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Use of metakaolin to stabilize sewage sludge ash and municipal solid waste incineration fly ash in cement-based materials

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HIGHLIGHTS

- Metakaolin was used to help immobilizing industrial wastes in cement-based materials.
- A dilution process (i.e. reduction of waste content) was tested and discussed.
- The solid residues had no significant effects on functional of cement-metakaolin mortars.
- Metakaolin was beneficial in decreasing the leaching of heavy metals.

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ABSTRACT

The landfilling of municipal incineration residues is an expensive option for municipalities. This work evaluates an alternative way to render waste inert in cement-based materials by combining the reduction of waste content with the immobilization properties of metakaolin (MK). The functional and environmental properties of ternary and quaternary binders using cement, metakaolin, and two industrial by-products from combustion processes (MSWIFA – Municipal Solid Waste Incineration Fly Ash and SSA – Sewage Sludge Ash) were evaluated. The binders were composed of 75% cement, 22.5% metakaolin and 2.5% residue. Results on the impact of residues on the functional and environmental behavior of mortars showed that the mechanical, dimensional and leaching properties were not affected by the residues. In particular, the use of metakaolin led to a significant decrease in soluble fractions and heavy metals released from the binder matrix. The results are discussed in terms of classification of the leaching behavior, efficiency and role of metakaolin in the immobilization of heavy metals in of MSWIFA and SSA, and the pertinence of the dilution process.

1. Introduction

The industrial by-products resulting from the incineration of municipal solid waste and sewage sludge cause several problems for their producers:

- A problem of storage on site.
- A potential risk of pollution since, when they are not stabilized, many heavy metals (e.g. Pb, Cd, Zn and Cu) in incineration residues such as MSWIFA can be easily leached into the environment under normal conditions [1].
- A problem of valorization when it is possible and authorized.
- A significant financial cost related to evacuation and landfilling when no valorization is possible or authorized.

Since landfilling is not a sustainable solution for these residues, many efforts are being made to reuse them in applications such as construction materials. The use of municipal solid waste fly ash (MSWIFA) and sewage sludge ash (SSA) in cement-based materials is reported in many studies (see the numerous references in [2–4]). Some of them show that these wastes have pozzolanic properties that contribute to the development of the compressive strength of pastes, mortars and concretes (e.g. [5–9] for MSWIFA, and [4,10,11] for SSA). A few authors have also used MSWIFA or SSA for the production of different kinds of binders such as Portland cement [12–15], sulfoaluminate cement [16] or alinite cement [17].

However, these wastes usually contain high proportions of heavy metals and their leaching potentially involves environmental problems, especially when large quantities of wastes are incorporated in cement matrices. For instance, Cyr et al. [4] showed that the use of 25 and 50% SSA in replacement of cement could lead to an increase of 50 and 100%, respectively, in the total heavy metals leached (11 elements tested in their study: Ti, V, Cr, Ni, Cu, Zn, As,

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Table 1
Chemical compositions of cement, metakaolin, sewage sludge ash (SSA) and municipal solid waste incineration fly ash (MSWI-FA).

(%)	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	TiO_2	Na_2O	K_2O	SO_3	P_2O_5	LOI
Cement	64.9	21.2	3.9	2.4	2.4	0.2	0.2	0.8	3.2	n.d.	1.8
Metakaolin	0.3	58.2	36.6	1.8	tr	1.6	0.02	0.05	0.04	n.d.	1.1
SSA	20.6	34.2	12.6	4.7	1.9	0.9	1.0	1.7	2.8	14.8	5.5
MSWIFA	30.6[a]	22.5	11.5	1.3	2.7	1.8	2.5	0.8	12.0	1.7	12.0

[a] Including 3.6% of free CaO.

Cd, Sn, Sb, Pb). Similar results were found with MSWIFA by Aubert et al. [7]: the replacement of 12 and 50% of cement by a treated fly ash induced an increase of toxic element (Cr, Ni, Zn, Cu, Pb, Cd, Sn, As) leaching by 50 and 158%, respectively.

Among the alternatives for stabilizing these wastes, geopolymers seem to be quite efficient [18–22]. In the case of cement-based materials, the use of blended cement has been reported to enhance the immobilization of certain heavy metals [23,24]. A few studies regarding the efficiency of metakaolin (MK) in the stabilization of hazardous wastes and toxic metals can be found in the literature [24–29]. For instance, Pera and Bonnin [27] showed that the use of 20% of MK led to a reduction in the heavy metals leached into the mixing water from pastes and mortars containing solutions of chromium, lead and cadmium. In another study, Pera et al. [28] found that chlorides and sulfates in MSWIFA (used as a partial replacement for the sand in mortar) were retained to a greater extent when MK was added to the mixture.

Another complementary possibility to help stabilize these wastes is to decrease the amount of wastes in the concrete, so as to limit their harmful impact on both the functional and the environmental properties.

The aim of this work is to combine two approaches, namely the immobilization properties of MK and the reduction of waste content, in order to stabilize SSA and MSWIFA in cement-based materials intended for applications where the risk for human health is minimized, which could be the case for road work concretes. This working hypothesis requires a feasibility study to evaluate the pertinence of this solution. The study, carried out in the laboratory, gives an evaluation of the impact of ternary and quaternary binders containing cement, metakaolin, municipal solid waste incineration fly ash and/or sewage sludge ash on the functional and environmental properties of concrete intended for non-structural applications. Considering the pozzolanic properties of metakaolin and the possibility of fixing heavy metals in the pozzolanic hydrates, the use of metakaolin should help to improve the properties of concrete containing residues.

2. Experimental procedures

2.1. Materials

The chemical compositions and trace analyses of cement, metakaolin, sewage sludge ash (SSA) and municipal solid waste incineration fly ash (MSWI-FA) are given in Tables 1 and 2. The cement used was a Portland cement, CEM I 52.5R according to EN 197-1, with a specific gravity of 3.15 g/cm^3 and a Blaine specific surface of 440 m^2/kg. The sand was a quartz sand with particle sizes between 0 and 2 mm in accordance with standard EN 196-1.

The metakaolin was obtained in the laboratory from the incineration of kaolinite at 700 °C for 5 h on a fixed bed. It was composed of an amorphous phase (Fig. 1) containing mainly silica and alumina due to the dehydroxylation of kaolinite (approx. 51%). The crystallized phases were quartz (SiO_2) and anatase (TiO_2). The density of the metakaolin was 2.55 g/cm^3, its mean equivalent diameter 58 μm and its specific surface area (BET) 10 m^2/g.

The sewage sludge ash was composed of quartz, calcium phosphate (whitlockite – $Ca_3(PO_4)_2$, which can contain Mg and Fe), calcium sulfate (anhydrite – $CaSO_4$), traces of plagioclase feldspars and a small amount of amorphous phase (Fig. 1). The density of SSA was 2.43 g/cm^3 and the particle sizes ranged between 0.7 and 90 μm, with a mean diameter of 19 μm. Trace element analysis revealed high amounts of copper and zinc but the overall heavy metal content was mainly among the lowest found in the literature for SSA (as reported by Cyr et al. [4]). The leaching results of raw SSA are given in Table 3. It is seen that all heavy metals except Cd were leached at less than 1% relative to the total amount of each element. Only Cd was leached at almost 10%.

The municipal solid waste incineration fly ash had a density of 2.51 g/cm^3 and a mean diameter of 195 μm. It contained significant amounts of calcium (including 3.6% of free lime), silica and alumina, and it presented a significant loss on ignition. X-ray Diffraction (XRD) measurement (Fig. 1) showed the presence of a small amount of amorphous phase and of many crystallized minerals, the main ones being sodium and potassium chlorides (halite – NaCl and sylvite – KCl), calcium sulfates (anhydrite – $CaSO_4$, bassanite – $CaSO_4{\cdot}½H_2O$), quartz (SiO_2) and calcite ($CaCO_3$). The other minerals found in smaller quantities included plagioclase feldspars, gehlenite ($Ca_2Al_2SiO_7$), hematite (Fe_2O_3), perovskite ($CaTiO_3$), titanite ($CaTiSiO_5$) and free lime (CaO). A small amount of metallic aluminum might also be present, as already reported by Aubert et al. [30] in a study on another MSWIFA. As for SSA, trace element analysis of MSWIFA showed that this sample of ash was in the lower range of heavy metal contents when compared to other data from the literature [31,32]. The leaching results of raw MSWIFA are given in Table 3. Higher proportions of heavy metals were leached compared to SSA, the highest values being for As and Pb, which reached around 50% of element released.

2.2. Sample preparation and test methods

The effects of SSA and MSWIFA on the hydration of cement and metakaolin were followed by X-ray Diffraction at 3, 7, 28 and 90 days. These reactivity tests were carried out on pastes made of cement, MK and waste in the following proportions: 50%–50%–0% for the reference, and 50%–40%–10% for the waste-containing pastes.

Table 2
Trace analysis of cement, metakaolin, sewage sludge ash (SSA) and municipal solid waste incineration fly ash (MSWI-FA).

(mg/kg)	As	Cd	Cr	Cu	Ni	Pb	Sn	Sb	Zn
Cement	0.5	0.2	80	50	65	2	2	0.6	90
Metakaolin	2	0.2	180	35	65	15	23	2	40
SSA	1	0.3	167	1195	80	21	53	4	2300
MSWIFA	1	0.3	365	350	48	50	58	18	6525