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A method developed to quantify lime and gypsum consumed by mineral additions

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ABSTRACT

This paper presents an original method developed to quantify the reactivity of mineral additions based on the measurement of the lime (CaO) and gypsum ($CaSO_4$, $2H_2O$) consumed by mineral additions in a paste. Three mineral additions were tested: a Siliceous Filler (SF), a natural pozzolan (Poz) and a Wastepaper Sludge Ash (WSA). The results obtained on SF, considered as a reference, show the efficiency of this method. Its application to Poz and WSA permits the quantity of lime and gypsum consumed by these additions to be evaluated and, thus, the amount of each component to be optimized in Hydraulic Road Binders.

1. Introduction

Mineral additions have long been used in cement-based materials and their use is standardized today for cement [1] and concrete [2]. These additions are either natural or artificial and the majority of them are by-products of industry (e.g. Ground Granulated Blast Furnace Slag (GGBFS), silica fume or coal fly ash). These mineral additions are used to replace a part of the clinker in cements for several reasons. The first one is economics, as such materials are generally much less expensive than clinker. Then, research on these additions has shown that they can improve some characteristics of cement-based materials. For example, it is clearly established today that pozzolanic additions improve the durability of concrete and that silica fume strongly reduces the porosity of high performance concrete and thus strongly increases both strength and durability [3,4]. Lastly, in recent years, the ecological impact of binders has become increasingly important. The production of clinker consumes a lot of energy and generates significant emissions of CO_2 in comparison with that of mineral additions. Also, the replacement of clinker by mineral additions makes it possible to reduce the carbon emissions of cements and their energy consumption [5]. Thus, even more than before, the advantages of using mineral additions in cement-based materials are seen as significant. Much research has been initiated to test new materials (natural materials or industrial by-products) for their potential use as mineral additions in cement-based materials. This could be interesting if the amounts produced are sufficiently high, if these materials do not lead to pollution and, finally, if they do not deteriorate, or better if they improve, the properties of cement-based materials.

In terms of reactivity, European standard EN 206-1 distinguishes two types of inorganic addition [2]: nearly inert additions (type I) and pozzolanic or latent hydraulic additions (type II). It is very useful to evaluate the reactivity of the mineral additions in binders, in particular to optimize the proportion of each component introduced into these binders. A method used frequently to quantify the reactivity of the mineral additions in cement-based materials is to measure the activity index and the *k*-values ("strength activity index" in ASTM C311 [6]). The activity index "*i*" is the ratio of the strength of a mortar containing 25% of addition and 75% of cement to the strength of a reference mortar (100% of cement). The *k*-values, used in particular in the concept of equivalent binder, are calculated by the relation $k = 3i - 2$. However, this method can be applied only for binders rich in cement. Nowadays, the trend is to develop new binders containing as little cement as possible, especially for Hydraulic Road Binders (HRBs) that have characteristics different from those of conventional cements [7]. The compositions of these binders are based on the use of reactive mineral additions (hydraulic, latent hydraulic or pozzolanic) activated by lime, gypsum or other activators, the proportions of which must be determined.

This paper presents an original method developed to quantify the reactivity of mineral additions used as major components in

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HRB. Two types of activators were studied: lime (CaO), which is necessary for the occurrence of the pozzolanic reaction, and gypsum ($CaSO_4$, $2H_2O$), which is known to be an excellent activator for numerous materials such as Ground Granulated Blast Furnace Slag (GGBFS) or coal fly ash [4], Basic Oxygen Furnace slag [8] and Wastepaper Sludge Ash [9].

The method presented in this paper was applied to pastes containing the tested mineral addition, gypsum and lime. The method consists of measuring the amounts of gypsum and lime consumed by the mineral addition in the paste at different ages. Three mineral additions were tested using this method: a Siliceous Filler (SF), a natural pozzolan (Poz) and a Wastepaper Sludge Ash (WSA). Firstly, the main characteristics (physical, chemical and mineralogical) of the mineral additions used in the study will be presented. The second part of the paper will be devoted to the description of the method developed and the presentation of the results. Finally, the results obtained will be applied to the optimization of HRB compositions.

2. State of the art

Numerous methods already exist for evaluating the pozzolanic activity of mineral additions. These methods will be quickly described in this section in order to highlight the originality of the method presented in this paper. Most of the methods found in the literature are based on the measurement of the consumption of lime by pozzolanic materials. Firstly, the ''Chapelle'' test measures the fixation of the lime in a solution saturated with lime and containing the tested addition at 90 °C. This test has been criticized by Ambroise et al. because the high temperature strongly modifies the kinetics of the reaction and the nature of the hydrates formed [10]. The standard procedure EN 196-5 ''Methods of testing cement – Part 5: Pozzolanicity test for pozzolanic cement'' is based on the same principle [11]. The pozzolanicity of pozzolanic cements is assessed by comparing the concentration of calcium ions present in the aqueous solution in contact with the hydrated cement with the quantity of calcium ions necessary for saturating a solution of the same alkalinity. The cement is considered to satisfy the test if the concentration of calcium ions in the solution is lower than the saturation concentration. In 2007, Garcia et al. developed an accelerated test to evaluate the pozzolanic activity of paper sludge waste [12]. This test is an alternative to the Chapelle test with longer durations (1, 7, 28 or 90 days) and a more moderate temperature (40 °C).

It is also possible to evaluate the pozzolanic activity of materials by measuring the compressive strength of mixtures containing the tested addition and lime. That is the case, for example, in the ASTM C311, ''Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete'' [6]. In this test, the 7-day and 28-day compressive strengths of mortar cubes with a 20% mass replacement of cement by pozzolan are compared to those of a control without pozzolan, at constant flow conditions. Bentz et al. have proposed an alternative method, in which the 20% pozzolan replacement for cement is performed on a volumetric basis and the volume fractions of water and sand are held constant [13]. Another example concerns the test specific to the pozzolans used in road foundations [14]. The reactivity of such pozzolans is evaluated from the compressive strength of a mixture containing pozzolan, lime (12%) and water (Proctor optimum) measured on cylinders 5 cm in diameter and 10 cm high, at 60 and 360 days. In another study, Argawal measured the pozzolanic activity of various siliceous materials [15]. The author worked on cement mortars by replacing a part (10%) of the cement by the addition to be tested. The originality of the method used by Argawal concerned the conservation of the samples in water at 65 °C to accelerate the occurrence of the pozzolanic reaction.

Finally, other mineralogical tools are often used to study the pozzolanic activity of materials, such as thermogravimetric analysis (TGA), which evaluates portlandite and calcite contents. But, the quantities of material tested with a conventional apparatus are often very low and thus the results are not representative of heterogeneous cement-based materials (some modern apparatus can test higher quantities of materials (between 2 and 3 g), thus reducing the severity of this problem).

This short review shows that methods to evaluate the reactivity of mineral additions exist but essentially concern pozzolanic activity. Many of these methods are carried out on solutions and often with excessive temperature to accelerate the reactions. This is very far from the real utilization of mineral additions in binders for concrete or road applications. In contrast, tests based on the evolution of compressive strength of mortar or compressed materials give results on the global efficiency of a mineral addition, but do not give information on its potential chemical reactivity. The method presented in this paper aims to provide such information and has the interest of being carried out on pastes and not on solutions.

3. Experiments

3.1. Materials

Siliceous filler was used as the reference in this study because it can be considered as chemically inert. The filler used was a commercial product with a fineness equal to 2000 cm^2/g and a SiO_2 content higher than 98.6%.

The pozzolan under study came from a French quarry where pozzolan is extracted, crushed, sifted and stocked as a 0/2 sand. The sample studied in this work was finely crushed in the laboratory.

The Wastepaper Sludge Ash (WSA) under study came from a paper mill equipped with an incinerator fed by biomass. This equipment uses the steam produced by the incineration of biomass to generate green electricity. After its passage in the turbine, the steam is reused in the paper making process, especially for the shrinkage of the paper. One half of the biomass incinerated is composed of waste coming from the paper mill (de-inking and waste water-treatment sludges in particular) and the other half comes from wood waste. The technology used in the boiler is a fluidized bed. As recommended by Directive 2000/76/EC, the sludge remains in the combustion zone for a few seconds (more than two) at 850 °C [16].

The gypsum and lime (CaO) were both pure commercial products of analytical quality.

3.2. Characterization procedures

3.2.1. Physical characterization

Specific surface area was measured by the Blaine test. This test was carried out according to European standard EN 196-6 [17]. The size distribution of the materials was analyzed by means of a laser particle size analyzer using a dry suspension with an air pressure of 0.5 bars. The density was determined by hydrostatic weighing of a powder sample in a non-reactive liquid (exxsol).

3.2.2. Chemical characterization

Major oxides composition was estimated on the basis of the macroelemental analysis carried out on digested samples by Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES). The loss on ignition (calcination at 1000 °C) was also measured according to European standard EN 196-2 [18]. The sulphate (SO_3) content was measured by ionic chromatography after acidic dissolution.