Proceedings of the 4th International Conference on Environmental Pollution and Remediation
Prague, Czech Republic, August 11-13, 2014
Paper No. 65

NOx De-pollution Using Activated Charcoal Concrete - From Laboratory Experiments to Tests with Prototype Garages

Matthieu Horgnies, Florence Serre, Isabelle Dubois-Brugger, Ellis Gartner
Lafarge Centre de Recherche
95, rue du Montmurier, Saint Quentin-Fallavier, France
matthieu.horgnies@lafarge.com; florence.serre@lafarge.com; isabelle.dubois-brugger@lafarge.com;
ellis.gartner@lafarge.com

Abstract **-** Nitrogen oxides released by car traffic affect the health of numerous people located in urban areas. This study shows that concrete doped with activated charcoal can absorb NO_2 and could be used to limit the pollution peaks in confined spaces. Samples of cement hydrates and hardened cement paste were exposed to air flows containing hundreds of ppbv of NO_2 and the absorption rate was measured. It is shown that pieces of concrete can continue to absorb a significant fraction of the NO_2 gas passing over their surfaces for long periods of time due to a reaction with the alkaline cement hydrates. Moreover, the presence of a small fraction of activated charcoal in the cement paste significantly improves and prolongs the adsorption of NO_2, especially in the presence of typical atmospheric CO_2 levels; and this additive is effective over a the whole range of typical exposure temperatures for concrete. Pilot-scale tests using prototype garages built with activated charcoal concrete confirm the continued absorption of NO_2 even in presence of other pollutants released by a petrol-engine generator. Subsequent leaching of the walls followed by ionic chromatography analyses show that the absorbed NO_2 gas is mainly converted to nitrate ions in the concrete.

Keywords**:** NOx, De-pollution, Activated charcoal, Concrete, Urban area, Prototype garage.

1. Introduction

Automotive traffic produces hazardous gaseous pollutants such as nitrogen oxides (NOx), which affect the health of numerous people living in urban areas (Mitchell et al., 2007; Blondeau et al., 2005; Wilkins et al., 2001). Thus, the development of de-polluting building materials able to significantly reduce NOx pollution in confined spaces (tunnels or underground parking) is a great challenge.

The main binding phase in concrete is hardened cement paste, which is a porous alkaline material rich in calcium hydroxide ($Ca(OH)_2$) and Calcium Silicate Hydrates (C-S-H) (Taylor, 1997; Odler, 2003; Allen et al., 2007). It has a high specific surface area, similar to that of oxides used for NOx adsorption in catalytic converters (Epling et al., 2004; Liu and Gao, 2011). We have previously shown that NO_2 is absorbed by ordinary hardened cement pastes at ambient temperatures because of its alkalinity (Horgnies et al., 2012; Krou et al., 2013). In addition, activated charcoals are reportedly excellent adsorbents for NOx (Gao et al., 2011; Jeguirim et al., 2004; Muckenhuber and Grothe, 2006; Yang et al., 2009; Zhang et al., 2008).

The main purpose of the present study was to establish NO_2 absorption rates for pure anhydrous and hydrated cement phases and for activated charcoal powder, in order to better understand the mechanism of action of the two together in hardened concrete. The influences of ambient temperature and atmospheric carbonation were investigated to estimate how these parameters would affect the absorption rate. Finally, NO_2 absorption rates were compared in two prototype garages, made with ordinary and activated charcoal concretes, in order to quantify the benefits of the activated charcoal concrete in a life-scale confined space.

2. Materials and Methods

2.1. Cement-based Materials

The two main hydrated phases created by the hydration of Portland cement are calcium hydroxide ($Ca(OH)_2$, also called portlandite,) and Calcium Silicate Hydrate (C-S-H). C-S-H is an amorphous, micro-porous colloidal phase of variable composition. Its average composition in fresh concrete is close to $(CaO)_{1.7}(SiO_4)(H_2O)_4$ but it loses water on drying. Both of these phases are highly alkaline and thus react rapidly with atmospheric CO_2 at the surface of concrete, a process called “carbonation.” This process proceeds very slowly but can ultimately convert all of the calcium in portlandite and much of the calcium in the C-S-H to calcium carbonate (which in turn leads to a decrease in the Ca/Si ratio of the C-S-H). In this study, reagent-grade $Ca(OH)_2$ was obtained from Sigma-Aldrich, Germany, and three different types of C-S-H were prepared by stirring CaO (Sigma-Aldrich, Germany) and silica (Aerosil 200, Degussa, Germany) together in water for long periods. The Ca/Si ratios of these three C-S-H preparations were 0.9, 1.5 and 1.7. After drying, all these phases were stored under vacuum to prevent any carbonation. An ordinary Portland cement (CEM I 52.5, Lafarge, France) was used to make cement pastes. A peat derived, steam-activated charcoal (SA2 from NORIT SA, Netherlands), was also used. The BET specific surface area of this activated charcoal (AC) was 695 m^2.g-1. In comparison, the BET specific surface areas of the C-S-H and cement paste samples were closer to 100 m^2.g-1.

Two types of hardened cement pastes were tested. Reference hardened cement pastes (R-HCP), were prepared by mixing 0.45 parts of water per 1 part of cement. Other hardened cement pastes (AC-HCP) were made with additions of activated charcoal (0.005 parts per part of cement), keeping the same water/cement (W/C) ratio. Previous work had shown that the addition of AC powder did not affect significantly the microstructure and the mechanical strengths of the cement pastes (Horgnies et al., 2012). Thin samples of hardened cement pastes, referred R-HCP-CO3 and AC-HCP-CO3 respectively, were subjected to an accelerated carbonation process (flow of 10% CO_2/90% N_2 gases at 90% RH). After 28 days of carbonation, tests done using phenolphthalein indicated a pH of less than 9 throughout the carbonated cement pastes, indicating effectively complete carbonation.

Finally, two prototype garages (dimensions: 4.0*2.0*2.2 m, **Fig. 1**) were built using reference and activated charcoal concretes, respectively. The volume was 17.6 m^3 for an exposed surface area of 17.6 m^2 (a part of the surfaces, especially the ceiling and floor, were insulated by sticking a plastic liner). The concretes were manufactured from Portland cement, limestone fillers, sand, gravels and admixtures (superplasticizer). Activated charcoal (AC) was added to the mix of depolluting concrete at an AC/cement ratio of 0.015. No special treatments were applied to the surfaces of these concretes after demoulding.

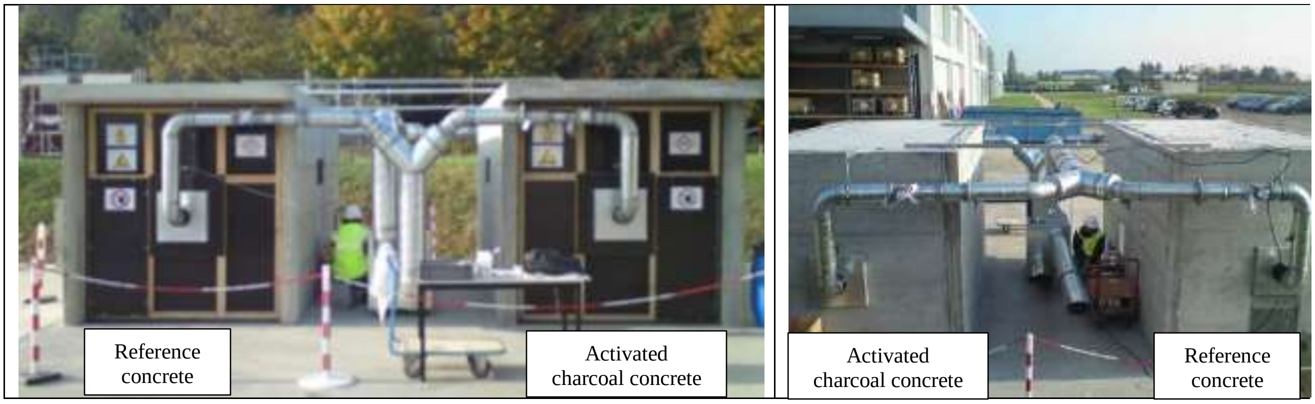

Fig. 1. Prototype garages at scale 1.

2.2. NOx Absorption Measurements

For experiments done in laboratory (**Fig. 2**), the system used two bottles of gases (from Air Liquide, France). The first bottle contained 1 ppm of NO_2 and 2 ppm of NO into nitrogen; this gas flow was mixed with gas from a second bottle containing pure nitrogen (N_2) gas. The N_2 gas was humidified to 60% relative humidity (RH) using a saturator before being mixed with the NOx and was then injected into a cylindrical reactor (made of quartz, volume of 1500 cm^3). A second such reactor without any samples inside was used as a reference reactor to give a baseline. An automatic NOx gas analyser ($AC_{32}M$ from Environnement SA, France, based on the chemiluminescence method) was coupled with the outlet of the reactor to measure the

NOx concentrations every two minutes. During the tests, the polluted gas injected was composed of 110 ppbv of NO_2 and 220 ppbv of NO. A residence time of 3.6 minutes was deduced from the ratio between the reactor volume and the gas flow rate (420 cm^3/min). The NOx absorption rates obtained with the different powders were studied using a specific modification of the substrate-holder described in a previous publication (Krou et al., 2013).

For experiments done in prototype garage, the system used one bottle of gas (from Air Liquide, France) containing 1 ppm of NO_2 and 2 ppm of NO in nitrogen. These gases were diluted with ambient air before being injected into the garages. The flow of polluted gas could be switched alternately to either garage with a residence time estimated to 14 minutes. In certain experiments, the NOx bottle was replaced by a petrol-engine generator, allowing simultaneous injection of multiple pollutants (NOx, CO, CO_2, VOCs, etc.), similar to gases released by automobile traffic. The automatic NOx gas analyser was alternatively coupled to the inlet or the outlet duct of the garage. Measurements of NOx concentration were done every 5 minutes.

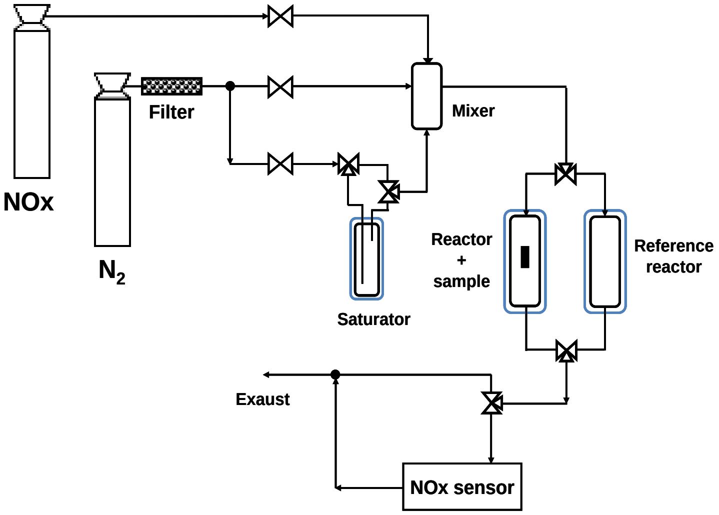

Fig. 2. Gas absorption system in laboratory.

2.3. Analyses by Ion Chromatography after Sample Leaching

The walls of the prototype garages, made of reference or activated charcoal concrete, were leached using a sponge soaked in ultra-pure water. The solutions were recovered by filtration and analysed by ion chromatography to determine the concentrations of nitrite (NO_2^-) and nitrate (NO_3^-) ion. The Spectra-Physics chromatograph consisted of an isocratic pump, a Rheodyne injection valve and a UV detector. The liquid mobile phase used was a solution of acetonitrile, octylamine and diamino-hydrogenophosphate in ultra-pure water. The pH of the mobile phase was buffered to a value of 6.1.

3. Results

3.1. Cementitious Powders

Fig. 3a shows the NO_2 concentrations as a function of time for powder samples of anhydrous cement, $Ca(OH)_2$ and C-S-H. NO_2 absorption by anhydrous cement was less efficient than by powdered $Ca(OH)_2$, C-S-H (1.5) and C-S-H (1.7). $Ca(OH)_2$ powder generally gave the highest absorption rate. For the two C-S-H powders with high Ca/Si ratios (1.5; 1.7), the NO_2 absorption rate was very high for the first 5 hours, while for the low Ca/Si (0.9) C-S-H powder it was about half of those values. After 15 hours, the C-S-H powders with high Ca/Si ratios showed absorption rates similar to $Ca(OH)_2$, whereas the rate for C-S-H (0.9) was barely better than that of the anhydrous cement. These observations confirm the significant role played by alkaline calcium species (presumably calcium hydroxide) in the absorption process. We hypothesize that NO_2 gas dissolves in the approximately two-molecule-thick adsorbed aqueous layer that is believed to cover the alkaline cement hydrates at 60% relative humidity (Baroghel-Bouny, 2007). Consequently, the NO_2

absorption rate should be related to the calcium hydroxide content of the adsorbed water, because it is well established that NO_2 reacted in alkaline aqueous solutions to give nitrite and nitrate ions (Ignarro et al., 1993). The following two disproportionation reactions appear thermodynamically possible:

$$Ca(OH)_2 + 3\ NO_2 \Rightarrow (Ca^{2+}, 2\ NO_3^-) + NO + H_2O \qquad (1)$$

$$2\ Ca(OH)_2 + 4\ NO_2 \Rightarrow (Ca^{2+}, 2\ NO_3^-) + (Ca^{2+}, 2\ NO_2^-) + 2\ H_2O \qquad (2)$$

However, given that excess oxygen is always present, reaction (1) seems unlikely; it is more likely that oxidation of any incipient NO would occur and that more nitrate than nitrite would thus form, overall.

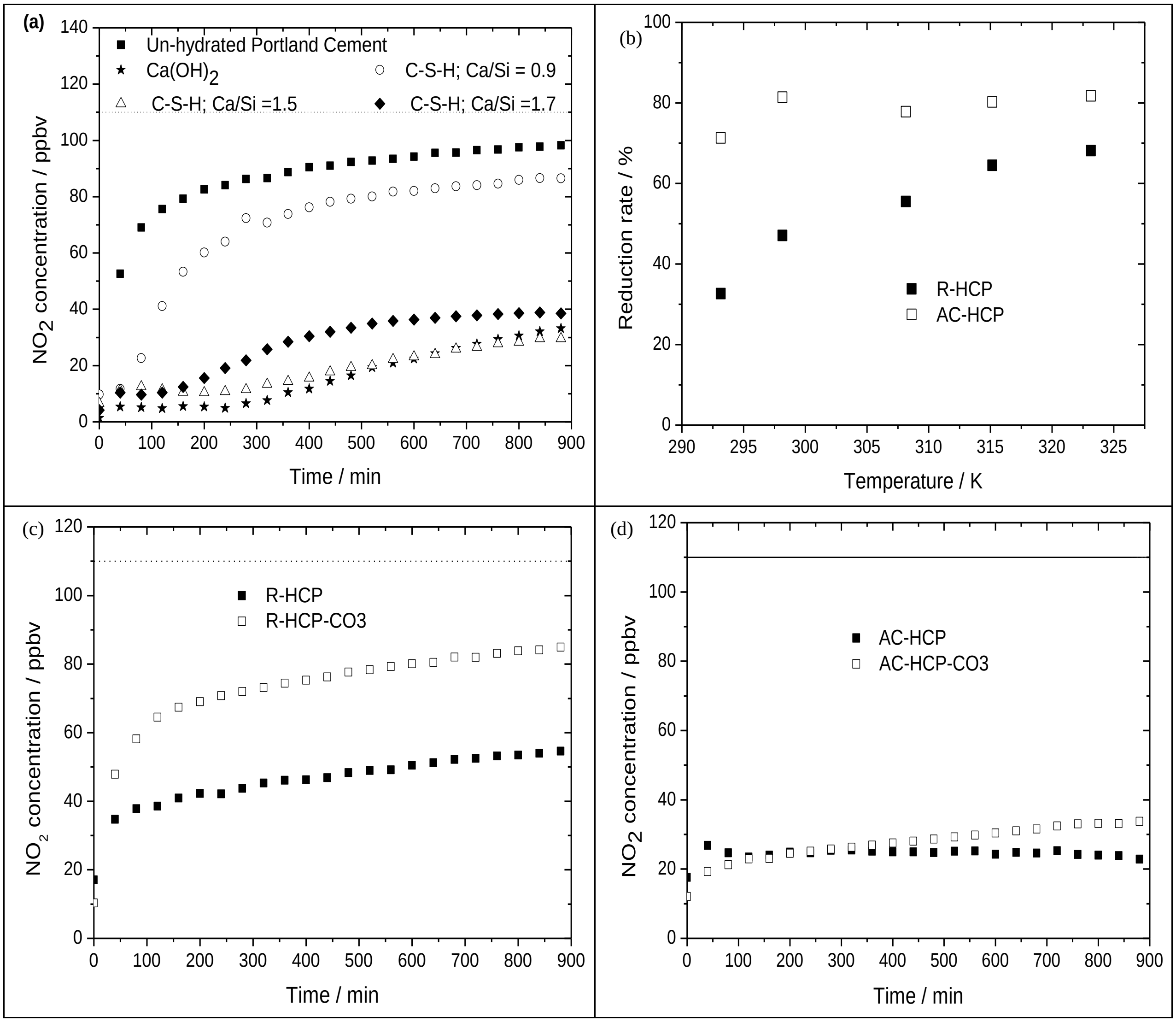

Fig. 3. NO_2 concentrations or absorption rates obtained in the laboratory reactor: (a) using different anhydrous or hydrated cement-based powders, (at 60% HR and 20°C); (b) using reference or AC-based hardened cement paste, (at 60% HR over a range of temperatures); (c) using hardened reference cement pastes, with or without carbonation (at 60% HR and 20°C); (c) using AC-based hardened cement pastes, with or without carbonation (at 60% HR and 20°C).

3.1. Influence of Temperature on the NO_2 Absorption Rate by Hardened Cement Pastes

NOx absorption rates were measured with R-HCP and AC-HCP samples at different temperatures (at 60% RH). No absorption of NO could be detected but, as seen in **Fig. 3b**, the NO_2 absorption rate for the reference cement paste increased with increasing temperature. The rate doubled from 20 to 50°C, indicating that NO_2 physisorption was almost certainly not the predominant mechanism in this case. We hypothesize that NO_2 effectively reacts immediately with R-HCP via reactions (1) or (2), the rates of which should be increased by increasing temperature. Concerning the AC-HCP sample, the NO_2 absorption rate was much higher (about 80%) and remained practically constant between 20 and 50°C. This suggests that NO_2 absorption in alkaline cement pastes containing AC is governed by two consecutive phenomena:

- NO_2 physisorption on the activated charcoal powder,
- reaction of the adsorbed NO_2 with the alkaline pore solution of the surrounding cement paste, which is favoured by the increase of the temperature.

3.2. Effect of Carbonation of Hardened Cement Pastes on their NOx Absorption Rates

Fig. 3c shows the variation of NO_2 absorption rate for the reference cement paste. The R-HCP sample was then able to absorb NO_2 with a absorption rate only 33% lower than the one measured with the $Ca(OH)_2$ powder. This result can be explained by the fact that the hardened cement paste contains, 28 days after demoulding, $Ca(OH)_2$ and C-S-H as major hydrated phases, which are supposed to be responsible for NO_2 absorption. However, the CO_2 present in the atmosphere (at ~380 ppmv) reacts with calcium hydroxide and C-S-H phases to form very stable calcium carbonates, which might affect the durability of the NO_2 absorption process. Indeed, NO_2 absorption experiments were done on R-HCP-CO3 sample. As shown by **Fig. 3c**, the NO_2 absorption rate (22%) was then two times lower with R-HCP-CO3 than with R-HCP.

Activated charcoal is known to have a very high physical adsorption capacity for many gases. NOx absorption experiments were done on AC-HCP sample in the same conditions as described above. **Fig. 3d** shows that a small addition of activated charcoal in the cement paste gave a significant positive effect on the NO_2 adsorption whereas adsorption of NO gas was not detected. The absorption rate was then 1.6 times higher than for the R-HCP. Furthermore, NO_2 absorption rate was very efficient and remained stable during all the experiment. To confirm this hypothesis, NOx absorption experiments were done using only AC powder. The results showed a NO_2 absorption rate close to 95% and stable throughout the exposure time (~5000 min), demonstrating the significant NO_2 sorption capacity of AC powder. The high affinity between NO_2 and AC can easily explain the enhanced NO_2 absorption rates of AC-HCP samples.

Finally, NOx absorption experiments were done using AC-HCP-CO3 to confirm the predominant role of activated charcoal. As shown by **Fig. 3d**, carbonation of the cement paste did not significantly affect the NO_2 absorption rate. After 900 minutes, the absorption rate was about 69% instead of 77% for the non-carbonated AC-HCP sample. This result indicates that the hardened cement paste matrix acts primarily as a dispersing medium and does not greatly interfere with the NO_2-adsorbing properties of the activated charcoal.

Fig. 4 shows the examples of NO_2 concentrations measured into the two prototype garages during over testing periods of about 3 hours and an airflow containing about 600 ppbv of NO_2. The temperature and the relative humidity were about 15-18°C and 40-60%, respectively. By comparing the measured NO_2 concentrations at the input and output of the garage, it appears that no NO_2 was absorbed by the reference concrete. However, an absorption rate of about 25% was observed for the garage made of activated charcoal concrete.

Table 1 summarises the NO_2 absorption rates measured during the different tests on the prototype garages, according to: (i) the type of concrete (reference/activated charcoal-based) constituting the walls; (ii) the NO_2 concentration injected at the input and (iii) the temperature and relative humidity, (depending on the weather). No significant absorption of NO_2 was detected for the reference concrete while a robust absorption rate of about 20-25% was observed for the activated charcoal concrete whatever the experimental conditions and the presence of other pollutants (CO, CO_2, VOCs, etc. released by the generator).

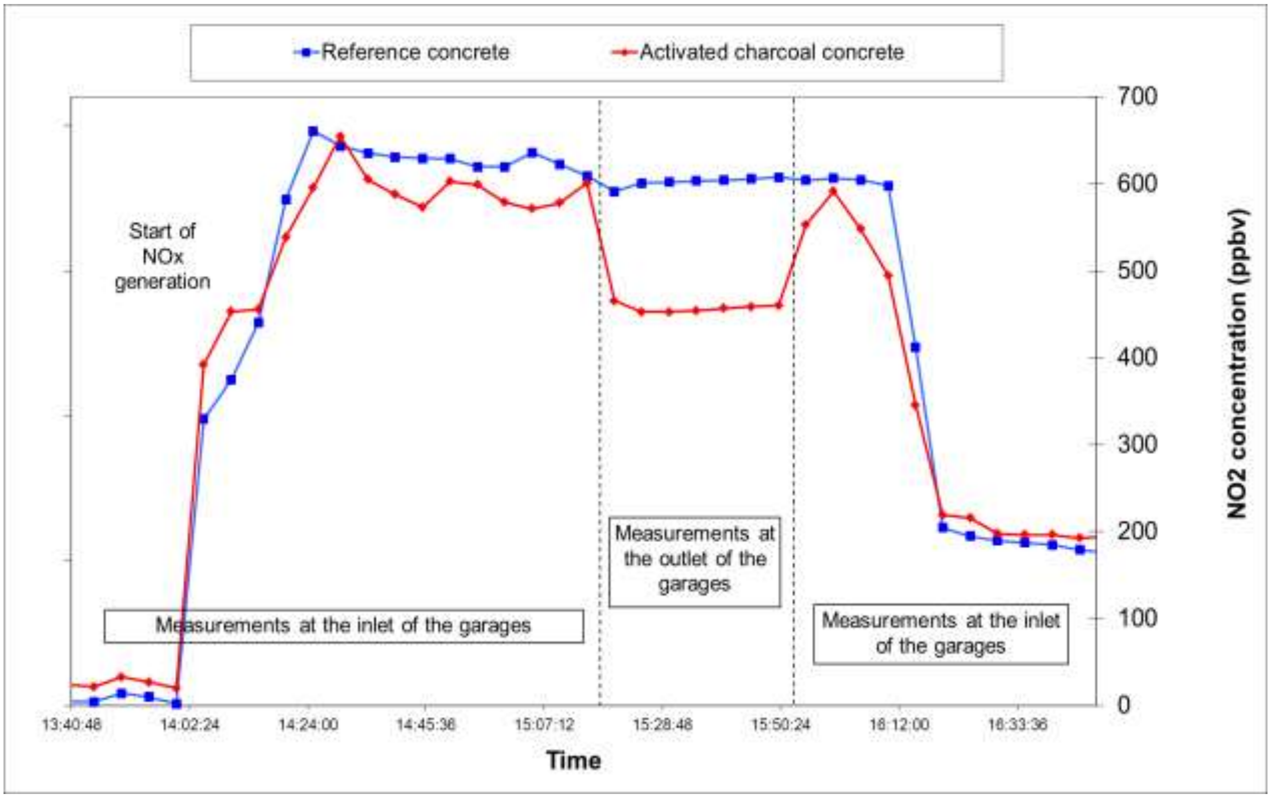

Fig. 4. Examples of NO_2 measurements in the prototype garages.

Table 1. Summary of the results obtained with the prototype garages.

Type of concrete	Age of concrete walls (relating to the carbonation time at ambient air)	Temperature (°C) and RH (%) during the tests	Generation of NOx	NO_2 concentration (ppbv)		NO_2 absorption rate (%)
				input	output	
Reference concrete	~ 3 months	3-4°C / 83-85 %	NOx bottle	105 (+/-3)	104 (+/- 1)	< 1%
				95 (+/-5)	93 (+/- 1)	< 1%
	~ 9 months	22-26°C / 34-45%	Generator	206 (+/-30)	200 (+/-2)	< 3%
				234 (+/-60)	226 (+/-3)	< 3%
	~ 12 months	21-23°C / 49-56%		200 (+/- 35)	200 (+/- 15)	< 1%
Activated charcoal concrete	~ 3 months	1-2°C / 75-88%	NOx bottle	220 (+/- 5)	175 (+/-5)	20%
				215 (+/-20)	165 (+/-2)	23%
				195 (+/-20)	152 (+/-1)	22%
		8°C / 56%		117 (+/-2)	90 (+/-1)	23%
	~ 9 months	15-18°C / 40-60%		600 (+/-50)	450 (+/-2)	25%
				240 (+/-20)	190 (+/-3)	21%
				185 (+/-15)	145 (+/-3)	22%
	~ 12 months	26-28°C / 30-34%	Generator	237 (+/-40)	181 (+/-2)	24%
				234 (+/-60)	182 (+/-2)	22%
				490 (+/-40)	360 (+/-5)	26%

The absence of absorption for the reference concrete can be explained by the presence of CO_2 in the atmosphere as well as by prior carbonation of the walls, which tends to reduce the reactivity of NO_2 with the alkaline medium. On the contrary, the lack of any significant effect of temperature, CO_2 and prior carbonation for the activated charcoal concrete garage supports prior smaller scale laboratory observations.

The solutions leached from the walls of the prototype garages after the gas absorption tests were analysed by ion chromatography. The results, shown in **Table 2**, show almost no nitrate or nitrite in the leachate from the reference concrete, but significant levels of nitrates (about three orders of magnitude higher) in the leachate from the AC concrete. The nitrate level in this leachate was also about 50x higher than the nitrite level.

Table 2. Nitrite and nitrate concentrations measured by ionic chromatography in the leaching solutions coming from the walls made of reference concrete and activated charcoal concrete.

Leachate / ion detected	Nitrites (NO_2^-) (mg/l)	Nitrates (NO_3^-) (mg/l)
From the walls of the reference concrete	0.04	< 0.02
From the walls made of activated charcoal concrete	0.28	13.20

4. Conclusions

Hydrated cement phases typical of the cement paste in hardened concrete can absorb a large amount of NO_2 gas from the surrounding atmosphere at similar rates over a wide range of conditions when exposed as powders. The most strongly alkaline phases, i.e. $Ca(OH)_2$ or C-S-H (with Ca/Si = 1.7), seem to have the highest absorption capacities.

In comparison, the rate of absorption of NO_2 by solid hardened cement paste specimens varies more as a function of temperature and exposure history. Carbonation by atmospheric CO_2 converts the highly alkaline hydrates to calcium carbonates, which are less reactive, so the NO_2 absorption rate can be greatly reduced.

Laboratory-scale experiments show that the addition of small percentages of activated charcoal (AC) powder to the cement paste boosts its NO_2 absorption, reduces its dependence on temperature and carbonation degree, and tends to prolong the depolluting effect.

Pilot-scale tests done with a pair of prototype concrete garages made with and without AC added to the concrete confirmed the general conclusions drawn from laboratory-scale tests:

- under the flow conditions tested, NO_2 absorptions of 20-25% were measured in the AC-concrete garage under both winter and summer weather conditions, while the reference garage gave almost no absorption.
- the depolluting effect of the AC concrete seems to be robust versus temperature, relative humidity and also the presence of other gaseous pollutants (CO_2, CO, benzene, toluene, formaldehyde) released by a generator.

Ion chromatography analyses of surface leachates showed that the absorption of NO_2 gas results in the creation mainly of nitrate ions in the concrete, with much smaller amounts of nitrite.

Future experiments are planned to model the very long-term evolution of the depolluting effect under various exposure conditions, and to study the influence of the state of the concrete surface.

Acknowledgements

The authors would like to thank TERA Environnement (Crolles, France) and the Institute of Chemistry of Poitiers: Materials and Natural Resources (ICP2M, UMR 7285 CNRS, France) for their helps during the experiments.

References

Allen A.J., Thomas J.J., Jennings H.M. (2007). Composition and density of nanoscale calcium-silicate-hydrate in cement, Nature Materials, 6, 311-316.

Baroghel-Bouny V. (2007). Water vapour sorption experiments on hardened cementitious materials Part I: Essential tool for analysis of hygral behaviour and its relation to pore structure, Cem. Concr. Res., 37, 414-437.

Blondeau P., Iordache V., Poupard O., Genin D., Allard F. (2005). Relationship between outdoor and indoor air quality in eight French schools, Indoor Air, 15, 2-12.

Epling W.S., Campbell L.E., Yezerets A., Currier N.W., Parks J.E. (2004). Overview of the fundamental reactions and degradation mechanisms of NOx storage/reduction catalysts, Catal. Rev. Sci. Eng., 46, 163-245.

Gao X., Liu S., Zhang Y., Luo Z., Ni M., Cen K. (2011). Adsorption and reduction of NO_2 over activated charcoal at low temperature, Fuel Process. Technol., 92, 139–146.

Horgnies M., Dubois-Brugger I., Gartner E.M. (2012). NOx de-pollution by hardened concrete and the influence of activated charcoal additions, Cem. Concr. Res., 42, 1348–1355.

Ignarro L.J., Fukuto J.M., Griscavage J.M., Rogers N.E., Byrns R.E. (1993). Oxidation of nitric oxide in aqueous solution to nitrite but not nitrate: Comparison with enzymatically formed nitric oxide from L-arginine, Proc. Nat. Acad. Sci., 90, 8103-8107.

Jeguirim M., Tschamber V., Brilhac J.F., Ehrburger P. (2004) Interaction mechanism of NO_2 with carbon black: effect of surface oxygen complexes, J. Anal. Appl. Pyrolysis, 72, 171–181.

Krou N.J., Batonneau-Gener I., Belin T., Mignard S., Horgnies M., Dubois-Brugger I. (2013). Mechanisms of NOx entrapment into hydrated cement paste containing activated charcoal – Influences of the temperature and carbonation, Cem. Concr. Res., 43, 51-58.

Liu G., Gao P.-X. (2011). A review of NOx storage/reduction catalysts: mechanism, materials and degradation studies, Catal. Sci. Technol., 1, 552-568.

Mitchell C.S., Zhang J., Sigsgaard T., Jantunen M., Lioy P.J., Samson R., Karol M.H. (2007). Current state of the science: health effects and indoor environmental quality, Environ. Health Perspect., 115, 958-964.

Muckenhuber H., Grothe H. (2006). The heterogeneous reaction between soot and NO_2 at elevated temperature, Carbon, 44, 546–559.

Odler I. (2003). The BET-specific surface area of hydrated Portland cement and related materials, Cem. Concr. Res., 33, 1049-2056.

Taylor H.F.W. (1997). Cement Chemistry, 2nd ed., Thomas Telford Publishing, London.

Wilkins C.K., Clausen P.A., Wolkoff P., Larsen S.T., Hammer M., Larsen K., Hansen V., Nielsen G.D. (2001). Formation of strong airway irritants in mixtures of isoprene/ozone and isoprene/ozone/nitrogen dioxide, Environ. Health Perspectives, 109, 937-941.

Yang J., Zhuang T.T., Wei F., Zhou Y., Cao Y., Wu Z.Y., Zhu J.H., Liu C. (2009). Adsorption of nitrogen oxides by the moisture-saturated zeolites in gas stream, J. Hazard. Mater., 162, 866-873.

Zhang W.J., Bagreev A., Rasouli F. (2008). Reaction of NO_2 with activated charcoal at ambient temperature, Indust. Eng. Chem. Res., 47, 4358-4362.