École Supérieure de Physique et de Chimie Industrielles de la Ville de Paris

3rd YEAR RESEARCH PROJECT

Superconductive cements

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1 Introduction

1.1 Hardened cement paste

Cement is the product of the reaction between water and cement powder. Such powder is obtained thanks to clinkering reaction, by heating up to 1500°C limestone and clay in a long rotating cylinder [1]. The reaction is complex and has a lot of products but the most important ones are the following reactive minerals: calcium oxide (CaO, that is called C), product of decalcination process of limestone, and silicon dioxide or silica (SiO₂) called S, contained in clay. The clinkering reaction leads to the formation, among other components, of different calcium silicates like alite (CaO)₃SiO₂ (C₃S) or belite (CaO)₂SiO₂ (C₂S) that are called clinker. In contact with water (called H), the clinker dissolves, forming a colloidal suspension of hydration products when the solution becomes over saturated in free calcium. The main products of hydration are calcium hydroxide Ca(OH)₂, called Portlandite, and calcium silica hydrates C-S-H. There is also water, different from the structural water included in the C-S-H group, adsorbed on the colloids. As the hydration goes on, the colloids grow and precipitate until reaching a percolation threshold and forming a gel that hardens to form a cement paste. The result of such hydration is called hardened cement paste. Cement is a porous material, and the porosity is controlled by the water to cement ratio (w/c), the ratio between water and cement powder initially used to make the cement paste (see a numerical simulation of hardened cement paste showing the porosity in Fig. 1a). The process of hydration of the clinker, that creates several hydration products, makes the cement a composite material. The main phases are Portlandite as discussed previously, and phases of calcium-silica-hydrates with different density, depending on their local packing fraction. Commonly, we make the distinction between the low density CSH phase and the high density CSH phase, as represented on Fig. [2] 1b. The goal of my internship was to create electronically conductive cement. The resistivity of standard hardened cement paste is about 10⁶Ω.m [3], this material is an insulator. Such cements could be used for example as electrodes for energy storage, electronically conductive with strong mechanical properties. How can one make such cement?

![Numerical simulation of hardened cement paste](image)

**FIGURE 1** – **Numerical simulation of hardened cement paste.** (a) Close-up view of the pore network for a hardened cement paste sample. The box size is L = 195.22 nm. (b) Numerical simulation of hardened cement paste showing the different phases of the cement, depending on the packing fraction of the CSH. In orange, high density CSH with high packing fraction, in blue low density CSH, with lower packing fraction. The size of the box is L = 585.54 nm. Images extracted from [2].

1.2 From standard to conductive hardened cement paste

In this study, we chose to incorporate conductive carbon black nanoparticles to the composition of cement. The carbon black nanoparticles are residues from combustion, and thus a cheap material, as cement is. The carbon black nanoparticles consist in unbreakable aggregates (about 300 nm) composed of nanometric carbon nodules (about 20 nm) and fractal shape [4].
Carbon black nanoparticles form breakable agglomerates of a microns thanks to Van der Waals forces [5]. The problem of adding carbon black nanoparticles to the cement composition is that carbon black is hydrophobic, making it difficult to mix with water during the synthesis of the cement paste. We overcame this problem by using a polymer, carboxymethyl cellulose (CMC), to disperse the carbon black nanoparticles. The polymer is hydrophilic enough to allow the synthesis of a cohesive cement paste [6], containing carboxymethyl cellulose and carbon black nanoparticles. Mishra et al already added carboxymethyl cellulose in cement and studied the influence on the mechanical properties at macroscale. They observed a drop in the mechanical properties at the macroscale above content of about 0.5\% wt in CMC [7]. Wen et al. [8] used mix of carbon fibers and carbon black nanoparticles to reinforce and make conductive hardened cement paste. In their study, a combination of both conductive particles gave the smallest value for the resistivity. Adding nanoparticles to reinforce cement (not necessarily conductive particles) has been studied a lot as reinforcement of hardened cement paste. For instance, Musso et al. [9] used carbon nanotubes to reinforce hardened cement paste, with a modified surface allowing the incorporation in the composition. They established that functionalizing the surface of the nanotubes worsened the mechanical properties. Moreover, Li et al. [10] observed a reinforcement of the hardened cement paste by adding carbon nanotubes treated in acid: improvement of the flexural and compression strengths, and failure strain of the cement matrix composites. Going beyond the sole mechanical properties at the mechanical properties at the macroscale, the objective of my internship was to answer the two following questions: are carbon-loaded cement electrically conductive? Does the presence of carboxymethyl cellulose and carbon nanoparticles affects the hydration scenario and the structural and mechanical properties of hardened cement paste?

![Carbon black nanoparticles, from nodules to agglomerates.](image)

**Figure 2** – Carbon black nanoparticles, from nodules to agglomerates. (a) Scheme of the hierarchy nodule - aggregate - agglomerate. Extracted from [11]. (b) Transmission Electron Microscopy (TEM) of Vulcan (left) and Ketjen (right) primary aggregates – inset is the primary particle size distribution determined using image analysis and the solid black line is the fit of this distribution to a Schultz distribution with polydispersity index of 0.30 being adequate to describe both Ketjen and Vulcan. Extracted from [12].

### 2 Materials and methods

#### 2.1 Sample preparation: synthesis and surface polishing

Cement paste is prepared by mixing Portland cement and distilled water, with a mechanical agitator equipped with stirring blades. The proportions set the water to cement (w/c) ratio, which controls the terminal properties of hardened cement paste. To prepare the carbon black loaded cement, sodium carboxymethyl cellulose (CMC, Sigma Aldrich, that will be called cellulose in the rest of the text) is first dispersed in distilled water under magnetic agitation for a day. Then, carbon black nanoparticles powder (PBX 55, Cabot Corp.) is added to this polymer solution and left under agitation until obtaining a homogeneous black ink, that we mix...
with cement. This dispersion is poured in a 2.2cm-diameter-cylindrical-mold, closed at its two extremities with paraffin. The cylinder is left in a calcium oxide solution to avoid the dehydration of the sample, that would lead to microcrack formation. The hydration creates C-S-H particles, that form a gel, which hardens as the hydration process goes on. After 7-day-curing, the cement is taken out of the bath.

For mechanical testing, we need a surface roughness of the sample that is typically smaller than the indentation depth, which requires a preparation of the samples surface. We start the preparation by cutting the cement paste, with a metallic saw equipped with a diamond blade, into cylindric specimens, of thickness ranging between 0.5 and 1 cm. The 2.2-cm-diameter of the sample is set by the mold (Fig.3.b). Then we make the top and bottom faces of the sample as parallel as possible and polish the surface [13]. By preparing the sample surface, we make sure that it is as flat as possible, to get rid of any surface effect during mechanical testing. To do so, we perform manual polishing using abrasive discs of silicium carbide of decreasing roughness : 35 µm (to set the parallelism between the two faces of the sample), 22, 14, 10 and 5 µm (Fig. 3c). We finish the polishing by gently brushing the specimen for a minute on a 1 µm abrasive disc mounted on a flat glass surface, which yields polished samples with a surface roughness lower than 500nm (Fig. 3d). We polish only one side of the sample for mechanical testing, and both sides for conductivity measurements.

**Figure 3** – **Pictures of samples of hardened cement paste at different steps of surface preparation** (a) Cement paste in the mold, after being taken out of the calcium oxide bath. (b) Specimen of hardened cement paste containing carbon black. (c) Specimen of hardened cement paste during the manual polishing step. Their faces are parallel but polishing is not over yet. (d) Polished surface of a sample containing carbon black. The surface has become optically reflective, which confirms that the surface roughness of the sample is lower than 1 µm.

In Fig. 4 are summarized the different cement samples prepared before and during my internship, and the parameters that were varied to study their influence on the mechanical and electrical properties : content in cellulose and carbon black nanoparticles, w/c ratio. In this report, the concentrations in cellulose and/or carbon black will be given in weight% with respect to the weight of the whole sample.

### 2.2 Mechanical testing

In this section, we present the techniques we use to test the mechanical properties of hardened cement paste at two different length scales : about 60 µm (microindentation) and about 1 µm (nanoindentation). The objective is to determine the influence of the cellulose and the carbon black nanoparticles on the mechanical properties of hardened cement paste. To do so, we perform several different mechanical tests, detailed hereafter.
Figure 4 – List of the different samples prepared to determine the influence of cellulose content, carbon black nanoparticles content and w/c ratio on the properties of hardened cement paste.

2.2.1 Microindentation and nanoindentation

Indentation consists in applying a load on a sample with an indenter, and measuring the indenter penetration depth into the material. The indenter used is a triangular Berkovitch pyramid, which is a sharp and geometrically self-similar indenter. From this experiment, in 1992, Oliver and Pharr introduced a method to measure the indentation modulus \( M \) and the hardness \( H \) of a material from indentation load-displacement data obtained during one cycle of loading and unloading (Fig. 5a) \[14\]. The indentation depth of the indenter \( d \) is measured (Fig. 5b), and we obtain a force vs depth curve (Fig. 5c) that we will explain thereafter. By maintaining a constant load in between loading and unloading phases, the material creeps, which makes it possible to determine the creep modulus \( C \) of the sample (Fig. 5d). The method is equivalent for micro- and nanoindentation, the difference being the maximum depth of indentation: 20 to 25 \( \mu \)m for microindentation and 300 to 400 nm for nanoindentation. Each microindentation experiment consists in performing a grid of 15x15 = 225 indents on the polished surface of the sample, separated by 300 \( \mu \)m, which corresponds to a grid of 4.5mmx4.5mm. A nanoindentation grid is composed of 21x21 = 441 indents, separated by 10 \( \mu \)m, which corresponds to a grid of 200\( \mu \)m x 200\( \mu \)m. This large number of indents allows us to analyze the results statistically. Following the Oliver and Pharr method, we can calculate the hardness \( H \) knowing the maximum load \( F_{\text{max}} \) applied on the sample, and the area \( B \) of the indenter in contact with the sample at \( F_{\text{max}} \): \( H = \frac{F_{\text{max}}}{B} \). The surface \( B \) can be determined by measuring the indentation depth \( d \) of the indenter, which in the case of the Berkovitch indenter is: \( B(d) = 24.5d^2 \). This method also allows us to calculate the indentation modulus of the sample \( M \), thanks to the force-depth data, knowing the effective stiffness \( S \), defined as the slope of the upper portion of unloading curve, that corresponds to elastic recovery (Fig. 5c). The stiffness \( S \) reads as follow:

\[
S = \beta \frac{2}{\pi^{1/2}} E_{\text{eff}} B^{1/2}
\]

where \( \beta \) is a dimensionless parameter of the order of a unity, and \( E_{\text{eff}} \) is the effective indentation modulus. \( E_{\text{eff}} \) takes into account the elastic deformation of both the sample and the indenter during the indentation test, and is defined below, where \( v \) is the Poisson ratio:

\[
E_{\text{eff}} = \frac{1-v_{\text{sample}}^2}{M} + \frac{1-v_{\text{indenter}}^2}{E_{\text{indenter}}}
\]

From the creep curve, Vandamme and Ulm developed a method to calculate the creep modulus \( C \) \[15, 16\]. In Fig. 5d, we see that after a few seconds, the depth of the indenter scales linearly with \( \log(t) \). We fit this curve to obtain the prefactor \( a \) in front of the logarithm. Knowing the maximum load \( F_{\text{max}} \), the maximum indentation depth \( d_{\text{max}} \) and the radius of the
projected area of contact during the holding phase \( B \), one can establish the following relation for the creep modulus \( C \):

\[
C = \frac{F_{\text{max}}}{2\pi B (d_{\text{max}})^{1/2}}
\]  

(3)

The creep modulus \( C \) is the inverse of a creep rate: the larger it is, the less the material deforms under constant external load. In our case, we chose the creep phase to be 180s long, based on previous experiments conducted in the lab [15, 16]. This allows us to see clearly the creep phase, that we can then fit reliably, and is a good compromise for the overall duration of the experiment (about 20 hours for microindentation and about 48 hours for nanoindentation).

2.2.2 Scratch test

The fracture toughness \( K_c \) of a material quantifies its ability to resist the propagation of a fracture. To measure the fracture toughness \( K_c \), we performed a scratch test, which consists in producing a scratch with an indenter on the surface of a sample (Fig. 6a). We use a Rockwell diamond indenter, with a conical-shape tip ending on a diamond sphere of radius \( R = 200 \mu m \). The test goes as follows: we prescribe a linear increase of the normal load from 0.5N up to 30N at a rate of 60N/min (Fig. 6b) while the sample moves horizontally at a speed of 6 mm/s, which generates a scratch of 3mm length (Fig. 6c). During the scratch test, the stress field ahead of the probe is assumed to be uniaxial: \( \sigma_{xx} = - \frac{F_T}{A} \), where \( A \) is the projected horizontal load bearing contact area, which depends on the depth of the indenter \( d \). With this experiment, we can plot the tangential force \( F_T \) measured during the test vs depth (Fig. 6d). We normalize the depth by the radius of the indenter \( R \), and \( F_T \) by \( [2p(d)A(d)]^{1/2} \) with \( p \) is the perimeter (Fig. 6e). The normalized tangential force converges to \( K_c \) for large enough depth [17, 18]:

\[
K_c = \lim_{d/R \to 0.4} \frac{F_T(d)}{[2p(d)A(d)]^{1/2}}
\]  

(4)

2.3 Electrical resistivity measurement

To measure the electrical resistivity \( \rho \) of the cement sample, we sandwich the cylindrical sample between two conductive graphite layers, connected to a power source (Fig. 7a). We
first measure the open circuit voltage of the sample by applying a zero current for 50s. We then apply a voltage ramp from 5V to 0V, with respect to the reference measured with the previous test, and measure the current I. Thanks to Ohm’s law $U = R \times I$, we determine the resistance $R$, then the resistivity $\rho$ of the sample knowing the thickness $L$ and radius $r$ of the sample: $\rho = \frac{R \cdot r^2 \cdot \pi}{L}$. We perform resistivity measurement on standard samples, which contain water (Fig. 6b). The ions contained in the water allow ionic conduction, that covers the electronic conduction. Indeed, the curve does not pass through the origin of the graph. We then store the sample for 2 weeks in a thermal chamber at 60°C, before performing the same measurement again (Fig. 6c). The water has evaporated as confirmed by measuring the mass of the sample, which is constant after two weeks. We obtain linear $U(I)$ curves, in respect with Ohm’s law, which allow us to determine the purely electronic conduction. The resistivity is smaller for dry samples than for standard ones, because there is only the electronic contribution to conduction.

**Figure 6** – Characteristics of the scratch test. (a) Scheme of a scratch test. Extracted from [19]. (b) We prescribe the vertical load $F_V$ and measure the tangential force $F_T$ and the penetration depth $d$ during a scratch test. (c) Picture of a 3mm long scratch. (d) Tangential force $F_T$ vs depth $d$. (e) Normalized tangential force vs normalized depth $d/R$. We can extract the value of the fracture toughness $K_C$: we average the value of the normalized force over the range of $d/R$ where the normalized tangential force is constant, i.e. range between the 2 vertical dashed lines. Here, $K_C = 1.7$ MPa.m$^{1/2}$.

**Figure 7** – Resistivity measurement : set up and curves (a) Scheme of the experimental set up: the sample, thickness $L$ and radius $r$, between two conductive layers connected to a power source. (b) Plot of $U$ vs $I$ for a standard sample. The linear fit is plotted is red dashed line. The resistivity $\rho$ is estimated from the resistance $R$, knowing the samples dimensions. (c) Plot of $U$ vs $I$ for the same sample, dried in a thermal chamber at 60°C for 2 weeks. The linear fit is plotted as a red dashed line. The resistivity is smaller for the standard sample than for the dry one, because of both ionic and electronic contribution to conduction.
3 Results and discussion

3.1 Resistivity measurement

In Fig. 8a is plotted the resistivity $\rho$ of the hardened cement paste vs the content in carbon black nanoparticles. All the standard samples show low resistivity and the resistivity decreases exponentially for increasing carbon black content. Without any specific treatment, cement still contains water, and we measure both ionic and electronic conduction. We first measure the open circuit voltage of the cement ($\bar{U}_{opc}$) for 50s, which is all the more close to zero than the sample is conductive. We perform a first resistivity measurement by applying a decreasing voltage ramp from 5V to 0V. We see that after applying this voltage ramp, $\bar{U}_{opc}$ is no longer close to 0V. The voltage ramp has indeed polarized the sample by mobilizing the ions contained in the sample, and we can measure a residual voltage. That residual voltage is also decreasing for increasing carbon black content (Fig. 8b). Knowing that carbon black is hydrophobic, it is possible that carbon black has increased the free water migration out of the cement. Therefore, there is less free water in cements highly loaded with carbon, smaller polarization and less ionic conduction. Once the samples were dried at 60°C for two weeks, we measure directly the electronic conduction, plotted in Fig. 8a. Below a threshold of about 3%wt. in carbon black, the samples are insulator, with resistivity greater than $10^6 \ \Omega \cdot m$. Above this threshold, which we interpret as the percolation threshold of the carbon black particles inside the cement matrix, the cement samples become conductive, and again the resistivity decreases exponentially for increasing carbon black content. The plot of $U_{opc}$ in Fig. 8c confirms that the samples contain a negligible amount of free water, since there is almost no difference between $\bar{U}_{opc}$ before and after voltage ramp: there is no polarization of the sample, therefore a negligible amount of free water in them.

![Resistivity of hardened cement paste containing 0.6%wt. of cellulose and various amounts of carbon black nanoparticles. (a) Resistivity of standard and dried samples. For the standard samples, there is both ionic and electronic conduction, whereas there is only electronic conduction in dry samples. The red dashed lines corresponds to the assumed carbon black content above which the dry samples are electronically conductive (formation of a percolated network of carbon black particles). (b) Measure of the open circuit mean voltage ($\bar{U}_{opc}$) before and after the voltage ramp for standard cement samples vs carbon black content. $\bar{U}_{opc}$ is larger after the voltage ramp, showing the presence of free water in the samples, that have been polarized. (c) Measure of the $U_{opc}$ before and after the voltage ramp for dry cement samples vs carbon black content. Above the percolation threshold, there is no difference before and after the voltage ramp: there is no polarization because there is a negligible amount of free water left in the samples.](image-url)
3.2 Mechanical properties of blank cement

We started by measuring the mechanical properties of hardened cement paste (w/c = 0.8 at 30 days) at different spatial scales. In Fig. 9 are plotted the probability density functions (pdf) of hardness $H$, indentation modulus $M$ and creep modulus $C$ obtained with microindentation and nanoindentation (Fig. 9) experiments on blank cement. Since the distributions of $H$, $M$ and $C$ are Gaussian (Fig. 9a,b,c), the blank cement is homogeneous at the scale probed by the microindenter, which is about 3 to 5 times the depth of the indent, i.e. about 60$\mu$m. However, the distributions for $H$, $M$ and $C$ are non Gaussian at the scale of the nanoindenter (Fig. 9d,e,f), which is about 3 to 5 times the depth of the indent, i.e. about 1$\mu$m. Hardened cement paste is heterogeneous at the scale of 1$\mu$m, composed of several phases (larger than 1$\mu$m but smaller than 60$\mu$m) with different mechanical properties. In order to determine the phases, we use a Gaussian Mixture Modeling algorithm : it allows to perform a deconvolution of the distributions of $H$, $M$ and $C$ into a superposition of gaussian distributions, corresponding to the different phases. Following a Bayesian Information Criteria, the GMM algorithm determines the most probable number of phase based on the values of $H$, $M$ and $C$ and gives the mean value and the standard deviation of the distribution of $H$, $M$ and $C$ for each phase. For the hardened cement paste, the GMM algorithm gives 4 different phases, plotted in Fig. 9d,e,f with the color legend displayed in Fig. 9h. Based on the mean value of $H$, $M$ and $C$ and previous studies, we were able to determine that the phases correspond to low density CSH (LDCSH), high density CSH (HDCSH), calcium hydroxide ($\text{Ca(OH)}_2$) and unhydrated clinker, with very high mechanical properties.

3.3 Influence of cellulose on hardened cement paste properties

In order to determine the influence of cellulose on the mechanical properties of cement at the spatial scale larger than 60$\mu$m, we performed a 25x 25 microindentation map, which corresponds to an area of 4.5mmx4.5mm on samples with different content in cellulose. For the samples containing increasing content of cellulose, the pdf of $H$, $M$ and $C$ are no longer Gaussian, and spread towards higher values of $H$, $M$ and $C$ (Fig. 10a to f). This shows that cement containing cellulose are heterogeneous at the scale probed by the microindenter (60$\mu$m). To understand this heterogeneity, we need to probe the sample a smaller length scales. To do so, we performed a 41x41 nanoindentation map on the sample containing 0.6%wt. cellulose. The distributions of $H$, $M$ and $C$ are not Gaussian (Fig. 11a,b,c), showing that the sample is heterogeneous at a scale of about 1$\mu$m (3 to 5 times the penetration depth of the nanoindenter). By applying the GMM algorithm, we see the different phases (Fig. 11f) : there are only three, not four as for the blank cement. We can first see that there is no unhydrated clinker in the cement containing cellulose : there is no value of $H$, $M$ or $C$ as high as those of the clinker, which has been fully hydrated. We also plotted the nanoindentation grid (Fig. 11e) where each square is an indent, the color corresponding to the phase it belongs to : low density CSH (LDCSH), high density CSH (HDCSH) and calcium hydroxide. We are here at a junction between a region of LDCSH and a region of HDCSH, of typical length larger than the size of the grid since we do not see the phases edges. Each phase (LDSCH and HDCSH) has a typical size larger than 100$\mu$m, which is larger than the size of the LDCSH and HDCSH phases observed in the blank hardened cement paste. When cement contains cellulose, LDCSH and HDCSH domains are bigger than in blank cement, creating heterogeneity at the microindentation scale (60$\mu$m).

We now summarize the results obtained with microindentation and scratch determined at the microscale on samples containing cellulose. In Fig. 12a, b and c. are plotted the values of respectively $H$, $M$ and $C$ corresponding to the position of the maximum of the pdf, and the fracture toughness $K_f$ versus cellulose content. The error bars on $M$, $H$ and $C$ correspond to the width of the distributions reported in Fig. 10. For w/c = 0.8 at 30 days, the cellulose content has no influence on $H$ and $M$. However, at lower w/c ratio (0.43), the mechanical properties are
FIGURE 9 – Mechanical properties of blank cement at the microscale and the nanoscale (w/c = 0.8 at 30 days). Distribution of (a) hardness $H$, (b) indentation modulus $M$ and (c) creep modulus $C$ for blank cement at the microscale. Distribution of (d) hardness $H$, (e) indentation modulus $M$ and (f) creep modulus $C$ for blank cement at the nanoscale. Each gaussian represents a different phase composing the material, the color code is given in (i) with the relative weight of each phase. (g) Picture of the nanoindentation map, which dimensions are 200 $\mu$m x 200 $\mu$m and contains 21x21 = 441 indents separated by 10 $\mu$m delimited by the red border. (h) Cluster map after gaussian mixture modeling. Each square represents an indent, the color code is given on (i). The black squares are the missed indents, for which the force vs depth curve was not exploitable.

Enhanced for increasing cellulose content. The ratio of 0.43 corresponds to the stoichiometric quantity of water to hydrate all the clinker initially introduced. Adding cellulose to the cement leaves less water to hydrate the clinker, which is left partially unhydrated, playing the role of local hard inclusions. Since the clinker has higher $H$ and $M$ than the C-S-H phases, globally the material is reinforced in presence of cellulose. However, there is no significant increase of $C$ at 30 days: creep seems to be insensitive to hard inclusions left. At 60 days, the aging of the blank cement associated with the hydration process reinforces the mechanical properties. There is no significant evolution of $H$, $M$ or $C$, but we can see that the cement with the highest cellulose
**FIGURE 10** – Probability density functions for $H$, $M$ and $C$ for various concentrations of cellulose for w/c = 0.8 at 30 days. Distribution of (a) hardness $H$, (b) indentation modulus $M$ and (c) creep modulus $C$ for blank cement and cement loaded with 0.6%wt. of cellulose. Cellulose loaded cement show non-Gaussian distributions. The distribution of $H$, $M$ and $C$ for cement loaded with 0.9% cellulose are added to the previous plots, respectively on (d), (e) and (f).

**FIGURE 11** – Results of nanoindentation on a cement sample containing 0.6%wt. of cellulose. The penetration depth of the indenter is typically 300nm, which gives access to the mechanical properties at a scale of 3 to 5 times $d_{max}$, i.e. about 1 $\mu$m. Distribution of $H$, $M$ and $C$ at the nanoscale. Each Gaussian represents a different phase composing the material, the color code is given in (f) with the relative weight of each phase. (d) Picture of the nanoindentation map, which dimensions are 200$\mu$m x 200 $\mu$m and contain 21x21 = 441 indents separated by 10 $\mu$m and delimited by the red border. (e) Cluster map after gaussian mixture modeling. Each square represents an indent, the color code is given in (f). The black squares are the missed indents, for which the force vs depth curve was not exploitable.
content has lower mechanical properties than the others. This suggests that the clinker hydration process is slower in presence of cellulose, and the hydration takes longer for increasing cellulose content. We also see a drop of $K_c$ for cellulose content beyond 1%wt (Fig. 12d).

Knowing $H$, $M$, $C$ and $K_c$, we can compute other physical quantities that we discuss below. At 30 days, the fracture energy, defined as $\gamma = K_c^2/M$ is smaller for cement containing cellulose than for hardened cement paste (Fig. 13a). At 60 days, the fracture energy is constant, independent of cellulose content for cement containing less than 1% cellulose. We observe a drop of the fracture energy beyond this cellulose content. Therefore, we choose a cellulose content of 0.6%wt in the rest of our study. We also plotted the plastic length, defined as $(K_c/H)^2$ and which corresponds to the typical length of plastic deformation at the tip of a crack in a material. A high plastic length indicates that the material can deform plastically. At 30 days, the plastic length is smaller for cement containing cellulose, as $H$ and $K_c$ are higher for blank cement. However, it seems to have a parabolic behavior at 60 days: there is a maximum of plastic length around 1% of cellulose content, after what it drops for higher cellulose content.

3.4 Influence of carbon black nanoparticles on hardened cement paste properties

3.4.1 Mechanical testing at the microscale

Let us first discuss the influence of carbon black nanoparticles on the mechanical properties of hardened cement paste at the microscale. In Fig. 14 are plotted the probability density functions of $H$, $M$ and $C$ for cement containing various amount of carbon black (CB). Like with the cellulose alone, the pdfs are non Gaussian, showing that the material is heterogeneous at the spatial scale probed by the indenter, i.e. 60$\mu$m. Moreover, we see that the peak of distributions tend to be shifted towards higher values of $H$, $M$ and $C$ for increasing carbon black content.

At 30 days for spatial scale larger than 60$\mu$m, the average value of $H$, $M$, $C$ and $K_c$ increase linearly with carbon content (Fig. 15a,b,c and d), cement is reinforced. We also see that the
Evolution of the mechanical properties of hardened cement paste reinforced with different concentrations of cellulose and different w/c ratios. Symbols encode the samples age and colors their w/c ratio. O : 30 days; ¶ : 60 days; red : w/c = 0.43; black : w/c = 0.8. The errorbars are calculated from the width of the pdf distribution of $H$, $M$ and $C$. Evolution of (a) the fracture energy $K_c^2/M$, (b) the plastic length $(K_c/H)^2$, (c) the ductility $M/H$ and (d) $C/H$ with cellulose content.

Probability density functions for $H$, $M$ and $C$ for various concentrations of carbon black for w/c = 0.8 at 30 days. The cellulose concentration is 0.6%wt. for all the cements except the blank reference, which does not contain cellulose.

dispersion of the distribution of $H$, $M$ and $C$, represented as errorbars, is independent of the load in carbon black. The reinforcement due to the aging (60 days) of the cement can only be seen on the blank cement, which has higher mechanical properties. At 60 days, there is so significant change of the mechanical properties for carbon black loaded cements, which stay the same as the ones at 30 days.

Like for the cement containing cellulose, we can compute physical quantities. The increase of $M$ and $K_c$ results in a linear increase of the fracture energy with carbon black content (Fig. 16a). There is no significant change in its value at 60 days for each carbon loaded sample. Carbon black content has no influence on plastic length at both 30 and 60 days. As both $M$
and $H$ increase with carbon content, the ductility $M/H$ remains unchanged for increasing carbon black content (Fig. 16c). Moreover, there is no significant variation of the ductility at 60 days, which is not affected by the aging of the cement. $C/H$ remains constant for increasing carbon black content at 30 days (Fig. 16d). As there is a slight increase of this ratio at 60 days, cement is consolidated with age, but their is no impact of carbon black content on this consolidation effect.

3.4.2 Mechanical testing at nanoscale

One can ask about the structure of the cement paste containing cellulose and carbon black nanoparticles. Are the carbon particles filling the pores of the cement, and the reinforcement due to filler effect, or is the structure of the cement modified by the carbon nanoparticles? To see the influence of carbon black nanoparticles on the structure of hardened cement paste, we performed nanoindentation on a cement containing 0.6%wt. of cellulose and 5%wt. of carbon black, and used the GMM algorithm together with the BIC criteria on the obtained distribu-
Results of nanoindentation on hardened cement paste containing 0.6%wt. cellulose and 5%wt. carbon black. The penetration depth of the indenter is typically 300nm, we see the mechanical properties of the material at a spatial scale typically larger than 1\(\mu\)m. Distribution of \(H\) (a), \(M\) (b) and \(C\) (c) at the nanoscale. Each Gaussian represents a different phase in the material, the color code is given in (f) with the relative weight of each phase. (d) Picture of the nanoindentation map, which dimensions are 200\(\mu\)m x 200 \(\mu\)m and containing 21x21 = 441 indents delimited by the red border. (e) Cluster mapping after Gaussian Mixture Modeling. Each square represents an indent, the color code is given in (f). The black squares are the missed indents, for which the force vs depth curve was not exploitable.

Assumptions of \(H\), \(M\) and \(C\) to determine the number of phases, which is four. Like for the cement containing cellulose, no phase corresponds to the clinker, which seems to have all been hydrated to low density CSH and high density CSH. The phases identifiable are low density CSH, high density CSH and calcium hydroxide, and a fourth phase. Considering the mean value of \(M\) for this unknown phase and the weight of that phase, we assume this is carbon black. This assumption has to be confirmed with chemical analysis of the indentation grid. Moreover, the mean values of \(H\), \(M\) and \(C\) for the 3 other phases seem to be shifted toward smaller values compared to those of the blank cement as illustrated in Fig. 18. In that figure are plotted the mean value of the hardness \(H\) (Fig. 18a), the indentation modulus \(M\) (Fig.18b) and the creep modulus \(C\) (Fig. 18c) for each phase: low density CSH, high density CSH, calcium hydroxide and carbon for hardened cement paste, cement containing 0.6%wt. cellulose and cement samples containing 0.6%wt. cellulose and various carbon black content. We can see that there is a sharp drop for \(H\), \(M\) and \(C\) when cement contains carbon black, compared to the reference sample and the sample with only cellulose. We observe the same trends for \(H\), \(M\) and \(C\) : the mechanical properties at nanoscale drop to lower values when cements contain carbon black. One could test some intermediate carbon black concentration at 1% or 2% to determine whether the mechanical properties drop abruptly even with minute amounts of carbon black. Since the mechanical properties of each phase are much smaller when cement contain carbon black, we can conclude that we do not observe filler effect, but rather a new structure of the hardened cement paste.
3.5 Influence of w/c ratio on mechanical properties at the microscale

To see the influence of water to cement ratio on the mechanical properties, we performed microindentation and scratch on cement samples at high stage of hydration (160 days) containing 0.6%wt. of cellulose and 3.3%wt. of vulcan carbon black nanoparticles (and so above the percolation threshold determined with the resistivity measures) for various w/c ratios. The results are plotted in Fig. 19. The mean value of C is globally unchanged by w/c ratio, but the mean value of H, M and \( K_c \) decreases for increasing w/c ratio. This result has been observed for hardened cement paste: when w/c increases, the hardened cement paste has higher porosity (more pores and bigger pores), which weakens the mechanical properties. Adding cellulose and carbon black nanoparticles to the composition of cement does not allow us to overcome the decrease of mechanical properties due to the increase of porosity.

**Figure 18** – Evolution of the mechanical properties of each phase for hardened cement paste, cement containing 0.6%wt. cellulose and various amount of carbon black. The blank circles of the legend represent the cement, and the colored ones contain 0.6%wt. cellulose + various carbon black concentrations. The values of \( H, M \) and \( C \) are the mean value of their distributions in each phase. Evolution of (a) hardness \( H \), (b) indentation modulus \( M \) and (c) creep modulus \( C \) for each phase composing the material. The red dashed line on each graph corresponds to the carbon black content beyond which the samples are electrically conductive.

**Figure 19** – Evolution of the mechanical properties of hardened cement paste with different w/c ratios and reinforced with cellulose (0.6%wt.) and vulcan carbon black nanoparticles (3.3%wt.) at 160 days. Evolution of the mean value (a) the hardness \( H \), (b) the indentation modulus \( M \), (c) the creep modulus \( C \) and (d) the fracture toughness \( K_c \) with water to cement ratio. The errorbars of \( H, M \) and \( C \) are the width of the pdf distributions of \( H, M \) and \( C \), not shown in this report.
4 Conclusion

We managed to synthesize samples of hardened cement paste containing conductive carbon black nanoparticles. The samples are electronically conductive when containing over 3%wt. of nanoparticles due to the presence of a percolated network of carbon particles. Moreover, beyond this conductivity threshold, the resistivity decreases exponentially for increasing carbon black content.

We studied the influence of cellulose on the mechanical properties of cement paste. At low water to cement ratio (w/c = 0.43), cellulose reinforces the material at the microscale by leaving unhydrated clinker in the cement paste. At high water to cement ratio (w/c = 0.8), we have observed a drop of the mechanical properties above a critical content of 1%wt. in cellulose. Under the 1%wt. limit, cellulose content has no influence on the mechanical properties at the microscale, but the cement paste is heterogeneous. This can be explained by probing the material at the nanoscale: we saw that the phases (LDCSH and HDCSH) composing the cement paste have a bigger size (of about 200$\mu$m) than those of the blank cement, which corresponds to the heterogeneity observed at the microscale. Moreover, all the clinker has been completely dissolved and turned into LD-and-HD-CSH.

We then studied the influence of carbon black nanoparticles on the mechanical properties of cement paste. At the microscale, the mean values of $H$, $M$, $C$ and $K_c$ increase linearly for increasing carbon black content, which means that the material is reinforced at age younger than 30 days. To study the structure at a smaller lengthscale and try to see the role of carbon in the structure, we performed nanoindentation on the samples. The mean values of $H$, $M$ and $C$ for each phase composing the material were smaller than for the blank cement. That means that the microstructure of the hardened cement paste has been modified by adding carbon black nanoparticles, which did not just fill the pores of the cement. We also observed the phase corresponding to the carbon black. If each phase is weaken with the presence of carbon black, globally the adhesion between the different phases must be stronger, which could justify the reinforcement of the mechanical properties measured at the microscale.
Références


