1 A concise and informative title:

2 **Enhanced thermoelectric effect of cement composite by addition of metallic oxide nanopowders**
3 **for energy harvesting in buildings**

4 Author names and affiliations:

5 **Tao Ji**, Ph.D. candidate, School of Materials Science and Engineering, Tongji University, Shanghai
6 201804, China.

7 **Xiong Zhang**, Professor, School of Materials Science and Engineering, Tongji University, Shanghai
8 201804, China.

9 **Weihua Li**, Professor, Cooperative Innovation Center of Engineering Construction and Safety in
10 Shandong Blue Economic Zone, Qingdao Technological University, Qingdao, 266033, China; Institute
11 of Oceanology, Chinese Academy of Sciences, Qingdao, 266071, China.

12

13 **Corresponding author : Weihua Li**

14 **E-mail: liweihua@qdio.ac.cn**

15 **Phone number: +86 13863961928**

16 **Contact address: Institute of Oceanology, Chinese Academy of Sciences, Qingdao, 266071, China.**

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1 **Abstract**

2 In this paper, metallic oxide nanopowders were incorporated in cement matrix to increase the
3 thermoelectric effect of cement composites. It can be seen from the result that the Seebeck coefficient
4 of these composites increased steadily with metallic oxide content. And the Seebeck coefficients of
5 these composites were measured to be higher than 1000 $\mu\text{V}/^\circ\text{C}$, which were about 10 times higher than
6 that of fiber reinforced cement composites indicated earlier. The increased surface density of the
7 electronic state near the Fermi energy level of the nanostructured metallic oxide is very possibly
8 responsible for the enhanced Seebeck coefficient of the cement composites. The high Seebeck
9 coefficient of this kind of cement composite is important for the potential application in energy
10 harvesting and air-conditioning system of future buildings.

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13 **Keywords**

14 Seebeck coefficient; cement composite; metallic oxide nanopowders; density of electronic state; energy
15 harvesting

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1. Introduction

Thermoelectric effect, providing a method for converting thermal energy to electrical energy, is expected to play an important role in dealing with energy shortage. For example, thermoelectric cooling technologies are gaining more interest in the field of energy conservation in buildings [1, 2]. In the former study of thermoelectric cooling technologies, thermoelectric devices made of traditional thermoelectric materials such as Bi_2Te_3 were installed on the wall and window [3]. But if the concrete wall possesses thermoelectric characteristics itself, the application of its thermoelectric effect will be more effective and convenient for energy harvesting and refrigerating. The concrete materials which possess thermoelectric effect for energy harvesting are characterized by zero energy consumption, environmentally friendly and low converting coefficient, so the benefits and drawbacks are clear.

Thermoelectric effect in cement based materials was firstly reported by Sun et al. [4, 5]. The reported material was made of cement paste, short carbon fibers and a disperser. And carbon fibers contributed the majority of the total thermoelectric effect in the composite. Almost at the same time, Wen and Chung researched the thermoelectric effect of carbon/steel fiber reinforced cement composites systematically. It was found that the Seebeck coefficient was about 5.5 and 68.0 $\mu\text{V}/^\circ\text{C}$ for carbon and steel fiber reinforced cement composites with a fiber content of 1.0% by mass of cement respectively [6, 7]. In addition, they pointed out the origin of the thermoelectric behavior of carbon/steel fiber reinforced cement paste [8, 9].

But the absolute thermoelectric power has to be increased greatly before its application in energy harvesting, so more attention was paid to increase the thermoelectric effect of cement composite since then. Substituting ordinary polyacrylonitrile fibers with bromine-intercalated carbon fibers, Wen and Chung increased the Seebeck coefficient of carbon fiber reinforced cement composite from 5.5 to 21.2

1 $\mu\text{V}/^\circ\text{C}$ [10]. Zuo et al. increased the Seebeck coefficient to $23.5 \mu\text{V}/^\circ\text{C}$ by incorporating carbon
2 nanotubes to carbon fiber reinforced cement composite [11]. Demirel and Yazicioglu obtained absolute
3 Seebeck coefficient up to $127 \mu\text{V}/^\circ\text{C}$ from carbon fiber reinforced lightweight concrete with silica fume
4 inside [12]. And Wei et al. obtained Seebeck coefficient up to $100.28 \mu\text{V}/^\circ\text{C}$ by incorporating 5.0%
5 Bi_2O_3 microparticles by mass of cement in the cement matrix [13]. However, these obtained Seebeck
6 coefficients are not high enough for their potential use in ambient energy harvesting, coolers or
7 structural health monitoring [14-16]. To increase the Seebeck coefficient of cement composites by
8 order of magnitude, incorporating new thermoelectric component may be an effective method.

9 Historically, the Seebeck effect was discovered early in the 19th century. In the 1950s, the field of
10 thermoelectric advanced rapidly when more and more heavily doped semiconductors exhibited good
11 thermoelectric effects. However, this field regained much attention until 1990s, when new research
12 directions were found to develop the next generation of thermoelectric materials. Two different
13 research approaches were proposed: one using new families of advanced bulk thermoelectric materials
14 [17–21], and the other using low-dimensional materials systems [22–24]. As a result of this guide,
15 Hochbaum et al. verified silicon nanowires as a kind of effective thermoelectric materials [25], and
16 Song et al. found the Seebeck coefficient of MnO_2 nanopowder was higher than $20000 \mu\text{V}/^\circ\text{C}$ [26].
17 Transition metal oxides are gaining increasing attention for their thermoelectric properties due to their
18 high temperature stability, tunable electronic and phonon transport properties and well established
19 synthesis techniques [27]. Based on the aforementioned promising properties, low-dimensional
20 transition metal oxide was chosen as thermoelectric component to increase the thermoelectric effect of
21 cement composites in this paper.

22 In this study, the nanostructured ZnO and Fe_2O_3 powder are incorporated in cement composites. It

1 shows that the introduction of ZnO and Fe₂O₃ powder can significantly influence the Seebeck
2 coefficient of cement composites. The giant Seebeck coefficient of higher than 1000 $\mu\text{V}/^\circ\text{C}$ is obtained
3 by incorporating a little metallic oxide nanopowders in the cement composites. Moreover, the
4 enhancement mechanism is discussed in detail and the potential application of the composites in energy
5 harvesting of future buildings is indicated.

6 **2. Material and methods**

7 **2.1. Cement paste specimens**

8 Portland cement (P) was used in conformance with Standard EN 197-1(2000), and the composition
9 and properties of available cement and silica fume are described in Table 1. ZnO and $\alpha\text{-Fe}_2\text{O}_3$ powder
10 were purchased from Macklin Biochemical Co., Ltd, Shanghai. The as-received ZnO powder was
11 50 ± 10 nm in diameter and spherical Fe₂O₃ was 30 ± 5 nm in diameter.

12 The dosage of silicon fume was fixed 15% by mass of cement, and the water/cement ratio was fixed
13 0.46. The dosage of ZnO and Fe₂O₃ nanoparticles into cement composites were 1.0, 2.0, 3.0, 4.0 or 5.0
14 wt% by mass of cement. The cement composites were prepared following the standard mixing
15 procedure (using a Perrier planetary mixer) which consists of the following steps: mixing the dry
16 components at low speed (60 rpm) for 30 s; joining the required quantity of kneading water and mixing
17 at low speed for 30 s; scraping down the sides of the mixer bowl for about 30 s and mixing at low
18 speed for 30 s. After mixing, the specimens were cast in steel molds with a size of $40\times 40\times 160\text{ mm}^3$ and
19 compacted with a vibrating table. After casting, the specimens were cured at $20 \pm 1^\circ\text{C}$ and $90 \pm 5\%$
20 humidity for 24 h, and then demolded. After demolding, the specimens were cured under standard
21 curing conditions for 14 days. Before the test of Seebeck coefficient, thermal conductivity and
22 electrical conductivity, samples were dried at 105°C for 24 h and then cooled at room temperature to

1 remove the moisture inside, under which treatment the heat transportation could be more uniform.

2 2.2. Characterizations of the ZnO and α -Fe₂O₃ nanoparticles

3 The ZnO and α -Fe₂O₃ nanoparticles in this work were identified by X-ray diffraction (XRD). XRD
4 pattern measurements were carried out by a Ultima IV diffractometer (Japan) using the Cu Ka ($k=$
5 1.5418 Å, tube voltage: 40 kV, tube current: 40 mA) at room temperature. XRD pattern scanned within
6 the range of 2θ from 10° to 80°, with a step width of 0.02° and an acquisition time of 0.01 s per step.
7 The crystalline phases were identified with the corresponding JCPDS diffraction data cards. The
8 particle sizes and morphologies of the nanoparticles were analyzed using a scanning electron
9 microscope (SEM) (Tabletop Microscope, S3400, HITACHI, Japan).

10 2.3. Electrical conductivity, thermal conductivity and Seebeck coefficient measurements

11 The electrical conductivity of the cement paste specimen with the size of 40×40×160 mm³ was
12 measured using the four-probe method, as illustrated in Fig. 1 [28]. The electrical conductivity
13 measurement involving the use of current contacts (A and D) in the form of copper wire adhered by
14 silver paste and voltage contacts (B and C) in the form of copper electrodes. Two Fluke B15
15 multimeters were used to test the current flowing through the specimen and the voltage between the
16 two copper electrodes. According to the definition of electrical conductivity of a specimen, σ can be
17 calculated by the following equation:

$$18 \quad \sigma = \frac{1}{\rho} = \frac{L}{S} \frac{I}{V} \quad (2)$$

19 where σ and ρ are the electrical conductivity and resistivity of the specimen, respectively; I and V are
20 the tested current and voltage values; L and S are the length and cross-sectional area of the specimen.

21 The thermal conductivity of the cement paste specimen with the size of 300×300×20 mm³ was
22 measured using a steady-state conductivity tester (DRH-300, China), as shown in Fig. 2. Prior to

1 conducting the test, all specimens were dried in an oven at 105 °C for 24 h and then cooled to room
2 temperature to remove the moisture inside. The specimen was placed between the cold plate and hot
3 plate, and the temperature difference between the two sides was controlled by the heating and cooling
4 system. The temperature value of the cold plate and hot plate was set as 20 °C and 70 °C respectively.
5 Thus the thermal conductivity of the cement paste specimen can be calculated by the formula as
6 follows:

$$7 \quad \kappa = \frac{I \cdot U \cdot d}{S \cdot \Delta T} \quad (1)$$

8 where κ is the thermal conductivity of the specimen, I and U are the current and voltage of the
9 heatmeter, respectively; d , S and ΔT are the thickness, cross-sectional area and temperature difference
10 between the two sides of the specimen.

11 The schematic of the apparatus for measuring thermoelectric voltage around room temperature was
12 shown in Fig. 3. Two ends of the hydrated cement composite samples were covered with a copper sheet.
13 Heat was applied through one side (40×40 mm²) to the other side of the specimen by a platelet
14 resistance heater. The hot side was heated automatically from room temperature to 70°C at a rate of
15 0.05°C, while the cold side of the specimen was kept at room temperature by contacting with the
16 flowing cold water. The temperature of both ends of the sample was monitored by K-type
17 thermocouples and thermoelectric power was measured by a Fluke B15 multimeter. Then the Seebeck
18 coefficient was obtained as the ratio of the thermoelectric power and temperature difference of the two
19 opposing surfaces.

20 **3. Results and discussion**

21 **3.1. Characterizations of the ZnO and α -Fe₂O₃ nanoparticles**

22 The crystalline structures of the ZnO and α -Fe₂O₃ powder were identified through XRD and the

1 relevant results are shown in Fig. 4. The diffraction peaks of (100) (002) (101) (103) (200) (112) (201)
2 (004) and (202) are observed from ZnO powder, as shown in Fig. 4(a), which match very well with
3 those of the standard ZnO (PDF 65-3411). The diffraction peaks of (012) (104) (110) (006) (113) (024)
4 (116) (211) (214) (300) (125) (208) and (220) are observed from α -Fe₂O₃ powder, as shown in Fig. 4(b),
5 which match with those of the standard α -Fe₂O₃ (PDF 89-0597). There are still several diffraction
6 peaks from 65.00° to 80.00° cannot be identified. However, the intensities of them are very weak,
7 which can probably be caused by noise signals.

8 The SEM images of the ZnO and α -Fe₂O₃ nanoparticles shown in Fig. 5 indicate that the ZnO
9 particles are blocky and α -Fe₂O₃ particles are nearly spherical. And the images indicate that both the
10 particles are nanostructured even though they are agglomerate in some parts.

11 3.2. Thermoelectric performance analysis of cement composites

12 The results of electrical conductivity of the cement paste specimens with different powder additions
13 are illustrated in Fig. 6. It can be seen that the electrical conductivities of all the cement composites
14 with ZnO powder are a little higher than the blank sample, and the electrical conductivity values
15 fluctuate around $1.70 \times 10^{-6} \Omega^{-1} \cdot \text{m}^{-1}$. The electrical conductivities of cement specimens with Fe₂O₃ show
16 a similar law and are approximately $0.20 \times 10^{-6} \Omega^{-1} \cdot \text{m}^{-1}$ less than that of the specimens with ZnO powder.
17 The electrical conductivity of the cement paste composite with metallic oxide powder reaches the
18 maximum value when the addition is 3.0%, and the maximum values are 51% and 26% bigger than that
19 of blank cement sample for ZnO and Fe₂O₃ respectively. Although ZnO and Fe₂O₃ are semiconductors,
20 their nanoparticles are characterized by high electrical resistivity because of a huge amount of pores.
21 So the cement paste composite with metallic oxide nanoparticles below 5.0% is insulating material, just
22 like the pure cement paste.

1 The results of thermal conductivity of the cement paste specimens with different powder additions
2 are illustrated in Fig. 7. It can be seen that the thermal conductivity of the cement composite with ZnO
3 powder decreases firstly and then increases with the addition of ZnO. The thermal conductivity of
4 cement composite with Fe_2O_3 inside shows a similar law of the specimens with ZnO powder. The
5 thermal conductivity of the cement paste composite with metallic oxide powder reaches the maximum
6 value when the addition is 5.0%, and the maximum values of ZnO and Fe_2O_3 sample are 8.7% and 7.2%
7 bigger than that of blank cement sample respectively. Although the thermal conductivity of blocky
8 metallic oxide usually ranges from 10 to 100 W/m·K, the thermal conductivity of their nanoparticles is
9 lower than 1 W/m·K because of numerous pores inside. The thermal conductivity of porous cement
10 paste composite is not only influenced by the component but also the structure such as the size, shape
11 and distribution of pores inside. So for cement paste composite with metallic oxide nanoparticles below
12 5.0%, the influence of ZnO or Fe_2O_3 on thermal conductivity is not obvious.

13 The relationship of thermoelectric power and temperature difference is shown in Fig. 8 and 9. Fig.8
14 shows that the relationship of thermoelectric power versus temperature difference is approximately
15 linear for cement composite specimens with 1.0, 2.0, 3.0, 4.0 and 5.0 wt% ZnO nanoparticles. And the
16 slopes of the curves increase with the dosage of ZnO nanoparticles. Compared with cement composites
17 with ZnO nanoparticles, the thermoelectric power of plain cement paste (with no metallic oxide
18 nanopowders) can be neglected. The relationship of thermoelectric power versus temperature
19 difference for the specimens with 1.0-5.0 wt% Fe_2O_3 nanoparticles inside (Fig. 9) was similar to that
20 shown in Fig. 8. Thermoelectric power of specimen with Fe_2O_3 inside shows little difference with that
21 of ZnO inside at the same dosage, which may be due to the difference in band structure and particle
22 size of metallic oxides [29].

1 The relationship between Seebeck coefficient and metallic oxide content of the tested specimens is
 2 illustrated in Fig. 10. It can be seen that Seebeck coefficient increases with the dosage of metallic oxide.
 3 At the dosage of 5.0 wt%, the largest Seebeck coefficients are measured 3300 and 2500 $\mu\text{V}/^\circ\text{C}$ for the
 4 specimens with ZnO and Fe_2O_3 respectively. Compared with cement composites with only 1.0 wt% ZnO
 5 or Fe_2O_3 nanoparticles, Seebeck coefficient of plain cement composite can be neglected. So the
 6 enhanced Seebeck coefficient of cement composites with ZnO or Fe_2O_3 nanopowders inside is due to
 7 the absence of metallic oxide. The two kinds of metallic oxide are appropriate for applications in
 8 cement composites due to their effective enhancement of Seebeck coefficient and low cost in economy.

9 The enhanced Seebeck coefficient of cement composites with ZnO or Fe_2O_3 nanopowders inside
 10 may be due to their surface electronic density of state (DOS) near the Fermi energy level. If the
 11 dimensionality of the material is decreased, a dramatic change in properties of material may be
 12 available. As the system dimensionality decreases, it is possible to cause dramatic differences in the
 13 density of electronic states (see Fig. 11), allowing new opportunities to vary Seebeck coefficient [29].

14 Fig. 11 shows that quantum dot structures exhibit sharper DOS compared to higher dimensional
 15 structures, and electronic structure with sharp maxima in the DOS like this is predicted to be the best
 16 for thermoelectric materials [30]. The Seebeck coefficient of a segmented nanowire is defined as [31]:

$$17 \quad S_{0D} = -\frac{1}{eT} \left(\frac{K_{(1)}}{K_{(0)}} \right) \quad (2)$$

$$18 \quad K_\alpha = \frac{4\tau}{\pi^2 h^2 d_w^2} \sum_{n,m} \int \frac{1}{g_{n,m}(E)} (E_{n,m} - E_F)^\alpha \left(-\frac{\delta f}{\delta E} \right) dE \quad (3)$$

19 where $\alpha = 0, 1$ or 2 , τ is the relaxation time of the carriers, T is the temperature, h is the Planck
 20 constant, e is the electron charge, d_w is the diameter of the wire, E_F is the Fermi energy, $f(E)$ is the
 21 Fermi–Dirac distribution function and $g_{n,m}(E)$ is the density of states of the n, m sub-band. From Eqs.(2)
 22 and (3) it is obvious that a sharp maxima in the electronic DOS will result in a strong increase in the

1 Seebeck coefficient.

2 The conversion efficiency of the thermoelectric materials is determined by a dimensionless
3 figure-of-merit (ZT), defined as

$$4 \quad ZT = (S^2 \sigma / \kappa) T \quad (4)$$

5 where S , σ , κ , and T are the Seebeck coefficient, the electrical conductivity, the thermal conductivity,
6 and the absolute temperature at which the properties are measured, respectively [23]. It can be seen
7 from Eq.(4) that ZT is influenced by Seebeck coefficient, electrical conductivity and thermal
8 conductivity simultaneously. From the measured parameters of the cement paste composite, the
9 influence of Seebeck coefficient on ZT is obvious, while the influence of electrical conductivity and
10 thermal conductivity can be ignored. It can be concluded that adding metallic oxide nanoparticles into
11 cement paste can increase its thermoelectric effect significantly.

12 3.3. Limitations and challenges

13 This work has limitations although it, for the first time, explored the influence of the metallic oxide
14 nanopowders on the thermoelectric performance of cement composites. Even though the Seebeck
15 coefficient of this cement composite is more than 10 times of fiber reinforced cement composites, the
16 thermoelectric efficiency of this cement composite is also very low compared with the small
17 commercial thermoelectric elements. Thus the actual application of this cement composite for energy
18 harvesting is hard to realize currently. Although the use of cement composite for energy harvesting is
19 challenging for its low efficiency, efforts can be made to increase it such as increasing Seebeck
20 coefficient, increasing electrical conductivity and decreasing thermal conductivity. This work made
21 efforts to increase the thermoelectric effect of cement paste by increasing Seebeck coefficient mainly,
22 but other efforts such as increasing the electrical conductivity by adding electric powder or fiber

1 materials can be considered. Considering the parameters Seebeck coefficient, electrical conductivity
2 and thermal conductivity are interdependent, any effort of changing them to improve thermoelectric
3 efficiency should be evaluated by ZT at last. As carbon fiber reinforced cement paste performs well in
4 electrical conductivity, it is interesting to see the effect of adding metallic oxide nanoparticles on its
5 thermoelectric effect. And this may be the focus of the next work of us.

6 **4. Conclusions**

7 The enhanced Seebeck coefficient of cement composites with metallic oxide nanopowders was
8 measured to be higher than $1000 \mu\text{V}/^\circ\text{C}$, which was more than 10 times higher than that of fiber
9 reinforced cement composites indicated earlier. The giant Seebeck coefficient is very possibly closely
10 related to the surface density of the electronic state near the Fermi energy level. From the measured
11 parameters of the cement paste composite, the enhanced Seebeck coefficient contributed most to the
12 enhanced thermoelectric efficiency, while the influence of electrical conductivity and thermal
13 conductivity can be ignored. Even though the thermoelectric efficiency of this cement composite is also
14 very low compared with the small commercial thermoelectric elements, this discovery will make it in
15 application of energy conservation and air conditioning in buildings very possible in the future.

16

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1 **Figure captions**

2 Fig. 1. Cement paste specimen for electrical conductivity measurements.

3 Fig. 2. Cement paste specimen for thermal conductivity measurements.

4 Fig. 3. The schematic of the apparatus for measuring thermoelectric effect around room temperature.

5 Fig. 4. XRD patterns of ZnO (a) and α -Fe₂O₃ (b) powder.

6 Fig. 5. SEM images of ZnO (a) and α -Fe₂O₃ (b) powder.

7 Fig. 6. The relationship between electrical conductivity and the weight fraction of ZnO and Fe₂O₃
8 powders in specimens.

9 Fig. 7. The relationship between thermal conductivity and the weight fraction of ZnO and Fe₂O₃
10 powders in specimens.

11 Fig. 8. Seebeck voltage versus the temperature difference for specimens with ZnO powders at the
12 amount of 0, 1.0 wt%, 2.0 wt%, 3.0 wt%, 4.0 wt % and 5.0 wt% by mass of cement.

13 Fig. 9. Seebeck voltage versus the temperature difference for specimens with Fe₂O₃ powders at the
14 amount of 0, 1.0 wt%, 2.0 wt%, 3.0 wt%, 4.0 wt % and 5.0 wt% by mass of cement.

15 Fig. 10. The relationship between Seebeck coefficient and the weight fraction of ZnO and Fe₂O₃
16 powders in specimens.

17 Fig. 11. Electronic density of states for a) a bulk 3D crystalline semiconductor, b) a 2D quantum well, c)
18 a 1D nanowire or nanotube, and d) a 0D quantum dot.

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Table 1
Compositions and properties of portlandcement (P) andsilica fume (S).

Material	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	TiO ₂	Density (g/cm ³)	Specifcsurface (m ² /kg)
P	21.42	5.63	2.70	63.32	1.91	3.43	0.68	0.29	3.12	346
S	95.80	1.76	0.10	0.40	0.52	-	0.87	-	2.46	19000

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