



Activation of Portland cement blended with high volume of fly ash using Na_2SO_4

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ABSTRACT

Increasing the replacement ratio of Portland cement clinker by supplementary cementing materials is one of the best strategies to reduce the impact of the cement and concrete industry on the environment. While fly ash is widely available particularly in developing countries where much of the construction activities are projected in the coming future, the replacement levels are limited to around 25–30% in practice owing to its low reactivity. This work studies the effect of sodium sulphate (Na_2SO_4) on the activation of Portland cement blended with 50 wt-% class F fly ash. Na_2SO_4 activation contributes to a significant strength increase both in the early and later ages. Flow table results indicate that mortar workability is improved. Mercury intrusion porosimetry after 28 days show considerable refinement of pore structure. An increase in the bound water content, cumulative heat release, ettringite content and reduction of portlandite and AFm content were measured.

1. Introduction

One of the major challenges faced by the construction industry worldwide is to cope up with its impact on the environment. Over the past several years, a great number of research has been performed on low carbon binders as an alternative for ordinary Portland cement (OPC) by partial replacement with supplementary cementitious materials (SCMs). These blended cements have been increasingly used and are presently more common than OPC. The global clinker factor (percentage of clinker in cements) is estimated to be around 77–78% and is only projected to reach around 71% by 2050 [1,2] unless new strategies are developed. The commonly used SCMs are coal combustion fly ash, ground granulated blast furnace slag (GGBFS), limestone etc. GGBFS owing to its high reactivity is permitted by the European standards for usage of 40–95% in cement (CEM III), but it is presently fully used and hence there is no potential for impacting the clinker factor.

On the other hand, only less than half of the fly ash produced globally is used in cement [3], because of its low/slow reactivity, high unburned carbon content and reduced early age performance. Although there is an increasing pressure worldwide for the reduction of coal production, major coal producers such as India and Australia are increasing their production to meet their energy demands [4,5] and there is only marginal decrease of production in the recent years from China and USA [6,7]. Together these four countries constitute to around 70% of the total coal produced around the world [8]. Increasing the replacement levels of fly ash in blended cements by enhancing its reactivity could potentially improve the global clinker factor

significantly.

In OPC-fly ash blended cements, fly ash pozzolanically reacts with $\text{Ca}(\text{OH})_2$ (portlandite) precipitated through the hydration of clinker phases. The kinetics of this reaction is primarily dependent on the alkalinity of the pore solution [9], temperature [10] and fineness of fly ash [11]. Hence different strategies were previously employed to increase the reactivity of fly ash in a blended system. Although increasing the curing temperature does contribute to a high early age strength, it is energy intensive and expensive. High temperature curing is indeed more feasible in tropical climates and precast products. Fly ash is often co-ground with clinker, but this is not desirable as the spherical shape of the particles, which contributes to the ball bearing effect and improved workability of concrete, is lost [12,13]. With increasing replacement levels of fly ash, the alkalinity of solution drops and hence there is reduced degree of hydration of fly ash [9,10].

To increase the alkalinity of blended cements, strong alkali hydroxides (NaOH and KOH) can be added [14,15]. Such additions of alkali hydroxides to blended cements with SCMs were found to increase early strength significantly. Better performances at later ages were only limited to systems with high cement replacement ratios, which fail to meet the performance standard of traditional OPC [14–16]. Although high concentrations of alkalis boost the reactivity of the SCM, it appears to negatively affect the cement hydration. There is a significant reduction in later age strength and increased porosity [17,18]. Also, high pH of NaOH/KOH solutions makes it less practical for general purposes as this imposes high risks for handling these caustic materials.

A promising alternative to alkali hydroxides is sodium sulphate

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(Na_2SO_4). Literature indicates that in blended cement systems with sodium sulphate, there is no strength reduction at later ages while there is a significant increase in the early age strength [19–21]. Potential advantages are that, compared to NaOH, sodium sulphate is much easier to handle. Sodium sulphate is pH neutral in a solution that avoids health and safety issues. Also, it has significantly lower heat release upon dissolution which makes it easier to handle. Compared to systems without alkali or with NaOH, a higher degree of hydration of the SCMs, and a higher bound water content were reported, both indicative for an overall enhanced reaction [22–24]. Moreover, addition of sodium sulphate has been found to generate lower total porosity than the addition of NaOH [16,19]. Finally, sodium sulphate has a lower economic and environmental cost when compared to the alkali hydroxides, in particular since it can be sourced as an industrial by-product.

This work intends to reaffirm the previous results and provide a deeper insight with a comprehensive experimental plan. The effect of additional sulphates on hydration and compressive strength development is further studied with addition of various amounts of gypsum. It has been previously reported that large amounts of Fe_2O_3 content in fly ash could have negative effect on hybrid systems with Na_2SO_4 [21]. In this work, a classified European siliceous fly ash with high amorphous content and moderate Fe_2O_3 content was used with an OPC cement and white cement. Different parameters such as effect of Na_2SO_4 on the strength development, mortar flow, heat release, bound water, setting time, hydration products and pore size distribution are investigated.

2. Experimental protocol

2.1. Materials

Two types of Portland cements were used in this study, OPC (CEM I 52.5) and white cement (WC, CEM II 42.5). The chemical and mineralogical compositions measured from XRF and XRD are given in Table 1. OPC has a higher C_3S content than WC while there is a large amount of calcite in WC. The high amount of calcite was also verified by TGA results. A classified siliceous European fly ash (Germany) was used in this study. This has a very high glassy content (~85% amorphous, Table 1) and a low mullite content. The particle size distributions of these materials measured by Malvern Mastersizer 2000 laser

Table 1

Oxide (XRF), mineralogical compositions (QXRD) and loss on ignition (TGA) of ordinary Portland cement (OPC), white cement (WC) and fly ash (FA) used in this study.

		OPC	WC	FA	
Oxide Composition (%)	CaO	63.4	71.4	3.5	
	SiO ₂	20.4	17.6	54.5	
	Al ₂ O ₃	4.5	3.7	26.5	
	Fe ₂ O ₃	3.9	0.3	6.6	
	SO ₃	4.6	5.1	1.3	
	MgO	1.7	1.0	2.0	
	Na ₂ O	0.1	-	1.0	
	K ₂ O	0.6	0.8	2.9	
	TiO ₂	0.5	0.1	1.1	
	ZnO	0.1	-	0.1	
	Mineralogical Composition (%)	C ₃ S M3	64.1	46.9	-
		C ₂ S beta	8.9	18.3	-
		C ₃ A cubic	5.7	3.3	-
C ₄ AF		11.7	0.6	-	
Gypsum		0.5	0.9	-	
Anhydrite		4.0	2.3	0.5	
Calcite		2.0	23.3	-	
Quartz		-	0.3	3.5	
Mullite		-	-	9.5	
Syngenite		1.7	2.1	-	
Amorphous		-	-	83.7	
Loss on Ignition (%)	20–600 °C	0.78	1.23	0.79	
	600–1000 °C	0.94	7.72	1.63	

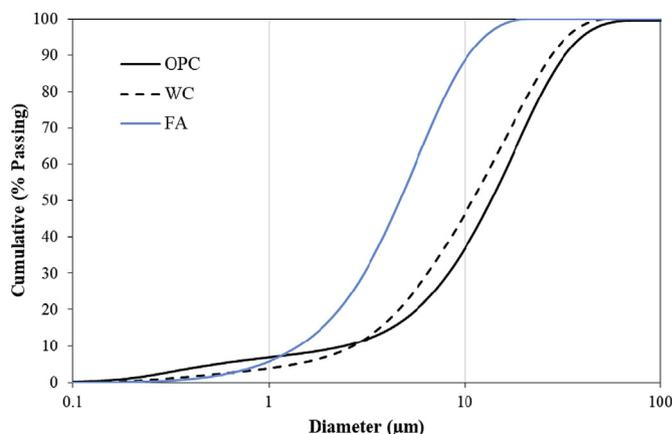


Fig. 1. Particle size distributions of ordinary Portland cement (OPC), white cement (WC) and fly ash (FA) used in this study.

diffraction are given in Fig. 1. Mean diameters (d_{50}) are 14, 11 and 4.6 μm for OPC, WC and FA respectively. The high fineness of fly ash is due to the mechanical classification used to separate particle sizes. This study also used technical grade gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and sodium sulphate (Na_2SO_4), both of which were purchased from Merck.

2.2. Experimental techniques

The flow table test on the fresh mortar and compressive strength test on the hardened mortar samples ($40 \times 40 \times 160$ mm) at 1, 7 and 28 days were performed following EN 196-1. The heat release was measured on pastes for 7 days for the most samples and 28 days for few samples using a TAMair 8 channel calorimeter. Such long measurement time with minimum heat loss was possible as the calorimeter was installed in a temperature controlled room at 20 °C. Around 10 g paste was used for each measurement, and equivalent thermal mass of water (considering the specific heat capacity) was used as reference. Thermogravimetric analysis (TGA) was performed at 1, 7 and 28 days by heating at 20–1000 °C using NETZSCH STA 409 PC at a heating rate of 10 °C/min. The bound water content was estimated as the mass loss until 600 °C and the Portlandite was determined using the tangent method [25]. X-ray diffraction was performed on Bruker D2 phaser diffractometer with Cu anode. The samples were side loaded to reduce the preferred orientation of the mineral phases. The setting of pastes was monitored using Vicomatic at 0.5 solution to binder (S/B) ratio. As the standard consistency was not used in the preparation of the pastes, this setting time shall not be termed as the standard setting time. The pore size distribution was determined after 28 days using mercury intrusion porosimetry (MIP). Elemental mapping for calcium (Ca), silicon (Si), aluminium (Al), sulphur (S) and sodium (Na) were performed using electron probe microanalyzer (EPMA, JXA-8530 F, JEOL) on polished paste samples which were embedded in resin after hydration stoppage.

2.3. Mix compositions and sample preparation

Pastes and mortars are prepared in a temperature controlled room at 20 °C using deionized water or Na_2SO_4 solution (0.75 M or 0.98 M). Pastes are prepared using an overhead mixer at 750 rpm for 2 min and mortars were prepared following the procedure described in EN 196-1 using norm sand (0–2 mm). The S/B ratio is fixed at 0.5 except for one mix which has a higher S/B of 0.55. It must be noted that the S/B ratio is used instead of water to cement (w/c) ratio in this paper. Therefore, the effective water to binder ratio of mixes containing Na_2SO_4 solution is always lower as additional solid particles are dissolved in water. The curing temperature is fixed at 20 °C.

Hydration was stopped for powder XRD and TGA using a freeze

Table 2
Composition of the mixes used in this study.

Mix ID	OPC (%)	WC (%)	FA (%)	gypsum (%)	Na ₂ SO ₄	S/B
OPC	100	-	-	-	-	0.5
OFA	50	-	50	-	-	0.5
NOFA	50	-	50	-	0.75 M	0.5
NOFA98	50	-	50	-	0.98 M	0.5
OFA30	70	-	30	-	-	0.5
NOFA60	40	-	60	-	0.75 M	0.5
NOFA0.55	50	-	50	-	0.75 M	0.55
OFA1g	49.5	-	49.5	1	-	0.5
OFA2g	49	-	49	2	-	0.5
OFA4g	48	-	48	4	-	0.5
WPC	-	100	-	-	-	0.5
WFA	-	50	50	-	-	0.5
NWFA98	-	50	50	-	0.98 M	0.5

dryer. The pastes were transferred to the freeze dryer after crushing (0.025 mbar pressure, -60 °C, 2 h). The solvent exchange technique with isopropanol [26] was used for arresting hydration and drying of samples for MIP (mercury intrusion porosimetry) and elemental mapping.

The mixes used in this study are given in Table 2 and the experimental plan is given in Table 3. OFA and NOFA indicates 50% replacement of OPC with fly ash without and with activation of Na₂SO₄ (at 0.75 M) respectively. NOFA98 indicates the molarity of Na₂SO₄ being 0.98 M. Similarly WFA and NWFA98 indicates 50% fly ash replacement with white cement, without and with activation with Na₂SO₄ at 0.98 M. OFA30 indicates 30% replacement of fly ash. OFA1g, OFA2g and OFA4g refer to OFA compositions with added gypsum (1,2 and 4% respectively). NOFA60 indicates 60% replacement of OPC with fly ash and activated with Na₂SO₄ at 0.75 M, while NOFA0.55 refers to 60% replacement of OPC with fly ash at a higher S/B ratio of 0.55.

3. Results

3.1. Compressive strength

Fig. 2 shows the compressive strength of all mixes listed in Table 2. Mix compositions to be studied more in depth were selected based on these strength results. With the increase in FA replacement ratio, there is a consistent reduction of strength till 28 days as expected. By 28 days, while OPC has a compressive strength of around 62.5 MPa, it is reduced to 47.4 and 33.2 MPa for 30% fly ash (OFA30) and 50% fly ash (OFA) respectively. On the other hand, when Na₂SO₄ is added, there is a considerable increase in the compressive strength. Mixes with 50% fly ash and 0.75 M Na₂SO₄ (NOFA) and 0.98 M Na₂SO₄ (NOFA98) had 28-day compressive strength which is marginally higher (64.6 & 65.7 MPa respectively) than that of the neat OPC mix at the same S/B ratio.

Table 3
Experimental plan for different mixes.

Mix ID	Compressive Strength & flow	Calorimetry	TGA	XRD	MIP	Vicat	EPMA
OPC	✓	28d	✓	-	✓	✓	-
OFA	✓	28d	✓	✓	✓	✓	✓
NOFA	✓	28d	✓	✓	✓	✓	✓
NOFA98	✓	7d	✓	-	✓	✓	-
OFA30	✓	-	-	-	-	-	-
NOFA60	✓	-	-	-	-	-	-
NOFA0.55	✓	-	-	-	-	-	-
OFA1g	✓	-	-	-	-	-	-
OFA2g	✓	7d	✓	-	-	-	-
OFA4g	✓	-	-	-	-	-	-
WPC	✓	7d	✓	-	✓	✓	-
WFA	✓	7d	✓	-	✓	✓	-
NWFA98	✓	7d	✓	-	✓	✓	-

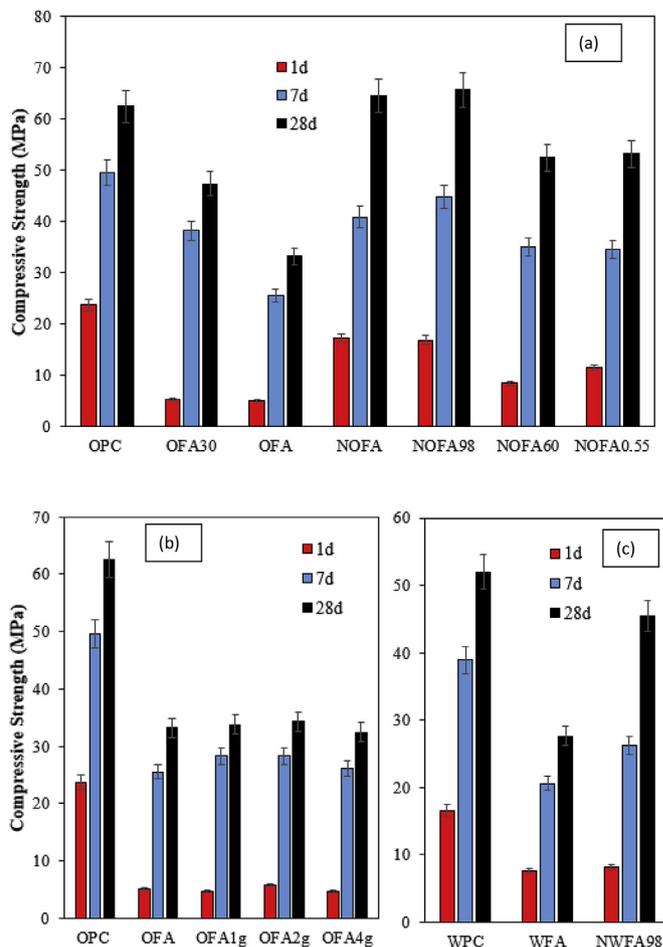


Fig. 2. Compressive strength of mixes in Table 2 at 1, 7 and 28 days.

Although the 28-day strength is higher with Na₂SO₄ solutions, the 1-day and 7-day strengths are on the lower side compared to OPC. Nevertheless, this is still higher than 30% fly ash blended cement. Even though the mix with 60% of fly ash and 0.75 M Na₂SO₄ (NOFA60) exhibits a lower strength (52.5 MPa) compared to OPC, it is still significantly higher than with 30% replacement with fly ash. With an increase in the S/B ratio, a reduction in strength is observed (NOFA0.55) but it is still higher compared to OFA or OFA30.

As previous researches have shown that the addition of calcium sulphates could also enhance the compressive strength in blended cements [22,27], the effect of added gypsum was investigated in Fig. 2 (b). Results indicate that there is no significant effect of the addition of gypsum, and maximum strength was obtained with 2% added gypsum content. This confirmed that the increase in strength in Fig. 2 (a) is not solely due to the additional sulphate content provided by Na₂SO₄. The effect of Na₂SO₄ activator was also investigated on WPC (Fig. 2 (c)). Addition of 0.98 M Na₂SO₄ with replacement 50% fly ash (NWFA98) has a lower compressive strength compared to neat WPC, but has a significant increase in compressive strength with respect to 50:50 fly ash-WPC system without addition of activator (WFA).

3.2. Flow table

Fig. 3 compares the flow diameter from flow table test (EN 196-1) for the different mixes. An increase in the flow is seen with increasing amount of fly ash content, which is expected due to the spherical shape of the fly ash particles enhancing the mortar workability due to the ball bearing effect [28]. There is a slight increase in the flow with Na₂SO₄ activator compared to the systems with the same amount of fly ash

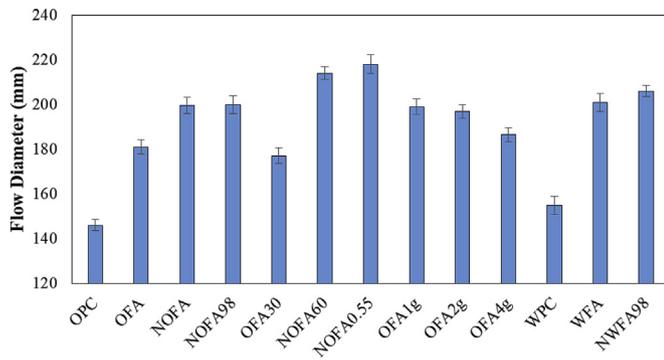


Fig. 3. Flow diameter of different mixes in Table 2.

without activator. This is particularly interesting as the water to solid ratio is lower in Na₂SO₄ systems as they have additional solids completely dissolved in water.

3.3. TGA

Fig. 4 compares the bound water content measured from TGA for different mixes at 1, 7 and 28 days. In blended cements, with Na₂SO₄ activator, there is an increase in the bound water content compared to the other blended cements. This corresponds to improved reactivity with Na₂SO₄ activator. Higher concentration of Na₂SO₄ improves the bound water content slightly. While NOFA and NOFA98 have comparable strength with respect to OPC, the total bound water content is significantly lower in systems with Na₂SO₄. Nevertheless, there is an overall good relationship between the compressive strength and bound water content (Fig. 5).

Fig. 6 compares the portlandite content measured from TGA using tangent method. OPC and WPC have the highest portlandite content. There is a slight decrease in the portlandite content from 7 days to 28 days for OPC which is attributed to experimental error. Carbonation of samples were not observed from TGA results. Compared to OFA and OFA2g, NOFA and NOFA98 indicate a higher portlandite content at 1 day and lower portlandite content by 28 days. This should be attributed to the increased hydration of the cement phases due to the activation by Na₂SO₄ during the initial days of hydration, and increased consumption of portlandite due to the pozzolanic reaction of the fly ash by 28 days. A lower amount of portlandite is also seen for NWFA compared to WFA at 28 days. The improved reactivity of fly ash with Na₂SO₄ is confirmed since a lower portlandite content and a higher bound water content are measured in these systems (Fig. 4).

3.4. Isothermal calorimetry

The heat release measured in isothermal calorimetry is shown in

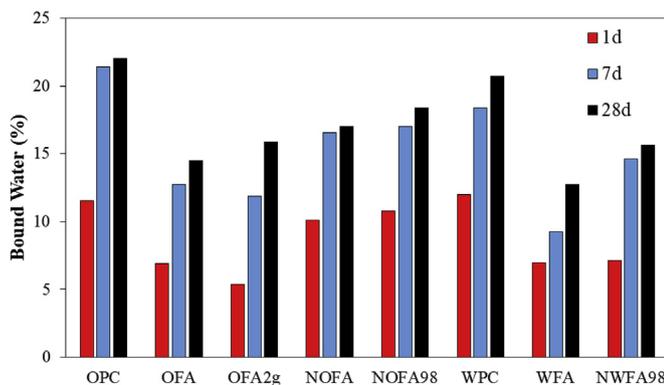


Fig. 4. Bound water content measured from TGA.

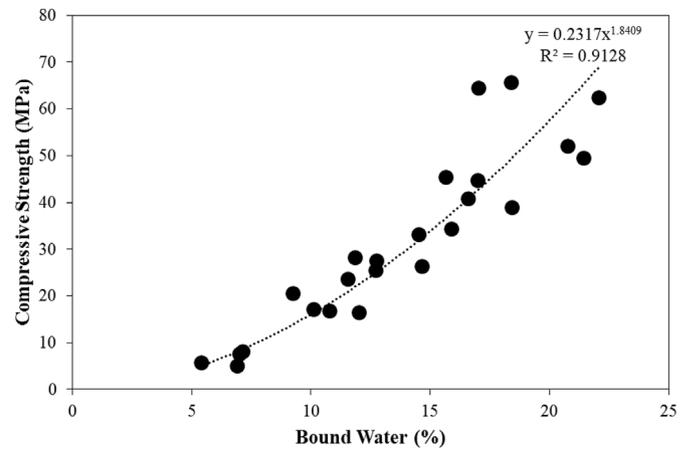


Fig. 5. Comparison of compressive strength (Fig. 2) with bound water content (Fig. 4).

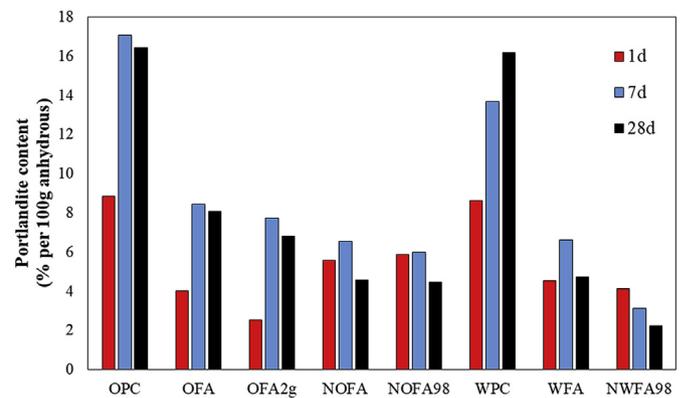


Fig. 6. Portlandite content per 100 g anhydrous from TGA using tangent method.

Fig. 7. Comparing the rate of heat release (Fig. 7 (a)), it could be seen that the induction period of NOFA and NOFA98 samples are comparable to OPC and there is an increase in the induction period for OFA and OFA2g. This increase in the induction period with the addition of fly ash is commonly reported in the literature [29,30]. There is a slight shift in the shoulder peak of OFA2g which is attributed to the delay in C₃A hydration due to increase in gypsum content. The cumulative heat release is shown in Fig. 7(b). No major deviation on the total heat release is observed with respect to NOFA and NOFA98, and between OFA and OFA2g although there is a slight increase in NOFA98 and OFA2g, which corresponds well with the results of compressive strength and TGA. While comparing the total heat release of the blended cements with and without Na₂SO₄, there appears to be a major increase in the heat with Na₂SO₄. This explains clearly the increase in strength and bound water content. Similar results could be seen for WPC as well (Fig. 7 (c) and Fig. 7 (d)). The induction period and the slope of the acceleration curve are similar for WPC and NWFA98 while there is an increase in the induction period and reduction in slope for WFA. Nevertheless, the total heat release between 24 and 48 h are similar for WFA and NWFA98. This also corresponds well with the similar compressive strength and bound water content for WFA and NWFA98. The heat release up to 28 days is further investigated for OPC, OFA and NOFA. The results show that NOFA continues to have higher heat release compared to OFA, but the difference between them slowly declines in time. OPC is consistently has a higher heat release. It should also be noted that the enthalpy of the pozzolanic reaction reported for fly ash (285 J/g [31]) is much lower than the enthalpy of reaction of OPC (~550 J/g [25]), based on enthalpy of reaction of different phases

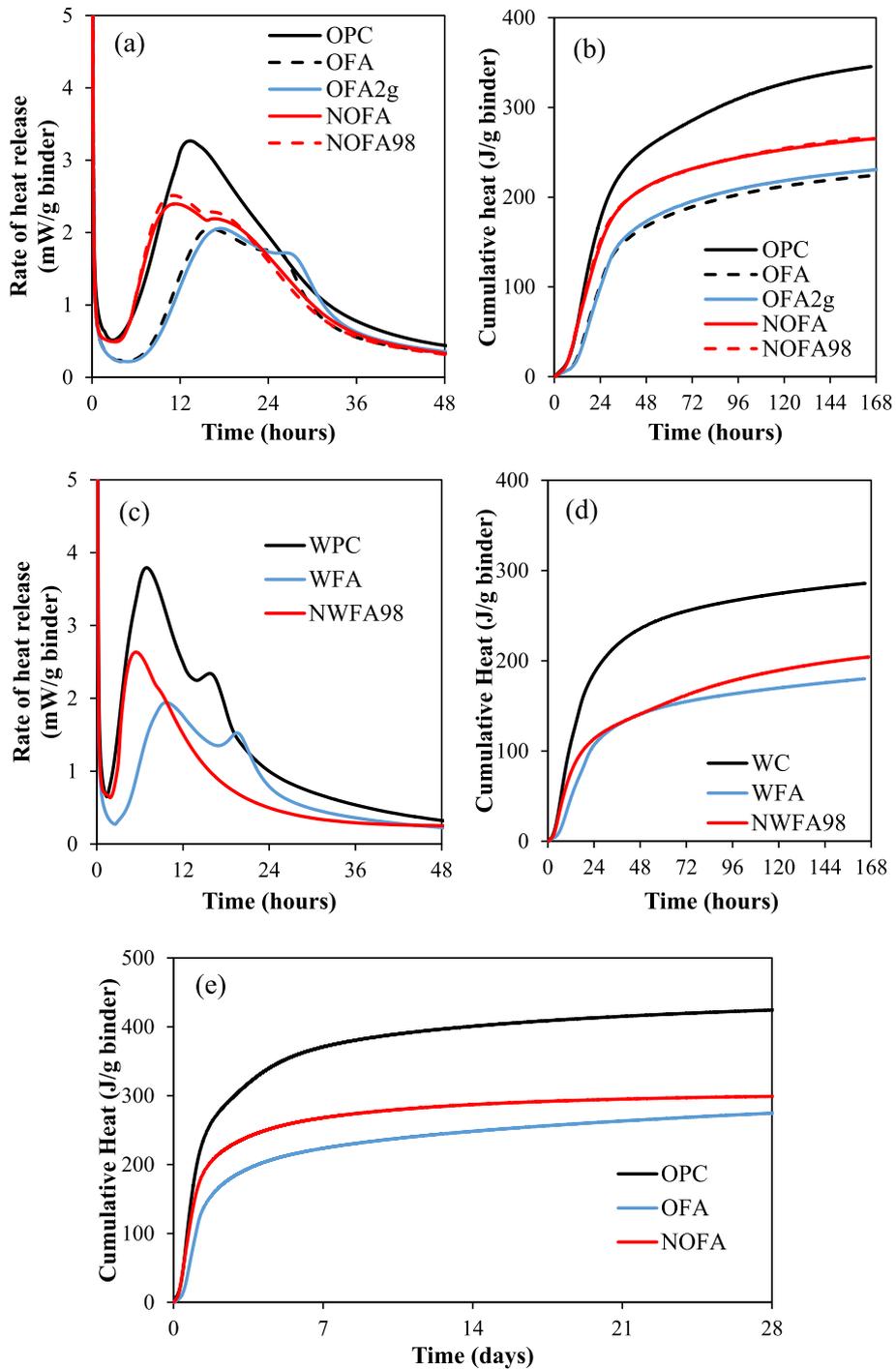


Fig. 7. Heat release from isothermal calorimeter.

and mineralogical composition).

Fig. 8 compares the cumulative heat release with compressive strength and bound water at 7 and 28 days. The results indicate that there is a good correlation between the compressive strength and cumulative heat until 7 days. The coefficients of the linear regressions are similar to those reported until 1 day of hydration [32]. On the other hand, if the 28-day strength is included, the R^2 value reduces. In this particular result (Fig. 8, b), there is only one point which stays away from the trend line, which is NOFA at 28 days. This should be attributed to the increase in degree of hydration of fly ash in NOFA after 28 days of hydration, as the enthalpy of reaction of fly ash is lower compared to that of OPC. Nevertheless, Fig. 8 (a) validates that the prediction of

compressive strength could be determined based on isothermal calorimetry for OPC-fly ash blended systems as well, till 7 days of hydration. This would imply more errors at higher ages as there would be increased reaction from fly ash and there would be other factors influencing the strength development, such as the pore structure and assemblage of hydration products. It should be further highlighted that a good correlation exists between the cumulative heat release and the bound water content. A positive intercept value of 1.61 of the linear regression equation is attributed to the omission of the heat produced in the initial 30–45 min.

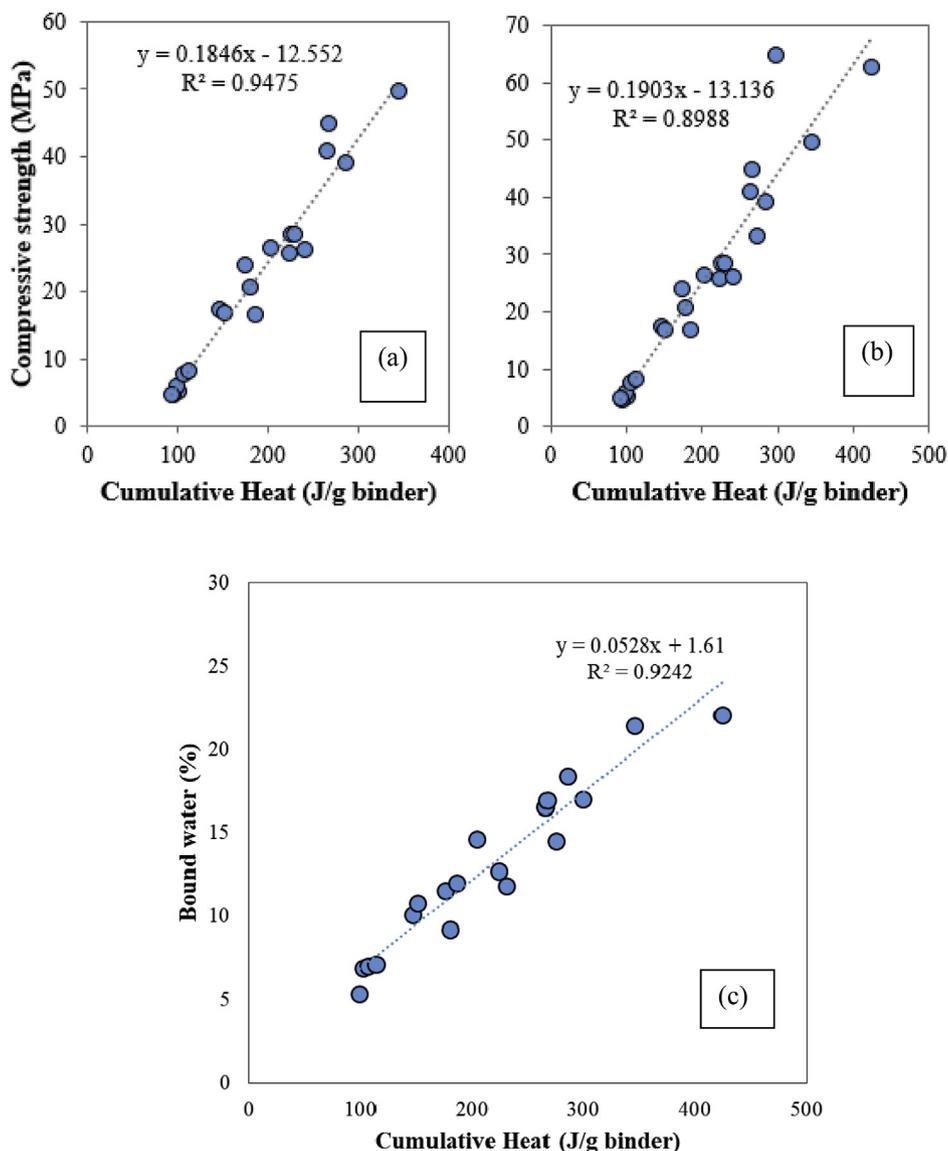


Fig. 8. Comparison of compressive strength and cumulative heat release a) until 7 days, b) until 28 days; c) - Comparison of cumulative heat with bound water content measured from TGA until 28 days.

3.5. Automatic Vicat

Fig. 9 compares the setting time measured by Vicat needle penetration for the different samples. The setting time of samples with Na_2SO_4 is similar to that of OPC, while there is an increase in the setting time of the fly ash blended cements without an activator. These results corresponds well with the calorimetry results from Fig. 7. Thus with addition of Na_2SO_4 , the increase in setting time due to the addition of fly ash is compensated. Similar results were also previously seen for hybrid systems based on Na_2SO_4 activator with very high fly ash content [22].

3.6. XRD

XRD allows us to further differentiate the hydration products in OFA and NOFA after 28 days of hydration (Fig. 10). The peaks of portlandite is lower in NOFA compared to OFA, which corresponds well with the portlandite content measured with TGA (Fig. 6). It can also be noted that the peak of ettringite is higher in NOFA at the cost of AFm phases. This is attributed to the increase in sulphate content provided by Na_2SO_4 solution. Increase in the ettringite content and reduction of

AFm phases with the addition of Na_2SO_4 was also previously reported [33].

3.7. EPMA

Fig. 11 and Fig. 12 shows the intensity normalized grayscale elemental maps of OFA and NOFA after 28 days of hydration. The normalization factor was chosen based on the concentration of these elements. Thus a higher normalization factor indicates a lower concentration and vice versa. An increase in the amount of Na and S elements is clearly visible for NOFA, which is expected due to the addition of Na_2SO_4 . The darker areas of Ca corresponds well with the brighter areas of Si and Al, which is attributed to the anhydrous fly ash. This is supported by the low amounts of Ca and high amounts of Si and Al present in the fly ash used in the study (Table 1) and also it correlates with the spherical shape of the fly ash particles.

3.8. MIP

Fig. 13 shows the pore size distribution of OPC, OFA and NOFA (Fig. 13 left) and WPC, WFA and NWFA98 (Fig. 13 right) measured

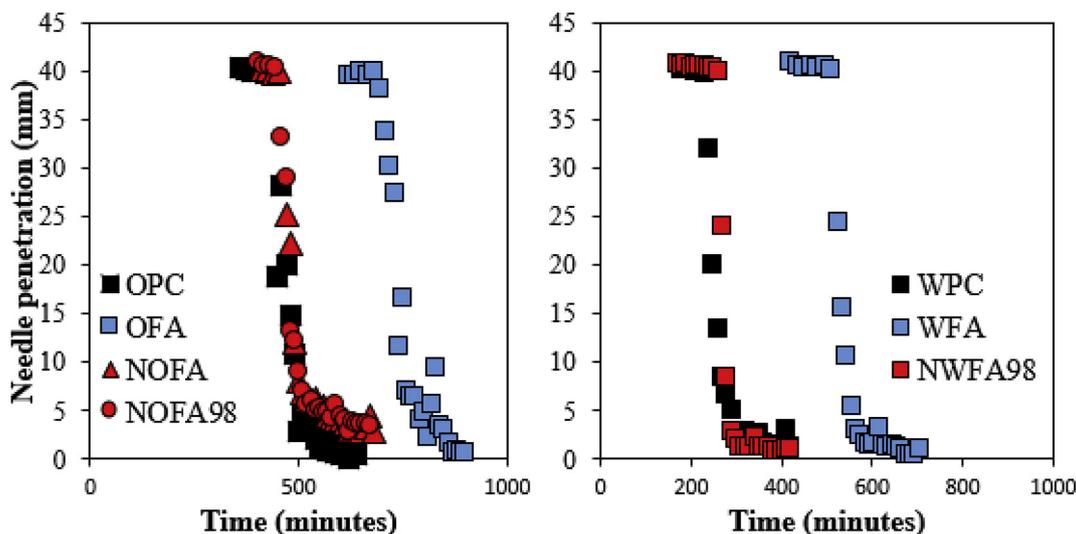


Fig. 9. Setting time of the studied compositions by means of Vicat needle penetration.

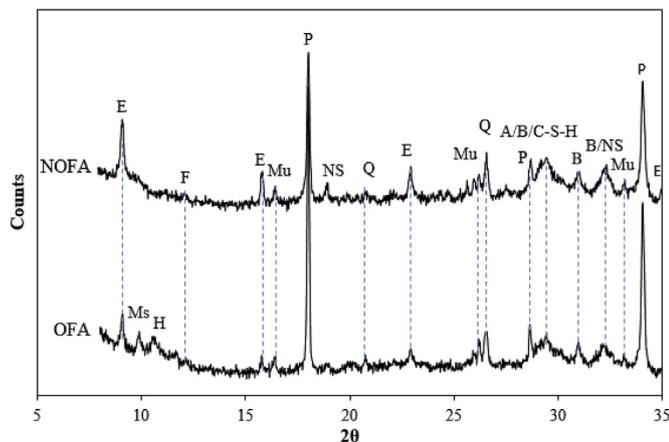


Fig. 10. XRD of OFA and NOFA after 28 days of hydration; A – Alite, B – Belite, F – Ferrite, E – Ettringite, Ms – Monosulphate, H- Hemicarbonate, Mu – Mullite, Q – Quartz, NS – Na₂SO₄, P – Portlandite.

after 28 days of hydration. NOFA has significantly lower porosity than OFA, which is even lower than the porosity of OPC. On the other hand, NWFA98 shows a lower porosity compared to WFA, while its porosity is higher compared to WPC. The pore size distributions also correspond well with the compressive strength results (Fig. 2). The lower total porosity of NOFA compared to OPC is probably due to the pore size refinement by fly ash pozzolanic reaction (beyond the limits of MIP) and due to a lower effective liquid to solid ratio.

4. Discussion

4.1. Compressive strength and influence of w/c ratio

It is well known that the w/c ratio has a significant effect on the compressive strength development as it influences the total porosity. In this work, as S/B was used in mixes with Na₂SO₄, the effective w/c ratio or w/s ratio is lower. The effective w/c ratio of NOFA is 0.45 due to the presence of dissolved Na₂SO₄ in the solution while that of OFA is 0.5. This has a positive influence on the compressive strength. Nevertheless, NOFA0.55 mix, which has an effective w/c ratio of around 0.5, still has 60% higher strength compared to OFA after 28 days of curing.

The effect of w/c ratio is not limited to the hardened properties, but also influences the fresh properties. Although the effective w/c ratio of NOFA is 0.45 compared to w/c ratio of 0.5 for OFA, the flow diameter

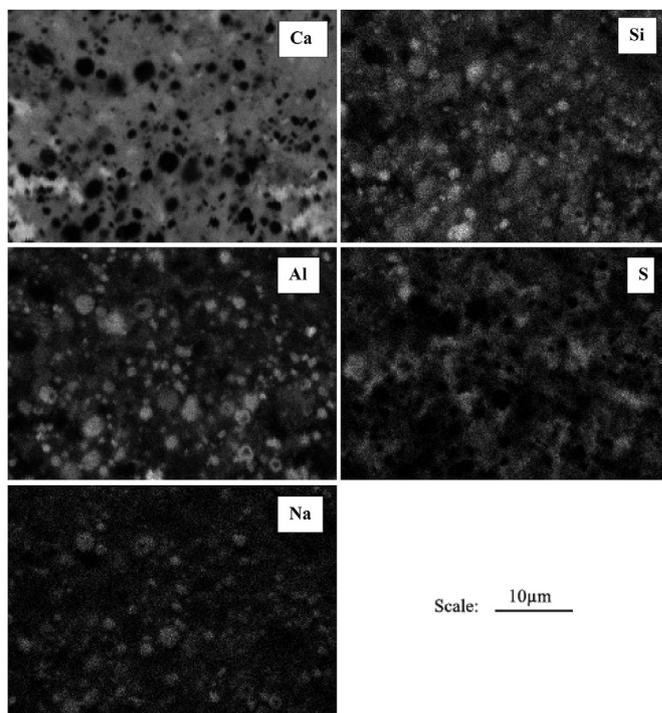


Fig. 11. Normalized grayscale maps for OFA after 28 days of hydration from EPMA. Resolution 270 × 170 pixels; Normalization factors of Elemental maps: Ca - 5, Si - 9, Al - 25, S - 35, Na - 75.

of NOFA is still on the higher side. A previous study also reported a decrease in the consistency of cement when Na₂SO₄ was added [34]. It must be noted that the S/B ratio of NOFA can be further reduced compared to OFA and OPC to achieve a similar mortar flow.

Previous study from Velandia et al. [21] reported a similar increase in strength after 28 days of curing (60–65%) for fly ashes having low Fe₂O₃ contents (4.39–4.92). They used similar proportions of 50% Portland cement and 50% fly ash, and the equivalent molarity of Na₂SO₄ was around ~0.5. On the other hand, the strength increase for fly ash with high Fe₂O₃ (9.77–10.21) content was significantly lower (12–27%). Lee et al. [19] reported a slight increase in strength (for cement blended with 40% fly ash) by 28 days with the addition of low amounts of Na₂SO₄ (0.5–1%) and a slight decrease with higher amounts (2–4%) for a fly ash which has 10.5% Fe₂O₃ content. The current work

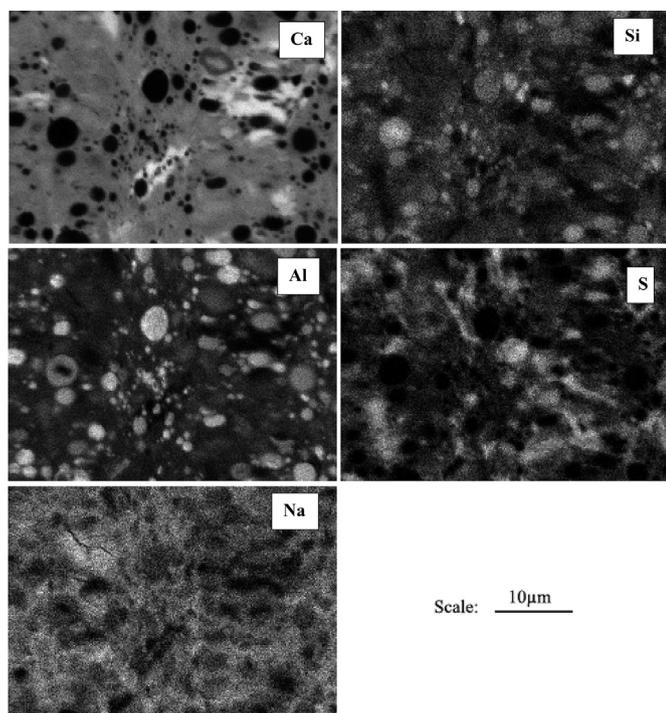


Fig. 12. Normalized grayscale maps for NOFA after 28 days of hydration from EPMA. Resolution 270 × 170 pixels; Normalization factors of Elemental maps: Ca - 5, Si - 9, Al - 25, S - 35, Na - 75.

uses a fly ash which has an Fe₂O₃ content of 6.6%. Velandia et al. [21] proposed that a negative effect could occur in activation of fly ash having high amounts of Fe₂O₃. This needs to be further investigated as Jueshi et al. [20] reported a significant increase in strength (~43%) after 28 days of curing with the addition of Na₂SO₄ at a 30% replacement level of fly ash which had 17.7% Fe₂O₃ content. It may be possible that the negative effect will only arise when iron is bound in the glassy phase of fly ash, and in the latter case, iron-oxide could be present as a separate mineral. In such case, a simple XRF technique based on determination of Fe₂O₃ might not be the appropriate technique to distinguish the fly ash which would have a positive effect in Na₂SO₄ activation.

4.2. Induction period

Isothermal calorimetry results show that (Fig. 7) there is an increase

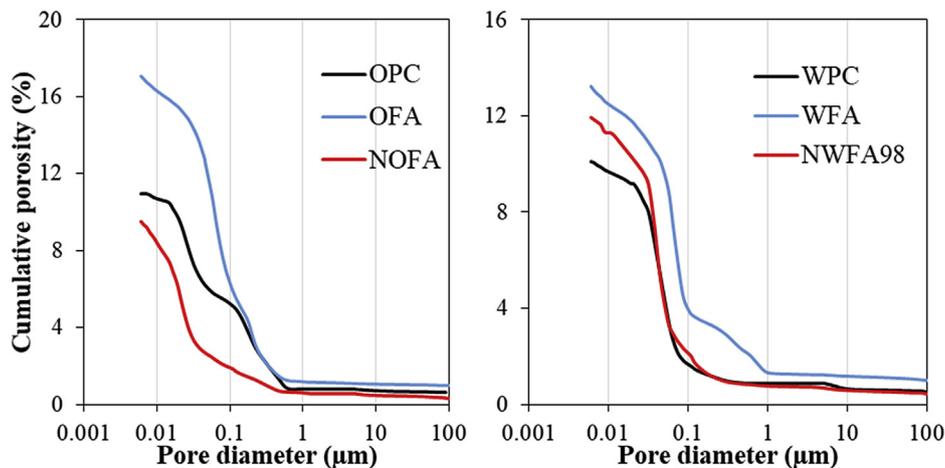


Fig. 13. Pore size distribution measured with MIP after 28 days.

in the induction period with the addition of fly ash. The effect of this increase in the induction period can be also derived from the vicat needle penetration test (Fig. 9), which indicates an increase in setting time. This increase in the induction period when Portland cement is partially replaced with fly ash, is compensated by the addition of Na₂SO₄. Fly ashes are known to increase the induction period of C₃S [35] and OPC hydration [29,36]. An increase in the effective w/c ratio for cement hydration due to the dilution effect is generally attributed to this effect [29,37]. Such retardation is not observed when OPC is replaced with inert fillers (quartz) or other SCMs (blast furnace slag, limestone etc.). Other possible explanation could be the interactions of alumina from the fly ash with alite hydration due to the chemisorption of Ca²⁺ ions on the fly ash surfaces, which would delay the precipitation of Ca(OH)₂ and C-S-H, thereby hindering the nucleation and growth process of alite hydration [36,38]. Nevertheless, the reason for this retardation is not very clear in the scientific literature.

4.3. Future perspectives

Although the studied blended systems are promising with respect to setting behaviour and strength development, a detailed testing of mechanical properties, rheological behaviour and durability properties at the concrete level needs to be further investigated. One of the crucial element is the volume stability. With the addition of Na₂SO₄, there is an increase in ettringite phase, which could lead to volume expansion. As there is an increase in the ettringite phase, and lower amounts of AFm, systems with Na₂SO₄ are expected to be more resistant to external sulphate attack as shown by the previous studies [39]. Furthermore, delayed ettringite formation when subjected to very high curing temperatures needs to be investigated.

5. Conclusion

The effect of sodium sulphate (Na₂SO₄) on the hydration of blended Portland cements with high volume of fly ash replacement is investigated. Two different Portland cements (OPC and white cement) and a classified class F fly ash were used. At 50% replacement of fly ash by cement, a considerable increase in compressive strength is achieved in the early and later ages with the addition of Na₂SO₄. The flow of mortar is higher in compositions with Na₂SO₄. Compressive strength at 28 days is even comparable to the levels of 100% OPC. Enhanced compressive strength by the addition of Na₂SO₄ is supported by an increase in the bound water content and cumulative heat release as well as significant pore size refinement. The addition of Na₂SO₄ results in a decrease in the portlandite and AFm phases but an increase in the ettringite phase.

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