Cement and Concrete Research 40 (2010) 1072–1080

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

The benefits of incorporating glycerol carbonate into an innovative pozzolanic matrix

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ARTICLE INFO

Article history:
Received 4 September 2009
Accepted 14 March 2010

Keyword:
Metakaolin (D)
Admixture (D)
Hydraulic lime (D)
Glycerol carbonate (D)

ABSTRACT

A green admixture, glycerol carbonate (GC), has been incorporated into an alternative binder composed of hydraulic lime and metakaolin. The new properties achieved are rapid hardening, an improvement of compressive strength and a reduction in shrinkage. A study of the rheological behaviour and monitoring of conductivity, pH and organic compounds concentrations in diluted solutions led to the conclusion of an early precipitation of calcium carbonate due to GC decomposition. This phenomenon is believed to be responsible for the early stiffening of the paste. XRD and TG analyses showed changes in the mineralogical hydrated phases formed in the presence of GC: calcium aluminium oxide hemi-carbonate hydroxide hydrate is the only aluminate phase existing in this mineralogical system and more C–S–H are formed. These differences could explain the enhancement in the paste mechanical performance. The study concludes that this innovative pozzolanic matrix has considerable potential as a binder in building ecocomposites.

1. Introduction

Sustainable development in the area of construction has led to much research work on the development of new building materials with low environmental impacts. These innovative materials aim to consume less energy in production than that required by conventional materials as well as reduce greenhouse gas emissions. They also aim to minimise waste throughout their life-cycle, i.e. from manufacture to demolition, and preferably use renewable raw materials.

The aim of our current work is to develop and characterize an alternative composite building material for non structural applications including vegetable renewable raw materials.

In this paper, we present results from a study on the properties of an alternative binder composed of hydraulic lime and metakaolin. In particular, the study explores the effects of the addition of a “green” organic admixture (glycerol carbonate) on the properties of the matrix.

Metakaolin (MK) is a pozzolanic admixture produced by flash calcination of kaolinite at 700 °C. It is mainly composed of quartz and silicium and aluminium oxides with an amorphous silico-aluminates mineralogical form. This latter phase is responsible for the pozzolanic activity of metakaolin which reacts with calcium hydroxide ($Ca(OH)_2$) to form C–S–H gel, calcium aluminate hydrates (C_4AH_{13} and C_3AH_6-hydrogarnet) and calcium alumino-silicate hydrates (C_2ASH_8-straetlingite) [1].

To formulate the binder, metakaolin was combined with a commercial natural hydraulic lime (NHL) produced by calcination and slaking of a pure chalky limestone with siliceous content. Its main mineralogical phases are the C_2S, the $CaCO_3$ and the $Ca(OH)_2$.

Environmental concerns led to the choice of this pozzolan-based binder. In fact, Portland cement is currently the most widespread binder in the world but its production generates large quantities of CO_2, which represent around 5% of the total GES emissions from human activity [2]. Most of the studies about the development of building ecomaterials suggest using aerial or hydraulic lime based binders ([3],[4],[5]) but lime production induces CO_2 emissions comparable to that of cement.

These emissions are of two types: those resulting from the conversion of carbon compounds of the raw materials during the manufacturing process and those produced by the combustion of fossil energy needed for the calcination of raw materials. According to Saint Astier, the carbon emissions in NHL5 production is approximately 0.635 t CO_2/t NHL5 which comprises 0.360 from raw material and 0.275 from coal [6].

Consequently, we chose to substitute 50% of NHL5 by metakaolin, a pozzolanic admixture.

Since the production of metakaolin does not generate any CO_2 emissions from chemical reactions and because the binder comprises 50% NHL and 50% MK, the resulting amount of CO_2 from the raw materials of our binder is approximately 0.180 t CO_2 /t binder.

The CO_2 emissions from the process of production of MK is about 0.175 t CO_2 /t MK [7], we could conclude that the amount of CO_2 from fuels for our binder is 0.225 t CO_2/t binder.

Finally, the total CO_2 emitted from the production of this alternative binder is about 0.405 t CO_2/t binder i.e. a reduction of 36% compared with the production of pure NHL5.

In order to improve the properties of the matrix, glycerol carbonate (GC), $CO_3C_3H_5OH$, presented in Fig. 1, was added to the

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doi:10.1016/j.cemconres.2010.03.009

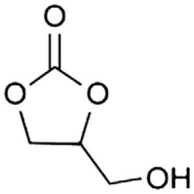

Fig. 1. Glycerol carbonate molecule.

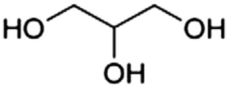

Fig. 2. Glycerol molecule.

mix. GC is prepared from a renewable raw material, the glycerol (Fig. 2), which is generated by the chemical conversion of vegetable oils. Glycerol is thus a co-product in the industrial productions of fatty acids (surface active agents) and of biodiesel [8]. The multivalorization of glycerol is necessary to consolidate economic balance of the biodiesel production as the world glycerol production could reach 2.2 millions of tonnes in 2010 [9].

Clean processes have been developed to prepare glycerol carbonate [10,11] and no R-phrase is mentioned in its Material Safety Data Sheet. Its chemical structure provides ideal physico-chemical properties for solvent, emulsifier or cosmetic formulations [12–14]. Glycerol carbonate (GC) is also used as a chemical intermediate, especially as monomer for the preparation of polyesters, polycarbonate or polyurethane [15]. Moreover, GC is authorized by ECOCERT® as an ingredient for a bioproduct formulation. ECOCERT specifications [16] take into account the natural origin of the molecule as well as the chemical processes required for the conversion of the natural molecules. Thus, GC can be used as a plasticizer for nail varnish formulations which meets the French charter “ecological cosmetic” [12]. In a previous study, Clements [17] studied the properties of glycerol carbonate as catalysts for the curing of cementitious mixtures. GC was also used by Nguyen [18] as an additive for cement mortar in order to reduce shrinkage, but initial results showed that GC contributed to a very fast hardening of the mortar and it was consequently discarded from the study.

In this work, GC was chosen for this very property, i.e. in order to improve the early age mechanical properties of our binder.

The aim of this paper is to investigate the effects of glycerol carbonate incorporation on the binder properties in both fresh and hardened states. At early age, the rheological behaviour of the binder was assessed, and the conductivity, pH and organic compounds concentrations in diluted solutions monitored. The latter monitoring was undertaken in order to understand the interactive mechanisms between the GC and the mineral species of the binder during the first hours after mixing. The mechanical properties and the dimensional variations of the hardened paste were also monitored. Finally, the results of microstructural investigations will be presented with the aim of understanding the mineralogical changes responsible for the aforementioned changes in material properties.

2. Experimental details

2.1. Materials

The metakaolin used is a commercial flash calcined metakaolin (Argicem of the Argeco Company) from the region of Fumel, France. Its chemical composition is given in Table 1.

The hydraulic lime (NHL5) comes from Saint Astier and has the composition presented in Table 2.

Glycerol carbonate (98%) was supplied by Huntsman (USA).

Table 1
Chemical composition of the metakaolin used [40].

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Loss of ignition
MK	68.7	25.7	2.3	0.7	tr	0.2	0.8

Table 2
Mineralogical composition of hydraulic lime NHL5 from St Astier [6].

	$Ca(OH)_2$	$CaCO_3$	C_2S	C_3A	C_2AS	C_4AF	$CaSO_4$	Insoluble
NHL5	22	23	43	0.7	1.3	0.7	0.7	5.6

2.2. Samples preparation

The reference paste was prepared with a water–binder ratio of 0.5 using a 1:1 mix of hydraulic lime (NHL) and metakaolin (MK). The GC paste was obtained with the addition of glycerol carbonate at a dosage rate of 1 wt.% of the binder. The mixing sequence is reported in Table 3.

Specimens were cast in 40 × 40 × 160 mm moulds and left for 48 h. Then, the prisms were demoulded and cured continuously under controlled conditions (100% or 50% relative humidity; 20 °C temperature) until the property tests were carried out.

2.3. Experimental methods on fresh paste

2.3.1. Rheological tests

The yield stress of the fresh paste was measured using an Anton Paar shear rheometer with a rotational cylinder measuring system. The test involves applying an increasing shear stress to the paste until the shear strain rate becomes significant, at which point the shear stress is measured and assumed to be equal the yield stress of the paste. The shear stress was increased at a rate of 1 Pa/s.

In the present test, a water–binder ratio of 0.58 was used, rather than the standard ratio of 0.5, because the flow test requires the mix to have greater fluidity than that of the standard mix.

The mixing sequence adopted is given in Table 3. At the end of mixing, the paste was immediately transferred into the rheometer, with measurements being taken at 0, 5, 11 and 15 min after transfer. As the mixing operation lasted 3 min and further 3 min was necessary to transfer the paste into the rheometer, the first test was actually undertaken 6 min after the first contact of water with anhydrous binder.

The tests were carried out at a controlled temperature of 20 °C.

2.3.2. Conductivity and pH monitoring

This method is based on the conductometric test of Vernet and is undertaken in order to study the reactivity of cement-admixture systems [19]. Measurements were performed using a double wall reactor maintained at a controlled temperature (20 °C). Conductivity and pH were continuously measured for 24 h and results were collected by a Consort multiplexer (model D230). Conductivity and pH electrodes are Radiometer Analytical instruments. The pH-electrode was calibrated using standard buffer solutions of pH 11.0 and 13.0. The conductivity electrode is a 2-pole conductivity cell. Its conductivity cell constant was determined using the conductivity standard solution of KOH. For the 0 to 20 mS/m measuring range, the frequency is 563 Hz and the peak to peak voltage is 100 mV.

The tests were carried out on diluted solution of 50% NHL and 50% MK with a water to solid ratio of 3. The solution was mixed with a magnetic stirrer. The Control binder and GC binder were tested, with the latter including the GC admixture at 4 wt.% of binder in order to maximise the interactions and to make the observations easier.

2.3.3. Chromatography HPLC

Filtered and diluted solutions (E/B = 4) of binder were analysed using an HPLC apparatus, which consisted of a P1500 Spectra Physics

Table 3
Mixing sequence.

Mixing sequence		1	2	3	4	5
Time		30 s	30 s	30 s	60 s	30 s
Speed		Low	Low	Low	Stop	High
Sample	Reference	NHL + MK	NHL + MK + W	NHL + MK + W	NHL + MK + W	NHL + MK + W
	GC	NHL + MK	NHL + MK + W	NHL + MK + W + GC	NHL + MK + W + GC	NHL + MK + W + GC

NHL: natural hydraulic lime; MK: metakaolin; W: water; GC: glycerol carbonate.

Analytical pump and an AS3000 auto-sampler. Detection was performed with a model Varian 350RI. Elution was done with 4.10^{-3} N H_2SO_4 at a 0.8 mL/min flow rate.

2.4. Experimental methods on hardened paste

2.4.1. Compressive and flexural strengths

Two series of strength tests were undertaken.

In the first of these, compressive and flexural strengths tests were performed in accordance with French Standard NF EN 196-1 on specimens with ages from 9 days to 8 months. These tests were conducted at constant load rates, with the rates for the compressive and flexural tests being 2.4 kN/s and 0.05 kN/s respectively.

During the second series, compressive and flexural strengths of specimens with ages from 2 to 14 days were tested using an alternative loading rig at constant displacement rates of 0.5 mm/min and 0.3 mm/min respectively.

For both series, a minimum of 2 flexural tests and 4 compressive tests were undertaken.

2.4.2. Total and endogenous shrinkages

Measurements of total and endogenous shrinkages were performed on 40 × 40 × 160 mm specimens using a retractometer accurate to 0.001 mm. The specimens were kept in a room at a constant temperature of 20 °C and constant Relative Humidity of 50% according to the French Standard NF EN 196-1.

The first measurements were performed immediately after demoulding, i.e. 48 h after casting.

The variations in mass of the specimens were determined with a scale accurate to 0.1 g.

The results presented are mean values from measurements taken of 3 different samples.

2.4.3. X-ray diffraction analysis (XRD)

The measuring system was a Siemens D5000 diffractometer using a Kα ($\lambda = 1.789$ Å) cobalt anticathode. The 2-Theta values ranged from 4°to70° and were recorded with a 0.02° step with an acquisition time of 10 s per step.

Measurements were performed on non-dried crushed samples which were 28 days old and which had been passed through an 80 µm sieve.

2.4.4. Thermogravimetric analysis (TG-DTG)

Thermogravimetric analyses were carried out on 28 days old samples from 200 to 300 mg in weight, using a Setaram thermo-analyser at a heating rate of 10 °C/min up to 900 °C.

TG techniques allowed the identification of amorphous hydrates such as calcium silicate hydrates (C–S–H). For this purpose, the measurements should be undertaken on dried samples, otherwise the free water evaporation may hide the decomposition of some hydrates. The selected technique was solvent-based drying. The crushed sample was mixed with acetone and then filtered to permit the evaporation of the water–acetone mixture.

Dried samples were then ground in an agate mortar and sieved to 80 µm.

3. Results and discussion

3.1. Fresh paste properties

As reported by a previous study [18], the incorporation of GC into the paste led to a quick stiffening of the paste at the end of mixing. Rheological measurements were consequently performed in order to quantify the stiffening observed.

3.1.1. Yield stress measurements

Yield stress evolution of the paste after the end of mixing was previously used for monitoring the setting process in cementitious materials [20]. Yield stresses of the control paste and of the GC paste 0, 5, 11 and 15 min after their transfer into the rheometer (i.e. 6, 11, 17 and 21 min after their first contact with water) are shown in Fig. 3.

The incorporation of GC has a clear influence on the structure of the paste in the early stages. From 0 to 15 min, the yield stress of the control paste remained almost constant whereas that of the GC paste exhibited a strong increase after 5 min. This enhancement results from the development of a solid structure in the system. However, according to the Vicat test definition, the material had not set, since the yield stress only reached 225 Pa, whereas the limit value detected by the Vicat needle is around 20 kPa [20]. But, this increase of yield stress is significant and results from chemical and/or physical mechanisms induced by the presence of GC.

3.1.2. Conductivity and pH monitoring

The results from conductivity and pH monitoring of two stirred diluted solutions, over a 24 h period, are presented with a logarithmic time scale in Fig. 4. One solution includes 1% GC whilst the other is a control with no GC. The logarithmic scale is used in order that the results during the first few minutes can be clearly observed.

In the longer term, both solutions show a conductivity maximum occurring more than ten hours after mixing. The decrease in conductivity observed after this maximum is caused by the precipitation of portlandite. In fact, at this time, the solution becomes supersaturated with respect to this hydrate [21]. The relatively long dormant period that precedes this phenomenon corresponds to the very slow reaction of β-C_2S with water, as exposed by Tamás [22]. It can be seen that the time to reach maximum conductivity is slightly

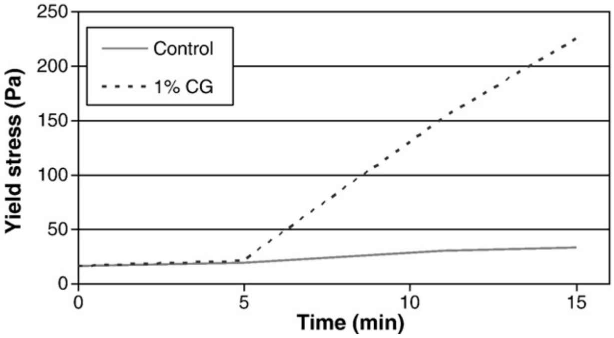

Fig. 3. Evolution of yield stress versus time for control and admixed paste.

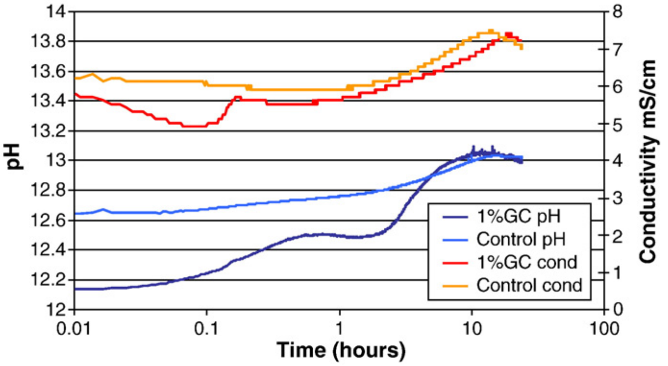

Fig. 4. Conductivity and pH monitoring of a control and a GC admixed solutions.

delayed for the solution containing GC in comparison with that of the control.

A more marked difference occurs at early age. The solution with GC exhibits a fall during the first 6 min (0.1 h), then the conductivity increases and its evolution becomes very close to that of the control. This drop in conductivity is related to the reduction of ion content in the solution which is associated with the formation of a solid precipitate.

This phenomenon is confirmed by the test shown in Fig. 5, that involves the addition of GC to a saturated calcium hydroxide solution. A white precipitate is almost immediately formed whereas nothing happens in the control container.

The evolution of pH is also modified by the presence of GC in the solution. Its initial pH is lower than that of the control and it only reached the same level after five hours. It also exhibited a plateau from 10 min to 2 h.

These observations show that GC does not just induce a time lag in the evolutions of pH and conductivity, as do other setting agents or retarding admixtures [23], but GC really modifies the mechanisms of the reactions, in that it gives rise to the early precipitation of a new compound.

3.1.3. HPLC analyses

Chromatograms of binder diluted solutions showed the near immediate decomposition of GC in this alkaline medium. This result is confirmed by a previous study [24] which presented two consecutive mechanisms. First, hydrolysis of GC occurs in alkaline medium and leads to the formation of glycerol and CO_2. Then, glycerol may generate diglycerol by polymerization.

Glycerol and diglycerol were actually detected by HPLC (Fig. 6.) 10 min after the start of the test.

The dosage of solution revealed that more than 60% of the initial GC had decomposed after 10 min.

Fig. 5. $Ca(OH)_2$ saturated solution precipitation test. A: GC. B: control.

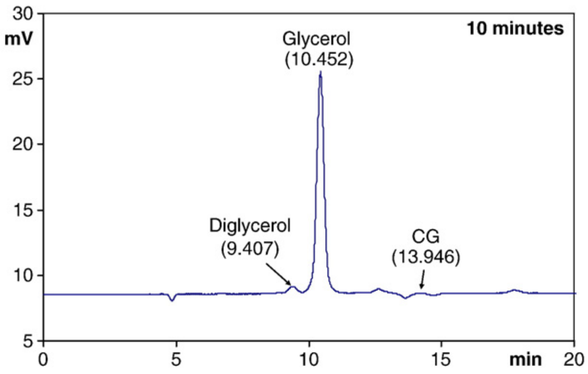

Fig. 6. HPLC chromatogram of filtered diluted solution containing GC 10 minutes after the mixing.

The hydrolysis reaction of glycerol carbonate in an alkaline environment is illustrated in Fig. 7 and this reaction leads to the formation of glycerol and CO_2.

At a pH higher than 12, CO_2 is converted in CO_3^{2-} ions through step 2 illustrated in Fig. 8. As the solution is saturated in calcium ions, we could make the hypothesis that the latter reacts with the carbonate ions which originate in step 2, which leads to the precipitation of calcium carbonate (Fig. 8, step 3).

According to the mechanism proposed, the precipitate observed in Fig. 5 would be calcium carbonate whose presence can be correlated to the drop of conductivity (Fig. 4). Moreover, HO^- ions are consumed by step 2, which suggests a lower initial pH with GC as observed in Fig. 4.

The ulterior evolution of pH can be explained by the increase of the dissolution rate of $Ca(OH)_2$ (from NHL) caused by the consumption of Ca^{2+} in step 3, acting as “calcium pump”. As 2 molecules of OH^- are released for 1 molecule of portlandite dissolved, the concentration of OH^- in solution and subsequently pH would increase.

Finally, the delay of precipitation of portlandite observed with GC could be attributed to the consumption of a part of calcium ions by step 3. The amount of calcium in solution would then be lower than for the control and the supersaturated state in portlandite would consequently occur later.

The investigations carried out on fresh paste led to the conclusion that the incorporation of GC into our pozzolanic binder induces stiffening at very early age. This phenomenon would be caused by the formation of solid calcium carbonate. This compound would result from the reaction between calcium ions from mineral species and carbon dioxide from the decomposition of GC in an alkaline medium.

3.2. Shrinkage reducing effect

The study undertaken by Cornac et al. [25] demonstrated the shrinkage-reducing effect of glycerol incorporated into cement mortars. In order to explore the effect of GC on dimensional variations of the pozzolanic binder, weight loss, endogenous and total shrinkages of the paste have been measured over a period of time.

After 330 days, the incorporation of GC to the paste leads to a reduction of total shrinkage of 30% and to a reduction of endogenous shrinkage of more than 85% (Fig. 9).

At the same time, the weight losses of control and admixed paste are 22.6% and 21% respectively. These values are close to one another but the drying kinetics of the two specimens is significantly different (Fig. 10). The paste containing GC reached its final mass in 20 days, whereas the control paste needed more than 60 days.

These results show that GC modifies the desiccation and hydration mechanisms in three ways, each governing a different stage of the process, which may be seen in a plot of total shrinkage versus weight loss, in the manner proposed by Neville [26] (Fig. 11).

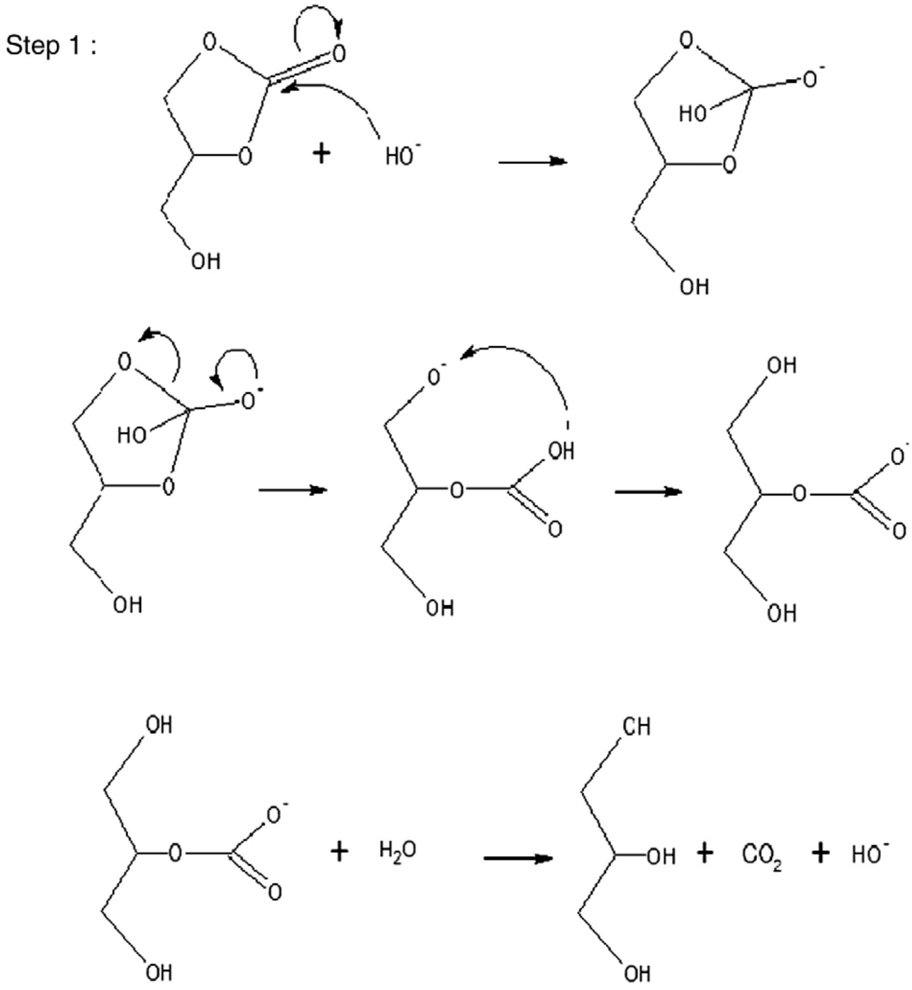

Fig. 7. Hydrolysis mechanism of GC.

First, at early age, GC accelerates water evaporation from big pores without generating additional shrinkage compared to the control (first linear part of the curves on Fig. 11).

In a second stage, GC modifies the endogenous shrinkage, as indicated by the shortening of the second linear part of the curve for the GC paste (Fig. 11).

Neville [26] and Tazawa [27] have attributed the phenomenon of endogenous shrinkage to two mechanisms:

- the absorption of water from capillarity to permit hydration that leads to the development of capillary stresses,
- the difference of volume between the hydrated reaction products and the reactants (anhydrous phases plus water).

GC could influence the first phenomenon as it is a surface agent that reduces the surface tension. At 25 °C, the surface tension of water is about 72 mN/m whereas that of GC is 45.5 mN/m [24]. But, as shown in Section 3.1.3, GC is also partly decomposed in alkaline environment and forms mainly glycerol. The surface tension of glycerol is about 63 mN/m. The pore solution would then contain a mix of GC and glycerol and its surface would be set between 45.5 and 72 mN/m. This decrease leads to the reduction in the negative capillary pressures responsible for shrinkage. The correlation between the reduction of surface tension and the decrease of endogenous shrinkage has been confirmed by a number of authors [28–33].

Furthermore, the incorporation of GC could also affect the second mechanism, as it can modify the nature and, consequently the volume, of hydrated phases. This hypothesis needs to be confirmed by mineralogical analyses.

Finally, a third step is visible in Fig. 11, as identified by the curved portion of the lines, which results from a gain of mass of the specimens and is probably linked with the carbonation of the paste. This part is much more pronounced in the GC curve. This result shows that GC has a clear influence on long term carbonation processes of the paste.

The drying kinetics observed with GC here (Fig. 10) is different from that seen in previous studies [28–30,34] with shrinkage-reducing agents (SRA). These authors observed a reduced drying rate in systems with SRA whereas we observe an increase of the drying kinetics with GC.

Step 2 : $CO_2 + 2\,HO^- \longrightarrow CO_3^{2-} + H_2O$

Step 2 : $CO_3^{2-} + Ca^{2+} \longrightarrow CaCO_3 \downarrow$

Fig. 8. Possible reactions inducing the preipitation of cacite.

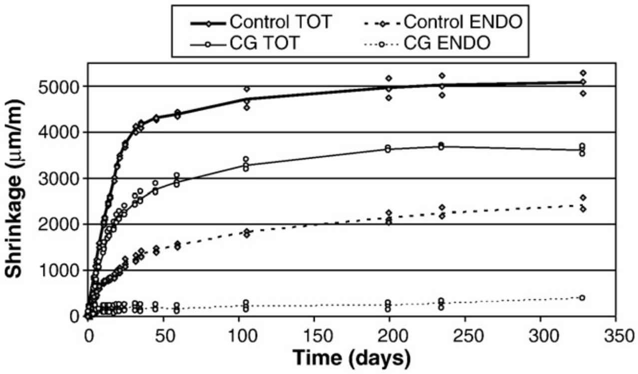

Fig. 9. Total and endogenous shrinkage of control paste and GC admixed paste.

This difference can be explained by the existence of different drying mechanisms. Coussot [35] identified three different drying mechanisms namely, surface evaporation, capillarity and evaporation from the interior of the sample. In our binder, due to the excess of water, the evaporative process could be predominant. In which case, the drying kinetics would be linked to the evaporation rate of the bulk solution which would be more important with GC as it is more important for solution containing SRA [28].

3.3. Mechanical properties

Mechanical properties were assessed for the binder with and without GC.

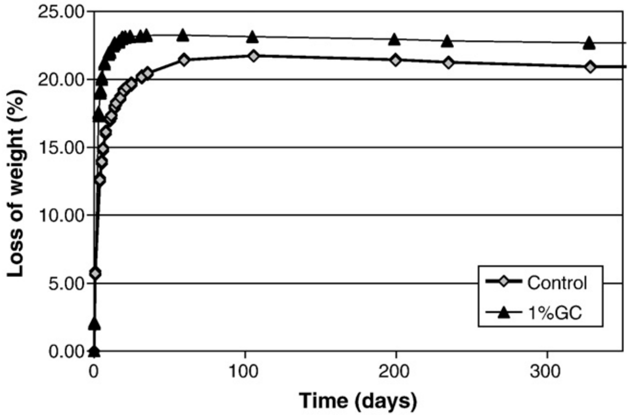

Fig. 10. Loss of weight of control paste and GC admixed paste.

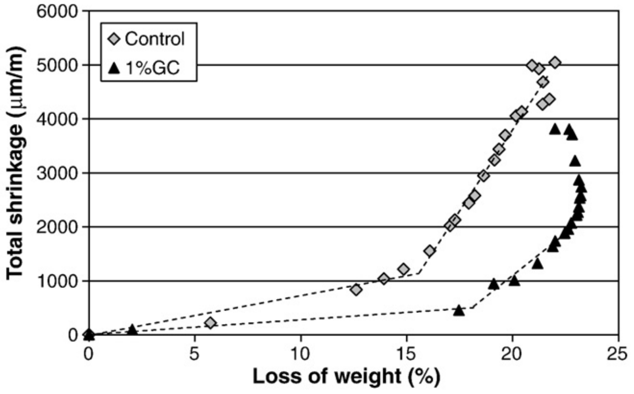

Fig. 11. Total shrinkage versus loss of weight for control paste and GC admixed paste.

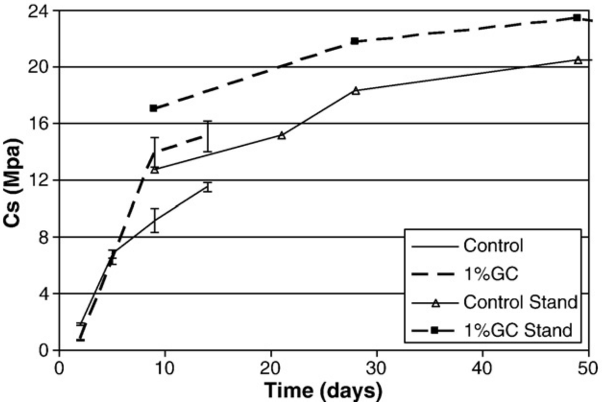

Fig. 12. Influence of GC on the compressive strength of the paste from 2 to 49 days.

Fig. 12 shows the compressive strength of control and GC paste at 2 to 49 days (results from two series of measurements are given as exposed in Section 2.4.1). From 2 to 5 days their properties are very close to one another, but from 9 to 49 days, the incorporation of GC led to an enhancement of the compressive strength of around 4 MPa. After 9 days, this represents an improvement of compressive strength of approximately 50%.

In the long term (Fig. 13), there is a reduction in strength of the GC paste, the properties of both pastes converged and then from 240 days the strength of the control paste exceeded that of the GC paste. This evolution is probably linked to an influence of GC on the carbonation processes of the paste, which would also be consistent with the long term shrinkage measurements.

As already mentioned, the early age compressive strength of the binder is similar to that of the control, thus, the mechanisms responsible for the rapid stiffening of the binder (see part 3.1 Fresh paste properties) cannot be directly responsible for the enhancement of mechanical properties from 9 to 49 days.

In order to verify that the glycerol resulting from the degradation of GC was not responsible for this improvement, we tested the mechanical performances of paste with 1% of glycerol. The results, which can be seen in Fig. 13, show that the incorporation of glycerol to the paste did not lead to a clear enhancement of the compressive strength.

3.4. Microstructural characterization

3.4.1. X-ray analyses

Fig. 14 shows the mineralogical characterization by XRD of the control paste and of the paste including 1% of GC, after 14 days of curing.

First, we can observe that after 14 days, the portlandite was almost totally consumed by the pozzolanic reaction, with the only peak visible

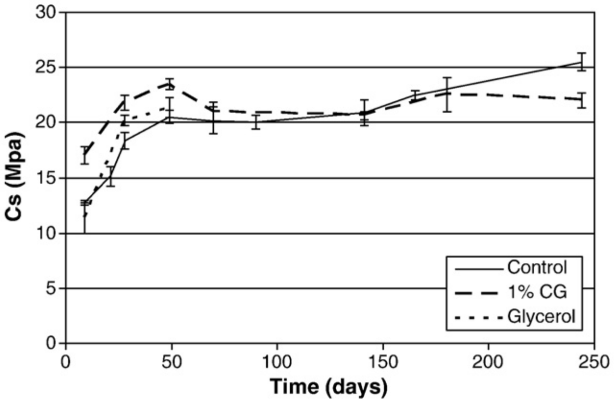

Fig. 13. Influence of GC and of glycerol on the compressive strength from 9 to 240 days.

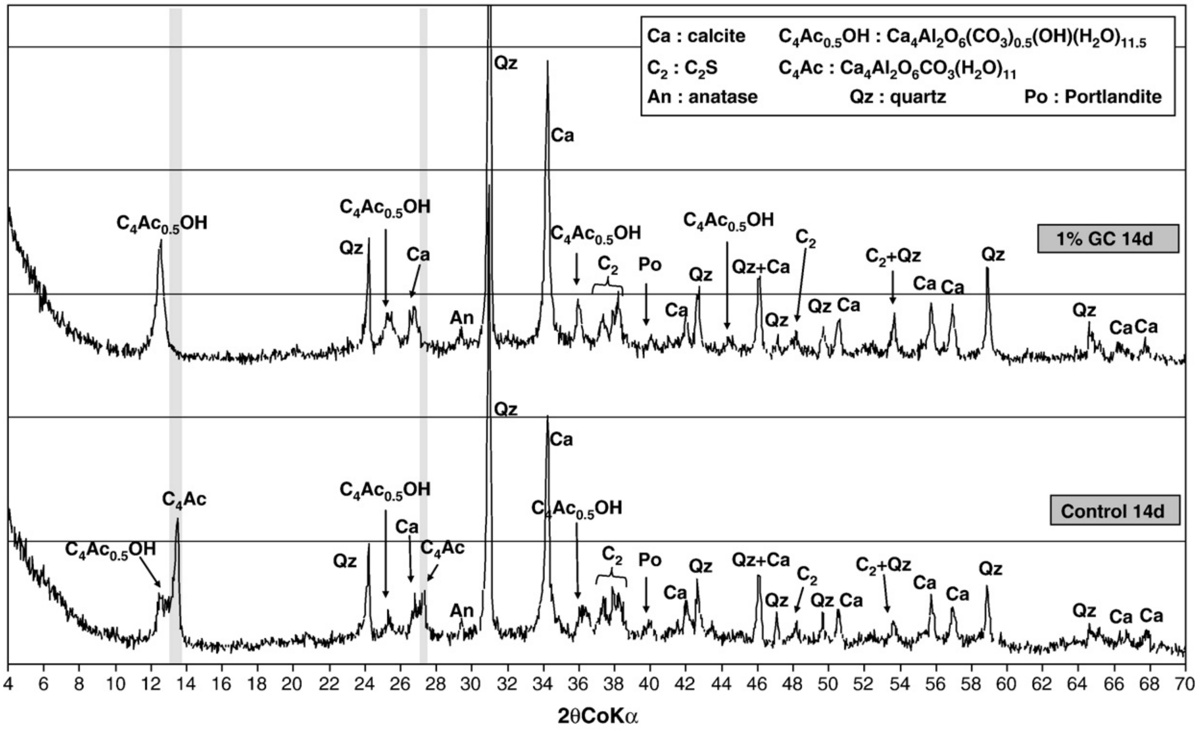

Fig. 14. Mineralogical analysis by XRD of the control binder and of the paste with 1% of GC after 14 days of curing.

being the main one at 39.8°. Some anhydrous phases are still present (C_2S) and the peaks of the quartz from MK and the calcite from NHL are also visible.

Considering the hydrated phases, for the control paste, the peaks of calcium aluminium oxide carbonate hydrate, $Ca_4Al_2O_6CO_3\cdot(H_2O)_{11}$ (noted C_4Ac), are observed as well as those of calcium aluminium oxide hemi-carbonate hydroxide hydrate, $(Ca_4Al_2O_6(CO_3)_{0.5}(OH)\cdot(H_2O)_{11.5}$ (noted $C_4Ac_{0.5}(OH)$). By contrast, for the 1% GC paste, the peaks of $C_4Ac_{0.5}(OH)$ are much higher than for the control paste and C_4Ac is not present at all.

The existence of both of these forms of calcium carboaluminate in hydrated systems containing C_3A and $CaCO_3$, has been already described in the literature by Bonavetti *et al.* and Kakali et al. [36,37].

Friás Rojas et al. [38,39] also identified calcium carboaluminate hydrated phases in a mix of MK and aerial lime. The formation of these hydrated phases has been attributed by the authors to the presence of CO_2 and/or $CaCO_3$ in the pastes. The origin of these species can be the atmospheric CO_2 at the moment of mixing, the use of a slightly carbonated lime or the presence of carbonic gas dissolved in mixing water [39]. In our case, these three conditions are satisfied, mixing occurs in presence of atmospheric CO_2, NHL contains a large amount of calcite and the decomposition of GC leads to the production of CO_2 into the solution.

The difference between the two pastes could be attributed to the modification of chemical equilibrium due to the presence of GC. Precipitation of calcite at early age in presence of GC could lead to a higher rate of dissolution of portlandite, and consequently to the

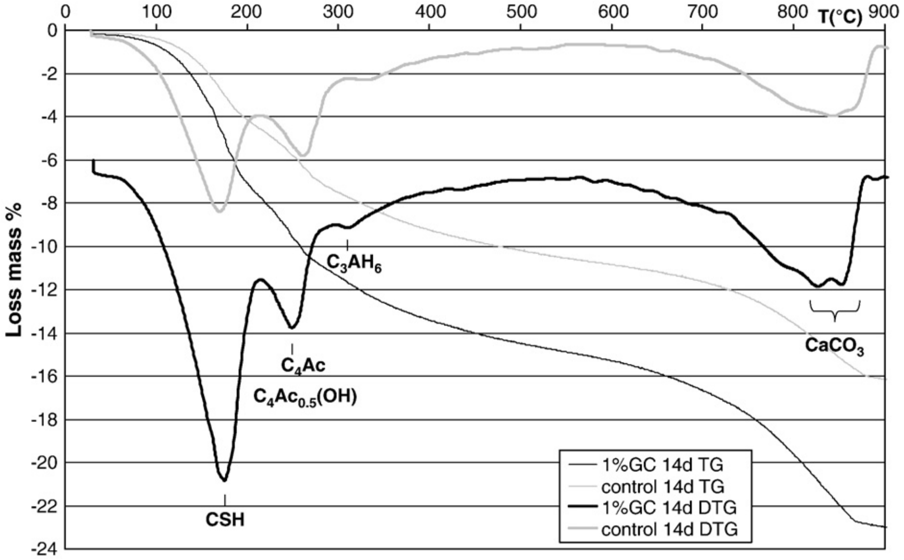

Fig. 15. TG and DTG thermograms of control paste and paste containing 1% of GC after 14 days of curing.

liberation of hydroxyl ions in solution. This higher amount in solution could induce a displacement of the chemical equilibrium in favour of calcium aluminium oxide hemi-carbonate hydroxide hydrate.

3.4.2. TG-DTG analyses

Fig. 15 shows the thermogravimetric analyses of the control paste and of the paste including 1% of GC, after 14 days of curing. The results have been filtered and derivatives calculated with the Peakfit software.

The total consumption of portlandite by the pozzolanic reaction after 14 days is confirmed by the thermal analysis (the dehydration of portlandite occurs between 520 and 570 °C).

The thermogravimetric analyses revealed the presence of hydrogarnet, C_3AH_6 (wide band with a maximum situated at about 310 °C). These aluminates are usual products of the reaction of MK with $Ca(OH)_2$. They were not visible with XRD due to the overlapping with the peaks of quartz.

According to Friás Rojas et al. [38], C_4AcH_{11} and $C_4Ac(OH)H_{11.5}$ have thermodynamic properties similar to C_4AH_{13}, their decomposition would then probably correspond to the peak with a maximum for 250 °C.

The large peak above 700 °C corresponds to the decarbonation of calcium carbonates which have more or less crystallised. Calcium carbonates mainly come from the anhydrous initial components, as they represent 23% in mass of the NHL. But, it is noted that the peak is more prominent for the paste containing 1% GC. These additional calcium carbonates would result from the initial precipitation due to GC decomposition.

The main difference between the two pastes is related to the intensity of the peak attributed to the CSH (which decomposes in the temperature range of 150–180 °C). In GC paste, this peak is much more pronounced than in the case of the control paste. Consideration of this finding with respect to the observed enhancement in mechanical properties, brought about by the incorporation of GC (see Section 3.3), would suggest that higher compressive strengths are associated with greater quantities of C–S–H in the paste.

According to previous work, the hydration of calcium silicates is accelerated in pastes containing $CaCO_3$ [37], the additional quantity of calcite formed in the presence of GC is then considered to induce a more rapid hydration of C_2S and subsequently results in a larger amount of CSH.

4. Conclusion

This study shows the potential of a new and innovative ecomaterial for building applications which is formed from metakaolin, hydraulic lime and glycerol carbonate.

The incorporation of GC brings about an early formation of solid structure in the paste, which is attributed to the precipitation of calcite.

In the case of production by prefabrication, this property could permit an immediate form removal.

The significant reduction of shrinkage induced by GC, which is attributed to lower surface tensions in the capillary fluid, should reduce the level of microcracking.

Finally, the improvement of early age mechanical strength is considered to be due to the greater quantities of C–S–H present in the GC paste compared with that present in the control paste.

The monitoring of hydration by XRD and DTG, as well as complementary NMR analyses, are being performed in order to confirm the mechanisms of action of GC on the development of the hydrates and in order to study the effect of GC on the long term behaviour of the paste.

This paper was the first part of a study aimed at optimising this mix for its use as a binder for a building ecomaterial. A second article will present work on the improvement of thermal and hygroscopic properties of the material by the incorporation of light vegetable aggregate, i.e. stalks of peeled hemp and sunflower stalks, as well as work on improving the ductility of the material by the inclusion of vegetable fibres, i.e. flax, hemp and yucca fibres.

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