Doctoral School on Engineering Sciences
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Extended summary

Photocatalytic cement applications in civil engineering

Curriculum: Materials, Water and Soil Engineering

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Abstract. In civil engineering works, the application of photocatalytic cement is functional to the aesthetic conservation and to the abatement of pollutant concentrations, both for existent constructions, and for new ones. Specimens were realized and tests on field were conducted in order to evaluate photocatalytic pervious concrete, cements and coatings.

Keywords. Photocatalytic Cement, Pervious Concrete, Concrete Lining, Tunnel Coating, Photocatalysis on TiO_2, Kinetic Model for Oxidation of NO, Photocatalytic and Pervious Pavements.

1 Executive summary

Photocatalytic process allows to reduce concentrations in air of photochemical pollutants and to keep the surface white and clear. Also, it is capable to capture and dispose of compounds as innocuous salts. For these reasons, taking into account the joint of oxidative photocatalytic process and traditional cement turns to be useful in application of cement with addition of TiO_2. A wide and significant contribution can be given to the environmental aspects among sustainable constructions.

On the one hand, pervious concrete mix design and photocatalytic pervious concrete, mortars and paints specimens were tested in laboratory in order to evaluate the mechanical characteristics and photocatalytic activity. Pervious concrete pavements were studied for the realization as road infrastructures, also replacing natural aggregate with recycled ones.

On the other hand, pervious concrete and photocatalytic pervious concrete were tested on field. Their activity and capability to drain water were verified.

An experimental research was carried out inside a highway tunnel painted with photocatalytic coatings: paints and a coat. Photocatalytic coatings and grout were applied to a highway surface, on field.

Results from applications and monitoring systems of a photocatalytic concrete pavement, a tunnel and a highway pavement are showed.

1.1 Cement involved

The main material involved in this study is cement, in several applications in civil engineering. Three typologies are the ones related to the realizations: a traditional Portland cement II/A-LL 42.5 R, a photocatalytic cement, the grey TX Aria® 42.5 R, another photocatalytic cement, the white TX Arca® 42.5 R. Both two cements can be described as A-LL and B-LL, respectively, and they also conformed to the UNI EN 197-1.

Another product, which was tested, is the i.active COAT®, a coat that can be sprinkled directly over the surfaces of a tunnel, for example. Its aggregate has dimensions inferior to 0.7 mm and the final density of the product is 1,750 kg/m^3. These photocatalytic materials are produced and marketed by Italcementi® S.p.A..

Therefore, photocatalytic coatings and paints were studied, especially in their applications in tunnels and accessories.

2 Pervious concrete

2.1 Concrete laboratory

First of all, the design of pavements was tackled. In fact, mix designs were set in the laboratories in order to establish the right quantities of cement, aggregate, water. Above all, natural aggregates were substituted for recycled aggregates, only from concrete demolition, until 100%, and photocatalytic cement was tested.

The main characteristic that the designed pervious pavements must have is permeability. For this reason, the coexistence of two antithetical qualities, like permeability, i.e. open porosity, and mechanical resistance had to be sorted out.

Tests with different mixes, ingredients, compaction effort for the realization of specimens, compression and traction tests were conducted. Also tests with a falling-head permeameter simulating the conditions in streets (specimen dimensions: 85x15x14 cm) were performed. The permeameter was realized in the laboratories of the Department just to simulate this particular condition, of bidimensional filtration.

An adequate strength to compression for application to roads and pavements was achieved. The obtained resistance was 15 ÷ 20 MPa also with recycled aggregates and photocatalytic cement. The coefficient of permeability, the *k* of Darcy, can be said $1.0 \cdot 10^{-2}$ m/s. This is a medium value obtained, considering all the mixtures realized, taking into account that in case of less porous mixtures the *k* value decreased but not so much as it could be expected.

Figure 1. Pervious concrete inside permeameter of laboratory

3 Photocatalysis

3.1 Laboratory of photocatalysis

3.1.1 Plug-flow tests

Several samples were made in pervious concrete, mortars and grout, with photocatalytic cement to be tested in laboratory of photocatalysis. The samples had dimensions of 15x8 cm, in surface, and thickness 0.1, 1.0 or 7.0 cm, depending on the typology of material. In fact, pervious concrete could not have a thickness inferior to 4.0 cm, because of its 7-15 mm aggregate. The samples having an inferior height needed to be laid down over a support in pyrex, while the pervious concrete samples only needed to have the side surfaces sealed.

According to the Italian regulations, in particular UNI 11247, the approach consisted in testing the materials in plug-flow, varying the flux and the concentration of the tracing compound, the inorganic NO_x. However, 1500 Ncm^3/min and 0.500 ppm of NO_x were the most recurring values adopted.

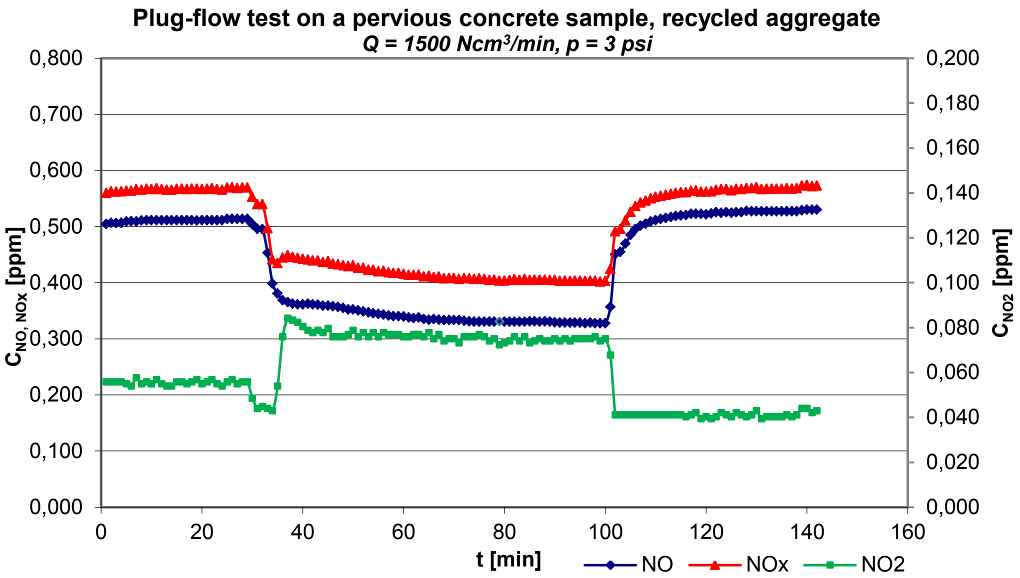

Figure 2. Graphic-example of a plug-flow test on a pervious concrete sample

Results varied, due to the content of photocatalytic cement, superficial porosity, colour, age of the samples, hydraulic retention time. Anyway, it can be affirmed that the most performing materials were the ones tested after a sufficient period of curing (after 14 days at least) and the ones having got a wider external surface exposed to the light of the lamp used. The lamp used in this kind of test was a UV-A lamp able to irradiate among 20 and 40 W/m^2 of irradiance, depending on how much close to the sample it was set.

A typical graphic is inserted, as example (Fig. 2). The second graph (Fig. 5) shows the efficiency of these materials, calculated as the starting concentration of NO versus the concentration of NO during the UV-A irradiation, the light phase.

Durability and the age of the samples were analysed. It was observed that the longer the samples are cured, the better results in efficiency they have. After 14 days, referring to pervious concrete specimens, it is possible to achieve satisfactory values. At the 60^{th} day of curing, efficiency values do not get better anymore.

The behaviour of specimens exposed to carbonation was studied. The process of carbonation was intended as a mere process of artificial aging. Many differences were sorted out: samples exposed to NO_x or realized with nitrites of sodium could discharge nitrites, when irradiated by the UV-A lamp.

3.1.2 Batch tests

Samples got from laboratory's mixtures were also tested in batch. They were put inside a 12.9 l box, with a fan and a PID sensor, to come to data from the surveying of the decay of organic tracers (MEK). Decay curves and α coefficients were obtained, in accordance with the theory of the indoor pollution modelling.

3.2 Image analysis

Analyses on images, 3D and 2D scans were run. Their results are extremely useful for evaluating materials' surfaces, referring to the high specific surfaces and corresponding depollution performances of this concrete. In fact, it was clear that there is a correspondence between the percentage of surface directly exposed to sunlight, the surfaces of the superficial pores and the efficiency recorded.

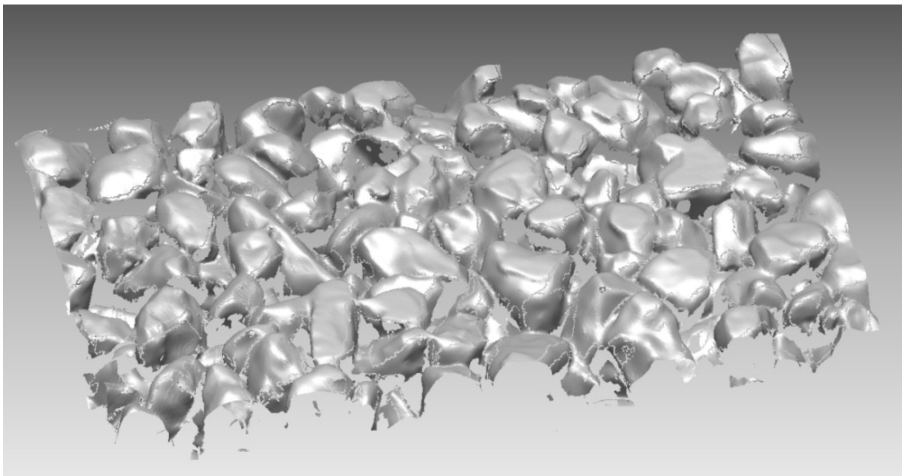

Figure 3. 3D pervious concrete scanning

Moreover, images of samples taken from applications in tunnel and pavements were analysed in order to establish the number of black particles attached to the surface (carbon particles), the toning of the colour of their surface (how white they can last) and the quantity of photocatalyst which was still present on the surface (in case of cold coatings application).

In addition, images from 2D scans were helpful to estimate the porosity of pervious concrete specimens.

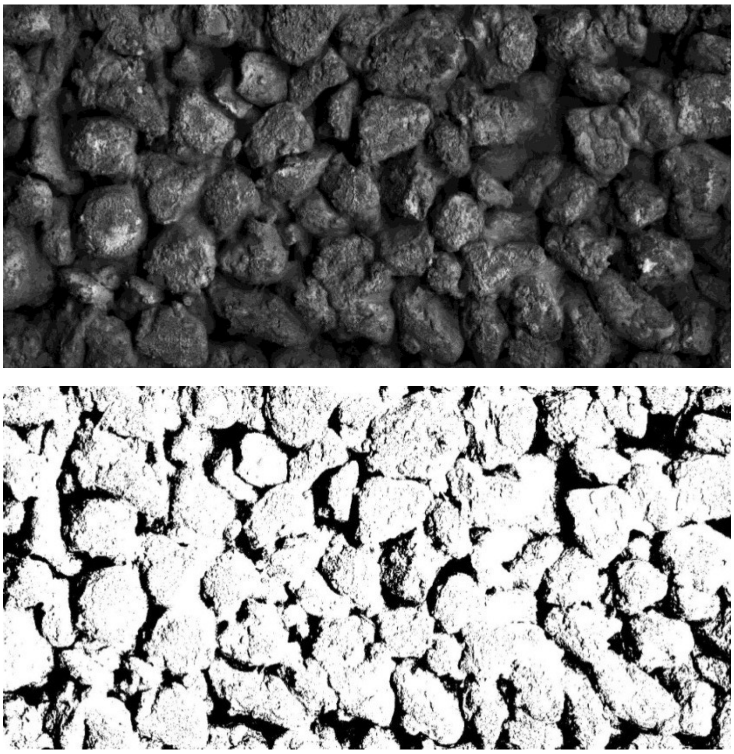

Figure 4. 2D scanning of a pervious concrete sample and image processing

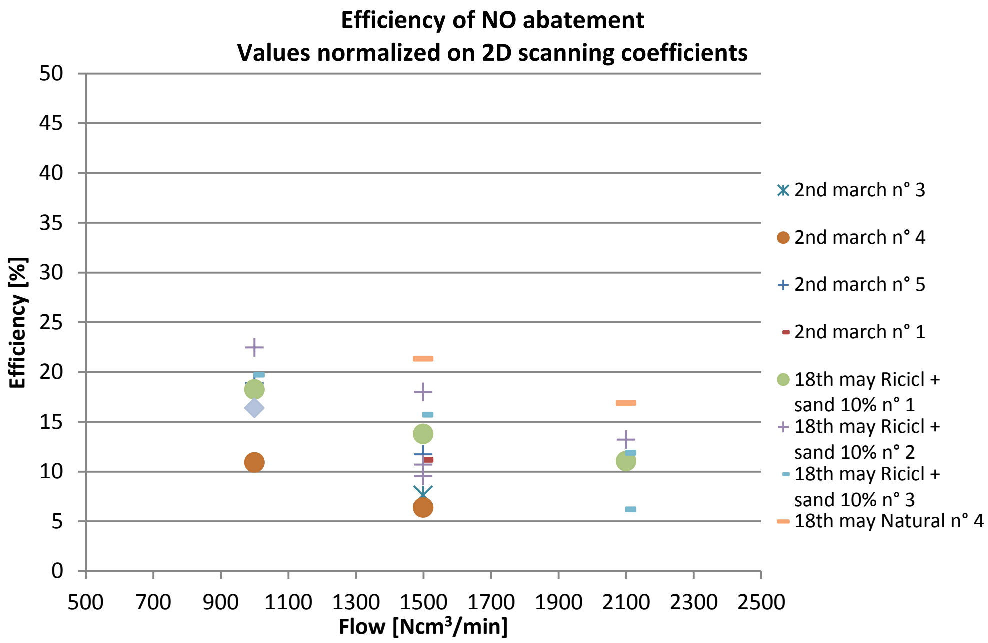

Figure 5. Graphic of efficiency of samples in plug-flow tests

4 Pervious concrete application on field

Pervious concrete pavements are made by binding open-graded aggregate with cement. The most crucial stage is the consolidation, after the placement, in construction. For this reason, it is extremely useful having the chance to test and improve pervious pavement features working on a test-field. In fact, despite three ways to compact cubic samples of laboratory were performed, evaluating on full-scale tests is always the most reliable method.
A pervious pavement, with traditional cement, was realized in a place susceptible to problems of serviceability: an underpass, close to fields, a road with heavy load traffic, because of many transits of truck mixers.

Figure 6. Pervious concrete, roadway pavement

After two years, three cylindrical samples were pulled out for mechanical tests and, above all, permeability tests, to estimate how much k could have been reduced by the debris of the underpass. These tests showed that the presence of sediments like sand and silty clay reduced the permeability from $3.50 \cdot 10^{-3}$ m/s to $3.60 \cdot 10^{-4}$ m/s. This estimated reduction can be weakened by washing the sample, removing the fine-grained silty sand and clay. Then, the k value was $4.23 \cdot 10^{-4}$ m/s.

Some defects and distresses occurred in a portion of the area. In particular, during visual inspections of the surface, a stretch mark area was recognized. There was an area resulting in a surface depression and higher porosity. It was stated to demolish this area and to install a new pervious concrete mixture, with white photocatalytic cement. The compression resistance was satisfactory and five samples for the photocatalysis laboratory were made.

Figure 7. Photocatalytic pervious concrete slab

After 23 days, a new visual inspection was done and four cylindrical samples were taken to laboratories. New tests on the overlay construction in photocatalytic pervious concrete (photocatalytic tests in plug-flow and batch and image analyses) were effected.

Table 1. Permeability tests on pervious concrete samples

Pervious concrete samples. Traditional and photocalytic cement *Cores from slab and on field test pavement*				
sample	5	1	1	1
typology	TX Active®	Pre-washing	Pre-washing	Post-washing
mass of a volume unit [daN/m^3]	2,108	2,063	2,063	2,063
k [m/s]	$2{,}92 \cdot 10^{-3}$	$3{,}65 \cdot 10^{-4}$	$2{,}59 \cdot 10^{-4}$	$4{,}23 \cdot 10^{-4}$

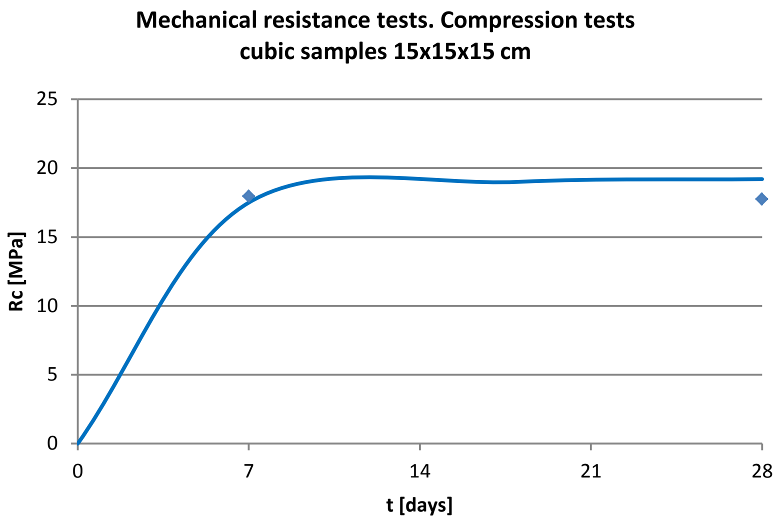

Figure 8. Compression resistance of pervious concrete cubic samples

5 Photocatalytic process in road environment: application in a highway tunnel

The aim of this application is to evaluate photoactivity of TiO_2 coating at a highway tunnel, illuminated by UV-A lamps. Measuring campaigns were intended at finding an in situ measurement strategy organized together with continuous monitoring and with grab sampling, with the aim of checking the pollution reduction through photocatalytic surface reactions on wall paint. The analysis focused on all the aspects linked to vehicular traffic emissions, macro and micro climate conditions and the reduction of air pollutants at the highway portal tunnel.

Figure 9. Photocatalytic tunnel

The tunnel was coated with three different products. These results are the ones obtained by the application of a photocatalytic coat, with TiO_2, as described in paragraph 1.

Instant samples were collected by means of steel cylinders, where the air from the North tunnel (painted with TiO_2), and South tunnel (not painted) were vacuum-emptied. The samples were taken by car which travelled the whole length of the tube tunnel at a fixed speed of about 80 km/h, paying attention to avoid closeness to trucks, cars, or any other type of vehicles.

Meteorological and traffic data were obtained from a local station belonging to the highway authority. It was observed that for a day of good weather conditions at the tunnel entrance, there was a typical wind rotation caused by the influence of convection cell of sea and land breezes. Concerning the tunnel exposure to the wind, it was observed that the prevalent winds persist mostly in the direction opposite to the traffic flow. Due to this condition, a kind of cap-effect occurs on North tunnel, amplifying the concentration of polluting agents.

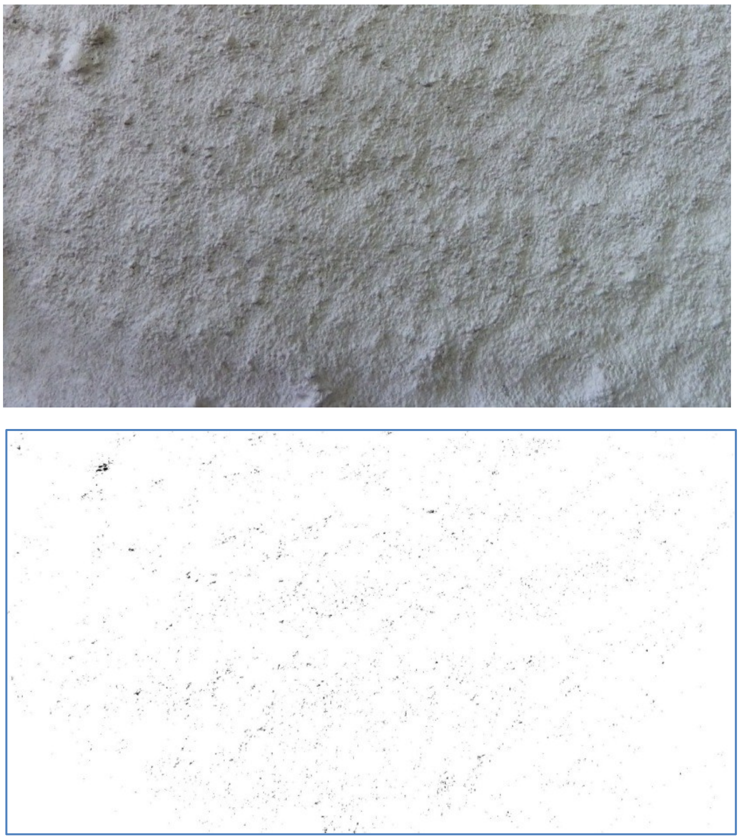

Figure 10. Photocatalytic sample and relative image processing, photocatalytic tunnel

Samples of the coat directly applied on the surfaces of the tunnel were analysed in laboratory of photocatalysis in order to evaluate colour, particles (image analyses) and photocatalytic activity at every sampling. The coat is applied on wooden (transpiring) and PVC samples of dimensions of a card, 12.5x16 cm.

Analyses of samples of air collected from the tunnel pointed out the levels of CO_2, CH compounds and mostly the ratio NO/NO_x for both tunnel, the one with TiO_2 and the one with traditional paint.

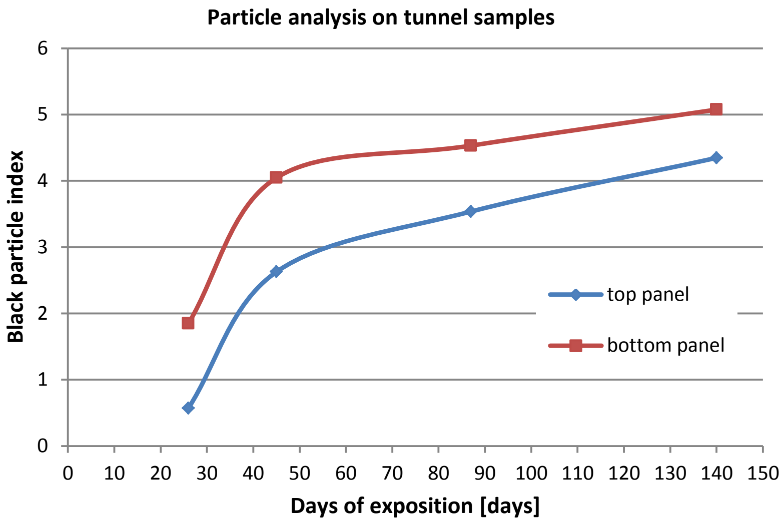

Figure 11. Particle analyses on photocatalytic samples, photocatalytic tunnel

6 Photocatalytic products on a highway pavement

Photocatalytic products can be applied also on pavements as surface layers or coatings. In this on field test, three different commercial coatings were evaluated. One product consisted on a photocatalytic grout, the other two products were paint, in a spray application, over bituminous porous asphalt of a highway.

A monitoring system was designed in order to control the behaviour of these materials for two years. Six sampling were made and all the cylindrical samples were tested in photocatalysis laboratory. Image analyses were run, as well.

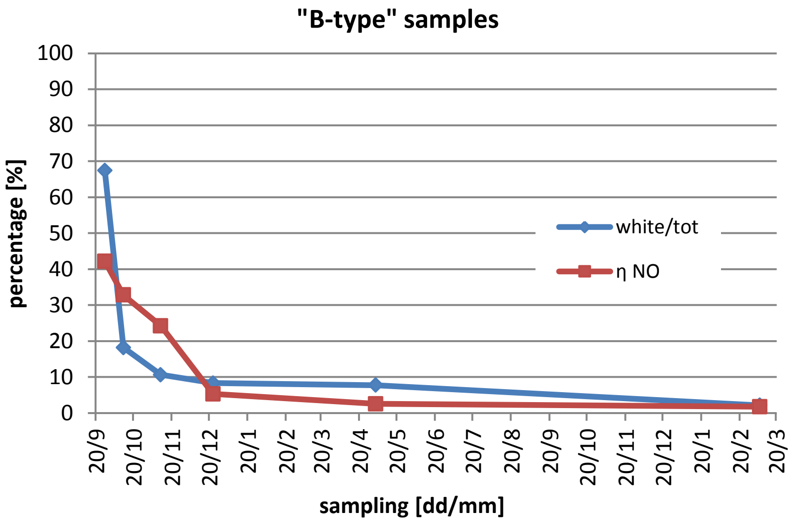

Figure 12. Comparison between image processing and efficiency of photocatalytic samples

The results were linked to the traffic, the number of vehicles which transited during the period, and to the weather data, in order to add photocatalytic analyses' data to the conditions the materials were exposed.

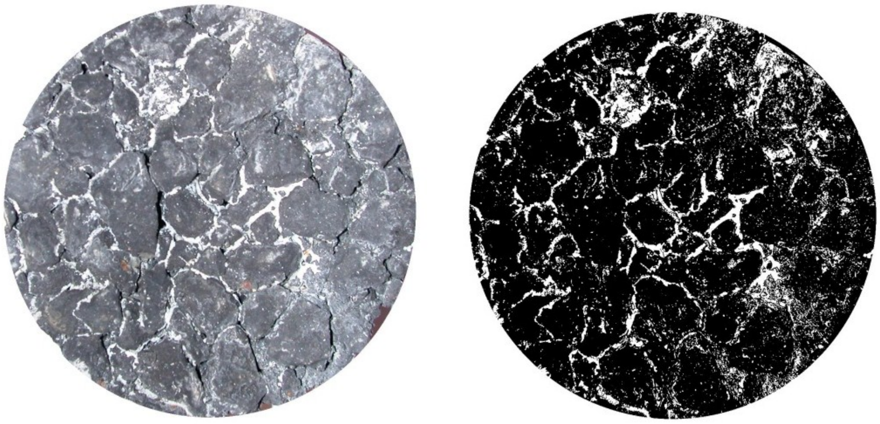

Figure 13. Highway pavement surface and image processing

7 Proposal of a batch model for the abatement of NO_x

In this section of this study, the proposal of a new method for the analyses in batch with inorganic NO_x. The aim consists in obtaining information by parameters like kinetic constants and adsorption constant. Samples of the gas inside the 12.9 l box were taken and lead to analysis with the chemiluminescence NO_x analyser. The decay and/or generation curves of NO, NO_x and NO_2 were acquired.

The beginning model was again the indoor pollution, in its expression $C(t) = C_0 \cdot e^{-\alpha \cdot t}$, starting with the coefficient α. Then, referring to the model of Moulis and Krýsa, it is possible to come to a modified solution, where NO_x concentration, the generation of NO and the disappearance of NO_2, at the end of the phase with UV-A lamp on, are described.

$$c(t)_{NO_x} = W \frac{K(c(0) - k \cdot t) - \ln \frac{1}{K \cdot c(0)}}{K} + a \cdot t \cdot e^{-k_1 \cdot t}$$

Where K is the adsorption constant, k the kinetic constant, a the coefficient of NO generation, k_1 the decomposition rate of NO_2, W the Omega function.

Some values of K and k parameters were available from plug-flow tests, according to the Langmuir-Hinselwood model. For this reason, the experimental curves where fitted by the modified Moulis Krýsa model, introducing K of the plug-flow analyses as beginning value of the interpolation.

Table 2. Parameter values, analyses in batch model

sample	**UV-A**	K [m³/mg]	k [mg/(m²·min)]	k_1 [min⁻¹]	a [mg/(m³·min)]
pervious c. on field test	on	0,476	0,0768	0,1838	0,0166
pervious c. on field test	off	3,654	0,0146	0,0110	0,0072

Data obtained are summed up in a table and the behaviour of samples compared (pervious concrete, cylindrical samples in pervious concrete, samples of grout, coat "card") allows to conclude that there is a correspondence between adsorbing and kinetic properties of each sample. Inside the table there is also the parameter α which describes the NO generation.

8 Conclusion

The joint of oxidative photocatalytic process and traditional cement turns to be useful in application of cement with the admixture of TiO_2 and it was showed through samples made in laboratory and the full-scale application, both for pervious concrete and coatings for surfaces of civil engineering constructions.

Analyses on images, 3D and 2D scans were designed and run. Their results are extremely useful for evaluating materials' surfaces, referring to the high specific surfaces and corresponding depollution performances of this concrete.

Then, monitoring systems were designed and verified in order to study and evaluate the proper parameters which are considered to be the ones that control applications on field.

Results from applications and monitoring systems of a photocatalytic concrete pavement, a tunnel and a highway pavement are showed.

Moreover, pervious concrete mixtures were settled and the full-scale application allowed to conclude that adequate compression strength can be achieved and that a photocatalytic cement can be the binder for a layer or an overlay of pervious concrete. In addition, the use of pervious concrete pavements boasts favourable environmental effects. In fact, pervious concrete is a firm and strong pavement and highly permeable. These features make the pavement a wise choice for applications in areas where it is fundamental that water can freely drain. Its colour, then, makes the surface clear at night and, finally, noise is reduced. If the material has a high infiltration rate, hydraulic operas can be limited or even absent.

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