1 **Expansive concretes with photocatalytic activity for pavements:**
2 **enhanced performance and modifications of the expansive hydrates**
3 **composition.**

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10 **Abstract**

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12 For the first time, the sustainability and functionality of expansive concretes have been
13 increased through the addition of a photocatalytic agent (PhAg). The inclusion of the
14 PhAg mainly modifies the properties of the fresh concrete and the resulting expansion
15 obtained in different curing conditions. PhAg particles act as nucleation sites that
16 increase and accelerate the formation of the expansion hydrates with the subsequent
17 enhancement in the expansion performance. In fact, some modifications in the chemical
18 composition of the expansive hydrates formed is detected due to the inclusion of the
19 PhAg. However, since expansive hydrates are expected to growth in the surface of the
20 PhAg, the photocatalytic activity decreases.

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23 **Keywords:** Expansive Concrete; Self-Compacting Concrete; Photocatalysis;
24 Mechanical Properties; Expansion, Microstructure.

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1. Introduction.

The use of concrete pavements has grown over the past few decades due to their higher durability and longer structural life than asphalt pavements. The service life of concrete pavements depends on many factors such as the material properties, applied loads, environmental conditions and maintenance practices. These factors or the combined actions of some of them can promote the formation of cracks. The cracks can reduce the load carrying capacity of the pavement and are also preferential ways for ingress of aggressive agents into the concrete, thus even promoting the reinforcement corrosion [1-3]. But initial crack formation in concrete pavements is also caused by concrete shrinkage and thermal gradients even before the application of external loads [4-9]. Since repairing the damage is usually difficult and expensive, exhaustive studies are being performed to control the formation of cracks in concrete pavements [10]. In this sense, inorganic expansive agents are being used to develop expansive concretes that effectively reduce shrinkage and the related crack formation. In fact, the application of expansive concretes to construction projects is increasing nowadays [11-18]. Two types of expansive agents are considered in this study: ettringite-based (type-K) or CaO-based (type-G). The curing conditions [15,19,20], the cement composition and the use of different supplementary cementitious materials (SCM) are going to influence the expansive performance obtained [21].

The application of expansive concretes in pavements allows a strong decrease of expansion or contraction joints, thus reducing the fabrication time consuming and the related maintenance costs. Additionally, the fabrication time can be reduced by using

self-compacting concretes (SCC) in order to make easier the delivery and casting on site. Previous papers have demonstrated the feasibility of producing expansive self-compacting concretes with good properties [20-25]. Within this regard, to increase the fines content of the SCC the use of fly ashes (FA) better than granulated blast furnace slag (GGBS) is recommended [26].

Thus, the use of expansive concrete increases the sustainability of the pavements. However, in order to improve this issue, new functionalities should be implemented in the concrete mix design. One of the research lines focuses on the incorporation of photocatalytic properties in concretes. Even though important works on construction photocatalytic materials have been carried out by different research groups concerning air decontamination [27-34], self-cleaning [35-37], self-sterilizing [38], anti-fogging properties and even pollen or deposited soot elimination [39,40], no references have been found in literature including photocatalytic materials in expansive concretes.

The positive effects of photocatalysis are achieved when different nanoparticles, mainly TiO_2 , are incorporated in the cementitious materials. The modifications promoted in the cementitious materials when TiO_2 nanoparticles are incorporated have been evaluated in recent years considering different aspects. Although some contradictory results have been published, mainly with respect to the resulting strength performance, some phenomena have been clearly evidenced. For example, the early degree of hydration is significantly enhanced by small dosages of nano- TiO_2 powder since they act as potential nucleation sites for the accumulation of hydration products and a refinement of the porosity structure occurs [34,41,42]. High contents of TiO_2 nanoparticles (>1%) can increase the total porosity and reduce the resulting compressive strength [43].

Regarding the photocatalytic activity, several authors highlighted the improvement promoted in this activity when increasing the roughness surface of the cementitious materials [44-46] but this influence is less significant for the self-cleaning activity [47]. Additionally, the photocatalytic activity depends on the chemical nature of the cement and SCM used [34].

The use of TiO_2 nanoparticles for pavements has been already postulated to refine the pore structure of cementitious materials giving better results than nano- SiO_2 particles [41]. However, as said, the combination of expansive agents and photocatalytic agent (PhAg) in a same concrete has not been investigated yet. Thus, this paper is focused on the design and evaluation of expansive concretes with additional photocatalytic properties to be used as concrete pavements. The combination of both concrete technologies is expected to join the benefits promoted by each one separately, that is, the reduction of the fabrication time consuming and the related maintenance costs caused thanks to the use of expansive concretes, plus the air decontamination, self-cleaning, self-sterilizing and anti-fogging properties caused by the photocatalytic activity. In fact, possible implementations of some of these properties could also occur. In this sense, the influence of the addition of a PhAg based on TiO_2 nanoparticles in the properties of expansive concretes is evaluated as well as the influence of the use of two types of expansive agents in the photocatalytic efficacy. In any case, the sustainability of the concrete pavements market is expected to increase strongly with the combination of both concrete technologies.

2. Experimental.

2.1 Materials and concrete mix proportions.

Five different concrete mixes were evaluated. Four of them were expansive concretes and three of them had photocatalytic properties. The cement used was CEM I 42.5R according to EN 197-1 [48]. Three siliceous aggregate fractions were used: 12/20 mm, 4/12 mm and 0/4 mm. Class F low CaO fly ashes was also used to increase the fine content. A type-K agent and a type-G agent were selected as expansive agents (ExAg). The first one is based on calcium sulfoaluminate and the second one is based on calcium oxide. The concretes based on type-K agent contained 15% in weight cement of ExAg and the concretes based on type-G contained 5%. The different ExAg content used are due to without water curing higher contents of type-K agent generated similar expansions than lower contents of type-G [20,21]. Moreover, similar concretes with 15% of type G agent and cured under water suffered from significant cracking due to the high expansion obtained. For this reason, the percentage of type-G agent used has been lower than the one of type-K agent. It is well known that modifications in the cement content, w/c ratio and chemical additives contents promote modifications in the expansion performance [12-26]. Thus, the w/c ratio and the cement content were maintained constant in all the cases. The content of the polycarboxylate based superplasticizer was also maintained constant. The nominal compositions of the five evaluated concrete mixes are shown in Table 1.

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Table 1. Composition of the concrete mixes developed (kg/m³).

	<i>EK</i>	<i>EG</i>	<i>PEK</i>	<i>PEG</i>	<i>P</i>
<i>Water</i>	195	195	195	195	195
<i>CEM I 42.5R</i>	385	385	385	385	385
<i>FA</i>	116	116	116	116	116
<i>Medium aggregate (4/12)</i>	654	669	645	659	666
<i>Sand (0/4)</i>	924	945	910	930	940
<i>Superplasticizer</i>	5	5	5	5	5
<i>Agent type-K</i>	58	-	58	-	-
<i>Agent type-G</i>	-	19	-	19	-
<i>Photocatalytic agent</i>	-	-	13.5	13.5	13.5

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128 EK and EG were SCC but the inclusion of the “photocatalytic agent” eliminated the
 129 self-compacting properties in the other three concretes (PEK, PEG and P) as shown in
 130 section 3.1. Photocatalytic concretes incorporated a 3.5% of TiO₂ (Aeroxide® P25) on
 131 weight of cement. This TiO₂ content was increased with respect to the percentage
 132 usually used in previous studies in order to guarantee that the effect was noticeable.
 133 Previous studies were mainly based on mortars while concretes are used in the present
 134 paper with the subsequent decrease in cement content with respect to the total material
 135 weight.

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137 **2.2 Methods.**

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139 *2.2.1 Characterization of the concrete properties.*

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The fresh state of the fabricated concrete mixes was assessed in all the cases by measuring air content (EN 12350-7) [49] and density (EN 12350-6) [50]. Since the w/c ratio was maintained constant in all the concrete mixes and previous results have shown that the addition of PhAg promotes a decrease of workability [34], the fresh state of concretes with photocatalytic activity (PEK, PEG and P concretes) was assessed by measuring the consistency (EN 13350-2) [51] but the fresh state of the SCC (EK and EG) was assessed by measuring the filling ability tests according to EN 12350-8 standard (slump flow and $T_{50\text{cm}}$ spread time) [52] and the passing ability J-ring flow test according to EN 12350-12 [53].

The mechanical properties of the concretes were evaluated in free and restraining expansion conditions. The compressive strength according to EN 12390-3 [54] was measured in Ø100 x 200 mm sized cylindrical concrete samples at 7, 28 and 90 days. In all cases three samples were considered. Most of the specimens were maintained at 20°C under water until testing but three samples for each concrete mix were maintained at 20°C in their own steel molds. In this last case water loss was avoided by wrapping the exposed face in retractable film. The influence of the confinement in the concrete strength gain was assessed by measuring the compressive strength of the samples cured in their mold at 28 days.

The microstructure of the fabricated concretes was also characterized in smaller cylindrical specimens (Ø 75 mm x 150 mm sized). Half of these specimens were cured under water but the other half of the specimens were maintained in the same conditions of the samples fabricated to evaluate the influence of the confinement in the compressive strength (that is, in their own molds and wrapped in retractable film). In all

the cases 1cm^3 of concrete sample was cut at 2 and 28 days of curing to measure the total porosity and the pore size distribution by using a Mercury Intrusion Porosimeter (MIP, Micromeritics porosimeter Model 9320). BSEM with EDAX analyses were also made at 28 days of curing. The samples, once embedded into an epoxy resin, cut, polished and coated with carbon were inserted in a scanning electron microscope Hitachi S-4800. This equipment has an energy dispersive analyzer BRUKER 5030.

For the photocatalytic samples, transport properties were carried out by measurement of the steady and non-steady state chloride diffusion coefficients through the matrixes. The steady (D_s) and non-steady (D_{ns}) state chloride diffusion coefficients were determined using the multi-regime method [55] that was standardized as EN 83987 [56]. The test is based on measuring the amount of chlorides arriving in the downstream cell (anolyte) accelerated by an electrical field, by means of measuring the conductivity of that solution instead of analysing chlorides in it. Distilled water was introduced in the compartment where the anode was placed (anolyte), while the cathodic compartment was filled with a solution 1 M NaCl. The voltage drop applied was of 12 V DC. Black steel bars were used as electrodes. Periodically during the experiment, conductivity of the anodic compartment was monitored to know the flux of chloride ions. Prior to the migration tests, the specimens were pre-treated for water saturation under vacuum using the procedure described in the standard ASTM C1202-97 [57].

The expansion under uniaxial restraining as measured in prismatic specimens according to the ASTM C878 “Standard Test Method for Restrained Expansion of Shrinkage-Compensating Concrete” [58]. Six prismatic specimens 254 x 76 x 76 mm size were fabricated per concrete mix and cured at $20\pm 2^\circ\text{C}$ and wrapped in retractable film during

6 hours. Then, half of the specimens were cured under water at $20^{\circ}\text{C}\pm 2^{\circ}\text{C}$ and the other half of the specimens were maintained at $20^{\circ}\text{C}\pm 2^{\circ}\text{C}$ but wrapped in retractable film. A digital comparator was used to measure the longitudinal restraining expansion. The accuracy of the comparator was 0.002 mm.

2.2.2 Photocatalytic efficiency

2.2.2.1 Characterization of the NO_x degradation

Borosilicate glass reactor designed according to the specifications of ISO 22197-1 was used to analyze the efficiency of the concretes to remove NO_x [59]. An image of the reactor used is shown in Fig. 1. The total volume of the reactor was 2.81 liters. The surface of the samples was irradiated to $10 \text{ W/m}^2 \pm 0.5 \text{ W/m}^2$ by using an UV lamp (Osram Ultravitalux 300 W). This lamp emits UVA radiation at an optimum of 365 nm and it was located outside the reactor. 1000 ± 50 ppb of NO gas diluted in normalized air was used as initial concentration. The bottle of NO contained a small amount of NO₂ in equilibrium with the NO. Two mass flow controllers were used to prepare the mixture supplying a flow rate of $3 \text{ L}\cdot\text{min}^{-1}$ circulating on the sample in laminar flow. When the NO concentration in the reactor was equilibrated (after 30 min), the lamp was turned on. RH was controlled at 30% and temperature was that of the ambient air in the laboratory (around 23°C) for all the tests. Light was on for 90 minutes and the modifications in NO and NO₂ concentrations were continuously recorded by a Chemiluminescence NO_x analyzer (model AC32M Environmental S.A.). The next equation was used to calculate the amount of NO_x (NO+NO₂) removal:

$$\%NO_{x\text{removed}} = [(NO_{x0} - NO_x) / NO_{x0}] \cdot 100 \quad (\text{Eq. 1})$$

Where: NO_{x0} is the initial NO_x concentration and NO_x is the final concentration after the irradiation test.

Fig. 1. Reactor designed to analyze the efficiency of the concretes to remove NO_x .

Cilindrical samples of 75 mm diameter and 10 mm height were introduced into the reactor, made from cutting specimens of 75 mm diameter and 150 mm height from the bulk of the specimen.

2.2.2.2 Characterization of the self-cleaning ability

The discolouration of Rhodamine B (RhB) was monitored in order to determine the self-cleaning ability of the concretes. The RhB was applied on the surface of the photocatalytic material. RhB was selected as it is used in the standard UNI 11259:2008 [60] for construction materials although dye-sensitisation has been reported [61]. Some modifications were made with respect to the procedure given in UNI 11259 standard. For example, in order to obtain homogeneous distribution of the colour over the entire

surface, the solution used in the current study were 6 ml of solution RhB ($0.0083 \text{ g}\cdot\text{L}^{-1}$) instead of 0.5 ml of RhB solution ($0.5 \text{ g}\cdot\text{L}^{-1} \pm 0.005 \text{ g}\cdot\text{L}^{-1}$) as recommended.

At different times of illumination, the colour measurements were directly taken on the surface of each specimen (bulk samples) with a portable spectrophotometer CM-2300d-Konika Minolta. The mean value of a series of at least 4 measurements was calculated for each chromatic characterization. The results were expressed according the CIELAB system using the readings of the parameter a^* whose chromaticity goes from red to green. The percentage of discolouration was expressed according to Eq. 2.

$$\% \text{ of colour change} = [(a^*_0 - a^*_t) / a^*_0] \cdot 100 \quad (\text{Eq. 2})$$

Where: a^*_0 is the colour intensity of the specimens before the UV irradiation and a^*_t is the colour intensity of the specimens after t hours of irradiation.

3. Results and discussion.

3.1. Characterization of the fresh state of the fabricated concretes.

Table 2 summarizes the main parameters measured in the fresh state of the developed concretes. The most evident phenomenon is the decrease of the workability of the concretes when adding the PhAg. In fact, the fabricated concretes lost the self-compacting characteristics. This decrease in the workability has been also detected in non-expansive cementitious materials and it was probably due to the extremely fine size and high specific surface area of the incorporated TiO_2 particles which caused higher

water demand for obtaining similar flow ability [34,62,63]. In fact, different types of photocatalytic powder particles tend to reduce the amount of free water in the mixtures that acts as lubricant upon flowing although their action is mostly defined by the physical characteristics, namely the particle size and the specific surface area [64]. The decrease of the concrete fluidity in the photocatalytic concretes is also higher when adding the expansive agent type-K. The higher decrease in fluidity detected in PEK concrete with respect to PEG concrete must be mainly related to certain interactions between type-K expansive agent and TiO₂ particles since previous studies have demonstrated that the expansive agents do not limit the self-compacting requirements [20,21,23,24]. Regarding the air content, the expansive SCC without PhAg shows the highest values but the differences are not very significant. Consequently, higher density values have been measured in the photocatalytic concretes, although again the differences are not very significant.

Table 2. Main characteristics of the fresh state of the concretes developed.

<i>Concrete mix</i>	<i>Consistency (mm)</i>	<i>Slump flow (mm)</i>	<i>T₅₀ (s)</i>	<i>J-ring flow (mm)</i>	<i>Density (kg/m³)</i>	<i>Air content (%)</i>
<i>EK</i>	-	570	1.5	520	2.19	2.8
<i>EG</i>	-	650	1.5	620	2.20	3.0
<i>PEK</i>	85	-	-	-	2.33	2.5
<i>PEG</i>	200	-	-	-	2.36	2.1
<i>P</i>	195	-	-	-	2.23	2.6

3.2. *Physic-mechanical and durability performance of the fabricated concretes.*

Although contradictory results have been published, the decrease of the mechanical strength when using the photocatalytic agent in cementitious materials was observed in previous studies [34,43]. However, this reduction was mainly attributed to the diminution of the amount of cement in total sample and the lower fluidity of the mixes with the photocatalytic agent that promoted lower homogeneity in the specimens. Nevertheless, according to the results shown in Fig. 2, the inclusion of the PhAg does not limit the compressive strength of the expansive concretes developed. In fact, in free expansion regime, the higher compressive strength is measured in P concrete (with PhAg but without ExAg) during all the test period. The lower compressive strength of the expansive concretes in free expansion regime could be related to the formation of microcracks as a result of the expansion generated. These microcracks would limit the concrete strength and this limitation is higher in the concretes with type K agent due to the higher ExAg content used. In fact, the free expansion of the concretes with type K agent cured under water is quite higher than the one of the concretes with type G agent (see section 3.3). The compressive strength values obtained in the concretes with type G agent are very similar to those measured in the non-expansive concrete.

Fig. 2. Compressive strength evolution of the developed concretes. Res = restraining conditions.

In free expansion, any significant difference is detected in the concretes with type K agent but really similar values are obtained during all the test period. Considering the concretes with ExAg type G, the compressive strength is always slightly higher when the PhAg is included in the concrete mix. Type G agent promotes the formation of portlandite and this formation can be increased by the nucleation effect of powder particles of low size that provide additional sites for the nucleation of this hydrate [65-68]. Since PhAg has very low particle size, it can also provide additional sites for the nucleation of portlandite thus accelerating the initial hydration of the concrete with ExAg type G. The acceleration of the early hydration of conventional Portland cementitious materials due to the inclusion of nano-TiO₂ particles has already been demonstrated [69].

In restraining conditions (28 days) only the use of type K agent generates some differences. The higher compressive strength value shown by PEK concrete must be

related with its higher expansion (see section 3.4). In these conditions K-concretes show higher strength values than G-concretes. This phenomenon is only related to the higher type K content used that promotes higher volume expansion. This higher expansion coupled with the deficit of free spaces would promote the precipitation of expansive hydrates in pores and cracks thus reducing the porosity of the concrete with the subsequent contribution to the concrete strength [20,70]. The higher expansion of PEK with respect EK in restraining conditions also explains the higher compressive strength of the former (see section 3.3).

Table 3 shows the total porosity values measured at 2 and 28 days of curing in the fabricated concretes (in free and restraining expansion conditions) and Fig. 3 their pore size distribution at 28 days. Initially (at 2 days) any significant difference is detected between the porosity results of the different concretes since the hydration processes are in their beginnings. However, lower total porosity is detected when using the PhAg. This phenomenon agrees with an acceleration of the hydration reactions due to the addition of the photocatalytic agent. In fact, PEG concrete shows the lowest total porosity at 2 days. The reduction in the total porosity when adding the PhAg is also noticeable at 28 days of curing and agrees with previous works [34, 41-43]. Regarding the pore size distribution at 28 days, the most refined structure occurs in P concrete. Thus, the addition of TiO_2 could act as effective filler of voids leading to a refinement of the porosity. The addition of the ExAg type G slightly increases the pore distribution towards bigger pores, mainly when the photocatalytic agent is absent, although the resulting pore structure is still very refined. The addition of the expansive agent type K increases this phenomenon (see Fig. 3 up). However, this higher shift of the pore distribution towards bigger pores can be only due to the higher type K agent content

used with respect to the type G content. Regarding the differences between the porosity resulted under restraining or free expansive conditions, lower total porosity is always generated in the confined samples at 28 days. This lower porosity of the confined samples agrees with their higher mechanical properties.

Table 3. Percentage of total porosity of the concretes developed after 2 and 28 days of curing.

<i>Time</i>	<i>Expansion</i>	<i>EK</i>	<i>EG</i>	<i>PEK</i>	<i>PEG</i>	<i>P</i>
<i>2 days</i>	Free	19.1	20.4	17.7	14.7	15.7
	Restraining	17.7	20.5	23.0	15.9	-
<i>28 days</i>	Free	14.6	16.2	12.4	14.2	12.6
	Restraining	13.1	15.3	12.0	13.2	-

Fig. 3. Pore size distribution of the concretes at 28 days. Up: concretes with type K agent; down: concretes with type G agent.

The steady state and non-steady state diffusion coefficients, D_{ef} , and D_{ap} respectively, calculated according the multiregime migration procedure, are presented in Fig. 4. Any

noticeable change for both types of coefficients takes place due to the addition of the expansive agents, being very compact samples with quite a low effective diffusion coefficient. From the ratio between both coefficients, low ability for combination of chlorides can be deduced after 28 days of maturity.

Fig. 4. Steady state, Def, and non-steady state, Dap, diffusion coefficients, for the photocatalytic mixes after 28 days of curing.

3.3. Influence of the curing conditions in combination with PhAg addition in the expansion regimes of the concretes developed.

Two different curing regimes were considered in order to measure the expansion behavior of the concretes developed in longitudinal restraining conditions. Fig. 5 shows the results of the samples wrapped in retractable film and maintained at $20\pm 2^\circ\text{C}$ while Fig. 6 shows the results of samples cured under water at $20\pm 2^\circ\text{C}$. The expansion of P concrete was not measured since it had not got any ExAg.

Fig. 5. Evolution of the longitudinal restraining expansion of the specimens wrapped in retractable film and maintained at 20°C.

Fig. 6. Evolution of the longitudinal restraining expansion of the specimens cured under water at 20°C.

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379 According to the results shown in both figures, the inclusion of the PhAg does not alter
380 the expansion performance of the concrete with type G agent in any of the curing
381 conditions considered. When there is water curing, the maximum expansion reached is
382 maintained during all the test period; however, a very slight decrease is detected in the
383 samples wrapped in retractable film. However, when using type K agent, a strong
384 influence of the PhAg in the resulting expansion is measured being even stronger in the
385 samples cured under water. The higher expansion obtained when using the PhAg could
386 be related to the fact that it can act as nucleation sites for the new hydrates formed due
387 to their very low particle size [34,41,42]. The higher expansion obtained with the PhAg
388 with the type K agent is detected from the very beginning of the hydration processes.
389 This characteristic may be noticeable with both ExAg since both are based on the
390 formation of cement hydrates. However, the lower type-G content used can explain the
391 non-influence of the PhAg in this case. The same physical activity was described for
392 limestone filler but recent studies have demonstrated certain chemical effect that also
393 influences the hydration reactions [65-68]. The possible influence of the use of the
394 PhAg in combination with the type-K agent is evaluated in section 3.4. Anyway,
395 regardless of the higher value obtained in PEK concrete with respect to EK concrete, the
396 expansion regimes obtained are influenced by the curing conditions. The maximum
397 expansion value, once reached, is maintained for water curing, but a clear decrease of
398 the expansion further occurs in the specimens wrapped in film. In fact, this further
399 decrease is more significant than in the concretes with type-G ExAg. Thus, regardless of
400 the use of PhAg, the water curing has more influence in the expansive concretes based
401 on the use of calcium sulfoaluminate agents (type-K).

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According to the obtained results, the incorporation of PhAg in the composition of expansive concretes influences the expansion regime obtained when type K expansive agent is used. Regardless of the curing conditions, the total expansion achieved is higher when PhAg is used in combination with type K ExAg. However, this phenomenon is not detected when using the expansive agent type G, at least with the content used in the present study.

3.4. Microstructural development of the fabricated concretes.

PEK and EK samples, under both free and restraining conditions, were observed by BSEM in order to detect an explanation for the higher expansion resulted in the former. In both conditions the presence of pores is lower in the concrete with PhAg which agrees with the lower and more refined porosity detected by MIP. In the concretes without photocatalytic agent, higher content of cement anhydrous phases is detected in the confined specimens than in the ones cured under water. Regarding the ettringite phases observed, different morphologies are found in both curing conditions. According to the BSEM images shown in Fig.7, in both curing conditions most of the ettringite phases formed are a kind of amorphous hydrate or at least they have a cristallinity degree lower than the typical one detected in ettringite directly formed from Portland cement anhydrous phases. Thus, possibly the ettringite formed from the anhydrous phases of the expansive agent type K has different morphology (or even crystallinity) than that formed from the anhydrous phases of Portland cement. The morphology of the ettringite phases formed in the expansive concretes with phtocatalytic activity is very similar to that detected in the samples without ExAg (see Fig. 7 down).

Some differences are also detected in the chemical composition of the ettringite hydrates formed in each curing conditions. Table 4 shows the A/C and $\bar{S}/C$ ratios calculated according to the EDX microanalysis made in the ettringite phases detected. The values given in the table correspond to the mean value of more than 25 EDX microanalysis each. The contents of the different elements could be overestimated as a result of the size of the area of the microanalysis and the presence of unreacted microparticles of the ExAg surrounding the ettringite hydrates. In the chemical composition of the ettringite nodules formed in the expansive SCC without PhAg cured under water, calcium enrichment is detected. Since the hydration of the expansive agent is faster than the one of the anhydrous of the cement, in the samples cured in their mold and wrapped in film the available water is lower and firstly will hydrate the anhydrous of the expansive agent. Thus, initially will be higher relative dissolution of sulfur and aluminum with respect to calcium than the one expected from the anhydrous cement particles. On the contrary, in the samples cured under water, the higher water availability will promote the almost complete dissolution of all the anhydrous cement particles thus decreasing the relative proportion of sulfur and alumina dissolution with respect to calcium dissolution.

In the ettringite phases formed in PEK samples, an enrichment of sulfur is clearly detected with respect to the samples without PhAg and also of alumina in the concretes cured under water. Thus, higher or faster availability of S and Al is detected in the concretes with PhAg. This higher availability could be due to the interaction of the extremely small particles of the PhAg and the anhydrous phases of the expansive agent. In this sense, PhAg particles can act as nucleation sites for the formation of ettringite thus accelerating the hydration of the anhydrous phases of type-K agent. Since the

hydration of the ExAg is faster than the one of the anhydrous of the cement, this acceleration of the hydration would mainly focus on the ExAg particles. In fact, the acceleration of the hydration reaction of the ExAg particles agrees with the higher expansion observed in PEK samples with respect to EK samples.

Table 4. Chemical composition of the ettringite hydrates formed in the concretes with type K expansive agent.

<i>Sample</i>	<i>Expansion condition</i>	<i>Ettringite composition</i>	
		<i>Al/C</i>	<i>S/C</i>
<i>EK</i>	Free (under water)	0.162	0.220
	Restraining	0.176	0.234
<i>PEK</i>	Free (under water)	0.203	0.288
	Restraining	0.180	0.246

Fig. 7. Ettringite morphology in the concretes with expansive agent type K. BSEM images x4000.

Therefore, the BSEM study reflects a physical interaction of the PhAg with the ExAg that promotes a faster hydration of the anhydrous phases of the type-K agent. This faster hydration promotes some modifications in the chemical composition of the resulting ettringite phases.

3.5. Photocatalytic efficiency.

Fig. 8(a-c) presents the results of diminution of NO for each material when starting the illumination of each specimen. In Fig. 8d, it can be seen that the incorporation of PhAg in the composition of expansive concretes decreases the photocatalytic activity for NO_x

as compared with the plain photocatalytic concrete, especially the one with type K expansive agent, that exhibit a 36% less of photocatalytic activity than the P sample.

Fig. 8. a-c) Photocatalytic removal of NO ; d) Percentage of degradation of NOx.

To evaluate the influence of PhAg in the composition of expansive concretes on self-cleaning efficiency, decomposition of the RhB has been carried out. Two bulk specimens of each mix have been tested, taking 4 points of measurement in each specimen, in order to smooth problems related to irregular distribution of the color. The average coefficient of variation (%) for the points taken at each step of the procedure, for the different samples have been 18% and 30% for P, 22% and 15% for PEG and 12% and 8% for PEK samples, which is within the range of bias allowed for concrete specimens. The results of decoloration are given in Fig. 9, where the average for each mix after 4 and 26 hours of irradiation is presented. In agreement with the results for NOx, the specimens without expansive agents present higher photocatalytic

activity, being the samples PEK those that give smaller values. Anyway, according to the standard UNI 11259:2008, the three materials are photocatalytic as R4 and R26 are higher than 20 % and 50% respectively.

Fig. 9. Average of decoloration of RhB (%) at 4 and 26 hours of irradiation, according to the standard UNI 11259:2008

The lower photocatalytic activity of the expansive concretes, mainly PEK, agrees with the role of the PhAg particles as nucleation sites for ettringite when using type-K agent and possibly for portlandite when using type-G agent. The growth of both hydrates on the surface of the PhAg particles could limit their photocatalytic activity.

4. Conclusions.

Expansive concretes with the inclusion of photocatalytic agents have been developed in this work. The PhAg decreases the workability of the concrete mixes but does not modify the mechanical properties while a refinement of the microstructure/porosity is

obtained. The most important conclusion of this study is the physical interaction detected between the particles of PhAg and ExAg. PhAg particles seem to act as nucleation sites that increase and accelerate the formation of the expansion hydrates with the subsequent increase of the resulting expansion. This effect is clear in the samples with 15% of type K agent where the resulting expansion is almost twice when using PhAg in the two curing regimes considered. Thus, the expansive hydrates are expected to grow in the surface of the PhAg, which in turn decreases its photocatalytic activity. Moreover, the chemical composition of the ettringite formed from the ExAg type-K is slightly modified due to the higher and faster hydration of the ExAg particles promoted by the inclusion of the PhAg. Since the content of type-G agent used was quite lower (5%), the effect in the resulting expansion has not been detected in the present study.

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