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STUDY OF EARLY HYDRATION OF OPC-HAC BLENDS BY MICROWAVE AND CALORIMETRY TECHNIQUE

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ABSTRACT

The early hydration of the Ordinary Portland Cement (OPC)-High Alumna Cement (HAC) system has been investigated by using the microwave and calorimetry methods. It is found that the hydration process of OPC-HAC systems vary with the HAC proportion. The pastes containing 20 and 25% HAC show a feature of fast setting. And the pastes containing 33% and 50% HAC show quite unusual patterns in the dielectric ε, conductivity σ and heat-evolution rate R curves. We find that the microwave method is more sensitive to the cement hydration than that of calorimetry method. The correlation of the microwave measurement results with the calorimetry measurement results is discussed. © *1997 Elsevier Science Ltd*

Introduction

OPC-HAC based expansive cement is useful for repair and rehabilitation of urban infrastructure (1–4). However, the setting time of the OPC-HAC blend varies with the proportion of the two cements, and the fast set control is a problem that has limited the actual application of OPC-HAC systems. Thus, understanding of the hydration mechanism and the fast set behavior of OPC-HAC systems is important to the application of this system in expansive cement. The optimum proportion resulting in minimum setting time are reported about 70% HAC and 30% OPC (5,6). Recently, the impedance measurement technique was applied to investigation of the hydration process and setting behavior of OPC-HAC systems (7). The evidence indicates that the impedance and capacitive response are sensitive to ionic concentration changes in the liquid phase and microstructure development of the hydrating pastes.

Various electrochemical methods involving Potential measurement (8,9), conductivity measurement (10–15) and a.c. impedance measurement (7,16–21), have been used in the study of cement hydration. A novel microwave measurement which has been successfully used in the study of hydration of OPC, OPC-slag blend and mortars (22–24) has been developed. In this work, we used the microwave method together with the conduction calorimetry method to investigate the early hydration of OPC-HAC system. We also discussed the correlation between microwave measurement results and calorimetry measurement results.

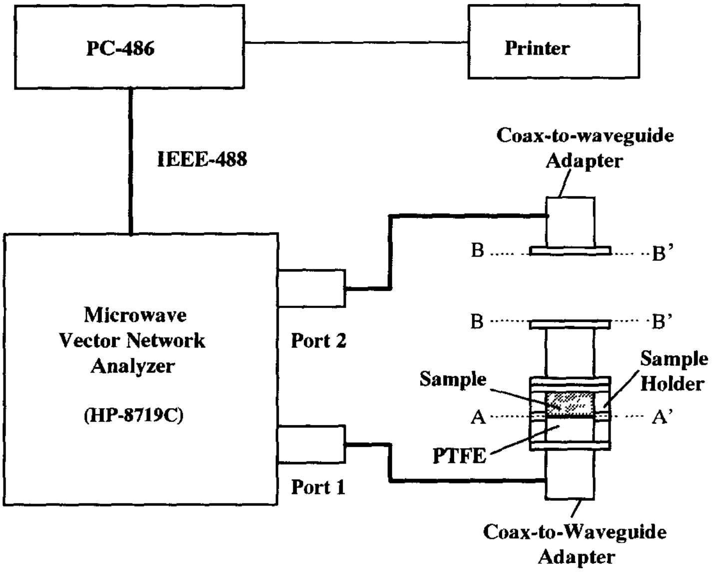

FIG. 1.
A schematic diagram of the microwave method set-up.

Measurements and Sample Preparation

Investigations of the electric property of materials at microwave frequencies are typically conducted by filling a rectangular wave-guide section with a sample of the material and then determining the complex dielectric constant from measurements of the reflection and/or transmission coefficients of the dominant waveguide mode. The equipment used in this work consists of a microwave vector network analyzer with a coax-to-waveguide adapter and a sample holder consisting of a section of the standard WR-90 waveguide. A personal computer is set up to receive data and then performs subsequent numerical analysis. Materials measurement software is used for all necessary network analyzer control, calculation, and data presentation. A schematic diagram of the experimental set-up is shown in Figure 1. The measurement is carried out at the frequency of 9.5 GHz. The details of the dielectric constant and electrical conductivity measurement can be refereed in reference 22.

OPC and HAC were used to make OPC-HAC blends in this work and their compositions are given in Table 1. The OPC-HAC cement blends were prepared by mixing the required amounts of solids with de-ionized water at a water to solid ratio of 0.4. The first electric measurement was made about 5 minutes after mixing with water. Further measurements were

TABLE 1
Component Oxides (wt%) of Cements Used

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	SO_3	Ig-loss
OPC	63.9	20.5	5.7	3.0	1.2	0.27	0.39	2.2	0.7
HAC	38.4	5.1	31.2	15.8	0.5	0.02	0.04	0.10	0.5

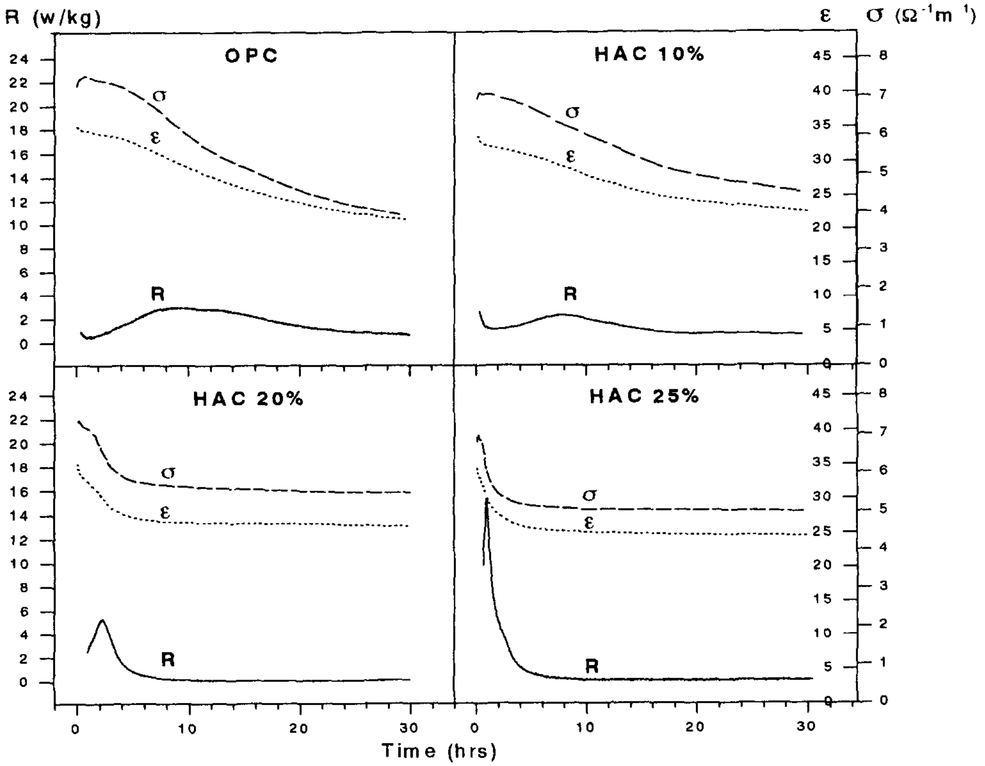

FIG. 2.

Variation of the electric constant ε, conductivity σ and the heat evolution rate R of OPC-HAC system during hydration.

made at intervals of 5–10 minutes during the first 5 hours and then at intervals of 0.5–2 hours over the next 25 hours. The heat evolution rate was measured using JAF Conduction Calorimeter. All measurements were made at 23°C.

Results

The variation of dielectric constant ε, electrical conductivity σ and heat-evolution rate R of OPC with time are shown in Figure 2. The conductivity σ curve is characterized by a first rapid increase accompanied by a rapid decreased in dielectric constant ε within 20 minutes after gauging with water. Thereafter a very slowly decreasing period in both ε and σ curves lasts for about 4–5 hours. At ~2 hours the value of the ε is ~34 and the value of the σ is ~7.5 Ω^{-1} m^{-1}. A drastic drop in ε and σ is observed after this slow change period. At ~20 hours both ε and σ change at a slow rate and at ~28 hours the values of the ε is ~23 and the value of the σ is ~4.2 Ω^{-1} m^{-1}. The relationship between the two electric parameters (ε and σ) and the chemical processes of OPC hydration has been discussed in the reference 23. The heat evolution rate R of the OPC shows a broad peak with a peak value R ~ 3 w/kg at 8 hours.

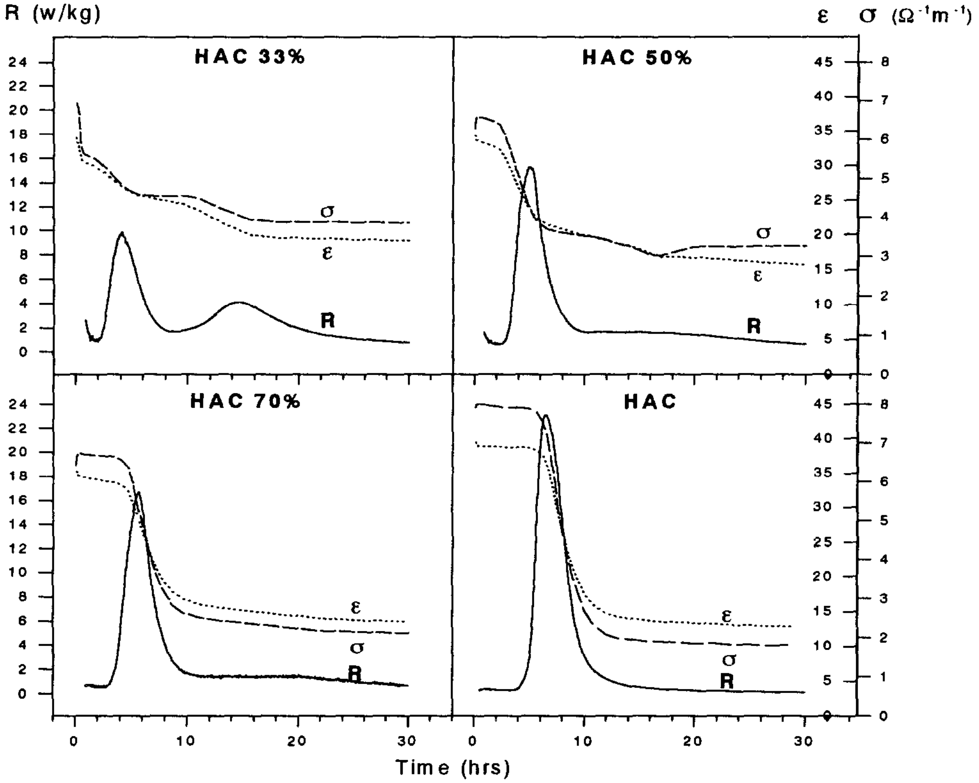

FIG. 3.

Variation of the electric constant ε, conductivity σ and the heat evolution rate R of OPC-HAC system during hydration.

The dielectric constant ε curve, conductivity σ curve and heat-evolution rate R curve of the HAC (see Figure 3) are very much different from that of the OPC. Comparing with the OPC, the HAC has a higher initial values of ε and σ (at 2 hours the ε is $\sim$39 and the σ is $\sim$8 Ω^{-1} m^{-1}) and a much smaller ε and σ values at 28 hours (the ε is $\sim$14 and the σ is $\sim$2 Ω^{-1} m^{-1}). We noted that for the HAC the slow change period lasts for about 6 hours. At $\sim$6 hour both ε and σ curves drops dramatically. At $\sim$12 hours the values of ε and σ are already close to their 28 hours values. The R curve of the HAC is also very much different from that of the OPC. It has a high and sharp peak. At $\sim$7 hours the peak reach the maximum with a R value of 23 w/kg, which is 7–8 times greater than that of the OPC.

The ε curve, σ curve and R curve of the OPC-HAC blends vary with the HAC proportion. For the paste containing 70% HAC, the curves are similar to that of the HAC (see Figure 3). But the values of ε and σ are smaller than that of the HAC at 2 hours, and greater at 28 hours. The drastic drops of ε and σ values are found to occur in the earlier time at 4–5 hours (see Figures 4 and 5). The peak or R curve of this specimen also occurs earlier at $\sim$6 hours, with a smaller R value of $\sim$17 w/kg as shown in Figure 3. For the paste containing 10% HAC, its ε, σ and R curves are similar to that of the OPC (see Figure 2). But the values of ε and

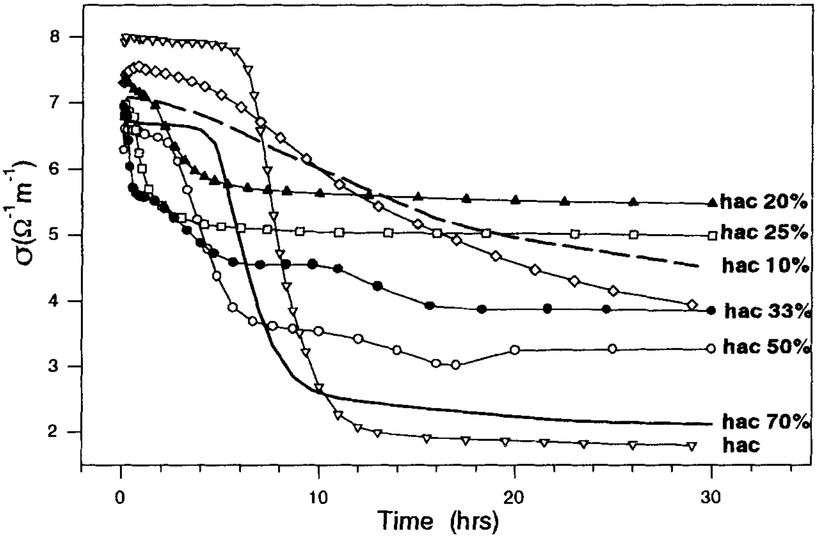

FIG. 4.
Variation of conductivity σ of OPC-HAC system with time.

σ are smaller than that of the OPC at 2 hours, and greater at 28 hours (see Figures 4 and 5). The R peak of this specimen is also smaller and occurs earlier compared with that of the OPC.

The OPC-HAC blends with HAC compositions of 20%, 25%, 33% and 50% behave very differently from OPC and HAC (see Figures 2 and 3). For the paste containing 50% HAC, the HAC component seems to play a dominant role as the R curve has the feature of HAC, but the R peak occurs earlier than that of 70% HAC sample (see Figure 6). Its ε and σ curves

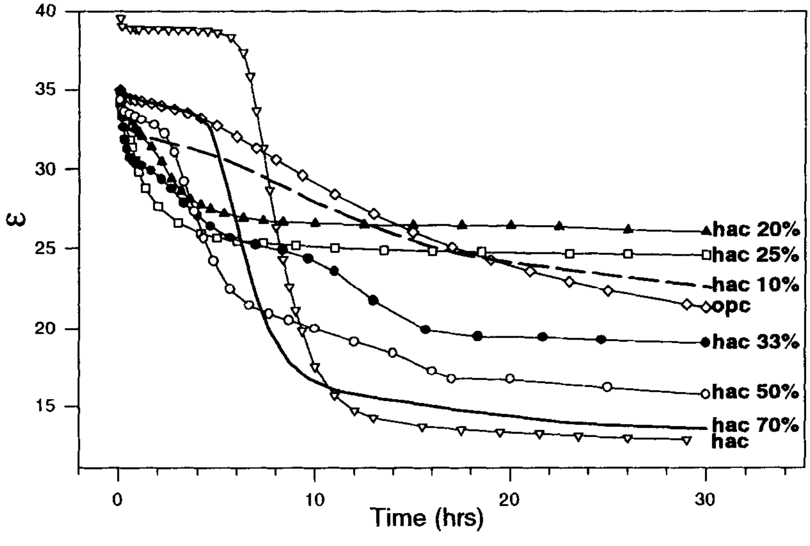

FIG. 5.
Variation of dielectric constant ε of OPC-HAC system with time.

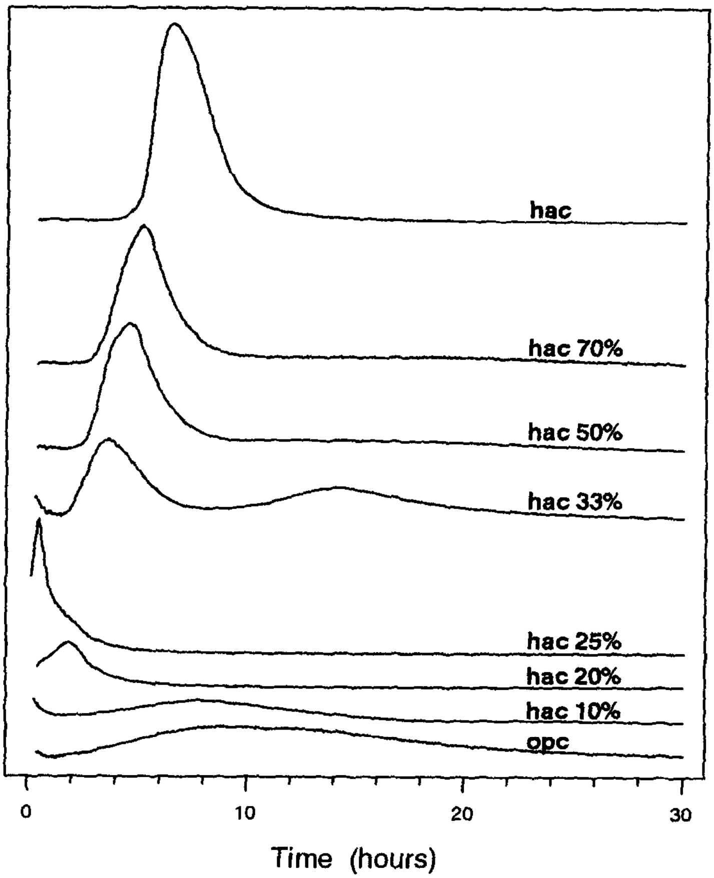

FIG. 6.
Heat evolution rate of OPC-HAC system during hydration.

are quite different from that of the HAC. After gauging with water, the σ increases and the ε decreases in the first 10 minutes and then they change slowly. At ~2 hours both of them drop dramatically and then at ~6 hours the ε and σ start to change slowly. At ~12 hours the ε and σ start to drop quickly again. At ~16 hours the ε decrease slows its rate but the σ increases surprisingly.

For the paste containing 33% HAC, there are two peaks in the R curve (see Figure 3). The first peak occurs at ~4 hours and is similar to the R perk in pure HAC sample. The second peak occurs at about 12–14 hours and is smaller than the first peak. There are three fast drops in the ε and σ curves in this sample (see Figure 3). The first starts in the very early time at ~15 minutes. The second occurs at ~2 hours. The third takes place in the later time (at 10–12 hours). After ~16 hours the values of ε and σ change little.

For the paste containing 20% HAC, the R curve has a much smaller perk comparing with 33% HAC sample (see Figures 2 and 3). This peak occurs earlier at ~3 hours. The fast drops in the ε and σ curves also occur earlier at 2–3 hours. After ~6 hours the ε and σ curves are almost unchanged. For the paste containing 25% HAC, shortly after mixing with water both

ε and σ decrease rapidly and after ~5 hours the decreases in the ε and σ slow down and eventually reach a relatively constant value. Corresponding with the earlier drop in the ε and σ curves, there is in the R curve a sharp and high peak with a R value of ~15.5 w/kg at ~1 hour. The unusual changes in the ε, σ and R curves are primarily due to the fast setting, which may be caused by the preferential reaction of gypsum with the HAC and by an increase in pH value due to the presence of the OPC. The fast setting causes accumulation of the hydrates around the cement grains so that the further hydration is impeded. That is why the pastes containing 20 and 25% HAC have a higher ε and σ values than that of the OPC after ~16 hours (see Figures 4 and 5).

Discussion

From Figures 2 and 3, we found that the results of microwave method correlate with the results of calorimetry method quite well. According to the traditional definition of the four periods of cement hydration based on the heat-evaluation rate curve, the change in electric responses ε and σ of cement pastes can also be divided into four stages:

(i) The Initial Stage. This stage begins immediately after the cement mixing with water. The initial dissolution of cement grains into water and the formation of AFT, CH, CAH_{10} etc. make ε and σ change quickly. This stage lasts for a very short time and coincides with the pre-induction period in the heat-evolution rate curve, where the exothermic wetting of cement grains and initial hydration of cement cause the first peak in σ curve.

(ii) The Slow Change Stage. This stage corresponds to the induction period in the heat-evolution rate curve. Within this stage the ε and σ of hydrating cement pastes change at a very low rate. Two opposing effects—the increase in ion concentration in liquid phase and the reduction in mobility of ions due to the formation of the diffuse double layer—cause the ε and σ of the pastes change slightly. This stage terminates when the ion concentration reaches over-saturation and the nucleation of hydrates begins. In all our microwave results, this stage will last a little longer than the induction period in the heat-evolution rate curve. This is possibly because the changes in the ε and σ are determined not only by the ion concentration in the liquid phase but also by the development of microstructure. The rapid condensation of the microstructure of cement paste may commence shortly after the beginning of the precipitation of the hydrates.

(iii) The Rapid Decrease Stage. This stage coincides with the acceleration period in the heat-evolution rate curve and is characterized by the rapid decrease in ε and σ. Due to the renewed hydration, a large amount of water and ions are combined into the hydrates. The rapid condensation of the microstructure and the adsorption of ions onto the enormous surface of hydrates reduce the mobility of ions. These effects all cause the fast drop in ε and σ. We noted that in the pastes containing 30 and 50% HAC two decreases in ε and σ curves are observed during this stage. In the heat-evolution rate curves of these pastes there are also two peaks in the acceleration period (The second R peak in the 50% HAC sample is not as apparent as in the 33% HAC sample).

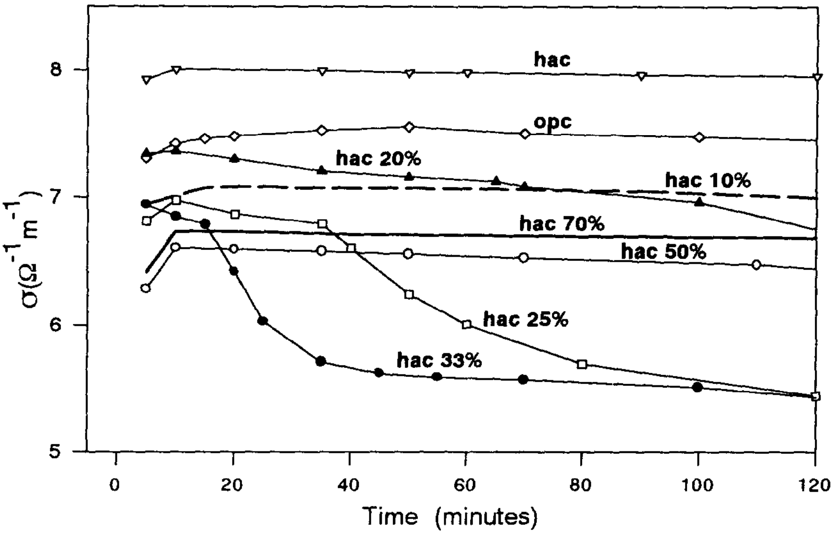

FIG. 7.
Variation of conductivity σ of OPC-HAC system within the first 2 hrs of hydration.

(iv) The Final Slow Change Stage. After the rapid drop of ε and σ, the changes in both electric parameters slow down and the values of ε and σ finally change little. This stage occurs at the same time when the deceleration and diffusion period in heat-evolution rate curve takes place. In some OPC-HAC pastes such as the paste containing 50% HAC, there is a slight rise in ε and σ in this stage. This rise may be due to the conversion of CAH_{10}, and C_2AH_8 to C_3AH_6 which can release water and increase the porosity of the paste matrix.

The differences in the values of ε and σ before and after their rapid decreases are of cause related to the ratio of OPC/HAC. The more the HAC, the larger the drop in the ε and σ. This is because the hydration of the HAC will take more water than the hydration of the OPC. But the final values of ε and σ of the pastes containing 20% and 25% HAC are greater than those of the pure OPC paste. This may be ascribed to the fast setting in these pastes, which impedes further hydration and leading to a heterogeneous distribution of hydrates so that a higher porosity formed in the paste resulting in higher ending values of ε and σ.

From Figures 2 and 3, we found that the fast drops in the ε and σ curves correspond in general to the peak in the R curve. But they do not correspond exactly. For example, for the HAC paste the peak position in the R curve occurs before the inflection point (at which the curve changes from turning downward to turning upward) in the ε and σ curves. While for the paste containing 50% HAC the R peak position occurs after the inflection. This possibly shows that the changes in ε and σ may correspond to the different mechanism in the cement hydration process, unlike the change in the heat-evolution rate. Another evidence for this is that in the paste containing 50% HAC there is a rise in the σ curve after ~16 hours whereas the R curve has no apparent change at the same time. We think that the changes in the σ may correspond mainly to the development of microstructure of cement paste.

It is known that the calorimetry method is not very suitable for the study of cement hydration at very early stages as the cement sample takes about 20–30 minutes to reach equilibrium in the water bath of the calorimeter. But the microwave measurement can start in 5 minutes so that microwave method is particularly suitable for studying the fast setting behavior of OPC-HAC system. Figure 7 shows that after 15 minutes the σ of the paste containing 33% HAC starts a fast drop. We also see a fast drop in the σ curve of the 25% HAC paste at 35 minutes. More works are needed to determine what corresponds to these early fast drop in the σ curves.

Conclusions

The microwave and calorimetry methods are used to study the early hydration of OPC-HAC system. We found that HAC has very different measured results of dielectric constant ε, conductivity σ and heat-evolution rate R from OPC. The hydration process of OPC-HAC systems vary with the HAC proportion. The hydration of the pastes containing 70% HAC is quite similar to that of the HAC, whereas the hydration of the pastes containing 10% HAC is quite similar to that of the pure OPC. The pastes containing 33% and 50% HAC have quite unusual patterns in ε, σ and R curves. Both the pastes containing 20 and 25% HAC have a feature of fast setting. Generally speaking, the correlation of microwave measurement results and the calorimetry measurement results is exist though these two techniques may not correspond exactly to the same mechanism of cement hydration. We found the microwave method is more sensitive to the cement hydration than the calorimetry method, and it is more suitable to study very early cement hydration, especially in the complex system like OPC-HAC system.

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