Cement and Concrete Research 42 (2012) 1348–1355

Contents lists available at SciVerse ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

NO_x de-pollution by hardened concrete and the influence of activated charcoal additions

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ARTICLE INFO

Article history:
Received 16 April 2012
Accepted 21 June 2012

Keywords:
Adsorption (C)
Concrete (E)
Characterization (B)
Microstructure (B)
NO_x de-pollution

ABSTRACT

The atmospheric pollution by nitrogen oxides affects the health of millions of people located in urban areas. Our work demonstrates that, even in the absence of photocatalysts, concrete walls can strongly absorb NO_2 and limit the intensity of pollution peaks. Our results show that concretes can continuously absorb a significant fraction of NO_2 from the surrounding atmosphere over long periods, probably due to a reaction with strongly alkaline cement hydrates. Moreover, the introduction of a small amount of activated charcoal into the concrete mix can significantly enhance and prolong this NO_2 absorption without greatly increasing total porosity or decreasing strength. We hypothesize that the NO_2 is adsorbed irreversibly by a neutralization reaction with the alkaline aqueous solution covering the surfaces of the hydrates and the activated charcoal. Simple calculations suggest that walls made of activated charcoal concrete could ameliorate the problem of NO_2 pollution peaks in road tunnels and parking garages.

1. Introduction

Environmental pollution is an important issue with respect to sustainable development [1,2]. Nitrogen oxides (NO_x) are common toxic gaseous pollutants produced by combustion processes, and especially by automotive traffic. They affect the health of hundreds of millions of human beings, especially in urban areas. The term "NO_x" represents two separate molecular species: nitrogen dioxide (NO_2) and nitric oxide (NO). According to the World Health Organization (WHO), NO_2 is the more toxic of these two gases [3]. It is also a precursor of ozone, which is the other major toxic atmospheric pollutant in urban areas [4,5]. These hazardous gases readily diffuse into buildings [6,7] and contaminate tunnels and underground car parks [8].

It has been suggested that NO_x pollution in cities or on roads could be treated by photocatalysts such as titanium dioxide (TiO_2) and zinc oxide (ZnO) [9–11]. Under UV-irradiation, these particles create hydroxyl radicals that can oxidize NO to NO_2, the latter gas being potentially more readily removed from the atmosphere by mineralization after a series of reactions [12,13]. Photocatalytic reactions of this type were first discovered in Japan [14] in the 1970s and they have been widely studied ever since as an approach to treating both indoor and outdoor air pollution [15]. Pigments based on the anatase form of titanium dioxide have been incorporated into concretes to create so-called "photocatalytic" or "self-cleaning" walls and pavements, such as those described by Beeldens and Van Gemert [16], Ballari et al. [17] and by Maury Ramirez et al. [18]. The idea of using this approach to reduce NO_x pollution has been discussed by Poon and Cheung [19], Hassan et al. [20] and Guerrini [21]. However, the potential of these photocatalytic systems to de-pollute the outdoor atmosphere has not been clearly demonstrated [22,23]. Folli et al. [24] recently observed apparently photocatalytic removal of both NO and NO_2 from gases passed over white cement mortars containing TiO_2 powders. They observed no detectable increase in NO_2 corresponding to the observed decrease in NO, which is different from what is observed with pure TiO_2 powders. They interpreted this as being due to the stabilization of both nitrite and nitrate ions due to the high pH of the cement matrix.

Despite much recent interest in photocatalysis, the reaction between NO_x and ordinary concretes has not been studied in detail, although it is known that NO_2 can easily dissolve in basic aqueous solutions [25] to produce nitrites and nitrates. Only a few authors (Spicer et al. [26], Wade et al. [27], Gröntoft and Raychaudhuri [28], Yamanaka [29] and M. Nicolas [30]) have dealt with the question of how adsorption or absorption of pollutants by residential materials can influence the indoor atmosphere. We believe that the preliminary study described in this paper is the first specifically devoted to the quantification of NO_x absorption by ordinary concretes.

In addition, we will describe tests that confirm our contention [31] that the incorporation of activated charcoal into a fresh concrete mix can greatly enhance the absorption rate of NO_2 by the hardened product. Activated charcoals and other activated carbons are among the best known of industrial adsorbents. They are widely used to decontaminate water by adsorbing organic residues such as pesticides [32], or to

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doi:10.1016/j.cemconres.2012.06.007

decontaminate air by adsorbing mercury [33] and other hazardous vapors [34]. Stavropoulos et al. [35], Yi et al. [36] and Seo et al. [37] have established that activated carbon can be used effectively to remove many volatile organic compounds (VOC) from the indoor atmosphere.

In this paper, the properties of a concrete containing activated charcoal are investigated and its NO_x de-polluting performance is compared to those of an ordinary concrete and a reference building stone (dolostone). Finally, the NO_x absorption rates measured are used to estimate the magnitude of the de-polluting effect considering the volumes of an underground parking garage and a road tunnel.

2. Experimental

2.1. Materials

2.1.1. Activated charcoal powder

Activated charcoal (AC) was manufactured from peat and was activated under water steam. AC (SA2 from NORIT, The Netherlands) was then used as an additive for concrete. The nitrogen BET specific surface area of AC was 695 m^2/g.[1] The particle size distribution of AC was measured by laser granulometry[2]; results are shown in Fig. 1.

2.1.2. Hardened concrete samples

The reference "ordinary concrete" (O-C) mix was a very fluid mix typical of a self-compacting concrete, prepared with an ordinary Portland Cement (CEM I 52.5 PMES from Lafarge, France), mixed with limestone filler, sand (0–4 mm), gravel (5–10 mm), water and a superplasticizer in the mass proportions 1.00:0.51:2.17:1.77:0.55:0.0103. The superplasticizer was a commercial polycarboxylate polyethylene-oxide comb polymer (Optima 206 from Chryso, France) with an active solid content of 21%. An "activated charcoal concrete" (AC-C) was made using the same cement, AC powder, limestone filler, sand, gravel, water and superplasticizer in the respective mass proportions: 1.00:0.015: 0.495:2.15:1.75:0.59:0.0103.

The test samples were prepared by pouring the fresh concrete into 15.0 × 13.5 × 3.0 cm steel molds coated with a vegetable oil (DEM Eco 2 from Chryso) for easy demolding. All samples were removed from their forms after 20 h and curing continued for over a month at 20 °C and 50% relative humidity. These specific conditions of curing were chosen because they are close to those expected during the manufacturing of building facades or walls of parking. The samples were then cut in half to make slices of 1.5 cm in thickness with a final volume of about 0.3 dm^3. As shown in Fig. 2, a surface area of 202 cm^2 of concrete (previously in contact with the mold) was exposed to the atmosphere of the reactor while a thick layer of a polyurethane-based sealer (Pantectonique R51 from Seigneurie-Sigmakalon, France) coated all the other faces of the concrete samples.

2.1.3. Sample made of dolostone

A sedimentary dolostone, comprising mainly calcite ($CaCO_3$) and dolomite, ($CaMg(CO_3)_2$), was used as the reference substrate; it had a total porosity of only 0.8%. The samples were cut to approximately 15.0 × 13.5 × 1.5 cm, the same size as the cut concrete samples, and they were coated in the same way.

2.2. Methods

2.2.1. Slump flow test

The workability of the fresh concrete was determined according to the NF EN 12350 slump-flow (spreading) test 5 min after the start of mixing.

2.2.2. Compressive strength tests

Compressive strength tests were done according to ASTM C39, using 16 × 32 cm cylinders cast from the same mix and moist cured for 7 days after demolding.

2.2.3. Mercury intrusion porosimetry (MIP)

The porosity of the concrete samples was investigated by a mercury intrusion porosimetry technique (Autopore IV from Micromeritics, USA). The pressure range of the porosimeter was from sub ambient up to 400 MPa, covering the pore diameter range from about 360 μm to 3 nm. Tests were carried out on 10 × 10 × 10 mm^3 samples cut from the core of the concrete. The samples were dried in an oven at 45 °C overnight before being tested.

2.2.4. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS)

Selected concrete samples were cut and then polished with ion beam (Cross-Polisher from JEOL, Japan) before being characterized using a high-resolution field-effect gun digital scanning electron microscope (SEM FEG Quanta 400 from FEI Company, USA; using an accelerating voltage of 15 keV and a current intensity of 1 nA). Images of the cross-sections were made in back scattering electron mode (BSE) and polished with ion beam polishing (Cross-Polisher from JEOL, Japan). EDS spectrometry was used to map the distribution of specific elements such as carbon that characterized the activated charcoal.

2.2.5. Description of the de-polluting analyses

The gas flow reactor system used in our study is shown in Fig. 3. The reactor, shown in Fig. 4 was made of fused quartz and had an internal volume of 3.8 dm^3. Details of the reactor and test conditions are given in Table 1. The gas was injected into the reactor via 5 holes to homogenize the flow pattern. NO_x concentrations were measured continuously over 20 h. Considering the ratio of the free (unsealed) surface area of the small samples (202 cm^2) to the free volume of the reactor (3.8 dm^3) minus the volume occupied by the samples (0.3 dm^3), the "effective volume/surface ratio" was 17.3 cm. (Note: this ratio can be considered to be twice the average distance between a molecule in the gas and the active solid surface.)

We mixed two gases (from Air Liquide, France): the first contained 1000 ppbv of NO_2 and 2000 ppbv of NO in a nitrogen carrier, and the second one being pure nitrogen. A portion of the second gas flow passed through a humidifier in order to obtain the desired 60% relative humidity in the final mixture. The desired NO_x concentrations in the mixed gases fed into the reactor were checked by the gas analyzer using a bypass to short-circuit the reactor. This allowed frequent direct comparison of the gases entering and leaving the reactor.

The mixed gas was injected into the chamber containing the solid samples. An automatic NO_x gas analyzer ($AC_{32}M$ from Environnement SA, France, based on the chemiluminescence method) was coupled with the outlet of the reactor to measure the NO_2 and NO concentrations downstream of the reactor. Measurements were recorded every minute. The uncertainty of the measurement was about 1 ppbv (conforming to the norm NF EN 14211 [38]).

The instantaneous percentage reduction in pollutant gas concentration at the reactor outlet, calculated according to Eq. (1), is herein referred to as the "absorption efficiency" (AE) for each individual pollutant (e.g. AE_{NO_2} and AE_{NO}):

$$AE_{pollutant} = \frac{\left(C_0 - C_{sample}\right)}{C_0} * 100 \qquad (1)$$

(where C_0 and C_{sample} are the simultaneous concentrations of the pollutant, at the outlet of the bypass and of the reactor containing the solid sample, respectively). The evolution of these concentrations was followed over a long period of continuous exposure of the sample to the gas flow.

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[1] Measured at −196 °C after first degassing at 200 °C for 4 h, using a BET surface area analyzer from Micromeritics Tristar II 3020, Norcross, USA.

[2] Mastersizer 2000, Malvern Instruments, UK.