ATILH
ASSOCIATION TECHNIQUE DE L'INDUSTRIE DES LIANTS HYDRAULIQUES

DECRYPTAGE N°1

Cement and the assessment of volatile organic compound emissions

Volatile Organic Compounds (VOCs): any organic compound with an initial boiling point between 50 °C and 286 °C.

Total Volatile Organic Compounds (TVOCs): the sum of volatile organic compounds whose elution occurs between n-hexane and n-hexadecane included, detected using the ISO 16000-6 method.

Key Points

- **Emission measurements of volatile pollutants from cements in mortar form were carried out according to ISO 16000-11.**
- **Measurements show that cements emit one tenth of regulatory VOC limits.**
- **In the indicative list, published on 21 January 2016, of products falling within the scope of decree No. 2011-321 of 23 March 2011 on the labelling of construction products which give off volatile pollutant emissions, cement and concrete are mentioned as products not covered by the scope of this decree. The standard label is therefore not placed on these products.**

INTRODUCTION

Decree No. 2011-321 of 23 March 2011(9) introduces an obligation to indicate on a label placed on a product or its packaging, the emission characteristics of volatile organic pollutants, once the product is implemented.

The decree of 19 April 2011 (8) on the labelling of construction products gives definitions of volatile organic compounds (VOCs) and total volatile organic compounds (TVOCs), the list of substances consistent with Article R221-27 of the French Environmental Code, the criteria to be measured, the emissivity classes and the characteristics of the label.

Decree No. 2011-321, published in its initial version in 2011, applies mainly to finished products, including precast and cast-in-place concrete products. For cements, only those delivered in bags are concerned.

Further information with regard to labelling procedure can be found on the French Ministry for Territorial Cohesion's "instructions for use" sitepage (http://www.cohesion-des-territoires.gouv.fr/etiquetage-des-produits-de-construction).

A cement is an anhydrous mineral powder manufactured by grinding with an organic milling agent. In order to be incorporated into concrete, said powder must first be hydrated. Anhydrous cement is therefore a "semi-finished" product: attempting to characterise the emissivity of the powder's volatile organic products referred to in the decree would not make any sense. Furthermore, since cement is designed to be used with admixtures in concrete, mortar or cement-based plastering applications, only those volatile organic compounds which contribute to the overall potential emissivity of the final product should be extracted.

It thus appeared necessary to distinguish between the characterisation of bagged cements and that of finished construction products such as concrete, whose placement requires mixing cement, aggregates, water and possibly admixtures.

The decree of 19 April 2011 refers to the series of NF EN ISO 16 000 standards which set out the sampling method for solid, liquid and combined products (Part 11), the test chamber method (Part 9), and the sampling and analysis methods for emitted compounds (Parts 3 and 6). The decree remains unclear about manufacturing conditions of the cement-based test samples.

To provide necessary insight, a parametric study was undertaken to determine the test conditions applicable to the study of specialty cements available in bags so as to characterise their regulatory emission class as provided for by decree No. 2011-321 of 23 March 2011.

In principle, estimating cement's contribution to an overall property of a concrete or mortar (in this case emissivity of volatile organic compounds) is very similar to estimating cement's contribution to the mechanical strength of concrete. As pertains to mechanical strength, the cement industry can only estimate the contribution of cement through a conventional test determining the mechanical strength of a mortar in which cement is the sole variable, all other parameters being held equal (nature and granulometry of the sand, rigidity and internal surface condition of the mould, dimensions of the specimens, sand/cement ratio, water/cement ratio and mixing, placing and preservation conditions).

We therefore proceeded similarly for volatile organic compounds by testing a mortar specimen produced under the conditions of standard NF EN 196-1, i.e. a [standard Sand/Cement] ratio = 3 and a [Water/Cement] ratio = 0.5.

Under these conditions, the influence of the various processing parameters likely to alter the emission of VOCs have to be determined, such as the maturation time (period of time between demoulding and placement in test chamber) and the duration of exposure in the test chamber.

STUDY METHOD AND ANALYTICAL TECHNIQUES

The study was carried out in two stages, the first of which was a parametric study of the placing criteria a priori able to influence outcome on a single quality of common cement, a CEM I according to standard NF EN 197-1, placed without demoulding oil, so as to only obtain the cement's signature.

This preliminary stage made it possible to define the operating conditions used later in the study on bagged cements of different natures.

Preparation of the test specimen

For each placement condition (without demoulding oil), a 16 x 16 x 4 cm test specimen was prepared and introduced directly into the emission test chamber. Without masking any of the specimen surfaces, its emitting surface is equal to 0.069 m^2.

Conditioning in emission test chambern

The test specimens were conditioned under controlled conditions of temperature (23 ± 2 °C) and relative humidity (50 ± 5%) in a glass emission test chamber with a volume of 51 litres, in accordance with the requirements of standard NF EN ISO 16000-9.

VOCs and aldehyde sampling conditions

Sampling and analysis of volatile organic compounds were carried out in accordance with standard NF ISO 16000-6 and those of formaldehyde and other carbonyl compounds in accordance with standard NF ISO 16000-3. VOCs and aldehyde sampling was carried out by pumping them onto a specific adsorbent, before the start of the test (D0), then after 2, 7, 14, 28 and 90 days (± 2 days) of conditioning the test pieces in the emission chamber.

Methods for Measuring VOCs and Aldehyde

The equipment used for VOCs analysis at the CSTB in Grenoble was a Perkin-Elmer ATD400 thermo-desorber and a gas chromatograph (Varian Saturn 3800), coupled with a mass spectrometer (MS) for identification, and a flame ionisation detector (FID) for quantification.

The main identified VOCs were quantified using their own response factor, or by default using the toluene response factor as the sum of identified and unidentified VOCs with the toluene response factor.

PRELIMINARY PARAMETRIC STUDY

Operating protocole

The cement chosen was an CEM I 52.5N-type Portland cement representative of the current cements according to standard NF EN 197-1 on an industrial manufacturing sample with its usual grinding agent.

Mortar formulation (cement-sand-water) was carried out according to standard NF EN 196-1, i.e. with a [Sand/Cement] ratio = 3, a [Water/Cement] ratio = 0.5 and without demoulding oil, in order to only obtain the signature of the cement.

The mortar thus manufactured was placed according to standard conditions in a stainless steel mould defined in standard NF EN 196-1, from which the central partitions had been removed to obtain a prismatic test specimen with effective dimensions of 16 x 16 x 4 cm. After being stored in the mould for 24 hours, the mortar was removed from the mould and placed in maturation conditions by a full immersion in water at 20 °C.

Parameters studied

The parametric study investigated the influence of curing time and the given exposure time at maturity on emissivity:

- **Curing time before test:** 14 and 28 days, under standard conditions (in water at 20 °C). Twenty-eight days is the normative duration used for measuring the mechanical strength of cement; it was chosen as a reference for this reason. With regard to volatile organic compounds, this is a realistic duration because building sites still have a maximum “natural” ventilation (door and window frames already installed being rare instances). The 14-day deadline was chosen to take into account rapid constructive provisions and thus assess a possible impact on the operators present on the site.
- **Exposure duration:** for each of these durations (14 and 28 days), volatile organic compounds emissivity was measured sequentially after increasingly lengthy times in the emission test chamber: 3, 7, 14, 28, and 90 days.

The test specimens were made in the cement producer’s laboratory and sent to the test laboratory under wet conditions and in a sealed bag within the time required to meet the 14 and 28-day durations.

Exposure chamber tests (“wall” exposure scenario) and volatile organic compounds measurements were carried out within the set durations by the CSTB laboratory in Grenoble (Saint-Martin-d’Hères).

- **Parameters measured**

The emissivity characteristics of volatile organic products were measured with reference to the list of 12 compounds set out in the decree of April 19, 2011 (8). The absence of category 1 and 2 carcinogenic, mutagenic or reprotoxic (CMR) compounds as defined in the decrees of April 30, 2009 and May 28, 2009 was also verified.

Units: surface emission factors are expressed in µg/m^2.h, while VOCs exposure concentrations (Cexp) are expressed in µg/m^3.

Results

Test results are expressed in Figure 1 and plotted against the Cexp limit value for formaldehyde which is the most demanding (10 µg/m^3), not counting CMR compounds whose limit is 1 µg/m^3.

It is concluded that the maximum emissivity values are obtained after 28 days of curing and 7 days of exposure. For lengthier exposure times (up to 90 days), a decrease in emissivity is observed. Finally, the values obtained for toluene should be compared with its relevant limit concentration, 300 µg/m^3.

In all cases, all measured concentrations correspond to the A+ emissivity rating defined in decree No. 2011-321 of 23 March 2011 (emission class: very low). Given the absence of demoulding oil, this emission level corresponds strictly to the contribution of cement, with sand considered as non-emitting.

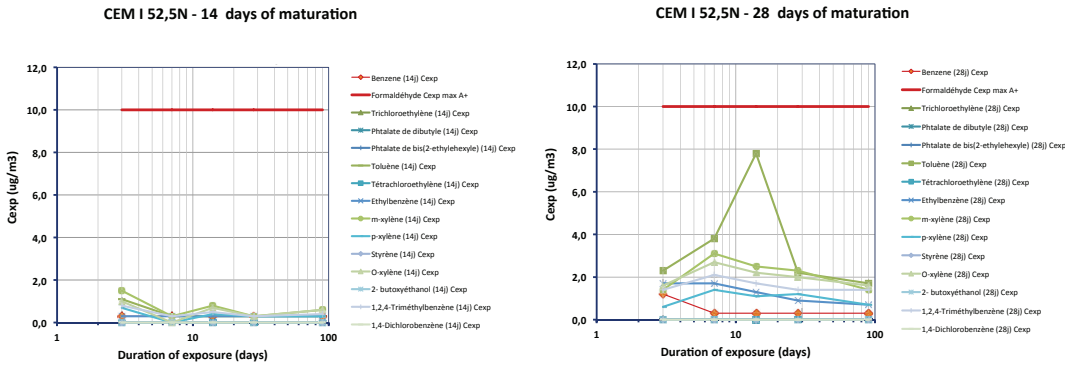

FIGURE 1 - VOCs emissivity as a function of exposure time (3, 7, 14, 28 and 90 days) of cements in EN196-1 mortar form. Left - results after 14 days of curing; right - after 28 days of curing.

For the remainder of the study, specialty cements will be studied under the same conditions (after 28 days of curing and 7 days of exposure), but placed using demoulding oil. This option was chosen in view of the positive results yielded by the preliminary study and the fact that these oils are considered free of volatile organic compounds. Specialty cements were therefore placed under the customary daily quality control conditions.

STUDY OF COMMON AND SPECIALTY CEMENTS IN BAGS

List of binders studied

The binders tested were:

- Natural hydraulic Lime NHL 3.5 CE compliant with standard NF EN 459-1,
- Natural prompt cement CNP PM NF compliant with standard NF P15-314,
- Calcium aluminate cement (CAC) compliant with standard NF EN 14647, and
- Masonry cement MC 12,5 CE NF compliant with standard NF EN 413-1 with air-entraining agent (compliant with standard NF EN 934-2).

All of the samples above were produced through industrial manufacturing, i.e. comprising a grinding-aid agent.

Implementation: Mortar NF EN 196-1 (Sand/Cement = 3, Water/Cement = 0.5) with demoulding oil. The cement samples were made in the producers' respective laboratories and sent to the test laboratory in wet conditions in waterproof bags.

Specimen dimensions: 16 x 16 x 4 cm

Experimental conditions: curing time, 28 days under standard conditions (20 °C in water); measurement deadline, after 7 days in the test chamber.

Parameters measured: emissivity characteristics of volatile organic compounds contained in the 11 compounds set out in the decree of 19 April 2011, and the absence of category 1 and 2 carcinogenic, mutagenic or reprotoxic compounds (CMR), as defined in the decree of April 30, 2009 and May 28, 2009.

Units: surface emission factors are expressed in µg/m^2.h while VOCs exposure concentrations are expressed in µg/m^3.

Results

Emissivity values are expressed in Figure 2 alongside the limit values. It should be noted that in all cases, the results are very far below the limit values, for total VOCs as well as for individual compounds, applied to the binders used in the presence of demoulding oil.

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For all cements tested, the values obtained are compatible with an A+ emissivity rating.

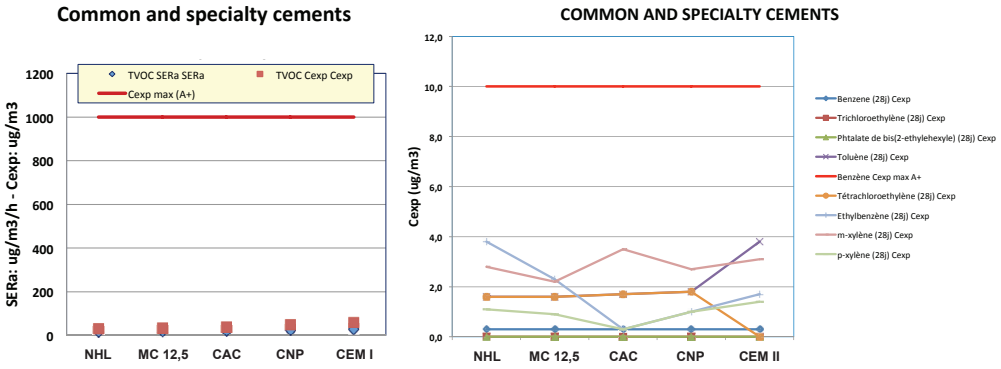

FIGURE 2 - Emissivity values of specialty binders compared to standard cements (CEM I), for total VOCs (left) and individual VOC compounds (right) yielding a non-zero value.

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Conclusion

- **Under the maximum emissivity conditions determined by the parametric study (implementation on mortar, 28 days of curing in water at 20 °C then 7 days of exposure in the emission chamber), the characterization of bagged cements shows that their emissivity class in VOCs is commensurate in all cases to A+ level, the lowest emissivity rate according to decree No. 2011-321 of 23 March 2011 and to the corresponding decree of 19 April 2011.**
- **In addition, the emissions of the test specimens comply with the requirements of the decrees of 30 April 2009 and 28 May 2009 relating to emissions of category 1 and 2 CMR compounds (exposure concentrations at 28 days below 1 µg/m³).**
- **Cement was removed from the products concerned in the 26 January 2016 edition of the *"Indicative list of products falling within the scope of decree No. 2011-321 of 23 March 2011 relating to volatile pollutant emission labelling on construction products or wall or floor coatings or paint and varnish."***

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