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ASSOCIATION TECHNIQUE DE
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DECRYPTAGE N°4

# Cement & concrete: dust emissions

**Inhalable fraction:** sum of an aerosol's thoracic and alveolar fractions
**Thoracic fraction:** subfraction of aerosol particles, median diameter < 10 micrometers
**Alveolar fraction:** subfraction of aerosol particles, median diameter < 4 micrometerss
**Crystalline silica:** sum of a material's pure siliceous content (quartz + cristobalite + tridymite minerals)

## Key Points

- An anhydrous cement is a very fine granular powder mineral material with particle size distributions ranging from 0.2 to 100 micrometers (µm). The proportion of alveolar particles varies with a cement's composition but remains minor.
- The natural or artificial constituents of cement may contain crystalline silica, which is harmful to health when inhaled as fine dust.
- Pure cement (CEM I) and the vast majority of limestone cements (CEM II/LL) and slag cements produced in France (CEM II/A-S and CEM III) do not contain crystalline silica.
- Only slag and ash cements (CEM V) or pozzolanic cements (CEM II/A-P or CEM II/A-M P-LL) are likely to contain a minute fraction of crystalline silica.
- Sanding/drilling hardened concrete can emit dust in varying quantities, making it necessary for individuals to protect themselves.
The alveolar dust fraction also varies and depends directly on the concrete composition. The dust emitted by these treatments may contain a fraction of crystalline silica, very rare in the case of drilling.
- In all cases, the dust emitted by the sanding/drilling of concrete may contain a small proportion of nanoparticles ($d<100$ nm) but cannot be classified as "nanoparticulate" due to a percentage in number far below the set value of 50%.

## INTRODUCTION

Working with pulverulent materials (cement) or processing hardened materials (concrete) creates a potential risk of exposure to the fine particles given off by these materials. It is therefore important to characterise the emission potential of inhalable dusts, especially their alveolar fraction, as well as their potentially toxic element content (crystalline silica) in order to implement appropriate prevention and/or protection measures.

In the light of recent regulatory provisions *(European Carcinogens and Mutagens Directive)* and questions raised by users, a need to carry out measurements characterising these dust emissions, both in terms of their size (inhalable fraction and possible presence of nanoparticles) and their physical constitution (mineralogy), has been identified. The present article has been divided into two sections, that of common cements and their main constituents (unhydrated cements), followed by a characterisation of dust emissions during sanding/drilling treatments on hardened concrete.

Readers should not infer direct link between the characterisations performed here and an occupational exposure context, and even less with an exposure limit value. For anhydrous cements, measurements were carried out to characterise potential risks by identifying, on the one hand, the alveolar fraction liable to be released in indoor or outdoor contexts, as these materials are handled and, on the other hand, their crystalline silica content, without comparing the values to a quantitative threshold.

Tests on concrete are closer to actual conditions without being strictly comparable, given the many parameters affecting exposure conditions.

## CHARACTERISATION METHODS

The characterisation methods were chosen with a view to comparing potential alveolar fraction emissions from different materials in a given situation, not to obtain reference values based on a simulation of exposure conditions. We have nevertheless striven to come as close as possible to the reality of material processing operations, namely the generation of aerosols, in order to simulate the dispersion in the air of anhydrous cements and the treatment of concrete by sanding/drilling operations. Treatments and measurements were carried out under the following conditions:

### Performing the measurements

Measurements were performed in a confined enclosure with a volume of 2.5 $m^3$ ("aerotest" test chamber) inside which were placed the mechanical load and metrology devices. The test volume was connected to a ventilation system with absolute filtration to confine the test, ensure the operator's safety, and lower the concentration of airborne particles until they were completely gone, based on measurements by a Grimm 1.108 optical particle counter.

### Aerosol generation for the cements

Aerosols were generated by placing a 1 kg mass of raw powder in a funnel outside the test chamber connected to a 25 mm diameter tube extending down into the experimental volume at a distance of 55 cm above the impact plate.

### Collecting the alveolar fraction

The alveolar fraction was collected using an individual CIP10-R recovery device, described in Appendix A of standard NF X-262, equipped with an alveolar fraction selector, a particle collection cup and a rotating cup. The collection rate was 10 L/min, maintained 10 minutes after the end of solicitation.

### Analysing the collected samples

- Quantifying alveolar fraction: the alveolar fraction was determined by weighing, using a Sartorius Genius ME254S balance with a measuring range [0.01 g - 250 g], a tolerance of +/- 0.5 mg and a resolution of 0.0001 g.
- Crystalline silica content was calculated by X-ray diffraction (DRX) determination according to standard NF X 43-295 concerning the detection of quartz, cristobalite and tridymite. These dosages are expressed in mg in each sample mass, the limit of quantification being in the order of 10 micrograms (10 µg).

## ANHYDROUS CEMENTS AND THEIR CONSTITUENTS

### Another look at cement composition

Cements are composed of main constituents ranging from 6 to 100% by mass, secondary constituents ranging from 0 to 5% by mass, and di-hydrated calcium sulphate (gypsum, $CaSO_4$, $2H_2O$) as a setting regulator (3 to 6% by mass).

The main constituents are clinker (hydraulic active ingredient produced by burning a mixture of limestone and clay at 1 450 °C) and other constituents of variable hydraulicity, which can be natural limestone, blast furnace slag, fly ash or natural pozzolan, as pure additions or in combinations. These composition criteria are used to classify the 27 cement types set out in standard NF EN 197-1: 1997.

The results presented here concern two CEM I cements (clinker+gypsum) made up of two distinct clinkers, a single MC 12.5 masonry cement (clinker+limestone+ash+gypsum) according standard NF EN 413-1 and a CEM V (clinker+slag+ash+gypsum). The pure constituents were: 3 blast furnace slags and 2 fly ashes produced in France, one limestone, one natural pozzolana and one natural gypsum.

### Results

**Alveolar fraction from cements' aerosols.** For CEM I, CEM I PM-ES (sulphate resisting) cements, and MC 12.5 masonry cement, it varies between 2.1 and 5.5 mg/kg (0.00021 to 0.00055% respectively). CEM V cement has a much higher alveolar fraction (21.4 mg/kg, or 0.00214%).

This result is confirmed by data on alveolar fractions collected from cement constituent aerosols: around 13 to 18 mg/kg for blast furnace slag and 21 to 23 mg/kg for fly ash, much higher than that of CEM I cements (2 to 4 mg/kg).

Limestone, gypsum and pozzolan have alveolar fraction values ranging from 2 to 7 mg/kg, which remain consistent with the CEM I and MC 12.5 masonry cement values. These data are summarised in Figure 1.

**Proportion of crystalline silica** contained in the alveolar fraction is determined by X-ray diffraction, an analytical method that identifies and quantifies the mineralogical forms present. In all cases except pozzolan, crystalline silica is only present as *quartz*. In the case of pozzolan, *cristobalite* is present. Lastly, crystalline silica's third mineralogical form, *tridymite*, was never detected (Table 1).

CEM I cements do not contain crystalline silica, explained by a clinkerisation reaction that combines one part $SiO_2$ with three parts CaO to form tricalcium silicate ($C_3S$), and one part $SiO_2$ with two parts CaO to form bicalcium silicate ($C_2S$). Several studies (1, 2) of industrial clinkers and laboratory clinkers have shown that in all cases, silica, even crystalline silica with grain sizes upwards of 100 µm, is totally "digested" and combined with the available lime to form at a minimum $C_2S$, which may exceed the $C_3S$ amounts present (5, 6).

The alveolar fractions of aerosols formed from CEM V cement and MC 12.5 contain 0.3% and 0.4% crystalline silica, respectively (Figure 1 - quantification in Table 1), attributable to fly ash. Cement constituents including limestone, gypsum, and slag used in the cements tested do not contain crystalline silica, whereas fly ashes (from French power plants) may contain between 0.3 and 1.7%; pozzolan may contain up to 2% of the substance (Figure 2 - quantification in Table 1). These values are representative only of the samples studied and are not typical values, the determination of which would require an exhaustive study.

From a geological standpoint, limestone may contain silica, mostly under the form of innocuous clay minerals. Geological science considers the presence of quartz or crystalline silica in limestone as a "siliceous accident", the most emblematic of which are chalk flints, far from being situationally representative.

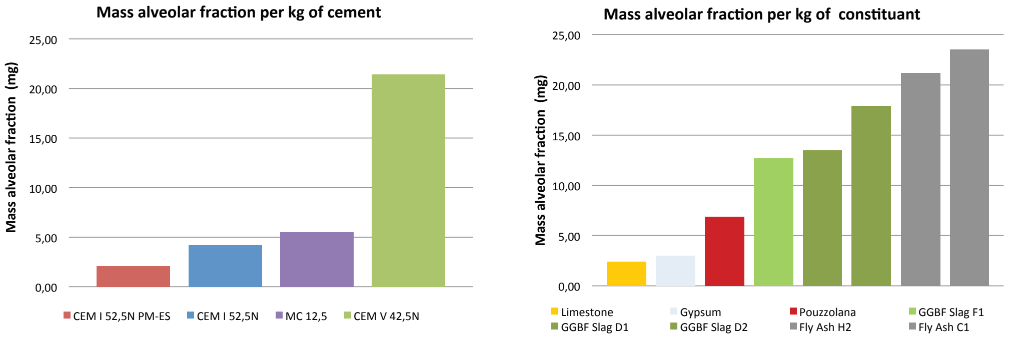


FIGURE 1 - Alveolar fraction (%) of the aerosols of common cements (left) and their constituents (right).

Moreover, crystalline silica is generally speaking a “poison” for the cement industry. A “mechanical poison” for crushing and grinding equipment (vertical and horizontal mills), due to the extremely abrasive nature of quartz in particular, causing excessive wear rates. Silica is also a “chemical poison”, because at the tens of microns scale, quartz particles constitute a considerable local reserve of silica, resistant to calcium saturation due to quantity ratios and calcium’s low mobility.

In conclusion, the proportion of alveolar fraction given off by aerosols depends directly on cement composition, as does the crystalline silica content. Thus, while CEM I type cements contain no crystalline silica, other cement families may contain some, depending on their composition, with the presence of fly ash, blast furnace slag or pozzolan being an indicator of potential occurrence.

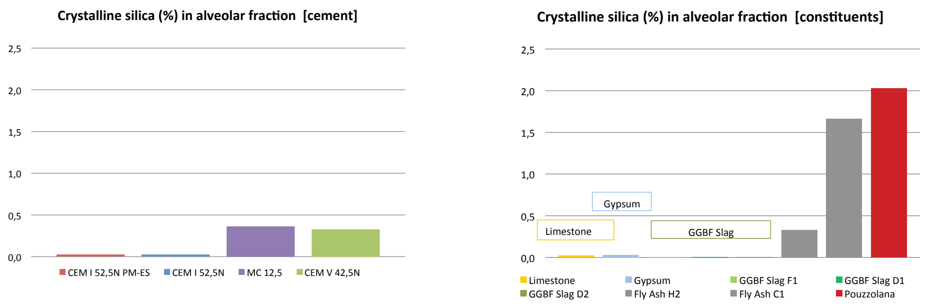
## HARDENED CONCRETE TREATED BY SANDING/DRILLING

### Compositions of the concretes studied

To account for possible variations due to concretes’ different manufacturing regions, we have distinguished four main classes of aggregates and produced four distinct concretes, respectively composed of limestone aggregates, chert aggregates, granitic aggregates and silico-calcareous aggregates.

These formulations are comparable (Table 2): they were manufactured using the same CEM I 52.5N SR3 Vicat cement from the St-Egrève plant (France), and the entire granular skeleton (sand, stone chippings and gravel) is petrographically homogeneous so as to best highlight the crystalline silica sources.

Each of these concretes was cast in the form of a prismatic test mould measuring 28 x 28 x 7 cm and stored for up to 28 days under standard conditions (cured in water at 20 °C then stored in a controlled atmosphere at 20 °C and 65% relative humidity). On day 21, the specimens were sawn into two equal halves (28 x 14 x 7 cm) and



FIGURES 2 - Percentage of crystalline silica alveolar fraction in the cements (left) and in cement constituents (right).

| Nature | Code | Initial mass of analysed powder | | Aerosol mass | Quartz content | Cristo-balite content | Trydymite content | Crystalline silica content | f SC1 (fAlv) |
|---|---|---|---|---|---|---|---|---|---|
| | | g | mg | mg | % | mg | mg | **mg** | % |
| CEM I 52,5N | C1 | 1 000,00 | 1 000 000,00 | 4,20 | 0,00 | 0,00 | 0,00 | **0,00** | 0,0 |
| CEM I 52,5N PM-ES | D2 | 1 000,00 | 1 000 000,00 | 2,10 | 0,00 | 0,00 | 0,00 | **0,00** | 0,0 |
| CEM V 42,5M | A3 | 1 000,00 | 1 000 000,00 | 21,40 | 0,07 | 0,00 | 0,00 | **0,07** | 0,3 |
| MC 12,5 | B4 | 1 000,00 | 1 000 000,00 | 5,50 | 0,02 | 0,00 | 0,00 | **0,02** | 0,4 |
| | | | | | | | | | |
| Limestone | B5 | 1 000,00 | 1 000 000,00 | 2,40 | 0,00 | 0,00 | 0,00 | **0,00** | 0,0 |
| GGBF Slag D1 | A7 | 1 000,00 | 1 000 000,00 | 13,50 | 0,00 | 0,00 | 0,00 | **0,00** | 0,0 |
| GGBF Slag D2 | A8 | 1 000,00 | 1 000 000,00 | 17,90 | 0,00 | 0,00 | 0,00 | **0,00** | 0,0 |
| GGBF Slag F1 | C6 | 1 000,00 | 1 000 000,00 | 12,70 | 0,00 | 0,00 | 0,00 | **0,00** | 0,0 |
| Fly Ash H22 | C10 | 1 000,00 | 1 000 000,00 | 21,20 | 0,07 | 0,00 | 0,00 | **0,07** | 0,3 |
| Fly Ash C1 | A9 | 1 000,00 | 1 000 000,00 | 23,50 | 0,39 | 0,00 | 0,00 | **0,39** | 1,7 |
| Pouzzolana | D11 | 1 000,00 | 1 000 000,00 | 6,90 | 0,00 | 0,14 | 0,00 | **0,14** | 2,0 |
| Gypsum | D12 | 1 000,00 | 1 000 000,00 | 3,00 | 0,00 | 0,00 | 0,00 | **0,00** | 0,0 |

Table 1 - Quantification of crystalline silica in cements and cement main constituents.

| | Sand 1 | Gravel 1 | Gravel 2 | Cement CEM I 52,5N | Water | W/C | S/G |
|---|---|---|---|---|---|---|---|
| | kg/m$^3$ | kg/m$^3$ | kg/m$^3$ | kg/m$^3$ | L/m$^3$ | | |
| Chert concrete | 0/4 C | 4/20 C | | | | | |
| | 895 | 997 | | 300 | 167 | 0,56 | 0.90 |
| Silico-Calcareous concrete | 0/4 SCL | 6.13/10 CL | 11,2/22,4 | | | | |
| | 802 | 349 | 785 | 300 | 172 | 0.57 | 0.71 |
| Granit concrete | 0/4 C | 6/10 CL | 10/20 CL | | | | |
| | 802 | 347 | 779 | 300 | 168 | 0.56 | 0.71 |
| Limestone concrete | 0/4 C | 6/16 C | 16/22,4 | | | | |
| | 808 | 358 | 797 | 300 | 170 | 0,57 | 0,70 |

Table 2 - Comparison of concrete mix design.

sent to two separate laboratories for dust emission characterisation: CSTB Champs-sur-Marne to quantify inhalable fraction and silica content after removing the concrete skin; CEA-PNS for characterising the potential nanoparticle content produced by sanding the skin as well as the test sample's underlying internal mass.

## Sanding and drilling conditions for concretes

**The test samples were sanded** using a concrete sander equipped with a diamond wheel (BOSH Concrete - diameter 125 mm). The test was performed manually for a cumulative time of 35 seconds after removing the skin from the concrete. The CIP collection system was placed at a distance of 1 meter from the test sample. The collection of suspended particles in the volume continued for 10 minutes after sanding was completed. For the "nano-particulate" component, sanding was carried out directly on the concrete skin, then on its inner part after stripping from it a thickness of around 2 to 3 mm.

**The test samples were drilled** using an impact drill with an SDS socket and a 10 mm diameter drill with 3 cutters. The test consisted of 6 holes 5 cm deep, drilled by the operator. The CIP collection system was placed at a distance of 50 cm from the test sample. The collection of suspended particles in the volume was continued for 10 minutes after completion of drilling.

## Dust emitted by sanding hardened concrete

### • Alveolar fraction and its silica content

The alveolar fraction masses collected are relatively significant and range from 3 to 7 mg, with minimum mass being generated by sanding the chert-based concrete and maximum mass by sanding the limestone-based concrete (Figure 3). This result is explained by differences in hardness and therefore in the resistance to sanding of these two materials.

Crystalline silica content was inversely proportional to alveolar fraction emissions of the quartz aerosol, always detected, with *cristobalite* only present in granite in very small quantities (0.08mg); *tridymite* was never detected

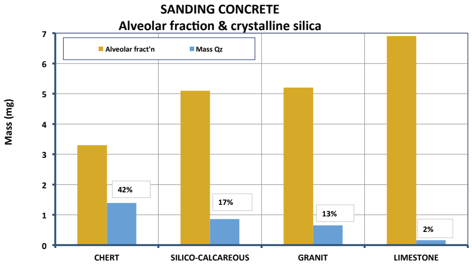


FIGURE 3 - Proportion of alveolar fraction emitted by the concretes and their crystalline silica content

### • Dust emission and particle size distribution

For the four concretes studied, the amount of dust (in number of particles/cm$^3$) emitted by sanding concretes varies greatly from one sample to another and from one configuration to another.

**Concerning sanding of the "skin",** granite-based concrete (400,000 p/cm$^3$) is 4 times more emissive than silico-calcareous based concrete (120,000 p/cm$^3$). Limestone and chert-based concretes are the least emissive (N <50,000 np/cm$^3$) and only chert-based concrete shows roughly 10% of particles below 100 nm (Figure 4, left).

**During "internal" sanding** (inner part underneath the concrete skin), granite-based concrete proves even more emissive (920,000 p/cm$^3$) than other concretes, with dust density remaining below 200,000 p/cm$^3$. Granite and silico-calcareous concretes generated a minor fraction of particles smaller than 100 nm (21 and 3% respectively). For limestone and chert-based concretes, no particles were smaller than 100 nm (Figure 4, right).

The vast majority of the particles emitted have a size distribution in the range of 160 to 220 nm, very similar to that of anhydrous cements. Since the proportion in number of particles smaller than 100 nm was at most 21%, as shown by the particle size distributions in Figure 5, these dusts cannot be classified as "nanoparticulate" under the terms of the "Nano" decree (n°2012-232 of 17 February 2012).

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## Dust emitted by drilling hardened concrete

### • The alveolar fraction and its silica content

Drilling concrete generated a quantity of alveolar fraction much lower (less than 1 mg) than the sanding operation. This result is explained by a worked surface smaller than that used for sanding. Correlatively, the proportion of crystalline silica was, as with sanding, inversely proportional to the quantity of dust generated, ranging from 0.60 to 0.03% (Figure 6, left).)

### • Dust emission and particle size distribution

The quantity of dust emitted by drilling concrete was of the same order of magnitude as dust from sanding the skin. The particle size distribution was roughly centred in the 170-220 nm range. Generally speaking, the concrete drilling operation generated between 3 and 18% nanometric size particles, except in the case of limestone aggregate concrete, which did not generate any (Figures 6 and 7).

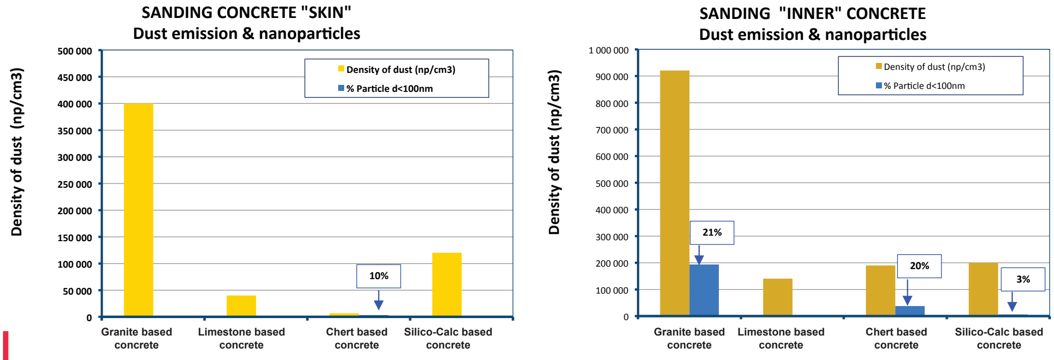

**FIGURE 4 - Sanding concrete: dust emission (np/cm$^3$) and proportion of particles smaller than 100 nm from sanding "skin" (left) and sanding "inner part" (right).** *Y-axis values on the right is twofold those on the left.*

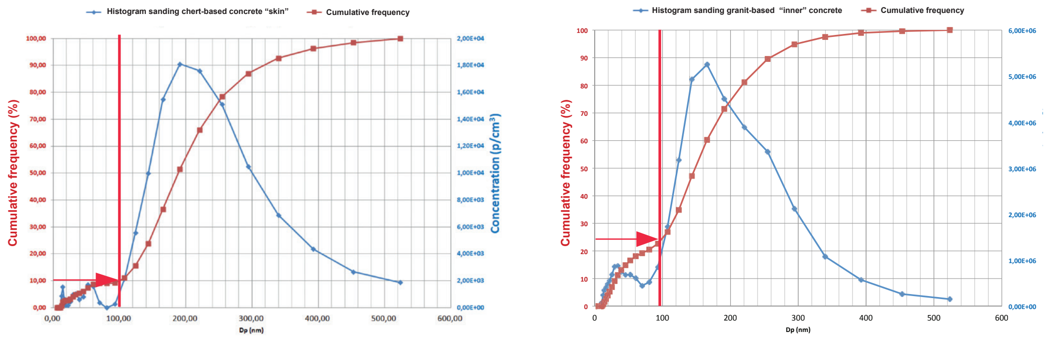

**FIGURE 5 - Sanding concrete: particle size distribution and quantification of % of particles < 100 nm. Left: "skin" sanding of flint-based concrete; right: "inner part" sanding of granite-based concrete.**

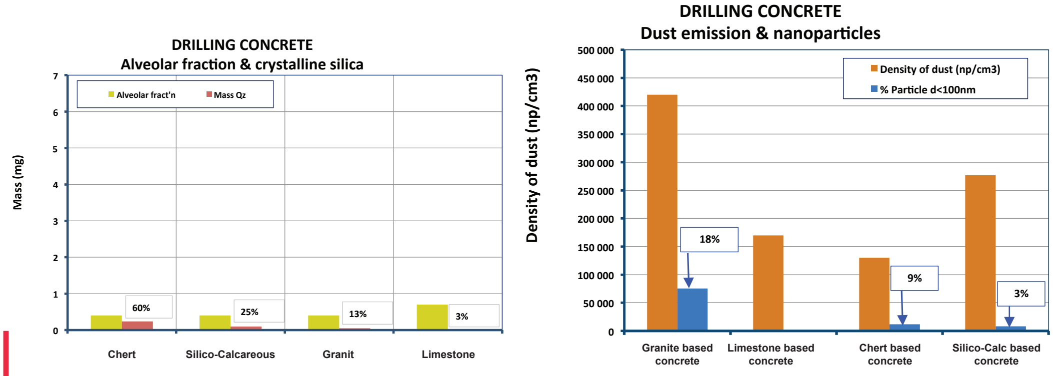

**FIGURE 6 - Drilling concretes: alveolar fraction and crystalline silica content generated during concrete drilling (left); dust emission and nanoparticle fraction generated during concrete drilling (right).**

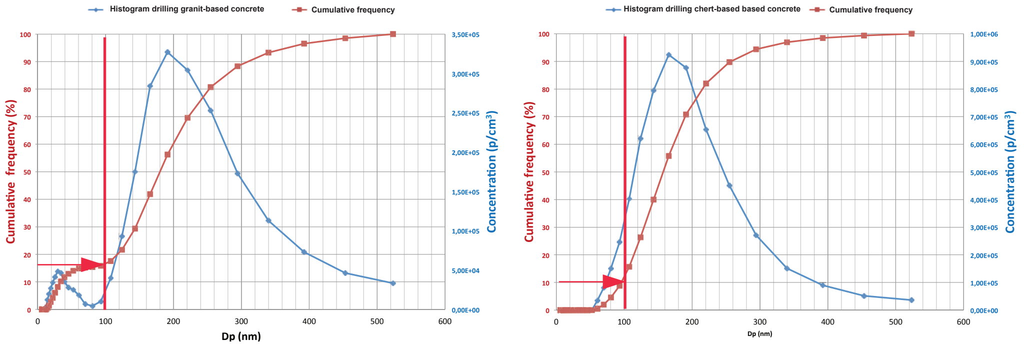

**FIGURE 7 - Drilling concretes: particle size distribution of dust generated by drilling. On the left, the curve for granite-based concrete; on the right, the curve for chert-based concrete.**

## CONCLUSIONS

Characterisation of the dust emitted by anhydrous cements and their constituents, as well as that emitted during the sanding/drilling operations on four concretes based on four different aggregate types covering the major petrographic families found in France, demonstrated that:

- Cement aerosols' alveolar fraction is low (maximum 0.0025%) and directly depends on the nature and proportion of their constituents. The proportion of crystalline silica in the alveolar fraction is zero for CEM I cements and depends essentially on the presence of fly ash and/or pozzolan in other cases.
- The alveolar fraction emitted during concrete sanding/drilling operations depends on the type of operation performed and the type of aggregate used. Crystalline silica content is inversely proportional to the amount of alveolar fraction emitted.
- Dust emitted may contain a small proportion of nanoparticles, except for limestone-based concretes. In these cases, the proportion by number of particles smaller than 100 nm was at most 21%. According to the French "Nano" decree, these dusts are therefore not classified as "nanoparticulates".

These data only constitute the intrinsic characterisation of materials under repeatable lab conditions. Under no circumstances should any link to exposure limit values be inferred, since these exposures have not been characterised and quantified.

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Design: Studio ***201***

Published: DECEMBER 2018

Cover photo:
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## Summary tables of measurements on concrete

- "Crystalline silica" data for concrete sanding/drilling operations

| Ref | Sanding | Alveolar fract'n | Mass Qz | Masse C | Mass Tryd | Cryst.Sil. Tot | % CrSil/ AlvFrac |
|---|---|---|---|---|---|---|---|
| | Unit | mg | mg | mg | mg | mg | % |
| | Detection limit | 0.1 | 3 µg | 3 µg | 3 µg | | |
| | Quantification limit | 0.5 | 10 µg | 10 µg | 10 µg | | |
| 1 | Chert | 3.3 | 1.39 | < 3 µg | 0 | 1.39 | 42 |
| 2 | Silico-Calcareous | 5.1 | 0.86 | < 3 µg | 0 | 0.86 | 17 |
| 5 | Granit | 5.2 | 0.57 | 0,08 | 0 | 0.65 | 13 |
| 3 | Limestone | 6.9 | 0.16 | < 3 µg | 0 | 0.16 | 2 |
| 4 | Blank | | < 3 µg | < 3 µg | | | 0 |

| Réf | Sanding | Alveolar fract'n | Mass Qz | Mass Cb | Mass Tryd | Cryst.Sil. Tot | % CrSil/ AlvFrac |
|---|---|---|---|---|---|---|---|
| | Unit | mg | mg | mg | mg | mg | % |
| | Detection limit | 0,1 | 3 µg | 3 µg | 3 µg | | |
| | Quantification limit | 0,5 | 10 µg | 10 µg | 10 µg | | |
| 6 | Chert | 0,4 | 0,24 | < 3 µg | 0 | 0,24 | 60 |
| 7 | Silico-Calcareous | 0,4 | 0,10 | < 3 µg | 0 | 0,10 | 25 |
| 10 | Granit | 0,4 | 0,05 | < 3 µg | 0 | 0,05 | 13 |
| 8 | Limestone | 0,7 | 0,2 | < 3 µg | 0 | 0,02 | 3 |
| 9 | Blank | | < 3 µg | < 3 µg | | | 0 |

- "Nanoparticulate" data for concrete sanding/drilling operations

| Dust amounts values from graphs cpc | Back-ground | Density of dust ($np/cm^3$) | | | $d_{50}$ (nm) | | | % Particle d < 100nm | | | Visu Particle d < 100nm | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Sand. Skin | Sand. Inner | Drilling | Sand. Skin | Sand. Inner | Drilling | Sand. Skin | Sand. Inner | Drilling | Sand. Skin | Sand. Inner | Drilling |
| Granit based concrete | $1,5x10^4$ | $4,0x10^5$ | $9,2x10^5$ | $4,2x10^5$ | 210 | 160 | 190 | 0 | 21 | 18 | 30 - 50 nm | 30 - 50 nm | + |
| Limestone based concrete | $1,5x10^4$ | $4,0x10^4$ | $1,4x10^5$ | $1,7x10^5$ | 220 | 210 | 230 | 0 | 0 | 0 | - | - | ε |
| Chert based concrete | $1,1x10^4$ | $6,5x10^3$ | $1,9x10^5$ | $1,3x10^5$ | 200 | 140 | 170 | 10 | 20 | 9 | ε | ε | ε |
| Silico-Calc based concrete | $1,4x10^4$ | $1,2x10^5$ | $2,0x10^5$ | $2,7x10^5$ | 200 | 180 | 190 | 0 | 3 | 3 | - | ε | ε |

ε: visualised particles <1%

## Conclusion

- Sanding/drilling operations carried out on concretes can generate the emission of crystalline silica in alveolar dust and in some cases, a small proportion (20% maximum) of particles smaller than 100 nm (i.e. 0.1 µm).
- In order to limit risks of exposure, it is imperative to protect oneself by using sanding/drilling machinery equipped with dust extraction systems at the source, hydraulic capture, as well as by wearing the appropriate individual protective gear (masks, glasses) (7).

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