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Microstructure and hardened state properties on pozzolan-containing concrete

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HIGHLIGHTS

- SEM microstructure analysis as a tool to evaluate pozzolan's effects in concrete.
- Effect of two chemically and physically different pozzolans in concrete behaviour.
- Comparison of concrete rheology controlled by water or a water reducing admixture.
- Impact of type of workability control over microstructure and hardened state features.

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ABSTRACT

The homogeneous state of the concrete in the fresh state has consequences on their properties in the hardened state. The use of pozzolanic concrete must be carefully evaluated, because the physical and chemical differences of each pozzolan have consequences on concrete hardened state properties. In this work, two physical and chemically different pozzolans were used to evaluate the effect on concrete microstructure and its basic hardened state properties. Scanning electron microscopy (SEM) was used and can be an effective tool in the analysis of the microstructure allowing a better understanding of the properties of concrete in hardened state. It allows showing that the differences in the two pozzolans (metakaolin and diatomite) promote different microstructures as well as different final properties of pozzolanic concrete. Moreover, it was also shown that the use of a water reducing agent, to adjust workability instead of water, promotes an improvement in both the microstructure and the hardened state features such as porosity and mechanical strength.

1. Introduction

It is widely accepted the use of pozzolanic materials such as fly ash and microsilica as partial replacement of Portland cement to produce mortars and concretes [1]. Pozzolans are natural or artificial fine materials which can partially replace cement in mortars and concretes. The main component of the pozzolan is amorphous silica which, in the presence of water, reacts with calcium hydroxide ($Ca(OH)_2$), forming compounds with cementitious properties. Some pozzolanic materials have also amorphous alumina in their composition, which can be very reactive, producing aluminosilicates such as in cements. The effectiveness of a pozzolan depends on its pozzolanic reactivity and this concept may include two factors, namely, the maximum amount of calcium hydroxide that can react with the pozzolan and the speed at which the pozzolanic reaction occurs [2]. However, beyond the pozzolanic reactivity, these materials, being very fine, can also have a "filler" effect, promoting a decrease in the total porosity of the system due to the filling of voids and capillary pores. The packing mechanism is greatly enhanced by the addition of very fine particles leading to densification. It was also demonstrated, using a simulation system, that the finer particles tend to concentrate near the transition zone of the cementitious matrix interface and the aggregates (IZT), leading to a reduction in the porosity and increasing the internal cohesion, since there is an increased action of van der Waals forces between the particles due to the increased proximity between them [3].

Besides silica fume and fly ash, metakaolin (MK) has been also studied as a pozzolanic material. The metakaolin is usually obtained from the calcination of kaolinite-rich clays at tempera-

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tures ranging between 600 and 800 °C, depending on the characteristics of the raw material. However, some authors [4] consider that the optimum calcination temperature should be always determined in order to obtain maximum strength. Moses and Cabrera [5] have studied the distribution of the pore diameter and the degree of hydration of cement pastes with metakaolin content (10, 15, 20 and 25%) for a water/cement ratio of 0,55 and observed a decrease in porosity for 28 days. For longer ages, the total porosity increases when compared with formulations without the pozzolan. Observing the works that have been done on the use of metakaolin in cement-based materials, it appears that the use of this pozzolanic material improves the behaviour of mortars and concretes. This beneficial effect is mainly due to the high pozzolanic reactivity of metakaolin that, on one side, reacts rapidly and extensively with calcium hydroxide resulting from the hydration process of cement and, on the other hand, accelerates the hydration reaction of cement. The calcium silicate hydrate formed is in the form of a gel that penetrates the pores, promoting the decrease of the average pore size and increasing the number of smaller pores. This effect is also observed in the interfacial transition zone (ITZ) between the binder and the aggregate, promoting densification. The refinement of the pores and densification of the interfacial transition zone can justify the improvement in mechanical strength, the decreased water absorption by capillarity, improved resistance to chemical attack and the increased durability [6].

Diatomite (D) is a natural material from a sedimentary rock, formed mainly by the deposition of microscopic organisms with a crystalline and amorphous silica shell [7]. Diatomite was used as a pozzolan, directly after milling or after a heat treatment at about 1000 °C followed by grinding. Subjecting this material to thermal treatment shows an increase in the content of amorphous silica and grinding reduces it particle size. The hydraulic and pozzolanic activity of silica mineral additions depends on its crystalline or amorphous state as well as on its size and particle shape [8]. The study of diatomite as partial replacement of cement is still recent but some authors have shown that its use in the production of mortar and concrete does not improve its mechanical properties, due to its nature and low pozzolanic reactivity [7,9]. A disadvantage of the use of diatomite in the production of mortar and concrete is the need for a very high amount of water which promotes a simultaneous reduction in the mechanical strength [10,11].

However, Ergun [12] has also studied the effect of diatomite on the mechanical properties of the concrete where cement was replaced by diatomite (5% to 10%), maintaining the water constant and using a constant amount of a water reducing agent. The compressive strength of the concrete increased with diatomite. Ergun [12] considered that this behaviour was due to the combination of this pozzolan (containing highly reactive amorphous silica) with a water reducing admixture which allows the use of lower amounts of mixing water.

Scanning electron microscopy (SEM) is recognized as a good tool to evaluate the microstructure of materials, including mortars and concretes. Some authors [13–15] have studied the interfacial transition zone (IZT) between the cement matrix and aggregates by SEM, for instance, Rossignolo [14] has used SEM to determine the thickness of the IZT. Diamond [15] studied the effect of a water reducing agent in the concrete microstructure and found that concretes containing this admixture are more homogeneous and without agglomerates that usually promote density variations in the material. Oertel et al. [16] have also analysed particle and agglomerates size of silica fume with SEM and its results indicate that, if particles agglomeration is prevented, a higher mechanical strength will result in the concrete.

The aim of this work was to use the microstructure analysis by SEM to better understand the hardened state characteristics of concrete containing two physically and chemically different pozzolans, specifically, a metakaolin and a diatomite.

2. Materials and methods

In this study, the formulation for the reference concrete mixture was obtained using the Faury method [17]. The standard or reference concrete (named B_0,6W) constitution involves Portland cement (CEM type I 42.5R) as a binder, a siliceous natural sand and two types of crushed limestone as coarser aggregates [18].

Metakaolin (MK) was used as a partial cement substitute material in contents of 10, 20 and 30% (wt%). This material is a dehydroxylated aluminium silicate, with a general formula of $Al_2O_3.2SiO_2$. It is an amorphous non-crystallized material constituted of lamellar particles. This MK presents a pozzolanic index (measured by the modified Chapelle test according to NF P18-513:2010) of 1100 mg $Ca(OH)_2$/g of metakaolin and a specific surface area (BET) of 17 m^2/g [19,20].

Diatomite (D) was used as a partial cement substitute in contents of 3, 5, 8 and 10% (wt%). This diatomite, previously calcined and grinded, presents a specific surface area (BET) of 9 m^2/g. The Chapelle test was not conducted in diatomite since its residence time in contact with the calcium hydroxide ($Ca(OH)_2$) is not enough to obtain reliable results. Alternatively, a comparative study adapted for these two pozzolans to evaluate their reactivity was performed. This test compares the compressive strength of lime based mortars with metakaolin or with diatomite, based on the pozzolan reaction with hydrated lime. The choice of lime as a binder was made to ensure the availability of calcium hydroxide to react with pozzolans. This method consisted of producing a reference lime based mortar whose composition is 80% of sand used in the study and 20% of hydrated lime (with 90% $Ca(OH)_2$). In the pozzolan-containing mortars, lime was replaced with 50% of diatomite or metakaolin.

Table 1 presents the results obtained for the pozzolanic characterization of the employed pozzolans (metakaolin and diatomite). The compressive strength (Rc) of the base lime mortar and the lime mortars with metakaolin or diatomite at different curing times (at 20 ± 5 °C and 60 ± 5% RH) confirms that the metakaolin have higher pozzolanic reactivity.

Yilmaz and Ediz [10] showed with SEM that diatomite is very porous and does not show a very high surface area even after calcination and grinding. It was considered important to determine the diatomite water absorption. An expedite method (an adaptation of the EN 1097-6 standard) was developed where a diatomite sample is diluted in water and then passes through a filter that retains particles larger than 8 μm. When all the free water has passed through the filter, the material filled of water is scraped with a spatula and weighed (Fig. 1). The difference between the weight of wet material and dry material, relative to the dry material weight, is the percentage of water absorption of diatomite The experiment was repeated 10 times for two different amounts of sample (1 and 5 g). The average value of water absorption presented by the diatomite was higher than 96%.

Table 1
Values of compressive strength (Rc) for the pozzolanic evaluation of metakaolin and diatomite.

Composition	Rc (MPa) 3 days	Rc (MPa) 7 days	Rc (MPa) 28 days
Base mortar	0,29	0,29	0,47
Mortar with MK	1,01	2,99	3,73
Mortar with D	0,41	0,62	1,08