

## OPTIMAL COMPOSITION OF CALCIUM ALUMINOSILICATE GLASS PARTICLES USED AS SUPPLEMENTARY CEMENTITIOUS MATERIALS

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### ABSTRACT

In this work, we investigate the potential use of CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass particles as supplementary cementitious materials (SCM). A requirement for the glass as a useful candidate for SCMs is that the overall CO<sub>2</sub> emissions caused by cement production should be reduced significantly by replacing part of the cement with glass. This can be obtained by compositional modifications aiming at minimizing both the “process CO<sub>2</sub>” and “fuel-derived CO<sub>2</sub>” linked with glass production and maximizing the pozzolanic reactivity of the glass. A high pozzolanic reactivity ensures an acceptable performance of the final mortar or concrete. Based on the glass characteristics and testing of pozzolanic reactivity, we find that the glasses prepared from the naturally occurring minerals (clay, limestone and sand) are promising SCMs.

### KEYWORDS:

CO<sub>2</sub> emission, Portland cement, supplementary cementitious materials, pozzolanity.

### INTRODUCTION

CO<sub>2</sub> emissions from human activity are widely recognized as the major cause of global warming observed over recent decades. Energy intensive industries are therefore making considerable efforts to reduce their CO<sub>2</sub> emissions. The production of Portland cement (PC) is one of these energy intensive industries, and it is estimated that the cement industry today accounts for approximately 5% of the global man-made CO<sub>2</sub> emissions (Damtoft, et al., 2005; Rehan & Nehdi 2005; Worrel, et al., 2001). Most of this CO<sub>2</sub> originates from the decarbonation of limestone which constitutes 80-85% of the raw materials for clinker production. This is referred to as “process CO<sub>2</sub>”. One strategy for reducing the CO<sub>2</sub> emissions from the cement industry is to reduce the clinker content in the cement. The clinker is partly substituted by alternative materials producing so-called composite cements. These alternative materials are referred to as supplementary cementitious materials (SCMs). It is important that the SCMs contribute positively to the final cement performance. Most SCMs are either latently hydraulic, such as granulated blast furnace slag, or pozzolanic, such as fly ash or silica fume. A pozzolan is defined as a silica or aluminosilica containing material that alone does not possess hydraulic reactivity but when mixed with calcium hydroxide and water reacts to form strength giving hydration products (Taylor, 1997). These materials are usually by-products from other industries and therefore do not contribute to the CO<sub>2</sub> emission of the cement production. In practice, the use of these materials is limited by their availability, transport costs and competition with other industries. At present they are almost fully utilized in Western Europe. Further reduction of the clinker content, therefore, requires new sources of alternative SCMs (Damtoft, et al., 2005; Rehan & Nehdi 2005; Worrel, et al., 2001). In addition, the demand for cement, especially in developing countries is expected to rise significantly over the coming decades placing even greater burden on the cement industry to reduce emissions (Damtoft, et al., 2005; Humphreys & Mahasanen 2002).

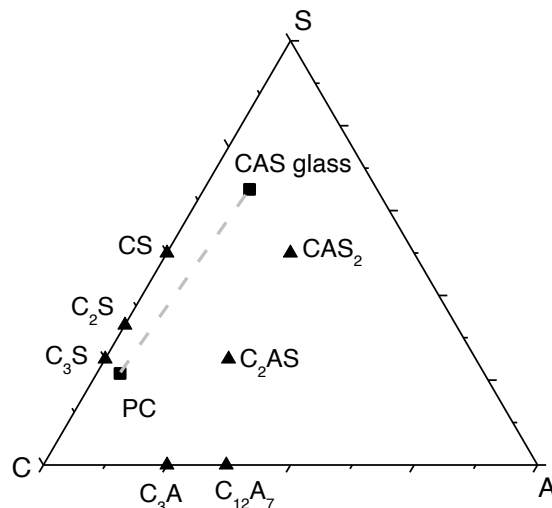
Possible candidates for alternative SCMs are calcium aluminosilicate (CAS) glass particles. CAS glass is composed of the same oxides found in Portland cement and the thermodynamic instability of glass is

expected to provide hydraulic reactivity. Hence the glass is expected to take part in the strength giving reactions occurring during cement hydration. In recent years, several studies have focused on the use of waste glass as SCMs. These studies have confirmed the hydraulic reactivity of the glass when mixed with cement. Glass can thus be considered as a pozzolan. Waste glass is however also a limited resource (Shi & Zheng 2007; Shayan & Xu 2006; Shi, et al., 2005; Schwarz, et al., 2008). In this work, we attempt to engineer CAS glass particles having a composition optimized for utilization as an SCM. This is done by considering both the extent to which the glass will take part in the hydration reactions and thus contribute to the strength of the composite cement, but also the amount of CO<sub>2</sub> released during glass production. In practice this is done by taking into account the consumption of limestone, practical melting temperature and pozzolanity of the glass. The first two characteristics are related to the energy and therefore CO<sub>2</sub> consumption during production.

For full scale production to be economically viable, the glass particles must be produced from low cost and locally available raw materials. Conventional raw materials i.e., clay, limestone and sand are therefore chosen. The raw materials are of course mixed in other proportions than for cement production. Investigations were first performed on a three component model system, i.e., the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system (Moesgaard & Yue 2009; Moesgaard, et al., in press). These are the major oxides in the raw materials and account for 90% of the oxides in PC. Subsequently impurities present in naturally occurring minerals were introduced to test the effects on the characteristics of the glass. Four glass compositions were investigated in this work corresponding to the optimum composition found from investigations on the three component model system (Moesgaard & Yue 2009; Moesgaard, et al., in press) (C<sub>26</sub>A<sub>9</sub>S<sub>65</sub>) and three compositions based on the naturally occurring minerals (referred to as the CLS glasses). The compositions of the glasses and that of ordinary PC are given in Table 1 and illustrated by the ternary CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> phase diagram shown in Figure 1.

**Table 1: Oxide compositions (mol%) of the five glasses investigated.**

	PC cement	C <sub>26</sub> A <sub>9</sub> S <sub>65</sub>	CLS <sub>1N</sub>	CLS <sub>5N</sub>	CLS <sub>9N</sub>
SiO <sub>2</sub>	19.2	64.9	59.1	56.1	53.9
Al <sub>2</sub> O <sub>3</sub>	3.5	9.3	8.2	7.9	7.7
Fe <sub>2</sub> O <sub>3</sub>	1.5	-	3.0	2.9	2.8
CaO	70.8	25.8	22.1	21.2	21.3
MgO	1.5	-	4.2	3.9	3.9
K <sub>2</sub> O	0.3	-	1.7	2.0	1.6
Na <sub>2</sub> O	0.2	-	1.2	5.4	8.2
SO <sub>3</sub>	2.8	-	<0.1	0.2	0.2
TiO <sub>2</sub>	0.2	-	0.5	0.5	0.5



**Figure 1: Molar ternary CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> phase diagram. Squares indicate the compositions of Portland cement (PC) and the CAS glasses under investigation (Table 1). Selected binary phases within the relevant compositional range are indicated by triangles. The traditional nomenclature with C, A and S representing CaO, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, respectively, is used. Mixes of PC and the glass particles plot along the dashed line.**

## EXPERIMENTAL

The glasses were synthesized by melting the batch in a Pt<sub>90</sub>Rh<sub>10</sub> crucible in air atmosphere (furnace: model SF6/17 Entech, Ängelholm, Sweden). For the model system glass, the batch was obtained by mixing the analytical chemicals SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and CaCO<sub>3</sub>. A two-step melting process was carried out. First, the batch was melted at 1550°C for 2 hours. The melt was subsequently quenched in water to obtain crushed fragments. The crushed glass was remelted at 1550°C for another 2 hours and cast on a graphite plate. The glass was annealed at 800 °C, i.e. at approximately the glass transition temperature ( $T_g$ ), for 10 minutes, and cooled slowly after switching off the furnace.

Clay (bentonite) for glass preparation was provided by Dantonit A/S Odense, Denmark. Sand and limestone were provided by Aalborg Portland A/S, Aalborg, Denmark. Analytical Na<sub>2</sub>CO<sub>3</sub> was introduced to provide additional Na<sub>2</sub>O. Prior to melting in the Pt<sub>90</sub>Rh<sub>10</sub> crucible the clay was heat treated at 900°C for 3 hours (heating rate of 10°C/min) to remove any organic material. The batch was homogenized using a mortar and then melted at 1450°C for 3 hours. The melt was cast on a graphite plate and annealed at 700 °C or 650 °C for 10 minutes, and naturally cooled inside the furnace. The chemical compositions of the glasses were determined by standard wet chemical analysis at Aalborg Portland A/S.

In the low viscosity range (approx. 10<sup>0</sup>-10<sup>3</sup> Pa·s), the viscosity ( $\eta$ ) was measured using concentric cylinder viscometry. The furnace was a box furnace (model HT 7, Scandiaovnen A/S, Allerød, Denmark) and the viscometer head was a Physica Rheolab MC1 (Paar Physica, Stuttgart, Germany).

For tests of pozzolanicity, the glass was ground to pass a 75  $\mu$ m sieve. 1.00 g glass powder (1.5·10<sup>-2</sup> mol) and 1.00 g Ca(OH)<sub>2</sub> (1.3·10<sup>-2</sup> mol) were mixed with 100 mL freshly boiled water and stored in a closed container for 7 days at 40°C. During storage the mixture was shaken with a horizontal rotary motion. The mixture was filtered and the filtrate was stored for further analyses. For solid-state NMR investigations the collected solid was dried over silica gel in a desiccator. For determination of the mass of unreacted glass the collected solid was washed with a weak acetic acid solution to dissolve remaining Ca(OH)<sub>2</sub> and any hydration products formed. The washed glass was dried over silica gel in a desiccator.

Solid-state<sup>29</sup>Si MAS (magic angle spinning) NMR (nuclear magnetic resonance) spectra were recorded at 39.8 MHz on a Varian INOVA-200 (4.7 T) spectrometer whereas the<sup>27</sup>Al MAS NMR spectra were recorded at 104.2MHz on Varian INOVA-400 (9.39 T) (14.09 T) spectrometers. The <sup>27</sup>Al and <sup>29</sup>Si isotropic chemical shifts were reported relative to a 1.0 M aqueous solution of AlCl<sub>3</sub>·6H<sub>2</sub>O and neat tetramethyl silane (TMS), respectively.

## RESULTS AND DISCUSSION

The initial investigations on the three component CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system focused on the compositional range of the eutectic compositions of anorthite-wollastonite-tridymite and anorthite-wollastonite-gehlenite. This compositional range involves significantly lower CO<sub>2</sub> emission from decarbonation compared to Portland cement. Furthermore the eutectic compositions correspond to minimum temperature on the liquidus surface implying that the glasses can be produced at relatively low temperatures. Last but not least, it is expected that glasses within this compositional range can be produced without forced cooling (Mysen & Richet 2005). From these investigations we chose to focus on the eutectic composition of anorthite-wollastonite-tridymite, i.e. C<sub>26</sub>A<sub>9</sub>S<sub>65</sub> (Table 1) (Moesgaard & Yue 2009; Moesgaard, et al., in press). In this work this composition is targeted using the naturally occurring minerals. The target composition is obtained by mixing the raw materials in the following proportions by weight; 63% bentonite, 31% limestone, 6% quartz sand. This corresponds to the CLS<sub>1N</sub> glass. The subscript indicates the molar content of Na<sub>2</sub>O. The use of these minerals introduces approx. 10% impurities (Table 1). These are mainly MgO, Fe<sub>2</sub>O<sub>3</sub> and alkali oxides. CLS<sub>5N</sub> and CLS<sub>9N</sub> containing 5 and 9 mol% Na<sub>2</sub>O, respectively, is produced to investigate the effect on the characteristics of the glass of introducing additional alkali oxide. In an industrial scale production the alkali content could be increased e.g. by addition of cement kiln dust or Na<sub>2</sub>SO<sub>4</sub>.

### CO<sub>2</sub> emissions from glass production

During cement production most of the CO<sub>2</sub> emission is caused by decarbonation of limestone, i.e., the so-called “process CO<sub>2</sub>”. As limestone is also used to provide the CaO in the glass this is also an important factor during glass production and the quantity of “process CO<sub>2</sub>” released during production is directly linked to the CaO content of the material. Minor variations in the composition of PC are observed worldwide depending on the local raw materials deposits. PC of the composition given in Table 1 results in the release of 516 kg “process CO<sub>2</sub>” per tonne cement produced. In contrast the production of the glasses C<sub>26</sub>A<sub>9</sub>S<sub>65</sub> and CLS<sub>1N</sub> results in 180 and 175 kg “process CO<sub>2</sub>” per tonne glass. This constitutes only approx. 30% of the CO<sub>2</sub> released from decarbonation during production of PC. Comparable quantities of “process CO<sub>2</sub>” are released from the three CLS glasses.

The other major contributor to the CO<sub>2</sub> released from cement and glass production is the so-called “fuel-derived CO<sub>2</sub>”. This is derived from the burning of fossil fuels needed to obtain the high temperatures of production and can be reduced by choosing a composition with a relatively low melting temperature hereby reducing the operating temperature of the melting furnace (Beerkens, 2004; Conradt, 2000). The temperature of importance during glass production is the so-called practical melting temperature ( $T_{pm}$ ). In this work  $T_{pm}$  is defined as the isokom temperature corresponding to a viscosity of 10 Pa·s. This viscosity will ensure a reasonable flow and workability of the glass melt.  $T_{pm}$  is determined by interpolation from the viscosity-temperature data determined by viscometry (Table 2). From the table it is observed that  $T_{pm}(C_{26}A_9S_{65})$  is even higher than the production temperature of PC (1450-1500°C). The introduction of approx. 10% minor components from the minerals has a pronounced effect on the melting temperature which is reduced by almost 200°C from C<sub>26</sub>A<sub>9</sub>S<sub>65</sub> to CLS<sub>1N</sub>. The introduction of additional Na<sub>2</sub>O further reduces the practical melting temperature.

**Table 2: Practical melting temperature ( $T_{pm}$ ) and degree of pozzolanic reactivity for the four compositions under investigation.  $T_{pm}$  is given as the isokom temperature at  $\eta = 10 \text{ Pa}\cdot\text{s}$ , and the degree of pozzolanic reactivity refers to the reactivity of the glass (wt%) with  $\text{Ca}(\text{OH})_2$  and water after 7 days.**

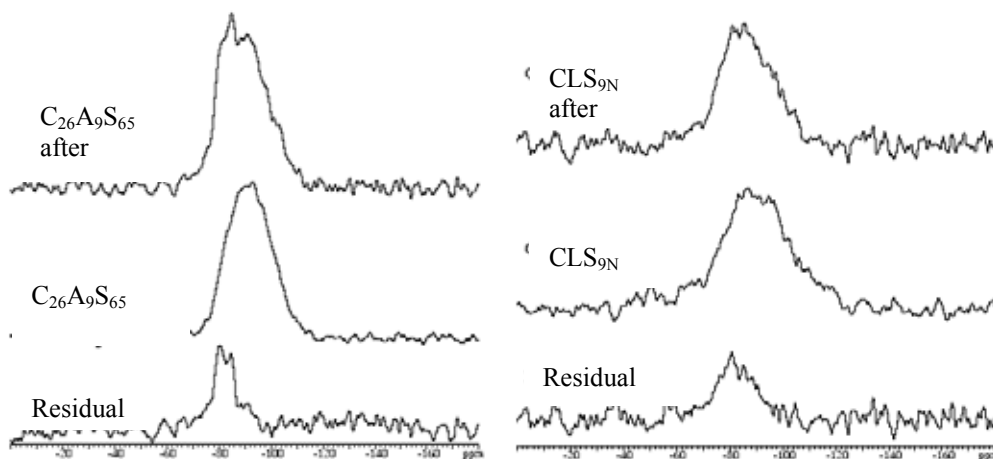
	$\text{C}_{26}\text{A}_9\text{S}_{65}$	$\text{CLS}_{1\text{N}}$	$\text{CLS}_{5\text{N}}$	$\text{CLS}_{9\text{N}}$
$T_{pm} \text{ (}^\circ\text{C)}$	1527	1346	1329	1285
Degree of pozzolanic reactivity (%)	11.6	14.1	16.3	21.6

The CLS glasses can be produced at temperatures significantly lower than used for cement production. This is expected to have a pronounced effect on the “fuel-derived  $\text{CO}_2$ ” especially by reduction of the major energy losses, i.e. the heat carried by the flue gas and the furnace wall and opening losses. Particularly the wall and opening losses are of importance as this energy normally cannot be recovered (Sardeshpande, et al., 2007). Another parameter affecting the “fuel-derived  $\text{CO}_2$ ” is the energy of reactions. During glass production the energy of fusion ( $\sim 500 \text{ kJ/kg}$  glass) (Bouhifd, et al., 2007) is of importance, whereas the energy of calcination ( $\sim 1800 \text{ kJ/kg}$   $\text{CaCO}_3$ ) is relevant for both glass and cement production. The reduced content of CaO in the CLS glasses relative to PC will therefore affect both the “process  $\text{CO}_2$ ” but also the “fuel-derived  $\text{CO}_2$ ”.

### Pozzolanicity of glass

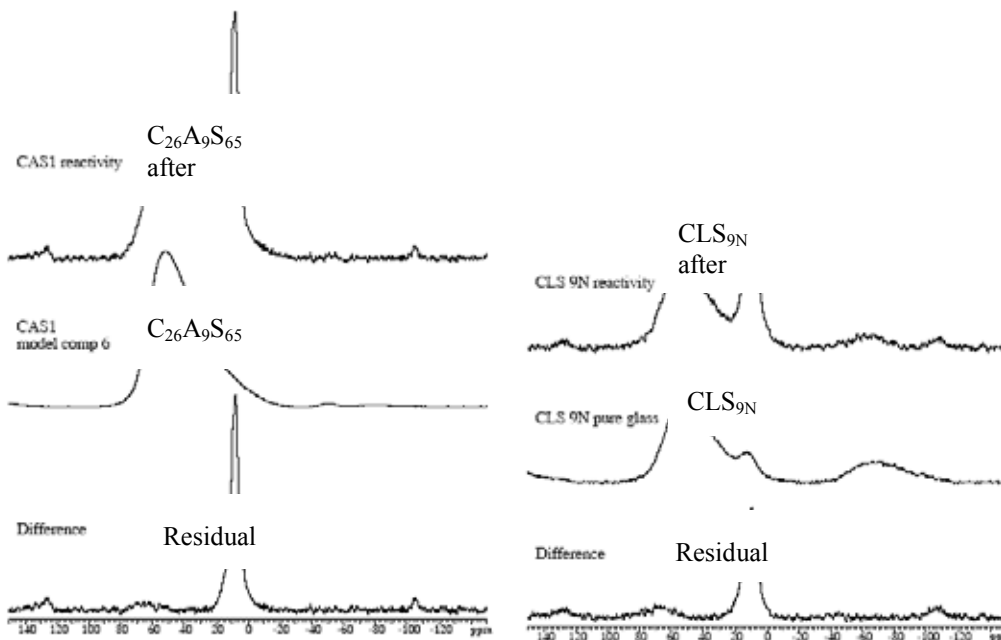
The SCMs are most often less reactive than PC. Therefore a partial substitution of PC with SCM will reduce the compressive strength compared to the pure cement. The most significant reductions are most often observed for the early strength (Shi & Zheng 2007; Massazza 2007). To ensure acceptable performance of the final mortar or concrete without being forced to increase the content of the composite cement it is of importance to minimize this reduction in compressive strength. This is possible if the SCM exhibits pozzolanicity and therefore contributes to the strength giving reactions taking place during hydration. In this work the pozzolanic reactivity of the glasses is tested as the reactivity of glass particles in a saturated  $\text{Ca}(\text{OH})_2$  solution. The alkalinity of the  $\text{Ca}(\text{OH})_2$  solution resembles the pore solution of cement paste and mortar. The degree of pozzolanic reactivity is quantified as the fraction of glass that has reacted with  $\text{Ca}(\text{OH})_2$  and water after 7 days.

During cement hydration Si is mainly incorporated into the C-S-H phase. This is an amorphous calcium silicate hydrate. The C-S-H phase is formed as the isolated  $\text{SiO}_4$  tetrahedra within alite and belite, i.e.,  $\text{Q}^0$  units, react with water to form polymerized chains consisting of  $\text{Q}^1$  and  $\text{Q}^2$  units. The formation of C-S-H can thus be followed by means of  $^{29}\text{Si}$  solid state MAS NMR as this method allows one to distinguish between  $\text{SiO}_4$  tetrahedra of different degrees of polymerization, i.e.,  $\text{Q}^0$ ,  $\text{Q}^1$  etc (Taylor 1997; Odler 2007). The chemical shift of tetrahedrally coordinated Si in silicates and aluminosilicates is expected in the range -60 to -120 ppm. An increasing degree of polymerization results in resonances at lower ppm-values (Lippmaa, et al., 1980; Mägi, et al., 1984; Klinowski 1984). Figure 2 shows the  $^{29}\text{Si}$  NMR spectra of  $\text{C}_{26}\text{A}_9\text{S}_{65}$  and  $\text{CLS}_{9\text{N}}$ . Spectra are recorded before and after the reaction with  $\text{Ca}(\text{OH})_2$  and water. For both samples the broad resonances reveal the amorphous nature of the glass composed of various  $\text{Q}^n$  units giving rise to resonances in the entire range -60 to -120 ppm. In addition, Figure 2 illustrates the difference between the two which is obtained by subtracting the spectrum obtained before the pozzolanicity test from the spectrum obtained after the test. To account for differences in the samples an appropriate scaling factor is used to ensure that the resonance from the original glass cancels out in the residual plot. For both samples the difference between the two is visualized as a resonance in the range -70 to -90 ppm. This corresponds to Si in  $\text{Q}^1$  and  $\text{Q}^2$  units indicating that a chain-like silicate structure forms during reaction with  $\text{Ca}(\text{OH})_2$  and water. A C-S-H like phase is thus formed. The presence of paramagnetic iron within  $\text{CLS}_{9\text{N}}$  causes the reduced signal-to-noise ratio observed for this glass compared to  $\text{C}_{26}\text{A}_9\text{S}_{65}$ .



**Figure 2**  $^{29}\text{Si}$  MAS NMR spectra of  $\text{C}_{26}\text{A}_9\text{S}_{65}$ (left) and  $\text{CLS}_{9\text{N}}$ (right). The “residual” spectra show the scaled resonance after the pozzolanic test minus the resonance before the pozzolanic test.

Throughout the hydration of PC Al is primarily incorporated into crystalline calcium aluminate hydrates. The Al hydration can be followed as a gradual conversion of tetrahedrally coordinated monomeric  $\text{AlO}_4$  units into octahedrally coordinated  $\text{AlO}_6$  hydrates (Taylor 1997; Odler 2007).  $^{27}\text{Al}$  MAS NMR can be used for this purpose as Al in tetrahedral coordination and in octahedral coordination give rise to signals in the range 55 to 80 ppm and -15 to 20 ppm, respectively (Merzbacher, et al., 1990; Muller, et al., 1981). Figure 3 shows the  $^{27}\text{Al}$  NMR resonances of the two samples before and after the pozzolanic test as well as the residual spectrum. For  $\text{C}_{26}\text{A}_9\text{S}_{65}$  (before the test) a broad resonance is observed, which corresponds to Al in tetrahedral coordination. Amorphous materials give broad peaks whereas crystalline phases cause narrow peaks. In addition to tetrahedrally coordinated Al,  $\text{CLS}_{9\text{N}}$  (before the test) also contains a small fraction of Al in octahedral coordination.



**Figure 3:**  $^{27}\text{Al}$  MAS NMR spectra of  $\text{C}_{26}\text{A}_9\text{S}_{65}$ (left) and  $\text{CLS}_{9\text{N}}$ (right). The “residual” spectra show the scaled resonance after the pozzolanic test minus the resonance before the pozzolanic test.

After the pozzolanic test, a sharp peak is observed for both samples in the range 0 – 20 ppm. Thus a crystalline phase containing Al in octahedral coordination forms as the amorphous calcium aluminosilica reacts with  $\text{Ca}(\text{OH})_2$  and water. This indicates the presence of a separate Al hydrate phase. This clearly shows that the glasses are reacting as pozzolanic materials.

The degree of pozzolanic reactivity is quantified as the fraction of glass that is reacting during the test (Table 2). The introduction of impurities from the natural minerals is observed to increase the reactivity and the introduction of additional  $\text{Na}_2\text{O}$  further increases the reactivity.

## CONCLUSION

In this work, we tested the applicability of CAS glasses made from natural minerals as a partial replacement of cement clinker. The objective of the replacement is to reduce the  $\text{CO}_2$  emissions from cement production. ~175 kg  $\text{CO}_2$  is released from the decarbonation of the raw materials used to produce one tonne of glass, whereas ~516 kg “process  $\text{CO}_2$ ” is released in the production of one tonne cement. The temperature of glass production affects the amount of “fuel-derived  $\text{CO}_2$ ”. The glasses based on naturally occurring minerals can be produced at temperatures that are 100-150°C lower than the temperature needed to produce Portland cement. Taking into account the energy of fusion for glass production, the “fuel-derived  $\text{CO}_2$  emission” involved in the production of glass and Portland cement clinker is approximately equal. NMR investigations proved that the glasses are pozzolanically active. The pozzolanicity is higher for the glass obtained using natural raw materials than the glass obtained using pure oxides. Introduction of additional  $\text{Na}_2\text{O}$  further increases the pozzolanicity.

In general, the glasses show good potential as supplementary cementitious materials. The use of the glasses in composite cements is also expected to result in an overall  $\text{CO}_2$  reduction in cement production. This is mainly due to the significantly lower raw material derived  $\text{CO}_2$  emission from glass production process compared to production of Portland clinkers.

## ACKNOWLEDGEMENTS

The Danish National Advanced Technology Foundation is acknowledged for financial support. We thank Ralf Keding (Section of Chemistry, Aalborg University) for assistance with the glass preparation and for useful discussions.

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