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Rheological behaviour of fresh cement pastes: Influence of synthetic zeolites, limestone and silica fume

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ABSTRACT

New generation concretes have specific properties, often obtained by using additives, and these properties are strongly affected by rheological characteristics of the fresh cement paste. In this work small amplitude oscillations were adopted to investigate the effects of synthetic zeolite, limestone and silica fume on the rheological properties of fresh pastes. Time sweep tests were used to describe paste evolution with time evidencing that zeolite is more able to increase the rate of structure development with respect to other additives. Frequency sweep tests evidenced that zeolite, at least at low concentration, is able to improve the mechanical strength and to increase the liquid-like behaviour of the paste. Adopted rheological tests and data analysis are suitable to describe paste structure and evolution with time and synthetic zeolite seems able to give better properties to cement paste than other additives can.

1. Introduction

New generation concrete, such as self-compacting concrete (SSC), high-performance concrete (HPC), or ultra-high-performance concrete (UHPC), is characterised by specific properties often based on the equilibrium between a low water to powder ratio and a required high workability. These characteristics are strictly related to the rheological properties of the cement paste adopted in concrete preparation, i.e. the continuous phase where larger aggregates are dispersed, and they are usually obtained by means of proper additives such as superplasticizers, viscosity modifying admixture and fine materials. Interaction among the various materials adopted in cement paste preparation can cause wide variations in workability, which are also controlled by the specific materials and proportions used [1]. Moreover, poor dispersion and inhomogeneity during mixing and placing can cause the cement particles to coagulate and cluster in the mix water, resulting in alternating regions of low and high porosity hardened paste and yielding a nonhomogeneous microstructure. Thus, the performance of concrete is a direct result of microstructure development of the cement paste during its mixing, setting and hardening process and it is relevant to know properties of the base cement paste to characterise mechanical properties of the final concrete.

Currently, the mechanical properties of both fresh cement paste and concrete are mainly assessed by using empirical tests such as the mini-cone slump and the EN445 cone tests for pastes, mortars and grouts or the slump-flow and the V-funnel tests for HPC and SCC [1,2]. Even though these procedures can be useful for a qualitative, on field, assessment of material performance, it is worth noting that they are only able to give an "index" more or less related to yield stress as a final result. Moreover, the difficulties in describing the complex kinematic conditions, adopted during these tests, make it almost impossible to analyse the local strain and stress tensor values; as a consequence only "indices" dependent on the adopted procedures can be obtained and their analysis is mainly based on previous "experience."

Therefore, these empirical devices do not seem suitable to describe the specific characteristics of more innovative materials [1]; this is a well-known issue also arisen investigating different complex materials, like bitumens, where the empirical procedures have proved unsuitable to describe the microstructure of novel modified systems [3].

As a consequence there is a need for a more fundamental and quantitative description of both concrete and paste behaviour; rheology, being able to relate macroscopic properties and material microstructure, can be extremely useful for this purpose. In fact, in recent years measuring rheological properties of fresh cementitious composites has become more and more important, as evidenced by the large number of scientific works on this topic [4,5], and has proved able to solve problems in production and placement uses and to help in developing novel optimal formulations and in designing formworks in a more rational way [2].

It is worth noting that, quite often, only flow properties are measured, evidencing a non-linear relationship between viscosity and shear rate which is described by a large number of different models [4,5]. Even though such studies are able to give important information

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on the flow ability of cement, they do not allow information to be obtained about fundamental phenomena, such as the evolution of structure of cement paste and the relationship between mechanical properties and material microstructure, because the obtained information (for example the viscosity) is determined by the adopted kinematic conditions (for example the shear rate value). When material properties are required, it is necessary to adopt techniques able to measure parameters independent of the specific kinematic conditions. This can be obtained by performing the so-called “asymptotic kinematics” [6], i.e. tests where the adopted conditions allow measurement of the “asymptotic” values of the material parameters that are determined only by the material characteristics and are not affected by the amplitude of the applied load. Among the different potential approaches [6] small amplitude oscillations are probably the most common tests: in this case sinusoidal deformations are applied to the sample by using small amplitudes that are able to guarantee the linear behaviour of the material [7]. As a result of the test, two dynamic moduli are measured: storage modulus, G', related to the elastic behaviour and loss modulus, G'', related to the viscous behaviour. According to the theory of linear viscoelasticity, dynamic moduli are related to the material function (i.e. the relaxation spectrum) present in the constitutive equation of linear viscoelasticity which, in turn, is determined by the material structure [8]. In fact, the linear response of materials is often widely investigated because it can give information on their molecular structure [7].

Starting from these considerations, the use of small amplitude oscillations, when investigating the behaviour of cement paste, can give information about the paste structure (and its changes) from mixing up to setting. Rheological tests in the linear viscoelastic region can be used to compare the type and dosage of mineral admixture that improve concrete properties [9] or to investigate the effect of the water/cement ratio [10]. In addition, the evolution in moduli with time can be used, in a profitable way, to investigate the continuously changing cement paste structure during hydration. For example Banfill et al. [11] used oscillatory rheological measurements conducted with a spade-shaped probe, coupled with calorimetric tests, to carry out a preliminary study of the structure evolution of a Portland cement with time; Vlachou and Piau [12] investigated the microstructural evolution of an oil well cement slurry by using SEM, X-ray diffraction and oscillatory tests (with a specially designed tool) in linear viscoelastic conditions; Nachbaur et al. [13] proposed a special mixer-type tool to carry out dynamic tests during the very first minutes following the end of mixing, which are unobtainable with classical tools. More recently, oscillatory tests were performed to study paste hydration by using mainly commercial rotational rheometers equipped either with classical parallel plate geometry [14,15] or with specific tools [16].

Starting from these considerations, in the present work the effects of selected mineral addition on the rheological properties of cement pastes were studied by using small amplitude oscillation tests. Fines or mineral admixtures, such as limestone, dolomite, fly ash, silica fume, glass or quartzite filler, are widely used in high performance concrete (HPC) and/or self-consolidating concrete (SCC) to obtain specific properties; moreover, in recent years, both natural and synthetic zeolites have shown interesting properties when used as a mineral addition [14,17]. Even though the effects of these admixtures on mechanical properties of hardened systems were investigated (see for example the work by Sabet et al. [17]) few data are available on their influence on material microstructure and its evolution during setting. Therefore, new data and new data analysis procedures can be useful to improve the current knowledge concerning mineral admixtures effects, mainly synthetic zeolite, on the microstructure and mechanical properties of cement pastes.

In this work the structure development of pastes during early hydration was investigated by analysing the time evolution of dynamic moduli measured in linear viscoelastic conditions and a rate of structure development, under isothermal condition, was obtained according to a procedure already adopted to investigate the gelation rate of food gelling systems (like pectin) where the structure of material changes with time as the effect of gelling agents.

Moreover, the material behaviour was evaluated at a constant time from paste preparation and the obtained parameters were related to the amount and type of mineral admixtures, with the aim of evaluating their effects and the most interesting formulations.

2. Materials and methods

2.1. Materials

All samples were prepared by using a TERMOCEM (Italcementi, Italy) slag cement CEM III/A 32.5 N (UNI EN197-1), whose composition is reported in Table 1.

In this work both mineral admixtures and fines were used; limestone was used as fine particle, whereas the mineral admixtures were silica fume (Mapeplast SF, Mapei, Italy), with particle size ranging between 0.01 μm and 1 μm (according to data supplied by the manufacturer) and synthetic Zeolite 5A. The Zeolite 5A was produced by ionic exchange of a Zeolite 4A: 250 g of 4A has been contacted with 1 l of a 1 M aqueous solution of calcium nitrate at room temperature [18]. The Zeolite 4A was prepared starting from a system having the composition: 3.2 Na_2O, 1 Al_2O_3, 1.90 SiO_2, and 95 H_2O; the sodium aluminate was added to a solution of sodium hydroxide and after the homogenisation the silica source was added. The solution was stirred for 15 min at room temperature and then submitted to hydrothermal treatment, in static conditions, for 7 days [18]. The obtained Zeolite 5A has a ratio of ionic content ($Ca^{+2}/(Ca^{+2}+Na^{+})$) of approximately 0.9 [18]. Composition of admixtures and fines is reported in Table 1.

Particle size distribution of cement, zeolite and limestone was determined by using a MasterSizer 2000 (Malvern Instruments, UK), and the experimental data were analysed using the Malvern software. Obtained results are shown in Fig. 1.

The neat cement paste was prepared by using a water to cement ratio of 0.45, a value adopted also in other rheological investigations in the literature [10,15,19–21]. The base formulation (named A1, see Table 2) was then modified by preliminarily mixing the cement with the selected additive, using the desired additive to cement ratio (Table 2). The cement–additive mixture, obtained in this way, was then adopted for the modified cement preparation keeping the water/solids ratio always constant and equal to 0.45.

2.2. Cement paste preparation

Cement paste was prepared by mixing, in a beaker, distilled water and cement (or the cement–additive mixture) using an RGL 100 overhead stirrer (Heidolph, Germany) with a speed range from 60 rpm to 1250 rpm and a maximum torque of 120 N·cm; the stirrer speed can be controlled through a detached control panel working over 10 positions (1 corresponding to 60 rpm and 10 corresponding to 1250 rpm). A BR 14 collapsible blade impeller (two blades, blade size 90 × 10 mm)

Table 1
Composition of adopted raw materials.

Composition (% w/w)	Cement	Silica fume	Limestone
SiO_2	28.33	97.56	4
CaO	50.10	1.04	52.4
Al_2O_3	7.37	0.28	0.33
Fe_2O_3	2.01	0.12	0.14
MgO	4.22	0.29	1.05
Na_2O	0.49	0.23	0.06
SO_3	2.89	–	–
Cl	0.034	–	–
K_2O	–	0.48	0.02
CO_2	1.16	–	–
Ignition loss	3.4	–	42