

## MICROMECHANICAL CHARACTERIZATION OF CEMENT PASTE MODIFIED BY NANOCCLAYS

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**ABSTRACT.** This work deals with the comparison of micromechanical properties and microstructure of cement pastes with additives used in concrete to reduce the lateral pressure on the formwork. This work is a steppingstone for broader investigation of the lateral pressures on different cement mixtures. The work focused on two additives used for the purpose, namely calcined clay (metakaolin) and a type of nanoclay sepiolite. A scanning electron microscope was used to describe their microstructure. Micromechanical properties of both cement composites were investigated by nanoindentation. Large statistical grids of indents were performed on three sample types: plain cement paste and two mixtures containing the enhancing additive of metakaolin and nanoclay. From the evaluated results in the form of property histograms, the modulus of elasticity, hardness and creep parameter were derived. It was found that in the cement paste with metakaolin the amount of C-S-H gel increased compared to the control mixture. Increased portlandite and the amount of unhydrous clinker was found in the cement paste with nanoclay. Nanomechanical response of individual phases was derived from overall property histograms by statistical deconvolution. The results were confirmed by electron microscopy. The micromechanical research was supplemented with the measurement of the compressive strength on cubes at the macroscopic level.

**KEYWORDS:** Cement, hydration, metakaolin, nanoclay, nanoindentation.

### 1. INTRODUCTION

In the construction industry, concretes in their fresh state are cast into formworks. Ordinary concretes are vibrated to support their flow and to overcome their high viscosity. The casting process of tall structures is done in steps to allow mixture compaction and stepwise vibration. Lateral pressures introduced by the ordinary concretes on formwork diminish relatively soon after casting due to the very high mixture viscosity and prolonged casting times. In contrary, self-compacting concretes (SCC) are characterized by low viscosity with no need of additional vibration to fill the formwork [1–4]. SCC are usually poured into formwork in one step filling the whole height of the structure (e.g. a column or a wall). The long-lasting mixture flowability is usually maintained by additives (plasticizers) and hydration retarders and even after casting the mixture behaves like a fluid that introduces high lateral pressures on the formwork.

However, the development of high lateral pressures in the SCC mixtures can be controlled by special additives that control viscosity and workability of the mixtures in the fresh state and simultaneously control development of thixotropic behavior and early strength development of the mixture. Such additives can be in the form of hydration modifiers or some nanoparticles [1–6]. So far, the effect of the additives on the microstructure and micromechanical properties of the resulting hardened concrete was not well studied. Thus, this work deals with the comparison

of micromechanical properties [7–10] and microstructure of cement pastes modified with additives that are used in SCCs to reduce the lateral pressure on the formwork [1–6].

There are several ways how to reduce the lateral pressure in the mixture. One of the ways is to change thixotropy of the concrete by non-reactive additives. It was found that the thixotropy can be increased and the pressure can be reduced by nanoclay minerals or derived materials [1–6]. The other way of reducing pressures is to modify hydration kinetics and hydration products by additives such as metakaolin. Metakaolin reacts with dissolved clinker minerals in cement paste and forms calcium-silica hydrates (C-S-H) [6].

### 2. TESTED MATERIALS

Cement pastes modified by two additives, metakaolin and nanoclay, were tested in hardened state in this work. Firstly, metakaolin which is a calcined clay with the chemical composition: 53.1% SiO<sub>2</sub>, 41.7% Al<sub>2</sub>O<sub>3</sub>, 1.1% Fe<sub>2</sub>O<sub>3</sub> and other minor oxides, was used. It is prepared as a granulated powder with a similar grain distribution as cement. Metakaolin particles have angular shape with mean size which can range from 1 to 10 μm (Figure 1). Metakaolin reacts with cement during hydration. It reduces the amount of portlandite in the hydrated cement and increases the main hydration product that is calcium-silica-hydrate gel (C-S-H) [6]. The nanoclay sepiolite was used for

Sample	Cement [g]	Metakaolin [g]	Sepiolite [g]	Water [g]
C	450	—	—	202.5
CM	445.5	4.5	—	202.5
CS	445.5	—	4.5	202.5

TABLE 1. Composition of cement pastes.

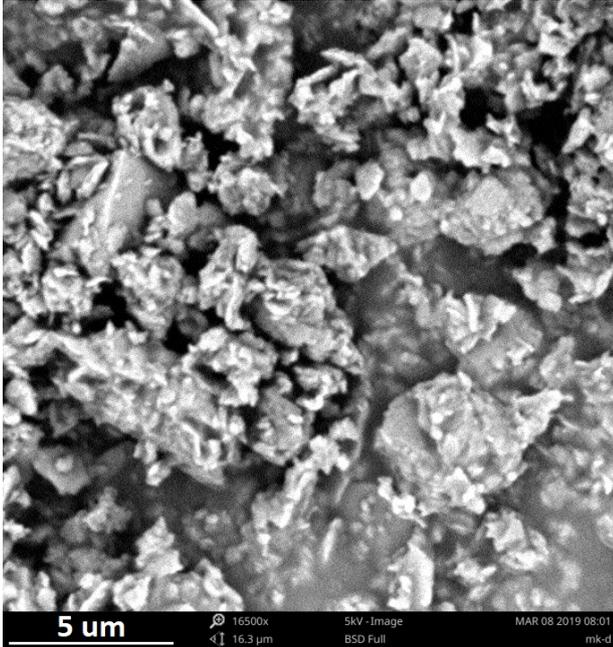


FIGURE 1. SEM image of metakaolin.

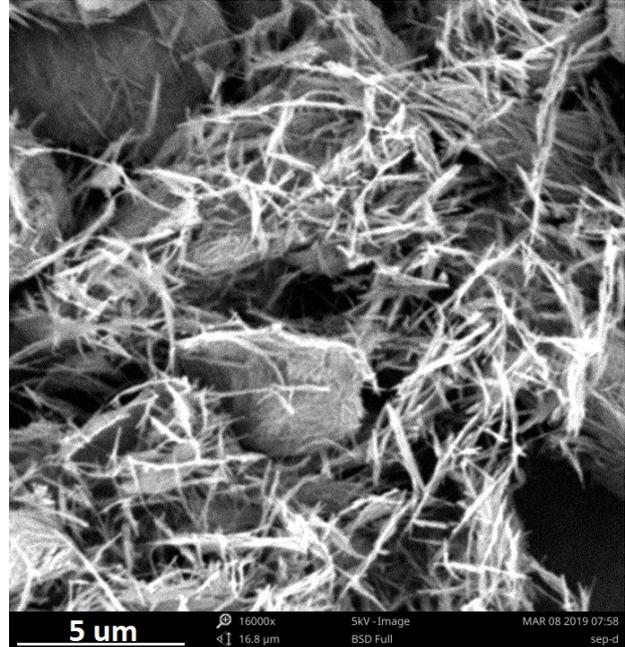


FIGURE 2. SEM image of sepiolite.

the second part of the samples. Its chemical formula is  $\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ . Sepiolite particles have tiny elongated shape (Figure 2). They have typical length of 1 to 2  $\mu\text{m}$  and width of several tens of nanometers. Sepiolite does not dissolve in water and it does not react with cement, but it works on reorganization of the crystallites in plastic stage of the mixture. It also binds more water upon mixing which lowers workability. The resulting microstructure contains larger amount of unhydrous clinker.

The micromechanical properties of the three cement paste mixtures with the composition defined in Table 1 were tested. All mixtures are based on Portland cement CEM I 42,5R and the additives described earlier. Equal water to binder ratio 0,45 was used for all samples. The amount of additives was chosen as 1% of weight of cement. Samples were cast into cylindrical plastic molds with height of 65 mm and diameter of 30 mm. They were demolded after three days from casting and stored in water for additional 25 days. After hardening, the samples were cut into discs and placed in an acetone bath to prevent further hydration. The surface of samples were grinded and polished by a metallographic procedure and prepared for testing by nanoindentation. Along, six cubic specimens (40x40x40 mm) were made for compressive strength testing.

### 3. METHODS

#### 3.1. NANOINDENTATION

The main objective of the paper was to compare nanomechanical properties of the cement paste modified by metakaolin or sepiolite with pure cement paste. Therefore, series of 400 indents were done on each sample. Each consisted of a matrix of 20x20 indents. The separation of indents was 10  $\mu\text{m}$ . A load-controlled test with the load function lasting for 26 seconds to the maximum force of 2000  $\mu\text{N}$  was prescribed for each indent. The function had a trapezoidal shape (Figure 3). The first part of the function was a linear loading with speed of 40 mN/min lasting for 3 seconds. The second part was a constant loading for 20 seconds and the last part of the function was a linear unloading with speed of 40 mN/min lasting for 3 seconds. A typical response (load-depth) for various phases in the material is shown in Figure 5. Material properties were evaluated for each indent by the Oliver and Pharr method [11]. Some defective indentations caused by local porosity or roughness were eliminated from considerations. The Oliver and Pharr [11] method was used for obtaining reduced modulus,  $E_r$  and hardness,  $H$  for single indents and property histograms were constructed for each matrix. The evaluation was complemented by creep indentation parameter  $CIT$ . The parameters are defined as

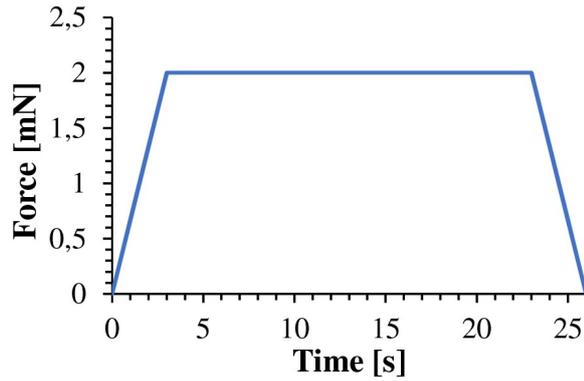


FIGURE 3. Load function of indents.

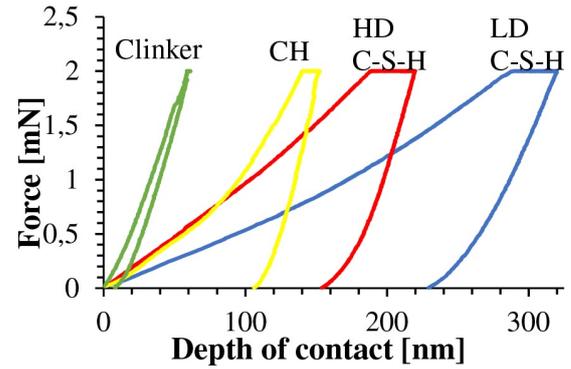


FIGURE 5. Indentation curves.

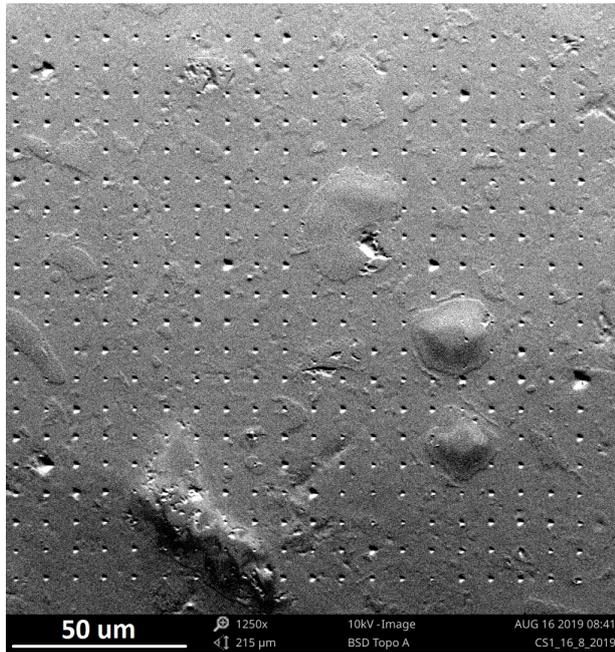


FIGURE 4. Topography of the surface.

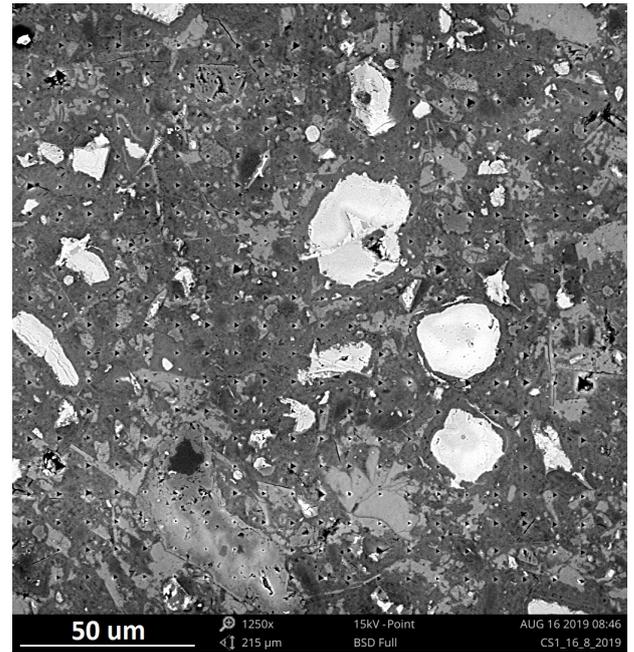


FIGURE 6. BSE images (phase composition).

follows.

$$E_r = \frac{S\sqrt{\pi}}{2\beta\sqrt{A_c}} \quad (1)$$

where  $S$  is the unloading tangential stiffness,  $\beta$  is a tip shape correction coefficient and  $A_c$  is the contact area,

$$H = \frac{P_{max}}{A_c} \quad (2)$$

where  $P_{max}$  is the maximum indentation force,

$$CIT_{(P,t_1,t_2)} = \frac{h_2 - h_1}{h_1} \times 100 \quad (3)$$

which is defined as a relative change between indentation depths  $h_1$  encountered at the time  $t_1$  and  $h_2$  at the time  $t_2$ , respectively. The  $CIT$  is dependent on the contact force  $P$  and time of holding period.

Note, that the reduced modulus can easily be used to calculate Young's modulus of isotropic materials [11] knowing Poisson's ratio of the material ( $\nu=0.2$  was assumed for all phases in this work).

### 3.2. MICROSTRUCTURAL ANALYSIS

The basic microstructural analysis was performed by scanning electron microscope (SEM). Back scattered electrons (BSE) images together with energy dispersive x-ray spectroscopy (EDS) analysis are very effective way for exploring the phase of cement paste at the level of micrometers. Topography of the surface (Figure 4), BSE images (phase composition) (Figure 6) and EDS maps of cement pastes were acquired. The distinction between the microstructural phases could be done from these images but it was not attempted in this work that concentrated on statistical evaluation of micromechanical results as shown later.

### 3.3. MACROSCOPIC LEVEL

The paper was supplemented by the compressive strength measurements performed in a standard electro-mechanical press on 40x40x40 mm cubes (Figure 7).

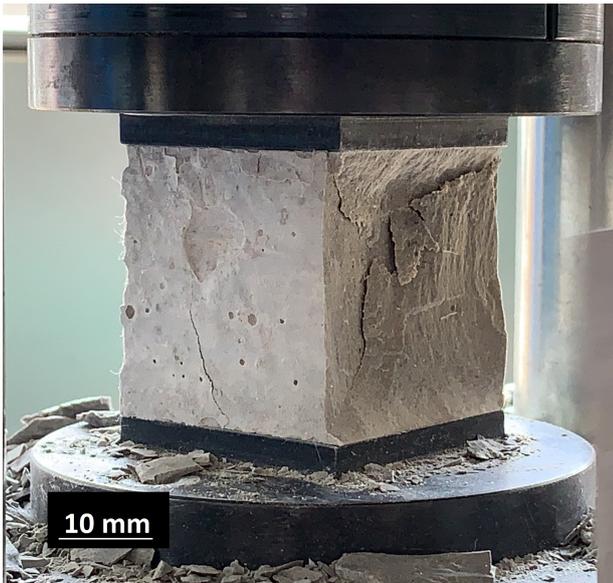


FIGURE 7. Test of cement paste cube for compressive strength.

## 4. RESULTS AND DISCUSSION

### 4.1. MODULUS OF ELASTICITY

Figure 8 shows histograms of modulus of elasticity for mixtures of cement pastes. Values were calculated from merged results of nanoindentation. The histograms show a similar trend for all mixtures. The main peak in CM sample appears between 11 to 51 GPa, between 16 to 66 GPa on CS mixture and 13 to 61 GPa on C sample, respectively, with the mean of 25 GPa for CS and C and 22 GPa for CM (Figure 8). The results show that the wrapping curve of elastic modulus for CM has shifted to the left compared to the control mixture. This confirms the assumption that the amount of portlandite in the hydrated cement is reduced and the calcium-silica-hydrate gel (C-S-H) content increases. The results of CS mixture show similar values compared to the control mixture C.

### 4.2. HARDNESS

Figure 9 shows histograms of hardness of cement pastes. Values were calculated from merged results of nanoindentation. Similarly, to results of  $E$ , the histograms show similar trend for all mixtures. The main peak of hardness measured on CM and C is around 1.0 GPa. In CS mixture the hardness has the main peak around 0.9 GPa, thus similar. It can be concluded that the results are qualitatively as well as quantitatively equivalent.

### 4.3. CREEP INDENTATION PARAMETER $CIT$

Figure 10 shows histograms of  $CIT$  of cement pastes. Values were calculated from merged results of nanoindentation. Again, similar trend for all mixtures was encountered. The highest mean  $CIT$  value is exhibited by the mixture with metakaolin suggesting the role

of increased C-S-H content on increased creep. However, the differences between the samples are not large and the mixtures can be considered as equivalently creeping.

### 4.4. COMPRESSIVE STRENGTH

The results of compressive strength were measured on the six samples cubes for each mixture. Average value was calculated and was supplemented by standard deviation. The average compressive strength of control mixture (C) was  $65,9 \pm 5,7$  MPa. For mixture with sepiolite (CS) the average compressive strength was  $63,6 \pm 1,1$  MPa. The average compressive strength of mixture with metakaolin (CM) was  $63,1 \pm 3,4$  MPa. It can be concluded that the average compressive strength of mixtures with additives were at about 95% of the control mixture. Thus, the additives of metakaolin and sepiolite do not have considerable effect on macromechanical properties.

### 4.5. EDS ANALYSIS

On the samples EDS analysis map were made (Figure 11). The results are shown in Table 2. Comparison of results of mixture from EDS analysis shows small change in volume concentration of chemical phases except carbon that is largely present in CS samples. This is a consequence of organic pollution of the raw sepiolite used for sample preparation.

Element	C W. C. [%]	CM W. C. [%]	CS W. C. [%]
O	72.63	68.74	59.17
Ca	15.89	20.21	17.78
Si	5.98	7.07	6.24
Al	3.28	2.11	1.82
Mg	1.4	0.89	0.53
S	0.82	0.97	0.48
C	-	-	12.95

TABLE 2. Weight concentrations of elements.

## 5. CONCLUSIONS

The presented paper provides nanomechanical and microstructural results of cement pastes with special additives in the form of nanoclays and calcined clay minerals used for the control of lateral pressures in fresh mixtures. Nanoindentation was used to obtain microscale hardness, elastic and creep properties. Values of Young's moduli, hardness and creep indentation parameter,  $CIT$ , were calculated from large statistical sets of nanoindentation. The results of elastic moduli indicate a statistically significant shift towards lower values on CM samples. This is a consequence of the hydration process where the amount of portlandite in the hydrated cement is reduced and the main hydration product, the calcium-silica-hydrate gel increases. The sepiolite in CS samples does not

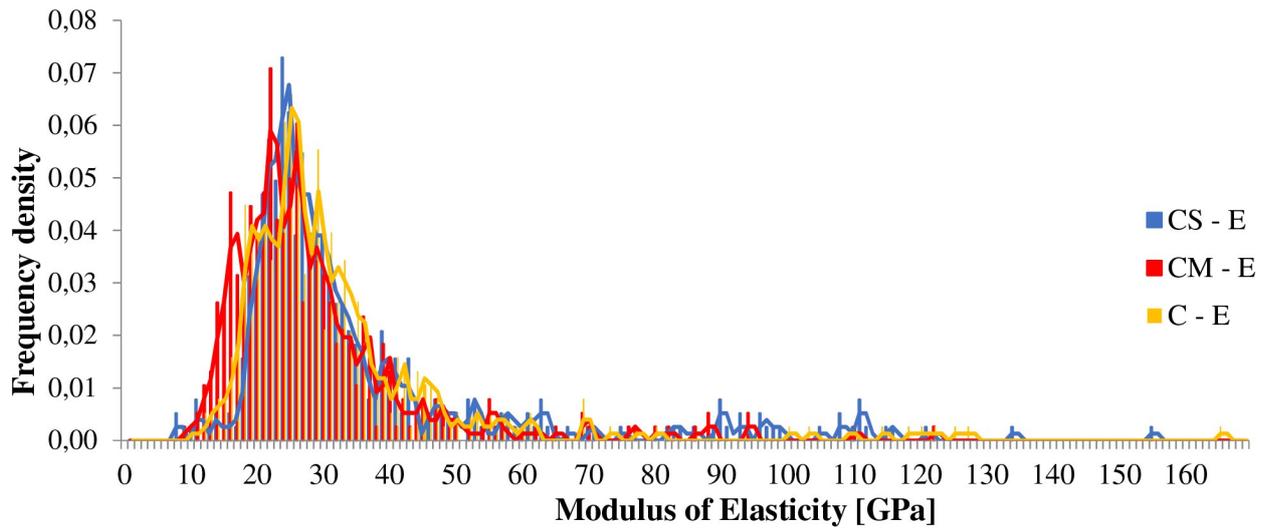


FIGURE 8. Histogram of modulus of elasticity with trend line for cement pastes CS, CM and C.

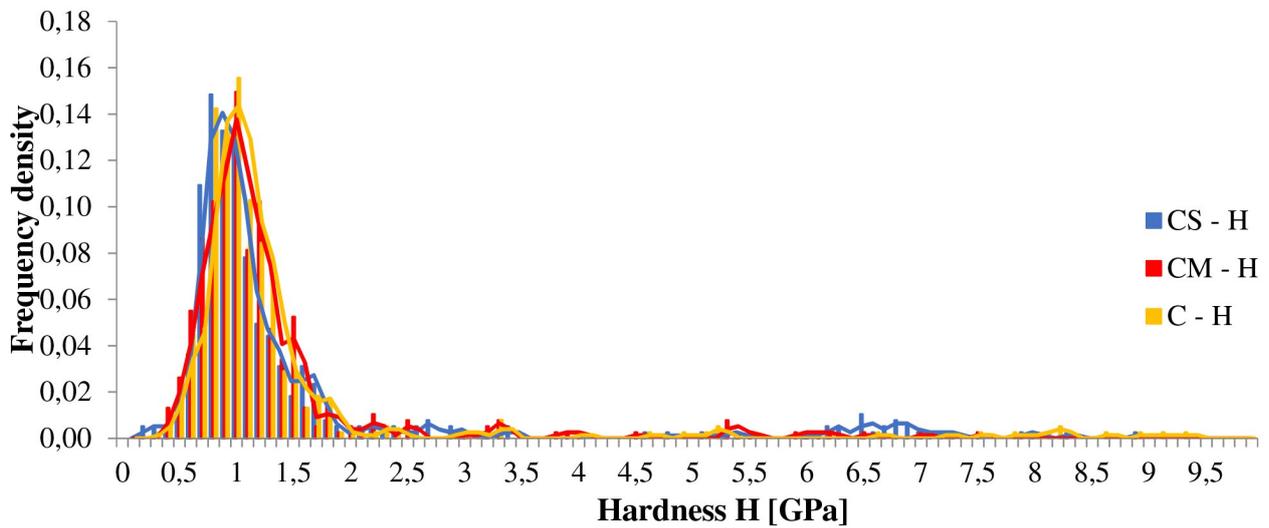


FIGURE 9. Histogram of hardness with trend line for cement pastes CS, CM and C.

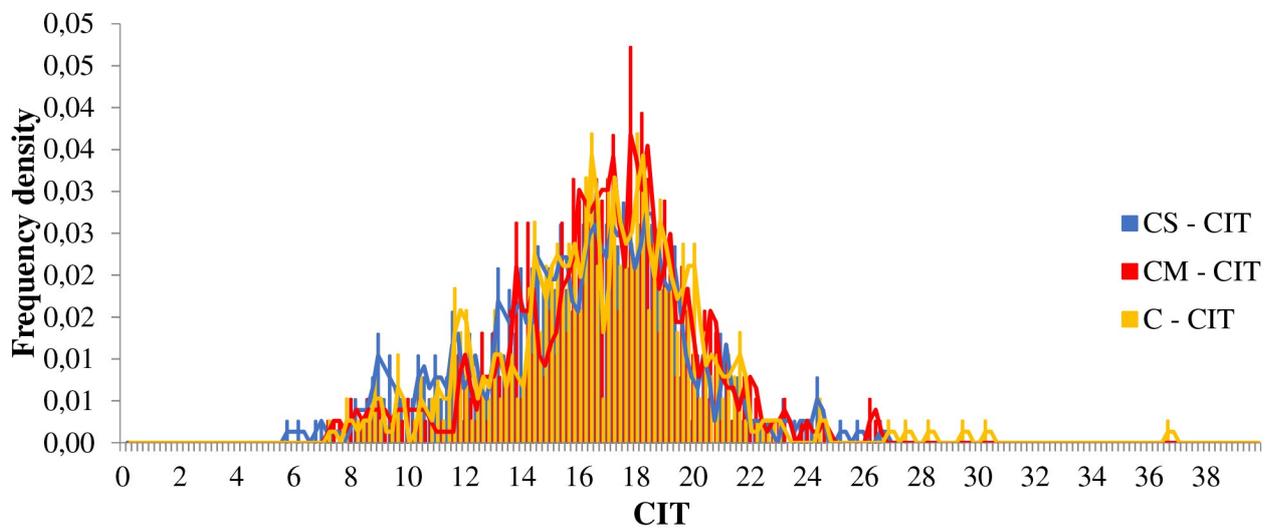


FIGURE 10. Histogram of CIT with trend line for cement pastes CS, CM and C.

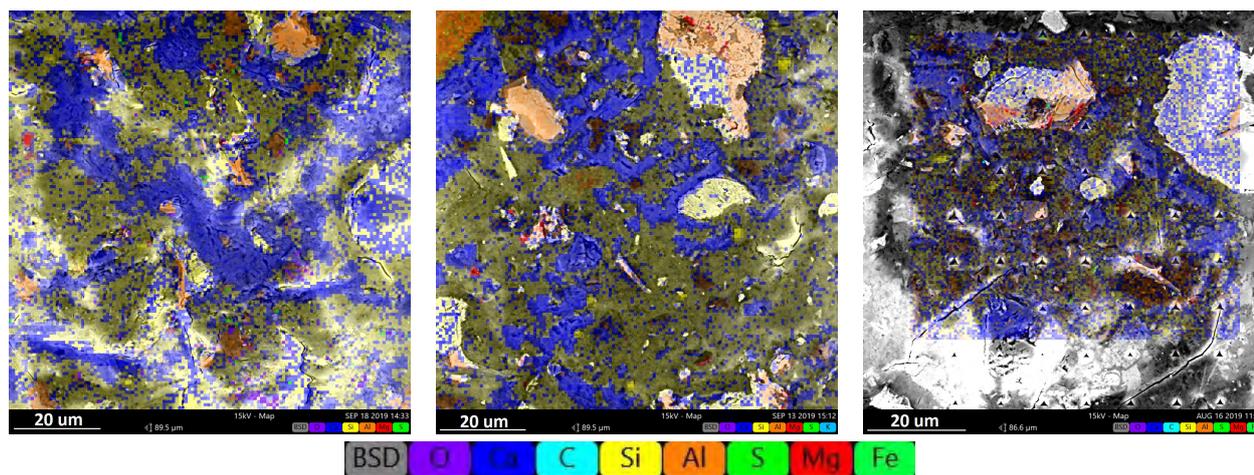


FIGURE 11. Maps of chemical elements from EDS analysis: a) C, b) CM and c) CS.

appear to statistically influence elastic modulus on microscale. The hardness and creep were also found statistically equivalent on all samples.

The average compressive strength of modified samples was found to be 95% of the control mixture meaning very little macroscopic influence of additives was observed. EDS analysis shows small change in concentrations of chemical elements except the presence of carbon in CS samples which is a consequence of the raw material organic pollution.

The work described in this paper confirmed mechanical compatibility of the additives with nil or very little influence on micro and macroscopic mechanical properties of the hardened samples. The work is a steppingstone for future lateral pressure investigations.

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