Ion monitoring solutions in cements using electrical spectroscopy

E. Menéndez
IETCC “Eduardo Torroja” (CSIC),
C/ Serrano Galvache, 4. 28033 Madrid (España),
e-mail: emm@ietcc.csic.es

J. de Frutos
POEMMA R&D Group, ETSIT (UPM),
Ciudad Universitaria 28040 – Madrid.

Recibido el 14 de agosto de 2008; aceptado el 8 de diciembre de 2008

This work proposes a new procedure to study the appearance and combination of different ions in the first steps of cement hydration. The suitable conditions of work are identified, and these conditions are applied to ordinary Portland cement and also to two cements with a partial substitution by fly ashes and slags. With the results obtained is clear that the measurement process permits the discrimination of phenomena that appear in a short space of time, and which it is not possible by the traditional methods of cement test. The responses found are very different for the different families of materials studied and these are related with the presence of ions in the material.

Keywords: Electrical impedance; cement; hydration; electrochemistry.

En este trabajo, se plantea un nuevo procedimiento para estudiar la aparición y combinación de diferentes iones en las etapas iniciales de hidratación del Cemento. Se determinan las condiciones idóneas de aplicación del mismo, y se aplica en el estudio de un cemento Portland ordinario, un cemento con adición de ceniza volante y un cemento con escoria de horno alto. Se pone de manifiesto que este procedimiento de medida permite la discriminación de fenómenos que se producen en cortos espacios de tiempo y cuya discriminación no es posible aplicando los procedimientos habituales de ensayo de cemento. Se obtienen respuestas muy diferentes para cada familia de material estudiado y se relaciona esta respuesta con la presencia de iones en el material.

Descriptores: Impedancia eléctrica; cemento; hidratación; electroquímica.

PACS: 82.45.-h; 84.37.+q; 81.70+q

1. Introduction

In the hydration of cement without addition, hydrated calcium silicates (C-S-H) are formed as main products which act as a matrix in the cement, also calcium hydroxide (CH) (portlandite) are formed, which is formed both in the matrix and in the interior of the pores. Also, the reaction of the aluminates and ferritealuminates, in the presence of gypsum, gives rise to the formation of ettringite (C₆₃₅₆₃₃₂₃₂) which, in the second stage and without sulfur, could react with the aluminates to form monosulfoaluminate 3C₄ASH₁₂, with these compounds appearing both in the matrix and in the porous areas of the material [1,2]. For its part, the hydration of the cements with additives requires the study of the hydration mechanism both in Portland cement and in each of the additives, as well as the interaction process. In the case of cements with fly ash, the hydration products formed are the same as those indicated for cement [3]; while in cements with slag, as well as the hydration products of the cement, a new hydro-calcite type phase is formed [4]. On the other hand, it must be taken into account that when additions are used, the reaction kinetics is modified [5].

At the beginning of the nineteen nineties the electrical impedance spectroscopy began to be used habitually for the study of cement pastes [6] analyzing Portland cement pastes with a water:cement ratio of 0,27 at three stages of hydration (1, 10 and 100 days), with different ways of processing the material and study conditions [7-9], and to relate the impedance spectra and its relationship with the microstructural characteristics [10] or with the manufacturing process [11,12], the setting conditions and the type of electric contact [13,14]. In general, in recent years, this technique has been used in cements to study its microstructural evolution and, in particular, the structure of the pores [6-12,15]. Several models of equivalent circuits have been proposed to estimate the significant physical parameters of the electrical responses according to the structure, distribution and size of the pore, together with the degree of hydration [12-18] always for periods of more than 24 hours, in which the stability of the material which allows the impedance arcs had been studied.

In this work, we propose a new procedure for studying the initial reactions to hydration in these materials, based on the measurement of their electrical impedance at different frequencies and according to time. In the use of the aforementioned electrical impedance spectroscopy it is essential to determine the impedance arcs in high and low frequency ranges. This demands measurement times of more than 30 minutes for each measurement, in which many of the initial and intermediate states are lost. On the other hand, the hydration process has with it significant changes in the presence of ions in solution which give rise to significant changes in the electrical response of the material. The intention of this work is to relate the said electrical response to the presence of ions.
ION MONITORING SOLUTIONS IN CEMENTS USING ELECTRICAL SPECTROSCOPY

Table I. Chemical composition of the cements and components.

<table>
<thead>
<tr>
<th></th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>SO$_3$</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>TiO$_2$</th>
<th>P$_2$O$_5$</th>
<th>P.F.</th>
<th>Cl$^-$</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM I</td>
<td>20.05</td>
<td>5.19</td>
<td>2.20</td>
<td>62.04</td>
<td>3.60</td>
<td>2.83</td>
<td>0.30</td>
<td>0.86</td>
<td>0.24</td>
<td>0.14</td>
<td>2.52</td>
<td>0.03</td>
<td>100.00</td>
</tr>
<tr>
<td>CEM II-A/S</td>
<td>22.00</td>
<td>6.18</td>
<td>2.22</td>
<td>59.20</td>
<td>4.29</td>
<td>2.34</td>
<td>0.28</td>
<td>0.81</td>
<td>0.32</td>
<td>0.12</td>
<td>2.20</td>
<td>0.04</td>
<td>100.00</td>
</tr>
<tr>
<td>CEM II-A/V</td>
<td>22.84</td>
<td>7.46</td>
<td>2.82</td>
<td>57.40</td>
<td>2.10</td>
<td>2.60</td>
<td>0.85</td>
<td>0.28</td>
<td>0.06</td>
<td>0.33</td>
<td>3.20</td>
<td>0.06</td>
<td>100.00</td>
</tr>
<tr>
<td>SLAG</td>
<td>38.42</td>
<td>11.31</td>
<td>1.54</td>
<td>40.76</td>
<td>6.54</td>
<td>0.24</td>
<td>0.00</td>
<td>0.32</td>
<td>0.71</td>
<td>0.02</td>
<td>0.00</td>
<td>0.14</td>
<td>100.00</td>
</tr>
<tr>
<td>FLY ASH</td>
<td>50.17</td>
<td>28.19</td>
<td>4.07</td>
<td>6.62</td>
<td>1.74</td>
<td>0.27</td>
<td>0.28</td>
<td>0.57</td>
<td>1.51</td>
<td>1.07</td>
<td>5.50</td>
<td>0.01</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Figure 1. Microstructure of the non hydrated ashes and slag used as an addition in the C-II-V y C-II-S compositions, respectively.

Figure 2. Different microstructures at 7 days of hydration of the three compositions. Obtained by a Scanning Electron Microscope.

Figure 3. Heat of Hydration as a function of time for the three compositions.

and consequently to the chemical reactions that take place in the material. These results are complemented by a microstructural analysis using a scanning electron microscope. In order to establish the potentiality of the technique, we use three different materials; the first will serve as a reference and will be made up of Portland paste, while the other two will correspond to the paste with the addition of fly ash or slag.

2. Experiment procedure

2.1. Materials for the tests

Three pasts have been designed and analyzed with a 1:3 water:cement ratio. The comparative response of a reference material (C-I) made up of traditional Portland cement without addition is analyzed in relation to two other cements with the partial substitution of clinker for 12.1% slag (C-II-S) or 7.9% fly ash (C-II-V). The different composition of the cements influences both the development of the hydration, and the microstructure of the products formed during the hydration. The chemical composition of the cements, slag and fly ash used for the manufacture of the cement pastes, is detailed in Table I.

The microstructure of the addition also has a significant influence on the behavior during the hydration, as does the observed electrical response. The analysis of the additions of fly ash and slag, by means of a scanning electron microscope, is detailed in Fig. 1. In Fig. 2, the different hydration products from in each of the test pastes can be seen for different stages.

2.2. Semi-adiabatic calorimetry

The analysis of the heat generated during the initial stages of the process of hydration in the cements allows us to see its evolution as well as quantifying the heat generated. The heat in hydration is a function of the nature of the cement and is between 10-50°C.
The cement material is introduced, after being mixed, into a Dewar dish with a thermally insulated lid, in which a thermocouple is inserted into the central part to register the heat produced over period of time. The hydration temperature is registered using a voltmeter. In this case the temperature is measured every 5 seconds, for a total period of 48 hours. The obtained data are showed in Fig. 3. It can be seen different behaviors for each of then, although it is difficult to relate the differences with the processes that are taking place.

2.3. Measuring the electrical impedance

A modification is proposed in this work of the Impedance Spectroscopy technique which consists of measuring the dielectric response of the material from the first instants of the hydration at different frequencies. From these measurements it is a question of determining the processes that take place in the material, both from the analysis of the impedance arcs, taking into account the dynamism of the response, and the specific analysis of the response at different frequencies. In order to complete this information and analyze the potentiality of our technique, we complement the information by taking measurement of the heat during the hydration to see to what extent both studies complement each other. In order to carry out these dielectric measurements, a specific sample holder has been developed that allows the response of the material to be obtained form the first stages of the hydration. This disposition allows data to be taken before initiating the hydration process. The impedance measurements have been taken using a 1260 A Impedance/Gain-phase Solartron analyzer with a 1296 A dielectric measuring module, which allows analysis within the range of frequencies from 10 µHz to 10 MHz, of $10^2$ to $10^{17}$Ω impedances, with a frequency resolution of 1 in 65,000,000 together with the possibility of applying a DC bias in the range of ±40.95 V. Software specifically developed by the authors has been to handle the results.
through the Solartron ZPlot software package. In the initial step, so as to be able to carry out the study of this process, the electric response values of the material are acquired with continuous cycles of data in the range of $10^0$ Hz to $10^{-3}$ Hz in a logarithmic sweep. The disadvantage of this process is that each cycle needs at least 30 minutes to be carried out, thus making the initial response of the hydration process of little use. However, it does help us to differentiate the chemical processes that take place, as well as the possibility of associating them to the electrical response obtained. With these data, a measurement strategy is determined with frequencies that allow, on the one hand, the chemical processes to be studied, and on the other, the initial response of the hydration.

As has already been stated, the electrical response is significantly modified as a result of their different composition.

3. Results and discussion

The $Z''(Z')$, for each of the sample chosen is detailed in Fig. 4 at different times for the three samples. The lack of well-defined arcs, the difficulty in determining relaxation times, and especially the period of time necessary to complete each cycle (approximately 2,000 seconds) makes it difficult to determine the processes related to the hydration from this information.

In order to get the information that we are looking for, we have represented (Fig. 5) the evolution of an electric parameter, $Z'$, normalized to the frequency to enable us to visualize the phenomena better. With these values superimposed, we have included the curve corresponding to the hydration heat in the material since, as has already been said, the specific heat measurements have been used in order to understand the reactions that take place in the process.

From the previous figures, a behavior can be seen that is clearly different in all of the pastes and with different responses for each frequency. On the other hand, the hydration process determined by the calorimeter shows a behavior similar to the electrical response at high frequencies. However, alterations in the response of the pastes at low frequencies can be seen. It can be seen that the measurement of the impedance, and especially its working frequency, is a potent tool for determining the phenomena and chemical processes that take place in these materials during the initial stages of hydration. Each range of frequencies provided different information. Thus the high frequencies allow the general behavior of the material to be determined in a similar manner to the hydration heat, although with a small gap in the time with respect to it. For its part, studies at low frequencies clearly show the presence of different phenomena and reactions that are taking place in the hydration process.

The limitation that we have found is that, in order to carry out the studies at low frequencies, each measurement takes longer than some of the phenomena that take place in shorter periods of time and are not visualized. At frequencies of more than 1 Hz, the results that are obtained are sufficiently discriminative of the phenomena that take place, and require sufficiently short measurement times so that phenomena in the measurement process do not disappear.

In order to make a first analysis of the processes studied, the results obtained from the three pastes tested are compared with the hydration values (Fig. 3) and the impedance values determined at 1 Hz and according to time (Fig. 6). The electrical response at 1 Hz which provides information on the processes is taking place in the material are also detailed.

The different heats produced by hydration have a very similar behavior (Fig. 3), which is why the analysis is difficult to use in order to deduce the types of phenomena that are taking place, while the electrical response has very significant changes between them. In all cases, a reduction begins in the impedance within about two hours, but while in the case of C-I the process is continuous, reaching a minimum, and rising again later, in the case of the C-II-V once started it undergoes a recovery and later reduces again reaching the minimum with a delay with respect to C-I of approximately 2 hours. For its part, the C-II-S starts with a reduction in the impedance in the same range as C-I but with a very small variation. Afterwards, and with a delay of more than 3 hours, shown a recovery and an intense final reduction, with a delay with respect to C-I of about 7 hours.

The different delays seen in the hydration process with respect to the C-I, result from the nature of the additions.
In the hydration in the C-I paste, a first step with a significant presence of ions is identified (where there is an increase in calcium hydroxide in solution that is released on the surface of the C3S with an increase in the pH). A reduction in the presence of carriers comes about between 2.5 and 4 hours later, which is associated with the inactive period (in which the grains of clinker become coated with hydration products which keeps the reaction latent) this stage is prolonged for the time it takes for the water to penetrate the grains of clinker. A gradual increase in carriers is seen after this period as a result of the release of ions from the particles of clinker, when the water penetrates the coating in a controlled diffusion process. From this step a continuous hydration process takes place with the reaction of the less reactive compounds, such as C2S.

For its part, in the hydration of the C-II-V paste, a reduction in the presence of carriers is seen between 2.5 and 3.5 hours which are associated with a reduction in calcium hydroxide in solution, because of the coating of the grains of clinker. A second period of latency in the hydration is seen between 3.5 and 6.5 hours, in which a coating with the hydration products would be produced both on the grains of clinker and those of the fly ash. A significant increase in carriers, associated with the penetration of water in the particles and the release of ions for the formation of the hydration products is seen from this stage. The double period reduction of the carriers, associated with the latency periods of the grains of clinker become coated with calcium hydroxide in solution, because of the coating of the grains of clinker. A second period of latency in the hydration is seen between 2.5 and 4 hours which are associated with a reduction in calcium hydroxide in solution that is released on the surface of the C3S with an increase in the pH). A gradual increase in carriers is seen after this period as a result of the release of ions from the particles of clinker, when the water penetrates the coating in a controlled diffusion process. From this step a continuous hydration process takes place with the reaction of the less reactive compounds, such as C2S.

4. Conclusions

At frequencies of less kHz, singularities appear that could be associated to the different stages in the hydration process which takes place in the material. Although to get the suitable information it is necessary to establish a compromise between the information obtained and the time needed to obtain the said information. It is considered that for the suitable use of this measurement procedure, in materials based on cement, the optimum choice is to take the measurements in consecutive cycles in the range of 1 Hz to 1 kHz, sweeping on a logarithmical scale and with 2 points per power ten. In this way response sequences are obtained at periods of several seconds, which allows the processes that take place in the hydration in the early stages to be followed.

For the study of hydration in the initial stages, is not usual use impedance spectroscopy, due to that the arcs of impedance require a long period of measurement and, consequently, throughout the measurement cycle of material is could produce an evolved since the inception of the measure until the end of it.

Acknowledgements:

This work has been possible to the financing of the Spanish MEC (project MAT2007-66845-C02-02) and of the action 139/Q06 0915-110 financed by the CAM-UPM.