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Physical performances of blended cements containing calcium aluminosilicate glass powder and limestone

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ABSTRACT

This work explores the suitability of calcium aluminosilicate (CAS) glass particles as an alternative to conventional supplementary cementitious materials (SCMs) such as fly ash and blast furnace slag. The reason for adding CAS glass particles to the cement blend is to reduce the CO_2 emission of cement production at the same level of performance. For this purpose, blended cement mortars containing 30 wt.% clinker replacement are characterized with respect to workability and mechanical performance. The results indicated that real emission reductions are possible, particularly for combinations of finely ground limestone and CAS glasses which resulted in significantly higher strengths than would be predicted from the individual contributions of each constituent.

1. Introduction

The production of Portland cement accounts for approximately 5% of the global anthropogenic CO_2 emissions [1–4]. For an efficient process ~2/3 of the CO_2 emission comes from the calcination of limestone which makes up about 80% of the raw materials. This is referred to as the "raw materials CO_2 emission" and accounts for 500–550 kg CO_2 per ton of cement clinker. The other major contributor is the "fuel-derived CO_2 emission" constituting 250–300 kg CO_2 per ton of clinker for an efficient kiln. The demand for cement, especially in developing countries, is expected to at least double by 2050 [1,4,5]. Therefore, emissions per ton of cement must be halved just to maintain the status quo. Several levers have been identified for achieving this, such as improved process efficiency, increased use of supplementary cementitious materials (SCMs), increased use of biofuels, and carbon capture and storage [4]. This paper deals with innovative SCMs based on calcium aluminosilicate (CAS) glasses and limestone. The incentive for this is that traditional SCMs such as fly ash and granulated blast furnace slag are already in short supply in some parts of the world such as Europe [1,3,6]. An important consideration in developing these new SCMs is that they must make a significant contribution to standard, early or 28 day concrete strengths since it makes little sense to lower the clinker factor by e.g. 30% if correspondingly more cement is needed to achieve a given concrete strength. In addition, the use of the new SCMs must of course provide a significant reduction in the overall CO_2 emissions associated with production of the blended cements compared to ordinary Portland cement (OPC).

Previous work by the present authors showed that CAS glasses produced from natural sources of clay, limestone and sand (CAS_{1N} and CAS_{9N} in Table 1) are pozzolanically reactive in a $Ca(OH)_2$ solution [7]. A chain-like silicate structure consistent with the C–S–H phase is detected by means of the ^{29}Si NMR and an Al containing hydration product consistent with the calcium aluminate hydrate phases formed during OPC hydration is detected by ^{27}Al NMR. The introduction of additional Na_2O into CAS_{9N} reduces the melting temperature of the glass and enhances its glass forming ability on cooling, in addition to increasing its grindability and pozzolanic reactivity [7]. In this work, the physical performance of blended mortars containing 30 wt.% clinker replacement is investigated. Blended cements containing only the CAS glasses or a combination of both glass and limestone are examined.

2. Experimental procedures

Commercially available cement containing approximately 96% clinker and 4% gypsum was used to prepare mortars for physical tests. The mineralogical composition of the clinker (Bogue) and the chemical composition of the cement are given in Tables 1 and 2. The content of free lime was measured by titration in alcohol. The preparation and characterization of the CAS glasses are described in [7]. The chemical compositions of the glasses and other SCMs are given in Table 1. Clay, limestone and sand were used as raw materials for the glass preparation. The clay was provided by Dantonit A/S, Odense, Denmark and the limestone and quartz sand were provided by Aalborg Portland A/S, Aalborg, Denmark. The subscript of the CAS

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Table 1
Chemical composition in wt.%. L.O.I. refers to the Loss On Ignition. For cement, limestone and fly ash XRF was used to determine the chemical composition. Atomic absorption spectrometry and spectrophotometry were used for the two glasses CAS_{1N} and CAS_{9N}. L.O.I. and the content of SO_3 were not determined for CAS_{1N} and CAS_{9N}.

Component	Cement	Limestone	CAS_{1N}	CAS_{9N}	Fly ash
SiO_2	19.0	4.4	53.0	51.0	55.2
Al_2O_3	5.8	0.4	13.4	12.4	24.7
Fe_2O_3	3.9	0.2	7.5	6.5	8.5
CaO	65.1	52.9	20.4	17.9	4.7
MgO	1.0	0.4	2.6	2.4	1.8
K_2O	0.4	0.1	2.1	2.0	1.6
Na_2O	0.3	<0.1	1.1	7.8	0.9
SO_3	3.7	0.1	–	–	0.6
L.O.I.	0.9	41.7	–	–	1.9

Table 3
Characteristics of the replacement materials.

Material	Surface area (m^2/kg) [a]	Mean diameter (μm) [b]
Pure cement	575	7.7
CAS_{1N}	338	16.2
CAS_{9N}	371	14.4
$CAS_{9N\text{-fine}}$	629	6.0
$CAS_{9N\text{-fiber}}$	619	6.2
Fly ash	330	20.1
Inert filler (quartz)	Diameter <90 μm	
Limestone	1288	2.7

[a] Determined by air permeability using the Blaine method.
[b] Determined by laser diffraction.

glasses refers to the molar content of Na_2O. In CAS_{9N} the Na_2O content has been increased by addition of Na_2CO_3. In industrial scale production additional alkali oxide can be introduced e.g. by recycling cement kiln dust or from albite or granite high in alkali oxide or directly as Na_2SO_4. CAS_{9N} was ground to two different finenesses and spun into fibers. For comparison the fibers were ground to the same fineness as one of the other CAS_{9N} samples (Table 3). Fibers are produced to compare the effect of using glasses with varying degrees of deviation from structural equilibrium conditions. The fibers were produced by Rockwool International A/S, Hedehusene, Denmark using the cascade spinning process, which is a type of centrifuge process drawing fibers by throwing out droplets of the melt [8].

Blended cement mortars containing 30 wt.% clinker replacement were prepared according to Table 4. For all mortars a water to cement ratio of $w/cm = 0.5$ was employed, where cm is the total content of cementitious materials including SCMs. In addition, the sand to cement ratio of the mortars was 1:3. The particle diameter of the sand in use was in the range of 0–2 mm.

The flow of the fresh mortar was measured using a flow table according to ASTM C230-80 (although tamped 20 rather than 25 times). The initial setting behavior was evaluated based on the heat of hydration during the first 18 h after preparation of the mortar using adiabatic calorimetry. Approximately 200 g of mortar was used for the measurement. Mortar prisms of $2 \times 2 \times 15$ cm^3 were made and stored in the molds for $24 \pm 1/2$ h at 20 ± 1 °C and a relative humidity of at least 95%. Hereafter the prisms were demolded and placed in water in the curing room (20 ± 1 °C) for a final hydration time of 2, 28 or 90 days. Each prism was cut in three for determination of compressive strength. The compressive strength was determined according to EN 196-1 except for the smaller prism size [9].

Thermogravimetric analyses of paste samples were performed using a simultaneous thermal analyzer (NETZSCH STA 449 C Jupiter, Selb, Germany). Three pastes were prepared: a reference containing 100% cement, a paste containing 30% limestone and a paste containing both 20% limestone and 10% CAS_{9N} fine (the sample with the largest surface area). For the pastes a water to cement ratio of $w/cm = 0.4$ was employed. For the thermal analyses 30–40 mg of ground paste was used. It was heated from 30 °C to 975 °C using a heating rate of 20 °C/min. The thermal analyses were performed immediately after the 90 days of hydration.

Powder X-ray diffraction patterns were obtained on a STOE diffractometer using capillary sample tubes. Cu–K_α radiation was employed in the range of $2\theta = 2$ to 127° with an interval of 0.015°. The generator conditions were 40 kV and 40 mA. The phases were identified by comparison with peaks from the reference samples of the International Centre for Diffraction Data database. Paste samples with $w/cm = 0.4$ were ground and investigated immediately after 90 days of hydration.

Table 2
Mineralogical composition (wt.%) of clinker.

Component	C_3S	C_2S	C_3A	C_4AF	Free lime [a]	LFS (−) [b]
Clinker	63.4	9.2	8.4	12.0	1.4	1.02

[a] The content of free lime is measured by titration in ethanol.
[b] LSF is the lime saturation factor.

3. Results and discussion

3.1. Comparison of the supplementary cementitious materials

The performance of blended cements containing the two CAS glasses is compared to that of the blended cements containing finely ground quartz, i.e., an inert material not participating in the chemical reactions, and fly ash as a traditional SCM. The glasses and fly ash were ground to similar fineness.

For all the prepared mortars (Table 4), standard mortar workability is slightly improved with increased slump on the flow table of 2–8% compared to the pure cement mix. Thus the addition of CAS glass does not increase the water demand.

Calorimetric results are shown in Fig. 1. For all blended cements the heat of hydration is lower, indicating that the clinker is replaced by a material which is less reactive during the early stages of hydration. The two glasses appear to make little or no contribution to early hydration, as similar heat development patterns are observed for the blended cements containing glass and inert filler (quartz). On

Table 4
Composition of the prepared mortars.

Material	Composition (wt.%)				$P/(P+L)$ [a]
	Cement	Pozzolan	Limestone	Inert filler	
Pure cement	100	0	0	0	–
CAS_{1N}	70	30	0	0	1.00
	70	20	10	0	0.67
	70	10	20	0	0.33
CAS_{9N}	70	30	0	0	1.00
	70	20	10	0	0.67
	70	10	20	0	0.33
$CAS_{9N\text{-fine}}$	70	30	0	0	1.00
	70	20	10	0	0.67
	70	10	20	0	0.33
$CAS_{9N\text{-fiber}}$	70	30	0	0	1.00
	70	10	20	0	0.33
Fly ash	70	30	0	0	1.00
	70	20	10	0	0.67
	70	10	20	0	0.33
Inert filler (quartz)	70	0	0	30	1.00
	70	0	10	20	0.67
	70	0	20	10	0.33
Limestone	70	0	30	0	0.00

[a] P includes both the pozzolans (CAS glass and fly ash) as well as the inert filler and L refers to limestone.

the other hand, the fly ash appears to make a significant contribution to the amount of early heat formation. The reason for this is believed to be that the finely ground fly ash acts as nucleation sites for the early alite hydration [10,11].

The strength development up to 90 days is shown in Fig. 2, normalized to the strength of the pure cement mortar ($\sigma/\sigma_{\mathrm{rel}}$). The pozzolanic reactivity of the glass and fly ash is shown by the strengths of the mortars containing these materials which is significantly higher than that of the mortar containing quartz, i.e. relative strengths of 70 to 75% at 90 days compared to 55% for the quartz. The relative strength development of the quartz containing mortars reaches a plateau already after 28 days, whereas the strength of the remaining three blended cements continues to increase up to 90 days.

Fig. 3 shows the effect of grinding the glass to a higher surface area (over 600 m^2/kg as shown in Table 3), which as expected results in a significant acceleration of strength development. At 90 days the strength in increased from 73% to 93% by means of increasing the surface area.

The CAS glasses were obtained by cooling the glass melt fast enough to avoid crystallization. The degree of disorder in the glass depends on the cooling rate. The faster the cooling rate the higher the temperature at which the structure is frozen-in, and the higher the entropy and thus the degree of disorder of the final glass. A higher degree of disorder should result in a higher degree of reactivity in the blended cement. To test this hypothesis, two glasses with different degrees of structural disorder were produced at different cooling rates. High cooling rates can be achieved by drawing thin fibers from the glass melt. In this work, discontinuous fibers with diameters of 3–15 μm were produced from the CAS_{9N} melt using the centrifugal spinning process [8] giving a cooling rate of about 10^6 K/s. In contrast, the glasses, which were cast onto a graphite plate, i.e., the normally cooled glasses, were cooled at about 10^3 K/s. The cooling rate is calculated using the procedure reported in ref. [12]. The excess energy stored in the structure of the fiber glass is about one order of magnitude larger than for the normally cooled glass (≈80 J/g vs. ≈7 J/g) [12]. The fibers were ground to a surface area comparable to the surface of the fine CAS_{9N} particles (629 m^2/kg) to compare the reactivity of the glasses. From Fig. 3, it is seen that the strength of the blended cement mortar containing the fast cooled fibers reaches 98% at 90 days compared to 93% obtained for the mortar containing normally cooled glass. The effect on reactivity of the degree of structural disorder within the glass is thus significantly less than the effect of the surface area.

4. Synergetic effect of limestone and pozzolan

In terms of volume, limestone is probably the most common clinker replacement material used today. Its role in accelerating strengths is reported to be both physical and chemical as it reacts with available alumina to form the so-called CO_2–AFm phase [6,13–17]. The quantity of limestone taking part in these reactions is however limited and reported to be in the range of a few percent to about 10%, depending among other things on the C_3A content [6,16–18]. In addition, limestone is reported to accelerate the early alite hydration [17–21]. This might compensate the reduction in early strength caused by addition of the CAS glasses (Figs. 2 and 3).

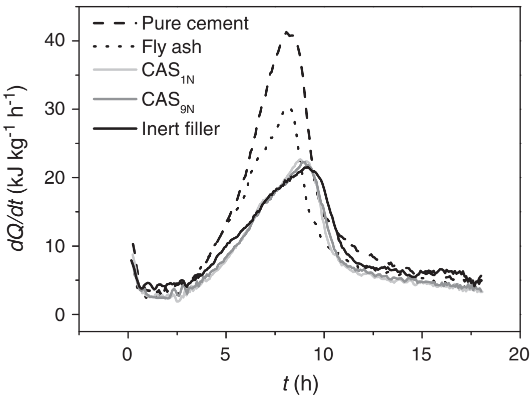

Fig. 1. The rate of heat evolution (dQ/dt) as a function of hydration time (t). The inert filler is quartz.

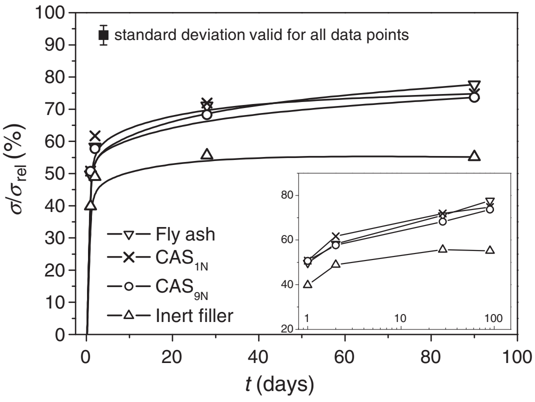

Fig. 2. Strength development of blended cement mortars containing different SCMs. The strength is given relative to the strength of pure Portland cement mortar ($\sigma/\sigma_{\mathrm{rel}}$) as a function of hydration time (t). The uncertainty associated with the experimental error of the method is given as the single standard deviation error bar. The inset shows the strength development on a logarithmic time scale.

Calorimetric results (Fig. 4) show that the early rate of heat development of the Portland limestone cement is intermediate between the pure cement reference and the sample containing 30% CAS glass. This could be due to the acceleration of C_3S hydration in the presence of $CaCO_3$. Heat development in the sample containing both limestone and glass is faster than the sample containing 30% glass, but slower than the sample containing 30% limestone. The total early heat formed in this blend is higher than in the limestone or glass blends on their own. We have no immediate explanation for this. Since it is unlikely that significant carboaluminate reaction would occur so early, increased alite hydration from heterogeneous nucleation must somehow be involved. It is however worthy noting that the heat of hydration for the ternary blend is higher than what would be expected from a simple sum according to the content of each component.

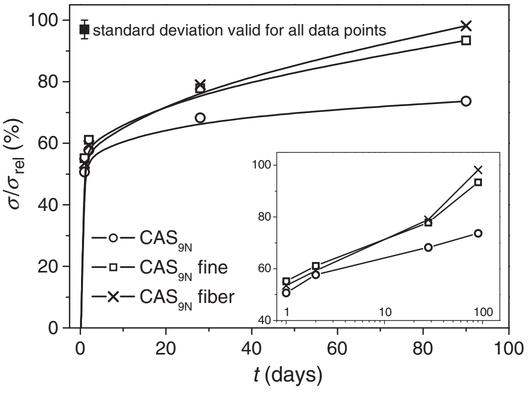

Fig. 3. Strength development of blended cement mortars containing CAS_{9N} with varying surface area and excess internal energy. The strength is given relative to the strength of pure Portland cement mortar ($\sigma/\sigma_{\mathrm{rel}}$) as a function of hydration time (t). The surface areas of the samples are: CAS_{9N} (371 m^2/kg), CAS_{9N} fine (629 m^2/kg) and CAS_{9N} fiber (619 m^2/kg). The uncertainty associated with the experimental error of the method is given as the single standard deviation error bar. The inset shows the strength development on a logarithmic time scale.

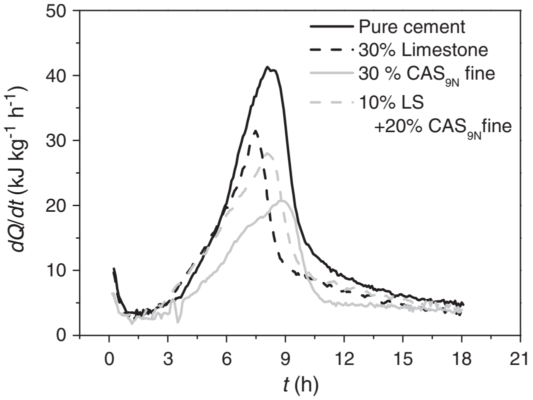

Fig. 4. The rate of heat evolution (dQ/dt) as a function of time (t) for the limestone containing mortars. LS refers to the limestone.

Fig. 5 shows the compressive strengths of the mortars as a function of the $P/(P+L)$ ratio. After 1 day hydration the strength of the limestone containing mortar has reached 66% relative to the pure cement reference. This is significantly higher than the 1 day strength obtained for blended cements containing either CAS glass or fly ash (Fig. 5). This is probably the result of increased hydration of the alite by heterogeneous nucleation of C–S–H on the fine limestone particles described in the literature [18,19,21]. For the ternary blends containing both pozzolan (fly ash or CAS glass) and limestone or inert filler and limestone the 1 day strengths can roughly be estimated from the content of each component. Thus, limestone can, to some extent, compensate for the reduced early strength of the blended cements containing CAS glass.

After 90 days hydration a significant synergetic effect is observed on the samples containing both limestone and CAS_{9N}, i.e., they exhibit significantly higher strengths than would be predicted from the individual contributions of each component (Fig. 5). Furthermore, the strength of the ternary blends exceeds that of the blended cements containing limestone as the only cement additive. Increased surface area significantly increases the strength development (Fig. 6) and for the mortars containing 20% $CAS_{9N\text{-fine}}$ and 10% limestone, the 90 days compressive strength even exceeds that of the pure cement. An effect of increasing the amount of energy stored in the glass during production is not observed for the blended cements containing both glass and limestone.

Fig. 7 shows the X-ray diffractograms of the three blended cements hydrated for 90 days. This validates the formation of monocarbonate in the samples containing limestone. Significant amounts of unreacted calcite are also indentified in these samples. This confirms that just a fraction or the carbonate is reacting chemically with available alumina forming the calcium monocarboaluminate [17,18,21–23]. Portlandite, ettringite and C–S–H are furthermore identified in all samples and monosulfate is found in the two-component blends containing either 30% CAS glass or 30% limestone. Thus the addition of CAS glass does not alter the hydration phase assemblage relative to the assemblage normally formed during hydration of ordinary Portland cement [6].

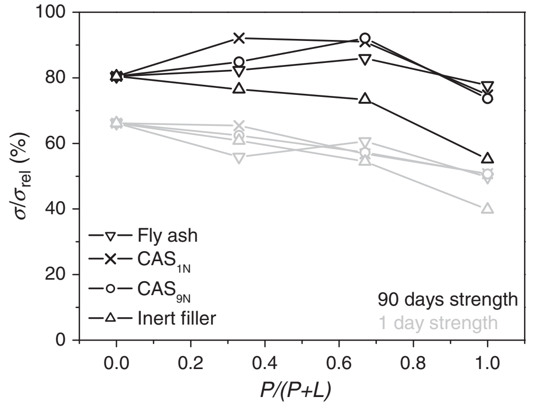

Fig. 5. Relative compressive strength (σ/σ_{rel}) of the mortars containing different SCMs as a function of $P/(P+L)$. P is the content of pozzolan (including the inert filler) and L is the content of limestone both in wt.%.

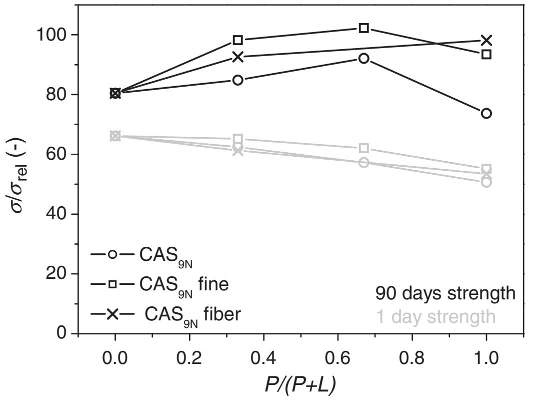

Fig. 6. Relative compressive strength of blended cement mortars containing CAS_{9N} with varying surface area and excess internal energy as a function of $P/(P+L)$. The strength is given in percentage relative to the strength of pure Portland cement mortar (σ/σ_{rel}). The surface areas of the samples are: CAS_{9N} (371 m^2/kg), CAS_{9N} fine (629 m^2/kg) and CAS_{9N} fiber (619 m^2/kg). P is the content of pozzolan (including the inert filler) and L is the content of limestone in wt.%.

The formation of hydration phases after 90 days is also investigated using thermal gravimetric analysis on paste samples (Fig. 8). The mass loss in the temperature range up to ~300 °C corresponds to the loss of water both from pore solution and from the different calcium silicate and calcium aluminate hydrate phases formed in the paste. In the temperature range of 440–540 °C $Ca(OH)_2$ is decomposed to CaO and water giving rise to the second mass loss. For the samples containing limestone a significant mass loss is furthermore observed in the temperature range of ~700–810 °C. This corresponds to the decarbonation of $CaCO_3$. From the observed mass loss the content of non-reacted $CaCO_3$ can be determined. The latter is used to calculate the degree of limestone reactivity. For the Portland limestone cement containing 30% limestone the degree of limestone reactivity is ~9%, whereas it is increases to ~16% as both limestone and CAS_{9N} is added to the same blended cement. The presence of the glass thus causes a larger fraction of the limestone to react chemically thus contributing to the formation of hydration phases. In that way, the combination of the physical filler effect of the limestone and the chemically cementitious reactivity of both limestone and fly ash or CAS glasses can be exploited to a greater extent.

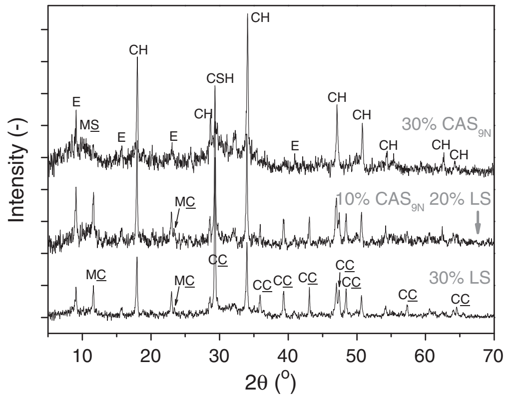

Fig. 7. X-ray diffractograms for the three blended cements. CH = portlandite, C$\underline{C}$ = calcite, E = ettringite, M$\underline{C}$ = monocarbonate, CSH = C-S-H and M$\underline{S}$ = monosulfate. LS: limestone.

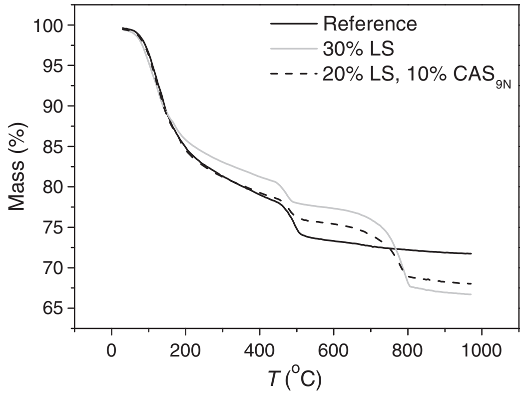

Fig. 8. Thermal gravimetric analyses of cement pastes hydrated for 90 days. LS refers to limestone.

The relatively high Al_2O_3 content of the glass compared to OPC is believed to be the reason of the increased reactivity. This is supported by previous studies indicating that a high C_3A content favors the consumption of carbonate in Portland limestone cements [14,16]. The conversion of monosulfate to monocarbonate releases sulfates resulting in the formation of ettringite. This is in agreement with the XRD analyses where no monosulfate was observed for the blended cement containing both limestone and CAS_{9N}. A larger AFt/AFm ratio is thus expected in the limestone containing cements. This will also contribute to a larger strength by an increase in the total volume of hydration products.

A similar synergetic effect in the late strength is reported previous on ternary blended cements containing both limestone and fly ash. In this study the degree of clinker substitution is 35 wt.% and the largest synergy effect is observed for small amounts of limestone (5 wt.%). This study confirms the conversion of monosulfate to monocarbonate and ettringite to be the reason for the enhanced late strength [24,25].

4.1. Evaluation of the raw materials CO_2 emission

In order for CAS glass particle to be useful SCMs less CO_2 must be released from the production of blended cements compared to pure cements for similar mortar or concrete performances. The production of blended cement includes both the production of cement clinker and that of CAS glass. To obtain a measure of the CO_2-release relative to the performance of the final concrete, the amount of CO_2 (given in kg) released during production of cement and SCM is normalized by the 90 days compressive strength (given in MPa) obtained for the given blended cement mortar. This is defined as the parameter m_{CO2}/σ.

The global average specific thermal energy consumption for production of PC is estimated to be 3.7 GJ/t clinker corresponding to the release of 250–300 kg fuel derived CO_2 per ton of clinker [4]. An efficient melting tank for glass production operating at a maximum temperature of 1600 °C has a thermal energy consumption of ~4 GJ/t [26,27]. The use of CAS glasses as SCMs sets no requirements to the homogeneity of the glass, and the glasses can thus be produced at considerably lower temperatures (1300–1350 °C) and with significantly reduced refining times than used for normal glass production [7]. These large continuous glass melting tanks producing up to several hundred tons of glass per days are often fired on fossil fuels with most new furnaces using natural gas where available. Therefore the fuel derived CO_2 emission is estimated to be comparable or slightly less for glass production than for production of Portland cement clinker. In the following calculations the fuel derived CO_2 release is approximated to 275 kg/t cement or glass. This corresponds to a glass melting tank fired on 100% natural gas or on a combination of coal and alternative fuels (often waste materials) in relative proportions corresponding to that used for cement production. No fuel derived CO_2 emission is linked to the use of fly ash, limestone and the inert filler.

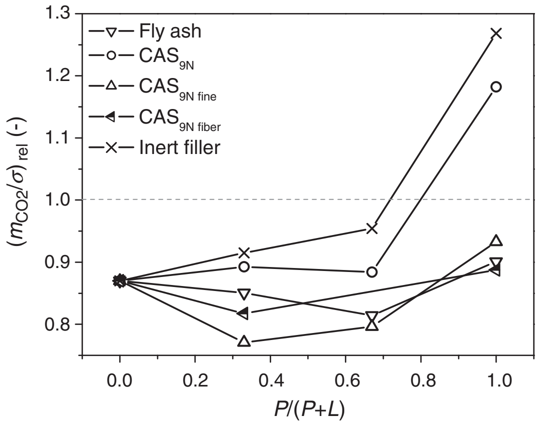

Fig. 9. Relative raw materials CO_2 emission $(m_{CO2}/\sigma)_{rel}$ as a function of $P/(P+L)$. $(m_{CO2}/\sigma)_{rel} < 1$ indicates blended cements with a reduced CO_2 emission relative to the mechanical performance compared to pure cement. This limit is indicated by the dashed grey line. The CAS_{9N}, CAS_{9N} fine and CAS_{9N} fiber samples have surfaces areas of 371 m^2/kg, 629 m^2/kg and 619 m^2/kg, respectively.

Limestone is the major raw material used in the production of PC clinker accounting for 500–550 kg CO_2 per ton of clinker. For the production of the CAS glasses limestone accounts for approximately one third of the raw materials resulting in a raw materials CO_2 emission of approximately 175 kg CO_2 per ton of glass. When limestone is used as a clinker replacement, it is mixed with the cement after clinker burning, and hence, no CO_2 is released since calcination is avoided. The same goes for fly ash and the inert quartz as these will not contribute to any raw materials CO_2 emission neither to any fuel derived CO_2 emission associated with cement production.

The measure m_{CO2}/σ includes the CO_2 contributions from both fuel and raw materials. Fig. 9 compares m_{CO2}/σ for the different blended cements relative to that of pure cement as a function of the $P/(P+L)$ ratio. If $(m_{CO2}/\sigma)_{rel} < 1$ the CO_2 per mechanical performance is reduced for the blended cement compared to the pure cement. This is the case for all the blended cements except for those containing 30% inert filler and 30% of the coarse CAS_{9N}. If CAS glass is added as the only SCM, it must therefore be ground to a high surface area to effectively reduce CO_2 release relative to the mechanical performance. When both limestone and CAS glass are added, the relative CO_2 emission can be reduced by approximately 20% for the same 90 days compressive strength as obtained for OPC. CAS glasses can therefore be considered a good alternative to the limited resources of traditional SCMs especially when mixed with limestone.

Another alternative to the traditional by-product SCMs is clay mineral heat treated at 600–900 °C. This yields poorly crystalline or amorphous calcined clays exhibiting pozzolanity. The use of calcined clays in blended cements is however reported to increase the water demand significantly thus requiring addition of superplasticizer [28–30].

5. Conclusion

Calcium aluminosilicate glass has been shown to be a viable alternative to the traditional SCMs. The combination of limestone and CAS glass in the same blended cement provides higher late strengths than predicted from the individual contributions of each constituent. This is probably related to the rather high alumina content in the glass which causes a larger part of the limestone to participate in the hydration reactions. Combined with the pozzolanity of the CAS glasses this provides blended cements with late strengths even higher than obtained with the pure Portland cement. Real reductions in the CO_2 emission of ~20% are possible for the same cement strength and performance compared to pure PC. This yields lower emission than achieved using fly ash or combinations of fly ash and limestone.

Acknowledgements

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