

MECHANICAL PERFORMANCES OF BLENDED PORTLAND CEMENTS CONTAINING OPTIMIZED CALCIUM ALUMINOSILICATE GLASS PARTICLES

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ABSTRACT

In this work, we investigate the mechanical performance of blended Portland cements containing the optimized calcium aluminosilicate (CAS) glass described in Moesgaard, et al., 2010a. The glass is investigated in mortars with a water to cement ratio of 0.5, and both fibers and particles from molded glass, ground to different finenesses, are investigated. From strength development and workability of fresh mortar it is concluded that the glass shows promising results as a supplementary cementitious material (SCM), and even more promising results have been obtained with combinations of glass and finely ground limestone where significantly higher strengths are observed than would be predicted from the individual contributions of each constituent.

KEYWORDS:

CO₂ emission; Portland cement; supplementary cementitious materials (SCMs); pozzolanity.

INTRODUCTION

As already described in Moesgaard, et al., 2010a cement is a global growth industry and huge amounts are needed for infrastructure development, housing and industrial estates in the developing countries, and as 1 tonne of clinker is typically associated with 0.8 tonnes CO₂ emitted, new technologies are needed to decouple the growth in cement production from a corresponding growth in CO₂ emissions. Several sources have already recognized this and a recent study (WBCSD-CSI & IEA, 2009) identified the increased use of SCMs as one of four necessary levers to achieve this goal. Substitution of clinker by SCMs is already increasing. This mainly involves the increased use of industrial by-products such as blast furnace slag and fly ash from coal fired power stations. However, as the processes for producing steel and electricity are replaced with new technology associated with less CO₂ emission, the availability of the traditional SCMs are diminishing. The amount of available conventional SCMs of 1.2 Gt/year forecasted by 2050 will therefore limit the reduction in clinker content to 73 %, if a global cement production of 4.4 billion tonnes per year is assumed; a reduction of only 6 % points compared to 2006 (WBCSD-CSI & IEA, 2009). Further reduction of the clinker content thus requires new sources of alternative SCMs (Damtoft, et al., 2005; Rehan & Nehdi 2005; Worrel, et al., 2001).

If the increased additions of SCMs are to make a real impact it is important that they do not result in a significant loss in the performance of the cement. Lower strengths for example mean that more cement is needed to achieve the same concrete strength resulting in little or no reductions in CO₂ per unit of concrete. In order to achieve a reasonable strength of the composite cement it is therefore important that the alternative material takes part in the hydration reactions contributing to the final strength.

Several potential calcium aluminosilicate (CAS) glasses have already been identified and the suitability of these glasses as SCMs has been confirmed from the measurement of pozzolanic reactivity using solid-state

^{27}Al and ^{29}Si magic angle spinning NMR on glass samples submerged in a $\text{Ca}(\text{OH})_2$ solution (Moesgaard, et al., 2010a). The hydraulic reactivity is assumed to derive from the structural disorder, i.e. thermodynamic instability, within the glassy materials. The Ca^{2+} , Na^+ and K^+ ions released into the pore solution, as Portland cement is mixed with water, will result in a highly alkaline environment with pH values of 13.4-14.0 (Lawrence, 2007). In the alkaline environment the glassy network will break down forming depolymerized Si- and Al-oxyhydroxides. As the CAS glasses are composed of the same oxides found in Portland cement these oxyhydroxides are expected to take part in the formation of hydration products similar to those formed during hydration of cement.

However, the strength contribution alone is not sufficient to provide a suitable SCM. The workability of the paste, mortar, or concrete also has to be acceptable. In this work, the cement clinker is partly substituted by CAS glass, or a combination of both glass and limestone. The composite cements are investigated in relation to workability of the fresh mortar, setting behavior and compressive strength of mortars at various periods of hydration. Finally, the effect of reduction of clinker content on the CO_2 emission linked with cement production is evaluated. Measurements on fly ash are used for comparison, and finely ground quartz is used as inert filler.

EXPERIMENTAL

The preparation and initial investigation of the CAS glass, $\text{CLS}_{9\text{N}}$, is described in Moesgaard et al. 2010a. The nomenclature refers to the raw materials, clay, limestone, and sand from which the glass is prepared by mixing in the proportions 63 wt% clay, 31 wt% limestone, and 6 wt% sand. The subscript indicates the molar content of Na_2O . Additional Na_2CO_3 is introduced to provide the rather high content of Na_2O . The glass has been ground to two different finenesses and spun into fibers, which have been subsequently ground to the same fineness as one of the $\text{CLS}_{9\text{N}}$ samples (Table 1). The fibers are produced by Rockwool International A/S, Hedehusene, Denmark using the cascade spinning process, which is a type of centrifuge process (Širok, et al., 2008).

Commercially available cement consisting of 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 2 and 3. The content of free lime was measured by wet chemistry. Composite cement mortars containing 30 wt% clinker replacements were prepared using the replacement materials stated in Table 1. In addition, composite cements containing both pozzolan (P), i.e. glass or fly ash (including the inert filler), and limestone (L) were prepared. $P/(P+L)$ ratios of 0, 0.33, 0.67 and 1 were investigated. For all mortars a water to cement ratio of $w/c = 0.5$ by mass was employed, with c representing the total content of cement and replacement material. The cement to sand ratio of the mortars was 1:3 and the particle diameter of the sand in use was in the range 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 investigated by measuring the heat of hydration during the first approximately 18 hours after preparation of the mortar using semi-adiabatic calorimetry. Approximately 20 g of mortar was used and the heat of hydration was determined from the temperature variations measured by the calorimeter. Mini-RILEM $2 \times 2 \times 15 \text{ cm}^3$ mortar prisms were made and stored in the moulds for $24 \pm \frac{1}{2}$ hours at $20 \pm 1 \text{ }^\circ\text{C}$ and a relative humidity of at least 95%. Hereafter, the specimens were demoulded and placed in water in the curing room ($20 \pm 1 \text{ }^\circ\text{C}$) for final hydration. Compressive strengths were measured directly after demoulding (1 day strengths) and after 2, 28 and 90 days of hydration in total, and each specimen was cut into three before measurement. The density of the prisms was determined by weighing.

Table 1: Characteristics of the Portland cement (PC) and replacement materials.

Material	PC	CLS _{9N}	CLS _{9N} fine	CLS _{9N} fibres	Fly ash	Inert filler (quartz)	Limestone
Surface area (m ² /kg) ^a	575	371	629	619	330	-	1288
Mean diameter (μm) ^b	7.7	14.4	6.0	6.2	20.1	D _{max} < 90 μm	2.7

^a Determined by air permeability using the Blaine method.

^b Determined by PSD analysis

Table 2: Mineralogical composition (wt%) of clinker according to Bogue.

Component	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	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 wet chemistry

^b LSF is the lime saturation factor.

Table 3: Chemical composition in wt%. L.O.I. states the loss on ignition. For Portland cement (PC), limestone and fly ash XRF is used to determine the chemical composition, whereas wet chemistry is used for the glass CLS_{9N}. L.O.I. and the content of SO₃ are not determined for CLS_{9N}.

Component	PC	CLS _{9N}	Fly ash	Limestone
SiO ₂	19.0	51.0	55.2	4.4
Al ₂ O ₃	5.8	12.4	24.7	0.4
Fe ₂ O ₃	3.9	6.5	8.5	0.2
CaO	65.1	17.9	4.7	52.9
MgO	1.0	2.4	1.8	0.4
K ₂ O	0.4	2.0	1.6	0.1
Na ₂ O	0.3	7.8	0.9	< 0.1
SO ₃	3.7	-	0.6	0.1
L.O.I.	0.9	-	1.9	41.7

RESULTS AND DISCUSSION

Comparison of the different supplementary cementitious materials

The workability was evaluated based on the flow of the fresh mortars, and it was found that the flow of the mortars containing glass increased by 2-8 % compared to the flow of the mortars containing pure cement. Addition of 30 wt% SCMs does not increase the water demand and mortars can be produced under the same

conditions as pure cement. This is a major advantage compared to clay based SCMs for example, which invariably increases the water demand requiring additional water or super plasticizer to maintain sufficient workability (He, et al., 1994).

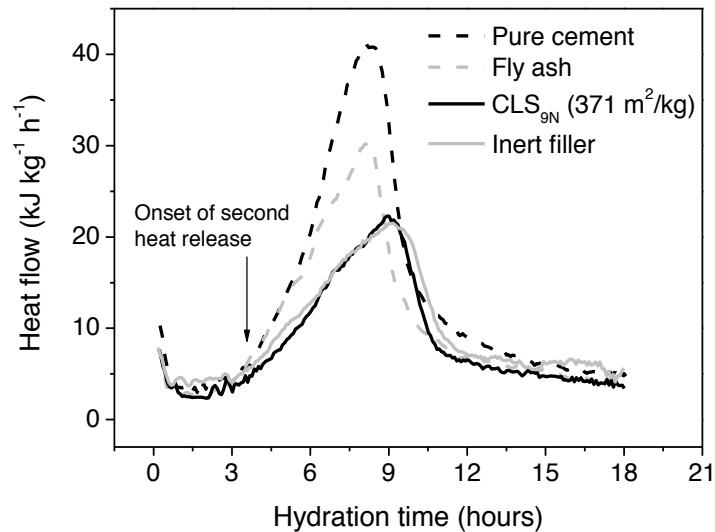


Figure 1: Setting behavior of mortar measured as the rate of heat evolution within the first 18 hours of hydration.

Figure 1 compares the heat flow within the first 18 hours of hydration for mortar containing pure cement, i.e., a reference sample, and the three different types of composite cements all containing 30 wt% of the SCMs or 30 wt% inert filler. It is observed, that the replacement of 30wt% of the cement with an alternative material changes the setting behavior. The total energy release is reduced indicating that the cement is replaced by a less reactive material. Similar heat flow patterns are observed for the composite cement containing the CAS glass and the cement containing the inert material indicating negligible early age pozzolanicity of the CLS_{9N} glass. Fly ash on the other hand does react to some extent during these early stages as indicated by, more heat formation than the inert filler and glass. The onset of the second heat release can be used as a measure of the initial setting time. No significant changes in the onset are observed by the introduction of 30 wt% cement replacement. For the mortars containing CAS glass and quartz the rate of heat evolution observed for the main peak is however slower, and a slightly prolonged working period before the mortars solidifies (20-25%) is expected for these composite cements.

Figure 2 shows the development in compressive strength of the composite cement mortars which all contain 30 wt% cement replacement. The strength is given relative to the strength of the mortar containing pure cement, i.e. as σ/σ_{ref} . The pozzolanicity of the glass and fly ash is apparent as the strength of the mortars containing these materials is significantly higher than the strength of the mortar containing 30wt% quartz. The strength of the sample containing quartz remains at 55% of the reference whilst, the mortars containing fly ash and glass continue to gain strength.

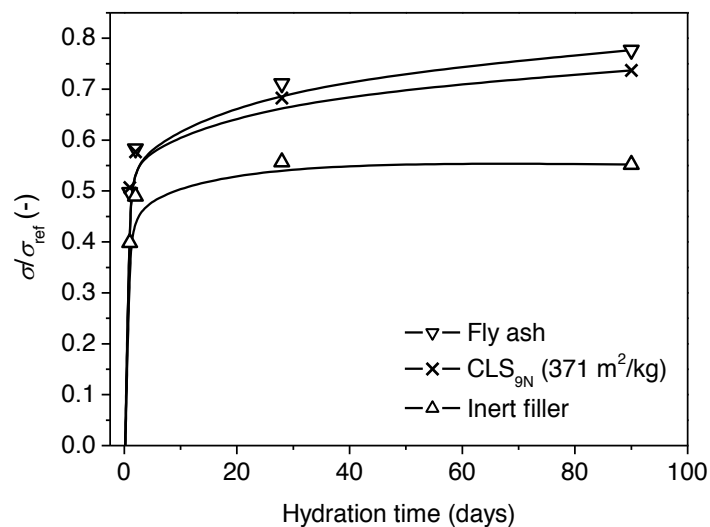


Figure 2: Strength development of composite cement mortars containing different clinker replacement materials. The strength (σ) is given as the relative strength to a pure Portland cement mortar (σ_{ref}). The solid lines should be regarded as guides for the eyes.

As expected from the results of the pozzolanity test (Moesgaard, et al., 2010a) the CAS glass contributes to the strength of the composite cements. Comparable performance is observed for the composite cements containing CAS glass and fly ash of similar fineness. A tendency of the fly ash to provide a slightly higher strength is however observed. A detailed discussion of the results can be found in Moesgaard, et al., 2010b.

Effect of particle size and cooling rate during glass production

During cement hydration, the reactions progress inwards from the surface of the particles. The particle size of the pozzolanic material is therefore expected to affect the rate of hydration and therefore the strength development. This phenomenon is evaluated from the results obtained on the three mortars containing different forms of CLS_{9N} (Table 1). The relative strength development is shown in Figure 3, and the increased surface area is observed to have significant impact on the strength over the course of hydration. The effect is most pronounced at longer hydration times.

The CLS_{9N} composition has also been used to draw thin glass fibers, and the cooling rate of this process is approximated to be in the range of 10^6 K/s, i.e., the glass is hyper-quenched. This is in contrast to the normally cooled glasses for which the cooling rate is approximated to be in the range of 10^3 K/s. The approximations of cooling rates are made according to the procedure of Yue, et al., 2004. The excess energy stored within the fiber glass is therefore significantly larger than for the normally cooled glass, proving a more disordered structure (Yue, et al., 2004). The fibers are ground to a surface area comparable to the CLS_{9N} (629 m²/kg) particles, and it is investigated (Figure 3) whether this increased energy stored within the fibers, i.e. the greater instability of the glass, has an effect on the reactivity of the glass. From Figure 3 the composite cement mortar containing the hyper-quenched glass has a slightly higher strength during late hydration than the mortar containing normally cooled glass, indicating that the glass with the highest thermodynamic instability has the greatest reactivity. Considering the uncertainty associated with the measurements, however, it is difficult to draw any firm conclusions.

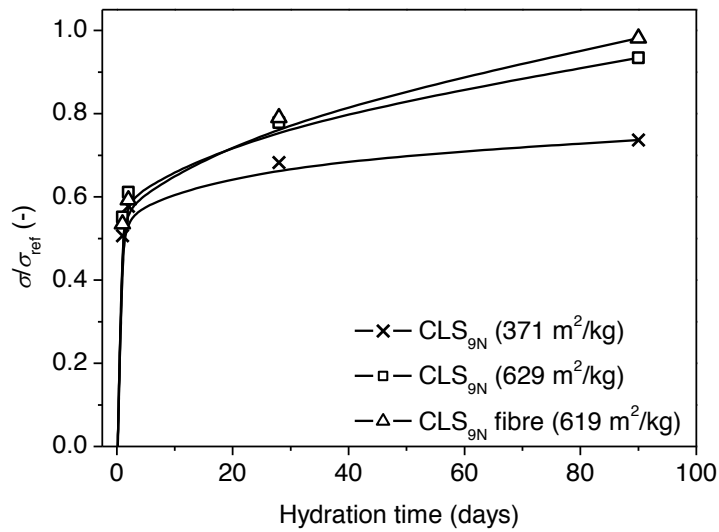


Figure 3: Strength development of composite cement mortars containing 30 wt% CLS_{9N} with varying fineness and excess internal energy. The strength is given as σ/σ_{ref} . The solid lines should be regarded as guides for the eyes.

Composite cements containing both glass and limestone

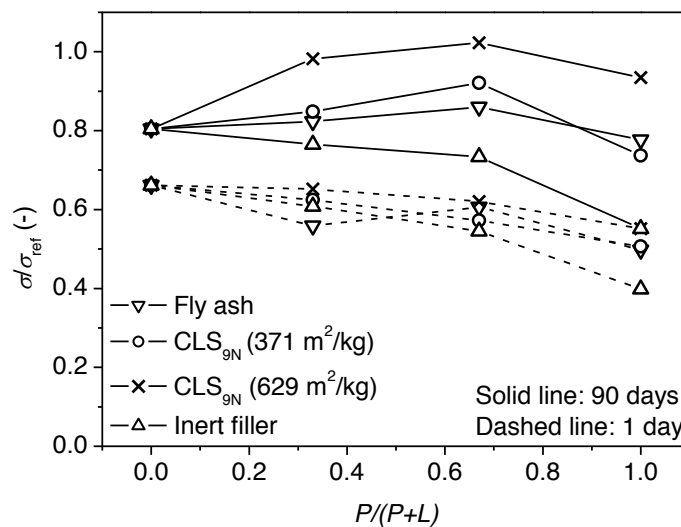


Figure 4: Relative compressive strength (σ/σ_{ref}) as a function of $P/(P+L)$ for mortars with 30% cement replacement. P is the content of pozzolan (including the inert filler) and L is the content of limestone in wt%.

The hydration of the mortars containing limestone was evaluated from the heat development. The degree of hydration of Portland limestone cement mortar with 30% cement replacement was midway between the pure cement reference and the sample containing 30% CLS_{9N}. The degree of hydration in the mortars containing both limestone and glass was higher approaching that of the reference cement without cement replacement (data not shown). This behavior is consistent with the measurements of early strength. In Figure 4 the

compressive strength of the mortar samples is plotted as a function of the $P/(P+L)$ ratio. Here P is the content of pozzolan also including the inert material and L is the limestone content. After 1 day's hydration the highest strength is observed for the composite cement mortars containing limestone as the only cement replacement material. The lowest strengths are observed for the samples containing 30% of the pozzolan (CLS_{9N}, fly ash or the inert material).

After 90 days of hydration the behavior is markedly changed for the mortars containing pozzolans participating in the strength giving reactions. At the early stage of hydration, mortars containing limestone as the sole replacement material exhibit still a slightly larger strength than the mortars containing only the fly ash or the coarse CLS glass. At the long duration of hydration however, a synergetic effect is observed between the limestone and the pozzolan and the samples containing both exhibit the highest strengths (Figure 4). It is presumed that the synergetic effect originates from a reaction between accessible aluminosilicates and limestone, forming the pore-filling phase, calcium monocarboaluminate hydrate. This is explained in greater detail in Moesgaard, et al., 2010b.

For the composite cements containing the fine CLS glass particles (CLS_{9N} 629 m²/kg) the lowest strength is observed at $P/(P+L) = 0$, i.e. when no glass is present. For the sample containing 20% CLS_{9N} and 10% limestone the 90 days compressive strength even exceeds that of the pure cement. Increased thermodynamic instability (drawing of fibers) does not seem to have an effect on the compressive strength of the mortars containing both limestone and CLS_{9N} (data not shown).

CO₂ emission

For the CAS glass particles to be an effective solution towards reducing the CO₂ emission of cement production, reasonable mortar or concrete performances must be obtained per mass of CO₂ released for the composite cements including CAS glass as an SCM. To obtain a measure of the CO₂-release relative to the performance of the final concrete, the amount of CO₂ (given in kg) released from raw materials during production of cement and SCM is divided by the obtained compressive strength (given in MPa) of the given composite cement mortar. This is defined as the parameter m_{CO_2}/σ . Limestone is the major raw material used in the production of PC clinker accounting for 500-550 kg CO₂ per tonne clinker (close to 1.2 tonnes limestone is needed to produce 1 tonne clinker). For the production of the CLS glasses limestone accounts for approximately one third of the raw materials resulting in a raw materials CO₂ emission of approximately 180 kg CO₂ per tonne glass. When limestone is used as a clinker replacement it is mixed with the cement after the burning, and therefore does not involve any CO₂ emission. This is of course also the case with fly ash and the inert quartz. Figure 5 compares m_{CO_2}/σ for the different composite cements relative to that of pure cement as a function of the $P/(P+L)$ ratio. Lower raw material CO₂ emissions, i.e., less than 1, are observed for all the composite cements except for the cement containing 30% inert filler and 30% of the coarse CLS_{9N}. If CLS glass is added as the only SCM it must therefore be ground to a high surface area to effectively reduce CO₂ emissions relative to the mechanical performance. When both limestone and CLS glass are added, the relative "raw materials CO₂ emission" can be reduced by 20-25%. CAS glasses, especially when mixed with limestone, can therefore be considered as a good alternative to the limited resources of conventional SCMs.

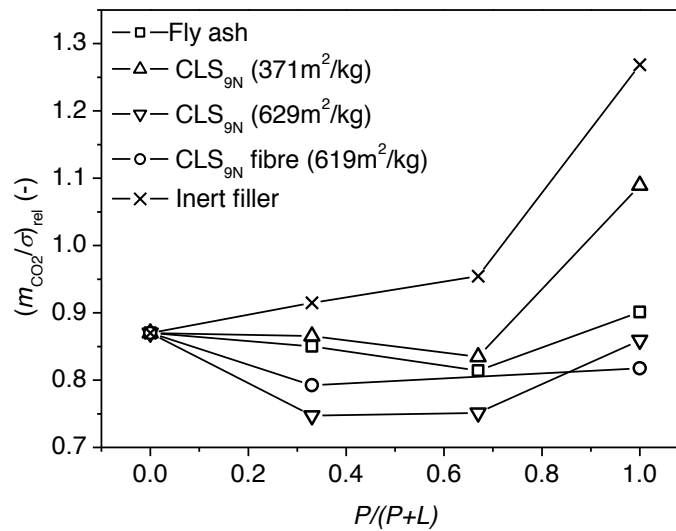


Figure 5. Relative raw materials CO₂ emission ($(m_{\text{CO}_2}/\sigma)_{\text{rel}}$). The CO₂ emission (m_{CO_2}) is given in kg of CO₂ released from raw materials during production of cement and alternative materials divided by the compressive strength (σ in MPa) of the composite cement mortars.

CONCLUSION

The goal of this investigation was to evaluate whether a refined calcium aluminosilicate glass, CLS_{9N}, which in earlier work was found to have pozzolanic properties (Moesgaard, et al., 2010a), can be used as an SCM. Mortars based on composite cements with 30% cement replacement were found to exhibit very promising flow behavior, and the water demand is unaffected by the addition of CAS glasses, which is a major advantage over natural pozzolans such as calcined clays. Initial setting behavior is found to be reasonable. Acceptable levels of late strength are also observed. The late strength of the composite cement mortars is in the range 70-90% of the strength of pure cement and is strongly dependent on particle size of the glass. The early strength, however, is only 50 to 60% of the early strength of mortars with pure cement. The pozzolanicity of the CAS glasses is therefore most pronounced at longer periods of hydration.

The combination of limestone and CAS glass provides higher late strengths than would be predicted from the individual contributions from each constituent. The high alumina content of the glass is believed to result in a higher degree of reaction of the limestone compared to normal Portland limestone cements. In this way, the beneficial effects of limestone both as a filler material and as a reactive component can be exploited to a greater extent. Combined with the pozzolanicity of the CAS glasses late strengths can be achieved which are even higher than the strengths of pure cement mortars. It is concluded that CAS glasses provide a promising alternative to traditional SCMs, achieving not just reduced emissions per tonne cement, but crucially real emissions reductions per unit of concrete produced to the same strength specification.

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