NEW METHOD FOR ASSESSING ENDOGENOUS MICROCRACKING IN CEMENTITIOUS MATRIX IN EARLY AGE

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This article presents a study on the microstructural evolution of the cementitious matrix at early stages of hydration. The main objective was to follow the development of the interfacial zone between cement paste and granular inclusions during the hardening process. For this purpose, the "simple replica" method was used. This technique consists in observing a facsimile of the polished sample surface. This prevents drying and cracking of the sample during observation under vacuum with a scanning electron microscope (SEM). The study was conducted on Portland cement mortars containing glass beads with diameters of 3 and 8 mm. The effects of inclusion size and temperature were analysed at different time of observation, between 8 and 120 hours of hydration. The results showed a progressive separation between cement paste and glass beads, and the presence of microcracks in the matrix kept at 40°C.

Keywords: *Cementitious matrix, glass beads, microstructure, replica method, endogenous microcracking*

1. Introduction

In the hydrating mortar or concrete, there are two distinct phases, the chemically reactive material known as cement paste and the inert material known as aggregates. The presence of aggregates locally disturbs the temperature gradient field induced by the heat of hydration. This effect is clearly (or significantly) larger on the surface than in the interior. This phenomenon is likely to cause a non-uniform development of material properties, particularly between the cement paste surrounding the aggregates and the bulk of cementitious matrix. The temperature and hydration degree gradients may have an impact on the fields of thermal strains and stresses as well. Consequently, they affect the evolution of the mechanical properties of the material. The influence of aggregates on the early-age mechanical behavior of mortars and concretes has been investigated in the literature [1, 2].

At an early age, a cementitious matrix manifests volume variations of physicochemical origins. This phenomenon is linked to Le Chatelier and autodesiccation contraction of the porous network. Around aggregates, these deformations are partially prevented and the induced tensile stresses are likely to cause microcracking in the matrix [1, 2]. This microcracking is a form of diffuse damage, which may have material behaviour consequences at the macroscopic scale and particularly on its transport properties [3].

In order to study the development of these phenomena at the microscopic scale, a method called "simple replica" is proposed. This method was developed in the 1980s and used in particular for monitoring the evolution of microcracks in concretes [4]. This method of investigation has recently been used to characterize the microcracking of cementitious materials caused by long-term pathologies [5-8]. It consists in observing a facsimile of the previously polished sample surface. The technique has the advantage of not introducing microcracks generated by the sample drying while in the observation chamber of the microscope.

This study was conducted on mortars prepared with 3 and 8mm glass beads in different cementitious matrices. The effect of inclusion size, granular concentration and the water/cement (w/c) ratio on microstructure development at the cement paste/inclusion interface are analysed at various times. Progressive separation between cement paste and glass beads was observed for the matrix kept at 40°C.

Table 1

Chemical composition of cement (% g/g massic)*

Cement	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O
Content (%)	20.2	4.9	2.8	64.4	0.9	3.1	1.0	0.2

**Data listed in the technical sheet provided by the manufacturer.*

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2. Materials and methods

The cement used in this study is a Portland cement known as CEM I 52.5 N CE CP2 NF produced by the COUVROT factory in France. It matches the European standard NF EN 197-1 [**9**]. The density and Blaine fineness of the applied cement are 3390 kg/m^3 and 400 m^2/kg, respectively. The chemical composition of the cement is given in Table 1. Application of Bogue's formulas to the chemical composition of the cement gave the following mass distribution of the main phases: 66% of C_3S, 13% of C_2S, 11% of C_3A and 7% of C_4AF.

The aggregates used for the mortars are artificial and non-porous. They consist of dry glass beads with diameters of 3.35mm and 8mm. The choice of glass beads as aggregates is of great importance. Indeed, the possible local impact induced by the dehydration around the sand grains can easily be highlighted to better understand the chemical affinity perturbation process alone.

The impact of the sand grains and their interactions within the cement paste is out of this paper's scope. Mortar was prepared with water-cement ratios (w/c) of 0.30 and 0.50, by mixing the solid components with water in accordance with the European standard [9]. The mortar was placed inside 40 × 40 × 160 mm metal moulds. The mortar composition is given in Table 2.

Table 2

Composition of mortars

Materials	Dosage (g)	
	Mortar M1	Mortar M2
Cement	300	300
Water	150	90
Glass beads Ø 3,35 mm	/	300
Glass beads Ø 8 mm	600	/
Water/Cement (E/C)	0.50	0.30
Glass beads /Cement (B/C)	2	1

After preparation, the specimens were removed from the molds, sawn and polished to produce replicas of different maturities (8h - 10h - 24h - 72h - 120h). Between each time, the samples were kept in endogenous conditions. Samples denoted "M1-20" and "M2-20" were stored in a controlled temperature room (20 ± 1°C) and a second series "M2-40" was stored in an oven at 40 ± 1°C.

3. Observations with replica method

To pursue the development of the interfacial zone between cement matrix and granular inclusions (in our case glass beads) during the hydration process, the "simple replica" method was used. The single replica technique was firstly developed by Ollivier [4] and further used by a series of researchers [5- 8, 10-13] for the visualization of cement-based materials. The Laboratory of Materials and Durability of Constructions (LMDC) in France first developed this technique in the 1980s for monitoring the evolution of cracking in concrete. This technique has the advantage of not introducing artefacts in the observation of microcracks in cement-based materials [5, 6].

After the preparation stage, the SEM observation can be carried out on whole sample. The processes of the single replica can be summarized as below:

- Moulds removed from the specimens,
- Saw and polish specimens after 8h–10h–24h–72h–120h,
- Hold all specimens in adiabatic conditions during the experiments,
- Spray methyl acetate on the specimens,
- Apply bioden film (cellulose acetyl) on the polished surface,
- Remove the bioden film and put specimen on the brass support after the solvent evaporates,
- SEM observation of the metalized replica.

An EVO40 (Carl Zeiss®) was used to perform the scanning electron microscopy (SEM) observations in the current study.

4 Results

4.1. Observation at 20°C

Figures 1 to 3 present the observations performed at 20°C on the M1and M2 replicas mortars at different times.

The first observations were carried out after 24 hours on the M1 mortar. Before this time, the mortar showed relatively low cohesion, particularly between paste and inclusions. This allowed for loosening of glass beads during sawing and polishing of samples. Moreover, the Bioden film does not adhere well to a wet matrix. After 24 hours, the material can be cut without major difficulties. It is therefore possible to make a replica for the polished surface of specimens.

Figure 1 does not highlight the microcracking of the matrix of M1 mortar. Even at higher magnifications, it was not possible to distinguish microcracks in the material. It is important to note that at the center of the matrix and on the outskirts of some glass beads, the Bioden film is torn (Figures 1 and 2). This suggests a low quality of film adhesion to the matrix, and very porous cement paste/glass bead interface. This highly degraded aspect of the film is not present around all grains.

Taking into account the high w/c ratio of the matrix, it is unlikely that the degradation of the film around the inclusions is due to matrix damage caused by the endogenous restrained shrinkage. Two phenomena can explain the rupture of the film:

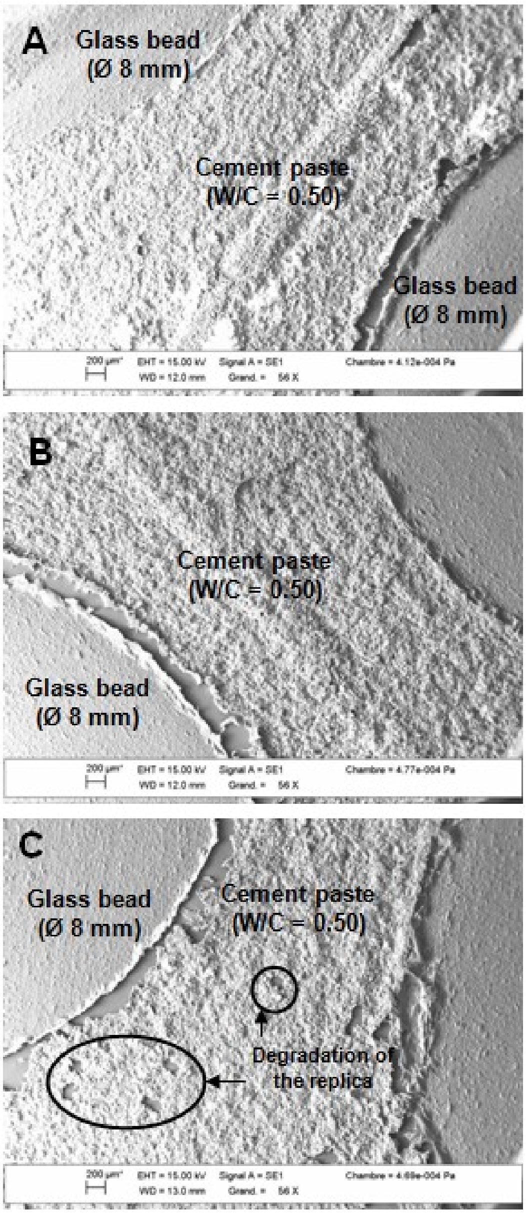

Fig. 1 - Observation of the cement paste/inclusion interface on replica mortar "M1-20" (T = 20±1°C) at different maturities. A. Age: 24h; B. 72h; C. 120h (×56 – Secondary electrons, in vacuum).

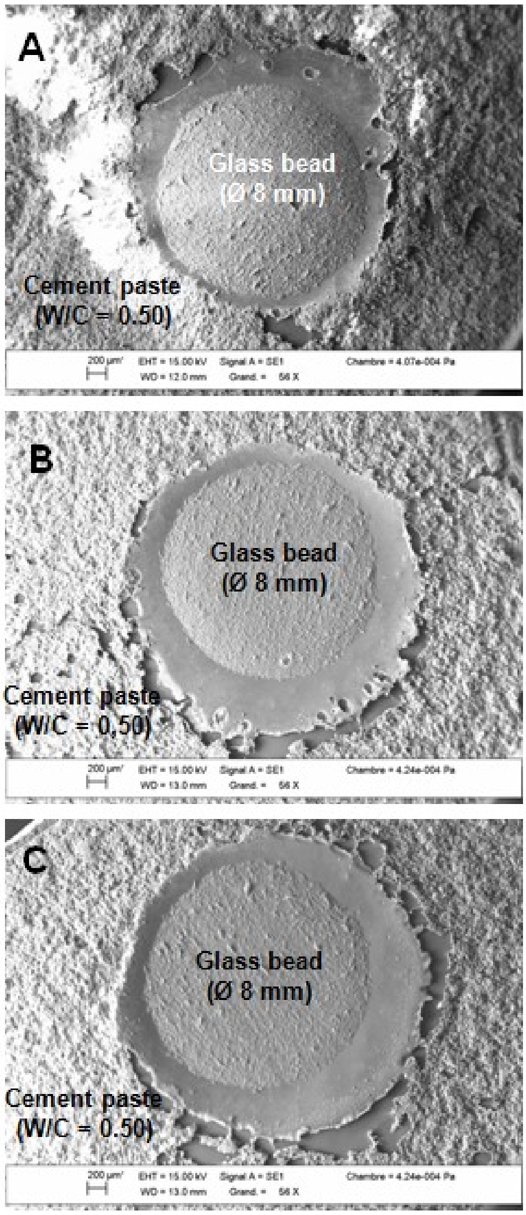

Fig. 2 - Dissymmetry in cement paste/inclusion interface probably related to localized bleeding. Observation on mortar replica "M1-20" (T = 20 ± 1°C) at different maturities. A. Age: 24; B. 72h; C. 120h (×56 - Secondary Electrons, in vacuum).

- the first is related to the conditions of sample preparation. The sawing and polishing may result in a slight loosening of some glass beads, unseen to the naked eye, resulting in a microscopic separation between the glass beads and the cementitious matrix. During the replica realization, the Bioden film is unable to find any support in the separation area, and it tears during its application or removal;
- the second explanation is the material behaviour. For medium or high w/c ratios (≥ 0.50), the material may be subject to bleeding of a portion of its mixing water. Bleeding is a phenomenon that occurs at two levels: at the macroscopic scale, it manifested by a superficial water layer above the material, and at the microscopic scale, it is mainly located around the upper parts of the aggregates.. This phenomenon is amplified by the fact that the glass beads are non-porous and thus do not absorb water from the mixture (Figure 2). This results in a very porous cement paste/aggregate to which the Bioden film adheres and degrades the interface.

Replicas obtained on matrix materials with a w/c ratio of 0.30 shown in Figure 3 are of a better quality: the film does not have as much damage as replicas of the M1 mortar. Furthermore, the mortar matrix M2 appears denser than the other samples. In addition, it clearly shows a clean break of the Bioden film around the inclusions indicating, as previously on the one hand, a cement paste / glass bead interface richer in water and, on the other hand, a separation between the inclusion

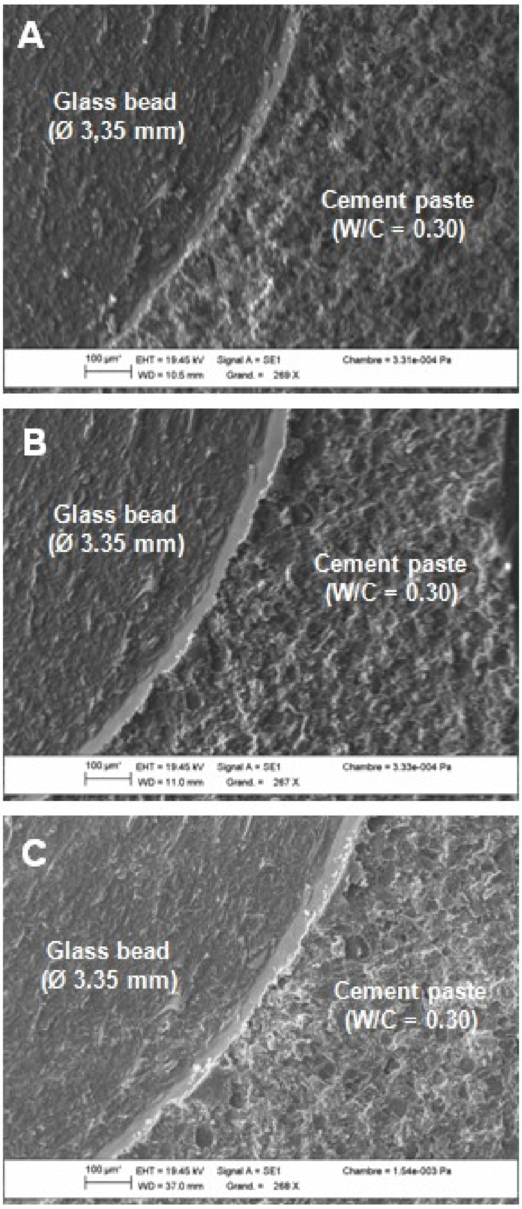

Fig. 3 - Observation of the cement paste/inclusion interface on mortar replicas "M2-20" (T = 20 ± 1°C) at different maturities. A. Age: 10 am; B. 24; C. 120h (× 268 - Secondary Electrons, in vacuum).

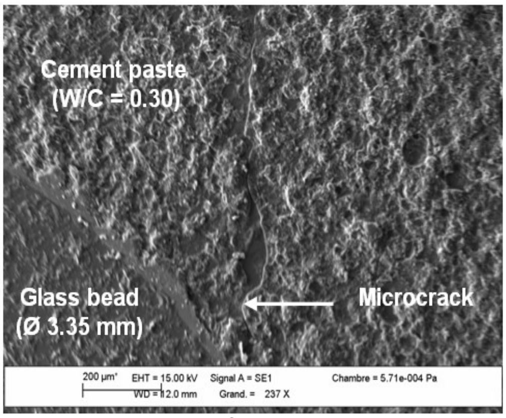

Fig. 4 - Microcracking of the matrix observed on mortar replica "M2-40" (T = 40 ± 1°C) for 10 hours of hydration (×237 - Secondary Electrons, in vacuum).

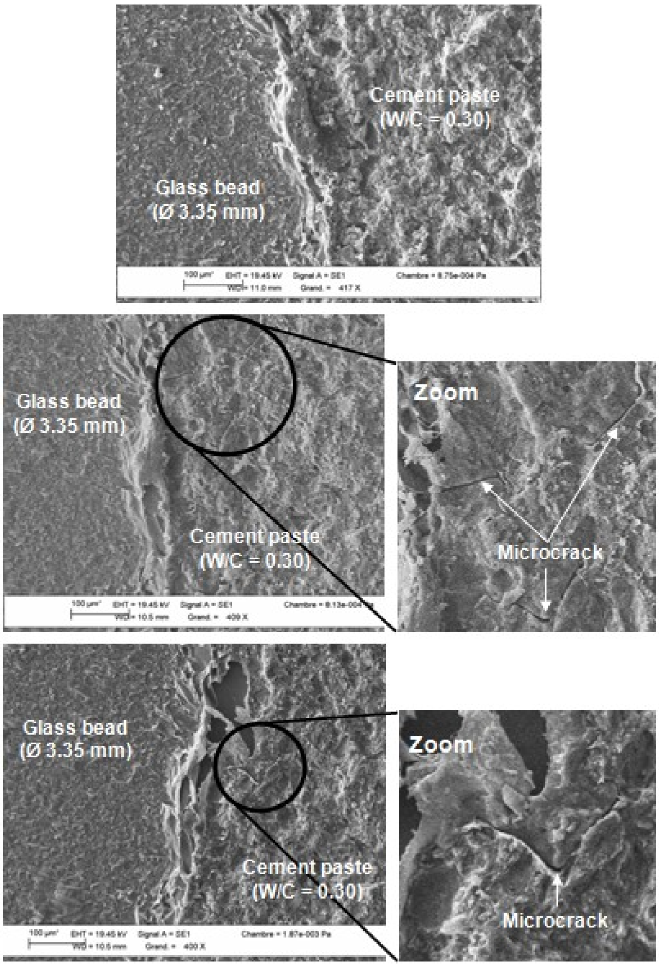

Fig. 5 - Evolution of microcracking of the matrix observed on mortar replicas "M2-40" (T = 40 ± 1°C) at different maturities. A. Age: 8h; B. 12; C. 24 (×400 - Secondary Electrons, in vacuum).

and the cement matrix.. The width of this "interface", corresponding to the thickness of the tear film, increases over time. This seems to highlight a dimensional change of the matrix that can be likened to the autogenous shrinkage. Note that no microcracking is visible within the cement matrix. Indeed, in the observed area, the deformations of the cement paste are not prevented by the presence of the inclusion.

4.2. Observations at 40°C

To investigate the effect of storage temperature on the evolution of the microstructure of the mortar M2, a series of samples were stored at 40°C throughout the period of investigation. Figures 4 and 5 show the observations performed on this mortar replica at different ages. As at 20°C, degradation of Bioden film is not observed except for at cement paste/glass bead interfaces. The same reasons explained above (paragraph 4.1) can be advanced to explain this phenomenon.

Furthermore, examining the microscopic photos reveals the presence of microcracking in the cement paste/inclusion interface after 10h of hydration (Figure 4). These very fine microcracks radiate from the inclusions and spread a few tens to a few hundreds of microns into the heart of the cement paste. Two phenomena can explain the development of this microcracking:

- First, differential expansion of glass inclusions and paste, causing tensile stresses within the matrix;
- Second, the generation of stresses due to the accelerated development of endogenous shrinkage of mortar subjected to 40°C. It has indeed been shown that the increase in temperature gives rise to increased cracking of Portland cement paste [2].

The decoupling of these two phenomena (thermo-mechanical and/or chemical-mechanical microcracking) should be the subject of further research work.

5. Conclusions

Two preliminary objectives were targeted in this study. One is the assessment of the using the "simple replica” method to study the microstructure of a cementitious matrix at very young ages. The second is to analyse the evolution of the microstructure in the time immediately after preparing the mortars. Preliminary results are promising but need to be further explored:

- The excessive humidity and lower cohesion of mortar with a medium w/c ratio (w/c = 0.50) did not allow replica preparation before 24h of hydration. After 24h, the mortar replicas clearly demonstrated an asymmetry of the interface due to microscopic bleeding around the inclusion zones.
- The mortar with w/c ratio of 0.30 stored at 20°C showed a gradual separation over time between the glass beads and the matrix. This is probably related to early dimensional changes of the matrix maintained endogenous conditions.
- The mortar stored at 40°C showed microcracks radiating from the inclusions and propagating several tens of microns into the paste after 10h of hydration. The stresses at the origin of this microcracking can be thermo-mechanical or chemo-mechanical.

The more accurate identification of causes is currently undergoing a new research campaign.

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