Characterization and performance of cement-based thermoelectric materials

Ruchita Jani[a], Niall Holmes[a*], Roger West[b], Kevin Gaughan[c], Xiaoli Liu[d], Esther Orisakwe[e], Conrad Johnston[e], Ming Qu[d], Jorge Kohanoff[e], Lorenzo Stella[e], Hongxi Yin[f]

[a] School of Civil and Structural Engineering, Technological University Dublin, Ireland
[b] Department of Civil, Structural and Environmental Engineering, Trinity College Dublin, Ireland
[c] School of Multidisciplinary Technologies, Technological University Dublin, Ireland
[d] Lyles School of Civil Engineering, Purdue University, West Lafayette, Indiana, USA
[e] School of Mathematics and Physics, Queen's University Belfast, United Kingdom
[f] International Centre for Energy, Environment & Sustainability, Washington University in St Louis, St Louis, Missouri, USA

E-mail : - ruchita.jani@mytudublin.ie, niall.holmes@tudublin.ie, rwest@tcd.ie, kevin.gaughan@tudublin.ie, liu2251@purdue.edu, e.orisakwe@qub.ac.uk, conrad.johnston@qub.ac.uk, mqu@purdue.edu, j.kohanoff@qub.ac.uk, l.stella@qub.ac.uk, hongxi.yin@wustl.edu

ABSTRACT: Thermoelectric materials enable direct conversion of thermal energy to electricity. Ambient heat energy harvesting could be an effective route to convert buildings from being energy consumers to energy harvesters, thus making them more sustainable. There exists a relatively stable temperature gradient (storing energy) between the internal and external walls of buildings which can be utilized to generate meaningful energy (that is, electricity) using the thermoelectric principle. This could ultimately help reduce the surface temperatures and energy consumption of buildings, especially in urban areas. In this paper, ongoing work on developing and characterizing a cement-based thermoelectric material is presented. Samples are fabricated using cement as a base material and different metal oxides (Bi_2O_3 and Fe_2O_3) are added to enhance their thermoelectric properties. A series of characterization tests are undertaken on the prepared samples to determine their Seebeck coefficient, electrical and thermal conductivity. The study shows that cement paste with additives possesses physical properties in the range of semiconductors whereby, initially, the resistivity values are low but with time, they increase gradually, thus resulting in lower electrical conductivity. The thermal conductivity of the cement paste with additives is lower than the control sample. Seebeck coefficient values were found to be relatively unstable during the initial set of measurements because the internal and external environment needed to be kept in a thermally stable condition to achieve steady results. The detailed analysis helped determine and eliminate the source of errors in the characterization process and obtain repeatable results. Parameters such as moisture content, temperature and age were found to have a significant impact on the properties of cement based thermoelectric materials.

KEY WORDS: Cement composites; Thermoelectrics; Seebeck Coefficient; Electrical Conductivity; Thermal Conductivity.

1 INTRODUCTION

Urbanization is increasing rapidly all over the world and so is the impact of anthropogenic activities. According to an estimate by UN urbanization projections, as of 2018, 55% of the world's population now resides in urban areas [1]. Pavements, roads and buildings absorb incident solar radiation leading to a 10-20˚C rise in their surface temperatures as compared to their surroundings in summer [2], causing the Urban Heat Island (UHI) effect [3]. 60 % of urban surface area is now covered by low albedo and heat absorbing materials [4]. On average, the electricity consumption in meeting cooling needs in summer was 13% higher in urban areas compared to rural areas [7]. Mitigation measures applied for alleviating the UHI effect helped reduce the surface temperature of buildings but had limited influence on reducing its overall impact [8].

Heat harvesting is a promising route to generate electrical energy from ambient heat which in turn helps reduce the surface temperature of buildings and pavements. Several technologies like photovoltaics, thermoelectrics, periodic kinetic, EM wave, airflow, etc have been studied for this purpose. The miniscule amount of power available from them and the complexities involved in their operation has restricted their application [9]. There exists a relatively stable thermal gradient between indoor and outdoor air in buildings [11]. Thermal energies from these gradients could be captured and converted into electricity using the thermoelectric (TE) phenomenon. Cement-based thermoelectric materials can be a useful route to harness absorbed thermal energy in buildings. This paper describes the use of cement based TE materials to harvest the waste heat stored in buildings by converting it into a useful form of energy, thus making them more sustainable.

2 LITERATURE REVIEW

The thermoelectric effect is a phenomenon where heat energy is directly converted into electric energy. The performance of TE materials can be assessed using a dimensionless parameter known as the figure of merit (ZT), which is mathematically represented by Equation 1. In this equation S, σ, κ and T stand for Seebeck Coefficient, Electrical Conductivity (EC), Thermal Conductivity (TC) and Absolute Temperature respectively. A TE material can be used for practical applications if its ZT value is greater than or equal to 1 [12].

$$ZT = \left(\frac{S^2.\sigma}{\kappa}\right)T \quad (1)$$

A superior TE material should have a high electrical conductivity to minimize joule heating, a large Seebeck coefficient for maximum conversion of thermal to electrical energy and a low thermal conductivity so that thermal shorting could be prevented [13]. The percolation phenomenon in cement was first observed in 1998 by Sun et al. in a carbon fibre reinforced cement (CFRC) composite, where a Seebeck coefficient of 17μV/˚C was obtained for a 1% concentration of carbon fibres [14]. Since then, cement-based TE materials have garnered substantial interest from researchers worldwide.

Addition of Bismuth Telluride in a CFRC mix led to a Seebeck coefficient of 35.5μV/°C [16]. Adding micro sized Fe_2O_3 and Bi_2O_3 were found to have a Seebeck coefficient of 92.6 and 100.3 μV/˚C respectively for a 5 wt. % concentration in the cement matrix [17]. However, the electrical and thermal conductivity of the resulting samples were not studied [17]. The use of nano sized metal oxide powders resulted in higher Seebeck coefficients as compared to micro sized additives [18].

Enhancing TE performance by introducing metal oxide powders helped improve the Seebeck coefficient but the EC values of the composite showed limited improvement. Other compounds such as carbon and steel fibres, graphite, carbon-based nano materials have also been used to improve the thermoelectric performance of cement. The biggest challenge in this endeavour is that high EC and Seebeck coefficient values could be obtained separately for samples but not simultaneously in the same specimen under similar operating conditions [19]. Maintaining a low TC value is essential to improve conversion efficiency of a TE cement composite.

Thermal and electrical conductivity are properties which are dependent on each other, increasing one will lead to an increase in the other and vice-versa. Hence, increasing EC whilst limiting the value of TC for a material is a difficult task to achieve. Characterising TE materials in general has its own share of problems, particularly at elevated temperatures which can cause inaccuracies as high as 50% in the measurement [20]. Even a small degree of inhomogeneity within the sample can result in large variations in TE properties [21]. This fact causes difficulty in achieving repeatable and reliable results for TE materials especially when electrochemical reactions and phase transitions are taking place within the sample [20]. It is still difficult to determine for how long was the TE phenomenon observed in enhanced cement-based TE materials, was it obtained from a dry or saturated sample or did curing time and changing degree of hydration taking place within its internal structure with age have any influence on it.

So far, just one study by Wei et al. has investigated the impact of moisture on the Seebeck coefficient and electrical conductivity of enhanced cement composites [22]. They found that the observed TE phenomenon can be attributed to a high moisture content in the sample. In this work, an attempt has been made to study the main thermoelectric properties of cement paste enhanced with micro sized Fe_2O_3 and Bi_2O_3 particles. Several challenges and errors were encountered while measuring the Seebeck coefficient and electrical conductivities for them. The methods adopted to solve the errors to produce stable results are highlighted and the intricate factors having an impact on the characterization process from the material and the measurement point of view are identified.

3 EXPERIMENTAL WORK

3.1 Material Specification

Cement samples were prepared using a 42,5 R CEM I cement from Irish Cement Ltd (described in Table 1) of particle size of about 15 microns and Bismuth trioxide powder with a purity of 99.5 % and maximum particle size of 50 microns. The Ferrous oxide powder used had 95% of its particles of size less than 53 microns. No aggregates were used.

3.2 Sample Preparation and Curing

Three set of samples were prepared; one was the control sample which consisted of only cement and water mixed with a water to cement (w/c) ratio of 0.45. The other two sets of samples were made of 5% Bi_2O_3 and 5% Fe_2O_3 weight by mass of cement respectively.

Table 1. CEM I chemical composition

Contents	Percentage (%)	
SiO_2	18.29 %	* Here the Chloride content of the cement is not included as it was not available from the reports
Al_2O_3	5.08 %	
Fe_2O_3	2.78 %	
CaO	63.89 %	
SO_3	2.64 %	
F. Cao	1.57 %	
LOI	2.79 %	
Na_2O Eq.	0.59 %	

The dry contents were blended thoroughly in a container and thereafter the required amount of water was added to form a wet paste mix using an automatic mortar mixer. The prepared mixture was poured into a stainless-steel mould of size 160 × 40 × 40 mm^3. The mould containing the mix was compacted using a vibrating table to remove air bubbles. The samples for thermal conductivity tests were of cylindrical shape (100mm diameter x 200mm long). The prepared mix was allowed to set for 24 hours and was then demoulded. Samples were later subjected to water curing in a tank for a period of 7 days. The curing tank temperature was maintained at 20 ± 1°C. Once the samples were removed from the curing tank, it took up to 6 hours for the surfaces to become dry and thereafter the measurements were made. In between the tests, they were allowed to rest in the laboratory environment under ambient temperature and humidity conditions.

3.3 TE Characterization methods

3.3.1 Seebeck Coefficient Tests

The experimental setup used for measuring the Seebeck coefficient was assembled in the laboratory and could measure the voltage difference generated as a result of subjecting the prepared cement sample to a fixed temperature gradient. A 3-D schematic of the insulated sample and the schematic of the setup are shown in Figure 1. It consisted of a silicone mat heater connected to a DC power supply powered by the mains. One of the square end (40mm × 40 mm) of the sample was heated by the silicone mat heater while it was enclosed on the four longitudinal sides using an insulating material having a thermal conductivity of 0.022 W/m-K. K-Type thermocouples were embedded into the samples during casting to monitor the temperature distribution across the sample length while subjecting it to a temperature gradient. The opposite end of the heated side was exposed to ambient temperature. Temperature sensors (K-Type) were also attached to the sample at both ends. Weights were applied to ensure adequate thermal contact existed between the sample and the heater. The sample was surrounded by insulation to minimise heat losses.

The samples had woven meshes of 300µm diameter copper wire embedded into them during the casting procedure for connecting them to the data acquisition unit for measuring voltage difference and resistance. The Seebeck coefficient tests were carried out by measuring the voltage difference between the two copper meshes in the sample. The temperature difference while measuring the Seebeck coefficient was recorded at the same point as the voltage difference. The data acquisition was carried out by connecting the electrical wires and temperature sensors to a Digital Multimeter combined with a Data Logging and Acquisition Unit.

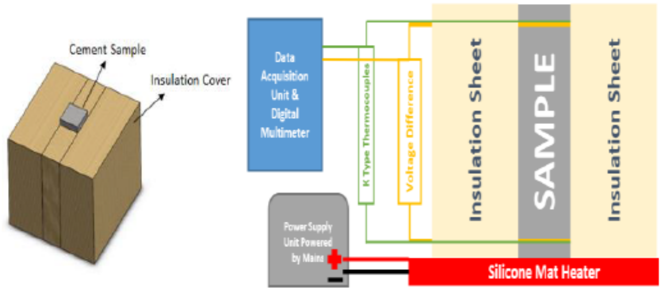

Figure 1. Schematic of the experimental set up

3.3.2 Electrical Conductivity Tests

The electrical resistance of the sample was determined using the 2 Wire DC method. The samples were connected to a Digital Multimeter and Data Acquisition unit (Figure 2.) using the copper meshes embedded in the cement samples. The electrical connections were made by soldering tinned copper wires (high temperature resistant) to the copper meshes. The tinned copper wires were connected to the data logging unit. Electrical conductivity was derived by measuring the electrical resistance of the sample and obtaining its resistivity by considering its geometric factor (length and cross-sectional area).

3.3.3 Thermal Conductivity Tests

The thermal conductivity (TC) tests followed the transient line source (TLS) method [23]. A cylindrical sleeve (100 mm long and 2mm diameter) was inserted into the sample to house the THERMTEST TLS-100 probe (see Figure 3). The measurements were carried out at room temperature and repeated 10 times with the average reading taken as the final TC value.

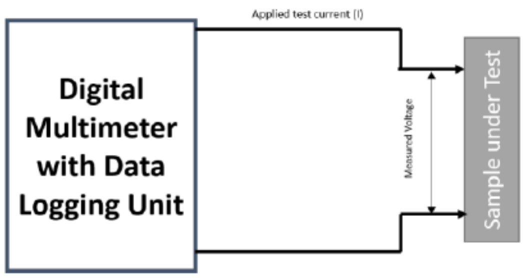

Figure 2. 2W DC resistance measurement method

Figure 3. Thermal Conductivity test set-up

4 RESULTS AND DISCUSSIONS

4.1 *Seebeck Coefficient Tests*

The initial set of Seebeck coefficient tests were carried out on plain cement samples in saturated conditions. It was observed that despite not subjecting the sample to any temperature gradient, a small DC voltage was generated. The Seebeck coefficient values for the control sample, when a constant temperature gradient (80°C) was maintained across the sample, is shown in Figure 4 and were found be in the range of -1×10^{-5} to -1×10^{-6} µV/°C. However, despite similar conditions throughout, a significantly higher Seebeck voltage was obtained from the same sample as shown in Figure 4. The sample was kept in a similar condition (insulated) throughout the testing period and moisture escape was not allowed. This could be a result of the moisture present in the sample as it was in a saturated condition.

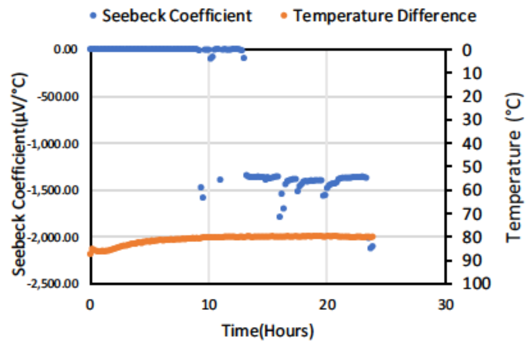

Figure 4. Seebeck Coefficient of control sample at fixed ΔT

The Seebeck coefficient tests were also carried out for the Bi_2O_3 and Fe_2O_3 cement composites with all saturated samples yielding a small DC voltage (less than 100mV) despite not being subjected to a temperature gradient. When a constant temperature gradient was established across the sample, the Seebeck voltage showed an unusual sinusoidal pattern which shifted from positive to negative upon a change in temperature, as shown in Figure 5 and Figure 6 respectively. This pattern was observed when specimens were subjected to heating, so it was difficult to arrive at a particular value or range of values for Seebeck coefficient thus measured for metal oxide containing samples. Hence, a thorough analysis was carried out to find the sources of error and mitigate them as described in detail in Section 4.4.

4.2 *Electrical Conductivity Tests*

The initial set of EC tests were carried out on the control sample at room temperature, without a temperature gradient. The EC value observed for a saturated control sample was found to be 0.07 S/m while after drying (for 24 hours at 105˚C), it reduced drastically to 2×10^{-4} S/m. Tests were simultaneously carried out for three different samples made and cured at the conditions described in Section 3.2. After curing samples in a water tank for 7 days, they were subjected to ambient temperature and humidity conditions for 14, 60 and 90 days with conductivities measured over a 24hr period. As expected, the EC value for the 14-day old sample was the highest at 0.06 S/m, while the conductivity decreased to 0.016 and 4×10^{-4} S/m for 60- and 90-days old samples respectively.

Similarly, EC tests for saturated Bi_2O_3 and Fe_2O_3 cement composites were carried out at room temperature. The Bi_2O_3 sample displayed a higher conductivity value of 0.09 S/m while the control and Fe_2O_3 cement composite samples had EC values of 0.07 and 0.06 S/m respectively. Conductivity values were found to decrease gradually with time for all measurements carried out (Figure 7). It was clear from the results that initially due to a high moisture content (with conducting ions present in the sample), the electrical conductivity is comparatively higher. With time as the sample approaches equilibrium with the relative humidity of the environment and the internal changes in its structure due to the continuous changes in degree of hydration taking place, the conductivity reduces gradually. The electrical conductivity values were still found to be falling in the range of conductivity found in semiconductors [24]. Cementitious materials enhanced with composite materials have two ways of electrical conduction, namely electronic and electrolytic [25]. The former is the result of the motion of free charge carriers in the conductive path formed by the additives. The latter is the result of motion of ions present in their porous structure. Electronic conduction plays the essential role of imparting electrically conductive properties to cement-based TE materials. To measure its effect, electrolytic conduction needs to be eliminated by drying the sample but doing so leads to a significant drop in conductivity values [26].

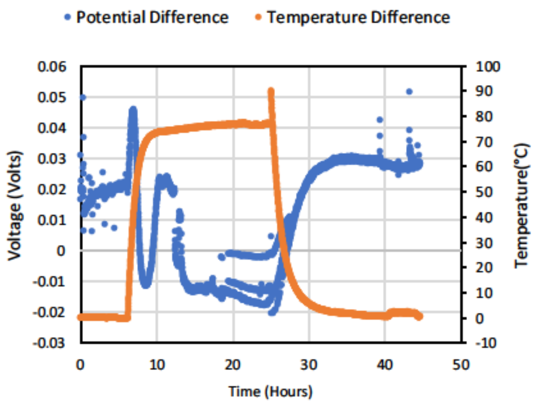

Figure 5. Voltage readings from 5% wt. Bi_2O_3 sample

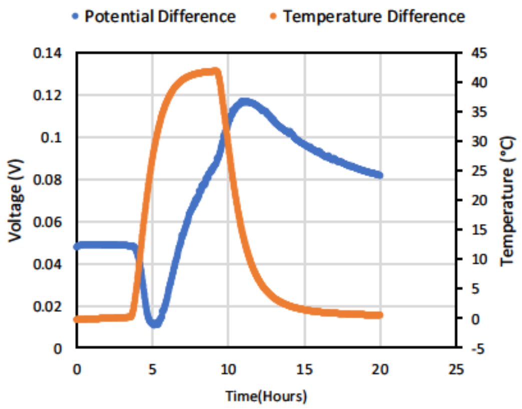

Figure 6. Voltage readings from 5 wt.% Fe_2O_3 sample

During DC resistance measurements at room temperature, a polarization effect as a result of using DC current in the form of a low voltage was detected in the sample (100-500mV) that interfered with the resistance measurements. This voltage reduced during the natural transition of the sample from saturated to a dry state.

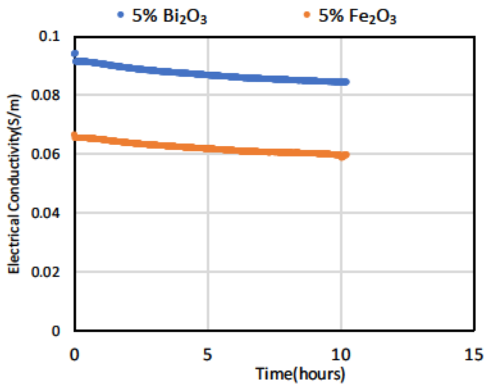

Figure 7. Electrical conductivity of 5 wt.% Bi_2O_3 and 5 wt.%Fe_2O_3 saturated sample

4.3 Thermal Conductivity Measurements

During the TC measurements, it was ensured that the instrument used was in thermal equilibrium with the sample before each test was carried out. The TCs of the control, Bi_2O_3 and Fe_2O_3 cement samples were found to be 1.15, 1.044 and 1.022 W/m-K respectively, in the saturated condition. The coefficient of variation observed for the measurements were found to be 1.6 %, 1.9 % and 1.5 % respectively which was acceptable. The Bi_2O_3 and Fe_2O_3 cement composite respectively saw a reduction of 9.2 % and 11.1 %, in their thermal conductivity values as compared to the TC of the control sample.

4.4 Troubleshooting the measurement process

The Seebeck coefficient is not a conventional property of a cementitious material. The Seebeck voltage is usually found to have a linear relationship with the applied temperature gradient for semi-conductors. However, while measuring the same for enhanced cement composites, the results obtained were highly inconsistent and it wasn't possible to get steady values of the quantity at fixed temperature gradients. Since low level voltage measurement (µV) were involved in the measurement process and knowing the extent to which multiple connections and the thermal gradient could influence them [27] , a thorough analysis was carried out to find the source of errors. The first possible source of error studied was instrumental. The instrument is specified to be capable of measuring voltage on the microvolts scale with an accuracy of 100 nV but it is still subject to offset and temperature drift. In order to determine its offset voltage, the instrument was disconnected from all circuits and the test lead wires were shorted together to find if the meter showed a true zero volts.

The procedure was carried out four times and the voltage obtained was in the range of 1×10^{-6} and 1×10^{-7} V for each. To avoid external electrical interference, additional components were added to the experimental setup. Firstly, a 3mm thick aluminium sheet covered with a neoprene rubber sheet was placed at the bottom which 'grounded' the instrument. Furthermore, the instrument required a warmup time of 30 minutes before taking any measurements. However, despite following these measures, the results continued to show unsteadiness due to thermal drift. It was, therefore, decided to warm up the instrument until a steady temperature was established providing constant DC voltages at thermal equilibrium.

The DC voltage measured for a Fe_2O_3 sample with no temperature gradient is shown in Figure 8. A steady voltage of 60-65mV was obtained for a significant amount of time. Later, the sample was subjected to a 45˚C temperature difference and, having switched the instrument on in advance, the measurements were taken after the gradient was established. The Seebeck coefficient was measured from the cold to hot end (negative) for a 30-minute time interval and was found to follow a steady pattern, as shown in Figure 9. This procedure and assessments were carried out for a 10-day period while maintaining a constant temperature gradient of 45°C without disturbing the system. The resulting voltage obtained ranged from 130-170 mV where it reduced gradually day by day. In order to cancel out offset, the voltage obtained was measured in both directions, i.e. from hot to cold end and vice-versa and the magnitude from both the directions was found to be same, but of opposite sign. Another set of results is shown in Figure 10.

These measurements were carried out first by using the automatic feature of the data logger. Later the values were confirmed to be in a similar range by using the manual function of the instrument and with two other Multimeter's (Fluke and Iso-tech). These tests helped achieve stable results for the Seebeck coefficient and eliminated source of errors from the instrument in the measurement process.

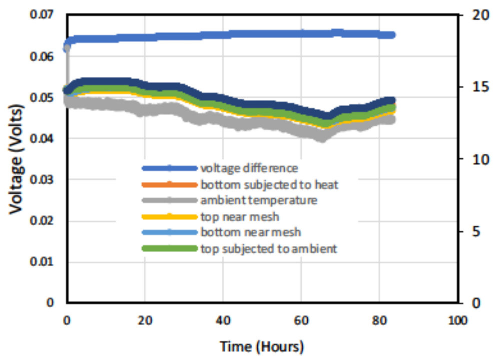

Figure 8. Potential difference obtained from a Fe_2O_3 cement composite at zero temperature gradient

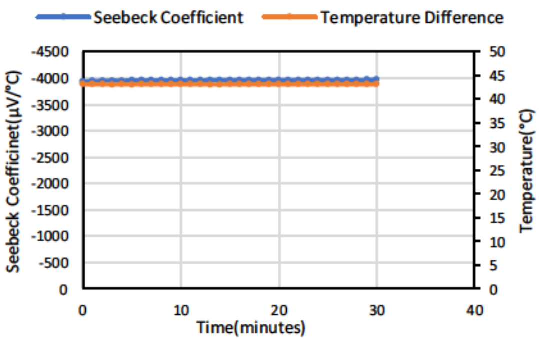

Figure 9 Seebeck Coefficient for saturated Fe_2O_3 cement composite over a 30 minute interval

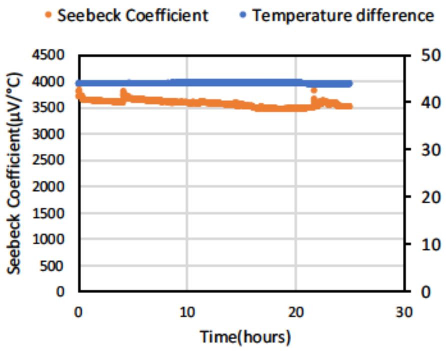

Figure 10 Seebeck Coefficient at fixed temperature difference over 1-day time period for 5% Fe_2O_3 cement composite

Seebeck tests were repeated for the saturated Fe_2O_3 samples with different temperature gradients. They were obtained by manually adjusting the voltage supplied to the heating plate. For the 30-50˚C range (with a 5˚C step), the observed Seebeck voltage had a proportional response. Thereafter, both Bi_2O_3 and Fe_2O_3 cement composites were dried in an oven for 24 hours at 105˚C. The Seebeck tests were repeated for those samples and the values obtained for a dry sample were significantly lower. They were found to be in a similar range (in terms of magnitude) to the Seebeck coefficient reported for other metal oxide-based cement composites.

There was still a transition observed from positive to negative values in the measurements. However, this phenomenon could be deemed temporary as it wasn't possible to maintain the sample in a dried state beyond a point in time. When it was subjected to ambient conditions, its moisture content increased. The Seebeck Coefficient obtained from a dried Bi_2O_3 cement composite is shown in Figure 11 where the values fell from +80 to -80µV/˚C, mostly remaining in the negative range after steady state was achieved. Similarly, the Seebeck coefficient for the cement composite with Fe_2O_3 showed values of -20µV during the temperature rise taking place up to +30µV when it stabilised, as shown in Figure 12. When continuing the tests, the coefficient varied from +20 to -60µV/˚C over a 68-hour time period. Thus, it can be observed that the Seebeck coefficient fluctuated between positive and negative in dried samples, unlike the saturated samples. The reason for the transition is not known yet and needs to be investigated further.

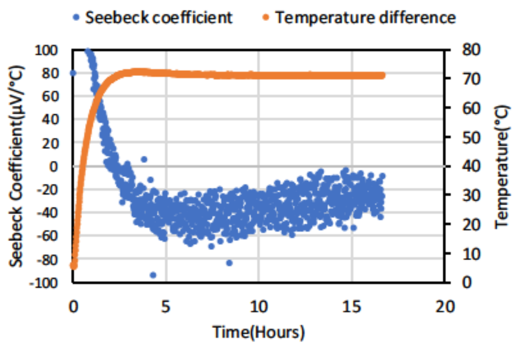

Figure 11. Seebeck Coefficient obtained from dried Bi_2O_3 sample

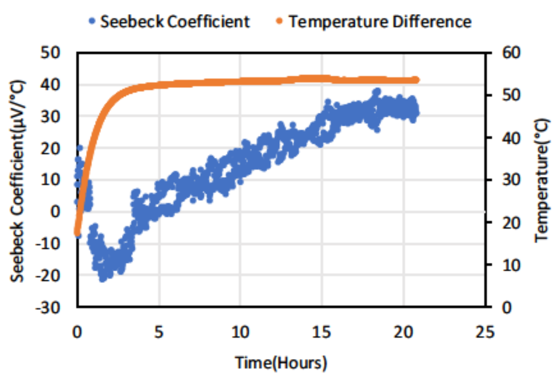

Figure 12. Seebeck coefficient values after drying the Fe_2O_3 sample in oven in 24 hours

5 CONCLUSIONS

In this work, an attempt to develop and characterize a cement-based TE material was made by adding micro sized metal oxide powders to the cement matrix. The following conclusions were drawn from the experimental work carried out:

- The Seebeck Coefficient of the metal oxide enhanced cement samples were high in saturated states but decreased significantly when dried;
- The electrical conductivity observed was high for those samples with a high moisture content but decreased gradually with time. The conductivity values dropped drastically in the dry state as compared to saturated.
- The DC resistance method is deemed unfit for measurements due to polarization effects generated by DC current in the sample during resistance measurement;
- Thermal conductivity of the enhanced cement composites was found to be lower than the control sample;
- There is a crucial impact of age and moisture content of the enhanced cement composite on the thermoelectric properties it possesses, and detail investigation of its influence is required to be carried out;
- A detailed analysis is also required to determine the properties of enhanced TE materials in a controlled manner. Future work will consist of undertaking measurements using an automatically controlled system to subject the sample to varying temperature gradients (20˚C - 80˚C).

ACKNOWLEDGMENTS

This research is supported through a US-Ireland grant tri-funded by the Science Foundation Ireland (SFI, 17/US/3424), National Science Foundation (NSF, 1805818) and the Department for the Economy of Northern Ireland (DfE, USI 127). The authors would like to thank the laboratory technicians at TU Dublin and TCD for their technical support.

REFERENCES

[1] Ritchie, H. and Roser, M. (2018), *Urbanization*. Published online at OurWorldInData.org.
Retrieved from: 'https://ourworldindata.org/urbanization'

[2] Taha, H., Sailor, D. and Akbari, H. (1992), *High-albedo materials for reducing building cooling energy use*. California Institute of Energy Efficiency, Berkeley, United States.

[3] Phelan, P., Kaloush, K., Miner, M., Golden, J., Phelan, B., Silva, H., and Taylor, R. (2015), 'Urban Heat Island: Mechanisms, Implications, and Possible Remedies', *Annual Review of Environment and Resources*, 40, 285-307.

[4] Ang, B., Wang, H. and Ma, X. (2017), 'Climatic influence on electricity consumption: The case of Singapore and Hong Kong', *Energy*, 127, 534-543.

[5] Levinson, R., Akbari, H., Berdahl, P., Wood, K., Skilton, W. and Petersheim, J. (2010),'A novel technique for the production of cool colored concrete tile and asphalt shingle roofing products', *Solar Energy Materials and Solar Cells*, 94, 946-954.

[6] Akbari, H. and Leanna, R. (2001), *Characterizing the fabric of the urban environment: A case study of Salt Lake City*, Utah.

[7] Santamouris, M., Cartalis, C., Synnefa, A. and Kolokotsa, D. (2015),'On the energy impact of urban heat island and global warming on the power demand and electricity consumption of buildings—A review', *Energy and Buildings*, 98,119-124.

[8] Yildiz, F. (2009), 'Potential Ambient Energy-Harvesting Sources and Techniques', *Journal of Technology Studies.*

[9] Matiko, J., Grabham, N., Beeby, S. and Tudor, M. (2013), 'Review of the application of energy harvesting in buildings', *Measurement Science and Technology*, 25.

[10] Ahmad, S., Muieebu, M. and Farooqi, M. (2019), 'Energy harvesting from pavements and roadways : A comprehensive review of technologies, materials, and challenges', *International Journal of Energy Research*, 43, 1974 -2015.

[11] Ouldboukhitine, S., Belarbi, R., Jaffal, I. and Trabelsi, A. (2011), 'Assessment of green roof thermal behavior: A coupled heat and mass transfer model', *Building and Environment*, 46, 2624-2631.

[12] Tritt,T., (2002) *Thermoelectric Materials : Principles , Structure , Properties , and Applications*. Encyclopedia of Materials: Science and Technology.

[13] Matsumoto, R., Hoshina Y. and Akuzawa, N. (2009), 'Thermoelectric Properties and Electrical Transport of Graphite Intercalation Compounds', *Materials Transactions Online*.

[14] Sun, M., Li, Z., Mao Q. and Shen, D. (1998), 'Study on the Hole Conduction Phenomenon in Carbon Fiber-Reinforced Concrete', *Cement and Concrete Research*, 28, 549-554.

[15] Sun, M., Li, Z., Mao Q. and Shen, D. (1998), 'Thermoelectric percolation phenomena in carbon fiber-reinforced concrete', *Cement and Concrete Research*, Volume 28, Issue 12, Pages 1707-1712.

[16] Yao, W. and Qiang, X. (2014), 'Preparation and thermoelectric properties of bismuth telluride – carbon fiber reinforced cement composites', *Journal of Functional Materials*.

[17] Wei, J., Hao, L., Geping, H. and Chunli, Y. (2014), 'Enhanced thermoelectric effect of carbon fiber reinforced cement composites by metallic oxide/cement interface', *Ceramics International*. 40. 8261-8263.

[18] Ji,T., Xiong Z. and Weihua, L. (2016), 'Enhanced thermoelectric effect of cement composite by addition of metallic oxide nano powders for energy harvesting in buildings', *Construction and Building Materials*. 115. 576-581.

[19] Wei, J., Zhao, L., Zhang, Q., Nie, Z. and Hao, L.(2018), 'Enhanced thermoelectric properties of cement-based composites with expanded graphite for climate adaptation and large-scale energy harvesting', *Energy and Buildings*, 159, 66-74.

[20] Snyder, G. and Toberer , E. (2008),'Complex thermoelectric materials', *Nature Materials*, 7, 105–114.

[21] Chen, N., Gascoin, F., and Snyder, G. (2005), 'Macroscopic thermoelectric inhomogeneities in $(AgSbTe_2)_x(PbTe)_{1-x}$', *Applied Physics Letters*, 87, 171903.

[22] Wei, J., Zhang, Q., Zhao, L., Hao, L. and Nie, Z. (2017), 'Effect of moisture on the thermoelectric properties in expanded graphite/carbon fiber cement composites', *Ceramics International*, 43, 10763-10769.

[23] International A., ASTM D5334 – 14, *Standard Test Method for Determination of Thermal Conductivity of Soil and Soft Rock by Thermal Needle Probe Procedure*, West Conshohocken, PA 2014.

[24] Singh, A., Mishra, M., Chandra, A. and Dhawan, S. (2011), 'Graphene oxide/ferrofluid/cement composites for electromagnetic interderence shielding application', *Nanotechnology*, 22.

[25] Xie, P., Gu, P. and Beaudoin, J. (1996), 'Electrical percolation phenomenon in cement composites containing conductive fibres'. *Journal of materials science*, 31,4093 – 4097.

[26] Su, J., Yang, C., Wu, W. and Huang, R. (2011), 'Effect of moisture content on concrete resistivity measurement', *Journal of the Chinese Institute of Engineers*, 25, 117 -122.

[27] Tectronix, *Low Level Measurements Handbook – 7th* Edition.