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11th ACI/RILEM INTERNATIONAL CONFERENCE ON CEMENTITIOUS MATERIALS AND ALTERNATIVE BINDERS FOR SUSTAINABLE CONCRETE

SP-349

Editor:
Arezki Tagnit-Hamou



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11th ACI/RILEM INTERNATIONAL CONFERENCE ON CEMENTITIOUS MATERIALS AND ALTERNATIVE BINDERS FOR SUSTAINABLE CONCRETE

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PREFACE

In July 1983, the Canada Centre for Mineral and Energy Technology (CANMET) of Natural Resources Canada, in association with the American Concrete Institute (ACI) and the U.S. Army Corps of Engineers, sponsored a five-day international conference at Montebello, Quebec, Canada, on the use of fly ash, silica fume, slag and other mineral by-products in concrete. The conference brought together representatives from industry, academia, and government agencies to present the latest information on these materials and to explore new areas of needed research. Since then, eight other such conferences have taken place around the world (Madrid, Trondheim, Istanbul, Milwaukee, Bangkok, Madras, Las Vegas, and Warsaw). The 2007 Warsaw conference was the last in this series.

In 2017, due to renewed interest in alternative and sustainable binders and supplementary cementitious materials, a new series was launched by Sherbrooke University (UdeS); ACI; and the International Union of Laboratories and Experts in Construction materials, Systems, and Structures (RILEM). They, in association with a number of other organizations in Canada, the United States, and the Caribbean, sponsored the 10th ACI/RILEM International Conference on Cementitious Materials and Alternative Binders for Sustainable Concrete (ICCM2017). The conference was held in Montréal, QB, Canada, from October 2 to 4, 2017. The conference proceedings, containing 50 refereed papers from more than 33 countries, were published as ACI SP-320.

In 2021, UdeS, ACI, and RILEM, in association with Université de Toulouse and a number of other organizations in Canada, the United States, and Europe, sponsored the 11th ACI/RILEM International Conference on Cementitious Materials and Alternative Binders for Sustainable Concrete (ICCM2021). The conference was held online from June 7 to 10, 2021. The conference proceedings, containing 53 peer reviewed papers from more than 14 countries, were published as ACI SP-349.

The purpose of this international conference was to present the latest scientific and technical information in the field of supplementary cementitious materials and novel binders for use in concrete. The new aspect of this conference was to highlight advances in the field of alternative and sustainable binders and supplementary cementitious materials, which are receiving increasing attention from the research community.

To all those whose submissions could not be included in the conference proceedings, the Institute and the Conference Organizing Committee extend their appreciation for their interest and hard work.

Thanks are extended to the members of the international scientific committee to review the papers. Without their dedicated effort, the proceedings could not have been published for distribution at the conference. The cooperation of the authors in accepting reviewers' suggestions and revising their manuscripts accordingly is greatly appreciated.

The assistance of Chantal Brien at the Université de Sherbrooke is gratefully acknowledged for the administrative work associated with the conference and for processing the manuscripts, both for the ACI proceedings and the supplementary volume.

Arezki Tagnit Hamou, Editor

Chairman, eleventh ACI/RILEM International Conference on Cementitious Materials and Alternative Binders for Sustainable Concrete (ICCM2021).
Sherbrooke, Canada
2021

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EFFECT OF MINERAL ADDITIONS ON THE SELF-HEALING ABILITY OF CEMENTITIOUS MATERIALS

Carol Namnoum, Benoît Hilloulin, Maxime Robira, Frédéric Grondin, Ahmed Loukili.

Synopsis: The production of cement by calcination of limestone releases large amounts of carbon dioxide. Development of concrete quality lead to optimize the sustainability and maintenance phases of concrete structures, so, using supplementary cementitious materials (SCM) is one of the methods adapted to reduce the environmental impact of cement production. In addition, self-healing of concrete appears as a process to considerably improve the durability of a damaged structure [1]. As revealed by most analyses, mineral additions can be used to improve the autogenous healing ability of cementitious materials [2].

In this study, the influence of using a combination of SCMs, such as ground granulated blast furnace slag and metakaolin, on the mechanism of autogenous crack healing was assessed in ternary formula. Self-healing evolution was characterised by means of mechanical tests carried out on notched mortar samples with different substitution ratios. The mechanical recovery was investigated after the healing period. Moreover, the micro-chemical structure of the healing products was determined using various techniques (TGA, SEM/EDS and XRD). The primary results showed that using metakaolin and ground granulated blast furnace slag together greatly improve the healing efficiency.

Keywords: Autogenous self-healing, ground granulated blast furnace slag, metakaolin, mechanical properties, SEM/EDX, TGA, XRD.

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INTRODUCTION

Around the world, the concern for sustainable development is present in every field of civil engineering, because cement is qualified as a major source of carbon. The valorization of secondary materials is the one of the methods to be followed to reduce the harmful emissions attributed to the process of portland cement production. Incorporation of mineral additions such as fly ash, silica fume, ground granulated blast furnace slag and metakaolin can improve permeability and strength of structures only over the long term, compared to portland cement that has better mechanical properties at early age. On the other hand, self-healing appears as a promising phenomenon to the durability of structures by blocking the penetration of aggressive agents and restoring the original mechanical properties of the structure. The intrinsic ability of concrete to heal is described by the continuous hydration of unhydrated cementitious particles and/or the precipitation of calcium carbonate [3]. Autogenous healing process is observed when unhydrated particles of clinker react with water to form secondary hydration products like portlandite and C-S-H, which can fill the crack and lead to mechanical recovery like strength and stiffness recovery. Different studies involve that autogenous healing potential is restricted to small crack and it requires the presence of water [4]. This type of healing depends on the cracking age, the presence of sustained mechanical load and the type of cementitious material [4] [5].

The intrinsic healing capacity of cement-based materials can be improved by mineral additions. From different research studies, the chemical reaction of minerals can form products that fill and heal cracks [4]. Through hydration reaction of slag with water in the presence of portlandite $\text{Ca}(\text{OH})_2$, additional hydration products like C-S-H gel were formed at the crack surface. Their latent hydraulic properties explain their significant role in self-healing processing [5]. As found in several studies, the mineralogy of reaction products formed in cracks is obviously different from the hydration products in bulk matrix. Self-healing in SCM cement paste lead to complex mineralogy of healing products in cracks compared to self-healing in

portland cement paste as the reaction mechanism of SCM is more complicated than that of portland cement.

In recent years, we notice the great interest of using metakaolin as supplementary cementitious materials. The importance of metakaolin is its contribution to improve the strength of the mixture at a young age. It has a strong pozzolanic reaction that induces the formation of C-S-H gel and C-A-S-H as healing products. The highly active pozzolanic reaction of metakaolin with respect to the latent hydraulic properties of slag can explain this equilibrium of functions leading to improved mechanical behavior [6]. Indeed, these two SCM characterized by their fineness allow to improve microstructure density, the presence of both MK and Slag has no adverse effect on the development of strength. However, ternary blend mix including MK and Slag can have some improved properties [7]. Initial hydration of ternary mixture containing MK and Slag produces C-S-H products and alumina phases as C_2ASH_8 , C_4AH_{13} and C_3AH_6 [7].

In this paper, self-healing capacity of mortars including supplementary cementitious materials is presented. More specifically, the aim was to test the mechanical properties of the mortars containing SCM following the self-healing process. Specimens mortars were designed and pre-cracked using controlled crack creation procedures, self-healing potential of mortars immersed in water was assessed by quantification of mechanical recovery. In order to gain insight into the chemical process of self-healing in SCM cement paste, the reaction products formed in cracks were characterized by using scanning electron microscope (SEM) equipped with an energy dispersive spectroscopy (EDS), Thermogravimetric analysis (TGA) and X-ray diffraction test. To distinguish the newly formed reaction products from the bulk paste, artificial gaps were made [8].

RESEARCH SIGNIFICANCE

With the increasing development of ternary formulations motivated by economic and environmental considerations in the first place, it is important to see what happens - if it takes place – during the self-healing phenomenon. The development of ternary formulations favorable to healing could be useful for on-site industrial applications.

MATERIALS AND EXPERIMENTAL PROGRAM

Materials, mixture proportions and exposure conditions of healed samples

Mortar mixtures were prepared with water to binder mass ratio of 0.4. The constituents of mortar mixtures are (0/2) sand, CEM I 52.5 N portland cement and different types of supplementary cementitious materials (SCM) was added as partial volume substitution of cement up to 30%. Chemical compositions of binders used are detailed in Table1.

Two different mortar formulations are prepared. The reference mixture (100C) was designed with 100% of portland cement, 15MKS: 70% of PC, 15% of metakaolin (MK) and 15% of ground granulated blast furnace slag (GGBFS). Details of the mortars mixture proportions are illustrated in Table2.

By using a concrete mixer with a capacity of 10 to 100 l, specimens of dimensions 7x7x28 cm (2.75 x 2.75 x 11.0 in) [Fig. 1] and 4x4x16 cm (1.57 x 1.57 x 6.29 in) were cast. All preparations were carefully vibrated into two layers on a horizontal vibrating table in order to minimize the

amount of occluded air. The samples were demolded after 24 hours of cure in water at $20 \pm 2^\circ \text{C}$. A notch of depth 7 mm and thickness 5 mm was made at the middle of $7 \times 7 \times 28$ cm specimens to locate the cracks during the mechanical tests. As a first step, mortars samples are pre-cracked after two days of casting by means of three point bending test. Samples were then cured in water at 20°C for 26 days. Finally, three point bending tests were performed on either uncracked or pre-cracked samples and results were compared with those obtained from reference sample. This comparison of load-CMOD curves allow the evaluation of stiffness and strength recovery. Three samples were prepared for each type of mixture; two samples were pre-cracked using three point bending test to obtain crack opening equal to $10 \mu\text{m}$, whereas the third one was left uncracked.

In parallel, compressive test was performed on $4 \times 4 \times 16$ cm specimens at 2, 7 and 28 days. The tests were carried out on three specimens and the average values were retrained. An overview of experimental program is presented by [fig.2].

Chemical & mineralogical analysis of the self-healing products

In the aim of assessing microstructure of healing products, SEM/EDS, TGA and XRD analysis have been performed. Since there is a difficult to examine the formed reaction products in a real crack, artificial cracks were prepared following the methodology proposed by [8]. As shown in [fig. 3], $4 \times 4 \times 16 \text{ cm}^3$ cement paste specimens were prepared with the same constituents mentioned before but except the sand. After 2 days, the specimens were cut into slices of 1 cm width. Then, the slices have been pressed together using a plastic clamp while the gap measured between two slices was less than $100 \mu\text{m}$. Following that, the specimens were immersed in water for 4 weeks, to promote the development of healing products between the flat slices by further hydration.

After self-healing period, the cement paste slices were separated and dried by vacuum for 2h. The slices were observed by SEM equipped with EDS to determine the morphology of healing products formed between each two flat slices and their chemical structures. As mentioned in [7], the planar gaps have no influence on the chemical natures of the healing products formed by further hydration.

The healing products were scratched off from the sliced surfaces. Analysis of mineralogy was performed using TGA and XRD tests. In addition, the internal part of cement paste matrix were grounded into powder and tested in order to differentiate the primary hydrate phases from the healed products formed between the slices.

X-ray diffraction (XRD) measurements were performed on a Bruker D8 phaser instrument. Scans were conducted with a step size of 2.5° , for 0.1 s per step between 5° and 60° . TGA tests were performed in nitrogen atmosphere at 0.6 bars. The heating rate was $20^\circ \text{C}/\text{min}$ and the final temperature is 1400°C .

Assessment of mechanical recovery due to self-healing

In order to evaluate the impact of healing process on mechanical properties, three steps were followed: i) Pre-cracking: Creation of the crack, ii) Immersion healing, iii) Reloading and characterization of mechanical gains.

After the first two stages described beforehand, the corresponding specimens were reloaded in order to identify the mechanical properties regained after healing process. At this time, the reference sample were loaded to obtain an identical crack width of the pre-cracked samples before healing and then they are reloaded immediately in order to characterize the residual mechanical properties for the unhealed specimens [9].

In order to determine the mechanical gains associated with healing, the reload curves of the specimens pre-cracked and then healed are compared to the loading curves of the test specimens' uncracked reference having undergone the same healing conditions [9,10]. Healing performance was quantified by means of two indexes of mechanical recovery related to strength and stiffness recovery respectively (1) (2).

$$IR.Res = \frac{F_{healed} - F_{unhealed}}{F_{ref} - F_{unhealed}} \quad (1)$$

$$IR.Rig = \frac{K_{healed} - K_{unhealed}}{K_{ref} - K_{unhealed}} \quad (2)$$

Where F_{healed} is the maximum strength of the healed samples during reloading, F_{ref} is the maximum strength of reference sample loaded at 28 days and $F_{unhealed}$ is the reloaded-maximum strength of reference sample. Concerning the stiffness K , it was calculated by drawing a tangent on the loaded and reloaded curve. K_{healed} is maximum stiffness of the healed samples during reloading, K_{ref} is the maximum stiffness of reference sample and $K_{unhealed}$ is the reloaded-maximum stiffness of reference sample.

RESULTS AND DISCUSSION

Self-healing products morphology:

SEM/EDS results

After 26 days of immersion following artificial cracking at 2 days, the morphology of self-healing products formed on sliced surfaces of all mortar specimens was observed by using SEM/EDS. The observation of the sliced surfaces was performed directly without any processing. [Fig. 5 (a), (b)] displays the morphology of sliced surface for the reference mixture (100C), and 15MKS after 26 days of healing. Self-healing products observed for reference sample (100C) are ettringite, which is normal in case of continued hydration of anhydrate particles of portland cement. [Fig. 5 (b)] shows the morphology of healing products formed on sliced surface for the sample containing metakaolin and GGBFS as supplementary cementitious materials (SCM). Evidence of C-S-H gel and ettringite formation was found in the cracks. These results are similar to the products resulting from the pozzolanic reaction of metakaolin and the hydration reaction of GGBFS. Moreover, we do not notice the presence of stralingite, which is simply one of the hydration products of metakaolin [11]. The products formed after healing process are the same in a real crack and an artificial crack. Moreover, it was observed that the needles ettringite have a large volume and therefore can easily fill the crack, the other products are denser.

TGA results

TGA test was performed to characterize the reaction products formed in cracks. The differential TG (DTG) profiles of bulk cement paste and healing products formed in cracks were shown in [Fig. 6]. Self-healing phenomenon starts at 2 days of specimen age and the healing time is 26 days. For all the samples, DTG profiles exhibit a remarkable weight loss of each sample at the temperature between 110 °C and 200 °C. The weight loss of these samples at the temperature of 110 °C to 200 °C can be attributed to the loss of chemically bound water of C-S-H and ettringite

[12]. It can also be observed that at this temperature the relative proportion of C-S-H in the healing products is smaller than in the bulk paste. When the temperature increases from 410 °C to 550 °C, there is a remarkable weight loss in the profile of healing products, which is caused by the decomposition of portlandite [13]. For 15MKS, small peaks are noticed at 190 °C and 280 °C in the DTG profiles of the healing products formed between the slices. This could be attributed to the decomposition of monocarboaluminate, hydrotalcite and hemicarboaluminate that they have not been observed but they participate in the diversification of healing products, and therefore a better filling of the crack [14]. As shown in [Fig. 6 (a, and b)], the peaks between 660 °C and 840 °C of healing products can be contributed by the decomposition of calcite [15]. According to [16], the presence of calcite, monocarboaluminate and hemicarboaluminate is related to the carbonation of reaction products in cracks. In fact, once the reaction products between the gaps are exposed to the air with a 50% and 70% HR a carbonation reaction of these particles evolves rapidly [16]. In addition, the ingress of CO₂ between each two slices is accelerated by the porous morphology of reaction products presents in gaps [16]. Therefore, carbonation of these particles is considered as a significant part of self-healing procedure [16].

XRD results

The characterization of healing products by using TGA and XRD test gave information on mineralogical components of products formed in cracks during the healing process. [Fig.7] shows the XRD results of the self-healing products formed when the self-healing starts at 2 days. XRD patterns of ternary binders (15MKS) in [Fig.7 (b)] demonstrate the presence of Gehlenite, portlandite, hydrotalcite and calcite as self-healing products. Regarding to the calcite, its sources are various. Portlandite precipitates during the normal hydration process of clinker. Furthermore, the presence of Gehlenite was reported to the chemical reaction of metakaolin and GGBFS in presence of portlandite [6]. For the reference sample (100C), the newly formed reaction products are calcite and portlandite, which is observed with TGA result.

Mechanical properties recovery

The compressive strength of these different samples of mortars is shown in [Fig. 8]. Incorporation of metakaolin and GGBFS in mortar as partial replacement of portland cement, increases early strength of mortar. 15MKS mortar sample has a compressive resistance rate equal to 55 MPa, which is close to the reference sample (100C) at 28 days. The highly active pozzolanic reaction of metakaolin with respect to the latent hydraulic properties of GGBFS can explain this balance of functions, which improves compression resistance at young age [16].

The results of [Fig. 9] show after 4 weeks of healing greater mechanical strength with the composition incorporating MK and GGBFS as supplementary cementitious materials. These results can be attributed to the healing of the crack through the formation of healing product that restores the continuity between the two faces of the crack. We can also conclude that the stiffness gains of this composition are clearly more significant than the resistance gains. This is explained by a different microstructure of CSH sheets compared to those from the first hydration and the fact that the crack is not completely filled in its volume [18]. In addition, it should be noted that the other formulations have a potential close to the reference (100C) that shows the positive impact of SCM on healing.

[Fig. 10] shows the typical stress – CMOD curves obtained for beam specimens pre-loaded at 2 days and immersed in water for 4 weeks. For both mixtures, stiffness gains was shown due to

formation of healing products that refilled the cracks [Fig. 10(a) and (b)]. However, the recovery of materials strength is more evident for 15MKS specimens than the reference one. These results indicate clearly that new healing products have precipitated in cracks and mechanically bind the crack faces.

CONCLUSIONS

Through this study, the autogenous healing potential of cementitious materials containing SCMs was studied. Self-healing efficiency of each mixture was assessed through quantification of mechanical recovery and the correspondent self-healing products were identified using SEM/EDS, TGA and XRD tests. The experimental results obtained can be summarized as follows :

- From TGA results, the ternary mixture shows newly hydration products compared to portland cement paste like monocarboaluminate, hydrotalcite and hemicarboaluminate. Moreover, XRD results indicate the presence of gehlenite, portlandite, hydrotalcite as healing products derived from ternary mixture containing metakaolin and GGBFS.
- Mechanical recovery of ternary mixture contained metakaolin and GGBFS as partial replacement of cement were improved after the self-healing process. This result was shown by a rapid recovery of stiffness and a slight improvement in flexural strength.

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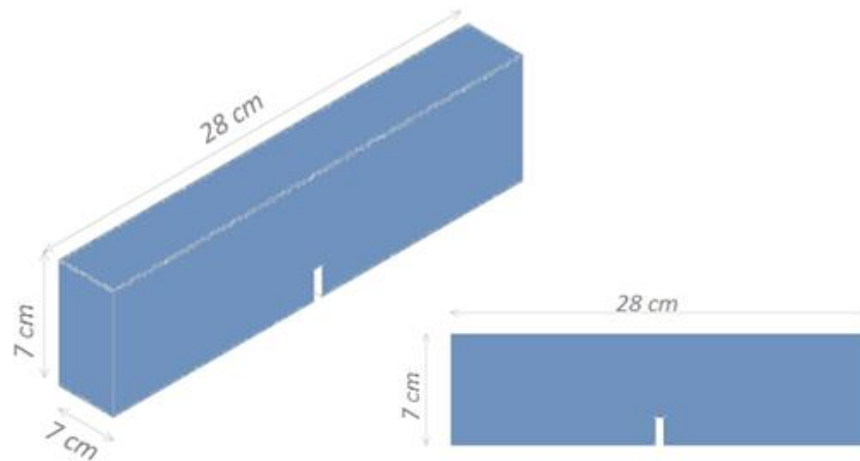


Fig. 1- Dimensions mortar specimens.

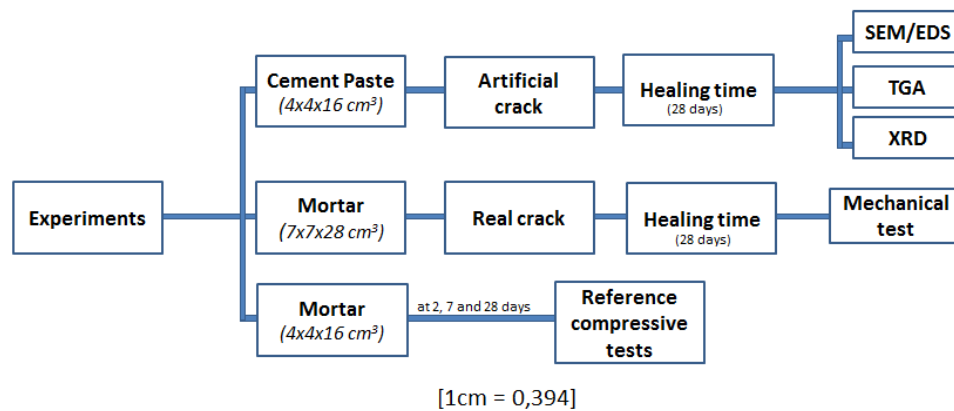


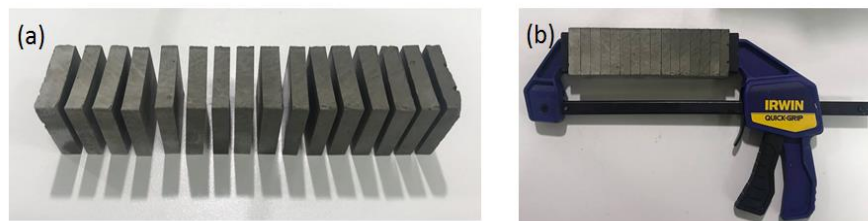
Fig. 2–Flow chart structure of the experimental program

Table 1- Chemical compositions of portland cement and mineral additions used in this study

	PC	Slag
SiO₂	19.6	37.7
Al₂O₃	4.5	10.2
Fe₂O₃	2.3	0.6
CaO	63.7	43.8
MgO	3.9	6.4
SO₃	2.6	0.1

Table 2—Compositions of different mixtures per one m³ (per 61023.7 in³)

	100C	30MK	15 MKS
C (kg/m³)	709 (44.26 pcf)	496 (30.96 pcf)	496 (30.96 pcf)
V_{paste}(l/m³)	530	530	530
W/ B	0.4	0.4	0.4
MK (kg/m³)	-	177	88
S (kg/m³)	-	-	98,5

**Fig. 3**—Slices cut from 40x40x160 mm cement paste specimen (a), slices pressed together using clamp (b).

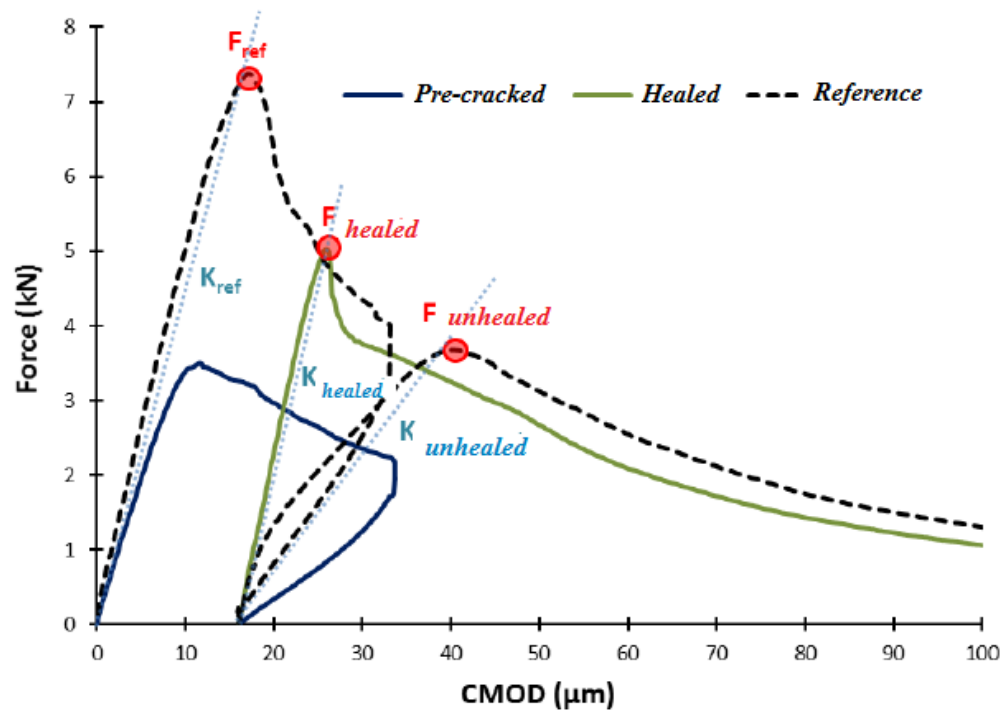


Fig. 4- Principle for determining mechanical gains from bending curves [9].

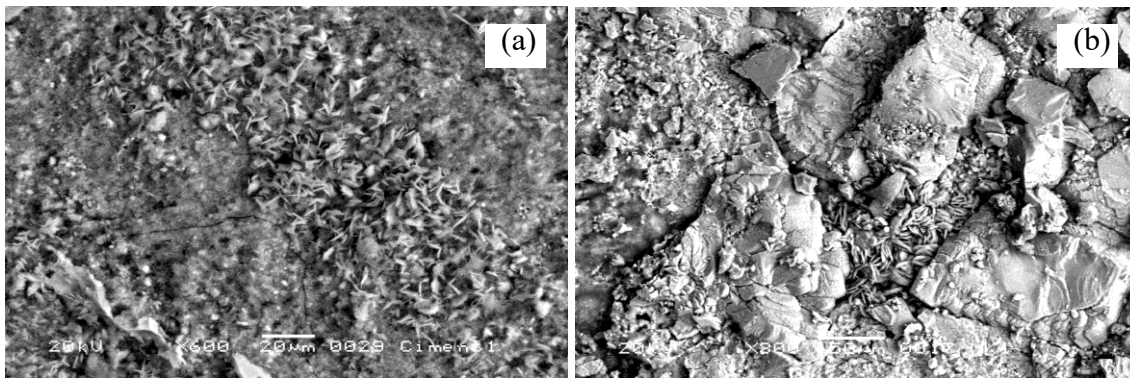


Fig. 5- SEM observations of healing products within an artificial crack after 4 weeks of healing for: a) 100C b) 150KS.

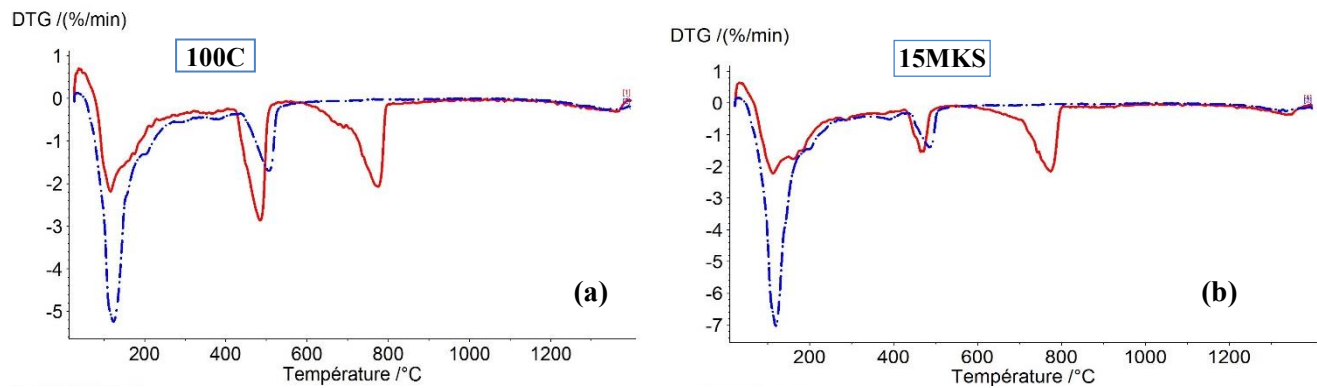


Fig. 6-DTG profiles of cement paste (dashed blue line) and healing products (continued red line) for each of the following mixtures: (a) - 100C, (b) – 15MKS.

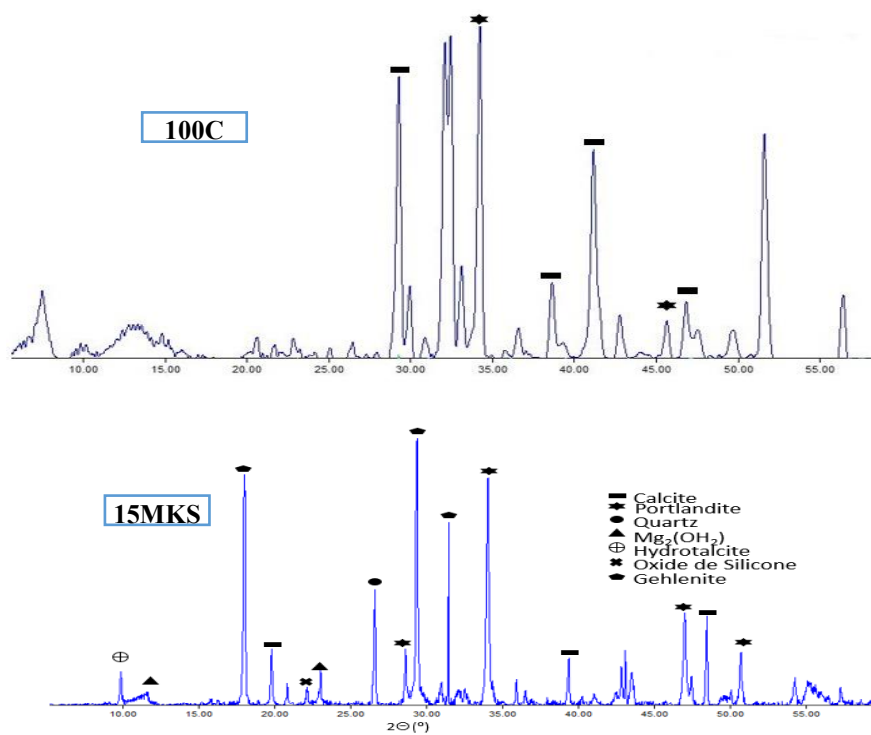


Fig.7-XRD analysis for cement paste and ternary formula after 28 days of healing

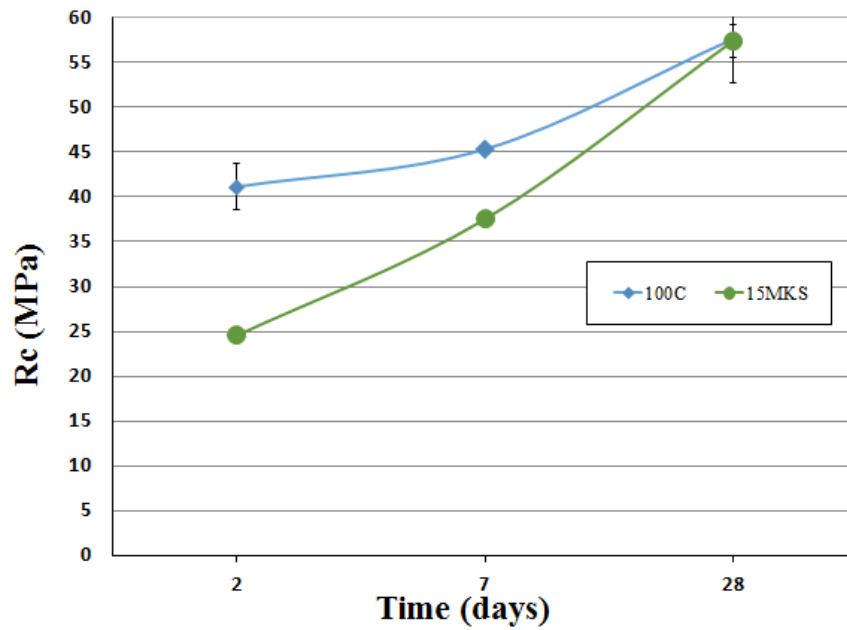


Fig. 8 – Compressive strength evolution of different mixtures prepared at 2, 7 and 28 days

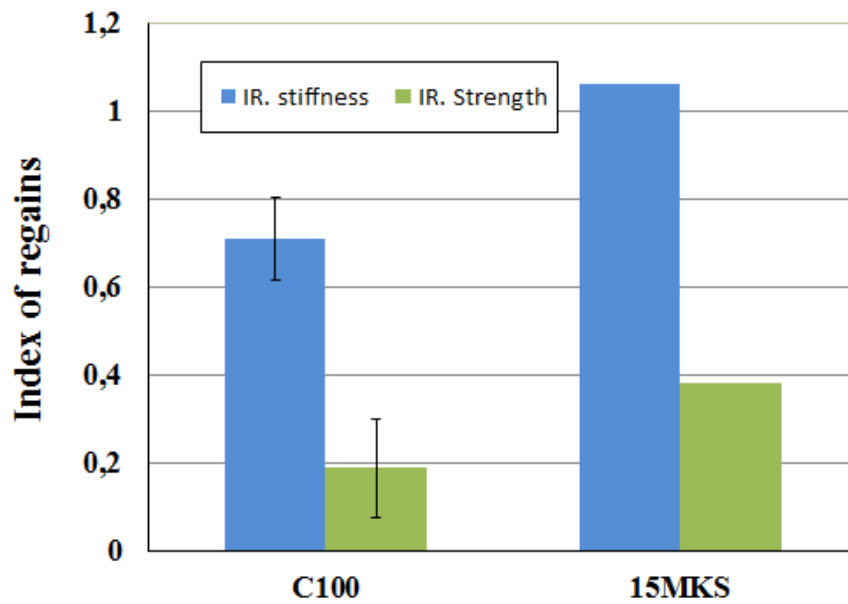


Fig. 9– Influence of different supplementary cementitious materials on mechanical properties of healed mortar series 100C and 15MKS

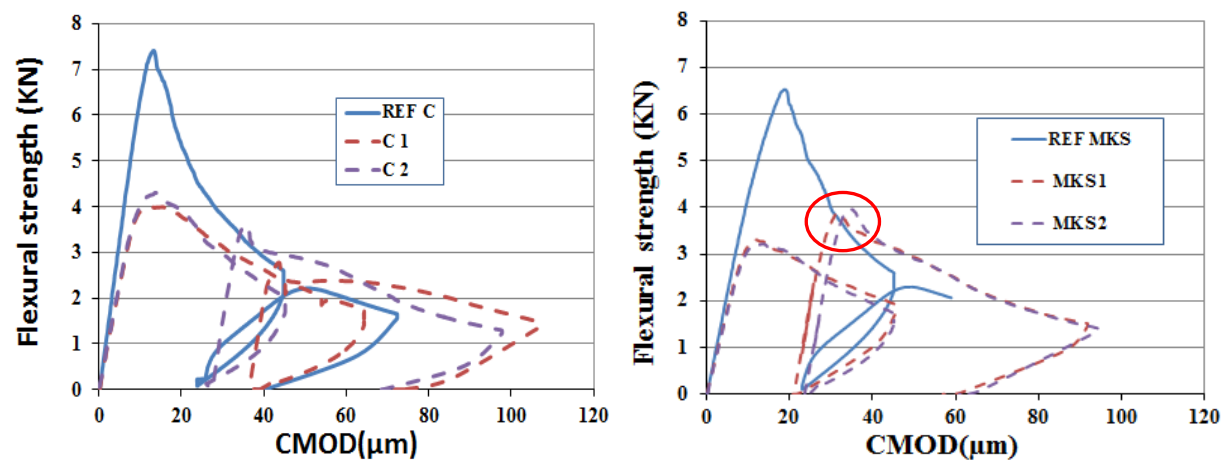


Fig. 10–Effect of different mixture on Flexural stress – CMOD behavior of mortar specimens: (a) with 100% of cement and (b) with 15% of Mk and 15% of Slag (preloading and reloading of healed specimens is represented by dotted red/purple curve while the reference one is represented by a continuous blue curve)

Hydration of MgO/hydromagnesite Blends

Alexander German, Frank Winnefeld, Pietro Lura

Synopsis: MgO/hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, abbreviated as HY) blends are cementitious materials, which set and harden when mixed with water. These blends reach acceptable strengths and therefore can potentially be used as binders in mortars and concrete. In case MgO is derived from carbonation of magnesium silicates and subsequent calcination, MgO/HY blends offer the possibility to be used as alternative binders with reduced carbon footprint compared to normal portland cement-based products.

This study focuses on the characterization of hydration products and mechanical properties of MgO/HY blends. Hydration of solely MgO leads to formation of brucite ($\text{Mg}(\text{OH})_2$) without any strength-building properties. In contrast, by blending MgO with hydromagnesite, it is possible to produce mortar samples with a strength of up to 11.0 ± 0.4 MPa (1595 ± 58 psi) after 28 d. Moreover, blending with hydromagnesite accelerates early hydration of MgO. XRD and TGA studies of hydrated blends revealed the presence of brucite and of a poorly crystalline, unidentified hydrate phase. The latter might play an important role in strength development.

Keywords: Alternative binder, artinite, brucite, cement, eco-friendly, hydromagnesite, magnesia

INTRODUCTION

Rising global demand for concrete as cheap, versatile construction material and the shift towards sustainable, environmental friendly building materials cause conflicting interests. This is mainly due to high CO₂ emissions associated with the manufacture of portland cement, the main binder of concrete. The production of portland cement clinker is based on the calcination of limestone and the subsequent clinkerization process at 1450°C. The calcination of limestone is an emission intense manufacturing step, during which fossil-bound CO₂ is emitted. It is estimated that currently 8% of worldwide CO₂ emissions can be attributed to the cement industry [1]. With regard to rising population especially in developing countries, production of portland cement will further increase in near future, resulting in higher amounts of emitted CO₂ which could represent 18-24% of worldwide CO₂ emissions in 2050 [1]. Different CO₂ mitigation strategies as modernization of cement plants, use of alternative fuels, and supplementary cementitious materials (SCM's) have been implemented by the cement industry to save emissions. However, these strategies are limited, and thus alternative binders with a substantially lower carbon footprint are of high interest to face future market development towards higher sustainability.

An example for such an alternative binder system are magnesium oxides derived from magnesium silicates (MOMS) [2]. The concept of MOMS is based on an industrially viable extraction process of MgO from magnesium silicate minerals such as forsterite (Mg₂SiO₄) or serpentine (Mg₃Si₂O₅(OH)₄), to avoid the release of fossil-bound CO₂ from carbonates, as it is the case for the calcination of limestone. In 2009 Vlasopoulos and Cheeseman patented the product Novacem, a magnesia-based cement, in which MgO and a basic magnesium carbonate such as hydromagnesite (HY) act as binders [3]. The MgO is derived in two steps: (1) Carbonation of magnesium silicates via hydrothermal synthesis of MgCO₃ and (2) subsequent calcination. However, as it was not possible to establish a large-scale manufacturing process for extracting MgO from magnesium silicates, the product was never introduced into the market. What remains from the pioneer work on Novacem is the MgO/HY binder system, whose hydration products are not yet fully understood and thus examined in this study.

EXPERIMENTAL PROCEDURE

Materials

Caustic MgO and hydromagnesite powders were used to prepare blends of 70/30, 60/40, and 50/50 wt% MgO/HY. Pastes and mortars were produced with a water-to-cement ratio (w/c) of 0.75. To enhance the workability, 2.7 wt% polycarboxylate ether-based superplasticizer (solid content: 41.8%) was added to the blends. Pure MgO samples were used as reference materials for the experiments.

Sample preparation

Heat development during hydration was monitored with a TAM Air isothermal calorimeter at 20°C (68 °F) for 72 h. MgO and MgO/HY pastes were produced by mixing homogenized powders with water and superplasticizer with a spatula by hand for 2 min. Glass vessels were filled with 6-8 g (0.013-0.017 lb) of paste, sealed, and transferred into the calorimeter.

For measurement of compressive strength, MgO and hydromagnesite were homogenized by a Turbula Mixer for 2 h. The binder was mixed with water, superplasticizer, and sand resulting in a sand/binder ratio of 3:1 following the EN 196-1 standard adapted for the production of 100×25×25 mm³ (3.94×0.984×0.984 in³) mortar prisms. Subsequently, the moulds were stored for 24 h in a humidity chamber at 96% relative humidity. The compressive strength was measured on MgO/HY mortars with a hydraulic press after 1, 2, 7, and 28 d applying a pressure load of 0.5 MPa/s (72.52 psi/s). Mortars consisting solely of MgO lacked sufficient cohesion; therefore, no representative compressive strength was measurable.

For thermogravimetry (TGA) and X-ray diffraction analysis (XRD), the samples were produced by mixing the powders with water and superplasticizer in PET vessels, which were sealed and stored at 20°C (68°F). Hydration was stopped after 6 h, 1, 2, 7, and 28 d by solvent exchange using isopropanol and diethyl ether according to [4]. The obtained samples were dried for 5 min at 40°C (104°F) and crushed with a mortar to a size smaller than 63 µm (2.5×10⁻³ in). TGA was conducted with the instrument STA 449 F3 Jupiter. 50 mg (1.10×10⁻⁴ lb) of each sample were filled in alumina crucibles and heated from room temperature to 980°C (1796°F) with a heating rate of 20 K/min in a nitrogen atmosphere (50 ml/min (6.54×10⁻⁵ yd³/min)).

The crystalline phases were examined by XRD. The samples were measured at diffraction angles of 2θ = 3-115° (45 min) in θ/2θ configuration with a diffractometer X'Pert Pro using CuKα radiation and the X'Celerator detector.

RESULTS

Isothermal Calorimetry

A substantial difference in heat development was measured between pure MgO samples and MgO/HY pastes. It was found that additions of hydromagnesite to MgO led to a higher heat development during hydration (see **Figure 1**). The main hydration peak was measured for both MgO and MgO/HY pastes after 3 h. Superplasticizer additions of 2.7% resulted in minor retardation and slightly higher heat release. The degree of hydration was determined by comparing experimental data with the hydration enthalpy of MgO (930 J/kg (0.40 Btu/lb)) [5]. After 72 h, MgO and MgO/HY pastes reached hydration degrees of approximately 60%, corresponding to 81 wt% of hydrated MgO contents of the impure, technical raw material.

Compressive strength

MgO/HY mortars displayed compressive strengths of 11.0 ± 0.4 MPa (1595 ± 58 psi) after 28 d (**Figure 2**). Compared to MgO mortars, which lacked cohesion, it is possible to produce MgO/HY mortars with significant strength, showing that hydromagnesite plays a key role in strength development in this type of binder. However, it is noteworthy that an increase of the amount of hydromagnesite does not lead to higher compressive strengths. It is rather the opposite case, as blends with the lowest hydromagnesite content as the 70/30 wt% MgO/HY mortars show the highest compressive strength in this study.

Thermogravimetry (TGA)

Figure 3 shows the TGA results obtained from an unhydrated and a hydrated 70/30 wt% MgO/HY paste, which was stopped after 6 h, 1 d, and 28 d. The unhydrated blend showed the first dehydration peak at about 80-100°C (176-212°F) due to loss of loosely bound water. The dehydration peaks at 270°C (518°F), 438°C (820.4°F), and 535°C (995°F) can be attributed to different dehydration stages of hydromagnesite as described in literature [6]. The dehydration peak at 750°C (1382°F) occurs due to dehydration of dolomite ($\text{CaMg}(\text{CO}_3)_2$), which is present as an impurity in the MgO. The hydrated blends showed a somewhat different result, as can be seen from the prominent dehydration peak at 405-430°C (761-806°F), which gains gradually intensity with advancing hydration, indicating the formation of brucite. The dehydration peaks of hydromagnesite show the opposite effect, indicating the consumption of hydromagnesite. With advancing hydration, a dehydration peak at 90-110°C (194-230°F) occurs. Similar to the brucite peak, this dehydration peak increases. In addition, none of the TGA data reported in literature for the identified phases (brucite, hydromagnesite, and dolomite) show the presence of a dehydration peak at this temperature range.

X-ray diffraction (XRD)

Figure 4 shows diffraction patterns of unhydrated and hydrated MgO pastes stopped after 6 h, 1, 2, 7, and 28 d. With progressing hydration, MgO reacts to brucite, resulting in the decrease of MgO reflection intensities at $2\theta = 36.5^\circ$, 42.9° . Simultaneously, two brucite reflections appear after 6 h of hydration at $2\theta = 18.6^\circ$, 37.9° . Due to use of industrial-grade MgO as raw material, several additional phases as talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$), calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$) and a phyllosilicate from the chlorite group were detected. Since the reflections of these phases did not gain or lose intensity for samples with different hydration time, it is assumed that their impact on the hydration products by chemical reaction or alteration is negligible.

Diffraction experiments of hydrated 70/30 wt% MgO/HY pastes show that a poorly-crystalline form of brucite is the main crystalline reaction product, recognizable by broad brucite reflections at $2\theta = 19.1^\circ$ and 37.9° (**Figure 5**). In addition, diffraction patterns indicate that besides some impurities, unreacted MgO and hydromagnesite are present after 28 d of hydration. Two weak diffraction signals at $2\theta = 10.8^\circ$ and 16.6° occur, which match with reflections of artinite ($\text{Mg}_2\text{CO}_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$), indicating the possible presence of a poorly-crystalline, artinite-like phase.

DISCUSSION

The results obtained by isothermal calorimetry highlight the important role of hydromagnesite in the hydration process. As is shown by the cumulative heat curves of MgO and the MgO/HY blends, early hydration is influenced by hydromagnesite, which significantly accelerates hydration, and therefore causes a much stronger heat development. In comparison, the MgO paste shows a steadier hydration process. Both samples show a similar degree of hydration of 60% for MgO. It remains unclear whether the acceleration caused by hydromagnesite is due to enhanced formation of brucite through the creation of additional crystallization sites or due to the formation of an additional phase, which is accompanied with a strong heat release.

Compressive strength measurements proved that the addition of hydromagnesite led to the development of higher cohesion in comparison to mortars consisting exclusively of MgO. As pure hydromagnesite does not contribute to strength in its initial form, we suggest that hydromagnesite is involved in the formation of a strength-providing phase. However, we do not exclude the possibility that hydromagnesite has an impact on the morphology of brucite, which might have led to higher cohesion of the mortar through intergrowing of the crystals.

This study showed that 70/30 wt% MgO/HY mortars reached a compressive strength of 11.0 ± 0.4 MPa (1595 ± 58 psi) after 28 d. The relatively low compressive strength can be explained by the high water demand ($w/c = 0.75$), which is needed to obtain a sufficient workability. The experiments showed that increasing strength does not correlate with increasing hydromagnesite contents. Since pure MgO mortars do not show a measurable compressive strength, there must be an optimum in which MgO/HY blends reach decent compressive strength. However, the difference in strength between the 70/30, 60/40, 50/50 wt% MgO/HY mortars are relatively low to achieve a significant strength optimization.

A strong dehydration peak of brucite was identified at 405-430°C (761-806°F) in hydrated MgO/HY blends by TGA. As expected, the brucite peak gains intensity with higher degree of hydration. This result is supported by XRD, which shows the gradual intensity increase of reflections of the poorly-crystalline form of brucite at $2\theta = 19.1^\circ$ and 37.9° for samples with long hydration times.

The dehydration peak in TGA at 90-110°C (194-230°F) raises the question of the origin of this weight loss. It cannot be explained by the decomposition of hydromagnesite, brucite or dolomite. Similar to the brucite dehydration peak, this peak gains intensity with advancing hydration. In previous studies [7-9] a dehydration peak in the same temperature range was found in a MgO/HY blend by TGA coupled with FTIR. By means of FTIR measurements, the authors

identified a water release in this temperature range. Thus, it is likely that the dehydration peak observed in this study might belong to an unidentified hydrate phase. Moreover, XRD measurements showed two weak diffraction signals at $2\theta = 10.8^\circ$ and 16.6° , which indicate the presence of a poorly-crystalline, artinite-like phase, which might be the hydrate phase causing the TGA hydration peak at 90-110°C (194-230°F). This phase might be, besides the poorly-crystalline brucite, the strength-providing phase in mortars made of MgO/HY blends.

CONCLUSION

Calorimetric measurements showed that the addition of hydromagnesite to MgO leads to a higher heat development during hydration, which reaches its maximum after 3 h. Furthermore, it was observed that superplasticizers cause a slight retardation of the hydration reaction in MgO/HY pastes. The compressive strength was only obtained for MgO/HY mortars. Mortars for which solely MgO was used showed too low cohesion for obtaining significant compressive strength data. It was found that MgO/HY mortars with a high MgO content (70/30 wt% MgO/HY) exhibited the highest compressive strength of 11.0 ± 0.4 MPa (1595 ± 58 psi) after 28 d. The relatively low strength can be explained by the high w/c of 0.75, which is needed to obtain a good workability for casting. In future, the water demand might be lowered by careful selection of superplasticizers.

Another important aspect of this study was the investigation of phases formed during hydration. TGA measurements indicated the presence of a hydrate phase, losing bound water at 90-110°C (194-230°F). Due to the fact that this dehydration peak gains intensity with advancing hydration, we postulate that an unknown hydrate phase is present in hydrated MgO/HY blends. This is supported by XRD results in which reflections of a low-crystallinity form of brucite and a nearly amorphous phase were measured. Reflections of the nearly-amorphous phase at $2\theta = 10.8^\circ$ and 16.6° matched with positions of artinite reflections, indicating an artinite-like phase, which was previously reported by [7-9] as well. This, so far, unidentified phase might be related to strength development in MgO/HY binders, and therefore, be of interest for future studies.

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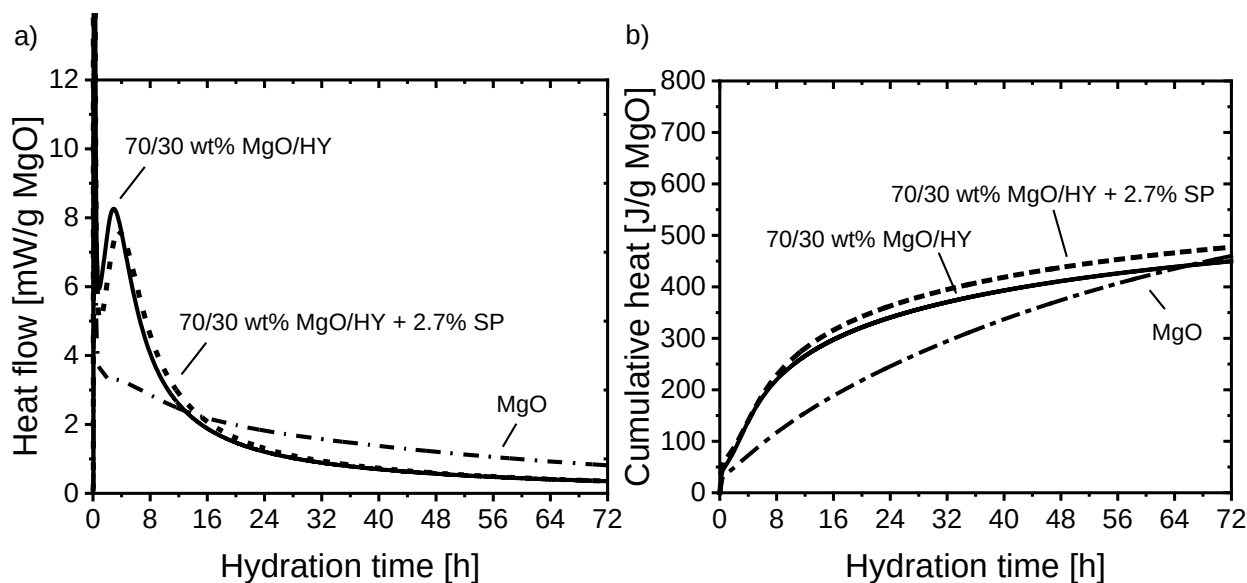


Fig. 1—Isothermal calorimetry of MgO and 70/30 wt% MgO/HY pastes. a) Heat flow, b) cumulative heat. Unit conversion: kg = 2.20 lb, m = 39.4 in.

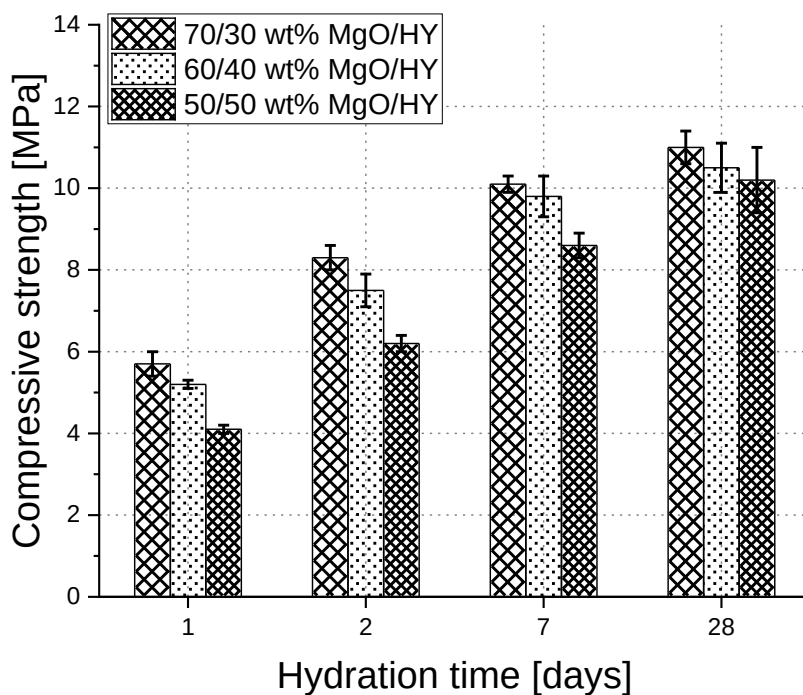


Fig. 2—Compressive strength development of MgO/HY mortars.

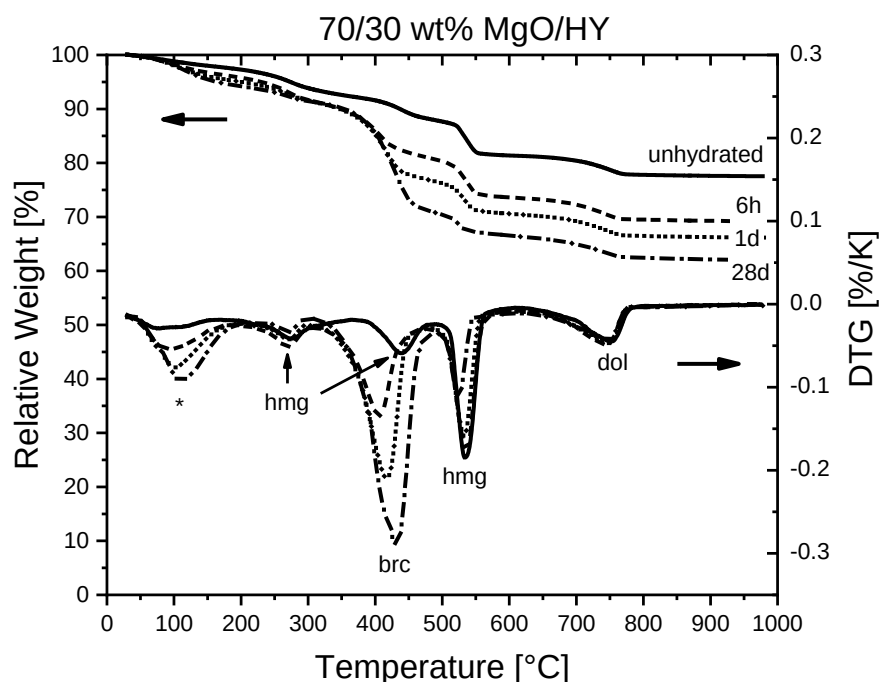


Fig. 3—TGA results of an unhydrated and a hydrated 70/30 wt% MgO/HY paste after 6 h, 1 d, and 28 d of hydration. *brc* = brucite ($\text{Mg}(\text{OH})_2$), *dol* = dolomite ($\text{CaMg}(\text{CO}_3)_2$), *hmg* = hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$), * = temperature range of an unidentified phase in the MgO/HY blends. Unit conversion: $^\circ\text{C} = (^\circ\text{F}-32)/1.8$.

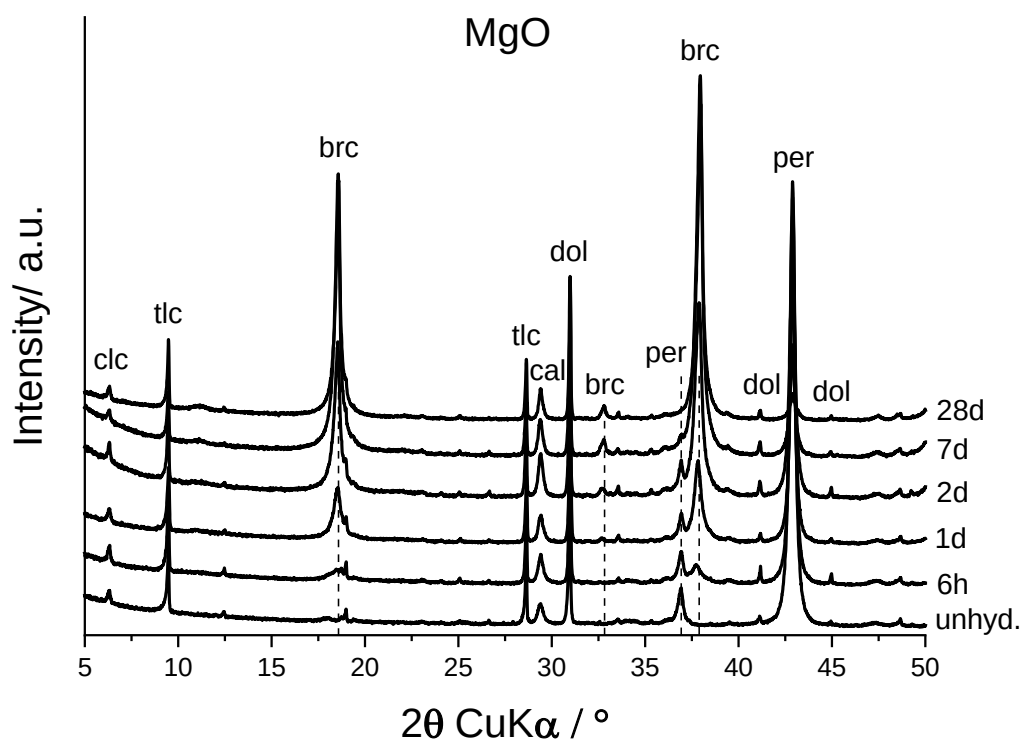


Fig. 4—Diffraction patterns of unhydrated and hydrated MgO pastes after 6 h, 1, 2, 7, and 28 d of hydration. *brc* = brucite ($\text{Mg}(\text{OH})_2$), *cal* = calcite (CaCO_3), *clc* = phyllosilicate from the chlorite group, *dol* = dolomite ($\text{CaMg}(\text{CO}_3)_2$), *per* = periclase (MgO), *tlc* = talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$).

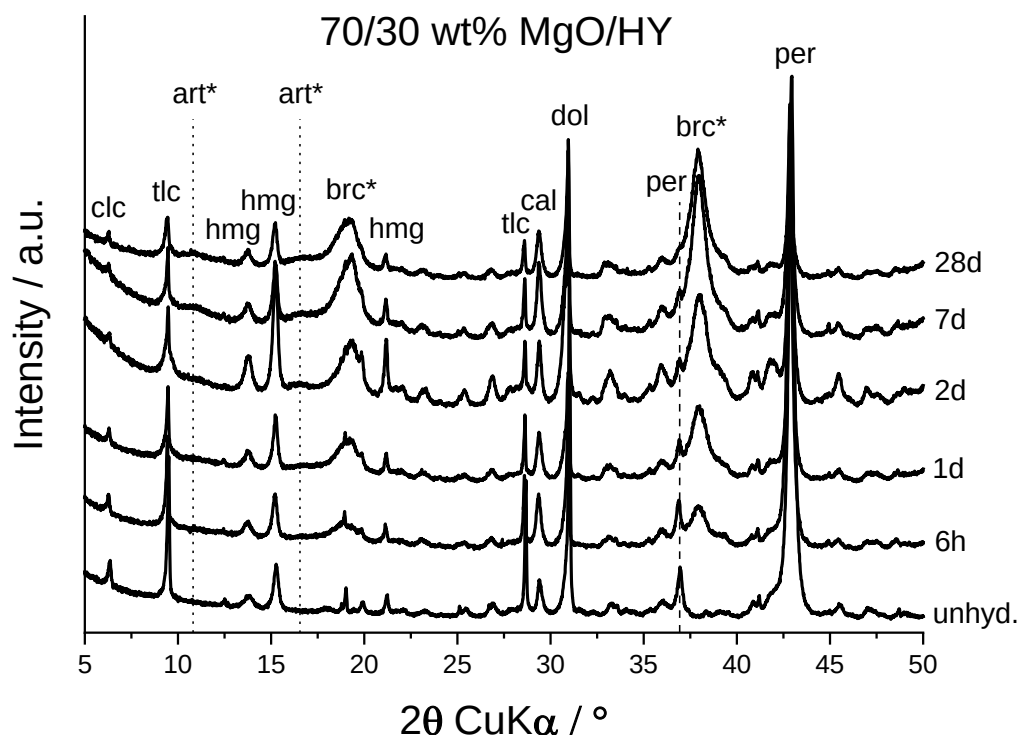


Fig. 5—Diffraction patterns of unhydrated and hydrated 70/30 wt% MgO/HY pastes after 6 h, 1, 2, 7, and 28 d of hydration. *art** = poorly-crystalline artinite-like phase, *brc** = poorly-crystalline brucite phase ($\text{Mg}(\text{OH})_2$), *cal* = calcite (CaCO_3), *clc* = phyllosilicate from the chlorite group, *dol* = dolomite ($\text{CaMg}(\text{CO}_3)_2$), *hmg* = hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$), *per* = periclase (MgO), *tlc* = talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$).

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Early-Age Shrinkage of Cement Paste Containing Humic Substances as that from River Dredging Sediments in France

Hamza Beddaa, Amor Ben Fraj, Francis Lavergne and Jean Michel Torrenti

Synopsis: Dredged river sediments can be considered as a promising alternative for conventional aggregates in concrete. However, the effect of sediments' properties and particularly their organic matter (OM) content on those of the concrete have to be assessed. Indeed, the organic weight fraction of organic matter in sandy sediments dredged in the Seine watershed is highly variable as it varies from 0 wt% to 10 wt% of the dry matter. This research aims at assessing the effects of humic substances (HS) on the early age behavior of a cement paste. HS are organic compounds resulting from the chemical, physical and microbiological transformation of animals and plants residues and which are also the most representative component of sediments organic matter. A soluble HS, potassium humate, is added as partial substitution of cement; 0.2 wt%, 0.5 wt% and 1 wt%. The results indicate that HS causes a delay of both chemical and autogenous shrinkages by retarding the hydration process. In addition, the chemical shrinkage amplitude is not significantly affected by the presence of HS in the mixture, while the autogenous shrinkage is decreased especially for the high w/b (water/binder; binder=cement+HS) ratios, due to bleeding. Furthermore, for high rates (2% and 3%), this bleeding could generate a delay of setting between the top and the bottom of the sample causing cracks due to a restrained shrinkage in the upper part of the sample.

Keywords: autogenous shrinkage, chemical shrinkage, dredging sediments, humic substances

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Francis Lavergne recently authored articles dealing with monitoring and modeling the effects of supplementary cementitious materials such as silica fume, fly ash or nano-silica. He and his coworkers depict concrete as an evolving multi-scale composite material: the hydration chemistry and resulting volume fractions of solids are to be connected to mechanical properties of concrete such as its strength and its basic creep compliance. He participated in extending Eshelby-based homogenization schemes to aging linear viscoelasticity.

Jean Michel Torrenti is the director of the Materials and structures department of IFSTTAR. He is also professor at Ecole nationale des ponts et chaussées. His research concerns mechanics of concrete and its coupling with durability aspects: behavior of concrete at early age, creep, leaching and is applied to model the behavior of structures such as bridges, nuclear power plants and nuclear waste storage. He is co-author of several books concerning concrete and concrete structures.

INTRODUCTION

The accumulation of sediments at the bottom of waterways slows the flow down, impedes transport activities and raises the flood risk. Therefore, it is essential to maintain waterways through regular dredging operations. In the Ile-de-France region and its surrounding more than 100,000 m³ [$\approx 131,000$ yd³] of sediments are dredged each year from rivers, canals and hydraulic annexes (1-3). In recent years, dredged sediments have received considerable interest as promising alternatives for civil engineering materials (4-7).

Sediments, however, contain a significant weight fraction of organic matters, which may affect the quality of the formulated cementitious material. Indeed, soluble humic substances (humic acid and fulvic acid) delay the setting and negatively affect the compressive strength at early age (8-12). Actually, the effect of humic acids is comparable to that of a water reducer (calcium lignosulfonates) as it improves the workability, extends the dormant period and decreases the compressive strength at early age in a similar manner, as shown in (8). In the course of this study, the occurrence of cracks right after setting has been noticed as high weight fractions of soluble humic substances are introduced (1.5 wt% and 2 wt% of the cement (Fig. 1)).

Such an early age cracking is likely induced by early age shrinkage (13-15). Indeed, the temperature rise induced by cement hydration and its gradient are likely very limited since the considered paste samples (4x4x16 cm³) are small and humic substances slows the hydration. Hence, the early age cracking is either triggered by plastic shrinkage, drying shrinkage or autogenous shrinkage. Since the samples have been prevented from drying as they were stored (the molds are covered), the early age cracking likely results from internal stresses induced by autogenous shrinkage which is the apparent volume change due to the chemical shrinkage. This chemical shrinkage is also called Le Chatelier's contraction. Prior to the setting of the cement paste, the cement paste freely shrinks as the volume of the water and cement consumed by chemical hydration reactions exceeds that of the created hydration products. As the cement paste solidifies, its solid skeleton resists to this contraction: the chemical shrinkage keep increasing due to hydration reaction, but it results in the porosity being partly filled with bubbles of water vapor. The resulting capillary tension must be balanced by internal stresses in the visco-elastic solid skeleton, which therefore globally shrinks (16-18). Such a

cracking induced by autogenous shrinkage may trigger lower strength and durability issues: it is therefore to be investigated.

This paper aims to study the early age shrinkage of the cement paste prepared with various substitution rates of humic substances for different water/binder (w/b) ratios. The results of this study complete those reported in (8), which was more focused on the effect of HS on the rheology, the hydration and the compressive strength of a cement paste. The chemical and autogenous shrinkage of cement pastes containing humic substances is presently investigated. Moreover, an industrial product featuring known weight fractions of humic and fulvic acids has been considered to carry out these studies, while the amounts of these acids in dredged sediments likely vary from one place to another. Therefore, two methods are applied to quantify these amounts in sediments dredged at various locations in the Seine watershed. The first is based on colorimetric tests and the second on leached organic matter in a basic solution as the interstitial solution of concrete.

MATERIALS AND EXPERIMENTS

Materials

The experiments were performed on CEM I 52.5 N cement, as it mainly contains clinker (91.3 wt%) , gypsum (4.9 wt%) and limestone (3.8 wt%) (Table 1). The physical and chemical composition of cement are reported in Table 1. As the cement is not blended with any supplementary cementing material, the observed effect can therefore be attributed to interactions between the portland cement, gypsum and humic substances.

The considered humic substance is a potassium humate. It is produced by incorporating a humic substance to an alkaline solution of potassium hydroxide. Hence, the fulvic and humic acid contained in the humic substance are released in the solution. The insoluble elements, such as humin, are removed by centrifugation and the solution is dried to retrieve humic substances as a soluble powder made of salt of humic and fulvic acids and potassium. The resulting humic substances are a standard product sold as a fertilizer and its properties are reported in Table 2. The amount of potassium added by incorporating potassium humate to the cement is significantly lower than that readily released by the cement, as long as potassium humate represents less than 1wt% of the solid content.

This study is conducted on three water/binder (w/b) ratios: 0.35, 0.42 and 0.50. The cement was mixed with humic substances for 2 min in order to yield a homogeneous binder before addition of water according to the protocol described in Fig. 2.

Methods

Chemical shrinkage—Chemical shrinkage is the variation of absolute volume due to the hydration reactions of the cement. It is measured by hydrostatic weighing method. Once prepared, a small amount of the paste 15 to 20 g [0,033 to 0.044 lbs] is introduced into a cylindrical flask. The remainder of the flask volume is carefully filled with distilled water. The set is immersed under water (20°C [68°F]) and suspended by a nylon thread at a balance with a precision of 0.0001 g, which is linked to a device to record the mass of the samples under water for 120 hours with a time step of 5 min (Fig. 3). The chemical shrinkage is calculated according to the following equation:

$$\Delta V(t) = \frac{W_w(t)}{\rho_w * M_c} \quad (1)$$

Where;

$\Delta V(t)$: the chemical shrinkage (mm³=g of cement), at time (t),

$W_w(t)$: the variation of the sample weight under water (g), at time (t),

ρ_w : the water density at 20 C [68°F] (0.9982 g=cm³ [62.310lb=ft³]),

M_c : the cement mass in the sample (g).

Autogenous shrinkage—Autogenous shrinkage is the apparent volume change due to the chemical process of hydration of cement. To follow the autogenous deformations, a volumetric method is used. 50 to 70 g [0,110 to 0.154

lbs] of cement paste are placed into a latex membrane which is then closed and immersed in a thermostatic water bath at 20°C [68°F]. The sample is suspended by a nylon thread at a balance with a precision of 0.0001 g. The balance is linked to a device to record the variation mass (Fig. 3). The autogenous shrinkage is calculated according to the same equation (1).

Heat of hydration—An isothermal calorimetry test is designed to continuously measure the heat flow and the heat output for a cement paste at a constant temperature. The apparatus used for this test is a TAM AIR isothermal microcalorimeter. Calorimetry testing requires a small amount of paste, i.e. approx. 10 grams. Once prepared and weighed, the paste is introduced into the microcalorimeter (the time required does not exceed 10 minutes), which has been linked to an apparatus for recording the released heat flow. The paste remains in the microcalorimeter for a few days. All calorimetry tests presented herein are performed at $20^{\circ} \pm 1^{\circ}\text{C}$ [$68 \pm 2^{\circ}\text{F}$] (19).

RESULTS AND DISCUSSION

Chemical shrinkage

The effect of humic substances on the chemical shrinkage over time is shown in Fig. 4 for rates 0%, 0.2%, 0.5% and 1 wt% with the various w/b ratios: 0.35, 0.42 and 0.50. As seen on Fig. 4, for the different w/b, a very slight variation is recorded as function of humic substances rate on the chemical shrinkage value after 120 hours. Besides, as the hydration is delayed by the addition of humic substances, the kinetic of chemical shrinkage is also slowed down as the amount of HS is increased.

The relationship between the chemical shrinkage and the heat of hydration, as a parameter that reflects the progress of hydration, is depicted in Fig. 5; higher cumulative heat and higher chemical shrinkage result from a higher hydration rate. The figures show a near-linear relationship between the chemical shrinkage and the cumulative heat for the low rates (0%, 0.2% and 0.5%) while for 1 wt%, an increase in chemical shrinkage is observed during the dormant period when there is no heat released. The possible explanation is that the dissolution of cement and humic substances, which occurs during this period, might reduce significantly the paste volume whereas the released heat is less significant. Furthermore, after five days, chemical shrinkage slightly increased with w/b ratio, compared to the clear increase that can be seen for the heat of hydration.

The possible explanation is that during a chemical shrinkage test, the permanent contact between sample and water ensures more hydration of cement, especially for low w/b ratio. This can be proved by a deviation of the curves (Fig. 5) towards the end, which corresponds to a clear increase in the chemical shrinkage kinetics compared to that of the heat released. This observation is less visible for w/b = 0.42 and unnoticed for w/b = 0.50; the material does not need extra water to ensure complete hydration of the cement.

The near constant chemical shrinkage for different HS rates shows that the presence of humic substances does not alter the volume variation between the fresh and the hardened state of one paste to another, therefore, it is likely that they have not modified the cement hydration products.

Autogenous shrinkage

The autogenous shrinkage of the cement paste with various HS rates and for different w/b ratios (0.35, 0.42 and 0.50) has been plotted vs the age from 10 min after the first water-cement contact up to 120 hours (Fig. 6).

The density of the fresh cement paste is computed according to the first measure of the cement paste weight under water. It clearly decreases as the rate of HS is increased (Table 3). A potential explanation for such a decrease of density is that the humic substances act as an air entrainment. Thus the drop of compression strength measured in (8) can be fully or partially attributed to the porosity increase.

The autogenous shrinkage curve features three phases; the evolution of autogenous shrinkage and that of chemical shrinkage are similar during the first phase. At this moment, the paste is still soft and the deformation follows perfectly the chemical shrinkage. After setting, the second phase is called "the knee point period", which has a transition from chemical shrinkage to self-desiccation shrinkage (15). The autogenous shrinkage is indeed much smaller than the chemical shrinkage during the final deceleration phase since the hardened solid skeleton is able to oppose the capillary pressure. This shrinkage is due to the creation of vapor bubbles inside the matrix induced by the consumption of water present in the pores, which leads to a capillary depression within the system and thus a deformation called self-

desiccation. The autogenous shrinkage globally increases with the w/b ratio as the knee point occurs later. Indeed, the formation of a percolated solid skeleton able to withstand the stress induced by a capillary pressure is likely delayed as water occupies a larger volume fraction. As adding HS extends the dormant period and slows down hydration reactions (8), the chemical shrinkage increases more slowly. The knee point also occurs later, but for lower chemical shrinkage strains. As this phenomenon is visible for cement paste featuring high w/b ratios (0.42 and 0.50), it may be related to bleeding, which densifies the packing of cement particles and leads to earlier setting. Indeed, for higher rates (2 wt% and 3 wt% for example), bleeding causes a very significant setting delay between the top and bottom of the same sample which can last for days (see Fig. 7). Since the water flowing from the bottom to the top of sample contains a significant rate of soluble HS, the HS/cement ratio increases and this can explain the notable delay observed between the top and bottom of the same cement paste. Consequently, the deformations due to shrinkage of the upper part of the paste can be restrained by the bottom which is hardened earlier. This restrained shrinkage is the main cause of the cracking observed on the top of the samples with the high HS contents (Fig. 1).

Fig. 8 shows the evolution of the autogenous shrinkage in term of the cumulative hydration heat. The transition from the chemical shrinkage to self-desiccation is observed with less heat released for lower w/b ratios or for higher HS rates (especially for w/b=0.42 and w/b=0.50), it provides further evidence that the setting occurs with low hydration degree for lower w/b ratios or higher HS rates.

COMPARISON BETWEEN HUMIC SUBSTANCES AND ORGANIC MATTER IN SEDIMENTS

The organic matter content present in the sediments of Paris region varies between 0 and 10 wt% of dry matter (3). Nevertheless, these amounts of organic matter, measured according to European standard EN12457-2 (21), are not made of soluble humic substance. For instance, it likely contains a significant fraction of humus, which is not soluble in alkaline solutions. Hence, measuring the amount of soluble humic substances in actual dredged sediments provides a valuable insight on their reuse as aggregates for concrete.

Methods

Colorimetric test- EN1744+A1—The first method is based on the estimation of humic substances content of aggregates from the color formed when the sample is put in a solution of sodium hydroxide, for humic acid content. All these tests are performed in strict accordance with the European Standard 1744-1+A1 (21). This study is carried out on eight sands with 30%vol of different sandy sediments and 70%vol of a conventional sand. The use of only 30% of the sediment makes it possible to avoid a dark color for all the samples and therefore the comparison will be possible. The results will be compared to those of conventional sand with various rates of humic substances as detailed in Table 4. Considering the concretes studied in calorimetry below, the rates added of HS are equivalent to 0%, 0.02%, 0.05%, 0.1%, 0.15% and 0.2% wt of cement. While the standards 1744-1+A1 compares the resulting color to a reference color and discards aggregates darker than the reference owing to their soluble organic content, the amount of soluble HS corresponding to this threshold is not reported.

Leaching test—The second method is the leaching test. Humic and fulvic acids are soluble in alkaline solutions such as the interstitial solution of concrete (10; 22). Leaching tests are therefore performed according to European Standard EN12457-2 (20), on the eight sediments, so as to quantify the humic substances content as that leached organic matter in the basic solution. The tests are carried out using a basic solution (NaOH 1g/l [0.0624 lb=ft³]) for 24 hours.

Calorimetry test-Langavant method—The heat released by cement hydration is measured by means of semi-adiabatic calorimetry tests (the Langavant method), according to European Standard EN196-9 (23). A sample of the freshly prepared concrete is poured into an insulated calorimeter, and the temperature change is driven by both the heat released due to hydration and the calibrated heat loss of the calorimeter. Hence, the heat released by hydration could be computed using the temperature history once the heat capacity of the sample had been estimated. For this purpose, the temperature was measured every 10 minutes. Table 5 shows the different concrete mixture proportions used in this study.

Results

The colorimetric results are shown in Fig. 9. The samples SS7, SS8, CSHS10, CSHS15 and CSHS20 are the only samples that prove darker than the color defined as reference by the colorimetric test (21). These aggregates therefore contains an amount of soluble HS that is considered as significant. Moreover, the soluble HS content of the sand formulated as mixtures of conventional sand and sandy dredged sediments is likely lower than that existing in CSHS15. Furthermore, the semi-adiabatic tests confirm that the amount of soluble HS is low, as the time of appearance of the maximum heat flow is not delayed by more than 3 hours (Table. 6). In addition, the three mixtures featuring the brightest colors (Fig. 9-(a)) during the colorimetric tests also features the shortest dormant period as observed during the semi-adiabatic calorimetric tests. Therefore this method is reliable for quantifying the humic acid content present in a sediment and thus to predict the effect of this organic matter on hydration, compressive strength and early shrinkage. Nevertheless, the sample are almost black as the rate of humic substance becomes very high and ranking the sample according to their color becomes difficult. To set this drawback, it can be suggested to use less sediment and compare the resulting color to that obtained for references featuring known amount of soluble humic substances. The dilution ratio is finally accounted for as the color is turned into an equivalent weight fraction of soluble HS per weight of sediment.

Measuring the total amount of organic matter before and after leaching also provides a way to estimate the amount of soluble HS in dredged sediments (Table 7). Indeed, the sediments featuring a bright color also feature a small, or negative, difference of mass attributed to leaching. Nevertheless the measured contents of the leached organic matter are quite high. Indeed, it can reach 10% wt of the sandy sediment S7 and it exceeds 1% wt for others sediments (S5 and S8). Such contents can occur a hydration delay of more than one day, while the calorimetry results show a much lower delay (Table 6). Therefore, the results of the leaching test overestimate the contents of humic substances in sandy sediments. Other components of the sediment might have been leached out of the sample since the leaching test lasts 24 hours and the leached products might also be transparent, thus leaving the colorimetric test unaffected.

CONCLUSION

The presence of HS (humic substances) causes a delay of hydration process up to one day for a rate of 1% wt of cement. This effect is attributed, by Beddaa et al (8), to the adsorption of polymers on cement particles and then the inhibition of hydrates formation. Consecutively, Le Chatelier's contraction is also delayed by the presence of HS.

After five days, the amplitude of chemical shrinkage is largely independent of the HS rate and it increases slightly with the increase of w/b ratio. The quasi-linear relationship between chemical shrinkage and hydration heat is observed for cement paste with a low HS rates, while for C990HS10 for example, this linearity is observed only after the dormant period where the increase of the measured shrinkage is not due to Le Chatelier's contraction but it is attributed to the sedimentation of the solid particles.

Up to five days, the autogenous shrinkage decreases by the addition of HS for high w/b ratios (0.42 and 0.50). This could be explained by the decrease of w/b due to bleeding and then the setting is possible for a low hydration degree. For high rates of humic substances, the bleeding becomes more remarkable and a delay of setting is observed between the top and the bottom of the sample. The earlier hardening of the lower part restrains the shrinkage of the upper one. When the shrinkage restrained, the tensile stresses appeared. Then, they probably exceeded the tensile strength of the paste and they induce cracks on the top of the sample.

The measurement of the amount of humic acids in sediments is necessary before their use in cementitious materials so as to limit the appearance of cracks due to shrinkage. The colorimetric method described in European Standard EN 1744-1+A1 (21) is quite reliable for measuring the soluble humic acids content in sandy sediments.

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Table 1—Chemical composition and physical properties of cement.

Chemical compound	wt. %	Constituents	Characterization of constituents	wt. %
CaO	63.1	Clinker (91.3 wt.%)	C ₃ S	66
SiO	19		C ₂ S	11
Al₂O₃	5.4		C ₃ A	10
F e₂O₃	2.6		C ₄ AF	8
K₂O	1	Limestone(3.8 wt.%)	CaCO ₃	90.0
MgO	2	Calcium sulphate(4.9 wt.%)	Gypsum	100.0
Na₂O	0.1		Anhydrite	0.0
SO₃	3.5			
MnO	0.0			
T iO₂	0.3			
Cl⁻	0.02			
S⁻	0.02			
Physical characteristics				
Density (g/cm³)			3.11 [194.13 lb/f t ³]	
Specific surface Blaine (cm²/g)			3854 [1880 f t ² /lb]	

Table 2—Properties of humic substances (HS).

Assay (dry substance)	95%
Organic matter	78.5%
Insoluble matter	<5%
pH-value	12
Total humic extracts (humic and fulvic acids)	65% (53%, 12%)
Potassium (K₂O) soluble in water	17%
Color	Black

Table 3—Density of the fresh paste for different mixtures.

Sample	Density (g/cm ³ [62.428 lb/f t ³])		
	w/b=0.35	w/b=0.42	w/b=0.50
C1000	2.151	1.952	1.883
C998HS2	2.009	1.931	1.872
C995HS5	1.984	1.910	1.847
C990HS10	1.963	1.902	1.833

Table 4—Names of different sands and the weight proportions of their constituents.

Conventional sand containing different hmic substances rates								
Sample	CS	CSHS2	CSHS5	CSHS10	CSHS15	CSHS20	CSHS50	
Conventional sand (%wt)	100	99.9924	99.9810	99.9620	99.9430	99.9240	99.8100	
Humic substances (%wt)	0	0.0076	0.0190	0.0380	0.0570	0.0760	0.1900	
Conventional sand incorporated by 30%vol of sandy sediments								
Sample	SS1	SS2	SS3	SS4	SS5	SS6	SS7	SS8
Sediment name	S1	S2	S3	S4	S5	S6	S7	S8
Conventional sand (%wt)	70.208	71.872	71.738	72.246	71.659	73.303	73.402	72.395
Sediments (%wt)	29.792	28.128	28.262	27.754	28.341	26.697	26.598	27.605

Table 5—Mixture proportions.

Type of mixture	CC	CCHS20	CCHS50	CS1	CS2	CS3	CS4	CS5	CS6	CS7	CS8
Cement (kg)	335	335	335	335	335	335	335	335	335	335	335
Conventional sand (kg)	881,1	881,1	881,1	616,77	616,77	616,77	616,77	616,77	616,77	616,77	616,77
Sediments (kg)	0	0	0	261,72	241,38	242,98	236,94	243,93	224,63	223,50	235,18
Humic substances (kg)	0	0.670	1.675	0	0	0	0	0	0	0	0
Conventional coarse aggregates (kg)	814,4	814,4	814,4	814,4	814,4	814,4	814,4	814,4	814,4	814,4	814,4
Effective water (kg)	184,25	184,25	184,25	184,25	184,25	184,25	184,25	184,25	184,25	184,25	184,25
Total water (kg)	244,29	244,29	244,29	238,22	249,06	260,38	251,38	251,71	270,58	268,38	255,47
W/C	0,55	0,55	0,55	0,55	0,55	0,55	0,55	0,55	0,55	0,55	0,55

Table 6—The delay of the time appearance of maximal heat flow for different mixtures in comparison with reference one (CC).

Sample	CCHS10	CCHS20	CCHS50	CS1	CS2	CS3	CS4	CS5	CS6	CS7	CS8
The delay of the main flow (hours)	0.82	1.33	4.99	0.77	1.09	-0.58	1.83	1.13	2.73	2.09	1.25

Table 7—The organic matter content before and after a leaching test on sediments.

Sample	S1	S2	S3	S4	S5	S6	S7	S8
Total Organic matter content (%)	2.11	1.69	1.86	2.60	3.32	3.95	14.88	3.66
Organic matter content after leaching (%)	1.91	2.12	2.31	2.41	1.35	3.53	4.15	2.39



Fig. 1—Appearance of cracks just after setting for a cement paste with 2 wt% of humic substances and $w/b=0.42$.

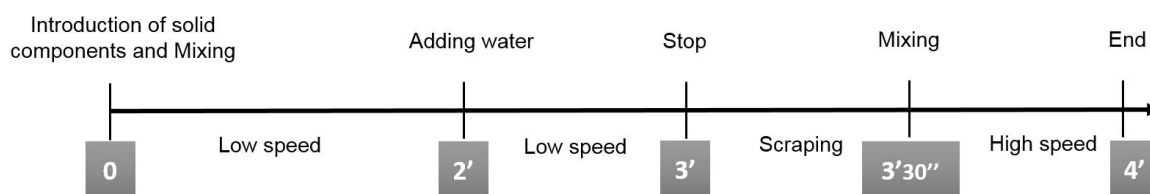


Fig. 2—Mixing procedure.

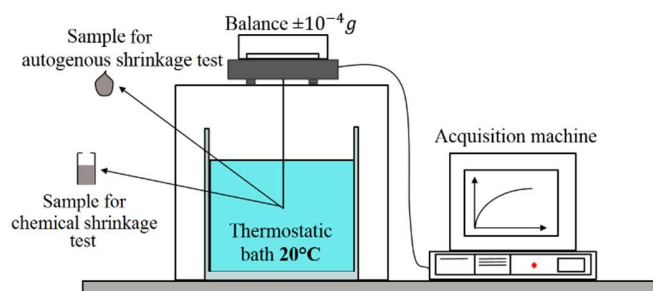


Fig. 3—Device for chemical and autogenous shrinkages.

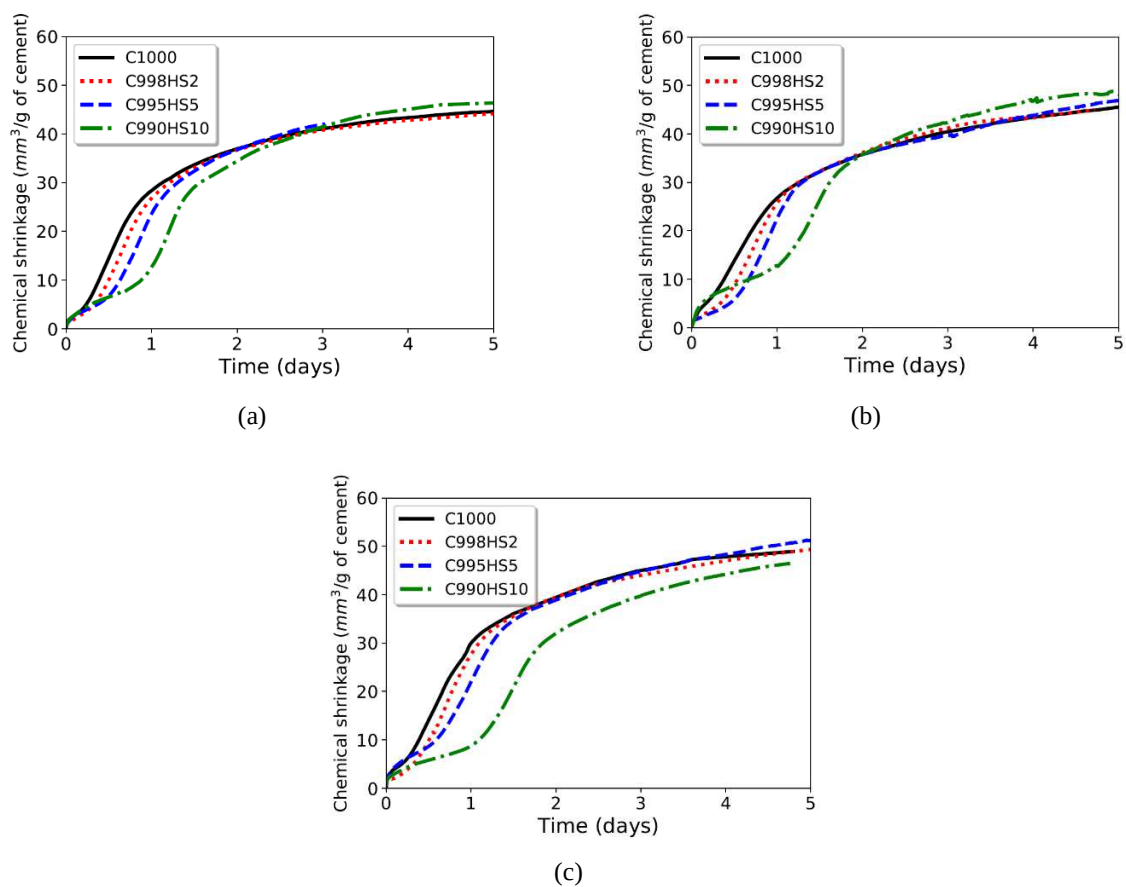


Fig. 4—Chemical shrinkage for different HS contents: (a) $w/b=0.35$; (b) $w/b=0.42$; (c) $w/b=0.50$.

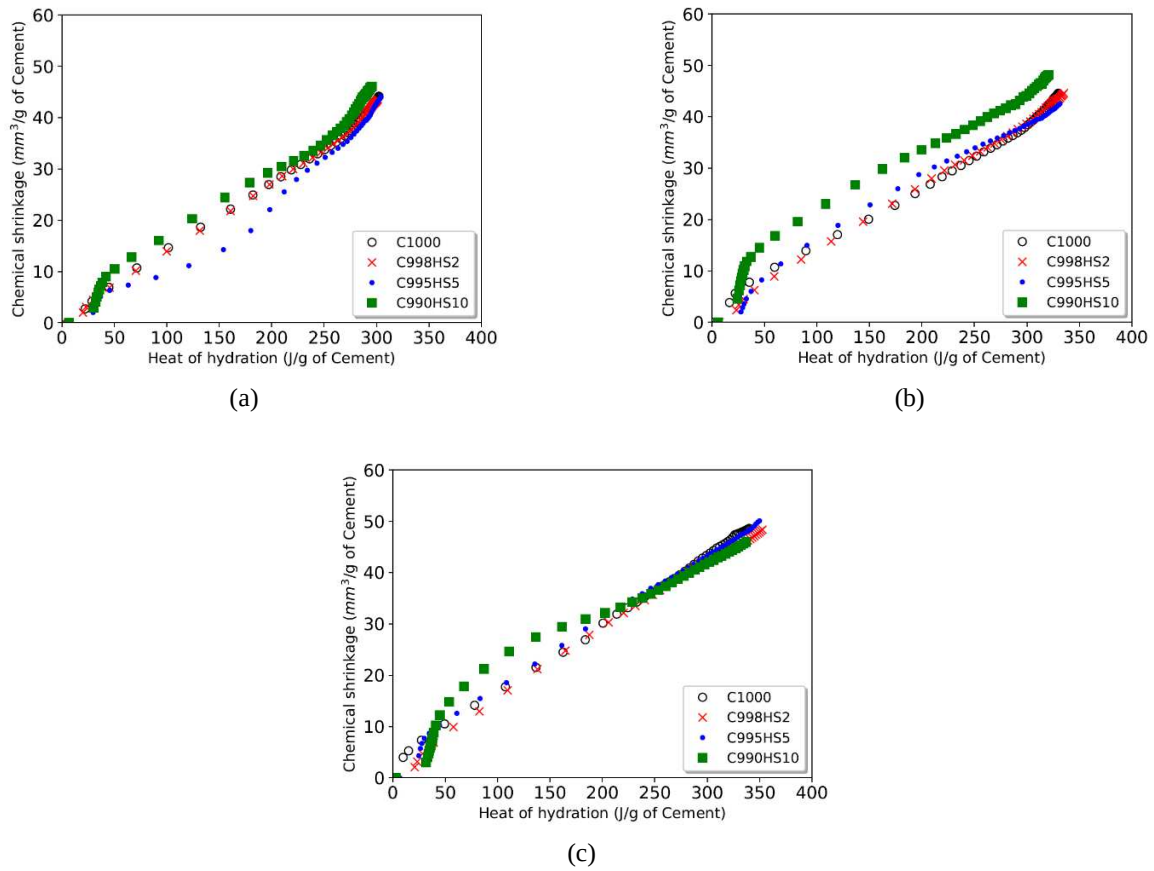


Fig. 5—Relationship between the chemical shrinkage and the cumulative heat for different HS contents: (a) w/b=0.35; (b) w/b=0.42; (c) w/b=0.50.

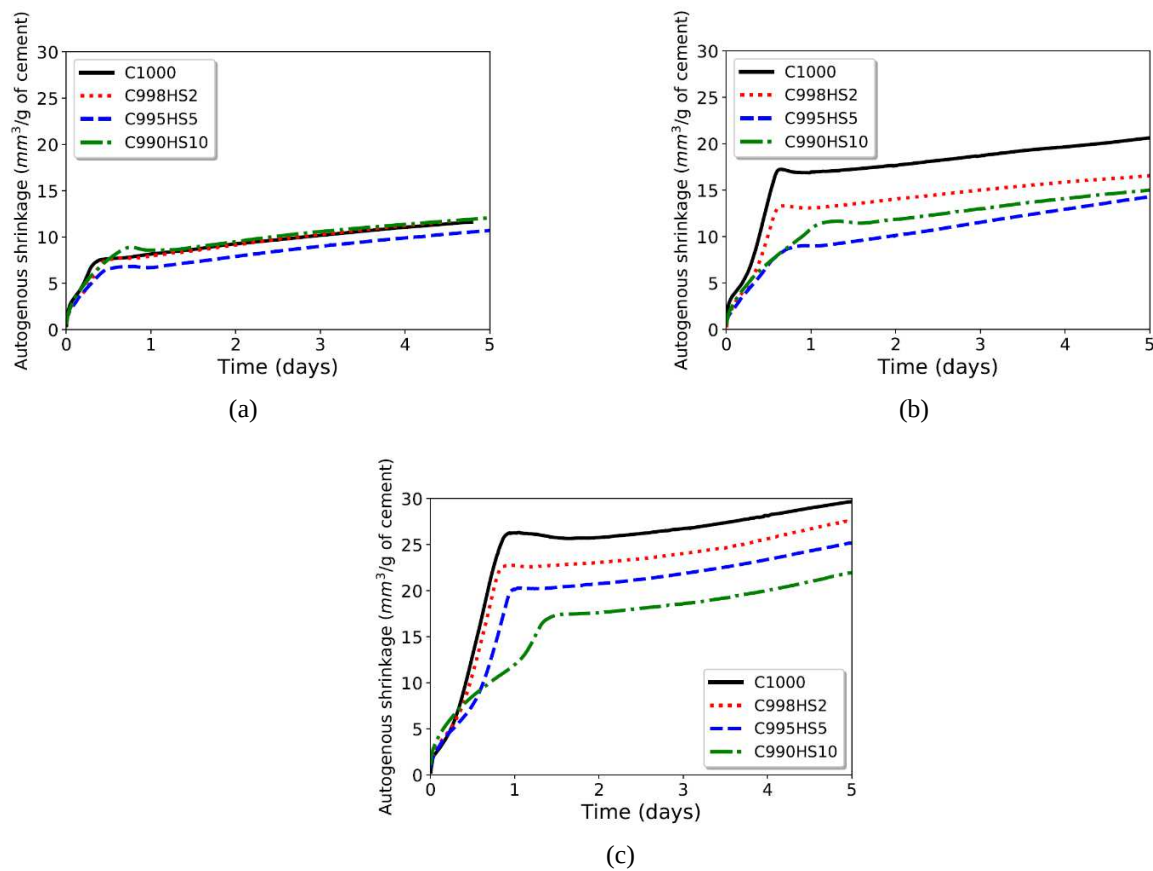


Fig. 6—Autogenous shrinkage for different HS contents: (a) $w/b=0.35$; (b) $w/b=0.42$; (c) $w/b=0.50$.

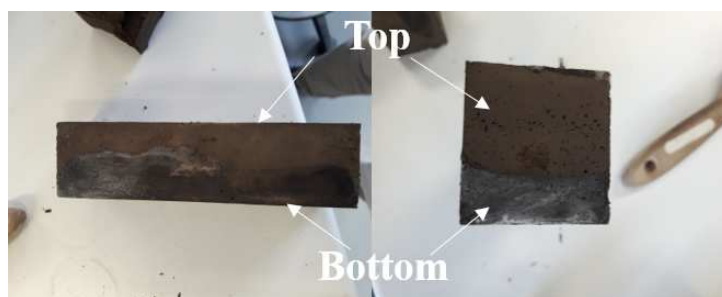


Fig. 7— Setting delay for the upper part of the sample compared to the lower part.

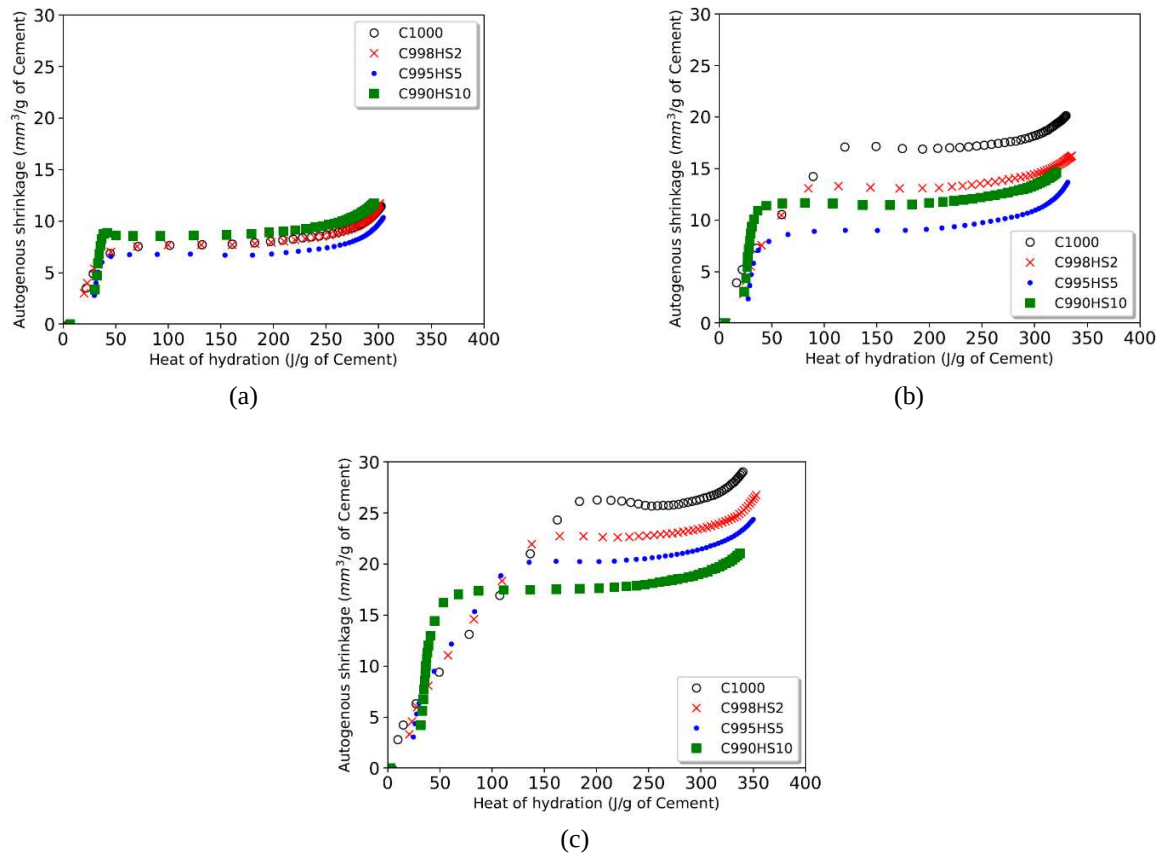


Fig. 8—Relationship between the autogenous shrinkage and the cumulative heat for different HS contents: (a) w/b=0.35; (b) w/b=0.42; (c) w/b=0.50.