



Evaluation of municipal solid waste incineration filter cake as supplementary cementitious material

V. Caprai^{*}, K. Schollbach, M.V.A. Florea, H.J.H. Brouwers

Department of Built Environment, Eindhoven University of Technology, Eindhoven 5600 MB, the Netherlands

HIGHLIGHTS

- The presence of LDH in early hydration is observed with increasing FC content.
- The formation of LDH causes a delay in the C_3S reaction.
- The reaction degree of PC slightly rises increasing the replacement rate.
- Within 5% replacement, the FC does not negatively influence the binder properties.

ARTICLE INFO

Article history:

Received 18 January 2019

Received in revised form 27 February 2020

Accepted 20 March 2020

Keywords:

Municipal solid waste incineration filter cake

Supplementary cementitious materials

Minor additional constituent

Double layer hydroxides

Cement reaction degree

ABSTRACT

Worldwide, the incineration of household waste generates high amounts of Municipal Solid Waste Incineration (MSWI) bottom ashes (BA). In some European countries, the Filter Cake (FC) is also collected (below 0.25 mm) by the wet sieving treatment of coarse BA (4–32 mm). By using centrifugation, the presence of readily soluble contaminants in FC is decreased. In addition, for reducing the leaching of heavy metals the use of FC in combination with cement represents a valuable option, due to cement immobilization capacity and the FC appropriate particle size and chemical composition. However, to the best of the authors' knowledge, FC has not often investigated as binder replacement. Therefore, this paper addresses the suitability of FC as substitution for CEM I 52.5 R, between 1 and 20% replacement, by mass. Due to its porous structure, the FC lowers the bulk and particle density of the mixtures and increases the water demand, and widens the particle size distribution. The XRD analysis evidences the formation of layered double hydroxides (LDH) in the early stage of the reaction (1, 2, 7 days) incorporating contaminants as Cl. Kinetically, the hydration of C_3S is delayed according to the FC replacement without affecting the long-term flexural strength. Despite this, the presence of FC minimally contributes to the increase of cement reaction degree. Tested accordingly to the EN 124-57, the 28 days mortars fulfill the Dutch legislation for contaminants leaching as unshaped material, independently on the substitution rate.

© 2020 Elsevier Ltd. All rights reserved.

1. Introduction

An effective recycling method for municipal solid waste (MSW) is becoming necessary in the European Union, where only in 2014, 2530 million tons of waste have been produced by households and other economic activities [10]. The use of MSW as fuel for waste-to-energy plants has grown by 24% between 2010 and 2014, a preferential option compared to incineration without energy recovery. However, despite the risk of air, water, and soil pollution, 47% of the incinerated waste is still landfilled, in the form of incineration bottom ash (BA) [10]. To reduce the landfilling, recycling of the MSWI BA is supported in the Netherlands through the “Green

Deal” [5], which restricts the use of by-products as MSWI bottom ash to specific applications, by 2020. Additionally, a new standard is established named the Soil Quality Decree [31], which regulates the leaching of contaminants into the environment of those applications and by-products. Innovative wet separation treatments applied to the coarser BA fraction ensure low contamination and a more straightforward application of the by-product [2]. However, an additional waste stream is produced called MSWI filter cake (FC), by accumulating the finest and most contaminated particles removed from the bigger fractions. Due to the wet sieving and centrifugation applied during its collection, chlorides and sulfates concentrations in FC are lower than in dry sieved BA fines, whereas the presence of heavy metals is hardly reduced, restraining its applicability. To limit the release of those contaminants into the environment, the application of BA in combination with cement (PC) has been proposed [6,14,17,19]. The presence of cement favors the

^{*} Corresponding author.

E-mail address: v.caprai@tue.nl (V. Caprai).

immobilization of ions in the cement matrix, limiting the leaching of the contaminants into the environment [11,24].

Commonly, dry sieved BA fines (BA-S, Fig. 1) have a small particle size, wide availability and often present hydraulic or pozzolanic phases affecting the cement hydration [28] and thus facilitating their application as supplementary cementitious material (SCM). However, despite the similar chemical and physical properties of FC and BA-S [4], the wet separation of FC limits its reactivity, which is mainly exhausted in contact with the washing water or during weathering [4]. Due to the limited application of this wet sieving treatment, not much knowledge is available about the behavior of FC in combination with cement. Moreover, despite its low reactivity, FC can be used, as cement substitution within a rate of 5% wt., defined as Minor Additional Constituent (MAC) [9]. The fineness of the FC and the presence of small amounts of calcium carbonate have been reported by other studies as beneficial in the cement hydration, providing the surface for nucleation and growth of reaction products [21]. Despite this, the use of FC as SCM or as MAC has so far not been evaluated in any study. Its influence on the physical properties and reaction products of the cement as well as its impact on the binder reaction degree are unclear.

Therefore, this study presents an accurate evaluation of the potential application of FC as SCM and MAC in CEM I 52.5 R, using replacements between 1% and 20% wt. The effects of FC on the early stage of hydration (reaction kinetics and phase formation) are studied by isothermal calorimetry and X-ray Powder Diffraction (XRD). The binder reaction degree and the mechanical performances are measured until the age of 91 days, by thermogravimetric analysis and according to EN 196-1, respectively. The leaching assessment of the final products is also presented according to the Dutch Soil Quality Decree [31], performing one batch leaching tests on the granular material (EN 124-57) [13].

2. Methodology

2.1. Materials

Fig. 1 displays the production process of the filter cake (FC) used in this study. Initially, the bottom ash below 32 mm was divided

into a fine and a coarse stream, called FBA (below 4 mm) and CBA (between 4 mm and 32 mm) respectively, by dry sieving. Due to the adhesion of fine and highly contaminated particles to the core of coarser particles, a wet separation treatment was applied to the coarser BA fraction (4 mm–32 mm) for removing those residues. From the collection of those fines (side product on the washing treatment), the wet sludge was produced and further processed by using a centrifuge to remove water and lower the soluble contaminants, such as Cl^- and SO_4^{2-} . After treatment, the obtained filter cake has a moisture content (MC) of around 50% that was reduced to 28% due to outdoor storage.

CEM I 52.5 R without the addition of the standard Minor Additional Constituent (MAC) was provided by ENCI (NL) and dry mixed in the cement plant with the FC, in different replacement rates (1, 3, 5, 10, 15, 20% wt). Table 1 displays the binder mix proportion used in this study. The high Blaine surface area of CEM I 52.5 R compared to other types of cement makes it the most sensitive to the modifications in PC hydration when additives are included, and therefore it was the most suitable binder for evaluating the FC influence on the PC hydration. The mortars were made by using standard inert sand (98% SiO_2 , Norm Sand, ISO 679, EN 196-1), according to the legislation EN 196-1. The samples in the form of loose powder were named as FCn, where n indicates the replacement rate applied (%wt.), mainly used for the determination of the physical properties of the blended mixtures before hydration. The mortar samples were called PC_m (reference without FC) or FCn_m, where n is the replacement level (%), and m stands for the hydration time (days).

2.2. Methods

Firstly, FC was dried at 60 °C for 72 h, to avoid the modification of mineral phases. The PSD was measured by laser diffraction (Mastersizer 2000, Malvern). The particle density of the dry powder was tested using a Helium pycnometer (AccuPyc II 1340), while the bulk density was measured using a conventional pycnometer. The chemical composition of the by-product was determined by X-ray Fluorescence spectrometry (PANalytical Epsilon 3 range, standardless OMNIAN method), on pressed powder. The loss of ignition was evaluated by heating the samples to 1100 °C for 4 h

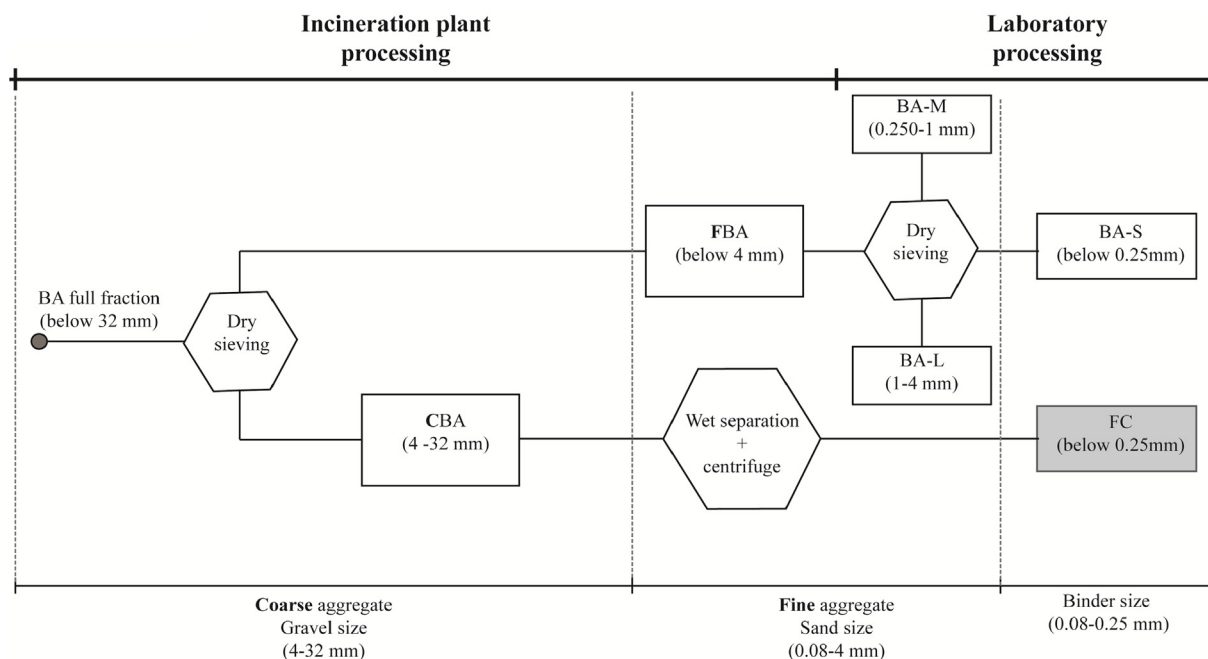


Fig. 1. Production process of MSWI filter cake.

Table 1

Mix proportions and nomenclature applied in this study.

Loose powder sample	Harden paste sample (m = curing days)	% wt*. FC	% wt*. PC
PC	PC_m	0	100
FC1	FC1_m	1	99
FC3	FC3_m	3	97
FC5	FC5_m	5	95
FC10	FC10_m	10	90
FC15	FC15_m	15	85
FC20	FC20_m	20	80

*based on the total binder mass.

and measuring the mass loss at a constant relative humidity (RH). The specific surface area and total pore volume were measured using nitrogen adsorption measurements (Micromeritics, Tristar II 3020V1.03). The water demand of the powders was determined by the Punkte test [38]. The evaluation of the metallic aluminum content was done by treatment in an alkaline environment (NaOH solution, 3 M) for 24 h [39]. Total organic content (TOC) was measured with the Behr CS30HT Coulometric carbon/sulphur analyser at 550 °C.

2.3. Mineralogical analysis

The crystalline phases in the FC and the blended pastes were identified by X-ray Powder Diffraction measurements (XRD), with a D2 (Bruker) using a Co tube, fixed divergence slits (0.2 mm) and a step size of 0.02. All the samples were ground using a pestle and mortar, and sieved below 80 µm before testing, to ensure the preservation of the mineral phases. For the blended mixtures, hydration products at 1, 2, and 7 days were evaluated after stopping hydration using 1-Propanol (Sigma-Aldrich, anhydrous, 99.7%) and subsequent oven drying at 60 °C for 24 h.

2.4. Reaction kinetics

The influence of FC on PC hydration was evaluated using Isothermal Calorimetry (TAMAIR), for the first 3 days of reaction. The samples were tested using a liquid to solid ratio (L/S) of 0.5. For assessing the impact of FC, the normalisation of the released heat was based on the mass of PC. Furthermore, all the cumulative heat curves were recorded 20 min after the beginning of the reaction to avoid any influence from the handling and stirring time and ensuring the stabilisation of the calorimetry conditions.

2.5. PC hydration degree

The cement reaction degree of the mixtures was evaluated by using thermogravimetric analysis (TGA) (Jupiter STA 449 F1, Netzsch), purged using synthetic air, by determining the mass loss caused by the decomposition of the main hydration products and carbonated phases [18,26,37]. All specimens were tested at a temperature range of 40–1100 °C at a rate of 10 °C/min. The reaction degree of the pastes was determined by chemically bonded water and portlandite content. Seven main parameters were considered: the total mass loss (w_t , between 40 and 1100 °C), the mass loss of physically and chemically bound water (w_p and w_c decomposing between 40 and 105 °C and 105–1100 °C, respectively), the mass loss of the carbonated phases (w_{C1} , 600–900 °C) and the mass loss of calcium hydroxide (w_{CH} , between 420 and 490 °C [30]). Moreover, due to the presence of volatile substances but also carbonated phases in FC (Table 2), their contribution was also quantified (Section 3.6) (w_{VS} , between 105 and 550 °C [7], and w_{C2} , 600–900 °C, respectively) and used for correction of the w_t mass loss propor-

tionally to FC content in the sample. For every time step considered, the mass of the carbonated phases not belonging to the FC was assumed as carbonated portlandite (CH), according to the reaction [22]:



Its corresponding CH mass (w_{CCH}) was determined based on the equation:

$$w_{CCH}(t) = (w_{C1}(t) - (\%FC * w_{C2})) * \frac{74.0927}{100.0869} \quad (2)$$

and added to w_{CH} to quantify the total CH of the system (w_{CHTOT}):

$$w_{CHTOT}(t) = \frac{w_{CH}(t) + w_{CCH}(t)}{\%PC} \quad (3)$$

The mass of the carbonated phases and volatile substances in FC (Table 2) is calculated based on their weight percentage in the sample (%FC). The chemically bound water (w_c) was therefore determined according to the equation:

$$w_c(t) = \frac{w_t(t) - w_p(t) - (\%FC * w_{C2}) - (\%FC * w_{VS}) + w_{CCH}(t)}{\%PC} \quad (4)$$

The w_c at any hydration time (t) is normalized for the mass percentage of the PC (%PC) in the sample, as it was assumed that reaction products were only formed by the PC hydration [26]. The analysed pastes have water to binder ratio (w/b) of 0.5, and the samples were tested after different curing times (t) (1, 7, 28, 91 days).

2.6. Mechanical performances

The mechanical performances of the mortars were tested according to EN 196-1 (EN 196-1, 2005), on prisms of 160 × 40 × 40 mm for flexural strength and on cubic specimens of 40 × 40 × 40 mm for compressive strength. The samples were demoulded after 24 h and then cured in humidified air (97% RH). Water curing was not carried out to avoid interferences with the leaching test. The final impact of the replacement on the performances of the mortars is determined by using the equation:

$$S = \frac{f_m - (f_{pc} * PC\%)}{(f_{pc} * PC\%)} * 100 \quad (5)$$

where, S (named strength coefficient) describes the influence of the FC on the strength performances of the mixtures compared to the reference sample [–], f_m is the compressive strength measured in the blended mixture (MPa), f_{pc} is the compressive strength measured for the reference sample (MPa) and the %PC is the mass percentage used in the investigated sample [% wt.].

Table 2

Physical properties of the binder (PC) and FC used in this study.

Material		FC	PC
Bulk density	g/cm ³	0.84	1.1
Particle density	g/cm ³	2.55	3.08
BET surface area	m ² /g	34.63	1.5
Water demand	% dw*	88.8	23.22
Total pore volume	cm ³ /g	0.098	–
MCI	% dw*	28	0.1
Metallic Al	% dw*	0.1	–
TOC	%dw*	5.9	–
CaCO ₃	% dw*	16.4	–

*based on the dry binder mass.

2.7. Leaching assessment

The leaching behaviour of the granular MSWI FC and the final mortars (crushed below 4 mm) were tested according to the EN 12457-2 (one-stage batch leaching test [13], under continuous shaking at 250 rpm for 24 h with liquid to solid ratio (L/S) 10 (ES SM-30, Edmund Buhler GmbH). After filtration, a part of the solutions was acidified with 0.2% HNO₃ and tested by ICP/OES for heavy metal content, according to NEN-EN 6966 [23]. The remaining suspensions were tested by ion chromatography (IC) (Thermo scientific Dionex ICS-1100) for Cl⁻ and SO₄²⁻ anions. The limit for the leaching of contaminants has been set by the Dutch Soil Quality Decree, where a column test was applied instead of the one batch leaching test. Comparability between the one batch leaching test and the column test has been established by other studies [12,29], due to the overestimation of contaminants concentration of the one batch leaching test (using the same L/S ratio). The study provides an estimation of the retention rate in the hydration products, calculating the theoretical leaching of the final product based on the leaching of the raw FC and hydrated PC paste at 28 days. The retention rate is determined using the equations:

$$R = \frac{(R_t - R_e)}{R_t} \quad (6)$$

$$R_t = (r_1 * L_{FC}) + (r_2 * L_{PC28}) \quad (7)$$

where, R_e is the effective leaching measured in the one batch leaching test, R_t is the theoretical leaching value calculated using Eq. (6), L_{FC} is the leaching of granular FC [mg/kg] (Table 5), L_{PC28} is the leaching of 28 days reference mortars in granular shape [mg/kg] (Table 5), r_n is the rate of each material in the sample [%]. A positive value for the retention rate indicates the beneficial effect of cement, as the reaction products retain pollutant into the matrix (theoretical value higher than the effective). Contrarily, a negative value corresponds to a higher concentration of pollutant in solution than the one expected (theoretical value lower than the effective), signifying the possible dissolution of phases incorporating contaminants during the hydration process.

3. Results and discussion

3.1. Materials characterization

In Table 2 a comparison of the physical properties of PC and FC is provided. FC shows a lower bulk and particle density compared to PC, in agreement with the high porous structure detected. The nitrogen adsorption measurements display that FC has a pore volume 32 times and a surface area 23 times higher than PC. These properties are mainly related to the presence of ultrafine ashes located on the core of the FC particles, denominated as “fragile zone” [40]. The poor consolidation of those ultrafine ashes on the FC core results in a contribution of the porosity of the material. The metallic Al is limited to 0.13% wt., a value which does not result in expansion behaviour during the application in mortars. FC shows a broader particle size distribution (Fig. 2) than cement since its d_{min} and d_{max} range between 0.025 mm and 0.25 mm.

The FC has an estimated content of calcium oxide around 32% wt. (from XRF, Table 3). However, most of the Ca²⁺ is not available for the reaction because it is mainly present in the form of CaCO₃ (from TGA, Table 2, and Fig. 9) and amorphous phases. Preliminary characterization of FC by EN 459-2 shows the absence of free lime in the FC studied, most likely due to the wet separation technique and weathering process. Compared to PC, FC shows a higher con-

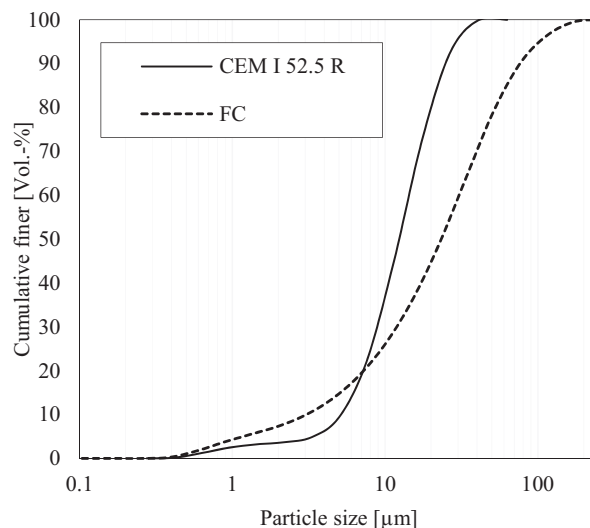


Fig. 2. Particle size distribution of CEM I 52.5 R (PC) and MSWI Filter Cake (FC).

Table 3

Bulk chemical composition (XRF) of the materials applied in this study.

Oxides	FC % wt.	PC % wt.
MgO	1.92	1.52
Al ₂ O ₃	8.84	3.88
SiO ₂	15.32	15.82
P ₂ O ₅	1.12	0.49
SO ₃	2.45	3.94
K ₂ O	0.88	0.58
CaO	32.72	68.38
TiO ₂	1.90	0.28
MnO	0.47	0.09
Fe ₂ O ₃	10.29	3.69
CuO	0.64	0.02
ZnO	1.16	0.12
Cl ⁻	0.35	0.02
Other compounds	0.54	0.29
LOI	21.4	0.99

tent of alumina (≈8% wt.) and iron oxide (≈10% wt.). The high LOI confirms the high content of carbonates as well as the content of volatile matter, remaining after incineration (TOC = 5.9, Table 2). Analysing the XRD diffraction pattern in Fig. 3, FC is characterised by different weathering products, such as calcite and gypsum. Calcite is mainly formed due to the carbonation of lime during the natural weathering, whereas gypsum is formed by the precipitation of sulphates and calcium ions during water quenching treatment [2,32]. The presence of Aft phases is often detected in the BA fine fraction treated in a wet environment [2]. However, due to its low stability, in this study the Aft decomposes during the drying procedure (60 °C, 72 h), reorganizing as gypsum/anhydrite and aluminum oxide. The presence of gypsum largely contributes to the high leaching of sulphates, during the environmental impact assessment. Alumina-containing phases are known to be present either in minerals (e.g., gehlenite and feldspar, Fig. 3) or in the amorphous phases of BA but also as aluminum hydroxides derived from the hydrolysis of metallic Al [35] or ettringite decomposition. Silica is detected in the form of quartz, but it is also present in the incineration slag, identified as gehlenite (Ca₂Al(AlSi)O₇) and feldspar. Moreover, it is known from the literature that a certain amount of silica is present as amorphous phase.

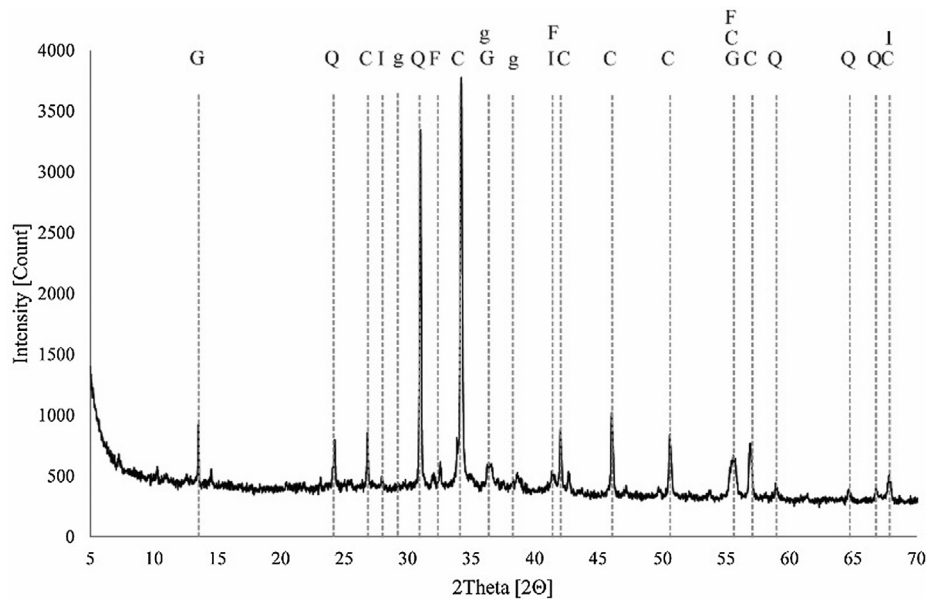


Fig. 3. XRD analysis of the FC. Q – Quartz, C – Calcite, G – Gypsum, g – Gehlenite ($\text{Ca}_2\text{Al}(\text{AlSi})\text{O}_7$), I – Iron oxide (Fe_2O_3), F – Feldspar.

3.2. Influence of the FC on the dry physical properties of the mixtures

After replacing cement with FC, the modification of the physical properties of the dry mix are measured. Although the d_{\min} is not affected, the presence of FC leads to the coarsening of the PC d_{\max} value (Table 4), which was expected based on the PSD of the raw materials (Fig. 2).

Due to its higher porosity and BET surface area (Table 2), the substitution of FC results in a drop in bulk and particle density by 11% and 8%, respectively for a maximum replacement of 20% wt. (Fig. 4a) and b)). In the MAC range (1–5% wt.), the modification of bulk density is relatively small (5% for 5% wt.). Here a minimal difference in the water demand is also observed (−0.8% for 3% wt. and +0.8% for 5% wt.), caused by the addition of coarser FC (Fig. 2 and Table 4). On the contrary, the 20% wt. replacement leads to a 10% higher water demand compared to the reference, caused by the high porosity of the FC (Table 2).

3.3. Influence of FC in the early stages of hydration

The XRD analysis in the early stages of the reaction is performed on hydrated pastes using plain PC with increasing FC replacement. The results are displayed in Fig. 5 at different ages (1, 2 and 7 days). Independently of the curing time, the reaction products of the reference are qualitatively similar to the ones including FC. Unreacted phases, such as alite (A) and belite (B) are detectable. Typical formations of ettringite and portlandite are also observed. However, depending on the replacement rate, the formation of layer double

hydroxides (LDH) is visible in early stages of hydration (Fig. 5a, b, c)). Those minerals are identified as hydrocalumite ($\text{Ca}_8\text{Al}_4(\text{OH})_24(\text{CO}_3)\text{Cl}_2(\text{H}_2\text{O})_8$, d-spacing 3.35) and calcium monocarboaluminate phases ($\text{Ca}_4\text{Al}_2\text{O}_6(\text{CO}_3)0.5(\text{OH})11.5\text{H}_2\text{O}$, d-spacing 8.11). The formation of LDH incorporating Cl^- in the presence of MSWI BA has been reported before [33]. The formation of LDHs is known to be part of the PC reaction during the first hours of hydration [27]. According to Plank et al. [27], LDHs are precursors of sulphoaluminate phases such as Aft and AFm, and therefore their presence is linked to the alumina, sulphates and calcium availability. For the analysed system, the increasing content of the FC causes a higher $\text{Al}_2\text{O}_3/\text{SO}_3$ ratio (Fig. 6), due to the lower content of SO_4^{2-} and to the higher content of alumina of FC compared to PC (Table 3). In FC aluminate phases available for reaction derive from the dissolution of aluminum hydroxides, gehlenite phases, feldspar, and amorphous incineration phases all soluble in the hydration alkaline environment [8,16]. As a result, the lower amount of SO_4^{2-} prompts to the formation of LDHs, more than additional Aft or AFm phases. The presence of those reaction products is known to be beneficial for the intercalation of inorganic anions, such as chlorides. This fact is also confirmed in this study, where some of the LDH characterized by XRD are incorporating Cl^- (hydrocalumite), and their presence is increasing in parallel with FC content. During the cement hydration, the presence of calcium monocarboaluminate is also reported by Kakali et al. [15], indicating the preferential formation of this phase compared to monosulfate in the presence of calcite. In this system, an increasing CaCO_3 amount is present due to the FC itself, as shown in Fig. 3 and Table 2 and, as for

Table 4

Characteristic sizes (d_{\min} , d_{10} , d_{50} , d_{90} , d_{\max}) of the mixtures tested in this study.

Mixture	d_{\min} μm	d_{10} μm	d_{50} μm	d_{90} μm	d_{\max} μm
PC	0.41	5.16	12.35	27.79	63.00
FC1	0.41	4.24	11.97	26.19	63.00
FC3	0.41	4.08	12.24	24.68	39.81
FC5	0.41	4.21	13.00	29.03	63.00
FC10	0.41	3.80	11.93	24.38	39.81
FC15	0.41	2.76	9.98	24.41	39.81
FC20	0.41	3.83	11.21	26.75	63.00
FC	0.41	3.1	23.4	78.5	261.50

Table 5

Environmental impact of the mortars including 5 and 20%wt. FC in CEM I 52.5 R. FC indicates the leaching of the FC as a loose powder, while PC_28 is the reference leaching value for cement mortars at 28 days. Values in bold overcome the legislation limit.

Elements	Leaching assessment values					Retention rate*	
	SQD Unshaped material mg/kg d.s.	FC mg/kg d.s.	PC_28 mg/kg d.s.	FC5_28 mg/kg d.s.	FC20_28 mg/kg d.s.	FC5_28 %	FC20_28 %
pH	–	11.3	11.7	11.8	11.5		
Antimony (Sb)	0.32	2.4	<0.10	<0.1	<0.1	53.5	82.14
Arsenic (As)	0.90	<0.3	<0.30	<0.3	<0.3	–	–
Barium (Ba)	22.00	0.4	13.80	14.7	14.1	–12.0	–26.8
Cadmium (Cd)	0.04	<0.02	<0.02	<0.02	<0.02	–	–
Chromium (Cr)	0.63	0.2	<0.02	0.2	0.3	–589.0	–435.7
Cobalt (Co)	0.54	<0.02	<0.03	0.02	0.03	32.2	–7.1
Copper (Cu)	0.90	1.3	0.2	0.13	0.28	49.0	33.3
Lead (Pb)	2.30	0.1	0.1	<0.1	<0.1	–	–
Molybdenum (Mo)	1.00	0.7	0.12	0.06	0.1	59.7	57.6
Nickel (Ni)	0.44	0.07	0.06	<0.05	<0.05	17.3	19.3
Selenium (Se)	0.15	<0.2	<0.2	<0.2	<0.2	–	–
Tin (Sn)	0.40	<0.1	<0.1	<0.1	<0.1	–	–
Vanadium (V)	1.80	<0.1	<0.1	<0.1	<0.1	–	–
Zinc (Zn)	4.50	0.4	0.05	0.08	<0.05	–18.5	58.3
Chloride (Cl)	616	2966	35.80	45.25	63.92	75.1	89.7
Sulphate (SO ₄ ²⁻)	1730	21,179	56.30	52.34	70.13	95.3	98.3

*The positive value indicates the rate of incorporation of the contaminants in the hydrated cement while a negative value corresponds to the more significant release of those ions in solution compared to what expected.

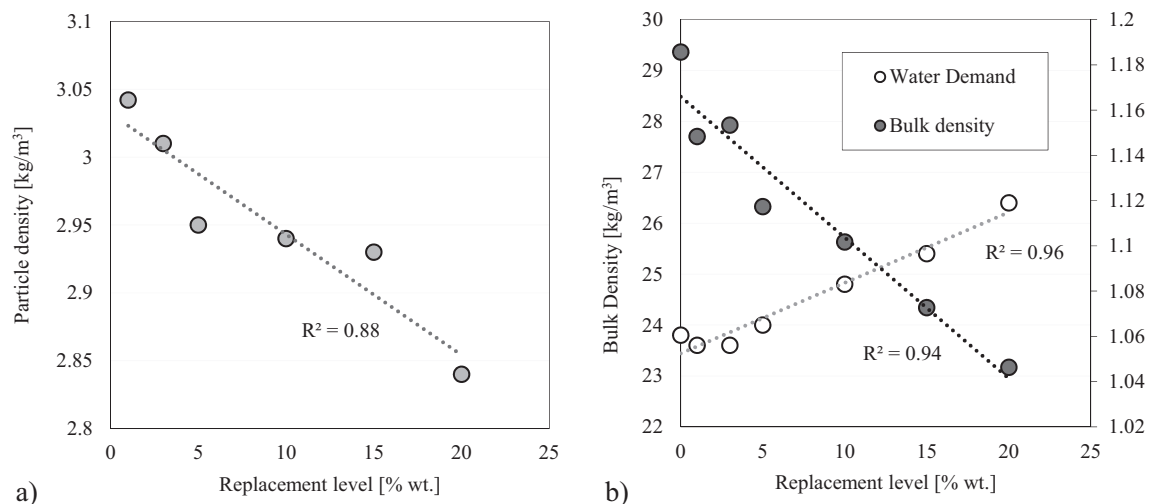


Fig. 4. Impact of FC on the physical properties of PC, for different replacement levels a) Particle density b) Bulk density and water demand.

literature, it results in the formation of monocarboaluminates rather than monosulfate phases.

3.4. Influence of the reaction kinetics

The reaction kinetic has been evaluated by isothermal calorimetry. Analyzing the normalized heat curves (Fig. 7a)), a shift in the C₃S hydration peak is observed, increasing with the replacement level. Within 5% replacement (FC5) the induction period is postponed by 30 min, while the delay reaches more than 2 h for higher substitution (FC20). Other studies have observed the same behavior in the presence of BA fines [26,34].

On the other hand, the intensity of the C₃S hydration peak is stable at $\approx 5.00 \times 10^{-3}$ W/g_{cement} independently of the replacement. This trend indicates that the main C₃S reaction is not affected by the presence of FC [3]. The presence of an extended dormant period is often related to the content of sulfates and aluminates [36]. As shown in Fig. 6 the alumina content of the blended mixtures increases with the replacement level, as well as the CaCO₃ amount, favoring the formation of LDH together with Aft phases (Fig. 5a))

[33]. Therefore, it appears that the combination of aluminates and carbonates released by the FC reaction has prolonged the induction period of PC, by the formation of LDH.

As far as the cumulative heat is concerned, an increment in the released heat is recorded in the blended pastes caused by the presence of FC. This phenomenon can be connected to the delay in the C₃S reaction visible in Fig. 7a). The available alumina uses the calcium in solution for the LDH formation, accelerating Ca²⁺ rate of diffusion [20]. Due to the extended dormant period, the higher concentration of dissolved species (Ca, Si and Al) in solution results in a higher reaction degree of PC after 3 days of reaction.

3.5. Mechanical performances

Fig. 8a) displays the spread flow of the mixtures according to the replacement levels. Due to the high surface area and pore volume of the FC, the water demand of the blended mixtures increases (Fig. 4b)). The presence of 1–5% FC causes a similar reduction in the slump ($\approx 7\%$), while a further increase in the substitution reduces the slump by 28%, compared to the reference.

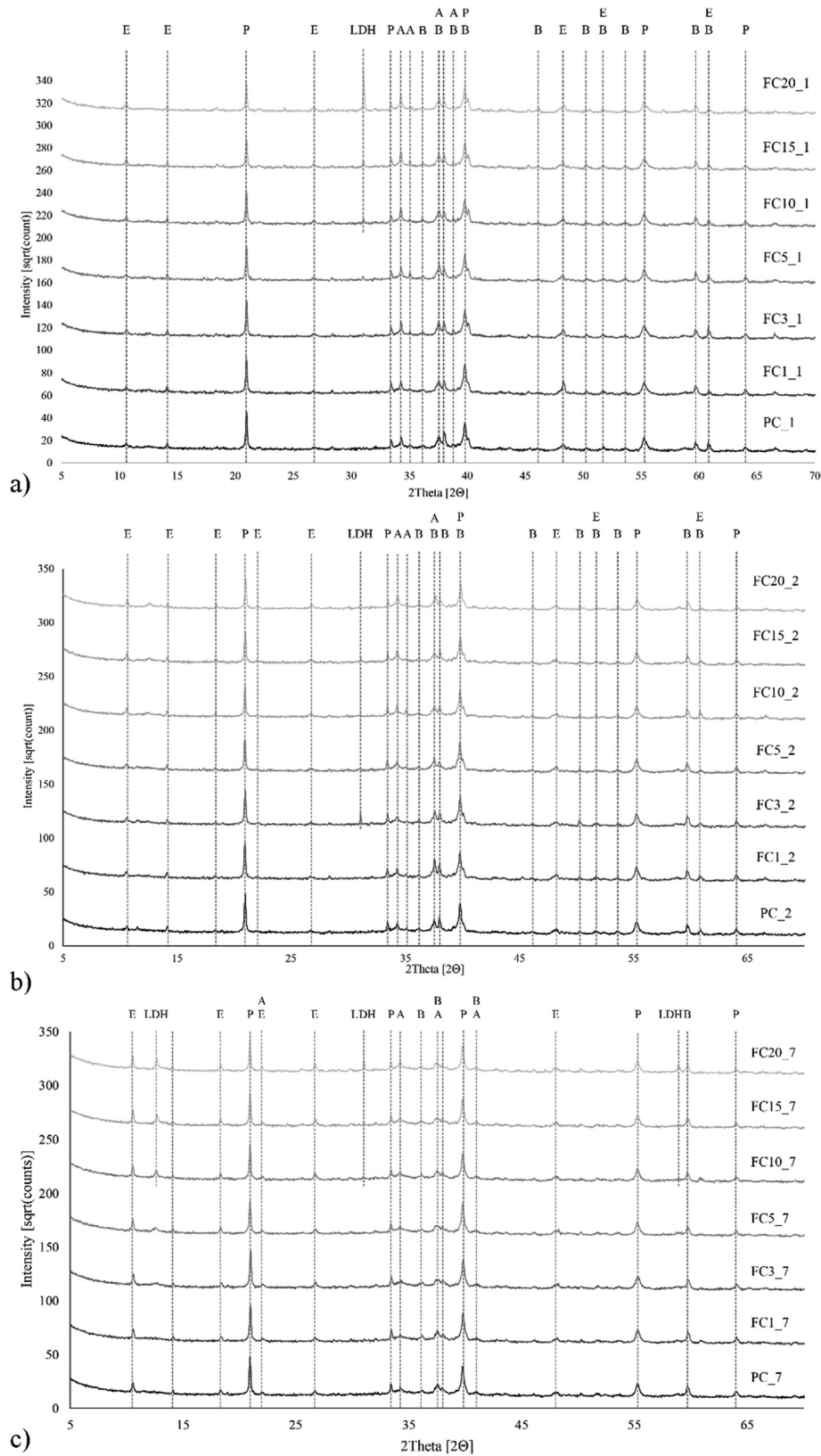


Fig. 5. XRD analysis of the mixtures including FC a) after 1-day b) 2 days and c) 7 days of reaction. A – Alite, B – Belite, E – Ettringite, P – Portlandite, LDH-layered double hydroxide.

Fig. 8b) and c) represent the flexural and compressive strength as a function of the FC replacement level. The early flexural strength (1 and 7 days) is inversely proportional to the

replacement, due to the contribution of the delay of the C_3S reaction. However, in later stages it stabilized at ≈ 4.0 MPa at 28 days and 6.5 MPa at 91 days, showing lower dependence on the

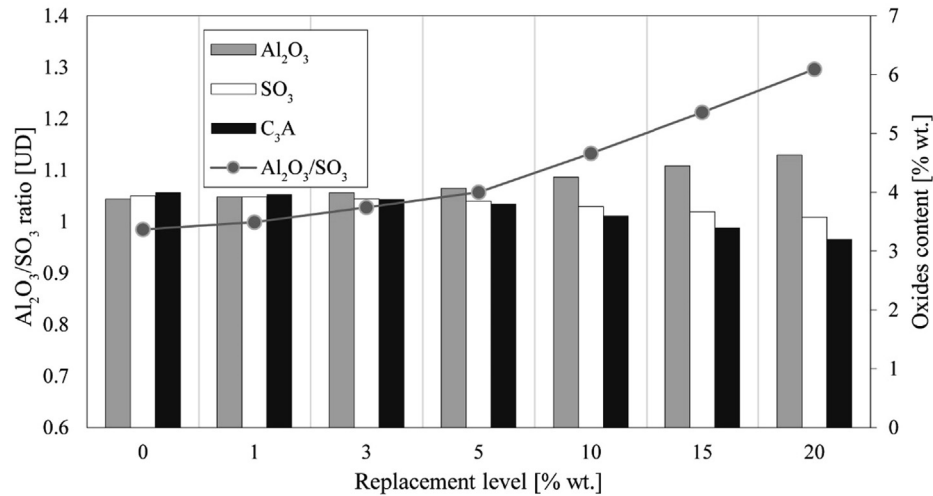


Fig. 6. Alumina, C₃A and sulphate content of the samples, as a function of the replacement level. Replacement level 0% indicates the plain reference PC.

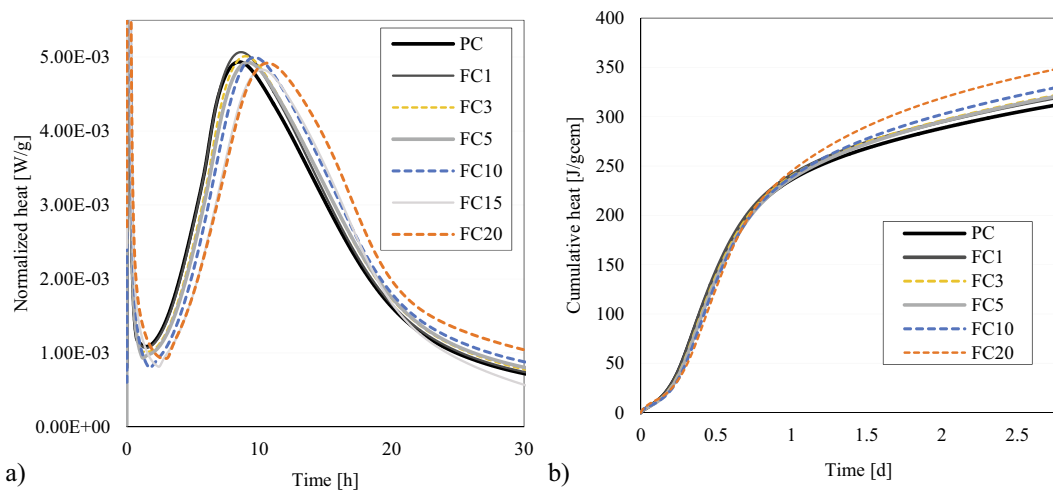


Fig. 7. a) Normalized heat of the first 30 h and b) Cumulative heat of the PC-FC mixtures including different replacement levels of FC, for a hydration period of three days.

presence of FC. The compressive strength decreases with the increase of the replacement level independently of the age. The main aspects affecting the behavior of the pastes are the porosity of the FC, and the reduction of the content of phases contributing to the strength development, such as C₃S and C₂S. Within a replacement of 5% wt. the compressive strength decreases by 9% compared to the reference sample, while for the higher replacement level (FC20) it drops up to 16%. Fig. 8d) shows the performances of the blended mixtures compared to the reference sample, by the strength coefficient *S*. The main contribution of FC (positive value of *S*) is observed at 7 days and at 91 days, where except for FC1, all the other mixtures improve the performances of the paste compared to cement. Increased compressive strength recorded at 7 days is in agreement with the higher reaction degree measured with calorimetry already at 3 days. As for the cumulative heat, the strength coefficient is improving according to the higher FC replacement, underlining a correlation between the FC content, the reaction degree and the strength of the blended mixtures. On the other hand, the higher performances at 91 days are due to the minimal pozzolanic activity of FC, developing at longer curing time. Low performances at 1 day are reflecting the delay in the C₃S reaction shown in Section 3.4 and Fig. 7a), limiting the formation of strength contributing reaction products.

3.6. Hydration degree evaluation

Analyzing the plain FC sample (Fig. 9), a total mass loss of $\approx 27\%$ wt. is recorded within 1100 °C. Between 105 and 550 °C, the decomposition of volatile substances is measured [7] ($w_{VS} = 10.97\%$ wt.). Moreover, the mass loss between 600° and 900 °C ($w_{C2} = 7.3\%$ wt.) corresponds to the thermal decomposition of carbonated phases, most of which is detected as calcium carbonate (Fig. 5). These mass losses are deducted from the chemically bonded water (w_b) calculation of the blended pastes proportionally to the FC content because they would be counted as reaction products otherwise, while they are not contributing to the hydration degree of the paste.

Fig. 10a) displays the non-evaporable water trends for the different pastes, normalized for the PC mass percentage of the sample. Compared to PC, in the early stages of reaction (1 day) the trend of chemically bonded water looks constant. For longer curing times, the presence of FC minimally affects the reaction degree of PC: the amount of chemically bound water in the samples is slightly rising with increasing FC substitution, indicating that a small amount of additional reaction products is formed in the presence of FC. Observing Fig. 10b), the presence of FC causes a reduction in the total CH mass with respect to its content, starting in the

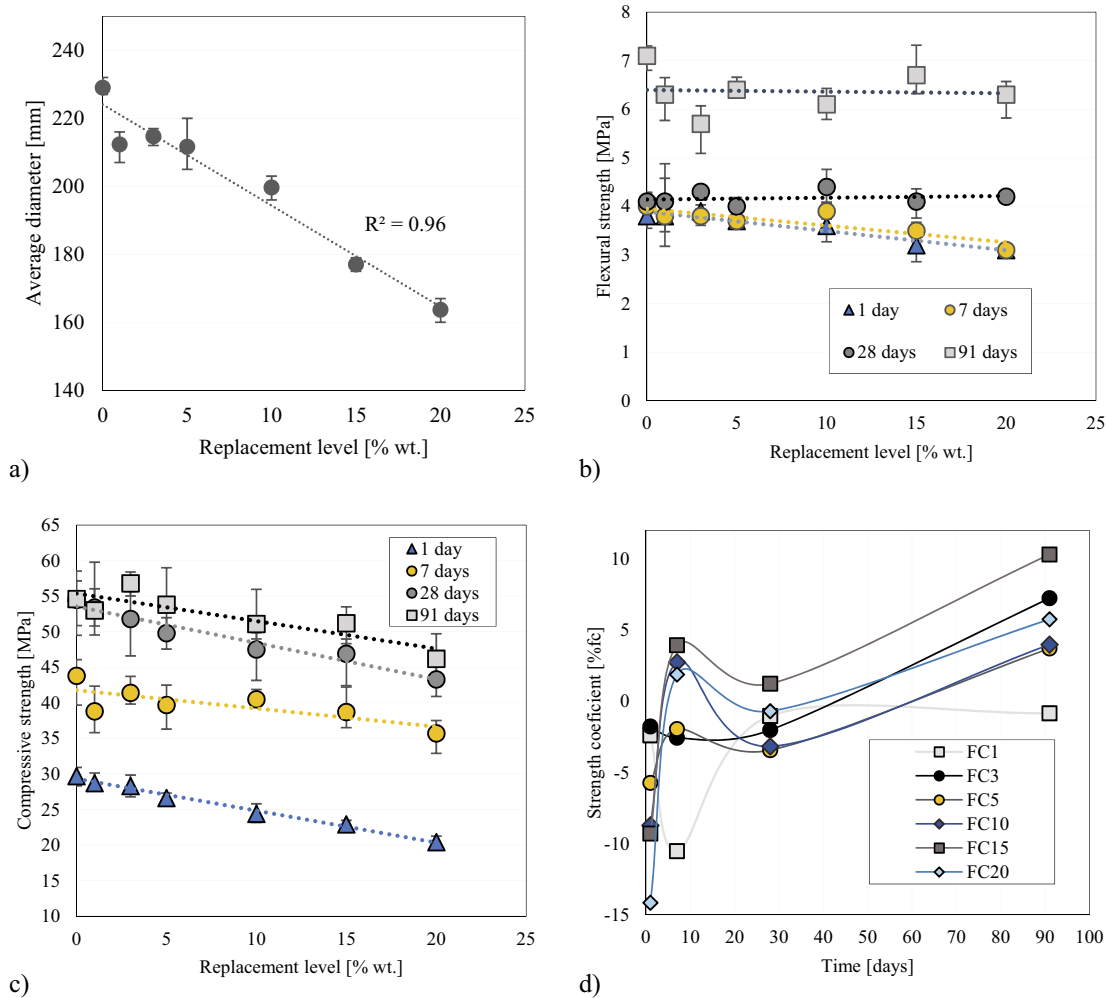


Fig. 8. a) Spread flow diameter of the mixtures, b) Flexural strength and c) Compressive strength in time as a function of the FC replacement level, d) strength factor for the blended mixtures at different curing times.

early stages of hydration. The amount of CH of the reference is, in fact, higher than in the other samples already at 1-day hydration. As shown in Section 3.3 (Fig. 5), part of the calcium ions of the system are used for the production of additional reaction products, e.g., double layer hydroxides, during the same period. Therefore, the lower content of CH in the blended systems is suspected to

be related to the lower availability of calcium ions, used for the LDH formation in early stages more than for the gel formation in later stages of hydration. This lower availability of Ca^{2+} affects the CH content for the whole hydration time (Fig. 10b). In agreement with this, the 91 days the compressive and flexural strength is not improved compared to the reference (Fig. 9b)) indicating a minimal pozzolan contribution typically to the later stages of hydration [25]. It appears that the low content of pozzolanic phases available for reaction (SiO_2 is mainly in the form of quartz, Fig. 5) does not lead to the formation of additional reaction products, e.g., C-S-H gel, and therefore is not contributing to the strength development. Additional factors such as the introduction of a more porous material, but also the lower cement phases' content caused by the substitution, might be equally responsible for the differences observed.

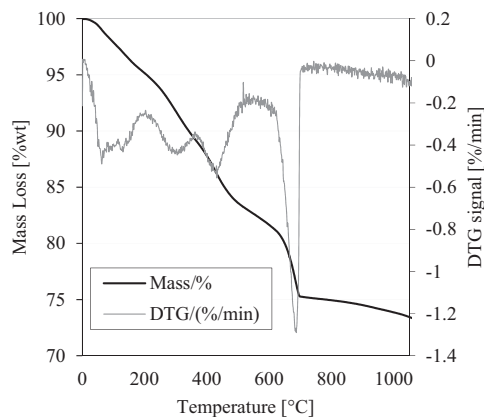


Fig. 9. TG analysis of plain filter cake, for the estimation of the organic mass loss between 105 and 550 °C.

3.7. Leaching assessment

The environmental impact is addressed by comparing the leachates concentrations to the limits imposed by the SQD (Table 5). The pure FC exceeds the limits for Cl^- and SO_4^{2-} (5 and 12 times more than the permissible level, respectively) while it minimally overcomes the concentration limit for Cu. High concentrations of Sb are also measured exceeding by 6.5 times the legislation threshold.

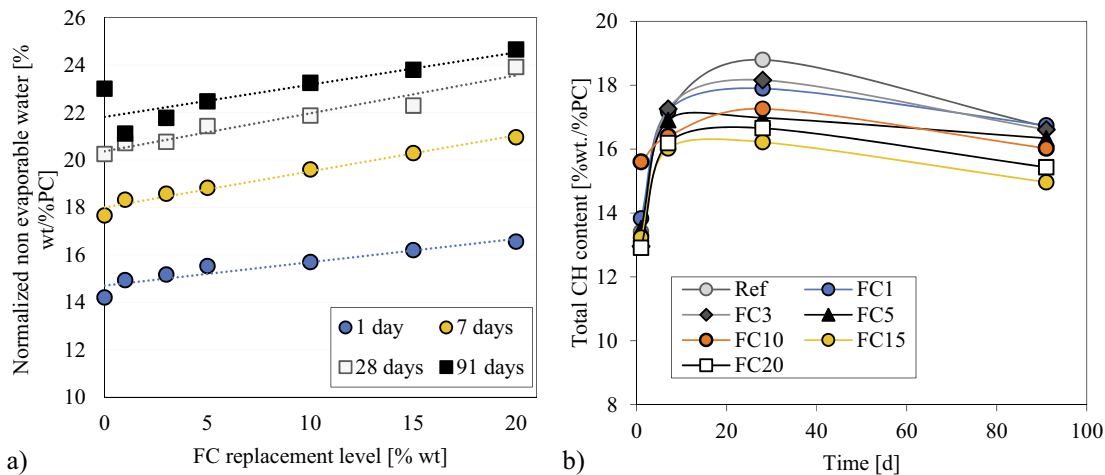


Fig. 10. Quantification of the reaction degree a) by mass loss of the chemically bonded water and b) by CH mass loss in function of the time of the pastes containing different FC amounts. The 0% represents the trend of the plain PC. Those parameters are normalized for the amount of PC in the sample since it is assumed that w_{CH} and w_b are produced by PC only [26].

Once the FC is placed in the cement paste, the leaching of those contaminants is highly reduced, either because of the dilution effect caused by the binder substitution and also due to the immobilization of part of those contaminants in the cement reaction products. Observing the retention rate in Table 5, and as shown in Fig. 5, the formation of hydrocalumite contributes to the immobilization of chlorides, for a total reduction in the Cl leaching by 56%, compared to the theoretical one. The decrease of sulfate leaching by 93% is also observed, due to their immobilization within reaction products such as ettringite (Aft) and monosulfates (AFm) [5]. Heavy metals like Cu and Sb also ranges within the 50% retention compared to the theoretical leaching. Overall, even for the highest FC replacement level (20% wt.) paste, the strict SQD legislation has been respected for all the contaminants [31].

4. Conclusions

This study evaluates the application of MSWI filter cake (FC) as supplementary cementitious material (SCM) and Minor Additional Constituent (MAC) for CEM I 52.5 R (PC). The following conclusions can be drawn:

- The use of FC within the allowed MAC substitution rate (5% wt.) does not modify the physical and mechanical properties of the mixtures. The differences measured are within 5% of the reference, which is well within the experimental error. Therefore the FC can be a suitable candidate for the application as MAC in cement production.
- With increasing FC content, physical properties are affected: the water demand increases by 11% while the particle and the bulk density are lowered for a maximum of 8% and 10% for FC20, respectively.
- In the blended systems, the higher availability of alumina provided by FC causes the formation of double layer hydroxides in the early stages of hydration. The reaction products formed include phases such as hydrocalumite and monocarboaluminate, which contribute to the retention of contaminants, incorporating chlorides.
- Kinetically, the presence of FC causes a prolonged induction period and a consequent delay in the C_3S reaction, proportional to the FC content. This behavior is mainly related to the production of LDH phases in the early stages of hydration. The maximum delay is achieved for FC20 with 2 h, while for smaller replacement such as FC5 only a 30 min retardation is observed.

- The flexural strength is stable at 28 and 91 days independently of the replacement level. On the other hand, the highest replacement level (FC20) reduces the compressive strength by 20% and 16%, at 28 and 91 days respectively.
- The blended pastes show a higher amount of non-evaporable water, indicating a slightly higher degree of reaction in the PC paste. At early stages of hydration, the CH content is lower for all pastes including FC suggesting the use of calcium ions for LDH formation instead of CH production. For the same reason, the higher amount of non-evaporable water does not lead to higher mechanical performance.
- The leaching of contaminants according to the one batch leaching test complies with the soil quality decree (SQD) independently of the replacement rate, due to the high immobilization capacity of PC also in reaction products as LDH. A complete column test is recommended, to also compare the results coming from the same methodology.

credit authorship contribution statement

V. Caprai: Conceptualization, Software, Formal analysis, Investigation, Resources, Writing - original draft. **K. Schollbach:** Conceptualization, Software, Validation, Resources, Writing - original draft. **M.V.A. Florea:** Validation, Supervision, Project administration. **H.J.H. Brouwers:** Conceptualization, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors would like to acknowledge the financial support provided by NWO domain Applied and Engineering Science, formally NWO (Nederlandse Organisatie voor Wetenschappelijk Onderzoek), the Netherlands, under the project number 13933: "Environmental concrete based on treated MSWI bottom ash." Moreover, for equipment support, the authors would like to acknowledge the group Chemical Engineering and Chemistry, Chemical Reactor Engineering, Eindhoven University of Technology.

References

- [2] Q. Alam, M.V.A. Florea, K. Schollbach, H.J.H. Brouwers, A two-stage treatment for Municipal Solid Waste Incineration (MSWI) bottom ash to remove agglomerated fine particles and leachable contaminants, *Waste Manage.* 67 (2017) 181–192, <https://doi.org/10.1016/j.wasman.2017.05.029>.
- [3] R. Alizadeh, L. Raki, J.M. Makar, J.J. Beaudoin, I. Moudrakovski, Hydration of tricalcium silicate in the presence of synthetic calcium-silicate-hydrate, *J. Mater. Chem.* 19 (2009) 7937–7946, <https://doi.org/10.1039/b910216g>.
- [4] V. Caprai, M.V.A. Florea, H.J.H. Brouwers, Evaluation of the influence of mechanical activation on physical and chemical properties of municipal solid waste incineration sludge, *J. Environ. Manage.* 1–12 (2017), <https://doi.org/10.1016/j.jenvman.2017.05.024>.
- [5] V. Caprai, K. Schollbach, H.J.H. Brouwers, Influence of hydrothermal treatment on the mechanical and environmental performances of mortars including MSWI bottom ash, *Waste Manage.* 78 (2018) 639–648, <https://doi.org/10.1016/j.wasman.2018.06.030>.
- [6] C.R. Cheeseman, A. Makinde, S. Bethanis, Properties of lightweight aggregate produced by rapid sintering of incinerator bottom ash, *Resour. Conserv. Recycl.* 43 (2005) 147–162, <https://doi.org/10.1016/j.resconrec.2004.05.004>.
- [7] J. Corton, I.S. Donnison, M. Patel, L. Bühle, E. Hodgson, M. Wachendorf, A. Bridgewater, G. Allison, M.D. Fraser, Expanding the biomass resource: sustainable oil production via fast pyrolysis of low input high diversity biomass and the potential integration of thermochemical and biological conversion routes, *Appl. Energy* 177 (2016) 852–862, <https://doi.org/10.1016/j.apenergy.2016.05.088>.
- [8] J. Davidovits, *Geopolymer Chemistry and Applications*, Institute Geopolymere, 16 rue Galilée, F-02100 Saint-Quentin, France, 2008..
- [9] EN 197-1, European standards, 2000..
- [10] Eurostat, 2017. Eurostat Statistics explained [WWW Document]. URL: https://ec.europa.eu/eurostat/statistics-explained/index.php/Waste_statistics#Total_waste_generation..
- [11] M.L.D. Gougar, B.E. Scheetz, D.M. Roy, Ettringite and C-S-H Portland cement phases for waste ion immobilization: a review, *Waste Manage.* 16 (1996) 295–303, [https://doi.org/10.1016/S0956-053X\(96\)00072-4](https://doi.org/10.1016/S0956-053X(96)00072-4).
- [12] J.L.T. Hage, E. Mulder, Preliminary assessment of three new European leaching tests, *Waste Manage.* 24 (2004) 165–172, [https://doi.org/10.1016/S0956-053X\(03\)00129-6](https://doi.org/10.1016/S0956-053X(03)00129-6).
- [13] J. Holm, J.B. Hansen, CEN EN 12457 leaching test : Comparison of test results obtained by part 1 and 2 with test results obtained by part 3 Dorthe Lærke Baun Jesper Holm Jette Bjerre Hansen Margareta Wahlström, 2003..
- [14] B. Juric, L. Hanzic, R. Ilić, N. Samec, Utilization of municipal solid waste bottom ash and recycled aggregate in concrete, *Waste Manage.* 26 (2006) 1436–1442, <https://doi.org/10.1016/j.wasman.2005.10.016>.
- [15] G. Kakali, S. Tsivilis, E. Aggeli, M. Bati, Hydration products of C 3 A, C 3 S and Portland cement in the presence of CaCO 3, *Cem. Concr. Res.* 30 (2000) 2–6, [https://doi.org/10.1016/S0008-8846\(00\)00292-1](https://doi.org/10.1016/S0008-8846(00)00292-1).
- [16] D. Kartikaningsih, Y.J. Shih, Y.H. Huang, Boron removal from boric acid wastewater by electrocoagulation using aluminum as sacrificial anode, *Sustain. Environ. Res.* 26 (2016) 150–155, <https://doi.org/10.1016/j.serj.2015.10.004>.
- [17] H.K. Kim, H.K. Lee, Use of power plant bottom ash as fine and coarse aggregates in high-strength concrete, *Constr. Build. Mater.* 25 (2011) 1115–1122, <https://doi.org/10.1016/j.conbuildmat.2010.06.065>.
- [18] V. Kocaba, E. Gallucci, K.L. Scrivener, Cement and concrete research methods for determination of degree of reaction of slag in blended cement pastes 42 (2012) 511–525..
- [19] I. Lancellotti, C. Ponzoni, M. Chiara, B. Luisa, Incinerator bottom ash and ladle slag for geopolymers preparation, *Waste Biomass Valoriz.* 5 (2014) 393–401, <https://doi.org/10.1007/s12649-014-9299-2>.
- [20] B.W. Langan, K. Weng, M.A. Ward, Effect of silica fume and fly ash on heat of hydration of Portland cement, *Cem. Concr. Res.* 32 (2002) 1045–1051, [https://doi.org/10.1016/S0008-8846\(02\)00742-1](https://doi.org/10.1016/S0008-8846(02)00742-1).
- [21] B. Lothenbach, G. Le Saout, E. Gallucci, K. Scrivener, Influence of limestone on the hydration of Portland cements, *Cem. Concr. Res.* 38 (2008) 848–860, <https://doi.org/10.1016/j.cemconres.2008.01.002>.
- [22] G. Montes-Hernandez, A. Pommerol, F. Renard, P. Beck, E. Quirico, O. Brissaud, In situ kinetic measurements of gas-solid carbonation of Ca(OH)2 by using an infrared microscope coupled to a reaction cell, *Chem. Eng. J.* 161 (2010) 250–256, <https://doi.org/10.1016/j.cej.2010.04.041>.
- [23] NEN-EN 6966, Milieu – Analyse van geselecteerde elementen in water, eluaten en destruaten – Atomaire emissiespectrometrie met inductief gekoppeld plasma, The Netherlands, 2005..
- [24] W. Nocun-Wczelik, J. Malolepszy, Studies on immobilization of heavy metals in cement paste-CSH leaching behaviour, in: *Proceeding of the International Congress on the Chemistry of Cement*, vol. 4, 1997..
- [25] A. Palomo, A. Fernández-Jiménez, G. Kovalchuk, L.M. Ordoñez, M.C. Naranjo, Opc-fly ash cementitious systems: study of gel binders produced during alkaline hydration, *J. Mater. Sci.* 42 (2007) 2958–2966, <https://doi.org/10.1007/s10853-006-0585-7>.
- [26] I. Pane, W. Hansen, Investigation of blended cement hydration by isothermal calorimetry and thermal analysis, *Cem. Concr. Res.* 35 (2005) 1155–1164, <https://doi.org/10.1016/j.cemconres.2004.10.027>.
- [27] J. Plank, D. Zhimin, H. Keller, F.v. Hössle, W. Seidl, Fundamental mechanisms for polycarboxylate intercalation into C3A hydrate phases and the role of sulfate present in cement, *Cem. Concr. Res.* 40 (2010) 45–57, <https://doi.org/10.1016/j.cemconres.2009.08.013>.
- [28] A. Poletti, R. Pomi, G. Carcani, The effect of Na and Ca salts on MSWI bottom ash activation for reuse as a pozzolanic admixture, *Resour. Conserv. Recycl.* 43 (2005) 403–418, <https://doi.org/10.1016/j.resconrec.2004.07.004>.
- [29] M.J. Quina, J.C.M. Bordado, R.M. Quinta-Ferreira, Percolation and batch leaching tests to assess release of inorganic pollutants from municipal solid waste incinerator residues, *Waste Manage.* 31 (2011) 236–245, <https://doi.org/10.1016/j.wasman.2010.10.015>.
- [30] K. Scrivener, R. Snellings, B. Lothenbach, *A practical guide to microstructural analysis of cementitious materials* edited, a practical guide to microstructural analysis of cementitious materials (2016). doi:10.7693/wl20150205..
- [31] Soil Quality Decree [WWW Document], 2015. URL: http://wetten.overheid.nl/BWBR0023085/BijlageA/geldigheidsdatum_09-10-2015..
- [32] P. Tang, Municipal solid waste incineration (MSWI) bottom ash – from waste to value (Ph.D. thesis), Eindhoven University of Technology, The Netherlands, 2017.
- [33] P. Tang, M.V.A. Florea, P. Spiesz, H.J.H. Brouwers, Application of thermally activated municipal solid waste incineration (MSWI) bottom ash fines as binder substitute, *Cem. Concr. Compos.* 70 (2016) 194–205, <https://doi.org/10.1016/j.cemconcomp.2016.03.015>.
- [34] P. Tang, M.V.A. Florea, P. Spiesz, H.J.H. Brouwers, Characteristics and application potential of municipal solid waste incineration (MSWI) bottom ashes from two waste-to-energy plants, *Constr. Build. Mater.* 83 (2015) 77–94, <https://doi.org/10.1016/j.conbuildmat.2015.02.033>.
- [35] H.-T. Teng, T.-Y. Lee, Y.-K. Chen, H.-W. Wang, G. Cao, Effect of Al(OH)3 on the hydrogen generation of aluminum–water system, *J. Power Sour.* 219 (2012) 16–21, <https://doi.org/10.1016/j.jpowsour.2012.06.077>.
- [36] L. Xu, P. Wang, G. De Schutter, G. Wu, Effect of calcium aluminate cement variety on the hydration of portland cement in blended system, *J. Wuhan Univ. Technol. Mater. Sci. Ed.* 29 (2014) 751–756, <https://doi.org/10.1007/s11595-014-0991-7>.
- [37] Q. Zeng, K. Li, T. Fen-Chong, P. Dangla, Determination of cement hydration and pozzolanic reaction extents for fly-ash cement pastes, *Constr. Build. Mater.* 27 (2012) 560–569, <https://doi.org/10.1016/j.conbuildmat.2011.07.007>.
- [38] M. Hunger, H.J.H. Brouwers, Photocatalysis applied to concrete products, *ZKG International* 62 (2) (2009).
- [39] C.B. Porciúncula, N. Marcilio, I. Tessaro et al., Production of hydrogen in the reaction between aluminum and water in the presence of NaOH and KOH, *Brazilian Journal of Chemical Engineering* 29 (2) (2012).
- [40] A. Saffarzadeh et al., Impacts of natural weathering on the transformation/neoformation processes in landfilled MSWI bottom ash: A geoenvironmental perspective, *Waste Management* 31 (12) (2011).