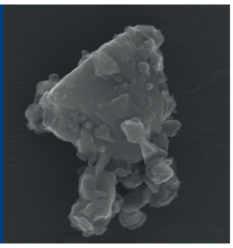
ATILH
ASSOCIATION TECHNIQUE DE L'INDUSTRIE DES LIANTS HYDRAULIQUES

DECRYPTAGE N°2

Cements and nanomaterials: Are cements likely to contain nanoscale particles?



Pulverulent: a granular material of finely divided powder

Nanoparticles: particles of matter smaller than 100 nanometres (np), or 1/10 micrometre (ultra-fine particles).

Key Points

- **Nanomaterials are materials whose size or structure has at least one dimension between 1 and 100 nm (0.001 to 0.1 micrometres), as stipulated by ISO/TS 80004-1:2015. This nanometric size endows them with distinctive and innovative physical, chemical and biological properties. For a material to be considered nanoparticulate, at least 50% of it (by number and not by volume) must be composed of particles having at least one dimension less than or equal to 100 nm.**
- **Measurements and characterisation studies carried out on cements during manufacturing, collected at cement plants or from shipping bags and tanks, show that the common cements covered by standard NF EN 197-1, specialty cements such as ultra-fine cement for injection, calcium aluminate cement (NF EN 14647), as well as prompt natural cement (NF P15-314), are not concerned by the French “Nano” decree.**
- **Their manufacturing characteristics (constitution, grinding method) are such that if cements contain nanoparticles, they do so in proportions varying between 4 and 6%, or at most 14% for the finest cements. Said characteristics are another reason why cements are not concerned by the French “Nano” decree.**

INTRODUCTION

Nanomaterials have become ubiquitous in our daily lives. From cosmetics to clothing, automobiles to building construction, few industries can afford to overlook the development of these new materials 50,000 times smaller than the diameter of a hair. Seemingly limitless technological innovation now appears possible within highly technical, high-stakes domains such as nanomedicine, in which scientists hope to keep in check diseases once considered highly aggressive. Besides the proven benefits from said advances, other innovations are more disputable, such as the field of “nano-additivated” textiles which lend products (T-shirts, socks, etc.) anti-odour properties. The flip side of these technological advances is that after more than a decade of scientific work, nanomaterials are being held up in the mainstream media as potentially hazardous. At the same time, for census purposes, the French Ministry of Ecology, Sustainable Development and Energy has made it mandatory to declare the use or import of nanoparticulate materials exceeding 100 grams.

Though the properties of manufactured nanomaterials are paving the way for a wi de variety of promising technological developments, the quantitative assessment of risks and exposure to nanomaterials are fraught with uncertainties. Pending proof of danger and a thorough toxicological response, the current approach has consisted of reducing exposure to nanoparticulate substances to the extent possible.

It is therefore only natural to wonder what incentives there might be to incorporate nanoparticles into cements. Owing to these materials' significant cost (1 kg of cement ≈10 eurocents; 100 g of nano ≈ 10 - 1,000 €), the incorporation of nanomaterials should logically result either in the introduction of a highly specific and otherwise unattainable use property or in the improvement of a conventional use property for the same cost, which is as yet not the case. But the question of nanoparticles unintentionally produced during the manufacturing process is worth exploring.

The challenge at hand is to avoid a delayed health crisis, as with asbestos. The trouble with doing so is that the term “nanomaterials” covers an extremely broad spectrum of subjects, with definitions yet to be finalised worldwide or even within Europe's borders. Further complicating matters, nanomaterials can be naturally occurring (salt spray, volcanic ash...) or linked to human activities, anthropogenic. Within manmade nanomaterials, scientists have recently begun to draw distinction between intentional nanomaterials (materials produced to provide a specific property) and unintentional nanomaterials, which include combustion-related materials (fossil energies, biomasses, etc.), vehicle fumes and industrial activities which emit nanometric substances.

The present study sought to confirm whether and how cements positioned themselves, as products deriving from traditional and historical industrial activity, *vis-à-vis* nanomaterials. Do cements contain nanomaterials? Taking the question further, do certain cement-related activities generate substances in the nanoparticulate state (work on concrete, cement plant activities, etc...)?

NANOMATERIALS

The scientific community has acknowledged that novel and specific properties are present in materials whose dimensions are equal to or less than 100 nm, wich is why this value is mentioned in the various national and international definitions related to nanomaterials.

According to the International Organization for Standardization (ISO/TS80004), “a nanomaterial is a material with an external dimension at the nanoscale or an internal structure or surface structure at the nanoscale”. The latter must measure “between approximately 1 and 100 nm” [1].

The European Commission has published the following recommended definition (2011/696/EU): “a nanomaterial is a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm-100 mm” [2].

In France, the mandatory Declaration (R-Nano, decree No. 2012-232 of 17 February 2012) states that a substance in the nanoparticulate state is a: ”...substance intentionally manufactured at the nanoscale, containing particles, unbound or in the form of aggregates or agglomerates, with a minimal proportion of particles presenting, in the number size distribution, one or more external dimensions ranging between 1 nm and 100 mm." This minimal proportion is set at 50% of the number size distribution, in the decree of 6 August 2012 associated with the R-Nano decree [3].

We chose to characterise the different cements in this study based on the "Nano" decree in order to situate the samples in relation to the all-important 50% number threshold. It bears noting that this threshold encompasses isolated particles as well as those embedded in larger structures such as agglomerates and aggregates, which from a practical standpoint require the implementation of sophisticated techniques and protocols.

NANOMATERIAL CHARACTERISATION PROTOCOL

The purpose of this study was to determine the characteristic sizes, shape and size distribution of different cement samples in powder form. Characterisation was carried out in two stages at the NanoSafetyPatform (NSP) of the Commission for Alternative Energies and Atomic Energy (French CEA, Commissariat à l'Énergie Atomique et aux Énergies Alternatives) at the Grenoble site:

- Visualisation of the powder using Scanning Electron Microscopy (SEM) techniques directly after placement on a medium.
- Dispersion of each cement powder into the air for real-time measurement of particle size distribution.

The combination of the two previous analysis methods makes it possible to avoid the possible biases generated by manipulation of the sample (placement on the electron microscope visu-alization medium). Moreover, air dispersion is more representative of pulverulence problems of the product. These are not standardised methods for determining the "nano" character of a substance, but protocols developed and tested within NSP and implemented in the framework of intercomparing [4] or projects such as Nanomet [5].

CHARACTERISATION OF INDUSTRIAL CIMENTS

Characterised samples consist, on the one hand, of cements as finished products placed on the market, to assess the "end user" risk and, on the other hand, of their constituent elements (e.g. clinker fresh out of the kiln) collected during manufacturing in a cement plant to assess the "manufacturing operator" risk.

For the first tests, all types of cements were studied, but we give only the results for CEM V type cements, which are representative of the finest cements, as well as those of specialty cements such as calcium aluminate cement, and CEM III for injection or prompt natural cement.

The second type of test carried out by the NSP, consisted of collecting atmospheric samples in a cement plant, near the kiln, near the cement mill and finally in the bagging plant immediately after a cleaning operation with compressed air.

Materials and Methods

Wide Range Aerosol Spectrum (WRAS)

The WRAS system combines use of an SMPS (Scanning Mobility Particle Sizer) and a Dustmonitor for monitoring aerosol particle size distribution over a wide range spanning from 5.5 nm to 32 nm µm. A Grimm dust measurement device was used, working on a classification principle based on electric and optical mobility; the counting principle is based on an optical Condensation Nucleus Counter (CNC) and Optical Particle Counter (COP).

Scanning Electron Microscopy (SEM) Characterisation

Before observation, the sample was placed on a porous polycarbonate membrane for easy viewing. This sample was then metallised (the sample was rendered conductive in order to avoid charge accumulation) by depositing a thin layer of platinum.

A Hitachi Model 5500 SEM Set was used for observations. The SEM employed enables high resolution imaging of a sample's surface up to a few nanometres.

The surface is scanned by primary electrons; the bouncing back of secondary electrons (SE) enables observation of the material's relief. The working voltage in kV and the magnification used are indicated next to each of the SEM images provided in this article.

Powder air dispersion

This test consisted of resuspending the sample to be analysed in aerosol form using a RBG1000-type Pallas rotary brush generator. Powder was placed in a piston rising at a speed of 10 mm/h; the powder was then continuously dispersed using a rotating brush with a speed set at 1,200 rpm. A 3 m^3/h scavenging air was used to transport the powder into the sampling chamber.

The aerosol was then analysed using various devices, a GRIMM SMPS and a GRIMM WRAS system. This line of instruments is capable of measuring sizes ranging from a few nanometres to a few tens of microns.

RESULTS FOR FINISHED PRODUCT CEMENTS

Results after direct characterisation

SEM imaging of a conventional cement does not show nanometric structures. The largest population is mostly made up of micron-size particle aggregates/agglomerates (therefore 10 times larger than the maximum “nano” size), as represented in Figure 1. On certain photographs, a few individual nanometric structures can be observed on top of the principal micrometric particles; it remains unclear whether these are individual particles or mere surface roughness. Identical results are obtained on other samples, such as prompt natural cement (see Figure 2).

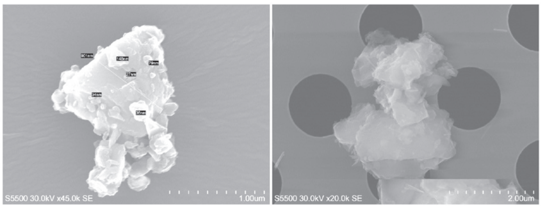


FIGURE 1 - SEM image of CEM V cement at 45 k and 20 k magnification

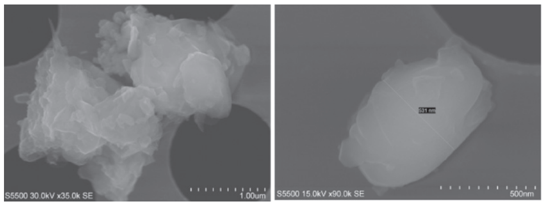


FIGURE 2 - SEM image of prompt natural cement at 35 k and 90 k magnification

Results following air dispersion

In our final stage of SEM observations, air dispersion and particle size distribution tests were performed for each cement according to the protocol discussed earlier in this study.

Visualisation of the results as a cumulative fraction (see Figure 3 for the CEM V cement sample and Table 1 summary) showed that the samples all displayed particle proportions under 100 nm, well below the 50% by number criterion.

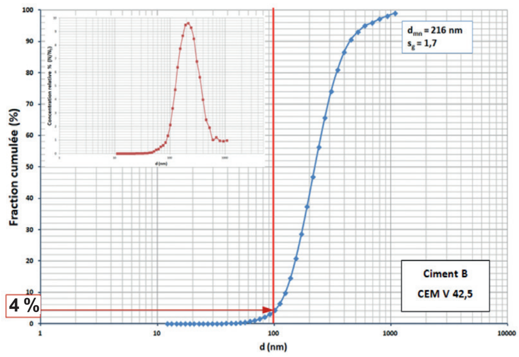


FIGURE 3 - Particle size distribution histogram (red-brown curve) and cumulative curve (blue) for CEM V/A 42.5 cement (containing clinker, fly ash and slag as main constituents). The intersection with the 100 nm limit indicates the % by number of particles smaller than 100 nm.

This approach (visualisation and particle size distribution), as well as the complementary measurement of the specific BET surface (by gas adsorption with a BELSORP-Max apparatus, BEL Japan brand) was applied to all cements. The results are summarized in Table 1 below:

Sample Reference	Cement Type	Median Diameter (d50) [SMPS]	% Inf. 100nm [SMPS]	Specific Surface [BET]
		nm	%	m^2/g
B	CEM V/A 42,5	216	4	1,5
C	CEM III Injection	172	13	2,6
D	CAC	175	14	6,0
E	Prompt cement	222	6	3,0
	“Nano” classification if :	N/A	> 50	> 60

Table 1: Results after cement air dispersion

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These results show that the dispersion of all tested cements in the air yielded some ultrafine particles (less than 100 nm). However, the quantitative granulometry curves show these quantities to be well below the 50% threshold cited in the "Nano" decree. The fact that all the cements analysed, including the finest ones (CAC as well as cements for injection) show a particle size distribution centred over a range of 170 to 200 nm, suggests that for the silicates and aluminates constituting the cements, the grinding process at implemented energy levels generates highly homogeneous particle sizes (low-spread histograms). Median diameter is a mere indicator here, since it is derived from distributions obtained on all the particles measured through the analytical chain, i.e. both the isolated particles and the aggregates or agglomerates constituting them. The decree stipulates however that each single particle making up the aggregates or agglomerates should be counted.

RESULTS FOR SAMPLES COLLECTED IN CEMENT PLANTS

The objective here was the identification, characterisation and evaluation of a possible incidental resuspension of aerosols and in particular nanometric particles, during various operations carried out in an active cement plant, in order to evaluate the "manufacturing operator" risk with regard to cement components (clinker fresh out of the kiln, for example).

Measurement series were carried out at various workstations: in a clinker storage hall, near the kiln, near the cement mill and finally in the bagging plant, immediately after a cleaning operation with compressed air.

The problem examined consisted of a "typical" dust build-up like that encountered in industrial sanitation settings (see Figure 4), with submicronic and micron-size particles. The post-resuspension characterisation of some samples (see Figure 5, characterisation of a cement collected at a bagging plant) shows particles below 100 nm to be exceedingly rare.

It appears that the problem of unintentional emissions of nanometric size particles is quite insignificant in a cement plant. In addition, since the cement plant is located near a highway and the workstations are in open buildings, we find carbon nanoparticles, probably coming from the urban pollution, intermixed with mineral aggregates / conglomerates particles.

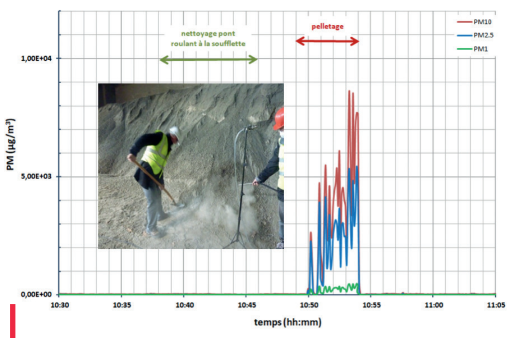

FIGURE 4 - PM evolution (particulate matter measuring 1 µm, 2.5 µm and 10 µm) during ambient measurement and clinker shovelling.

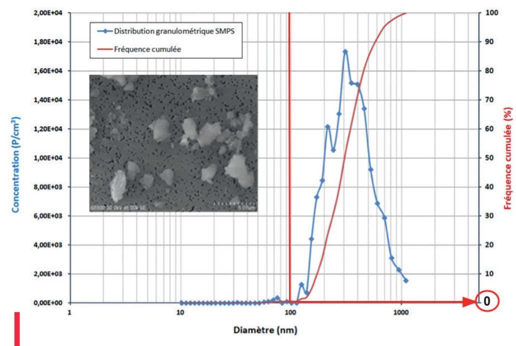

FIGURE 5 - Histogram of particle size distribution (blue curve) and cumulative curve (red-brown curve) for cement sampled at the bagging station. The intersection with the limit at 100 nm yields the percentage by number of particles smaller than 100 nm.

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Conclusion

- **The full study of the cements as "finished product" supplied by ATILH, showed an absence of nanometric structures when the finest samples tested were observed using a scanning electron microscope. Very small particles (less than 100 nm) may be visualised occasionally.**
- **The air dispersion of each cement powder showed the presence of some ultrafine particles (less than 100 nm), though in minute proportions, far short of the 50% threshold necessary for classification as a nanoparticular substance.**
- **Within the current regulatory framework, cements are therefore not classified as "nanoparticles". Periodic monitoring of this characteristic will be carried out by ATILH and CEA/PNS (2018 programme).**
- **The study of samples collected in a cement plant during manufacturing operations confirms these conclusions: the process generates few or no nanoparticles. The only nanoparticles found are representative of typical urban pollution morphologies.**