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Permeability and mechanical properties of cement mortars colored by nano-mineral additives

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Abstract: This work concerns a preliminary study on issues that relate primarily to the permeability of cementitious materials under the influence of some specific inexpensive additions that can play an important role in preserving the environment. We studied the addition of dyes in the presence of TiO_2 on the Portland cement mortar. The used dyes are a yellow powder containing iron oxyhydroxide (FeO (OH)), a blue-based powder tellurate manganese ($MnTe_2O_5$) and red powder containing iron oxide (Fe_2O_3). We measure the setting time, permeability and mechanical properties of Portland cement mortars colored with nano-mineral oxides mentioned previously. Test results indicate that the addition of nano-particles has a little influence on the setting time, improves penetration resistance that is due the affinity of the pore structure of mortar and slightly improves the resistance to compression for low levels of nanoparticles of TiO_2.

Keywords: Portland cement mortars, nano-particles, permeability, penetration, pore structure.

1 Introduction

The additions were introduced in the composition of cementitious materials several decades ago. Incorporated in low quantities, they change their characteristics to fresh and / or hardened state. The desired effects mainly affect the workability and the setting kinetics and / or hardening.

The challenge today is to succeed in raising the overall level of specific qualities of used construction materials. The new cementitious materials must offer all together: exceptional mechanical strength, excellent surface appearance, ease of implementation with the potential recovery of by-products of different origins. The characterization of these properties is defined through a range of tests, studies, convenience and control, carried out on fresh and hardened materials.

In this study, the influence of three mineral pigments, yellow-containing iron hydroxide (FeO (OH)), blue-based manganese tellurate ($MnTe_2O_5$) and red oxide containing iron (Fe_2O_3) is performed on Portland cement mortars with titanium oxide TiO_2. This oxide is the most widely used white pigment as a colorant; it is not toxic and has replaced the lead-based colorants. It is manufactured from titanium ore, chemically inert and insoluble in almost all liquids except strong acids.

Several researchers have introduced TiO_2 in cementitious materials as a photocatalyst for the degradation of pollutants from the atmosphere as (NO_x, SO_x and NH_3) [1,3]. The titanium oxide located on the surfaces of concrete can trap volatile molecules by the photoelectric effect of sunlight. The generation of electron-hole pairs by absorption of photons of energy allows charge carriers to react with the chemical species on the surface of the material, giving rise to the electron and hole reduction to oxidation. The mechanisms of recombination of photogenerated electron-hole pairs are reconstructed by the cycles of sunlight. Various authors [1,2] reported that concentrations of 4.5 to 5% by weight of TiO_2 could be incorporated into the clinker as a normal rate. Quantities of TiO_2, not incorporated, may lead to the formation of phases $CaOTiO_2$, $2CaOTiO_2$ and $3CaOTiO_2$ [4,5]. The presence of small amounts (<5%) TiO_2 increases, apparently, the hydraulic activity of cement [5]. The increase of activity can be attributed to deformation of the crystal lattices of alite and belite resulting from the substitution of the Si^{4+} ions by Ti^{4+} and the formation of solid solutions [5,6].

The permeability of concrete, which can be defined as its ability to be penetrated by external media fluid such as liquids, gases, various aggressive ions and other pollutants[7,8], is considered one of the most important properties which affect the durability of concrete [9]. Low permeability decreases the penetration and movement of fluids in concrete and is therefore beneficial. A concrete with a greater permeability allows more rapid penetration of fluids, which causes rapid deterioration of the concrete. The permeability of concrete is strongly affected by the pore structure of concrete. It is principally related to the distribution and size of pores and closely related to the connectivity of pores, while the compressive strength of concrete is also governed by the porosity. [10-12].

The permeability of concrete is based mainly on the pore structure and its changes and developments. There are three types of factors that affect the permeability of concrete [13]. The first are factors that influence the pore structure of the original concrete such as water / cement ratio, mineral admixtures (such as silica fume, fly ash and blast furnace slag) and the additive agents. The second is the factors that influence the development of the pore structure of concrete, including the state of hardening, age and activity of binder. The third is the penetration such that the hydraulic gradient, time of penetration and the chemical composition of media penetration.

Zhang and Li [14] have reported that the addition of nano-particles refines the pore structure of concrete and improves resistance to chloride penetration on concrete. The affinity of the pore structure and resistance to chloride penetration of concrete is increased with decreasing content of nano-particles. The pore structure and chloride penetration of concrete containing nano-TiO_2 are higher than that of concrete containing the same amount of nano-SiO_2.

The objective of this study is to evaluate experimentally the influence of mineral powders colored yellow, blue and red with TiO_2 on the properties of Portland cement mortars. The aim is to compare the setting time, permeability characteristics and mechanical strength of mortar binders. Different percentages of TiO_2 are used with three colors, in prepared mixtures.

2 Experimental

The mortars were prepared as cylindrical specimens (8cm * 4cm) using molds BVC. The mortars are made of clinker by adding 5% of each color (red, blue and yellow) using two different amounts of TiO2 (1 and 3%) with standard sand. Hydration is done with a water cement ratio W / C = 0.5. Standards AFNOR (French Standards Association) have been respected to mix the mortars and mold filling. After demolding, the samples were stored in water for 14 days, and then dried in an oven at 105 ° C for two days.
The principle of the apparent permeability is to maintain a constant difference pressure of gas, helium, between the two limits of the sample and measuring the resulting flow. The experimental principle is based on measuring the flow rate for a given pressure gradient. Subsequently, we defined the apparent permeability gas K_A calculated from the overall flow of gas through the sample measured by direct application of Darcy's law.
After measuring the apparent permeability, cylindrical specimens are subjected to increasing load until failure to define the quality of mechanical strength of mortars. The compressive strength f_c is the ratio between the breaking load and the cross section of the specimen.

3 Results and discussions

3.1 Characterization by X-ray diffraction

Analysis of raw materials is reported in Table 1. It shows the mineralogical composition of the used clinker which is composed of a normal phases: alite (3CaO, SiO_2), belite (2CaO, SiO_2), Celite (3CaO, Al_2O_3) and ferrite (4CaO, Al_2O_3, Fe_2O_3). The dyes are mainly composed of calcium carbonates of different varieties and low percentages of pigments. Titanium oxide is analyzed, shows that it consists of 100% Anatase TiO_2.

Table 1. Analysis by X-ray diffraction of materials used anhydrous

Material analyzed	Mineral phase identified	% Phase / subject
Clinker	Alite C_3S	46.4
	Bélite C_2S	35.8
	Celite C_3A	14.3
	Ferrite C_4AF	3.5
Blue dye	$CaCO_3$	98.5
	$MnTe_2O_5$	1.5
Yellow dye	$CaCO_3$	76
	$MnTe_2O_5$	24
Red dye	$CaCO_3$	97
	Fe_2O_3	3
Titanium oxide	Anatase	100

3.2 Determination of setting time

The objective of the trial is to determine the workability of the mixtures, by measuring the time of beginning and end of the setting time. The experimental device is Vicat apparatus that measures, under the effect of a load, time of penetration of a needle when she stops at a distance from the surface of the dough sample. The results are expressed in minutes in Table 2.

Table 2. Vicat test results for samples 1% TiO_2

Sample	Mixture without added	Blue mortar	Yellow mortar	Red mortar
start of setting	5h40mn	5h50mn	5h10mn	5h30mn
End of setting	8h30mn	8h50mn	8h20mn	8h40mn
Setting time	170 mn	180mn	190mn	190mn

These results indicate that mortars are known in the standards of workability that exceed five hours. The time taken for all samples is about three hours with an extension of 10 min for the blue sample and 20 minutes for yellow and red. These variations are very minimal and do not influence the properties of workability of mortars.

3.2 Measurement of the apparent permeability

Following curves “figure 1” present the evolution of apparent permeability of mortars as a function of mineral powders addition.

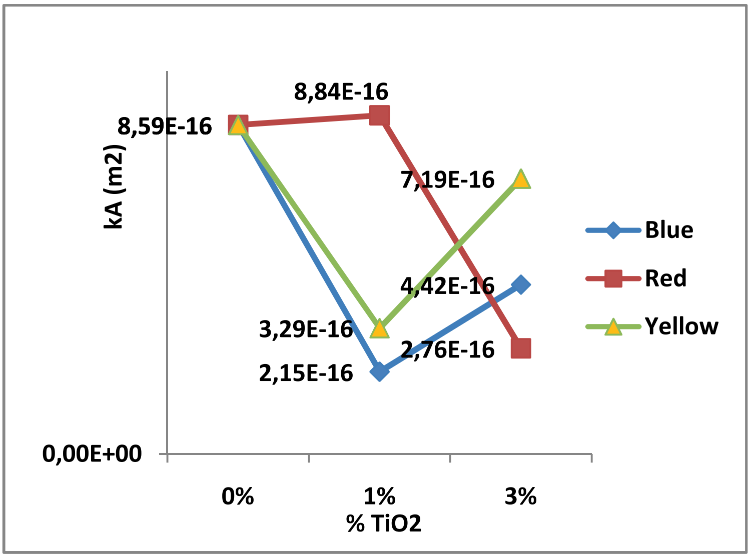

Fig. 1. The apparent permeability of different mortars

The addition of mineral powder containing the dye and TiO_2 reduces the apparent permeability of mortars, except for the red mortar with 1% TiO_2. The addition of 1% TiO_2 in mortars blue and yellow lowers their gas permeability and if we increase the amount of TiO_2, the permeability increases also, but less than regular mortar. Contrary, for the red mortar, the addition of 1% TiO_2 does not decrease the permeability; it drops only at the addition of 3% of TiO_2. Strengthening or reducing the penetration resistance is mainly due to improvement or degeneration of the pore structure. Over the pore structure is finer; the resistance to penetration is enhanced. By the addition of nano-particles, the pore structure is refined, so that the resistance to penetration is enhanced. The pore structure of the dough with a small amount of TiO_2 (1%) and more advanced significantly [14].

Zhang [14] explain the mechanism to refine the pore structure of the dough by nano-particles as follows. Assuming that the nano-particles are uniformly dispersed in the cement and each particle is contained in a cube model, the distance between the nano-particles can be determined. After hydration starts, hydrates spread and envelop the nanoparticles as kenel. If the content of nano-particles and the distance between them are appropriate, the crystallization will be controlled in a suitable condition limiting the growth of $Ca(OH)_2$ crystal by nano-particles. In addition, nano-particles in cement paste as kernel can also promote the hydration of cement due to their high activity. This makes the cement matrix more homogeneous and compact. Therefore, the pore structure is obviously refined such that the paste containing nano-TiO_2 in an amount of 1% by weight of binder.

With the increasing content of nano-particles, refining the pore structure of the paste is low. This can be attributed to the distance between the nano-particles decreases with increasing content of nano-particles, and crystal $Ca(OH)_2$ cannot grow enough because of limited space and the amount of crystal is decreased, causing the ratio of crystal / CSH gel to become smaller and shrinkage and creep of the cement matrix increases [15], so the pore structure of cement matrix is relatively coarse.

The addition of nano-particles refines the pore structure of the paste. On the one hand, nano-particles can act as a filler to increase the density of concrete, causing the porosity of the concrete to decrease significantly. On the other hand, nano-particles cannot only act as an activator to accelerate the hydration of cement due to their high activity, but also act as a nucleus in the cement paste which makes the size of the crystal $Ca(OH)_2$ and the exposure of small crystals $Ca(OH)_2$ more random.

3.2 Measurement of compressive strength

The following curves in Figure 2 illustrates the evolution of the addition of mineral powders on the compressive strength of mortars.

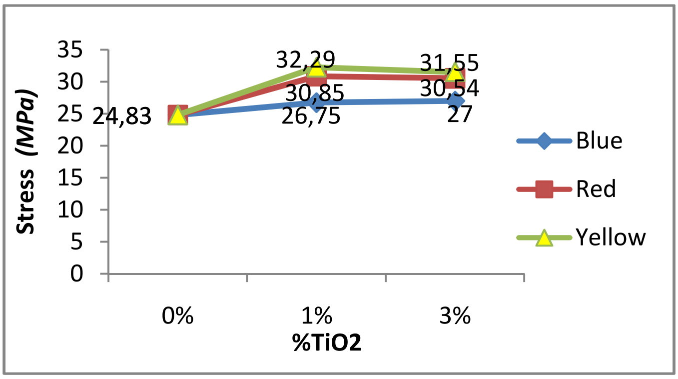

Fig. 2. Stress of different mortars

The addition of TiO_2 in colored mortars increases its compressive strength compared to ordinary mortar. With a small amount of TiO_2 (1%) the compressive strength increases slightly compared to an addition of 3% as it is shown in the literature [6].

The permeability of concrete is closely related to the connectivity of the pores, but the compressive strength of concrete is governed by the porosity [11, 12]. The compressive strength is an important factor affecting the resistance to penetration.

4 Conclusion

We can conclude that:

(1) The addition in mortars, blue dye, yellow or red at a fixed rate of 5% by mass and low percentage of TiO_2 (1% by mass) has little influence on the workability of fresh mortars or on their setting time.

(2) The addition of nano-particles improves the penetration resistance of a mortar. Resistance to penetration is beneficial when adding a small amount of nano-TiO_2. The strengthening or reducing of the resistance to penetration is mainly due to improvement or degeneration of the pore structure of concrete. By adding nano-particles, the pore structure of concrete is refined, so that the resistance to penetration is enhanced.

(3) The incorporation of dyes with small amounts of TiO_2, improves the mechanical strength of mortar. This is due to the increased kinetics of hydration of C_3S and C_2S mineral that are the main minerals ensuring the development of mechanical strength of the mortar, and substitution of silica by titanium which enhances the durability of the mortar.

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