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CINCOS'12

Congresso de Inovação na
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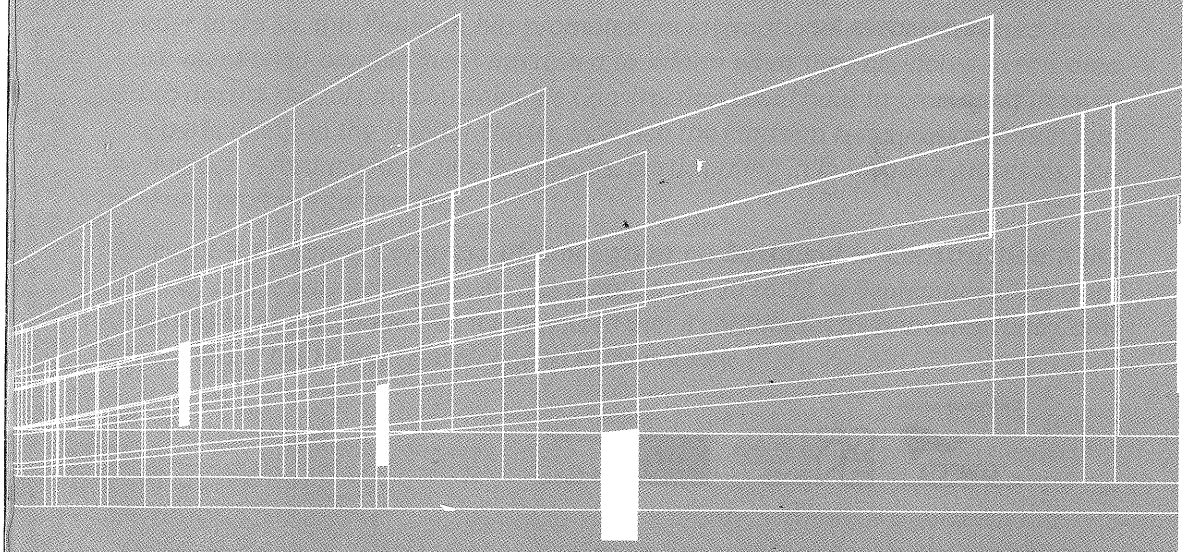
Congress of Innovation on Sustainable Construction

Inovação na Construção Sustentável

Innovation on Sustainable Construction



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A **Plataforma para a Construção Sustentável** (www.centrohabitat.net) é hoje uma rede que congrega empresas, centros de I&D, autarquias e outros agentes comprometidos com este tema da sustentabilidade e em usá-lo como mote para a inovação. O seu interesse abrange toda a fileira do Habitat e tem como objectivo principal concentrar recursos para valorizar empresarial e socialmente o conhecimento sobre a sustentabilidade do ambiente construído.

De modo a concretizar este objectivo, entende a Plataforma promover um evento internacional dirigido às empresas, centros de I&D, autarquias e demais entidades interessadas em divulgar o que fazem nesta área e discutir o papel que a Construção Sustentável pode ter sobre a Inovação, particularmente, no cluster Habitat Sustentável, de que é a entidade gestora a nível nacional.

Assim surgiu o **Congresso de Inovação na Construção Sustentável** (**CINCOS'12**) realizado em Aveiro (Portugal) de 20 a 22 de Setembro de 2012 e a partir do qual se elaborou este livro, repositório de conhecimentos que se pretende útil para a Inovação e Competitividade do cluster Habitat e sua sustentabilidade.

*The Portuguese **Sustainable Construction Platform** (www.centrohabitat.net) is a network linking companies, research centres, municipalities and other agents concerned with the theme of Sustainability and in using it as a driving force for Innovation. The Platform aims to concentrate resources in order to value technology and knowledge transfer to companies and local governance, namely, about sustainability of the built environment.*

In order to do so, this Platform has promoted an international event addressed to the above-mentioned organizations interested to inform what they are doing in this area and to discuss the role that Sustainable Construction could have in promoting Innovation, particularly, in the Habitat cluster, in which the Platform is the national management entity. A forum where different agents, participating in innovation processes, can meet and promote partnerships.

*The event was named **Congress of Innovation on Sustainable Construction** (**CINCOS'12**), and it was held in Aveiro (Portugal), from 20 to 22 of September 2012, from which this book was made and, it is expected that it contributes to Innovation and Competitiveness of the Habitat cluster and its sustainability.*

Monitoring hydration in lime-metakaolin composites

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Abstract

This paper describes a study of the micro-macro property relationships relating to hydraulic setting reactions in air lime - metakaolin mixtures. The application of electrochemical impedance spectroscopy (EIS) to monitor the on-going hardening processes is discussed together with the recorded changes in the chemical, physical and mechanical properties. Scanning electron microscopy (SEM) and bulk characterisation techniques including thermal analyses (TGA/DSC), mercury intrusion porosimetry (MIP) and mechanical property measurements were applied to evaluate structure and composition. Electro-mechanical impedance (EMI) measurements were taken on samples and used to monitor changes in the mechanical properties of the paste. Results showed a clear relationship between the chemical and structural development of the paste while electro-mechanical impedance was sensitive to hydration. Changes in electrical-chemical and mechanical impedance show potential for the development of in-situ sensors for monitoring of lime based composite materials.

Keywords: *Electrochemical Impedance, Electromechanical impedance, Lime, Metakaolin*

Introduction

Impedance spectroscopy (or electro-chemical impedance spectroscopy, EIS) is a non-destructive technique commonly used to study processes in a range of materials including ceramics, polymers and composites. Over the past 30 years its use in the construction industry has been mostly confined to cement hydration and rebar corrosion in concrete [1, 2]. Only limited work has been carried out in applying this technique to lime binders [3, 4, 5]. The ability of impedance spectroscopy to monitor setting reactions in lime based materials would allow the construction industry to estimate strength development based on quantitative data. This is particularly important in the early days and weeks after mixing when strengths are low and environmental vulnerability to processes such as frost damage is high. Data obtained from EIS is mainly related to the chemical and physical characteristics of the material and does not directly measure mechanical characteristics.

In addition to EIS, electro-mechanical impedance (EMI) is a non-destructive technique whose potential has been shown in the construction industry for both, structural health monitoring (SHM) and strength development monitoring in concrete [15]. EMI applica-

tions are of great interest to the construction industry because, unlike other techniques, the sensors used are inexpensive and simple to use. Furthermore, these sensors have excellent mechanical strength, flat response over a wide frequency range and broad dynamic response [6]. Research on SHM dates back to the 1990's [7; 8] while research on strength development monitoring has only begun in recent years [9, 10, 11].

Experimental

The hydraulic reactions between calcium hydroxide, amorphous silica and aluminum hydroxide were followed using a paste of lime and metakaolin. A commercially available hydrated lime classified as a CL 90 according to EN 459-1 [12] and a metakaolin manufactured by Imerys Minerals Ltd was used [5]. According to previous research [13, 14], optimum mechanical properties were obtained from a 10:1 mixture of lime to metakaolin by weight ratio, therefore a similar mix ratio has been adopted in this study with no added water.

Due to the small quantities of material, the required mixing was performed by hand in a plastic container. A mixing time of approximately eight minutes was adequate to obtain a homogeneous mixture (water-lime ratio of 1.2:1). After mixing, the paste was immediately cast into stainless steel moulds. Evaporation of water and carbonation were minimized by covering the top surface of the moulds that were open to air with a thin layer of plastic. In order to reduce the above mentioned processes during the curing time, the moulds were inserted into a polystyrene box where the temperature was controlled by a thermal bath at 20ºC±1. Inside the box a beaker containing water was left to maintain humidity at near 100% along with a Petri dish containing lime putty to adsorb excess carbon dioxide contained in the atmosphere.

Before sealing the boxes, the cell was connected to the impedance analyzer and the test was started. The first measurement was recorded one hour after the initial mixing.

Throughout a three week period when EIS measurements were acquired, chemical, physical and mechanical tests were performed on the paste after 1, 2 and 3 weeks. In order to evaluate the response of impedance spectroscopy to the hydraulic reactions, a similar test with only lime was also performed.

Mechanical compression tests were performed immediately after removal of the specimens from the sealed boxes. Due to the differences in environmental condition, fragments collected for physical and chemical measurements were kept in air tight plastic in order to minimize any potential micro-structural changes. Samples used for scanning electron microscopy (SEM) and mercury intrusion porosimetry (MIP) analysis were dried in a desiccator for 15 hours; however this was not necessary for thermal analysis where humid samples were used.

Impedance spectroscopy was performed using a Solartron SI 1260 Impedance/Gain-Phase Analyzer. Measurement acquisition was controlled with SMaRT (Solartron Materials Research and Test; Solartron Mobrey Ltd) software version 2.7.0. Impedance sweeps were taken hourly for three weeks over the frequency range 1MHz to 10Hz and a V_{rms} potential of 10 mV. During impedance measurements, the sample was housed in an open top polycarbonate reaction cell of internal dimensions 50 x 50 x 50 mm containing two 50 x 50 x 3mm stainless steel electrodes on opposing faces. Connections were made using screened coaxial leads to the voltage and current terminals. The sample impedance, Z(f) at a frequency, f, is described in [5] along with calculation of the relative permittivity (ε'_r) and ac conductivity (σ) of the sample at a given frequency.

Compressive strengths of the samples were determined using a Instron 'Fastrack' 8800 digitally controlled servo hydraulic system with 100 kN load cell at a loading speed of 0.2 mm/min. Microstructural information relating to phases within the hardened samples was obtained from fresh surface fractures using a Scanning Electron Microscope JEOL JSM6480LV.

Thermal analysis was performed using a SETARAM thermo gravimetric - differential scanning calorimetry (TG-DSC) model TGA 92-1750 thermal balance with a 1600°C module. Analysis was made using a dynamic regime, with a temperature rate of 10°C/min up to 950°C, starting from 20°C. During testing, nitrogen gas was flowed inside the furnace in order to avoid any reaction between the samples and atmospheric oxygen or carbon dioxide. In order to have a sample with an average content of moisture, fragments from the inner and the outer regions of the sample were crushed with a pestle and mortar prior to particles greater than 250µm being removed with a sieve.

Mercury intrusion porosimetry was performed using a Micrometrics AutoPore III utilizing ports for both low and high pressure. A WIN9400 series version 2.00 software by the Micrometrics Instruments Corporation allowed analysis of data downloaded from the Micrometrics Interface Controllers. Penetrometers (pen and stem) for solid samples with 5 ml volume from Micrometrics where also used.

EMI tests were carried out on two lime-metakaolin specimens, each sealed in plastic tubes of diameter 46 mm and height 50 mm. In order to reduce water evaporation and exclude carbon dioxide, and thus carbonation, the two moulds were closed at each ends with plastic sheets and sealed inside plastic bags. The specimens were de-moulded after one week curing and stored in a conditioning chamber at 30°C. A piezo-concrete composite sensor [16] was embedded at the mid height of each specimen. EMI measurements were performed with an Agilent 4980A Precision LCR meter in the frequency range between 50 and 350kHz, recording 100 readings and at 1 Volt tension. At each frequency within this range, the values of the real part (conductance) and the imaginary part (susceptance) of admittance were recorded together with the related frequency. Measurements were acquired for the paste at ages between 6 and 19 days.

Results and discussion

Electrochemical Impedance Spectroscopy (EIS) - A decrease in dielectric constant (that describes the electric polarizability) and a relatively small increase in ac conductivity with frequency was observed and is shown in Figure 1. The sum of all polarization processes operating within the lime-metakaolin structure contribute to this value at a given frequency of applied field. These processes, which may be superimposed, each have a characteristic relaxation frequency defining the polarisation behaviour. The permittivity exists across the entire frequency range under study and is indicative of a spread of relaxation frequencies. At the lower frequencies the dielectric constant rises to anomalously high values of around 10^8. This behavior is attributed to the dominating influence of electrode polarization below this frequency. Previous work suggests polarisation is a combination of electric double-layer polarization and an interfacial polarization processes [3]. The presence of conductive species, such as water can also lead to very high relative permittivity [17]. With hardening time, a decrease is recorded both, in conductivity and in relative permittivity.

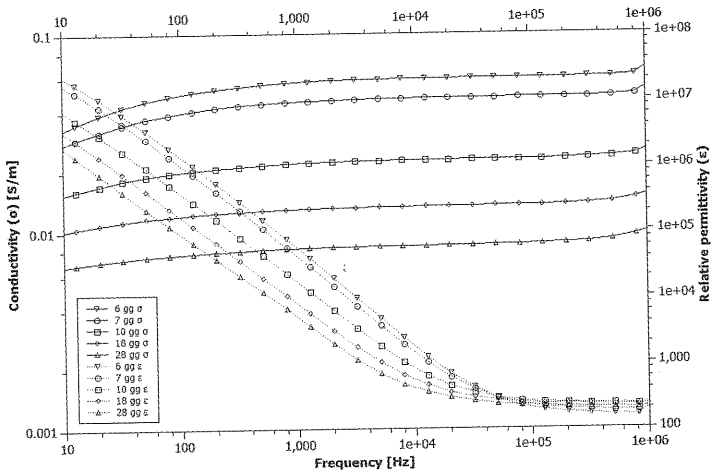

Figure 1. Conductivity and Relative Permittivity as function of frequency

Compression test - Results from the compression test performed on a one week old sample are shown in Figure 2, which clearly demonstrates a maximum resistance of about 0.30 MPa and a low slope of curve (E=557 MPa). After two weeks the above mentioned slope increases up to about 8000 MPa and the maximum load reaches 0.40 MPa. At the end of the third week maximum load rises again, 0.44 MPa, but little change is recorded in the slope of the curve (E=845 MPa). At the end of fourth week maximum load rises again, 0.55 MPa and the slope of the curve remains almost constant. In all samples the peak is followed by a gradually reduction of resistance without breaking of sample.

Scanning electron microscopy (SEM) - The microstructure of a fresh fracture surface is characterised by the presence of metakaolin plates randomly scattered in a porous matrix, mainly made of non-crystalline compounds. Plates can be single or grouped in packs of 2-8 plates and it is often possible to recognise plate fragments intimately mixed and incorporated into the lime matrix. In a one week old sample it is possible to observe bridges of amorphous phases between two plates and the growth of amorphous structures on the edge of the plates as shown in Figure 3. Metakaolin plates were readily identifiable in the one week old paste.

However it is noteworthy that due to the progress of the reaction of metakaolin with lime the plates became covered and harder to identify in the two and three week old pastes. In fact, the SEM, microstructure of the four week old sample showed a higher compactness compared with the microstructure of the one week old sample.

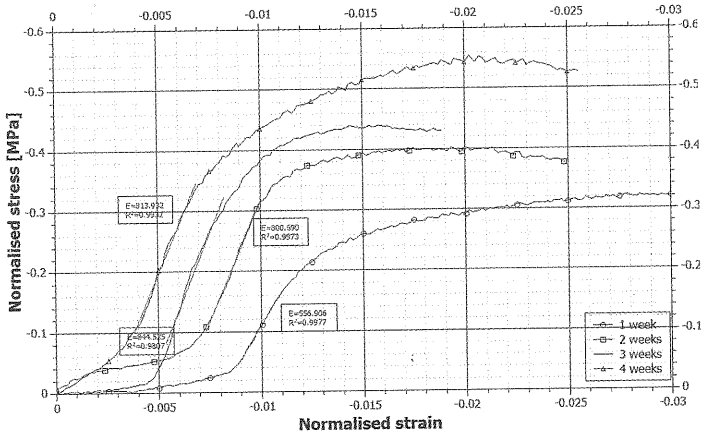

Figure 2. Stress-strain plot for lime-metakaolin paste for one to four weeks

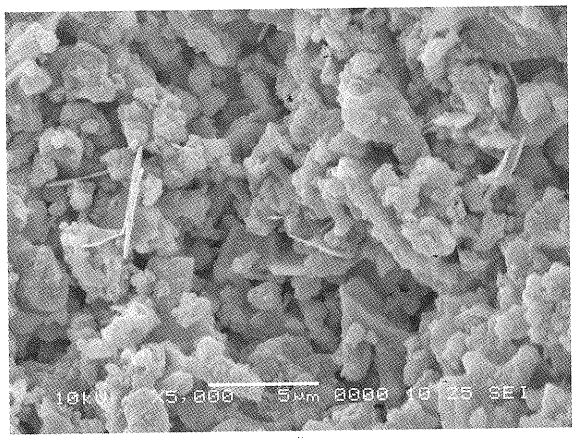

Figure 3. SEM of lime-metakaolin paste aged for one week

Thermal analyses - The endothermic reaction and weight loss due to dehydration of CSH occurs in the temperature range 110-140°C [18, 19, 20] however this is not evident due to a large amount of water evaporation from the pores. Calculations demonstrate a decrease of these compounds between the first and the second week, while their amount remains almost the same between the second and the fourth week.

The DSC curves in Figure 4 show a peak between 140-200°C attributed to the dehydration of the hydraulic compound stratlingite (C_2ASH_8). A second less pronounced peak which is visible by close inspection of the one week old sample between 200-270°C, is attributed to hydrogarnet C_4AH_{13} [17, 18, 20]. A large endothermic peak at about 490°C is due to the dehydration of calcium hydroxide. In the two-week old sample, this peak consists of two overlapping peaks attributed to the presence of calcium hydroxide of different crystallinities. According to the test set up, a very small amount of calcium carbonate was detected by the thermal analysis.

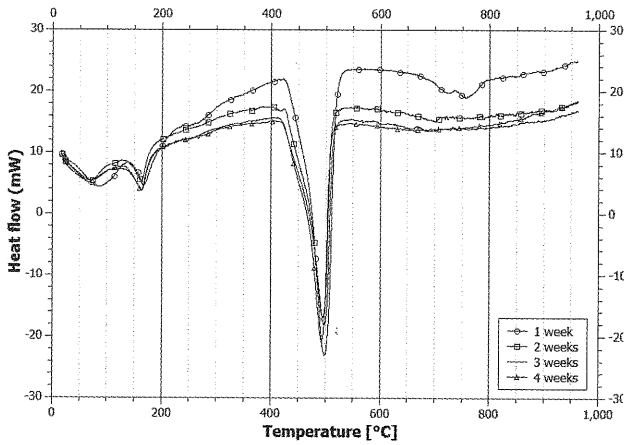

Figure 4. DSC plot of lime-metakaolin paste aged up to four weeks

Mercury Intrusion Porosimetry (MIP) - Mercury intrusion porosimetry of lime-metakaolin paste aged up to four weeks is shown in Figure 5. Results of the one week old sample show that pores are mainly in the 400-1200 nm diameter range but a small quantity of smaller pores in the 20 nm and 6 nm ranges are also present. Results on the two week old samples show that after one week porosity remains constant but a slight increase is noticeable in the 9 nm diameter pores. This small increase is shown also in the total intrusion volume of mercury and the reduction in volume of median pore diameter.

In contrast to the week one and three, a significant pore reduction in the porosity is apparent in the fourth week [22, 23].

Electro Mechanical Impedance (EMI) – The PZT patches mounted in both samples exhibited uniform behaviour with hydration in the lime-metakaolin pastes tested. The real and imaginary components of the extracted mechanical impedance were found to exhibit a response similar to that of a parallel spring damper (Kelvin-Voigt) combination [7, 15] in the frequency range 70-120 kHz. The variation of k and c was monitored with progression of hydration. The system parameters k and c both showed a decrease with time with the exception of a small initial increase in the beginning. A typical response from one of the samples is shown in Figure 6. The variation of c is similar to that observed for concrete curing [15], however, k exhibited a somewhat opposite trend. More experiments are underway to verify the observation in this particular case. Nevertheless, there is no doubt that both parameters are sensitive to hydration of lime.

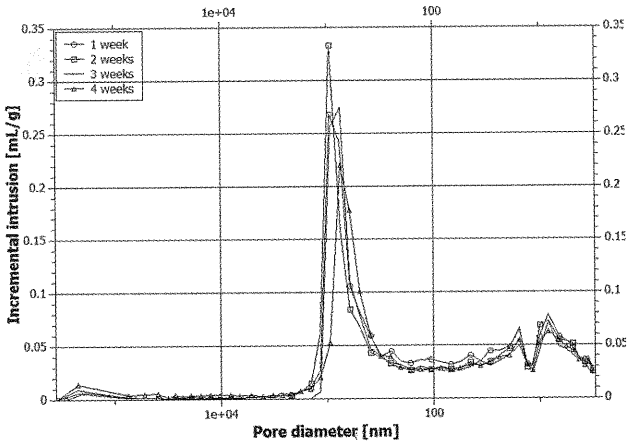

Figure 5. Mercury intrusion porosimetry plot of lime-metakaoline paste aged up to four weeks

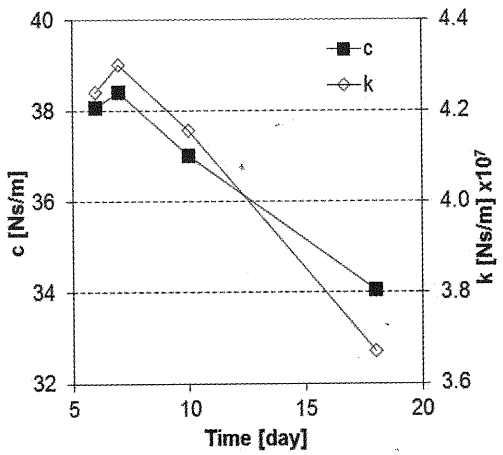

Figure 6. Variation in system parameters k and c as a function of hydration time

Discussion

Results of thermal analysis suggest that samples contain a certain amount of water after three weeks and that negligible carbonation had taken place. This observation is also supported by the absence of angular calcium carbonate crystals in the SEM micrograph. Consequently, the only reaction that can be taken into consideration for the mechanical and physical properties of hardened samples is the hydration process of silica and alumina. Furthermore, according to previous research, thermal analysis suggests a specific sequence in the silica and aluminum hydrated compounds. By the end of the first week mainly the CSH, the stratlingite and the C_4AH_{13} hydrogarnet are formed. As these compounds are not stable [18] they begin to transform into C_3ASH_6 hydrogarnet over the longer term. This is demonstrated in the second and third week by a new peak consistent with hydrogarnet (C_3ASH_6) [5]. The noticeable difference from the thermal calorimetry, attributed to the degree of crystallisation in $Ca(OH)_2$ phases, may be a consequence of calcium hydroxide recrystallization during the experiment. However, the constant proportion of calcium hydroxide detected in all of the samples suggests that all the calcium needed by the reaction with the metakaolin is acquired during the first week. Consequently, changes visible in the hydraulic phases are mainly due to the modifications of the hydraulic compounds developed during the first week, rather than formation of new phases. Results from the MIP support the theory that the recrystallisation and hydration reactions modify the pore size distribution and structure. These can also be attributed to the changes in the electrical response identified by impedance spectroscopy. A reduction in freely rotational water molecules associated with the formation of the hydraulic phases is consistent with the results. Changes in the mechanical properties of the mixes, attributable to hydration, were detected by the electro mechanical impedance technique.

Conclusions

This paper demonstrates the potential of impedance spectroscopy to study and monitor the reaction between lime and metakaolin. Changes of impedance response with time are believed to be associated with reaction kinetics. Impedance behaviour with time was consistent with results obtained

from the complementary techniques. The EMI technique is sensitive to changes in extent of hydration in a lime-metakaolin paste. This study highlights the importance of impedance spectroscopy and the electromechanical impedance technique as potential tools for the non-destructive monitoring and evaluation of lime based hydraulic binders.

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