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Effect of Nano-SiO₂ from Rice Hull Ash on the Conductivity of Cement Paste

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The electrical conductivity of simulated cement paste matrix with water-to-cement ratio of 0.50 and 2.0 % amorphous nanosilica, synthesized from rice hull ash, has been related to the effect of hydration stages on the ions dissociated in the capillary pore solution of the cement paste mesostructure. The increase in ions, as the hydration proceeded, has also been implied by the increasing trend of the conductivity spectra obtained from the complex impedance spectroscopy in the frequency region from 100 kHz to 20 MHz. To consider the effect of capillary pores, a comparable set of cement paste with similar macrostructure has been established using a modified method of simple grinding and pelletizing techniques. From the results of the Kramers-Kronig validation test, the impedance data have been found to exhibit causal, linear, and stable behavior in the high frequency region from 6 to 20 MHz.

1. Introduction

In recent years, research on pore structure of concrete has been gaining interest because of its implication on the durability against chemical attacks in extreme environment.¹⁻⁴ The mesostructure pores serve as the ion transport paths for chloride and sulfate ingress that can reduce the service life of concrete.⁴ However, several techniques such as the incorporation of admixtures are being introduced for pore refinement and hydration acceleration.⁵

In an agricultural country, recycling rice hull ash (RHA) as one of the byproducts of agro-industrial processes into a useful construction material has been one of the promising innovations in establishing a more resilient and sustainable infrastructure.⁶⁻⁸ Recently, the intervention of nanotechnology has played a huge role in advancing the construction materials to improve the mechanical properties of concrete.^{9,10} Synthesized from RHA, amorphous nanosilica (nano-SiO₂) has promoted the compressive strength and chloride resistance of concrete because of the high reactive surface area of nano-SiO₂.¹¹

From complex impedance spectroscopy, the frequency-dependence of the electrical conductivity of cement paste has been associated with the physical phenomena such as hydration kinetics and ion diffusion.^{4,12} The conduction mechanism is highly dependent on the moisture, ions, and pore and solid phases from capillary sites.^{4,13} With these multiple considerations, several studies have proposed techniques in experimenting a control factor to explain significantly the conduction mechanism in concrete.¹⁴

The conduction mechanisms of concrete, mortar, and cement paste largely differ with each other because of the differences in their major components. Among the three, the cement paste can have small specimen size because of the high degree of homogeneity of the phases.¹⁵

In the mesostructure of cement paste, the electrical conductivity is primarily caused by the capillary pore solution with ions dissociated in the dissolution of calcium hydrate and alkali salts in water.⁴ The conductivity of pores and solid phase is relatively negligible in terms of the magnitude of the ions as hydration products.¹⁶ In the initial hydration stage, an increase in the conductivity is primarily caused by the

ions dissociated after the water is reacted with the cement.¹⁷ However, a decrease in conductivity is caused by the development of the larger pore networks to facilitate the development of hydrated compounds such as ettringite.¹⁸

In the low-frequency region, the dynamic behavior of ions in the pore solution of the cement paste matrix can be explained using the power-law behavior relating the frequency and the conductivity. In this case, the hopping mechanism of charges can then be associated with the disordered system of the cement paste matrix.¹⁹ In this study, the effect of amorphous nano-SiO₂ on the electrical conductivity of simulated cement paste matrix samples, with similarly comparable macrostructure, was analyzed using the conductivity spectra in the frequency region from 100 kHz to 20 MHz in explaining the ion dynamics in the capillary sites.

2. Materials and Methods

2.1. Sample preparation

The cement paste was a mixture of 2.0 % amorphous nano-SiO₂ by weight of type I cement powder at 0.50 water-to-cement ratio. The white nanosilica powder was synthesized from rice hull ash and its amorphous structure was characterized by another study using the same material.²⁰ In order to consider the conductive ions from the hydration only, distilled water with no ion content was used in preparing the fresh paste mixture.

In a polyvinyl chloride mold with 0.5-inch diameter, the fresh paste mixture was casted and allowed to harden for 24 hours under room temperature, humidity and pressure. The hardened mixtures were demolded and cured in a container filled with water under the same ambient condition for 7, 14, 21, and 28 days.

For each curing period, the hardened cement paste samples were powdered with a maximum diameter of 100 μm. Three 0.25-g and 1-mm thick discs were then pelletized for a one-minute press loading of 200 MPa. Similar procedures were performed for control mixture without nano-SiO₂.

2.2. Complex impedance spectroscopy

From 100 kHz to 20 MHz, the complex impedances were measured by the Keysight Impedance Analyzer E4990A. The contribution of pellet-electrode interface was neglected by applying non-contacting technique. Prior to any measurement, the short and open calibrations were performed to set the initial conditions of the instrument. The corresponding conductivity (σ), which is the real component of the inverse of impedance, was computed using Equation 1.

$$1. \quad \sigma = \frac{t}{A} \frac{Z'}{(Z')^2 + (Z'')^2}$$

where, t and A are the thickness and area of the samples, respectively. The Z' and Z'' were the measured real and imaginary components of the impedance, respectively.

Kramers-Kronig validation test

The Kramers-Kronig (KK) relations evaluate the impedance spectra for stability, causality, and linearity.^{21,22} The stability refers to the unchanging magnitude of an impedance point after the reapplication of electric field. The causality pertains to the sole effect of electric field on the impedance data. The linearity checks the non-linear KK behavior caused by the perturbation peaks.²³ For these criteria, the KK relations assume a combination of parallel connections of resistive and capacitive elements.²⁴ From one component of the measured impedance, the other component can be computed using the Equations 2 and 3.

$$2. \quad Z'(\omega) = Z'(\infty) + \frac{2}{\pi} \int_0^{\infty} \frac{xZ'(x) - \omega Z''(\omega)}{x^2 - \omega^2}$$

$$3. \quad Z''(\omega) = \frac{2\omega}{\pi} \int_0^{\infty} \frac{Z'(x) - Z''(\omega)}{x^2 - \omega^2}$$

where, ω and x are the angular frequency and arbitrary point, respectively.

The difference between the actual and KK-validated impedance data can be expressed using residual (Δ) for each frequency point using Equations 4 and 5.

$$4. \quad \Delta = \frac{Z_m - Z_c}{|Z|}$$

$$5. \quad |Z| = \sqrt{[Z'(\omega)]^2 + [Z''(\omega)]^2}$$

where, Z_m , Z_c , and $|Z|$ were the measured, computed, and total impedance, respectively.

2.3. Universal power law behavior

The frequency-dependence of conductivity of disordered systems such as the cement paste was modeled using a power-law behavior.²⁵ The conductivity spectra can then be fitted using Equation 6.

$$6. \quad \sigma(\omega) = A\omega^S + \sigma_0$$

where, A , S , and σ_0 are the frequency-independent amplitude, physical constant, and conductivity at direct current, respectively.

3. Results and Discussion

In the 10^5 - 10^7 Hz spectra shown in Figure 1, the conductivity of cement paste pellet with and without amorphous nano-SiO₂ generally showed plateau and the dispersive behaviors in the low and high frequency regions, respectively.^{19,26} As the frequency increased, the conductivity also increased exhibiting a power-law behavior. This implied that the conduction of cement paste samples followed a hopping transport mechanism.²⁷

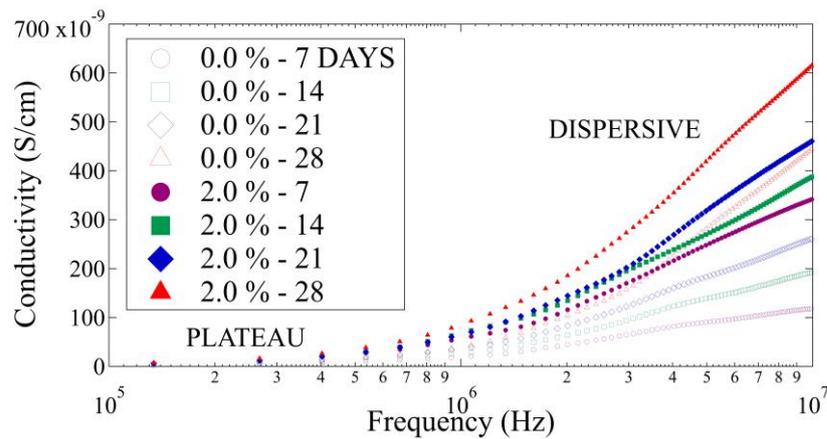


Figure 1. Frequency-dependence of electrical conductivity of cement paste with and without amorphous nano-SiO₂ at varying curing period.

Moreover, the DC conductivities of all samples were found to be negligible compared to AC conductivities.¹⁹ The conductivity was independent of frequency as it reached a constant value in the plateau region of low frequency. Similar results have also been obtained from this simplified power-law behavior from other studies on polymer-cement composites.^{19,25} In the sample preparation, air bubbles and large voids did not significantly contribute to the DC conductivity because of the similar macrostructure of the pellet. Hence, only the capillary voids and pore solution ions have significantly affected these conductivity measurements.

The parameter S ranged from 0.65 to 0.72 for cement paste samples with nano-SiO₂. This indicated that the hopping mechanism of ions behaved in a translational manner, rather than localized states with S greater than 1.0.²⁷

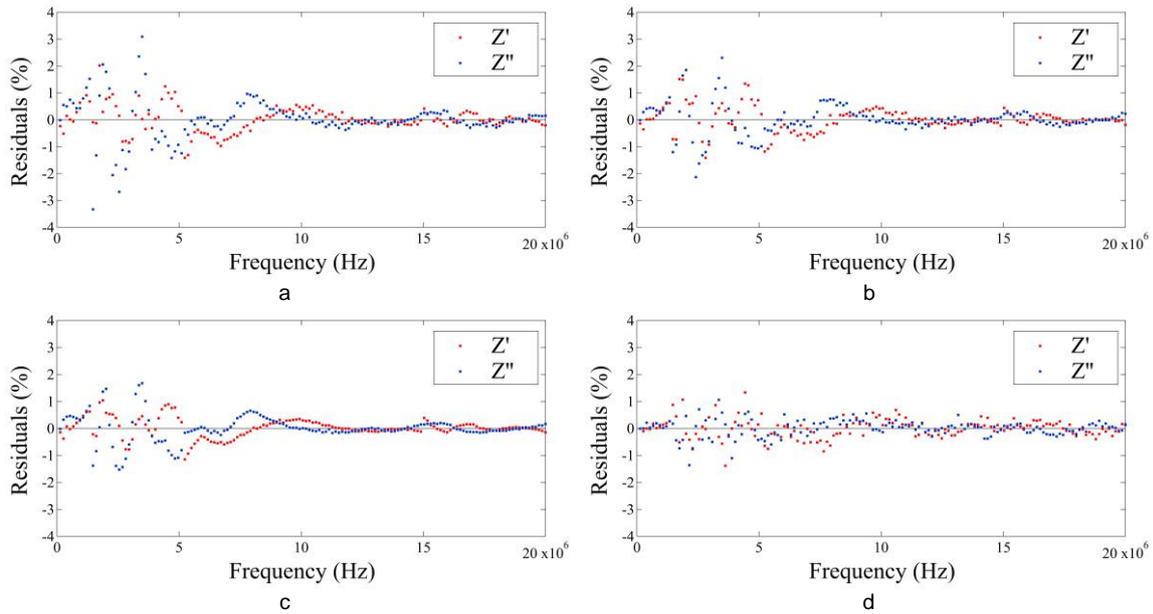


Figure 2. Residuals of impedance on cement paste sample without amorphous nano-SiO₂ at (a) 7, (b) 14, (c) 21, and (d) 28 curing days.

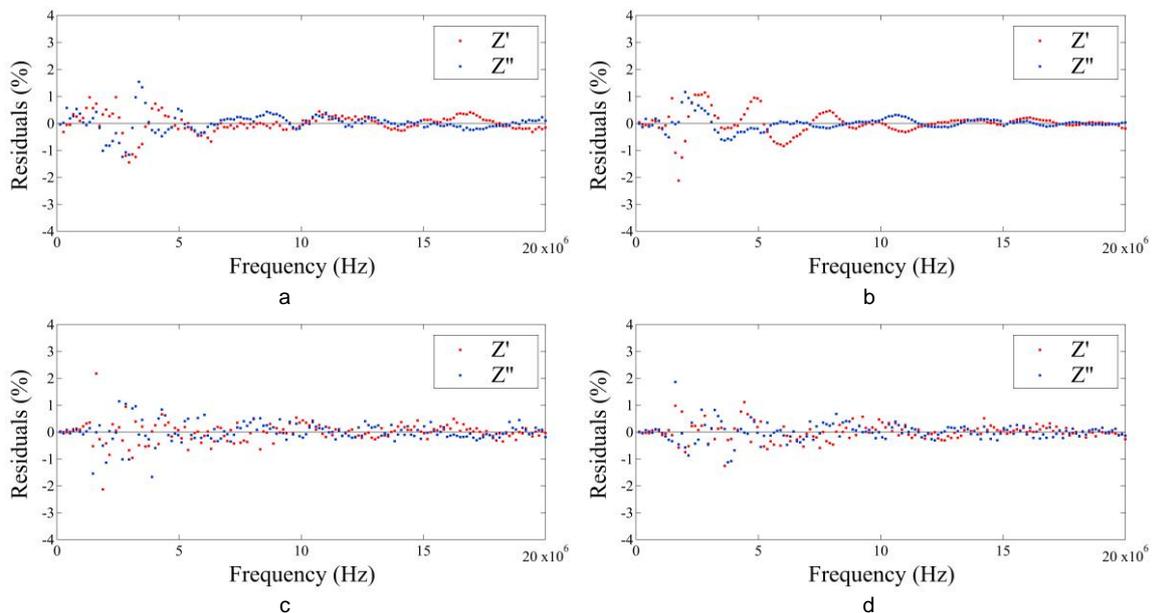


Figure 3. Residuals of impedance on cement paste sample with 2.0% amorphous nano-SiO₂ at (a) 7, (b) 14, (c) 21, and (d) 28 curing days.

Referring to Figures 2 and 3, the causality, linearity, and stability of impedance measurements were observed in the high frequency regions. Although some residuals up to 3.0% were observed in the low frequency region below 6 MHz, most of the impedance points resulted in at most 1.0% residual, indicating a set of representative impedance measurements of the electrical properties of cement paste pellet.

At 28-day curing period, the conductivity dramatically increased as implied by the relative differences in the dispersive region. For all frequencies, the conductivity of cement paste with nano-SiO₂ was higher than that of control sample. This may be caused by higher number of ions because of the hydration by curing or the pozzolanic reaction by nano-SiO₂.^{14,17}

In the pore solution, the ion concentration increases because the volume of the water only is reduced due to drying.¹⁴ The number of ions increases because of the charge carriers as products of the hydration induced by nano-SiO₂.¹⁷ Among the pore solution ions, the OH⁻ ions significantly contribute to the measured conductivity of the cement paste sample.²⁸ Therefore, the conductivity spectra of cement paste samples can be postulated from the contribution of ions and other phases in the cement paste mesostructure since the resistivity of air bubbles and large voids were disregarded by the modified method of simple grinding and pelletizing techniques. The addition of amorphous nano-SiO₂ to the cement paste has caused further pozzolanic activity that improved mechanical properties in the mesoscale analysis of cement paste as one of the concrete phases. Similarly, the trend of the conductivity has showed an agreement between the pore solution ions and the hydration stages of cement paste.

Conclusion

The electrical conductivity of cement paste pellet with amorphous nano-SiO₂ has been related to the pore solution ions by establishing a set of comparative samples that highlighted the contribution of the mesostructure including the solid phase and ions in the capillary sites. Moreover, the curing period and addition of nano-SiO₂ on the conductivity of cement paste demonstrated the effects of hydration and pozzolanic activity on the microstructure of the compounds. Lastly, the impedance measurements followed the causality, linearity, and stability of KK relations.

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References

1. Banavar JR, Koplik J and Winkler KW. Physics and chemistry of porous media II: Ridgefield, CT, 1986. American Institute of Physics; 1987.
2. Schwarz N, DuBois M and Neithalath N (2007) Electrical conductivity based characterization of plain and coarse glass powder modified cement pastes. *Cement and Concrete Composites* **29**(9): 656-666.
3. Tang SW, Cai XH, He Z, Zhou W, Shao HY, Li ZJ, Wu T and Chen E (2017) The review of early hydration of cement-based materials by electrical methods. *Construction and Building Materials* **146**: 15-29.
4. Wu L, Dai P and Li Y (2016) Determination of the transport properties of structural concrete using AC impedance spectroscopy techniques. *Journal of Engineering* **2016**.
5. Nmai CK (1995) Corrosion-inhibiting admixtures: passive, passive-active versus active systems. *Special Publication* **154**: 565-586.
6. Al-Khalaf MN and Yousif HA (1984) Use of rice husk ash in concrete. *International Journal of Cement Composites and Lightweight Concrete* **6**(4): 241-248.
7. Zhang MH, Lastra R and Malhotra VM (1996) Rice-husk ash paste and concrete: some aspects of hydration and the microstructure of the interfacial zone between the aggregate and paste. *Cement and Concrete Research* **26**(6): 963-977.
8. Chindapasirt P and Rukzon S (2008) Strength, porosity and corrosion resistance of ternary blend Portland cement, rice husk ash and fly ash mortar. *Construction and Building Materials* **22**(8): 1601-1606.
9. Wang L, Zheng D, Zhang S, Cui H and Li D (2016) Effect of nano-SiO₂ on the hydration and microstructure of portland cement. *Nanomaterials* **6**(12): 241.
10. He X and Shi X (2008) Chloride permeability and microstructure of Portland cement mortars incorporating nanomaterials. *Transportation Research Record: Journal of the Transportation Research Board* **2070**: 13-21.
11. Ronquillo GJB, Madlangbayan MS, Ignacio MCCD, Peralta EK and Peralta MM (2016) Morphological and characterization-based verification of the properties of concrete with amorphous nanosilica synthesized from rice hull ash. *Asia Life Sciences* **25**(1): 311-324.
12. Dotelli G and Mari CM (2001) The evolution of cement paste hydration process by impedance spectroscopy. *Materials Science and Engineering: A* **303**(1): 54-59.
13. Brantervik K, Berg A, Niklasson GA, Hedberg B and Nilsson LO (1990) Percolation effects in the electrical conductivity of porous cement mortar. *EPL (Europhysics Letters)* **13**(6): 549.
14. Rajabipour F and Weiss J (2007) Electrical conductivity of drying cement paste. *Materials and Structures* **40**(10): 1143-1160.

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15. Scrivener KL (1997) Microscopy methods in cement and concrete science. *World Cement Research and Development* **28(9)**: 92-112.
 16. Rajabipour F (2006) In situ electrical sensing and material health monitoring of concrete structures. Ph.D. Dissertation. Purdue University.
 17. Andrade C, Blanco VM, Collazo A, Keddam M, Novoa XR and Takenouti H (1999) Cement paste hardening process studied by impedance spectroscopy. *Electrochimica Acta* **44(24)**: 4313-4318.
 18. Topçu İB, Uygunoğlu T and Hocaoğlu İ (2012) Electrical conductivity of setting cement paste with different mineral admixtures. *Construction and Building Materials* **28(1)**: 414-420.
 19. Zihlif AM, Ayish IO and Elimat ZM (2013) The AC electrical behavior of cement-polymer composite. *Journal of Thermoplastic Composite Materials* **26(9)**: 1168-1179.
 20. Ignacio M CCD, Peralta EK, Peralta MM, Elepano AR and Suministrado DC (2014) Thermophysical properties of nanosilica-in-fluid dispersion (nanofluid) derived from rice hull ash. *Philippine Journal of Crop Science* **39(1)**: 20-29.
 21. Lasia A (2014) *Electrochemical impedance spectroscopy and its applications*. Springer, New York.
 22. Orazem ME and Tribollet B (2011) *Electrochemical impedance spectroscopy (Vol. 48)*, John Wiley & Sons, Hoboken, New Jersey.
 23. Boukamp BA (2004) Electrochemical impedance spectroscopy in solid state ionics: recent advances. *Solid State Ionics* **169(1)**: 65-73.
 24. Boukamp BA (1995) A linear Kronig-Kramers transform test for immittance data validation. *Journal of the Electrochemical Society* **142(6)**: 1885-1894.
 25. Greenhoe BM, Hassan MK, Wiggins JS and Mauritz KA (2016) Universal power law behavior of the AC conductivity versus frequency of agglomerate morphologies in conductive carbon nanotube - reinforced epoxy networks. *Journal of Polymer Science Part B: Polymer Physics* **54(19)**: 1918-1923.
 26. Funke K (1995) Mechanisms of ionic conduction in solid electrolytes. *Zeitschrift für Physikalische Chemie* **188(1-2)**: 243-257.
 27. Badr S, Sheha E, Bayomi RM and El-Shaarawy MG (2010) Structural and electrical properties of pure and H₂SO₄ doped (PVA) 0.7 (NaI) 0.3 solid polymer electrolyte. *Ionics* **16(3)**: 269-275.
 28. Snyder KA, Feng X, Keen BD and Mason TO (2003) Estimating the electrical conductivity of cement paste pore solutions from OH⁻, K⁺ and Na⁺ concentrations. *Cement and Concrete Research* **33(6)**: 793-798.