Electrical Joule heating of cementitious nanocomposites filled with multi-walled carbon nanotubes: role of filler concentration, water content, and cement age

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Abstract

In the study at hand the Joule heating effect of electrically conductive cementitious nanocomposites filled with different loadings of multi-walled carbon nanotubes (MWCNTs) is investigated. Nanofiller dispersions were initially prepared via ultrasonication in deionized water (d-H2O) utilising a commercial superplasticizer as surfactant. Electrically percolated nanocomposites were fabricated via shear mixing and subsequent casting into moulds. Storing the prepared samples under different humid conditions enabled explanation of the role of water content as well as cement age on Joule heating performance. All prepared specimens were investigated at ages of 3 d, 7 d and 28 d by applying two different DC bias voltages. Infrared-thermography (IR-T) images were recorded after 1 min, 5 min and 10 min in order to visualize the differences in the Joule heating effect as a function of time, keeping contact with the DC bias voltage. The observed results showed a significant dependency of the Joule heating effect on water content as well as on filler concentration. Moreover, increasing cement age provided more effective electrical heating. This work elucidates the complexity of the electrical heating phenomena occurring in cementitious/MWCNT nanocomposites via the well-known Joule heating effect because it contributes to the understanding of the underlying mechanism. The main parameters used and the corresponding results are envisaged to be applicable for large-scale, heatable concrete structures in future respecting buildings temperature, aerial control, de-icing, thermal management, and better energy efficiency, etc.
Keywords: Joule heating effect, electrical heating, carbon nanotubes, cement and concrete, nanocomposites

(Some figures may appear in colour only in the online journal)

1. Introduction

The exceptional, multi-functional properties of carbon nanotubes (CNTs) have advanced them to become one of the most intensely investigated nanomaterials in designing nanocomposites. In the field of cement and concrete, CNTs have been widely investigated with the aim of enhancing Young’s modulus as well as compressive and flexural strengths [1–7]. However, there exist a great plenty of different materials of much lower cost and easier processability in improving mechanical properties as such. In fact, the main advantage of utilising CNTs for designing nanocomposites is their multifunctionality, arising from their unique physicochemical properties and, in particular, the use of their electrical conductivity and their 1D geometry, all of which allow CNTs to create electrically conductive networks within a host matrix. Accordingly, much attention has been given in recent years to the use of CNTs in designing cementitious matrices with fully new functions, often also described as ‘smart’ materials [8, 9]. With this in mind, research has been conducted on developing stress–strain sensitive cement/CNT nanocomposites, otherwise reported as ‘piezo-resistivity’ effect [4]. Furthermore, thermoelectric properties for use in harvesting potentially wasted thermal energy have been explored [10, 11].

A very attractive function in the design of new CNT nanocomposites is electrical heating via the well-known ‘Joule’ effect, also called Ohmic or resistive heating. Here an applied voltage induces an electrical field, resulting in the movement of a charge-carriers through the resistor. A collision of charge-carriers results in energy dissipation in the form of heat. This effect can be realized using alternating (AC) as well as direct current (DC). For DC setups the electrical power (P) of the heating element can be described as follows:

\[ P = I^2 \times R \]  \hspace{1cm} (1)

or

\[ P = U^2 / R \]  \hspace{1cm} (2)

where \( I \) is current, \( R \) the resistance, and \( U \) the applied voltage.

For cementitious matrices modified using carbon-based materials, the Joule heating effect was initially reported for carbon-fibre (CF) reinforced composites [12, 13]. Such materials can be easily applied in heating and de-icing applications, as shown for continuously aligned CFs in a concrete slab [14, 15]. However, the alignment of continuous CFs is related to the anisotropic distribution of the thermal energy generated and the localisation of the heating effect within the concrete, which requires more time for the complete heating of the structural element. Hence, for a more homogenous temperature distribution, dispersed carbon fillers represent a more promising approach. Still, it is noteworthy that for dispersed carbon fillers also temperature peaks can occur within a concrete slab [16]. Further critical aspects for developing heatable cementitious composites are the required voltage, filler content and impact on the composite’s mechanical properties. Galao et al. reported on concrete composites with 2% of short CFs for icing prevention using AC and DC setups at an applied bias voltage of 20 V [17]. According to [18] the Joule effect can be further enhanced by incorporating electrically conductive aggregates. Hambach et al. conducted studies on CF cementitious composites applying 12 V AC and showed that flexural strength is not diminished during electrical heating at 60°C for 4 weeks [19].

A few studies have also been conducted on the utilisation of carbon nanofillers for electrical heating of cementitious matrices. The feasibility of self-heating concrete was demonstrated by utilizing a carbon nanofibre paper under a constant DC bias voltage of 20 V [20]. Galao et al. developed self-heating cement nanocomposites with up to 5 wt.% dispersed carbon nanofibre. In this study, an improved heating effect in terms of temperature and heating rate with higher CNF loadings was found [21]. However, relatively high voltages of up to 150 V were applied, which make these systems relatively difficult in practical application. Lower CNF contents and applied voltages were used to accelerate hydration and to avoid frost damage via Joule heating [22]. Moreover, carbon-based fillers, such as carbon black [23], expanded graphite [24] and graphene nanoplatelets [25] also have been recently reported to be suitable for the electrical heating of cementitious matrices. There have been only a few studies conducted on the use of CNTs for the Joule heating of cementitious matrices, for CNTs are excellent candidates due to their high electrical conductivity and potential to create percolated networks by their 1D geometrical characteristics. Lee et al. demonstrated that at relatively high voltages the heating performance with 1 wt.% of CNTs can be achieved only with sufficient filler dispersion [26], while single-walled carbon nanotubes perform better than multi-walled carbon nanotubes (MWCNTs) [27]. In another study [28], an optimal CNT content of approximately 1% was established with regard to heating and mechanical properties. An acceleration of cement hydration was reported for cementitious nanocomposites with only 0.6 wt.% CNT content [29]. Gomis et al. compared the self-heating and de-icing properties of cements with different carbon fillers such as graphite, different short carbon fibres, CNF and CNT. They found the best performance using CNTs at 5 wt.% within voltages ranging between 5 V and 150 V and high water-to-cement ratios of up to 1.5 [30]. Kim et al. showed that hybrid-filled cementitious composites with CF and non-dispersed CNTs are very effective with regard to electrical heating and less sensitive to differing water-to-cement ratios [31, 32]. However, many fundamental aspects of developing
electrifying the electrical conductivity and Joule heating performance of the commercially MWCNTs used in the study at hand. A MWCNT dispersion at a concentration of 1.25 mg ml$^{-1}$ (100 mg of MWCNT powder was used for the bucky paper) has been initially prepared via ultrasonication for 5 min at 70% using an ice bath and a high-range water reducing admixture MasterRheobuild 30 based on napthalenesulfonate (NS). The bucky paper has been fabricated following a vacuum filtration process through a polycarbonate membrane (0.4 µm pore size; 47 mm diameter). After filtering the MWCNT dispersion, the resulting filter cake was dried at 80 °C overnight for 16 h. The final bucky paper film was peeled off from the membrane and the thickness was measured to be approximately 100 µm. The following steps included the preparation of the MWCNT bucky paper (figure 1(a)); as well as two digital photos of the resulting self-standing and flexible bucky paper film (figure 1(b)), and a scanning electron microscopy (SEM) micrograph showing the film morphology with entangled and randomly distributed long MWCNTs (figure 1(c)).

2.2. Characterization techniques

The experimental setup for measuring the Joule heating effect is illustrated in figure 2. It consisted of a FLUKE 289 Multi-meter, which was connected to a PC for the continuous logging of temperature values at a frequency of 1 per sec, over a testing period of 10 min. The two-point-probe method was employed to measure the volume resistance due to difficulty in installing electrodes inside cement paste, as similarly reported in other studies [36]. Notice that because the contact resistance is much smaller than the resistance of samples, the advantages of the four-point-probe method over the two-probe method are not significant. The presented graphs in this work, additionally contain data logging without applied voltage in the first 30 s to demonstrate the response of the investigated nanocomposites. A K-type thermocouple was inserted in the holes prepared in the samples for measuring the temperature, while current measurements were performed simultaneously. Two different DC voltages were applied, 15 V and 30 V to investigate the effect of the applied voltage on the Joule heating effect. Figure 2(b) shows schematically the method used to contact the samples in order to perform the Joule heating experiments.
To reduce contact resistance silver paste ACHESON 1415 from Plano GmbH, Germany was applied to the surface of the samples at an interelectrode distance of 1.2 cm. The contacts were finally connected to copper tape to ensure stable and reliable measurement. IR-T was employed in order to measure the surface temperature of the samples using an IR camera (Seek Thermal UWAAA CompactPRO Imaging Camera).

A MWCNT bucky paper film has been cut in small rectangular pieces of 20 mm × 12 mm × 0.1 mm, while silver paste has been deposited in order to create metallic contacts at an interelectrode distance of 12 mm. IR-T images have been captured by applying a voltage bias of 5 V at time intervals of 1, 5 and 10 min, as for the nanocomposite samples. It should be mentioned that neither 15 nor 30 V have been applied to the bucky paper sample in order to avoid extremely high Joule heating effect, considering that at 5 V already a temperature raise of 100 °C has been reached. SEM investigation was performed by means of an FEI NanoSem 200 (FEI, Eindhoven/The Netherlands) at an operational voltage of 2 kV. It was utilized to study the morphology of the bucky paper as well as nanocomposite’s fractured surfaces.

The DC electrical resistance (R) of the cement/MWCNT nanocomposites was measured using a standard two-probe method by means of a digital multimeter (Voltcraft VC860) at an interelectrode distance of 1.2 cm. Silver (Ag) paste was applied in order to reduce contact resistance. As stated in the previous study [10], the contact resistance is much smaller than the resistance of the samples, thus in this case the advantages of the four point-probe method over the two-probe method are not significant. The resistance values were used then in order to derive the electrical volume resistivity (ρ) and electrical conductivity (σ) according to the dimensions of the samples measured. The electrical conductivity of MWCNTs in the form of bucky paper film has been measured also using a two-probe method and it was found to be in the range of $1.28 \times 10^2$ S m$^{-1}$.

3. Results and discussion

3.1. Influence of filler concentration on electrical conductivity of cementitious nanocomposites

In assessing the electrical conductivity of cement/MWCNT nanocomposites, the different phenomena occurring during cement hardening in conjunction with the MWCNT charge-carrier transport mechanisms need to be considered. For electrically conductive cement nanocomposites with carbon-based nanoinclusions, a superposition of ionic and electron conductivity is present [37]. With high water content the ionic conductivity is dominant, whereby in the dried state electron conductivity is preeminent [38]. Moreover, the distance between the fillers affects the conductive path and the carrier transport via a ‘hopping’ or a ‘tunnelling’ mechanism. Specifically, charge-carrier transport, due to an electron or hole tunnelling between the conductive filler, is only possible up to 2–3 nm distance [39]. Hence, for dispersed fillers a specific concentration is required to reach this interparticle distance and an electrically percolated network.

As seen in the SEM micrographs for the sample containing 1.1 wt.% of MWCNTs, a high amount of individually dispersed MWCNTs can be found throughout the whole cementitious matrix (figure 3, left). More specific, MWCNTs are well dispersed within the calcium silicate hydrate (CSH) structures of the matrix. Nevertheless, adjacent MWCNTs are also located close to each other with a high number of crossing points creating a well-percolated MWCNT network and extended number of MWCNT–MWCNT junctions, which may enable further the electrical current efficiently to pass through the whole sample.

The electrical conductivity of the nanocomposites is shown in figure 4 for samples after 28 d of hydration. All nanocomposites possess an electrical conductivity in the range of $10^{-1}$ S m$^{-1}$–$10^0$ S m$^{-1}$, means an electrically percolated MWCNT network is present for both prepared samples.
systems. As demonstrated in the SEM images above, this achieved by the MWCNT network within the cementitious matrix. Due to the pronounced number individualized MWCNTs, hopping and tunnelling mechanisms can occur throughout the nanocomposites.

As also expected, a better electrical conductivity is found with higher MWCNT loading. The higher number of MWCNT in the mixture results in a denser network. The is related to a reduction of MWCNT–MWCNT distances as well as a higher number of MWCNT–MWCNT interactions. Since the critical distance for electron tunnelling between individual MWCNTs is between 2–3 nm, for a denser MWCNT network electron tunnelling effects are more likely, explaining the higher measured electrical conductivity for higher MWCNT loading.

In figure 5 the influence of water on the electrical conductivity of the nanocomposites is also represented. In particular, the sample containing 1.1 wt.% of MWCNT is very sensitive to moisture. The highest electrical conductivity was found for samples with 1.1 wt.% MWCNT in the dried state. With increasing water content the electrical conductivity is reduced, as also reported in [10, 40]. The moist and wet samples possess a water film surrounding the MWCNTs, which acts as a barrier to the charge-carriers; cf figure 6. And this impairs the electrical conductivity of the nanocomposites [10].

In combination with the water and MWCNT loading, the age of nanocomposites influences their electrical conductivity, as seen in figure 5 for the moist nanocomposites. Almost all nanocomposites with the same filler loading have an electrical conductivity in the same range. Note, dried cementitious matrices without MWCNT as reference samples cannot be measured with the multimeter. At younger ages, 3 d and 7 d, for the samples containing 0.9 wt.% MWCNTs, similar electrical conductivity was measured, which is slightly smaller at 28 d. With 1.1. wt.% filler loading, increased electrical conductivity is seen during the first 7 d of hydration. This can be explained by the reduction of the free water content and densification of the cement morphology with increasing age (cf schematic illustration in figure 6). When mixing the MWCNT suspensions with the cement, one portion of the dispersed MWCNTs will be incorporated into the hydrating cementitious matrix, in particular during formation of calcium silicate hydrate (CSH) and ettringite. After 3 d of hydration the
samples still have a significant amount of micro- and macro-sized pores; see figure 6(a). Moreover, after only 3 d of hydration a large amount of pore water containing a significant portion of MWCNTs is still only physically bound in the porous structures; see figure 6(a).

With ongoing cement hydration, the porosity of the nanocomposites is further reduced; see figure 6(b). Thus, more pore water is consumed and one part of the dispersed MWCNT is further bound into the cementitious matrix. But another part of the MWCNTs will be further confined in a smaller volume in the remaining porous structure. Those will be in particular the larger, non-dispersed MWCNT agglomerates. Similar to an increase in MWCNT content, this filler confinement within the pore channels is related to a reduction of the MWCNT distances. More MWCNT junctions become present in the microstructure. Simultaneously, less water molecules around the MWCNTs are present. Both effects enable the observed increase in electrical conductivity after 7 d; see figure 6(b). After 28 d slightly decreased electrical conductivity is seen for both MWCNT loadings. This is induced by further cement hydration processes and, hence, a densification of the cementitious matrix, which is potentially related to a formation of an

\[ \text{Figure 5. Influence of age on the electrical conductivity of moist nanocomposites containing different amount of MWCNTs.} \]

\[ \text{Figure 6. Schematic illustration of the development of the MWCNT interconnected network within a cementitious matrix and the occurring charge-carrier mechanisms (hopping–tunnelling) as a function of time.} \]
insulating cementitious matrix between individual MWCNTs and suppressing electron tunnelling effects. Note that these changes in electrical conductivity are also reflected in the Joule heating performance, as discussed later in section 3.3; cf figures 12 and 15.

3.2. Influence of filler concentration on Joule heating effect of cementitious nanocomposites

The filler concentration drastically influences the heating performance of cementitious nanocomposites, as shown in figure 6 for dried samples at an age of 28 d measured using an applied voltage of 15 V. After starting the experiment, a typical Joule heating curve shape is observed, which is mathematically described in [30]. It can be clearly seen that with higher MWCNT loading a more pronounced Joule heating effect occurs, as similarly reported for CNF-modified cement pastes tested at significantly higher voltages [21]. For the samples with only 0.9 wt.% MWCNT content, an absolute temperature rise of ∼3 K is observed within the 10 min test. At the same time, an absolute temperature increase of ∼18 °C is seen for the sample with the higher MWCNT loading. This is explained by the higher electrical conductivity of the sample, as shown above (cf figure 4). In its specifics a more pronounced tunnelling and hole conduction mechanism is present among the single MWCNTs and within MWCNT network, respectively. This is related to a more efficient charge-carrier transport responsible for the current that passes through in the electrical field. Furthermore, this is directly associated with more pronounced electron collisions responsible for the Joule heating effect. Due to these higher charge-carrier collisions, energy is dissipated in the form of heat, which results in the higher measured temperatures.

The observed differences in the temperature measurements are confirmed by the time-resolved IR-T images, shown in figure 7 for thermally dried nanocomposites containing 0.9 wt.% and 1.1 wt.%. It should be mentioned that these images are recorded on the samples’ surfaces, whereby the temperature curves were recorded via a thermocouple inserted into the core of the samples. The visible dots in the centre of all samples represent those holes where the thermocouple was placed. For the sample with lower MWCNT loading only a slight increase (2 °C–3 °C) in the surface temperature was observed after 1 min; see figure 7 top. This surface temperature is rather non-homogeneously distributed. Also, no clear difference can be observed between the nanocomposite and the attached electrodes. With increasing time, only a marginal temperature increase on the surface is observed, whereby for the thermocouple measurements a slight increase of about 6 °C was still found; cf figure 6. However, after 10 min the surface temperature distribution appears more homogenous and clearly centrally located between the attached electrodes.

The more electrically conductive nanocomposite with 1.1 wt.% MWCNT loading already shows a significant temperature increase of up to 33 °C after 1 min; see figure 7—lower case images. It can be clearly seen that this increase is particularly pronounced in between the two electrodes, which translates exactly to the applied electrical field. In addition, a very homogenous distribution of the surface temperature can be seen, induced by the very well dispersed and homogenously distributed MWCNTs. As a result, temperature increases of up to 36 °C after 5 min could be observed. In the sample area outside the two electrodes a temperature rise is also seen, which can be traced back to the thermal conductivity of the nanocomposites. However, this heating is clearly less effective, and homogenous temperature distribution will require much time. However, after 10 min, no further significant increase of the surface temperature was seen. It is important to mention that the final surface temperature is clearly lower than the temperature measured via thermocouple in the core of the sample, indicating a decreasing temperature gradient towards the samples’ surface.
Figure 8. Time-resolved infrared images of the nanocomposites recorded at 15 V with 0.9 wt.% (top) and 1.1 wt.% MWCNT (bottom) loading, respectively.

In figure 8, the time-resolved IR-T images of the produced bucky paper are illustrated by applying 5 V of DC. As it can be observed, already after a very short time of 1 min, the MWCNT film reached approximately 100 °C. This is explained by the higher electrical conductivity ($1.28 \times 10^2$ S m$^{-1}$) of the BP compared to investigated nanocomposites. However, after 10 min the Joule heating effect is only slightly further increased up to approaching 108 °C.

In figure 9, the role of applied voltage is demonstrated for dried samples containing 1.1 wt.% at the age of 28 d. It can be seen that significantly higher temperatures can be obtained with higher applied voltages, as reported also by Galao et al for CNF-modified cement pastes utilising very high voltages [21]. Within the first 8 min, approximately 90 °C is reached, increasing further over time. Due to the higher applied voltage, a higher current is induced by the electrical field, as seen in figure 10, resulting in a more pronounced charge-carrier transport. This is directly related to the increasing frequency of charge-carrier collision and consequently a significantly higher temperature increase. According to equations (1) and (2), the power of the electrical heater is determined by the material’s resistance, as well as the applied voltage or induced current, respectively. Since voltage across or current through the sample contribute in a positive manner, a significant increase in the heating effect is observed. Moreover, the shapes of the recorded curves are very similar; only the slopes differ. Initially a more pronounced slope is observed, which levels off over longer time periods. The observed results fit well with the work by Gomis et al, who described this typical shape mathematically, based on the Newtonian law [30], and confirmed that the degree of heating is adjustable in response to the applied voltage.
3.3. Influence of cement age and water content on Joule heating effect

Since cementitious matrices are hygroscopic materials and consist of physical and chemical bound water, the role of water content in respect of the Joule heating effect in cementitious composites should be investigated. As shown in figure 11 for samples with 1.1 wt.% MWCNTs measured with 30 V after 28 d of hydration, the water content has a clear influence on the Joule effect. In contrast to the observations by Gomis et al [30], who reported higher temperatures with increasing moisture content, in the present study water impairs Joule heating behaviour; see figure 11. As already discussed above, the dried sample shows excellent heating behaviour with an electro-thermally induced increasing temperature up to 90 °C within the first 8 min; cf figure 14. For the moist sample, stored under laboratory conditions to contain both the remaining physically bound and the environmental water, the heating effect early on is less pronounced. This can be traced back to the higher resistivity of the nanocomposites, as reported in [10, 40] and shown in figure 3. As discussed in section 3.1, electrical conductivity is hampered by water layers among the MWCNTs, in this way supressing the electron tunnelling mechanism [10]. This correlates to a smaller electrical current induced within the applied electrical field; see figure 12. Thus, fewer charge-carrier collisions occur, and consequently the Joule heating is less effective.

Surprisingly, the wet sample does not yield a pronounced Joule heating effect within the timespan of the investigation.
In the beginning a slight increase with a typical shape can be observed, followed by a clear reduction in temperature. On the one hand, this might be explained again by the insulating water layer surrounding the MWCNTs, whereby this is rather unlikely since all the samples showed significant electrical conductivity, cf figure 3, and a clearly measurable electrical current, cf figure 12. On the other hand, the conductive properties of cementitious nanocomposites underlie a superposition of ionic and electron conductivity. For CF reinforced cement Wen and Chung reported that in the wet state, i.e. water saturated state, the ionic conduction dominates, whereby in the dry state the electron conduction is preeminent [38]. This might be in line with the study at hand, which shows that in the wet state electron movements and collisions are fewer and less vigorous, and no further warming is observed. The ions present in the cement pore solution do not contribute to the Joule heating effect, and no electrical heating can be obtained under wet conditions. Moreover, the wet curve further indicates an interesting physical phenomenon. Considering the measurement curve in more detail, a cooling effect of the sample can be observed at ~3 min. This can indicate that the Joule heating effect from the electron movement (cf figure 12) induces water evaporation, which would tend to cool the samples. As long as a significant amount of water is present in the sample, thermal energy is consumed in water evaporation and no heating effect can be obtained. It is here worthy of note that the authors continued these experiments for up to 8 h and could not measure a further temperature increase.

Another significant parameter for the Joule heating effect of cementitious nanocomposites is the material’s age, as seen in
Figure 13. Influence of moisture on the induced electrical current for nanocomposites containing 1.1 wt.% MWCNTs at 28 d and tested at 30 V.

Figure 14. Influence of age on Joule heating effect for dry nanocomposites containing 1.1 wt.% tested at 30 V.

Figure 13 for the dried samples with 1.1 wt.% MWCNTs. Here the potential contributions of water in the form of an insulating layer, evaporation, and ion conductivity are suppressed. For nanocomposites at younger ages, a less pronounced Joule heating effect was observed. This is explained by the densification of the nanocomposite morphology; cf figure 5. The nanocomposites possess at a young age very porous structures. With further cement hydration, the CNT network is more narrowed, and the distances between the CNTs are reduced; cf section 3.1. and figure 5. More electron tunnelling in the MWCNT network is possible and, thus, a more pronounced charge-carrier transport occurs. This is directly related to more electron collisions, resulting in a more pronounced Joule heating effect.

Moreover, the densification of the cement morphology is directly related to an increase in thermal conductivity, which additionally supports Joule heating throughout the sample. For the samples stored under lab conditions, i.e. moist samples, all the 3-d samples showed less pronounced heating performance. However, for the moist samples the behaviour at different ages is more complex (figure 13). The most pronounced Joule effect is observed for the 7 d samples and less pronounced heating for the youngest specimen (3 d). In this connection the parameters to consider is the different content of physically bound water in the nanocomposites as well as their changed morphology of time. As discussed above, among the MWCNTs water molecules build an insulating film, which reduces the electrical conductivity of the samples, in particular for nanocomposite at younger ages; cf figure 5(a). With further cement hydration, more water is bound in the crystal structure of the matrix. Additionally, physically bound water could further evaporate...
over time, which also reduces the insulating layer around the electrically conductive MWCNTs. At very young ages also, a very porous structure is present, which becomes denser over time. The densification of the MWCNT network within the first 7 d reduces the distances between the MWCNTs; cf section 3.1, and figure 5. Thus, more electron tunnelling and, hence, more charge-carrier collisions occur, resulting in more pronounced Joule heating. Hence, within the first 7 d both effects improve the electrical conductivity of the samples; cf figure 4. Hence they contribute clearly to the Joule heating effect.

However, after 28 d a slight decrease in the heating performance can be seen. This tendency is fully in line with the reduced electrical conductivity observed after 28 d, as seen in figure 4. As described in section 3.1, further cement hydration is related to the densification of the nanocomposite’s matrix. The cementitious matrix is further incorporated within the MWCNT network, resulting in a partial increase of the MWCNT–MWCNT distance, which is related to the suppression of more pronounced electron tunnelling effects. This example shows the complexity involved in developing heatable cementitious nanocomposites due to their specific material features, such as weight ratios, water content, and age.

4. Summary and conclusions

The main parameters responsible for electrothermal Joule heating effect in cementitious nanocomposites with carbon-based nanofillers have been systematically investigated for the first time. In this regard, the role of MWCNT concentration, water content, and nanocomposite age have been studied by applying two different DC bias voltages; namely 15 V and 30 V. Complex interactions of the investigated parameters were observed, showing a superposition of different effects due to the underlying electronic and ionic conduction mechanisms as well as changes in morphology.

All investigated nanocomposites were electrically conductive and, therefore, capable to be used as electrical heat generators. Thereby, the surface temperature was slightly smaller than the core temperature of the nanocomposites. With higher MWCNT loading and higher the applied voltage, the better was the obtained Joule heating effect, due to more charge-carrier movement and more frequent electron collisions. Moisture impaired significantly the Joule heating effect of the MWCNT nanocomposites, explained by the reduced electrical conductivity of nanocomposites due to an insulating water film surrounding the MWCNTs. Fully wet samples did not show a significant heating effect within the investigation period.

With regard to cement age, the Joule heating effect is promoted within the first days of hydration. This was induced by a higher electrical conductivity of the samples, due to their smaller water content and densified morphology. However, after 28 d of hydration the heating effect is slightly smaller due to further cement hydration and matrix densification.

The results show the challenges to assess and discuss the Joule heating effect in cementitious nanocomposite. However, they could facilitate the selection of proper parameters for designing ‘smart’ cementitious nanocomposites for potential de-icing, thermal management in buildings, etc, and can be also transferred to other cementitious composites with carbon-based nanofillers, such as graphene or carbon black.

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