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Dielectric properties of fly ash geopolymers with two types of potassium activators

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Abstract- The interest for geopolymer materials for cement and binder applications has increased in recent years due to their compliance with green chemistry and low cost. In this study, we show the dynamics of water in fly ash-based geopolymers using low-temperature broadband dielectric impedance spectroscopy (BDS). Confined water has a major influence on properties such as durability and performance because it affects the porosity and pore size distribution. Hence, the dielectric measurements allow probing of the porous structure of the geopolymers.

I. INTRODUCTION

Geopolymers[1] are amorphous inorganic polymers formed through an alkali activated polycondensation reaction of aluminum and silicon oxides dissolved in the presence of a high pH activator. Geopolymers can be cast and shaped at room temperature and harden without sintering. Their use has been increasing in recent years due to their compliance with green chemistry, their low cost and sustainability,[2] their good insulating properties, their stability at high temperature and their high mechanical strength.[3] Those properties make them ideal eco-friendly building blocks, which can be used as large volume replacements for different kinds of composite for building materials and energy storage devices.[2] Precursors for geopolymers include natural minerals such as montmorillonite[4] and bentonite,[5] mineral derivatives, such as metakaolin,[6] and industrial wastes, such as fly ash.[7,8] Free alkali ions, water molecules, and hydroxyl ions are the conducting and polarizing species in geopolymers that determine the electrical and dielectric properties. Alkali ions play a charge-balancing role or are actively bonded into the matrix. However, their role in the molecular structure of geopolymers is not clearly understood. [5,6]

Broadband dielectric impedance spectroscopy (BDS) has given important insights describing the characteristics of water in cementitious materials.[9-12] With BDS, the electrical and dielectric properties of a material can be studied across a large frequency range. This enables measurement of the resonance frequencies of water bound in the pores of a material and the dynamics of this water on different time scales.[9] The mobility of microstructurally bound water is dependent on the pore size and connectivity.[10] Important information on solvent response times comes from dielectric relaxation measurements. Many dynamic processes, such as proton and cation mobility, charge recombination, and transient solvation, are interpreted in terms of the dielectric relaxation, the corresponding Debye relaxation time, and tetrahedral displacement mechanisms.[13] Debye relaxation is dependent on temperature. The measurement of the dielectric response at different temperatures allows deconvolution of each relaxation time and the calculation of the activation energy for each corresponding process.[9-12] In geopolymers, dielectric relaxation is also an indicator of the binder's phase evolution. While this phenomenon has been documented in the early stages of curing,[11,14] it has never been previously been applied to the phase change during the aging of geopolymers.

In this investigation, the objectives are: 1) to prepare geopolymers by reacting a mixture of fly ash (Fig.1A) and silica fume (Fig.1B) with potassium carbonate and potassium hydroxide activators in water and to fabricate a harden disk after curing (Fig.1C); (2) to deconvolve the different conduction and polarization mechanisms present in the geopolymers using low-temperature BDS (Fig.1D); to evaluate the effects of (3) aging over a 2-year period; and (4) annealing on the dielectric response.

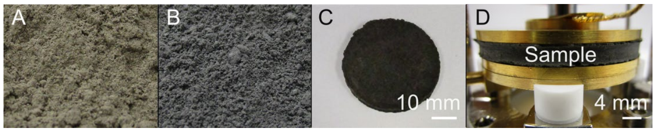

Fig. 1: Photographic images of: (A) fly ash, (B) silica fume, (C) a geopolymer disk sample and (D) a geopolymer disk sample sandwiched into the parallel plate capacitor cell of the BDS system.

II. EXPERIMENTALS

A. *Preparation of the geopolymers*

All the samples were prepared in duplicate by mixing ACS reagent grade potassium carbonate (99.9 %) or potassium hydroxide (85 %) in distilled water in the presence of industrial grade silica fume (95.2 % SiO_2, 4.8 % water) and fly ash (55.3 % SiO_2, 21.4 % Al_2O_3, 2.11 % K_2O). The proportions were calculated to obtain K/Al/Si ratios of 1.4:1:2.85 and 1:1:2.5 and water-to-binder (w/b) ratios of 0.25 and 0.20 respectively, for the carbonate and the hydroxide-based samples. The K/Al/Si and w/b ratios were optimal to form a flowable paste with good dielectric properties once hardened. The mixtures were prepared at room temperature in a low-shear mixer at 500 rpm and mixed for 30 minutes, then casted into high density polyethylene molds into disks (40 mm diameter/4 mm thickness) which were sealed to prevent moisture loss during curing at 60°C for 2 days. After 2 days of curing, the samples were unsealed and cured at 60°C for an extra day. For the annealing procedure, the samples were transferred immediately into a hot furnace and annealed at 200, 300 or 400 ºC for 3 hours at atmospheric pressure with a temperature ramp of 10ºC/min. All samples were stored in an airtight plastic bag prior analysis.

B. Broadband dielectric impedance spectroscopy

Dielectric properties (imaginary permittivity, Tan δ) were measured on a Novocontrol Technologies BDS system equipped with a parallel plate capacitor cell (PPCC) and a liquid nitrogen tank. The disk-shaped material samples were placed between two parallel brass electrodes (40 mm diameter/2 mm thickness) to form a capacitor. To measure the dielectric properties, the formed capacitor was subjected to alternating current of amplitude 3 Volts and frequencies between 0.1 to 10^6 Hz. The measurement was repeated at temperatures ranging from -125°C to 75°C to determine the temperature dependence of the dielectric relaxation. The relaxation time and activation energy values were calculated with Matlab.

III. RESULTS AND DISCUSSION

The interaction between an external electric field and the permanent molecular dipoles within the geopolymer is measured using the permittivity (ε’) and its imaginary part (ε’’) as a function of the frequency (Fig.2) on a logarithmic scale.[9,10] The permittivity is a complex function and is a measure of the electric polarizability of a dielectric. The net polarization[15] is the sum of dipolar, ionic, electronic, and atomic polarizations. For the range of frequencies used in this study (0.1 to 10^6 Hz), the ionic and the dipolar polarization mechanisms are the two main contributors. Electronic and atomic polarizations are weaker, and their values are usually constant over the microwave frequencies. A material containing more dipolar species (water, hydroxyl) in its structure will exhibit greater permittivity in the presence of the electric field.

In the case of geopolymers, ε’’ values are dependent on the type of starting materials, the proportions, the method of mixing and curing, and the range of frequency used in the BDS measurements.[7,8,16] Dielectric relaxation in solids is conventionally modeled as a Debye process to describe the decay of polarization over the frequency range.[17] At low frequencies, the dipolar molecules found in geopolymers have more time to rotate and orient themselves in the direction of the applied alternating electric current.[18] This results in a greater ε’’, shown in Fig.2, and is consistent with prior studies .[7,8,14] As the frequency increases, an increasing proportion of the water molecules cannot change orientation fast enough due to constraints on their mobility related to their confinement in the geopolymer pores. As a result, the ε’’decreases with higher frequencies.

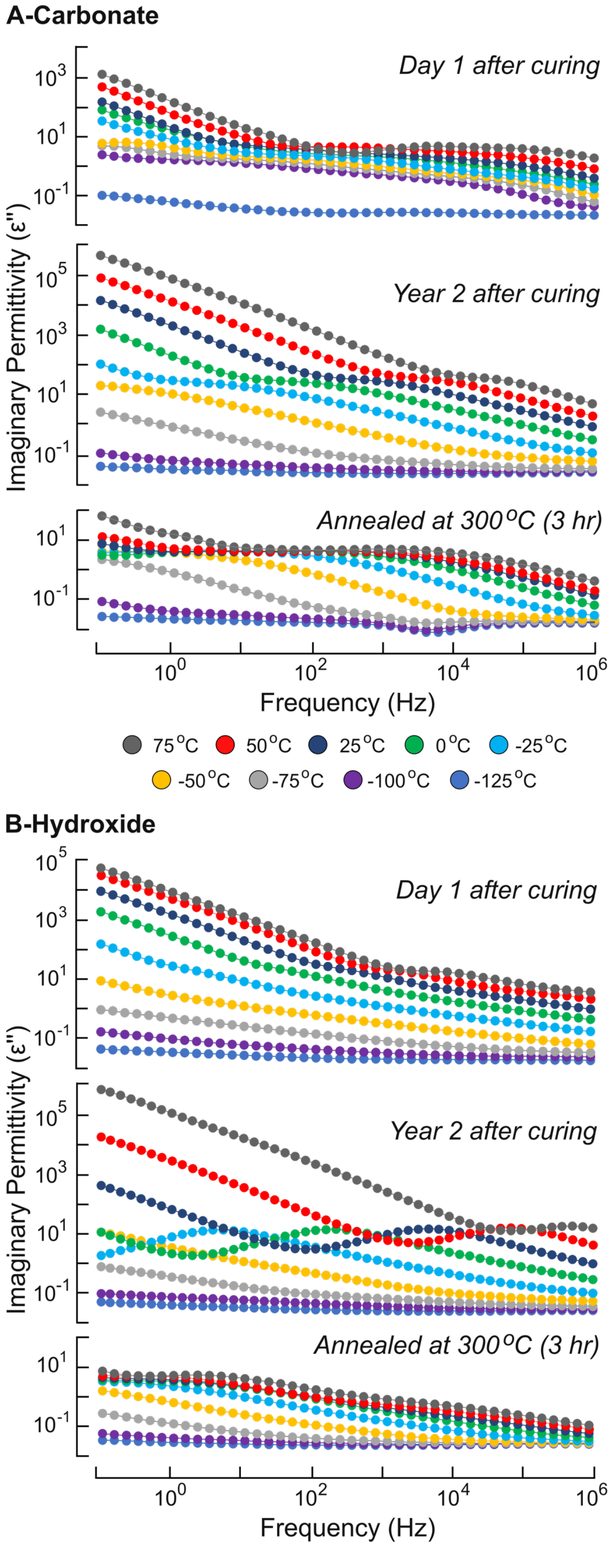

Fig.2: Effect of time and annealing on the evolution of the dependence of the imaginary permittivity with temperature and frequency for: (A) the carbonate and (B) the hydroxide-based geopolymers.

The mobility of bound water molecules in the pores of the geopolymer changes with temperature, causing a corresponding shift in the frequency dependence of ε’’. At the lowest temperatures (-125ºC), the bound water is substantially below the freezing point and consequently mobility is low. Even at very low frequencies, the ε’’ is flat, indicating minimal contributions from the dipolar water molecules. At higher temperatures, near and above the melting point, the ε’’ is strongly dependent on the frequency. Higher temperature increases the mobility of the water molecules and the asymmetric shape of the peaks in Fig.2, suggests that multiple dielectric relaxation processes are active. The dielectric response can be modeled as a Debye relaxation with a distribution of relaxation times.[13]

Fig.2 shows an increase in the ε’’ for both the carbonate (A) and the hydroxide (B) based geopolymers over two years of aging at room temperature. A similar trend was observed at ages of 3, 7, 14 and 45 days (not shown). After 2 years of aging, the ε’’ response is more symmetrical, with multiple well-defined strong processes, particularly for the hydroxide samples (Fig.2B). Interestingly, the carbonate-based samples show important lower dielectric values compared to the hydroxide-based samples at day 1. This effect disappears with aging. This may be related to the solubility of potassium carbonate which is lower than that of potassium hydroxide and retards the initial stages of the polycondensation reaction.[11,14]

Upon annealing the geopolymers at 300ºC, Fig.2 shows that ε’’ is decreased. Similar observations were accounted for annealing at 200 and 400ºC (not shown). This may be attributed to the loss of bound water molecules from the pore network by evaporation during the heat treatment. Furthermore, the dielectric loss tangent (Fig.3) on annealed samples showed clearly that the minimum loss tangent is obtained at higher frequencies with carbonate and hydroxide samples annealed at 300ºC, compared to temperatures of room temperature, 200 and 400ºC. The dielectric loss is the amount of energy lost by heating during the interaction of the applied electrical field with the dipoles and is measured by the ratio ε’’/ ε’. It is a good indicator to measure the ability of a capacitor to charge and discharge each half cycle. When the samples are heated to 300ºC, the bound and adsorbed water molecules are removed from the sample. However, at higher temperatures (400ºC), a recrystallization of the amorphous geopolymers is possible, which could change the porosity and increase dielectric loss.[19,20]

For a more detailed analysis, the imaginary permittivity (ε’’) values can be deconvolved by using standard fitting functions for water in confinements, such as the symmetric Cole–Cole (CC) or Debye functions to describe each relaxation process.[9,10,17] Relaxation time is a measure of the time scale needed for the dipole to reorient itself in the system after its perturbation by the external electrical field. When the temperature of the sample increases, the mobility of the dipole is increased, causing a decrease in the relaxation period. This indicates that water relaxing via the main processes are independent from the pore network developed during hydration.[9,10,14] Furthermore, three-dimensional X-ray microtomography and BET (Brunauer-Emmett-Teller) analysis for the physical adsorption of gas molecules on a solid surface will be used in a near future to characterize the pores with more precision. This will allow to measure their size, evaluate their distribution, observe their evolution in the network, and correlate the findings with the dielectric properties of the geopolymers.

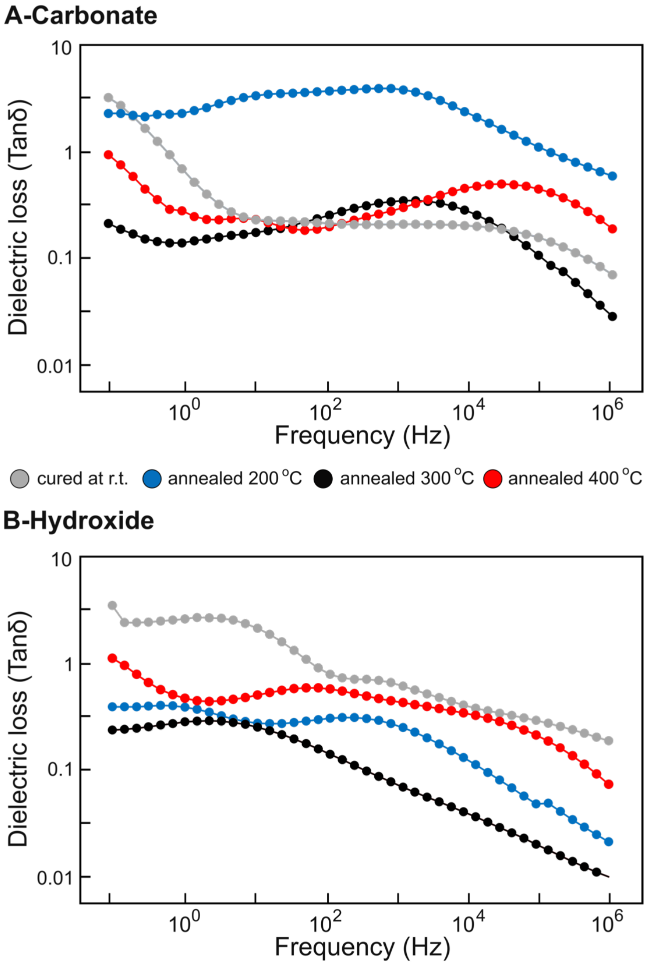

Fig.3: Effect of annealing temperatures on the evolution of the dependence of the dielectric loss with frequency for: (A) the carbonate and (B) the hydroxide-based geopolymers.

IV. CONCLUSION

The current work seeks to gain a new understanding of the nature of the relaxation phenomena in geopolymers, deconvolve the behavior mechanistically, and determine the effect of aging and heat on these properties. This topic has not previously been explored for geopolymers, presenting an opportunity to contribute to the understanding of conduction and polarization in these materials.

This improves the understanding of the dynamics of bound water in geopolymer materials and provide an additional avenue for material assessment, microstructural evaluation, and quality assurance for geopolymers. In a near future, the dielectric performance of geopolymers activated with lower environmental impact bases such as potassium silicate and sulfate will be examined. This work contributes to strengthen understanding of the dielectric properties of geopolymers and how they could be used as a high-performance dielectric.

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