ICCC 2023 - Guidelines for citation and reuse

Please cite the conference proceedings as following:
Thailand Concrete Association, Ed. *Further Reduction of CO2 -Emissions and Circularity in the Cement and Concrete Industry, 16th International Congress on the Chemistry of Cement 2023 - ICCC2023* (Bangkok 18.-22.09.2023). Bangkok, 2023. Available at: https://www.iccc-online.org/archive/

Please cite individual papers as following:
Author. Title. In: Thailand Concrete Association, Ed. *Further Reduction of CO2 -Emissions and Circularity in the Cement and Concrete Industry, 16th International Congress on the Chemistry of Cement 2023 - ICCC2023* (Bangkok 18.-22.09.2023). Bangkok, 2023. Available at: https://www.iccc-online.org/archive/

Organized by

TCA
สมาคมคอนกรีตแห่งประเทศไทย
Thailand Concrete Association

THE 16TH INTERNATIONAL CONGRESS ON THE CHEMISTRY OF CEMENT
ICCC 2023
BANGKOK THAILAND

ICCC 16th 2023

INTERNATIONAL CONGRESS ON THE CHEMISTRY OF CEMENT

CONGRESS PROCEEDING VOLUME III

Further reduction of CO_2-emission and circularity in the cement and concrete industry

SEPTEMBER 18-22, 2023

CENTARA GRAND & BANGKOK CONVENTION CENTRE @CENTRALWORLD

Co-Sponsor by

aci American Concrete Institute Always advancing
SEADMA
ACF
gcca Global Cement and Concrete Association
ASTM INTERNATIONAL

Contact infomation :
Email: iccc2023.tca@gmail.com
Website : https://www.iccc2023.org/

Preliminary Investigation of 0-3 Lead Zirconate Titanate – Lime Calcined Clay Cement Composites

A. Alchaar[1] and K. Celik[2,*]

[1] *New York University Abu Dhabi, Abu Dhabi, United Arab Emirates*
asa7916@nyu.edu
[2] *New York University Abu Dhabi, Abu Dhabi, United Arab Emirates*
kemal.celik@nyu.edu

ABSTRACT

The development of cement-based piezoelectric composites (CPCs) was found to have great potential in sensor applications for concrete structural health monitoring. Popular CPCs are made of lead zirconate titanate (PZT) and ordinary Portland cement (OPC). Efforts continue to densify such composites to lower the energy-intensive polarization requirements or make them more efficient in composite response. Recently, adding alumino-silicate-based materials (kaolin) was found to cause refined microstructure, hence improving the dielectric and piezoelectric properties of CPCs. In this study, CPC was fabricated using limestone calcined clay cement (LC^3) with 50% PZT as a functional phase to observe the composite's densification and assess its viability in the CPCs field. Results show that the microstructure is less porous with LC^3 compared to conventional composites. In addition, the dielectric loss was found to be 0.54, similar to conventional CPCs. However, relative permittivity was found to be far lower than those of conventional CPCs. This was owed to the quick moisture loss after curing, the relatively lower relative humidity of curing, and irregularities at the electrode surfaces. The presented preliminary results can indicate a potential in this composite to have improved dielectric properties and lower polarization needs.

KEYWORDS: *Smart materials, piezoelectric, PZT,* LC^3*, smart cement*

1. Introduction

Over the last 2 decades, cement-based piezoelectric composites (CPCs) have been investigated as smart sensors for structural health monitoring (SHM) applications. They comprise ordinary Portland cement (OPC) and a piezoelectric material such as lead zirconate titanate (PZT). Research has shown that such composites have better compatibility with concrete and are superior to normal piezoelectric composites like polymer-based ones. The enhanced compatibility of CPCs results from better volume stability and a lower acoustic impedance mismatch with the host concrete (Dong & Li, 2005). CPCs can be fabricated with ten different connectivity patterns, including 0-3, 1-3, and 2-2 (Chen et al., 2019). 0-3 configuration is the most popular due to the relatively easier fabrication (since ceramic is added as a powder) and overall better performance (Ding et al., 2021). However, the piezoelectricity of such composites requires activation through polarization. This is because ceramic particles have different dipole directions, which cannot be controlled during fabrication. It is important to note that dipoles of a smart material shall be in the same direction to exhibit a piezoelectric behavior (Chen et al., 2019). Polarization is an energy-intensive process that is performed by applying an external electric field using a high-voltage direct current (DC) power supply for a specific duration and at a certain temperature. Ever since it was developed, CPCs have been characterized by the evaluation of piezoelectric strain factor (d_{33}), electromechanical coupling coefficient (K_t), and dielectric constant (ε_r) (Li et al., 2002). Research efforts continue to enhance the piezoelectric performance (especially the d_{33} parameter) of CPCs by optimizing the poling process, fabrication techniques, and microstructure. The latter is specifically important due to the complexity of hydration products and the microstructure heterogeneity. The densification of CPCs can improve the connectivity between piezoelectric particles and the host cement matrix and lower the porosity at interfacial regions. This is key to pushing the levels of d_{33} higher because porosity leads to discontinuities in stress transfer and dramatically increases polarization requirements (Ding et al., 2021). **Figure 1** shows Scanning Electron Microscopy (SEM) micrographs for OPC-PZT composites at different magnifications. It can be observed that despite the relatively good bond between cement hydration products and PZT particles (Chaipanich et al., 2013), pores take up a considerable part of the interface.

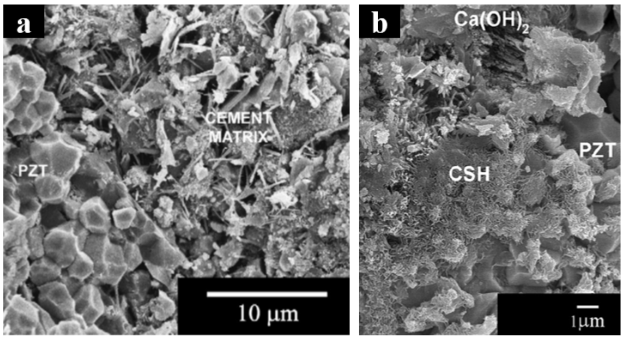

Figure 1. SEM micrographs of (a) CPC with 50% PZT (Chaipanich et al., 2007) and (b) CPC with PZT at large magnification (Chaipanich et al., 2013)

Several attempts to densify CPCs were recently made by incorporating supplementary cementitious materials (fly ash, silica fume, slag, and kaolin) and conductive fillers (carbon black and carbon nanotubes). Furthermore, the use of kaolin (alumino-silicate-based additive) has shown promising results in enhancing CPCs by lowering porosity to 1.86%, according to Pan et al (2015). While kaolin performs well as an additive, limestone calcined clay cement (LC^3) can perform similarly as a cementitious matrix. LC^3 is a recently developed sustainable binder with 20% less thermal energy requirement. It allows ~45% clinker replacement, larger binder density, and finer microstructure. Thereby, it significantly improves the mechanical and durability properties of cement. This is because alumina from calcined clay undergoes normal pozzolanic reactions and reacts with limestone carbonates (Sharma et al., 2021). This work is a preliminary investigation of the versatility of LC^3 as a matrix in CPCs with PZT as a functional phase. It is believed that CPCs made with LC^3 instead of OPC will be denser, especially at interfacial zones, which can lead to reducing polarization requirements and improving piezoelectric properties. In that context, this study sheds light on the dielectric properties and microstructure of 0-3 PZT-LC^3 composites.

2. Methodology

2.1 Materials

The composite was fabricated with 50% PZT by volume. Water and polycarboxylate-based superplasticizers were used to fluidize the mixture before casting. The matrix phase comprises (by weight) 50% OPC type I, 30% high reactivity calcined clay (acquired from TARA, India), 15% Limestone, and 5% Gypsum. PZT was acquired as hollow spherical agglomerates 50-150 µm from APC International Ltd, United States.

2.2 Fabrication

Normal mixing and distribution method was employed in fabricating the composite. Samples were cast with size 15 x 15 x 3 mm and left to dry at ambient temperature for 2d. After drying, samples were cured at 60° C and relative humidity (RH) of ~90% for 4d. Part of the samples was coated with conductive silver paint on both surfaces to form electrodes for dielectric measurements.

2.3 Experiments

Capacitance and dielectric loss were measured using an impedance phase analyzer (Keysight E4980A/AL Precision LCR Meter) at the age of 10 days, ambient temperature, and unpoled status. Measured capacitance was used to calculate the relative dielectric permittivity (ε_r) as a parallel plate condenser using the formula

Ct/ε$_0$A, where C is the capacitance, t is the thickness of the sample, ε$_0$ is the permittivity of free space (8.854 pF/m), and A is the electrode area. In addition, the impedance spectrum of the composite was recorded to observe electromechanical coupling. Finally, the microstructure of the composite was characterized through a scanning electron microscope (SEM, Quanta 450 FEG) with an operating voltage of 10 kV.

3. Results and Discussion

SEM micrographs of the composite are shown at different magnifications in **Figure 2**. Compared to OPC-based composites, the microstructure is observed to be denser, as expected. In addition, there were hardly any indications of calcium alumino-silicate hydrates (C-A-S-H, which is the main hydration product of LC3). Getting high-resolution images at large magnification was challenging because of the charging effect. Besides, PZT particles can be seen surrounded by the matrix products with some porosity at the interface.

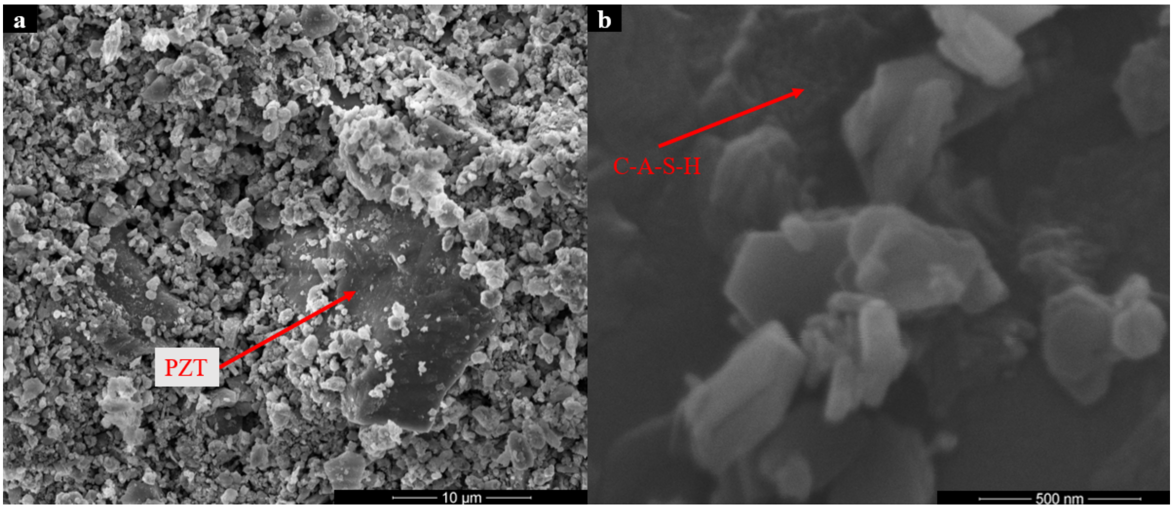

Figure 2. SEM micrographs of LC^3-PZT Composite at (a) medium and (b) high magnifications

The impedance spectrum of the composite can be seen in **Figure 3**. A spike in the phase curve was observed at ~17 kHz, which can indicate coupling. However, coupling was not captured by the analyzer in the impedance spectrum.

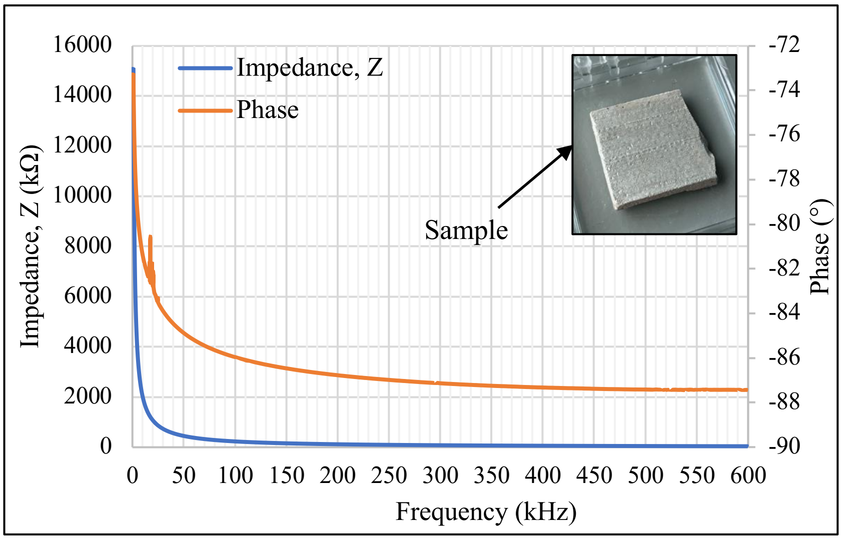

Figure 3. (a) Impedance spectrum of the LC^3-PZT composite with the sample shown

The composite exhibited a dielectric constant ε$_r$ of 22 and a dielectric loss (D) of 0.54. Conventional PZT-OPC 0-3 composites have ε$_r$ that can reach up to 167 and D down to ~0.79 (Ding et al., 2021). In addition, Pan et al (2015) reported an ε$_r$ up to 252 and D of 0.58 when kaolin was added as a cement replacement by 10%. It is important to note that for CPCs, higher relative permittivity is desired as it indicates charge generation in the application of an external electric field and therefore tells about the polarizability of the material. On the other hand, lower dielectric loss (D) is desired for polarization efficiency. In this study, the measured dielectric loss is comparable to previous research, but the dielectric constant is 10-25% of the values reported for similar composites. There are some probable causes for a low ε_r. First, LC^3 formulation has a higher fineness level than OPC, meaning a higher surface area and water requirement. In addition, samples were cured at RH of ~90% only, rather than 100%, due to the chamber's capability. As a result, composites have low moisture levels and fewer free water particles. Furthermore, silver-painted surfaces were observed to have non-uniformity. Such issues can significantly reduce permittivity and add up resistance to the composite.

4. Conclusions

This study presents a preliminary investigation of cement-based piezoelectric composites (CPCs) using limestone calcined clay cement (LC^3) as a matrix with 50% PZT as a functional phase. The use of LC^3 densified the composite and improved its dielectric properties. This will favor developing cement-based smart materials as polarization requirements can be reduced while maintaining good piezoelectric behavior. Previous research has shown several improvements in the dielectric, piezoelectric, and morphological properties of CPCs when kaolin was incorporated as an alumino-silicate cement replacement additive. Interestingly, LC^3 has a nature similar to kaolin but is considered a matrix rather than an additive. The dielectric loss was demonstrated to be 0.54, which is reasonable. However, the spectral analysis of impedance showed a spike in the phase, which can resemble coupling, but resonant frequencies of impedance and admittance were not captured. In addition, dielectric permittivity was 10-25% of those achieved in previous works with similar composites. This was due to the low post-curing internal moisture and the presence of irregularities at the electrode surfaces of samples. Nonetheless, the refined microstructure, observed through SEM micrographs, confirmed the densification of the composite. Future work will attempt to fabricate composites with different mixing parameters, maximizing relative humidity in curing, monitoring moisture levels, and achieving better surface quality of electrodes. In that way, improved dielectric properties are expected to be exhibited by the composite.

Acknowledgments

The authors are grateful to Juan Esteban Villegas and staff members at the Core Technology Platforms at New York University Abu Dhabi (NYUAD) for helping in the experimental work of this study. This material is based upon works supported by the NYUAD Center for Smart Engineering Materials (NYUAD-CSEM), funded by Tamkeen under NYUAD RRC Grant No. CG011.

References

Chaipanich, A., Jaitanong, N., & Tunkasiri, T. (2007). Fabrication and properties of PZT–ordinary Portland cement composites. *Materials Letters*, *61*(30), 5206–5208. https://doi.org/10.1016/j.matlet.2007.04.031

Chaipanich, A., Rianyoi, R., Potong, R., Jaitanong, N., & Chindaprasirt, P. (2013). Compressive Strength and Microstructure of 0–3 Lead Zirconate Titanate Ceramic-Portland Cement Composites. *Ferroelectrics*, *457*(1), 53–61. https://doi.org/10.1080/00150193.2013.847333

Chen, J., Qiu, Q., Han, Y., & Lau, D. (2019). Piezoelectric materials for sustainable building structures: Fundamentals and applications. *Renewable and Sustainable Energy Reviews*, *101*, 14–25. https://doi.org/10.1016/j.rser.2018.09.038

Ding, W., Liu, Y., Shiotani, T., Wang, Q., Han, N., & Xing, F. (2021). Cement-Based Piezoelectric Ceramic Composites for Sensing Elements: A Comprehensive State-of-the-Art Review. *Sensors*, *21*(9), 3230. https://doi.org/10.3390/s21093230

Dong, B., & Li, Z. (2005). Cement-based piezoelectric ceramic smart composites. *Composites Science and Technology*, *65*(9), 1363–1371. https://doi.org/10.1016/j.compscitech.2004.12.006

Li, Z., Zhang, D., & Wu, K. (2002). Cement-Based 0-3 Piezoelectric Composites. *Journal of the American Ceramic Society*, *85*(2), 305–313. https://doi.org/10.1111/j.1151-2916.2002.tb00089.x

Pan, H. H., Yang, R.-H., & Cheng, Y.-C. (2015). *High piezoelectric properties of cement piezoelectric composites containing kaolin* (P. J. Shull, Ed.; p. 94370R). https://doi.org/10.1117/12.2085452

Sharma, M., Bishnoi, S., Martirena, F., & Scrivener, K. (2021). Limestone calcined clay cement and concrete: A state-of-the-art review. *Cement and Concrete Research*, *149*, 106564. https://doi.org/10.1016/j.cemconres.2021.106564