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# HYDRATION MECHANISMS OF SEWAGE SLUDGE ASHES USED AS CEMENT REPLACEMENT

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## Abstract

The influence of sewage sludge ash (SSA) on the hydration of Portland cement (OPC) was investigated in this study. Blending OPC with SSA was found to influence the kinetic of hydration, notably the alite dissolution. This retardation effect has been attributed to the presence of the orthophosphate ions ( $\text{PO}_4^{3-}$ ). However, SSA releases only a small fraction of  $\text{PO}_4^{3-}$  into solution, which is deemed insufficient to precipitate calcium phosphates compounds on noticeable levels at least. On the other hand, an enhancement of the engineering-scale properties (i.e. mechanical and durability) and portlandite consumption are observed when SSA is used. This is explained by the formation of AFm phases, which leads to changes in the total volume of the solid and thus the properties of the systems. These experimental results were confirmed by thermodynamic modelling, showing that the additional alumina released by SSA results in the formation of higher amount of AFt and AFm phases.

## Keywords

Sewage sludge ash, cement hydration, AFm phase, kinetics, phase assemblage

## 31 I. INTRODUCTION

32 Sewage sludge is an inevitable by-product produced during waste water treatment.  
33 Depending on its quality (with regards to pollutant concentrations), different methods can be  
34 used to dispose of this waste. However, due to the current environmental awareness, many of  
35 these disposal practices have been subject to more or less legal limitations: ocean dumping  
36 has been banned since 1998 for environmental reasons (Urban Waste Water Directive  
37 98/15/EC), a cautionary application to soils as a fertilizer has been advocated by some  
38 countries for health concerns (Council Directive 86/278/EEC), and finally limits have been  
39 introduced for biodegradable wastes going to landfills in order to reduce the emissions of  
40 methane and carbon dioxide from these sites (Waste Landfill Directive 1999). Within this  
41 legislative context, incineration has become one of the most environmental friendly disposal  
42 options and has received increasing attention, particularly in Europe [1]. Nevertheless, the  
43 incineration process only diminishes the wastes weight by nearly 70% ( $\approx 70\text{--}90\%$  by volume),  
44 generating residual sewage sludge ashes (SSA) as an ultimate by-product to deal with [2]. In  
45 the past decades, these ashes have been usually landfilled due the relatively low amounts  
46 generated each year (estimated of 1.2 Mt in 2004 in USA and Europe [3]). However, the rising  
47 amount of sludge being incinerated urges the search for alternative means to reuse or  
48 recycle the SSA.

49 The construction field has provided a brand new recovery channel for this waste through its  
50 use in bricks, tiles, ceramics, lightweight materials, aerated concrete, soil stabilization [2–17].  
51 Recently, some studies have also suggested a potential use as replacement or in substitution  
52 to cement and reviewed the properties of the SSA-blended mortars and/or concretes from a  
53 technological and engineering point of view [2,3,18–25]. On the one hand, SSA tends to  
54 increase the water demand, to reduce the workability and to delay the setting of concrete  
55 and mortars. On the other hand, however, acceptable strength activity indexes for  
56 replacement rates below 20 wt.% (i.e. standard for pozzolanic activity) and a high  
57 consumption of portlandite (amounts of  $\text{Ca}(\text{OH})_2$  fixed) have been reported when the SSA are  
58 used. These observations have inferred to SSA the characteristic of being pozzolanic  
59 [19,21,23,26] and aroused the interest in its use as an alternative supplementary cementitious  
60 material (SCM).

61 Despite the promising results of the SSA as cement component, there is still little  
62 information available about its hydration mechanisms and its impact on the phase  
63 assemblage of the cementitious matrix. In addition to the low alumina and silica contents  
64 compared to conventional SCMs, several authors have reported the presence of phosphate in  
65 SSA, often in form of iron- or magnesium-bearing whitlockite (WH,  $\text{Ca}_9(\text{Mg,Fe})(\text{PO}_4)_6\text{PO}_3\text{OH}$ )  
66 [3,26–29], calcium aluminium phosphates ( $\text{Ca}_9(\text{Al})(\text{PO}_4)_7$ ) [30], aluminium or iron phosphates  
67 ( $(\text{Al,Fe})\text{PO}_4$ ) [29–31], or hydroxyapatite (HAP,  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ ) [28,29]. Hence, the composition  
68 of SSA makes its chemistry distinguishable from the cement based materials. Furthermore,  
69 the portlandite consumption and the compressive strength gains might be related to the

70 formation of other compounds than C-S-H (e.g. hydroxyapatite [22,26], or hydrogarnet [3])  
 71 and thus SSA cannot be simply considered as a pozzolanic SCM [26].

72 In this respect, the aim of this paper is to identify and quantify the changes in the hydration  
 73 products upon the addition of SSA. First, the hydraulic and pozzolanic reactivity of SSA is  
 74 investigated using isothermal calorimetry and X-ray diffraction. Then, the effects of replacing  
 75 10 and 20 wt.% of the cement by SSA are investigated in terms of macro-scale properties and  
 76 phase assemblage of cementitious matrix. Finally, thermodynamic modelling was employed  
 77 to validate the experimental observations.

## 78 2. MATERIALS AND METHODS

### 79 2.1 Materials

80 In this work, the cement pastes and mortars were prepared using a commercially available  
 81 Portland Cement (OPC) from Ciment Quebec and conforming to ASTM C150 [32], a class F fly  
 82 ash (FA) from Lafarge, and a sewage sludge ash (SSA) obtained by incinerating an urban  
 83 sewage sludge (from Grenoble region, France) in a fluidized bed furnace at 850 °C. The  
 84 chemical and physical properties of the raw materials and the characterisation technics  
 85 employed are summarized in Table 1. Besides, Table 2 shows the mineral composition  
 86 obtained by X-ray diffraction combined with the Rietveld refinement, whereas Fig. 1 displays  
 87 the particle size distributions determined by laser granulometry of the aforementioned  
 88 materials.

89 *Table 1. Chemical and physical characterizations of the studied materials OPC, SSA, FA.*

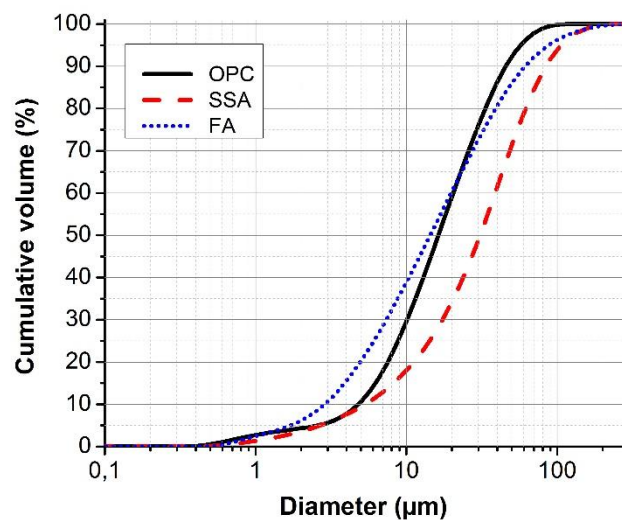
	<b>OPC</b>	<b>SSA</b>	<b>FA</b>	<b>Method/Instrument</b>
<b>SiO<sub>2</sub></b>	19.5	28.6	46.4	
<b>CaO</b>	60.5	20.1	4.5	
<b>Al<sub>2</sub>O<sub>3</sub></b>	4.4	17.6	23.2	
<b>Fe<sub>2</sub>O<sub>3</sub></b>	2.6	4.4	16.5	
<b>Na<sub>2</sub>O</b>	0.3	0.6	0.8	
<b>K<sub>2</sub>O</b>	0.9	1.9	1.9	
<b>P<sub>2</sub>O<sub>5</sub></b>	0.9	19.5	0.4	Phillips PW-2600 X Fluorescence Spectrometer
<b>SO<sub>3</sub></b>	4.0	2.0	0.7	
<b>Mn<sub>2</sub>O<sub>3</sub></b>	0.1	0.0	0.0	
<b>MgO</b>	2.9	2.3	1.0	
<b>TiO<sub>2</sub></b>	0.2	1.5	1.1	
<b>Cr<sub>2</sub>O<sub>3</sub></b>	0.0	0.1	0.0	
<b>SrO</b>	0.2	0.1	0.1	
<b>ZnO</b>	0.0	0.2	0.2	
<b>Loss On Ignition (LOI)</b>	2.7	0.7	2.7	LOI at 1000°C
<b>Equivalent alkali</b>	0.9	1.8	2.1	Na <sub>2</sub> O <sub>eq</sub> (%) = Na <sub>2</sub> O + 0,658 x K <sub>2</sub> O (%)

<b>D<sub>50</sub> (μm)</b>	16.3	30.8	14.4	Malvern's Mastersizer 2000 laser granulometer
<b>Density</b>	3.11	2.62	2.51	Pycnometry
<b>Blaine (m<sup>2</sup>/kg)</b>	395	845	387	Blaine fineness
<b>BET (m<sup>2</sup>/g)</b>	1.26	5.2	-	Micromeritics ASAP2010
<b>Lime fixed (mg per g)</b>	-	362	512	Pozzolanic test NF P18-513

90

Table 2. Mineral composition of the studied materials.

	<b>Chemical formula</b>	<b>OPC</b>	<b>SSA</b>	<b>FA</b>
<b>Alite</b>	$Ca_3SiO_5$	52.1		
<b>Belite</b>	$Ca_2SiO_4$	11.5		0.8
<b>Aluminate</b>	$Ca_3Al_2O_6$	4.3		
<b>Ferrite</b>	$Ca_3FeAlO_5$	8.6		
<b>Lime</b>	$CaO$		0.9	
<b>Portlandite</b>	$Ca(OH)_2$			1.1
<b>Periclase</b>	$MgO$	0.6		0.5
<b>Gypsum</b>	$CaSO_4 \cdot 2H_2O$	3.4		2.0
<b>Bassanite</b>	$CaSO_4 \cdot 1/2H_2O$	2.6		
<b>Anhydrite</b>	$\gamma-CaSO_4$	0.3	3.1	0.8
<b>Apthitalite</b>	$K_{2.25}Na_{1.75}(SO_4)_2$	0.2		
<b>Calcite</b>	$CaCO_3$	3.3		2.7
<b>Quartz</b>	$SiO_2$	0.3	14.7	9.1
<b>Hematite</b>	$Fe_2O_3$		0.4	0.5
<b>Mullite</b>	$Al_{4.5}Si_{1.5}O_{9.75}$			1.7
<b>Microcline - Feldspars</b>	$KAlSi_3O_8$		4.4	
<b>Whitlockite</b>	$Ca_7Mg_2P_6O_{24}$		27.9	
<b>Hydroxyapatite</b>	$Ca_5(PO_4)_3(OH)$		0.3	
<b>Amorphous/unidentified</b>		12.8	48.3	80.6



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*Fig. 1. Particle size distribution of OPC, SSA and FA.*

93

## 94 **2.2 Methods**

### 95 *2.2.1 Samples preparation*

96 The hydraulic and pozzolanic activities of SSA were evaluated through mixture with water,  
97 KOH solution, and calcium hydroxide+water (NF P18-513 2012) [33]. The water to solid mass  
98 ratio was fixed to 1 to achieve a good rheology of the pastes. For the CH-SSA systems, two  
99 mass proportions were used 50 wt.% SSA and 25 wt.% SSA, which in the following will be  
100 respectively referred to as 50SSA50CH and 25SSA75CH. All the mixtures were prepared using  
101 a propeller mixer (2 min, 2000 rpm).

102 Standard mortar cubes (5x5x5 cm) were prepared with a binder:sand:water ratio (by weight)  
103 of 1:2.75:0.485 according to ASTM C109. The blended cements were prepared by replacing  
104 commercial Ordinary Portland Cement (OPC) with sewage sludge ash (SSA) according to the  
105 following percentages: 0, 10, and 20% by weight. After demolding, the specimens were  
106 immersed in a lime-saturated solution until the age of testing. The blended mortar cubes  
107 were used to evaluate the effect of SSA on compressive strength and electrical resistivity,  
108 while the mortars with neat OPC were used, for comparison purpose, as control samples.

109 The phase changes due to the inclusion of SSA were investigated using cement pastes at a  
110 water to binder ratio of 0.485. Two replacement levels (10 and 20 wt. %) were used for the  
111 SSA-blended systems. The pastes were cast in plastic containers, sealed, and stored in a  
112 desiccator with soda-lime to avoid CO<sub>2</sub> contamination. Before the testing ages of 1, 3, 7, 14,  
113 28, 56, 91, 180, and 300 days, the hardened pastes were manually ground ( $d_{50} \approx 40 \mu\text{m}$ ) and  
114 the hydration was immediately stopped by placing the sample in isopropanol for 15 min.  
115 Afterwards, the isopropanol was filtered and removed by solvent exchange with diethyl ether  
116 followed by a short vacuum drying process [34,35].

### 117 *2.2.2 Isothermal calorimetry*

118 The hydration heat evolution of the control and the SSA-blended pastes (weight  
119 replacements of 10, 20, and 30%) was analysed using a TAM Air isothermal calorimeter (TA  
120 instruments). For each mixture, a sample of about 4.5 g at a water to binder weight ratio of  
121 0.485 was placed in an ampoule and inserted into the calorimeter cell. The heat  
122 measurements were collected continuously during the first week (7 days) of hydration.

### 123 *2.2.3 Thermogravimetric analyses (TGA)*

124 Thermogravimetric investigations were carried out with a TA instrument SDT Q600 over a  
125 temperature range of 30–1000°C at a heating rate of 20 °C/min. The measurements were

126 performed on about 50 mg of the ground sample (after the hydration stoppage), placed in a  
127 150  $\mu$ L alumina crucible. Nitrogen with a flow of 50 mL/min was used as a purging gas. TGA  
128 was used to determine the chemically bound water and the mass loss corresponding to the  
129 portlandite decomposition.

#### 130 2.2.4 X-ray diffraction analyses (XRD)

131 X-ray powder diffraction was used to identify the mineralogical composition of both raw  
132 materials and hydrated pastes. X-ray Data were collected using a PANalytical X'pert Pro MRD  
133 diffractometer equipped with a PIXcel 1D detector. The analyses were performed on back-  
134 loaded samples in a Bragg-Brentano ( $\theta$ - $2\theta$ ) geometry, using Soller slits of 0.04 rad. Further  
135 details concerning the XRD operating parameters are reported in Table 3. On the other hand,  
136 an Alfa Aesar  $\alpha$ - $\text{Al}_2\text{O}_3$  corundum, calibrated to 98.2% crystalline content using a certified  
137 corundum standard from the National Institute of Standards and Technology (NIST 676a),  
138 was used as an external standard to quantify the amorphous content of the samples [36]. The  
139 standard was scanned frequently to take into account the decay of the X-ray tube.

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Table 3. Instrumental settings for X-ray data collection

	<b>Powder XRD</b>
<b>Current/Voltage</b>	50 mA / 40 kV
<b>Angular range</b>	5 to 70° $2\theta$
<b>Detector's active length</b>	3.347° $2\theta$
<b>Step size</b>	0.0263° $2\theta$
<b>Counting Time</b>	176 s
<b>Measurement time</b>	30 min
<b>Vertical spinning</b>	8 rpm
<b>Divergence slit</b>	0.5°
<b>Anti-Scatter slit</b>	0.5°
<b>Scan mode</b>	Continuous

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#### 142 2.2.5 $^{27}\text{Al}$ nuclear magnetic resonance

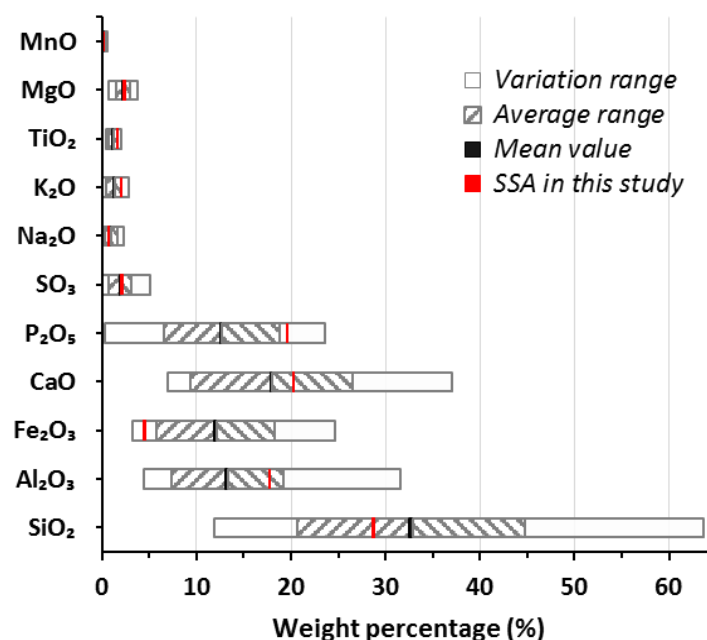
143  $^{27}\text{Al}$  NMR spectroscopy is a powerful tool to analyse the structure of both amorphous and  
144 crystalline materials, at a local scale. It provides insight on the geometrical configuration of  
145 the nucleus and the coordination of the atoms as a function of the chemical shift.  $^{27}\text{Al}$  magic-  
146 angle spinning NMR (MAS NMR) spectra were performed at a frequency of 130.3 MHz using  
147 a Bruker Avance III (11.74 T magnetic field). The spectrometer was equipped with a 4 mm  
148 probe head operating at a spinning frequency of 11.5 KHz. The record was carried out with a  
149 pulse length of 1.5  $\mu$ s and a relaxation delay of 5 s. The chemical shift was referenced using  
150  $\text{Al}^{3+}_{\text{aq}}$  in a 0.1 M  $\text{AlCl}_3$  aqueous solution.

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### 152 3. OVERVIEW OF SEWAGE SLUDGE ASHES

#### 153 3.1 Variability of the composition

154 The main elements present in SSAs as reported in the literature are silicon, aluminium, iron,  
155 calcium and phosphorus. Fig. 2 illustrates the variation range and average weight percentage  
156 of the major components of SSAs, compiled from former studies [2,3,7–9,15,19,21,30,31,37–  
157 56]. Given the wide range of variation of the oxides (e.g.  $\approx 62$  wt.% for  $\text{SiO}_2$ ), it can be  
158 concluded that the sewage sludge ashes present a very high variability. Indeed, the  
159 composition of SSAs could be heavily influenced by several factors such as the type of the  
160 effluents (urban, industrial, etc.), the treatment processes (e.g. removal of phosphates [43]),  
161 the incineration process, etc. Fig. 2 also shows that the oxide composition of the SSA studied  
162 here fall into the average regions (except  $\text{Fe}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$ ). Therefore, the SSA in this study  
163 might be considered representative of other SSAs to some extent. It should also be noted  
164 that the amount of oxides intervening in the pozzolanic reaction ( $\text{SiO}_2 + \text{Al}_2\text{O}_3 < 50$  wt.%) are  
165 low compared to conventional SCMs, with a significant part expected to be inert (in form of  
166 quartz and feldspars). On the other hand, SSA contains high levels of  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$ ,  
167 mainly in the form of calcium phosphates minerals (whitlockite). The presence of high  
168 amount of  $\text{CaO}$  is related to the use of lime in the water treatment process. Furthermore,  
169 other minor minerals have been observed such as hematite and anhydrite, in addition to a  
170 vitreous (or unidentified) phase of  $\approx 48$  wt.%, as shown in Fig. 3. Similar observations have  
171 been reported by Cyr and al. [3].

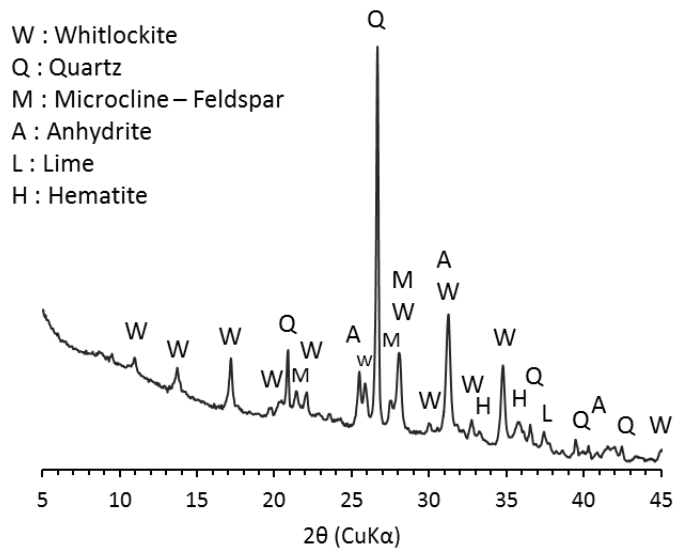


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173 Fig. 2. Variability of the chemical composition of the studied SSA (in red) compared to other SSA found in the  
174 literature.

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*Fig. 3. X-ray diffraction pattern of the investigated SSA, with the identification of the main phases.*

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### 3.2 Reactivity of SSA

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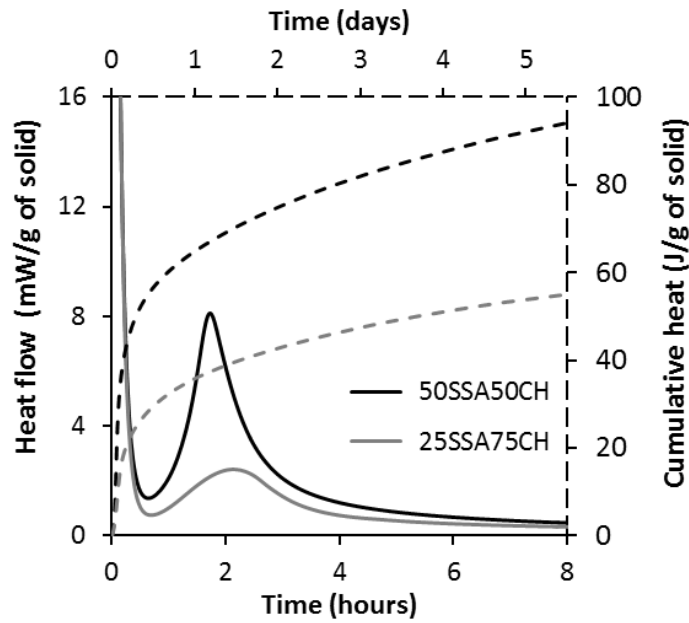
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The hydraulic and pozzolanic properties of SSA were evaluated using isothermal calorimetry and XRD analyses. The mixtures with distilled water and KOH solution (0.1 mol/L, i.e. pH = 13) showed no significant heat release or hardening, thus it can be concluded that SSA has no self-cementitious or hydraulic properties. These observations concur with the results of former studies, showing no phase changes except the dissolution of gypsum [3,22]. On the other hand, however, the heat flow curves of the SSA-CH mixtures displayed a distinguishable peak about two hours following the initial contact with water. Fig. 4 illustrates the heat flow evolution per g of solid, as measured by isothermal calorimetry. The cumulative heat values after six days of reaction were 96 and 56 J per g of solid for the 50SSA50CH and 25SSA75CH mixtures, respectively. Although this is an indication that the SSA reacts in presence of calcium, further investigations are required to assume the pozzolanic activity of SSA. In this respect, XRD analyses were simultaneously employed to follow the phase change in the CH-SSA within the first hours of reaction.



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*Fig. 4. Heat flow calorimetry results of the SSA-CH systems at w/s ratio of 1. Solid lines represent the heat flow over the first hours while the dashed lines show the evolution of the cumulative heat during the first days. The results are normalised per g of solid.*

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In order to predict the phases that might form in SSA-CH mixtures, the fraction of elements mobilized in the solution upon the dissolution of SSA was calculated. For this purpose, SSA was placed in two mediums: distilled water (neutral pH) and KOH solution (pH = 13). The solutions were sealed for a month (to avoid contamination) and the elements in the solution were quantified using ICP-AES. The results are reported in [Table 4](#). On the other hand, given the weak solubility of the crystalline phases composing SSA (e.g. quartz, whitlockite, feldspar), it is expected that the majority of element governing its reaction are provided by the glassy phase ( $\approx 48$  wt.%). Therefore, the average composition of the SSA amorphous phase was calculated by subtracting the contribution of the crystallized phases from the bulk composition determined by X-ray fluorescence. As shown in [Table 4](#), the SSA amorphous phase is mainly composed of alumina ( $\approx 17.3$  wt.%) and silicon ( $\approx 11.9$  wt.%). These observations are in line with the ICP-AES results, showing that the aluminium and, to some extent phosphates, are the most soluble phase while the dissolution of other elements is negligible. Therefore, combining these information, the calcium aluminates hydrates (probably AFt, hydrogarnet or AFm) are the most likely phases to form in presence of portlandite. Furthermore, with the majority of  $P_2O_5$  being inert in the structure of the whitlockite (13.26 out of 19.5 wt.%), only 0.644 wt.% has dissolved in KOH solution. Consequently, it is realistic to assume that the phosphate will not heavily impact the products of hydration.

*Table 4. Composition of the glassy phase of SSA.*

	<b>Amorphous phase composition (wt.%)</b>	<b>Dissolved amount in distilled water (wt.%)</b>	<b>Dissolved amount in KOH solution (wt.%)</b>
pH		<b>9.7</b>	<b>12.1</b>

<b>SiO<sub>2</sub></b>	11.93	0.003	0.003
<b>CaO</b>	4.95 + 1.28*	0.790	> 0.001
<b>Al<sub>2</sub>O<sub>3</sub></b>	17.34	0.025	1.580
<b>Fe<sub>2</sub>O<sub>3</sub></b>	3.97	> 0.001	> 0.001
<b>Na<sub>2</sub>O</b>	0.62	0.031	> 0.001
<b>K<sub>2</sub>O</b>	1.21	0.080	0.169
<b>P<sub>2</sub>O<sub>5</sub></b>	6.84	0.002	0.644
<b>SO<sub>3</sub></b>	0.24 + 1.82*	1.242	0.746
<b>MgO</b>	1.39	0.007	> 0.001

\*Anhydrite

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217 **Fig. 5** depicts the X-ray diffractograms of the 50SSA50CH mixture at different ages of  
 218 hydration. After two hours of hydration, the XRD patterns revealed the apparition of the  
 219 characteristic peaks of monocarboaluminates ( $C_4A\bar{C}H_{11}$ ) and ettringite, respectively at 7.6 Å  
 220 and 9.7 Å. The amounts of monocarboaluminates and ettringite increased while the  
 221 portlandite peaks intensity decreased within the first hours of hydration. These results are in  
 222 agreement with the fact that aluminium is the main element being introduced to the system  
 223 upon the dissolution of SSA. At 7 days, besides the formation of gypsum due to the  
 224 hydration of anhydrite, a second peak appeared around 8.2 Å. This peak was attributed to the  
 225 formation of hemicarboaluminates ( $C_4A\bar{C}_{0.5}H_{12}$ ). The increase of its intensity with reaction time  
 226 coincides with the decrease in the portlandite content. Similar observations were reported by  
 227 [57,58], showing that the excess of portlandite in a mixture containing monocarboaluminates  
 228 results in the formation of hemicarboaluminates. Furthermore, the diffraction patterns  
 229 showed no sign of ettringite after 28 days although the presence of monocarboaluminates  
 230 are reported to stabilise the AFt phase [59]. Instead the remaining hydration products were  
 231 hemi- and monocarboaluminates, and gypsum.

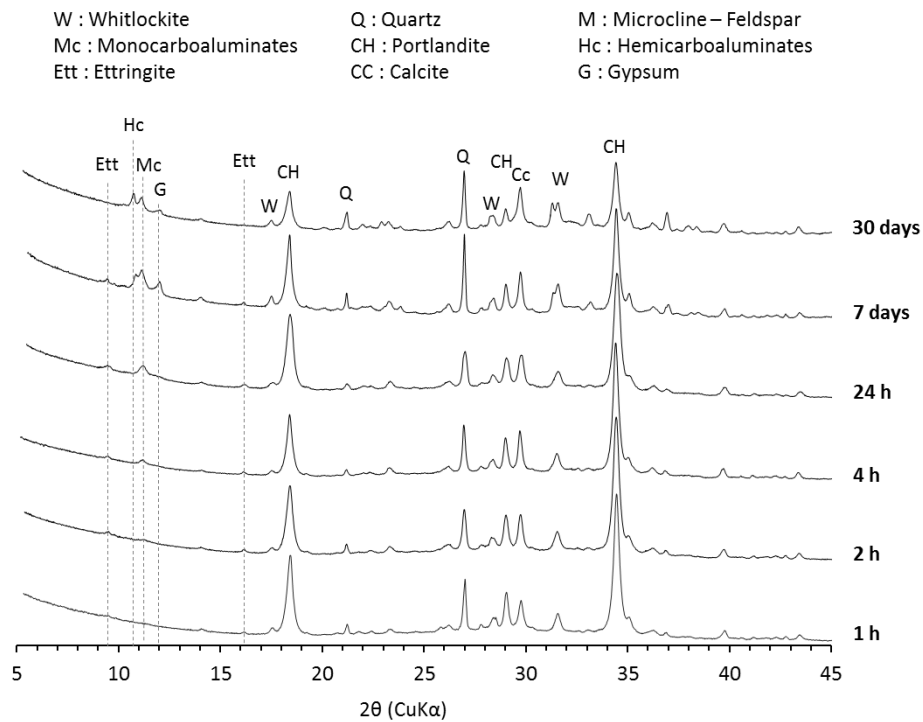


Fig. 5. XRD patterns of 50SSA50CH system at different hydration times.

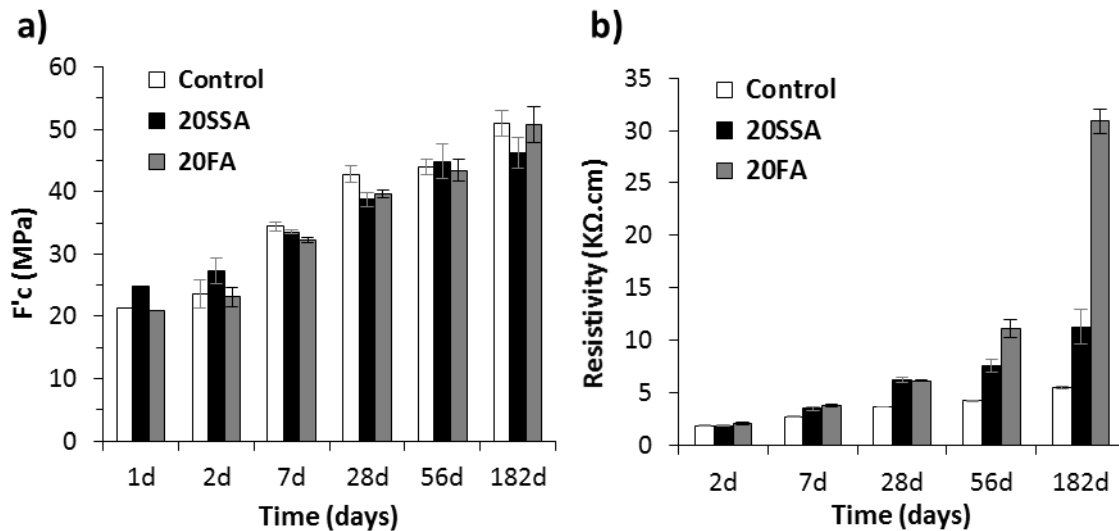
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## 234 4 INFLUENCE OF SSA ON CEMENT HYDRATION

### 235 4.1 Compressive strength and electrical resistivity

236 The influence of sewage sludge ashes on compressive strength ( $f'_c$ ) and electrical resistivity  
 237 was investigated by comparing the behaviour of mortars containing 20% SSA (20SSA) to a  
 238 control (OPC) and a 20% FA-blended (20FA) mortars. Fig. 6 presents the measured  
 239 compressive strength and resistivity of the produced mortars at 1, 2, 7, 28, 56, and 182 days  
 240 of hydration. The compressive strength results of 20SSA showed a steep increase in the first  
 241 days of hydration, that exceed both control and 20FA mortars. However, after 28 days of  
 242 hydration, the strength of the control and 20FA surpassed the mortar containing SSA. On the  
 243 other hand, the blended systems (20FA and 20SSA) show a higher resistivity than the control  
 244 (respectively 5.5, 11.3 and 30.9 K $\Omega$ .cm for control, 20SSA and 20FA at 182 days). This is more  
 245 likely related to a more refinement of the microstructure and pore distributions.



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Fig. 6. a) Compressive strength,  $f'_c$  (MPa) and b) Electrical resistivity ( $k\Omega \cdot cm$ ) of OPC, 20SSA and 20FA mortars.

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## 4.2 Hydration kinetics and setting time

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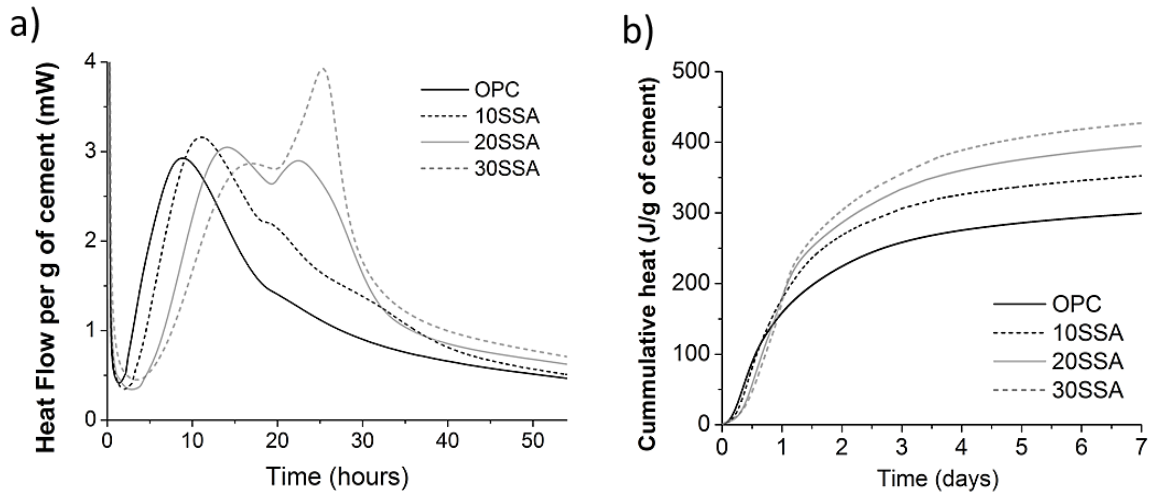
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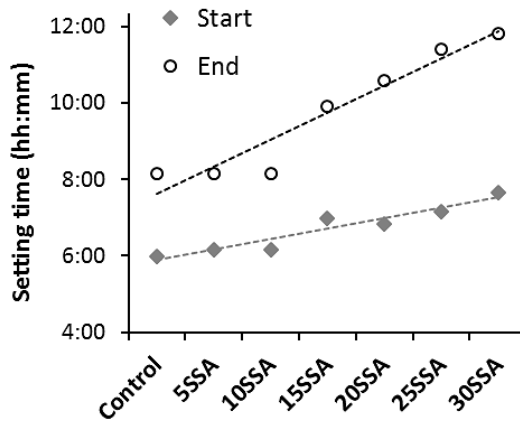
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The heat evolution curves of the control and SSA-modified pastes, normalised to the amount of cement, are displayed in Fig. 7. The pastes containing SSA can be clearly discerned as they show a second peak (around 20–30 hours of hydration) as opposed to the control (OPC) heat curve where only the main peak of hydration is observed. Steeper heat liberation is observed on the second peak in the pastes with higher SSA content, and thus the apparition of the second peak could be explained by the reactivity of the SSA replacements. Furthermore, an extension of the acceleration period and a shift of the first heat peak maximum towards later ages has been observed on the heat curves when SSA is used. These results are consistent with the Vicat needle measurements (NF EN 196-3), showing the retardation effect of SSA. As shown in Fig. 8, increasing SSA content led to a further delay in both the initial and final setting times compared to a control mortar. For a 30% SSA replacement, the initial setting was obtained 1:40 after the control while the setting time was increased by 2 hours, so a total delay of 3:40. Similar observation has been reported by previous studies [3,43,60].



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Fig. 7. Influence of the SSA substitution rate on the heat liberation: a) Heat flow and b) cumulative heat per g of cement



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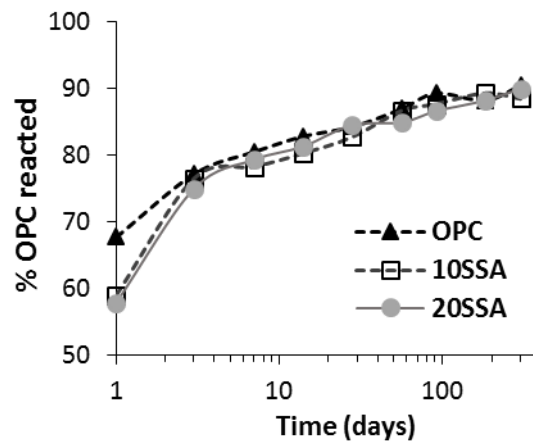
Fig. 8. Influence of SSA substitution rate on the setting time

268 The delay in the cement hydration and setting time when SSA is used could be explained by  
 269 the presence of the orthophosphate ions ( $\text{PO}_4^{3-}$ ), which are known to inhibit the growth of  
 270 crystals [61]. In fact, several authors have reported the retarding effect of the orthophosphate  
 271 on the cement hydration [62–64]. In the same manner that gypsum (particularly sulphates)  
 272 slows down the reaction of  $\text{C}_3\text{A}$ , the adsorption of phosphates ions on the reactive sites of  
 273  $\text{C}_3\text{S}$  hinders its dissolution rate [61]. Furthermore, Benard et al. [65] have shown a  
 274 discontinuity of the retarding effect above a pessimum phosphate concentration of 0.2 mol/L.  
 275 This change of behaviour have been attributed to the precipitation of hydroxyapatite, due to  
 276 the saturation of the silicate dissolution sites. However, the solubility of  $\text{P}_2\text{O}_5$  in SSA (see  
 277 [Table 4](#)) is rather low, and thus the adsorption of phosphates ions on the different phases  
 278 constituting the cementitious matrix is more likely than the formation of calcium phosphates  
 279 compounds.

280

### 281 4.3 Clinker phases evolution

282 The degree of hydration of clinker as function of time is given in Fig. 9, as measured by XRD-  
 283 Rietveld refinement. Similarly to the calorimetry observations, the inclusion of SSA seems to  
 284 delay the hydration of cement at early age. For instance, only 57% of clinker has reacted in  
 285 the 20SSA system whereas the cement dissolution was faster in the neat OPC system with  
 286 over than 65% having reacted within the first day of hydration. Eventually, the cement  
 287 hydration in SSA blended systems reaches similar degree of reaction as the control.  
 288 Moreover, the influence of SSA on the individual clinker phases' hydration is summarized in  
 289 Table 5. Upon the addition of SSA, the hydration of alite was slowed down, notably in the  
 290 first days of hydration. The hydration of  $C_3A$ , on the other hand, seems also to be delayed but  
 291 only marginally. In contrast, no discernible effect were observed on the belite and ferrite rates  
 292 of hydration. The effect of SSA on the hydration of alite is probably related to the adsorption  
 293 of the orthophosphates ions on its surface, as explained above.



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Fig. 9. Degree of the reaction of cement as measured by XRD-Rietveld refinement

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Table 5. Evolution of clinker phases as a function of hydration time. The value are normalised to the cement content (g per g of cement).

	Time (days)	$C_3S$	$C_2S$	$C_3A$	$C_4AF$
OPC	1	12.5	7.8	1.1	3.3
	3	6.4	7.4	0.8	2.8
	7	4.7	6.7	0.8	2.6
	14	3.6	6.5	0.6	2.4
	28	3.5	6.0	0.4	2.1
	56	2.4	4.9	0.5	2.2
	91	1.9	4.0	0.5	1.8
	182	2.2	4.1	0.5	2.1
10SSA	1	19.1	6.6	2.0	3.6
	3	8.2	5.9	1.3	2.6
	7	7.3	5.5	1.2	2.6
	14	6.3	5.6	0.8	2.3

	28	5.8	4.6	0.8	2.0
	56	3.8	4.0	0.7	1.7
	91	3.2	3.8	0.6	1.9
	182	2.4	3.2	0.7	1.8
	300	2.7	3.6	0.7	1.7
20SSA	1	19.8	6.9	2.1	3.5
	3	9.1	6.4	1.1	2.6
	7	6.9	5.8	0.9	2.2
	14	6.0	5.7	0.6	2.0
	28	4.8	4.7	0.5	1.8
	56	4.8	4.3	0.8	1.7
	91	3.9	4.1	0.5	1.7
	182	3.0	3.9	0.4	1.7
	300	2.5	3.3	0.3	1.5

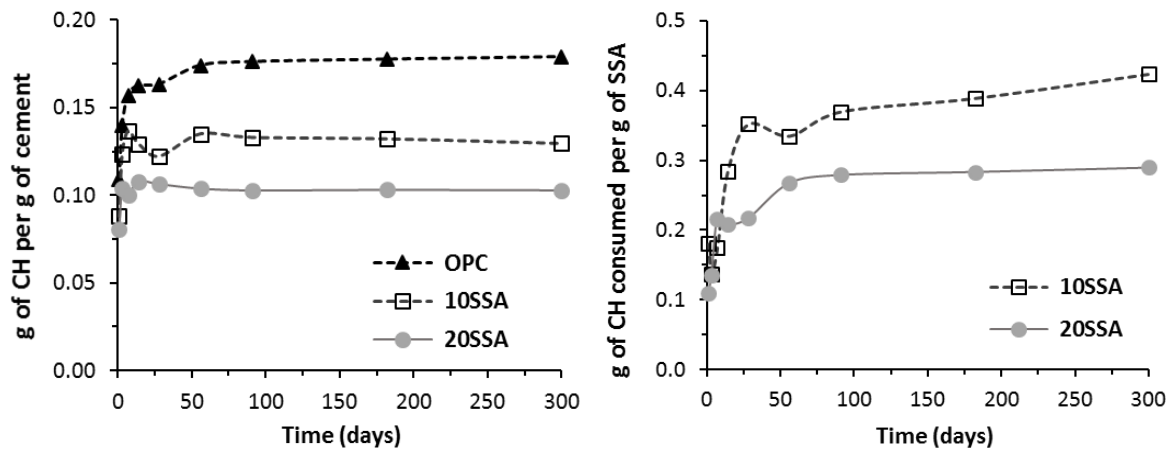
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#### 299 4.4 Portlandite consumption

300 The replacement of cement by SSA leads to the formation of lesser amount of portlandite,  
301 which is even lower when normalised back to the mass of cement. Fig. 10(a) shows the  
302 evolution of the portlandite content normalised to cement content, as measured by the  
303 tangent method from the DTG curves (derivative of the thermogravimetric curve) [35].  
304 Furthermore, the consumption of portlandite per g of SSA, calculated by subtracting the  
305 expected amount of CH produced by each g neat OPC, is given in Fig. 10(b). The results show  
306 that the increase of SSA substitution rate results in the decrease of portlandite content (0.13  
307 vs. 0.10 g per g of cement for 10SSA vs. 20SSA at 300 days). However, the reactivity of SSA  
308 seems to be higher in the 10SSA with 0.42 g of CH consumed by g of SSA compared to 0.29  
309 g of CH per g of SSA in the 20SSA mix. Additionally, the majority of CH is consumed within  
310 the first days while no significant change occurs at later age (56 days and onwards),  
311 particularly for 20SSA mix. This might be related to the type and/or the amounts of the  
312 hydrates which will be discussed subsequently. It is worth mentioning the amount of CH  
313 measured by XRD-Rietveld are in line with the TGA results (+/- 1 wt.%).

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Fig. 10. : a) Evolution of the amount of calcium hydroxide (CH) per g of cement and b) Evolution of CH consumed by the reaction in SSA in blended systems (g per g)

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#### 4.5 AFm and AFt phases

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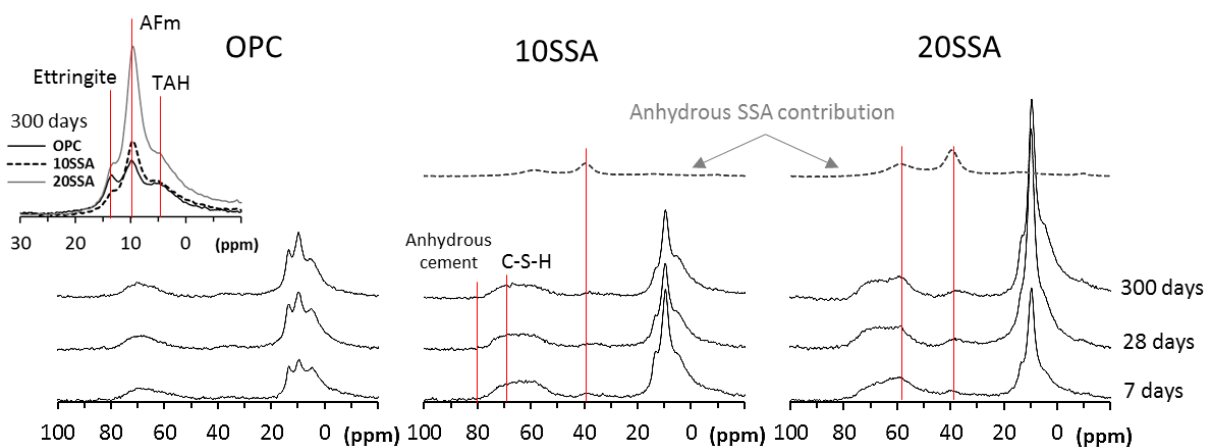
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Fig. 11 presents normalised  $^{27}\text{Al}$  MAS NMR spectra of the OPC, 10SSA and 20SSA systems hydrated for 7, 28, and 300 days. The spectra yield three distinguishable resonances between 100-50 ppm over the spectral range for the Al(IV) (i.e. Al in tetrahedral coordination). The observed peaks with centers at  $\approx 81$  ppm and  $\approx 70$  ppm are respectively assigned to Al substituting for Si in the alite/belite and the C-S-H phase [59,66,67]. On the other hand, the broadened signal with low intensity at about 58 ppm, appearing only in the blended systems, is attributed to the contribution of SSA. It is worth mentioning that the Al incorporation in C-S-H increases with the SSA inclusion and with reaction time. Moreover, the SSA displays another peak around 39 ppm, which intensity decreases for higher curing time. At lower frequencies, the chemical shift region for Al in octahedral coordination (from -10 to 20 ppm) shows three peaks which are attributed to the presence of (i) ettringite at  $\approx 13.5$  ppm, (ii) AFm phases at  $\approx 9.8$  ppm and finally (iii) unknown "Third Aluminate Hydrate" at about 5 ppm [68–70]. Even though the  $^{27}\text{Al}$  MAS NMR spectra show clearly an increase in the AFm content in the SSA-blended systems, the fine distinction between the different AFm phases is not possible [59,66,71]. In fact, the monosulfoaluminates, hemi- and monocarboaluminates have very similar chemical shift and quadrupole coupling parameters, and thus their contribution cannot be deconvoluted using the  $^{27}\text{Al}$  NMR spectra alone. Therefore, the occurrence of the AFm phases in SSA-modified pastes was further investigated using XRD.

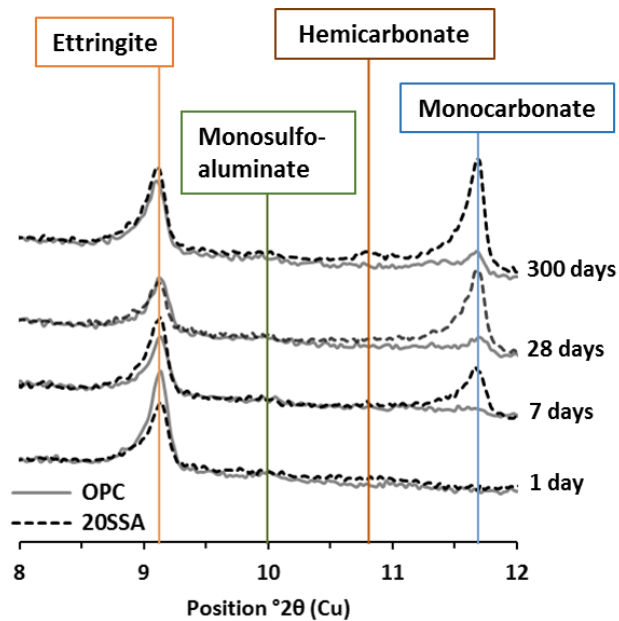


337

338 Fig. 11.  $^{27}\text{Al}$  MAS NMR spectra of hydrated OPC, 10SSA and 20SSA for 7, 28 and 300 days. In the upper left corner,  
 339  $^{27}\text{Al}$  MAS NMR spectra over a (-10)–30 ppm range, used to compare the ettringite and AFm phases contents in the  
 340 300-days hydrated systems

341 Fig. 12 displays details of the XRD diffractograms of hydrated OPC and 20SSA systems for 1,  
 342 7, 28 and 300 days. The patterns are compared over an angular range of  $8\text{--}12^\circ$   $2\theta$  ( $\text{CuK}\alpha$ ),  
 343 which allows the distinction between the various AFm phases. Overall, the identified  
 344 crystalline phases are ettringite and monocarboaluminates, which are common to both OPC  
 345 and 20SSA. Moreover, a low intensity reflection of the hemicarboaluminates is detected in  
 346 the 300 days hydrated 20SSA sample. Quantitatively, the amounts of ettringite and  
 347 monocarboaluminates in the blended system are higher than the OPC systems after 300 days  
 348 of hydration (respectively 10.9 and 11.0 vs. 8.2 and 2.8 g per g of cement). As  
 349 aforementioned, this could be explained by the aluminium content in the SSA and the initial  
 350 presence of limestone in cement. Indeed, the ettringite, formed during the reaction between  
 351  $\text{C}_3\text{A}$  and calcium sulphates, might convert to monosulfoaluminates ( $\text{C}_4\text{A}\bar{\text{S}}\text{H}_{12}$ ) upon the  
 352 depletion of free sulphate and/or the continuing supply of Al to the system. Furthermore, in  
 353 presence of calcite, the  $\text{SO}_4^{2-}$  in the interlayer of monosulfates are substituted by  $\text{CO}_3^{2-}$ , which  
 354 leads to the formation of calcium carboaluminates hydrates [57,59,72,73]. Additionally, these  
 355 observations are in line with the  $^{27}\text{Al}$  NMR results, showing the decrease of SSA signal at  
 356 about 39 ppm (i.e. dissolution of aluminium in SSA).

357



358

359 *Fig. 12. Diffraction patterns of hydrated Portland cement (OPC, full grey line) and modified cement with 20 wt.%*  
 360 *sewage sludge ash (20SSA, dotted line) at 1, 7, 28 and 300 days of hydration. The diffractograms are compared in an*  
 361 *angular window of 8–12° 2θ (CuKα), which allows the identification of AFm and AFt phases.*

#### 362 4.6 Chemically bound water content

363 The non-evaporable water content is typically used to assess the degree of reaction of the  
 364 plain Portland cements [35,74,75]. However, the interpretation of the bound water becomes  
 365 more complicated when the SCMs are incorporated in the pastes. This comes down to the  
 366 fact that SCMs and clinker phases reaction occurs simultaneously, which makes it a difficult  
 367 task to separate the contribution of each material in the measured bound water. In this study,  
 368 the non-evaporable water content of SSA-modified pastes was contrasted to a control in  
 369 order to highlight the differences in hydration process between the binders. Therefore, the  
 370 bound water was measured by thermogravimetric (mass loss at 1000 °C without the  
 371 carbonates contributions) and the results are normalised to cement content of the systems.  
 372 To accurately determine the amount of bound water, the sample was prepared as follows: the  
 373 hardened pastes were ground then immersed in isopropanol for 15 min to replace the  
 374 unbound water in the capillary pores, the isopropanol was then removed by diethyl ether and  
 375 the powders were subsequently subject to short vacuum drying to remove the residual  
 376 solvents.

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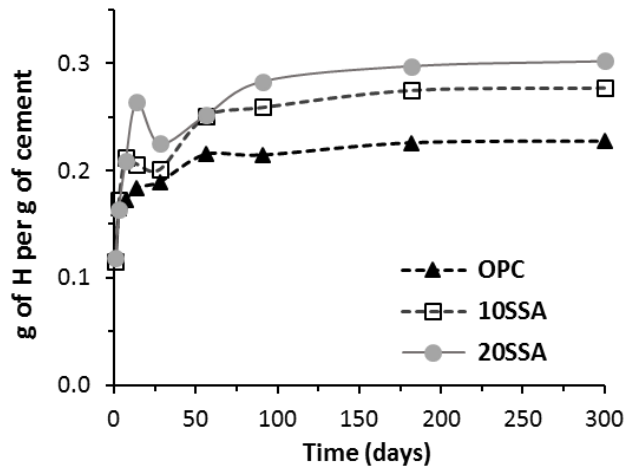
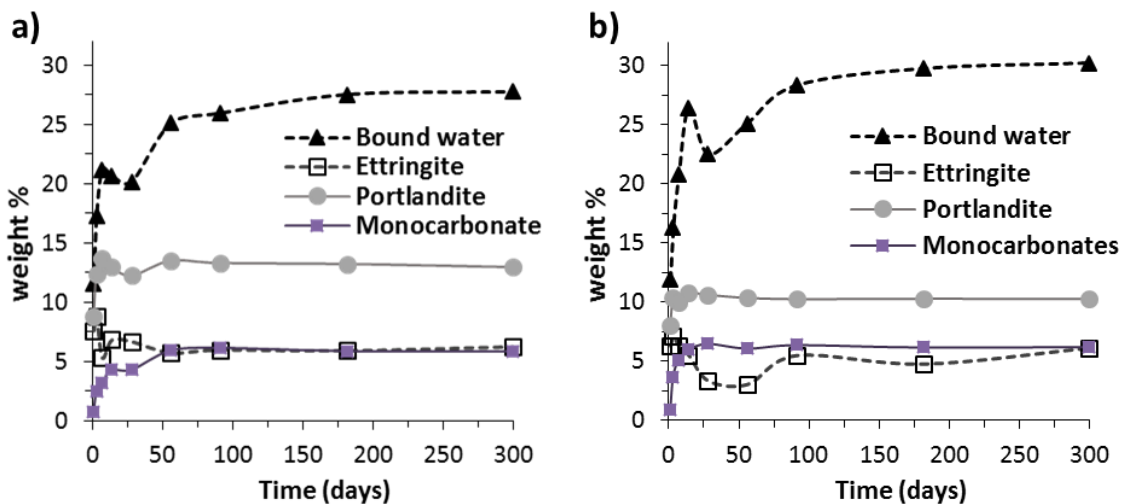


Fig. 13. Evolution of bound water content per g of cement as a function of time.

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380 Overall, the SSA blends have a slightly higher amount of bound water per g of binder.  
 381 However, the differences are more significant when the non-evaporable is reported to the  
 382 cement content, as shown in Fig. 13. It could be explained by the different type of product  
 383 formed during the hydration (e.g. monocarboaluminates) as shown by XRD/Rietveld results.  
 384 Furthermore, the SSA modified systems shows a loss in the bound water between 7 and 56  
 385 days. More interestingly, this loss coincides with the dissolution of ettringite and the  
 386 formation of the monocarboaluminates phase, as shown in Fig. 14. The ettringite content  
 387 decrease is probably related to the depletion of alumina during the formation of  
 388 monocarboaluminates, which is considered as the most stable phase. However, the  
 389 continuous supply of Al through the dissolution of SSA amorphous phase resulted in the  
 390 precipitation of ettringite after 56 days, and thus the increase of bound water.



391

392 Fig. 14. Evolution of the main phase as a function of time in the systems a) 10SSA and b) 20SSA. The ettringite and  
 393 monocarboaluminates are expressed in wt.% in hydrated sample, while the bound water and portlandite content are  
 394 normalized to the cement content.

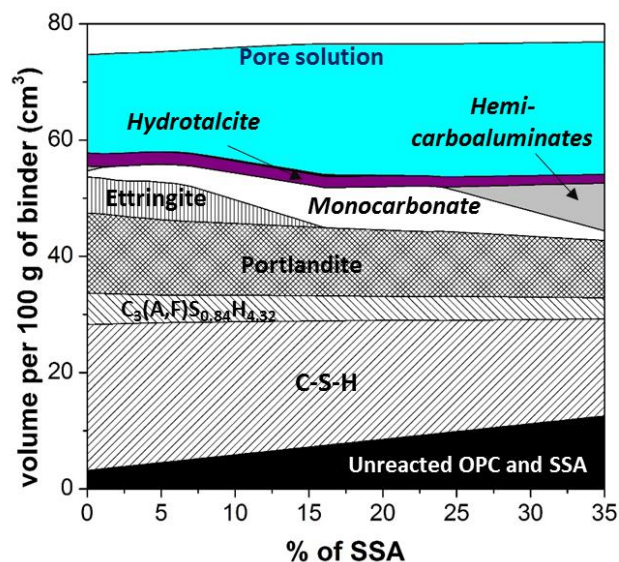
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## 397 5. DISCUSSION

398 The partial replacement of cement by SSA results in a delay in the setting time of the cement  
399 paste (around 2 hours with 20 wt.% SSA). This could be explained by the slowdown of the  $C_3S$   
400 hydration due to the adsorption of orthophosphate ions on the dissolution site of this phase.  
401 This assumption is confirmed by the XRD-Rietveld results, showing a retardation in the alite  
402 degree of reaction, particularly within the first days of hydration. Nonetheless, the overall  
403 hydration of cement seems unaffected at later age. Furthermore, the use of SSA leads to the  
404 apparition of a second peak on the heat flow curve. This heat liberation has been attributed  
405 to the formation of calcium aluminate hydrates due the continuous supply of aluminium to  
406 the system upon the dissolution of the amorphous phase of SSA. On the other hand, the  
407 majority phosphates in SSA are in form of whitlockite, a calcium phosphate mineral with a  
408 weak solubility [76], whereas the remaining amount (about 6.84 wt.%) is included in the  
409 amorphous phase. However, the dissolution of the amorphous  $P_2O_5$  is found to be very low,  
410 therefore the formation of hydroxyapatite (or other calcium phosphate compounds) is  
411 deemed unlikely.

412 The compressive strength of SSA cements surpass that of neat OPC at early age. This is  
413 because of the change in the phase assemblage, which is governed by the bulk composition  
414 of the system [59,77,78]. Indeed, the SSA contains high amount of reactive aluminium, and  
415 thus the formation of AFt and AFm phases is promoted. As confirmed by the experimental  
416 results, the ettringite and AFm phases (notably monocarboaluminates) content in SSA blends  
417 is higher than in the neat OPC system. Therefore, these modifications in the hydration  
418 products lead to changes in the total volume of solid, and thus the mechanical and durability  
419 properties. These observations are in line with the thermodynamic simulation (see Fig. 15),  
420 showing the formation of ettringite and monocarbonates, while the formation  
421 hemicarbonates instead of monocarbonates is calculated for higher replacement level. It  
422 should be noted that simulated phase assemblage here is based on the assumption that 90%  
423 of the cement has reacted whereas 50% of the amorphous phase of SSA has dissolved.  
424 Overall, the thermodynamic modelling agrees well with the experimental observations. It is  
425 also worth mentioning that the XRD patterns have revealed the simultaneous occurrence of  
426 AFt, hemi-, and monocarboaluminates in the 20SSA system at 300 days (see Fig. 12) while the  
427 model did not predict the coexistence of these phases. This could be explained by the  
428 amount of SSA assumed to dissolve (i.e. alumina introduced to the system) and/or the  
429 amount of calcite available to react (i.e. the increase of  $CO_2$  promote the formation of  
430 hemicarboaluminates over the monocarbonates).



431

432 *Fig. 15. Thermodynamic modelling of the phase assemblage as a function of the SSA addition. Only 50% of the SSA*  
 433 *amorphous phase is assumed to react.*

434 **6. CONCLUSION**

435 In this work, the influence of the partial replacement of cement by SSA on its hydration and  
 436 the phase assemblage of the cementitious matrix is investigated. The following conclusions  
 437 can be drawn according to the findings of this study:

- 438
- 439 • As evidenced by the calorimetry results, the inclusions of SSA delays to hydration of  
 440 the cement, particularly the alite, due to the presence of orthophosphate ions.
  - 441 • Even though the chemical and mineralogical composition of SSA appears to fluctuate  
 442 significantly, only the amorphous phase seems to participate in the reaction.
  - 443 • Being the most soluble element, aluminium is found to affect the amount of formed  
 444 AFt and AFm phases, notably the monocarboaluminates. These experimental  
 445 observations have been confirmed by thermodynamic modelling.
  - 446 • The enhancement of the macro-scale properties of mortars can be explained by the  
 447 changes in the solid volume, as a result of the formation of different hydrates.
  - 448 • The fraction of phosphates mobilised into solution is considered insufficient to form  
 calcium phosphates compounds.

449 Considering the reaction products and the macro-scale results, the use of SSA as a cement  
 450 component is feasible. However, further studies are still require to extend the boundaries of  
 451 knowledge concerning the long-term and durability aspects of SSA blended cements.

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