

# DIELECTRIC CHARACTERIZATION AT HIGH FREQUENCY (1 MHz - 1.8 GHz) OF A PORTLAND CEMENT AT THE EARLY STAGES OF HYDRATION

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*The aim of the present paper is to demonstrate that by using frequencies  $> 10^6$  Hz, it is possible to get information about phenomena at the interface between cement and water, and therefore to follow hydration in a cement based material at the early stages. Disks of Portland type cement was prepared with water to cement weight ratio, W/C, equal to 0.4. The samples cured for 10 hours at 20 °C and 50 % relative humidity were tested electrically at 10, 14, 16, and 18 hours after mixing. The experimental technique was based on high frequency measurements (1 MHz to 1.8 GHz) with a 4291 A Hewlett-Packard apparatus. This frequency range is useful to follow phenomena at the cement / water interfaces during hydration or, equivalently, hardening of the cement based material. The complex permittivity as a function of frequency was studied in relation to the time after mixing. The progressive passage of water from an electrolytic form to hydrated phases was identified. It corresponds to the relaxation of the real part of the permittivity at  $2.2 \times 10^6$  Hz and approximately  $10^6$  Hz, respectively. A Cole-Cole type distribution, taking into consideration the degree of heterogeneity,  $\alpha$  (with  $0 < \alpha < 1$ ), of the material, was proposed to fit the experimental data points. It is shown that  $\alpha$  increases from 0.37 to 0.48 as the hardening time goes from 10 to 18 hours.*

## INTRODUCTION

The long-term behaviour of cement paste is closely related to its state at a young age and in particular water content and distribution. Experimentally, it is a challenge to develop non-destructive techniques to characterize the cement-based systems. Several groups have investigated electrical measurements either by looking at the DC electrical conductivity, by using impedance spectroscopy up to 1 MHz [1-12], or by microwave dielectric measurements between 100 kHz and 20 GHz, via the time-domain reflectometry method [13]. In this latter case, the characterizations have been carried out on cements, either after curing for 1 hour or after curing for 57 days. The authors report relaxation phenomena at frequencies of ~ 100 and 1 MHz for the cement being set for 57 days related to the orientation of the different types of hydrated water in the calcium silicate hydrates, C-S-H.

The aim of the present communication is to demonstrate that by using frequencies between  $10^6$  and  $1.8 \cdot 10^9$  Hz, it is possible to follow hydration in cement based material at the early stages and to have a signature of its heterogeneity.

## EXPERIMENTAL PART

The measurements were carried out between 1 MHz and 1.8 GHz with the 4291A Hewlett-Packard apparatus. Instead of the vector-voltage-current-ratio measurement method (usable at low frequencies), the principle is to

measure the reflection coefficient of an electromagnetic wave sent on the tested sample. The measurement frequency test signal being applied to the sample is terminated at the test port and detects the vector-voltage-ratio of the reflected wave,  $V_{ref}$ , to the incident wave,  $V_{inc}$ , to measure the reflection coefficient. The complex reflection coefficient,  $\Gamma^*$ , is defined as:

$$\Gamma^* = \frac{V_{ref}}{V_{inc}} = \Gamma_x + i\Gamma_y \quad (1)$$

The complex reflection coefficient value and the normalized complex impedance value of the sample,  $Z_R^*$ , are related by the following formula:

$$Z_R^* = \frac{1 + \Gamma^*}{1 - \Gamma^*} \quad (2)$$

where  $Z_R^*$  is defined as:

$$Z_R^* = \frac{Z^*}{Z_0} \quad (3)$$

where  $Z^*$  is the complex impedance of the tested material and  $Z_0$  is the characteristic impedance of the coaxial line (50  $\Omega$ ).

The next stage is to relate the complex dielectric permittivity,  $\epsilon^*$ , of the cement with its complex impedance. For an alternating field, the complex permittivity is given by:

$$\epsilon^* = \epsilon' - i\epsilon'' = \epsilon_0 (\epsilon'_R - i\epsilon''_R) \quad (4)$$

where  $\epsilon_0$  is the permittivity of vacuum and  $\epsilon'$  (resp.  $\epsilon'_R$ ) and  $\epsilon''$  (resp.  $\epsilon''_R$ ) are the real and imaginary parts of the permittivity (resp. relative permittivity).  $\epsilon^*$  is related to the complex admittance,  $Y^* (\frac{1}{Z^*})$ , as follows:

$$\frac{Y^*}{i\omega} = \epsilon^* L(\omega) = \epsilon^*_R \epsilon_0 L(\omega) \quad (5)$$

where  $L(\omega)$  is a geometrical factor which takes into consideration the edge effects as specified by Hewlett-Packard.

The samples were prepared in form of cement disks (diameter 20 mm ; thickness: 2.5 mm) with mirror like surfaces. No electrode is coated onto the samples. The tested materials made from Portland cement (CEM 52.5, Lafarge) were mixed with distilled water with a water to cement weight ratio  $W/C = 0.4$ . After mixing for 1 min with a blender, the paste was simultaneously vibrated and de-aerated under low pressure ( $\sim 10^{-1}$  bar) for 4 min. Then it was poured into a cylindrical mould with mirror polished faces. The samples were cured for  $t_0 = 10$  hours at 20 °C and 50 % relative humidity. After this curing delay, the cement was tested electrically at 20 °C and at  $t_1 = 0, 4, 6, 8$  and 140 hours. The times reported on the various figures correspond to the total time after mixing, i.e.  $t_0 + t_1$ . In addition a disk of Portland cement dried at 110 °C for 24 hours (called anhydrous cement) was prepared and tested electrically.

### RESULTS AND DISCUSSION

Figure 1 shows the variations of the real part of the relative permittivity as a function of frequency. The data points at various hydration stages are located between the dielectric curves for water and for anhydrous cement in the whole frequency range. It is the signature of the progressive passage of water from an electrolytic form containing ions to hydrated phases. The curves for the hydrated cement pastes show a typical behaviour of dielectric materials where the real part of the relative permittivity decreases from its relaxed value at low frequencies to its unrelaxed value at high frequencies [14]. Figure 2 presents the variations of  $\epsilon'_R$  and  $\epsilon''_R$  versus frequency determined for the material from 10 to 18 hours after mixing. It can be noticed that the dielectric behaviour of hydrated cement is very sensitive to curing time. For a given frequency, the drop of  $\epsilon'_R$  and  $\epsilon''_R$  as the time after mixing increases is particularly marked.

The equation used to describe a relaxation process characterized by a single relaxation time,  $\tau_0$ , has the form [15]:

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_1 - \epsilon_\infty}{1 + i\omega\tau_0} \quad (6)$$

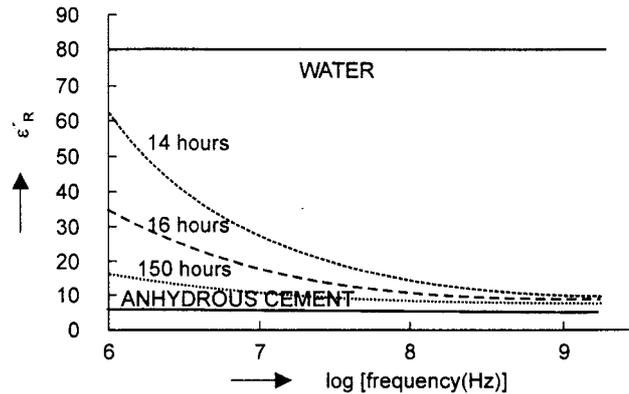
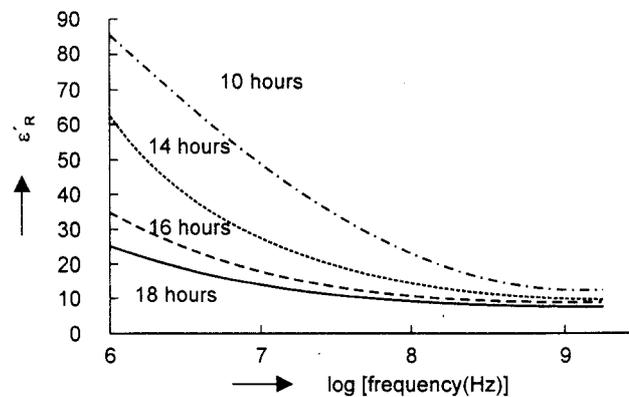
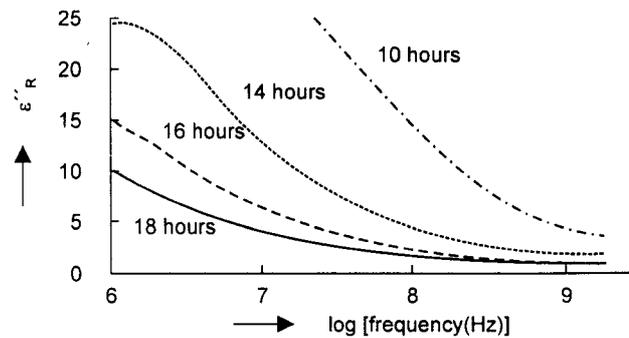


Figure 1. Evolution of the real part of the relative permittivity as a function of frequency for a Portland type cement ( $W/C = 0.4$ ). The values correspond to  $t_0 + t_1$  where  $t_0 = 10$  hours and  $t_1$  ranges between 0 and 140 hours.



a)



b)

Figure 2. Variations with respect to frequency of the real (a) and of the imaginary parts (b) of the relative permittivity of a Portland cement cured for different times.

The values correspond to  $t_0 + t_1$  where  $t_0 = 10$  hours and  $t_1$  ranges between 0 and 8 hours.

where  $\epsilon_1$  and  $\epsilon_\infty$  refers to the permittivity at low and high frequencies, respectively. This equation does not fit perfectly the data points in figure 2. The consideration of only one relaxation time appears to be too simplified.

A better fit of our experimental data is found if we consider that several relaxation times are involved, as observed in a typical ceramic based material [16, 17]. In this case, the expression given by K.S. Cole and R.H. Cole [13, 16] describing the variations of the complex permittivity can be used:

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_1 - \epsilon_\infty}{1 + (i\omega\tau_0)^{1-\alpha}} \quad (7)$$

where  $\alpha$  is a coefficient representing a distribution of relaxation times. It is readily seen that for  $\alpha=0$ , the expression reduces to equation (6). Table 1 lists the parameters leading to the best fit of our data points for each curing time between 10 and 18 hours.

The value of  $\epsilon_1$  decreases regularly with setting time. It corresponds to the passage of water from the liquid state to an hydrated phase. Relaxation frequency  $f_0 = 2.4 \cdot 10^6$  Hz appears from 14 hours and its value slightly decreases with setting time. According to ref.[13], this frequency value around 1 MHz could correspond to the orientation of water molecules that are attached to the calcium silicate via chemical bonding. The complete distribution of the relaxation times can be obtained by applying the Cole-Cole equation:

$$G(\ln\tau) = \frac{1}{2\pi} \frac{\sin\pi\alpha}{\cosh\left\{(1-\alpha) \ln\left(\frac{\tau}{\tau_0}\right)\right\} - \cos\pi\alpha} \quad (8)$$

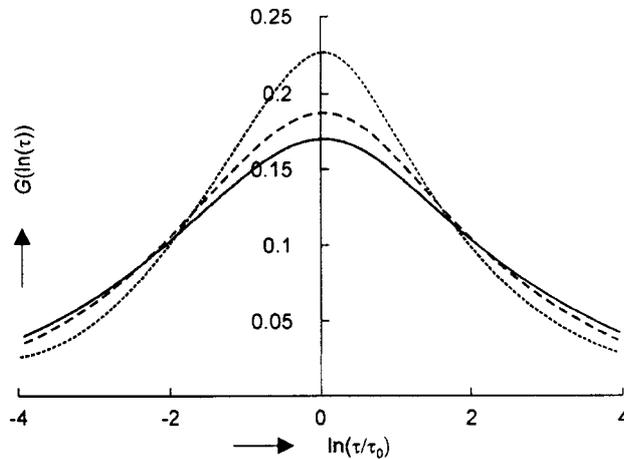


Figure 3. Distribution of relaxation times deduced from the Cole-Cole equation (8). The corresponding coefficients are given in table 1.

..... 14, - - - - 16, ———— 18 hours after mixing

Figure 3 shows this distribution plotted for the Portland cement cured from 14 to 18 hours. In each case, the distribution is symmetric. Its width or, equivalently, the  $\alpha$  value increases with the setting time (table 1). This

fact indicates that the longer time after mixing brings the more heterogeneous behaviour of water molecules linked to calcium silicate.

Table 1. Parameters used in equation (7) to simulate the data on figure 2.

| $t_0 + t_1$ (hours)            | 10                   | 14                  | 16                 | 18                 |
|--------------------------------|----------------------|---------------------|--------------------|--------------------|
| $\epsilon_1$                   | $81\epsilon_0$       | $79\epsilon_0$      | $55\epsilon_0$     | $42\epsilon_0$     |
| $\epsilon_\infty$              | $9.5\epsilon_0$      | $8.6\epsilon_0$     | $7.8\epsilon_0$    | $7.1\epsilon_0$    |
| $\tau_0$ (s/rd)                | $0.71 \cdot 10^{-8}$ | $6.7 \cdot 10^{-8}$ | $14 \cdot 10^{-8}$ | $20 \cdot 10^{-8}$ |
| $f_0$ (MHz)                    |                      |                     |                    |                    |
| $(f_0 = \frac{1}{2\pi\tau_0})$ | 22                   | 2.4                 | 1.1                | 0.8                |
| $\alpha$                       | 0.37                 | 0.39                | 0.45               | 0.48               |

For the cement paste cured for 10 hours, a relaxation phenomenon at  $f_0 = 22 \cdot 10^6$  Hz can be noticed. This frequency value is higher in an order of magnitude than that for a cement paste cured between 14 and 18 hours. Such value can be considered as characteristic of the relaxation of water molecules that are attached to the calcium silicate via hydrogen bonds [13], though our value is smaller than what is reported in the literature (i.e.  $\sim 100$  MHz).

### CONCLUSION

The aim of the present communication was to show the possibilities offered by high frequency measurements (1 MHz up to 1.8 GHz) for characterizing cement based materials at the early stages of hydration. The frequency range is suitable to obtain information about phenomena occurring at the water - cement interface during hydration. In the present case, we studied Portland type samples prepared with water to cement ratio 0.4. The electrical characterizations were carried out from 10 to 18 hours after mixing and involved the measurement of the complex permittivity as a function of frequency. The permittivity indicates relaxation phenomena at  $2.2 \cdot 10^6$  Hz and around  $10^6$  Hz between 10 and 14 hours after mixing, respectively. These frequencies are characteristics of the vibration of water molecules either adsorbed, via hydrogen bonding, at the surface of cement particles, or incorporated in hydrates. In other words, as cement hardening proceeds, water combines progressively with other chemical species at the surface of cement particles to give hydrates. The technique described in this letter enables a very fine tracking of the modifications in the state of water to be achieved. Future work will be focused on the study of these phenomena in relation to the chemical interfacial interactions between cement and water as complete understanding of the physical chemistry of cement hydration is still a challenge [18].

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DIELEKTRICKÁ CHARAKTERIZACE  
PORTLANDSKÉHO CEMENTU  
PŘI VYSOKÝCH FREKVENCÍCH (1 MHz - 1,8 GHz)  
V POČÁTEČNÍCH FÁZÍCH HYDRATACE

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Dlouhodobé chování cementových kaší úzce souvisí s jejich stavem krátce po jejich smísení s vodou, a závisí zvláště na obsahu a rozdělení vody. Experimentálně je zajímavé sledovat charakteristické vlastnosti systémů na bázi cementu nedestruktivními metodami. Cílem této práce bylo prokázat, že použitím frekvencí vyšších než  $10^6$  Hz je možné získat informace o jevech na rozhraní mezi cementem a vodou, a tím sledovat počáteční fáze hydratace cementových materiálů.

Měření byla prováděna v rozmezí od 1 MHz do 1,8 GHz na přístroji Hewlett-Packard 4291A. Zkušební vzorky byly připravovány z cementu Lafarge CEM 52.5 smísením a destilovanou vodou. Vodní součinitel činil 0,4. Vzorky kaší byly ponechány tuhnout a tvrdnout po dobu 10 h při teplotě 20 °C a 50% relativní vlhkosti. Po dobu byly vzorky zkoušeny vysokými frekvencemi v intervalech  $t_1 = 0, 4, 6$  a 8 h (celková doba po zamísení činila  $t_0 + t_1$ ). Mimo toho byl rovněž připraven a zkoušen vzorek portlandského cementu vysušený při teplotě 110 °C po dobu 24 h (tak zvaný bezvodý cement).

Během postupujícího tuhnutí a tvrdnutí se změny reálné části relativní permitivity jako funkce frekvence nacházejí mezi dielektrickými křivkami pro vodu a pro uvedený bezvodý cement. Jde prakticky o záznam přeměny elektrolytické iontové formy vody do hydratovaných fází. Křivky hydratované cementové kaše vykazují typické chování dielektrického materiálu, kde se skutečná část relativní permitivity snižuje ze své klidové hodnoty při nízkých frekvencích na vybuzené hodnoty při vysokých frekvencích. Relaxační jevy lze pozorovat při frekvencích cca.  $10^7$  Hz 10 h po zamísení, a při cca.  $10^6$  Hz po více než 14 hodinách po zamísení. Tyto relaxační frekvence odpovídají molekulám vody adsorbovaných na částicích cementu, ale také již vázaným do hydratovaných sloučenin. Pro vyjádření experimentálních dat bylo navrženo rozdělení typu Cole-Cole. Metodu lze využít pro studium heterogenity materiálů a pro sledování jevů hydratace cementu.