Avestia Publishing
International Journal of Environmental Pollution and Remediation
Volume 4, Year 2016
Journal ISSN: 1929-2732
DOI: 10.11159/ijepr.2016.002

NOx De-Pollution Using Innovative Mortars and Concretes - From Garage Prototypes to Tunnel Pilot

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Abstract *- Air pollution generated by transportation (cars, trucks, etc.) affects the health of millions of persons around the world. Some of the most toxic air pollutants are composed of nitrogen oxides (especially nitrogen dioxide, NO2) and volatile organic compounds (VOCs). These gas pollutants affect also the environment by promoting the formation of ground-level ozone and micro-particles harmful to human health and ecosystems. These compounds are responsible for the rise of acute respiratory diseases, asthma and allergies in urban areas.*

The patented technology of de-polluting concrete does not rely on photo-catalysis and can function perfectly well without sun light, which is especially suitable for use in confined areas prone to pollution peak (tunnels or parking garages). The experiments done in laboratory demonstrated that the addition of certain activated carbons into the mix improves the NO2 absorption properties without affecting the mechanical strength of concrete.

In order to demonstrate the interest of this innovation, two parking garages were built with the walls made of a de-polluting concrete or covered by a de-polluting mortar. The tests done using gasoline generator as a source of pollutants confirmed a significant abatement of NO2. The de-polluting effect still detected after one year of aging (carbonation) helped us in scheduling a field test in a tunnel located in the region of Lyon (France). This field-test consisted in spraying the de-polluting mortar on the walls of the ventilation plant located at the top of a chimney of a motorway tunnel. The results after 6 months of trials confirm a significant NO2 reduction rate in the air released by the chimney.

Keywords: Air pollution, concrete, mortar, tunnel, confined spaces, NOx, parking.

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1. Introduction

Hazardous gaseous pollutants, such as nitrogen oxides (NOx), are mainly produced by car and truck traffic. They affect the health of millions of people by worsening allergic, respiratory and cardiovascular diseases [1-2]. Indeed, the development of new de-polluting materials that could reduce the NOx concentrations in confined spaces (such as in office or residential buildings, but also in basements, underground garages, industrial plants, warehouses and motorway tunnels) could improve the life quality in urban areas [3-4].

We have previously shown that ordinary Portland cement pastes are porous alkaline material that can absorb NO_2 at ambient temperature until the complete carbonation of the paste [5]. In addition, the activated carbons are known to be excellent adsorbents for NO_2 [6-8] and can be added to the mix of mortar and concrete [9]. The validity of the solution at a lab scale has been demonstrated previously [9-10] and the challenge is now to prove that it works in-situ in prototypes.

The objectives of this paper consist in presenting: (i) the NO_2 reduction rates in instrumented garage boxes built with de-polluting building materials (ii) the results of a field test undertaken in the ventilation plant of a chimney of a motorway tunnel.

2. Presentation of the de-polluting material

It is well established that NO_2 can react in alkaline aqueous solutions to give nitrite and nitrate ions [11]. The most strongly alkaline phases like $Ca(OH)_2$ of the hydrated cement pastes show a high absorption capacity but this effect is temporary. Indeed, the NO_2 reduction rate by the reference cement paste is affected

Date Received: 2015-01-10
Date Accepted: 2015-12-06
Date Published:2016-05-12

by carbonation caused by atmospheric CO_2: this gas converts the highly alkaline hydrates to calcium carbonates, which are less reactive with NO_2. Laboratory-scale experiments show that the addition of small percentages of activated carbon (AC) powder to the cement paste increases the NO_2 reduction rate and reduces the influence of carbonation, by prolonging the de-polluting effect.

Two types of hardened cement pastes were tested in a lab reactor. The reference cement pastes were prepared by mixing 0.45 parts of water per 1 part of cement. Other cement pastes were manufactured with additions of a selected activated carbon, keeping the same water/cement (W/C) ratio. Previous work showed that the addition of AC powder did not affect significantly the microstructure and the mechanical strengths of the cement pastes [9]. Finally, the composition of the polluted gas was modified by diluting the NOx in ambient air in order to quantify the NO_2 abatement in presence of carbon dioxide (380 ppmv of CO_2). The addition of activated carbon in the cement paste improved significantly the NO_2 abatement. Figure 1 evidences a stable NO_2 abatement close to 70%, even in presence of CO_2, which reacts with the cement-based hydrates present at the surface of the hardened paste.

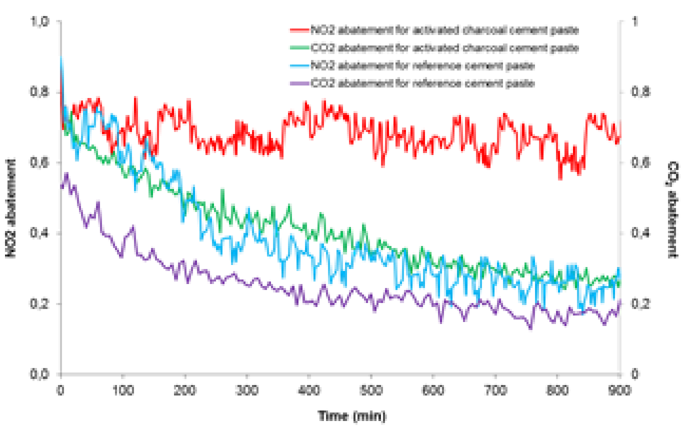

Figure 1. Variations of the NO_2 and CO_2 abatements using reference and activated carbon cement pastes.

NOx absorption experiments confirmed the predominant role of the activated carbon powder. The NO_2 absorption in the alkaline cement pastes is then governed by two consecutive phenomena:

- NO_2 physisorption on the activated carbon powder,
- Reaction of the adsorbed NO_2 with the alkaline pore solution of the surrounding cement paste, which depend on its carbonation.

3. Pilot tests done in parking boxes

3.1. Description of the instrumented parking boxes

Two garages (dimensions: 4.0x2.0x2.2 m, see Figure 2) were built using walls made of reference concrete and activated carbon concrete, respectively. The volume was 18 m^3 for an exposed surface area of 18 m^2 (the ceiling and floor were insulated by sticking a plastic liner). The both concretes were manufactured from Portland cement, limestone fillers, sand, gravels and admixtures (superplasticizer). Activated carbon was added to the mix of de-polluting. No special treatment was applied to the surfaces of these concretes after demoulding. For the measurements done in the garages, a petrol-engine generator was used, allowing the injection of multiple air pollutants, similar to the ones released by the road traffic. The concentrations of NOx were measured every 5 minutes using an automatic gas analyzer. The estimated residence time is 14 minutes.

Figure 2. Picture of the garages made of reference (left) and activated carbon concrete (right).

3.2. NO_2 abatement measured in the parking boxes

Table 1 compares the NO_2 abatements measured during the different tests, according to: (i) the NO_2 concentration injected at the input of the garages, and (ii) the conditions in terms of temperature and relative humidity. By comparing the concentrations measured at the input and output of the garage, no significant absorption of NO_2 was detected in the garage, while an abatement of 20-25% was observed in the garage made of activated carbon concrete, whatever the weather conditions and even in presence of other pollutants released by the generator.

Table 1. De-polluting tests undertaken using the garages made of reference concrete or activated carbon mortar and concrete.

Material type	T (°C)	RH (%)	Input NO2 concentration (µg/m3)	Output NO2 concentration (µg/m3)	NO2 absorption rate (%)
Reference concrete	24	39	421	407	< 3
Reference concrete	22	53	382	382	< 1
AC concrete	27	32	453	346	24
AC concrete	27	32	937	688	26
AC mortar	31	29	721	402	44
AC mortar	24	52	604	335	45
AC mortar	28	34	717	411	42
AC mortar	20	71	476	279	41

The absence of absorption for the reference concrete can be explained by the presence of CO_2 in the atmosphere leading to a carbonation of the surface of the walls, which tends to reduce the reactivity of NO_2 with the alkaline medium [12]. On the other hand, no effect of carbonation is observed on the NO2 reduction measured in the activated carbon concrete garage supporting the laboratory scale observations. The solutions leached from the walls of the garages were analyzed by ion chromatography after the gas absorption tests. The results showed almost no nitrate or nitrite in the leachate from the reference concrete and significant levels of nitrates and nitrites in the leachate coming from the activated carbon concrete yet below the water quality standards [11].

3.3. Improvement of the NO2 abatement with a de-polluting spray mortar

One of the garages (previously used to study the NO_2 absorption on the reference concrete) was refurbished by spraying a new de-polluting mortar on the walls. This de-polluting mortar was mixed according to the same AC/cement ratio as the one used for the activated carbon concrete. The W/C ratio and the type and amount of admixtures of this spray mortar were designed to stick well on the walls. The overall porosity (measured by mercury intrusion porosimetry) of this de-polluting mortar was close to 30%, which is significantly higher than the one measured for the activated carbon concrete (about 15%). Figure 3 compares the NO_2 concentrations alternately measured at the inlet and at the outlet of the garage covered by the de-polluting spray mortar. The NO_2 concentrations were measured every 5 minutes and during a few hours using an automatic gas analyzer. The temperature and the relative humidity were about 28°C and 34%, respectively. NO_2 abatement close to 42% was detected by using the activated carbon mortar, which is a significant improvement compared with the previous tests done with a de-polluting concrete.

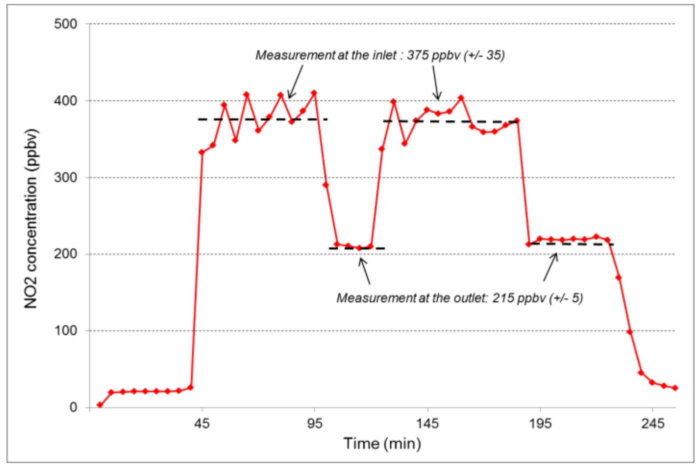

Figure 3. Examples of NO2 concentrations measured in the garage covered by a de-polluting spray mortar (1ppb = 1.912 µg/m3).

Table 1 summarizes the NO_2 abatements measured during the different tests carried out in the garage covered by the de-polluting spray mortar (using a residence time estimated to 14 min). A stable abatement of about 40-45% was always detected whatever the levels of NO_2 concentrations injected at the inlet of the garage. As previously demonstrated using the de-polluting concrete, the presence of other gas pollutants released the generator (CO, CO_2, VOCs) did not affect the NO_2 abatement. Final tests were also done by decreasing the residence time of the gas pollutants into the garage. As detailed in [12], the NO_2 abatement varies as a function of the residence time and decrease by 38% NO2 as the residence time is divided by a factor three. This last parameter was taken into account for planning bigger field-tests.

4. Pilot tests in a chimney of a motorway tunnel

4.1. Spray of the de-polluting mortar on the walls of the ventilation plant

The test done to assess the depolluting effect of the activated carbon mortar took place in 2014 at the top of a chimney of a motorway tunnel, which is located in the region of Lyon (one of the biggest cities of France). The length of this 4-ways tunnel is 1750 m and its traffic is about 50000 vehicles per day. The polluted air coming from the tunnel is extracted by five chimneys topped by a ventilation plant. Each ventilation plant can be separated in three distinct rooms: inlet room, fan room and outlet room (as detailed in Figure 4). The roof of the outlet room is partially open to release the polluted gas into the atmosphere.

The field test undertaken in September 2014 consisted in spraying more than 125 m^2 of de-polluting mortar on the walls of the inlet room. The final thickness of the layer of mortar was about 2 cm. As shown by the pictures of Figure 4, the activated carbon mortar was sprayed on the four walls of the inlet room (inside volume close to 200 m^3). Note that the turbulent polluted gas coming from the chimney is supposed to be in contact with the walls of the inlet room covered by the depolluting mortar, before being ejected into the outlet room thanks to the three extractors located in the fan room.

The methodology of measurements was scheduled to monitor the NO2 concentrations in the inlet and outlet rooms, before and after the spray of the de-polluting mortar. During the tests, the NO_2 concentrations were measured by regularly positioning at least six absorbent sensors (Radiello® code 166) in each room at a height of at least 45 cm and at less than 1 m from the air ejection. The validity of the measurement by these sensors was checked by the following experiments:

1. The data given by this type of sensor were previously validated during the pilot tests done in the garages by using an automatic gas analyzer, where we observed a good agreement between the two measurement methods.
2. Another test was performed recently inside the inlet room of the tunnel chimney to compare the Radiello® sensor and an automatic gas analyzer located at the same position. The NO2 concentration given by the sensor (942 µg/m3) was in good agreement with the average measured with the automatic NOx analyzer (991 µg/m3).
3. During the different tests, 2 sensors were positioned side by side to check the variability of the measurement. The average difference observed between two sensors located side by side is 6 %.

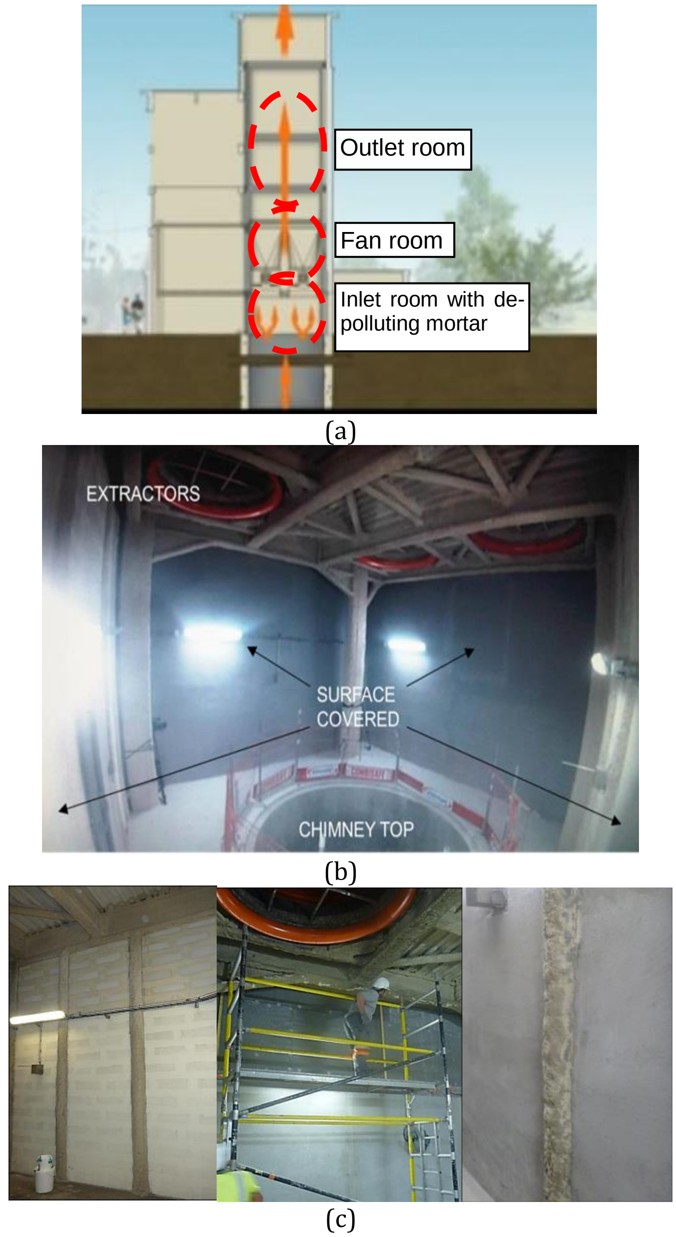

Figure 4. Field test done for a motorway tunnel: (a) schematic of the ventilation plant (the NO2 concentrations were measured in the inlet and outlet rooms at the top of one of the chimneys); (b) inlet room (6.3x6.3x5m) where the walls were covered by a de-polluting mortar; (c) photos before, during and after spray of the de-polluting mortar (from left to right).

A few series of tests detailed on Table 2 were carried out between 2014 and 2015 to measure the de-polluting effects obtained by the application of the mortar. Note that the tests were performed at a slow ventilation rate. One of the three fans was regulated in manual configuration at 300 rds/min, while the two others were closed. This allowed for an average air speed of 1.6 m/s with variations 1.4 to 1.8 m/s in the inlet room and a sufficient residence time for the air pollutants to react with the de-polluting walls.

Table 2. De-polluting tests undertaken using the garages made of reference concrete or activated carbon concrete.

Test series	T (°C) *	RH (%)*	NO_2 level (µg/m3) *	Traffic (vehicles per hour)	Sensor exposure time (in hours)
One month before spraying the mortar	28	No data	421	1700	18h
One month after spraying the mortar	21	64	450	Max 2000	6h
One month after spraying the mortar	20	62	600-653	Max 4000	18h and 53h
Five months after spraying the mortar	9	38	453	No data	6 h
Seven months after spraying the mortar	14	48	937	No data	3 h

* measured in the inlet room

4.2. Results one month before and after mortar application

Figure 5 compares the NO_2 concentrations measured in the inlet and outlet rooms, before and after the spray of the de-polluting mortar. All the absorbent sensors used to monitor the NO_2 concentrations were exposed for 18h to the pollutant gas flow. The levels of concentrations detected in the inlet room were similar to the one measured in the outlet room before the spray of the de-polluting mortar (according to the uncertainty of measurement), giving an average value close to 600 µg/m^3 of NO_2. However, the level of NO_2 concentrations measured in the outlet room decreased drastically after the spray of the de-polluting mortar in the inlet room, reaching an average value close to 200 µg/m^3 (for a NO_2 reduction rate of about 60%). Even if the comparison at two similar but different testing periods of time has to be taken cautiously, a significant effect of the material was observed on NO_2 concentration confirming the previous results obtained in lab and in the garage prototypes.

Figure 6 shows the NO_2 concentrations measured into the inlet and outlet rooms after the spray of the mortar in the inlet room. Several absorbent sensors were continuously exposed to the polluted gas flow for distinct periods (from 6h to 53h). In every case, the NO_2 concentrations detected into the outlet room were lower than the ones measured in the inlet room.

The average NO_2 reduction rate in 24h measured is of 48% with some variations observed depending on the exposure duration. Considering the concentrations measured during the longest periods of exposure (from 18h to 53h) characterized by a high traffic (peak close to 4000 vehicles per hour), the NO_2 reduction rate could reach over 60%, which is close to the rate calculated from the concentrations measured before and after the spray of the activated carbon mortar (see Figure 6). On the other hand, the NO_2 reduction goes down to 32 %, considering only the values measured for a period of 6h (9AM-3PM) characterized by a low traffic (maximum of about 2000 vehicles per hour), which could reduce the concentrations detected in the inlet room (and thus under-estimate the NO_2 reduction rate). Thus the higher the NO_2 concentration the more effective is the depolluting material. This may be explained by the fact a higher NO_2 concentration induces that more NO_2 gas penetrates faster into the material and react with it.

These first results about the NO2 reduction rate measured in this field test should be considered cautiously. Indeed, they were measured a few weeks after the spray of the activated carbon mortar. Other sets of measurements were then scheduled in order to confirm the robustness of the de-polluting effect.

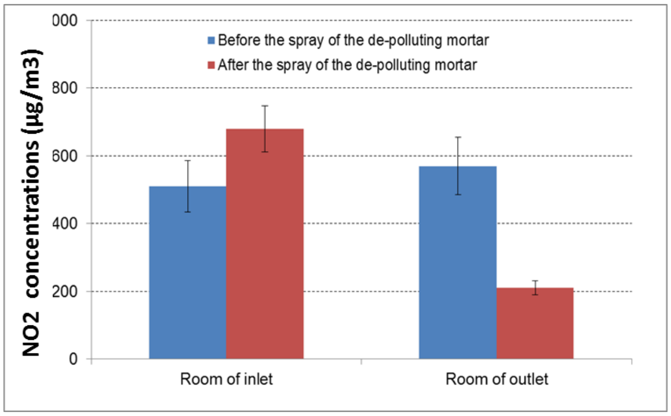

Figure 5. NO2 concentrations measured in the inlet and outlet rooms, before and after the spray of the de-polluting mortar (the absorbent sensors were exposed for 18h to the polluted gas flow).

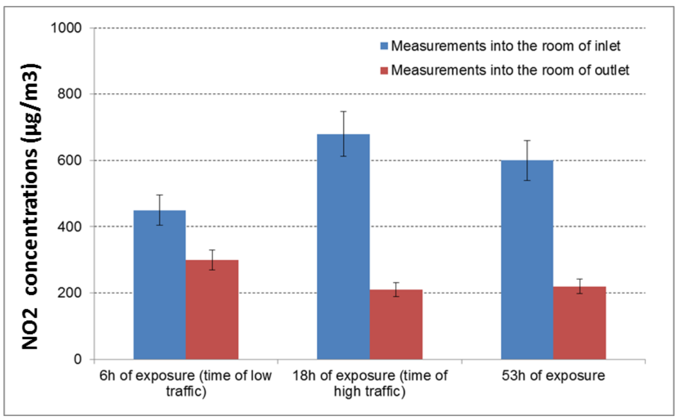

Figure 6. NO2 concentrations measured in the inlet and outlet rooms after the spray of the activated carbon mortar in the inlet room; the absorbent sensors were continuously exposed for different time durations (from 6h to 53 h).

4.3. Results measured five and seven months after the application of the mortar

Other tests done five and seven months after the application of the spray mortar, confirm the significant reduction rate of NO_2 due to the action of the de-polluting mortar containing activated carbon.

After 5 months, the level of pollution measured in the inlet room (Figure 7) was a bit higher than the ones measured previously but it may be due to a more intense traffic. However, the reduction rate of NO_2 deduced from the measurements done in the inlet and outlet rooms was similar to the ones measured one month after the application of the de-polluting mortar. The results after 5 months of test thus do not highlight any sign of saturation of the material as it was observed from the lab previous experiments (Figure 1).

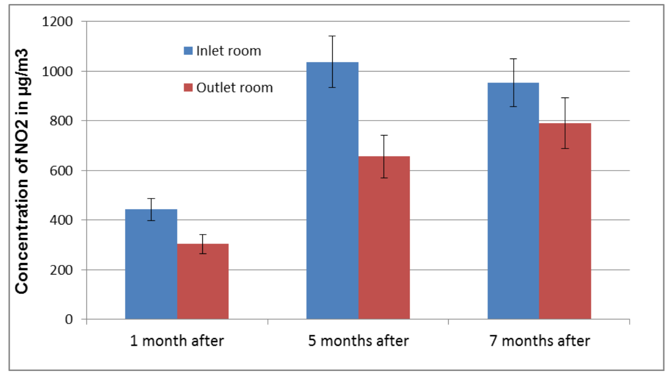

Figure 7. NO2 concentrations measured in the inlet and outlet rooms, 1, 5 and 7 months respectively, after the spray of the activated carbon mortar in the inlet room; the absorbent sensors were continuously exposed for 6h for the 1 and 5 months trial and 3h for the 7 months trial.

A decrease is detected after 7 months, but the NO_2 abatement of about 20 % is still significant. It is important to remind that the material is exposed to conditions where the pollution is particularly concentrated. It is thus possible to anticipate that the de-polluting effects should last for years in more common applications such as underground parking lot, where the NO_2 concentration is about 5 times lower. Tests after one year of exposure are being scheduled to confirm if the material gets saturated over time. In that case, a solution can be to wash the material with water and collect the nitrite and nitrate ions formed by reaction of gaseous NO_2 in the mortar [11]. This is a way to reactivate the de-polluting effect induced by the material.

4.4. Error measurement assessment

The fiability of the measurements with the Radiello® sensors was assessed by the following tests done during the last campaign:

1. Comparison with an automatic NOx analyzer: a test was performed inside the inlet room of the tunnel chimney to compare the Radiello® sensor and an automatic gas analyzer located at the same position. The NO_2 concentration given by the sensor (942 µg/m3) was in good agreement with the average recorded by the automatic NOx analyzer (991 µg/m3). Note that a peak over 1200 µg/m3 was observed in the middle of the rush hours, showing that the NO_2 concentration can strongly vary with traffic.
2. In four different locations of the inlet and oulet rooms, two sensors were positioned side by

side to check the variability of the measurements. The average differences observed between two sensors located side by side in the inlet room is 5.5 %, which is an acceptable error. The mean error in the outlet plenum is a bit higher (6.8%). This is probably due to the fact that the oulet room is in semi-open conditions where the air flux is more random.

3. According to the fabricants, the measurement with Radiello® sensor is difficult with air speeds higher than 10 m/s. The air speeds in the chimneys were also monitored using two anemometers located at the same position of two NO2 sensors. The average recorded is 1.6 m/s, all the values being comprised between 1.4 m/s and 1.8 m/s. It shows that the ventilation worked regularly during the tests.

These tests show some variability of the NO_2 measures, which remains acceptable for a full-scale pilot in real conditions.

5. Conclusion

The objective of this paper was to validate at a higher scale the laboratory-scale experiments showing that the addition of specific activated carbon powders to the cement paste increases durably the NO_2 reduction rate. Pilot-scale tests done with both garages built respectively in reference concrete and activated carbon concrete confirmed the general conclusions drawn from laboratory-scale tests: NO_2 reduction rates of 20-25% were measured in the activated carbon concrete garage whatever the weather conditions and after one year of carbonation while the reference garage gave almost no absorption.

Moreover, it was demonstrated that spraying a porous de-polluting mortar (containing activated carbon powder) can enhance the de-polluting effect (reaching a NO_2 reduction rate of 40-45% in certain conditions) even in presence of other gaseous pollutants (CO_2, CO, VOCs) released by a generator. The tests performed into the garages helped us to plan a test at a higher scale in a motorway tunnel.

This field test consisted in monitoring NO_2 before and after spraying about 125 m^2 of de-polluting mortar on the walls of the inlet room of the ventilation plant located at the top of a chimney of a tunnel located in the south-east of France. The first results confirm a significant NO_2 reduction rate by about a factor 2 by comparing the concentrations measured in the outlet room of the ventilation plant. The more recent results are also encouraging, since no decrease had been observed before 6 months of continuous exposure in the urban tunnel.

Future experiments are planned to model the long-term evolution of the de-polluting effect under various exposure conditions of ventilation in this tunnel where the traffic can reach about 50000 vehicles per day. Thanks to these encouraging results, other field tests are now on-going in different parking lots in Spain.

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