

Technological and environmental behavior of sewage sludge ash (SSA) in cement-based materials

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Abstract

Sewage sludge ash (SSA) is a waste material obtained from the incineration of wastewater sludge. The physical, chemical and mineralogical characteristics of SSA, and the evaluation of its use in cement-based materials, are presented in this paper. Results show that SSA is composed of irregular grains having a high specific surface area and thus leading to a significantly high water demand. A fraction of the ash is rapidly soluble (sulfates, aluminum and silica) and can create new-formed products in presence of lime. SSA induces short delays of cement hydration, probably due to both minor elements of the ash and dilution effect. Compressive strengths of mortars containing 25% and 50% of SSA are always lower than those of reference mortars but it is shown that SSA has a long-term positive effect which might be related to a slight pozzolanic activity. The amount of elements leached from SSA mortars is slightly higher than from the reference mortar without residue but it remains of the same order of magnitude. An extensive literature review was performed in order to compare the residue used in this study with others included in the same category. This analysis highlighted the principal characteristics that must be taken into account to use SSA correctly in cement-based materials. © 2007 Elsevier Ltd. All rights reserved.

Keywords: Sewage sludge ash; Characterization; Mineral admixture; Leaching; Waste

1. Introduction

The total production of sewage sludge for the United States of America (USA) and countries of the European Union (EU) approaches 17 Mt of dry solids per year (7 Mt in USA + 10 Mt in EU) [1]. The management of these sewage sludges between incineration, agricultural uses and landfill is reported in Fig. 1 [1–4]. Considering that between 300 and 400 kg of ashes are produced per ton of dried sludge and that a fraction of these sludges are incinerated (around 22% in USA and a mean value of 15% for the EU countries), it is obvious that about 1.2 Mt must be managed each year in USA and EU. This quantity is much smaller than that of other by-products such as coal fly ash (70 Mt and 44 Mt produced in USA [5] and EU [6] in 2003, respectively), which may explain the relatively limited research done on the recycling of SSA. Another reason for the lack of publications may be related to the fact that management of

sewage sludge by incineration processes is recent, as it was previously reused in agriculture.

Some research work has already been done on the use of this waste in construction materials, e.g. as a filler in asphalt concrete applications [7,8], bricks and tiles [9–22], raw material in a cement kiln [23,24], or for the manufacture of aggregates and lightweight aggregates [9,25–33]. The use of SSA in cement-based materials as cement or sand replacements is also reported in a few recent studies [34–57]. In a general way, these studies show that SSA reduces the workability of fresh mortars and tends to increase the setting time of cements [36,38,41–46]. Most studies also report a decrease of compressive strength of mortars and concrete when SSA is used as a cement or sand replacement: about 30% of decrease in the worst case found in the literature for 10% SSA [52]. Only a few authors have shown a strength similar to or greater than the reference with up to 5 [38], 10 [9] or even 15% [56] of SSA in mortars. Since SSA is a waste material, attention must be paid to its environmental impact when it is reused in other applications. However, little information is available about the environmental impact of SSA in cement-based materials [56] and no comparison has been

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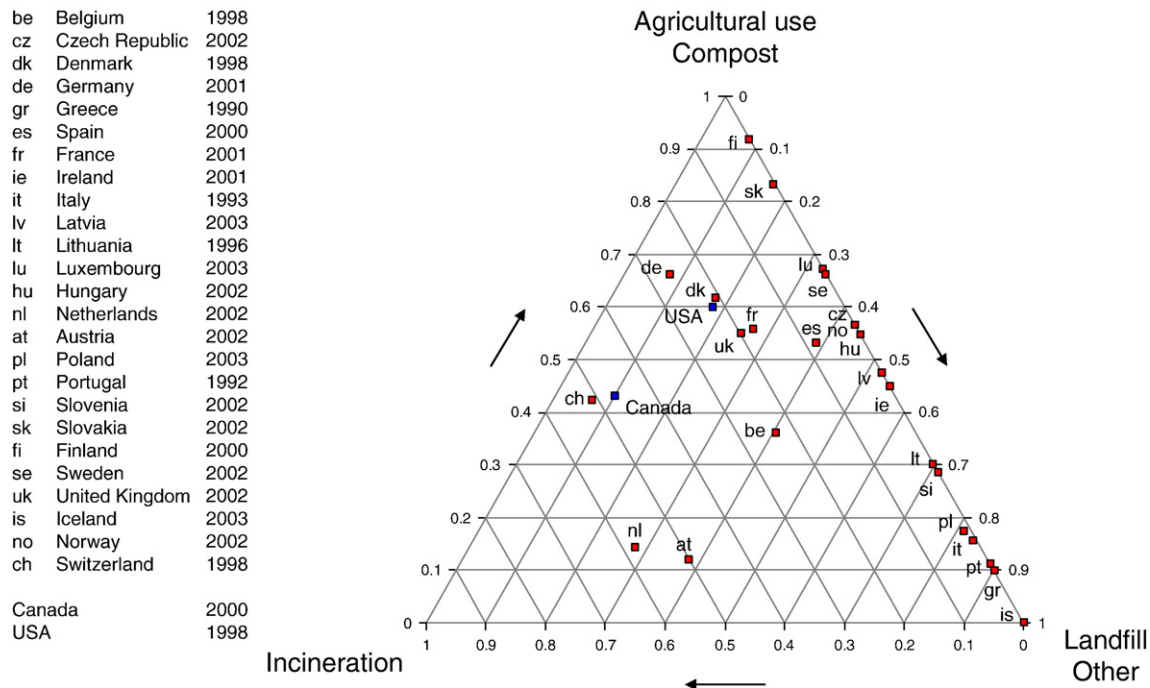


Fig. 1. Disposal of sewage sludge between incineration, agricultural use and landfill for European countries, Canada and United States. The years represent the last available data for each country [1–4].

made with reference concrete, so it is not possible to evaluate the pollutant potential of SSA.

A literature analysis shows that the effects of SSA on mortars and concrete properties are more or less noticeable, depending on the characteristics of the specific SSA used in each study. The inherent variability of this kind of residue remains one of the most important reasons for avoiding a systematic general-

ization of the results. So the aim of this work is to provide supplementary knowledge about the characteristics of SSA and its effect on the properties of cement-based materials. The results are then compared to those found in the literature in order to compare the residue of this study with others included in the same category. Considering the origin of SSA, its environmental impact is also evaluated. The analysis of the results should

Table 1

Experimental methods for the physical and chemical characterization of SSA, and for the study of the activity of SSA in cement-based materials

Property	Test method/standards
Density	Hydrostatic weighing
Particle size distribution	Laser granulometry
Specific surface area	Blaine (NF EN 196-6), BET (nitrogen)
Morphology	Scanning Electron Microscopy (SEM), coupled with elemental analysis (EDX)
Chemical analysis	Atomic adsorption with flame atomisation (major oxides)
	Inductively coupled plasma-mass spectrometry ICP-MS (minor elements)
Selective dissolution	Successive HCl and KOH attack
	–40 ml of HCl (37%)
	–100 ml of KOH (250 g/l)
	Soluble fraction (acid and base) NF EN 196-2
Mineralogy	X-ray diffraction (XRD); Co K α radiation ($\lambda = 1.789 \text{ \AA}$)
	2 θ step interval of 0.02° (5°–70°) and acquisition time of 10 s
Reactivity	
–with water (hydraulic reaction)	XRD of mixtures ash–water
–with lime (pozzolanic reaction)	XRD of mixtures Ca(OH) ₂ –ash–water (4:1:4 in mass)
Effect on cement hydration	
–mineralogical study	XRD of mixtures cement–ash–water
–setting time	Setting time using Vicat apparatus (NF EN 196-3)
–heat evolved	Semi-adiabatic (Langavant) calorimeter (NF P 15-436)
Effect on workability of mortars	Flowing under vibration using LCL apparatus (NF EN 12350-1)
Effect on mechanical properties of mortars	Compressive strength of 4 × 4 × 16 cm prisms (NF EN 196-1)
	Hydration times: 1, 7, 28, 84 days; Each value is the average of 6 tests
Effect on environmental behavior of mortars	Leaching tests on monolithic mortars (NF P X31-211) and on crushed mortars (EN 12457-2)

highlight the main characteristics that must be taken into account in order to use SSA correctly in cement-based materials. This paper includes a physical, chemical and mineralogical characterization of SSA, a technological study aiming to evaluate the residue's effect on the properties of mortars, and an environmental study, by means of leaching tests, which concerns the quantitative impact of the residue on the surrounding environment.

2. Materials and methods

The sewage sludge ash from this study came from a fluidized bed combustor operating at 850 °C. The experimental methods used for the physical and chemical characterization of ashes are shown in Table 1. It also gives the experimental program concerning the study of the activity of SSA in cement-based materials. The binder was a standard CEM I 52,5R as specified in European Standard EN 197-1, with a specific surface area (Blaine) of 400 m²/kg. The aggregate was a 0–2 mm quartz sand meeting the requirements of French standard NF EN 196-1.

The mortar mixtures were prepared according to French standard NF EN 196-1. They were composed of three parts of sand and one part of cement (by mass). The water–cement ratio was fixed at 0.50. The cement replacement rates were 25 and 50%. A naphthalene sulfonate based superplasticizer was used in mortars intended for compressive strength and leaching tests, at 0.17% and 0.56% dry matter compared to cement mass for mortars containing 25% and 50% of SSA respectively. The mixtures were cast in 4 × 4 × 16 cm moulds for the first 24 h and then the mortar prisms were sealed in plastic bags in a temperature controlled room at 20 °C.

The water requirement of SSA and mortar workability were determined in accordance with French Standard P 15–437, by measuring the flow time of vibrated mortars. The apparatus is composed of a vibrator fixed on a prismatic box which is separated in two parts by a removable barrier. After the mortar has been introduced on one side of the box, the barrier is removed and the vibrator starts. The flow time is the time for vibrated mortar to spread and reach a marker on the opposite side of the box. A short flow time characterizes a fluid material.

The leaching test for the environmental study (liquid–solid extractions) was carried out at 28 days of age in order to

evaluate the quantity of pollutant released by cement based materials containing SSA. Two tests were performed: NF P X31-211 on monolithic mortars (3 × 3 × 8 cm pieces) and NF EN 12457-2 on raw residue and crushed mortars (fragments finer than 4 mm). The former test aims to assess the release from intact products, while the latter concerns the product after its destruction. All the tests consisted of one leaching cycle of 24 h in stirred de-ionized water. The liquid/solid ratio was set at 10. Measurements on the leachates collected after filtration (0.45 µm) included pH, soluble fractions and minor-element content (Ti, V, Cr, Ni, Cu, Zn, As, Cd, Sb, Ba, Pb) using ICP-MS.

3. Results

3.1. Characteristics of SSA

The major and trace chemical compositions of SSA are given in Table 2. Table 3 gives a quantitative mineralogical composition obtained from X-ray diffraction measurement and selective dissolution (HCl and KOH). Tables 2 and 3 also present the compositions of other SSA found in the literature [17,31,43,49,51–54,56]. SSA is a polyphasic material made of several crystalline minerals (≈60%) and a vitreous phase (≈40%), characterized by a diffusion hump ranging between 25 and 45° 2θ Co (d between 4.14 and 2.34 Å). The chemical composition reported in Table 2 shows that SSA is mainly composed of silicon, calcium, phosphorus and aluminum. The amount of CaO and P₂O₅ is high compared to classical mineral admixtures such as fly ash, silica fume or metakaolin. These elements are combined to form about 26% of whitlockite β-Ca₃(PO₄)₂ (Table 3), a calcium phosphate mineral weakly soluble in a basic environment. SiO₂ and Al₂O₃ represent less than 50% of SSA. These oxides, which compose the reactive part of pozzolanic materials, are significantly lower in SSA than in other classical mineral admixtures. Fractions of silicon and aluminium are present as crystalline quartz (14%), feldspars and micas (9%), the rest being in the amorphous part of the ash. SSA also contains significant amounts of sulfate (2.8%) crystallized in the form of gypsum (SSA was humidified for transportation). The trace element analysis (Table 2) shows the presence of heavy metals such as zinc, chromium and copper.

Table 2
Chemical composition and trace analysis of SSA compared to other SSA found in literature

Oxide		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	P ₂ O ₅	SO ₃	Na ₂ O	K ₂ O	TiO ₂	MgO	MnO	LOI	
SSA (%)		34.2	12.6	4.7	20.6	14.8	2.8	1.0	1.7	0.9	1.9	0.06	5.5	
Other SSA ^a	Mean	36.1	14.2	9.2	14.8	11.6	2.8	0.9	1.3	1.1	2.4	0.3	6.1	
	Min	14.4	4.4	2.1	1.1	0.3	0.01	0.01	0.1	0.3	0.02	0.03	0.2	
	Max	65.0	34.2	30.0	40.1	26.7	12.4	6.8	3.1	1.9	23.4	0.9	41.8	
Elements (mg/kg)		As	Ba	Cd	Co	Cr	Cu	Ni	Pb	Sb	Sn	Sr	V	Zn
SSA		23	1430	14	669	2636	2483	621	720	73	283	623	63	7103
Other SSA ^b	Mean	87	4142	20	39	452	1962	671	600	35	400	539	35	3512
	Min	0.4	90	4	19	16	200	79	93	35	183	539	14	1084
	Max	726	14600	94	78	2100	5420	2000	2055	35	617	539	66	10000

^a [8,13,17,18,23,24,28,32,33,36,38,39,41–46,48–50,53,54,56,59–76].

^b [8,17,18,23,24,28,31,48,56,57,64,69,70,72,74,76].

Table 3
Mineralogical composition of SSA of this study compared to those found in the literature [17,31,43,49,51–54,56]

	This study	Monzo et al. [43]	Roland [54]	Pan et al. [51–53]	Dyer and Dhir [49]	Fontes et al. [56]	Cheeseman et al. [31]	Anderson et al. [17]
Silicon oxide	✓	Q 14%	✓	✓	✓	✓	✓	✓
Calcium oxide		✓	✓	✓	✓	✓	✓	✓
Iron oxide		✓	✓	✓	✓	✓	✓	✓
Calcium sulfate	✓	Ma	✓	✓	✓	✓	✓	✓
Calcium phosphates	✓	A	✓	✓	✓	✓	✓	✓
Feldspar	✓	HAP CPH	✓	✓	✓	✓	✓	✓
Micas	✓	W 26%	✓	✓	✓	✓	✓	✓
Glass	✓	P 6%	✓	✓	✓	✓	✓	✓
Other minerals	✓	3% 40%	✓	✓	✓	✓	✓	✓

A (anhydrite— γ -CaSO₄), C (calcite — CaCO₃), CPH (calcium phosphate hydrate—Ca₃(PO₄)₂·xH₂O), G (gypsum — CaSO₄·2H₂O), H (hematite — Fe₂O₃), HAP (hydroxylapatite — Ca₅(PO₄)₃(OH)), Ma (magnetite — Fe₃O₄), Mo (moganite — SiO₂), Mu (muscovite — KAl₂(Si₃Al)O₁₀(OH,F)₂), O (orthoclase — KAlSi₃O₈), P (plagioclase), Q (quartz — SiO₂), W (whitlockite — β -Ca₃(PO₄)₂ or Ca₇Mg₂P₆O₂₄)

Remarks:

a: no diffusion hump detected on XRD diagram

b: slight diffusion hump detected on their XRD diagram

c: other minerals such as ettringite, silicon carbide (SiC), iron sulfite (FeSO₃), Gehlenite (Ca₂Al₂SiO₇), tridymite (SiO₂), rutile (TiO₂), fredericksonite (Mg₂MnBO₅)

d: minor peaks may correspond to aluminium phosphate (AlPO₄), aluminium oxide chloride hydroxide (Al₄O₅(OH)₄Cl), iron silicite (FeSi₂) and calcium copper fluoride (CaCuF₄).

The comparison of chemical and mineralogical compositions with literature results reveals a high variability between the different types of SSA. Table 2 gives a literature data of the oxide contents (mean, minimum, maximum) taken from between 31 and 80 oxide content values of SSA available in the literature [8,13,17,18,23,24,28,32,33,36,38,39,41–46,48–50,53,54,56,59–76]. Significant differences were found for each of the oxide contents, as attested by the large spaces between the minimum and maximum values for each element. For example the SiO₂ content varied between 14 and 65% of the whole mass of ash. Almost all oxides from the SSA studied here were near the mean values. So from a composition point of view, the SSA of this study might be considered as representative of other SSAs. The trace element analysis reported in Table 2 shows that, compared to other SSA (between 1 and 23 trace content values were available in literature [8,17,18,23,24,28,31,48,56,57,64,69,70,72,74,76], depending on the element), only Co and Cr were present in higher concentrations.

All the papers of the literature giving a mineral composition of SSA (Table 3) indicate the presence of quartz. Some SSA also contain calcium phosphates (whitlockite or hydroxylapatite, probably depending on the composition of the sludge and the temperature and time of incineration), calcium sulfates, iron oxides and feldspars. Other minerals than those found in this study have been identified (calcite, moganite, hematite, magnetite and other minor minerals). A few authors detected the presence of an amorphous phase, ranging between 50 and 74% of the whole ash. These values were higher than the one found here. It is noteworthy that a few XRD measurements showed no evidence of an amorphous phase [51–54]. These results also confirm the high variability of this type of residue.

The physical characteristics of SSA are summarized in Table 4, with other results available in the literature. The particle size distribution ranges between 1 and 100 μ m, with a mean diameter around 26 μ m. The Blaine and BET specific surface areas are 640 and 19 000 m²/kg, respectively. The latter value, which is quite high, can be related to the morphologic irregularities of the grains and their open porosity. An important consequence of this high specific surface area is the significant water demand, which affects the workability of mortars when the same amount of water is used in the mixtures with and without SSA (see results in this paper). Compared to other SSA, the residue studied here had particles finer than the mean values for diameter and specific surface area.

3.2. Effect of SSA on technological properties of mortars

3.2.1. Reactivity of SSA

In order to assess the hydraulic and pozzolanic activity of SSA, two types of mixtures were prepared and analyzed using XRD: SSA with water and SSA with CH and water. For the first mixture (pH of 8.3), no hardening had occurred several weeks after mixing the SSA with water and, except for the dissolution of gypsum, no other phase changes were detected with XRD. So, the conclusion was that SSA did not present any hydraulic activity.

Table 4
Physical properties of SSA compared to other SSA found in literature

		Density	Mean diameter (μm)	Specific surface area	
				Blaine (m^2/kg)	BET (m^2/g)
SSA		2.64	26	640	19 000
SSA in literature	Mean	2.61	44	450	15 100
	Min	2.19	8	160	10 200
	Max	3.00	200	600	23 100
References		[32,38,51,53,54,56]		[16,32,36,38,51,53,54]	[33,51,56]

The pozzolanic reaction was evaluated with XRD by following phase changes with time of a mixture composed of SSA, CH and water, in mass proportions of 4:1:4, respectively. It must be kept in mind that this test is not always representative of what really happens in hydrated cement pastes, since some hydrated minerals could appear only in CH paste, as is the case for metakaolin [77]. However, it gives a first evaluation of the potential of reactivity of the powder and it simplifies the mineralogical study of the mixture, since the hydrates of cement do not disturb the analysis of the reactivity proper to the ash.

The XRD evolution of phase changes at 1, 21 and 150 days is given in Fig. 2, in comparison with the dry mixture before the addition of water. It can be seen that SSA reacted in the basic environment and some of the reactions happened very quickly, creating a few new-formed phases. Gypsum was totally dissolved at 1 day and the sulfates combined with Ca, Al and water to form ettringite. This early formation of ettringite should

not be harmful to mortar since it appears in a young and plastic material. XRD analysis also shows a high consumption of CH, since it disappeared almost entirely within the first 3 weeks. Calcium reacted with aluminum and silica to form hydrated aluminates (essentially C_4AH_{13} , which was sometimes carbonated — $\text{C}_4\text{A}\bar{\text{C}}_{0.5}\text{H}_{11.5}$) and aluminosilicates (essentially hydrated gehlenite — C_2ASH_8). The formation of these hydrates required a plentiful source of aluminum (and silica), which probably came from the partial decomposition of the vitreous phase. However, it was almost impossible to detect any evolution of the diffuse hump which characterizes C–S–H. Nevertheless, these reactions had mechanical consequences since they led to a modest but significant strengthening of the paste.

Most conclusions reported in the literature about the reactivity of SSA were deduced from the results of compressive strength tests, by measuring the strength activity index [32,41,44,45,51–53]. Monzo et al. [43] and Dyer et al. [49]

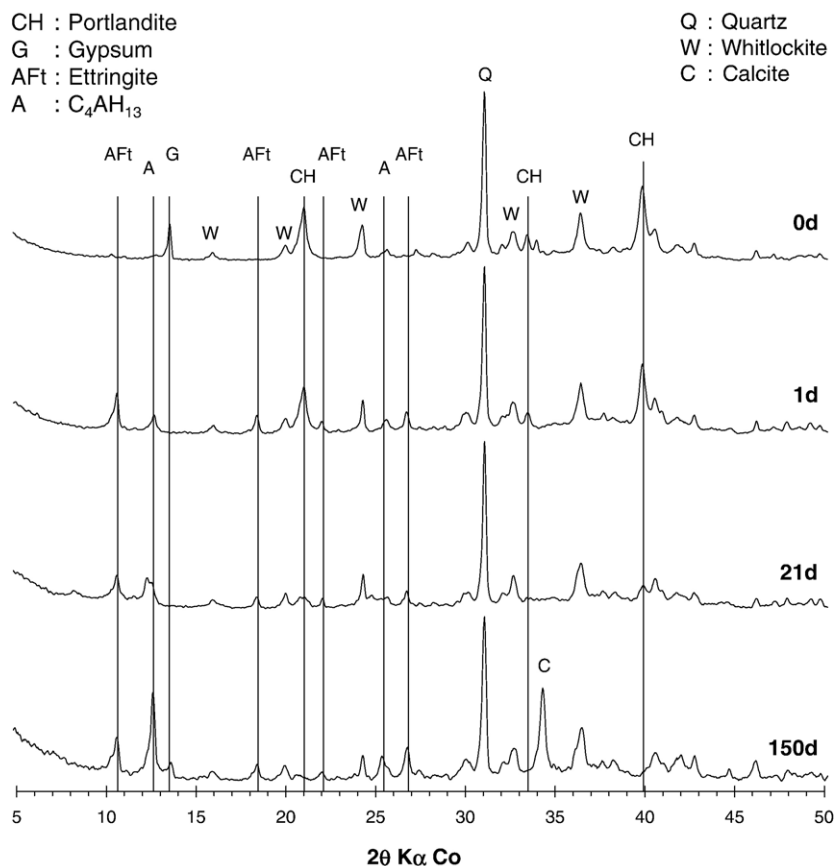


Fig. 2. Phase changes assessed by XRD between 0 and 150 days for CH–SSA–H₂O paste.

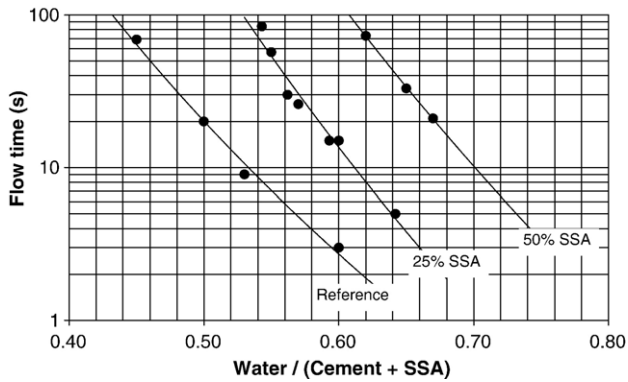


Fig. 3. Flow time of mortars containing 0, 25 and 50% of SSA.

tried to evaluate the reactivity of SSA using physicochemical methods. The former [43] used thermogravimetric analysis to quantify the consumption of CH on SSA/CH mixtures cured at 40 °C. Their results showed that CH decreased from 29% to 16% in the first three days of curing. An increase of the hydration water was also measured. However, it must be kept in mind that the increase of temperature tends to activate the pozzolanic reaction. Dyer et al. [49], in a study on four SSAs, used an isothermal conduction calorimeter and XRD to assess the hydration of cement pastes containing SSA. As in our study, they observed the presence of hydrated carboaluminates ($C_4A\bar{C}H_{11}$ and $C_4A\bar{C}_{0.5}H_{11}$) and aluminosilicates (C_2ASH_8). They also detected other minerals such as monosulfate (C_2ASH_{12}).

3.2.2. Water requirement and mortar consistency

The effect of SSA on the workability of cement-based materials was studied by measuring the flow time of vibrated mortars. Fig. 3 shows the flow time of mortars containing 0%, 25% and 50% of SSA. All mixtures contained the same amount of sand and binder (cement and SSA). Only the amount of water

was changed in order to increase or decrease the water–binder ratio. It can be seen that the use of SSA led to a significant decrease of workability, which depends on the amount of SSA. For a given water–cement ratio (e.g. 0.60), the flow time increased from 3 s (reference mortar) to 15 s and more than 100 s for 25 and 50% SSA, respectively. Thus, in order to maintain the consistency of mortars (e.g. 20 s), it was necessary to increase the water content compared to the reference mixture: +17% and +34% of water for mortars with 25% and 50% SSA, respectively.

Fig. 4 presents results from the literature [38,43,46,52,53,57] giving the increase of water demand of mortars and pastes containing SSA as a cement replacement. Except for the low SSA content, there is an increase of the water demand of the cement-based materials, which can reach more than 50% for high replacement rates. Our results deduced from Fig. 3 show a water demand in the same order of magnitude as other SSA. As stated earlier, the water demand of SSA is related to the high specific surface area of the grains, which are mainly composed of small sintered particles. This water requirement can lead to a decrease in the mechanical performance of mortars unless a superplasticizer is used to counteract this effect. However, the cost of such an admixture should be taken into account and its use may not be justified, as is the case for other mineral admixtures such as silica fume, since SSA has a low pozzolanic activity and does not lead to a significant gain in performance (compared to silica fume).

3.2.3. Setting time and early hydration

Vicat needle (French Standard NF EN 196-3) was used to determine the setting time of non-plasticized mortars. Initial setting was obtained after 3 h, 4 h and 30 mins. and 6 h for mixtures containing 0, 25 and 50% SSA, respectively. So increasing fractions of SSA induced higher setting delays compared to a control mortar (delays of 1 h and 30 min and 3 h for 25 and 50% SSA, respectively). Fig. 5 gives the relative setting

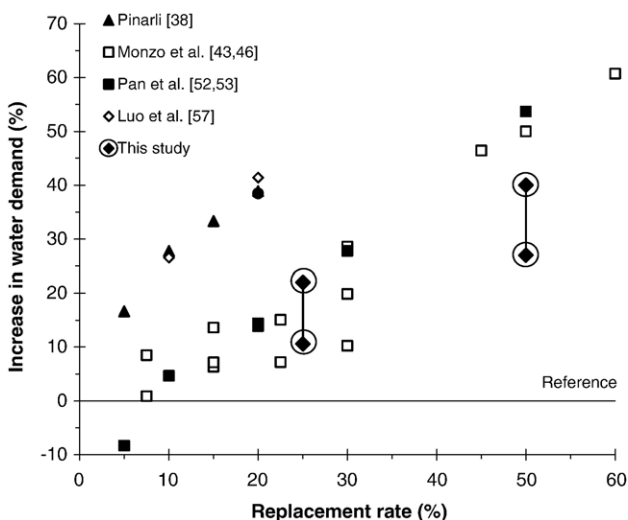


Fig. 4. Increase in water demand (%) of mixtures containing SSA compared to SSA-free mixtures. Comparison between our results and those found in literature [38,43,46,52,53,57].

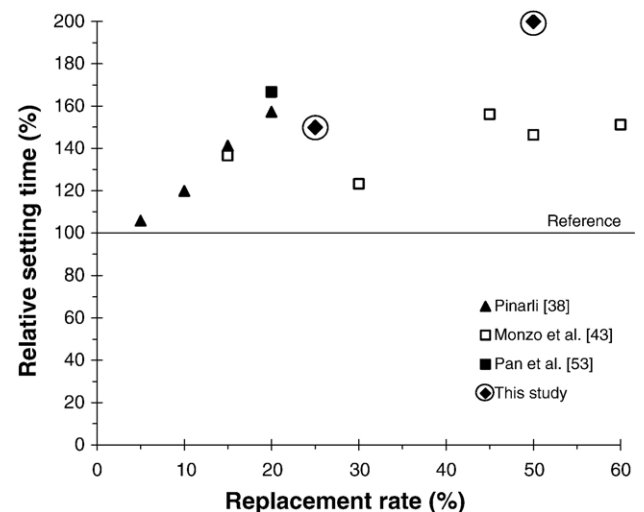


Fig. 5. Relative setting time of mixtures containing SSA compared to SSA-free mixtures. Comparison between our results and those found in literature [38,43,53].

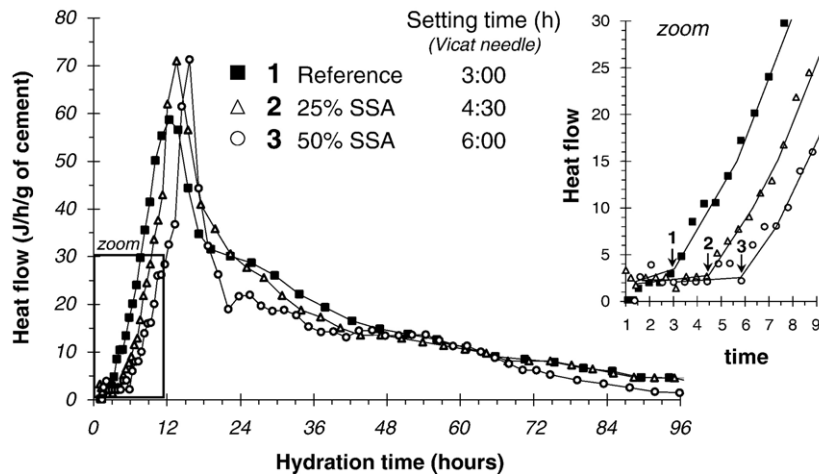


Fig. 6. Hydration heat flux and setting time (Vicat needle) of mortars without SP containing 0, 25 and 50% of SSA.

times of mixtures containing SSA relative to reference mixtures with cement only. It permits our results to be compared with those found in literature [38,43,53]. It can be seen that the result for 25% SSA is in an average range compared to other SSA, while, for high replacement rates (50%), a higher setting delay is obtained.

The setting delays observed using the Vicat needle were confirmed by calorimetric measurements on mortars made with a Langavant calorimeter (NF P 15-436) [78]. Fig. 6 shows the

heat flow of mortars with SSA compared with reference mortar. It must be noted that the hydration time was corrected [79–81] with an Arrhenius law in order to compare all mixtures at the same heat evolved and at an equivalent hydration temperature of 20 °C. This law is considered to be the most accurate one for describing the effect of temperature on simultaneous chemical reactions, as in cement materials [82–85]. It requires a knowledge of the activation energy E , which was fixed to 43 kJ/mol for all the mortars tested [86].

As shown on Fig. 6, the reference mixture's heat flow started earlier than SSA mixtures' ($\Delta t = 1$ h and 30 min and 3 h for 25 and 50% SSA, respectively) and the starting times are similar to the setting times measured using the Vicat needle (zoom on Fig. 6). A part of the delay could be due to the dilution of cement when SSA are used in mortars, since less cement implies less heat evolved at young age and so less thermal activation of the cement. The dilution effect has already been suggested by authors using other mineral admixtures such as coal fly ashes [87]. These short delays could also be due to some

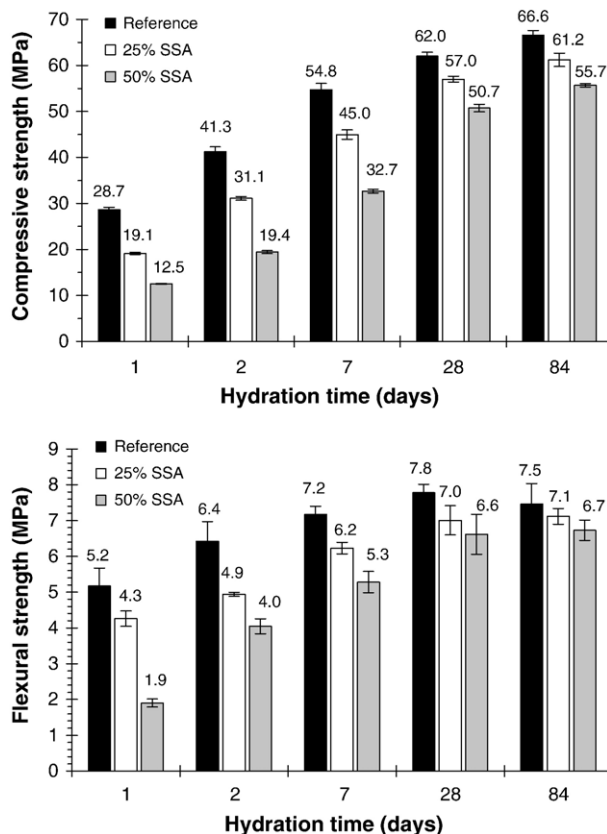


Fig. 7. Compressive and flexural strengths of mortars containing 0, 25 and 50% of SSA.

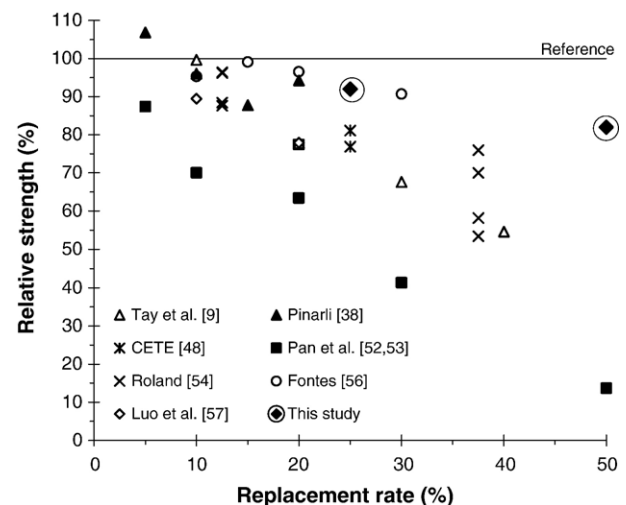


Fig. 8. Relative compressive strengths of mixtures containing SSA compared to SSA-free mixtures. Comparison between our results and those found in literature [9,38,48,52–54,56,57].

Table 5
Calculation of the water absorbed by SSA

Replacement rate (%)	0%	25%	50%
Required w/b^a to maintain the flow time at 20 s (Fig. 3)	0.50	0.585	0.67
Excess of water absorbed by SSA- $\Delta w/b$	–	0.085	0.17
Coefficient of water absorption by SSA (%)	–	34%	34%

$$\omega = \frac{\Delta w/b \cdot b}{p \cdot b} = \frac{\Delta w/b}{p}$$

Cement (g)	450	337.5	225
SSA (g)	0	112.5	225
Total water (g)	225	225	225
Absorbed water (g)	0	38	76
Effective water (g)	225	187	149
w/b (total)	0.50	0.50	0.50
w/b (effective)	0.50	0.42	0.33
w/c (total)	0.50	0.67	1.00
w/c (effective)	0.50	0.55	0.66

^a b and w are the masses of binder (cement+SSA) and water, respectively.

minor elements present in SSA, which may dissolve in the pore solution and then affect the hydration of the cement. Zn [88,89] and P [88,90,91] are two elements known to perturb cement hydration.

The total heat evolved after 4 days (96 h) of hydration at 20 °C was 315, 372 and 413 J/g of cement for mortars with 0, 25 and 50% SSA, respectively. So even if the early hydration of cement was delayed, the total heat evolved expressed per gram of cement increased with the addition of SSA. These results could be related to either a rapid activity of the ash in a basic environment, or an activation effect on the hydration of cement [92]. However, as will be seen in the next section, this does not lead to an improvement in mechanical performance at young ages.

3.2.4. Compressive and flexural strength

Fig. 7 gives the compressive and flexural strengths at 1, 2, 7, 28 and 84 days for superplasticized mortars containing 0, 25

and 50% of SSA in replacement of cement. From this figure, it can be seen that, even if relatively high strengths are obtained (more than 50 MPa at 28 days), the increase of replacement level led, for all hydration times, to a decrease in compressive strength. As shown on Fig. 8, our results are in accordance with those found in the literature [9,38,48,52–54,56,57], but the decrease of strength observed here is less marked since the results are in the higher range of compressive strength.

The delay of early hydration when SSA was used probably affected the early strength and may be responsible for the poor short-term results. However, the gaps between SSA and reference mortars reduced significantly over time, since the strengths were only 8% and 16% less than the reference at 3 months for 25 and 50% SSA, respectively (Fig. 7). So the short-term negative effect of SSA was strongly reduced after 28 days. These results could probably be related to a slight pozzolanic activity of SSA.

The kinetics of the SSA mortar's strengthening looked that of coal fly ash mortars, but important differences remained. The activity of SSA made its effect felt more quickly, since 28 days were sufficient to reduce the gap between SSA and the reference. In the case of coal fly ash, a few weeks more are often necessary for pozzolanic activity to take place [92]. However, the long-term strength gap with the reference mixture is significantly higher than for mortars with coal fly ash, for which the activity index is often near or greater than one. This difference is surely due to the small amount of amorphous phase in SSA, leading to modest pozzolanic activity, as stated earlier.

Feret's law [93] (Eq. (1)) can be used to correct the measured compressive strength (S) to account for the water that is not available to hydration because it is absorbed by the SSA.

$$S = F \left(\frac{c/\rho_c}{c/\rho_c + w_e/\rho_w} \right)^2 \quad (1)$$

where c and w_e are the masses of cement and effective water respectively, ρ_c and ρ_w are the density of cement and water respectively, and F is a parameter which takes account of the characteristics of the cement and aggregate used. In our case,

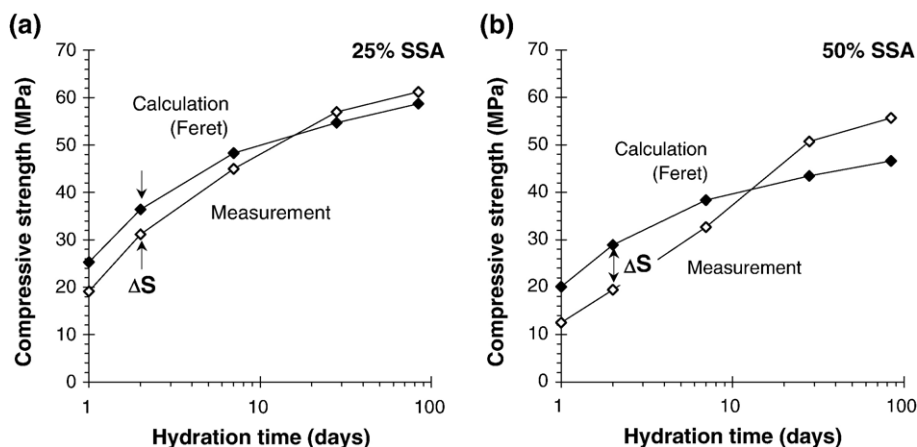


Fig. 9. Comparison of compressive strength measurements and compressive strength calculations according to Feret's law, for mortars containing (a) 25% and (b) 50% of SSA.

F was calculated using the reference mortar containing only cement and siliceous sand.

The effective water was calculated from the difference between the initial water in mixtures and the water absorbed by SSA (Table 5). The absorption of water by SSA (ω) was evaluated using Eq. (2).

$$\omega = \frac{\Delta w/b}{p} \tag{2}$$

where $\Delta w/b$ is the increase in the water–binder ratio (binder=cement+SSA) required to maintain a constant flow time (Fig. 3) and p is the replacement level (0.25 or 0.50). In the case of a flow time of 20 s, which corresponded to the reference mortar at a w/b of 0.50, the absorption of SSA was 34% (Table 5). So the effective water–cement ratio of 25% and 50% SSA mortars used for the calculations were 0.55 and 0.66, respectively (instead of 0.67 and 1.0 if absorption had been neglected).

The comparisons of calculated and measured strengths are given in Fig. 9. It can be seen that, for the two replacement levels, the measured strengths up to 7 days were lower than the calculated ones. Knowing that the calculations were performed considering the real amount of free water and cement in the mixture, it can be concluded that SSA had a negative effect on short-term performance. However, this negative effect was transformed to a long term positive effect, since the measured strengths exceeded those calculated after 28 days. This is probably due to the long-term activity of SSA.

In short, the use of SSA in mortars having the same water–binder ratio (0.50) led to an overall decrease of compressive strength for all hydration times. However, considering the water absorption of SSA, which reduced the effective w/c ratio but necessitated the use of a superplasticizer, SSA had a long-term positive effect compared to cement alone. In all cases, the use of a superplasticizer with SSA should minimize the loss of strength but the increase of cost is unfavorable to high replacement rates. It would probably have been more realistic to test SSA in a saturated surface dry condition. Pre-saturation of SSA would have reduced the quantity of superplasticizer required to achieve a plastic mortar, thus improving the economics of utilization. However, the strengths would have been reduced as a function of the higher free w/c . Finally, it must be kept in mind that strength is only one characteristic of importance with regard to the performance of a mineral admixture in concrete and other

Table 6
Results of leaching tests (concentrations of minor components leached, soluble fractions and pH of monolithic and crushed mortars)

	Monolithic mortars			Crushed mortars		
	Ref	25% SSA	50% SSA	Ref	25% SSA	50% SSA
Total, 11 elements ($\mu\text{g/kg}$)	115.7	177.2	243.0	608.2	642.5	919.3
Soluble fraction (g/kg)	5.0	4.0	3.3	31.9	30.2	21.5
pH	11.6	11.6	11.4	12.6	12.5	12.3

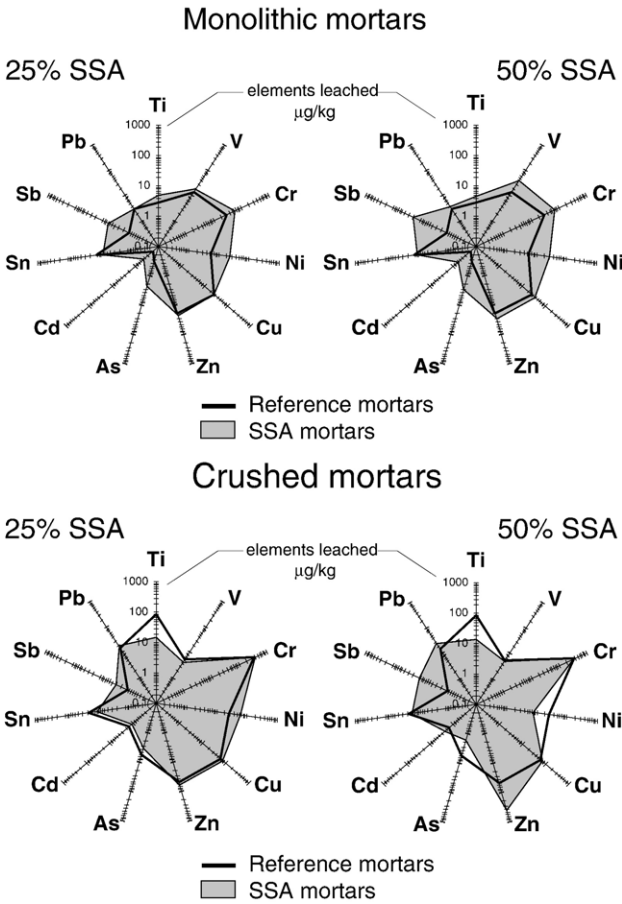


Fig. 10. Leaching of heavy metals of monolithic and crushed SSA mortars compared to reference mortars.

aspects of performance should be taken into account before any use is considered on a larger scale.

3.3. Effect of SSA on leaching behavior of mortars

Table 6 gives the concentrations of leached minor components (in $\mu\text{g/kg}$ of mortar), the total soluble fraction and the pH at $L/S=10$ of monolithic and crushed mortars containing 0, 25 and 50% SSA. It can be seen that lower soluble fractions were obtained when SSA was used. These reductions could be related to the decrease in cement content of SSA mortars (25 and 50% less cement than reference), which probably implied less decalcification of the matrix. As expected, crushed mortars released between 3 and 6 times more heavy metals on average than monolithic mortars, mainly because of their high available surface area. Fig. 10 compares the leaching data between each SSA mortar and its corresponding reference. In the case of monolithic mortars, the increase of SSA resulted in higher amounts leached for almost all heavy metals. This could be due to the higher porosity of SSA mortars at 28 days, and also to the higher heavy metal content of the mortars when using SSA, leading to an increase of the amount of heavy metal available for leaching. For crushed mortars, heavy metals were leached more or less than from reference mortars, the overall behavior being a slight increase for 25% SSA. The significant increase

for 50% SSA was due to the leaching of Zn and Sb. Nevertheless, considering the uncertainty and the dispersion of this kind of measurements, the results remain of a similar order of magnitude for all mortars.

Only a few references are available in the literature about the leaching behavior of SSA in construction materials. Most of them concern SSA in bricks and tiles [13,14,20], and (to the authors knowledge) only Fontes et al. [56] present leaching results of SSA in cement-based materials. However, their results are not comparable with ours since they used a different test to evaluate the environmental behavior of SSA in concrete. Moreover, no comparison with reference concrete was available.

4. Conclusion

This paper aimed to improve our knowledge of the characteristics of SSA and its effect on the properties of cement-based materials. Results were compared with those found in the literature in order to situate our residue with respect to others included in the same category. This analysis highlighted the principal characteristics that must be taken into account in order to use SSA correctly in cement-based materials:

4.1. Morphology of SSA grains

All SSA, including the one studied here, are composed of irregular particles having a porous structure. These particle shapes, which are related to the method of incineration (fluidized bed combustion), thus lead to a high water demand when SSA is used in mortars: +17% and +34% of water for mortars with 25% and 50% SSA, respectively.

4.2. Amount of amorphous phase

SSA presented only a limited content of SiO_2 and Al_2O_3 , the two oxides responsible for the pozzolanic activity in cement-based materials. Moreover, a fraction of these oxides were in a crystallized form, thus limiting the pozzolanic activity of SSA compared to other classical mineral admixtures. In our case, the amorphous content was evaluated at around 40% and XRD measurements showed a notable consumption of CH, which provided a slight but significant long-term activity, as proved by the compressive strength activity index (mortars with superplasticizer) reaching 92 and 84% at 3 months for 25 and 50% replacement of cement, respectively.

4.3. Trace element content

Due to their origin (waste materials), SSA always contain trace elements which are mostly heavy metals. In our case, the main heavy metals were zinc, chromium and copper, which occurred in concentrations greater than 2 g per kg of residue. These concentrations are notably lower than those found in other incineration residues such as MSWI fly ashes [58].

The presence of heavy metals in SSA had two main effects: one on the technological properties of cement-based materials and the other on the surrounding environment.

The heavy metals of SSA probably affected the cement hydration and so the setting time of the mortars. Results obtained from Vicat needle and calorimetric measurements showed delays in setting and hydration of 1 h and 30 min and 3 h for 25 and 50% SSA, respectively. The compressive strength development of mortars at early ages was also affected.

The environmental impact of SSA used in mortars was checked by means of leaching tests. It was shown that the leaching behavior of mortars containing SSA was of the same order of magnitude as the reference mortar without residue. However, it must be kept in mind that more environmental tests must be performed before any large scale use is undertaken.

Considering these results, the reuse of sewage sludge ash in cement based materials is conceivable and could present a good alternative to landfilling, depending on the evolution of regulations on the reuse of waste materials. Other technological and environmental tests should be performed, including field scale experiments, before any industrial applications take place.

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