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Experimental Study about the Influence of Storage Conditions of Bulk Cement on the Early-Age Stiffness Evolution of Cementitious Pastes

Luigi Cieri [1], Paolino Cassese [1], Giovanni Fabbrocino [2,3], Antonio Occhiuzzi [1,4] and Carlo Rainieri [1,*]

[1] Construction Technologies Institute (ITC), Italian National Research Council (CNR), 80146 Naples, Italy
[2] Department of Biosciences and Territory, University of Molise, 86100 Campobasso, Italy
[3] Construction Technologies Institute (ITC), Italian National Research Council (CNR), 67100 L'Aquila, Italy
[4] Department of Engineering, University of Naples "Parthenope", 80143 Naples, Italy
* Correspondence: rainieri@itc.cnr.it

Abstract: The effects of uncontrolled storage and curing temperature on the early-age mechanical behavior of cement are under-investigated issues, and the few available studies in the literature analyze their influence mainly from a chemical-physical point of view. The present study, on the contrary, aims at studying the effects of temperature and, above all, cement prehydration due to uncontrolled storage from a phenomenological perspective through the application of the EMM-ARM method. In particular, the influence of those factors on the early-age evolution of the Young's modulus of cement pastes produced from Portland as well as pozzolanic cement is experimentally assessed. The obtained results confirm the possibility of exploiting the EMM-ARM method to characterize those effects on a phenomenological basis, sorting back to the comparison of the curves of prehydrated cement with reference ones in controlled storage conditions. As a result, the methodology shows promising applicative perspectives for acceptance checks of the materials before use.

Keywords: cement paste; pozzolanic cement; Portland cement; early-age elastic modulus; storage conditions; EMM-ARM

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1. Introduction

Italy is characterized by a large heritage of masonry buildings, most of them located in minor centers and valuable historical centers, which often exhibit poor structural conditions due to age and the impact of natural events, like earthquakes [1]. As a result, the demand for effective and sustainable structural interventions aimed at combining the preservation of their architectural and cultural features and a rational increase in their level of safety is high. In the last decades, different strengthening techniques have been designed to offer an increase in the static and seismic capacity of masonry structures and limited invasiveness of the interventions so that the principles of preservation and restoration can be respected [2].

In this context, techniques based on the use of textile-reinforced mortar (TRM), or fiber-reinforced cementitious matrix (FRCM) are largely established for historic masonry structures [3,4]. Several natural lime mortars have been recently proposed as inorganic matrices in order to replace traditional cement-based mortars to achieve better historical compatibility with the masonry substrate and higher environmental sustainability. Indeed, the use of hydrated lime and pozzolan in various proportions yields binders characterized by high mechanical and durability performance with a reduction in the cement content [5,6]. The pozzolanic component provides good protection against chemical attacks, making it suitable for aggressive environments, and its activity contributes to the achievement of material mechanical performance after casting in a slow and continuous fashion over time [7]. Furthermore, it is worth noting that pozzolan is largely known and adopted in the Mediterranean area, particularly in Southern Italy [8].

The evolution of the stiffness of the cementitious materials may play a key role in many retrofit and upgrading structural interventions: the assessment of the matrix structural features, such as setting time and hardening, indeed supports the accurate definition of the work sequence as well as the analysis of the capacity of members associated with the activation of the reinforcement effectiveness, and the prediction of the long-term stiffness. Specifically, Young's modulus considerably changes during the early age phase after casting basically due to hydration reactions [9]. Various destructive and non-destructive techniques have been proposed in the literature for the early-age mechanical characterization of cement-based materials. The majority of those tests can only be performed after setting time, i.e., after some days of curing [10]. In the second half of the last century, several non-destructive test methodologies to evaluate the mechanical properties of cement-based materials since setting time have been proposed [11]. Among them, maturity methods are based on temperature measurements during curing; they are mainly applied on-site, and their reliability strictly depends on adopted maturity functions. Measurements of the variation of the dielectric properties of the material can also be correlated with the hydration process and mechanical properties evolution. In the case of methods based on ultrasonic waves, the reflection coefficient is used as an indicator of hydration to qualitatively describe the mechanical evolution since setting time. The Radon exhalation method consists of exploiting the properties of this noble gas to monitor the hydration of the cement and identify the setting time. Further details about the abovementioned methods can be found in [11].

A very promising non-destructive method based on vibration measurements has been recently proposed to assess the evolution of Young's modulus E in cementitious materials: the so-called E-modulus Measurement through Ambient Response Method (EMM-ARM) [9,12]. It has been widely applied in the literature and validated using extensive comparisons with the results of destructive as well as non-destructive techniques [13].

The development of chemical reactions in the early ages might be affected by factors such as exposure to moisture, which might cause premature hydration (prehydration) of the cement. Prehydration leads to a considerable delay in hydration reactions with an increase in setting time and reduced mechanical performance. Calcium silicates, calcium aluminates, and calcium sulfates react with water vapor to form hydration products on the surfaces of the cement particles that reduce the reactivity of cement to water during normal hydration [14]. The phenomenon is worthy of investigation because it can occur during production as well as storage in the absence of appropriate countermeasures. Relative humidity (RH) of the environment and duration of exposure determine the extent of prehydration. Despite its undesired effects, prehydration has been poorly investigated: a few research studies [14–17] focused on chemical and physical approaches to assess the effect of prehydration on Portland cement are available in the literature.

The original contribution of the present research in the area of knowledge is represented by the use of a mechanical testing methodology, the EMM-ARM, to investigate the effect of prehydration since the very early ages from a phenomenological viewpoint. Furthermore, particular attention has been paid to pozzolanic cement, which has not been investigated through EMM-ARM so far (see Section 2).

The paper is organized as follows. The outcome of a detailed literature review focused on EMM-ARM applications is reported in Section 2 to further remark on the contribution of the present study. In Section 3, the experimental campaign is described, and the EMM-ARM theoretical background is summarized along with some proposed changes in data processing with respect to the original procedure. Section 4 finally illustrates and discusses the obtained experimental results.

2. EMM-ARM in the Literature

EMM-ARM is a non-destructive technique that indirectly measures the early age evolution of the Young's modulus of cementitious materials since casting through the solution of an inverse problem. This requires the identification of the fundamental frequency of a properly designed beam from its ambient vibration response. More details about the theoretical background of the method and the experimental testing procedure are provided in Section 3.2; herein, an extensive literature review about relevant applications of the methodology is reported to point out established outcomes and less investigated threads. The review is presented according to chronological order, whereas Table 1 summarizes the main outcomes of the literature review in terms of (i) tested materials, (ii) cement typology, (iii) curing conditions (temperature and/or relative humidity, RH), and (iv) investigated experimental variables.

The EMM-ARM method was originally proposed by Azenha et al. [9] for continuous monitoring of concrete E-modulus evolution since casting. The results were validated by comparison with those obtained from ordinary compression tests carried out after setting time (typically at 3, 7, 14, and 28 days after casting). A different experimental setup was proposed later to characterize cement pastes and mixtures with retarding and accelerating additives [12]. The influence of the composition of cement pastes on the evolution of the E modulus was investigated by EMM–ARM in [18]. In particular, the study focused on the influence of different water-to-cement (w/c) ratios and contents of limestone filler, fly ash, silica fume, and metakaolin. The procedure was able to continuously catch the performance changes due to the variation in the composition; w/c ratio and filler typology strongly affected stiffness evolution over time.

A case study aimed at assessing the reliability of the methodology for in situ applications was discussed in [19]. The Authors tried to adapt the setup used in a laboratory environment to field conditions, but some problems were revealed. The use of multiple accelerometers was proposed, and Stochastic Subspace Identification (SSI) [20] was used to estimate the fundamental natural frequency.

Silva et al. [21] investigated the extension of the EMM-ARM to sand-cement samples extracted by stabilized soils; in particular, the study faced the problem of mold geometry and sampling techniques. A good match with the results of cyclic compression tests was found. A detailed and extensive study [22] compared the results obtained using EMM-ARM with those provided by other conventional non-destructive and destructive techniques in the presence of different temperatures during the test, as well as various constituent materials. An in-situ application of EMM-ARM to stabilized soils is reported in Azenha et al. [23], where an assessment of the influence of mold geometry and different mixes of cement was carried out.

The results of a round-robin test involving three independent laboratories are presented in [13]: the experimental program encompassed eight different automatic destructive and non-destructive techniques to evaluate the evolution of stiffness in concrete at early ages. Evidence of a good agreement among the estimates provided by the different techniques is documented.

Granja et al. proposed some improvements to the conventional test setup to simplify in situ applications [24]. The influence of biomass ashes on the evolution of concrete early-age Young's modulus was studied through the EMM-ARM. In particular, cement was partially replaced by biomass ash, which reduced the stiffness within the first 28 h and also largely increased the electrical conductivity of the mix [25].

The influences of recycled aggregates and curing temperature on the evolution of the Young's modulus of concrete at early ages were investigated in [26] through EMM-ARM and other non-destructive techniques, obtaining results in good agreement with each other.

The possibility of reproducing the evolution of cement paste mechanical properties obtained through EMM-ARM by means of numerical simulations of paste microstructure was studied in [27]. In particular, three-dimensional lattices and Finite Element models were applied, obtaining promising results.

A considerable influence of water/lime ratios on the behavior of natural hydraulic lime mortars at early ages was proved by Garijo et al. by applying EMM-ARM and cyclic compression tests in parallel [28].

Table 1. Summary of EMM-ARM applications reported in the literature.

Study	Material [1]	Cement [2]	Curing	Experimental Variables
[9]	C	CEM I 42.5 R	T = 20 °C RH = 50%	Methodology
[12]	CP M	CEM I 52.5 CEM IV/A 32.5R (FA)	N.A. [3]	Methodology Additive
[18]	CP	CEM I 42.5R	T = 20 °C RH = 50%	w/c ratio Filler
[19]	C	CEM I 42.5R	T = 9.2 °C RH = N.A.	Mold (in-situ application)
[21]	SC	CEMI42.5R	N.A.	Mold Sampling (in-situ application)
[22]	CP	CEM II/B-L 32.5N CEM I 42.5R	T = 20 °C; 40 °C	w/c ratio Temperature
[23]	M; SA	CEM I 42.5 R CEM II/B-L 32.5N	N.A.	Mix composition
[13]	C	CEM I 52.5N PMES CP2	T = 19.2 ± 0.5 °C	Methodology validation (Round Robin)
[24]	C	CEM I 52.5 N PMES CP2 CEM II 42.5R CEM II/A-L 42.5R	T = 20 ± 2 °C	Mold Mix composition (in situ application)
[25]	C	CEM I 52.5R-SR 3	T = 20 °C	Filler
[26]	C	CEM I 52.5 S/SR-3	T = 20 °C; 40 °C	Temperature Mix composition
[27]	CP	WCAP	T = 20° C	w/c ratio
[28]	HLM	N.A.	T = 20 °C RH = 95%	w/c ratio
[29]	LCM	CEM I 42.5 R	T = 20 °C RH = 95%	w/c ratio
[30]	LCM	CEM I—42.5 R	N.A.	Temperature Mix composition
[31]	CP	WCAP	T = 20° C	w/c ratio

[1] Concrete (C), Cement Paste (CP), Mortar (M), Sand-Cement (SC), Soil Admixture (SA), Hydraulic Lime Mortar (HLM), Lime-Cement Mortar (LCM). [2] White Cement Aalborg Portland (WCAP). [3] N.A.: Not Available data.

In Ref. [29], EMM-ARM is applied to the analysis of mixed lime-cement mortars, and a comparison between its results and those of cyclic compression tests is reported. More in detail, cement was replaced by lime in different proportions, and a stiffness decrease was observed at increasing amounts of lime.

Other studies [30] on lime-cement mortars investigated the effect of temperature on curing at an early age for different lime contents, pointing out how high temperature during curing increases the reactivity of the mix and shortens the dormant period of cement.

The most recent studies combined the results of EMM-ARM and H-Nuclear Magnetic Resonance with numerical modeling to associate Young's modulus with C-S-H evolution in cement pastes [31]. Finally, other studies by Azenha and his research team were focused on developing a cost-effective and open-source test system to perform EMM-ARM tests, reducing the costs of the experimental equipment and the complexity of the elaboration procedure associated with the original system [32–34]. These studies have not been added to Table 1 because no experimental tests were carried out.

In summary, AMM-ERM has been extensively applied to analyze the early-age mechanical behavior of cementitious materials. Its reliability has been largely established in comparison with classical destructive and non-destructive techniques, including standard compression tests at a given time. Several tests have been carried out on concrete, whereas mortar and, particularly, cement pastes have been less investigated.

Among the studies focused on mortar, a few considered the presence of supplementary materials in the mix (e.g., fly ash, silica fume, etc.), but none of these considered the influence of pozzolan despite its widespread use. In addition, a phenomenological investigation about the issue of prehydration due to uncontrolled storage of the bulk material through EMM-ARM has not been an object of research so far.

3. Experimental Campaign

3.1. Materials and Test Nomenclature

Eight tests were carried out on cementitious pastes using two types of cement: (i) CEM IV/B (P) 32.5 R, pozzolanic cement with a clinker content between 45% and 64%, and (ii) CEM II/A LL 42.5 R, limestone Portland cement with a clinker content between 80% and 94%; w/c ratio was kept constant in all tests and equal to 0.5; curing additive (Mapei Mapecure SRA, following the recommended dosage of 0.33% of cement weight) was added to reduce shrinkage, being representative of real applications. The mix for the generic single specimen was prepared by using 225 g of cement, 112.5 g of water, and 0.75 g of additive.

The specimens were prepared by using cement right after bag opening as well as after given periods of uncontrolled storage. Specifically, four and two different storage periods were considered for pozzolanic (0, 30, 240, and 360 days) and Portland (0 and 240 days) cement pastes, respectively. After the opening, an uncontrolled storage method with the cement kept in the original bag without the use of a proper airtight container was considered, while the material was exposed to controlled temperature (T) and humidity conditions (T = 20 ± 0.5 °C; RH = 35 ± 5%). Thus, the time of exposure to the reference environmental conditions represented the experimental variable governing the prehydration phenomenon. In addition to storage, a preliminary investigation on the effect of curing temperature on the early-age behavior of pozzolanic cement paste was carried out. Particularly, two different temperature values were considered to simulate different operating scenarios: 15 °C and 20 °C.

Table 2 shows specifications and nomenclature of test specimens.

Table 2. Test specimens and experimental variables.

Specimen	Material	Experimental Variable	
		T (°C)	Time (Day)
C325d0	CEM IV/B (P) 32.5 R-SR	20 ± 0.5	0
C325d30	CEM IV/B (P) 32.5 R-SR	20 ± 0.5	30
C325d240	CEM IV/B (P) 32.5 R-SR	20 ± 0.5	240
C325d360	CEM IV/B (P) 32.5 R-SR	20 ± 0.5	360
C425d0	CEM II/A-LL 42.5 R	20 ± 0.5	0
C425d240	CEM II/A-LL 42.5 R	20 ± 0.5	240
C325T20	CEM IV/B (P) 32.5 R-SR	20 ± 0.5	0
C325T15	CEM IV/B (P) 32.5 R-SR	15 ± 0.5	0

The generic specimen was identified through the string CXXXvYYY, where C stands for cement paste, XXX represents the cement compressive strength (i.e., 32.5 or 42.5 N/mm^2), v specifies the considered experimental variable (storage days, d, and curing temperature, T), and YYY the corresponding value.

3.2. Specimens and Test Setup

The specimen comprised a composite cantilever consisting of an acrylic tube filled with cement paste. Further details can be found elsewhere [12]. The mold used for the preparation of the sample is a 500 mm long acrylic tube characterized by internal (ϕ_i) and external (ϕ_e) diameters equal to 16 mm and 20 mm, respectively. Before casting, a polystyrene cap (Figure 1a), weighing less than 0.1 g, was glued to the free end of the tube. Then, the mix was prepared as reported in Section 3.1. Once the mixture was ready, the pouring phase was executed as follows: (i) the acrylic tube was inclined at approximately 15° with respect to the vertical; (ii) the mix was poured by applying a slight pressure by means of a flexible tube starting from the capped end of the beam; (iii) a mild vibration was externally applied to the tube to eliminate voids and air bubbles. After casting, the specimen was placed in a vertical position, and a purge system (Figure 1b) was mounted on the free end of the specimen. The purge system consisted of a nut glued onto a washer and a bolt. It acted like a plug: by gently screwing the bolt, the remaining air bubbles were removed. At the end of the operations, the specimen was positioned horizontally and placed within the clamping device depicted in Figure 1c,d in order to obtain a composite cantilever beam with a free span equal to 400 mm.

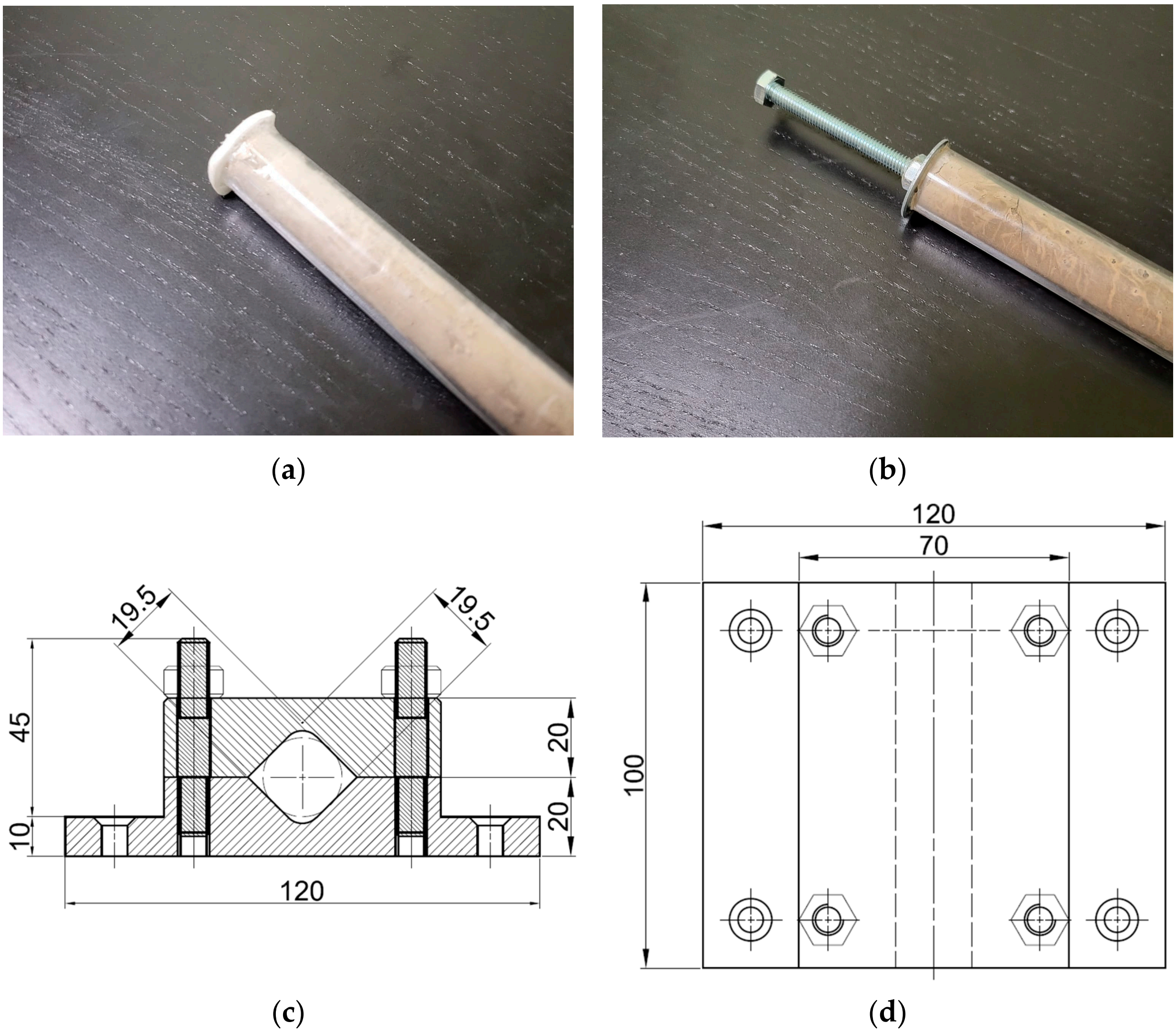
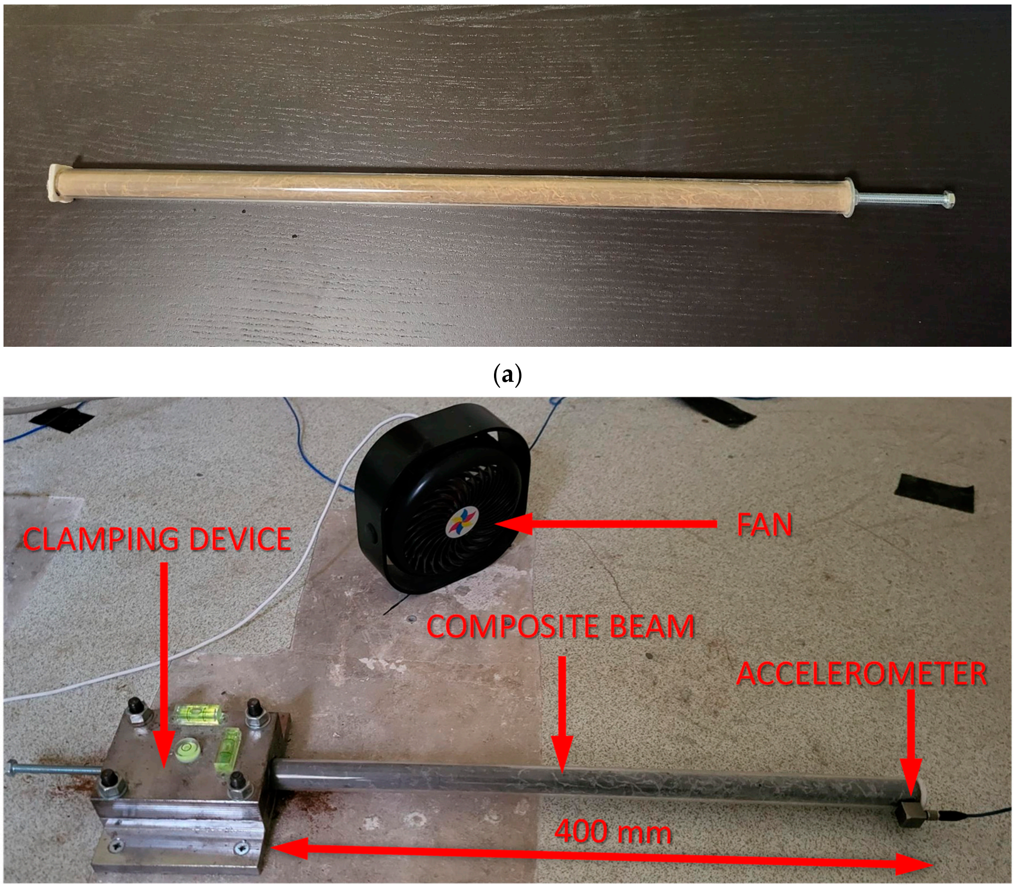


Figure 1. Views of specimen ends after casting (**a**,**b**), and scheme of clamping device (**c**,**d**).

The described specimen preparation procedure allows for achieving conventional controlled curing conditions in agreement with the original procedure [12].

The restraint system consisted of two steel plates: the lower one was fixed to the strong floor of the laboratory, and the upper one was screwed onto it after positioning the specimen; a torque wrench was used to gradually tighten the bolts while controlling the tilt angles by means of integrated bubble levels (see Figure 2). Notice that, with respect to the original setup proposed by Azenha et al. [12], a slight modification of the configuration of the clamping device was introduced to prevent undesirable localized stress concentrations on the acrylic tube.



(**a**)

(**b**)

Figure 2. General view of the specimen (**a**) and of the experimental setup (**b**).

In Figure 2, general views of the specimen (Figure 2a) and of the experimental setup (Figure 2b) are shown. A piezoelectric accelerometer with 7.5 g weight and 1 V/g sensitivity was glued to the free end of the beam. A low-power fan was used to improve the signal-to-noise ratio (by increasing the vibration response of the specimens without significantly altering the broadband nature of the excitation) in view of the identification of the fundamental natural frequency. The data acquisition system consisted of programmable hardware controlled by the S2-DDA software v.2.0.0 [35]. It was characterized by a 24-bit resolution and analog anti-aliasing filter. A sampling frequency of 100 Hz was adopted coherently with the expected value of the fundamental natural frequency of the beam.

It is worth noting that adhesion plays a primary role in test execution and data processing. Even if an anti-shrinkage additive is added to the mixes in order to preserve the specimens from possible losses of adhesion between the outer acrylic tube and the inner cement paste, specific after-test checks have been carried out in agreement with the original methodology [12], by cutting and visual inspections.

3.3. Data Processing Procedure

EMM-ARM [9,12] is an experimental methodology that provides indirect measurements of the Young's modulus of cementitious materials cast inside an acrylic cylindrical beam since the very early ages after casting. Young's modulus is obtained by solving an inverse problem starting from the fundamental natural frequency of the composite beam identified by Operational Modal Analysis [36]. The applied input is, therefore, not measured, but it is assumed to be broadband with a smooth spectrum in the band of interest. In order to continuously and automatically track over time the evolution of the fundamental natural frequency of the composite beam and of the associated Young's modulus of the inner cementitious material, an automated version of the simple Peak-Picking technique is needed. The automatic dynamic identification procedure was implemented in the LabVIEW environment. Acceleration time series were analyzed in 15-min blocks, with a total duration of 120 h for all tests. The Normalized Power Spectral Density (NPSD) [12] was estimated from each record by applying the Welch procedure with 50% overlap and the application of the Hanning window. In the original procedure [12], a pondered average of the 40 highest energy points in the NPSD was used to estimate the fundamental natural frequency. Conversely, in this work, an Automatic Peak Detection (APD) algorithm was used. This automatic procedure is based on an algorithm that fits a quadratic polynomial to sequential groups of data points by setting a suitable threshold. The curves obtained with both methods are compared in Figure 3. The APD curve (in red) is characterized by reduced scatter and, therefore, enhanced results with respect to the original procedure.

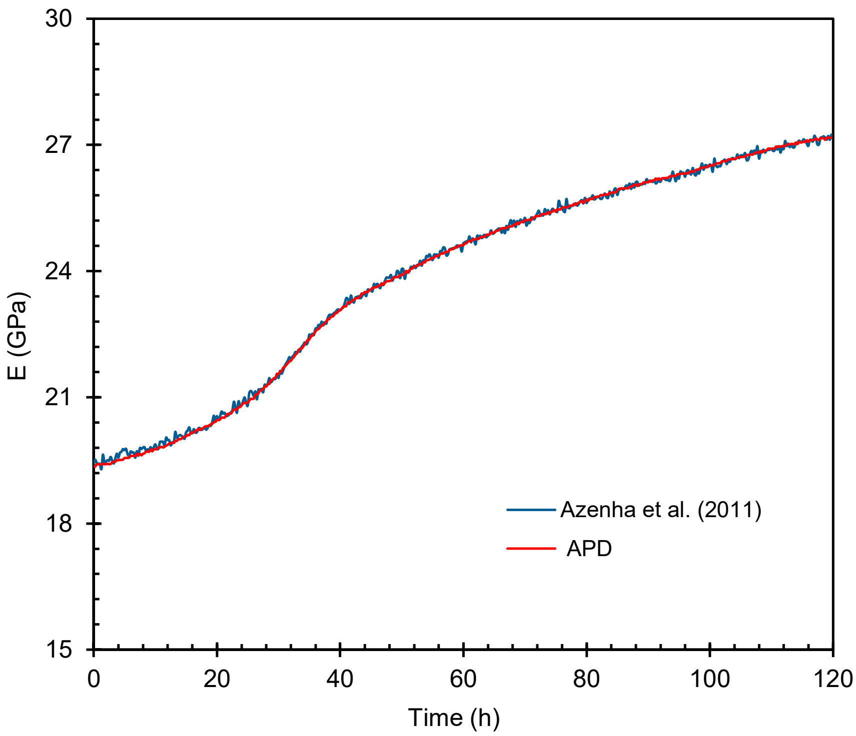


Figure 3. Comparison between the algorithm used by Azenha et al. (2011) [12] and the APD procedure used in the present study.

The estimated natural frequency is used afterward to evaluate the elastic modulus E by iteratively solving Equation (1):

$$a^3[\cosh(aL)\cos(aL)+1]+\frac{\omega^2 m_1}{EI}[\cos(aL)\sinh(aL)-\cosh(aL)\sin(aL)]=0 \quad (1)$$

where E is the composite elastic modulus, I is the second moment of inertia of the composite cross-section, $\omega = 2\pi f$ is the circular natural frequency of the fundamental mode, m_1 is the added mass of the sensor at the free end of the cantilever, L is the free-span length (equal to 400 mm), and the term a is the coefficient given in Equation (2), in which $\overline{m}$ is the uniformly distributed mass.

$$a = \sqrt[4]{\frac{\omega^2 \overline{m}}{EI}} \quad (2)$$

An initial value $(EI)_0$ of the bending stiffness is required to iteratively find the solution of Equation (1), taking into account Equation (2); it can be computed under the assumption that the mass m_1 of the sensor is small compared to the cantilever mass:

$$(EI)_0 \cong \frac{\overline{m}L^4\omega^2}{1.8751^4} \tag{3}$$

Once Equation (1) is iteratively solved to obtain the final value EI of the bending stiffness of the composite cantilever beam, the elastic modulus of the inner cementitious material E_c can be obtained as per Equation (4):

$$E_c = \frac{64EI}{\pi\phi_i^4} - E_a\frac{\phi_e^4 - \phi_i^4}{\phi_i^4} \tag{4}$$

where ϕ_e and ϕ_i are the outer and inner diameters of the acrylic tube, respectively, and E_a is the elastic modulus of the acrylic tube. This is obtained according to the same testing and data processing procedure but with the acrylic tube filled with water so that the Young's modulus of the inner material is null while the global mass of the beam is well known. The interested reader can refer to [12] for more details.

Constant coefficients in Equation (4) (i.e., $\overline{m}$, E_a, L, ϕ_e, and ϕ_i) were individually determined. L, ϕ_e, and ϕ_i were measured by distance meter and caliper. The weight of the composite beam was also measured to compute $\overline{m}$. Finally, E_a was determined by a preliminary test of the tube filled with water, as previously mentioned. The preliminary test to estimate the value of E_a has been carried out before the preparation of each composite specimen to properly account for the variability of the elastic modulus of acrylic among different tubes associated with different production stocks.

4. Results and Discussion

4.1. Benchmark Response Curves

Before starting the experimental campaign, according to Table 2, some pilot tests were carried out in order to optimize the layout and check the effectiveness of the procedure.

Two pilot tests were performed in parallel on specimens produced from Portland (CEM II/A) and pozzolanic (CEM IV/B) cement pastes, respectively; the tests aimed at experimentally reproducing well-established theoretical results. Specifically, it is known from the literature that the high content of clinker in CEM II/A cement produces very quick hardening with high stiffness reached in a reduced amount of time, with nearly the final value approached after 28 days of curing. Conversely, the low content of clinker characterizing CEM IV/B cement yields slower hardening with respect to the previous case in the same initial period. Such theoretical trends were confirmed by the experimental outcomes, as shown in Figure 4. Figure 4a shows the evolution of the elastic modulus E as a function of time for the two specimens. A time window of 120 h since casting was considered, and the value of E was normalized with respect to the maximum value E_{max} recorded in that period for the considered specimen in order to improve comparability of the curves: in fact, these refer to cement types characterized by different final strength and stiffness properties. Furthermore, a 23-term moving average was applied to smoothen the curves and further reduce the noise influence.

The incremental ratio R of E/E_{max} computed over the time interval of 15 min is reported in Figure 4b, together with a detailed view of the trends, while the curves of the elastic modulus approach the maximum value. Figure 4b points out that the CEM II/A curve grows faster and higher than the CEM IV/B one. Indeed, at the point of inflection, R is equal to 0.32 1/h for the CEM II/A curve and 0.22 1/h for the CEM IV/B curve. From 72 to 120 h (see top of Figure 4b), the CEM II/A curve is almost approaching zero, i.e., the maximum stiffness, whereas the CEM IV/B curve is still far from the horizontal axis. In fact, the fitting lines (dotted lines) yield R values at 120 h equal to 3×10^{-4} 1/h and 3.2×10^{-3} 1/h, respectively.

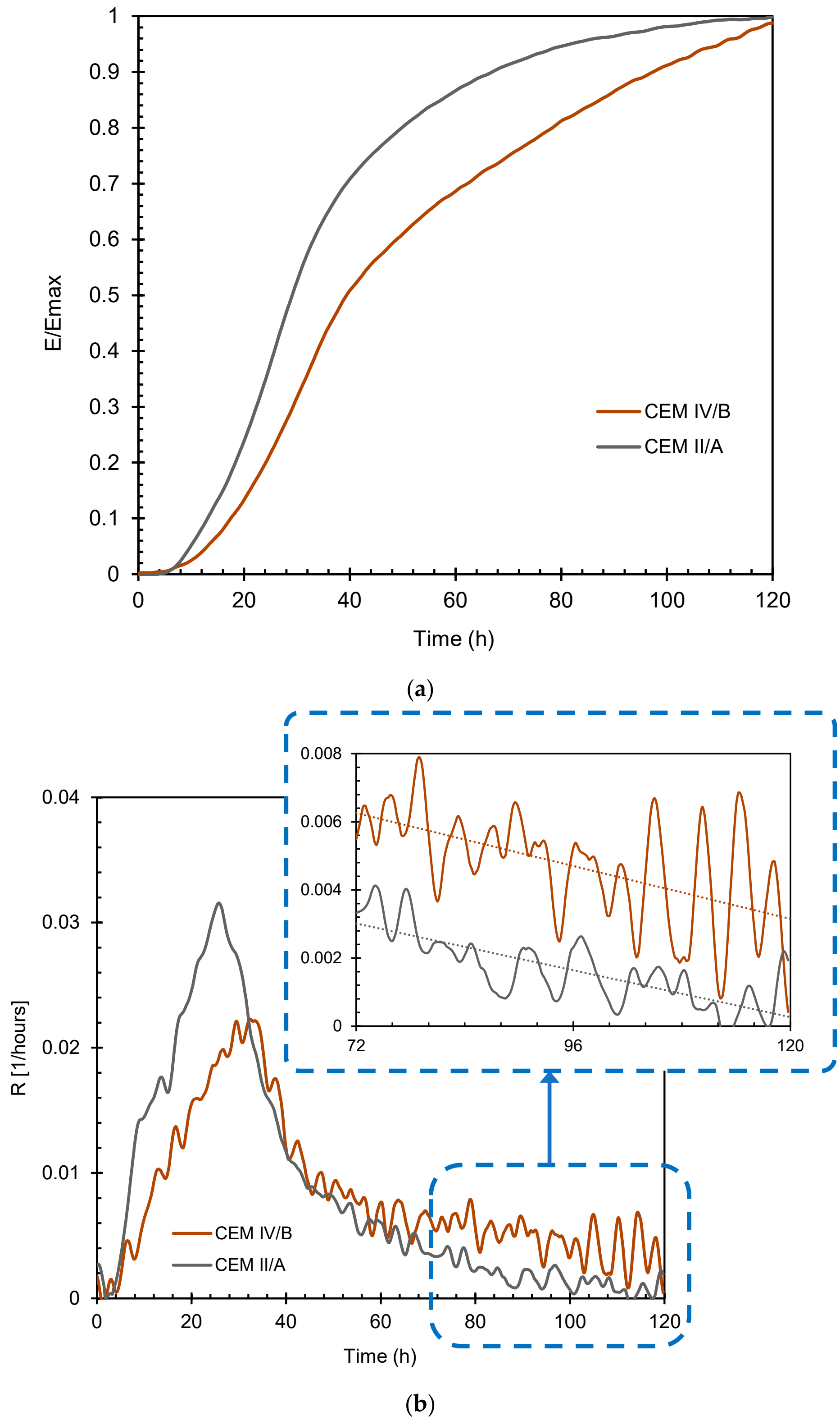


Figure 4. (**a**) dimensionless curves of CEM II/A and CEM IV/B; (**b**) incremental ratio of dimensionless curves.

4.2. Effect of Storage

The effect of storage on early-age mechanical properties, specifically in terms of elastic E-modulus, was investigated on both CEM II/A- and CEM IV/B-based cement pastes, according to the scheme of Table 2. Starting from the recorded accelerations and applying the procedure described in Section 3, the fundamental natural frequency and E-modulus of the tested composite beams were obtained. Figure 5 shows the results for the pozzolanic CEM IV/B cement paste.

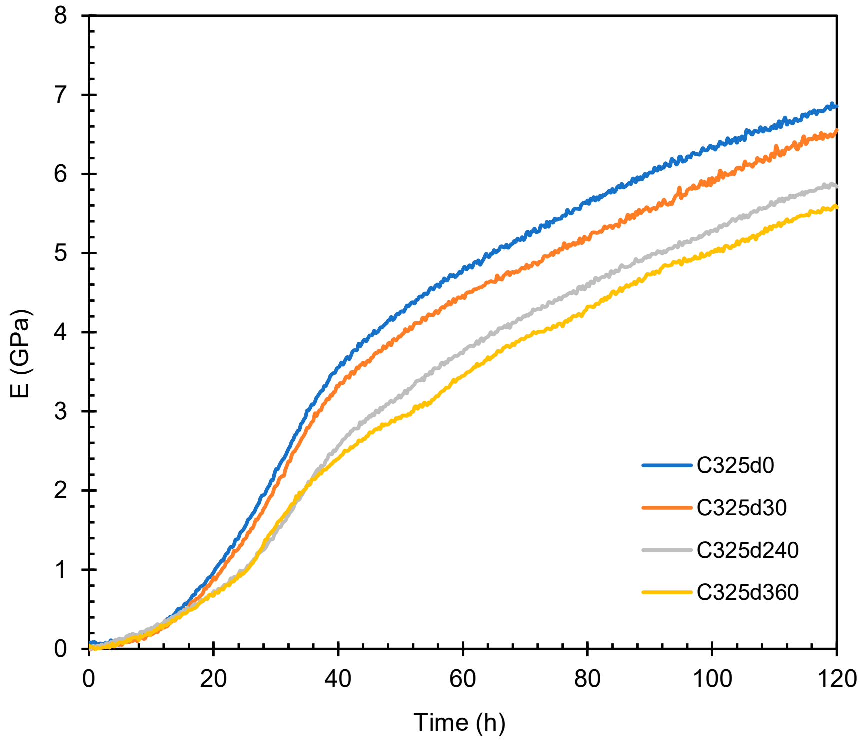


Figure 5. Elastic modulus vs. time for CEM IV/B cement paste at different storage times.

As known, from a phenomenological point of view, after mixing cement with water, the hydration process starts. At a microscopic level, the process is characterized first by a period of almost no reaction, which is called the dormant period, with the initial formation of ettringite; production of C-S-H (calcium silica hydrate) and calcium sulfoferrite characterizes the subsequent setting and hardening phases [37]. From macroscopic EMM-ARM results, an initial dormant period of between 1 and 2 h since the beginning of the test was observed for all tested specimens. The dormant period is characterized by nearly zero values of the Young's modulus. Setting and hardening stages took place afterward. During such a phase, the stiffness monotonically increased, as expected, regardless of the storage time. However, a considerable effect of storage time on both E modulus absolute value and hardening time was experimentally observed. The E modulus and hardening rate, i.e., stiffness value reached in a certain period, reduced as storage time increased. In particular, 30 days of storage (see specimen C325d30) caused a decrease in E equal to 8% on average during the observation period (i.e., 120 h); cement stored for 360 days (see specimen C325d360) yielded, on average, a 26% reduction in the Young's modulus over the whole observation period. For specimens C325d240 and C325d360, the elastic modulus assumed very similar values in the first 36 h of observation, whereas larger differences were observed thereafter; this result seems to suggest that prehydration completely affected the formation of the first reaction products.

At the end of the observation, i.e., after 120 h, the elastic modulus reached the following values: 6.85 GPa for C325d0, 6.55 GPa for C325d30, 5.83 GPa for C325d240, and 5.57 for C325d360. Therefore, 1-, 8-, and 12-month storage caused respectively 4.4%, 14.9%, and 18.7% reduction in E modulus. It is noteworthy that, as expected, after 5 days of observation, the E vs. time curves do not show a clear plateau because the significant presence of pozzolanic delays the achievement of the long-term stiffness.

Two experimental tests were also carried out on CEM II/A cement paste. In the present case, a reduced number of tests have been carried out with respect to CEM IV/B because they mainly addressed existing knowledge, even if from a different (phenomenological rather than chemical–physical) point of view. Specifically, two different storage conditions were considered: new material (right after the opening) and material stored for 240 days (i.e., 8 months) in uncontrolled conditions. Figure 6 shows E vs. time curves for an observation window of 120 h after casting.

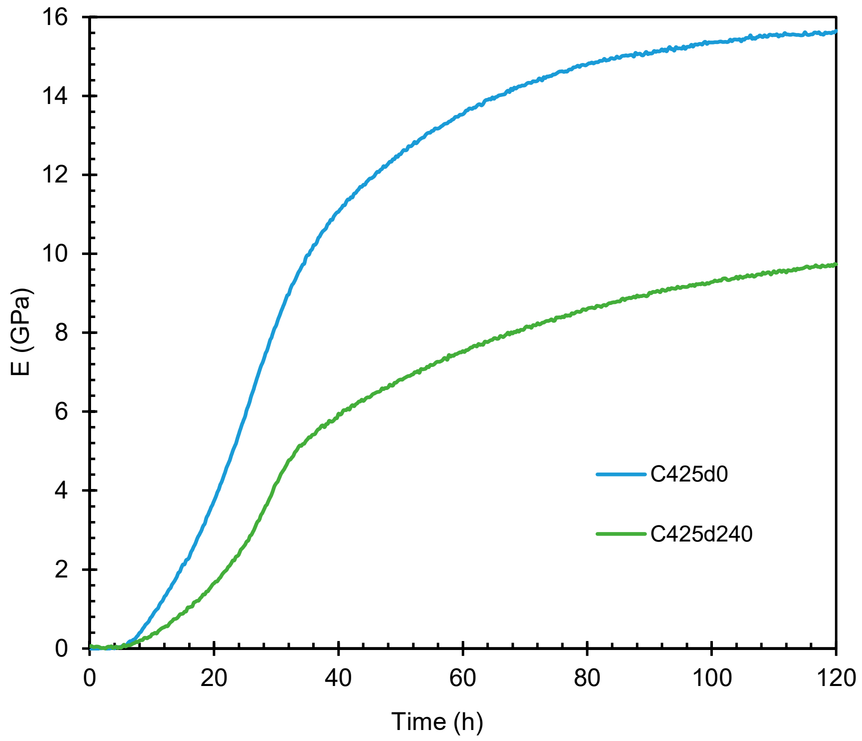


Figure 6. Elastic modulus vs. time for CEM II/A cement paste at different storage times.

In this case, the reduction in the elastic modulus is more significant with respect to the pozzolanic CEM IV/B cement paste. Unlike the pozzolanic CEM IV/B cement pastes, at the end of the observation period, the curves showed a substantial reduction in slope because of approaching the maximum long-term stiffness value. The values of the elastic modulus at 120 h were equal to 15.6 GPa and 9.7 GPa for the C425d0 and C425d240 specimens, respectively, corresponding to a final reduction of 38%. The observed results and differences with respect to pozzolanic cement pastes can be associated with the higher clinker content in CEM II/A cement with respect to CEM IV/B, which makes CEM II/A more sensitive to prehydration [15].

4.3. Effect of Temperature

Some applications of EMM-ARM are available in the literature focused on the assessment of the effect of operating temperature on CEM I and CEM II cement-based materials [22,26,30]. In this work, the effect of different curing temperatures on the early age mechanical properties of pozzolanic CEM IV/B cement paste was investigated by means of the EMM-ARM methodology considering two temperature values equal to 15 °C and 20 °C, the latter assumed as control value, in order to simulate different operating scenarios. Figure 7 shows the results observed in terms of elastic modulus vs. time.

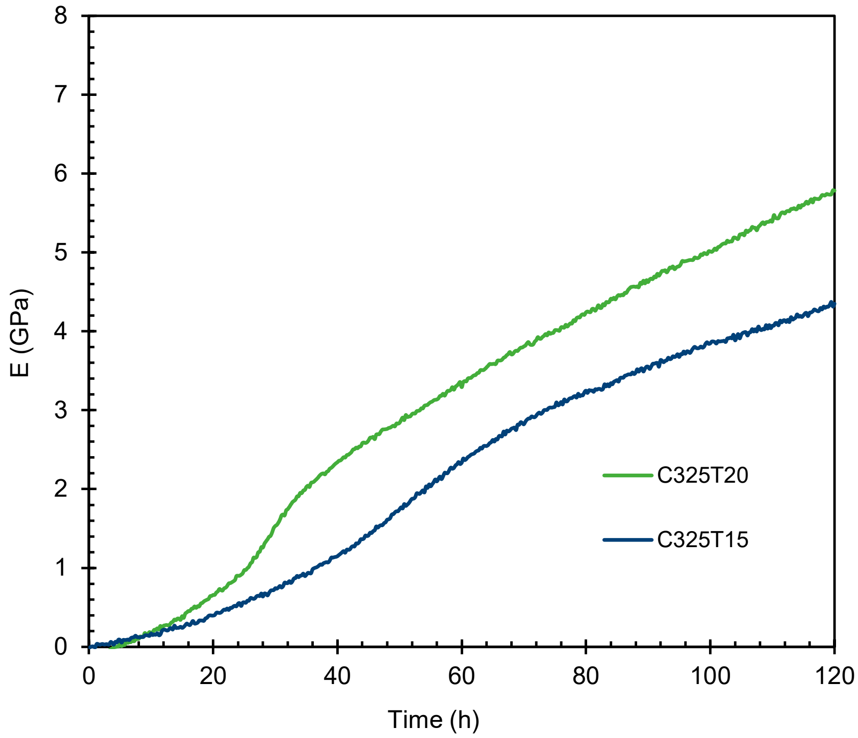


Figure 7. Elastic modulus vs. time for CEM IV/B cement paste at 15 °C and 20 °C.

The 15 °C curing temperature (see specimen C325T15) was characterized by a relevant change in setting and hardening phases as well as a significant drop of the elastic modulus with respect to the control condition (namely, 20 °C). After 120 h of maturation, in fact, a reduction in E equal to 25% for specimen C325T15 (E = 4.34 GPa) with respect to the corresponding control value at 20 °C was observed. The results confirmed the expected trends since the hydration reactions and the rate of the kinetic reactions are affected by temperature decreases.

5. Conclusions

The present work aimed at studying the effects of cement prehydration due to uncontrolled storage from a phenomenological point of view through the application of the EMM-ARM method for the characterization of the early-age evolution of the elastic modulus of cement pastes. Attention has been focused on Portland (CEM II/A) as well as pozzolanic (CEM IV/B) cement; the latter has never been investigated by EMM-ARM. In addition to storage time, which was assumed as the control variable for prehydration, specific tests have also been carried out to assess the influence of curing temperature on the early age evolution of the Young's modulus of pozzolanic cement pastes. A total of eight experiments were conducted, six of which were on CEM II/A and CEM IV/B specimens stored for different periods of time up to one year, and the remaining two on CEM IV/B specimens cured at two different temperatures typical of environmental Mediterranean scenarios.

Based on the obtained results, the following conclusions can be drawn:

- The material stored in uncontrolled conditions undergoes phenomena that have negative effects on both Young's modulus and hardening rate as storage time increases. The observed trend was very marked for CEM II/A, characterized by higher clinker presence, with a reduction in the elastic modulus after 240 days of storage equal to 38% at 120 h since casting. The pozzolanic cement (CEM IV/B) proved to be less sensitive to the phenomenon of prehydration, with an 18.7% reduction in the elastic modulus observed at 120 h since casting on specimens produced from cement stored for one year; nevertheless, the effect cannot be neglected;

- a reduction in curing temperature of 5 °C with respect to the reference ordinary value of 20 °C induces a delay in the Young's modulus evolution of pozzolanic cement paste, with a 25% reduction in E at 120 h since casting.

In summary, the present study confirms that the EMM-ARM method can be used to assess the possible effect of cement prehydration based on a phenomenological approach. Considering that prehydration due to uncontrolled storage significantly affects the early-age evolution of the Young's modulus of the cement paste, the present study demonstrates the applicability of EMM-ARM for the phenomenological characterization of the effect of uncontrolled storage and, therefore, prehydration on the mechanical properties of cement paste, with particular attention to pozzolanic as well as Portland cement. In this framework, a further applicative perspective of the EMM-ARM technique might be its application as an additional experimental test in the context of the CE marking qualification procedure of cement-based materials [38], with specific reference to the verification of constancy of performance. Thus, it might be attractive for acceptance checks of cementitious materials before use or commercialization.

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