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DIELECTRIC PROPERTIES OF FLY ASH GEOPOLYMERS

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Abstract

Alkali-activated materials made with fly ash and potassium activator have sensing properties. This article studies their dielectric behavior and compares the material properties when activated with potassium hydroxide and potassium carbonate. The complex dielectric permittivity of the samples was measured through broadband dielectric spectroscopy. Isothermal measurements were conducted through a frequency range from 0.1 to 10^6 Hz, consecutively performed at different temperatures by increasing the temperature from -125°C to 75°C with discrete steps. The study identifies two relaxation mechanisms, one caused by the weakly bound water. The impact of the free water is so strong that it is not possible to clearly distinguish the two alkaline activators without further studies.

Keywords: Fly-ash alkali-activated materials, dielectric properties, potassium hydroxide, potassium carbonate

1. INTRODUCTION

Self-sensing and piezoelectric structural materials can benefit for new concepts of structural health monitoring. These sensing building blocks can be integrated in a structure to follow the load over time, for example. Previous research showed that the resistance of fly ash (FA) alkali-activated materials (AAM) vary more when a load is applied compared with metakaolin AAM and the resistance does not really vary for granulated blast furnace slag AAM, and concrete made with Portland cement.[1] The sensitivity of the FA AMM made with potassium hydroxide was greater than made with sodium hydroxide.[2, 3] When comparing potassium hydroxide and potassium carbonate activator, cyclic voltammetry shows a greater hysteresis and charge accumulation with potassium carbonate activator.[4] The objective of this study is to analyze the dielectric behavior or FA AAM made with potassium hydroxide and potassium carbonate.

Frequency-domain dielectric spectroscopy also known as broadband dielectric spectroscopy (BDS) is a powerful tool to investigate charge carrier motions, dipolar relaxation mechanisms and electronic conductivity for any non-metallic material and it is particularly relevant in the case of hydrophilic inorganic materials such as geopolymers. This technique has been successfully used for example to explain ionic and electronic conductivity and grain (or interfacial) polarization in the case of bentonite as a function of water contain[6] as well as ionic diffusion processes in the case of montmorillonite saturated with alkali cations.[7] In that later case, the low frequency plateau in the real part of the complex conductivity curve was (rightly or wrongly) assigned to ionic conductivity and its temperature dependency was observed to fit fairly well an Arrhenius-type dependency allowing the calculation of the activation energy. Accordingly, BDS can give significant and rather unique insights describing the dynamic of water motion in cementitious materials.[5] For example, the mobility of microstructurally bound water is dependent on the pore size and connectivity and many dynamic processes, such as proton and cation mobility, charge recombination, and transient solvation, can be interpreted and explained in terms of the dielectric relaxation with a characteristic time constant that is dependent upon temperature. In the specific case of geopolymers, the dielectric properties were found to be reasonably well correlated with both the rate of porosity and the variations in the binders during geopolymerisation. [8]

Furthermore, in almost all cases of hydrophilic ceramic containing a significant amount of water, massive low frequency dispersion (LFD) is usually observed. This particular type of dielectric response is characterized by a large increase of both real and imaginary parts of the complex permittivity at similar rates towards low frequencies. It has been observed, possibly for the first time, forty years ago in the case of humid ceramic [9] as well as biopolymers over a range of temperatures and frequencies. The true nature of low frequency dispersion is still not completely understood despite being properly recognized in the literature for decades [10, 11] and it leads to (apparently) huge permittivity at low frequencies along with massive dielectric losses. It seems however clear that it involves slow carriers such as ions or hopping electrons but this form of charge transport is also accompanied with charge storage in complete contrast to conventional direct current transport. This has led to the idea of using these materials in energy storage application as long as the dielectric losses can be mitigated.[12] Another, and probably more promising, idea is to use carbon black loaded cementitious materials as electrodes in the fabrication of supercapacitors taking advantage of the huge effective surface resulting from the material porous structure and the dynamic of charge carrier motions.[13]

2. EXPERIMENTAL

The samples were prepared in duplicate by mixing ACS reagent grade potassium hydroxide (85 %) or potassium carbonate (99.9 %) 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 1:1:2.5 and 1.4:1:2.85 and water-to-binder (w/b) ratios of 0.20 and 0.25 respectively, for the hydroxide and carbonate-based samples. The K/Al/Si and w/b ratios were optimal to form a flowable paste with good dielectric properties once harden. The carbonate-based activator at 0.2 was too thick (not flowable) and the dielectric response of the hydroxide-based activator at 0.25 was too low. The mixtures were prepared at room temperature in a low-shear mixer at 500 rpm and mixed for 30 minutes, then cast 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. All samples were stored in an air-tight plastic bag prior analysis.

The complex dielectric permittivity of the samples was measured through broadband dielectric spectroscopy using a broadband dielectric spectrometer. The disc-shaped specimens were sandwiched between plated brass electrodes in order to form a plane-plane capacitor configuration as shown in Figure 1 and the samples were placed in an environmental chamber that was continuously flushed with nitrogen. Isothermal measurements were conducted through a frequency range from 0.1 to 10^6 Hz under an excitation voltage of 3 V. Measurements on each specimen were consecutively performed at different temperatures by increasing the temperature from -125°C to 75°C with discrete steps. The samples were weighted before and after their measurement and were found to have lost approximately 10% of their water content.

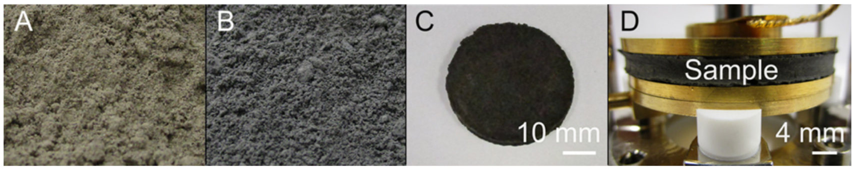

Figure 1: Photographic images of: (A) fly ash, (B) silica fume, (C) a geopolymer disk sample and (D) a geopolymer disk sample sandwiched into the parallel plate capacitor cell of the BDS system.

3. RESULTS AND DISCUSSIONS

Figures 2 and 3 show the real and imaginary permittivities of hydroxide and carbonate and based geopolymers as a function of frequency at different temperatures from -125°C to 75°C respectively. The effect of curing time and annealing was presented in a previous report.[14] These results are in good agreement with prior studies [8, 15] that also reported LFD-type behaviour, where both the real and imaginary parts were plotted in the same graph featuring sharp increases of both towards low frequencies.[8]

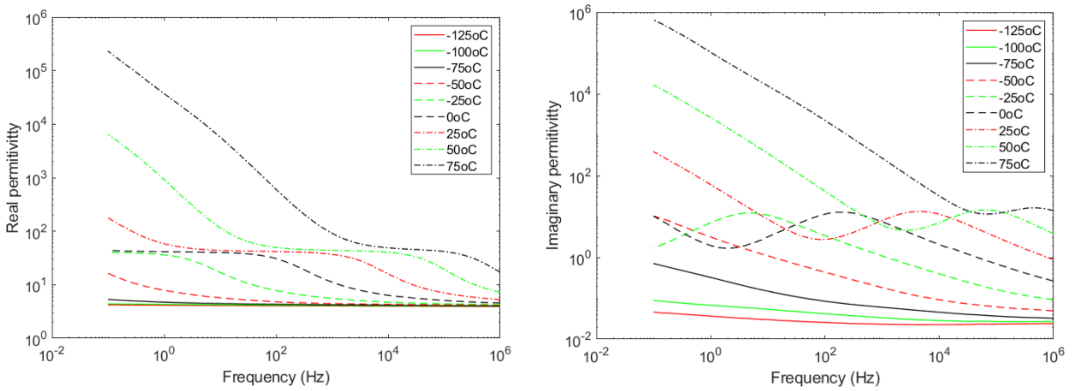

Figure 2: Real (left) and imaginary (right) permittivities of a hydroxide-based geopolymer 2 years after fabrication

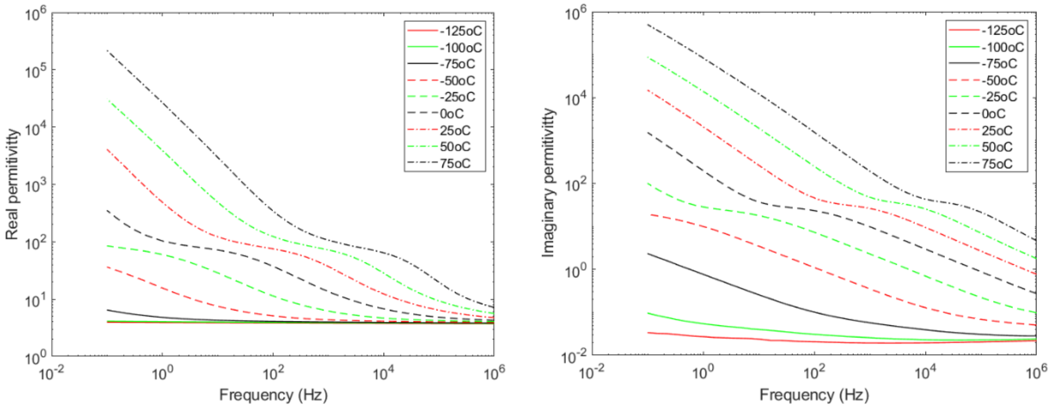

Figure 3: Real (left) and imaginary (right) permittivities of a carbonate-based geopolymer 2 years after fabrication

Figure 4 shows a strikingly good example of LFD with both real and imaginary parts of the complex permittivity featuring parallelism between the two branches at low frequencies complying with a frequency dependency in the form of $\hat{\varepsilon} \propto (j\omega)^{-n}$ where the exponent n is usually slightly below 1 (0.84 here). But the main feature of the dielectric response spectrum is the presence of relaxation processes. Indeed, in the case of geopolymers in equilibrium with atmospheric moisture one or two relaxation processes can be observed as a function of the amount of absorbed water. Figure 5 shows the dielectric response of a carbonated-based geopolymer, in a drier condition than the measurement shown in Figure 3, featuring two distinct relaxation peaks. In order to enhance the contribution of the relaxation processes to the total dielectric losses, the imaginary part of the complex permittivity can be calculated from the real part using the following expression:

$$\varepsilon''_{rev}(\omega) \cong -\frac{\pi}{2}\frac{\partial \varepsilon\prime(\omega)}{\partial \ln(\omega)} \tag{1}$$

This equation was used to treat the data shown in figure 5 as shown in Figure 6 in the form a 3D mapping of the dielectric losses. It is an approximation of the Kramers-Kronig equations [16, 17] and allows to remove a large part of the contributions from charge fluctuations to the dielectric losses. ε''_{rev} means the dielectric loss related to reversible processes, leading to charge storage, such as dipolar or interfacial polarization. The two relaxation processes as well as their activation with temperature can be clearly distinguished. The low temperature (or high frequency) process remarkably spans over the entire frequency range moving from low to high frequencies when the temperature changes form -70°C to 40°C. A second process appears at a higher temperature, slightly below the freezing point, and is also thermally activated as the temperature is increased. Figure 6 (right) shows the relaxation mapping for both processes, with the time-honoured labels alpha and beta used simply to indicate the order of appearance from high to low temperatures. Both processes were found to follow an Arrhenius-type temperature dependency for temperature below freezing, which is consistent with ionic polarization in confined space, with a noticeable decrease of the activation energy at temperatures above freezing point. The high temperature process is believed to be related to weakly bounded water as it disappears upon drying (after an isothermal step at 100°C under nitrogen) as shown in the inset of the right part of Figure 5.

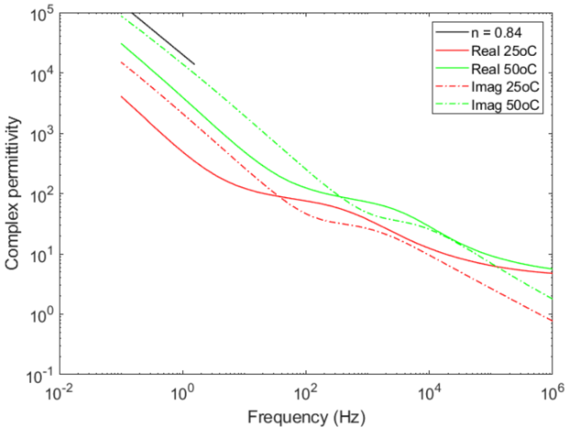

Figure 4: Dielectric response at 25 and 50°C of a hydroxide-based geopolymer

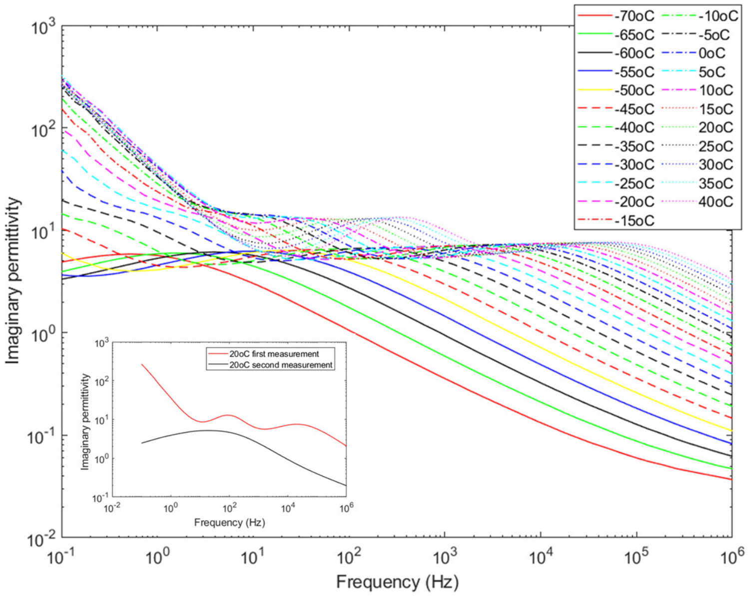

Figure 5: Imaginary permittivity over a range of temperatures (right) of a carbonate-based geopolymer.

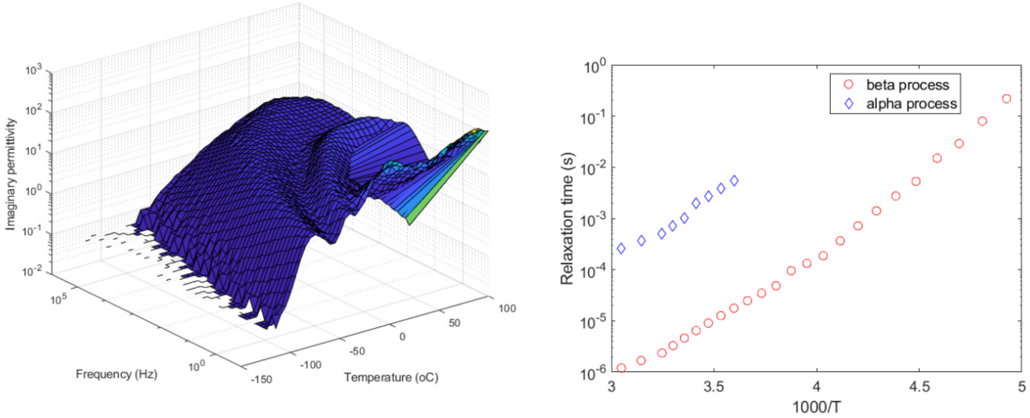

Figure 6: a) Dielectric loss of a carbonate-based geopolymer calculated from the real permittivity using the Kramers-Kronig equations (left) and relaxation map of the two relaxation modes (right).

4. CONCLUSION

Alkali-activated materials (AAM) made with fly ash (FA) activated by potassium are self-sensing. This article studied the dielectric behaviour of FA AAM and made with potassium hydroxide and with potassium carbonate. Within a certain range of water content, two relaxation processes are visible in the measurements. One process occurred at the low temperature (or high frequency) moving from low to high frequencies when the temperature changes form -70^{o}C to 40^{o}C. A second process occurred at a higher temperature, slightly below the freezing point, and is also thermally activated as the temperature is increased. This later process disappeared upon drying and it is associated with weakly bounded water. The impact of water is so strong that it is not possible to clearly distinguish the two alkaline activators without further studies.

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REFERENCES

[1] Di Mare, M. and C.M. Ouellet-Plamondon, Greener, smarter, stronger: Self-sensing construction materials from one-part alkali-activated materials. *Materials Letters*, **349**, 2023, 134830.

[2] Di Mare, M. and C.M. Ouellet-Plamondon, Highly piezoresistive, self-sensing, one-part potassium-activated inorganic polymers for structural health monitoring. *Materials Today Sustainability*, **20**, 2022 100261.

[3] Di Mare, M., *et al.,* Combined Experimental and Computational Prediction of the Piezoresistivity of Alkali-Activated Inorganic Polymers. *The Journal of Physical Chemistry C*, **126**, 2022, 14995-15000.

[4] Di Mare, M. and C. Ouellet-Plamondon, The effect of composition on the dielectric properties of alkali activated materials: A next generation dielectric ceramic. *Materials Today Communications*, **32**, 2022, 104087.

[5] Goracci, G., *et al.,* Dynamics of nano-confined water in Portland cement - comparison with synthetic C-S-H gel and other silicate materials. *Scientific Reports*, **7**, 2017, 8258.

[6] Saltas, V., Vallianatos, F. and Triantis D., Dielectric properties of non-swelling bentonite: The effect of temperature and water saturation. *Journal of Non-Crystalline Solids*, **354**, 2008, 5533-5541.

[7] Salles, F., *et al.,* Diffusion of Interlayer Cations in Swelling Clays as a Function of Water Content: Case of Montmorillonites Saturated with Alkali Cations. *The Journal of Physical Chemistry C*, **119**, 2015, 10370-10378.

[8] B., Al-Mattarneh, H., Achara, B. E., Mohammed, B. S. and Nuruddin, M. F, Dielectric Properties for Characterization of Fly Ash-Based Geopolymer Binders, *Construction and Building Materials,* **189**, 2018, 19-32.

[9] Ramdeen, T., Dissado, L.A. and Hill, R.M., Influence of adsorbed water on the dielectric response of a ceramic material. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, **80**, 1984, 325-340.

[10] Jonscher, A. K., The Universal Dielectric response: Part III. *IEEE Electrical Insulation Magazine*, **6,** 1990, 19-24.

[11] Jonscher, A. K., Dielectric relaxation in solids, *J. Phys. D: Appl. Phys.,* **32**, 1999, R57-R70.

[12] Di Mare, M., Ouellet-Plamondon, C., The effect of composition on the dielectric properties of alkali activated materials: A next generation dielectric ceramic. *Materials Today Communications*, **32**, 2022.

[13] Chanuta, N., Stefaniuka, D., Weaverb, J.C., Zhuc, Y., Shao-Hornc, Y., Masica, A. and Ulma, F.J., Carbon–cement supercapacitors as a scalable bulk energy storage solution. *Proceedings of the National Academy of Sciences (PNAS),* **120**, 2023, 1-7.

[14] Brisebois, P. P., Di Mare, M., and Ouellet-Plamondon, C. M, Dielectric properties of fly ash geopolymers with two types of potassium activators, *IEEE Conference on Electrical Insulation and Dielectric Phenomena,* 2022, 491-494

[15] Hanjitsuwan, S., Hunpratub, S., Thongbai, P., Maensiri, S., Sata, V. and Chindaprasirt, P., Effects of NaOH Concentrations on Physical and Electrical Properties of High Calcium Fly Ash Geopolymer Paste. *Cement and Concrete Composites,* **45** (2014) 9-14.

[16] Pinto, G.M., Helal, E., Ribeiro, H., David, E., Fechine, G.J.M., Demarquette, N.R., Use of Kramers-Kronig Transform and Vogel-Fulcher-Tammann Equation to Probe the Molecular Dynamics of Polyamide 10.10 Nanocomposites, *IEEE Conference on Electrical Insulation and Dielectric Phenomena,* 2023, 18-21.

[17] Steeman, P. A. M. and Van Turnhout, J., A numerical Kramers-Kronig transform for the calculation of dielectric relaxation losses free from Ohmic conduction losses. *Colloid Polym. Sci.,* **275**, 1997, 106-115.