass–ceramics, ceramic frits, ceramic pigments and plastic materials [5]. As far as cement materials are concerned, the most promising class of thermally-treated CA seems to be that with $C/S > 1.4$, where a number of phases possessing good hydraulic properties, such as dicalcium silicate (belite, Ca_2SiO_4), tricalcium silicate (Ca_3SiO_5), calcium aluminoferrite ($Ca_2(Al,Fe)_2O_5$), mayenite ($Ca_{12}Al_{14}O_{33}$), ye'elimite ($Ca_4Al_6O_{12}(SO_4)$), are formed.

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They sum to about 70 wt%, and the resulting product resembles a belite-rich clinker, making it a potential secondary raw material for the building industry. In this regard, it has been tested successfully in place of cement in concrete [11].

The use of CA as a raw material for clinker production has been already proposed [12–16], however, its industrial application has been limited by the high investments required in order to eliminate risks to health during manufacturing.

Airborne exposure to workers in cement production plants can be avoided by employing in the raw mix the CA inertization product (i.e. a non-hazardous material) instead of asbestos containing material. The inertization product could be obtained in a different plant, specifically dedicated to the thermal treatment of ACM. In the process described in Gualtieri et al. [5], grinding, the most critical step when considering CA slates, is accomplished safely after thermal treatment. A further advantage of operating in a specific inertization production plant, is that chemical and mineralogical characteristics of the secondary raw material could be readily optimized for each recycling solution adopted for the end product [3].

Used and standardized in China for over 30 years [17–20], calcium sulfoaluminate (CSA) cements are receiving increasing attention in Europe as pressure for reducing CO_2 emissions during cement manufacturing is strengthened. As a consequence, the principal actors on the market have developed specific products [21,22]. Although sulfoaluminate clinker compositions may vary, they all contain ye'elimite. Its content usually ranges between 30 and 70 wt% [23], while other minor phases, such as belite, calcium aluminoferrite, anhydrite ($CaSO_4$), gehlenite ($Ca_2Al(AlSi)O_7$), mayenite or lime (CaO) may be present.

CSA clinkers are usually produced from limestone, bauxite (mainly constituted by aluminium hydroxides), and calcium sulphate (anhydrite or gypsum) [17–20,24]. Clinker manufacturing is accomplished similarly as for ordinary Portland cement (OPC), although the maximum temperatures attained may vary from 1250 to 1350 °C, at least 100 °C below those required for OPC. In terms of CO_2 emissions, this advantage adds to a reduction in the amount of limestone employed in the raw feed, and by lower grinding energy requirements [17,25,26].

Many efforts have been devoted to the introduction of various industrial by-products or waste materials in belite-sulfoaluminate cements (containing around 20–30 wt% of ye'elimite) [27,28]; examples are known for CSA clinkers as well [29]. As a continuation of our previous investigations on thermally treated CA in view of their safe recycling [10], this work describes for the first time the formulation of CSA clinker compositions (i.e. with ye'elimite contents > 50 wt%) obtained using the inertization product of CA.

Table 1
Chemical and mineralogical analyses for the thermal inertization product of CA employed in the raw mixes. Chemical analyses obtained with XRF are expressed as oxide wt%. Phase fractions are expressed as wt% with standard deviations in parentheses. CAT1 and CAT2 data correspond to sample 23 and 18, respectively, in Viani et al. [10]. Abbreviations used: C_4AF, calcium aluminoferrite; $C_5S_2\bar{S}$, silicosulphate ($Ca_5Si_2O_9(SO_4)$); L.O.I., loss on ignition.

	CAT1	CAT2
SiO_2	33.1	32.6
Al_2O_3	4.9	4.04
CaO	49.2	51.8
Na_2O	0.00	0.16
K_2O	0.01	0.54
MgO	7.67	3.66
Fe_2O_3	2.12	1.89
TiO_2	0.2	0.2
P_2O_5	0.07	0.16
SO_3	2.6	4.76
L.O.I	0	0
β Belite	62.0 (6)	69.7 (6)
C_4AF	5.5 (1)	8.2 (1)
Akermanite	2.8 (2)	–
Merwinite	1.1 (1)	1.0 (1)
Mayenite	7.3 (1)	–
Lime	1.5 (1)	5.0 (1)
Periclase	5.0 (1)	2.9 (1)
Anhydrite	1.3 (1)	3.0 (1)
$C_5S_2\bar{S}$	–	0.8 (1)
Ye'elimite	–	4.0 (1)
Amorphous	13 (1)	5.4 (7)

2. Experimental

2.1. Materials and sample preparation

In this work, two different samples of CA inertization product, named CAT1 and CAT2, have been employed. They have been fully characterized elsewhere [10,30] and their chemical and mineralogical analyses are reported in Table 1. Other raw materials were reagent grade calcite ($CaCO_3$), gypsum ($CaSO_4{\cdot}2H_2O$) and the aluminium hydroxide gibbsite ($Al(OH)_3$). Formulations adopted, named Mix1 and Mix2, are reported in Table 2. They have been defined in relationship with available chemical data from commercial CSA cements as reported by Álvarez-Pinazo et al. [22]. Points corresponding to each clinker formulation have been reported as molar fractions in the system $CaO–SiO_2–Al_2O_3–SO_3$ (see Fig. 1).

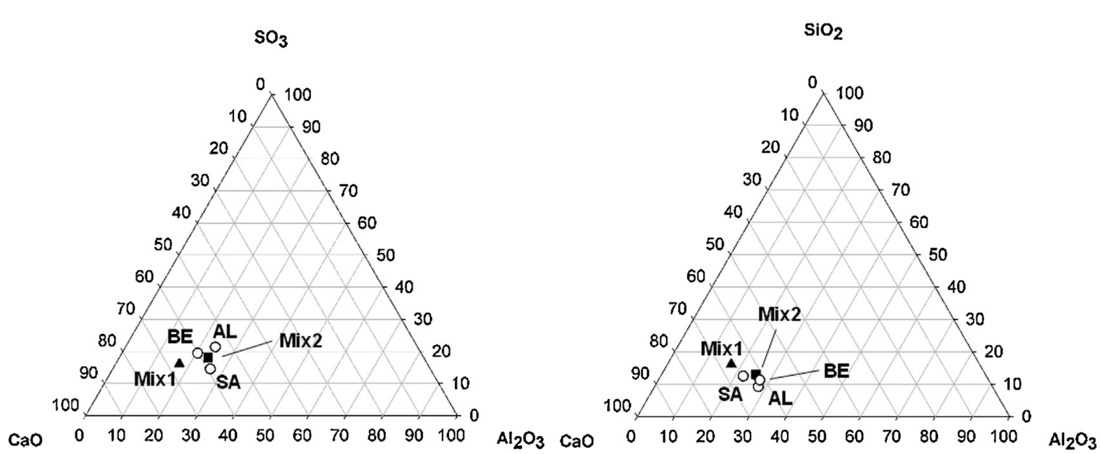

Fig. 1. Points corresponding to raw mixes for CSA clinkers studied (Mix1 and Mix2), and compositions corresponding to commercial CSA cements as reported by Álvarez-Pinazo [22], plotted as mol% of oxides, in the $CaO–SiO_2–Al_2O_3$ and $CaO–SiO_2–SO_3$ ternary diagrams. Legend: AL = ALIPRE® by Italcementi group; BE = BELITH_CS10 by Belith; SA = S.A. cement by Buzzi Unicem.