In this study, piezoelectric properties of 0–3 type cement-based piezoelectric composites influenced by pozzolanic materials are investigated, where the piezoelectric inclusion is PZT and the cement-based matrix includes 50% cement, or a mixture of 40% cement and 10% pozzolanic materials in volume. Three pozzolanic materials containing silica fume, blast furnace slag and F grade fly ash were selected. The cement-based piezoelectric composites were made by applying 80MPa to form disk-like shapes. Experimental results show that the piezoelectric properties of the composites reach a plateau behavior after the 14th day of the polarization. The piezoelectric composite with fly ash always has the shortest trigger time of polarization, the specimen with blast furnace slag is the second, and the silica fume composite takes the longest trigger time. The silica fume specimen owns higher dielectric properties and denser structures which enhance piezoelectric strain constant $d_{33}$ values up to 34.43 pC/N if the polarization is completed. The cement-based piezoelectric composites containing blast furnace slag also can increase the piezoelectric strain constant, but this did not achieve for the composites with fly ash. The value of piezoelectric voltage constant $g_{33}$ for the cement-based piezoelectric composites adding fly ash is 23.7 mV-m/N, near PZT piezoelectric ceramics. Meanwhile, cement-based composites containing pozzolanic materials do not raise the electro-mechanical coupling factor.

Keywords: Piezoelectric properties, Cement, Pozzolana, Polarization.

1. Introduction
Cement-based piezoelectric composites have been attracted considerable attention more than ten years (Li et al., 2002; Wen et al., 2002; Sun et al., 2004; Dong and Li, 2005; Chaipanich, 2007; Li et al., 2009). For the applications of sensors and actuators in civil engineering structure, 0–3 cement-based piezoelectric composites developed to overcome the matching problem in concrete structures that conventional piezoelectric ceramics or polymers do not contact synchronously with concrete (Huang et al., 2006; Dong et al., 2007; Jaitanong, 2008).

Most literatures and reports for 0–3 cement piezoelectric composites discussed the piezoelectric and dielectric properties affected by volume fraction and particle size of piezoelectric ceramics, poling time, poling temperature, poling field, curing time, the thickness and the forming of specimens (Li et al., 2002; Sun et al., 2004; Dong and Li, 2005; Li et al., 2005; Cheng et al., 2005; Huang et al., 2006; Dong et al., 2007; Huang et al., 2007; Jaitanong, 2008; Chaipanich, 2008; Pan and Chen, 2011).

Pozzolanic materials, such as silica fume, slag and fly ash, are commonly used in concrete to enhance the strength and durability. The dielectric and piezoelectric properties of cement-based piezoelectric composites containing pozzolanic materials are seldom studied until PZT-silica fume cement composites was reported (Chaipanich, 2007), where PZT is lead zirconate titanate, a kind of piezoelectric ceramic.

Here, we study the effect of pozzolanic materials on cement-based piezoelectric composites with three pozzolanic materials: silica fume, blast furnace slag and fly ash. Cement-based piezoelectric composite was made by 50% PZT and 50% cement-based binder, in volume. Four cement-based piezoelectric composites were tested, one of the binders is 100% cement (PC), and the others are 20% cement binder in volume replaced by pozzolanic materials. For convenience, the binder with silica fume, slag...
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and fly ash is referred as SF, SL and FA, respectively.

2. Materials and Manufactures

PZT particles are uniformly distributed to cement-based binders, so-called 0–3 cement piezoelectric composites. Particle diameter of PZT is 75~150 μm, and the PZT properties include a specific gravity of 7.9, piezoelectric strain factor \(d_{33}\) of 470 pC/N, piezoelectric voltage factor \(g_{33}\) of 24 mV-m/N, and relative dielectric factor \(\varepsilon_r\) of 2100.

Cement is type I Portland cement with the fineness of 349 m²/kg and specific gravity of 3.16. The specific gravity, particle diameter and the fineness of silica fume are 2.2, 0.15 μm and 20,000 m²/kg, in turns. Blast furnace slag was produced from CHC Resources Corporation (Taiwan), where a fineness of 572 m²/kg and specific gravity of 2.87 were used. Fly ash belongs to F grade produced by Hsinta thermal power plant (Taiwan) with a fineness of 326 m²/kg and specific gravity of 2.11. The main chemical components of materials are shown in Table 1, where silica fume has 95.01% SiO₂, similar to quartz but not the same. All materials in Table 1 have similar components but with different fraction.

PZT power combined with the binder was mixed by solar-planetary mill without adding water. Then, the mixed materials were pressed into disks of 15 mm diameter and 10 mm thickness under 80 MPa by MTS machine for 3 minutes. The specimens were cured in a temperature of 90°C and relative humidity of 100% for 7 days before polarizations. After curing, the specimens sequentially were polished to a 2 mm in thickness, coated with silver paint and baked for 30 minutes at 150°C in oven. Poling voltage was applied to the specimen at 1.5 kV/mm, in a 150°C silicone oil bath for 45 minutes. During the polarization, voltage increase was carefully applied to prevent from current breakdown of the specimens. We also measured trigger time and applied voltage increment until the design poling voltage reaches.

3. Results and Discussion

After poling, the specimens were placed in the air for 24 h before the measurements. The piezoelectric strain factor was directly measured by \(d_{33}\) Piezometer, and the other electric properties were captured by Impedance Phase Analyzer. The piezoelectric voltage factor and the dielectric permittivity of each specimen were calculated as (Huang et al., 2007).

\[
g_{33} = \frac{d_{33}}{\varepsilon_r \times \varepsilon_0} \quad (1)
\]

\[
\varepsilon_r = \frac{C \cdot t}{A \cdot \varepsilon_0} \quad (2)
\]

where vacuum dielectric constant \(\varepsilon_0 = 8.854 \text{ pF/m}\), Capacitance C was measured at 1 kHz, \(t\) and \(A\) are specimen thickness and electrode area.

3.1. Material age effect

We recorded the piezoelectric strain factor of four cement-based piezoelectric composites and calculated its increase rate by day, shown in Figure 1. For all specimens, increase rates vary dramatically between 10% and 20%, at the first 5 days and, after that, the increase rates gradually go to a plateau behavior with 0% to 8% increment. Similarly, the increase rate of relative dielectric factor in Figure 2 also shows the same tendency. The variations of piezoelectric properties for cement-based piezoelectric composites with or without pozzolanic materials become lower after the polarization of 5 days.

<table>
<thead>
<tr>
<th>Chemical component</th>
<th>Cement</th>
<th>Silica fume</th>
<th>Slag</th>
<th>Fly ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>21.24</td>
<td>95.01</td>
<td>33.36</td>
<td>46.26</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.44</td>
<td>–</td>
<td>14.19</td>
<td>19.47</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.44</td>
<td>–</td>
<td>0.37</td>
<td>5.72</td>
</tr>
<tr>
<td>CaO</td>
<td>64.51</td>
<td>–</td>
<td>42.63</td>
<td>4.90</td>
</tr>
<tr>
<td>MgO</td>
<td>2.35</td>
<td>–</td>
<td>5.80</td>
<td>1.53</td>
</tr>
</tbody>
</table>
To distinguish the pozzolanic effect for composites adding silica fume, slag and fly ash, Figure 3 shows $d_{33}$ behavior in terms of the day after polarization. Piezoelectric composite with Silica Fume (SF) always has the highest $d_{33}$, SL lies in between, and FA does not affect $d_{33}$, compared with PC composites. The value of capacitance $C$ for the composite containing Fly Ash (FA) is even less than for PC, shown in Figure 4. All materials for $d_{33}$ and $C$ become stable after 14 days, and the value at 14-day is about 90% of 21-day.

From Eqs. (1) and (2), we calculate $\varepsilon_r$ and $g_{33}$, the results are shown in Figures 5 and 6. In Figure 5, pozzolanic effect of SF composites is also the most effective for the relative dielectric factor, and FA is the less. However, for piezoelectric voltage factor in Figure 6, the $g_{33}$ value of FA is close to $24 \times 10^{-3}$ V-m/N, almost the same as PZT piezoelectric ceramic.

To find the thickness electromechanical coupling coefficient $K_t$, the formula was
used as follows (Huang et al., 2007).

\[ K_t^2 = \frac{\pi f_m}{2 f_n} \tan \left( \frac{\pi f_n - f_m}{2 f_n} \right) \]  

(3)

where \( f_m \) = frequency at minimum impedance and \( f_n \) = frequency at maximum impedance. In Figure 7, the fluctuations of \( K_t \) are pretty small with increasing the material ages for all cement piezoelectric composites. It seems that pozzolanic materials do not affect \( K_t \) except SF composite.

### 3.2. Pozzolanic materials effect

From Figures 3–6, the piezoelectric properties for all cement piezoelectric composites are gradually steady after 14 days, we adopt the properties after the polarization of 14-day to compare pozzolanic materials effect, here, and shown in Table 2.

In Table 2, the capacitance in SF is 140.7 pF higher than that in the others materials. Silica fume has much effective to cement piezoelectric composites, shown in Figure 4. Meanwhile, compared with PC, \( d_{33} = 33.1 \text{ pC/N} \) in SF has 31.9% increment. SL can also improve \( d_{33} \), but the efficiency is less SF, only 12% increment. Nevertheless, FA has no increase to \( d_{33} \). The effect of pozzolanic materials for \( d_{33} \) is plotted in Figure 8. The relative dielectric factor \( \varepsilon_r \) depends on the capacitance C shown in Eq. (2), SF is still the most effective to improve \( \varepsilon_r \).

From Eq. (1), piezoelectric voltage factor \( g_{33} \) is affected by \( d_{33} \) and \( \varepsilon_r \). As cement-based composites contains Fly Ash (FA), \( g_{33} = 23.37 \text{ mV-m/N} \). This is 1.9% increment compared with PC composite.

### Table 2. Piezoelectric properties at 14-day.

<table>
<thead>
<tr>
<th>Property</th>
<th>PC</th>
<th>SF</th>
<th>SL</th>
<th>FA</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (pF)</td>
<td>96.7</td>
<td>140.7</td>
<td>120</td>
<td>94.1</td>
</tr>
<tr>
<td>( \varepsilon_r )</td>
<td>124</td>
<td>180</td>
<td>153</td>
<td>120</td>
</tr>
<tr>
<td>( d_{33} ) (pC/N)</td>
<td>25.1</td>
<td>33.1</td>
<td>28.1</td>
<td>25.1</td>
</tr>
<tr>
<td>( g_{33} ) (mV-m/N)</td>
<td>22.94</td>
<td>20.29</td>
<td>19.81</td>
<td>23.37</td>
</tr>
<tr>
<td>( K_t ) (%)</td>
<td>13.48</td>
<td>12.41</td>
<td>13.27</td>
<td>13.58</td>
</tr>
</tbody>
</table>
Table 3. Trigger time and voltage increment.

<table>
<thead>
<tr>
<th>Time Voltage</th>
<th>PC</th>
<th>SF</th>
<th>SL</th>
<th>FA</th>
</tr>
</thead>
<tbody>
<tr>
<td>(min)</td>
<td>10.25</td>
<td>82.17</td>
<td>26.33</td>
<td>9.83</td>
</tr>
<tr>
<td>(kV/min)</td>
<td>0.293</td>
<td>0.037</td>
<td>0.114</td>
<td>0.305</td>
</tr>
</tbody>
</table>

Table 2, SF and SL will reduce $g_{33}$ compared with PC although their $d_{33}$ increase.

From the observation of experiment, it takes time to pole the specimen successfully. Table 3 shows trigger time (min) from the beginning to reach 1.5 kV/mm and applied voltage increment (kV/min). PC and FA are easy to be poled with voltage increment of 0.293 kV/min and 0.305 kV/mm, in turns. Trigger time for PC and FA specimen takes about 10 min. However, to trigger SF successfully needs 82 min at least for one specimen because applied voltage increment of SF is pretty small. If we applied voltage increment more than 0.037 kV/mm, SF specimen is easy to breakdown by applied voltage. This is a disadvantage when silica fume is used in cement-based piezoelectric composites.

4. Conclusions

The effect of pozzolanic materials on 0–3 cement-based piezoelectric composites is investigated. The specimens were cured in 90°C water for 7 days, and then, poled by voltage fields at 150°C for 45 minutes. The results are concluded as follows.

1. The piezoelectric properties of cement-based composites are steady after the polarization of 14 days, no matter what pozzolanic materials are added.
2. Compared with PC, cement piezoelectric composite containing silica fume (SF) can increase 31.9% of $d_{33}$, and 12% increment for SL. However, adding fly ash to cement piezoelectric composites (FA) does not improve $d_{33}$.
3. The piezoelectric voltage constant $g_{33}$ of FA is 23.7 mV-m/N, close to PZT piezoelectric ceramics.
4. In general, pozzolanic materials have less effect to the electromechanical coupling factor for all cement-based piezoelectric composites.
5. Although adding silica fume can improve the piezoelectric properties, to trigger SF is difficult.
6. The piezoelectric properties of FA are almost the same as PC though FA is easy to trigger successfully. Adding fly ash to increase piezoelectric properties does not have much benefit.
7. Considering the results of piezoelectric properties increment and trigger time, blast furnace slag is a compromising selection to increase the piezoelectric properties for cement-based composites.

Acknowledgments

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