NO_2 AND VOCS DEPOLLUTION IN GARAGE PROTOTYPES USING INNOVATIVE CONCRETES AND MORTARS

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ABSTRACT
Air pollution produced by road traffic is an issue for public health and is responsible for the rise of acute respiratory diseases in urban areas. Some of the most toxic air pollutants, composed of nitrogen oxides (especially nitrogen dioxide, NO_2) and volatile organic compounds (VOCs), are significantly detected in the poorly ventilated areas. The depolluting cement-based materials studied by LafargeHolcim do not rely on photo-catalysis and function without sunlight, which is especially suitable for use in polluted confined areas (such as tunnels or parking garages). The experiments carried out in the laboratory demonstrated that an addition of activated carbons into concrete and mortar improved the absorption properties of these noxious gases without affecting their mechanical properties and durability. Two parking garages of 18 m^3 were built with internal walls made of depolluting concrete (or coated by a depolluting mortar) to measure their performances. The tests conducted using a gasoline-based generator (to produce a cocktail of air pollutants) confirmed a significant reduction of the NO_2 rate and noticeable abatements of certain VOCs (such as benzene and toluene).
Keywords: air pollution, NOx, VOCs, concrete, mortar, activated carbon, parking garage.

1 INTRODUCTION

Because each human being breathes about 15,000 L of air per day, minimizing the air pollution is essential to maintain a good life quality in urban areas and to reduce the risks of respiratory and cardiovascular diseases [1]–[4]. A poor air quality is a result of a number of factors, mostly including pollutants emissions coming from the combustion of fossil fuels. Indeed, motorcycles, cars and trucks traffic is responsible of the main hazardous gaseous pollutants emissions, such as nitrogen oxides (NOx), but also of a part of VOCs emissions. Indeed, the development of new depolluting materials that could reduce the NOx and VOCs concentrations in confined areas (such as in the garages of the commercial/office/residential buildings, but also in motorway tunnels) could improve the air quality [5], [6].

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 [7]. In addition, the activated carbons are known to be excellent adsorbents for NO_2 [8] and can be added to the mix of mortar and concrete without affecting their mechanical properties and intrinsic durability [9]. It was also proved that cement paste containing activated carbon additive could adsorb certain types of VOCs [10]. The validity of the solution at a lab scale was demonstrated previously and the challenge is now to prove that it works in-situ in real pilot tests.

The objectives of this paper consist in presenting the NO_2 and VOCs reduction rates measured in instrumented parking garage with internal walls made of depolluting concrete or coated by a depolluting mortar.

2 CEMENT-BASED DEPOLLUTING MATERIALS

It is well established that NO_2 can react in alkaline aqueous solutions to give nitrite and nitrate ions [11], [12]. The most strongly alkaline phases like calcium hydroxide ($Ca(OH)_2$) and

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Calcium Silicate Hydrates (C-S-H) of the hydrated cement pastes showed a high absorption capacity but this effect is temporary [7]. Indeed, the NO_2 reduction rate by the reference cement paste is affected by carbonation caused by atmospheric CO_2: this gas converts the highly alkaline hydrates to calcium carbonates [13], which are less reactive with NO_2. Previous laboratory-scale experiments [7], [14] showed that the addition of a small rate of activated carbon (AC, SA2 from Cabot Corp.) powder into the cement paste increases the NO_2 reduction rate (even in presence of ambient concentrations of CO_2) and prolongs the depolluting effect. According to these previous works, we hypothesized [7] that the NO_2 absorption in the alkaline cement pastes could be governed by two consecutive phenomena: (i) NO_2 physisorption on the activated carbon (AC) powder; and (ii) reaction of the adsorbed NO_2 with the alkaline pore solution of the surrounding cement paste, which depends on its carbonation.

Thanks to the results using hydrated cement pastes obtained in laboratory, new depolluting concrete and depolluting sprayed mortar were both designed using an AC powder/cement ratio of 0:015. The overall porosity of these depolluting concrete and mortar (measured by mercury intrusion porosimetry) was close to 15 and 30%, respectively.

3 TESTS CONDUCTED IN PARKING GARAGES

3.1 Description of the instrumented parking garages

Two garages made of concrete (4.0 × 2.0 × 2.2 m; Fig. 1) were built: one using reference concrete (without activated carbon), and another one using the depolluting concrete. The volume was about 18 m^3 for an exposed internal surface area of 18 m^2 (the ceiling and floor were insulated by sticking a plastic-based liner). The residence time of the gases was

Figure 1: External and internal views of the instrumented parking garages.

estimated to about 14 minutes according to the ventilation conditions used. After performing the sets of tests to compare the NO_2 and VOCs reduction rates between the reference and the depolluting concrete, one of the garages was refurbished by spraying a depolluting mortar on the internal walls.

A petrol-engine generator was used to inject a cocktail of air pollutants (relatively similar to the ones released by the road traffic) into the garages. Whether for the NOx or VOCs abatements measurements, the generated pollutants were fully screened. For the NOx abatement experiments, the concentrations were measured every 5 minutes using an automatic gas analyser (AC32M from Environnement SA, based on the chemiluminescence method).

The analysis of the VOCs was a two-steps passive measurement: the VOCs sampling was performed using Radiello® tubes followed by an analytical analysis (as described in literature [15]). In fact, two different chemical Radiello® tubes (Radiello® Code 165 and Radiello® Code 145) were used to trap the aldehydes and non-aldehyde VOCs, respectively. Fig. 2 details the 26 most abundant species detected in the reference garage (in order of their mass concentrations, showing more than 90% of the total VOCs mass). The experimental configuration (confined volume) induced high amounts of benzene and toluene but the nature of detected pollutants was consistent with literature [16].

3.2 NO2 reduction rates measured in the parking garages

Table 1 compares the NO_2 reduction rates measured during the different tests, according to: (i) the concentrations injected at the input of the garages, and (ii) the conditions of temperature and relative humidity (RH). By comparing the concentrations measured at the input and output of the garage, no significant absorption of NO_2 was detected in the reference garage while an abatement of 20–25% was observed in the garage made of depolluting concrete (even in presence of the other gases released by the generator such as VOCs, CO, CO_2, etc.).

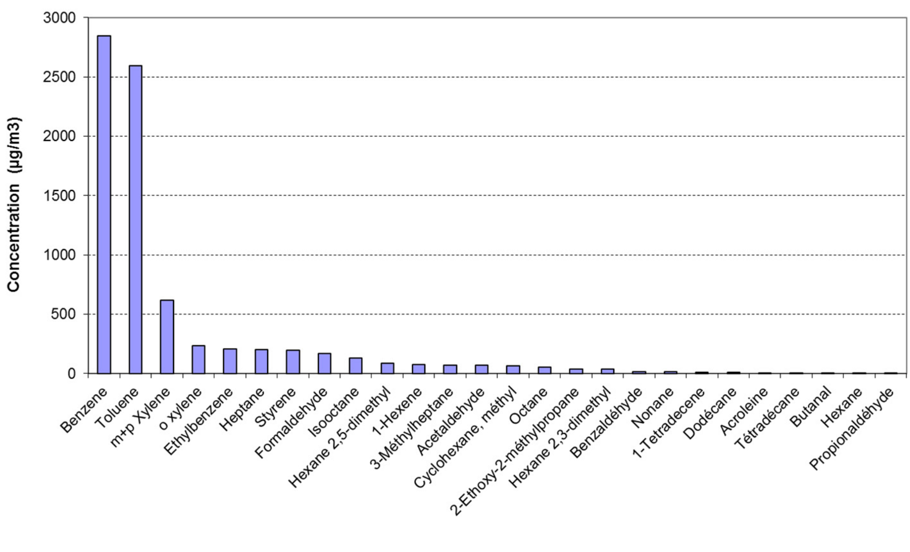

Figure 2: Concentration (µg/m^3) of the 26 most abundant VOCs collected after one hour of measurement in the reference garage.

Table 1: Depolluting tests undertaken using the parking garages.

Materials	Experimental conditions and results					
	Exp.	T (°C)	RH (%)	Input NO_2 concentration (µg/m³)	Output NO_2 concentration (µg/m³)	NO_2 absorption rate (%)
Reference concrete	A	24	39	421	407	<3
	B	22	53	382	382	<3
Depolluting concrete	C	27	32	453	346	24
	D	27	32	937	688	26
Depolluting mortar	E	31	29	721	402	44
	F	24	52	604	335	45
	G	28	34	717	411	42
	H	20	71	476	279	41

The absence of NO_2 abatement in 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 (as already shown using laboratory experiments [7], [9]). On the other hand, carbonation did not affect the NO_2 abatement detected in the garage made of depolluting concrete (supporting the previous laboratory scale measurements [7], [14]). Moreover, the solutions leached from the walls of the garages were analysed by ion chromatography after the gas absorption tests. The results showed that almost no nitrate or nitrite in the leachate coming from the reference concrete but significant levels of nitrates and nitrites in the leachate coming from the depolluting concrete yet below the water quality standards [10].

Higher NO_2 reduction rates (close to 40%) were measured in the refurbished garage where about 18 m² of internal walls were coated by a depolluting mortar (containing activated carbon and showing a higher overall porosity than the depolluting concrete). Fig. 3 details the measurements done during the experiment "H" (see Table 1). A reduction rate of 41% was calculated by comparing the NO_2 concentrations measured at the inlet and at the outlet of the garage.

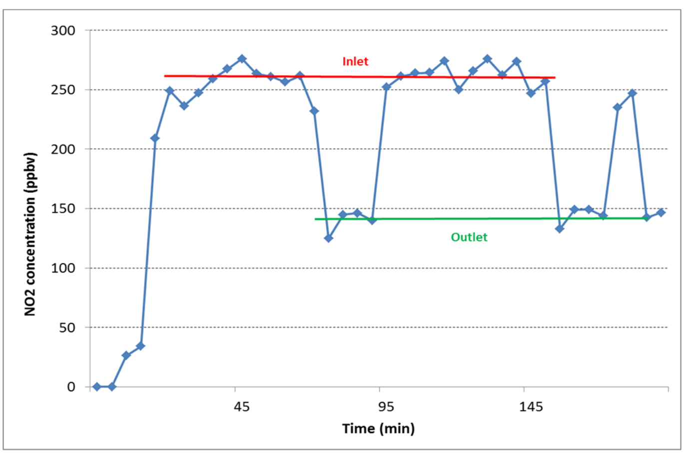

Figure 3: Example of NO_2 concentrations measured in the garage: experiment "H" with internal walls coated by a depolluting mortar (1 ppbv = 1.912 µg/m³).

3.3 VOCs reduction rates measured in the parking garages

The VOCs tests were performed within four campaigns over a period of one year which allowed us to cover different relative humidity (from 24% to 86%) and temperature (from 4°C to 33°C) conditions. The Radiello® tubes were exposed as long as the petrol-engine generator was operating (from 30 to 150 min). Note that for an inlet NO_2 concentration of 200 ppbv, the inlet concentrations of VOCs varied from 460 µg/m³/h (total aldehydes) to 4111 µg/m³/h (total aromatic pollutants).

Table 2 summarizes the difference of the main VOCs reduction rates in favour of the garage made of depolluting concrete (compared to the reduction rates measured in the reference garage). For each type of VOC, the reduction rates were then more significant in the garage made of depolluting concrete than in the garage made of reference concrete. These abatements were averaged over three tests campaigns gathering different weather conditions. The concrete containing activated carbon allows a better aldehyde rate reduction of 11% and a better aromatic VOCs rate reduction of 22% (e.g. 38% for benzene).

Some desorption tests were undertaken (Radiello® tubes exposed in the garage after the end of the adsorption tests). No specific release was detected after five days for the six main pollutants adsorbed by the depolluting concrete garage (benzene, toluene, ethylbenzene, styrene, 2, 3, 4 trimethyl pentane, heptane). However, non-negligible releases were observed for ethyltoluene and trimethylbenzene.

4 CONCLUSION

The objective of this paper was to validate at a higher scale the laboratory experiments showing that the addition of activated carbon powder in cement-based materials can durably increase the NO_2 reduction rate, and to a lesser extent, the VOCs adsorption.

Pilot-scale tests done in garages prototypes confirmed the general conclusions drawn from laboratory-scale tests: NO_2 reduction rates of 20–25% were measured in the garage made of depolluting concrete (even after more than one year of carbonation) while the reference garage gave almost no proof of abatement.

Table 2: Difference of reduction rates in favour of the garage made of depolluting concrete (compared to the VOCs reduction rates measured in the reference garage).

VOCs	Inlet rate (µg/m³/h)	Improvement of reduction rates in favour of the depolluting concrete (%)
Formaldehyde	255	11
Acroleine	15	56
Benzene	829	38
Heptane	108	18
Pentane, 2, 3, 4-trimethyl-	69	41
Toluene	1570	16
M+p xylene	771	16
o-Xylene	253	24
Ethyltoluene	82	34
Trimethylbenzene	60	52

Improvements of VOCs reduction rates (of 11% for aldehydes-based pollutants and 22% for aromatic compounds) were highlighted using depolluting concrete whatever the weather conditions. Moreover, it was demonstrated that spraying a porous depolluting mortar can enhance the depolluting effect (reaching a NO_2 reduction rate of 40–45%) even in presence of other gaseous pollutants released by the petrol-based generator.

These tests done into the garages helped us to plan another test at a higher scale in a road tunnel. Future experiments are also planned to model the long-term evolution of the depolluting effect under various exposure conditions of ventilation.

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